## POLITECNICO DI TORINO

Master's Degree in Electronic Engineering



Master's Degree Thesis

#### Molecular Electronic Sensors Modeling: From Theory to Applications

Supervisors Prof. Gianluca PICCININI Prof. Mariagrazia GRAZIANO Engr. Yuri ARDESI

Candidate Fabrizio MO 252976

October 2020

To the memory of my beloved mother and to my dear father. They have always believed in me, and, by sustaining and inciting me, they made possible all this, and much more...

### Summary

In the last twenty years, the impressive development of molecular electronics and its related technology made possible the establishment of molecular electronic sensors (MES). In particular, the advancements in molecular synthesis engineering and the evolution towards sub-photolithographic processes allowed to fabricate molecular sensors whose working principle is different from conventional molecular chemo-sensors. Indeed, in MES, the detection involves the electric current flow instead of other chemical-physical phenomena, thus making possible a direct integration with conventional electronic circuitry. Pollution, chemical compounds, humidity, temperature and light sensors are realizable by modulating the molecular channel conductivity, exploiting quantum phenomena such as intermolecular or photon interactions. The potential applications are many and varied: gas sensors for industrial processes or environment monitoring, e-noses for non-invasive disease diagnostics, wearable/implantable bio-sensors and single-molecule detection in biochemical processes. MES are promising for several reasons, among which: potentially high sensitivity, selectivity and detectability, huge integrability, fast response time, low cost, label-free detection.

The first part of this work is a literature review of the theoretical physical-chemical modeling of MES. Molecular channel electronic structure, intermolecular interactions and transport state-of-the-art modeling techniques are introduced from the applicative standpoint of the electronic engineer, without requiring any extra notion w.r.t. the standard electrical/electronic engineering MSc background. To this purpose, the rigorous and purely quantum mechanical Non-Equilibrium Green's function (NEGF) theory is introduced, without the requirement of the second quantization formalism. The information provided in this part should be enough to perform an aware and correct setting up of atomistic simulations and to judiciously interpret the results.

The second part is instead focused on developing a general and complete methodology for the design of a MES. This crucial point is still lacking in the literature, even if it should be the first step toward the engineering and industrialization of the design process. To this purpose, the  $C_{60}$  fullerene molecule is used as molecular channel, and the device-level design is performed suggesting a possible general methodology for the choice of the device optimal geometry and other device parameters. Then a complete characterization of the designed gas sensor is performed, analyzing the performances in terms of sensibility, selectivity and sensor response. This allows the potential development of a "black-box"-like model of the MES, to be used in designing the conditioning circuit, being also the starting point toward a design by levels of abstraction, analogously to what is well established in semiconductor companies.

#### Acknowledgements

I must thank my colleague and dear friend Chiara Elfi Spano with which I had the honor of working with on the interdisciplinary workshop "Innovative Systems" during the a.y. 2018/19 and 2019/20. Some parts of the present work were definitively clear to me only after the long discussions with her, while others were conceived together, as part of such a workshop. In particular, sections 3.5, 3.6, 5.1, 5.8, 5.16, and 5.17 are partially the result of the study we carried out together. Moreover, appendix F is entirely taken from the work we developed together, and the material reported in appendices G.1, G.2 and G.3 was in great part, again, conceived together.

## **Table of Contents**

Li	st of	Tables	KVII
Li	st of	Figures	XXI
A	crony	yms	XLI
1	<b>Intr</b> 1.1 1.2 1.3	coduction and motivations         Conventional electronics and beyond CMOS: toward molecular electronics .         Molecular electronic sensors         Context, motivations and organization of this work	1 10 19
Ι	$\mathbf{M}$	olecular devices modeling	23
2	<b>Brie</b> 2.1 2.2 2.3	ef review of quantum mechanicsWave-particle duality	25 32 37 39 43 46 53 56 59 61 93
	2.5	Schrödinger's equation	94 95 100 106
3	Mo	lecular electronic structure	117
	$3.1 \\ 3.2$	Molecular Hamiltonian and the Born - Oppenheimer approximation The SCF procedure	118 120

	3.3	<b>B</b> A brief mention on the Hartree-Fock method		. 123
	3.4	Taxonomy of methods for electronic structure ca	lculations	. 125
	3.5	The DFT method		. 131
		3.5.1 Kohn-Sham Hamiltonian		. 133
		3.5.2 Exchange-correlation functionals		. 135
		3.5.3 DFT and fitting parameters		. 138
		$3.5.4$ DFT and basis sets $\ldots$ $\ldots$ $\ldots$		. 138
	3.6	5 The Extended Hückel theory and semi-empirical	$\mathrm{methods}\ .\ .\ .\ .\ .\ .$	. 142
		3.6.1 The semi-empirical approach		. 142
		3.6.2 The EHT method		. 145
	3.7	' Intermolecular interactions		. 146
		3.7.1 van der Waals and intermolecular interac	tions $\ldots$ $\ldots$ $\ldots$ $\ldots$	. 146
		3.7.2 Quantum modeling of intermolecular inte	eractions	. 150
		3.7.3 Supermolecular approach and DFT corre	ctions	. 151
4	An	n introduction to transport in molecular dev	ices	155
	4.1	A simple model for transport through quantum	dots	. 155
		$4.1.1  \text{Levels broadening}  \dots  \dots  \dots  \dots  \dots$		. 161
		4.1.2 Multi-level quantum dot		. 164
		4.1.3 Quantum conductance		. 166
		4.1.4 Electrostatic source and drain capacitance	es	. 167
		4.1.5 Charging effect $\ldots$ $\ldots$ $\ldots$ $\ldots$		. 169
		4.1.6 Self consistent algorithm and total electro	ostatic effect	. 170
		4.1.7 Gating the quantum dot: a three termina	als model $\ldots$ $\ldots$ $\ldots$ $\ldots$	. 171
		4.1.8 Quantum capacitance		. 172
		4.1.9 Final considerations		. 175
	4.2	2 Mesoscopic systems		. 176
	4.3	B The transmission formalism		. 177
		4.3.1 The transmission function $T$		. 178
		4.3.2 Bütticker's formula		. 179
		$4.3.3  \text{Linear response}  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  $		. 180
		4.3.4 Non-coherent transport		. 182
	4.4	Molecular devices linear response and coherent t	$ransport \dots \dots \dots \dots \dots$	. 183
	4.5	The non-equilibrium Green's function formalism		. 186
۲	The	a Nan Fauilibrium Crean's Function formal		107
9	I ne	The shares of a sum estimate	ISIN	100
	0.1	5.1.1 The change of perspective in formulae		. 100
	5.9	1D retarded and advanced Creen's functions		. 191
	0.2 5-2	Differenced and advanced Green's functions		. 195
	0.0 5 4	Figenfunction expansion and matrix representation		. 190 107
	0.4	5.4.1 Figenfunction expansion and matrix representat.	1011	. 197 100
		5.4.2 An important relation		. 198
		5.4.2 All important relation		. 199
	55	Croop's function poles		. 200
	0.0			. 201

5.6 Time domain impulse response	201
5.7 A remark on notation	203
5.8 "Contact-ing" the Schrödinger's equation: an intuitive introduction .	204
5.9 A more rigorous introduction: the contact self-energy	208
5.9.1 Evaluation of the contact self-energy $\Sigma$	210
5.9.2 The total system and the device Green's functions	213
5.9.3 The Dyson's equation	215
5.9.4 The impulse response $G_D$	215
5.9.5 A "good" contact	216
5.10 Density matrix, density of states and spectral function	217
5.10.1 Density matrix $\ldots$	217
5.10.2 Density of states and local density of states	220
5.10.3 Spectral function $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	221
5.10.4 Spectral function and density matrix	222
5.11 Summary of one contact system equations and some useful relations .	222
5.12 Contact self-energy, levels broadening and finite lifetime	224
5.12.1 The physical origin of broadening and the LDOS $\ldots \ldots \ldots$	224
5.12.2 Finite lifetime of broadened states	225
5.12.3 The broadening function $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$	227
5.13 The two contacts case $\ldots \ldots \ldots$	228
5.14 Inflow, outflow and terminal current	231
5.14.1 One contact case $\ldots \ldots \ldots$	231
5.14.2 Two contacts case $\ldots$	232
5.14.3 Many contacts case and terminal current	233
5.15 Transmission with NEGF	233
5.15.1 Transmission formalism vs NEGF	236
5.15.2 Landauer's formula, small bias and thermal broadening $\ldots$	237
5.15.3 Channel proper modes and maximum conductance	239
5.16 Summary of NEGF transport equations	240
5.17 The general procedure for the current calculation	242
5.17.1 A "toy" pseudocode $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	244
5.17.2 The general procedure: a real example	247
5.17.3 Mixing schemes	250
5.17.4 Poisson's solver in $Quantum$ -Wise $ATK$	251
5.17.5 Density matrix and contour integral	252
5.18 The general self-energy concept and incoherent transport	253
5.18.1 Bütticker's probes and scattering	254
5.18.2 The general approach and the scattering self-energy	256
5.18.3 The general approach: a summary of transport equation with in	100-
herent scattering	259
5.18.4 Incoherent scattering and transmission	260
5.18.5 Dissipated power	262
Transport regimes in nano-devices	265
6.1 Coulomb blockade	265

6

6.2	2 Transport mechanisms		268
6.3	Modeling approaches: strong	vs weak coupling case and corrections	272
	6.3.1 Strong coupling case		272
	6.3.2 Weak coupling case as	nd the Single Electron Transistor	273

#### II Molecular electronic sensors

7	Mo	lecular	electronic sensors	281
	7.1	Worki	ng principle	. 282
		7.1.1	Chemical adsorption: physisorption and chemisorption	. 282
		7.1.2	Gas molecular electronic sensors	. 285
		7.1.3	Single molecule event detection with molecular electronic sensors .	. 287
		7.1.4	Light molecular electronic sensors	. 287
		7.1.5	Humidity and temperature molecular electronic sensors	. 288
		7.1.6	DNA sequencing with molecular SETs	. 288
	7.2	Metho	odological approach: gas sensors	. 289
8	$\mathbf{C}_{60}$	-based	ammonia gas sensor	293
	8.1	Device	e structure and geometry	. 294
		8.1.1	The $C_{60}$ fullerene $\ldots$	. 294
		8.1.2	The initial geometry	. 295
	8.2	Prelin	ninary equilibrium properties of the device	. 296
		8.2.1	DFT equilibrium simulations settings	. 296
		8.2.2	A remark on transmission function $T(E)$ in $ATK$	. 296
		8.2.3	DFT equilibrium simulations results	. 299
		8.2.4	EHT equilibrium simulations	. 302
	8.3	Device	e geometry engineering	. 305
		8.3.1	Equilibrium DOS and $T(E)$ and contact distance	. 305
		8.3.2	Device orbitals (MPSH) and contacts distance	. 308
		8.3.3	Physisorption, chemisorption and equilibrium distances	. 313
		8.3.4	$C_{60}$ orientation and geometry optimization	. 314
		8.3.5	<i>I-V</i> characteristic and contact distance	. 317
		8.3.6	Geometry for maximum sensitivity	. 318
		8.3.7	The final $C_{60}$ -wire geometry	. 327
	8.4	Equili	brium properties of the final $C_{60}$ -wire sensor	. 327
	8.5	EHT 1	non-equilibium calculations validation	. 329
	8.6	Non-e	quilibrium properties and $I-V$ characteristics $\ldots \ldots \ldots \ldots \ldots$	. 331
		8.6.1	Sensitivity to different $NH_3$ orientations $\ldots \ldots \ldots \ldots \ldots \ldots$	. 333
		8.6.2	Selectivity to common atmospheric gases: the $C_{60}$ ammonia gas	
			sensor failure	. 335
		8.6.3	The $C_{60}$ lead sulfate gas sensor proposal $\ldots \ldots \ldots \ldots \ldots$	. 339
9	$\mathbf{C}_{60}$	-based	lead sulfate gas sensor	343
	9.1	The P	$bSO_4$ molecule $\ldots$	. 344

#### $\mathbf{279}$

9.2	Device structure and geometry
	9.2.1 The distance from contacts
	9.2.2 The final geometry $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 34$
9.3	Preliminary equilibrium properties of the final $C_{60}$ -wire sensor $\ldots \ldots 34$
9.4	EHT non-equilibrium calculations validation
9.5	Non-equilibrium properties and <i>I-V</i> characteristics
	9.5.1 Sensitivity to different PbSO <sub>4</sub> orientations
	9.5.2 Selectivity to common atmospheric gases: the $PbSO_4$ gas sensor
	proposal
	9.5.3 Possible choice for the $PbSO_4$ gas sensor bias voltage $\ldots \ldots 33$
	9.5.4 Sensitivity to different $PbSO_4$ distances
	9.5.5 Sensitivity to different $PbSO_4$ concentrations
	9.5.6 Transmission eigenstates in real space: an insight in detection mech-
	anism
9.6	Sensor LUT-based circuit model
97	Sensor capacitances and "dynamic" resistances
0.1	971 Cadence circuital dynamic model
9.8	Sensor response time estimation
0.0	9.8.1 Estimated interaction time and sensor response
0.0	Cating the sensor 38
5.5	9.9.1 Gate control and choice of the gate voltage
	9.9.2 Sensor sensitivity and selectivity 30
	9.9.3 Sensor response to PbSO, concentration
	9.9.5 Sensor response to PbSO, distance
	$9.9.4$ Sensor response to 1 bb04 distance $\dots \dots \dots$
0.10	5.5.5 Sensor response time
9.10	
10 A g	limpse on the $C_{eo}$ -based nitric oxide gas sensor 40
10 1	Preliminaries 4
10.1	The C <sub>co</sub> wire sensor 40
10.2	The sensor with gate 40
10.0	Final remarks
10.1	
1 Con	clusions and future works 41
11.1	Summary of the results
	11.1.1 Part I
	11.1.2 Part II
11.2	What is next?
11.2	
Bibliog	graphy 42
A Add	litional quantum mechanics related topics
A 1	Solution of second order homogeneous differential equations
11.1	Solution of second of definition of a second of the second

	A.3	<i>MatLab</i> implementation of the finite difference method for the 1D finite height quantum well	A7
	A.4	<i>MatLab</i> implementation of the finite difference method for the 1D potential barrier (and step)	A11
В	Add	litional molecular electronic structure related topics	B1
	B.1	Hartree approximation and electron correlation	B1
$\mathbf{C}$	NE	GF useful calculations	C1
	C.1	Fourier transform of Green's function	C1
	C.2	Impulse response of time dependent Schrödinger equation	C2
	C.3	Some useful relations	C3
		C.3.1 A useful theorem	C3
		C.3.2 Equation 5.38: device density matrix $[\rho_D]$	C4
		C.3.3 Equation 5.39: $A(E) = i [G(E) - G^{\dagger}(E)] \dots \dots \dots$	C4
		C.3.4 Broadening function equation: $\Gamma = i [\Sigma - \Sigma'] = \zeta A_R \zeta' \ldots \ldots$	C5
		C.3.5 Equation 5.39: $A_D = G_D \Gamma G_D^{\dagger} = G_D^{\dagger} \Gamma G_D$	C5
		C.3.6 Equation 5.40: $[G^n] =  G_D \Gamma G_D^{\dagger}  f_{FD} = [A_D] f_{FD} \dots \dots \dots \dots$	C6
	C.4	One contact inflow and outflow	C7
	C.5	Transmission function calculations	C10
р	Cha	opter 8 - Additional images graphs and material	D1
Ľ	D.1	Additional images and graphs relative to section 8.1	D1
	D.2	Additional images and graphs relative to section 8.2	D4
	D.3	MatLab code used for exponential fitting of the transmission spectrum peaks	
		at 1 eV	D5
	D.4	Additional images and graphs relative to section 8.3	D6
		D.4.1 <i>MatLab</i> code for exponential interpolation with 3D plots $\ldots$ .	D14
	D.5	Additional images and graphs relative to section 8.4	D16
	D.6	Additional images, graphs and material relative to section 8.5	D16
		D.6.1 MatLab code for implementing trapezoidal integration of equilibrium	<b>D</b> 4 0
		transmission spectra	D16
	D 7	D.6.2 Graphs for the case of 3 and 5 ammonia molecules	D20
	D.(	Additional images and graphs relative to section 8.0	D22
		D.7.1 Zoom in of light 8.52 for $V_D = 0.2$ V and $V_D = 1.4$ V	D22
		$D.7.2$ Sensitivity of the $C_{60}$ whe to additional pollutants	$D_{20}$
$\mathbf{E}$	Cha	pter 9 - Additional images, graphs and material	E1
	E.1	Additional images and graphs relative to section 9.2	E1
	E.2	Additional images and graphs relative to section 9.4	E3
	E.3	Additional images and graphs relative to section 9.5	E4
	<b>Б</b> (	E.3.1 Different $PbSO_4$ orientation geometries	E4
	E.4 E.5	Additional material relative to section 9.5.4	E6
	上.5 日子	Additional material relative to section 9.5.5.	E7
	Ľ.0	Additional material relative to section 9.5.0	E10

		E.6.1 Additional material relative to section 9.5.6: two opposite oriented	
		$PbSO_4$ molecules	E15
	E.7	Argon transmission eigenstates analysis	E17
	E.8	Additional images and graphs relative to section 9.9	E21
	-	E.8.1 Sensor response time (gate case): section 9.9.5	E26
$\mathbf{F}$	An	perative introduction to the free available tool Huckel-IV 3.0	F1
$\mathbf{G}$	Cha	ter 9 - Molecular electronic sensor circuit level parameters and	
	mod	ling	G1
	G.1	LUT-based model: <i>verilogA</i> code	G1
		G.1.1 LUT data: the "C60_PbSO4_sensor_ATK.txt" file	G2
	G.2	Device capacitances and "dynamic" resistances calculations	G3
		G.2.1 Gate capacitance calculation	G11
		G.2.2 Source and drain electrostatic capacitance calculation, by means of	
		the parallel plate approximation	G12
		G.2.3 Quantum capacitance calculation	G14
		G.2.4 Equilibrium total electrostatic capacitance calculation	G15
		G.2.5 Source and drain capacitances calculation	G16
		G.2.6 Gate resistance calculation	G19
		G.2.7 Source and drain "dynamic" resistances calculation	G21
	G.3	Sensor time constant and response time estimation	G24
		G.3.1 $MatLab$ code for the time constant estimation $\ldots \ldots \ldots \ldots \ldots$	G24
		G.3.2 <i>MatLab</i> output figures for time constant estimations	G27
	G.4	MatLab code for the interaction time estimation	G29
	G.5	LUT-based model (gate case): $verilogA$ code	G30
н	Cha	ter 10 - Additional images, graphs and material	H1

### List of Tables

1.1	Advantages and drawbacks of moletronics (i.e. molecular electronic technol- ogy) w.r.t. conventional CMOS technology	8
1.2	Main features of molecular electronic sensors (MES).	14
1.3	Comparison of different gas sensing technologies. SSES (solid state electro- chemical sensors) and QCM (quartz crystal microbalance) are not considered in this work (see [29] and references herein for details). A comparison is provided in detail in [29]	15
2.1	Quantum mechanical operators that are associated to physical observables in both position space and momentum space	55
8.1	ATK-DFT equilibrium calculator settings. If not differently stated, all the DFT simulations were performed with these settings	297
8.2	ATK-DFT equilibrium DOS calculator settings. If not differently stated, all the DOS simulations were performed with these settings	298
8.3	ATK-DFT equilibrium transmission spectrum calculator settings. If not differently stated, all the transmission spectrum simulations were performed	
	with these settings	298
8.4	ATK-SE (EHT) equilibrium calculator settings. If not differently stated, all the EHT simulations were performed with these settings.	303
8.5	ATK-SE (EHT) non-equilibrium $I$ - $V$ characteristics calculator settings. If not differently stated, all the non-equilibrium $I$ - $V$ characteristic simulations were performed with these settings	317
8.6	Mean percentage current variation values, averaged over the range $[0,2]$ V of applied voltage, due to the presence of 1, 3, 5 NH <sub>3</sub> molecules, for all the considered distances between the contacts and the C <sub>60</sub> fullerene (EHT	
	method).	326
8.7	Major atmosphere constituents	336
9.1	Mean absolute and percentage current variation values, averaged over the range $[0,2]$ V of applied voltage, due to the presence of 1 and 2 PbSO <sub>4</sub> molecules, for all the considered distances between the contacts and the C <sub>60</sub> fullerene (EHT method)	347

9.2	Maximum absolute deviation between the cubic spline interpolation and the linear interpolation of the current values in function of the $PbSO_4$	
	concentration, for the various considered bias points	360
9.3	Transmission eigenvalues for the three main transmission spectrum peaks	
	within the bias window at $V_D = 0.8 \text{ V}$ , for the sensor with a single PbSO <sub>4</sub>	
	molecule nearby the fullerene	363
9.4	Source and drain capacitance and "dynamic" resistance values calculated	
	from the <i>Huckel-IV</i> current-voltage characteristic with $V_c = 0.65$ for the	
	fullerene molecular wire. The average values and the values at $0.8\mathrm{V}$ are	
	reported. Notice that the approximated (parallel plates) source and drain	
	capacitances resulted to be: $C_s = C_d = 1.89516e-18$ F. The $C_s$ and $C_d$	
	values at 0.8 V are the arithmetic mean of those at 0.775 V, that are: $C_s =$	
~ <b>-</b>	$C_d = 2.171e-21$ F, and those at 0.825 V, that are: $C_s = C_d = 3.3978e-21$ F.	382
9.5	Rise and fall times for the drain and source voltages and the drain current	
	of the sensor, evaluated by means of the "Transient Measurements" tool in	
	Cadence environment. The quantities are defined with reference to figure 0.20. The undersheet and every sheet are provided in $%$ with the steady	
	state (final) value	383
96	MatLab estimated time constant and transient duration defined as 7 times	000
0.0	the relative time constants. The considered quantities are defined with	
	reference to figure 9.20. The time constants are defined with a graphical	
	method	384
9.7	MatLab estimated interaction time accordingly with the described approxi-	
	mations and method	386
9.8	Absolute average current variations $ \Delta I_D $ and percentage average current	
	variations $ \Delta I_D _{\%}$ in the voltage ranges [0,1] V and [0,2] V; both in the case	0.01
0.0	of the sensor wire and transistor structures.	391
9.9	Absolute maximum errors from linearity for the different blas voltages, in the ease of the C lead sulfate senser with sets	204
0.10	Source and drain capacitance and "dynamic" resistance values calculated	594
3.10	from the Huckel-IV current-voltage characteristic with $V = 0.625$ for the	
	fullerene molecular transistor. The average values and the values at $0.8 V$	
	are reported. Notice that the approximated (parallel plates) source and	
	drain capacitances resulted to be: $C_s = C_d = 1.89516e-18$ F. The $C_s$ and $C_d$	
	values at 0.8 V are the arithmetic mean of those at 0.775 V, that are: $C_s =$	
	$C_d = 8.8539e-18$ F, and those at $0.825$ V, that are: $C_s = C_d = 8.2754e-18$ F.	
	The gate capacitance and resistance were evaluated starting from the device	
	geometry (parallel plate approximation); thus only one (average) value is	
0.11	reported.	396
9.11	MatLab and Cadence estimated time constants and transient duration.	
	The considered quantities are defined with reference to figure 9.30. The $MatLab$ time constants $\sigma$ are estimated with a graphical method. Notice	
	that <i>Cadence</i> failed in identifying correctly the rise fall edges for the current	307
9 1 2	Bough estimation of the static active dissinated power for the wire and the	.531
0.14	gate PbSO <sub>4</sub> sensors.	399

10.1 10.2	<i>MatLab</i> and <i>Cadence</i> estimated time constants and transient duration. The <i>MatLab</i> time constants $\tau$ are estimated with a graphical method Absolute average current variations $ \Delta I_D $ and percentage average current variations $ \Delta I_D _{\%}$ in the voltage ranges [0,1] V and [0,2] V; both in the case	406
10.3	of the sensor wire and transistor structures. $\dots \dots \dots$	408 412
E.1	Maximum absolute deviation between the cubic spline interpolation and the linear interpolation of the current values in function of the target-fullerene distance, for the various considered bias points.	E6
F.1	Huckel-IV parameters used for the C <sub>60</sub> molecular wire simulations. First column: parameter. Second column: set value. Third column: brief explanation.	F8

# List of Figures

1.1	Possible taxonomy of emerging memory devices and a comparison among few of them (bottom-left) in terms of relevant features for a future commer- cialization. Black line: FeFET memory; grey line: FTJ memory; red line: ReRAM memory; green line: Mott memory; purple line: macromolecular memory; orange line: molecular memory; blue line: carbon-based memory. The classification is coherent with the one reported in [5]	4
1.2	Possible options for emerging logic devices. The devices are differentiated according to whether the structure or the material are conventional or innovative (abscissa axis) and whether the information representation is based on electron charge or on some non-charge entity (ordinate axis). Only three groups are possible since a conventional FET material and structure is intrinsically a charge-based device. The classification is in accordance	1
1.3	with the one from [5] Example of a molecular FET structure. In this case the PDT (phenyl dithiol) molecule is used. The yellow atoms are the gold source and drain contacts; the two dark yellow atoms are the sulfur anchoring groups; grey atoms are carbon and white hydrogen. The light purple region is the gate insulator (continuum approximation) while the white/light grey region is the metal gate contact. The figure was generated in <i>Quantum-Wise ATK</i> software.	5
2.1	Experimental arrangement for observing electron diffraction through crys- talline material (left); and diffraction patterns of electrons on the photo- graphic plate (right).	30
2.2	Davisson and Germer experimental arrangement for observing Bragg scat- tering of electrons.	31
2.3	A monochromatic continuous wave train corresponding to an unlocalized particle (top); and an example wave packet corresponding to a localized particle within the distance $\Delta x$ (bottom); $\lambda$ is the monochromatic wavelength,	
2.4	$v_g$ is the group velocity of the pulse envelope	34
	unnormalized	73

2.5	Wave-function squared modulus corresponding to an incoming electron from left side, with energy $E = 1.4 \text{ eV}$ (a) and $E = 1.989 \text{ eV}$ (b) toward a potential step of height $U_0 = 2 \text{ eV}$ . The wave-functions and their squared moduli are unnormalized.	74
2.6	Rectangular potential energy barrier. The barrier height is $U_0$ , its width is $W$ . Incident (from left), reflected and transmitted paths are shown. The three regions are: $I$ for $x < 0$ ; $II$ for $0 \le x \le W$ ; and $III$ for $x > W$	76
2.7	Wave-function (a) and wave-function squared modulus (b) corresponding to an electron with energy $E = 0.82 \text{ eV}$ incoming from left toward a potential barrier of width 0.5 nm and height $U_0 = 1 \text{ eV}$ . The wave-function and its squared modulus are unpermalized	79
2.8	Rectangular potential energy barrier transparency example. The barrier height is of about $U_0 = 4.5 \text{ eV}$ while its thickness is 20 nm. The transmission coefficient is calculated both starting from analytical theoretical formulae (following the approach of [97]), and with a numerical method. The numerical method is an implementation of a Finite Element Method for the solution of the Schrödinger's equation, conceptually similar to what will be presented in section 2.4.1. The two methods provide very similar results indeed the two curves are well overlapped. Notice the resonance peaks and the non-null	10
2.9	transmission also for $E < U_0$	79 81
2.10	Permitted energy eigenvalues in a 1D potential energy well with $L = 10 \text{ nm}$ and $U_0 = 1 \text{ eV}$ . Notice that they are discrete, and only 17 bound states are possible for this specific quantum well. In black the quantum well shape (in eV).	85
2.11	First four wave-functions corresponding to the first four energy levels of figure 2.10. The same quantum well is considered: 1D potential energy well with $L = 10 \text{ nm}$ and $U_0 = 1 \text{ eV}$ . Notice that the exponential tails in the classical forbidden regions. The wave-functions are unnormalized; in black the quantum well shape (in eV).	85
2.12	Squared moduli of all the 17 wave-functions corresponding to the 17 energy eigenvalues of figure 2.10. The same quantum well is considered: 1D potential energy well with $L = 10 \text{ nm}$ and $U_0 = 1 \text{ eV}$ . The squared moduli are positioned at a height corresponding to their relative eigenvalue for aesthetic reasons. They are unnormalized; in black the quantum well shape (in eV)	86

- 2.13 Infinite height 1D potential energy well. The well height is  $\infty$  at x = 0 and x = L; the well width is L, the potential has even symmetry. . . . . . .
  - 87

91

- 2.14 General potential energy shape example, typical of a central force problem. At large x value the interaction vanishes thus  $U(x) \to 0$ . Instead for x = 0the potential energy tends to infinity  $U(x) \to \infty$  because of the repulsion. For small x values an attractive interaction occurs and U(x) is negative. On right side of the potential shape is reported the Hamiltonian operator spectrum (energy eigenvalues), discrete for negative energies (bound states) and continuous for positive energies (free states).
- 2.15 Wave-function corresponding to an electron tunneling through two consecutive potential barriers. The first barrier is 0.5 nm thick and 1 eV of height, the second is 0.25 nm thick and 2 eV of height. The electron energy is  $E = 0.73 \,\mathrm{eV}$ . Notice the exponential decay within the barriers; the wavefunction is unnormalized. The graph was generated with the MatLab code reported in appendix A.4. 91
- 2.16 Wave-function squared modulus corresponding to an electron tunneling through two consecutive potential barriers. The potential shape and the structure is the same of figure 2.15. Notice the exponential decay within the barriers; the wave-function is unnormalized. The graph was generated 92
- 2.17 Confinement in a quantum well. The well is 10 nm long and 1 eV tall. Inside it a barrier of 5 nm of width and height 0.8 eV is present. The potential shape is the curve in black. In total 13 bound states are present in this structure. Their wave-functions are reported in this graph; they are unnormalized and they are placed at an height corresponding to their relative energy eigenvalues. Notice the degeneracy and the spacing between the energy levels. The graph was generated with the *MatLab* code reported in appendix A.3. 92
- 2.18 Confinement in a quantum well. The well is the same of picture 2.17. Here four wave-functions are reported, they correspond to energy levels:  $E_3 = 0.174 \,\text{eV}$  (top left),  $E_8 = 0.662 \,\text{eV}$  (top right),  $E_{10} = 0.815 \,\text{eV}$  (bottom left) and  $E_{11} = 0.855 \,\text{eV}$  (bottom right). Notice the exponential decay in the central region (of height  $0.8 \,\mathrm{eV}$ ) of the top ones, while the bottom ones are free in that region (oscillating). The wave-functions are unnormalized. The graph was generated with the MatLab code reported in appendix A.3. 93
- 3.1Schematic representation of the converge toward the exact solution of the electron correlation methods. On abscissa axis the basis sets are considered while on ordinate axis the different electron correlation methods are considered. 130
- A summary of the main classes of functionals with examples (a); and a 3.2comparison among them (b). RMS stands for Root Mean Square, MAD for Mean Absolute Deviation. The comparison is performed with experimental
- 3.3 A qualitative example of comparison between STO and GTO functions. The exponential 1s STO orbital is compared with three different GTO possible functions.  $\ldots \ldots 140$

4.1	Electron transport through a single level quantum dot. Four electron fluxes are considered: $\Phi_{S,dot}$ from source to dot, $\Phi_{dot,S}$ from dot to source, $\Phi_{D,dot}$ from drain to dot, $\Phi_{dot,D}$ from dot to drain. Two net fluxes are then defined: the net flux from source to dot $\Phi_S$ , and the net flux from drain to dot $\Phi_D$ . The x-axis is from source to drain, while the drain to source current is
4.2	conventionally flowing from drain to source
4.3	distribution
4.4	LUMO) are supposed known from electronic structure calculations 105 Qualitative example for the two level quantum dot of figure 4.3. The LUMO level causes the first plateau at $\pm 1$ V while the HOMO the second at $\pm 1.4$ V. Notice the conductance gap around the zero bias condition (0 V), and notice that it is equal to the double (for both positive and negative biases) of the energy interval that separates the closest dot energy level to the dot
4.5	Fermi level
4.6	Quantum dot capacitive model. In this simplified model the molecular quantum dot -i.e. the channel- is assumed to be without physical extensions, i.e. zero-dimensional
5.1	General Self-Consistent procedure for the solution of the NEGF transport and Poisson equations
5.2	Schematic representation of the model for considering incoherent scattering within the NEGF framework. The various electron inflows and outflows are
5.3	sketched
8.1	Initial geometry of the $C_{60}$ fullerene ammonia gas sensor. The $C_{60}$ -contacts distances were fixed at around 2.7 Å, no special orientation of the $C_{60}$ was considered. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations)

XXIV

8.2	Device equilibrium DOS with different ammonia molecule concentrations: 1, 3 and 5 NH <sub>3</sub> molecules were considered.	301
8.3	Device equilibrium transmission spectra with different ammonia molecule concentrations: 1, 3 and 5 NH <sub>2</sub> molecules were considered	301
8.4	Device equilibrium transmission spectra with different ammonia molecule concentrations: 1, 3 and 5 $NH_3$ molecules were considered.	302
8.5	Device equilibrium transmission spectra with different ammonia molecule concentrations: 1, 3 and 5 $NH_3$ molecules were considered (EHT method).	304
8.6	Device equilibrium transmission spectra with different ammonia molecule concentrations: 1, 3 and 5 $NH_3$ molecules were considered (EHT method).	304
8.7	Device equilibrium transmission spectra with different ammonia molecule concentrations: 1, 3 and 5 $NH_3$ molecules were considered (EHT method).	305
8.8	Device equilibrium DOS with different molecule-contact distances: 2.7 Å, 3.0 Å, 3.3 Å, 3.6 Å, 4.0 Å, 5.4 Å (EHT method)	306
8.9	Device equilibrium transmission spectra with different molecule-contact distances: $2.7$ Å, $3.0$ Å, $3.3$ Å, $3.6$ Å, $4.0$ Å, $5.4$ Å (EHT method)	307
8.10	Device equilibrium transmission spectrum peaks at around 1 eV values and their interpolation with an exponential fitting curve. The different considered molecule-contact distances are: $2.7$ Å, $3.0$ Å, $3.3$ Å, $3.6$ Å, $4.0$ Å, $5.4$ Å (EHT method). On abscissa axis the distance between the fullerene and the contacts, on ordinate axis the transmission peak value (at 1 eV).	308
8.11	MPSH of the HOSO (Highest Occupied System Orbital) and the LUSO (Lowest Unoccupied System Orbital) of the $C_{60}$ molecular wire with molecule- contact distances of 5.4 Å. The two colors (teal and fuchsia) are referred to the phase (negative or positive) of the MPSH. The figure was generated by ATK software [125], [126] (used for performing the simulations)	310
8.12	MPSH of the HOSO (Highest Occupied System Orbital) of the $C_{60}$ molecular wire with molecule-contact distances of 4 Å and 3 Å, respectively. The two colors (teal and fuchsia) are referred to the phase (negative or positive) of the MPSH. The figure was generated by $ATK$ software [125], [126] (used	
8.13	for performing the simulations)	311 312
8.14	Equilibrium geometry for chemisorption with gold-carbon bond length of 2.4 Å, and with the hexagons on the gold surfaces. Top-left (a): the C <sub>60</sub> orientation. Lighted up atoms are the ones of the first contact layer, notice that the fullerene hexagon is centered on a vacancy. Top-right (b): the distance of 2.4 Å is measured. Bottom-left (c): side view. Bottom-right (d): top view. The figure was generated by $ATK$ software [125], [126] (used for	014
	XXV	314
	1111	

8.15	Device equilibrium transmission spectra with different molecule-contact distances: 2.4 Å (both with casual/non-special orientation and with the	
	hexagons on gold surfaces one), 2.7 Å, 3.0 Å, 3.3 Å, 3.6 Å, 4.0 Å, 5.4 Å (EHT method).	315
8.16	Current-voltage $(I-V)$ characteristics for the various considered distances between the contacts and the C <sub>60</sub> fullerene: 2.4 Å (both with casual/non- special orientation and with the hexagons on gold surfaces one), 2.7 Å, 3.0 Å, 3.3 Å, 3.6 Å, 4.0 Å, 5.4 Å (EHT method).	318
8.17	Dependence of current values on the distance between the fullerene and the contacts for a fixed voltage: $V_D = 1$ V. The exponential fitting performs well. Top: linear scale, bottom: semilogarithm scale.	319
8.18	Device current as a function of the applied voltage and the contacts distance. Red dots are the simulated points, while the surface corresponds to the exponential interpolation. Purple dots are those below the semi-transparent	
8.19	surface. A general good agreement is present (EHT method) Current-voltage $(I-V)$ characteristics for distances between the contacts and the C <sub>60</sub> fullerene of 2.7 Å; the cases with 0, 1, 3, and 5 NH <sub>3</sub> molecules are considered (EHT method)	320
8.20	Absolute variations of current due to the presence of 1, 3, 5 NH <sub>3</sub> molecules, for distances between the contacts and the $C_{60}$ fullerene of 2.7 Å (EHT	320
8.21	method)	321
	between the contacts and the $C_{60}$ fullerene of 2.7 Å; the cases with 0, 1, 3, and 5 NH <sub>3</sub> molecules are considered (EHT method). Bottom (b): Interpolated absolute variations of current due to the presence of 1, 3, 5 NH <sub>3</sub> molecules, for distances between the contacts and the $C_{60}$ fullerene of	
8.22	2.7 Å (EHT method)	322
8.23	Absolute variations of current due to the presence of 1 NH <sub>3</sub> molecule, for all the considered distances between the contacts and the $C_{60}$ fullerene (EHT	J2J
8.24	method)	324
8.25	method)	325
8.26	method)	326 328
	XXVI	520

8.27	Equilibrium transmission spectra of the final ammonia sensor geometry, in the cases of 1, 3, 5 $NH_3$ molecules (EHT method)	328
8.28	Integral difference of the final ammonia sensor equilibrium transmission spectra in the cases of 1 NH <sub>3</sub> molecule. The results obtained with the two methods: DFT (blue curve) and EHT (red/orange curve) are compared. The ellipse is around the considered range of bias windows, i.e. up to 2 V. The integrals were performed with trapezoidal numerical method in <i>MatLab</i> , over the bias windows from $0.1 \text{ V}$ to $4 \text{ V}$ with a step of $0.1 \text{ V}$ .	330
8.29	Top (a): Current-voltage characteristics for the final sensor geometry, the cases with 0, 1, 3, and 5 $NH_3$ molecules are considered (EHT method). Bottom (b): Interpolated (cubic spline) current-voltage characteristics for the final sensor geometry, the cases with 0, 1, 3, and 5 $NH_3$ molecules are considered (EHT method).	332
8.30	Top (a): Absolute current variations for the final sensor geometry, the cases with 0, 1, 3, and 5 $NH_3$ molecules are considered (EHT method). Bottom (b): Interpolated (cubic spline) absolute current variations for the final sensor geometry, the cases with 0, 1, 3, and 5 $NH_3$ molecules are considered	
8.31	(EHT method)	333
8.32	cases (EHT method)	335 338
8.33	Absolute current variations (with sign) to lead sulfate (PbSO <sub>4</sub> ) and other common atmospheric gases. Different orientations of PbSO <sub>4</sub> are considered (EHT method). $\dots \dots \dots$	341
9.1	Top (a): Average current variations in the case of 1 and 2 PbSO <sub>4</sub> molecules. The arithmetic mean is over the half voltage range: $[0,1]$ V and considers absolute values of the current variations. Bottom (b): Average current current variations in the case of 1 and 2 PbSO <sub>4</sub> molecules. The arithmetic mean is over the full voltage range: $[0,2]$ V and considers absolute values of the current variations.	346
9.2	Current variations in the case of $1 \text{ PbSO}_4$ molecule for the casual orientation of the fullerene and for the special chemisorption equilibrium orientation (hexagons toward the gold surfaces). On average the latter presents better performances.	348
9.3	Equilibrium transmission spectra calculated with DFT method for the cases of $0, 1, 2 \text{ PbSO}_4$ molecules.	349

9.4	Equilibrium transmission spectra calculated with EHT method for the cases	240
05	of $0, 1, 2$ PDSO <sub>4</sub> molecules	349
9.0	Integral difference of the final lead subtained sensor equilibrium transmission $\frac{1}{2}$	
	spectra in the cases of 1 PDSO <sub>4</sub> molecule. The results obtained with the	
	The allingsid is around the considered range of bigg windows i.e. up to 2V	
	The employed is around the considered range of bias windows, i.e. up to $2 v$ .	
	The integrals were performed with trapezoidal numerical method in <i>MatLab</i> ,	250
0.6	Top (a): $IV$ characteristics with 0, 1, and 2 DbSO, molecules (FUT)	300
9.0	method) Better (b): Interpolated (cubic spline) I.V. characteristics with	
	0.1 and 2 PbSO molecules	259
0.7	$0, 1, and 2.10504$ indecutes. $\dots$ $2.20504$	252
9.1	<i>U</i> horestoristics obtained with four different orientations of the lead	აკა
9.0	sulfate molecule (FHT method)	254
0 0	Absolute current variations (with sign) to lead sulfate (PbSO <sub>4</sub> ) and other	004
9.9	common atmospheric gases. Different orientations of $PbSO_4$ are considered	
	(EHT method)	355
9 10	Top (a): $I-V$ characteristics with different PbSO <sub>4</sub> molecule orientations the	000
0.10	possible bias choice is highlighted by means of an ellipse - $V_D = 0.8$ V (EHT	
	method). Bottom (b): Enlargement of the graph (a) around the chosen bias	
	point.	356
9.11	Current values for different PbSO <sub>4</sub> distances at $V_D = 0.8$ V. Black circles:	
	simulated data. Blue line: cubic $3^{rd}$ order spline interpolation. Red/Orange:	
	linear interpolation.	357
9.12	Current values for different $PbSO_4$ distances at different bias voltages.	
	The chosen bias voltage $(0.8 \text{ V})$ corresponds to the red line. Red dots are	
	simulated values, the surface corresponds to cubic spline interpolation curves.	
	Notice the greater variations/oscillations for larger bias points	358
9.13	Current values for different PbSO <sub>4</sub> concentrations and for $V_D = 0.8$ V. Black	
	circles: simulated values; blue curve: cubic $3^{rd}$ order spline interpolation;	
	red/orange: linear interpolation	359
9.14	Current values for different $PbSO_4$ concentrations at different bias voltages.	
	The chosen bias voltage $(0.8 \text{ V})$ corresponds to the red line. Red dots are	
	simulated values, the surface corresponds to cubic spline interpolation curves.	200
0.15	Notice the worse linearity for larger bias points.	360
9.15	Current-voltage characteristics in the case of 0, 2, and 2 with "opposite	
	direction" $PDSO_4$ molecules. Notice the current improvement in the latter	961
0.16	Case	301
9.10	ransmission eigenstate (top view) corresponding to the transmission eigen- value $2.540207e^{-1}$ with quantum number $ON = 1$ transmission peak at	
	value 5.540507e-1 with quantum number $QN = 1$ , transmission peak at operary $E = 0.04 \text{ eV}$ the geometry is the one with two PbSO, molecules	
	with opposite directions and with a bias voltage $V_{\rm D} = 0.8 V$ . The surface	
	corresponds to an iso-transmission surface the colors correspond to different	
	phases. The figure was generated by $ATK$ software [125] [126] (used for	
	performing the simulations).	366
	<b>I</b>	

XXVIII

9.17	Transmission eigenstate (full view) corresponding to the transmission eigen- value with quantum number $ON = 0$ , transmission peak at energy $F =$	
	value with quantum number $QN = 0$ , transmission peak at energy $E = 0.28 \text{ eV}$ the geometry is the one with a single PbSO, molecule, with the SO.	
	group pointing down toward the fullerene with opposite direction and with	
	a bias voltage $V_{\rm D} = 0.8 \mathrm{V}$ . The surface corresponds to an iso-transmission	
	surface the colors correspond to different phases. The figure was generated	
	by $ATK$ software [125] [126] (used for performing the simulations)	367
9.18	Circuit symbol for the PbSO. MES Notice the drain terminal (D) source	001
9.10	terminal (S) and the fictitious terminal "N $PbSO4$ " that represents the	
	number of lead sulfate molecules nearby the sensor. In vellow the instance	
	name The image is generated by <i>Cadence Virtuoso</i> software used for	
	performing circuit level simulations.	369
9 1 9	Left (a): LUT-based model testbench schematic Right (b): Result of the	
0.10	transient simulation with the circuit in (a). The red line is the Vdd voltage.	
	i.e. the DC voltage of the top DC generator in (a). DC voltage between	
	ground and D. The vellow line is the fictitious voltage step applied to the	
	N_PbSO4 input terminal of the sensor (the bottom generator in (a)). The	
	blue line is the sensor drain to source current, varying from $10.527 \mu\text{A}$ to	
	13.573 µA. The image is generated by <i>Cadence Virtuoso</i> software, used for	
	performing circuit level simulations	371
9.20	Circuit schematic for the sensor circuital model including $C_s$ , $C_d$ , $R_s$ and $R_d$ .	
	The image is generated by <i>Cadence Virtuoso</i> software, used for performing	
	circuit level simulations.	379
9.21	<i>I-V</i> characteristics obtained with <i>ATK</i> and with <i>Huckel-IV 3.0</i> tool. The	
	ellipse highlight the chosen bias point, i.e. $0.8$ V. Notice the different values	
	of the fitting parameter $V_c$ . Depending on what is bias range of interest	
	a different $V_c$ values can be used. For $V_D = 0.8$ V the best agreement is	901
0.00	Obtained with $v_c = 0.05$	991
9.22	aurrent of the circuit in figure 0.20. The analysis was carried out in <i>Cadanae</i>	
	$Virtuge^{\mathbb{B}}$ environment. The current and voltage values are not of interest.	
	in this analysis so they are not considered (they are wrong): the transient	
	duration is instead significant of the sensor response time.	383
9.23	Equilibrium transmission spectra with and without the PbSO <sub>4</sub> molecule for	000
0.20	the wire configuration (a) and the transistor one (b).	389
9.24	MES structure with gate contact. The fullerene orientation and distance	
0	from source and gate contacts are unchanged. The gate terminal is added	
	at the bottom. The purple region is the gate insulator, i.e. $ZrO_2$ (dielectric	
	constant 25.0) with thickness 5.1 Å. The white/light grey region is the metal	
	contact. The figure was created with $ATK$ software, used for performing	
	the simulations.	390
9.25	Current-voltage characteristics with and without the PbSO <sub>4</sub> nearby the	
	fullerene, both in the case of the wire sensor and in the transistor-based	
	sensor one. For the transistor sensor the gate voltage was fixed at $V_{GS} = 2.5$ V	.391

<ul> <li>9.27 Current flowing in the sensor with the gate structure in function of applied drain-to-source bias V<sub>D</sub> and of the number of PbSO<sub>4</sub> molect nearby the molecular channel. Red points are simulated data, the surface obtained by merging the spline (3<sup>rd</sup> order cubic) interpolating curves. 'red line corresponds to the chosen bias point of 0.8 V; a good linearity present</li></ul>	the iles e is
<ul> <li>applied drain to source bias VD and of the function of 1 bbo4 indeced nearby the molecular channel. Red points are simulated data, the surface obtained by merging the spline (3<sup>rd</sup> order cubic) interpolating curves. 'red line corresponds to the chosen bias point of 0.8 V; a good linearit present.</li> <li>9.28 Current flowing in the sensor with the gate structure in function of applied drain-to-source bias V<sub>D</sub> and of the distance of PbSO<sub>4</sub> molecular channel. Red points are simulated data, the surface obtained by merging the spline (3<sup>rd</sup> order cubic) interpolating curves. 'red line corresponds to the chosen bias point of 0.8 V; a good linearit present.</li> <li>9.29 LUT-based ideal model test-bench schematic. Notice the circuit symfor the PbSO<sub>4</sub> MES. Notice the drain terminal (D), source terminal and the fictitious terminal "N_PbSO4" that represents the number of I sulfate molecules nearby the sensor. In addition a gate terminal (G present. In yellow the instance name. The image is generated by Cade Virtuoso software, used for performing circuit level simulations.</li> <li>9.30 Circuit schematic for the sensor circuital model (with gate) including C<sub>a</sub>.</li> </ul>	e is
<ul> <li>obtained by merging the spline (3<sup>rd</sup> order cubic) interpolating curves. 'red line corresponds to the chosen bias point of 0.8 V; a good linearit present.</li> <li>9.28 Current flowing in the sensor with the gate structure in function of applied drain-to-source bias V<sub>D</sub> and of the distance of PbSO<sub>4</sub> molec from the molecular channel. Red points are simulated data, the surface obtained by merging the spline (3<sup>rd</sup> order cubic) interpolating curves. 'red line corresponds to the chosen bias point of 0.8 V; a good linearit present.</li> <li>9.29 LUT-based ideal model test-bench schematic. Notice the circuit symfor the PbSO<sub>4</sub> MES. Notice the drain terminal (D), source terminal and the fictitious terminal "N_PbSO4" that represents the number of I sulfate molecules nearby the sensor. In addition a gate terminal (G present. In yellow the instance name. The image is generated by Cade Virtuoso software, used for performing circuit level simulations.</li> <li>9.30 Circuit schematic for the sensor circuital model (with gate) including C<sub>a</sub>.</li> </ul>	
<ul> <li>red line corresponds to the chosen bias point of 0.8 V; a good linearit present.</li> <li>9.28 Current flowing in the sensor with the gate structure in function of applied drain-to-source bias V<sub>D</sub> and of the distance of PbSO<sub>4</sub> molec from the molecular channel. Red points are simulated data, the surface obtained by merging the spline (3<sup>rd</sup> order cubic) interpolating curves. Tred line corresponds to the chosen bias point of 0.8 V; a good linearit present.</li> <li>9.29 LUT-based ideal model test-bench schematic. Notice the circuit symfor the PbSO<sub>4</sub> MES. Notice the drain terminal (D), source terminal and the fictitious terminal "N_PbSO4" that represents the number of I sulfate molecules nearby the sensor. In addition a gate terminal (G present. In yellow the instance name. The image is generated by Cade Virtuoso software, used for performing circuit level simulations.</li> <li>9.30 Circuit schematic for the sensor circuital model (with gate) including C<sub>1</sub>.</li> </ul>	Гhe
<ul> <li>present</li></ul>	y is
<ul> <li>9.28 Current flowing in the sensor with the gate structure in function of applied drain-to-source bias V<sub>D</sub> and of the distance of PbSO<sub>4</sub> molec from the molecular channel. Red points are simulated data, the surface obtained by merging the spline (3<sup>rd</sup> order cubic) interpolating curves. 'red line corresponds to the chosen bias point of 0.8 V; a good linearity present</li></ul>	392
<ul> <li>red line corresponds to the chosen bias point of 0.8 V; a good linearit present.</li> <li>9.29 LUT-based ideal model test-bench schematic. Notice the circuit sym for the PbSO<sub>4</sub> MES. Notice the drain terminal (D), source terminal and the fictitious terminal "N_PbSO4" that represents the number of I sulfate molecules nearby the sensor. In addition a gate terminal (G present. In yellow the instance name. The image is generated by <i>Cade Virtuoso</i> software, used for performing circuit level simulations.</li> <li>9.30 Circuit schematic for the sensor circuital model (with gate) including C<sub>1</sub>.</li> </ul>	the cule e is Γhe
<ul> <li>9.29 LUT-based ideal model test-bench schematic. Notice the circuit sym for the PbSO<sub>4</sub> MES. Notice the drain terminal (D), source terminal and the fictitious terminal "N_PbSO4" that represents the number of I sulfate molecules nearby the sensor. In addition a gate terminal (G present. In yellow the instance name. The image is generated by <i>Cade Virtuoso</i> software, used for performing circuit level simulations</li> <li>9.30 Circuit schematic for the sensor circuital model (with gate) including C<sub>ade</sub></li> </ul>	y 18 204
<ul> <li>for the PbSO<sub>4</sub> MES. Notice the drain terminal (D), source terminal and the fictitious terminal "N_PbSO4" that represents the number of I sulfate molecules nearby the sensor. In addition a gate terminal (G present. In yellow the instance name. The image is generated by <i>Cade Virtuoso</i> software, used for performing circuit level simulations.</li> <li>9.30 Circuit schematic for the sensor circuital model (with gate) including C<sub>au</sub></li> </ul>	э94 bol
<ul> <li>present. In yellow the instance name. The image is generated by Cade Virtuoso software, used for performing circuit level simulations.</li> <li>9.30 Circuit schematic for the sensor circuital model (with gate) including C<sub>a</sub>.</li> </ul>	(S), ead ) is
9.30 Circuit schematic for the sensor circuital model (with gate) including $C_{aa}$	nce 205
	$C_{I}$
$C_g, R_s, R_d$ and $R_g$ . The image is generated by <i>Cadence Virtuoso</i> softwork used for performing circuit level simulations.	are, are, $397$
10.1 Current flowing in the wire NO sensor in function of the applied drain source bias $V_D$ and of the number of NO molecules nearby the molecu- channel. Red points are simulated data, the surface is obtained by merge the spline ( $3^{rd}$ order cubic) interpolating curves. The red line correspon- to the PhSO <sub>4</sub> sensor operating hiss point: 0.8 V	-to- ılar çing nds 404
10.2 Current variations (absolute with sign) obtained with $PbSO_4$ and	NO
molecules nearby the wire $C_{60}$ wire sensor	405
10.3 $I$ - $V$ characteristics obtained with the C <sub>60</sub> sensor with gate alone and w a single NO molecule with different relative orientations w.r.t. the fuller "Flat": the NO molecule is oriented with the bond axis parallel to transp direction, i.e. with N and O atoms at same distance from fullerene.	vith ene. oort "O
down": the NO molecule is oriented with oxygen atom pointing down tow	ard
the fullerene. "N down": the NO molecule is oriented with nitrogen at	om
pointing down toward the fullerene.	408
10.4 Current variations due to the different orientations of NO, and to ot common atmospheric chemical species	ner 400
10.5 Current flowing in the NO gate sensor in function of the applied drain source bias $V_D$ and of the number of NO molecules nearby the molecules	405 -to- 1lar
channel. Ked points are simulated data, the surface is obtained by merge the spline $(3^{rd} \text{ order cubic})$ interpolating curves. The red line correspondence of the spline ( $3^{rd} \text{ order cubic})$ interpolating curves.	ng
to the PbSO <sub>4</sub> sensor operating bias point: $0.8$ V	nds

10.6	Current flowing in the sensor with the gate structure in function of the applied drain-to-source bias $V_D$ and of the distance of the NO molecule from the molecular channel. Red points are simulated data, the surface is obtained by merging the spline ( $3^{rd}$ order cubic) interpolating curves. The red line corresponds to the chosen bias point of 0.8 V; a good linearity is present.	411
A.1	Graphic solution of the system of the two equations (A.3) and (A.4). In blue: $k \tan\left(k\frac{L}{2}\right)$ ; in orange: $-k \cot\left(k\frac{L}{2}\right)$ ; in black: the functions $\beta_k = \sqrt{k_0^2 - k^2}$ for various $k_0$ . The only possible solutions are the intersection points, highlighted with red circles, between $\beta_k = \sqrt{k_0^2 - k^2}$ and the functions $k \tan\left(k\frac{L}{2}\right)$ and $-k \cot\left(k\frac{L}{2}\right)$ . These intersection points correspond to discrete values of $k$ and thus of energy $E$	Α7
B.1	IP is the Ionization Potential while EA is the Electron Affinity. The ionization potential includes the repulsive potential from $N_e - 1$ electrons while the electron affinity that of $N_e$ electrons, thus the latter is higher in energy by the single electron charging energy $U_0$ .	B2
D.1	Initial geometry of the C <sub>60</sub> fullerene ammonia gas sensor, with a single NH <sub>3</sub> molecule. The C <sub>60</sub> -contacts distances were fixed at around 2.7 Å, no special orientation of the C <sub>60</sub> was considered. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations).	D1
D.2	Initial geometry of the $C_{60}$ fullerene ammonia gas sensor, with a single NH <sub>3</sub> molecule. van der Waals spheres are shown. Since they are intersected, the interaction should be strong. The $C_{60}$ -contacts distances were fixed at around 2.7 Å, no special orientation of the $C_{60}$ was considered. The figure was generated by <i>ATK</i> software [125], [126] (used for performing the simulations)	D9
D.3	Initial geometry of the C <sub>60</sub> fullerene ammonia gas sensor, with a single NH <sub>3</sub> molecule. The ammonia C <sub>60</sub> distance is of about 2.2 Å The C <sub>60</sub> -contacts distances were fixed at around 2.7 Å, no special orientation of the C <sub>60</sub> was considered. The figure was generated by $ATK$ software [125], [126] (used for a sufficient the simulation)	52
D.4	Initial geometry of the C <sub>60</sub> fullerene ammonia gas sensor, with three NH <sub>3</sub> molecule. The C <sub>60</sub> -contacts distances were fixed at around 2.7 Å, no special orientation of the C <sub>60</sub> was considered. The figure was generated by $ATK$	D2
D.5	software [125], [126] (used for performing the simulations) Initial geometry of the $C_{60}$ fullerene ammonia gas sensor, with five NH <sub>3</sub> molecule. The $C_{60}$ -contacts distances were fixed at around 2.7 Å, no special orientation of the $C_{60}$ was considered. The figure was generated by $ATK$	D3
D.6	software [125], [126] (used for performing the simulations) Equilibrium DOS per unit energy obtained with various DFT-based method. All curves are overlapped apart for the DFT-1/2 correction that is different.	D3 D4

D.7	Equilibrium transmission spectrum obtained with various DFT-based method. All curves are overlapped apart for the DFT-1/2 correction that is different.	D4
D.8	Current-voltage $(I-V)$ characteristics for 2.4 Å of distance between the contacts and the C <sub>60</sub> fullerene. The two orientations casual/non-special and with the hexagons on gold surfaces one are considered.	D6
D.9	Dependence of current values on the distance between the fullerene and the contacts for a fixed voltage: $V_D = 0.4$ V. The exponential fitting performs well. Top: linear scale, bottom: semilogarithm scale.	D7
D.10	Dependence of current values on the distance between the fullerene and the contacts for a fixed voltage: $V_D = 1.6$ V. The exponential fitting performs well. Top: linear scale, bottom: semilogarithm scale.	D8
D.11	Absolute variations of current due to the presence of 1, 3, 5 NH <sub>3</sub> molecules, for distances between the contacts and the $C_{60}$ fullerene of 2.4 Å (EHT method).	D9
D.12	Absolute variations of current due to the presence of 1, 3, 5 NH <sub>3</sub> molecules, for distances between the contacts and the $C_{60}$ fullerene of 3.0 Å (EHT method).	D9
D.13	Absolute variations of current due to the presence of 1, 3, 5 NH <sub>3</sub> molecules, for distances between the contacts and the $C_{60}$ fullerene of 3.3 Å (EHT method).	D10
D.14	Absolute variations of current due to the presence of 1, 3, 5 NH <sub>3</sub> molecules, for distances between the contacts and the $C_{60}$ fullerene of 3.6 Å (EHT method).	D10
D.15	Absolute variations of current due to the presence of $3 \text{ NH}_3$ molecules, all the considered distances between the fullerene and the contacts are compared (EHT method).	D11
D.16	Absolute variations of current due to the presence of $5 \text{ NH}_3$ molecules, all the considered distances between the fullerene and the contacts are compared (EHT method).	D11
D.17	Percentage variations of current due to the presence of $1 \text{ NH}_3$ molecules, all the considered distances between the fullerene and the contacts are compared (EHT method).	D12
D.18	Percentage variations of current due to the presence of $1 \text{ NH}_3$ molecules, only the distances $2.4 \text{ Å}$ (both with the chemisorbed and the casual orientations), $2.7 \text{ Å}$ and $3.0 \text{ Å}$ are compared for clarity (EHT method). All the curves are instead reported in figure D.17.	D12
D.19	Percentage variations of current due to the presence of $3 \text{ NH}_3$ molecules, all the considered distances between the fullerene and the contacts are compared (EHT method).	D13
D.20	Percentage variations of current due to the presence of 5 $NH_3$ molecules, all the considered distances between the fullerene and the contacts are compared (EHT method).	D13

XXXII

D.21	Device current as a function of the applied voltage and the contacts distance. Red dots are the simulated points, while the surface corresponds to the exponential interpolation. Purple dots are those below the semi-transparent surface. A general good agreement is present (EHT method). Voltage up to 0.8 V only are considered.	D14
D.22	Equilibrium transmission spectrum of the $C_{60}$ molecular wire with the final sensor geometry; the DFT and EHT methods are compared	D16
D.23	Integral difference of the final ammonia sensor equilibrium transmission spectra in the cases of $3 \text{ NH}_3$ molecule. The results obtained with the two methods: DFT (blue curve) and EHT (red/orange curve) are compared. The ellipse is around the considered range of bias windows, i.e. up to $2 \text{ V}$ .	D20
D.24	Integral difference of the final ammonia sensor equilibrium transmission spectra in the cases of 5 NH <sub>3</sub> molecule. The results obtained with the two methods: DFT (blue curve) and EHT (red/orange curve) are compared. The ellipse is around the considered range of bias windows, i.e. up to 2 V	D21
D.25	Zoom-in of the current-voltage characteristics for the final sensor geometry. The two different ammonia orientations are considered along with various atmosphere constituents (EHT method). Top (a): curves at $V_D = 0.2$ V; bottom (b): curves at $V_D = 1.4$ V	D22
D.26	Top (a): Absolute current variations with sign for methane $CH_4$ and butane $C_4H_{10}$ (EHT method). Bottom (b): Absolute current variations with sign for methane $CH_4$ and butane $C_4H_{10}$ along with common atmosphere constituents (EHT method)	D23
D.27	Absolute current variations with sign for NO along with other common atmospheric chemical species (EHT method).	D24
D.28	Absolute current variations with sign for $NO_2$ along with other common atmospheric chemical species (EHT method).	D24
D.29	Absolute current variations with sign for PbCl <sub>2</sub> along with other common atmospheric chemical species (EHT method).	D25
D.30	Absolute current variations with sign for PbO along with other common atmospheric chemical species (EHT method).	D25
E.1	Absolute current variations for various atmospheric gases and for $PbSO_4$ with the two fullerene orientations: the casual one and the equilibrium chemisorption one, with hexagons toward gold (EHT method)	E1
E.2	Top (a): Absolute current variations (magnitude) due to lead sulfate single- molecule, for the different considered distances between the fullerene and contacts. Bottom (b): Absolute current variations (with sign) due to lead sulfate single-molecule, for the different considered distances between the	
	fullerene and contacts (EHT method).	E2

XXXIII

E.3	Integral difference of the final lead sulfate sensor equilibrium transmission spectra in the cases of 2 PbSO <sub>4</sub> molecule. The results obtained with the two methods: DFT (blue curve) and EHT (red/orange curve) are compared. The ellipsoid is around the considered range of bias windows, i.e. up to 2 V. The integrals were performed with trapezoidal numerical method in <i>MatLab</i> , over the bias windows from $0.1 \text{ V}$ to $4 \text{ V}$ with a step of $0.1 \text{ V}$ .	E3
E.4	Geometry labeled as "PbSO <sub>4</sub> " simply. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations)	E4
E.5	Geometry labeled as $PbSO_4$ "left-right". It corresponds to a rotation w.r.t. a vertical rotation axis. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations)	E4
E.6	Geometry labeled as $PbSO_4$ "up-down". It corresponds to a rotation w.r.t. a rotation axis parallel to the transport direction. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations)	E5
E.7	Geometry labeled as $PbSO_4$ "SO-down". The figure was generated by $ATK$ software [125], [126] (used for performing the simulations).	E5
E.8	Geometry labeled as $PbSO_4$ "Pb-down". The figure was generated by $ATK$ software [125], [126] (used for performing the simulations)	E6
E.9	Maximum absolute deviation between the cubic spline interpolation and the linear interpolation of the current values in function of the target-fullerene distance, for the various considered bias points. Notice the chosen bias point at $V_D = 0.8$ V; it is a good compromise among the possible choices. For $V_D$ grater than 1 V the current variations/oscillations are much more marked.	E7
E.10	Maximum absolute deviation between the cubic spline interpolation and the linear interpolation of the current values in function of the PbSO <sub>4</sub> concentration, for the various considered bias points. Notice the chosen bias point at $V_D = 0.8$ V; it is a good compromise among the possible choices.	E7
E.11	Current values for different PbSO <sub>4</sub> concentrations and for $V_D = 0.8$ V. Black circles: simulated values; blue curve: cubic $3^{rd}$ order spline interpolation; red/orange: quadratic interpolation. The latter is exactly overlapped to the cubic interpolation thus meaning a perfect agreement and a quadratic sensor response for $V_D = 0.8$ V	E8
E.12	Current values for different PbSO <sub>4</sub> concentrations and for $V_D = 0.2$ V. Black circles: simulated values; blue curve: cubic $3^{rd}$ order spline interpolation; red/orange: linear interpolation. Strongly non linear sensor response is present for $V_D = 0.2$ V.	E8
E.13	Current values for different PbSO <sub>4</sub> concentrations and for $V_D = 0.4$ V. Black circles: simulated values; blue curve: cubic $3^{rd}$ order spline interpolation; red/orange: linear interpolation. The sensor response for $V_D = 0.4$ V is very linear.	E9
E.14	Equilibrium transmission spectra in the case of 2 $PbSO_4$ molecules and in the case of 2 $PbSO_4$ molecules oriented in opposite directions	E9

E.15 Transmission spectrum with a PbSO<sub>4</sub> molecule for a bias  $V_D = 0.8$  V. Abscissa axis: transmission; ordinate axis: energy (eV);  $\varepsilon_{L,R}$  are the two contacts Fermi levels, and the energy values in between them correspond to the one within the bias window. The red arrows highlight the three main transmission peaks within the bias window, at energy 0.04 eV, 0.28 eV and  $0.4 \,\mathrm{eV}$ . The figure was generated by ATK software [125], [126] (used for E.16 Transmission eigenstate (full view) corresponding to the transmission eigenvalue 5.654839e-1 with quantum number QN = 0, transmission peak at energy  $E = 0.04 \,\mathrm{eV}$ , the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \,\mathrm{V}$ . The surface corresponds to an isotransmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simu-E.17 Transmission eigenstate (top view) corresponding to the transmission eigenvalue 5.654839e-1 with quantum number QN = 0, transmission peak at energy  $E = 0.04 \,\mathrm{eV}$ , the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \,\mathrm{V}$ . The surface corresponds to an isotransmission surface (smaller transmission value w.r.t. the one of figure E.6), the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations). . . . . . . E11 E.18 Transmission eigenstate (full view) corresponding to the transmission eigenvalue 2.229667e-2 with quantum number QN = 1, transmission peak at energy  $E = 0.04 \,\mathrm{eV}$ , the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \,\mathrm{V}$ . The surface corresponds to an isotransmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simu-E.19 Transmission eigenstate (top view) corresponding to the transmission eigenvalue 2.229667e-2 with quantum number QN = 1, transmission peak at energy  $E = 0.04 \,\text{eV}$ , the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \,\mathrm{V}$ . The surface corresponds to an isotransmission surface (smaller transmission value w.r.t. the one of figure E.6), the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations). . . . . . . E12 E.20 Transmission eigenstate (side view) corresponding to the transmission eigenvalue 8.373195e-1 with quantum number QN = 0, transmission peak at energy  $E = 0.28 \,\mathrm{eV}$ , the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8$  V. The surface corresponds to an isotransmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).  $\ldots$   $\ldots$   $\ldots$   $\ldots$   $\ldots$ EI2

E.21	Transmission eigenstate (full view) corresponding to the transmission eigenvalue 2.119902e-1 with quantum number $QN = 1$ , transmission peak at energy $E = 0.28 \text{ eV}$ , the geometry is the one with a single PbSO <sub>4</sub> molecule and with a bias voltage $V_D = 0.8 \text{ V}$ . The surface corresponds to an isotransmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations).	E13
E.22	Transmission eigenstate (full view) corresponding to the transmission eigenvalue 6.899972e-1 with quantum number $QN = 0$ , transmission peak at energy $E = 0.4 \text{ eV}$ , the geometry is the one with a single PbSO <sub>4</sub> molecule and with a bias voltage $V_D = 0.8 \text{ V}$ . The surface corresponds to an isotransmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations).	E13
E.23	Transmission eigenstate (side view) corresponding to the transmission eigenvalue $3.125305e-1$ with quantum number $QN = 1$ , transmission peak at energy $E = 0.4 \text{ eV}$ , the geometry is the one with a single PbSO <sub>4</sub> molecule and with a bias voltage $V_D = 0.8 \text{ V}$ . The surface corresponds to an isotransmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations).	E14
E.24	Transmission eigenstate (full view) corresponding to the transmission eigenvalue $8.513583e-2$ with quantum number $QN = 2$ , transmission peak at energy $E = 0.4 \text{ eV}$ , the geometry is the one with a single PbSO <sub>4</sub> molecule and with a bias voltage $V_D = 0.8 \text{ V}$ . The surface corresponds to an isotransmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations).	E14
E.25	Transmission eigenstate (top view) corresponding to the transmission eigenvalue 5.594843e-1 with quantum number $QN = 0$ , transmission peak at energy $E = 0.04 \text{eV}$ , the geometry is the one with two opposite oriented PbSO <sub>4</sub> molecules and with a bias voltage $V_D = 0.8 \text{V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations).	E15
E.26	Transmission eigenstate (top view) corresponding to the transmission eigenvalue 8.684692e-1 with quantum number $QN = 0$ , transmission peak at energy $E = -0.16 \text{ eV}$ , the geometry is the one with two opposite oriented PbSO <sub>4</sub> molecules and with a bias voltage $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations).	E15
E.27 Transmission eigenstate (top view) corresponding to the transmission eigenvalue 7.872365e-1 with quantum number $QN = 0$ , transmission peak at energy $E = 0.16 \text{ eV}$ , the geometry is the one with two opposite oriented PbSO <sub>4</sub> molecules and with a bias voltage $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations).	E16	
--	-----	
E.28 Transmission eigenstate (top view) corresponding to the transmission eigenvalue 6.032937e-2 with quantum number $QN = 1$ , transmission peak at energy $E = 0.16 \text{ eV}$ , the geometry is the one with two opposite oriented PbSO <sub>4</sub> molecules and with a bias voltage $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations).	E16	
E.29 MPSH (zoomed in) for the HOSO level of the system $C_{60}$ + Ar (side view).		
The considered bias point is $1.6 \text{ V}$ . The figure was generated by $ATK$ software [125], [126] (used for performing the simulations)	E18	
E.30 Transmission eigenstate (full view) corresponding to the main transmission eigenvalue with quantum number $QN = 0$ for the transmission peak at energy $E = 0.32 \text{eV}$ , and with a bias voltage $V_D = 1.6 \text{V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations)	E19	
E.31 MPSH for the LUSO level of the system $C_{60}$ + Ar (side view). Notice again the argon orbitals polarization. the considered bias point is 1.6 V. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations)	E19	
E.32 Transmission eigenstate (side view) corresponding to the main transmission eigenvalue with quantum number $QN = 0$ for the transmission peak at energy $E = 0.2 \text{ eV}$ , and with a bias voltage $V_D = 0.4 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations)	E20	
E.33 Transmission eigenstate (side view) corresponding to the second transmission eigenvalue with quantum number $QN = 1$ for the transmission peak at energy $E = 0.2 \text{ eV}$ , and with a bias voltage $V_D = 0.4 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by $ATK$ software [125], [126] (used for performing the simulations)	E20	
E.34 Absolute current variations due to the presence of the $PbSO_4$ molecule for the case of the wire sensor and the transistor-based one. $\ldots \ldots \ldots $	E21	
E.35 Percentage current variations due to the presence of the $PbSO_4$ molecule for the case of the mine sense and the transition hand are	201	
for the case of the wire sensor and the transistor-based one E	121	

E.36	Current-voltage characteristics for 0, 1, and 2 $PbSO_4$ molecules nearby the conducting channel, in the case of the gated sensor. Notice that a good variation occurs among them and thus it is expected the sensor to be able	EOO
E 97	Comment explositions due to 1 and 2 DECO medicular membra the second station	$\mathbf{E}ZZ$
E.37	channel, in the case of the gated sensor. $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	E22
E.38	Sensor current in function of the number of $PbSO_4$ molecules for $V_D = 0.4$ V. Black circles: simulated data; blue line: spline interpolation; red/orange line: straight line interpolation.	E23
E.39	Sensor current in function of the number of $PbSO_4$ molecules for $V_D = 0.8$ V. Black circles: simulated data; blue line: spline interpolation; red/orange line: straight line interpolation.	E23
E.40	Sensor current in function of the number of $PbSO_4$ molecules for $V_D = 0.8$ V. Black circles: simulated data; blue line: spline interpolation; red/orange line: second order polynomial interpolation.	E24
E.41	Sensor current in function of the number of $PbSO_4$ molecules for $V_D = 1$ V. Black circles: simulated data; blue line: spline interpolation; red/orange line: straight line interpolation.	E24
E.42	Sensor maximum deviation from linearity in function of the applied bias, for different $PbSO_4$ concentrations. It is the maximum difference between the straight line interpolating curve and the spline $3^{rd}$ order interpolating curve. Notice the low error at $0.8 V. \ldots \ldots \ldots \ldots \ldots$	E25
E.43	Sensor current in function of the PbSO <sub>4</sub> molecule distance from the sensor for $V_D = 0.8$ V. Black circles: simulated data; blue line: spline interpolation; red/orange line: straight line interpolation	E25
E.44	Sensor maximum deviation from linearity in function of the applied bias, for different $PbSO_4$ distances. It is the maximum difference between the straight line interpolating curve and the spline $3^{rd}$ order interpolating curve. Notice the low error at $0.8 \text{ V}$ .	E26
E.45	<i>I-V</i> characteristics obtained with <i>ATK</i> and with <i>Huckel-IV 3.0</i> tool. The ellipse highlight the chosen bias point, i.e. 0.8V. Notice the different values of the fitting parameter $V_c$ . For $V_D = 0.8$ V the best agreement is obtained with $V_c = 0.625$	E26
G.1	Drain voltage in function of time for the circuit of figure 9.20. The interpolating straight lines are also shown, and the red circle highlight their intersection point, useful to determined graphically the time constant	G28
G.2	Source voltage in function of time for the circuit of figure 9.20. The interpolating straight lines are also shown, and the red circle highlight their intersection point, useful to determined graphically the time constant	G28
G.3	Drain current in function of time for the circuit of figure 9.20. The interpolating straight lines are also shown, and the red circle highlight their intersection point, useful to determined graphically the time constant	G29

XXXVIII

H.1	I-V characteristics with and without the NO molecule both in the case of	
	the wire sensor and in the case of gated one (EHT method)	H1
H.2	Current variations in the gate sensor with both the lead sulfate $PbSO_4$	
	and the nitric oxide NO, for all the (main) possible orientations of such	
	molecules. Notice the behavior at 0.8 V.	H2
H.3	Sensor maximum deviation from linearity in function of the applied bias,	
	for different NO concentrations. It is the maximum difference between the	
	straight line interpolating curve and the spline $3^{rd}$ order interpolating curve.	
	Notice the low error at $0.8 \text{ V}$	H2
H.4	Current values for different NO concentrations and for $V_D = 0.8$ V. Black	
	circles: simulated values; blue curve: cubic $3^{rd}$ order spline interpolation;	
	red/orange: linear interpolation	H3
H.5	Current values for different NO distances from the sensor and for $V_D =$	
	$0.8$ V. Black circles: simulated values; blue curve: cubic $3^{rd}$ order spline	
	interpolation; red/orange: linear interpolation	H3

## Acronyms

2DLM 2D (Two-Dimensional) Layered Material **ANN** Artificial Neural Network B88 Becke functional B3LYP Becke-3 parameters-Lee-Yang-Parr functional **BLYP** B88-LYP functional CMOS Complementary Metal Oxide Semiconductor **CNDO** Complete Neglect of Differential Overlap **CNT** Carbon NanoTube **CNT FET** Carbon NanoTube FET **DFT** Density Functional Theory **DIBL** Drain Induced Barrier Lowering DNA DeoxyriboNucleic Acid **DRAM** Dynamic Random Access Memory  $\mathbf{DZ}$  Double Zeta **DZP** Double Zeta Polarized EHT Extended Hückel Theory **FD** Finite Difference method **FEM** Finite Element Method **FET** Field Effect Transistor **FinFET** Fin Field Effect Transisotr

GAA Gate All-Around	
---------------------	--

GAA FinFET Gate All-Around FinFET

**GGA** Generalized Gradient Approximation

 ${\bf GNR}$ Graphene Nano-Ribbon

**GNR FET** Graphene Nano-Ribbon FET

GTO Gaussian Type Orbitals

HD High Density process / low power process

 ${\bf HF}$  Hartree-Fock method

**HP** High Performances process

**IC** Integrated Circuit

 ${\bf IR}~{\rm InfraRed}$  radiation

**IRDS** International Roadmap for Devices and Systems

**ITRS** International Technology Roadmap for Semiconductors

LCAO Linear Combination of Atomic Orbitals

LDA Local Density Approximation

LSDA Local Spin Density Approximation

LTI Linear Time Invariant (system)

 ${\bf LUT}$  Look Up Table

LYP Lee Yang Parr functional

MCBJ Mechanically Controlled Break-Junctions

 ${\bf MES}\,$  Molecular Electronic Sensor

**NEGF** Non-Equilibrium Green's Function

**NEMS** Nano Electro-Mechanical System

**MolFET** Molecular Field Effect Transistor

**MOSFET** Metal Oxide Semiconductor Field Effect Transistor

NW Nano-Wire

 $\mathbf{NW}\ \mathbf{FET}$  Nano-Wire FET

**OPTX** OPTimized eXchange functional

**PBE** Perdew Burke Ernzerhof functional

 $\ensuremath{\textbf{PEC}}$  Perfect Electrical Conductor

 $\mathbf{PKZB}$ Perdew-Kurth-Zupan-Blaha functional

 ${\bf ppb}\,$  parts per billion

 $\mathbf{ppm}$  parts per million

**ppt** part per trillion

 ${\bf PZ}$ Pentuple Zeta

 ${\bf QD}\,$  Quantum Dot

 ${\bf QFT}$ Quantum Field Theory

 ${\bf QZ}$ Quadruple Zeta

 $\mathbf{QZP}\ \mbox{Quadruple}$ Zeta Polarized

 ${\bf QW}$ Quantum Well

 ${\bf QWire}\,$  Quantum Wire

 ${\bf RNA}$ Ribo<br/>Nucleic Acid

 ${\bf SAM}$  Self-Assembled Monolayer

 ${\bf SCE}$  Short Channel Effect

SCF Self Consistent Field procedure/approximation

 ${\bf SET}$  Single Electron Transistor

 ${\bf SGF}$  Surface Green's Function

 ${\bf Si\text{-}NW}$ Silicon Nano-Wire

**SNR** Signal to Noise Ratio

**SS** Subthreshold Slope (figure of merit)

 ${\bf STM}\,$  Scanning Tunneling Microscopy

 ${\bf STO}$ Slater Type Orbitals

XLIII

**TFET** Tunnel FET

**TPSS** Tao-Perdew-Staroverov-Scuseria functional

 ${\bf TZ}$  Triple Zeta

 ${\bf TZP}$  Triple Zeta Polarized

**ULSI** Ultra Large Scale of Integration

 ${\bf VLSI}$  Very Large Scale of Integration

 ${\bf VSXC}$ Voorhis-Scuseria eX<br/>change-Correlation functional

 ${\bf VOC}$ Volatile Organic Compound

# Chapter 1 Introduction and motivations

The purpose of this first introductory chapter is to provide a brief overview of both the background and the motivations behind this work, and also to introduce the basic lexicon and few preparatory concepts that will be useful in the rest of this thesis. In section 1.1 it is briefly introduced what "molecular electronics" is, and why during last decades it got great attention at research level. In section 1.2 it is explained what the term "molecular electronic sensor" refers to and in which sense it is generally different from "molecular sensor". Moreover the basic working principle of molecular electronic sensors is qualitatively introduced. Then, in section 1.3, the reasons that motivated this work and the background in which it finds place are clarified; and, finally, the structure of the rest of this work is illustrated.

#### 1.1 Conventional electronics and beyond CMOS: toward molecular electronics

Since the invention of the Integrated Circuit (IC) technology and the fabrication of the MOSFET more than fifty years ago, a tremendous and incessant progress, in terms of electronic devices design and fabrication processes, allowed to continuously reduce the physical dimensions of transistors, reaching nowadays the so-called Ultra Large Scale of Integration (ULSI), in which the number of transistors integrated in a single chip can be far beyond one billion [1]. This was possible thanks to the introduction of the CMOS logic (the negligible standby power of complementary MOS logic allowed to overcome the  $10^4$ devices per chip opening the way for the VLSI era), and to the steady improvement of lithography technologies [2]. The main advantage of the transistor scaling lies in the larger amount of devices, and thus functional blocks, that can be integrated in a single chip, making use of almost the same number of photolitographic masks, thus reducing the cost per unit while increasing the functionalities. Together with the higher packing density, other advantages in shrinking the transistor dimensions are the higher circuit speed and performances and the lower power dissipation per device (nevertheless since also the device sizes are scaled, the resulting power density may be dramatically high, depending on the specific type of adopted scaling policy) [2].

The scaling process empirically followed the well known Moore's law, firstly introduced by Gordon Moore in 1965, that stated that the number of transistors that could be put on a single chip was doubling every year [3]. Surprisingly, this trend continued for many years (and decades!) with only a small slowing down: the number of transistors integrated in a single IC doubled every 18 months or even every 2 years or so [4]. The reason for this slowing down of the scaling pace is double: from the system standpoint a great challenge in scaling is currently given by the power dissipation (one refers to "dark silicon era" meaning that only a portion of the chip can be switched on at the same time due to power constraints) and interconnection bandwidth [5]; while from the other side there are also technological drawbacks, beside the above mentioned advantages, in reducing the transistor sizes, that required several smart device improvements [2]. In particular, even if the basic operating principles of large and scaled MOSFETs are the same, the small ones are affected by non-idealities such as Short Channel Effect (SCE), threshold voltage roll-off, Drain Induced Barrier Lowering (DIBL), velocity saturation, high field effects (e.g. gate oxide breakdown) and so on... As mentioned above, these non-ideal effects required for careful device design strategies, along with technology improvements, in order to be counteracted and overcome [2]. These device ameliorations gave rise to the current device structure: the so-called FinFET [2], [5].

In addition to these effects, and due to the nanometric scale dimensions of current devices, another class of important non-idealities must have been considered, i.e. the quantum mechanical effects, such as the increasing tunneling through the gate dielectric or the carrier density shape modifications due to the quantum confinement [2]. Even more important is a fundamental limit that is going to be reached soon from the semiconductor industries: with the approaching of the channel physical length to the typical thermal wavelength of electrons (that is around 8 nm at room temperature) there will be no way of controlling the electron flow from the source to the drain, and thus to make a functioning transistor. Indeed if the source to drain energy barrier thickness is less than the electron de Broglie wavelength, the electron direct tunneling probability from source to drain would be so high (it is an exponential phenomenon with the barrier thickness - see e.g. chapter 2) to make impossible to switch-off the transistor [2].

Currently, the last technological node that seems will go into production soon, appears to be the 5 nm one, as expected from the last International Roadmap for Devices and Systems (IRDS) reports [5], [6], [7], and as announced from some companies (e.g. TSMC [8] that proclaimed volume production in 2020 and Samsung Electronics [9] that plans to put it in full operation in the second half of 2021). In the IRDS 2020 report it is expected the 5 nm node to have a gate physical length (i.e. source to drain spacing) of 18 nm for High-Performance (HP) process and 20 nm for High-Density/low-power (HD) process [5]. Again in this report it seems the next technological node (expected in 2022) will be the 3 nm one with a gate length of 16 nm for HP and 18 nm for HD. Notice that the physical spacing between source and drain in these technological nodes is greater than the previously mentioned limit of 8 nm, due to the electron room temperature de Broglie wavelength. Finally, again in the IRDS 2020 report, previsions for future trends up to 2034 are made, in which the source to drain spacing is stuck at 12 nm [5].

In light of the above mentioned fundamental and intrinsic limit, it is legitimated the question: "what will be next?". Indeed it appears that sooner or later an alternative to

conventional silicon devices will be necessary. Nobody can answer today to this question, and what the future technology will be depends on many factors, among which the cost will very likely play a central role. Nevertheless the last International Technology Roadmap for Semiconductor (ITRS) report in 2015 [4] and the successive IRDS ones [7], [6] and [5] (in 2017, 2018 and 2020 respectively) try to summarize the possible answers to that question in their sections named "Beyond CMOS". The driving interest of the research in these innovative beyond CMOS technologies is to maintain the circuit scaling cadence and to sustain the performance gain started with CMOS scaling process [4]. This is referred as "more Moore" in the ITRS and IRDS reports. Next to this attempt, also another reason is behind this front of research, that is the "more than Moore", i.e. the trend of accomplishing an heterogeneous integration of multiple functions (not only information processing and storing but even its transmission/reception or sensing and measuring, etc...) as a new paradigm for system architectures [4], [5]. Consequently the beyond CMOS research is not only carried on at device level, but all abstraction levels are simultaneously involved. Novel computing paradigms for beyond CMOS technologies were investigated in the last years [7]. [6], [5], and some of them (such as big data, internet of things, artificial intelligence, neural networks, etc...) require high performance and efficiency which is increasingly difficult to fulfill with the saturating "more Moore" CMOS technologies [5].

During the last decades, the explored and proposed beyond CMOS solutions are many and various, and the current landscape is extremely ample [5]. In figure 1.1 is summarized a possible taxonomy of emerging beyond CMOS memory devices (top) and there is also a comparison among few of them (bottom-left); while figure 1.2 summarizes a possible taxonomy of emerging beyond CMOS logic devices. As evident several solutions exist in both the fields, even if many of them are just "emerging" proposal, in the sense that they were proved at research level but advantages w.r.t. CMOS may be at moment only potential, i.e. at the present there may be important technological limits that are still unsolved. Nevertheless they are somehow promising or interesting enough to be still considered as a valid research topics for the next years [5]. An introduction to all of them falls outside the purposes of this work (interested readers can refer directly to the IRDS 2020 report [5] and references therein). However they constitute the current background in which "molecular electronic sensors", main subject of this work, find place.

ITRS and IRDS reports clearly state that the technologies they consider are somehow promising substitute of conventional CMOS at short-term, as bridging technologies between current CMOS and future beyond CMOS, but nothing is said about the long-term beyond CMOS technologies [5]. Indeed it is reasonable supposing that the transition between conventional electronics and the future one will be gradual, with, at the beginning, a coexistence between CMOS and beyond CMOS technologies, until (for some reasons) one technology will "win" above the others and will become the dominant one. Thus at the beginning, i.e. during the next years, an important or even discriminant factor for the success of new technologies will likely be the compatibility with standard CMOS technology and with standard CMOS architectures, since a coexistence even within the same IC, will be very probable [5], [10]. Nevertheless this is not the only feature to be considered in comparing the beyond CMOS technologies. Several factors should be accounted for, see e.g. fig. 1.1 (bottom-left), such as the already mentioned process cost, the performances in terms of speed and dissipated power (or energy efficiency), the scalability (that should be -at least potentially- superior to current CMOS one), etc... At least some of these features are required to a new technology to be further considered as a potential substitute of CMOS, and this holds true for all the technologies reported in figures 1.1 and 1.2.



Figure 1.1: Possible taxonomy of emerging memory devices and a comparison among few of them (bottom-left) in terms of relevant features for a future commercialization. Black line: FeFET memory; grey line: FTJ memory; red line: ReRAM memory; green line: Mott memory; purple line: macromolecular memory; orange line: molecular memory; blue line: carbon-based memory. The classification is coherent with the one reported in [5].

In light of this, promising new technologies for the next future, i.e. at short-term, seem to be e.g. the Tunnel FET (TFET), the Nano-Wire FET (NW FET) and the Carbon NanoTube FET (CNT FET), etc... The TFET appears able to overcome the CMOS thermal intrinsic limit of  $60 \,\mathrm{mV/dec}$  for the subthreshold slope (SS). While there is no difficulty in switch it off (contrary to conventional CMOS) there are at the moment still difficulties in achieving an enough large ON current (due to the ON state barrier through which tunneling happens, that is too wide thus leading to a small tunneling probability - see also chapter 2). It presents also optimal compatibility with CMOS processes and architectures. For memories, the landscape is more extended and ample and here I would just like to cite the macromolecular memories, in which the basic cell is essentially a capacitor whose dielectric is a polymer (i.e. a molecular chain), eventually embedding small molecules or nanoparticles (e.g. the  $C_{60}$  fullerene that will be cited again in next chapters of this work). The logic state ("0" or "1") can be stable at room temperature and present a resistive, ferroelectric or capacitive nature depending on the specific nature of the sandwich [5]. The programming power (tens of nW) seems to be enough low for extremely low-power applications [5]. An evolution toward miniaturization of these memories are the macromolecular ReRAM or even the molecular memories. The latter are memory

Beyond CMOS Memory Technologies

applications of the so-called molecular Single Electron Transistor (SET), that will be cited again in next chapters of this work.



Figure 1.2: Possible options for emerging logic devices. The devices are differentiated according to whether the structure or the material are conventional or innovative (abscissa axis) and whether the information representation is based on electron charge or on some non-charge entity (ordinate axis). Only three groups are possible since a conventional FET material and structure is intrinsically a charge-based device. The classification is in accordance with the one from [5].

As mentioned, the ample set of all these possible devices essentially constitutes the wide landscape in which nowadays molecular electronics and molecular electronic sensors find place. Before going on in clarifying better what molecular electronics is, where it is precisely placed in terms of its technology features and why it is intimately linked with molecular electronic sensors, a deeper look to the capabilities that are required to novel beyond CMOS technologies is given.

For many years the technology advancements were driven by memories (DRAMs especially), in which the demand for increased capability drove to a huge research effort in scalability of the basic cells and thus transistors. Instead during the last years the driving force gradually became the processing unit, requiring for extremely low power functioning and increased cache memories capability and performances [5]. In these terms, the novel logic switches, in order to be considered potential replacements for current CMOS ones, should possess one or more of the following fundamental capabilities [5]:

- scalability: increase in the device density (and thus decrease the cost) beyond that achievable by ultimately scaled CMOS
- speed: increase beyond CMOS in speed performances (switching speed)

- power: reduction of the switching energy and thus of the overall power consumption
- novel computing schemes: enabling of innovative computing paradigms or information processing functions that cannot be performed as efficiently with conventional CMOS

Molecular electronics gained particular attention during last three decades from scientific community because of its intrinsic interesting capabilities [11], [12]. In December 2005, the ITRS officially noted that molecular electronic components will need to be integrated into silicon manufacturing in order for Moore's law to continue to hold true [13], [11]. With the term "molecular electronics", sometimes also called "moletronics" [11], [14], it is conventionally intended that field of electronics in which the fundamental units for computing are devices based on single molecules or, alternatively, small packets of molecules [15]. It is an interdisciplinary field that includes physics, chemistry, materials science and engineering [14]. In particular all the electronic components can be realized by means of single (or small packets of parallel) molecules, thus transistors, diodes, resistors, capacitors, etc... can be all implemented as molecular devices [14].

As a title of example in figure 1.3 is reported a scheme of a molecular transistor. Notice that source, drain and gate contacts are quite conventional, a gate dielectric is still present (in general a front and a back gates can be present) and the main distinctive feature is that the channel is constituted by a single molecule, chemically bonded with the source and drain contacts and "suspended" above the gate dielectric. Thus the active portion of the device is a single molecule.



Figure 1.3: Example of a molecular FET structure. In this case the PDT (phenyl dithiol) molecule is used. The yellow atoms are the gold source and drain contacts; the two dark yellow atoms are the sulfur anchoring groups; grey atoms are carbon and white hydrogen. The light purple region is the gate insulator (continuum approximation) while the white/light grey region is the metal gate contact. The figure was generated in *Quantum-Wise ATK* software.

Sometimes with the term "molecular electronics" is indicated a much wider class of devices, including some macromolecular-based (or polymer-based) devices and transistors, and also optoelectronic devices such as organic light-emitting displays (or even liquid crystal displays), organic photovoltaic devices, chemical sensors and so on... that are built starting from (organic) molecular processes, but present a much larger active region than the one of small molecule devices, like the transistor mentioned so far [14], [16]. These devices were the first practical results of research on the field of molecular electronics mainly pioneered by Forrest Garret [11] during the 1980s.

The use of single molecules as basic building blocks for realizing electronic devices potentially represents the next (or even the ultimate) limit of miniaturization of electronic devices, beyond the CMOS intrinsic limit, and up to the basic "bricks" of matter [17], [18]. Indeed molecules are the fundamental entities of matter, or better of compound materials (atoms should be more correctly the fundamental basic entities of matter but they are so only for single elements). And this is more correct the more the employed molecules are small, e.g. the benzene ring with a dimension of the order of 1 nm (while it may be not true at all, as already mentioned, for the so-called macromolecules that can be hundreds or thousands of times bigger than the benzene ring - think e.g. to proteins, enzymes, DNA, or bio-macro-molecules in general).

Since the beginning of the century several molecular device prototypes were demonstrated in literature [12], [18], even if, actually, the idea of making electronic devices by means of single molecules is not so young. The term "molecular electronics" was coined in 1958 (even if the meaning was slightly different: it was referred to a bottom-up material engineering from molecules to devices), when the US Air Force and Westinghouse Electric Company adopted it to describe their radical joint research program, that unfortunately was a failure [11]. In the mid 1970s the term "molecular electronics" went back to vogue (with the conventional meaning explained above) and in 1974 the first molecular rectifier (actually the first single molecule electronic device) was proposed [19]. This was a purely theoretical device, in which an isolated molecule was supposed to present rectifying properties. The first prototypes were instead successfully realized only after more than twenty years, because of technological limits [11]. The current technology allows for the fabrication of single molecule devices or even for the simultaneous creation of thousands of them, with a reasonable reliability and yield, even if currently the technological process variability is still the main issue in molecular electronics [15], [17], [12], [16], [18]. For example, the manipulation of single molecules is possible by means of Scanning Tunneling Microscopy (STM) methods, that make possible even to act on a single molecule, e.g. by breaking or modifying it to perform the synthesis of specific structures [12], [16], [20]. Moreover the synthesis and anchoring (even with the desired orientation) of millions or billions of molecules is made possible by means of Self-Assembled Monolayer (SAM) techniques, in which a sequence of chemical reactions, under given conditions, is able to self-assembly molecules in between break-junctions or above a substrate [15], [18]. From the standpoint of contacting the molecule the difficulty is mainly due to the creation of reliable and clean (typically metal or graphene) contact gaps, of the order of the nm. For example this is achievable by means of Mechanically Controlled Break-Junctions (MCBJ) or through controlled electromigration, electroburning or etching processes [12], [18], [21], [22], [23]. Hence at moment, after more than twenty years of ameliorations in the techniques for the construction of molecular devices, it is possible to fabricate single molecule devices with a yield of the order of  $25\% \div 40\%$  (better performances are often obtained with graphene contacts) [21], [22], [23]. As mentioned, the low yield and the high process variations are at the moment the main unsolved issues in molecular electronics from the technological standpoint, leading to low reliability of fabricated devices. The high process variations, moreover, lead to a wide variance on measured current-voltage characteristics. Other problems concern the large parasitics, especially for the interconnection, that are actually the main Achilles' heel of this technology (precisely like in the ultra-scaled CMOS case). Another very remarkable drawback is the usually poor  $I_{ON}/I_{OFF}$  ratio (for conventional molecules it is of the order of few tens [12] even if improvements up to few hundreds seem possible [24], [25]) and the too low  $I_{ON}$  value. Instead, the main potential advantage w.r.t. to CMOS is the huge scalability: molecules as fundamental entities of matter push the scalability to the ultimate intrinsic limit of miniaturization, potentially beyond the 8 nm thermal limit of silicon devices [11], [15]. The SAM processes are compatible with the conventional CMOS process. Even if they require few extra steps to be performed w.r.t. to standard CMOS process, these extra steps are generally few and can be performed such that the remaining steps of standard processes are not affected at all [18]. Moreover the parallel and simultaneous fabrications of billions of molecular devices, accessible with the SAM processes, allows to potentially further decrease the cost per unit below the CMOS one. Due to the small dimensions and currents, molecular devices have other potential advantages w.r.t. CMOS: they seem to be intrinsically low power, even if compared with conventional CMOS [14], [24], [12]; and moreover due to the small amount of electrons (thus mass) that are moved through a so tiny device, molecular electronic components are potentially faster that CMOS ones (potentially smaller intrinsic relaxation times), even if parasitics constitute currently a big conflicting effect to this benefit. In the words of Mark A. Reed and James Tour: "molecular electronics is the ultimate step in small, cheap and fast" [11]; nevertheless, mainly due to the previously cited technological still unsolved problems, these are currently only potential advantages. Table 1.1 summarizes the molecular electronics pros and cons illustrated up to now.

 Table 1.1: Advantages and drawbacks of moletronics (i.e. molecular electronic technology) w.r.t. conventional CMOS technology.

Advantages of moletronics w.r.t. CMOS	Drawbacks of moletronics w.r.t. CMOS		
huge scalability	process variations		
low cost (thanks to SAM)	low yield and reliability		
CMOS process compatible	large parasitics		
low power	poor Ion/Ioff ratio		

In summary, in terms of the previously discussed novel technology capabilities, molecular electronics presents:

- scalability: far beyond the conventional CMOS
- speed: potentially faster than CMOS, still very limited
- power: potentially lesser than CMOS, still limited

 novel computing paradigms: molecular electronics open the way to several interesting new processing principles, e.g. in neuromorphic system [11], [26]. The main strong point in this direction seems to be the possibility of synthesizing *ad hoc* organic molecules, able to perform innovative basic operations, intended as the basis for the new computing paradigm [11], [26].

Currently molecular electronics seems to catch the attention as potential beyond CMOS technology at long-term, in the words of Mark A. Reed (2009) [11]:

"Even though in many ways I was responsible for the generation of this new incarnation of molecular electronics, I'm a critic. Because I don't see it going into electronic devices in the future. Yet. If I'm going to take my money today, I'm going to put it on silicon. But that doesn't mean that I don't think that there's potential. [...] My job description (unlike someone at Intel) is to explore the physics, explore the potential over a lifetime. So my time horizon is 20, 30, 40 years. [...] On top of that, there's an additional part of my job description, which is [...] is there any important physics to be learned from it?"

Indeed even if the initial goal of molecular electronics was to effectively substitutes the conventional CMOS devices, due to the above discussed drawbacks, it resulted clear that, at least at short-term, it would have been not possible to successfully accomplish this task [15]. This is the main reason why molecular electronics does not assume a central role in the last ITRS and IRDS reports (that are focused on short-term promising technologies) [4], [5]. Nevertheless nobody can today know what will happen at long-term, and if the molecular electronics technological limits and disadvantages will be overcome, leading to a much better promising technology w.r.t. CMOS one, or not.

Moreover, the research in this field led to important irrefutable achievements: it opened the way to a set of technologies aimed in the development of novel molecular devices that find place in several potential field of applications [15]. Molecular electronic sensors are examples of this. The developed technological processes and techniques for molecular electronics are exploitable for building a new class of sensing devices that became subject of research in the last few years: the "molecular electronic sensors" [22], [23], [27], [28], [29], [30], [31]. They are also the subject of this entire work. A molecular electronic sensor is essentially a molecular wire (i.e. a molecule or a packet of molecules in between two contacts) or a molecular transistor, in which the conductance of the molecular channel, the device capacitance, etc.. are changed depending on the presence or not of a target substance or chemical species (e.g. gas sensor). In general they can also sense the temperature, the light (even in the far InfraRed -IR- gap) and other chemical-physical quantities [22], [27], [29], [31], [32].

Molecular electronic sensors will be presented more in detail in the next section, and then they will be widely considered in the rest of this work. Moreover they are a possible short-term answer to the "more than Moore" trend, allowing for hybrid integration of molecular sensors along with conventional CMOS electronics within the same IC, to the end of performing the sensing and the post-processing of several chemical-physical quantities in a unique low-cost ultra-scaled system [10]. In conclusion, the constant and incessant scaling pace during the last sixty years promoted the research not only in the silicon industry field but even in the beyond CMOS field. In a very rich, prosperous and ample landscape, molecular electronics represents only a possibility among the others for the long-term future of ultra-scaled electronics. At the same time the theoretical and experimental research in this field opened the way to the fabrication of sensors, that can be accessed at short-term end, for the advancements in the "more than Moore" trend. They are also a first potential market arrival point for molecular electronics, able to potentially become a driving force for the research in this fascinating field.

#### **1.2** Molecular electronic sensors

The purpose of this section is to provide an overview about molecular electronic sensors and the context in which they find place today, in terms of currently used sensing devices. As mentioned at the end of the previous section, the recently developed both theoretical and experimental techniques and technologies for molecular electronics (beyond the photolithography limit) allowed for the fabrication of single molecule devices (or even small packets of molecules), to be used like conventional electronic devices (both digital and analog) or like sensing devices. The latter application is briefly introduced in this section and it is the subject of the rest of this work, widely investigated in the next chapters.

A molecular electronic sensor (sometimes shortened MES) is a molecular wire, i.e. a single molecule or a packet of molecules in between two contacts, or alternatively a molecular transistor, i.e. a molecular wire with one or more electrostatically coupled gate contacts, in which the channel conductance (or sometimes capacitance or other physical properties) is suitably and uniquely changed by the detection of chemical or physical events, such as the presence of a given chemical compound in proximity of the channel (gas sensor) or alternatively chemically bonded with the channel (chemical compound sensor for interacting gases, liquids etc...), or the absorption of a photon at a given wavelength by the device, or again the change in the relative ambient humidity, temperature, and so on... Even single electron charge detection or more in general the proximity electrical charge detection is possible. Examples of MES, from which the above reported definition was derived, are reported in literature during recent years, e.g. [21], [22], [23], [32], [33], [34], [35], [36], [37], [38], [27], [28].

It is important that regardless of the specific chemical/physical phenomenon that produce the MES channel conductance variation, the sensor or device physical model for transport is always the same, and it coincides with the physical model for transport in mesoscopic systems (i.e. in that systems small enough to make classical physical out of its regime of validity but big enough to make a standard quantum mechanical approach unmanageable [39]). The physical model for transport in mesoscopic systems will be investigated more in details in the chapters of part I of this work. Thus once the final details of the molecular conducting channel are known, the transport calculations will be performed always in the same manner. The differences from an application to another are mainly two: the specific molecule used as conducting channel for a specific MES, and the physical or chemical event that causes the variation in the channel conductance (or device capacitance, etc...). Concerning the employed molecule for the MES, depending on its specific electronic and transport features different conductive behaviors may exist [12], [17], [15], [14], [40], [41], [24], [25], [42]. The specific molecule is not the only variable that influences the transport. Also the contact material (e.g. metal, graphene, etc...), its quality or orientation and the way through which the molecule is anchored (the anchoring group) to the contacts (and if the anchoring is of good quality or strong/weak) influence the transport features [12], [43], [44], [45], [33], [46]. Instead, concerning the physical or chemical phenomenon at the basis of the conductance variation, each specific case is different depending on the particular event that should be detected. In the case in which some physical parameters such as temperature or humidity are to be detected, the possible range of values should be considered during calculations (e.g. the temperature will affect the Fermi-Dirac statistics and thus the occupation of the electronic states within the channel) and the corresponding conductance sensitivity is easily found. In other cases the presence of an electrical charge in proximity of the channel can affect the conduction due to Coulomb interaction with the electrons within the channel, or the absorption of a photon at a specific wavelength can vary the number of carriers that take part to the conduction thus changing the resulting electrical current (exactly like in conventional optoelectronic devices). Again, the creation of a chemical bond between a target molecule and the channel molecule will obviously change the channel transport properties thus resulting in a current variation. From the standpoint of the physical/chemical event to be detected, the simplest case (along with the temperature or humidity variation) is the one in which the presence of a target chemical compound in proximity of the molecular channel of the sensor makes varying its conductance in an appreciable way, due to weak chemical/physical interactions such as the van der Waals ones. The latter is essentially the only case considered in this work. Notice that this could be the case in which a barely chemically interacting molecule is used as conducting channel, and it interacts through van der Waals forces with a target chemical substance, thus leading to a gas sensor [23], [32], [33], [34].

The MES functioning principle is quite similar to the conventional FETs-based sensor that constitute the current state of art in electronic sensors or bio-sensors [30]. For example in a GNR FET based gas sensor the detection of the target substance is possible because of the conductance modulation due to direct interaction between the graphene nano-ribbon (i.e. the FET channel) and the target molecule (through van der Waals interaction or through "chemisorbed" interaction - i.e. with the creation of a chemical bond between the surface and the adsorbate [47], that is the target molecule) [48], [49], [50]. Otherwise the detection of whatever chemical compound or substance in gas or liquid solution is possible by means of conventional CMOS/MOS FETs, floating gate FETs and other FETs structures, again thanks to a modulation of the channel conductance, that can be enhanced by means of chemical interactions between the target molecules and specific receptors anchored to the gate [30].

Notice that, especially in biological applications, the biosensor target substance is often called "analyte", where the analyte is a substance or chemical constituent that is of interest in an analytical procedure [51], in this case the sensing or measuring process.

Currently the FETs used for sensing applications are mainly two-dimensional (2D) devices such as thin-film FETs or Organic FETs (OFETs), in which a sheet of organic material, e.g. graphene or other organic polymers, is placed between the source and drain contacts and its conductance is modulated by the event that should be detected [52]. Other possible devices are very miniaturized conventional FETs, CNT FETs, NW FETs (both silicon NW or other materials NW), etc... [29], [28], [27], [31], [53]. In all these devices the working principle is always the same: the conductance of the channel is varied depending if the target substance is present (and in what concentration) in proximity of the sensor or not; or alternatively depending if the target substance is chemically bonded (i.e. chemisorbed [47]) with the channel or not. Actually, the most general functioning principle should be expressed as follows: the sensor conductance is varied accordingly to the chemical or physical event to be detected [54], [30], [29]. Indeed, not only gas sensors are possible, but, exactly like in the case of MES, many other chemical or physical events and quantities can be detected. For example, a 2D FET can be mechanically strained thus leading to a Nano-Electro-Mechanical System (NEMS) or sensor, able to detect strain and mechanical deformations [55], [56].

Anyway, the point now is that the functioning principle of molecular electronic sensors and FET-based sensor is essentially the same [30], [27]. This should not be surprising since both are essentially FETs (or wires), even if in MES the channel is a single molecule (or a packets of molecules). Nevertheless, in general, 2D devices are at the present favoured in literature for two main reasons. Firstly, they can be fabricated with current technology without the molecular electronic fabrication issues mentioned in the previous section (such as the low yield, etc...) and thus many recent papers report the prototyping and demonstration of sensors [29], [52], [31], [57], [58], [59], [60], [61], [62], [63], [64]. Then, in a 2D device the interacting portion of the device is the 2D surface or sheet of organic material, thus the interaction region is bigger, leading to a greater sensor sensitivity e.g. to the target substance/gas or chemical-physical event in general [30], [53], [52], [29]. In this regard, for example in [58], the authors state:

"2D-layered materials (2DLM) have an exceptionally large surface-area-to-bulk ratio, and thus adsorbed gases can greatly modify their properties, making them promising candidates for gas detection".

The potentially lower sensitivity of MES w.r.t. current 2D devices is a significant drawback, at least for gas sensors. The problem can intuitively viewed as follows: a gas sensor should detect the presence of specific substances (pollutants, toxic particles, certain chemical compounds, etc...) that are present in the monitored environment at least in a given concentration, often expressed in parts per million (ppm) or parts per billion (ppb), e.g. accordingly to the legislative regulations [65]. The target is thus a minor portion of the total air in the environment, and in order to be detected it should be in proximity of the MES, i.e. nearby a tiny molecular device. This can constitute a limit in terms of sensitivity if a single device based on single is used instead of a 2D device for the reasons expressed above. Nevertheless a trivial solution could be to put several MES in parallel, thus increasing the interaction surface and maintaining the advantage of great miniaturization of the device [22], [54]. Notice that depending on the specific application and thus on the specific chemical/physical event that should be detected and measured by means of the MES, the sensitivity issue can be not present or completely solved [27], [28], [54]. Other issues, as

already pointed out, are concerning the current fabrication processes of molecular devices (see the discussion in the previous section 1.1), and the small currents involved in the sensing process (see again section 1.1). The latter could be a limiting factor for detection due to the noise that unavoidably afflicts the system. Nevertheless also these issues can be often overcome (even if not always easily), for example by increasing the complexity of the front end electronics such as the signal conditioning circuit of the sensor [21], [66], [67], [68], [69], [70], [71], [72].

Besides these drawbacks the main advantages in exploiting molecular electronic sensors are generally their high selectivity, i.e. it is possible to choose *ad hoc* molecules to be used as conducting channel such that the device responds to the target event only (without the usage of intermediate recognition elements), high sensitivity, generally linked again to the possibility of choosing *ad hoc* molecules for the device channel (even if as mentioned this sometimes is not true at all for gas sensors if compared to 2D devices), real-time detection, indeed the current modulation occurs within the transit or relaxation time of the device, that is of the order of conventional electronic response times, and label-free detection. These advantages together with the above discussed drawbacks are summarized in table 1.2. The last mentioned advantage needs a bit of discussion, indeed the conventionally used lexicon must be introduced. When biosensors are taken into consideration (see below for a summary of possible application fields of molecular electronic sensors) one usually distinguishes between labeled detection processes (or sensing with label) and label-free detection processes. The distinction between the two is well explained in [54]:

"In the most general case a biosensor consists of at least two functional components: a molecular recognition element (receptor - it can be a natural, synthetic, bio-inspired molecule) that selectively interacts with its target analyte (e.g. ions, DNA, antibodies, cells, microorganisms, etc...) and a physicochemical transducer (e.g. the molecular wire/transistor). The latter converts the bio-recognition information into a measurable quantity, being in general an electrochemical, electrical, optical, magnetic, mass-sensitive, or thermal signal. Due to the fact that biological analytes are often hard to detect purely on basis of their intrinsic physical properties, biosensors often require labels such as enzymes and fluorescent or radioactive molecules attached to the targeted analyte. As a result, the final sensor signal corresponds to the amount of labels, representing the number of bound target molecules. As a drawback, label-based technologies are often labor- and cost-intensive as well as time-consuming. In addition, labeling of biomolecules can block active binding sites and alter the binding properties. Altogether, this may adversely affect the affinity-based interaction between the recognition elements and the target molecules. In contrast, labelfree biosensing technologies, by definition, do not require the use of labels to facilitate measurements. Instead, they utilize intrinsic physical properties of the analytes, such as molecular weight, size, charge, electrical impedance, dielectric permittivity, or refractive index, to detect their presence in a sample." (adapted from [54]).

From this definition it should be clear that molecular electronic sensors are always labelfree sensors, in which the target analyte makes the molecular channel conductance (or capacitance, etc...) varying, making possible the detection. Notice that in general all

Sensor feature	MES performance			
selectivity:				
sensor response only	high			
in presence of the target				
sensitivity:	potentially high			
ample variation of conductance/capacity	(not always true			
in response to target	especially for gas sensors)			
concentration variations				
accuracy	potentially high			
signal-to-noise ratio (SNR)	can be critical			
	due to the low currents			
	in molecular devices			
response time	fast			
real-time detection:	good/fast			
sensor response speed	(comparable with current electronics)			
linearity	good (depending on device structure)			
repeatability	good			
	(may deteriorate in long-scale times			
	due to molecular stress			
	e.g. variations of temperature/humidity			
	or applied field)			
reliability	good			
	(can be worsened by process			
	variations and device stress)			
labeled / label-free	label-free			
reversibility	good (may be in contrast			
	with selectivity)			
stability/drift over device life-time	good			
	(depending on process variations			
	and device stress)			
cost	(potentially) low - see sec. 1.1			
size	small (potentially suitable for			
	wearable/implantable bio-systems)			

 Table 1.2: Main features of molecular electronic sensors (MES).

FET-based biosensors are label-free. Indeed even in the case in which a biological entity is detected by means of a bio-macro-molecule (a protein, antibody, enzyme, etc...) chemically bond to the FET channel on one side and to the target analyte on the other side, from the above definition, it is a label-free sensor. For example a virus detection in a clinical solution (or even in air), that is made possible thanks to the FET conductance modulation due to the presence or not of the bond between the virus specific antibody that is anchored at the FET channel (e.g. a 2D graphene sheet) and the virus itself, is a label-free detection process [73], [74]. Label-free biosensing methods have made enormous progress in recent years due to their ability for rapid and inexpensive bio-detection even in small reaction volumes. Moreover, they lend themselves for integration into lab-on-chip platforms and allow monitoring the concentration of target analytes in real time [54]. In this regard molecular electronic sensors may be the next generation toward higher miniaturization, selectivity and sensitivity of label-free real-time sensors for biological applications and single molecule event detection [27].

The FET-based (standard FETs, 2D FETs, OFETs, CNT FETs, NW FETs, GNR FETs, molecular FETs or whatever kind of FET) sensors are not the only possible of biosensors. Another broad class of biosensors or chemosensors (i.e. chemical-sensors) are the so called "electrochemical sensors", that have similar important features in terms of sensors characterization (such as sensitivity, selectivity, real-time, labeled/label-free, etc...) to the FET-based ones [53]. An electrochemical sensor is usually a label-free sensors often suitable for real-time detection of biological or chemical substances (often in solutions). In few words it is constituted by an electrode (usually an inert metal -e.g. gold- or graphene/polymeric electrode) immersed in the biological or clinical solution that contains the target molecule or chemical compound, above which suitable receptors (such as antibodies, enzymes, proteins, organic molecules/polymers, etc...) are anchored to it and suspended in the solution. The target analytes (molecules, bio-macro-molecules, ionic species, etc...) are then chemically bonded to the receptors producing a change in the resistance of the portion of solution in between the electrode and the top-side of bio-solution (or alternatively in between two contacts). This is then detected by means of amperometric methods or voltammetric methods (sometimes dynamic techniques are used: conductometric methods). Notice that if the electrical resistance is varied due to the presence of the target analyte the sensor material is often referred as chemoresistor [31], [53], [28], [29]. A comparison between FET-based sensors and chemoresistors (electrochemical sensors) is reported in table 1.3 (SSES -solid state electrochemical sensors- and QCM -quartz crystal microbalance- are not considered here - see [29] and references herein for details). In this optics, MES have the advantage of having high selectivity and low cost (for the rest they are analogous to FETs).

Table 1.3: Comparison of different gas sensing technologies. SSES (solid state electrochemical sensors) and QCM (quartz crystal microbalance) are not considered in this work (see [29] and references herein for details). A comparison is provided in detail in [29].

Sensor technology	Sensitivity	Selectivity	Speed	Cost	Size
Chemoresistor	high	medium	high	low	small
FET	high	medium	high	medium	small
SSES	high	good	high	low	large
QCM	high	poor	medium	high	medium

The other ample class of above mentioned biosensors are the labeled ones, in which a label is exploited in order to make detectable a given event or bio-(macro)-molecule or substance in general. Labels have the role of converting the bio-recognition information into a measurable quantity, e.g. electrochemical, electrical, optical, magnetic, mass-sensitive, or thermal signal [54]. For example a widely spread labeled sensors are the one exploiting fluorescence (i.e. photon re-emission) depending if the target is present or not (with an intensity dependent on concentration). More in general, in optical molecular sensors a chemical reaction occurs between the target analytes and the labels such that photons at a given wavelength (typically in the ultra-violet or visible range) are emitted (or absorbed) and detected with conventional optical or optoelectronic sensors [54], [75]. These classes of sensors are beyond the purposes of this work and they will be no more considered. Nevertheless notice that they are called "molecular sensors" as well. In particular, in this regard, a "molecular sensor" or "chemosensor" is a molecular structure (organic or inorganic complexes) that is used for sensing of an analyte to produce a detectable change in a signal (often electromagnetic radiation but it is not said - see before). The chemosensor working principle is based on interactions occurring at the molecular level. usually involving the continuous monitoring of the activity of a chemical species in a given matrix such as solution, air, blood, tissue, waste effluents, drinking water, etc... and it is a labeled detection process [75]. As already said, since chemosensors are based on molecular recognition at molecular level, they are often referred as "molecular sensors" [75], even if they are completely different from the "molecular electronic sensors" that are the subject of this work. For this reason and in order to avoid confusion, so far I have always specified "electronic" together with "molecular sensors". In the next chapters if no misunderstanding is possible I will sometimes shorten the name in "molecular sensors", even if I will always refer to "molecular electronic sensors" (MES).

At this point it should be clear what molecular electronic sensors are, their basic working principles, and the ample background in which they find place. Moreover the basic lexicon was briefly introduced.

In conclusion to this introductory section, I would like to briefly summarize the possible fields of application of MES, on the basis of what is the current state-of-art in sensing science. The following list details some of the possible applications of molecular electronic sensors, and even if it is very likely incomplete, it gives the idea of the plenty fascinating applications of this emerging field of electronics and sensing:

gas sensor: this application was already discussed above, the recent years demand is for on-line/*in situ* detection of gases for both outside and inside environment monitoring [29]. Possible markets are related to pollution and pollutants detection of particles, molecules, heavy metals, to chemical industrial processes monitoring (toxic gases can be a collateral product in case of fault in some industrial processes), or fault in public or private buildings (e.g. carbon monoxide or methane emission in dangerous concentrations) [29], [65], [53]. The main substances to be detected in these applications are usually formaldehyde (HCHO), benzene (C<sub>6</sub>H<sub>6</sub>), acetone (C<sub>3</sub>H<sub>6</sub>O), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>), ammonia (NH<sub>3</sub>), hydrogen sulfide (H<sub>2</sub>S), ozone (O<sub>3</sub>), nitric oxide (NO), nitrous oxide (NO<sub>2</sub>), methane (CH<sub>4</sub>), butane (C<sub>4</sub>H<sub>10</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), and so on... [29], [65].

- environment monitoring: for air-quality tests and gas concentrations monitoring in outside and inside environments see above (gas sensor); for soil or water pollution monitoring the application is similar but the sensor is designed to be used in solutions in which the target analyte is present. Usually in this last application field the detection of the following chemical compounds is of importance: ammonia (NH<sub>3</sub>), methane (CH<sub>4</sub>), nitric oxide (NO), sulfur dioxide (SO<sub>2</sub>) and heavy metals [29], [53]. It is possible to include in the environment monitoring set of applications the outdoor/indoor air quality tests, factory emission detection, vehicle exhaust control of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitric oxide (NO), nitrous oxide (NO<sub>2</sub>) and all the related applications [29].
- public security: the public security, especially anti-terrorism, is becoming extremely urgent [29]. The applications, in this field, mainly focus on the detection of the explosives and/or the nerve agents. Normally, the vapor pressure of explosives, e.g. 2-methyl-1,3,5-trinitrobenzene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are 9 ppb, 4.9 ppt, and 0.25 ppt, respectively. Therefore, the detection of explosives needs ultra-sensitive sensors, exactly like MES potentially are [29].
- diagnostics/bio-medical: diagnosis of health conditions via detection and classification
  of volatile organic compounds (VOCs) or biomarkers into one or combination of
  body fluids released as a result of a disease evolvement in the human body [29].
  The monitoring of biomarkes is in general performed by means of the analysis of
  exhaled breath, skin/sweat, feces, urine, saliva, breast milk, blood, interstitial fluid,
  cerebrospinal fluid, tears, seminal fluid and intestinal gas [31]. Even virus detection
  in clinical solution is currently performed by means of FET-based sensors [73], [74];
  thus leaving the door opened for a possible replacement with molecular electronics
  sensors (to be still verified if and in what cases it would be possible).
- food industry: sensors are used for the detection of toxic/polluting substances in food items, or to monitor the presence of pesticides. Moreover they are also exploited to monitor the shelf life or fungi contamination in vegetables and fruits or meat/fish spoilage [29]. Again, the brand and/or the place of origin of tobacco can be recognize by means of e-nose (electronic nose) based sensing systems [29].
- agricultural production: sensors are used for monitoring production processes, disease detection, identify insect infestations in their infant stage, and soil/water pollution (environment or pesticides etc...) [29].
- e-nose or e-tongue: all the fields of application mentioned up to now can be also the applications of e-noses (electronic noses) or e-tongues (electronic tongues) [29]. An e-nose (e-tongue) is mainly constituted by three parts: a sensor, a conditioning circuit or front-end circuit, and a post-processing usually real-time on-line unit [29]. The latter very often employs algorithms (implemented both in hardware and in software) based on Artificial Neural Network (ANN) computing paradigms [29]. The sensor can be in general a molecular electronic sensor.

- wearable/implantable sensors: wearable and implantable electronics is gaining popularity and interest in recent years [76], [77], [78], [79]. It may be a relevant next-future market for biosensors and for implementing generic tasks with biological data collection and transmission to smartphones for more complex post-processing [78], [79], [80]. In terms of sensed quantities, mainly human bio-signals are monitored (especially in sport applications), such as heart beat. Moreover real-time wearable physiology monitoring, e.g. temperature, pH, sweat and metabolytes measuring or multi-ion monitoring (potassium, sodium, etc...), is becoming relevant and important in various applications even already on market [80], [81]. In this field molecular electronic sensors may become valid substitutes to conventional FET-based sensors due to their high selectivity and sensitivity. Furthermore, due to their huge scalability they can play a central role for implantable systems, especially considering the recent advancements in biodegradable and biocompatible materials and molecules [82], that can potentially open the way to implantable biosensors that are nontoxic or spontaneously ejected or disintegrated/decomposed from the human body.
- single-molecule detection: this is an emerging field in sensing science, in which the ٠ presence of a single molecule is detected [27]. Usually the detection happens in real-time allowing for the detection also in the case in which the target molecule has a limited life-time of few milli- or micro-seconds (or even less), for example because it is an unstable product of a more complex chemical reaction [27], [83]. The process can be labeled or label-free [83], if a molecular electronic sensor is used to this end, it is label-free [27], [28]. The purposes of single-molecule detection can be e.g. the experimental proof of predicted chemical reactions (or chains of reactions) through the measurement of the type and life-time of intermediate compounds, the better understanding of biological and bio-chemical dynamic processes, useful both in biology and medical researches, the early detection of analytes for disease diagnostics, etc... [27], [28], [83]. Other interesting applications are in real-time DNA sequencing. Often single electron transistors (SETs) that are used to this end are comprehensive of a nanogap (that can be natural, such as specific enzymes, or artificial like graphene nanogaps) to which an applied electric field allows for the scrolling of the DNA nucleotides through it at a constant velocity. The conduction through source and drain contacts changes depending on what nucleotide is present in that moment within the nanogap, allowing for DNA real-time sequencing [84], [35], [36], [85], [86]. In this field the single-molecule recognition is fundamental, and MES may become and alternative to conventional techniques or integrate and ameliorate them [27]. The single-molecule detection is sometimes referred as the ultimate limit in analytical chemistry, allowing for visualizing the dynamic processes of chemical/biological interactions with single molecules at single-event sensitivity [27], enabling the study of stochastic fluctuations under equilibrium conditions and the observation of time trajectories and reaction pathways of individual species in non-equilibrated systems, and the direct observation of novel microscopic quantum effects and fundamental discoveries of underlying molecular mechanisms in organic reactions and biological processes that are not accessible in ensemble experiments [27]. All this is becoming reality thanks to molecular electronic sensors.

## 1.3 Context, motivations and organization of this work

In the wide landscape presented in the previous section, the MES are still at an embryonic level. At the moment it is still untimely talking about production or commercialization of molecular electronic sensors, exactly like it is untimely thinking of substituting conventional electronics with molecular electronics. Nevertheless, I personally agree with the aforementioned critical standpoint, about this subject, of Mark Reed [11], and in this optics much work has still to be done in this field to gain much knowledge on the physics, the chemistry and above all the electronics and information processing paradigms to manage such innovative systems. Then, as I already mentioned, it may also be (but no one knows) the research in the MES field become an important milestone toward the development of molecular electronic systems. Without getting lost in daydreams, the facts are that the present work is actually a pioneering work in this fascinating field of science. The context in which it finds light, is an increasing demand in small, low cost, real time and label-free chemo- and bio- sensors, also in light of the applications mentioned at the end of the previous section, like the emerging field of single molecule detection, that can only be performed by means of innovative electronic devices, like MES are. The motivations behind this work are, above all, the ones reported previously, concerning what can be learnt in approaching the study of this novel class of devices. Moreover, at the present, the literature is still lacking of a unique and complete work that collect in a critical way all what is needed to perform analyses, simulations and finally the design of this class of devices. In particular the main purpose of this work is the attempt of providing a general investigation methodology to be used as reference (within its limits) for next works and toward an engineering of the design and the analysis of MES. To this purpose this work is organized as follows.

The first part of this work is essentially a literature review of the MES theoretical physical-chemical modeling techniques. The treated topics are quite well established in literature, and the main point of this part is to collect all the needed theoretical aspects, also belonging to very different fields, within the same document. In addition, since the only topics assumed for granted are the basic mathematical and physical knowledges, common to all engineering and scientific backgrounds, this document should be accessible without any extra requirement to electronic engineers. This part is conceived to be a reference for understanding the meaning of the many input parameters of atomistic simulations that are usually required to be set up. Since very often the calculations are performed by means of commercial tools (like *Quantum-Wise ATK* used in this work), the task of setting up simulations may appear to be easy. Nevertheless a great amount of knowledge is actually required to avoid wrong settings and consequently unreliable results. This is the reason why this part is so long.

The second part is instead focused on developing a general and complete methodology for the design and the analysis of a MES, by means of three cases of study, namely a  $C_{60}$  gas sensor for ammonia detection, a  $C_{60}$  gas sensor for lead sulfate detection, and a  $C_{60}$  gas sensor for nitric oxide detection. In literature there is still very few about the topics covered in this part, and the great majority of the papers are still focusing on theoretical simulation studies rather than on prototypes. For this reason this part of the work is a pioneering attempt to "put order" in the large landscape of possible analyses and simulations one can perform on MES, in order to identify the analyses that are effective and useful to extract information and eventually figures of merit of such a kind of novel devices. The advantage of treating these topics by means of real cases of study is obviously the direct feedback about critical issues of such novel devices.

A brief presentation of the topics covered in the various chapters is now presented.

#### Part I:

Chapter 2 is aimed in reviewing quantum mechanics, i.e. the theory in which the MES models have their roots. Since this work assumes the reader to have an electronic engineer background, the treated topics may or may not be already known, depending on the specific course of study, and for this reason also the very basics were recalled. All the needed topics to get a complete comprehension of the next chapters, that in turn are important to correctly set up simulations and deal with MES, are introduced and discussed there. Basic quantum mechanics results (like confinement, electron wave-functions and orbitals, etc...) are indeed the starting point of chapters 3 and 4, and it was chosen to recall them in order to have an homogeneous notation and lexicon. The matrix notation for quantum mechanical operators, widely used in chapter 5, is also introduced.

Chapter 3 is aimed in modeling the molecular channel electronic structure, i.e. the starting point for all the equilibrium and non-equilibrium modeling techniques of MES and transport through them. Moreover, intermolecular interactions and relative modeling techniques are discussed. They are of extreme importance for correctly modeling gas sensors, like those considered in the practical part (II) of this work. The useful information for setting up molecular electronic structure calculations, geometry optimizations, and molecular device simulations is reported and discussed. In particular, the focus is on concepts and approximations behind the specific methods. Then, a more in-depth insight is provided concerning the DFT (Density Functional Theory) and the EHT (Extended Hückel Theory) methods, since they are the ones used in the part II of this work. Finally, the advanced modeling techniques for weak interactions (like van der Waals ones) are briefly addressed with a focus on the recent supermolecular approach, suitable to correct DFT calculations. Such topics are the fundamentals for a correct setting up of atomistic simulation relatively to MES, especially for gas sensors or single molecule event detection, in which the working principle directly involves such kind of weak interactions.

Chapter 4 is focused on the transport through molecular devices. Such a complicated matter is introduced in this chapter by means of an oversimplified model, that allows to gain the physical intuition of what actually happen in such a kind of devices. All the main transport features of MES (and molecular devices in general) are introduced, along with a powerful and simple electrostatic treatment of the system. Moreover an introduction to transmission formalism is also provided.

In chapter 5 the transport through molecular devices is addressed by means the formal and general Non-Equilibrium Green's Function (NEGF) formalism, that allows not only to model transport in such devices in all their possible regimes of transport, but also to understand the meaning of the many parameters to be set up in atomistic simulations and the way to correctly set them up. Moreover, a practical and complete example is provided, being the occasion to introduce an interesting free tool for EHT + NEGF transport calculations through molecular systems: *Huckel-IV* tool, that will be also used in the practical part of this work for the sensor response time estimation.

In chapter 6 additional transport-related topics are addressed. A brief review of the transport mechanisms through molecules is provided, and the way of accounting for them in the NEGF framework is presented. Moreover, the Coulomb blockade phenomenon is also addressed, and the possible modeling approaches in Coulomb blockade transport regime are explained, with reference to the methods that are increasingly becoming popular in literature in recent years (e.g. DFT corrections).

#### Part II:

In chapter 7 the working principles of different molecular electronic sensor are introduced, with the gain of the part I of this work. A focus is provided on the concepts of chemisorption and physisorption, that are very useful whenever gas sensors are considered, and also in the moment in which metal electrodes are used to contact the molecular channel. Moreover the general methodology, followed in the next chapters of this work, will be introduced.

In chapter 8, the  $C_{60}$  fullerene molecule is used as molecular channel for an ammonia MES. This practical application is the occasion to develop a method for the device geometry choice and optimization, to develop a simple approach for validating the EHT non-equilibrium simulations starting from DFT equilibrium ones and to quantitatively estimate the sensor sensitivity and selectivity.

In chapter 9, after a brief repetition of the methodology steps already introduced in the previous chapter, the main non-equilibrium properties of a lead sulfate MES are analyzed. In particular the sensor selectivity, sensitivity to different target orientations, concentrations and distances are analyzed and verified. These properties, all together, allow to gain a complete understanding of the sensor detection capabilities. Then a detailed analysis on transmission eigenstates of the MES under study is performed. Finally, an equivalent static and an equivalent dynamic circuit models of the sensor are proposed, aimed in evaluating the functionality of circuits including the MES (LUT-based model) and the sensor response time (dynamic model). A gated device is also considered to verify the different performances in such a case.

Chapter 10 is dedicated to a brief study of the nitric oxide detection by the same device structure already analyzed in the previous two chapters. Both the molecular wire and the molecular transistor device structures are considered and the already introduced steps and methods, are exploited to provide a brief characterization of the nitric oxide detection by the  $C_{60}$ -base MES.

## Part I

# Molecular devices modeling

### Chapter 2

# Brief review of quantum mechanics

The purpose of this chapter is to review the fundamental topics of quantum mechanics that are necessary to understand the next chapters related to molecular device modeling. These topics are nowadays often covered in the electronic engineer background, and for example they are subject of bachelor's level courses at Politecnico di Torino. For this reason this chapter is intended to be a review of the main results to be kept in mind in the following of this work, rather than a complete introduction to quantum mechanics. Very good textbooks about quantum mechanics fundamentals, in my opinion, are the following: [87] (in Italian) that formally introduces all the topics without losing track of the physical insights, [88] that provides an excellent understandable introduction to these topics, even if sometimes the mathematical formalism is omitted, [89] that provides a complete, simple and understandable introduction to the fundamental topics without requiring particular prerequisite, [90] that provides an extreme simple and applicationoriented introduction to quantum mechanics, [91] that provides a very rigorous and formal introduction to basic quantum mechanics, and [92] that provides a formal introduction to some advanced topics sometimes required in rigorous modeling of molecular devices. Many other valid and excellent textbooks are anyway present in literature (just to mention one: the milestone "Principles of Quantum Mechanics" by Paul A. M. Dirac). Throughout all this chapter I will always refer to the previously cited books, even if not always explicitly.

#### 2.1 Wave-particle duality

The first question I will address in this introductory section is: "why quantum mechanics?". This entire work deals with molecular devices used as sensors. Molecules are the basic entities of matter and they can be composed of very few atoms (think for example to hydrogen molecule  $H_2$  that is composed of only two hydrogen atoms), as well as a very large number of atoms. In both cases the characteristic dimensions are very small when compared to classical entities (like a rugby ball or even a small marble). For example

the benzene ring has a characteristic dimension of less than 1 nm (it is around 5Å), and again the fullerene  $C_{60}$  (a molecule with sixty carbon atoms) has a diameter of approximately 7Å. In such microscopic systems novel physical effects arise. These novel effects and phenomena are not present in classical mechanics, that deals with the motion of macroscopic bodies, and in fact classical mechanics fails in accurately describing the motion and the interaction of such microscopic systems. The physical theory that, instead, correctly explains in a satisfactory manner the behavior of microscopic systems, like atoms and molecules, is quantum mechanics. Thus it must be considered the starting point in modeling molecular-based devices.

Quantum mechanics born at the beginning of the twentieth century, precisely to explain physical phenomena, especially at the microscopic scale, that were not explainable at all with classical physics. Actually, important unsolved problems by the end of nineteenth century were for example related to the interaction between electromagnetic radiation and matter, that did not result in accordance with the classical laws of electromagnetism (i.e. Maxwell's equations). Among them I only cite the blackbody radiation spectrum, the photoelectric effect, the Compton effect, the discrete spectral lines in atomic or molecular absorption or emission of radiation and natural radioactivity. The explanation of all these, classically inexplicable, phenomena was possible only after that in 1900 Max Planck assumed that energy exchange between electromagnetic radiation and matter is not continuous, but it can happen only by discrete amounts, called energy "quanta". In Planck's model an energy quantum has an energy E proportional to the electromagnetic radiation frequency f by means of the Planck's constant h ( $h = 6.62607015 \cdot 10^{-34}$  J·s):

$$E = hf \tag{2.1}$$

The Planck's assumption was in agree with the concept of photon (name coined by Lewis in 1926) introduced by Einstein in 1905, intended as an energy quantum of electromagnetic radiation. The interaction between electromagnetic fields and matter was thus rethought in terms of photons, meaning that only single photons interact with matter. This allowed to explain the photoelectric effect, the Compton effect and the blackbody radiation. The important conceptual consequence in this reasoning is that the electromagnetic radiation behaves like waves in some experiments and like a particle-based entity in others. This led scientists at the beginning of the twentieth century to accept the "dualistic" nature of the electromagnetic radiation. The wave nature of electromagnetic field is associated to physical quantities such as frequency or wavelength, while the particle-based nature is associated to a well defined energy and momentum. The connection among the two pictures is provided in equation (2.1). Moreover the modulus of the momentum associated to a photon, that is a particle with null mass since it is a quantum of electromagnetic energy, is provided by the following relativistic relation (introduced by Einstein in his work on special relativity):

$$p = \frac{E}{c} \tag{2.2}$$

where c is the light speed.

By putting together eq. (2.1) and eq. (2.2) it is possible to get (remember that  $c = \lambda \cdot f$ ):

$$p = \frac{h}{\lambda} = \hbar k \tag{2.3}$$

where  $\hbar$  is the reduced Planck's constant (i.e.  $\frac{h}{2\pi}$ ) and k is the wavenumber (i.e. the modulus of the wave vector  $\vec{k}$ ). The last relation can be then rewritten in vector form like (the wave vector is conventionally defined with the same direction of the propagation direction of the wave):

$$\vec{p} = \hbar \vec{k} \tag{2.4}$$

The just introduced quantities are the key points for the comprehension of many classically inexplicable phenomena, like the already mentioned photoelectric effect, Compton effect and blackbody radiation spectrum.

Instead the nature of atomic and molecular spectra was explained in a satisfactory way only after many other progresses were achieved, with a complete theory of microscopic world: the quantum mechanics. Nevertheless the intermediate achievements, even if sometimes they were *ad hoc* theories, are nowadays important in understanding the basic assumptions of quantum mechanics and its change of perspective w.r.t. classical physics. An important achievement I would like to briefly mention is the Niels Bohr's pioneering work on absorption and emission spectra of atoms, dated 1913. He assumed true the atomic structure demonstrated by Rutherford, with a central nucleus around which electrons rotate. Classically such a system cannot exist since it would be unstable, indeed electrons are charge particles and in a circular orbit around the nucleus (i.e. accelerated motion) they should emit electromagnetic radiation loosing their own energy until they should collapse toward the nucleus. Bohr started from the obvious prove that atoms are essentially stable (since they exist), and assumed that well determined orbits were possible such that electrons (for some unknown reasons) can rotate around the nucleus without radiate. Even if this assumption was in conflict with classical laws he quantified it. Indeed he supposed that such orbits were circular and that the only "permitted" orbits were the ones whose the modulus l of the electron angular momentum w.r.t. nucleus (that was considered point-like) was an integer multiple of the reduced Planck's constant:

$$l = n\hbar$$
 ,  $n = 1, 2, 3, ...$  (2.5)

The orbits for which this angular momentum quantization law holds were supposed to give rise to "stationary" states, thus leading to stable structures. Then Bohr used the concept of photon and extended the Planck's assumption supposing that an electron in a steady state E by means of the absorption of a photon of suitable energy, i.e. frequency f, in a unique process, could be excited in a steady state E' (with E' > E). Consequently, involving the conservation of energy, he stated that the energy difference should be equal the energy provided by the photon (Bohr's formula):

$$\Delta E = E' - E = hf \tag{2.6}$$

The reasoning was analogous for the emission of photons by atoms and molecules (with a transition toward ground state from excited states). This model admits only transitions
between stationary states, that have a quantized angular momentum l. Consequently the "permitted" energy levels of an atom are discrete, or at least a subset of the possible atomic energy levels are discrete, and they correspond to stationary states. This last concept constitutes the current conceptual importance of Bohr's model. The admission of having quantized quantities (see eq. 2.5) such as the energy levels or the angular momentum in microscopic systems is a revolutionary concept, that is naturally demonstrated by means of quantum mechanics. The difference between this model (or the Wilson-Sommerfeld model for quantized action integrals) and an authentic quantum theory, is in the fact that this first attempt introduces quantization *ad hoc* in a classical theory, while in quantum mechanics it arises naturally by solving the equations and enforcing boundary conditions.

The difficulties related to a complete and satisfactory explanation of the microscopic phenomena were emphasized by the fact that in some experiments the same physical quantities that showed a discrete nature, showed also a continuous nature, like the energy emitted by electrons in some well-defined conditions (e.g. the braking radiation of electrons). The first attempt in explaining why a fundamental property of a physical system, such as its energy, can sometimes appear discrete and sometimes instead continuous, was proposed by Louis de Broglie in 1924. He proposed an intrinsically "dualistic" nature, up to that time accepted for the electromagnetic radiation as mentioned above, also for "material" systems, i.e. microscopic systems of material particle. In particular de Broglie assumed that microscopic systems, up to that time seen as particles, could present also undulatory aspects. This is referred as the "wave-particle duality", and this is one of the fundamental conceptual achievements in quantum mechanics. More precisely de Broglie postulated that a particle of momentum  $\vec{p}$  (with modulus p) can be associated to a wave, characterized by means of a wavelength  $\lambda$ , that analogously to what happens with electromagnetic waves and photons, was given by:

$$\lambda = \frac{h}{p} \tag{2.7}$$

This relation is known as "de Broglie relation". It can be rewritten in vector form like:

$$\vec{p} = \hbar \vec{k} \tag{2.8}$$

where k is the wave vector with a modulus  $k = 2\pi/\lambda$ . In light of this, the different behavior of an electron can be explained as follows. A free electron that is braked (e.g. by Coulomb interaction) behaves like a traditional particle and thus it can posses (and emit) a continuous range of energy. Instead if it is bonded to an atom, it shows its wave nature, and the only allowed energy states are those corresponding to stationary waves. Indeed, from the standpoint of de Broglie, the Bohr's assumption corresponds to state that the only permitted orbits are those that include an integer number of electron wavelengths. And exactly like an acoustic wave in a room is said to be steady if the dimension of the room is an integer multiple of its wavelength, if the electron orbit length (i.e. circumference in case of circular orbits like in the Bohr's model) is an integer multiple of the the electron de Broglie wavelength, it is a steady state, with no loss (neither gain) of energy (as assumed by Bohr). Now one may wonder: "what is thus an electron? a wave or a particle?". The answer is both or neither. Or better: in the wave-particle duality picture an electron is

seen as a physical entity, that in some cases shows a particle-like behavior while in others a wave-like properties. In some experiments it is is well described by the classical concept of particle (with a given momentum and energy) and in others it is well described by the classical concept of wave (with a given wavelength and wave vector). The connection between the two descriptions is provided by the de Broglie relation (equations 2.7 and 2.8). In summary, the wave-particle duality states that with each particle is associated a wave field (sometimes called a matter field - not to be confused with waves of matter like acoustical or mechanical waves!). This is analogous to associate a photon to its electromagnetic field. The wave field describes the dynamical condition of a particle in the same sense that the electromagnetic field corresponds to photons which have precise momentum and energy. As already mentioned the connection between the wave field and the particle (e.g. electron) is provided by the de Broglie relation (eq. 2.7 and 2.8). Well, at this point a question may be: "what is the meaning of this wave field?". The answer is sometimes still controversial. According with the widely accepted and traditionally taught Copenhagen interpretation of quantum mechanics, the wave field has to be intended as a position probability field, as better discussed in section 2.3.1. In mathematical terms the wave field is represented by the so called "wave-function" (see section 2.3 and 2.3.1, 2.3.2 particularly) related to the electron or the microscopic entity. The wave-function  $\psi$  is a complex function of space and time that defines the wave field for the considered microscopic system:

 $\psi(x, y, z; t) : \mathbb{R}^4 \mapsto \mathbb{C}$ 

Thus more precisely the quantity that is associated to the meaning of position probability of the particle is the wave-function intensity  $|\psi(x, y, z; t)|^2$ , indeed a probability must be a real quantity (refer again to section 2.3.1). In this optics it is expected that whenever the motion of a particle is disturbed in such a way that the wave field associated with it cannot propagate freely, interference and diffraction phenomena should be observed, exactly like it happens for elastic waves or electromagnetic waves. Nevertheless the physical meaning of this wave field is associated to the probability of position of the particle, thus a perturbation in the wave-function  $\psi$  leads to a different position probability of the particle. That is, whenever the particle motion is somehow perturbed and the wave field modified, there is a different probability of finding the particle in the different regions of space, according to interference phenomena (typical of waves!) that modify the wave-function  $\psi$ . In this, the mentioned wave field or matter field is extremely different from the classical concept of matter waves in which e.g. the molecules of air are subjected to a well defined undulatory motion because of the propagation of an acoustical wave in air.

The first experimental evidence of the wave-like behavior of electrons was thanks the experiments of Davisson and Germer and of G. P. Thomson starting from the 1927. In the Thomson experiments a well collimated electron beam (of enough low energy to neglect electron-electron interaction) was sent through a thin crystalline film (see fig. 2.1 left) and then made impacting on a photographic plate. If the electron had behaved as classical particles a blurred image would have been observed focused around the center of the photographic plate, since each electron would undergo in general a different scattering by the atoms in the crystal. However the obtained result was analogous to the one obtained

with X-rays diffraction by a polycrystalline substance. As evident in figure 2.1 (right), the result clearly showed a wave like propagation and diffraction of the electron beam by means of the crystalline film. Notice that in the moment in which an electron impacted on the photographic plate it generated a small point, like it were a "small particle", even if during its propagation it underwent to a wave-like propagating behavior (indeed there were favoured "trajectories" and forbidden ones). By doing all the calculations starting from the spacing between crystal planes, and considering the laws for evaluating interference, the recovered value for the electron wavelength was in agreement (with the limits of the experimental error) with the one postulated by de Broglie (eq. 2.7).



Figure 2.1: Experimental arrangement for observing electron diffraction through crystalline material (left); and diffraction patterns of electrons on the photographic plate (right).

In the C. Davisson and L. Germer experiments an electron beam was sent at a given angle toward a crystal face and the diffracted electrons were observed at a symmetrically located detector (see fig. 2.2). It was found that the electron current registered by the detector had a maximum every time the so-called Bragg condition (derived for X-rays) was fulfilled, i.e. only for given angles  $\theta$  such that:

#### $2d \sin\theta = n\lambda$

where d is the separation between successive atomic layers, n is an integer multiple and  $\lambda$  is the de Broglie wavelength. Again this experiment allowed to highlight the wave-like propagation behavior of electrons and their undulatory diffraction patterns as a result of the interaction with the crystal layers.

Other famous experiments are the ones that make electron pass through a single or a double slit in a shielding panel. In the single slit experiment a small circular micro-hole is present on a opaque screen behind which a photographic plate is present. Again in this case, if the electrons were classical particles, moving on rectilinear trajectories, a strong sign should be present on the photographic plate in correspondence of the slit,



Figure 2.2: Davisson and Germer experimental arrangement for observing Bragg scattering of electrons.

with blurred signs around it due to interaction of the electrons with the slit edge. Thus a sort of a Gaussian distribution of the intensity should be present. Instead, exactly like in the previously mentioned experiments, even in this case concentric rings (similar to the one of figure 2.1 right) are present, showing the presence of "allowed" zones in which a large amount of electrons impact and "forbidden" zones in which no electron impacts. The diffraction pattern is again similar to the one obtained with diffracted light rays by a circular aperture.

The two slits experiment is analogous but two close slits are present. When only one of the two slits is opened the same result of the previous experiment is recovered, instead when both the slits are opened simultaneously an interference pattern is present on the photographic plate.

Once more the only possible explanation to these phenomena is that electrons (and in general whatever microscopic system - indeed analogous experiments with analogous results were carried on neutrons, protons and atoms) can posses a wave nature and thus they can interfere. Nevertheless notice that the wave nature of microscopic systems is not a collective phenomenon due to the interactions among them. Indeed the experiments described above lead to same results even if single electrons are sent one by one toward the photographic plate, and remember that before it was assumed that the electron energy was low enough to make negligible the interactions among them. Moreover also connecting a single electron with a single wave is generally wrong. Indeed, if it were so, a single electron would produce a diffraction figure on the photographic plate, eventually more marked if the number of electrons is increased. Instead as already mentioned a single electron produces on the photographic plate a single small spot, indicating that it is well localized (a posteriori) in the moment in which it impacts on it, showing its particle nature. Only when an enough large amount of electrons is considered the diffraction figure takes its shape. Again the impact regions and thus the propagating nature of electrons (or microscopic systems in general) are somehow not classical but linked with wave-like properties. And again everything becomes clear if the meaning of the wave field associated to electrons is considered: the intensity of the wave field, i.e.  $|\psi(x, y, z; t)|^2$ , must be interpreted as intimately related to the position probability amplitude, as mentioned above and discussed later in section 2.3.1. Thus to each electron is associated a well defined probability of impacting on a precise point of the photographic plate, and the waves are probability waves. Once again it should be clear now that wondering if an electron is a particle or a wave has no sense: it is a microscopic physical entity and thus it obeys to the physical laws that govern this world.

# 2.2 Particles, wave packets and indetermination principle

In the previous section it was reviewed the concept of wave-particle duality. Few words were said also on its physical interpretation and then some experiments (among the many) were briefly described to point out the correct interpretation of this revolutionary concept. In this section the main conceptual implications of this fact are considered.

A classical particle is a material object with a given spatial extension (that sometimes can be approximated like a dimensionless material point) and with a given trajectory. Instead a classical wave is a physical entity that shows opposite characteristics. A pure monochromatic wave (i.e. with a well define wavelength and thus in the de Broglie representation with a well defined momentum) has an infinite extension and it has no sense speaking about localization or trajectory. A "localization" of an undulatory system is possible only if wave packets are formed. A wave packet can be decomposed in the superposition of monochromatic waves of different frequencies (or wavelengths), and the greater is the number of superimposed monochromatic waves the smaller is the physical extension of the wave packet. This is essentially a Fourier decomposition (i.e. transform) of the wave packet. Indeed the wave packet of whatever waveform, or alternatively the pulse, can be considered localized if it presents an amplitude that is enough large only in a given region of space, such that it can be neglected outside of that region. In the wave-particle dual representation the wave field amplitude (or intensity) is linked to the probability of position of the system. Thus if the wave amplitude is non-negligible only in a given region of space, that is if the wave-function intensity  $|\psi(x, y, z; t)|^2$  is non-negligible only in a given region of space, it means the probability of finding the system represented by  $\psi$  outside that region is essentially null, and thus the system is localized.

In other words a monochromatic wave is non-localized since its amplitude is constant in all the (infinite) space, see figure 2.3 (top). Nevertheless a monochromatic wave has a well defined wavelength  $\lambda$ , and thus from eq. (2.7) a well defined momentum p. Moreover a phase velocity can be associated to a monochromatic wave. By definition the phase velocity is the velocity that an observer should have to see a constant phase of the wave. From classical wave theory it is well known that a monochromatic one-dimensional (x-direction) wave can be described in mathematical terms like (harmonic wave):

$$wave(x,t) = A \sin(kx - \omega t)$$

where  $\omega = 2\pi f$  is the angular frequency and A the amplitude, or alternatively by the

complex expression:

$$wave(x,t) = Ae^{i(kx-\omega t)}$$

where i is the imaginary unit.

The phase velocity  $(v_{phase} = \frac{\omega}{k})$  of this monochromatic wave is obtained by differentiating the phase of the wave and by setting it to zero (since by definition the observer sees a constant phase its derivative is set to zero). Exploiting the equations (2.1) and (2.7) it is obtained (*m* is the particle mass or effective mass if the effective mass approximation is considered):

$$v_{phase} = \frac{\omega}{k} = \lambda f = \frac{h}{p} \frac{E}{h} = \frac{E}{p} = \frac{p}{2m} = \frac{1}{2} v_{particle}$$
(2.9)

where the kinetic energy of the particle is used. In general the total energy of the particle is given by the sum of kinetic T and potential energy U:

$$E = T + U(x) = \frac{1}{2}mv_{particle}^{2} + U(x)$$
(2.10)

Here for simplicity U(x) = 0, thus:

$$E = \frac{1}{2}mv_{particle}^2 = \frac{p^2}{2m} \tag{2.11}$$

The phase velocity of a monochromatic wave field is equal to one-half the particle velocity, thus they are different. Nevertheless this has no particular implications since it is not possible to measure the phase velocity of a monochromatic wave directly (see [88] for details). The main point here is that a monochromatic wave has an amplitude (and an intensity) that is constant in all the space, thus it is non-localized, indeed (considering again the 1D example of before):

$$|\psi(x,t)|^2 = |wave(x,t)|^2 = |Ae^{i(kx-\omega t)}|^2 = |A|^2 = constant \ in \ x$$

Now it should be evident that a monochromatic wave field  $\psi(x,t) = Ae^{i(kx-\omega t)}$  does not provide information about the localization in space of a particle.

Instead a localized particle should be related to a wave field that has a large amplitude (or intensity) in the region of space in which the particle is localized and null or very small outside it. As already mentioned previously, a wave field with a large intensity only in a small region of space must be built by means of interference processes, by superposition of many monochromatic waves. Indeed a pulse can be localized, see figure 2.3 (bottom). It can be expanded as superposition of monochromatic waves by exploiting the Fourier transform (or series), thus it is effectively a wave-packet, intended as a set of monochromatic waves. In this regard think for example that the Fourier transform of a pulse (with a well define time -or spatial- support) presents a wide bandwidth in frequency domain that includes many different frequencies, while the spectrum of a monochromatic wave contains (ideally) only one frequency, i.e. it is a delta Dirac. From the basic physics and from the courses about signal processing and telecommunication theory, it is well known that the velocity



Figure 2.3: A monochromatic continuous wave train corresponding to an unlocalized particle (top); and an example wave packet corresponding to a localized particle within the distance  $\Delta x$  (bottom);  $\lambda$  is the monochromatic wavelength,  $v_g$  is the group velocity of the pulse envelope.

at which a wave-packet travels (think e.g. to amplitude modulation schemes) is not the phase velocity but instead the so-called group velocity, that is given by  $v_{group} = \frac{d\omega}{dk}$  (a derivation can be found in [88] or in any basic classical wave physics or signal processing book). Since the wave-packet (i.e. the pulse) is associated to the particle position, its envelope velocity must be equal to the particle velocity, that indeed is:

$$v_{group} = \frac{d\omega}{dk} = \frac{dE}{dp} = \frac{d}{dp} \left[ \frac{p^2}{2m} \right] = \frac{p}{m} \equiv v_{particle}$$
(2.12)

Now it is evident that a localized particle is associated to wave-field that is not monochromatic but given by a wave packet, whose group velocity corresponds to the particle velocity.

A crucial conceptual point is that when an electron shows its particle-like nature, e.g. through a position measurement, nothing is known about its wave-like nature since this corresponds to a well localized wave packet, thus containing a large range of frequencies or wavelengths. In terms of Fourier transform a small space support (small region of space in which the probability of finding the particle is non-negligible) corresponds to a wide frequency bandwidth, with many frequencies (i.e. wavelengths) within it. With the de Broglie relation (eq. 2.7) this corresponds to a wide range of momenta p. Consequently an electron with well defined position has a non-defined momentum p. Vice versa whenever

an electron shows its wave-like nature, e.g. through a momentum measurement, nothing is known about its particle-like nature since this corresponds to an unlocalized monochromatic wave, with a given value of p and thus a well-defined wavelength  $\lambda$ . This is the basic intuition behind the indetermination principle formulated in 1927 by Werner Heisenberg. It states that in a microsystem is not possible perform simultaneous measurements of position and momentum with arbitrary high accuracy. This limit is not related to measurement setup issues, but to the intrinsic nature of microscopic systems. This is a peculiar situation that is not preset in classical physics. Indeed in classical mechanics it is always possible to know with the desired accuracy both the position and the momentum of classical particles (within the measurement error and accuracy). Thus in classical physics it is possible to speak about trajectories, intended as the curve followed by classical particles for which the position and the velocity (or momentum) are simultaneously known. Instead in quantum mechanics, because of the wave-particle duality, in order to have a space localized wave packet it is necessary to superpose several monochromatic fields with different wavelengths  $\lambda$ , or with different wavenumbers k. Once again notice that if the Fourier transform of the wave packet (i.e. the pulse) is considered, the waveform result decomposed as a superposition of monochromatic waves, each with suitable amplitude (i.e. Fourier transform coefficient). Then recall also that the Fourier transform of a space coordinate x corresponds to a wavenumber  $k_x$ , and in 1D case the subscript can be omitted without confusion:

$$x \stackrel{\mathfrak{F}}{\longleftrightarrow} k$$

At this point if the wave packet extends over a region  $\Delta x$ , the values of the wavenumbers of the interfering waves that compose the wave packet and have appreciable amplitude fall within a range  $\Delta k$  such that:

$$\Delta k \sim \frac{2\pi}{\Delta x} \quad \Rightarrow \quad \Delta x \ \Delta k \sim 2\pi$$

Notice that the last expression follows directly from the theory of Fourier analysis. According with eq. (2.7) with  $\lambda = \frac{2\pi}{k}$ , different wavelengths  $\lambda$  or wavenumbers k mean that there are several values of p such that  $\Delta p = \hbar \Delta k$ , and therefore the previous expression becomes:

$$\Delta x \ \Delta p \sim h \tag{2.13}$$

The last expression constitutes a possible mathematical relation of the above introduced Heisenberg's indetermination principle (see section 2.5 for a more precise expression). Notice that it is a direct consequence of the Fourier transform analysis, as already pointed out. The physical meaning of eq. (2.13) is the following:  $\Delta x$  and  $\Delta p$  should be interpreted as the variance (or eventually standard deviation) of the position and the momentum of the considered microscopic system. Since their product is essentially constant and proportional to the Planck's constant h if one of the two physical quantities is known with whatever precision (i.e. with null variance and standard deviation) then the other one is completely unknown. In other words if a particle is within the spatial region  $x - \frac{1}{2}\Delta x$  and  $x + \frac{1}{2}\Delta x$  (that is  $\Delta x$  is the uncertainty on its position), its associated wave field is represented by superposing monochromatic waves of momenta between  $p - \frac{1}{2}\Delta p$  and  $p + \frac{1}{2}\Delta p$ , where  $\Delta p$ 

is related to  $\Delta x$  by means of eq. (2.13). The information about the localization in space is obtained at the expense of the information about its momentum, or velocity, thus as already said in quantum mechanics there is no more the concept of trajectory. It is not possible to accurately determine both the position and the momentum simultaneously ( $\Delta x = 0$  would imply  $\Delta p \rightarrow \infty$  and vice versa). The Heisenberg's uncertainty principle holds true in general for each pair of canonically conjugated variables (i.e. for all that variables that are connected by means of a time derivative operation), and not only for position and momentum. This again is a consequence of the Fourier transform properties:

$$\frac{d}{lt} \stackrel{\mathfrak{F}}{\longleftrightarrow} i\omega \tag{2.14}$$

where  $\omega = 2\pi f$  and *i* is the imaginary unit (sometimes depending on the sign convention in the exponent in the Fourier transform definition the previous relation is written with a minus sign:  $-i\omega$ ). Considering that f = E/h it is easily recovered the previous result. In addition to the position and momentum uncertainty relation and to all the canonically conjugated variables uncertainty relation, an interesting uncertainty relation needs a brief comment: the time-energy uncertainty relation. Indeed starting from eq. (2.14) it is possible to write:

$$\Delta t \ \Delta \omega \sim 2\pi \tag{2.15}$$

Again the physical meaning is suddenly clear when the Fourier theory is considered. As well known, if the time duration of a wave packet, i.e. the time support of a pulse, is very short in time, then to represent that pulse in terms of Fourier transform (or series) as superposition of monochromatic waves, a wide frequency bandwidth is necessary. Thus to define the exact time at which a particle passes through a given point, the pulse should in fact have a short duration  $\Delta t$ . But to build up such a pulse different harmonic waves with different frequencies are to be used. Then these harmonic waves will have an appreciable amplitude in the frequency range  $\Delta \omega$  centered around the frequency  $\omega$ . Multiplying both members of eq. (2.15) by  $\hbar$ , recalling that  $E = hf = \hbar \omega$  and  $2\pi\hbar = h$  the energy-time uncertainty relation is found:

$$\Delta t \ \Delta E \sim h \tag{2.16}$$

The uncertainty relation (2.16) needs a remark on its physical interpretation and another relative to its formal correctness. The physical meaning of equation (2.16) should be interpreted as related to unstable or excited systems. Equation (2.16) states essentially that in order to determine the energy E of a system with an uncertainty  $\sim \Delta E$  a time of the order of  $\Delta t$  is necessary. This means that in order to measure the energy of a stable system with a perfectly defined energy it should be necessary an infinite time. Thus a correct interpretation of eq. (2.16) is in terms of lifetime of excited states. For example if an electron in an atom for some reason is excited and goes in an excited state, then after some time it will suffer a radiative transition by means of which it looses its excess energy and goes into a stationary state, namely the ground state. Unfortunately it can be shown that there is no mean of predicting exactly how long the electron will remain in the excited state before it makes the transition. At most it is possible to speak about transition probability per unit time that the electron jumps back to the ground state. Therefore the average time interval the electron stays in the excited state is named lifetime of that state (it is inversely proportional to the transition probability), and it can be known with an uncertainty of the order of  $\Delta t$ . Hence the energy of the excited state cannot be known exactly, but only within an uncertainty range of the order of  $\Delta E$ . The shorter is the lifetime (and thus  $\Delta t$ ) the larger is the uncertainty on the excited state energy  $\Delta E$ . For the ground state, whose lifetime is infinite (since the system is stable and cannot suffer of a transition toward a state of lower energy) the lifetime and thus  $\Delta t$  is infinite, while its energy can be known with the desired accuracy ( $\Delta E \rightarrow 0$ ).

Coming to the formal correctness of eq. (2.16), a good discussion is provided in [87]. In extreme summary the fact is that despite the name "principle" the Heisenberg's indetermination principle can be demonstrated and indeed it a theorem. As already mentioned the demonstration holds for all the canonically conjugated variables. Nevertheless the total energy of a system E and the time t are not canonically conjugated variables (the total energy of a system cannot be determined as the time derivative of the time - it has no meaning). Formally this trouble comes out because the time in quantum mechanics is not considered a "physical observable" but instead like a free parameter. In quantum mechanics, as will be clarified in section 2.3.4, to each physical observable a specific operator is associated, but since the time is a parameter it is not an operator. Thus if one uses the same procedure used for the demonstration of the Heisenberg's indetermination principle a conceptually wrong relation is recovered. Nevertheless it is possible to formally demonstrate the time-energy uncertainty relation proceeding with slightly different arguments. Thus a similar expression to eq. (2.16) can be formally showed using non-relativistic (let's say "standard") quantum mechanics, and its physical interpretation is conventionally the one I have reported above.

# 2.3 The Schrödinger's equation

Classical mechanics was developed for describing the detailed motion of macroscopic bodies under the assumptions that these bodies are localized in space and can be observed without appreciably disturbing their motion. These assumptions are in general made implicitly rather than stated in a precise way, but they are at the basis of the classical formalism. As briefly summarized in the previous sections 2.1 and 2.2, it is no more possible talking about localization in a classical way when microscopic entities are considered. Moreover measurements on some physical observable related to microscopic systems show the evidence that such quantities (like the energy levels of atoms and molecules) are quantized, and this is again unexpected with classical mechanics. Quantum mechanics is instead capable of catch all these physical insights. The first issue to address in a novel physical theory of mechanics is how to represent the state of the system under study and then how to determine the dynamics of the system state, i.e. its time evolution. The state of the system is represented by means of the so called "wave-function"  $\psi(x, y, z; t)$ :

$$\psi(x, y, z; t) : \mathbb{R}^4 \mapsto \mathbb{C}$$

this complex function represents the wave field associated to each microscopic particle or system. It is a function of space (in the three variables x, y, z) and time t. Its meaning and its properties will be described more in details in sections 2.3.1 and 2.3.2 respectively. The time evolution of the system described by  $\psi$  can be determined by means of the Schrödinger's equation, firstly introduced by Erwin Schrödinger in 1926:

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r};t) = \hat{H}\psi(\vec{r};t)$$
(2.17)

where:

- *i* is the imaginary unit
- $\hbar$  is the reduced Planck's constant (already introduced)
- $\vec{r} = (x, y, z)$  is the position vector in the 3D space
- $\frac{\partial}{\partial t}$  indicates the derivation operation w.r.t. the time t
- $\psi(\vec{r};t)$  is the wave-function that represents the system state at the time instant t
- $\widehat{H}$  is the so called Hamiltonian (quantum mechanical) operator

Before going on few words concerning the Hamiltonian operator are needed. In quantum mechanics to each physical observable (such as the energy, the position, the momentum, the angular momentum and so on...) a mathematical operator is associated. By making use of such mathematical operator (that can be e.g. a differential operator) it is possible to make previsions and calculations about that specific physical quantity and then predict the set of its possible values. A more detailed introduction to quantum mechanical operator (and their origins) is reported in section 2.3.4. In classical rational mechanics the system total energy E, given by the sum of the kinetic energy T and the potential energy U, is equal to the so called Hamiltonian H of the system (this holds if the body constraints are time-independent, otherwise the Hamiltonian H is a scalar function of the system total energy). Thus H = T + U = E corresponds to the total energy of the system. Since as already mentioned in quantum mechanics to each physical observable a mathematical operator is associated, to the total energy of the system an operator, i.e. the Hamiltonian operator, is associated. Generally to distinguish the operator from the observable the symbol  $\hat{}$  is positioned on top. Thus  $\hat{H}$  is the quantum mechanical operator associated to the total energy of the system, i.e. the system Hamiltonian, and it can be used to find the possible set of energy values (from here on indicated with E) for that specific system. In section 2.3.4 this concept will be further discussed.

The Schrödinger's equation is the most important equation in (non-relativistic) quantum mechanics. As already pointed-out it provides the dynamics of the system, i.e. its time evolution. Starting from the knowledge and the hypothesis about the system under study it is possible to derive an explicit expression for the Hamiltonian operator  $\hat{H}$ , that is known. Then by solving the Schrödinger's equation the wave-function is obtained, that is: the system state (represented by  $\psi$ ) is found by solving the Schrödinger's equation. More precisely equation (2.17) is referred as the time-dependent Schrödinger's equation, and indeed it provides the time evolution of the system ( $\psi$  in eq. (2.17) is function of time). Starting from the knowledge of the system state at initial time instant  $t_0$ , i.e. starting from  $\psi(\vec{r}; t_0)$ , the state  $\psi(\vec{r}; t)$  at whatever time instant t can be found by solving the Schrödinger's equation (2.17). The general solution of eq. (2.17) will be addressed in section 2.3.5.

The Schrödinger's equation was the fundamental starting point for the development of a complete quantum theory. Indeed the quantization of some physical properties (such as the energy) arises naturally as a consequence of the enforced boundary conditions used in the solution of the Schrödinger's equation for a specific system (and the same quantity -e.g. the energy- results quantized or continuous depending exactly on the specific boundary conditions), contrarily to the initial attempts briefly discussed in section 2.1, in which the quantization was introduced *ad hoc*.

The Schrödinger's equation is often compared for importance and meaning to the well known Newton's second law of dynamics, i.e.  $\vec{F} = m\vec{a}$  (where  $\vec{F}$  is the total force acting on the body of inertial mass m and  $\vec{a}$  is its acceleration); and analogously to it there exist no demonstration of the Schrödinger's equation. This equation was the result of the exceptional intuition of Erwin Schrödinger and at most it is possible to provide some "arguments of plausibility" that are aimed in intuitively justify it. In this regard a good treatment is provided in [87] (in Italian) or in [93] (in English). Here I only point out that the purpose of the Schrödinger's equation is to provide the wave field  $\psi(\vec{r};t)$  that is associated to a microscopic system, and thus some similarities with a conventional wave equations are expected. In particular embedded within the Hamiltonian operator Hthere is a space second order derivative (see section 2.3.4 for details), and in eq. (2.17)a first order derivative in time appears. In a classical, let's say standard, wave equation it is expected to have also a second order derivative in time, nevertheless this is what distinguish the Schrödinger's equation from a standard wave equation. The reason behind the first order time derivative is linked to the validity of superposition principle for the wave-function. Indeed as clarified in section 2.3.2 a fundamental physical requirement for the wave-function  $\psi$  is that the superposition principle holds, i.e. if  $\psi_A$  and  $\psi_B$  are possible states for a microscopic system, then a linear combination of them must be again a state for that system. This requires firstly the Schrödinger's equation to be linear (as it is, since derivative operators are linear), and then to have non-dynamic coefficients (if dynamic coefficients were present different wave-functions corresponding to different coefficient values would be solutions of different equations thus making the superposition principle no more valid). The latter requirement implies a first order time derivative instead of a second order one in eq. (2.17).

# 2.3.1 Wave-function physical meaning

The first implication of the wave-particle duality (section 2.1) is that it is not possible to talk about trajectories for microscopic system because of the Heisenberg's uncertainty principle (section 2.2) that states the impossibility of knowing at the same the position and the momentum of a microscopic particle. Moreover the revolutionary fundamental concept of the wave-particle duality is that to each particle is associated a wave field, that is somehow represented by means of the complex field  $\psi(\vec{r};t)$ . The purpose of this section is to definitively clarify the physical meaning of the wave-function, i.e. of  $\psi(\vec{r};t)$ , that is associated to a microscopic particle.

The wave-function  $\psi(\vec{r};t)$  precisely represents the amplitude of the wave field (sometimes called matter field [88]) that is associated to a particle. From the mathematical standpoint a "field" is a function of more variables whose domain and codomain are the same, e.g. in physics very often four variables are used (three for the space coordinate and one for the time coordinate) thus for example  $f : \mathbb{R}^4 \to \mathbb{R}^4$ . A scalar field is instead a scalar function of more variables. For example the temperature, that links a scalar value to each point in space at each time, is a scalar field: *temperature* :  $\mathbb{R}^4 \to \mathbb{R}$ . In the case of the wave-function:

$$\psi(x, y, z; t) : \mathbb{R}^4 \mapsto \mathbb{C}$$

It means that a complex scalar value  $\psi$  is associated to each point of space at each time instant; thus  $\psi$  is a (complex) scalar field. The complex value  $\psi$  has to be intended as the amplitude of the wave field that is associated to a given microscopic system. From classical theory of waves it is well known that the intensity of a wave (linked to its energy or power) is proportional to the square of its amplitude. By analogy in quantum mechanics the intensity of the wave field is  $|\psi(\vec{r};t)|^2 = \psi(\vec{r};t)\psi^*(\vec{r};t)$ , since the wave-function already corresponds to the wave field amplitude. In this case the wave-function is in general a complex function of space and time, and its modulus squared must be considered, since the intensity of a wave field is by definition a real scalar quantity.

The physical meaning of the wave-function and of its modulus squared, i.e. the physical meaning of the intensity of the wave field associated to microscopic entities, becomes then clear if the experiments on electrons described in section 2.1 are considered. In the moment in which it is accepted that the electrons impacting on the photographic plate are described by a wave field, it is possible to associate the intensity of the electrons tracks on the photographic plate to the wave field intensity, i.e.  $|\psi(\vec{r};t)|^2$ . Where the wave field is more intense,  $|\psi(\vec{r};t)|^2$  is larger, and thus  $|\psi(\vec{r};t)|^2$  must be somehow proportional to the distribution of the electrons on the photographic plate. Notice at this point that  $|\psi(\vec{r};t)|^2$  does not describe a collective property of the electrons, indeed as mentioned in section 2.1 the same interference patterns are obtained also sending one electron at a time. Moreover each electron hits the photographic plate in one specific point (leaving a well define point-like sign), thus the wave field cannot be interpreted as a matter wave, in which there is a collective motion of the particles involved (think for example to a mechanic wave in a string, the particles of the string oscillate in a well defined way but the phenomenon is obviously extremely different from the one noticed for electrons). Consequently this wave field should be considered like a wave field of probability. The probability should then be interpreted as probability of position, i.e. of finding the microscopic system in that specific point at that specific time. Consequently the intensity of the wave field, that is its amplitude squared, i.e.  $|\psi(\vec{r};t)|^2$ , should be somehow proportional to the probability of finding the microscopic system (e.g. the electron) in that place at that time. More precisely the wave-function modulus squared is conventionally interpreted as the position probability density (i.e. probability per unit volume) of the system that it describes. For this reason the wave-function is also called "amplitude of position probability".

To be more quantitative: the probability of finding the microscopic system described by the

wave-function  $\psi(\vec{r};t)$  in the (3D) neighbourhood  $d\vec{r}$  around the point  $\vec{r}$  at the time instant t is given by:  $|\psi(\vec{r};t)|^2 d\vec{r}$ . Where in this notation (similar to one of [87])  $d\vec{r} = dxdydz$ . In summary,  $|\psi(\vec{r};t)|^2 d\vec{r}$  is interpreted as the probability of finding the system between  $\vec{r} = (x, y, z)$  and  $\vec{r} + d\vec{r} = (x + dx, y + dy, z + z)$  at the time instant t. The total position probability can be recovered integrating over the entire volume V the probability density:

$$P = \int_{V} \left| \psi(\vec{r}; t) \right|^2 d\vec{r} \tag{2.18}$$

where P corresponds to the probability of finding the system described by  $\psi$  within the volume V, and as already mentioned  $|\psi(\vec{r};t)|^2$  is the probability per unit volume.

This interpretation of the wave-function squared modulus like a probability density is universally accepted and it is the conventional interpretation provided in all basic courses of quantum mechanics [87]. It is usually referred as the "Copenaghen" interpretation of quantum mechanics, mainly due to the works, done in Copenaghen, by Bohr and Heisenberg during the 1927 and after the second world war by Wolfgang Pauli, even if the first idea of associating to the intensity of the wave field the meaning of probability density is due to Max Born. Other interpretations of quantum mechanics are possible, and even if their treatment is outside the scope of this work, I would like to briefly mention the so called "statistic" interpretation of quantum mechanics. In this interpretation the probability associated to the wave field has to be interpreted like applied to a set of systems or particles but not to a single system or particle. In this interpretation the amplitude of the wave field has a more abstract physical meaning related to the statistics of obtaining a given configuration (e.g. a given diffraction pattern on the photographic plate) that is represented by the wave-function. The difference w.r.t. the Copenaghen interpretation can appear subtle at a first read, but the main diversity is exactly that in the Copenaghen interpretation the wave field meaning of probability is associated also to a single particle. In the statistic interpretation the probability arises from the fact that there is an intrinsic limit in the knowledge of microscopic system, that nevertheless behave in a deterministic way. Notice that the limit is intrinsic and not related to instrumentation limits (see section 2.2). If there were not this intrinsic limit then a deterministic description would be possible. Instead in the Copenaghen interpretation the probabilistic meaning of the wave field is intrinsic. To better clarify this point consider the two slits experiment presented at the end of section 2.1. In this experiment when a single slit is open the diffraction pattern of figure 2.1 is recovered, instead when both are open a different shape is obtained, that evidently presents interference patterns. The electrons in such an environment are described by two wave-functions  $\psi_A$  and  $\psi_B$  depending if the electron passes through one slit (A) or the other (B). The two wave-functions  $\psi_A$  and  $\psi_B$  alone corresponds exactly to the diffraction patterns of figure 2.1, correctly aligned to the slit A or B. When both slits are opened then the electrons, that can pass through one or the other slit, are described in general by a wave-function  $\psi_C$  that is the superposition of the wave-functions of before:  $\psi_C = \psi_A + \psi_B$ . This effectively corresponds to the interference pattern that appears on the photographic plate when both the slits are opened. Thus if  $\psi_A$  and  $\psi_B$  are solution of the Schrödinger's equation (2.17) for that system, also  $\psi_C$  must be solution of the same equation, i.e. the superposition principle must hold. This is exactly the reason why the Schrödinger's equation is linear and with non-dynamic coefficients, as discussed previously.

And since the Schrödinger's equation is linear and with non-dynamic coefficients  $\psi_C$  is actually solution for the Schrödinger's equation. The electron state before it impacts on the photographic plate, in the case in which both the slits are open, is represented by  $\psi_C = \psi_A + \psi_B$ , i.e. it is the sum of two states. In the Copenaghen interpretation the electron, before impacting onto the plate, is actually in two different states simultaneously, i.e. in both states  $\psi_A + \psi_B$ . In the moment in which a detector is used to understand toward which slit the electron is passing, then there happens the so called "collapse" of wave-function, that means that electrons are no more in the state  $\psi_C$  but they collapse in one of the two states  $\psi_A$  or  $\psi_B$  that constitute  $\psi_C$ . The collapse of the wave-function in the Copenaghen interpretation is actually intended as a change of state of the electrons, that from the state  $\psi_C$  collapse to the state  $\psi_A$  (or  $\psi_B$ ) because of the measurement process. The measurement procedure in microscopic system always interact strongly with the system and force this transition of state. Instead in the statistic interpretation of quantum mechanics, writing  $\psi_C = \psi_A + \psi_B$  is a way to quantify that some electrons pass through A, and thus are represented by  $\psi_A$  and others trough B (represented by  $\psi_B$ ), but since it is not possible to know toward which aperture they pass the description is given by  $\psi_C = \psi_A + \psi_B$ . The state  $\psi_C$  is then a sort of collective state, that is the result of the experiment only when an enough large number of electrons are considered, while the single electron will not be in two states ( $\psi_A$  and  $\psi_B$ ) at the same time but only in one of them  $(\psi_A \text{ or } \psi_B)$ . In this picture the electron wave-function collapse is not intended as a state transition from  $\psi_C$  to  $\psi_A$  or  $\psi_B$  but is intended as the revelation of the actual state of that specific electron, that can be either  $\psi_A$  or  $\psi_B$ .

As mentioned many other interpretations are possible and they are not discussed here. The difference between these two should have been useful in highlight the widely accepted Copenaghen interpretation. The point is that all such interpretations are a boundary matter between physics and metaphysics (or philosophy), and indeed they are the subject of many science philosophy debates.

Independently of what is the correct interpretation of quantum mechanics, and thus of what are the features of the world we are living in, the practical importance of this theory is that it provides the means to predict the behavior of microscopic systems and to design novel devices based on them. In the following of this work the Copenaghen interpretation will be considered.

So far only the modulus of the wave-function was considered. Since it is a complex function it has also a phase. The wave-function phase is useful in interference phenomena, for example when more states are superimposed, to correctly find the total state (like done previously with the two slit experiment). The interference patterns between wave-functions are indeed the results of the phase mismatch between different wave-functions.

Notice again that the wave-function (in the Copenaghen interpretation) describes a single microscopic system and not a statistic set of systems. Nevertheless also in the Copenaghen interpretation it is possible to consider the wave-function as representative of statistic properties of a set of identical systems, at least if the number of considered identical systems is enough large. For example if a set of  $N_A \sim 6 \cdot 10^{23}$  (Avogadro's number) of identical systems is considered, and the wave-function has a probability of 10% to find the single system in a given volume, then it is possible to say that volume contains the 10% of the considered systems.

A final remark is now provided by means of an example. An atom is a quantum system, and it is known form basic chemistry that it is constituted by a nucleus of protons and neutrons around which the electrons are present, like they were in "orbit" around the nucleus. Since it is not possible to talk about trajectories (and thus orbits), and keeping in mind the wave-function meaning explained above, the wave-functions that are solutions of the Schrödinger's equation for an atom, are to be intended as the amplitude of the position probability wave field. Thus their moduli squared, when integrated over the space, provides a surface in the 3D space that corresponds to the high probability region. The higher is  $|\psi|^2$  the higher is the probability of finding the electron in that space region. In general the wave-function modulus squared are the so called atomic orbitals (usually indicated with  $1s, 2s, 2p_x, 2p_y, 2p_z$ , etc...), usually presented in the basic chemistry courses. It is well known that the 1s orbital has the shape of a sphere around the atomic nucleus. Well, that sphere is the region in which it is most probable to find the electron that is in that specific state (with that specific energy, angular momentum modulus and orientation and spin). In this optics atomic and molecular orbitals correspond simply to high probability regions, in which it is highly probable to find that electrons.

Finally notice that the wave-function describes the microscopic system and it contains all the information that is possible to get about the system.

## 2.3.2 Wave-function properties

Once understood the physical meaning (Copenaghen interpretation) of the wave-function as the amplitude of the position probability wave field associated to the microscopic system (see section 2.3.1), a set of properties that the wave-function must satisfy is immediately derived. In particular the probability of finding a given particle in all the space must be 100% (if the particle exists it must be inside the universe). Then it follows immediately that:

$$P = \int_{All \ space} |\psi(\vec{r};t)|^2 \, d\vec{r} = 1$$
 (2.19)

This condition is called the "normalization condition" [88]. Indeed it imposes a limitation on the possible forms of the wave-function  $\psi$  since it is not always possible to satisfy eq. (2.19). In particular  $\psi$  must decrease rapidly when the coordinates x, y, z are large in order to ensure the integral to exist. More precisely the wave-function must be a square-integrable function (or quadratically integrable function), that means:

$$\int_{-\infty}^{+\infty} |\psi(\vec{r};t)|^2 \, d\vec{r} < \infty \tag{2.20}$$

The usual notation for indicating a square-integrable wave-function over the space region V is:  $\psi \in L^2(V)$ . If it is supposed to have an electron under test, it can be considered like certainly confined in the laboratory in which the experiments takes place, thus said V the volume of the laboratory, the normalization condition becomes:

$$P = \int_{V} |\psi(\vec{r};t)|^2 d\vec{r} = 1$$
(2.21)

and the wave-function must be square-integrable in the domain  $V: \psi \in L^2(V)$ .

*Example 2.1:* Let's consider for example a 1D wave-function (where K is a real constant,  $K \in \mathbb{R}$ ):

$$\psi(x;t) = \begin{cases} K &, & if \ 0 < x < x_0 \\ 0 &, & otherwise \end{cases}$$

The normalization condition implies that:

$$\int_{-\infty}^{+\infty} |\psi(x;t)|^2 dx = 1 \quad \Rightarrow \quad \int_0^{x_0} |K|^2 dx = 1 \quad \Leftrightarrow \quad |K|^2 x_0 = 1 \quad \Leftrightarrow \quad K = \frac{1}{\pm \sqrt{x_0}}$$

Thus assuming for example the positive sign solution the normalized wave-function, to which it is possible to associate the meaning of position probability density is:

$$\psi_N(x;t) = \begin{cases} \frac{1}{\sqrt{x_0}} &, & if \ 0 < x < x_0\\ 0 &, & otherwise \end{cases}$$

such that:

$$\int_{-\infty}^{+\infty} |\psi_N(x;t)|^2 \, dx = \int_0^{x_0} \left| \frac{1}{\sqrt{x_0}} \right|^2 \, dx = \frac{1}{x_0} x_0 = 1$$

where the subscript N is used to point out that  $\psi_N$  is the normalized wave-function.  $\Box$ 

Other direct consequences of the (normalized) wave-function physical interpretation as probability density are that it must be a monodromic function (i.e. it provides a single complex scalar value and not a complex vector) since it has no sense talking about more than one probability values of finding the particle in a given point. It must be everywhere limited (the probability cannot be infinite in a point or region of space) and that it must be continuous (if a 1D wave-function in space is considered, it has no meaning talking about a left-side probability or right-side probability around a point  $x_0$  in which a discontinuity is present, thus the left and the right limits should be equal and the wave-function is continuous). Another property that is possible to demonstrate is that the wave-function must also have continuous first derivatives. The latter property follows from a continuity equation (analogous to the well known continuity equation for the electrical current), that is intimately linked with the concept of continuity of the total probability. In few words the fact the total probability must be conserved (i.e. if at a given time instant  $t_0$  there is a particle in a given region of space, at another time instant  $t_1$  the particle does not disappear if no particular interactions occur, thus the integral over all the space of the wave-function even at  $t_1$  must be unitary, that corresponds to a total probability conservation) implies that the total probability must satisfy a continuity equation, and thus must have a continuous first derivative.

The last two properties, i.e. the wave-function must be continuous with continuous first derivative, imply that the wave-function must be of class  $C^1$ :  $\psi \in C^1(V)$ , where V is the volume of definition of the wave-function. From the mathematical standpoint this is also a direct implication of the fact that  $\psi \in L^2(V)$ . Indeed it is possible to show that:

$$\psi \in L^2(V) \Rightarrow \psi \in H^2(V) \Rightarrow \psi \in C^1(V)$$

where  $H^2$  is the so called Sobolev space. This last relation is often seen in the numerical methods courses.

The last important property to be satisfied by wave-function is the superposition principle. This is a direct consequence of the de Broglie assumption of wave-particle duality. Indeed in order to localize a particle in space it is necessary to consider a wavepacket, as described in section 2.2. A wave-packet is obtained thanks to the interference of monochromatic waves, i.e. it is constituted by a superposition of wave-functions, thus the superposition principle must hold. This point was also clarified in the previous section 2.3.1 when the two slits experiment was considered as an explicative example for the wave-function physical meaning. Two are the equivalent statements that summarize the validity of the superposition principle. First, wave-functions that differ only for the normalization constant (i.e. they are different only because of a different multiplicative constant) represent the same state. So the two wave-functions  $\psi$  and  $\psi_N$  considered in example 2.1 are representing the same physical state.

Second, if a system can be in a state described by the wave-function  $\psi_A$  and also in another state described by the wave-function  $\psi_B$  (see e.g. the two slits experiment), it can also be in whatever state that is a linear combination of the two:

$$\psi = \alpha \psi_A + \beta \psi_B \quad , \quad \alpha \; , \; \beta \; \in \mathbb{C} \tag{2.22}$$

The last statement can be rephrased as: the set of all wave-functions that describe all possible physical states of a given quantum system constitute a vector space.

In this regard notice that if a system is in the state  $\psi = \alpha \psi_A + \beta \psi_B$ , the result of measurement on it can be either  $\psi_A$  or  $\psi_B$ , and it is said (as already pointed out) that the wave-function  $\psi$  collapse into either  $\psi_A$  or  $\psi_B$ .

As already pointed out in the previous sections the Schrödinger's equation is totally linear and with non-dynamic coefficients. This ensures the validity of the superposition principle (and indeed the Schrödinger's equation was "built" up to satisfy it).

In summary the properties of a wave-function are the following:

- it must be square-integrable:  $\psi \in L^2(space)$ .
- it must be normalized such that it can be interpreted as position probability density, the normalization condition is given by eq. (2.19).
- it must be a monodromic function (i.e. it provides a single -complex- scalar value and not a vector, the codomain is C).
- it must be everywhere limited.
- it must be continuous.
- it must have continuous first derivatives.
- the superposition principle holds.

### 2.3.3 Expected values and momentum space

At the end of section 2.3.1 was pointed out that the wave-function contains all the information that is possible to get about the system. The purpose of this section is to further discuss this statement, by giving an introduction to the calculation of average values in quantum mechanics. More precisely the question addressed in this section is "what is the information that can be extracted from the wave-function?". First of all a fast review of average value and standard deviation is provided.

#### Expectation values review

From an experimental standpoint, from basic bachelor's level courses on physics and statistics, the expected value  $\langle F \rangle$  of a quantity F can be defined by doing a series of N measurements performed on identical systems in the same conditions (and thus described by the same wave-function). The arithmetic mean of the obtained measurement results is the average value:

$$\langle F \rangle = \frac{1}{N} \sum_{i} n_i f_i = \sum_{i} \nu_i f_i \tag{2.23}$$

where it is intended that during the N measurements of F, the value  $f_i$  was obtained  $n_i$  times, and where  $\sum_i n_i = N$ . The frequency at which the result  $f_i$  appears is then  $\nu_i = \frac{n_i}{N}$ . If the number of total measurements N is very large then the frequency  $\nu_i$  can be interpreted as a probability (see for example [94]):  $\nu_i \rightarrow P_i$  when  $N \rightarrow \infty$ . Thus equation 2.23 can be rewritten as:

$$\langle F \rangle = \frac{1}{N} \sum_{i} f_i P_i \tag{2.24}$$

The last relation holds for system in which quantization appears and thus discrete values of the quantity F are possible. It corresponds to the case of a discrete random variable [94]. If the quantity F can assume a set of continuous values then the previous equation is modified as follows (F is considered in the same way as a continuum random variable):

$$\langle F \rangle = \int f P(f) df$$
 (2.25)

where P(f) is the conventionally called probability density function, and P(f)df has the meaning of differential probability, i.e. of probability of finding a result between f and f+df when a measurement on F is performed. Finally recall that the definition of standard deviation (intended as the dispersion of the obtained results f when measurements on F are performed) is the following:

$$\Delta F = \sqrt{\langle F^2 \rangle - \langle F \rangle^2} \tag{2.26}$$

where the term under square root is called variance. The bigger is  $\Delta F$  the more the measured values are different among them. Notice that it corresponds to the notation used in section 2.2 for indicating the standard deviation of position, momentum, energy and time.

#### Expectation values in quantum mechanics

Coming now to the information that can be extracted from the wave-function, and considering the probabilistic meaning of wave-function itself, it is intuitive that a statistical information can be extracted from it. Indeed in quantum mechanics it is possible to evaluate the expected value  $\langle F \rangle$  of each physical observable F starting from the knowledge on the wave-function that represents the state of the system. In fact the wave-function squared modulus  $|\psi|^2$  corresponds exactly to the probability density function P(f) since it is interpreted as the position probability density, and  $|\psi|^2 d\vec{r}$  corresponds to the differential probability P(f)df (see section 2.3.1).

Thus the expected value for the position vector  $\vec{r}$  can be expressed as:

$$\langle \vec{r} \rangle = \int \vec{r} \left| \psi(\vec{r};t) \right|^2 d\vec{r}$$
(2.27)

in which the integral corresponds to a continuum sum over all the possible values of  $\vec{r}$  (usually they coincide with all the possible points in space), each multiplied by its probability:  $|\psi(\vec{r};t)|^2$ . Then  $|\psi(\vec{r};t)|^2 d\vec{r}$  is exactly the differential probability of before, i.e. the probability of finding  $\vec{r}$  in the infinitesimal volume in between  $\vec{r}$  and  $\vec{r} + d\vec{r}$ . Notice that eq. (2.27) is a vector equation that embeds three scalar equations in the three variables x, y, z. In general it is possible to show that whatever function  $F(\vec{r})$  of  $\vec{r}$  has an expected value that is:

$$\langle F(\vec{r})\rangle = \int F(\vec{r}) \left|\psi(\vec{r};t)\right|^2 d\vec{r}$$
(2.28)

indeed  $|\psi(\vec{r};t)|^2 d\vec{r}$  corresponds to the probability density function of position, and a function  $F(\vec{r})$  involves only the probability of position. In other words the probability density function of a function of the position vector corresponds to the position probability density. This point is clarified in the following example.

*Example 2.2:* The average value of the function F(x, y, z) = xy is given by:

$$\langle xy \rangle = \int xy \left| \psi(\vec{r};t) \right|^2 d\vec{r}$$
(2.29)

indeed  $|\psi(\vec{r};t)|^2 d\vec{r}$  is the probability of finding x at the time instant t between x and x + dx but also the probability of finding y between y and y + dy.  $\Box$ 

Equation (2.28) can be rewritten as:

$$\langle F(\vec{r})\rangle = \int \psi^*(\vec{r};t)F(\vec{r})\psi(\vec{r};t)d\vec{r}$$
(2.30)

Usually indicated symbolically as:

$$\langle F(\vec{r}) \rangle = (\psi, F\psi) \tag{2.31}$$

where (f, g) indicates the functional scalar product between the two functions f and g, that in the simple 1D case (i.e. f(x) and g(x)) is defined by:

$$(f,g) = \int f^*(x)g(x)dx$$
 (2.32)

The wave-function physical meaning is the one of position probability density. For this reason it is suitable for the definition of expected values of all those quantities  $F(\vec{r})$  that are function of the position  $\vec{r}$ . Nevertheless it is not suitable for the definition of expected values that are function of the momentum  $\vec{p}$ , or alternatively of the wave vector  $\vec{k}$  (linked to  $\vec{p}$  by means of the de Broglie relation:  $\vec{p} = \hbar \vec{k}$ ). In order to estimate the expected values of a whatever function  $F(\vec{k})$  of the wave vector (or momentum) it is necessary to consider as probability density function P(f) in equation (2.25) a suitable probability density. In particular in analogy to what done for a general function of the position, the momentum probability density must be considered, i.e. the probability of finding the particle momentum between  $\vec{p}$  and  $\vec{p} + d\vec{p}$ . The last statement correspond to finding the wave vector between  $\vec{k}$  and  $\vec{k} + d\vec{k}$ .

Fortunately the momentum probability density can be recovered by means of the Fourier transform as it will clear in a while.

#### Position space and momentum space

It is well known that the Fourier transform generate a correspondence between time t and frequency  $\omega$ : the Fourier transform of a signal that is a function of time s(t) is a function of frequency  $S(\omega) = \mathfrak{F}\{s(t)\}$ , where  $\mathfrak{F}$  indicates the Fourier transform. This correspondence is often indicated as:

$$t \stackrel{\mathfrak{F}}{\longleftrightarrow} \omega$$
 or alternatively:  $s(t) \stackrel{\mathfrak{F}}{\longleftrightarrow} S(\omega)$ 

Moreover recall the derivative property of the Fourier transform that associates to a derivative in time domain a multiplication by  $\omega$  in frequency domain:

$$\frac{d}{dt} \stackrel{\mathfrak{F}}{\longleftrightarrow} i\omega \tag{2.33}$$

where sometimes, depending on the sign convention in the exponent in the Fourier transform integral, the previous relation is written with a minus sign:  $\frac{d}{dt} \stackrel{\mathfrak{F}}{\longleftrightarrow} -i\omega$ .

The Fourier transform can be generally performed w.r.t. to any variable and not only the time. In particular it should be known that the Fourier transform of a function of the position (e.g. the wave-function  $\psi(\vec{r};t)$ ) is a function of the wave vector. In other words the (3D) space variable  $\vec{r}$  is linked by means of the Fourier transform to the wave vector  $\vec{k}$ :

$$\vec{r} \stackrel{\mathfrak{F}}{\longleftrightarrow} \vec{k}$$
 or alternatively :  $(x, y, z) \stackrel{\mathfrak{F}}{\longleftrightarrow} (k_x, k_y, k_z)$ 

that in the 1D case becomes simplifies in (if only x-coordinate is considered):

$$x \stackrel{\mathfrak{F}}{\longleftrightarrow} k_x$$

Again the meaning is that the Fourier transform of a function of position is a function of the wave vector:  $\vec{x} = t(\vec{z})$ 

$$\psi(\vec{r};t) \longleftrightarrow A(k;t) \quad or \; alternatively:$$

$$A(\vec{k};t) = \mathfrak{F}\left\{\psi(\vec{r};t)\right\} \quad and \quad \psi(\vec{r};t) = \mathfrak{F}^{-1}\left\{A(\vec{k};t)\right\}$$

where  $\mathfrak{F}$  indicates the Fourier transform and  $\mathfrak{F}^{-1}$  the Fourier inverse transform (or antitransform).

More quantitatively it is possible to define a 3D Fourier transform w.r.t. to space of the wave function as [87] (the integrals are to be intended as triple integrals in the three space variables, i.e.  $d\vec{r} = dxdydz$  and  $d\vec{k} = dk_xdk_ydk_z$ ):

$$A(\vec{k};t) = \mathfrak{F}\{\psi(\vec{r};t)\} = \frac{1}{\sqrt{(2\pi)^3}} \int \psi(\vec{r};t) e^{-i\vec{k}\cdot\vec{r}} d\vec{r}$$
(2.34)

and consequently:

$$\psi(\vec{r};t) = \mathfrak{F}^{-1}\left\{A(\vec{k};t)\right\} = \frac{1}{\sqrt{(2\pi)^3}} \int A(\vec{k};t) e^{+i\vec{k}\cdot\vec{r}} d\vec{k}$$
(2.35)

notice that the previous expressions in the 1D case simplify in:

$$A(k_x;t) = \mathfrak{F}\left\{\psi(x;t)\right\} = \frac{1}{\sqrt{2\pi}} \int \psi(x;t)e^{-ik_x x} dx$$
$$\psi(x;t) = \mathfrak{F}^{-1}\left\{A(k_x;t)\right\} = \frac{1}{\sqrt{2\pi}} \int A(k_x;t)e^{+ik_x x} dk_x$$

In summary, the Fourier transform links the so called "position space", in which the state of the system is represented by means of the wave-function  $\psi(\vec{r};t)$ , that is function of the position vector  $\vec{r}$ , to the so called "momentum space", in which the state of the system is represented by means of the Fourier transform of the wave-function  $A(\vec{k};t)$ , that is function of the wave vector  $\vec{k}$ . Sometimes the momentum space is called: "k-space".

An important theorem about the Fourier transform is the so called Plancherel's theorem (for the Fourier series the analogous of the Plancherel's theorem is the so called Fischer-Riesz, that has an analogous meaning). It states that if a function (of position, in this case)  $\psi(\vec{r};t)$ is Fourier transformed in a function (of the wave vector in this case)  $A(\vec{k};t)$ , and then the inverse Fourier transform is performed, it is obtained a function (of position)  $\psi'(\vec{r};t)$  that is different from the initial function at most in a numerable set of isolated points. It means that an integral equality holds. Moreover a corollary states that if the starting function  $\psi(\vec{r};t)$  is continuous (as it is for a wave-function - see section 2.3.2) then the obtained function  $\psi'(\vec{r};t)$  is pointwise equal to the original one:  $\psi(\vec{r};t)$ . The Plancherel's theorem has an extremely important conceptual consequence. In fact it states that the correspondence between a wave-function in the position space  $\psi(\vec{r};t)$  and its Fourier transform in the momentum space  $A(\vec{k};t)$  is an exactly biunivocal correspondence. In other words it means that the same information that is included in the wave-function  $\psi(\vec{r};t)$  in position space, is also included in its Fourier transform  $A(\vec{k};t)$  in the momentum space. Thus working with one representation or the other makes no difference. In mathematical terms the position space and the momentum space are "isomorphous". Given a wave-function in position space  $\psi(\vec{r};t)$ , its Fourier transform  $A(\vec{k};t)$  in momentum space is uniquely determined and vice versa.

A direct consequence is on the physical meaning of  $A(\vec{k};t)$ . Indeed if the wave-function  $\psi(\vec{r};t)$  is normalized to 1, and thus it is an amplitude of position probability, then its

Fourier transform  $A(\vec{k};t)$  is also normalized to 1, and it has the meaning of amplitude of momentum probability. This is a consequence of the so called Parseval's theorem that states that [90] (it holds true between any couple of functions linked by means of the Fourier transform):

$$(\psi,\psi) = (A,A)$$

where the notation  $(\cdot, \cdot)$  is used to indicate the functional scalar product, as pointed previously in eq. (2.32), and thus:

$$(\psi, \psi) = \int \psi^*(\vec{r}; t) \psi(\vec{r}; t) d\vec{r} = \int |\psi(\vec{r}; t)|^2 d\vec{r}$$
$$(A, A) = \int A^*(\vec{k}; t) A(\vec{k}; t) d\vec{k} = \int |A(\vec{k}; t)|^2 d\vec{k}$$

from which the Parseval's relation corresponds to:

$$(\psi,\psi) = (A,A) \quad \Leftrightarrow \quad \int |\psi(\vec{r};t)|^2 d\vec{r} = \int |A(\vec{k};t)|^2 d\vec{k}$$

Consequently a correctly normalized wave-function in position space, such that:

$$\int |\psi(\vec{r};t)|^2 \, d\vec{r} = 1$$

corresponds to a correctly normalized wave-function in k-space:

$$\int \left| A(\vec{k};t) \right|^2 d\vec{k} = 1$$

Thus  $A(\vec{k};t)$  has in general the meaning of amplitude of momentum probability, and its modulus squared has the meaning of momentum probability density, since its integral over all the possible values of the wave vector is normalized to 1 (from Parseval's relation):

$$(A, A) = \int A^*(\vec{k}; t) A(\vec{k}; t) d\vec{k} = \int \left| A(\vec{k}; t) \right|^2 d\vec{k} = 1$$

In conclusion, in position space  $\psi(\vec{r};t)d\vec{r}$  is the differential probability of finding the system described by  $\psi$  in the infinitesimal volume between  $\vec{r}$  and  $\vec{r}+d\vec{r}$ ; while in momentum space  $A(\vec{k};t)d\vec{k}$  is the differential probability of finding the system described by A with a momentum (or wave vector, remember always:  $\vec{p} = \hbar \vec{k}$ ) between  $\vec{k}$  and  $\vec{k} + d\vec{k}$ . This is exactly the momentum probability density we were looking for at the beginning of this digression about the Fourier transform.

Before going on notice that up to now the time dependence of the wave-function was not considered. It is generally possible to Fourier transform also w.r.t. time, and from time domain it is possible to go in frequency domain:  $t \leftrightarrow \mathfrak{F} \omega$ . By exploiting the Planck's relation:  $E = hf = \hbar \omega$  it is possible to rewrite the correspondence as:

$$\stackrel{\mathfrak{s}}{\longleftrightarrow} \stackrel{\mathfrak{s}}{\longleftrightarrow} \frac{E}{\hbar}$$

t

in this case one talks about the energy domain. Thus in the most general case the Fourier transform can be a 4D Fourier transform that corresponds to three Fourier transforms w.r.t. space (as explained above), that connect the position vector  $\vec{r}$  to the wave vector  $\vec{k}$ , and one w.r.t. time that connect the time domain t with the energy domain  $E/\hbar$ .

#### Expectation values in momentum space

At this point it is known how to evaluate the expectation values of position and of a whatever function of position from equations (2.27) and (2.28), and moreover it should be clear how it is possible to proceed in the case of expected values of momentum or functions of momentum. Indeed proceeding along the lines of what was done before for writing equations (2.27) and (2.28), it is possible to say that the expected value of the wave vector  $\vec{k}$ , expressed in the momentum space, is:

$$\langle \vec{k} \rangle = \int \vec{k} \left| A(\vec{k};t) \right|^2 d\vec{k} = \int A^*(\vec{k};t) \vec{k} A(\vec{k};t) d\vec{k}$$
(2.36)

that is:

$$\langle \vec{k} \rangle = \left( A, \vec{k}A \right) \tag{2.37}$$

and for a whatever function of the wave vector  $F(\vec{k})$ :

$$\langle F(\vec{k}) \rangle = \int F(\vec{k}) \left| A(\vec{k};t) \right|^2 d\vec{k} = \int A^*(\vec{k};t) F(\vec{k}) A(\vec{k};t) d\vec{k}$$
(2.38)

that is:

$$\langle F(\vec{k}) \rangle = \left(A, F(\vec{k})A\right)$$
 (2.39)

Nevertheless sometimes may be useful to recover an expression for these expected values in the position (real) space, instead that in momentum space. This can be done by Fourier anti-transforming the previous relations, thus eq. (2.36) can be Fourier anti-transformed to position space and the following expression is recovered (the demonstration for the 1D case is provided in example 2.3 below):

$$\langle \vec{k} \rangle = \int \psi^*(\vec{r};t) \left[ -i\nabla\psi(\vec{r};t) \right] d\vec{k}$$
(2.40)

that can be rewritten in symbol form like:

$$\langle \vec{k} \rangle = \left(\psi, \hat{\vec{k}}\psi\right) \tag{2.41}$$

in which the symbol  $\vec{k}$  must be intended as the differential operator:  $\vec{k} = -i\nabla$  (that comes out by considering the Fourier anti-transform).

Proceeding analogously for a whatever function F of the wave vector  $\vec{k}$ , it is possible to write:

$$\langle F \rangle = \left(\psi, \hat{F}\psi\right) \tag{2.42}$$

in which the symbol  $\hat{F}$  must be intended as the differential operator that is built by substituting  $\vec{k}$  with  $-i\nabla$  in the expression of F:  $\hat{F} = F(-i\nabla)$ .

Notice that these operators are a direct consequence of the Fourier transform.

At this point it is possible to recover the average values in position space of a whatever physical observable of interest that is function of position (such as the potential energy  $U(\vec{r})$ ), by means of equation (2.28), and of whatever function of momentum (such as the kinetic energy  $T = \frac{p^2}{2m}$ ) by means of equation (2.42) by properly substituting the function  $F(\vec{k})$  with its differential operator  $\hat{F} = F(-i\nabla)$  obtained by performing the following substitutions:

$$\vec{k} \leftrightarrow -i\nabla \quad and \quad \vec{p} \leftrightarrow -i\hbar\nabla$$
 (2.43)

that arise from the derivation property of the Fourier transform (and noticing the de Broglie relation  $\vec{p} = \hbar \vec{k}$ ).

*Example 2.3:* Here a proof for the previous relation is reported for the 1D case (for the 3D case see e.g. [87]):

$$x \stackrel{\mathfrak{F}}{\longleftrightarrow} k_x$$

the expected value of  $k_x$  in momentum space is:

$$\langle k_x \rangle = \int k_x \left| A(k_x;t) \right|^2 dk_x = \int A^*(k_x;t) k_x A(k_x;t) dk_x$$

by substituting the explicit expression of the Fourier transform for  $A(k_x; t)$  and its complex conjugate:

$$A(k_x;t) = \frac{1}{\sqrt{2\pi}} \int \psi(x';t) e^{-ik_x x'} dx'$$
$$A^*(k_x;t) = \frac{1}{\sqrt{2\pi}} \int \psi^*(x;t) e^{+ik_x x} dx$$

it follows:

$$\langle k_x \rangle = \frac{1}{2\pi} \int \int \int e^{+ik_x x} \psi^*(x;t) k_x e^{-ik_x x'} \psi(x';t) dk_x dx dx'$$

noticing that:

$$\frac{\partial}{\partial x'}e^{-ik_xx'} = -ik_xe^{-ik_xx'}$$

it follows (an integration by parts is required):

$$\langle k_x \rangle = \frac{1}{2\pi} \int \int \int e^{+ik_x(x-x')} \psi^*(x;t) \left[ -i\frac{\partial}{\partial x'} \psi(x';t) \right] dk_x dx dx'$$

and considering that the only term dependent on  $k_x$  is the exponential and that its integral corresponds to the definition of the delta Dirac function:

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{+ik_x(x-x')} dk_x = \delta(x-x')$$

it follows:

$$\langle k_x \rangle = \int \psi^*(x;t) \left[ -i \frac{\partial}{\partial x} \psi(x;t) \right] dx = \left( \psi, -i \frac{\partial}{\partial x} \psi \right)$$

The extension to the general 3D case requires the usage of a 3D delta Dirac function and the substitution of the partial derivative w.r.t. x with the nabla operator.  $\Box$ 

#### 2.3.4 Quantum mechanical operators and Hamiltonian operator

A fundamental assumption in quantum mechanics is that to each physical observable F a quantum mechanical operator  $\hat{F}$  is associated. It can be a differential operator, for example of the kind of the ones associated to the wave vector for the evaluation of its expected value in real space (see the discussion presented in the previous section 2.3.3). Actually, the origin of such operators has to be found exactly in the evaluation of the expected values. In particular they arise from the Fourier transform applied to the evaluation of expected values, like it was shown in the previous section. If each physical observable must be associated to an operator, then if position space expected values are considered, from equations (2.27), (2.31), (2.40) and (2.42) it is possible to derive the following associations, true in the (real) position space (where  $\vec{p} = \hbar \vec{k}$ ):

$$\vec{r} \rightarrow \vec{r}$$

$$F(\vec{r}) \rightarrow F(\vec{r})$$

$$\vec{k} \rightarrow -i\nabla$$

$$\vec{p} \rightarrow -i\hbar\nabla$$

$$F(\vec{k}) \rightarrow F(-i\nabla)$$

Thus the general rules for building the quantum mechanical operators in position space are:

- the operator associated to the position vector is equal to itself:  $\hat{\vec{r}} = \vec{r}$
- a general function  $F(\vec{r})$  of the position vector  $\vec{r}$  is thus unchanged and its quantum mechanical operator is equal to itself:  $\hat{F} = F(\vec{r})$
- the operator associated to the wave vector is equal to  $-i\nabla$ :  $\hat{\vec{k}} = -i\nabla$
- a general function  $F(\vec{k})$  of the wave vector  $\vec{k}$  is thus associated to a quantum mechanical operator obtained substituting in the expression of F the wave vector  $\vec{k}$  with  $-i\nabla$ :  $\hat{F} = F(-i\nabla)$

Of particular interest are the following quantities:

- the potential energy  $U(\vec{r})$  is a function of the position, thus its quantum mechanical operator in position space is equal to itself:  $\hat{U} = U(\vec{r})$
- the momentum  $\vec{p} = \hbar \vec{k}$  is a function of the wave vector thus its quantum mechanical operator is recovered by substituting  $\vec{k}$  with  $-i\nabla$  in its expression:  $\hat{p} = -i\hbar\nabla$
- the kinetic energy  $T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$  is a function of the momentum, i.e. of the wave vector, thus its quantum mechanical operator is recovered with the same procedure:

$$\widehat{T} = \frac{(-i\hbar\nabla)^2}{2m} = \frac{-\hbar^2}{2m}\Delta$$

where  $\Delta = \nabla^2 = \nabla \cdot \nabla = \left(\frac{\partial^2}{\partial x^2}, \frac{\partial^2}{\partial y^2}, \frac{\partial^2}{\partial z^2}\right)$  is the so called Laplacian operator (or Laplace operator).

Notice that the quantum mechanical operators are to be intended as mathematical entities that act on a specific function, i.e. the wave-function, that represent the physical states. It has no meaning of talking about an operator if it is not "applied" to a state function (in quantum mechanics the wave-functions represent the state of the system and sometimes they are simply called "states"). Notice that from the above discussion the quantum mechanical operators are differential operators in the space variables but not w.r.t. time. The time in quantum mechanics is a parameter to which no quantum mechanical operator is associated. As time goes by, the wave-functions in general change, i.e. the system state is modified. In the Schrödinger's wave mechanics the system states, i.e. the wave-functions, evolve in time. It is possible to point out a set of properties and operations concerning the quantum mechanical operators, for a reference see e.g. [87]. The only properties that I mention here and that will be useful later on, are the linearity (since they are differential operators they are linear) and that to each physical observable is associated an operator that is Hermitian, i.e. for which the following relation holds:

$$F^{\dagger} = F$$

where the symbol  $\dagger$  indicates the operation of complex conjugation (and transpose if F is in matrix form - see later). The important fact is that to an Hermitian operator is associated a physical observable that can assume real values, that is: if a measure is performed on the physical observable that is represented by an operator that is Hermitian, a real value is obtained. Since physical observables can always assume only real values, then the operators associated to them are always Hermitian.

At this point it is trivial to write down an explicit expression for the Hamiltonian operator  $\hat{H}$  that appears in the Schrödinger's equation (2.17). As already mentioned the classical Hamiltonian corresponds to the sum of the kinetic and potential energy: H = T + U, thus the quantum mechanical operator can be recovered with the rules just stated as follows (position space):

$$\widehat{H} = \widehat{T} + \widehat{U} = \frac{-\hbar^2}{2m} \Delta + U(\vec{r})$$
(2.44)

in which the linearity is exploited such that the Hamiltonian is recovered as the sum of the kinetic energy operator  $\hat{T}$  and the potential energy one  $\hat{U}$ . The last expression is exactly the one to be used in the Schrödinger's equation. The Hamiltonian operator is thus the quantum mechanical operator associated to the total energy of the system, and indeed it will be linked to the energy levels of the quantum system in sections 2.3.5 and 2.3.6.

In general in quantum mechanics to each physical observable a suitable operator (that is found by applying the previously mentioned rules) is associated, so one talks about the angular momentum operator, the squared angular momentum operator, and so on... In section 2.3.6 few more words will be said on their link to the physical observables they represent.

#### Quantum mechanical operators in momentum space

In section 2.3.3 it was already pointed out that is possible to express the expected value of a physical quantity also in the momentum space or k-space. In this case by proceeding in an analogous way to what done previously for obtaining the operators in position space, it is possible to get the following fundamental relations for the representation of operators in the momentum space:

$$\vec{r} \rightarrow +i\nabla_k = +i\hbar\nabla_p$$

$$F(\vec{r}) \rightarrow F(+i\nabla_k)$$

$$\vec{k} \rightarrow \vec{k}$$

$$\vec{p} \rightarrow \vec{p}$$

$$F(\vec{k}) \rightarrow F(\vec{k})$$

where  $\nabla_k = \left(\frac{\partial}{\partial k_x}, \frac{\partial}{\partial k_y}, \frac{\partial}{\partial k_z}\right)$  and  $\nabla_p = \left(\frac{\partial}{\partial p_x}, \frac{\partial}{\partial p_y}, \frac{\partial}{\partial p_z}\right)$ . Everything is then analogous: a function of the momentum is associated to an operator that is equal to itself, while a function of the position is associated to an operator built up in an analogous way of what presented previously. In table 2.1 the fundamental relations are summarized.

Table 2.1:	Quantum mechanical oper	ators that are	associated to ph	ysical observat	oles in both
	position space and momen	tum space.			

position space representation	momentum space representation
$\vec{r} \rightarrow \hat{\vec{r}} = \vec{r}$	$\vec{r} \rightarrow \hat{\vec{r}} = +i\nabla_k = +i\hbar\nabla_p$
$F(\vec{r}) \rightarrow \hat{F} = F(\vec{r})$	$F(\vec{r}) \rightarrow \hat{F} = F(+i\nabla_k)$
$ec{k}  ightarrow ec{k}  ightarrow ec{k} = -i  abla$	$\vec{k} \rightarrow \hat{\vec{k}} = \vec{k}$
$\vec{p} \rightarrow \hat{\vec{p}} = -i\hbar \nabla$	$ec{p}  ightarrow ec{p} = ec{p}$
$F(\vec{k}) \rightarrow \hat{F} = F(-i\nabla)$	$F(\vec{k}) \rightarrow \hat{F} = F(\vec{k})$

# 2.3.5 General solution of Schrödinger's equation

The purpose of this section is to provide a general methodology for solving the Schrödinger's equation (2.17). Considering the expression for the Hamiltonian operator of eq. (2.44), the Schrödinger's equation can be rewritten as:

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r};t) = \widehat{H}\psi(\vec{r};t) = \left[\frac{-\hbar^2}{2m}\Delta + U(\vec{r})\right]\psi(\vec{r};t)$$
(2.45)

It is partial differential equation of the second order in space and of the first order in time. Since  $\hat{H}$  is time-independent, the Schrödinger's equation is completely separable in the time and the space variables. Indeed the left-hand member:  $i\hbar \frac{\partial}{\partial t}\psi(\vec{r};t)$  depends only on time derivative while the right-hand one:  $\left[\frac{-\hbar^2}{2m}\Delta + U(\vec{r})\right]\psi(\vec{r};t)$  depends only on space derivatives. It is possible to show that this kind of separable equations present always factorized solutions of the kind (see e.g. [87]):

$$\psi(\vec{r};t) = \Psi(\vec{r})\phi(t)$$

where  $\Psi(\vec{r})$  is a function of space coordinates only and  $\phi(t)$  is a function of time only. Substituting this solution in the Schrödinger's equation:

$$i\hbar\Psi(\vec{r})\frac{\partial}{\partial t}\phi(t) = \phi(t)\hat{H}\Psi(\vec{r})$$

dividing both members by  $\Psi(\vec{r})\phi(t)$ :

$$i\hbar\frac{1}{\phi(t)}\frac{\partial}{\partial t}\phi(t) = \frac{1}{\Psi(\vec{r})}\widehat{H}\Psi(\vec{r})$$

where the left-hand member is function of time only and the right hand one of space only. Since the two members depend on different variables (time and space respectively) the equation is true if and only if the two members are equal to a certain constant, and said E this constant the equation can be rewritten as a system of two equations:

$$\begin{cases} i\hbar\frac{1}{\phi(t)}\frac{d}{dt}\phi(t) = E\\ \\ \frac{1}{\Psi(\vec{r})}\widehat{H}\Psi(\vec{r}) = E \end{cases}$$
$$\Rightarrow \begin{cases} i\hbar\frac{d}{dt}\phi(t) = E\phi(t)\\ \\ \widehat{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \end{cases}$$

The two equations can be solved separately. The first equation is a first order differential equation in time:

$$\frac{d}{dt}\phi(t) = -\frac{i}{\hbar}E\phi(t) \quad \to \quad \frac{d\phi}{dt} = -\frac{i}{\hbar}E\phi \quad \to \quad \int \frac{1}{\phi}d\phi = -\frac{iE}{\hbar}\int dt \quad \to \quad \ln\phi = -\frac{iE}{\hbar}t$$
56

Thus the solution of the first equation, that is the term that provides the time evolution of the state  $\psi(\vec{r}; t)$ , is the following:

$$\phi(t) = e^{-\frac{i}{\hbar}Et} \tag{2.46}$$

unless an inessential integration constant, that is now omitted. The second equation is called time-independent Schrödinger's equation, or steady state Schrödinger's equation:

$$\widehat{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{2.47}$$

indeed its solutions  $\Psi(\vec{r})$  are corresponding to stationary states that are time-independent. The solution for the steady state Schrödinger's equation is addressed in the next section. Here the point is that the factorized solutions for the time-dependent Schrödinger's equation (2.45) have the following form:

$$\psi(\vec{r};t) = \Psi(\vec{r})e^{-\frac{i}{\hbar}Et}$$
(2.48)

in this kind of solutions the time dependence is factorized and known, once the constant E is fixed. As it will be addressed in the section, the constant E corresponds exactly to the total energy of the system, this is indeed the meaning of the steady state Schrödinger's equation (see section 2.3.6). The solution of the steady state Schrödinger's equation provides indeed the energy values E characteristics of the system described by  $\hat{H}$ , and also the steady states  $\Psi_E(\vec{r})$ , i.e. the states that are stable, and thus with an infinite life-time as introduced in section 2.2. Notice that in the following the wave-functions  $\Psi_E(\vec{r})$  that are solutions of the steady state Schrödinger's equation will be indicated with a subscript E:  $\Psi_E(\vec{r})$ . Notice also that the steady state Schrödinger's equation represents an eigenvalue problem, in which the energy E is called "system eigenvalue" and the wave-function is called "eigenfunction" (or sometimes eigenvector). The correspondence with a usual eigenvalue problem should be clear if the Hamiltonian operator is expressed in matrix form (see section 2.4).

Moreover recall that each quantum mechanical operator that is associated to a physical observable, like e.g. the Hamiltonian operator  $\hat{H}$ , associated to the total energy of the system E, is said to be Hermitian.

It is possible to show that the eigenfunctions of an Hermitian operator are always orthogonal (and thus once normalized othonormal) and constitute a "complete" set of functions. A complete set of orthonormal functions is a set of functions that can be used as basis in the Fourier transform (or series for discrete systems). In particular if E (the eigenvalues) is a continuous variable, then it is said that the spectrum of the operator  $\hat{H}$  is continuous, and the set  $\{\Psi_E(\vec{r})\}_E$  can be used as a basis for the Fourier transform; instead if E(the eigenvalues) is a discrete variable, then it is said that the spectrum of the operator  $\hat{H}$  is discrete, and the set  $\{\Psi_E(\vec{r})\}_E$  can be used as a basis for the Fourier series. The completeness is intended in the sense of the Plancherel's theorem for the Fourier transform or in the sense of the Fischer-Riesz theorem for the Fourier series. The meaning of this two theorems was already pointed out, and in particular it is related to the biunivocal correspondence that the Fourier transform establishes. In particular when they hold (and they hold when a complete set is used as basis for the Fourier transform or series), it is possible to show that the Fourier transform (series) exist and converge to the original function.

From a practical standpoint, the important point of this treatment is that it is always possible to express the most general solution for the Schrödinger's equation as superposition of the factorized solutions that were presented above. In mathematical terms the way to superimpose an eventually infinite set of functions is indeed by means of the Fourier transform (or series), exactly like explained for the build up of the wave packet in section 2.2. Thus the most general solution  $\psi(\vec{r};t)$  of the Schrödinger's equation can be expressed as superposition of the factorized solutions found above:

$$\psi(\vec{r};t) = \oint dE \ C(E) \ \Psi_E(\vec{r}) \ e^{-\frac{i}{\hbar}Et}$$
(2.49)

where  $\Psi_E(\vec{r})$  are the solutions of the steady state Schrödinger's equation, E are the so called energy eigenvalues (i.e. the possible or "permitted" energy values for the system described by  $\hat{H}$ ), the symbol  $\oint dE$  indicates a summation (i.e. a Fourier series expansion) if the Hamiltonian operator spectrum is discrete (E is discrete), or an integral (i.e. a Fourier transform) if it is continuous, and C(E) are the Fourier series coefficients if the Hamiltonian operator spectrum is discrete while it is the Fourier transform if the Hamiltonian operator spectrum is continuous. Notice that in the most general case the Hamiltonian operator spectrum can be partially continuous over a range of E and partially discrete for other values of E (see later - section 2.3.7).

In both cases the coefficient can be evaluated accordingly to the notation:

$$C(E) = \left(\Psi_E(\vec{r})e^{-\frac{i}{\hbar}Et}, \psi(\vec{r};t)\right) = \int \Psi_E^*(\vec{r})e^{+\frac{i}{\hbar}Et}\psi(\vec{r};t)d\vec{r}$$

i.e. they are the projection on the factorized solutions  $\Psi_E(\vec{r})e^{-\frac{i}{\hbar}Et}$  of the general wavefunction  $\psi(\vec{r};t)$ . This corresponds exactly to the meaning of Fourier series coefficients, or Fourier transform (please refer to a signal processing book if not clear - e.g. [95] [96]).

In conclusion, the general solution of the time-dependent Schrödinger's equation was provided, and it was noticed that it can be expressed as a superposition (by means of the Fourier series/transform) of the factorized solutions of the Schrödinger's equation, that represent the states at a well defined energy. These factorized solutions have always a factor dependent on time multiplied by the solutions (the eigenfunctions) of the steady state Schrödinger's equation. The latter represent a well defined energy state, while the exponential term has an imaginary exponent (indeed the energy E, time t and  $\hbar$  are all real), thus leading to an oscillatory behavior in time with angular frequency:  $\omega = E/\hbar$ . These factorized solutions are solutions at a well defined energy E, solution of the steady state Schrödinger's equation. Thus the important insight of this section is that a whatever solution of the time-dependent Schrödinger's equation, can be expressed as a superposition of the factorized solutions that are the solutions at a well defined energy. In other words, they are the steady state solutions, and thus the solution of the steady state Schrödinger's equation is needed about that system, since the other solutions are simply a superposition of the steady state ones.

This is not, in principle, much different from the free response study of a Linear Time Invariant (LTI) system. Indeed in that case the system poles (think to an RC circuit for example), play the role of the steady states in quantum mechanics, and the general LTI system response can be always be recovered from the knowledge of the system poles (that e.g. determine the denominator of all the possible transfer functions).

# 2.3.6 Eigenvalue problems and steady state Schrödinger's equation

In the previous section it was pointed out that the general solution of the time-dependent Schrödinger's equation can be written as a superposition of the factorized solutions of the kind:

$$\psi(\vec{r};t) = \Psi_E(\vec{r})e^{-\frac{i}{\hbar}Et}$$

These factorized solutions are called steady states of the the system. Indeed they are completely determined if the wave-functions  $\Psi_E(\vec{r})$  (function of space only) are known, and the  $\Psi_E(\vec{r})$  correspond to the solutions of the so called steady state Schrödinger's equation:

$$\widehat{H}\Psi_E(\vec{r}) = E\Psi_E(\vec{r}) \tag{2.50}$$

that is a time-independent version of the Schrödinger's equation. Once the stationary (time-independent) states of the system are known then the generic state of the system can be recovered with eq. (2.49), but the fundamental point that I am stressing is that the knowledge about a given system is complete in the moment in which its steady states  $\Psi_E(\vec{r})$  are known.

This is similar to what is generally done in an electrical circuit with reactive elements. From circuit theory and LTI system theory should be well known that once the network poles (i.e. its proper modes, its steady states) are known, then everything about that system is known, since the general behavior of the network in presence of an external stimulus can be evaluated, also in transient behavior.

Here the name steady states comes from the fact the great majority of the interesting physical properties for these states is constant in time. This is a consequence of the fact that the time appears only in the complex exponent (thus defining an oscillating behavior with angular frequency  $\omega = E/\hbar$ ). As highlighted in section 2.3.3, in quantum mechanics we are often interested only in average quantities, and great importance is given to expected values of physical observables, that are easily recovered starting from the wave-function as explained in section 2.3.3. If a physical observable F that is not explicitly dependent on time is considered, then its expected value, if the system is in a steady state  $\psi(\vec{r};t) = \Psi_E(\vec{r})e^{-\frac{i}{\hbar}Et}$ , is given by:

$$\langle F \rangle = \left(\psi, \widehat{F}\psi\right) = \int \Psi_E^*(\vec{r}) e^{+\frac{i}{\hbar}Et} \widehat{F}\Psi_E(\vec{r}) e^{-\frac{i}{\hbar}Et} d\vec{r}$$

and the time dependence is removed:

$$\langle F \rangle = \int \Psi_E^*(\vec{r}) \hat{F} \Psi_E(\vec{r}) d\vec{r} = \left(\Psi_E, \hat{F} \Psi_E\right)$$
  
59

Thus the expected value is time-independent, reason for which these are called steady states.

The fact that whatever solution of the Schrödinger's equation can be expressed as superposition of steady states limits the system study to the research of its steady states, solution of the time-independent Schrödinger's equation. Starting from them, a complete understanding of the physical system behavior is obtained, as it will be clarified in section 2.3.7, where the steady state Schrödinger's equation will be effectively solved in few fundamental examples.

Moreover it is now clear that the time in quantum mechanics plays a minor role, and indeed no quantum mechanical operator is directly associated to it. Instead the system energy is likely the most important quantity for a system. It provides information concerning the actual state of a system and even about its history. This is usually well known to electrical engineers, since usually the state variables of an electrical network containing reactive elements (such as capacitors and inductors) are the voltages across the capacitors and the current that flows through inductors. These two quantities are indeed linked with the stored energy (that tells the "story" of the element) in those reactive elements:

$$W_C = \frac{1}{2}CV^2$$
 and  $W_L = \frac{1}{2}LI^2$ 

An additional point is now discussed concerning the steady state Schrödinger's equation (2.50), here reported for convenience:

$$\widehat{H}\Psi_E(\vec{r}) = E\Psi_E(\vec{r})$$

This is the so called "eigenvalue" equation for the Hamiltonian operator. The similarity with a conventional eigenvalue problem of linear algebra is evident by noting that the Hamiltonian operator can be expressed in a matrix form and the state wave-function in vector form (while E is a scalar real number), see section 2.4. In this equation the energy levels E (that represents the total energy of the system) are called "eigenvalues", and the wave-functions  $\Psi_E(\vec{r})$  are called "eigenfunctions". The physical meaning of this equation has to be intended as follows. The eigenvalue equation for the operator  $\hat{H}$  that is associated to the physical observable E, when solved, provides the eigenvalues E and the eigenfunctions  $\Psi_E$ . The system eigenfunctions  $\Psi_E$  are describing the possible system states in which the physical observable represented by  $\hat{H}$  assumes exactly the value E(without uncertainty), in each measurement of that physical observable when the system is in that specific state. Thus the set of eigenvalues E constitutes the set of all possible measurement results that are performed on the physical observable represented by  $\hat{H}$  on that system, and the set of eigenfunctions  $\{\Psi_E\}_E$  corresponds to the set of all possible steady states for that system, i.e. the proper modes of such a system.

In terms of Schrödinger's steady state equation this means that starting from the knowledge of  $\hat{H}$ , by solving the energy eigenvalue problem (i.e. eq. (2.50)), all the possible energy values E for that system are known, and all the related stationary states  $\Psi_E$  are known.

As mentioned it is possible to write an eigenvalue equation for each possible quantum mechanical operator. In general it is possible to show that, given an operator  $\hat{F}$  that represents a physical observable F, its eigenvalue equation is:

$$F\psi_i = f_i\psi_i \tag{2.51}$$

where  $f_i$  are its eigenvalues and  $\psi_i$  its eigenfunctions. The physical meaning explained above still holds: each time a measurement is performed on the physical observable F, the possible result can be one among the  $f_i$ , that means that the system was in the state  $\psi_i$ . This physical meaning is very evident when the general eigenvalue equation (2.51) is demonstrated. Indeed it is demonstrated by defining a quantum mechanical operator that represents the standard deviation (or variance) introduced in section 2.3.3 and by forcing it to zero, such that  $f_i$  in eq. (2.51) actually represents a possible result of a measurement (without uncertainty).

A complete demonstration of this relation is outside the purposes of this work. A detailed treatment is present in [87].

As already pointed out in the previous section, the operator  $\widehat{F}$  has a discrete spectrum if the set of its eigenvalues  $\{f_i\}_i$  constitutes a discrete set (i.e. is a numerable set); while it is said that the operator  $\widehat{F}$  has a continuous spectrum if the set of its eigenvalues  $\{f_i\}_i$ constitutes a continuous interval in  $\mathbb{R}$ . Moreover it is said that the operator  $\widehat{F}$  has a mixed spectrum if the set of its eigenvalues  $\{f_i\}_i$  is both continuous and discrete depending on the specific system state  $\psi_i$  that is considered.

It was already said that an operator associated to a real physical observable (such as the Hamiltonian operator associated to the total energy of the system) has the property of being Hermitian. It is possible to show that the eigenvalues of an Hermitian operator are always real (indeed they correspond to possible values of a measurement performed on the system), and moreover that its eigenfunctions are orthogonal (and after a normalization orthonormal) and constitute a complete set. If the set  $\{\psi_i\}_i$  is a complete then it is possible to use it as a basis for the Fourier series (if it is a discrete spectrum operator) or Fourier transform (if it is a continuous spectrum operator). This implies the validity of the already discussed Fischer-Riesz theorem (for the Fourier series) and Plancherel's theorem (for the Fourier transform). This allows to write whatever wave-function  $\psi$  as superposition of the operator eigenfunctions  $\{\psi_i\}_i$ , exactly like expressed in equation (2.49). With the notation of this section it becomes:

$$\psi = \oint dE \ C(E) \ \psi_i$$

with the same meaning of eq. (2.49). This last concept, that is generally true, will be important again when the matrix representation of quantum mechanical operators will be considered in section 2.4.

# 2.3.7 Solution of steady state Schrödinger's equation in few easy cases

In this section the solution of the steady state Schrödinger's equation in some important cases is addressed. The goal is to find the stationary states solution for the Schrödinger's equation that are the proper modes, i.e. the eigenfunctions, for a specific system, and also its eigenvalues (i.e. the system energy levels). The knowledge of these proper modes correspond to the complete knowledge about such a system, as widely discussed in sections 2.3.5 and 2.3.6. The equation to be solved is:

$$\widehat{H}\psi = E\psi \tag{2.52}$$

where the steady states (eigenfunctions) are simply indicated with  $\psi$  in this section, E are the eigenvalues, and  $\hat{H}$  is the Hamiltonian operator:

$$\widehat{H} = \frac{-\hbar^2}{2m}\Delta + U(\vec{r})$$

where  $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ , and  $U(\vec{r}) = U(x, y, z)$ . Very often it is possible to simply a lot the problem, that is a 3D problem, by separating it

Very often it is possible to simply a lot the problem, that is a 3D problem, by separating it into three 1D problems. This is possible whenever the Hamiltonian is completely separable, that corresponds to the possibility of separating the potential energy term U(x, y, z) into the sum of three independent contributions:

$$U(x, y, z) = U_x(x) + U_y(y) + U_z(z)$$

Indeed under this assumption the Hamiltonian is:

$$\widehat{H} = \frac{-\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] + U_x(x) + U_y(y) + U_z(z)$$

and it can be expressed as the sum of three independent contributions in the three variables:

$$\widehat{H} = \widehat{H}_x + \widehat{H}_y + \widehat{H}_z$$

where:

$$\hat{H}_x = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U_x(x)$$
$$\hat{H}_y = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + U_y(y)$$
$$\hat{H}_x = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + U_z(z)$$

In order to complete the separation of variable suitable expressions for the total eigenvalues and eigenfunctions must be recovered. In particular the total energy is given by the sum of the eigenvalues in the three directions:

$$E = E_x + E_y + E_z$$

while the wave-function is factorized in the product of the three wave-functions in the three directions:

$$\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z)$$

In this way the 3D problem becomes:

$$\left[\widehat{H}_x + \widehat{H}_y + \widehat{H}_z\right]\psi_x(x)\psi_y(y)\psi_z(z) = \left[E_x + E_y + E_z\right]\psi_x(x)\psi_y(y)\psi_z(z)$$

$$62$$

and by dividing both members by  $\psi_x(x)\psi_y(y)\psi_z(z)$  (that are always non-null since the interesting solutions are the non-trivial ones) and considering that  $\hat{H}_x$  applies only to  $\psi_x(x)$  (analogously for  $\hat{H}_y$  and  $\hat{H}_z$ ):

$$\begin{aligned} \hat{H}_{x}\psi_{x}(x)\psi_{y}(y)\psi_{z}(z) + \hat{H}_{y}\psi_{x}(x)\psi_{y}(y)\psi_{z}(z) + \hat{H}_{z}\psi_{x}(x)\psi_{y}(y)\psi_{z}(z) = \\ &= E_{x}\psi_{x}(x)\psi_{y}(y)\psi_{z}(z) + E_{y}\psi_{x}(x)\psi_{y}(y)\psi_{z}(z) + E_{z}\psi_{x}(x)\psi_{y}(y)\psi_{z}(z) \\ &\to \frac{1}{\psi_{x}(x)}\hat{H}_{x}\psi_{x}(x) + \frac{1}{\psi_{y}(y)}\hat{H}_{y}\psi_{y}(y) + \frac{1}{\psi_{z}(z)}\hat{H}_{z}\psi_{z}(z) = E_{x} + E_{y} + E_{z} \end{aligned}$$

the problem is divided into a system of three 1D problems (indeed the above equation is true if the three members at left-hand side are one-by-one equal to three members at right-hand side):

$$\begin{cases} \dot{H}_x \psi_x = E_x \psi_x \\ \hat{H}_y \psi_y = E_y \psi_y \\ \hat{H}_z \psi_z = E_z \psi_z \end{cases}$$

This separation of variables is possible because of the linearity of the Hamiltonian operator, and under the assumption of being able to separate the potential energy in the sum of three independent contributions as already pointed out. This is very often possible in many problems of practical importance and relevance. Once the variables are separated the 3D problem is divided into three 1D problems that can be solved independently the one from the others. The complete 3D solution is then recovered as already pointed out above: the total energy eigenvalues are obtained by summing the unidimensional ones while the total wave-function is the product of the unidimensional ones. For this reason in the following unidimensional problems will be considered.

#### One dimensional problems

According with the separation of variables it is very often possible to separate a 3D problem into three 1D problems. The 1D steady state Schrödinger's equation is (the subscripts "x" are omitted since in 1D no confusion is possible):

$$\hat{H}\psi(x) = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + U(x)\psi(x) = E\psi(x)$$
(2.53)

where the potential energy U(x) is linked with the (conservative) forces that are acting on the quantum system by means of the classical relation:

$$\vec{F} = -\nabla U$$
 that in 1D is:  $\vec{F}_x = -\frac{d}{dx}U(x)$  (2.54)

An important remark is needed. The important forces in the 1D problems to be addressed are the electrostatic forces. It is well known that the electrostatic field is conservative, and thus it can be expressed as the gradient of a scalar function, that is the electrostatic potential. Consequently eq. (2.54) holds between the electrostatic force (Coulomb force) and the potential energy. In this picture is evident that in "standard" (i.e. non-relativistic) quantum mechanics the forces, and thus the potentials and potential energies, are still
considered and evaluated as classical. The particle is the entity that behaves as nonclassical, due to the wave-particle duality. In some fields of application this is no more accurate and also the interactions must be quantized (no more classical); this procedure is called "second quantization", but it will not addressed in this work.

In the next examples the entity and the kind of the force acting on the particle will be supposed known. Consequently the potential energy U(x) is always supposed known. If the electrostatic interaction is repulsive the potential energy is conventionally positive. Nevertheless the potential energy is defined up to an additive constant, that can shift it. Thus the same concept can be reformulated as follows: if the electrostatic interaction is repulsive, the potential energy is of "barrier" type, i.e. in the region in which the repulsive force is acting a more positive potential is present w.r.t. the rest of the space. And the particle should overcome a potential is of "well" type, i.e. in the region in which the attractive force is acting a more negative potential is present w.r.t. the rest of the space; and the particle should overcome a potential barrier to leave that region of space and prevail on the attractive force.

Before proceeding with the examples, it is useful to highlight the general procedure and point out some useful remarks. The 1D Schrödinger's equation (2.53) can always be rewritten like:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + U(x)\psi(x) = E\psi(x)$$

$$\rightarrow \frac{d^2}{dx^2}\psi(x) + \frac{2m}{\hbar^2}\left[E - U(x)\right]\psi(x) = 0$$

$$k = \sqrt{\frac{2m}{\hbar^2}\left(E - U(x)\right)}$$
(2.55)

it becomes:

and said:

$$\frac{d^2}{dx^2}\psi(x) + k^2\psi(x) = 0$$
(2.56)

Notice that k has exactly the meaning of wavenumber. Indeed if the particle is free (no force is acting on it) then U(x) = 0 and thus the total energy E of the particle is equal to its kinetic energy:

$$E = T = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad \rightarrow \quad k = +\sqrt{\frac{2m}{\hbar^2}E} = +\sqrt{\frac{2m}{\hbar^2}T}$$

(where the positive solution of the square root is considered since the wavenumber  $k = 2\pi/\lambda$  is defined positive). In the case in which a force (attractive or repulsive) is acting on the particle, then it has both kinetic and potential energy, and the wavenumber is again given by the previous expression, in which the kinetic energy T is given by T = E - U(x):

$$k = \sqrt{\frac{2m}{\hbar^2} \left(E - U(x)\right)}$$
  
64

The potential shapes that will be addressed in this section will be always piece-wise constant, thus it will be (for some x)  $U(x) = U_0$ , constant in space. It follows that equation (2.56) becomes a second order ordinary differential equation with constant coefficients, indeed  $k^2$  depends on energy but not on space when  $U(x) = U_0$  is constant since it becomes:  $k = \sqrt{\frac{2m}{\hbar^2}(E - U_0)}$ . Its solution can be found exploiting the characteristic polynomial (to this purpose please refer also to appendix A.1):

$$\lambda^2 + k^2 = 0 \quad \rightarrow \quad \lambda_{1,2} = \pm \sqrt{-k^2} = \pm ik$$

where k was defined above. The solution of the equation is then:

$$\psi(x) = Ae^{+\lambda_1 x} + Be^{+\lambda_2 x} = Ae^{+ikx} + Be^{-ikx}$$
(2.57)

Notice that this holds in general if  $k \in \mathbb{R}$ , i.e. if  $E > U_0$ ,  $\forall x \in \mathbb{R}$ . In the case in which  $E < U_0$  for some value of x then k is purely imaginary. Anyway possible to define the function  $\beta_k$  such that it is positive real and get (see again also appendix A.1):

$$\beta_k = \sqrt{\frac{2m}{\hbar^2}} (U(x) - E) \quad \to \quad k = i\beta_k \quad , \quad \beta_k \in \mathbb{R} \quad , \quad k \in \mathbb{C}$$
$$\psi(x) = Ae^{+ikx} + Be^{-ikx} = Ae^{-\beta_k x} + Be^{+\beta_k x} \tag{2.58}$$

The constants A and B will be determined by enforcing the boundary conditions. Moreover notice that in the last case in which  $E < U_0$  the exponential terms in the solution (eq. (2.58)) have real exponents, thus they are non-propagating terms, and they correspond to exponentially attenuated wave-functions. Instead the solutions in the case of  $E > U_0$ correspond to propagating waves. Indeed in equation (2.57) the two exponential terms correspond to two harmonic waves propagating respectively toward positive x values (forward wave) and toward negative x values (backward wave). In order to better visualize it let's consider the solution of the time-dependent Schrödinger's equation. From the previous treatment of the general solution of the Schrödinger's equation in section 2.3.5, it is known that the steady states, i.e. the factorized solutions of the time dependent Schrödinger's equation, are those given by equation (2.48). Thus the total wave-function in the 1D problem must be still multiplied by an exponential term that contains the time dependence as follows:

$$\psi(x;t) = \psi(x)e^{-i\frac{E}{\hbar}t} = \psi(x)e^{-i\omega t}$$
(2.59)

where the Planck's relation  $E = \hbar \omega$  is used. Thus the total wave-function (in the case of  $E > U_0$ ) is:

$$\psi(x;t) = Ae^{+ikx}e^{-i\omega t} + Be^{-ikx}e^{-i\omega t}$$

The first term (the forward wave) can be rewritten as:

$$\psi(x;t) = Ae^{+i(kx-\omega t)}$$

that corresponds to a monochromatic plane wave in 1D. Its phase velocity can be estimated by differentiating the phase and set it to zero:

$$\phi(x,t) = kx - \omega t \quad \rightarrow \quad d\phi = \frac{\partial \phi(x,t)}{\partial x} dx + \frac{\partial \phi(x,t)}{\partial t} dt = k dx - \omega dt = 0$$
  
$$\rightarrow \quad v_{phase} = \frac{dx}{dt} = \frac{\omega}{k} \quad (positive)$$
  
65

Since  $v_{phase}$  is positive it is an harmonic forward wave. Analogous procedure for the second term leads to a phase velocity  $v_{phase} = -\omega/k$ , thus negative. It means that it is a backward propagating monochromatic wave.

It must finally said that it has no much sense talking about a 1D plane wave. Indeed a plane wave is a wave in which the wavefronts (i.e. the constant phase surfaces in the 3D space) are planes. The general 3D expression for a plane wave is the following:

$$\psi(\vec{r};t) = Ce^{i(\vec{k}\cdot\vec{r}-\omega t)} \tag{2.60}$$

The phase is:

$$\phi = \vec{k} \cdot \vec{r} - \omega t$$

Now the constant phase surfaces can be found by fixing the time instant at a given  $t_0$  and set the phase  $\phi$  constant, the result is:

$$\phi = constant \quad \Leftrightarrow \quad \vec{k} \cdot \vec{r} = k_x x + k_y y + k_z z = constant$$

The last expression correspond to a parametric equation of a plane, thus the wavefronts are planes. In 1D the harmonic plane wave of eq. (2.60) actually becomes :

$$\psi(x;t) = Ce^{i(k_x x - \omega t)} \tag{2.61}$$

from which the name used before. It is useful to notice that a plane wave has a purely parabolic energy dispersion relation. The energy dispersion relation is the relation that links the total energy E to the wavenumber k. For a plane wave of the kind of eq. (2.61) it was already pointed out that  $k = k_x$  is linked to the total energy of the particle by means of the de Broglie relation:

$$E(k) = \frac{\hbar^2 k^2}{2m}$$

Thus the energy dispersion relation E(k) is quadratic.

# 1D Free particle

A free particle, with no forces acting on it, is now considered as first practical example. The particle can be e.g. an electron. It was pointed out in the previous section that no forces acting on the particle means that the potential energy is constant in each point (indeed if  $\vec{F_x} = 0$  in eq. (2.54) then U(x) is constant). Since the potential energy is defined up to an additive constant then this constant can always be set such that the particle "feels" no potential energy but its energy E is only kinetic: U(x) = 0,  $\forall x \in \mathbb{R}$ . Thus the 1D steady state Schrödinger's equation (2.53) becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + U(x)\psi(x) = E\psi(x) \quad , \quad U(x) = 0 \quad \forall x \in \mathbb{R}$$
$$\rightarrow \frac{d^2}{dx^2}\psi(x) + k^2\psi(x) = 0 \quad , \quad k = \sqrt{\frac{2m}{\hbar^2}E} \in \mathbb{R}$$

The wavenumber is real since the total energy E, that equals in this case the kinetic energy, cannot be negative (indeed a negative energy E would lead to unacceptable solutions). By writing the characteristic polynomial as pointed out in the previous subsection, the solution of this equation turns out to be:

$$\psi(x) = Ae^{+ikx} + Be^{-ikx} \tag{2.62}$$

i.e. the superposition of a forward and a backward wave. Even if the wavenumber k is positive (by definition) there are two possible wave vectors (or propagation constants), that in this 1D case corresponds exactly to  $\pm k$ , and they appear in the two exponents. Indeed as already mentioned the first term  $Ae^{+ikx}$  is a forward wave, thus with positive propagation constant +k and momentum  $p = \hbar k$ ; while the second term  $Be^{-ikx}$  is a backward wave, with negative propagation constant -k and momentum  $p = -\hbar k$ . To both the terms, i.e. to both the wave-functions, the same energy value E is associated, indeed as already pointed out this is the case of an harmonic plane wave, with energy:

$$E(k) = \frac{\hbar^2 k^2}{2m}$$

Consequently to each energy value E (or eigenvalue in the notation of eigenvalue problems), two wave-functions are associated, with the two different propagation constant - see eq.(2.62). This is obvious if the dispersion relation E(k) is considered. Indeed it is parabolic and two symmetric values of the wavenumber, namely  $\pm k$ , lead to the same energy value E. It is said that the energy level E is degenerate with degeneracy equal to two, indeed two states, or wave-functions (namely  $Ae^{+ikx}$  and  $Be^{-ikx}$ ), are associated to the same energy eigenvalue E. Notice that there are no constraints on the possible range of values of E (apart that it must be non-negative), thus  $E \in \mathbb{R}^+$  and the Hamiltonian spectrum is thus continuous.

In general if no interaction occurs between the particle and external forces or entities it will persevere in its state of motion, thus if it assumed to be an incoming particle from negative to positive x values then its state will be simply the forward wave (B = 0 since it cannot be reflected since nothing is present apart it):

$$\psi(x) = Ae^{+ikx} \tag{2.63}$$

In the case in which the kinetic energy is null, that is E = 0, then the steady state Schrödinger's equation simplifies in:

$$\frac{d^2}{dx^2}\psi(x) = 0$$

thus the solution is very simple, and it is recovered by integrating two times in dx:

$$\psi(x) = A + Bx$$

Nevertheless in section 2.3.2 it was discussed that the wave-function must be limited, while here  $Bx \to \infty$  when  $x \to \infty$ , thus in order to ensure a limited wave-function everywhere B must be chosen equal to zero: B = 0.

An important remark is that a free particle is unlocalized. This is evident considering eq. (2.63). The magnitude squared of  $\psi(x)$  is constant (recall that  $|e^{\pm ikx}|^2 = 1$ ), and the same holds for the case of E = 0. Obviously the same again holds true for a single backward propagating wave. In general it is possible to rewrite the 1D wave-function of eq. (2.62) like:

$$\psi(x) = Ce^{ikx} \quad \to \quad |\psi(x)|^2 = |C|^2 \tag{2.64}$$

where depending on the sign of k (if it is accepted to embed the sign in k that becomes no more the wavenumber but the 1D propagation constant instead) the wave-function is a forward or backward wave. The point is that a free particle has the same probability of being in each point x of the space and it is unlocalized (indeed its squared magnitude is constant). This is even more clear considering that a wave-function  $\psi(x) = e^{\pm ikx}$  describes a particle whose momentum  $p = \hbar k$  is precisely known: that is  $\Delta p = 0$ . Indeed it is a monochromatic wave with a well defined k, and from the Heisenberg's uncertainty principle this requires  $\Delta x \to \infty$  corresponding to unlocalization in space. Notice that unlocalization corresponds to a continue range of energy E, i.e. a continuous spectrum of the Hamiltonian operator  $\hat{H}$ .

A final remark on the wave-function normalization is provided. In order to appreciate it let's consider again the last expression for the 1D plane wave of eq. (2.64). The modulus squared of the wave-function is constant everywhere. The problem is that the particle is supposed to be free in all the space, that corresponds to the fact that the potential energy is everywhere null. If in a region of space a force field is acting then this assumption is no more true, since a potential energy variation should appear in that region. In order to normalize the wave-function the following integral must be considered (see the normalization condition eq. (2.19)):

$$\int_{all \ space} |\psi(x)|^2 \, dx = \int_{-\infty}^{+\infty} |C|^2 \, dx = 1 \quad (impossible!)$$

Nevertheless the problem is that that integral does not converge since it is unlimited (infinite). In other words the wave-function is not square-integrable:  $\psi(x) \notin L^2(all \ space)$ . The problem is conceptual, because if the wave-function is not square-integrable it cannot be normalized, and thus it cannot be associated to the physical meaning of position probability density. This issue can be overcome in three possible ways.

First, the solution is to say that the universe, thus all the space is limited and not infinite. In this way, said V the volume of the entire universe, the integral is finite thus the wavefunction can be normalized similarly to what done in example 2.1 (section 2.3.2). For example assuming  $V = [0, x_0] \subset \mathbb{R}$  the solution in 1D becomes:

$$\int_{V} |\psi(x)|^{2} dx = \int_{0}^{x_{0}} |C|^{2} dx = |C|^{2} x_{0} = 1 \quad \Leftrightarrow \quad C = \frac{1}{\sqrt{x_{0}}}$$

This solution has very important and unsolved physical, metaphysical and even philosophic implications. Nevertheless the way of thinking is that the quantum mechanical systems are always confined at least in the laboratory in which the experiments are carried out. In this last optics it has sense. Thus a particle can be modeled as "free" even if it is not (since it is confined by external forces / materials). The continuous energy E would be

no more continue at all (see later - discretization arises from confinement), but since the laboratory is macroscopic (thus extremely larger that the particle itself) the energy levels are so close that it would be impossible to distinguish between two successive levels and they are at all practical effects considered continuous, thus making true the model and its interpretation as practical tool.

The second solution starts from the consideration that an infinite physical entity cannot be directly measured (since it is infinite) and thus believing that it may have an intrinsic physical reality is a matter of personal philosophy. Consequently the solution is very practical: independently on the existence or not of an infinite space, the solution consists in saying that even if  $\psi(x) \notin L^2(all \ space)$ , it keeps anyway the meaning of a relative probability:

$$\frac{\int_{V_1} |\psi(x)|^2 dx}{\int_{V_2} |\psi(x)|^2 dx}$$

In the moment in which  $V_1$  and  $V_2$  tend to infinity their ratio is finite, leading to a relative probability that is finite and can be suitably normalized. Nevertheless monochromatic plane waves are mathematically very simple and useful. Indeed the set of all the monochromatic plane waves (in 1D)  $\left\{\frac{1}{\sqrt{\Omega}}e^{ikx}\right\}_k$  can be shown to be orthonormal and complete, and thus it can be used as basis for the Fourier Transform (if k is continuous) or series (if k is discrete); and the usefulness of the Fourier analysis is of extreme both conceptual and practical importance in quantum mechanics, as it should be clear from the treatment of previous sections 2.2, 2.3.3, 2.3.5, 2.3.6. In this solution it is implicitly admitted their physical inconsistency.

The third solution is widely accepted. It is referred as "wide sense normalization". The mathematical procedure is quite similar to the one conventionally adopted for introducing (non formally) the concept of Fourier transform in signal processing courses [95], [96]. In few words it consists in limiting the domain to a finite domain (similarly to what done in first solution), but then to enforce periodic boundary conditions, such that the system is left open. This means the the wave-function does not tend to zero at the domain boundaries (that would mean confinement, indeed a null wave-function means no probability of finding the particle there), but instead it has the same phase condition at all the boundaries (i.e. the frontier) of the domain. Thus since the domain is limited a discretization occurs (see next examples to better understand this point). Nevertheless, then, the boundaries of the domain are made tend to infinity, and from a discrete system (Fourier series) a continuous system is obtained (Fourier transform). So the continuous case is recovered but the gain is that a normalization condition is found for the continuous case, i.e. for the unlocalized free particles (monochromatic harmonic plane waves). The normalization condition involves the functional theory, and in particular it involves the delta Dirac function. For the 1D case it is:

$$\int_{-\infty}^{+\infty} |\psi_k(x)|^2 dx = (\psi_k, \psi_{k'}) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i(k-k')} dx = \delta(k-k')$$

Sometimes in electromagnetic fields courses similar expressions are found for the modal functions. With this new delta Dirac normalization condition, that holds for continuous systems, it is then possible to normalize the unlocalized wave-function in a wide sense, and thus to assign them the meaning of position probability density as usual. A complete discussion with a focus on the important physical, metaphysical and philosophic implications of all the three solutions is provided in [87].

#### 3D free particle

In this section is recovered the expression for the wave-function of a free particle in the 3D space. Starting from the points gained in the previous section for the 1D free particle wave-function, and considering the separation of variables presented at the beginning of the section, it is possible to directly write the final expression for the wave-function. Indeed from the separation of variables it is possible to solve separately three 1D problems in x, y and z like already done in the previous subsection, and then the full 3D wave-function is given by the product of the three 1D wave-functions. By doing so:

$$\psi(x,y,z) = A_x A_y A_z e^{ik_x x} e^{ik_y y} e^{ik_z z} = C e^{i\vec{k}\cdot\vec{r}} \quad , \quad C = A_x A_y A_z \quad (generally \ complex)$$

If time is considered (see eq. (2.49) for the total solution of the time dependent Schrödinger's equation):

$$\psi(x, y, z; t) = Ce^{i\vec{k}\cdot\vec{r}}e^{-i\omega t} = Ce^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

Notice that it is a plane wave in the 3D space (as pointed out previously in this section). Since it is a monochromatic harmonic wave ( $\omega$  is fixed once E is fixed:  $E = \hbar \omega$ ), it is an unlocalized wave-function (see also section 2.2) and the same remarks done in the previous subsection are valid here. In particular its squared magnitude is constant and thus there is the same probability of finding the particle in each point of the 3D space.

#### Potential step

In this subsection the solution of the steady state Schrödinger's equation for the case of a potential step is addressed. It is supposed to have zero potential energy for x < 0 and a constant positive value  $U_0 > 0$  for x > 0:

$$U(x) = \begin{cases} 0 & if \ x < 0\\ U_0 & if \ x \ge 0 \end{cases}$$

For example this shape of the potential can be the mathematical simplified representation of the potential experienced by free electron in a metal nearby the surface. Indeed electrons in a metal can be considered as a free gas around the nuclei, but they are confined in the material (in normal conditions the metal does not emit electrons). Thus they experience no potential deep in the metal, but they "feel" a potential step (of height of the order of the work function) close to the surface, such that they are confined inside the metal. Thus the potential step can be a mathematical (abrupt) simplification of the (smoother) surface potential experienced by electrons in a metal [88].

In order to proceed it is better to solve separately the two cases for  $E < U_0$  and  $E > U_0$ . Case of  $E < U_0$ : In this case the classical mechanics predicts that the particle cannot be found in the region with x > 0. Thus it is a classical forbidden region. Think for example to a marble with kinetic energy E coming from left toward a potential barrier. The potential energy barrier can be a hillock, that can be overcome by the marble only if it has enough kinetic energy E to overcome the gravitational potential barrier  $U_0$ : i.e. if  $E > U_0$ . Otherwise the marble will go up a bit but then it will come back on the left side. Let's split the problem into two parts for negative (region I) and positive (region II) xvalues and then merge together the solutions by enforcing the wave-function properties presented in section 2.3.2. For x < 0 no potential is acting on the electrons thus the solution of the Schrödinger's equation is analogous to the one already found in the previous subsections for a free particle:

$$\psi_I(x) = Ae^{+ik_1x} + Be^{-ik_1x} , \quad k_1 = \sqrt{\frac{2m}{\hbar^2}E} \in \mathbb{R}^+$$

For x > 0 instead the Schrödinger's equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{II}(x) + U_0\psi_{II}(x) = E\psi_{II}(x) \quad \to \quad \frac{d^2}{dx^2}\psi_{II}(x) + k_2^2\psi_{II}(x) = 0$$
  
with:  $k_2 = i\beta_k$ ,  $\beta_k = \sqrt{\frac{2m}{\hbar^2}(U_0 - E)} \in \mathbb{R}^+$ 

that has the general solution (see also previously the general procedure for 1D problems):

$$\psi_{II}(x) = Ce^{+ik_2x} + De^{-ik_2x} = Ce^{-\beta_k x} + De^{+\beta_k x}$$

Nevertheless  $De^{+\beta_k x}$  is unacceptable since the wave-function must be everywhere limited and for  $x \to +\infty$  the term  $De^{+\beta_k x} \to +\infty$ ; thus D is set to zero: D = 0. The total wave-function is thus:

$$\psi(x) = \begin{cases} \psi_I(x) = Ae^{+ik_1x} + Be^{-ik_1x} \\ \psi_{II}(x) = Ce^{-\beta_k x} \end{cases}$$

A very important remark that makes quantum mechanics different from classical mechanics is that with quantum mechanics there is a certain probability of finding the particle (electron) in the region II even in the case it has an energy  $E < U_0$ . Indeed the wavefunction in the region II with x > 0 it is non-zero, but it is  $\psi_{II}(x) = Ce^{-\beta_k x}$ . Since  $\beta_k$  is real (ad positive) the probability of finding the particle on the other side of the potential step is exponentially decreasing with the distance x. Moreover the smaller is E w.r.t.  $U_0$ , the faster is the decay (see the expression for  $\beta_k$  above). In other words the exponential decay is faster if  $U_0$  is increased, and for  $U_0 \to +\infty$  the wave-function exactly zero at the boundary ( $\psi_{II}(x) \to 0$ , that means that if the potential step is infinitely high there is no probability of finding the particle in the classically forbidden region, and the classical result is recovered). In physical terms there is a given probability of finding the electrons beyond the metal surface, even this probability rapidly decays with the distance.

The constants A, B and C can be determined by enforcing the continuity on the wavefunction and its first derivative in x = 0:

$$\begin{cases} \psi_I(x=0) = \psi_{II}(x=0) \\ \frac{d\psi_I(x)}{dx}|_{x=0} = \frac{d\psi_{II}(x)}{dx}|_{x=0} \end{cases} \rightarrow \begin{cases} Ae^{+ik_10} + Be^{-ik_10} = Ce^{-\beta_k 0} \\ ik_1Ae^{+ik_10} - ik_1Be^{-ik_10} = -\beta_kCe^{-\beta_k 0} \\ 71 \end{cases}$$

These conditions yield A + B = C and  $ik_1(A - B) = -\beta_k C$ , which in turn give:

$$B = \frac{(ik_1 + \beta_k)A}{ik_1 - \beta_k} \quad and \quad C = \frac{2ik_1A}{ik_1 - \beta_k}$$

Notice that one parameter is free (indeed there are three unknowns A, B and C and only two equations; thus from Rouché-Capelli's theorem there are  $\infty^1$  solutions). A common choice is to assume A as known, since it represents the incoming (from left) wave amplitude, and normalized to 1. The incoming wave field intensity is thus  $|A|^2$ , while  $|C|^2$  is the intensity of the transmitted wave field and  $|B|^2$  the intensity of the reflected back wave field. Notice that:

$$|B|^{2} = \left|\frac{ik_{1} + \beta_{k}}{ik_{1} - \beta_{k}}A\right|^{2} = \frac{(ik_{1} + \beta_{k})}{(ik_{1} - \beta_{k})}\frac{(-ik_{1} + \beta_{k})}{(-ik_{1} - \beta_{k})}|A|^{2} = |A|^{2}$$

Therefore the incident and the reflected wave fields have the same intensity. This result should be interpreted by saying that all incoming (from left) particles reaching the potential step with an energy  $E < U_0$  bounce back, including also those that penetrate slightly into the region II. Thus at the end all the particles are reflected, and this is a consequence of the fact that the potential step extends infinitely at right side (for x > 0). If it were of finite width, and enough thin, there may happen that a particle can cross it even if it has an energy  $E < U_0$  (since the exponential decay may be not enough to ensure zero probability of finding the particle at right side). This is exactly what happens for enough thin potential barriers, see later in this section the potential barrier 1D problem.

In figures 2.4 and 2.5 few examples of interest concerning a potential step are reported. The figures were created in MatLab environment implementing a finite difference method for solving the Schrödinger's equation, following what is presented in section 2.4 (the code is reported in appendix A.4). Notice the exponential tails and the larger penetration in region II when the energy of the incoming particle is increased.

Case of  $E > U_0$ : In this case the classical prediction, if the particle is assumed coming from left, is that it always overcome the step, although it has a smaller velocity in region II than in region I. Nevertheless the quantum mechanical picture is different even in this case. Indeed there is a given probability of reflection even if  $E > U_0$ .

The solution of steady state Schrödinger's equation in region I is the same of before:

$$\psi_I(x) = Ae^{+ik_1x} + Be^{-ik_1x} , \quad k_1 = \sqrt{\frac{2m}{\hbar^2}E} \in \mathbb{R}^+$$

Instead for x > 0 the Schrödinger's equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{II}(x) + U_0\psi_{II}(x) = E\psi_{II}(x) \quad \to \quad \frac{d^2}{dx^2}\psi_{II}(x) + k_2^2\psi_{II}(x) = 0$$

with:  $k_2 = \sqrt{\frac{2m}{\hbar^2} \left( E - U_0 \right)} \in \mathbb{R}^+$ 



Figure 2.4: Wave-function (a) and wave-function squared modulus (b) corresponding to an electron with energy  $E = 0.354 \,\text{eV}$  incoming from left toward a potential step of height  $U_0 = 2 \,\text{eV}$ . The wave-function and its squared modulus are unnormalized.

It has the general solution:

$$\psi_{II}(x) = Ce^{+ik_2x} + De^{-ik_2x}$$

Since now  $k_2$  is real (positive) then both the forward and the backward waves are limited and mathematically acceptable.







Figure 2.5: Wave-function squared modulus corresponding to an incoming electron from left side, with energy E = 1.4 eV (a) and E = 1.989 eV (b) toward a potential step of height  $U_0 = 2 \text{ eV}$ . The wave-functions and their squared moduli are unnormalized.

Nevertheless assuming that the particle is incoming from left, once it overcomes the potential step there is no more reason why it could be reflected back (no other variations of the potential occurs, and if U(x) is constant the particle perseveres in its state of motion with no reflection or scattering phenomena).

For this reason D = 0 (no backward wave in the region II). Consequently:

$$\psi_{II}(x) = Ce^{+ik_2x}$$
 and  $\psi(x) = \begin{cases} \psi_I(x) = Ae^{+ik_1x} + Be^{-ik_1x} \\ \psi_{II}(x) = Ce^{+ik_2x} \end{cases}$ 

Applying then the boundary conditions on the wave-function and its first derivative continuity:

$$\begin{cases} \psi_I(x=0) = Ae^{+ik_10} + Be^{-ik_10} = \psi_{II}(x=0) = Ce^{+ik_20} \\ \frac{d\psi_I(x)}{dx}|_{x=0} = ik_1Ae^{+ik_10} - ik_1Be^{-ik_10} = \frac{d\psi_{II}(x)}{dx}|_{x=0} = ik_2Ce^{+ik_20} \\ \rightarrow \quad \begin{cases} A+B=C \\ k_1(A-B) = k_2C \end{cases} \rightarrow \quad B = \frac{k_1-k_2}{k_1+k_2}A \quad and \quad C = \frac{2k_1}{k_1+k_2}A \end{cases}$$

The important fact, as already pointed out, is that in this case B is not zero, thus a particle has a non-null probability of being reflected back in x = 0 due to the potential step even in it has an energy E greater than the step height:  $E > U_0$ . This is again an effect that arises only in quantum mechanics. Notice that this reflection is a characteristic behavior of all the wave fields whenever a region of discontinuity of the physical properties of the medium is present (analogously to the well known behavior of elastic or electromagnetic waves).

A final remark is provided concerning negative energies. If the calculations are repeated with  $E \leq 0$ , enforcing the boundary conditions it turns out that the only possible solution is  $\psi(x) = 0$  (i.e. the trivial one), that means no state is possible with negative or null energy (zero probability means no particle in that state). This holds is general, and as already pointed out for the free particle case, this is not surprising.

#### Potential barrier and tunnel effect

It is now considered a potential barrier of thickness W and height  $U_0$ , of the kind of the one in figure 2.6. The corresponding expression of the potential is:

$$U(x) = \begin{cases} 0 & if \ x < 0 & (region \ I) \\ U_0 & if \ 0 \le x \le W & (region \ II) \\ 0 & if \ x > W & (region \ III) \end{cases}$$

It is supposed to have an incoming particle (electron) of energy E from left side (as indicated in the picture). Analogously to the previously considered examples the case in which the incoming particle energy is negative or null ( $E \leq 0$ ) is not interesting since it leads to null states of the kind  $\psi(x) = 0$ . Thus only the case E > 0 is taken into account. *Case of*  $E < U_0$ : In this case from classical mechanics it is expected a full reflection of the incoming particles (as already described for the potential step). Nevertheless in quantum mechanics it turns out that there is a finite probability of finding the incoming particles on the right side of the barrier, thus there is a certain probability of transmission. This is referred as "tunnel effect".



Figure 2.6: Rectangular potential energy barrier. The barrier height is  $U_0$ , its width is W. Incident (from left), reflected and transmitted paths are shown. The three regions are: I for x < 0; II for  $0 \le x \le W$ ; and III for x > W.

In regions I and III the potential energy U(x) is zero, thus the steady state Schrödinger's equation is the one for the free particle already discussed. The general solutions in the two regions are:

$$\psi_I(x) = Ae^{ik_1x} + Be^{-ik_1x}$$
 and  $\psi_{III}(x) = Ce^{ik_3x} + De^{-ik_3x}$   
with:  $k_1 = k_3 = k = \sqrt{\frac{2m}{\hbar^2}E} \in \mathbb{R}^+$ 

In region I both an incident and a reflected wave fields are expected. Instead by supposing no other potential energy variations after W in region III only a transmitted wave is expected, thus it is chosen D = 0 (no backward wave in region *III*). In region *II* the Schrödinger's equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{II}(x) + U_0\psi_{II}(x) = E\psi_{II}(x) \quad \to \quad \frac{d^2}{dx^2}\psi_{II}(x) + k_2^2\psi_{II}(x) = 0$$

with: 
$$k_2 = i\beta_k$$
,  $\beta_k = \sqrt{\frac{2m}{\hbar^2}} (U_0 - E) \in \mathbb{R}^-$ 

that has the general solution:

$$\psi_{II}(x) = Fe^{+ik_2x} + Ge^{-ik_2x} = Fe^{-\beta_k x} + Ge^{+\beta_k x}$$

Since the barrier extends from x = 0 to x = W no constraints are present on  $\psi_{II}(x)$  since it results always limited. The fact that both a positive and a negative exponentials are presents has to be interpreted as follows. The incoming particle from left has a probability to be transmitted at x > 0, but this probability decays exponentially with space accordingly with  $Fe^{-\beta_k x}$ . Since in x = 0 there is a potential discontinuity there is a non-null probability of reflection that give rise to the backward term in region I. Analogously the potential discontinuity in x = W gives rise to a non-null probability of reflection of the (exponentially decaying) transmitted wave again region II. This is a backward propagating wave, that is exponentially attenuated (since  $E > U_0$ ), and corresponds to the term  $Ge^{+\beta_k x}$  (since it is propagating in -x direction it corresponds to an attenuated wave). Then if the barrier width W is finite (and enough thin) a non-negligible probability of finding the particle in the region III is present, described by the transmitted term:  $\psi_{III}(x) = Ce^{ik_3x}$ . Thus the total wave-function is:

$$\psi(x) = \begin{cases} \psi_I(x) = Ae^{ikx} + Be^{-ikx} & \text{if } x < 0 \quad (region \ I) \\ \psi_{II}(x) = Fe^{-\beta_k x} + Ge^{+\beta_k x} & \text{if } 0 \le x \le W \quad (region \ II) \\ \psi_{III}(x) = Ce^{ikx} & \text{if } x > W \quad (region \ III) \end{cases}$$

The quantum mechanical result for which it is possible to find the particle in region III even if it has an energy  $E < U_0$  has no classical analogous and is called "tunnel effect". It is at the origin of the gate current in conventional MOSFETs and in FinFETs. Notice that (as mentioned in the introductory chapter -section 1.1-) the tunneling is an exponential phenomenon with the barrier width W, thus a linear decrease in the barrier width leads to an exponential increase of the tunneling probability.

The values of the five constants A, B, C, F and G can be determined as done in the previous examples by enforcing the continuity on the wave-function and on its first space derivative in the discontinuity points x = 0 and x = W. The incoming wave field intensity  $|A|^2$  can be assumed to be known (indeed it is obtained a system of four equations and five unknowns). In this case usually the explicit expression of the final wave-function is not of interest. Instead the transmission and reflection coefficients T and R are usually considered interesting. It is possible to define them as:

$$T = \left| \frac{C}{A} \right|^2$$
 and  $R = \left| \frac{B}{A} \right|^2$ 

It can be verified that T + R = 1. The details on these calculation are not reported here, and are left to the interested reader. Good references can be [87] (in Italian) and [88]. An example of tunneling through a potential barrier is reported in figure 2.7, that is the output of a *MatLab* code (reported in appendix A.4) implementing a finite difference method based on the considerations of section 2.4.

Case of  $E > U_0$ : Similarly to what happens in the case of a potential step in this case it is classically expected that all the incoming particles reaching the barrier from left are transmitted. Instead with quantum mechanics a finite probability of reflection is present both at x = 0 and x = W, i.e. in the potential discontinuity points.

The same procedure already carried out for the previous case can be followed for obtaining the following result for the total wave-function in the three regions:

$$\psi(x) = \begin{cases} \psi_I(x) = Ae^{ikx} + Be^{-ikx} & \text{if } x < 0 \quad (region \ I) \\ \psi_{II}(x) = Ce^{ik'x} + De^{-ik'x} & \text{if } 0 \le x \le W \quad (region \ II) \\ \psi_{III}(x) = Fe^{ikx} & \text{if } x > W \quad (region \ III) \end{cases}$$
$$where: \quad k = \sqrt{\frac{2m}{\hbar^2}E} \in \mathbb{R}^+ \quad and \quad k' = \sqrt{\frac{2m}{\hbar^2}(E - U_0)} \in \mathbb{R}^+$$
$$77$$



Figure 2.7: Wave-function (a) and wave-function squared modulus (b) corresponding to an electron with energy E = 0.82 eV incoming from left toward a potential barrier of width 0.5 nm and height  $U_0 = 1 \text{ eV}$ . The wave-function and its squared modulus are unnormalized.

Notice that k corresponds to the wavenumber of a free electron and  $\hbar k'$  is the momentum of the particle while crossing the barrier. The values of the constants B, C, D and F can be determined as functions of A by applying the boundary conditions on wave-function continuity and on its first derivative continuity in x = 0 and x = W, again four equations are recovered and thus one free parameter, namely A, appears in the solution. The term  $Be^{-ikx}$  corresponds to a back reflected wave that has no classical analogous. It is possible

to define a reflection coefficient analogously to what done previously in the case of  $E > U_0$ . Instead of defining the transmission coefficient, in this case, it is possible to define the so called "transparency" T of the barrier:  $T = |F|^2/|A|^2$ . It is possible to show (see e.g. [88] or [87]) that there are values of  $E/U_0$  for which there is a perfect transmission, i.e. T = 1. These values of input energy E correspond to a particle de Broglie wavelength (inside the barrier)  $\lambda' = \frac{2\pi}{k'}$  that is an integer multiple of 2W:

resonance condition: 
$$\lambda' = \frac{2\pi}{k'} = \sqrt{\frac{2\pi^2\hbar^2}{m(E-U_0)}} = 2Wn$$
,  $n \in \mathbb{N} \setminus \{0\}$ 

This phenomenon is called "resonance effect". In figure 2.8 a pair of examples of transparency T as a function of particle energy E are reported for rectangular potential barriers. Notice the resonance peaks of transmission.



Figure 2.8: Rectangular potential energy barrier transparency example. The barrier height is of about  $U_0 = 4.5 \text{ eV}$  while its thickness is 20 nm. The transmission coefficient is calculated both starting from analytical theoretical formulae (following the approach of [97]), and with a numerical method. The numerical method is an implementation of a Finite Element Method for the solution of the Schrödinger's equation, conceptually similar to what will be presented in section 2.4.1. The two methods provide very similar results indeed the two curves are well overlapped. Notice the resonance peaks and the non-null transmission also for  $E < U_0$ .

## 1D potential well

The potential energy shape considered in this section has an opposite shape w.r.t. the potential barrier considered previously. An example is reported in figure 2.9. As mentioned at the beginning of the present section, a positive potential (e.g. of barrier type) corresponds to a repulsive interaction, instead a negative potential (e.g. of well type) corresponds to an attractive potential. In figure 2.9 (a) it is evident that the particle experiences a negative

potential in the region  $-\frac{L}{2} \le x \le +\frac{L}{2}$ , while it experiences a null potential in  $x < -\frac{L}{2}$  and  $x > +\frac{L}{2}$ . This means that there is an electrostatic attractive force acting on the particle in the central region, within the well, while around it the particle does not feel it and behaves like a free particle (since no potential is acting on it). In particular, also in this case it is convenient to separate the various cases depending on what is the total energy E of the considered particle (electron). If  $E < -U_0$  no state is possible (see previous subsections, here it is analogous) and this case is not of interest. If  $-U_0 \leq E \leq 0$  it is said that the particle is in a "bound state". Classically it cannot overcome the potential barrier (exactly as already seen for the potential step or the barrier) and go out of the well, thus the particle is classically confined within the well. Thus bound states are conventionally the ones with negative energy. Instead if E > 0 then the particle is classically free to move everywhere in the space (analogously to the barrier case), indeed it has enough energy to jump out of the well and move in the zero potential region. The states with positive energy are called "free states" or "continuum states". Indeed the solution of the Schrödinger's equation in this case is analogous to the one for the free particle, and the energy E is continuous:  $E \in \mathbb{R}^+$ . The sign convention on energy E is thus:

- bound states: with negative energy  $-U_0 \leq E \leq 0$ . They represent classically confined states. Analogously to the cases of the potential step and barrier in quantum mechanics there is a given probability of finding the particle outside the well (if it has a finite height). It will be shown in a while that these states have a discrete spectrum (of Hamiltonian operator), i.e. discrete energy levels.
- continuum states: with positive energy E > 0. They represent free particles moving with no particular constraints. These states have continuous range of eigenvalues  $(E \in \mathbb{R}^+)$ , thus the Hamiltonian spectrum is said to be continuous.

This convention is widely spread and often used, especially in chemistry. In which a negative energy level corresponds to a bound state, that means that the electron is confined in that chemical structure (e.g. atoms, molecules, crystal, etc...). The binding energy (or dissociation energy) is the amount of energy to make the electron free, thus it corresponds to the energy difference between the considered energy level and the zero-energy level (vacuum level). If that amount of energy is provided to the electron (e.g. in a molecule) it undergoes to a state transition from a bound state (in which e.g. it is kept in the molecule) to a free state. Thus the binding energy is exactly the amount of energy to be provided to an electron in a bound state in order to break its chemical bond and make it free.

Even if this convention is widely spread, in the practical solution of the steady state Schrödinger's equation addressed in this section it will be assumed to have zero potential inside the well, thus U(x) = 0 for  $-\frac{L}{2} \leq x \leq +\frac{L}{2}$ , and a positive potential value  $U_0$ (constant) outside the well. Since the potential energy is defined up to an additive constant the final result does not change and exactly the same results are recovered. The only thing that changes is the sign convention on states, that is now different from the one above. In particular the bound states will be the ones with energy  $0 \leq E \leq U_0$  and the free ones will be those with  $E > U_0$  (see figure 2.9 (b) ).



Figure 2.9: 1D potential energy well. The well height is  $U_0$ , its width is L, the potential has even symmetry. Left side (a) shows a potential well with the sign in accordance with the standard sign convention for bound and free states. The binding potential is negative  $-U_0$ , the bound states are those with energy  $-U_0 \leq E \leq 0$ , the free states are those with energy E > 0. Right side (b) shows the potential well considered here with positive  $U_0$ , and with the following sign convention. The bound states are those with  $0 \leq E \leq +U_0$ , the free states those with  $E > U_0$ .

With this convention, the potential shape is:

$$U(x) = \begin{cases} U_0 & \text{if } x < -\frac{L}{2} \\ 0 & \text{if } -\frac{L}{2} \le x \le +\frac{L}{2} \\ U_0 & \text{if } x > +\frac{L}{2} \end{cases}$$

Notice that this potential shape can be an oversimplification of the real the case of a free electron gas within a metal. If the positive ions potential shape is neglected, the potential inside the metal is flat and chosen equal to zero. Nevertheless the metal does not emit electrons, that are confined in it, and this corresponds in having an high potential barrier  $U_0$  at the metal interface. The height  $U_0$  of the potential barrier will be of the order of the metal work function, that corresponds to the energy to be provided in order to extract an electron from the metal.

As already said, the case with negative energy E < 0 is not of interest. Instead let's start from the free states with energy  $E > U_0$ . This case is similar to the already considered one of potential barrier with energy E greater than the potential energy barrier one. The procedure of proceeding is exactly analogous and contrarily to classical mechanics it turns out that there is a finite probability of reflection in the two discontinuity points  $x = -\frac{L}{2}$ and  $x = +\frac{L}{2}$ . It is possible to get explicit expressions for the transmission and the reflection coefficients, and also in this case it is possible to verify an energy dependence of these coefficients, with both transmission peaks and reflection peaks. A full treatment is provided in [87]. Notice that no constraints on the range of energy values is recovered thus they can be continuous.

The attention is now focused on the most interesting case: the one of bound states, i.e. with energy  $0 \le E \le U_0$ .

In region I the potential is  $U(x) = U_0 > E$  and the steady state Schrödinger's equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_I(x) + U_0\psi_I(x) = E\psi_I(x) \quad \to \quad \frac{d^2}{dx^2}\psi_I(x) - \frac{2m}{\hbar^2}\left(U_0 - E\right)\psi_I(x) = 0$$
  
$$\to \quad \frac{d^2}{dx^2}\psi_I(x) - \beta_k^2\psi_I(x) = 0 \quad \to \quad \frac{d^2}{dx^2}\psi_I(x) + k_1^2\psi_I(x) = 0$$

with:  $k_1 = i\beta_k$ ,  $\beta_k = \sqrt{\frac{2m}{\hbar^2} (U_0 - E)} \in \mathbb{R}^+$ 

The characteristic polynomial is:  $\lambda^2 - \beta_k^2 = 0$  from which the two roots are:  $\lambda_{1,2} = \pm \beta_k = \pm \sqrt{\frac{2m}{\hbar^2} (U_0 - E)}$ . The general solution is thus:

$$\psi_I(x) = Ae^{+\beta_k x} + Be^{-\beta_k x} \quad , \quad with: \ A, B \in \mathbb{R}$$

In order to ensure an everywhere limited wave-function B = 0, because otherwise the limit for  $x \to -\infty$  diverges. Thus the solution becomes:

$$\psi_I(x) = A e^{+\beta_k x} \quad , \quad A \in \mathbb{R}$$

In region II the potential is null: U(x) = 0. Thus the solution is the one for free electrons:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{II}(x) = E\psi_{II}(x) \quad \rightarrow \quad \frac{d^2}{dx^2}\psi_{II}(x) + k_2^2\psi_{II}(x) = 0$$
  
with:  $k_2 = k = \sqrt{\frac{2m}{\hbar^2}E} \in \mathbb{R}^+$ 

Since no confusion is possible  $k_2$  is simply called k. The characteristic polynomial is:  $\lambda^2 + k^2 = 0$ ; from which the two roots are:  $\lambda_{1,2} = \pm ik = \pm i\sqrt{\frac{2m}{\hbar^2}E}$ . The general solution is thus:

$$\psi_{II}(x) = Ce^{+ikx} + De^{-ikx} \quad , \quad with: \ C, D \in \mathbb{C}$$

No constraints are present on C and D since the exponentials are complex and the  $\psi_{II}(x)$  is limited everywhere.

In region III the potential is again  $U(x) = U_0 > E$ , thus the solution is formally the same of region I, with the same  $\beta_k$  (since  $U_0$  is supposed to be the same also  $\beta_k$  is the same). The solution can be written as:

$$\psi_{III}(x) = Fe^{+\beta_k x} + Ge^{-\beta_k x} \quad , \quad with: \ F, G \in \mathbb{R}$$

In order to ensure a limited wave-function everywhere F = 0, because otherwise  $\psi_{III}(x)$  would diverge for  $x \to +\infty$ . Thus the solution in region III becomes:

$$\psi_{III}(x) = Ge^{-\beta_k x} \quad , \quad G \in \mathbb{R}$$

In summary the total wave-function is:

$$\psi(x) = \begin{cases} \psi_I(x) = Ae^{+\beta_k x} & \text{if } x < -\frac{L}{2} & (region \ I) \\ \psi_{II}(x) = Ce^{+ikx} + De^{-ikx} & \text{if } -\frac{L}{2} \le x \le +\frac{L}{2} & (region \ II) \\ \psi_{III}(x) = Ge^{-\beta_k x} & \text{if } x > +\frac{L}{2} & (region \ III) \end{cases}$$

By enforcing the boundary conditions on continuity of  $\psi(x)$  and its first derivative in  $x = -\frac{L}{2}$  and in  $x = +\frac{L}{2}$  it is possible to find the values for the constants A, C, D and G. In order to do that it is simpler to rewrite the wave-function as follows:

$$\psi_{II}(x) = Ce^{+ikx} + De^{-ikx} = C \left[ \cos(kx) + i\sin(kx) \right] + D \left[ \cos(kx) - i\sin(kx) \right] = \\ = (C+D)\cos(kx) + (iC-iD)\sin(kx)$$

and said:  $K_1 = A$ ,  $K_2 = C + D$ ,  $K_3 = iC - iD$  and  $K_4 = G$  the wave-function becomes:

$$\psi(x) = \begin{cases} \psi_I(x) = K_1 e^{+\beta_k x} & \text{if } x < -\frac{L}{2} & (\text{region } I) \\ \psi_{II}(x) = K_2 \cos(kx) + K_3 \sin(kx) & \text{if } -\frac{L}{2} \le x \le +\frac{L}{2} & (\text{region } II) \\ \psi_{III}(x) = K_4 e^{-\beta_k x} & \text{if } x > +\frac{L}{2} & (\text{region } III) \end{cases}$$

The continuity conditions are:

$$\begin{cases} \psi_{I}(-\frac{L}{2}) = \psi_{II}(-\frac{L}{2}) & (cond. \ 1) \\ \psi_{II}(+\frac{L}{2}) = \psi_{III}(+\frac{L}{2}) & (cond. \ 2) \\ \frac{d}{dx}\psi_{I}(x)|_{x=-\frac{L}{2}} = \frac{d}{dx}\psi_{II}(x)|_{x=-\frac{L}{2}} & (cond. \ 3) \\ \frac{d}{dx}\psi_{II}(x)|_{x=+\frac{L}{2}} = \frac{d}{dx}\psi_{III}(x)|_{x=+\frac{L}{2}} & (cond. \ 4) \end{cases}$$

For example from (cond. 1) one gets:

$$K_1 e^{-\beta_k \frac{L}{2}} = K_2 cos(k \frac{L}{2}) - K_3 sin(k \frac{L}{2})$$
  

$$\rightarrow \quad K_1 e^{-\beta_k \frac{L}{2}} - K_2 cos(k \frac{L}{2}) + K_3 sin(k \frac{L}{2}) + K_4 \cdot 0 = 0$$

Proceeding analogously for the other three conditions an homogeneous linear system of four equations in four unknowns (that are  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_4$ ) is recovered. Then it is possible to select only non-trivial solutions by enforcing its determinant (in matrix form) to be null (a trivial solution corresponds to all four constants  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_4$  null, that means no state or null state  $\psi(x) = 0$ ). The result is a mathematical condition to be satisfied by both k and  $\beta_k$  that leads thus to a condition on the allowed energy values (since both k and  $\beta_k$  are function of energy E). It turns out that the only possible energy values for steady states in a quantum well are discrete. Nevertheless a full analytical solution is not possible in the case of finite height quantum well. Notice that the quantization here comes out naturally, by enforcing the boundary conditions on  $\psi(x)$ . This is the main difference between a quantum theory based on the Schrödinger's solution and the first attempts of Bohr, in which the quantization was introduced *ad hoc*. Thus bound states have quantized energy levels, that is: the Hamiltonian operator (in a bound system) has a discrete spectrum for  $0 < E < U_0$  (bound states), while has a continuous spectrum for  $E > U_0$  (free states).

The same result can be obtained in an another way by noting that the potential U(x) has an even symmetry, and thus exploiting symmetry conditions of the wave-functions. Nevertheless, also in this case a full analytical solution is not possible and at a certain point a numerical or graphical solution of a system is required. This procedure is highlighted in appendix A.2.

Of course whatever is the method used for the solution of this problem the final result does not change: a finite number of discrete energy levels are present (or allowed) in the quantum well. Thus discretization is the main feature of the bound states. It is possible to show that the number of quantized energy levels increases with the height  $U_0$  of the well and with the square of its length L. The quantity  $U_0 \left(\frac{L}{2}\right)^2$  is sometimes called the "binding power" of the well since it represents the strength of the bond. If the binding power is increased then the number of discrete energy levels is increased, i.e. the number of permitted bound states increases, thus meaning that the intensity of the attractive force is greater.

It is possible to solve numerically the steady state Schrödinger's equation for the case of a quantum well of height  $U_0$ . Examples of numerical results, obtained in *MatLab* environment by means of an implementation of the finite difference method presented in section 2.4 are reported in figures 2.10, 2.11 and 2.12. The *MatLab* code used to creates these figures is reported in appendix A.3. Notice that when the well is increased or enlarged the number of bound eigenstates is increased, as already pointed out.

In conclusion, the Hamiltonian operator, in the case of a finite height quantum well, presents a mixed spectrum: the bound states have discrete energy eigenvalues, corresponding to the discrete part of the spectrum, while the free states have a continuous range of energies E, thus corresponding to the continuous part of the spectrum.



Figure 2.10: Permitted energy eigenvalues in a 1D potential energy well with L = 10 nm and  $U_0 = 1 \text{ eV}$ . Notice that they are discrete, and only 17 bound states are possible for this specific quantum well. In black the quantum well shape (in eV).



Figure 2.11: First four wave-functions corresponding to the first four energy levels of figure 2.10. The same quantum well is considered: 1D potential energy well with L = 10 nm and  $U_0 = 1 \text{ eV}$ . Notice that the exponential tails in the classical forbidden regions. The wave-functions are unnormalized; in black the quantum well shape (in eV).



Figure 2.12: Squared moduli of all the 17 wave-functions corresponding to the 17 energy eigenvalues of figure 2.10. The same quantum well is considered: 1D potential energy well with L = 10 nm and  $U_0 = 1$  eV. The squared moduli are positioned at a height corresponding to their relative eigenvalue for aesthetic reasons. They are unnormalized; in black the quantum well shape (in eV).

# 1D infinite height potential well

In this section an infinite height quantum well is considered. The difference w.r.t. previous section is that  $U_0 \to +\infty$  at the well boundaries. In this case there are no continuum states, since there cannot exist particles with energy E greater than infinity:  $E > U_0 \to +\infty$ . Thus only bound states will be found. In this case it is possible to get an analytical solution, as it will be shown in a while. The procedure is always the same of the previously investigated 1D problems. Before summarizing the main steps notice that if in the finite height well it is made the limit for  $U_0 \to +\infty$ , the real decaying exponentials in the two classically forbidden regions I and III tend to zero. Thus it is expected to find perfectly confined wave-functions, that go to zero at the well boundaries.

The potential shape is assumed to be analogous to the one of figure 2.9 but with  $U_0 = +\infty$ . The calculations are a little bit simplified with a shift in the x-coordinate axis such that the well is in between x = 0 and L. Figure 2.13 represents the new potential shape. The fact that the potential energy blows up to infinity at the well boundaries represents that very strong forces are acting in the two boundary points x = 0 and x = L, resulting in a full reflection of the particle. Indeed  $\psi(x = 0) = 0 = \psi(x = L)$  means no probability of finding the particle in x = 0 and c = L, that means that it is completely reflected (conservation of matter and total probability holds).

The Schrödinger's equation in region I and III is analogous to the one already solved in the previous section, but with  $U_0 \to +\infty$ . It it possible to write the exponential functions



Figure 2.13: Infinite height 1D potential energy well. The well height is  $\infty$  at x = 0 and x = L; the well width is L, the potential has even symmetry.

and then make them tend to zero. The steps are summarized in the following equations:

$$\frac{d^2}{dx^2}\psi_I(x) + k_1^2\psi_I(x) = 0 \quad with: \quad k_1 = k_3 = i\beta_k \quad , \quad \beta_k = \sqrt{\frac{2m}{\hbar^2}(U_0 - E)}$$

The general solutions thus are:

$$\psi_I(x) = Ae^{+\beta_k x} + Be^{-\beta_k x} \quad , \quad \psi_{III}(x) = Ce^{+\beta_k x} + De^{-\beta_k x}$$

In order to ensure an everywhere limited wave-function it must be set: B = 0 and C = 0. And since  $\beta_k = \sqrt{\frac{2m}{\hbar^2} (U_0 - E)} \rightarrow +\infty$  when  $U_0 \rightarrow +\infty$  the two wave-functions tend to zero (for  $\psi_I(x)$  remember that x is negative x < 0, thus making the exponent negative since  $\beta_k$  is positive):

$$\psi_I(x) = Ae^{+\beta_k x} \to 0 \quad , \quad \psi_{III}(x) = De^{-\beta_k x} \to 0$$

In region *II* the Schrödinger's equation is the one for the free particle:

$$\frac{d^2}{dx^2}\psi_{II}(x) + k_2^2\psi_{II}(x) = 0 \quad with: \quad k_2 = k = \sqrt{\frac{2m}{\hbar^2}E} \in \mathbb{R}^+$$

whose solution is:

$$\psi_{II}(x) = \psi(x) = Fe^{+ikx} + Ge^{-ikx}$$

By enforcing the continuity in x = 0 one gets  $\psi(x = 0) = 0 = F + G$  from which G = -F, and so:

$$\psi(x) = Fe^{+ikx} - Fe^{-ikx} = F(e^{+ikx} - e^{-ikx}) = 2iFsin(kx) = Ksin(kx)$$

where K = 2iF is constant. The boundary condition in x = L leads  $\psi(x = L) = 0 = Ksin(kx)$ , but since the constant K cannot be null (otherwise  $\psi(x) = 0$  for each x value, but this means no state - trivial solution), it can be rewritten as:

$$sin(kL) = 0 \quad \Leftrightarrow \quad kL = 0 + n\pi \quad , \quad n \in \mathbb{N} \setminus \{0\}$$

Notice that n = 0 would lead to zero k value that is again the trivial solution. Moreover in general it would be mathematically acceptable an integer  $n \in \mathbb{Z} \setminus \{0\}$ , but for positive and negative symmetric n values the same wave-function would be recovered due to the *sin* function anti-symmetry, thus it has sense to choose  $n \in \mathbb{N} \setminus \{0\}$ . Solving for the momentum gives:

$$k = \frac{n\pi}{L}$$
,  $p = \hbar k = \frac{n\pi\hbar}{L}$ ,  $n \in \mathbb{N} \setminus \{0\}$  (2.65)

The energy eigenvalues of the particles are then given by:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad , \quad n \in \mathbb{N} \setminus \{0\}$$
(2.66)

In conclusion, the electrons (or particles) in an infinite height quantum well cannot have arbitrary energy values but only discrete values given by eq. (2.66), i.e. the energy is quantized. This is a general result that holds whenever quantum confinement occurs, due to a potential shape that confines the particles in a certain region of space. Notice again that quantization comes out naturally by enforcing the boundary conditions on the general solutions of the steady state Schrödinger's equation, and it is not introduced *ad hoc*. An acceptable wave-function that satisfies these boundary conditions is possible only for certain values of energy. In the case of a step or of a barrier the particles were not confined and indeed continuum states were present, with in general a continuous energy E. Moreover notice that the minimum energy for a particle in a quantum well is  $E_1 = \frac{\pi^2 \hbar^2}{2mL^2} > 0$ and not zero. This minimum energy is related to the uncertainty principle, indeed the uncertainty on the particle position is of the order of L:  $\Delta x \sim L$ . The particle is moving back and forth in the 1D well with a momentum p, leading to an uncertainty on the momentum of around  $\Delta p \sim 2p$ . The uncertainty principle (eq. (2.13)) requires  $\Delta x \Delta p \geq h$ , thus  $2Lp \geq h$  that is  $p \geq \pi \hbar/L$ , that gives:  $E \geq E_1$ . The existence of a "zero point energy", like  $E_1$ , is typical of all the quantum confinement problems.

Finally the wave-functions  $\psi(x) = Ksin(kx)$  can be normalized. From the normalization condition (eq. (2.19)):

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 \, dx = |K|^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right) \, dx = 1$$

The value of the integral is L/2, thus:  $|K|^2 \frac{L}{2} = 1$ , from which  $K = \sqrt{\frac{2}{L}}$ . Therefore the normalized wave-functions are:

$$\psi_{normalized}(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \quad , \quad n \in \mathbb{N} \setminus \{0\}$$
(2.67)

#### 3D potential well

In this section a 3D quantum well is considered. It means that the potential is of the kind of the one of figure 2.13 in all the three directions x, y and z. Since quantum confinement occurs in all directions, this structure is sometimes also called "quantum dot", or better: it can be an oversimplified representation of a real quantum dot. In general the lengths of the sides of potential "box" can be different, they are assumed to be  $L_x$ ,  $L_y$  and  $L_z$ . Assuming that the potential can be expressed as the sum of the three different wells (as happens for a potential box just described), it is possible to speed up the solution by exploiting the separation of variables presented at the beginning of this section. In this way the total energy of a particle (electron) inside the 3D potential box is simply the sum of the energy eigenvalues in the three directions:  $E = E_x + E_y + E_z$ . From equations (2.65) and (2.66) one gets:

$$k_x = \frac{n_x \pi}{L_x}$$
,  $k_y = \frac{n_y \pi}{L_y}$ ,  $k_z = \frac{n_z \pi}{L_z}$ ,  $n_x, n_y, n_z \in \mathbb{N} \setminus \{0\}$  (2.68)

and said:  $k^2 = k_x^2 + k_y^2 + k_z^2$ , the energy eigenvalues are then given by:

$$E = E_x + E_y + E_z = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m} = \frac{\hbar^2 k^2}{2m}$$
$$E = \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_y^2}{L_y^2} \right) \quad , \quad n_x, n_y, n_z \in \mathbb{N} \setminus \{0\}$$
(2.69)

Then the 3D wave-functions are given by the product of the 1D ones, thus:

$$\psi(x, y, z) = \psi(x)\psi(y)\psi(z) = K_x \sin(k_x x) K_y \sin(k_y y) K_z \sin(k_z z)$$

$$\rightarrow \quad \psi(x,y,z) = Csin\left(\frac{n_x\pi}{L_x}x\right)sin\left(\frac{n_y\pi}{L_y}y\right)sin\left(\frac{n_z\pi}{L_z}z\right) \tag{2.70}$$

where  $C = K_x K_y K_z = (2/L)^{3/2}$  (see eq. (2.67)). An interesting case is the one of  $L_x = L_y = L_z = L$ . In this case the above expressions become:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\pi^2 \hbar^2}{2mL^2} \left( n_x^2 + n_y^2 + n_z^2 \right) \quad , \quad n_x, n_y, n_z \in \mathbb{N} \setminus \{0\}$$
(2.71)

$$\psi(x, y, z) = Csin\left(\frac{n_x \pi}{L}x\right)sin\left(\frac{n_y \pi}{L}y\right)sin\left(\frac{n_z \pi}{L}z\right)$$
(2.72)

Notice that the energy eigenvalues depend only on  $(n_x^2 + n_y^2 + n_z^2)$ , this means that all the set of  $n_x$ ,  $n_y$  and  $n_z$  that provide the same value of  $(n_x^2 + n_y^2 + n_z^2)$ , provide also the same energy level. Nevertheless when  $n_x$ ,  $n_y$  and  $n_z$  are changed, even without changing E, they make changing the wave-function  $\psi(x, y, z)$ , thus the same energy level may correspond to different wave-functions or states and degeneracy occurs.

## General potential shapes

So far various cases were treated, and the main result is that the quantum confinement gives rise to energy quantization. This holds in general and not only for energy eigenvalues. Indeed in section 2.3.6 it was pointed out that the steady state Schrödinger's equation is the eigenvalue problem for the Hamiltonian operator  $\hat{H}$ , but in general it is possible to write an eigenvalue problem for each operator  $\hat{F}$  representing whatever physical observable F. By doing so an equation of the kind of:

$$F\psi_i = f_i\psi_i \tag{2.73}$$

is obtained. Its solutions corresponds to the physical observable eigenvalues  $\{f_i\}_i$  and eigenstates (or eigenfunctions)  $\{\psi_i\}_i$ . The meaning (that comes out from the way in which eq. (2.73) is derived - see section 2.3.6 for details), is the following: by performing a measurement on F it is possible to find as a result one of the possible  $\{f_i\}_i$  values, let's say  $f_n$ , that means that the system was in the corresponding state  $\psi_n$ . It is possible to verify that quantum confinement (of the kind of the quantum well investigated so far) does imply quantization, not only of energy levels but also of the other physical observables such as angular momentum and so on... This can be verified by solving the relative eigenvalue problems of the kind of eq. (2.73).

In general an operator can have a discrete spectrum (i.e. its eigenvalues are quantized), a continuous spectrum (i.e. its eigenvalues can assume each value in a real range of values with continuity) or a mixed spectrum (a mix of the previous cases is possible). For example in the general case of a potential energy of the kind of the one in figure 2.14, the Hamiltonian operator presents a mixed spectrum. Indeed, as indicated in the figure, for negative energies bound states are present (due to confinement) and its spectrum is discrete ( $E_1$ ,  $E_2$ ,  $E_3$ , etc... in the figure); while for E > 0 no confinement occurs and the energy is continuous (continuum states or unbound states).

It may be thus useful to gain an intuition about the physical insights of system under study, starting from the facts so far known. In figures 2.17, 2.18 2.15, 2.16 are reported some examples. In order to understand the physical results that can be obtained by a simulator it may be useful to intuitively draw the wave-functions specifying if they are propagating waves or attenuating in each region (before solving the equations). To this purpose a good reference may be [88].



Figure 2.14: General potential energy shape example, typical of a central force problem. At large x value the interaction vanishes thus  $U(x) \to 0$ . Instead for x = 0 the potential energy tends to infinity  $U(x) \to \infty$  because of the repulsion. For small x values an attractive interaction occurs and U(x) is negative. On right side of the potential shape is reported the Hamiltonian operator spectrum (energy eigenvalues), discrete for negative energies (bound states) and continuous for positive energies (free states).



Figure 2.15: Wave-function corresponding to an electron tunneling through two consecutive potential barriers. The first barrier is 0.5 nm thick and 1 eV of height, the second is 0.25 nm thick and 2 eV of height. The electron energy is E = 0.73 eV. Notice the exponential decay within the barriers; the wave-function is unnormalized. The graph was generated with the *MatLab* code reported in appendix A.4.



Figure 2.16: Wave-function squared modulus corresponding to an electron tunneling through two consecutive potential barriers. The potential shape and the structure is the same of figure 2.15. Notice the exponential decay within the barriers; the wave-function is unnormalized. The graph was generated with the *MatLab* code reported in appendix A.4.



Figure 2.17: Confinement in a quantum well. The well is 10 nm long and 1 eV tall. Inside it a barrier of 5 nm of width and height 0.8 eV is present. The potential shape is the curve in black. In total 13 bound states are present in this structure. Their wave-functions are reported in this graph; they are unnormalized and they are placed at an height corresponding to their relative energy eigenvalues. Notice the degeneracy and the spacing between the enrgy levels. The graph was generated with the *MatLab* code reported in appendix A.3.



Figure 2.18: Confinement in a quantum well. The well is the same of picture 2.17. Here four wave-functions are reported, they correspond to energy levels:  $E_3 = 0.174 \text{ eV}$  (top left),  $E_8 = 0.662 \text{ eV}$  (top right),  $E_{10} = 0.815 \text{ eV}$  (bottom left) and  $E_{11} = 0.855 \text{ eV}$  (bottom right). Notice the exponential decay in the central region (of height 0.8 eV) of the top ones, while the bottom ones are free in that region (oscillating). The wave-functions are unnormalized. The graph was generated with the *MatLab* code reported in appendix A.3.

# 2.4 Finite difference method and matrix representation

The purpose of this section is to illustrate how a differential operator, such as the Hamiltonian one  $\hat{H}$ , can be represented in matrix form. This will be useful to understand next theoretical topics in this thesis work, especially related to the Non-Equilibrium Green's Function formalism (see chapter 5). As already mentioned in the introductory sections of this chapter, this representation is also the foundation of the Heisenberg's formalism of quantum mechanics, the so called "matrix mechanics", in which operators are indeed matrices. The task will be addressed in two steps, following the approach of [89].

Firstly, a finite difference discretization of the steady state Schrödinger's equation is presented. It is interesting to notice that Heisenberg initially conceived his matrix mechanics, starting from finite difference discretization of differential operators. In particular he developed a theory that involved only physical quantities directly observable. In doing so, he exploited the Fourier analysis to rewrite the classical dynamic (differential) equations in finite difference equations for the state transition probabilities, from one state to another state of the quantum system. Notice that this formulation was initially conceived by Heisenberg, but in the form known today, it is the result of the work of many other scientists, among which Dirac produced a great contribution. Then, the general method for representing an operator in matrix form and the Dirac's notation will be briefly addressed.

# 2.4.1 Finite difference method for the solution of the steady state Schrödinger's equation

The 1D Hamiltonian operator is:

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)$$

It is possible to think of solving numerically the steady state Schrödinger's equation, and to do that it is necessary to discretize the domain x and the Hamiltonian operator.

The space axis can be discretized in N of nodes:  $x = (x_1, x_2, x_3, ..., x_n, ..., x_{N-1}, x_N)$ , in this way it becomes an array. Let's suppose a uniform spacing discretization, that means the the step between two nodes in the space array is constant and fixed to  $a = x_{n+1} - x_n$ (for each considered n). Since the potential energy shape U(x) is supposed known it can be also discretized in a set of N equidistant points:  $U = (U_1, U_2, U_3, ..., U_n, ..., U_{N-1}, U_N)$ , where the generic  $U_n$  is intended as:  $U_n = U(x_n)$ . The constant  $-\frac{\hbar^2}{2m}$  is unchanged. The second derivative operator can be instead discretized by means of a finite difference formula, that is intuitively derived from the geometrical meaning of derivative. In numerical methods courses the finite difference method is usually treated, nevertheless what is needed here is just the finite difference formula for the second order derivative. Thinking that the derivative is defined by means of a limit of the incremental ratio, it is possible to approximate the first order derivative with one of the two formulae (forward or backward finite difference formula):

$$\frac{d\psi}{dx} \sim \frac{\psi_{n+1} - \psi_n}{a}$$
 ,  $or: \frac{d\psi}{dx} \sim \frac{\psi_n - \psi_{n-1}}{a}$ 

where  $\psi_n = \psi(x_n)$  and  $a = x_{n+1} - x_n = x_n - x_{n-1}$ . The second order derivative can be obtained by deriving two times w.r.t. space, thus:

$$\frac{d^2\psi}{dx^2} \sim \frac{\frac{\psi_{n+1}-\psi_n}{a} - \frac{\psi_n-\psi_{n-1}}{a}}{a} = \frac{\psi_{n+1}-2\psi_n+\psi_{n-1}}{a^2}$$

It follows that the Hamiltonian operator, when it is applied to the wave-function  $\psi(x)$  in the node  $x_n$  of the discretized domain, becomes:

$$\widehat{H}\psi(x_n) = \widehat{H}\psi_n \sim -\frac{\hbar^2}{2m}\frac{\psi_{n+1} - 2\psi_n + \psi_{n-1}}{a^2} + U_n\psi_n$$

Notice that it depends on the potential only in that node  $U_n = U(x_n)$ , and on the wavefunction at nodes n - 1, n and n + 1. It is now defined the quantity  $t_0$  (accordingly with [89]):

$$t_0 = +\frac{\hbar^2}{2ma^2}$$
94

and the product of the Hamiltonian operator applied to  $\psi_n$  becomes:

$$\widehat{H}\psi_n \sim -t_0 \left(\psi_{n+1} - 2\psi_n + \psi_{n-1}\right) + U_n \psi_n = -t_0 \psi_{n-1} + \left(2t_0 + U_n\right) \psi_n - t_0 \psi_{n+1} \quad (2.74)$$

At this point the steady state Schrödinger's equation can be discretized exploiting the finite difference method, and it can be translated in a matrix equation:

$$\widehat{H}\psi = E\psi \quad \rightarrow \quad [H] \{\psi\} = E \{\psi\}$$

where the symbol [H] indicates a matrix of dimension  $N \ge N$  and the symbol  $\{\psi\}$  a column vector of dimension N. The product [H]  $\{\psi\}$  is a matrix product (rows by columns). Since the application of  $\hat{H}$  to  $\psi_n$  involves the nodes n - 1, n and n + 1 the Hamiltonian matrix [H] will be tridiagonal, with  $(2t_0 + U_n)$  on the main diagonal, and  $-t_0$  on the upper and lower diagonal (see eq. (2.74) for a reference). The final result is thus:

$$\begin{bmatrix} 2t_0 + U_n & -t_0 & 0 & 0 & 0 & \cdots \\ -t_0 & 2t_0 + U_n & -t_0 & 0 & 0 & \cdots \\ 0 & -t_0 & 2t_0 + U_n & -t_0 & 0 & \cdots \\ 0 & 0 & -t_0 & 2t_0 + U_n & -t_0 & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \cdots \\ \psi_n \\ \vdots \\ \psi_N \\ \psi_N \\ \end{bmatrix} = E \begin{cases} \psi_1 \\ \psi_2 \\ \cdots \\ \psi_n \\ \vdots \\ \psi_N \\ \end{pmatrix}$$

Notice that by performing the matrix product between [H] and  $\{\psi\}$  equation (2.74) is recovered.

# 2.4.2 Matrix representation of differential operators

The purpose of this section is to address the matrix representation of differential operators. In order to do that, the important concept of basis set will be also introduced. These topics will be further discussed in the next section, where the Dirac's notation will be addressed. In this section I will follow the approach of [89], while in the next one the one of [87].

In section 2.3.5 it was mentioned that the general solution of the time-dependent Schrödinger's equation can be always be expressed as superposition of the steady state factorized solutions, that are solution of the steady state Schrödinger's equation, i.e. of the Hamiltonian operator eigenvalue problem. This result was summarized in eq. (2.49), in which the general case of a mixed spectrum Hamiltonian was considered. Equation (2.49) is reported here for convenience:

$$\psi(\vec{r};t) = \oint dE \ C(E) \ \Psi_E(\vec{r}) \ e^{-\frac{i}{\hbar}Et}$$

The important fact, that enables to write the most general wave-function  $\psi(\vec{r};t)$  as a superposition of the steady state (time-dependent) wave-functions  $\Psi_E(\vec{r}) e^{-\frac{i}{\hbar}Et}$ , by means of the coefficients C(E), is that the steady state wave-functions are an orthogonal (or if

normalized an orthonormal) and complete set of functions. Exactly like an orthonormal set of N vectors can be used as a basis for a representation of each vector in the N-dimensional vector space, the orthonormal complete set of wave-functions can be used as a basis for the representation of whatever wave-function  $\psi(\vec{r};t)$ . Notice that "complete" means exactly that this procedure, namely the representation of a whatever function as superposition of the functions belonging to the orthonormal complete set, can be performed. In general, as pointed out in section 2.3.3, this procedure is analogous at all to perform a Fourier series expansion (for discrete systems) or transform (for continuous systems). Indeed as known from signal theory courses, the meaning of the Fourier analysis is to change the basis of representation of the function (signal) from time domain to frequency domain, or better: to express the signal as a superposition of purely harmonic (monochromatic) signals. A complete set of functions is thus a set of functions that can be used as basis for representing whatever function. The general function  $\psi(\vec{r};t)$  can be thus expressed as a linear combination (i.e. a superposition) of the basis functions, each suitably weighted by means of the coefficient C. These coefficient can be interpreted exactly like Fourier coefficients (see e.g. [96] and [95]), since the procedure is essentially a Fourier expansion. Moreover these (Fourier) coefficients have an analogous meaning to the coefficients of a vector w.r.t. a new vector basis for the vector space: i.e. they are the projection of the general function  $\psi(\vec{r};t)$  on the representation basis  $\Psi_E(\vec{r}) e^{-\frac{i}{\hbar}\vec{E}t}$ . For conventional vectors this corresponds to a scalar product, for functions it is the same but the scalar functional product must be considered. It is formally defined by equation (2.32). In the case of the projection of the general wave-function  $\psi(\vec{r};t)$  onto the basis set made by the steady states it becomes:

$$C(E) = \left(\Psi_E(\vec{r})e^{-\frac{i}{\hbar}Et}, \psi(\vec{r};t)\right) = \int \Psi_E^*(\vec{r})e^{+\frac{i}{\hbar}Et}\psi(\vec{r};t)d\vec{r}$$

Let's focus for the moment only in the case of a discrete spectrum of the Hamiltonian operator. In this case equation (2.49) becomes a summation:

$$\psi(\vec{r};t) = \sum_{i} C(E_i) \Psi_{Ei}(\vec{r}) e^{-\frac{i}{\hbar}E_i t}$$

i.e. it is a Fourier series (discrete case). The general 1D Fourier series expansion of the function f(x) in the basis of harmonic exponential functions  $\{e^{i\frac{2\pi n}{P}x}\}_n$  (where P is a constant often assumed equal to the period of f(x) or equal to  $2\pi$ ) is usually written as (see signal processing courses or [96] and [95]):

$$f(x) = \sum_{n} c_{n} e^{i\frac{2\pi n}{P}x} , \quad c_{n} = \frac{1}{P} \int f(x) e^{-i\frac{2\pi n}{P}x} dx = \left(e^{i\frac{2\pi n}{P}x}, f(x)\right)$$

From which it is evident that the coefficients  $C(E_i)$  are essentially Fourier coefficient, with the meaning discussed above, for the basis set  $\Psi_{Ei}(\vec{r}) e^{-\frac{i}{\hbar}E_it}$ . The difference w.r.t. to the usual Fourier series is only the choice of the basis set, that usually is the set of harmonic waves (complex exponentials). At this point it should be very clear what discussed above, and the general theory can now be addressed.

All these concepts hold in general and not only for the steady state wave-functions. In particular the only requirement to express whatever function (wave-function) as a superposition (summation) of basis functions is that the set of basis functions is orthogonal (if normalized orthonormal) and complete. This is always true for the eigenfunctions of an Hermitian operator. Thus if the quantum mechanical operator is Hermitian, it is possible to exploit its eigenfunctions as basis set. It is possible to show that all the quantum mechanical operators that represent physical observables (such as the Hamiltonian one, the momentum and the angular momentum ones, and so on...) are Hermitian.

In general it is thus possible to express whatever wave-function as a linear combination of suitable functions, that constitute the so called basis set. If the basis functions are indicated with  $\{u_m(\vec{r})\}_m$  then the wave-function can be written as:

$$\psi(\vec{r}) = \sum_{m} c_m u_m(\vec{r}) \quad , \quad c_m = (u_m(\vec{r}), \psi(\vec{r})) = \int u_m^*(\vec{r}) \psi(\vec{r}) d\vec{r} \tag{2.75}$$

where a time-independent wave-function was considered for simplicity (the general results do not change - see previously eq (2.49) and the discussion above), and the integral is generally a three dimensional integral in space  $(d\vec{r} = dxdydz)$ .

From the geometrical meaning pointed out previously it is possible to represent the wavefunction  $\psi$  simply by means of a column vector consisting of the expansion coefficients (exactly like is often done in linear algebra):

$$\psi(\vec{r}) \rightarrow \{c_1 \ c_2 \ \dots \ c_n \ \dots\}^T$$

where T indicates the transpose. Notice that in general the Fourier series involves an infinite number of basis functions  $\{u_m(\vec{r})\}_m$ , nevertheless also a finite number of basis functions can be used. The latter case is always the case to be used in a numerical implementations on computers. In the first case the dimension of the coefficients vector will be infinite, in the latter finite. A vector space with a infinite number of dimensions is called Hilbert space (that is indeed a generalization of the concept of vector space for infinite dimensions), thus in the first case the basis set is a basis (thus a coordinate system) for a representation in an Hilbert space of the wave-function. In the latter case if the (finite) dimension of the basis set is called M then the representation becomes:

$$\psi(\vec{r}) = \sum_{m=1}^{M} c_m u_m(\vec{r}) \quad thus: \quad \psi(\vec{r}) \quad \to \quad \{c_1 \ c_2 \ \dots \ c_M\}^T$$
(2.76)

Notice that this last case is not so different from the presented finite difference discretization of the steady state Schrödinger's equation in the previous section 2.4.1. In that case indeed it was:

$$\psi(\vec{r}) \rightarrow \{\psi(\vec{r}_1) \ \psi(\vec{r}_2) \ \dots \ \psi(\vec{r}_M)\}^T$$

An important point now is that the basis set  $\{u_m(\vec{r})\}_m$  can be chosen quite arbitrary, and if a good choice is made, i.e. the basis functions  $\{u_m(\vec{r})\}_m$  are similar to the wave-functions that appear in the considered problem, then it is possible to accurately represent the wave-function  $\psi(\vec{r})$  with just few terms (to the extreme if  $u_1 = \psi$  then only one term is necessary, with  $c_1 = 1$  - even if it has no sense).

By substituting the wave-function expansion into the steady state Schrödinger's equation one gets:

$$\hat{H}\psi = E\psi$$
 , with :  $\psi(\vec{r}) = \sum_{m} c_m u_m(\vec{r})$ 

$$\rightarrow \sum_{m} c_m \hat{H} u_m(\vec{r}) = E \sum_{m} c_m u_m(\vec{r})$$

since the Hamiltonian operator has to be applied to a function  $u_m$  cannot be taken out on the left, instead since  $\hat{H}$  is linear and  $c_m$  are constant in  $\vec{r}$  (they are the result of an integral in  $d\vec{r}$  thus the space dependency is lost) they can be taken out on the left. Then by multiplying both sides by  $u_n^*(\vec{r})$  and integrating over all  $\vec{r}$  yields to:

$$\sum_{m} c_m \int \widehat{H} u_m(\vec{r}) u_n^*(\vec{r}) d\vec{r} = E \sum_{m} c_m \int u_m(\vec{r}) u_n^*(\vec{r}) d\vec{r}$$

From which:

$$\sum_{m} H_{nm} c_m = E \sum_{m} S_{nm} c_m \tag{2.77}$$

where:

$$H_{nm} = \int u_n^*(\vec{r}) \hat{H} u_m(\vec{r}) d\vec{r}$$
(2.78)

$$S_{nm} = \int u_n^*(\vec{r}) u_m(\vec{r}) d\vec{r}$$
(2.79)

Equation (2.77) can be rewritten in matrix form as:

$$[H] \{c\} = E [S] \{c\}$$
(2.80)

where square brackets indicate a matrix and the curly ones a column vector (E is a scalar).

Example 2.4: To definitely get the point let's consider this example in which only two basis functions  $u_1$  and  $u_2$  are present. The summation over m is to be considered with n fixed (indeed eq. (2.77) was derived by multiplying the steady state Schrödinger's equation by a fixed function  $u_n^*(\vec{r})$ ), thus the left hand side term is:

$$\sum_{m=1}^{2} H_{nm}c_m = H_{n1}c_1 + H_{n2}c_2 = \begin{bmatrix} H_{n1} & H_{n2} \end{bmatrix} \begin{cases} c_1 \\ c_2 \end{cases}$$

where the product is a matrix product (rows by columns). This must hold for each n, that corresponds exactly to the matrix product between the matrix of elements  $H_{nm}$  (n is the row index and m the column one) and the column vector of the coefficients, that is:

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{cases} H_{11}c_1 + H_{12}c_2 \\ H_{21}c_1 + H_{22}c_2 \end{cases}$$

Indeed eq. (2.77) was written by multiplying the steady state Schrödinger's equation by  $u_n^*(\vec{r})$ , and thus in principle a system of equations of the kind of eq. (2.77) should be written for each *n* possible value. These equations are obtained by multiplying the steady state Schrödinger's equation by all the possible  $u_n^*(\vec{r})$ , one at time. And a system of equations of that kind can be though in matrix form, in which each row of the matrix corresponds to an equation of the kind of eq. (2.77) with a different *n* value, exactly as it happens in this simple example. This argument should have convinced of the validity of eq. (2.80). The final column vector (last equation right hand side) consist of the coefficient column vector of the wave-function that is the result of the application of the Hamiltonian operator to the state  $\psi$ .  $\Box$ 

Evaluating the integrals of eq. (2.78) and (2.79) is the most time-consuming step in this process. Nevertheless once they are known the conventional linear algebra can be used (much simpler than differential equations), and an almost direct numerical implementation is moreover possible.

Notice that [S] is called overlap matrix, and in the case of an orthonormal basis set it coincides with the identity matrix [I]. Indeed in that case the basis functions are supposed normalized such that the integral of eq. (2.79) is always null except when m = n, that corresponds to diagonal elements, for which it is normalized to 1. In the case of an orthonormal basis set the matrix form of the Schrödinger's equation becomes:

$$[H] \{c\} = E [I] \{c\} \rightarrow [H] \{c\} = E \{c\}$$

$$(2.81)$$

indeed the matrix product between E[I] and  $\{c\}$  and the scalar product between E and  $\{c\}$  are the same. Notice that now, with the matrix notation just introduced, the steady state Schrödinger's definitively resembles a standard eigenvalue problem, see especially the orthonormal basis set case of equation (2.81).

In general it is possible to have a complete set, that thus can be used as basis set, even if it is not orthonormal but simply a set of linear independent functions, from which the need of defining properly the overlap matrix. This point will be further addressed in the next section 2.4.3.

Supposing of exploiting the linear algebra instruments to solve the eigenvalue problem, one gets the energy eigenvalues  $E_i$  and the corresponding eigenvectors, or better their representation in the chosen basis. Thus the problem can be to turn back to real space and get  $\psi(\vec{r})$ , starting from the knowledge on the coefficient eigenvectors  $\{c\}_i$ . The solution is immediate when eq. (2.75) is considered. Indeed:

$$\psi_i(\vec{r}) = \frac{1}{\sqrt{Z_i}} \sum_m c_{mi} u_m(\vec{r}) \quad , \quad \psi_i^*(\vec{r}) = \frac{1}{\sqrt{Z_i}} \sum_n c_{ni}^* u_n^*(\vec{r})$$

where  $Z_i$  is a normalization constant for the *i*-th eigenfunction, that is chosen in order to satisfy the normalization condition eq. (2.19):

$$\int \psi_i^*(\vec{r})\psi_i(\vec{r})d\vec{r} = \frac{1}{Z_i} \int \sum_n \sum_m c_{ni}^* u_n^*(\vec{r})c_{mi} u_m(\vec{r})d\vec{r} = 1 \quad \to \quad Z_i = \sum_n \sum_m c_{ni}^* c_{mi} S_{nm}$$

A set of very simple, clear and useful examples for becoming familiar with this notation and related topics are reported in [89].
### 2.4.3 The Dirac's notation and Hilbert spaces

In this section the same topics of the previous one will be discussed, but with the gain of the Dirac's notation. Moreover the mathematical formalism behind the addressed topics will be also briefly discussed. In this section I will mainly follow the approach of [87], and also of [89].

As already mentioned in the previous section, eq. (2.75) corresponds a representation of the wave-functions  $\psi(\vec{r})$  in terms of the basis functions  $u_m(\vec{r})$  and this is not so different from the representation in a given basis of a vector in a given vector space. In this optics the wave-function  $\psi(\vec{r})$  can be seen as a state vector in the infinite dimensional function space called the Hilbert space. If the number of basis functions is finite (see eq. (2.76)) then the wave-functions  $\psi(\vec{r})$  corresponds to a state vector in the *M*-dimensional Hilbert space. The coefficients  $c_m$  in equations (2.75) and (2.76) are like components of the state vector  $\psi(\vec{r})$  along the basis functions  $u_m(\vec{r})$ , i.e. the coordinate system chosen as basis. Choosing a different basis set is exactly like choosing a different coordinate system, and the component  $c_m$  along the different axes change while the state vector  $\psi(\vec{r})$  is the same. In the Dirac's notation the state vector associated with a given wave-function  $\psi(\vec{r})$  is indicated with the so called "ket":  $|\psi\rangle$ , while the basis functions  $u_m(\vec{r})$  are indicated with the kets:  $|m\rangle$  (sometimes also with:  $|u_m\rangle$ ). In this notation equation (2.75) becomes:

$$|\psi\rangle = \sum_{m} c_m |m\rangle \tag{2.82}$$

Before going on let's recall the definition of vector space. A linear vector space V is a set of elements called vectors, in which a sum operation and a product by a scalar operation are defined. The sum operation has commutative and associative properties, and associates to each pair of vectors in V a third vector again in V (V is closed w.r.t. sum) in a unique way. The scalar product has distributive and property w.r.t. vectors and distributive and associative properties w.r.t. scalars, and it has for result a vector that is again element in V (V is closed w.r.t. scalar product). Notice that the scalar can be in general a complex number.

The concept of Hilbert space is a generalization of the concept of vector space for the case in which the basis vectors are indeed basis functions. Its elements are often indicated with the "ket" symbol introduced above. Analogously to conventional vector spaces, it is possible to define the scalar product between two functions in the Hilbert space. This concept was already introduced by means of eq. (2.32), and it is now rewritten pointing out the Dirac's notation:

$$\langle f|g\rangle = \int f^*(\vec{r})g(\vec{r})d\vec{r}$$
(2.83)

where f and g are any two functions. The similarity of this integral with a scalar product is seen very well considering that the integral has meaning of sum over a continuum  $d\vec{r}$ . Thus it sums all the products  $f^*g$ , that is effectively what a standard scalar product does: it sums the component by component products (if one works with complex numbers the complex conjugates of the first vector components are used, i.e.  $f^*$ ). Notice that the complex conjugate of the function f is indicated with the so called "bra"  $\langle f|$ . The scalar product is thus represented by the juxtaposition of  $\langle f|$  and  $|g\rangle$ , that is:  $\langle f|g\rangle$ . In order to represent functions in an Hilbert space W a basis set of functions is needed. Analogously to conventional vector spaces, a basis is constituted by a linearly independent set of generators. With the term "generators" it is intended that each function of the Hilbert can be expressed as linear combination of the basis functions. Thus said  $\{u_m\}_m$ the basis set for the space W:

$$|f\rangle = \sum_{m} c_m |m\rangle \quad , \quad \forall f \in W$$

while with linearly independent it is meant:

$$\sum_{m} c_m \left| m \right\rangle = 0 \quad \Leftrightarrow \quad c_m = 0 \quad , \quad \forall \ m$$

In general it is thus possible to have non-orthogonal basis set, from which the importance of the overlap matrix [S] of elements  $S_{nm} = \int u_n^*(\vec{r}) u_m(\vec{r}) d\vec{r}$ ; as already mentioned. The basis functions are orthogonal if their scalar products are null except for the case n = m. If they are also normalized to 1 then they said to be orthonormal. For an orthonormal basis set the following relation is satisfied:

$$\langle n|m\rangle = \int u_n^*(\vec{r})u_m(\vec{r})d\vec{r} = \delta_{nm} \quad , \quad \delta_{nm} = \begin{cases} 0 & if \ n \neq m\\ 1 & if \ n = m \end{cases}$$

where  $\delta_{nm}$  is the Kronecker's delta. If the basis set is non-orthogonal (see eq. (2.79) for the definition of  $S_{nm}$ ):

$$\langle n|m\rangle = \int u_n^*(\vec{r})u_m(\vec{r})d\vec{r} = S_{nm}$$
(2.84)

Again notice that for orthonormal basis sets the overlap matrix becomes the identity one: [S] = [I] (which is a diagonal matrix with ones on its diagonal).

### **Operators and matrix representation**

From linear algebra it is known that a linear application (e.g.  $\hat{H}$ ) can be represented in matrix form, thus it is intuitive that is possible to write a differential (i.e. linear) operator in a matrix form. Moreover it was already shown the procedure to turn the differential operator  $\hat{H}$  into a matrix representation [H] with the discussion about the steady state Schrödinger's equation. To this purpose see equations (2.77) and (2.78); where the latter is a definition for the elements  $H_{nm}$  of the matrix [H]. Equation (2.78) is now rewritten exploiting the Dirac's notation:

$$H_{nm} = \int u_n^*(\vec{r}) \left( \hat{H} u_m(\vec{r}) \right) d\vec{r} = \langle n | \hat{H} | m \rangle$$
(2.85)

where  $\widehat{H} |m\rangle$  indicates the application of the Hamiltonian differential operator to the basis function  $u_m$  (i.e. the state  $|m\rangle$ ), and the juxtaposition of the bra  $\langle n|$  with  $\widehat{H} |m\rangle$  indicates the scalar product. This holds in general for any operator  $\widehat{F}$ , that in matrix form becomes [F] with elements  $F_{nm}$ :

$$F_{nm} = \int u_n^*(\vec{r}) \left( \hat{F} u_m(\vec{r}) \right) d\vec{r} = \langle n | \hat{F} | m \rangle$$
(2.86)

Example 2.5: In order to prove the last statement let's start from the consideration that in general a differential operator  $\hat{F}$  acting on a state vector  $|\psi_1\rangle$  changes it into a different state vector  $|\psi_2\rangle$ . Usually only transformations such that  $|\psi_1\rangle$ ,  $|\psi_2\rangle \in W$  (with W considered Hilbert space), are of interest. From the above discussion it is known that (see eq. (2.75) where Dirac's notation is now used):

$$|\psi_1\rangle = \sum_m c_m |m\rangle$$
 ,  $c_m = \langle m|\psi_1\rangle = \int u_m^*(\vec{r})\psi_1(\vec{r})d\vec{r}$ 

As said above, the application of  $\hat{F}$  on the state  $|\psi_1\rangle$  produces a different state vector  $|\psi_2\rangle$ :

$$\left|\psi_{2}\right\rangle = \widehat{F}\left|\psi_{1}\right\rangle$$

The point now is how to get the matrix representation for  $\hat{F}$  such that the above relation can be written in matrix form as:

$$|\psi_2\rangle = [F] |\psi_1\rangle$$

In order to do that let's start from the first relation:

$$|\psi_2\rangle = \hat{F} |\psi_1\rangle = \hat{F} \sum_m c_m |m\rangle = \sum_m c_m \hat{F} |m\rangle$$

then it is possible to represent the new state vector  $\hat{F} |m\rangle$ , that represents the differential operator  $\hat{F}$  acting on the basis state  $|m\rangle$ , as a linear combination of the basis functions like:

$$\widehat{F}|m\rangle = \sum_{n} c_{n} |n\rangle \quad , \quad c_{n} = \langle n|\widehat{F}|m\rangle = \int u_{n}^{*}(\vec{r}) \left(\widehat{F}u_{m}(\vec{r})\right) d\vec{r} = F_{nm}$$

and thus, by substituting in the previous relation:

$$|\psi_2\rangle = \sum_m c_m \widehat{F} |m\rangle = \sum_m c_m \sum_n c_n |n\rangle = \sum_m \sum_n c_m \langle n | \widehat{F} |m\rangle |n\rangle = \sum_m \sum_n c_m F_{nm} |n\rangle$$

from which an explicit expression for the coefficient vector that represent the state vector  $\psi_2$  in the basis set is recovered:

$$|\psi_2\rangle = \sum_n \left(\sum_m c_m F_{nm}\right) |n\rangle = \sum_n K_n |n\rangle \quad , \quad K_n = \sum_m F_{nm} c_m$$

Indeed the last relation corresponds to a representation of the vector state  $\psi_2$  in the basis set  $|n\rangle$ , given by the set of basis functions  $\{u_n(\vec{r})\}_n$  (now the index is called *n* but in principle it can be called *m* as done previously for  $\psi_1$ ), by means of the coefficients  $K_n$ , that all together constitute the coefficient vector of  $\psi_2$  in the basis  $\{u_n\}_n$ . The coefficient vector definition  $K_n = \sum_m F_{nm}c_m$  can be interpreted in matrix form as (remember that the matrix product is row by column):

Where [F] is exactly the matrix of elements  $F_{nm}$  as defined above. In conclusion it follows that (again the summation over n is interpreted as matrix product - i.e. the scalar product of the coefficient column vector with the basis set vector):

where indeed:

$$|\psi_{1}\rangle = \sum_{m} c_{m} |m\rangle = \begin{cases} c_{1} \\ c_{2} \\ \dots \\ c_{n} \\ \dots \end{cases} \{u_{1} \quad u_{2} \quad \dots \quad u_{n} \quad \dots\} = \{c\} \{u\}^{T}$$

In the last equation the summation over m is interpreted as a scalar product between the coefficient column vector and the vector that has the basis functions for components  $(u_m \to |m\rangle)$ ; then it is interpreted as matrix product (rows by columns).  $\Box$ 

The overlap matrix elements  $S_{nm}$  were already written with the new notation in equation (2.84). The steady state Schrödinger's equation in matrix form was already written in equation (2.80). Notice again that if the basis set is orthonormal then [S] = [I] and the Schrödinger's equation becomes the one of eq. (2.81). From the discussion carried on in the example 2.5 above, it follows that is also possible to write the steady state Schrödinger's equation directly like:

$$[H] |\psi\rangle = E |\psi\rangle$$

Indeed:

$$[H]\sum_{m} c_{m} |m\rangle = E\sum_{m} c_{m} |m\rangle \quad \rightarrow \quad [H]\{c\}\{u\}^{T} = E\{c\}\{u\}^{T}$$

That corresponds exactly to eq. (2.81) with a multiplication (to the right) of both members by  $\{u\}^T$  (notice that previously  $\{u\}$  was assumed to be a row vector). Notice that the time-dependent Schrödinger's equation with the Dirac's notation

becomes:

$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle = \hat{H}\left|\psi\right\rangle$$

where the Hamiltonian operator can be intended in its differential or matrix form.

### Hermitian operators and some properties

Good references for all the properties of linear operators can be [87] (in Italian) and [91] (a practical introduction is also provided in [89]). In the following of this work it will not needed to handle operators in matrix operation (the only concepts needed are the ones already introduced), consequently all the properties of operators in Hilbert spaces are not introduced.

For example it is possible to perform changes of basis (in a similar manner to what is done in the linear algebra courses), to define the inverse operator (quite similarly to inverse matrix definition), to define operations on operators such as their product, the commutation and anti-commutation operations and so on...

In this section I will only mention a pair of properties that will be important in the next chapters of this work.

An operator is said unitary if its inverse  $F^{-1}$  equals its complex conjugate transpose  $F^{\dagger}$ :

$$F^{-1} = F^{\dagger} \to F^{\dagger}F = 1$$

where "1" is the identity operator:  $1|m\rangle = |m\rangle$ .

A linear operator  $\hat{F}$  is said to be Hermitian when its matrix representation equals its complex conjugate and transpose:

$$[F] = [F]^{\dagger}$$
, *i.e.*  $F_{ij} = F_{ji}^{*}$ 

It is possible to show that all the operators representing real physical observables are Hermitian and that an Hermitian operator has real eigenvalues. This has sense if one thinks to the physical meaning of eigenvalues: they are the only possible results of a measurement on the physical observable F represented by  $\hat{F}$ . Moreover it is possible to show that a matrix that is Hermitian in a given basis remains Hermitian also in any other representation. Another useful property of Hermitian operators is that their eigenfunctions are orthogonal (after normalization orthonormal) and thus linear independent and they can be used as basis set. Notice that a representation of an Hermitian operator (e.g.  $\hat{H}$ ) in the basis of its eigenfunctions is diagonal (thus in energy domain [H] is diagonal), and the diagonal elements are its eigenvalues (thus the energy eigenvalues in the case of [H]).

### The continuum case

In this section extra-topics that are not strictly required for understanding the next of this thesis about the modeling of molecular devices are reported for completeness, since they were beforehand mentioned in some sections. They will be introduced not rigorously, but with a focus on the meaning.

So far it was implicitly assumed that the basis set  $\{u_m\}_m$  constitutes a discrete set of functions, even if infinite. This is the case of the Fourier series theory. Nevertheless in equation (2.49) the symbol  $\oint$  was used to indicate the general case of a mixed spectrum Hamiltonian operator, meaning that a continuum basis set can also be chosen. Now it is

moment of definitively clarify this point by introducing the correct nomenclature.

It is well known that the maximum number of linearly independent vectors that can be extracted by a vector space V equals its dimensionality (e.g. the 3D space with coordinate axes x, y and z has dimensionality 3 - isomorphous to  $\mathbb{R}^3$ ). The same concept holds also for an Hilbert space W. In particular the Hilbert spaces can have a finite dimensionality (think to eq. (2.76) in which only M basis functions are used to represent the general state  $\psi$ ), or an infinite one (think to eq. (2.75) or (2.82) in which an infinite number of basis functions is used to represent the general state  $\psi$ ). Moreover in the latter case the dimensionality (thus with at least a part that is continuous). To understand better, think that the cardinality (i.e. the number of elements of a set) of the integer numbers sets such as  $\mathbb{N}$  or  $\mathbb{Z}$  is infinite countable, while the one of the real numbers set  $\mathbb{R}$  is infinite uncountable. For the Hilbert spaces the situation is similar. Hilbert spaces with finite dimensionality or with an infinite countable dimensionality are called "separable" Hilbert spaces.

To get the point, let's assume that the chosen basis set is the set of the eigenfunctions of the Hamiltonian operator (that is Hermitian and thus with a complete set of linearly independent eigenfunctions). In the case of quantum confinement (bound states) H has a discrete spectrum, i.e. the discrete eigenvalues  $E_i$  cannot assume each real value but only few discrete values. The corresponding eigenfunctions are thus a countable set of generators functions. More precisely if an infinite height quantum well is considered, the number of bound states is infinite, thus the eigenfunctions are an infinite countable set of functions. In this case a general state  $\psi$  can be represented in the Hamiltonian operator basis  $\{u_m\}_m$ by means of eq. (2.75), or with the Dirac's notation eq. (2.82). Otherwise if a finite height quantum well is considered, the number of bound states is finite, thus the eigenfunctions are finite countable set of functions. In this case a general state  $\psi$  can be represented in the Hamiltonian operator basis  $\{u_m\}_m$  by means of eq. (2.76). Nevertheless in this last case the finite height quantum well admits also a part of the Hamiltonian spectrum that is continuous: indeed for energies above the well height there is no constraint on the energy values, that can be continuous (real). Thus if both the bound and the unbound states of a finite quantum well are chose as basis for an Hilbert space representation, then its dimensionality will be infinite and uncountable, because of the continuum states (with energy eigenvalues that are an infinite range of real numbers).

In the continuum case of infinite uncountable dimensionality of the Hilbert space the previously relations must be reinterpreted as follows. The representation of the general state  $\psi$  as linear combination of the basis vector is no more a Fourier series expansion, but it becomes a Fourier anti-transform (think to the -not formal!- introduction of the Fourier transform as limit case of the Fourier series - see [96], [95]). Assuming that the chosen basis is the one composed by the Hamiltonian operator eigenfunctions (such that the notation is the one already used in section 2.3.5), and considering only the continuum part of  $\hat{H}$  spectrum:

$$\psi(\vec{r};t) = \int dE \ C(E) \ \Psi_E(\vec{r}) \ e^{-\frac{i}{\hbar}Et} = \int dE \ C(E) \ u_E$$

where the basis eigenfunctions are simply called  $u_E = \Psi_E(\vec{r}) e^{-\frac{i}{\hbar}Et}$ . The previous equation

corresponds to a Fourier anti-transform. The coefficients C(E) correspond instead to a Fourier transform w.r.t. to the basis  $u_E$ :

$$C(E) = (u_E, \psi(\vec{r}; t)) = \int dE u_E^* \psi(\vec{r}; t) = \int dE \Psi_E^*(\vec{r}) \ e^{i\frac{i}{\hbar}Et} \psi(\vec{r}; t)$$

Even in this case everything is analogous to what discussed in the previous sections. The main difference is in the normalization condition, that in the continuum case must involve the delta Dirac function instead of the Kronecker delta:

$$\langle n|m\rangle = \delta(n-m)$$

where  $\delta(n-m)$  indicates a delta Dirac. A delta Dirac is indeed a generalization of the Kronecker delta for the case of continuum systems, and indeed it appears also in the normalization condition of unbounded wave-functions (see section 2.3.7).

# 2.5 Few Other useful topics in quantum mechanics

The purpose of this section is to briefly summarize other important results of quantum mechanics. These are "extra" topics in the sense that they are not necessary to understand the rest of this work. Nevertheless they are important achievements and in my opinion a brief mention is due. A full treatment is present e.g. in [87].

### Correspondence principle

Bohr in 1923 stated the correspondence principle: a correct quantum theory must "contain" also the well known classical laws, in the sense that classical laws must be recovered from quantum predictions each time they are applied to a macroscopic (classical) system.

### Ehrenfest's theorem

Ehrenfest's theorem states that the time evolution of expected (average) values of physical observables, follow the same laws of the corresponding classical physics quantities.

The main consequence of this theorem is that in solid state physics, e.g. in conventional electronic devices, the classical physics can be used, if the physical quantities are intended to be average values. This is the main theoretical foundation for using classical physics in modeling conventional electronic devices, in which indeed average quantities (such as the mobility, the average velocity, etc...) are used. This allows to use the drift-diffusion set of equations for modeling electronic devices.

Notice that there is no a theoretical foundation for the widely used quantum corrections of such semi-classical models. Indeed there is no reason why a "bit" of quantum mechanics should be used in a semi-classical model (intended in the sense of Ehrenfest's theorem). Instead a purely quantum approach has all the reasons to be used in such devices, since indeed they are devices in which quantum mechanical effects are non-negligible and the classical approximation of physics (see above the Bohr's correspondence principle) does not hold. The non-equilibrium Green's function formalism, introduced later in this work, is a purely quantum mechanical approach for modeling transport in nano-electronic devices, thus it should be used.

### Coefficient vector physical meaning

Notice that for normalized wave-functions expressed in an orthonormal basis, the following relation holds (it is called the Parseval's relation):

$$\begin{split} \langle \psi | \psi \rangle &= \int \psi^* \psi d\vec{r} = \int |\psi|^2 d\vec{r} = 1 = \int \left( \sum_m c_m \, |m\rangle \right)^* \sum_m c_m \, |m\rangle \, d\vec{r} = \\ &= \int \left( \sum_m c_m^* \, \langle m | \right) \sum_m c_m \, |m\rangle \, d\vec{r} = \sum_m c_m^* c_m \int \, \langle m | m\rangle \, d\vec{r} = \\ &= \sum_m |c_m|^2 = 1 \quad (if \ normalized). \end{split}$$

The coefficients  $c_m$  are the projections of the wave-function  $\psi$  on the basis functions  $u_m$ :

$$c_m = \langle m | \psi_1 \rangle = \int u_m^*(\vec{r}) \psi_1(\vec{r}) d\vec{r}$$

if they are normalized such that the above summation of their squared moduli is 1, then their moduli squared represent exactly the percentage of the basis function  $u_m$  that is present in  $\psi$ .

This concept is important in the eigenvalues problems, because it provides a direct physical interpretation of the eigenvalues. Let's consider the generic eigenvalue equation:

$$\widehat{F}\psi_n = f_n\psi_n$$

where  $\psi_n$  are the eigenfunctions and  $f_n$  the eigenvalues. It was already mentioned (see section 2.3.6) that because of the way this general equation is derived, the physical meaning is that the eigenvalues  $f_n$  are the only possible results of a measurement on the physical observable F represented by the operator  $\hat{F}$ . If the system is in the state  $\psi_n$  then the result of the measurement will be  $f_n$ . Moreover since F is supposed to be a real physical observable for the system, then  $\hat{F}$  will be Hermitian, and thus the eigenfunctions  $\psi_n$  are linearly independent and orthogonal and can be used as basis set (see section 2.4.3). In this case, supposing also to have suitably normalized the  $\psi_n$ , one gets:

$$\psi = \sum_{n} c_n \psi_n \quad , \quad c_n = \langle \psi_n | \psi \rangle = \int \psi_n^* \psi d\vec{r} = (\psi_n, \psi)$$

At this point if the system is in the state  $\psi$ , that is a linear combination of the eigenstates  $\psi_n$ , then a measurement process will make the wave-function collapse into one of the eigenstates  $\psi_n$  and the corresponding obtained value will be the corresponding eigenvalue  $f_n$ . Let's now consider the average value of the observable F, that accordingly with eq.

(2.31) is (the Dirac's notation is also pointed out here, together with the previously adopted one):

$$\langle F \rangle = \langle \psi | \hat{F} | \psi \rangle = \int \psi^* \hat{F} \psi d\vec{r} = \left(\psi, \hat{F}\psi\right) = \left(\psi, \hat{F}\sum_n c_n \psi_n\right) = \left(\psi, \sum_n c_n \hat{F}\psi_n\right) =$$
$$= \left(\psi, \sum_n c_n f_n \psi_n\right) = \int \psi^* \sum_n c_n f_n \psi_n d\vec{r} = \sum_n c_n f_n \int \psi^* \psi_n d\vec{r} =$$
$$= \sum_n f_n c_n \left(\psi, \psi_n\right) = \sum_n f_n c_n c_n^* = \sum_n f_n |c_n|^2$$

where the following relations are used:

$$\widehat{F}\psi_n = f_n\psi_n \quad and \quad c_n^* = \left(\int \psi_n^*\psi d\vec{r}\right)^* = \int \psi_n^*\psi d\vec{r} = (\psi, \psi_n)$$

In conclusion:

$$\langle F \rangle = \sum_{n} f_{n} |c_{n}|^{2}$$

from which it is clear that the quantity  $|c_n|^2$  assumes exactly the meaning of probability of finding the eigenvalue  $f_n$  when a measurement is performed on F (if the coefficient are normalized to 1 as indicated by the Parseval's relation reported above).

In the case of a continuum spectrum it is possible to show an analogous relation, that has an analogous meaning (where c(f) is the Fourier transform):

$$\langle F \rangle = \int f |c(f)|^2 df$$

### Simultaneous measurements of physical observables

It was highlighted many times that in the moment in which a measurement is performed on a system, because of the measurement process, the system state changes from the generic state  $\psi$  to one of its possible eigenstates  $\psi_n$  (collapse of the wave-function) such that the result of the measurement is one of the possible eigenvalues  $f_n$ . The only case in which the system does not change state, when a measurement is performed on it, is when it is already (before the measurement) in one of its eigenstates  $\psi_n$  such that the result of the measurement is  $f_n$ . This is an intrinsic property of quantum systems.

Now a question may be when it is possible to perform simultaneous measurements on two different physical quantities F and G. The answer is that a simultaneous measurement of two distinct physical quantities F and G is possible if and only if the two operators  $\hat{F}$  and  $\hat{G}$  admit common eigenstates. Indeed if the measurement process cause the wave-function collapse, the state of the system must collapse in an eigenstate of both  $\hat{F}$  and  $\hat{G}$  such that it is possible to get a result for the measurement (that will be  $f_n$  and  $g_n$ ). It is possible to provide a rigorous demonstration for this statement, and to represent it by means of mathematical relations. Notice that this is also the origin of the Heisenberg's uncertainty principle. Indeed as mention in section 2.2 it is possible to provide a demonstration of the uncertainty principle (in spite of its name). The formal demonstration of the Heisenberg's indetermination principle leads to the following inequality:

$$\Delta r_i \Delta p_i \ge \frac{\hbar}{2}$$

where  $r_i$  and  $p_i$  are the *i*-th component of the position vector  $\vec{r}$  and of the momentum vector  $\vec{p}$  respectively (with i = x, y, z). In the 1D case:

$$\Delta x \Delta p \ge \frac{\hbar}{2}$$

Notice that  $\Delta f$  indicates the standard deviation of the quantity f, as defined in eq. (2.26). The uncertainty principle holds for each pair of canonically conjugate variables (linked by a time derivative) f and g:

$$\Delta f \Delta g \ge \frac{\hbar}{2}$$

And moreover it is possible to demonstrate the following energy-time uncertainty relation (that holds formally with the physical meaning introduced in section 2.2):

$$\Delta E \Delta t \ge \frac{\hbar}{2}$$

### Bohr's complementary principle

In classical physics, for a full description of a physical system with n degrees of freedom (e.g. in 3D, n = 3) it is necessary the simultaneous knowledge of n pairs of canonically conjugated quantities (like the position  $\vec{r} = (r_x, r_y, r_z)$  and the momentum  $\vec{p} = (p_x, p_y, p_z)$  such that the concept of trajectory is defined). Nevertheless because of the Heisenberg's uncertainty principle this is not possible in quantum mechanics. It follows that the full characterization of a physical system is determined by a complete set of simultaneously measurable quantities. The maximum number of simultaneously measurable quantities in a system with n degrees of freedom is n (think again to the Heisenberg's uncertainty principle). This is essentially the statement of the Bohr's complementary principle, that holds true for all the physical quantities that have a classical analogous. It can be stated as: the complete characterization of a quantum system with n degrees of freedom is possible by means of the choice of a complete set of at most n compatible physical quantities (i.e. for which the simultaneous measurement is possible). This characterization is not unique, but more than one complete set can be chosen, and the different choices correspond to equivalent descriptions of the same system, that are thus complementary.

Notice that when quantization occurs a given physical quantity can be expressed in function of an integer number (think for example to the energy in a quantum well), thus choosing n quantities corresponds in choosing n "quantum numbers" (i.e. integers) by means of which the state of the system can be characterized. Indeed the wave-function solution of the Schrödinger's equation will depend on n integer numbers, that are related to different physical quantities (e.g. the energy, the angular momentum, and so on...). This is the origin of the quantum numbers introduced in the basic courses of chemistry. Finally notice that in a quantum system, beside to classical degrees of freedom for which hold the previous discussion, there can be also purely quantum quantities (such as the spin) that have no classical analogous. The n quantities and the Bohr's complementary principle are referred to physical quantities that have classical analogous only. The knowledge on such purely quantum quantities can be considered separately and joined to the others. For example in the 3D space there are n = 3 degrees of freedom. From the Bohr's complementary principle only n = 3 physical quantities, that have classical analogous, can be used in quantum mechanics to provide its characterization. The quantum systems description in the 3D space is usually provided in terms of the quantum numbers n, l, m and s. The (principal) quantum number n is associated to the energy. As discussed in section 2.3.6 this is the most important physical quantity that provides information also about the history of the system. The angular momentum quantum number l is associated to the magnitude of the angular momentum (that is quantized and thus characterized by means of the integer l). The magnetic quantum number m is associated to the third component of the angular momentum (i.e. to angular momentum orientation, that is quantized and thus characterized by m). These three quantities have classical analogous and thus they provide a complete set (their simultaneous measurement is possible accordingly with Heisenberg's uncertainty principle). In addition the quantum number of spin s that provide information concerning the spin can be also used in the system description. Indeed it is associated to a quantity (the spin) that has no classical analogous. Other choices are in principle possible, in that case a complementary and equivalent descriptions of the system would be provided.

#### Systems of identical particles

In quantum mechanics holds the so called "principle of indistinguishability". In classical mechanics it is always possible to distinguish between two particles that are identical. Indeed it is possible to distinguish them thanks to different space localization or thanks to the concept of trajectory. Then, by means of the knowledge on their trajectories it is possible to understand always which of the two particles is. Instead in quantum mechanics this is no more true, because of the Heisenberg's uncertainty principle that makes no more possible talking of trajectories. For example, if two hydrogen atoms are considered, it is possible to distinguish between the two electrons in the two atoms only when they are at large distance, because of the spatial localization of such electrons. If instead the two hydrogen atoms are close (think e.g. to the hydrogen molecule  $H_2$ ) then the two electrons was initially belonging to what atom.

In a system of N identical particles (it can be also a molecule with N electrons) if two particles are exchanged a new wave-function is in principle obtained. For example in a molecule with N electrons the steady state Schrödinger's equation can be solved for a given configuration, and the eigenstate  $\psi_{\alpha}$  is obtained. Then, for example, two identical particles are exchanged, that could be: an electron 1 that is in a given quantum state described by a given set of quantum numbers  $\{n_1, l_1, m_1, s_1\}$  is exchanged with an electron 2 described by  $\{n_2, l_2, m_2, s_2\}$ ; and thus after the exchange the electron 1 is in the state described by  $\{n_2, l_2, m_2, s_2\}$  and the electron 2 is in the state described by  $\{n_1, l_1, m_1, s_1\}$ . Then, the steady state Schrödinger's equation can be solved again, and the wave-function

 $\psi_{\beta}$  is obtained. Both  $\psi_{\alpha}$  and  $\psi_{\beta}$  are solution of the steady state Schrödinger's equation for that system, and it turns out that the eigenvalues  $E_{\alpha}$  and  $E_{\beta}$  associated to the two wave-functions are equal:  $E_{\alpha} = E_{\beta}$ , that means that  $\psi_{\alpha}$  and  $\psi_{\beta}$  are degenerate (exchange degeneration). Thus in principle in a system of N identical particles there is a degeneracy equal to N! (indeed the same procedure can be iterated for each possible permutation of the states - i.e. each possible exchange of electron states). Nevertheless, because of the indistinguishability principle, since it is not possible to distinguish between the state  $\psi_{\alpha}$  and the state  $\psi_{\beta}$  (since the two exchanged electrons are indistinguishable), it means that the two states must be one the multiple of the other, such that they differ only for a multiplicative constant K (parallel vectors in an Hilbert space) and they are essentially the same state (see also superposition principle - section 2.3.2). Thus:  $\psi_{\beta} = K \psi_{\alpha}$ . If the two electrons are again exchanged the same reasoning leads to:  $\psi_{\beta} = K \psi_{\alpha} = K^2 \psi_{\beta}$ . From which must be  $K^2 = 1$  and thus only two cases are possible:  $K = \pm 1$ . The first case K = +1 leads to symmetric wave-functions, the second one K = -1 to anti-symmetric wave-functions. This means that:  $\psi_{\beta} = \pm \psi_{\alpha}$  and instead of getting an exchange degeneracy of N! it is obtained an exchange degeneracy equal to 2. Moreover it is an experimental evidence that for bosons (i.e. integer spin particles - e.g. photons) the only possibility is the symmetric one, with K = +1, while for fermions (i.e. fractionary spin particles - e.g. electrons) the only possibility is the anti-symmetric one, with K = -1. It means that if two (identical) bosons are exchanged of state then the same wave-function is obtained, while if two (identical) fermions are exchanged of state the anti-symmetric wave-function is obtained.

This is important because it is intimately linked with the Pauli exclusion principle. As known from basic chemistry courses, it states that in a given quantum system it is not possible to have two fermions (e.g. electrons) in the same quantum state (i.e. with all the quantum numbers -n, l, m, s- that are equal). Indeed it is possible to show (see e.g. [87]) that this would imply that their wave-function must be null (i.e. no state). And this follows directly from the requirement of having an anti-symmetric wave-function when an exchange of state is performed. Instead notice that it is possible to have two bosons in the same quantum state.

### Causality principle and time evolution operator

Also in quantum mechanics the causality principle must hold. In particular it states that once the initial state of the system is known, the physical laws that govern its time evolution must allow to predict the system state in each time instant. This is possible thanks to the direct application of the Scrhödinger's equation. Indeed it was alredy mentioned that the (time-dependent) Schrödinger's equation is the fundamental equation in quantum mechanics that allows to know the dynamics of the system, i.e. its time evolution (see sections 2.3 and 2.3.5). Such time evolution is then determined by the Hamiltonian operator of the system, that indeed appears in the Schrödinger's equation. Starting from the time-dependent Schrödinger's equation (2.17) it is possible to recover an expression for a quantum mechanical operator that is able to provide the time evolution of the state of the system. Such an operator is called "time evolution operator" and it is defined such that:

$$\psi(\vec{r};t) = \hat{S}(t,t_0)\psi(\vec{r};t_0)$$
(2.87)

The time evolution operator  $\hat{S}(t, t_0)$  is thus the operator that, when applied to an initial state  $\psi(\vec{r}; t_0)$  supposed known at the time instant  $t_0$ , is able to provide the state of the quantum system at the instant t (the final time instant). This operator is implicitly defined in the Schrödinger's equation. It is possible to show that [87]:

$$\widehat{S}(t,t_0) = e^{-\frac{i}{\hbar}H(t-t_0)}$$
(2.88)

Its main properties are:

$$\begin{bmatrix} \widehat{S}(t,t_0) \end{bmatrix}^{-1} = \begin{bmatrix} \widehat{S}(t,t_0) \end{bmatrix}^{\dagger} \quad i.e. \ it \ is \ unitary.$$
  
and :  $\widehat{S}(t_0,t_0) = 1$ 

### Different pictures in quantum mechanics

In section 2.4 it was derived a matrix representation for quantum mechanical operators. This representation is at the basis of the so called Heisenberg's matrix mechanics formalism (even if it was developed also thanks to many other scientists among which Paul Dirac). The purpose here is to briefly highlight the differences between the Schrödinger's and the Heisenberg's approaches.

In the Schrödinger's formulation (also called wave mechanics) the focus is on the wavefunction of a quantum system, and the time evolution (the dynamic evolution) of the system is expressed in terms of the wave-function itself. The state of a system is represented by means of the wave-function, and it evolves in time following the law of the Schrödinger's equation, that as mentioned in the previous section provides the time evolution of the state of the system. The mathematical formalism is the one of differential equations and indeed operators are differential (linear) operators. Notice that here the states depend on time and indeed they evolve in time, while the operators are fixed in time and they do not change.

Vice versa in the Heisenberg's approach the fundamental role is played directly by the observable quantities (the physical observables), that are represented by means of operators in matrix form. The matrix elements of the operators are quantum mechanical representations of the physical observables. In this approach the dynamics, i.e. the time evolution, is related to the time evolution of operators, while the states are unchanged in time. Thus, as time goes by, the state does not evolve in time, but the system simply changes its state, under the action of time-dependent operators that make the system passing through different states. The time evolution of the operators is derived from the time evolution laws of the physical quantities they represent. The mathematical formalism is essentially the one of linear algebra, thus algebraic (matrix) equations are considered instead of differential ones.

The two formalisms were derived in different ways at almost the same time. Even if slightly different, they lead to same predictions and they have essentially the same content (as already noticed by Schrödinger in 1926). In the following a brief deeper discussion is provided in order clarify the link between the two approaches.

Assuming that exists a linear (Hilbert) space W, that includes all the possible states of all the possible physical systems, then it will be always possible to represent the generic state  $\psi(\vec{r};t)$  as a vector  $|\psi\rangle$  in this linear space. The Dirac's notation introduced in section 2.4.3 is used to indicate that vector. The vector  $|\psi\rangle$  is thus the well known wave-function or state of a given physical system. The time evolution of a system can be evaluated in different ways in quantum mechanics. As already pointed out the two extremes are the Schrödinger's picture and the Heisenberg's one. The point now is how to switch between these two pictures.

In the Schrödinger's picture the states  $|\psi\rangle$  are seen as elements in the space W that evolve or change with time:  $|\psi\rangle = |\psi(t)\rangle \in W$ . The vector  $|\psi\rangle$  will thus change in time:  $|\psi(t)\rangle$ . Instead all the operators that do not involve an explicit time dependence (e.g. if they do not have a time derive like it happens with  $\hat{H}$ ), and they can be assumed to be unchanged as time goes by. The time evolution of the state will be given by the Schrödinger's equation:

$$i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle=\hat{H}\left|\psi(t)\right\rangle$$

or alternatively, as mentioned in the previous subsection, by the application of the time evolution operator:

$$|\psi(t)\rangle = \widehat{S}(t,t_0) |\psi(t_0)\rangle \quad , \quad \widehat{S}(t,t_0) = e^{-\frac{i}{\hbar}\widehat{H}(t-t_0)}$$

Instead in the Heisenberg's picture the states  $|\psi\rangle$  are time independent and thus unchanged in time, while operators are time dependent. The space W is seen as a static space, whose vectors  $|\psi\rangle$  do not change in time. While the operators evolve in time, under the laws that will be presented now. The states (that do not evolve in time) and the operators (that evolve in time) in the Heisenberg's picture are defined as (subscript H is used to indicate that they are in the Heisenberg's picture):

$$\begin{aligned} |\psi_H(t)\rangle &= \widehat{S} |\psi_H(t_0)\rangle = e^{-\frac{i}{\hbar}\widehat{H}(t-t_0)} |\psi_H(t_0)\rangle = |\psi_H(t_0)\rangle \quad constant \ in \ time \\ \widehat{F}_H &= \widehat{F}_H(t) = \widehat{S^{\dagger}}\widehat{F}_S\widehat{S} = e^{+\frac{i}{\hbar}\widehat{H}(t-t_0)}\widehat{F}_S e^{-\frac{i}{\hbar}\widehat{H}(t-t_0)} \quad changes \ in \ time. \end{aligned}$$

where  $\hat{F}_S$  indicates that the operator  $\hat{F}$  is represented like done so far in this work (section 2.4), i.e. it is the operator in the Schrödinger's picture.

The last two relations, and especially the one that defines the operators  $\hat{F}_H$  in the Heisenberg's picture, constitute the link between the two picture.

Example 2.6: Let's verify the correspondence between the two pictures, and thus that the two pictures are equivalent. In the Schrödinger's picture the operators  $\hat{F}_S$  are time independent. Nevertheless they matrix elements  $F_{mn}$  (in their matrix representation) are

time dependent:  $F_{mn}(t)$ . This because the matrix elements are scalar products between states, and the states depend on time:  $u_m(t)$ . Indeed:

$$F_{mn}(t_0) = \langle u_m(t_0) | \hat{F}_S | u_n(t_0) \rangle \quad \neq \quad F_{mn}(t) = \langle u_m(t) | \hat{F}_S | u_n(t) \rangle$$

In particular since the time evolution of states in the Schrödinger's picture can be evaluated by applying the time evolution operator:

$$|u_m(t)\rangle = \widehat{S} |u_m(t_0)\rangle = e^{-\frac{i}{\hbar}\widehat{H}(t-t_0)} |u_m(t_0)\rangle$$

Then the matrix element at time instant t is:

$$\begin{aligned} F_{mn}(t) &= \langle u_m(t) | \widehat{F}_S | u_n(t) \rangle = \left( u_m(t), \widehat{F}_S u_n(t) \right) = \left( \widehat{S} u_m(t_0), \widehat{F}_S \widehat{S} u_n(t_0) \right) \\ &= \int \left( \widehat{S} u_m(t_0) \right)^* \widehat{F}_S \left( \widehat{S} u_n(t_0) \right) d\vec{r} = \int \widehat{S}^{\dagger} u_m^*(t_0) \widehat{F}_S \widehat{S} u_n(t_0) d\vec{r} = \\ &= \int \widehat{S}^{\dagger} \left( u_m(t_0) \right)^* \widehat{F}_S \widehat{S} \left( u_n(t_0) \right) d\vec{r} \end{aligned}$$

Since the operator  $\widehat{F}_S \widehat{S}$  is acting on  $u_n(t_0)$ , that in Dirac notation is the ket  $|u_n(t_0)\rangle$ , and the operator  $\widehat{S}^{\dagger} = e^{+\frac{i}{\hbar}\widehat{H}(t-t_0)}$  is acting on  $u_m^*(t_0)$  that in Dirac notation is the bra  $\langle u_m(t_0)|$ , and noticing that the application of an operator on a bra is indicated with:  $\langle u_m| \widehat{F}$ , that in this case implies  $\widehat{S}^{\dagger} (u_m(t_0))^* = \langle u_m(t_0)| \widehat{S}^{\dagger}$ , the last relation can be rewritten as:

$$F_{mn}(t) = \langle u_m(t) | \hat{F}_S | u_n(t) \rangle = \int \hat{S}^{\dagger} u_m^*(t_0) \hat{F}_S \hat{S} u_n(t_0) d\vec{r} = \langle u_m(t_0) | \hat{S}^{\dagger} \hat{F}_S \hat{S} | u_n(t_0) \rangle$$

Since in the Heisenberg's picture the states are time independent:  $|u_{mH}(t)\rangle = |u_{mH}(t_0)\rangle$ (where subscript *H* indicates that this holds in the Heisenberg's picture), the correspondence between Schrödinger's picture operators and Heisenberg's picture operators is recovered:

$$\begin{aligned} F_{mn}(t) &= \langle u_m(t) | \hat{F}_S | u_n(t) \rangle = \langle u_m(t_0) | \hat{S}^{\dagger} \hat{F}_S \hat{S} | u_n(t_0) \rangle = \langle u_{mH}(t) | \hat{S}^{\dagger} \hat{F}_S \hat{S} | u_{nH}(t) \rangle \\ &= \langle u_{mH}(t) | \hat{F}_H | u_{nH}(t) \rangle \qquad , \qquad \hat{F}_H = \hat{S}^{\dagger} \hat{F}_S \hat{S} \end{aligned}$$

that correspond to what stated previously. Notice that the matrix elements  $F_{mn}(t)$  in the two pictures are the same, indeed they are intimately linked with the expected values of physical observables, and thus they must be unchanged (since directly linked to measurements). Moreover notice that the states in the Schrödinger's picture in this example were simply indicated with  $u_m$  with no subscript.  $\Box$ 

In addition to these two pictures a third one is also widely used in quantum mechanics. It is the so called "interaction picture". In this representation both the states and the operators are time dependent. It is particularly useful if the Hamiltonian operator (that appears also in the time evolution operator) can be written as the sum of an interacting part that accounts for the interactions among particles and a non-interacting one (whose eigenvalues and eigenfunctions can be calculated exactly). It is possible to show that the time evolution of operators and states in the interaction picture depends only on the non-interacting Hamiltonian, and thus it is simple to evaluate. This picture is often used in the second quantization formalism (see next section), that constitutes the background in which the non-equilibrium Green's function formalism finds place in its traditional formal derivation. In this work I will follow the approach of [89] and [39] in which such a formalism is introduced without the need of the second quantization formalism, and thus is made accessible also to electronic engineers in a fast way without too much effort.

### A brief mention about the second quantization

So far the presented quantum mechanical theory was the so called "first quantization" one. As seen, in this theory the concept of wave-particle duality and wave field allow to associated to each microscopic quantity both undulatory and particle behaviors. An important feature is that the forces acting on systems are still considered classical forces. Indeed the potential energy by means of which it is represented the interactions of the quantum systems under study and the rest of the world, can be still derived in a classical manner (e.g. it can be an electrostatic Coulomb potential, etc...). The force field is thus said to be non-quantized. The quantized quantities are the results of the double behavior of matter particles, to which a wave field is associated. This theory succeeded in explaining a wide range of phenomena, and in particular all the non-relativistic quantum mechanics).

Nevertheless this theory cannot still definitively explain some issues, especially related to the interaction between the electromagnetic radiation and matter. In order to get a quantum theory able to precisely describe and predict also such phenomena the so called "second quantization" and the so called "quantum field theory" were introduced.

As mentioned, in the first quantization the force fields are still classical, while the physical observables are associated to operators. Instead in the second quantization the force fields, and thus all the interactions between particles, are quantized. In order to do that the force fields are associated to the so called "field operators", in a similar way of what done in the first quantization with the physical observables. These field operators are able to create or annihilate a particle at a given time instant and in a given point, because of the action of the force field. The field operators are defined in an Hilbert space that is the so called the Fock's space. It was mentioned previously (see the subsection on systems of identical particles) that by exchanging two identical particles in a quantum system a new state is obtained, whose wave-function must be symmetric (bosons) or anti-symmetric (fermions) w.r.t. to the initial one. Usually these properties must be enforced on the wave-functions to get proper results. The Fock's idea at the basis of his proposed linear space, is to "embed" these symmetry properties directly in the way in which the states are represented in a given Hilbert space: namely the Fock's space. Therefore in Fock's space the mathematical operations of creation and annihilation are suitably defined, such that the Pauli exclusion principle and the correct symmetry on wave-functions is always guaranteed automatically whenever a particle is added (created) to the system or eliminated (annihilated) from it. This is the starting point for the so called relativistic quantum mechanics, that is the quantum field theory. In quantum field theory the so called canonical quantization (i.e. second quantization or quantization of

force fields) is used to build up the field operators in the Fock's space. Quantum field theory (QFT) is a relativistic theory that combines classical field theory, special relativity and quantum mechanics (but not general relativity). It is a theory that is able to definitely explain the interaction between electromagnetic radiation and matter (this specific branch of quantum field theory is called quantum electrodynamics), and many other phenomena. All the interactions (all kind of interactions, e.g. electromagnetic, gravitational, nuclear etc..) are quantized in QFT. For example the electromagnetic field is rethought in terms of photons (i.e. quanta of electromagnetic radiation), the gravitational field in terms of gravitons, and so on...

Notice that the existence of the spin comes out naturally in QFT by solving the relativistic Dirac's equation (the fundamental equation of QFT - for importance analogous to the Schrödinger's one in non-relativistic quantum mechanics). Instead in non-relativistic quantum mechanics (the one considered in this chapter and in this entire work) it is introduced from experimental considerations (usually presenting the Stern-Gerlach famous experiments) and with the phenomenological Pauli's correction of the Schrödinger's equation. The second quantization formalism, and especially the Fock's space and field operators, are of extreme importance also in the so called "quantum many-body" systems analysis and "quantum many-body perturbation theory". These two branches of quantum mechanics focus on systems constituted by many body, like it could also a molecule for example. Indeed a molecule with tens of atoms can also contains hundreds of electrons, thus making clear that it is a many-body system. The situation is even worse in solid state physics in which even a nano-scale crystalline device can include hundreds or thousands of atoms.

# Chapter 3 Molecular electronic structure

The first step in the study of the transport in whatever kind of device (also conventional 3D electronic devices) is to understand what are the possible electronic states within the conducting channel. Indeed the electronic states that will take part to the conduction (essential to understand the number of electrons involved in conduction and thus the electrical current) will be a subset of the allowed electronic states within the channel. In molecular electronic sensors, and in general in molecular electronic devices, the active part of the device is a single molecule (or at most a small packet of parallel molecules), and the electronic states that are permitted for a given molecular channel can be found by solving the steady state Schrödinger's equation  $H\psi = E\psi$ . They corresponds indeed to stable states within the molecule, that are stationary states. Consequently the first step in studying the conduction in a molecular device is to derive and handle the molecular Hamiltonian operator H. Even if molecules are small, they are already enough complicated, and often with enough atoms composing them, that this task can be very hard and challenging. This chapter focuses on how to deal with and to solve the steady state Schrödinger's equation for molecules, starting from the molecular Hamiltonian operator. Various methods for achieving the task of calculating the electronic structure of a molecular channel are briefly presented and reviewed. The purpose is to provide the needed information to be used in setting up atomistic simulations like the ones presented and discussed in the part II of this work. A good reference on these topics (also for beginners) can be for example [98] - many other references are present in literature.

In section 3.1 the Born-Oppenheimer approximation is addressed. It is the starting point for all the methods discussed in the rest of this chapter and it will be always assumed. Then in section 3.2 the general mean field method and its implications are discussed. This is the fundamental approximation around which all the other presented methods revolve. In appendix B it is further discussed with simple examples and application formulae to give the physical insights and sensibility to understand the approximations and hypotheses also used in the other methods. In section 3.3 the Hartree and Hartree-Fock methods are addressed. They assume the mean field approximation introduced in section 3.2. Next in section 3.4 the most used classes of methods for the evaluation of the electronic structure are presented. They all can be classified and understood starting from the Hartree-Fock method. Moreover the force field methods and the post-Hartree-Fock methods are briefly treated. Finally in section 3.5 and 3.6 two of the most widely spread methods are discussed, namely the Density Functional Theory (DFT) and the Extended Hückel Theory (EHT). They are also the only two methods employed in the practical part (part II) of this work. The chapter ends with a discussion of the intermolecular interactions and the methods for simulating them within the DFT environment in section 3.7.

# 3.1 Molecular Hamiltonian and the Born - Oppenheimer approximation

In section 2.3.4 it was reviewed that the Hamiltonian operator is the quantum mechanical operator associated to the total energy of the system, and in general it is given by the expression of equation (2.44), reported here for clarity:

$$\hat{H} = \hat{T} + \hat{U} = -\frac{\hbar^2}{2m}\Delta + U(\vec{r})$$

A molecule is a set of atom nuclei around which electrons are displaced, some of which (usually the so called valence electrons) are involved in chemical bonds between the atoms forming the molecule. Consequently the explicit expression of a molecular Hamiltonian corresponds to a many-body problem. Indeed even the simple benzene ring ( $C_6H_6$ ) consists of six carbon atoms (with atomic number  $Z_C = 6$ ) and six hydrogen atoms (atomic number  $Z_H = 1$ ) meaning that there are 42 electrons. The number of electrons within a molecule increase rapidly with the complexity of the molecule itself, reaching e.g. the number of 360 electrons for the  $C_{60}$  fullerene molecule. It is intuitive thinking that some approximations must be used to deal with the molecular Hamiltonian and the solution of the Schrödinger's equation for a molecular channel.

It is possible to write the general expression of a molecular Hamiltonian considering that the kinetic energy operator can be written as the sum of the kinetic energy operators of the  $N_e$  electrons and the  $N_n$  nuclei ( $\Delta$  is linear,  $\hat{T}$  is a linear operator and superposition of effects can be exploited):

$$\widehat{T} = \widehat{T}_e + \widehat{T}_n = -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \Delta_{r_i} - \sum_{j=1}^{N_n} \frac{\hbar^2}{2m_n} \Delta_{R_j}$$

where  $\Delta_{r_i} = \left(\frac{\partial^2}{\partial x_i^2}, \frac{\partial^2}{\partial y_i^2}, \frac{\partial^2}{\partial z_i^2}\right)$ ,  $\Delta_{R_j} = \left(\frac{\partial^2}{\partial x_j^2}, \frac{\partial^2}{\partial y_j^2}, \frac{\partial^2}{\partial z_j^2}\right)$  and where the coordinate vectors of electrons and nuclei respectively  $\vec{r_i} = (x_i, y_i, z_i)$  and  $\vec{R_j} = (x_j, y_j, z_j)$ .

Instead the potential energy operator (equal to the potential energy in real space) is constituted by three terms, that represent the three principal interactions among electrons and atomic nuclei:

- $U_{nn}$ : contribution due to Coulombic nuclei-nuclei repulsion
- $U_{ne}$ : contribution due to Coulombic electrons-nuclei attraction

•  $U_{ee}$ : contribution due to Coulombic electron-electron repulsion

Thus the general expression for the molecular Hamiltonian operator assumes the following form:

$$\widehat{H} = -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \Delta_{r_i} - \sum_{j=1}^{N_n} \frac{\hbar^2}{2m_N} \Delta_{R_j} + U_{nn} + U_{ne} + U_{ee}$$

that becomes rapidly unmanageable as the number of atoms in the molecule increases. The steady state Schrödinger's equation becomes very hard to be solved also with the help of today's computers, if no approximations are considered.

In the so called Born-Oppenheimer approximation [99] the kinetic and potential energy contributions of the nuclei are neglected. Indeed, since the nuclei are several tens of thousands times heavier than electrons, their velocities are a much less than those of electrons, and thus the electrons can respond quickly to variations in the nuclei configuration, maintaining the system state essentially unaltered. Consequently the nuclei are approximated as fixed in the reference coordinate system, that means that their kinetic energy (and kinetic energy operator  $\hat{T}_n$ ) is null. Moreover also the potential energy contribution  $U_{nn}$  related to nuclei-nuclei repulsion is neglected: indeed since they are fixed, they are supposed to be unaffected by repulsive forces among them, that are neglected. Therefore within the Born-Oppenheimer approximation, for a system with  $N_e$  electrons and  $N_n$  nuclei, the electronic Hamiltonian operator becomes:

$$\hat{H} = \hat{T}_{e} + U_{ne} \left( \vec{r_{i}}, \vec{R_{j}} \right) + U_{ee} \left( \vec{r_{i}}, \vec{r_{k}} \right) =$$

$$= -\sum_{i=1}^{N_{e}} \frac{\hbar^{2}}{2m_{e}} \Delta_{r_{i}} - \sum_{j=1}^{N_{n}} \sum_{i=1}^{N_{e}} \frac{Z_{j}q^{2}}{4\pi\varepsilon_{0}} \left| \vec{r_{i}} - \vec{R_{j}} \right| + \sum_{1 \leq i,k \leq N_{e}} \frac{q^{2}}{4\pi\varepsilon_{0}} \frac{q^{2}}{|\vec{r_{i}} - \vec{r_{k}}|}$$
(3.1)

where q is the elementary charge, -q is the electron charge,  $\varepsilon_0$  is the vacuum permittivity,  $Z_j$  is the *j*-th nucleus atomic number (equal to the number of protons of charge +q in the *j*-th atom). The previous expression is often called "many-body Hamiltonian", and it is often expressed in atomic units as [100]:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_{r_i}^2 - \sum_{j=1}^{N_e} \sum_{i=1}^{N_e} \frac{Z_j}{|\vec{r_i} - \vec{R_j}|} + \sum_{1 \le i,k \le N_e} \frac{1}{|\vec{r_i} - \vec{r_k}|}$$
(3.2)

Within this many-body framework the steady state many-body Schrödinger's equation assumes the following expression:

$$\hat{H}\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_{Ne}) = E\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_{N_e})$$
(3.3)

where  $\psi(r_1, r_2, ..., r_{Ne})$  is the wave-function of the many-body system of  $N_e$  electrons composing the molecule, i.e. it is a steady state for the entire molecule (in other words a molecular orbital). As mentioned at the beginning of this section its exact solution is an impossible task for systems having more than a few electrons, even within the Born-Oppenheimer approximation. Indeed as  $N_e$  increases, the number of degrees of freedom in the many-body Schrödinger's equation, after it is discretized (e.g. with a finite difference method or another numerical method), increases exponentially making the problem computationally infeasible even on the most powerful computers available nowadays. Just to give an idea of the order of magnitude of the problem, if  $r_i$  is discretized with an  $k \times k \times k$  grid (in the Fourier domain, remembering that  $\vec{r} \leftrightarrow \vec{k}$ ), the dimension  $N_H$  of H is  $k^{3N_e}$ , that means that for example with k = 32 and  $N_e = 5$ ,  $N_H$  is greater than  $3.5 \times 10^{22}$  [101].

Consequently several methods have been devised to find accurate approximated solutions. The choice of the approximated method to use, is a matter of suitability with the system under analysis and of numerical accuracy, and it will further discussed in this and successive chapters of the present work.

A final remark on the term "electronic structure" used in the introduction of this chapter: accordingly with [102] the electronic structure is the state of motion of electrons in an electrostatic field created by stationary nuclei. This corresponds in finding the eigenfunctions  $\{\psi\}_i$  and the eigenvalues  $\{E\}_i$  for a given structure. Notice that the eigenfunction moduli squared correspond to surfaces in the 3D space, that are high position probability surfaces, i.e. molecular orbitals in our case (in the coordinate space). Instead the eigenvalues  $\{E\}_i$ are the molecular energy levels corresponding to each orbital. Therefore the electronic structure is obtained by solving the steady state Schrödinger's equation, usually under the aforementioned Born-Oppenheimer approximation, i.e. in the clamped-nuclei case. Notice finally that the electron states that will participate to conduction, will be part of the permitted (steady) states of the molecule, from which the importance of knowing the electronic structure of molecular channels.

### 3.2 The SCF procedure

The electron-electron interaction, i.e. the term  $U_{ee}$  in eq. (3.1), is likely the main issue in solving the many-body Schrödinger's equation. In this section the Self Consistent Field (SCF) procedure for approximating the electron-electron interaction is addressed. I will follow the introduction of [89]. The treatment here has no pretension of being a formal detailed introduction to these topics, but more a conceptual introduction to understand the basic reasoning behind these topics, even to electrical and electronic engineers who have never seen these topics before. The purpose is indeed to provide the means to correctly set up practical and useful simulations, in commercial or free available softwares without getting lost. In order to do that not all the theoretical details are necessary, but at least the fundamental concepts.

The basic idea is to transform the many-body problem of equation (3.3) into a  $N_e$  singleparticle (one-body) problems, that are decoupled. Thus equation (3.1) is transformed in a system of  $N_e$  decoupled equations. In order to do that, the electron-electron potential  $U_{ee}$  is substituted with a suitable SCF potential  $U_{SCF}(\vec{r})$  that arises from all but one electrons. A single electron is thus considered at a time, and the  $U_{SCF}(\vec{r})$  potential to which it undergoes, arises from the remaining  $N_e - 1$  electrons. This because an electron does not "feel" any potential due to itself [89]. In order to calculate the potential  $U_{SCF}(\vec{r})$  a self consistent iterative procedure must be implemented. This because the considered (single) electron undergoes the sum of the attractive potentials of atomic nuclei, that are fixed under the Born-Oppenheimer approximation, and the aforementioned  $U_{SCF}(\vec{r})$ (representing the repulsive interactions with all the other electrons), that is unfortunately a function of the final (many-body) wave-function. In practice  $U_{SCF}(\vec{r})$  is derived from the electronic charge (think to a conventional electrostatic potential derived from a continuous charge density). The electronic charge in the 3D space depends on the wave-function (since this gives the high probability regions), and in turns the wave-function is a solution for the steady state Schrödinger' equation that contains  $U_{SCF}(\vec{r})$ . The self-consistent procedure can be summarized as follows [89]:

- 1. initial guess for the SCF potential  $U_{SCF}(\vec{r})$
- 2. solve steady state Schrödinger's equation and get the eigenvalues  $\{E\}_i$  and the eigenfunctions  $\{\psi\}_i$
- 3. calculate the electron density  $n(\vec{r})$
- 4. calculate the  $U_{SCF}(\vec{r})$  from  $n(\vec{r})$
- 5. if the new  $U_{SCF}(\vec{r})$  is significantly different (i.e. more than the chosen maximum tolerance) from the last guess (or initial guess at first iteration) then: suitably update  $U_{SCF}(\vec{r})$  and go back to step 2; if the new  $U_{SCF}(\vec{r})$  is enough close to the last guess (i.e. less than the chosen maximum tolerance) the result is considered converged and the calculation is complete

The electron density  $n(\vec{r})$  in step 3 can be calculated by summing up the probability distributions for all the occupied eigenstates:

$$n(\vec{r}) = \sum_{occupied \ i} |\psi_i(\vec{r})|^2 \tag{3.4}$$

The charge density is then given by the electron density multiplied the electron charge:  $-q \cdot n(\vec{r})$ . The SCF potential energy in step 4 is recovered from classical electrostatics by integrating the charge density  $-q \cdot n(\vec{r})$  over the entire volume V of interest:

$$U_{SCF}(\vec{r}) = \frac{(N_e - 1)}{N_e} \frac{q^2}{4\pi\varepsilon_0} \int_V \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'}$$
(3.5)

where the multiplicative factor  $(N_e - 1)/N_e$  finds the following explanation: the appropriate charge density for each eigenstate should exclude the electron eigenstate under consideration, since as mentioned no electron feels any repulsion due to itself. However it is more convenient to simply take the total charge density and scale it by the factor  $(N_e - 1)/N_e$  that "weights" it on all but one electrons. Notice that the total electronic charge in all the volume V is always equal to  $-qN_e$ . Further details on this procedure, and application examples can be found in [89].

Notice that the SCF approach allows to split the many-body problem into a system of  $N_e$  single-electron (one-body) problems:

$$\widehat{H}\psi = E\psi \quad \longrightarrow \quad \widehat{H}_i(n(\vec{r})) \quad \psi_i = E_i \quad \psi_i \quad , \quad i = 1, 2, ..., N_e \tag{3.6}$$

where the Hamiltonian operator  $\hat{H}_i$  of the single particle picture can be written from eq. (3.1) as follows (for the *i*-th electron of the system whose position vector is indicated simply with  $\vec{r}$  - no confusion is possible since it is the only electron in the single-electron Schrödinger's equation):

$$\hat{H}_{i}(n(\vec{r})) = \hat{T}_{e} + U_{ne}\left(\vec{r}, \vec{R}_{j}\right) + U_{SCF}\left(\vec{r}\right) =$$

$$= -\frac{\hbar^{2}}{2m_{e}}\Delta - \sum_{j=1}^{N_{n}} \frac{Z_{j}q^{2}}{4\pi\varepsilon_{0}} \left|\vec{r} - \vec{R}_{j}\right| + \frac{(N_{e} - 1)}{N_{e}} \frac{q^{2}}{4\pi\varepsilon_{0}} \int_{V} \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'}$$
(3.7)

notice that it is function of the electron density  $n(\vec{r})$ , given by equation (3.4). The SCF approximation (also called the Hartree approximation or the mean field approximation) is further discussed in appendix B.1, where a more quantitative, even if oversimplified, treatment is provided.

The main problem of this approximation is related to the so called "electron correlation". Indeed if the many-body picture is considered, it is possible to show that the electronelectron interaction is less than the one predicted by the single-electron picture with the mean field just introduced. In particular it is possible to show that the real SCF potential that accurately accounts for all the other electrons in the single-electron picture is given by the difference between two contributions. The first one is an SCF potential of the kind of the one of eq. (3.5), that is called the Hartree potential (name that comes from the original Hartree method that was the first SCF-based method). The second contribution is a contribution that represent the aforementioned electron correlation. Indeed the actual interaction energy is less than the one of eq. (3.5) because electrons can correlate their motion so as to avoid each other. From the wave-function standpoint this corresponds to the fact that the probability of finding two electrons simultaneously in two points  $\vec{r_1}$ and  $\vec{r_2}$  of the space is not simply proportional to the electron density n in the two points:  $n(\vec{r_1})$  and  $n(\vec{r_2})$ ; but it is somehow reduced because electrons "try to avoid each other". In other words the presence of an electron in a region of space, makes decreasing the probability of finding another electron in that region w.r.t. the case in which the first electron is not present. This electron correlation comes out by doing all the calculations on the multi-electron picture. The simple semi-classical expression of equation (3.5) does not account for this correlation, and thus the actual SCF potential should be given by:

$$U_{SCF} = U_{Hartree} + U_{XC} \quad , \quad with: \quad U_{Hartree} = \frac{(N_e - 1)}{N_e} \frac{q^2}{4\pi\varepsilon_0} \int_V \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'}$$

where  $U_{XC}$  is a negative term accounting for the correlation, and it is called "exchangecorrelation" potential. The accurate estimation of  $U_{XC}$  required great effort in research and it is still an unsolved problem for some specific branches of application in which high accuracy is required. Notice that the SCF approach is at the basis of many methods for the calculation of the electronic structure of molecules such as the DFT one that will presented in section 3.5. This topic is more quantitatively discussed in appendix B.1.

In conclusion to this section I would like to point out that, as also mentioned in [89], it is quite surprising that a single-electron picture with a suitable SCF can be often used as a reasonable accurate description of a multi-electron system. The fact that it works well has no convincing mathematical proof, but it is instead proved by many experiments in different conditions. Almost all the electronic structures of atoms, molecules and solids are somehow derived from this method, as will be discussed in section 3.4.

## 3.3 A brief mention on the Hartree-Fock method

The purpose of this section is to provide an insight in the Hartree and Hartree-Fock methods for the calculation of the electronic structure of molecules (or in general conductive channels or devices). These methods are important for understanding the taxonomy of the currently used classes of methods aimed in electronic structure calculations, that is indeed presented in the next section 3.4.

### The Hartree method

Like in any SCF-based method the starting point for the Hartree method is the Born-Oppenheimer approximation. Moreover it is assumed that the electrons are non-interacting, and thus it is possible to show that the many-body steady state Schrödinger's equation admits factorized solutions of the kind:

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{Ne}) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\dots\phi_{Ne}(\vec{r}_{Ne})$$

Thus in the original Hartree method the total many-body wave-function  $\psi(\vec{r})$  is initially approximated as the product (called Hartree product) of the single-electron wave-functions for the individual electrons of the system. Again notice that it holds only if each wavefunction of each electron is independent from the others (non-interacting electrons). Under these hypotheses the many-body problem becomes a set  $N_e$  single electron problems, as already mentioned. If the *j*-th single electron problem is considered, i.e. the *j*-th electron is considered, then the SCF potential in which it is immersed, that accounts for the repulsive interactions of all the electrons but the *j*-th one can be recovered starting from the electron density given by all the other electrons (be careful to the notation):

$$n_j(\vec{r}) = \sum_{i \neq j} |\phi_i|^2$$

and by solving the following Poisson's equation:

$$\nabla^2 V_{Hj}(\vec{r}) = -q \frac{n_j(\vec{r})}{\varepsilon_0}$$
123

where the charge density  $\rho_j(\vec{r}) = -qn_j(\vec{r})$  is now the charge density due to all the electrons except the considered one; it is supposed of having free space (thus  $\varepsilon_0$ ) around the nuclei and the electrons (if not so  $\varepsilon$  of the medium should be considered), and  $V_{Hj}(\vec{r})$  is the electrostatic potential (not potential energy) in the Hartree approximation (subscript "H") related to the *j*-th electron. The resulting SCF potential energy, that will appear in the *j*-th single-electron Schrödinger's equation, is thus:

$$U_{Hj}(\vec{r}) = -qV_{Hj}(\vec{r}) = -\frac{q}{4\pi\varepsilon_0} \int \frac{\rho_j(\vec{r})}{|\vec{r} - \vec{r'}|} d\vec{r'} = +\frac{q^2}{4\pi\varepsilon_0} \sum_{i \neq j} \int \frac{|\phi_i|^2}{|\vec{r} - \vec{r'}|} d\vec{r'}$$
(3.8)

This is the starting guess to be included in the Schrödinger's equation, that as mentioned previously must be solved self-consistently by means of an iterative procedure. The assumption that each electron feels the average potential  $U_{Hj}(\vec{r})$  is the mean field approximation, also called Hartree approximation.

Notice that this expression is essentially analogous to the one of eq. (3.5), and to the aforementioned Hartree approximation of eq. (B.5). Indeed if the summation is extended to all the electron states,  $n_j(\vec{r})$  becomes the total electron density  $n(\vec{r})$  and the corrective weight  $(N_e - 1)/N_e$  should be introduces, such that eq. (3.5) is recovered. This way of rewriting is possible thanks to the fact that the electrons are identical particles (see also section 2.5 - subsection about the systems of identical particles), and even if they exchanged the *j*-th electron is always subjected to the same SCF potential, that is:

$$U_{SCFj}(\vec{r_{j}}) = U_{SCF}(\vec{r}) = \frac{(N_e - 1)}{N_e} \frac{q^2}{4\pi\varepsilon_0} \int_V \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'}$$

In this way the many-body problem is divided into a system of  $N_e$  single electron problems, like done in eq. (3.6). These equations are in general non-linear and must be solved self-consistently.

### The Hartree-Fock method

The original Hartree method briefly summarized above was conceived by Hartree in 1927, and was called self-consistent field method [98]. Nevertheless it did not account for the Pauli's exclusion principle, and for the symmetry constraints on the total system wavefunction  $\psi$  due to the exchange of two identical particles (i.e. electrons on this case) of the system. As briefly discussed in section 2.5 (subsection on systems of identical particles), if two electrons are exchanged then the obtained wave-function for the total many-body system must be anti-symmetric. With the Hartree method this is not guaranteed and must be enforced a posteriori. Instead a way of directly embed this condition in the Hartree method is to consider the so called Hartree-Fock method [98].

In general it is possible to show that if the wave-function can be written as the product of the single-electron ones:

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{Ne}) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\dots\phi_{Ne}(\vec{r}_{Ne})$$

then if two electrons i and j are exchanged (i.e. the electron i that was in state  $\phi_i$  is now

in the state  $\phi_j$  and vice versa) an anti-symmetric wave-function is obtained [87]:

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_{Ne}) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\dots\phi_i(\vec{r}_i)\dots\phi_j(\vec{r}_j)\dots\phi_{Ne}(\vec{r}_{Ne}) = -\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_j, \dots, \vec{r}_{i}, \dots, \vec{r}_{Ne}) = -\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\dots\phi_j(\vec{r}_j)\dots\phi_i(\vec{r}_i)\dots\phi_{Ne}(\vec{r}_{Ne})$$

Considering all the  $N_e!$  possible permutations of the  $N_e$  single electron wave-functions  $\phi$ , the previous relation can be written as [87]:

$$\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_i ..., \vec{r}_j ..., \vec{r}_N e) = \frac{1}{\sqrt{N_e!}} \sum_P (-1)^P \ \hat{P}[\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) ... \phi_{Ne}(\vec{r}_N e)]$$

where P indicates the *P*-th permutation and  $\hat{P}$  is the operator that performs that permutation. The last expression can be interpreted as a determinant, the so called "Slater determinant", defined as follows [87]:

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_{Ne}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_1(\vec{r}_2) & \dots & \phi_1(\vec{r}_{Ne}) \\ \phi_2(\vec{r}_1) & \phi_2(\vec{r}_2) & \dots & \phi_2(\vec{r}_{Ne}) \\ \dots & \dots & \dots & \dots \\ \phi_{Ne}(\vec{r}_1) & \phi_{Ne}(\vec{r}_2) & \dots & \phi_{Ne}(\vec{r}_{Ne}) \end{vmatrix}$$

The exchange of two electrons correspond to the exchange of the two corresponding columns in the Slater determinant.

In the Hartree-Fock method the initial wave-function, given by the product of the single-electron ones, is built starting from the Slater determinant, such that it automatically embeds the anti-symmetrization on the total wave-function. This is the main conceptual difference w.r.t. the Hartree method. Many variants are possible and many ameliorations were proposed during years. Notice that also the Hartree-Fock method includes a self-consistent solution [98].

Finally notice that in modern Hartree-Fock methods the initial single-electron wavefunctions  $\phi_i$  are already a linear combination of atomic orbitals, and generally these atomic orbitals can be Gaussian type wave-functions or of other types (e.g. Slater-type orbitals, more sharp around the nucleus than a Gaussian function). In practice many basis sets (exactly in the sense of the concept of basis set introduced in section 2.4) can be used [98].

# 3.4 Taxonomy of methods for electronic structure calculations

In this section the attempt is to classify the various methods for the calculation of the electronic structure of molecules in such a way that the correct terminology is associated to each method and, more important, the main features of a method can be immediately understood by the knowledge on where it find place in the methods taxonomy. More than one classification are possible, depending on what specific feature is desired to be highlighted.

First of all a fundamental distinction is the one between *ab initio* methods and semiempirical ones. In *ab initio* methods the solution of the (many-body) steady state Schrödinger's equation is generated without reference to experimental data, and starting only from the first principles and physical constants. In contrast in semi-empirical models the solution is found by exploiting information from measurements or from *ab initio* methods. Moreover in semi-empirical methods, suitable fitting parameters are present, whose value is usually derived from a combination of theory (or *ab initio* calculations) and experimental observations.

Another possible classification is related to the kind of variables considered as the unknown of the Schrödinger's equation during the solution. So far these variables were assumed to be the wave-functions. Nevertheless in the mean field approximation the wave-functions are somehow derived from the electron density  $n(\vec{r})$  or analogously from the electron charge density  $\rho(\vec{r}) = -qn(\vec{r})$ . Indeed this variable appears both in the SCF potential and in the Schrödinger's equation that, once solved, provides the eigenfunctions  $\{\psi_i\}_i$ . Thus since the wave-functions are intimately connected with the electron density, it is possible to re-formulate the eigenvalue problem such that the unknown to be found is precisely the electron density (or the charge density). In light of this, it is possible to classify the methods between wave-function-based methods and density-based methods. Nevertheless things are more elaborated than this and each of these classes is further subdivided into different approaches [103], [104]:

- 1. Wave-function-based methods: an explicit form for the wave-function is written down and physical observables are calculated using that.
  - [a.] Perturbational: Møller-Plesset, diagrammatic methods, etc...
  - [b.] Variational: Hartree-Fock, configuration interaction, etc...
- 2. Density-based methods: the focus is shifted from the wave-function to the electronic density. The wave-function is not written explicitly. Examples are Thomas-Fermi approximation and density-functional theory (DFT).

In order to further appreciate the aforementioned terminology some considerations must be pointed out, and they start from the already discussed Hartree-Fock (HF) method.

First of all notice that the Born-Oppenheimer approximation is always assumed to be true. Under this approximation the coupling between the nuclei and electronic motion is neglected, and this allows the electronic part to be solved with the nuclear positions as parameters. In general the Born-Oppenheimer approximation is good, and it does not afflict significantly the accuracy of the final solution [98], [104]. The dynamics of a many-electron system is very complex, and consequently requires elaborate computational methods. A significant simplification, both conceptually and computationally, can be obtained by introducing independent-particle models, where the motion of one electron is considered to be independent of the dynamics of all other electrons [98]. This coincides in what was done in the self-consistent mean field approximation and the Hartree-Fock method, that were already discussed in sections 3.2 and 3.3. Notice that an independent-particle model means that the interactions between the particles is approximated, either by neglecting all but the most important one, or by taking all interactions into account in an average fashion. Within electronic structure theory, only the latter has an acceptable accuracy, and it is again exactly what was done with the SCF Hartree-Fock (HF) method. The key conceptual point in the understanding of the electronic structure methods is the HF theory. For this reason before going on in the treatment, its main features are summarized below (in the words of [98]):

- a. In the HF model, each electron is described by an orbital, and the total wave-function is given as a product of orbitals.
- b. Since electrons are indistinguishable fermions (particles with a spin of 1/2), the overall wave-function must be anti-symmetric (change sign upon interchanging any two electrons), which is conveniently achieved by arranging the orbitals in a Slater determinant.
- c. The best set of orbitals is determined by the variational principle, i.e. the HF orbitals give the lowest energy within the restriction of the wave function being a single Slater determinant.
- d. The shape of a given molecular orbital describes the probability of finding an electron, where the attraction to all the nuclei and the average repulsion to all the other electrons are included.
- e. Since the other electrons are described by their respective orbitals, the HF equations depend on their own solutions, and must therefore be solved iteratively.
- f. When the molecular orbitals are expanded in a basis set, the resulting equations can be written as a matrix eigenvalue problem.

The HF model is a kind of branching point, where either additional approximations can be invoked, leading to semi-empirical methods, or it can be improved by adding additional determinants, thereby generating models that can be made to converge towards the exact solution of the electronic Schrödinger's equation [98], [104].

Semi-empirical methods are derived from the HF model by further neglecting some integrals related to electron-electron interaction. Since the HF model by itself is only capable of limited accuracy, such approximations will by themselves lead to a poor model. Nevertheless a semi-empirical method can also provide very accurate results, depending on the specific case. Indeed the success of semi-empirical methods relies on turning the remaining integrals into parameters, and fitting these to experimental data, especially molecular energies and geometries. Such methods are computationally much more efficient than the *ab initio* methods, but they are limited to systems for which parameters exist. As mentioned, in such systems they can also reach significant good accuracy becoming competitors of *ab initio* methods, nevertheless the final result is strongly dependent on the specific considered case. A semi-empirical method is e.g. the Extended Hückel Theory (EHT), that will be addressed in section 3.6.

The HF theory only accounts for the average electron–electron interactions, and consequently neglects the correlation between electrons (see sections 3.2, 3.3 and appendix B.1). Methods that include electron correlation are typically computationally much more involved than the HF model, but can generate results that systematically approach the exact solution of the Schrödinger's equation. These methods are often called "electron correlation methods" or "post-Hartree-Fock methods". They will be mentioned again at the end of this section.

A different approach is instead the one of the Density Functional Theory (DFT), that in the original in the Kohn–Sham version can be considered as an improvement on HF theory, where the many-body effect of electron correlation is modelled by a function of the electron density. DFT is, analogously to HF, an independent-particle model, and is comparable to HF computationally, but provides significantly better results. The main disadvantage of DFT is that there is no systematic approach to improving the results towards the exact solution, like in the aforementioned electron correlation methods. The DFT method will be addressed in section 3.5.

Finally there exists a class of methods which is completely unrelated to all the others presented so far, and starts from a complete different approach. This includes the so called "Force Field" methods, also referred as "Molecular Mechanics" methods. They are very computationally effective methods, but also very rough. A brief discussion is reported at the end of this section, while a complete presentation can be found e.g. in [98].

### Electron correlation methods (the post-Hartree-Fock methods)

The main limit of the Hartree-Fock method (see section 3.3) is that the electron-electron interactions are completely neglected (this is indeed the hypothesis that allows for writing the many-body wave-function as the product of the single-electron ones). In general this is a limit of the SCF approach in which the electron-electron interaction is represented by means of a mean field. This is evident when the initial guess on the total many-body wave-function is considered. It is given by the product of single-electron ones in which the  $U_{ee}$  term is substituted my the mean field one  $U_{SCF}$ . The Hartree-Fock methods are for this reason called "independent-particle" models, indeed the motion of an electron is considered on the dynamics of all the others.

Successive generations of methods were derived from the original HF one, all aimed in better estimating the electron-electron interaction by means of the so called correlation potential (this holds true also for the DFT method - see section 3.5), to account for the electron-electron repulsion [104]. As mentioned in section 3.2 (and further discussed in appendix B.1) the point is that electrons can correlated their motion such that they avoid each other, and this correlation depends also on spin. As pointed out again in section 3.2 (and appendix B.1) the electron correlation results in an additional (negative) contribution of energy  $U_{XC}$  that must be added to the SCF potential within the Schrödinger's equation. In general the resulting HF many-body wave-function is able to account for the great majority of the total energy (let's say the 99%), but the small remaining part, that is due to the electron correlation, can be very important in describing chemical phenomena. Since the HF solution usually provides the  $\sim 99\%$  of the actual correct answer, the electron correlation methods normally use the HF wave-function as a starting point for improvements. For this reason they are also called "post-Hartree-Fock" methods. The basic concept is to superimpose to the HF wave-function  $\psi_{HF}$  a set of other wave-functions  $\psi_i$  such that the total wave-function becomes [98], [104]:

$$\psi_{TOT} = \psi_{HF} + \sum_{i} c_i \psi_i$$

where  $c_i$  are suitable coefficients. Notice that this approach can be interpreted as a "multi-determinant" approach. Indeed in section 3.3 it was mentioned that the HF wave-function  $\psi_{HF}$  can be interpreted as the Slater determinant of a matrix whose elements are atomic wave-functions (or in general they can be a suitable basis set of functions). If the same is applied to each additional  $\psi_i$  then the  $\psi_{TOT}$  can be found by calculating several determinants. The electron correlation methods are essentially different in how they calculate the coefficients  $c_i$ . Indeed once the basis functions are selected they are always the same in each considered Slater determinant for building the  $\psi_i$ , while by changing  $c_i$  it is possible to get different total wave-functions. There are mainly three methods to calculate the electron correlation and thus the coefficients  $c_i$ : the configuration interaction method, the many-body perturbation theory and the coupled cluster.

Notice that the functions  $\psi_i$  are already total many-body functions, i.e. they can in turn be represented as superposition of the chosen basis functions (that in section 3.3 were indicated with  $\phi_i$ ). To this purpose see also section 2.4. Analogously it is possible to think to the total wave-function  $\psi_{TOT}$ , called multi-determinant wave-function, as a superposition of the  $\psi_i$ , that defines a sort of "coordinate system" for the Slater determinants. In this optics the basis set determines the size of the one-electron basis (and thus limits the description of the single  $\psi_i$ ), while the number of included considered Slater determinants defines the size of the many-electron basis (and thus limits the description of the final  $\psi_{TOT}$ ).

At this point, in analogy with the Fourier series, notice that if the number of basis functions is increased then the accuracy generally increases, and for an infinite number of considered basis functions the reconstruction of the original function is obtained. This is the result of the already mentioned Fischer-Riesz theorem that states that (for a complete basis set) the original function can be exactly recovered as Fourier series expansion (unless a set of isolated points, that is empty if the initial function is continuous - like electron wavefunctions must be, see section 2.3.2). Consequently if the number of basis set functions is increased, the representation (in that basis set) of the single-electron wave-function  $\psi_i$ is ameliorated. And again if the number of considered Slater determinants is increased, the representation of the total multi-electron wave-function  $\psi_{TOT}$  is ameliorated. This is more than an intuitive reasoning, indeed it is possible to show that the electron correlation methods can systematically converge to the actual solution of the Schrödinger's equation. This happens if both the basis set and the number of determinants is increased. In particular the exact Schrödinger's equation is recovered if a complete basis set and a complete set of Slater determinants are used. In real applications this is not possible since it would imply the usage of an infinite number of functions or determinants, nevertheless if the number is correctly increased then the solution is closer to the real one. This concept is summarized in figure 3.1. On abscissa axis the basis sets are considered (see also section 3.5 -subsection on basis set- for the basis set names and their meanings), increasing the accuracy means moving toward greater abscissa coordinates. On ordinate axis the different electron correlation methods are considered (increasing the accuracy means moving toward greater ordinate coordinates).

I will not use in the rest of this work any electron correlation method and thus I will not further discuss them. A good presentation is in my opinion provided in [98]. I conclude this section with a mention of some of these methods, just to give the idea of how ample is



Figure 3.1: Schematic representation of the converge toward the exact solution of the electron correlation methods. On abscissa axis the basis sets are considered while on ordinate axis the different electron correlation methods are considered.

the current landscape (remember that three main approaches are possible for calculating the electron correlation):

- configuration interaction based correlation methods: the configuration interaction (CI) method, the multi-configuration self-consistent field, the multi-reference configuration interaction, etc...
- many-body perturbation theory based correlation methods: the Møller–Plesset (MP) perturbation theory, unrestricted Møller–Plesset and projected Møller–Plesset, etc...
- coupled cluster based methods: truncated coupled cluster (CC) methods, etc...

Notice that also other methods and approaches are possible such as the so called Quantum Monte Carlo (QMC) method (that provides a statistical estimation of energy - intended as integral of the wave-function), etc... [98], [104].

### Force field methods

This subsection has not the aim of being a complete introduction. It is essentially taken from [98], that instead provide a good introduction to the force field methods.

The "building blocks" in force field methods are atoms, i.e. electrons are not considered as individual particles. This means that bonding information must be provided explicitly, rather than being the result of solving the electronic Schrödinger's equation. In addition to bypassing the solution of the electronic Schrödinger's equation, the quantum aspects of the nuclear motion are also neglected. This means that the dynamics of the atoms is treated by classical mechanics, i.e. Newton's second law. For time-independent phenomena, the problem reduces to calculating the energy at a given geometry. Often the interest is in finding geometries of stable molecules or different conformations. The problem is then reduced to finding energy minima (in the principle that in nature a stable molecule is always in a configuration that minimizes its potential energy - ground state) on the potential energy surface. The electronic energy is thus written as a parametric function of the nuclear coordinates, and fitting the parameters to experimental or higher level computational data.

Moreover in force field methods the molecules are described by a sort of "ball and spring" model, with atoms having different sizes and "softness" and bonds having different lengths and "stiffness". The foundation of force field methods is the observation that molecules tend to be composed of units that are structurally similar in different molecules. For example carbons are essentially planar, or all C-H bond lengths are roughly constant in all molecules, being between 1.06 Å and 1.1 Å. If then the C-H bonds are further divided into groups, for example those attached to single-, double- or triple-bonded carbon, the variation within each of these groups becomes even smaller. This picture is not so different from the one widely used in organic chemistry, in which the organic molecules are seen as composed by the so called "functional groups". Force field methods are in a sense a generalization of these models, with the added feature that the atoms and bonds are not fixed at one size and length. As mentioned the main task in force field methods is almost always the one of minimizing the potential energy of the system, thus providing the stable configuration. In a force field model the energy can be written as a sum of different contributions: the energy function for stretching a bond between two atoms, the energy required for bending an angle, the torsional energy for rotation around a bond, the non-bonded atom-atom interactions energy and the coupling energy between the first three terms. Given such an energy function of the nuclear coordinates, geometries and relative energies can be calculated by optimization, i.e. by minimizing it. Stable molecules correspond indeed to minima on the potential energy surface, and they can be located by minimizing the total potential energy as a function of the nuclear coordinates.

## 3.5 The DFT method

In the Density Functional Theory (DFT) the focus is shifted from the wave-function to the electronic density. The DFT method treats again the electron-electron interactions in a mean field manner (see section 3.2): each electron is considered moving inside a mean field created by all other electrons of the system under analysis. Hence, instead of solving an interacting  $N_e$ -particles problem, it solves  $N_e$  non-interacting one-particle problems self-consistently, that is pretty much more manageable. With this approach it is possible to obtain the electronic structure of a system of a few tens to a few hundreds of atoms with reasonable accuracy and computational effort/time, if compared to traditional methods, such as Hartree-Fock theory and its descendants that include electron correlation.

The properties of a many-electron system, within the DFT framework, can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density  $n(\vec{r})$ . Before going on a note on semantics [98]: a function is a prescription for producing a number from a set of variables (coordinates); a functional is a prescription for producing a number from a function, which in turn depends on variables. A wave-function and the electron density are thus functions, while the energy depending on a wave-function or an electron density is a functional. Usually a function that depends on the variable x is indicated with f(x), instead a functional F depending on a function f(x) is conventionally indicated as F[f] (with square brackets).

The basis for the DFT is the Hohenberg-Kohn's theorem that states that the ground state electronic energy is completely determined by the electron density. In other words, there exists a one-to-one correspondence between the electron density of a system and its energy. The importance of the Hohenberg–Kohn's theorem is well understood if a system with  $N_e$  electrons is considered. A steady state wave-function for such a system contains  $4N_e$  variables (three spatial and one for spin - because of Pauli's exclusion principle the spin must be considered for discriminating among electron states). Instead the electron density  $n(\vec{r})$  for the same system only depends on three spatial coordinates, independently on the number of electrons of the system. Therefore while the complexity of a wave-function increases exponentially with the number of electrons, the electron density has the same number of variables, independent of the system size. Moreover it is possible to demonstrate that each different electron density yields a different ground state energy, thus confirming the one-to-one correspondence. The problem is that the functional connecting the system energy with the electron density is not known. Indeed it is not possible to find an analytical explicit expression for it. Thus the goal of DFT methods is to design functionals that accurately connect the electron density with the energy [104].

Density functional theory is conceptually and computationally similar to Hartree–Fock theory [98], but provides much better results and has consequently become a very popular method. The main problem in DFT is the inability to systematically improve the results, like it happens instead for the electron correlation methods (see previous section 3.4). In addition, despite the many successes of DFT, there are some areas where the current functionals are known to perform poorly (especially concerning weak interacting systems):

- in describing certain types of weak interactions, e.g. van der Waals interactions, where instead the correlation methods have great success
- in describing systems with loosely bound electrons (the self-interaction error in these cases is larger than the actual binding energy, and thus lead erroneously to an unbound electron)
- in predicting the binding energy of some kinds of chemical bonds that are predicted to be too stable
- large errors in predicting excitation energies in some conditions
- poor result in some cases of strong electron-electron interaction (see also chapter 6)

For many of these issues some kind of correction exists and can be employed to improve the final accuracy. Few other critical issues are present in addition to the ones presented here, for reference see [98]. The only issue of interest in this work is the first one, namely the poor modeling of some kind of weak interactions such as the intermolecular van der Waals interactions, nevertheless corrections exist to improve the DFT accuracy and they are briefly presented in section 3.7.

### 3.5.1 Kohn-Sham Hamiltonian

Early attempts at designing DFT models (i.e. Thomas–Fermi and Thomas–Fermi–Dirac methods) tried to express all the energy components (the kinetic and all the potential contributions) as a functional of the electron density. In this optics it is possible to write directly an expression for the total energy of the system  $E_{tot}$  (energy eigenvalues), corresponding to the classical Hamiltonian (not the Hamiltonian operator) of the system (n is the electron density):

$$H_{tot} = E_{tot} = T_e[n] + U_{ne}[n] + U_{ee}[n]$$

Notice that this formulation embeds the exchange-correlation within the functional  $U_{ee}[n]$  that represents the electron-electron interaction. Thus  $U_{XC}$  is not explicitly written. Unfortunately these methods had poor performance [98], mainly because it is very hard finding an enough accurate functional able to accurately express the kinetic energy term in function of the electron density. Although there have been some recent attempts at constructing such functionals, at the present this way is still unfeasible because of its poor accuracy [98]. Notice that this formulation of the many-body problem is completely orbital-free, indeed the wave-functions do not appear in this "pure" DFT approach. Notice also that if such functionals could be derived, the full potential of DFT in having only three variables independent of system size could be fully realized [104].

Nevertheless the current foundation for the use of DFT methods in computational chemistry is the introduction of some orbitals, as suggested by Kohn and Sham in 1965. These orbitals (i.e. wave-functions) are exploited to accurately represent the kinetic energy of the system. More precisely Kohn and Sham proposed that the electron kinetic energy should be calculated from an auxiliary set of orbitals, used for representing the electron density. As mentioned this assumption is the starting point of all the modern DFT methods. The gain in this approach is that it is possible to carry out very accurate calculations. Indeed the exchange–correlation energy  $U_{XC}$  (see section 3.2 and later in this section), which is a rather small fraction of the total energy, in this approach is the only unknown functional, and even relatively crude approximations for this term provide quite accurate computational models [98]. In the Kohn-Sham (KS) Hamiltonian the kinetic energy functional is split into two parts, one which can be calculated exactly, and a small correction term. Unfortunately price to be paid is that orbitals (i.e. wave-functions) are re-introduced and must be used to represent the kinetic energy term/operator which is not enough accurately represented in terms of electron density functional only. Thereby the complexity is increased from 3 (3 spatial variable of  $n(\vec{r})$ ) to  $3N_e$  variables, and the electron correlation re-emerges as a separate term,  $U_{XC}$  that must be summed up to the other potentials in the Hamiltonian. The KS model is closely related to the HF method, sharing identical formulas for the kinetic energy, electron-nuclear energy and Coulomb electron-electron energy (i.e. the Hartree potential of equations (3.5), (3.8) and (B.5)). In particular the many-body electronic Hamiltonian is re-conceived in terms of the one-electron Kohn-Sham Hamiltonian like [101]:

$$H_{KS}[n] = \sum_{i}^{N_e} \left[ -\frac{\hbar^2}{2m_e} \Delta_i + U_{eff}(\vec{r_i}) \right] = \sum_{i}^{N_e} H_{KSi}$$
(3.9)

where the so called effective Kohn-Sham potential  $U_{eff}(\vec{r_i})$  is defined as:

$$U_{eff}(\vec{r_i}) = U_H[n(\vec{r_i})] + U_{XC}[n] + U_{EXT}(\vec{r_i})$$
(3.10)

In equation (3.9) the first term is the kinetic energy of the *i*-th electron, while the second term is the potential energy of the i-th electron moving in the mean field created by the other electrons as well as in any external potential field (e.g. the electrostatic potential of ions or any other external field). The latter is detailed in equation (3.10). The first term in eq. (3.10) is the Hartree potential due to the mean-field electrostatic interaction between the electrons. It corresponds to the one of the already introduced equations (3.5), (3.8) and (B.5). The second one is the exchange-correlation potential, which arises from the quantum mechanical nature of the electrons and embeds all the many-particle interactions, thus it represents the correction term used to account for energy that the non-interacting reference system fails to capture. It corresponds exactly to the term introduced in section 3.2 (and in appendix B.1). Notice that these two terms are due to electron-electron interactions, which depend on the electron density  $n(\vec{r})$ , which depends on the wave-function  $\psi_i$  (that must be used and calculated for representing correctly the kinetic term), which in turn depend on  $U_{eff}$ . Therefore the problem of solving the Kohn-Sham equation has to be done in a self-consistent way, analogously to the SCF and HF methods. Usually in the KS method one starts with an initial guess for  $n(\vec{r})$  (instead of a wave-function guess like in the HF method), then calculates the corresponding  $U_{eff}$  and solves the Kohn-Sham equations for the  $\psi_i$ . From these, one calculates a new electron density and starts again. This procedure is then repeated until convergence is reached. A non-iterative approximate formulation, called Harris functional DFT, is also possible [101] [98].

The third term in equation (3.10) represents any other electrostatic field in the system. It can be separated into two contributions: the electrostatic potential due to electron-nuclei interactions and an eventual external potential arising from applied electrostatic fields (given by one or more external sources).

*Example 3.1:* Very often the KS Hamiltonian is presented in atomic units, instead of SI units. In that case its various terms can assume slightly different aspects, for example the kinetic term becomes:

$$\widehat{T}_e = -\frac{\hbar^2}{2m_e}\Delta \quad \rightarrow \quad -\frac{1}{2}\Delta$$

A generic potential energy contribution instead can be:

$$U_{potential} = \frac{q^2}{4\pi\varepsilon_0 r} \quad \to \quad \frac{1}{r}$$

Consequently the Hartree potential of eqs. (3.5) and (3.8) becomes:

$$U_H = \frac{q^2}{4\pi\varepsilon_0} \int \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'} \quad \to \quad \int \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'}$$
134

that is often written as a convolution product (indicated with the symbol \*):

$$U_H = n(\vec{r}) * \frac{1}{|\vec{r}|} = \int \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'}$$

with this notation the KS Hamiltonian becomes:

$$H_{KS}[n] = \sum_{i}^{N} \left[ -\frac{\hbar^2}{2m_e} \Delta_i + U_{eff}(\vec{r_i}) \right] \quad , \quad U_{eff}(\vec{r_i}) = n(\vec{r_i}) * \frac{1}{|\vec{r_i}|} + U_{XC}[n] + U_{EXT}(\vec{r_i})$$

as for example appear in some papers, like [101].  $\Box$ 

In summary, the many-body stationary Schrödinger's equation can be rewritten in  $N_e$  more manageable Kohn-Sham equations (since  $\hat{H} = \sum_{i}^{N_e} \hat{H}_{KSi}[n]$ ):

$$\widehat{H}\psi = E\psi \quad \to \quad \widehat{H}_{KSi}[n] \ \psi_i = E_i \ \psi_i \quad , \quad i = 1, 2, .., N_e$$
(3.11)

As mentioned the main problem with the DFT method is that the exact functionals for exchange-correlation term are not known, except for the free electron gas. Therefore other approximations are needed. They are the subject of the next subsection.

### 3.5.2 Exchange-correlation functionals

The main issue in DFT is how to estimate the exchange-correlation functional  $U_{XC}[n]$  that represents the electron-electron interaction in a precise way. The difference between various DFT methods is indeed the choice of the functional form for the exchange–correlation energy. It can be proven [98] that the exchange–correlation potential is a unique functional, valid for all systems, but an explicit functional form of this potential does not exist, except for special cases such as a uniform electron gas. Several functionals with different level of accuracy were developed [98], [104].

Notice that exchange–correlation functionals have a mathematical form containing parameters. There are two main philosophies for assigning values to these parameters, either by requiring the functional to fulfil theoretical criteria, or by fitting the parameters to experimental data, although in practice a combination of these approaches is often used [98]. The quality of exchange–correlation functionals will ultimately have to be settled by comparing the performance with experiments or high-level wave mechanics calculations. Such calibration studies, however, only evaluate the quality for the chosen selection of systems and properties. It has indeed been found [98] that the "best" functionals depend on the system and properties, some being good for molecular systems, others for delocalized (periodic) systems, and others again for properties such as excitation energies, etc... Since DFT is an active area of research, new and improved functionals are likely to emerge in future.

I will now introduce the main classes of functionals accordingly to what presented in [98]. For the next chapters of this work and for the purpose of setting up simulations it is just important to acquire the sensibility of the level of approximation of these functionals,
such that it is possible to choose the most suitable for the specific application, considering if a more refined should be better depending on the structure to be simulated (e.g. a more refined functional could be needed to capture the essential of the interactions that are not well represented within a DFT framework - see previously in this section). The main functional classes are thus briefly considered in the following, while a comparison among them is provided in figure 3.2.

Name	Variables	Examples
Local density GGA	$n^n, \nabla n$	LDA, LSDA, <i>X</i> <sub>α</sub> BLYP, OPTX, OLYP, PW86, PW91, PBE, HCTH
Meta-GGA Hyper-GGA	$n, \nabla n, \nabla^2 n$ $n, \nabla n, \nabla^2 n$ <i>HF exchange</i>	BR, B95, VSXC, PKZB, TPSS, <i>τ</i> -HCTH H+H, ACM, B3LYP, B3PW91, O3LYP, PBE0, TPSSh, <i>τ</i> -HCTH-hybrid
Generalized RPA	$n, \nabla n, \nabla^2 n$ HF exchange Virtual orbitals	OEP2

1	``
1.	s١
	a /
``	

Functional	RMS (kJ/mol)	MAD (kJ/mol)
HF	649	885
LSDA	439	510
PW91	80	99
PBE	87	93
PKBZ	75	29
BLYP	41	40
PBE0	50	28
OLYP	40	25
B3LYP	40	21
VSXC	39	14
HTCT	33	30
$\tau$ -HCTH	31	
$\tau$ -HCTH-hybrid	26	
TPSS		24
TPSSh		16

(b)

Figure 3.2: A summary of the main classes of functionals with examples (a); and a comparison among them (b). RMS stands for Root Mean Square, MAD for Mean Absolute Deviation. The comparison is performed with experimental data on a set of molecules, data are taken from [98].

#### LDA and LSDA:

The simplest model is the Local Density Approximation (LDA), where the electron density is assumed to be slowly varying, such that the exchange–correlation energy can be calculated using formulae derived for a uniform electron density. In particular, within this approximation,  $U_{XC}$  in a given spatial point  $\vec{r}$  is expressed only in terms of the electron density at that point  $n(\vec{r})$ . A simplified quantitative introduction is provided in [89], notice that the functional is usually taken proportional to the electron density to the power of 1/3 (in the same point):  $U_{XC}[n(\vec{r})] \propto [n(\vec{r})]^{1/3}$ . An straightforward improvement is obtained considering explicitly the electron spin, in the LSDA (Local Spin Density Approximation) functional.

### GGA:

A significant improvement in the accuracy can be obtained by making the exchange– correlation functional dependent not only on the electron density but also on its derivatives. In the so called Generalized Gradient Approximation (GGA) methods, the first derivative of the electron density is included as a variable within the exchange-correlation functional. GGA methods are sometimes referred to as non-local methods, although this is somewhat misleading since the functionals only depend on the density (and derivative) at a given point, not on a space volume [98]. The following functionals belong to this class: B88 (from A. D. Becke), OPTX (OPTimized eXchange), LYP (Lee, Yang and Parr), PBE (Perdew–Burke–Ernzerhof), OLYP (combination of OPTX and LYP) and BLYP (combination of B88 and LYP), etc...

#### Meta-GGA:

The logical extension of GGA methods is to allow the exchange and correlation functionals to depend on higher order derivatives of the electron density, with the Laplacian  $(\nabla^2 n(\vec{r}))$ being the second-order term. Alternatively, the functional can be taken to depend on the orbital kinetic energy density  $\tau$ . Inclusion of either the Laplacian or orbital kinetic energy density as a variable leads to the so-called meta-GGA functionals. Examples are: VSXC (Voorhis–Scuseria eXchange–Correlation), TPSS (Tao–Perdew–Staroverov–Scuseria), PKZB (Perdew–Kurth–Zupan–Blaha) that can be considered as the next improvement over the PBE functional, etc...

#### Hybrid or hyper-GGA:

In hybrid functionals a portion of exact exchange (from HF theory) is incorporated with the rest of the exchange–correlation energy from other sources (*ab initio* or empirical). The exact exchange energy functional is expressed in terms of the Kohn–Sham orbitals rather than the density (so often is called implicit density functional). One of the most commonly used versions is B3LYP (Becke, 3-parameter, Lee–Yang–Parr), other functionals in this class are B3PW91, O3LYP, PBE0 (also denoted PBE1PBE), etc...

#### Generalized RPA:

In Generalized Random Phase methods also virtual molecular orbitals are considered. These are molecular orbitals that are empty in ground state, but that can be occupied in excited states. The improvement seems to be effective especially for weak interactions such as the van der Waals ones (that are still a problem with conventional functionals). Examples are: Optimized Effective Potential (OEP) methods (e.g. OEP1, OEP2, ...).

# 3.5.3 DFT and fitting parameters

An important question is now addressed: "should DFT methods be considered *ab initio* or semi-empirical?" If *ab initio* is taken to mean the absence of fitting parameters, LSDA methods are *ab initio* but gradient corrected methods may or may not be. The LSDA exchange energy contains no parameters and the correlation functional is known accurately as a tabulated function of the density. Some gradient-corrected methods (e.g. the B88 exchange and the LYP correlation), however, contain parameters that are fitted to give the best agreement with experimental atomic data, but the number of parameters is significantly smaller than for semi-empirical methods. Functionals such as VSXC contains a moderate number of parameters (21), while other functionals such as PBE are derived entirely from theory and can consequently be considered *ab initio*. If instead *ab initio* is taken to mean that the method is based on theory, which in principle is able to produce the exact results, DFT methods are *ab initio*. The only issue is that current methods cannot yield the exact results, even in the limit of a complete basis set, since the functional form of the exact exchange–correlation energy is not known.

Although gradient-corrected DFT methods have been shown to give impressive results, even for theoretically difficult problems, the lack of a systematic way of extending a series of calculations to approach the exact result is a major drawback of DFT [98]. The results converge toward a certain value as the basis set is increased, but theory does not allow an evaluation of the errors inherent in this limit. Moreover although a progression of methods such as LSDA, BLYP and B3LYP has provided successively lower errors for a suitable set of reference data, there is no guarantee that the same progression will provide better and better results for a specific property of a given system. Indeed, LSDA methods may in some cases provide better results, even in the limit of a large basis set, than either of the more complete gradient-corrected models. The quality of a given result can therefore only be determined by comparing the performance for similar systems where experimental or high-quality wave mechanics results are available. In this respect, DFT resembles semi-empirical methods.

### 3.5.4 DFT and basis sets

One approximation in essentially all electronic structure calculation methods is the introduction of a basis set. Expanding an unknown function, such as a molecular orbital, in a set of known functions is not an approximation if the basis set is complete (see also chapter 2). However, a complete basis set means that an infinite number of functions must be used, which is impossible in actual calculations. An unknown molecular orbital can be thought as a function in the infinite coordinate system spanned by the complete basis set. When a finite basis set is instead used, only the components of the molecular orbital along those coordinate axes corresponding to the selected basis functions can be represented. The smaller the basis set, the poorer the representation. Also the type of used basis functions influence the accuracy. The better a single basis function is able to reproduce the unknown function, the fewer basis functions are necessary for achieving a given level of accuracy.

In mathematical terms each molecular orbital  $\psi_i$  is expanded in terms of the basis functions  $\{\phi_{\alpha}\}_{\alpha}$ , conventionally called atomic orbitals:

$$\psi_i = \sum_{\alpha} c_{\alpha} \phi_{\alpha}$$

Thus a molecular orbital is expanded as Linear Combination of Atomic Orbitals (LCAO). The expansion of the molecular orbitals leads to integrals of quantum mechanical operators over basis functions (see also section 2.4), and the ease with which these integrals can be calculated also depends on the type of basis function. And often the accuracy does not correspond to efficiency of calculation.

In principle any type of basis functions may be used: exponential, Gaussian, polynomial, cube functions, plane waves, etc... Nevertheless two very common functions are the Slater Type Orbitals (STO) and Gaussian Type Orbitals (GTO). Both STOs and GTOs can be chosen to form a complete basis. Historically, STOs were used due to their geometric similarity to the hydrogenic orbitals. They also remain a common choice in semi-empirical methods. However, they do have a significant drawback since there are no general and numerically stable solutions for the many-center integrals involving Slater-type orbitals. Consequently, Gaussian type orbitals are often the preferred choice. In figure 3.3 an example of STOs and GTOs is reported. The GTOs are inferior to the STOs in two respects. At the nucleus a GTO has a zero slope, in contrast to a STO which has a cusp (discontinuous derivative), and GTOs consequently have problems representing the proper behaviour near the nucleus. The other problem is that the GTO falls off too rapidly far from the nucleus compared with an STO, and the tail of the wave-function is consequently represented poorly. The increase in the number of GTO basis functions, however, is more than compensated for by the ease of which the required integrals can be calculated. In terms of computational efficiency, GTOs are therefore preferred.

There are mainly two guidelines for choosing the basis functions. One is that they should have a behaviour that agrees with the physics of the problem, since this ensures that the convergence as more basis functions are added is reasonably rapid. For bound atomic and molecular systems, this means that the functions should go toward zero as the distance between the nucleus and the electron becomes large. The second guideline is a practical one: the chosen functions should make it easy to calculate all the required integrals. To this purpose thinks again to the matrix formulation of quantum mechanics (section 2.4) in which an integral has to be one for each matrix element. Notice also that semi-empirical methods usually approximate (at least some of) these integrals by means of fitting parameters (usually the so called two-electrons integrals that appears in the electron-electron interaction terms). Exactly like in a Fourier series (indeed it can be seen exactly like a Fourier decomposition) as the number of basis functions increases, the



Figure 3.3: A qualitative example of comparison between STO and GTO functions. The exponential 1s STO orbital is compared with three different GTO possible functions.

accuracy of the molecular orbitals improves. Nevertheless the computational cost increases exponentially with the number of basis functions. Indeed it is possible to show [98] that (in the large basis set limit) the SCF procedure involves a computational effort that increases (at least) as the number of basis functions to the fourth power.

The first criterion suggest the use of exponential functions located on the nuclei, since such functions are known to be exact solutions for the hydrogen atom. Unfortunately, exponential functions turn out to be computationally difficult. Gaussian functions are computationally much easier to handle, and although they are poorer at describing the electronic structure on a one-to-one basis, the computational advantages more than make up for this. For periodic systems, the infinite nature of the problem suggests the use of plane waves as basis functions, since these are the exact solutions for a free electron (think also that Bloch waves are intimately linked with plane waves - each Bloch wave is constituted by a forward and a backward plane wave).

#### Basis set classification

The smallest number of functions possible is a minimum basis set. Only enough functions are employed to contain all the electrons of the neutral atom(s). For hydrogen (and helium) this means a single s-function. The next improvement of the basis sets is a doubling of all basis functions, producing a Double Zeta (DZ) type basis. The term zeta stems from the fact that the exponent of STO basis functions is often denoted by the Greek letter  $\zeta$ . A DZ basis thus employs two s-functions for hydrogen (called 1s and 1s'), and so on... The importance of a DZ over a minimum basis is clear if different chemical bond types are considered. For example a  $\pi$ -orbital is more delocalized than a  $\sigma$ -one. It will have a more diffuse electron distribution w.r.t. a  $\sigma$  bond. The optimum basis function exponent for representing a more delocalized orbital should be smaller than for representing a localized orbital. Moreover such an optimum exponent may vary with the direction (if e.g. in direction x a  $\sigma$ -bond occurs and in direction y a  $\pi$ -bond occurs). If only a single set of basis function is available (minimum basis), a trade-off will be necessary. Instead in a DZ basis, two sets of basis functions with different exponents are present. Thus, doubling the number of basis functions allows for a much better description of the fact that the electron distribution is different in different directions.

The next step up in basis set size is a Triple Zeta (TZ). Such a basis contains three times as many functions as the minimum basis; then Quadruple Zeta (QZ) and Quintuple or Pentuple Zeta (PZ or 5Z, but not QZ) are possible, and so on.

#### **Polarization function**

In most cases, higher angular momentum functions are also important, and these are denoted polarization functions. If methods including electron correlation are used, higher angular momentum functions are essential. Electron correlation describes the energy lowering by the electrons avoiding each other, beyond the average effect taken into account by Hartree–Fock methods. Polarization functions are added to the chosen basis. Adding a single set of polarization functions (*p*-functions on hydrogens and *d*-functions on heavy atoms) to the DZ basis forms a Double Zeta plus Polarization (DZP) type basis. Similarly Triple Zeta plus Double Polarization (TZ2P) can be formed.

Mixed basis sets are sometimes used, for example a DZP quality on the atoms in the active/central portion of the device part of the molecule and a minimum basis for the device leads. An important point (not discussed here) is to choose "balanced" basis set is to keep the error as constant as possible. The use of (not at all balanced) mixed basis sets should therefore only be done after careful consideration. A good treatment is provided in [98].

#### Plane waves

Rather than starting with basis functions aimed at modelling the atomic orbitals (STOs or GTOs), and forming linear combination of these to describe orbitals for the whole system, one may use functions aimed directly at the full system. For modeling extended (infinite) systems, for example, a unit cell with periodic boundary conditions, this suggests the use of functions with an "infinite" range. For example the outer valence electrons in metals behave almost like free electrons, which leads to the idea of using solutions for the free electron as basis functions. Indeed in periodic systems like crystals the solution of the Schrödinger's equation leads to the arise of energy bands, and the electrons in a band can be described by orbitals expanded in a basis set of plane waves, which in three dimensions can be written as a complex function. To this purpose notice that a Bloch wave-function (solution of steady state Schrödinger's equation) is similar to a plane wave and moreover can be expanded as a superposition of two (a forward and a backward) plane waves.

Therefore plane wave basis functions are ideal for describing delocalized slowly varying electron densities, such as the valence bands in a metal; and indeed plane wave basis sets have primarily been used for periodic systems. Nevertheless they can also be used for molecular species by using a supercell approach, where the molecule is placed in a sufficiently large unit cell such that it does not interact with its own image in the neighbouring cells. Placing a relatively small molecule in a large supercell to avoid selfinteraction consequently requires many plane wave functions, and such cases are handled more efficiently by localized Gaussian functions. A three-dimensional periodic system, on the other hand, may be better described by a plane wave basis than with nuclear-centred basis functions. Notice that the set of the all possible plane-waves (with all possible momentum values) can be shown to be a complete set, and for this reason they can be used as basis set.

#### Pseudo-potentials or effective core potentials

Systems involving elements from the lower part of the periodic table have a large number of core electrons. These are unimportant in a chemical sense, but it is necessary to use a large number of basis functions to expand the corresponding orbitals, otherwise the valence orbitals will not be properly described. This issue can be solved by modeling the core electrons by a suitable function, and treating only the valence electrons explicitly. The function modeling the core electrons is usually called an Effective Core Potential (ECP) in the chemical community, while the physics community uses the term Pseudopotential (PP). These terms results sometimes useful in understanding the principles behind some semi-empirical methods. A good treatment is again provided in [98].

# 3.6 The Extended Hückel theory and semi-empirical methods

In this section one of the most widely spread semi-empirical method, for the electronic structure calculation, in briefly addressed, namely the Extended Hückel Theory (EHT). Since it is a semi-empirical method the first part of this section is dedicated to an introduction to semi-empirical methods.

#### 3.6.1 The semi-empirical approach

As mentioned in section 3.5.4, the computational cost of performing an HF or a DFT calculation scales formally as the fourth power of the number of employed basis functions  $\{\phi_{\alpha}\}_{\alpha}$ . This arises from the number of integrals (especially the so called two-electrons integrals - see below) that are required for building the matrix form of quantum mechanical operators (see section 2.4). Semi-empirical methods reduce the computational cost by reducing the number of these integrals.

The first step in reducing the computational problem is to consider only the valence electrons explicitly (the ones in the outer shells that origin the chemical bonds and determine the main chemical-physical properties). The core electrons are accounted for by reducing the nuclear charge or introducing suitable functions for accounting them, that are not part of the basis set. To this purpose see also previously section 3.5.4, the part about the pseudo-potentials PP (or Effective Core Potential -ECP-), that are exactly the functions mentioned above. Furthermore, only a minimum basis set (the minimum number of functions necessary for accommodating the electrons in the neutral atom) is used for the valence electrons (to this purpose see again section 3.5.4). The large majority of semi-empirical methods to date use only *s*-type and *p*-type basis functions, and they are usually of Slater type orbitals (again refer to section 3.5.4), i.e. exponential functions.

The central assumption of semi-empirical methods is the Zero Differential Overlap (ZDO) approximation, which neglects all products of basis functions that depend on the same electron coordinates when located on different atoms. To be clearer, said  $\psi_i$  the *i*-th molecular orbital, it is expressed in terms of the basis set  $\{\phi_{\alpha}\}_{\alpha}$  (the atomic orbitals) as follows:

$$\psi_i = \sum_{\alpha} c_{\alpha} \phi_{\alpha}$$

Then said an atomic orbital on centre A as  $\phi_A$  and an atomic orbital on centre B as  $\phi_B$ , the ZDO approximation corresponds to  $\phi_A \phi_B = 0$ . Note that it is the product of functions on different atoms that is set equal to zero, not the integral over such a product. The consequences of the ZDO approximation are [98]:

- The overlap matrix S is reduced to a unit matrix: I
- One-electron integrals involving three centres (two that come from the basis functions and one from a quantum mechanical operator) are set to zero (these are product of the kind  $\langle \phi_A | \hat{F} | \phi_B \rangle$ , where  $\hat{F}$  is the quantum mechanical operator)
- All three- and four-centre two-electron integrals are neglected. These integrals come out in doing the calculations (in building the so called Fock matrix), and corresponds to products of the kind  $\langle \phi_A \phi_B | \phi_C \phi_D \rangle$

To compensate for these approximations, the remaining integrals are made into parameters, and their values are assigned based on calculations or experimental data or from other more accurate theoretical calculations [104]. Exactly how many integrals are neglected, and how the parameterization is done, defines the various semi-empirical methods. The following approximations are done possible:

- Neglect of Diatomic Differential Overlap (NDDO): in this approximation there are no further approximations than those mentioned above. The overlap matrix becomes:  $S_{mn} = \langle \phi_m | \phi_n \rangle = \delta_{mn} \delta_{AB}$ , where  $\delta$  indicates the Kronecker delta. Thus  $S_{mn}$  is null each time different basis functions are considered  $m \neq n$  but also each time different atom centers are considered  $A \neq B$ .
- Intermediate Neglect of Differential Overlap (INDO): in this approximation all twocentre two-electron integrals that are not of the Coulomb type, in addition to those neglected by the NDDO approximations are neglected.
- Complete Neglect of Differential Overlap (CNDO): in this approximation also the the one-centre two-electron integrals are neglected. Instead the approximations for the one-electron integrals in CNDO are the same as for INDO.

The important point to keep in mind is that all semi-empirical method assume the ZDO approximation (that is the NDDO), and then that successive approximation are possible,

and passing from NDDO, to INDO and to CNDO the approximations are worse, that means that more fitting parameters are present in that method. Fitting parameters that compensate for the neglected integrals and are used to represent the (few) integrals that are performed. Again fitting parameters that are derived from experimental data. Many different versions exist today, and they differ in the exact way in which these parameters are derived. Some of the names are CNDO/1, CNDO/2, CNDO/S, CNDO/FK, CNDO/BW, INDO/1, INDO/2, INDO/S and SINDO1. And moreover better performances are generally obtained with the following methods: MINDO, Modified NNDO, MNDO, AM1, PM5, etc...

Typical errors in semi-empirical methods are nowadays only slightly greater than the average DFT ones. For example typical errors on bond lengths are of the order of  $10^{-2} \div 10^{-3}$  Å, errors on angles of few degrees.

#### Semi-empirical methods performances

It is possible to show that semi-empirical methods formally scale as the cube of the number of basis functions in the limit of large molecules [98]. For this reason the current limit of semi-empirical methods at around 1000 atoms [98].

Semi-empirical methods share the advantages and disadvantages of force field methods: they perform best for systems where much experimental information is already available but they are unable to predict totally unknown compound types. Nevertheless, the dependence on experimental data is not as severe as for force field methods. Once a given atom has been parameterized, all possible compound types involving this element can be calculated.

Semi-empirical methods are zero-dimensional, just as force field methods are. There is no way of assessing the reliability of a given result within the method. This is due to the selection of a minimum basis set. The only way of judging results is by calibration, i.e. by comparing the accuracy of other calculations on similar systems with experimental data.

Notice that semi-empirical models provide a method for calculating the electronic wave-function, which may be used for predicting a variety of properties, e.g. the molecule polarization. Nevertheless from *ab initio* calculations that good results require a large polarized basis set including diffuse functions, and the inclusion of electron correlation, that are not considered in semi-empirical methods. Depending on the specific application the semi-empirical results can also be accurate. In this sense the result should be somehow validated by comparison with experimental data or more accurate *ab initio* approaches, as already mentioned above.

Generally semi-empirical methods, like force field ones, are not at all suitable for accurate estimations of molecule energy levels or for molecular geometry optimization, unless some modifications are considered. They instead are very computationally efficient and find applications in many fields in which qualitative results are enough.

#### 3.6.2 The EHT method

The extended Hückel method (EHT) is a semi-empirical LCAO method, which exploits all valence orbitals of the atoms as the basis functions. Contrarily to the original Hückel method, the extended one takes into account not only  $\pi$ -orbitals but also  $\sigma$  ones. These atomic orbitals are approximated with Slater Type Orbitals (STOs) which allows the overlap matrix  $S_{ij}$  to be calculated efficiently. As already mentioned (see section 3.5.4), the STOs are orbitals characterized by having a blunt exponential decay centered in the atom nuclei. In this way, by using this basis set, the matrix elements can be defined by very few parameters. In particular, the matrix elements of the Hückel Hamiltonian are described by the following equation [105]:

$$H_{ij} = \begin{cases} -E_i, & \text{if } i = j \\ \frac{c}{2}S_{ij}(H_{ii} + H_{jj}), & \text{if } i \neq j \end{cases}$$
(3.12)

where the diagonal elements (i = j) of the Hamiltonian are approximated with the valence orbital ionization energies  $E_i$ , taken either from experimental data or calculated by means of more advanced methods. The off-diagonal elements  $(i \neq j)$  are proportional to the overlap of the *i*-th and *j*-th orbitals weighted by a constant c that is usually taken equal to 1.75. Thus, given a molecular geometry, the overlap matrix and thereafter the Hamiltonian can be calculated.

Several variants are possible, but often the overlap integrals are actually calculated, i.e. the ZDO approximation is not invoked. It is possible having EHT methods with NDDO, INDO or CNDO. If the CNDO approximation is assumed, performances may be limited since it does not take into account electron-electron repulsive interactions.

Usually EHT methods are non-iterative. Since the diagonal elements only depend on the nature of the atom (i.e. the nuclear charge), this means for example that all carbon atoms have the same ability to attract electrons. But in general, it is unlikely that all carbon atoms have the exact same charge, i.e. owing to the different environments their ability to attract electrons is no longer equal. In order to overcome this drawback self-consistent EHT calculations can be performed. Such methods are called self-consistent (or charge-interaction) Hückel methods, and in these methods the matrix elements are modified by the calculated charge.

The main advantage of extended Hückel theory is that only atomic ionization potentials are required, and it is easily parameterized to the whole periodic table. Extended Hückel theory can be used for large systems involving transition metals, where it often is the only possible computational model [98]. Moreover in many cases show the correct trend for geometry perturbations corresponding to bond bending or torsional changes, and thus qualitative features regarding molecular shapes may often be predicted or rationalized from EHT calculations [98].

In summary, this approach requires only a fraction of the computational effort needed by the more elaborated *ab initio* methods and often provides reasonably accurate quantitative results that give insight into the essential physics (or chemistry) [106], [105].

Finally notice that recent work in this area has used an approach to parameterize against density functional results, thereby providing a computationally very efficient model capable of yielding fairly accurate results [98].

# 3.7 Intermolecular interactions

In the practical part (part II) of this work I will consider gas sensor applications. The structure will be mainly the one of a molecular wire, and depending on the presence of a target molecule in proximity to the sensor, the conductance of the molecular channel will be changed. The physical principle of the device is thus linked with weak intermolecular interactions, such as the van der Waals ones, that modify the channel molecular orbitals such that the transport is significantly changed. The aim of this section is to provide a review of the van der Waals intermolecular interactions and to briefly highlight how to consider them in a electronic structure calculation (mainly considering the DFT approach).

# 3.7.1 van der Waals and intermolecular interactions

In order to review the van der Waals forces it is better to firstly review briefly the different kinds of chemical bonds and chemical interactions between atomic elements. References can be [107], [108].

Valence electrons in atoms (i.e. the electrons in the most external shells of an atom) are those that generate the chemical bonds, and give rise to many chemical-physical properties of the considered element. Accordingly with Lewis theory, these electrons are those belonging to an incomplete octet, and the chemical bonds arise for the attempt of completing it. Covalent bonds are created between atoms with enough high electronegativity, in these kind of chemical bonds each atom provide one electron, such that two electrons are shared between them and constitute the bond. Covalent bonds can be pure (between atoms of the same element) or polar (between atoms of different elements). Moreover it can also be dative if a single atom provides both the electrons, and a double covalent bonds if two pairs of electrons are provided. Analogously a triple covalent bond involves three pairs of electrons. The triple is stronger w.r.t. the second that is stronger w.r.t. to the simple covalent one. This means that a greater amount of energy (binding energy) should be provided to break a triple bond w.r.t. a second one, and moreover the bond length of the triple will be lesser than the one of double (all analogous between double and simple bond). The covalent bond length is of the order of  $1 \div 2$  Å. Moreover ionic bonds are also possible, usually if the electronegativity difference between the two element is greater than 1.9. In this case an element provides one or more electrons to the other, and both becomes ions (positive ion the first one and negative the second one). The donor atom is called cation while the other is called anion. The ionic bond is the result of the electrostatic interaction between the two ions. It is usually the weaker among the mentioned bonds, but it is stronger than intermolecular interactions. Notice that usually a "clean" ionic bond is not possible and instead there is "a bit" of electron sharing between the anion and the cation.

In addition to these bonds it is possible to have also intermolecular interactions, i.e. physical-chemical interactions among molecules. Different molecules can undergo to attractive (or also repulsive) interactions. The intermolecular interactions are four in total:

the hydrogen bond and the van der Waals forces, that are in number three since they includes three different cases. These are at the origin of chemical bonds in hydrogen-bond solids and molecular solids respectively. Notice that they are weaker than intramolecular bonds described above (i.e. their binding energy is lower).

#### Hydrogen bond

The hydrogen bond is a particular case of electrostatic dipole-dipole interaction. It is formed between molecules in which an hydrogen atom is covalently bond with an atom with high electronegativity (and small dimensions), typically fluorine, nitrogen and oxygen. Due to the high electronegativity the electron has more probability of being found nearby the higher electronegativity atom. This means that its wave-function or orbital (the molecular orbital or the electron cloud) is spatially deformed toward the more electronegative atom. Consequently the molecule present a permanent electric dipole, with a small negative charge  $\delta^-$  close to the high electronegative atom and a small positive charge  $\delta^+$  close to the hydrogen atom. An example can be the water molecule  $H_2O$ . Because of this permanent electric dipole different molecules can be bond together, due to the electrostatic interaction. Thus there is the formation of weak (if compared to the above intramolecular bonds such as the covalent bonds) chemical bonds between the hydrogen atom of one molecule and the electronegative atom (e.g. F, N, O) of another molecule. Its binding energy is of the order of  $20 \div 50 \text{ kJ/mol}$ , and notice that this value is comparable (or even less!) with the typical errors of the DFT methods reported in figure 3.2 (b). This means that for these kind of weak interactions such a methods are not suitable, and indeed corrections must be used (as described below - subsection 3.7.3). The origin of this interaction is (in a semiclassical picture as the one just provided) an electrostatic interaction between two electrical dipoles. The fact that the hydrogen atom is very small, and the fact that it contains only one electron (thus there are no electrons that can somehow screen the electric field and thus the interaction) make the hydrogen bond particularly intense w.r.t. other intermolecular interactions (van der Waals), thus making the binding energy particularly high. Because of the reasons just mentioned this kind of intermolecular interaction is particularly important, and since it is possible only with hydrogen atoms it is called hydrogen bond. Notice that the hydrogen bond is directional (like the covalent bonds). Finally notice that it is possible to have hydrogen bonds even within the same molecule (if the molecule is large, i.e. made by an enough number of atoms), usually it happens between different functional groups composing the molecule.

#### van der Waals forces

Intermolecular interactions (i.e. interactions among molecules) are attractive or repulsive forces that mediate the interaction between molecules, they can occur between both polar and non-polar molecules. They have again an electrostatic nature, and they are usually referred as van der Waals forces. Intermolecular interaction (or binding) energy is very low ( $0.1 \div 10 \text{ kJ/mol}$ ) if compared with covalent or ionic bonds ( $100 \div 1000 \text{ kJ/mol}$ ), moreover the interaction distance is usually short (of the order of 4 Å) and the strength of interaction decreases rapidly with distance. The van der Waals forces are responsible of several interesting chemical and physical properties of materials, especially in changes of the state of aggregation of matter (solid to liquid, liquid to gas and vice versa). The van der Waals forces (named after the Dutch physicist Johannes Diderik van der Waals) include actually three different types of interactions:

• Keesom's interactions:

The Keesom interactions involve permanent dipoles. They result from the interaction of a permanent dipole with another permanent dipole. Indeed it is possible to have an electric permanent dipole in a polar molecule, and as already mentioned this may happen if there is one (or more) atom with a significantly higher value of electronegativity w.r.t. to the others composing the molecule. In this case the electron(s) has an higher probability of being found close to the high electronegativity atom, creating a (small) negative charge  $\delta^-$  around it. Consequently a (small) positive charge  $\delta^+$  is induced around low electronegativity atoms. As known from basic physics an electrical dipole generates an electric field that allows the polar molecules to interact. In particular in nature there always the trend of achieving a stable configuration (if no external stimuli are applied), that coincides with the achievement of the thermodynamic equilibrium (i.e. minimum potential energy configuration). If many permanent dipoles are present in the same volume one close to the other then they will align with opposites poles (i.e.  $\delta^+$  and  $\delta^-$ ) close the one to the other. Usually Keesom's interactions are negligible in gases due to the high kinetic energy of particles that allows for overcome the Keesom's interaction energies. Notice that it is also possible that the permanent dipoles have a different origin from the one specified above, for example they can be due to the presence of molecular ions or molecular multipoles (nevertheless the treatment does not change).

• Debye's interactions:

This kind of interaction occurs between a polar and a non-polar molecule. If a nonpolar molecule undergoes to an electric field then the electron clouds (or molecular orbitals) are distorted. Indeed the electrons have the inclination to go in opposite direction to the field. As a result the molecule is temporarily polarized. Thus an induced dipole is created. The same effect is obtained if a polar molecule is nearby the non-polar one. In that case opposite charges are attracted and the non-polar molecule results polarized, until the distance between the two molecules is not so big to make the interaction negligible. The intensity of the interaction is of course proportional to the strength of the permanent dipole of the polar molecule.

• London's interactions:

These interactions occur between a fluctuating dipole and an induced dipole. Indeed non-polar molecules can instantaneously become polar, due to motion of the electrons around the nuclear centers. Usually in a (neutral) atom the electron cloud is symmetric w.r.t. to the nucleus, nevertheless for short time intervals the electrons can be localized in a certain region of space giving rise to an instantaneous electrical dipole. This is called fluctuating dipole. Again the instantaneous electric field that is generated by this dipole can have effects on another atom/molecule nearby this one, originating an induced dipole. In response to the induced dipole the first atom/molecule can change its configuration, such that the total potential energy of the system is minimized. This means that opposite charges are attracted to the same side (as explained previously). Nevertheless this can have again effects on the induced dipole that can change again orientation (passing in between the neutral configuration). This mechanism is at the basis of the London interactions. The London interaction strength increases with the molecular molar mass.

It is possible to derive classical expressions for the Keesom, the Debye and the London interactions (not reported since non-relevant for the quantum mechanical treatment - see next section 3.7.2). Moreover all the intermolecular interactions are anisotropic, that means that they depend on the relative orientations of the involved molecules. This is obvious if their physical origin (above) is considered.

Notice that it is possible to have other intermolecular interactions, not included in the van der Waals one. Nevertheless they all have essentially an electrostatic origin. In particular it is possible to have ionic bonds/interactions between molecules. The principle is analogous to the one of ionic bonds reviewed before: a molecule (or a functional group) provides all the electrons of the bond (and becomes the cation) while the other is the anion. In addition other kind of dipole–dipole interactions are possible between molecules which have permanent dipoles. Also ion–dipole and ion–induced dipole interactions are possible. Notice that generally in the latter case ions are involved, giving rise to forces that are stronger than dipole–dipole interactions because the charge of any ion is greater than the charge of a dipole moment.

A mention is also due to the so called steric effects [107], [108]. They are non-bonding interactions that influence the shape (conformation) and reactivity of ions and molecules. Notice that steric effects result from repulsive forces between overlapping electron clouds. An example can be the real shape of benzene molecule that is non-planar, this because the repulsive forces between electrons (that correlate their motion to avoid each other) cause it to deform and assume the so called chair-like shape (bent instead of planar). These effects are in great majority again a consequence of electrostatic interactions and correlation between electrons.

Nevertheless the point that now should be clear is that all these kinds of interactions have essentially an electrostatic origin. For this reason they all have the same quantum mechanical treatment, that in practice is very simple: all these kind of interactions are automatically included in the considered system Hamiltonian (to this purpose refer also to the next section 3.7.2). Indeed once the geometry is chosen the Hamiltonian can be built following the methods described in the previous sections of this chapter, and the wave-functions satisfying the steady state Scrhödinger's equation are automatically accounting for all these effects, that indeed appear within the Hamiltonian as potential energy contributions, either relative to electron-nuclei interactions or to electron-electron interactions. Notice that choosing the geometry means to fix and optimize it by means of an optimization procedure aimed in minimizing the potential energy in order to obtain the equilibrium configuration. The problem in modeling all the intermolecular interactions is the fact that they have small interaction energies (van der Waals forces are of the order of  $0.1 \div 10 \text{ kJ/mol}$ ), that are often below or of the order of the root means square or maximum deviation errors of the DFT and the EHT methods (refer to figure 3.2 to have

an idea). This means that some kind of corrections are needed, and they are the subject of the next sections (refer especially to section 3.7.3).

# 3.7.2 Quantum modeling of intermolecular interactions

So far the classical models for intermolecular interactions were briefly reviewed. As mentioned, intermolecular forces between two molecules or atoms can be attractive or repulsive and occur from either momentary interactions between molecules (e.g. London dispersion force) or permanent electrostatic interactions between dipoles. The aim of this section is to point out how they are modeled with the quantum mechanical approach.

It was already noticed at the end of the previous section that the origin of intermolecular interactions is essentially the electrostatic attraction or repulsion between permanent or momentary dipoles or charges. Moreover it was highlighted that they result from the (both static and dynamic) geometry of the wave-functions, in the sense that the shape of the electron cloud and the electron correlation can somehow influence the interaction. Think for example to steric effects or to the deformation of the electron cloud due to the proximity of a charge/dipole/molecule. As already mentioned all these interactions are somehow already included within the molecular Hamiltonian.

The standard analytical approach for considering intermolecular interactions is by means of the so called Rayleigh-Schrödinger perturbation theory [109]. In this model the (weak) intermolecular forces are treated by means of a perturbational approach. In particular the total system Hamiltonian (for example of the system of two interacting molecules) is written as the sum of an unperturbed Hamiltonian and a perturbative term. In the case of two interacting molecules the first term is the sum of the two equilibrium (and unperturbed) molecular Hamiltonians, while the latter if the contribution considering the interactions between them. Once the total system Hamiltonian is known it is possible to proceed as usual in solving the Schrödinger's equation. Since it is a perturbative approach it holds true if the intermolecular interactions are weak w.r.t. to intramolecular ones (that are e.g. covalent bonds), and from the above discussion it is known that this hypothesis is usually true (van der Waals interactions for example involve energies in the range  $0.1 \div 10$ kJ/mol much lesser than covalent/ionic bonds  $100 \div 1000$  kJ/mol). This approach allows for evaluating the intermolecular forces, and it can be useful in considering them in wavefunction based methods like electron-correlation (post-HF) methods presented previously (see section 3.7), e.g. the Møller–Plesset Perturbation theory based methods [109]. A remark on the so called dispersion forces will be useful in the next section 3.7.3. Long-range intermolecular forces, also known as London or dispersion forces (see previous section 3.7.1), are well represented by the Taylor's second order expansion of the perturbative term. This procedure leads to an attractive potential with a leading term of the kind:  $-C_6 R^{-6}$  (where  $C_6$  is a constant and R is the distance). The classical explanation for this term was already provided in the previous section 3.7.1, and it involves the creation of temporary dipoles. London coined the name "dispersion effect" (from which the name "dispersion forces" or "London forces") for the attraction between noble gas atoms after he noted the presence of aforementioned terms that appeared in the equations for the intermolecular interactions, and that were analogous to oscillator strengths.

Other methods that include a perturbative approach in modeling of intermolecular interactions can be other electron-correlation methods (like the coupled cluster one) or the Quantum Monte Carlo (QMC) one.

Nevertheless all such electron correlation methods and the QMC one, have the great disadvantage of being unusable for large systems with more than few tens of atoms (let's say 50 atoms). Nevertheless a complete device, for example a molecular wire or transistor, can widely overcome that limit, also because the contacts should be considered as atomistic in order to make plausible predictions. For this reason DFT or semi-empirical methods are usually preferred. In such methods it is possible to consider intermolecular interactions by means of the so called "supermolecular approach". It is referred to all quantum chemical standard methods (e.g. DFT, EHT, etc...) that include some kind of correction aimed in modeling intermolecular interactions. Notice that the electron correlation should be considered in these approaches in order to get reliable results (especially for dispersion/London forces) [109], [110]. An important issue in supermolecular approaches is the basis of one molecule improves the basis of the other molecule, and it can give rise to artifacts, since the intermolecular interactions are distance dependent (see e.g. the above result on London forces). More details are provided in the next section.

# 3.7.3 Supermolecular approach and DFT corrections

The way of accounting for intermolecular interactions in electron correlation methods was briefly mentioned in the previous section. This section instead briefly introduces the supermolecular approach. Such an approach consists in introducing suitable corrections to both DFT and semi-empirical methods in order to account for intermolecular interactions (like hydrogen bond, van der Waals and London dispersion forces). It found recently applications in accurately predicting some large supramolecular complexes or bio-macromolecular geometries such as the simulation of protein folding [110].

Different methods (namely HF, DFT, and semi-empirical) are now considered and it is mentioned how to consider intermolecular interactions within them. A comparison among them is also proposed. The material of this section is mainly adapted from [110].

Hartree–Fock method can provide an adequately accurate for hydrogen-bonding interactions (with, however, significant underbinding) in some organic compounds. Nevertheless it fails spectacularly for considering dispersion (London) in bound complexes. A dispersion corrected Hartree–Fock method (the HFD method) was proposed [110], but it has important limits and thus the DFT-based methods are usually considered much better in terms of performance with comparable computational performances.

Traditionally, it has been generally believed that semi-empirical methods are not particularly well suited to hydrogen bonding problems [110]. Some semi-empirical methods have been re-parameterized and additional empirical terms were added to increase the accuracy for describing weak intermolecular interactions [110]. Others instead adopt some of the below mentioned DFT-D corrections in the semi-empirical environment [110]. In general is a good practice to consider unreliable a semi-empirical method for accurate estimation of weak intermolecular interactions, unless it is not "validated" for the specific case of interest by means of comparisons with experimental data or DFT methods (or more refined *ab initio* methods).

The situation is even worse for molecular mechanics (force fields) based methods. They are not generally high accuracy methods, even if the presence of many accurate experimental data can give good values for fitting parameters and thus fair results, but only in specific particular cases.

Instead DFT-based methods allow for the usage of corrections to consider electron correlations and weak intermolecular approaches that usually lead to very good results sometime comparable with the ones of post-HF or perturbative methods [110]. In general LDA accuracy can only be described as sporadic, and therefore its application in intermolecular interactions is not recommended. GGA functionals typically show repulsive behavior for dispersion bound complexes similar to Hartree–Fock method, with the corrections mentioned below they provide good results. Meta-GGA functionals show only marginal improvements over the GGA ones, while some hybrid-GGA functionals give reasonable answers for particular problems of interest, but should be used with extreme caution [110]. The main available DFT corrections for intermolecular interactions are:

• DFT-D (Grimme-D2 / Grimme-D3):

These class of corrections include empirical methods to account for dispersive interactions in practical calculations within the DFT framework. They were tested for a wide variety of molecular complexes resulting in good predictions. For example for stacked aromatic systems the DFT-D (BLYP) model seems to be even superior to standard perturbative approaches. The good results obtained, in a variety of diverse examples [110], suggest that the DFT-D approach is a practical tool for describing weak intermolecular interactions [110]. The dispersive energy is described by a damped interatomic potential of the form  $-C_6R^{-6}$  (see previously section 3.7.2). This simple approach has recently been improved regarding accuracy introducing less empiricism with the so called DFT-D2 (or Grimme-D2) model [110]. In particular in this new version the most important parameters (like R and  $C_6$ ) are computed ab *initio*, and general applicability to most elements of the periodic table was proved. An important change is present in the so-called DFT-D3 (or Grimme-D3) method [110], in which the  $C_6$  dispersion coefficients are dependent on the molecular structure which accounts for subtle effects, e.g., the hybridization state of an atom changes. The DFT-D methods do not only work for molecular complexes and intramolecular dispersion effects but are rather general [110].

- Range Separated and Dispersion Functionals (vdW-DF): In this method the non-local correlation is calculated explicitly in a non-empirical manner[110]. It is typically used with standard GGAs like PBE. The overall quality of wdW. DE results for tuning her complete completes is not better then with DET. D but
- vdW-DF results for typical non-covalent complexes is not better than with DFT-D but this method has the great disadvantage of requiring substantially more computation time (w.r.t. DFT-D ones).
  Dispersion Calibrated Effective Potentials (DCEP):
- It is a novel approach whereby the missing dispersion effect in traditional DFT methods is introduced using a suitably engineered effective core potential (ECP see also section 3.5.4).

In the practical of this work (part II) the first correction, namely the DFT-D (in its Grimme-D2 and Grimme-D3 verions) will be used for modeling molecular electronic gas sensors.

Important considerations concern the basis set. The electron density around one nucleus may be described by functions centred at another nucleus. This is especially troublesome when calculating small effects, such as energies of van der Waals or intermolecular interations or even hydrogen bonds, as explained in a while. It was said in section 3.5.4 that a complete basis should include an infinite number of basis functions and this is of course impossible. Moreover in order to have accurate results a great number of basis functions should be consider, but again this is often unfeasible in practice, due to the fact that the computational effort increases as the fourth power of the number of chosen basis functions. Thus the truncation of the basis set leads inevitably to an error (in particular an overestimation of the energy levels is often obtained). Usually the interest is in relative energies, e.g. ratio between energy levels, thus these errors are not so relevant in many practical cases (even if absolute errors are large -e.g. hundreds of kJ/mol- the relative ones are not). A balanced basis set (as mentioned in section 3.5.4) is able to provide a (more or less) constant error, thus leading to small relative errors (on ratio of energies). Moreover fixing the position of the basis functions to the nuclei allows for a compact basis set [98], otherwise sets of basis functions positioned at many points in the geometrical space would be needed, leading to a too large number of basis functions for practical implementations. When comparing energies at different geometries, however, the nuclear fixed basis set introduces an error, because as mentioned previously the various basis functions overlap in the nuclei. To better visualize the problem let's consider two water molecules. They may give rise to an hydrogen bond, and its energy can be estimated for example by considering the total energy of the system of two water molecules to which it is subtracted two times the energy of the single water molecule. Nevertheless different nuclear geometries leads to different superposition of the basis functions, thus different overlap errors, and in particular with more nuclei the basis set results improved because of basis functions overlap in the nuclei that lead to a whole amelioration of the completeness of the basis set (it is thus "more complete" than the basis set of the single water molecule). Consequently the system of two water molecules will have a more realistic energy w.r.t. to the isolated water molecules, that is a lower energy (the basis set truncation error results in an increase of the energy levels, since now a "more complete" basis set is used this truncation error is lesser and the energy is lower). And thus an overestimation of the hydrogen bond energy occurs, but it is wrong. This effect is known as the Basis Set Superposition Error (BSSE). In the limit of a complete basis set, the BSSE will be zero, and adding more basis functions will not give any improvement. The conceptually simplest approach for eliminating BSSE is therefore to add more and more basis functions, until the interaction energy no longer changes (that is: the two molecules basis set is no "more complete" than the single molecule one). Unfortunately, this requires very large basis sets and is unpractical. Mainly two corrections for BSSE are possible, namely the chemical Hamiltonian approach (CHA) and the Counterpoise (CP) correction. In the first case the basis functions mixing is prevented a priori in the way in which the Hamiltonian is built. In the latter the BSSE is reduced by re-performing all the calculations with the mixed basis set (in the previous example in the case of two water molecules). The two methods tend to give similar results [98].

In conclusion to this section, few recommendations are cited from [110]:

- Whenever possible, approximate methods (force field, semi-empirical or HF) that are unavoidable in many practical applications should be checked or benchmarked against large (or complete) basis set results or experimental/*ab initio* more accurate methods.
- Electron correlation or post-HF methods work fine but are feasible only for small systems (<50 atoms)
- When the issue of London dispersion interactions is carefully considered within DFT, this yields a similar or often even better performance than electron correlation or post-HF methods. The DFT-D method has proven as an accurate and robust computational tool. The main advantage of DFT-based approaches is that they can be applied also in electronically complicated situations (e.g. a complete molecular electronic device).
- The biggest problem in DFT is the choice of the functional approximation. Computationally cheap (meta-)GGAs (e.g., BLYP, PBE, or TPSS) can be recommended. The currently highest level of approximation in DFT is represented by double-hybrid functionals (e.g. B3PLYP) that also perform very well for non-covalent interactions, even if they should used carefully in some particular situations (see previous discussion).
- Semi-empirical methods (and this also holds for many force fields) mainly suffer from a poor description of the electrostatic interactions which is demonstrated by their notoriously bad performance for hydrogen-bonded systems (for which even the simplest GGAs work very well). Because also their description of polarization (induction) contributions to binding is deficient, these methods can only be recommended for non-polar systems or alternatively employed after a careful benchmark validation is provided.

# Chapter 4

# An introduction to transport in molecular devices

In the introductory section 1.1 it was briefly introduced the concept of molecular electronics, in which single molecules (or small packets of them) are exploited to create whatever electronic device. Then in section 1.2 the definition of molecular electronic sensors and their working principle were briefly introduced, only qualitatively. The purpose of this chapter is provide an overview of the transport features in such systems, while a rigorous introduction to transport is left to the next chapter. In section 4.1 an oversimplified model for transport through single molecule devices, or more generally through quantum dots (i.e. zero-dimensional systems), is provided. It is useful to catch the main physical insights of transport features in quantum dots. In section 4.2 it is introduced the concept of mesoscopic systems, to which quantum dots (and molecular) devices usually are considered to belong. In section 4.3 is very briefly addressed the Landauer-Büttiker transmission formalism for transport in mesoscopic systems. It is useful in a deeper understanding of the simple transport model presented in section 4.1, and in understanding some of the features of the more advanced Non-Equilibrium Green's Function (NEGF) formalism. The purpose of section 4.5 is to provide an introductory overview of the advantages of using the NEGF formalism for modeling transport in mesoscopic systems (while the formalism is presented in the next chapter).

# 4.1 A simple model for transport through quantum dots

The aim of this section is to provide an oversimplified model for the transport through quantum dots, i.e. zero-dimensional (0D) systems. Such a model is the one presented in the course "Micro & nano systems", taught at Politecnico di Torino during the academic year 2018/2019 by professors Mariagrazia Graziano and Gianluca Piccinini. It is analogous to the "toy model" introduced in the first chapter of [89], and moreover it is essentially the

same of the model presented in [90], exactly concerning the transport through quantum dots. In this section I will adopt the notation used in the above mentioned "Micro & nano systems" course, that can be slightly different from the ones of [89] and [90]. Even if this model is very simplified, the main physical insights of electronic transport in quantum dots can be easily understood, also in a quantitative way. For this reason I think it can be a useful preparatory treatment, before entering into the details of the more complete Non-Equilibrium Green's Functions Formalism (subject of next chapter).

A quantum dot, or zero dimensional system, is a system in which quantum confinement occurs in all the three spatial directions. Molecules can be thus thought as quantum dots (indeed electrons are confined within the molecule in all directions). A feature of quantum confinement is the arising of quantization, e.g. in energy levels. To this purpose one can think to a 3D quantum well, like presented in section 2.3.7 (the parts about the finite and the infinite height quantum wells). A first approximation can be the so called "bounding box" approximation. In which the quantum dot is though to be 3D infinite height quantum well with zero potential (i.e. flat potential) inside it. This is a strong simplification, but it is useful to highlight the discrete nature of energy levels inside the quantum dot. Indeed by proceeding as already done in section 2.3.7, and thus exploiting the separation of variables, and supposing  $L_x = L_y = L_z = L$  it follows (see equations (2.71), (2.72), (2.67)):

$$E = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad , \quad n_x, \ n_y, \ n_z \in \mathbb{N} \setminus \{0\}$$
$$\psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(n_x \frac{\pi}{L}\right) \ \sin\left(n_y \frac{\pi}{L}\right) \ \sin\left(n_z \frac{\pi}{L}\right)$$

that holds true if U(x, y, z) can be written as the sum of three independent contributions: U(x, y, z) = U(x) + U(y) + U(z). This is an oversimplification and it is wrong for molecules. The correct way of obtaining the energy levels (energy eigenvalues) of a molecule is to employ one of the methods described in the previous chapter 3. Anyway the important point is that a quantum dot, both in the oversimplification (and absolutely inaccurate and wrong) assumption of being a 3D infinite height quantum well, both in more accurate approximations (like the ones discussed in chapter 3), is a system characterized by discrete energy levels, due to quantization phenomena in all the three directions. Thus the electrons are not free to move in no direction, and they result confined. Nevertheless, it is possible to place a quantum dot in between two contacts and to have a current flowing between them. But as will be discussed in while, the current-voltage characteristics of such a system will have peculiar features, typical of 0D systems only, arising, precisely, from quantum confinement.

For the moment let's consider a quantum dot characterized by having a single energy level, denoted with  $E_L$ , placed in between two contacts (namely the source and the drain). Moreover it is assumed to have a strong coupling between the two contacts and the single-level quantum dot. This means that a strong chemical interaction is present, e.g. a covalent bond. Consequently electrons have no difficulty in passing from contacts to dot and vice versa. Indeed the electron wave-function at contact-dot interface (because of the presence of the chemical bond) envelopes both atoms in the contacts and in the dot/molecule, such that the electrons populating that orbitals have high probability of being localized both in the dot and in the contacts, making easy the passage between the two. If not so, it is said that the dot is weakly coupled to the contacts. The latter case corresponds to wave-functions that are not delocalized, thus making difficult for the electrons being exchanged between the contacts and the dot (since they are localized either inside the dot or the contact). In this case the electrons are required to "jump" from the contacts to the dot and vice versa in order to have an electrical current. This is possible whenever the electrons change their state for some reason and go in another state, that in terms of wave-functions means: the electrons "jump" from a wave-function to another. These physical processes are referred as "sequential tunneling" (or hopping - see also chapter 6), in the sense that two completely uncorrelated tunneling phenomena are required to make the electrons "jump" from the source to the dot and then from the dot to the drain. Nevertheless, as mentioned above, it is now assumed that a strong coupling occurs between contacts and dot such that the electrons can easily be transferred between the two systems without changing state. This corresponds to have "coherent tunneling". i.e. a single tunneling process that allows electron to flow from source to drain passing through the dot. It is possible to think to this single tunneling mechanism as a single plane wave that "carries" the electron from the source to the drain passing through the dot (indeed within the contacts -periodic structures- Bloch waves exist, that are not much different from plane waves in principle).

It is assumed to have an applied voltage  $V_{DS}$ , and that the number of electrons that the single energy level  $E_L$  of the dot is hosting is equal to N (notice that N can be only 0, 1, or 2). Notice that (since the contacts are assumed to be in equilibrium -due to their huge dimension when compared to the dot- the Fermi levels within the contacts are constant and differ of quantity  $-qV_{DS}$ ). The energy level  $E_L$  is assumed to be within the so called bias window, i.e. in between the drain Fermi level  $E_{FD}$  and the source one  $E_{FS}$ .

Because of charge conservation at steady state the two net fluxes of electrons from the source to the dot  $\Phi_S = \Phi_{S,dot} - \Phi_{dot,S}$  and from the drain to the dot  $\Phi_D = \Phi_{D,dot} - \Phi_{dot,D}$  should compensate, giving rise to (see also figure 4.1):

$$\Phi_S = -\Phi_D \quad \Leftrightarrow \quad \Phi_{S,dot} - \Phi_{dot,S} = -\left(\Phi_{D,dot} - \Phi_{dot,D}\right)$$

Notice that charge conservation is in general a consequence of the matter conservation, indeed the previous equation corresponds in saying that all the electrons that enter the dot from the source, exit from the dot toward the drain (no electron is created or annihilated within the dot); that is in agreement with the assumption of having coherent tunneling from source to drain.

In order to write explicit expressions for the four fluxes of figure 4.1 one more concept is needed. As mentioned it is supposed to have strong coupling between the contacts and the dot. The quality of the contact-dot interfaces is represented by means of the contact intrinsic times. The contact intrinsic times can be defined as the average amount of time required to an electron to move from the contact (the source or the drain) into the dot or vice versa to move from the dot into the source/drain contact. They are indicated with  $\tau_S$  (referred to source) and  $\tau_D$  (referred to drain). The smaller is the intrinsic time the stronger is the coupling between that contact and the dot. Indeed a small intrinsic time indicates that the electrons can be easily moved between the contact and the dot,



Figure 4.1: Electron transport through a single level quantum dot. Four electron fluxes are considered:  $\Phi_{S,dot}$  from source to dot,  $\Phi_{dot,S}$  from dot to source,  $\Phi_{D,dot}$  from drain to dot,  $\Phi_{dot,D}$  from dot to drain. Two net fluxes are then defined: the net flux from source to dot  $\Phi_S$ , and the net flux from drain to dot  $\Phi_D$ . The *x*-axis is from source to drain, while the drain to source current is conventionally flowing from drain to source.

indicating a strong coupling. In addition it is possible to define two energies: the so called contact coupling factors as follows:

$$\gamma_S = \frac{\hbar}{\tau_S} \quad , \quad \gamma_D = \frac{\hbar}{\tau_D}$$

that are the source coupling factor  $\gamma_S$  and the drain one  $\gamma_D$ . Notice that they have dimensions of energy since they are equal the reduced Planck's constant over a time. As mentioned, the lower is the intrinsic time the stronger is the coupling to the contact, that in terms of coupling factors becomes: the greater is the coupling factor the stronger is indeed the coupling between the contact and the dot.

An important remark is due concerning these two concepts. The intrinsic time can be seen as the average time interval needed to an electron to "jump" from a contact into the dot. But as mentioned it can analogously be seen as the average amount of time needed to an electron to "jump" from the dot into the contact. Considering the latter statement the intrinsic time acquires the meaning of average lifetime of the electrons inside the dot. Indeed if every  $\tau_S$  (or  $\tau_D$ ) an electron escape from the dot to go into the source (or drain) contact, then from the standpoint of the dot every  $\tau_S$  (or  $\tau_D$ ) an electron disappears (annihilates). In this optics the coupling factors  $\gamma_S$  and  $\gamma_D$  can be interpreted as an uncertainty on the energy of such electrons. To this purpose see also section 2.2, in which the time-energy uncertainty relation  $\Delta E \Delta t \sim \hbar$  was discussed. Indeed the fact that an electron can stay within the dot (thus in the energy level  $E_L$ , or better in the state with energy  $E_L$ ) only for an (average) amount of time  $\tau_S$  (or  $\tau_D$ ) means that the exact value of the energy level of that state has an uncertainty (a standard deviation) equal to  $\gamma_S = \hbar/\tau_S$  (or:  $\gamma_D = \hbar/\tau_D$ ). If instead the uncertainty on the energy eigenvalue were null (no uncertainty on the energy level thus it is exactly known) then the lifetime should be infinite, that implies no exchange of electrons between the contacts and the dot (isolated dot, with  $\gamma_{S,D} = 0$  and  $\tau_{S,D} \to \infty$ ). An uncertainty on the energy level means a broadening of the energy level, that is no more known exactly but only within a range of values centered in  $E_L$  (standard value / variance). And since the stronger is the coupling, i.e. the stronger is the chemical bond, between the contact and the dot, the greater is the coupling factor, a strong coupling means also more broadening of the dot quantized energy levels. These topics will addressed again later.

At this point it is possible to write the expressions for the electron fluxes of figure 4.1. In general a flux of charged particles (electrons in this case) is given by the number of particles that pass through a given cross-section area (contact area) in the unit time. Here the flux can be considered as the number of electrons that pass from the contact to the dot (or vice versa) in the entire area (thus not per unit area, but like it was already integrated over the cross-sections) in the unit time. Thus the flux of electrons from the source to the dot is given by the number of electrons that pass from the source to the dot over the source intrinsic time  $\tau_S$ . the number of electrons that with a unique tunneling process (i.e. coherent tunneling process) can pass from the source to the dot is given by two times (spin degeneracy) the Fermi-Dirac function referred to the source Fermi level  $E_{FS}$  evaluated at energy level  $E_L$ :  $f_{FD}(E_L, E_{FS})$ . Indeed two is the maximum number of electrons that can be hosted in  $E_L$  in the dot, and thus is the maximum number of electrons that can flow from the source toward the dot. The Fermi function evaluated for energy equal to  $E_L$ provides instead the probability of occupation of the energy level  $E_L$  within the source (since it is supposed coherent tunneling this is also the probability of having tunneling from source to the dot). The time in which an electron on average "jumps" from the source to the dot is  $\tau_S$  and thus it is the unit time. Thus:

$$\Phi_{S,dot} = \frac{2f_{FD}(E_L, E_{FS})}{\tau_S} = 2\frac{\gamma_S}{\hbar} f_{FD}(E_L, E_{FS})$$

Instead the flux of electrons from the dot toward the source is given by the number of electrons hosted in the dot N over the average time at which electrons pass from the dot to the source,  $\tau_S$ :

$$\Phi_{dot,S} = \frac{N}{\tau_S} = \frac{\gamma_S}{\hbar} N$$

Analogous reasoning for the drain contact lead to:

$$\Phi_{D,dot} = \frac{2f_{FD}(E_L, E_{FD})}{\tau_D} = 2\frac{\gamma_D}{\hbar} f_{FD}(E_L, E_{FD}) \quad , \quad \Phi_{dot,D} = \frac{N}{\tau_D} = \frac{\gamma_D}{\hbar} N$$

The net fluxes are defined as incoming fluxes (figure 4.1), thus they are given by:

$$\Phi_S = \Phi_{S,dot} - \Phi_{dot,S} \quad , \quad \Phi_D = \Phi_{D,dot} - \Phi_{dot,D}$$

At steady state the sum of the two net fluxes must be zero, because of charge (or matter) conservation, as stated previously. Thus:

$$\Phi_S + \Phi_D = 0 \quad \Leftrightarrow \quad \Phi_{S,dot} - \Phi_{dot,S} + \Phi_{D,dot} - \Phi_{dot,D} = 0$$
159

From which it is possible to find the number of electrons N in the energy level  $E_L$ :

$$\Phi_{S,dot} - \Phi_{dot,S} = -(\Phi_{D,dot} - \Phi_{dot,D})$$

$$\rightarrow \quad \frac{\gamma_S}{\hbar} \left[ 2f_{FD}(E_L, E_{FS}) - N \right] = -\frac{\gamma_D}{\hbar} \left[ 2f_{FD}(E_L, E_{FD}) - N \right]$$

$$\rightarrow \quad N = \frac{2}{\gamma_S + \gamma_D} \left[ \gamma_S f_{FD}(E_L, E_{FS}) + \gamma_D f_{FD}(E_L, E_{FD}) \right]$$
(4.1)

Once that N is known it is possible to write an expression for the electrical current flowing from drain to source. Since the net flux of electron from source to dot  $\Phi_S$  was already calculated as the flux of electrons over the entire cross section (it is already the actual number of electrons flowing from the source contact into the dot and then toward the drain), the electrical current can be written by directly multiplying it by the electron charge -q. At steady state the drain to source current is (the first minus sign is due to the fact that x-axis goes from source to drain while the current from drain to source):

$$I_{DS} = -(-q)\Phi_S = +q \left[2\frac{\gamma_S}{\hbar}f_{FD}(E_L, E_{FS}) - \frac{\gamma_S}{\hbar}N\right]$$

and considering the above expression for N:

$$\begin{split} I_{DS} &= \frac{q}{\hbar} \gamma_S \left[ 2f_{FD}(E_L, E_{FS}) - \frac{2\gamma_S}{\gamma_S + \gamma_D} f_{FD}(E_L, E_{FS}) - \frac{2\gamma_D}{\gamma_S + \gamma_D} f_{FD}(E_L, E_{FD}) \right] = \\ &= \frac{q}{\hbar} \frac{2\gamma_S}{\gamma_S + \gamma_D} \left[ \gamma_S f_{FD}(E_L, E_{FS}) + \gamma_D f_{FD}(E_L, E_{FS}) \right] + \\ &- \gamma_S f_{FD}(E_L, E_{FS}) - \gamma_D f_{FD}(E_L, E_{FD}) \right] = \\ &= \frac{q}{\hbar} \frac{2\gamma_S \gamma_D}{\gamma_S + \gamma_D} \left[ f_{FD}(E_L, E_{FS}) - f_{FD}(E_L, E_{FD}) \right] \end{split}$$

In conclusion the electrical current through a single energy level quantum dot is given by:

$$I_{DS} = \frac{q}{\hbar} \frac{2\gamma_S \gamma_D}{\gamma_S + \gamma_D} \left[ f_{FD}(E_L, E_{FS}) - f_{FD}(E_L, E_{FD}) \right]$$
(4.2)

This expression holds for any temperature  $T \ge 0$  K but it is not general at all. Indeed it was mentioned before that the meaning of the coupling factors  $\gamma_{S,D}$  is to broaden the energy levels, since they introduce an uncertainty over the energy level value. This issue will be discussed in a while, in the next section 4.1.1. Before discussing it a last remark is provided.

One may ask when the single level quantum dot conduct. In order to answer this question let's consider three cases:

1. In the first case the energy level  $E_L$  within the dot is supposed to be placed well above both the source Fermi level  $E_{FS}$  and the drain Fermi level  $E_{FD}$ . In this case both the Fermi-Dirac functions  $f_{FD}(E_L, E_{FS})$  and  $f_{FD}(E_L, E_{FD})$  will be essentially null, leading (see eq.(4.2)) to a null  $I_{DS}$ . Indeed in this case there are no occupied states in the source, thus no electron can flow into the dot (and proceed up to the drain). In this case  $N \sim 0$  (empty) and no electrical current flows.

- 2. In the second case the energy level  $E_L$  within the dot is supposed to be placed well below both the source Fermi level  $E_{FS}$  and the drain Fermi level  $E_{FD}$ . In this case both the Fermi-Dirac functions  $f_{FD}(E_L, E_{FS})$  and  $f_{FD}(E_L, E_{FD})$  will be essentially equal to 1, leading (see eq.(4.2)) to a null  $I_{DS}$ . Indeed in this case there are only occupied states both in the source and in the drain. Consequently there will be no possibility for the electrons to flow in free states (since there are no free states) within the dot or in the drain. In this case  $N \sim 2$  (occupied) and no electrical current flows.
- 3. In the last case the energy level  $E_L$  within the dot is supposed to be placed in between the source and the drain Fermi levels, like depicted in figure 4.1. In this case the source has occupied states at energy  $E_L$ , thus  $f_{FD}(E_L, E_{FS}) \sim 1$ , while the drain has unoccupied states at the energy  $E_L$ , thus  $f_{FD}(E_L, E_{FD}) \sim 0$ . From eq. (4.2) there is a non-null electrical current  $I_{DS}$ , and it is said that the energy level  $E_L$  within the dot is inside the bias window, where the bias window indicates exactly the energy interval  $qV_{DS}$  that separates the source Fermi level from the drain one. In this case there is conduction through the energy level  $E_L$ . Notice that if  $f_{FD}(E_L, E_{FS}) \sim 1$ and  $f_{FD}(E_L, E_{FD}) \sim 0$  the current saturates at the saturation value for the level within the bias window, that is:

$$I_{DS} = \frac{q}{\hbar} \frac{2\gamma_S \gamma_D}{\gamma_S + \gamma_D}$$

This is a general feature of transport through each 0D, but also 1D, 2D and 3D system: the electron states that take part to the conduction mechanism are only those in between the source and the drain Fermi levels. Otherwise, if no electron state is present in that energy interval, no electrical current originates.

# 4.1.1 Levels broadening

It was already mentioned in the previous section that the strong coupling between contacts and dot implies that the energy levels inside the dot are broaden w.r.t. the isolated dot. The physical origin of this phenomenon is indeed in the chemical bond that is generated between the dot and the contacts, that allows the electrons to easily move from the contacts to the dot and vice versa. In other words the energy-time uncertainty principle holds true and since the lifetime of an electron within the dot is limited (since it can escape from it), then an uncertainty on its energy eigenvalue is present. Again, it is possible to see the same physical phenomenon from another perspective. Let's consider the general solution of the time-dependent Schrödinger's equation, i.e. eq. (2.49) in section 2.3.5; that is reported here for clarity:

$$\psi(\vec{r};t) = \oint dE \ C(E) \ \Psi_E(\vec{r}) \ e^{-\frac{i}{\hbar}Et}$$

The steady state with an infinite lifetime have essentially no time dependence, since the exponential is a complex exponential (this feature was already discussed in section 2.3.5 and 2.3.6). Nevertheless in the present case it was said that the electrons can escape from the dot, giving rise to a finite lifetime. Thus the time dependence could be given by an

exponential decay in time, indeed from the general solution of the Schrödinger's equation it is known that the time-dependent solution (factorized) should be:

$$\phi(t) = e^{-\frac{i}{\hbar}Et}$$

and if a finite lifetime is considered it is intuitive thinking that the exponential could become real, giving rise to the exponential decay in time, meaning that the (position) probability of finding the electron in such a level decreases with time. Indeed this is exactly what happens, and said  $\tau$  the electron lifetime within the dot, the time dependence is of kind:

$$\phi(t) = e^{-t/\tau} = e^{-\frac{\tau}{\hbar}t}$$

A full demonstration of this equation will provided in the next chapter (see section 5.12); nevertheless what happens in doing the calculations is exactly that an imaginary part of the energy comes out, representing the exponential decay of the previous equation. In particular a complex energy  $E = E_L - i\gamma$  is considered, and when substituted into  $\phi(t) = e^{-\frac{i}{\hbar}Et}$  the following time-dependence is found:

$$\phi(t) = e^{-\frac{i}{\hbar}E_L t} e^{-\frac{\gamma}{\hbar}t} = e^{-\frac{i}{\hbar}E_L t} e^{-t/\tau}$$

Notice that the energy as physical observable will be always a real number. So one may ask what is the meaning of a complex energy, is it correct to consider it? The answer is yes. The energy will be always real when measured. The imaginary part of energy is thus only a model, a mathematical artifact for representing the effects of the contacts. Indeed if one consider all the entire system molecule plus contacts, there is no reason of using a complex energy, since the electrons do not disappear from the "dot + contacts" system, but simply move through it, flowing from the dot towards the contacts or vice versa. Nevertheless, in analogy with conventional electronic devices modeling, it is usually preferred to make calculations only on the isolated device, and to consider the effects on the contacts by means of suitable boundary conditions. This approach (that will be widely investigated in the next chapter) leads to significant simplifications in the analytical treatment and in practical calculations (as it will be explained). The way of modeling the fact that the electrons can escape from the device, without explicitly considering the contacts is exactly by means of an imaginary part of the energy, that can be thus intended as a boundary condition that represents the fact that the dot is not isolated but it is in between the two contacts, and the electrons can escape from the dot (open system). Indeed, as already clarified above, introducing an imaginary part of the energy allows to write the general solution of the Schrödinger's equation as multiplied by a real exponential in time, i.e. a finite lifetime state, like the physics intuitively tells us. The time constant of the finite lifetime state is called lifetime, and in the previous treatment is exactly the intrinsic time  $\tau_S$  for the source (or  $\tau_D$  for drain). Thus modeling the energy as a complex entity has the advantage of making the calculations only on the quantum dot (the active portion of the device), but considering as it is in the real world: in between the two contacts. From the standpoint of the device this means that the electron can "disappear" (annihilate) after a time  $\tau$ , and the probability of finding them in the dot is exponentially decaying with time. An infinite lifetime state has a lifetime that is infinite:  $\tau \to \infty$ , and it is possible to exactly

know its energy, that previously was said to be  $E_L$ . Thus the density of states per unit energy of a infinite lifetime state will be a delta Dirac, in energy domain, centered in  $E_L$ . Instead in the case of a finite lifetime state, there is an uncertainty on the exact value of the energy of the electrons in such a state. Thus the density of state per unit energy will be broadened (it is only qualitatively illustrated in figure 4.2). In practice, whenever an exponential decay is considered in time domain a Lorentzian distribution is recovered in energy domain. Thus the broadened density of states per unit energy will have a Lorentzian shape, of the kind:

$$D_{EL}(E) = \frac{\gamma/(2\pi)}{(E - E_L)^2 + (\frac{\gamma}{2})^2}$$
(4.3)

where  $\gamma = \gamma_S + \gamma_D$  and  $E_L$  is the energy level in the dot. Notice that it is possible to demonstrate the previous expression. In order to do that one should make the Fourier transform of the electron wave-function, considering the (real) decaying exponential in time, and then normalize it to 1 [90]. Notice also that the Fourier transform w.r.t. to time corresponds to the following correspondence of variable (between time variable t and angular frequency  $\omega$ ):

$$t \iff \omega = 2\pi f = 2\pi \frac{E}{h} = \frac{E}{\hbar}$$

From which it is clear that by Fourier transforming a wave-function that depends on time corresponds in going into energy domain, that is where the density of states per unit energy is defined (further details on this will be clarified in the next chapter). Notice that it is said that the time and energy domain are isomorphous (see also section 2.3.3), since they are biunivocally linked by means of linear application (the Fourier transform).



Figure 4.2: Qualitative pictorial representation of broadening of an energy level. Usually the broadening assumes a Lorentzian shape, thus  $D_{EL}(E)$  is a Lorentzian distribution.

A measure of the level broadening is provided by  $\gamma = \gamma_S + \gamma_D$ , indeed notice that if in equation (4.3) it is made the limit for  $\gamma \to 0$  then the denominator goes to zero more rapidly than the numerator (squared  $\gamma$  is present), such that the remaining function tends to infinite when  $E \to E_L$  (it is essentially a delta Dirac centered in  $E_L$ ).

Notice that the integral over all the energy axis of equation (4.3) is again equal to 2 (due

to spin degeneracy); indeed the integral w.r.t. energy of a density of states per unit energy should provide the number of states; and since  $D_{EL}(E)$  is the effect of the broadening of a single energy level  $E_L$  then it should again host two electrons (since it is a single electron state with spin degeneracy).

In order to consider the broadening in the previous expression for the electrical current through the molecular/dot wire, equation (4.2) should be modified as follows:

$$I_{DS} = \frac{q}{\hbar} \frac{2\gamma_S \gamma_D}{\gamma_S + \gamma_D} \int_{-\infty}^{+\infty} D_{EL}(E) \left[ f_{FD}(E, E_{FS}) - f_{FD}(E, E_{FD}) \right] dE$$
(4.4)

in which the integral over all the energies is aimed in recovering the full probability of occupation of the broadened level  $E_L$ . Notice again that the stronger is the coupling between the contacts, i.e. the greater is  $\gamma$ , the wider is  $D_{EL}(E)$ . If it is defined the transmission functions as:

$$T(E) = 2\pi \frac{\gamma_S \gamma_D}{\gamma_S + \gamma_D} D_{EL}(E)$$
(4.5)

then the las equation becomes:

$$I_{DS} = \frac{2q}{h} \int_{-\infty}^{+\infty} T(E) \left[ f_{FD}(E, E_{FS}) - f_{FD}(E, E_{FD}) \right] dE$$
(4.6)

# 4.1.2 Multi-level quantum dot

Let's now consider the case of a two-levels quantum dot. First of all a remark concerning the position of the Fermi level of the dot w.r.t. source and drain Fermi levels. In the moment in which the molecular wire is created a (small) amount of charge exchanging between the contacts and the dot occurs such that after a given time the thermodynamic equilibrium is reached. This means that the Fermi levels in the source, the drain and the dot are all aligned. In the moment in which there is an applied bias one may ask where the dot Fermi level is positioned w.r.t. to Fermi levels of source and drain contacts. The answer is not easy in general, and some *ab initio* calculations, regarding the entire device (dot/molecule plus contacts), should be performed to answer it. Nevertheless if it assumed of having similar coupling factors  $\gamma_S \cong \gamma_D$  then it is quite probable of having the Fermi level of the dot in the middle between the source and drain ones. This is in general an assumption, and for the moment no further discussion is provided. This topic is again considered under a different perspective in section 4.1.4.

Thus for the moment the considered case is the one of a molecular quantum dot with two energy levels, namely the HOMO (Highest Occupied Molecular Orbital) and the LUMO (Lowest Unoccupied Molecular Orbital), respectively placed below and above the dot Fermi level, that is supposed to be in the middle between the source and drain Fermi levels as mentioned above. The situation is summarized in figure 4.3. The relative positions of the LUMO and the HOMO w.r.t. the dot Fermi level are supposed to be known from electronic structure calculations (e.g. performed by means of the methods discussed in chapter 3).

Let's start by considering the thermodynamic equilibrium case. As mentioned above in this case all the Fermi levels are aligned. In the moment in which a small  $V_{DS}$  is applied



Figure 4.3: Qualitative representation of a two level quantum dot. The distances between the Fermi level in the dot  $E_{Fdot}$  and the two levels (HOMO and LUMO) are supposed known from electronic structure calculations.

neither the LUMO nor the HOMO are inside the bias window, thus the electrical current is null. Instead when the bias window reaches the value of 1 eV (i.e.  $V_{DS} = 1$  V) then the LUMO level starts conducting. This because the applied bias drops half between the source and the dot and half between the dot and the drain. Indeed it was supposed to have the dot Fermi level in the middle between the source and drain ones. Consequently a voltage equal to two times the difference between the LUMO and the Fermi level of the dot should be applied in order to have the LUMO within the bias window and thus an electrical current flowing from drain to source. If the applied voltage is further increased then when it reaches the 1.4 V the HOMO level starts conducting, again this is a consequence of the fact that it was assumed that the applied voltage drops equally from source to dot and from dot to drain. In summary, without broadening, the current-voltage characteristics will be similar to the one of figure 4.4 (dashed line). If broadening is considered then the solid line of figure 4.4 will be recovered. Indeed in the picture of figure 4.3 the energy is on ordinate axis and the effect of broadening is to make the levels entering before and exiting later from the bias windows, thus leading to a smoother characteristics. The greater the broadening the smoother (i.e. more linear) will be the current-voltage characteristics. The important point is that in this oversimplified model for conduction through quantum

dots the two energy levels contribute to conduction independently when they enter in the bias window. Thus, under these hypotheses, the extension of equation (4.4) to a generic number of discrete energy levels within the quantum dot is trivial: indeed it is sufficient to superimpose their effects by summing their density of states. This is exactly what is done with the following equation, in which the multi-level transmission function is defined as the sum over all the *i*-th levels in the dot:

$$T(E) = \sum_{i} 2\pi \frac{\gamma_{Si} \gamma_{Di}}{\gamma_{Si} + \gamma_{Di}} D_{ELi}(E)$$
(4.7)

where different coupling factors  $\gamma_{Si}$ ,  $\gamma_{Di}$  are in general possible for the different energy levels (it is not said that all the energy levels -i.e. all the dot orbitals- have the same



Figure 4.4: Qualitative example for the two level quantum dot of figure 4.3. The LUMO level causes the first plateau at  $\pm 1$  V while the HOMO the second at  $\pm 1.4$  V. Notice the conductance gap around the zero bias condition (0 V), and notice that it is equal to the double (for both positive and negative biases) of the energy interval that separates the closest dot energy level to the dot Fermi level.

coupling with the contacts -i.e. wave-function hybridization or chemical bond). The final expression for the electrical current through a multi-level quantum dot, even in the case of broadening (and at whatever temperature, that is account with the Fermi-Dirac distributions) is the following:

$$I_{DS} = \frac{2q}{h} \int_{-\infty}^{+\infty} T(E) \left[ f_{FD}(E, E_{FS}) - f_{FD}(E, E_{FD}) \right] dE$$
(4.8)

where the transmission spectrum (or function) T(E) is defined by eq. (4.7). Notice that the last expression resembles eq. (4.6).

# 4.1.3 Quantum conductance

If in equation (4.8) it is assumed to have perfect transmission, i.e. T(E) = 1 for each energy value E, the following expression is obtained:

$$I_{DS} = \frac{2q}{h} \int_{-\infty}^{+\infty} \left[ f_{FD}(E, E_{FS}) - f_{FD}(E, E_{FD}) \right] dE$$

Moreover by supposing of being at zero kelvin for simplicity, the two Fermi functions are 1 below the source and drain Fermi levels respectively while they are 0 above. Thus the integral becomes simply the difference between the contact Fermi levels:

$$I_{DS} = \frac{2q}{h} \left( E_{FS} - E_{FD} \right) = \frac{2q^2}{h} V_{DS}$$

where it was exploited the bias window definition:  $E_{FS} - E_{FD} = -qV_{SD} = +qV_{DS}$ . Notice that even if the transmission is unitary, i.e. all electrons are always transmitted by hypothesis through the quantum dot, the electrical current presents a finite slope, i.e. a well defined (and finite) conductance, that is (the factor two arose from spin degeneracy):

$$G_Q = \frac{2q^2}{h}$$

This conductance value is called "quantum conductance" or "contact conductance". It arises from the interface between the quantum dot and the contacts, indeed it is present even if a full transmission is supposed. The contact conductance limits the maximum slope of the current that cannot be infinite as predicted with classical physics for a conductor length that tends to zero. To this purpose remember that the classical (ohmic) conductance is:  $G = \sigma W/L$ , thus for a small conductor  $(L \to 0)$  it is expected a huge conductance. especially if transmission is unitary: T(E) = 1. Nevertheless the actual conductance has an upper limit, the so called quantum limit to conductance, that is indeed given by the quantum conductance value:  $G_Q = \frac{2q^2}{h} \sim (12.49 \mathrm{k}\Omega)^{-1}$ . Early experiments on mesoscopic systems (see also section 4.2 for a precise definition of mesoscopic systems), i.e. small conductors, underlined that the actual conductance was approaching to a limiting value, that was indeed  $G_Q$ . Notice that the physical origin of the quantum conductance, despite the name, has no an intimate relation with quantum mechanics [39]. Indeed it arises from the interface between the contact and the quantum dot (or the small conductor). Within the contact the current is carried by a huge number of possible electron states, or contact proper modes. Indeed a contact is usually a metal contact, and it presents allowed energy bands, composed by a set of continuum states, i.e. a continuum infinite number of states/modes. Instead within the quantum dot the current can flow only through the allowed discrete (and few!) electron states. This fact requires a redistribution of the current among the current-carrying modes/states leading to an interface resistance (the dot is like a sort of "bottleneck") [39]. It is possible to get rid of this resistance by making the contacts identical to the channel (i.e. the quantum dot). Nevertheless this has no sense because the contacts are by definition a large reservoir of electrons, and they should be "infinitely" more conducting than the conductor in order to justify the assumption that the applied voltage drops entirely across the channel.

#### 4.1.4 Electrostatic source and drain capacitances

In the moment in which there is a non null applied voltage conventional electrostatic capacitances should be considered. Indeed the movement of charges in response to the applied voltages would lead to capacitive effects. In total there are two effects on the channel potential that are linked to electrostatic capacitances:

- the electrostatic effect: quite conventional, it follows from the capacitance definition, i.e. from the fact that an applied bias would produce a variation in the channel (i.e. in the dot) charge.
- the charging effect: it is an effect that in general occurs also in conventional electronic devices, but is so small that it is in general negligible. Instead in nano-devices it is comparable to the electrostatic effect and must be considered in the system modeling. It is the subject of the next section.

Notice that in general the electrostatic effect and the charging effect are linked, as will be better clarified in the next section, and a self-consistent loop is necessary to ensure convergence.

Once the source and drain electrostatic capacitances are supposed known, the simple capacitive model of figure 4.5 can be considered. This is a linear (or better linearized) model, and conventional circuit theory can be used to find the total channel potential within the dot. Since it is a linearized model it holds only for small variations, or analogously small  $V_{DS}$  values. If not so a non-linear model should be considered, indeed the actual values of  $C_S$  and  $C_D$  are dependent on the applied voltage.

The equivalent circuit (figure 4.5 - right) is a simple capacitive divider, and since  $C_S$  and  $C_D$  are supposed known it is possible to easily estimate the effect of an applied  $V_{DS}$  on the channel potential. Notice that this model make also the additional assumption of having a zero-dimensional quantum dot, i.e. the physical extension of the quantum dot is completely neglected. Consequently it is also neglected the potential shape within the dot (that instead in general varies from point to point accordingly to the Laplace equation). And notice also that the source potential is taken as reference potential.



Figure 4.5: Capacitive (linearized) model for an ideal quantum dot with no physical extension (zero dimensions). Left: a representation of the molecular/dot wire physical structure; right: the equivalent linearized circuit.

The consequence of an applied  $V_{DS}$  voltage is the one of shifting the quantum dot energy levels. In particular the quantum dot Fermi level will be no more the one at thermodynamic equilibrium but instead it will be shifted in energy of the amount  $U_{Vds} = -qV_{dot}$ , where from the capacitive divider:

$$V_{dot} = V_{DS} \frac{C_D}{C_S + C_D} \quad \rightarrow \quad U_{Vds} = -q V_{dot} = -q \frac{C_D}{C_S + C_D} V_{DS}$$

In conclusion, the effect of an applied  $V_{DS}$  will be to create a bias window  $-qV_{DS}$  as explained previously, but also to shift the quantum dot energy levels (the quantum dot Fermi level) of the amount  $U_{Vds}$ . Usually the capacitive ratio is called "voltage division factor", and indicated with:

$$\eta = \frac{C_D}{C_S + C_D} = \frac{C_D}{C_{ES}}$$

where  $C_{ES}$  is the total electrostatic capacitance, defined as:  $C_{ES} = C_S + C_D$ . Notice that if  $C_S = C_D$  then  $\eta = \frac{1}{2}$ , that is exactly what was supposed in the previous sections by saying that the dot Fermi level was assumed to be in the middle between the source and drain Fermi levels. Indeed  $\eta = \frac{1}{2}$  implies that the Fermi level of the dot is  $1/2qV_{DS}$ higher than the source potential (that is the reference), and  $1/2qV_{DS}$  lower than the drain potential.

# 4.1.5 Charging effect

The charging effect arises from the motion of charged particles, i.e. electrons, toward/from the channel. In particular the amount of charge that is moved toward/from the channel alters the energy levels in the channel itself. In general the charging effects occurs also in conventional macroscopic electronic devices, where the presence of an extra electron can alter somehow the band diagram. Nevertheless in such devices the charging effect is so small that in general it results negligible. Instead in nano-devices it becomes comparable to the electrostatic effects and thus it must be considered in the system modeling. Indeed the perturbation of a quantum dot energy levels due to the presence of extra electrons can be large, of the order of the eV, and thus comparable to the effects of the applied bias. In response to a variation in the applied voltage, a given amount of charge  $Q_n = -q\Delta N$ is moved toward/from the channel, accordingly with the total electrostatic capacitance  $C_{ES}$  (see also previous section). Notice that  $\Delta N$  indicates the variation of the number of electrons inside the dot due to the applied bias, while the corresponding total charge is  $Q_n$ . As a consequence a voltage is established across the total capacitance of the system, indeed it is the result of the charge transferred from the contact(s) into the dot and the result affects the entire system:

$$\Delta V_{charging} = \frac{\Delta Q}{C_{tot}} = \frac{Q_n}{C_{ES}} = \frac{-q\Delta N}{C_S + C_D}$$

The potential energy corresponding to  $\Delta V_{charging}$  is called "charging energy", and it is equal to:

$$U_{charging} = -q\Delta V_{charging} = \frac{q^2}{C_{ES}}\Delta N \tag{4.9}$$

This potential contribution corresponds to the potential energy within the dot that is due to the transfer (through  $C_S + C_D$ ) of a given number of extra electrons  $\Delta N = N - N_0$ , where N indicates the current number of electrons within the dot and  $N_0$  the number of electrons in the dot at thermodynamic equilibrium. If a single electron is transferred toward the dot then  $\Delta N = N - N_0 = 1$ , that means a single extra electron is present, and the charging energy is:

$$U_{charging \ 1 \ eln} = \frac{q^2}{C_{ES}} \Delta N = \frac{q^2}{C_{ES}} = U_0$$
169

Consequently it is possible to rewrite the charging energy as:  $U_{charging} = U_0 \Delta N = U_0(N - N_0)$ . Notice that  $\Delta N$  can also be negative (meaning that the electrons are moving from the dot toward the contacts as a consequence of the applied bias).

The effect of the charge transferring toward/from the dot thus has again the effect of shifting the total potential of the dot of the amount  $U_{charging}$ ; i.e. the Fermi level of the dot is shifted of  $U_{charging}$ . To this purpose it is possible to have a dynamic level shifting of the dot levels. Indeed, if, on average, an extra electron is present within the dot due to the external bias  $V_{DS}$ , then the Fermi level of the dot is shifted upward of the (positive) quantity  $U_0$ , that means that both the LUMO and the HOMO are shifted upward of  $U_0$ . It may also happen that due to the charging effect one level (e.g. the LUMO) that initially was inside the bias window (thus conducting), then is shifted so much that exits from the bias window, thus reducing the total current. This can give rise to negative differential resistances.

Notice that the contribution  $U_{charging}$  can be superimposed (i.e. summed) to the electrostatic effect discussed in the previous section to get the total effect.

# 4.1.6 Self consistent algorithm and total electrostatic effect

The effect of an applied bias is to shift the dot energy levels of an amount  $U_{Vds} = -q \frac{C_D}{C_S+C_D} V_{DS}$ , and as a consequence of the applied bias a number of electrons N populates the dot, with  $N \neq N_0$  in general. Thus a charging energy arises and it has the effect of shifting the dot energy levels of the amount  $U_{charging}$ . The total effect of the applied bias is thus a superposition of the two aforementioned effects (under the hypothesis of a linear, or better linearized, system - i.e. for small variations or small  $V_{DS}$  values):

$$U = U_{Vds} + U_{charging} = -q \frac{C_D}{C_S + C_D} V_{DS} + \frac{q^2}{C_{ES}} \Delta N$$

In order to account of these effect the potential U can be used to shift the transmission function T(E), that becomes T(E - U), thus leading to a total current:

$$I_{DS} = \frac{2q}{h} \int_{-\infty}^{+\infty} T(E - U) \left[ f_{FD}(E, E_{FS}) - f_{FD}(E, E_{FD}) \right] dE$$
(4.10)

from which, by remembering the definition of transmission spectrum in equations (4.7) and (4.5), it follows that the density of states D(E) is shifted of the amount U:

$$D_{ELi}(E) \rightarrow D_{ELi}(E-U)$$

Nevertheless the density of states appears in the evaluation of the number of electrons within the dot N, that from eq. (4.1) is:

$$N_i = \frac{2}{\gamma_{Si} + \gamma_{Di}} \int_{-\infty}^{+\infty} D_{ELi}(E - U) \left[ \gamma_{Si} f_{FD}(E, E_{FS}) + \gamma_{Di} f_{FD}(E, E_{FD}) \right]$$

where the last expression is a straightforward generalization of the eq. (4.1) for the case in which broadening occurs in the level *i*-th. This holds for each energy level *i* of the dot (the total N is the sum of the various *i* since the relations are all linear:  $N = \sum_i N_i$ ). The point is that U depends on N, because of  $U_{charging}$  dependence from N, but N depends on U. Thus an iterative self-consistent procedure or algorithm must be used to evaluate the final effect of an applied bias.

# 4.1.7 Gating the quantum dot: a three terminals model

In the first chapter it was mentioned the possibility of realizing a molecular transistor, by adding a third electrostatically coupled gate terminal, see figure 1.3. In this section the capacitive model presented in the previous sections is suitably modified in order to account for the gating effect.

In figure 4.6 is represented a possible capacitive model including also the gate capacitance that arises from the device structure (again refer to figure 1.3). If the applied voltages  $V_{GS}$  and  $V_{DS}$ , and the electrostatic capacitances  $C_G$ ,  $C_S$  and  $C_D$  are known, the resulting channel potential can be simply found from two capacitive dividers. Exploiting the superposition of effects (i.e. linearized system hypothesis), the total average channel potential (this is the average potential inside the quantum dot, that in this model is considered without physical dimensions) is given by:

$$U_{tot} = U_{Vgs} + U_{Vds} + U_{charging} \tag{4.11}$$

where the two contributions  $U_{Vgs}$  and  $U_{Vds}$  can be evaluated by superposition of the effects. For estimating  $U_{Vgs}$  it is possible to set  $V_{DS} = 0$ , thus  $C_S$  and  $C_D$  are in parallel (toward ground since the source is taken as reference) and the effect of an applied  $V_{GS}$  is thus the one of shifting the energy levels in the dot of the amount:

$$U_{Vgs} = -qV_{dot}\big|_{V_{GS}} = -q\frac{C_G}{C_G + C_S / / C_D}V_{GS} = -q\frac{C_G}{C_G + C_S + C_D}V_{GS} = -q\frac{C_G}{C_{ES}}V_{GS}$$

where  $C_{ES} = C_G + C_S + C_D$  is the total electrostatic capacitance.

For estimating  $U_{Vds}$  it is possible to set  $V_{GS} = 0$ , thus  $C_G$  and  $C_S$  are in parallel and the effect of an applied  $V_{DS}$  is thus the one of shifting the energy levels in the dot of the amount:

$$U_{Vds} = -qV_{dot}\big|_{V_{DS}} = -q\frac{C_D}{C_D + C_G//C_S}V_{DS} = -q\frac{C_D}{C_G + C_S + C_D}V_{DS} = -q\frac{C_D}{C_{ES}}V_{DS}$$

where  $C_{ES} = C_G + C_S + C_D$  is the total electrostatic capacitance. The charging effect is given by same expression of previous section, i.e. eq. (4.9), that is now reported for clarity:

$$U_{charging} = \frac{q^2}{C_{ES}} \Delta N \tag{4.12}$$

where  $C_{ES} = C_G + C_S + C_D$  is the total electrostatic capacitance. Finally notice again that the set of equations presented so far needs to be solved self-consistently.


Figure 4.6: Quantum dot capacitive model. In this simplified model the molecular quantum dot -i.e. the channel- is assumed to be without physical extensions, i.e. zero-dimensional.

## 4.1.8 Quantum capacitance

The quantum capacitance represents the molecule states filling. The easiest way of introducing it (in my opinion) is the approach presented in [90]. In the moment in which the molecule-contact (source or drain contact) junction is created, a re-distribution of charges occurs between the molecule and the contacts and the thermodynamic equilibrium is achieved, with an alignment in the Fermi levels. A contact in order to be a "good" contact should have an enormous amount of states around the Fermi level, if compared to the channel ones, and thus it should be an unlimited reservoir of electron states for the channel. Under this approximation the contact Fermi level is essentially pinned. Instead the molecule/dot Fermi level is moved up or down in order to achieve the equilibrium. A small amount of charge can be already enough to produce a huge molecular Fermi level shift. Notice that even a fractional electron charge can be exchanged between the molecule and the contacts. Indeed if an electron is involved in a chemical bond between the contact and the dot/molecule (or the molecular anchoring group), the electron orbital (electron cloud) is partially in the contact and partially in the molecule, thus the electron is for a certain time localized inside the contact and for another time interval inside the molecule. On average, therefore, a charge less than q (less than an electron elementary charge) can be localized inside the molecule and considered as transferred charge in order to achieve the equilibrium. The amount of shift in the Fermi level depends on the amount of states in the dot around the Fermi level. In particular if a dot/molecule has a large density of states (per unit energy) around the Fermi level, the amount of Fermi level shift due to a given amount of charge transfer between the contact and the dot would be lesser than if the density of states would be small. The total number of electrons in the molecule is in general given by:

$$N = \int_{-\infty}^{+\infty} DOS(E) f_{FD}(E, E_F) dE$$
(4.13)

where DOS(E) is the (total) density of states per unit energy of the molecule (corresponding to the sum over all energy levels of the  $D_{ELi}(E)$  distributions), and  $f_{FD}(E, E_F)$  the Fermi-Dirac distribution. At zero kelvin the amount of occupied states (i.e. the number of electrons) is:

$$N = \int_{-\infty}^{E_F} DOS(E) dE \tag{4.14}$$

remember that  $N \in \mathbb{R}^+$  since a fractional charge can be transferred. From fundamental theorem of integral calculus:

$$\frac{dN}{dE} = DOS(E) \quad \Rightarrow \quad \frac{dN}{dE}\Big|_{E_F} = DOS(E_F) \tag{4.15}$$

and by supposing only small variations of Fermi energy (indicated with  $\delta E_F$ ):

$$\delta E_F = \frac{\delta N}{DOS(E_F)} = \frac{q^2}{C_q} \delta N = \frac{q}{C_q} Q_n \tag{4.16}$$

where it is defined the quantum capacitance as:  $C_q = q^2 DOS(E_F)$ , and where the total channel charge is  $Q_n = q\delta N$ . The notation is analogous to the one of [90], where " $\delta$ " indicates a small variation.

Equation (4.16) holds only for small variations and it is an linearized expression, useful for determining the amount of charge transferred between the contacts and the molecule, for reaching the thermodynamic equilibrium, once the Fermi level shift is known (or vice versa to find  $\delta E_F$  if  $Q_n$  is known). From eq. (4.16) it is evident that the greater is the quantum capacitance, the smaller is  $\delta E_F$  for a given  $\delta n$ .

The concept of quantum capacitance can be generalized for any (small) variation of the total channel potential due to whatever effect, such as the application of a bias. The concept of quantum capacitance is simple (and strictly holds) for small deviations from equilibrium, i.e. for linearized models. In particular with the notation of [89] (see chapter 7.3 for a more formal introduction of these concepts), said  $N_0$  the number of electrons in the molecule at equilibrium, N the number of electrons in the molecule outside the equilibrium,  $U_N$  the value of the channel potential such that  $N = N_0$  and U the current value of the channel potential, the following relation holds:

$$\delta N = N - N_0 \approx C_q \frac{U_N - U}{q^2} = C_q \frac{\delta U}{q^2} \quad \Rightarrow \quad -q\delta N = Q_n \approx C_q \delta V_{CH} \tag{4.17}$$

where  $\delta U = -q \delta V_{CH}$  is the (small) electrostatic potential variation that occurs in the channel, e.g. due to external bias (notice that in eq. (4.17)  $q^2$  can be thought as  $(-q)^2$ ). A full demonstration of eq. (4.17) is provided in [89] (chapter 7.3) and also in slightly different terms in [90]. Nevertheless it is reasonable thinking at eq. (4.17) like the generalization of eq. (4.16) in which the dot Fermi level  $E_F$  is substituted with the channel potential U.

In conclusion, the quantum capacitance is an additional contribution of capacitance

that represents the state filling in a nanodevice. More precisely, it is in general a measure of the amount of charge (electrons) that can be transferred into (or from) the molecule in a given bias condition, indeed it is intimately linked to the density of states within the molecular channel or the quantum dot.

In general the quantum capacitance should be considered in molecular devices capacitive balance. In order to do that let's consider once again the expression for the total channel potential shift U, that is given by eq. (4.11) and reported here for simplicity:

$$U = U_{Vgs} + U_{Vds} + U_{charging} = -q \frac{C_G}{C_{ES}} V_{GS} - q \frac{C_D}{C_{ES}} V_{DS} + q^2 \frac{\Delta N}{C_{ES}}$$
(4.18)

if a small variation of the number of electrons in the dot is considered, then  $\Delta N \to \delta N$  and thus:

$$\Rightarrow U = -q \frac{C_G}{C_{ES}} V_{GS} - q \frac{C_D}{C_{ES}} V_{DS} + q^2 \frac{\delta N}{C_{ES}}$$

$$\tag{4.19}$$

Remembering the definition of quantum capacitance and equation (4.17), it is possible to rewrite eq. (4.19) as follows:

$$U = -q \frac{Cg}{C_{ES}} V_{GS} - q \frac{Cd}{C_{ES}} V_{DS} - \frac{C_q}{C_{ES}} U$$

from which:

$$U = -q \frac{Cg}{C_{ES} + C_q} V_{GS} - q \frac{Cd}{C_{ES} + C_q} V_{DS}$$
(4.20)

that finally can be rewritten in terms of small (linearized) variations as:

$$\delta U = -q \frac{Cg}{C_{ES} + C_q} \delta V_{GS} - q \frac{Cd}{C_{ES} + C_q} \delta V_{DS}$$
(4.21)

The important point is that the quantum capacitance  $C_q$  should be considered in the same way as the electrostatic capacitances in the capacitive balance of the entire system, indeed it appears in equations (4.20) and (4.21).

A final remark: in 2019 the first experimental evidence of the quantum capacitance was possible [111], thus highlighting its increasing importance as the devices are scaled.

## 4.1.9 Final considerations

The model introduced so far for the transport through molecular quantum dot is an oversimplified model. In this model the broadening was essentially introduced ad hoc, even if an attempt of short qualitative and intuitive discussion was provided. The broadening is an extremely important feature of transport in nano-devices and more importantly it is a natural consequence of the quantum mechanical physical and mathematical modeling of nano-transport, as will be better clarified in next chapter. Moreover in the multi-level picture it was stated that the levels participate to conduction independently the one from the other. This is not always at all correct, as will be clarified in the next chapter. More important is the fact that when more energy eigenvalues are considered within the quantum dot, more coupling factors arise. This suggest to collect them within a matrix, and this is exactly the standard approach in non-equilibrium Green's functions theory in which matrices are considered instead of scalars. A more formally correct and comprehensive of all the effects (also those introduced *ad hoc* here or not yet introduced) treatment is provided in the next chapter. It is a purely quantum mechanical model for transport and it is very general, indeed it holds in all transport regimes, comprising also incoherent transport.

Despite of its limits, this oversimplified model is capable of collecting the main physical insights of the transport at nano-scale. Indeed the current saturation or plateau whenever an entire level (with entire level is intended the broadened  $D_{ELi}(E)$ ) is included in the bias window, and the conductance gap around the zero bias are well explained with this extremely simple model. Moreover, the origin of an asymmetric *I-V* characteristics is again explained if a voltage division factor  $\eta$  different from one half is taken into account. And again the possibility of a negative differential resistance arises naturally from the concept of having a channel energy level exiting from the bias window. Still the capacitive model is capable of catching many interesting insights in a straightforward manner, especially when also the quantum capacitance is taken into account.

Since the advantages seem to be more than the above discussed drawbacks, one may ask the reason for introducing a more refined model, that is also a little bit more involved in the formalism, instead of continuing using this one, eventually with some *ad hoc* corrections. The answer is that the physical phenomena are very rarely uncorrelated like in this "toy" model. For example, a subtle effect of the applied bias voltage is to modify the density of states within the quantum dot, and also its transmission function (or spectrum) T(E). Transmission peaks due to different energy level can merge together, totally separate, modify in height, width, shape, entering or exiting in unforeseen ways, and all these effects can be correlated. Thus the model presented so far is of extreme importance because it allows to keep always in mind in a straightforward manner the physical intuition of what happens in a real case, but in order to make quantitatively correct previsions on actual transport behaviors of nano-devices a more refined model is needed. As already mentioned, it is the so called non-equilibrium Green's functions formalism (NEGF), that is the subject of the next chapter.

# 4.2 Mesoscopic systems

It was already mentioned that due to the small dimensions of molecules (of the order of the nanometer), a classical approach to transport cannot catch the essence of the transport features in such a system. Indeed the correct way of proceed should take into account quantum mechanics. In particular, molecular electronics modeling is based on the physical treatment of mesoscopic systems, i.e. that systems whose dimensions are intermediate between the microscopic and macroscopic ones [39]. Mesoscopic conductors are much larger than microscopic objects like atoms (of the order of tens of hundreds of picometers) but not large enough to be "ohmic" conductors [39]. Molecular devices, especially when the considered molecules are composed by some tens of atoms (and this is the typical case), belong to the class of mesoscopic system. The purpose of this section is to point out the features of such systems.

A conductor usually shows ohmic features if its dimensions are much larger than each of the following three characteristic length scales [39]:

- The de Broglie wavelength: it is related to the kinetic energy of the electrons, indeed it is  $\lambda = \frac{h}{p} = \frac{h}{mv}$ .
- The mean free path: it is the distance that an electron travels before its initial momentum is destroyed. It is the consequence of scattering phenomena, arising from interactions among electrons and phonons, etc...
- The phase-relaxation length: it is the distance that an electron travels before its initial phase is destroyed (think to the phase of the wave-function). Again it is due to interactions among electrons and phonons or between an electron and another electron. In the latter case (under the assumption that the scattering phenomenon between two electrons is elastic i.e. any the momentum lost by one electron is picked up from the other) the main effect is affecting the phase-relaxation time and thus the phase-relaxation length without affecting the mean free path (the situation is different if a phonon is involved in the scattering process). Notice that rigid (i.e. static) scatterers (such as an impurity atom or a well defined molecular geometry) do not influence the phase-relaxation since the phase relation between electrons interacting or not with these static scattereres is constant in time leading to constant transmission coefficient and constant phase relation. Only dynamic scatterers (electron-electron interactions etc...) lead to phase-relaxation.

These three scale lengths vary widely from one material to another and they are also strongly affected by temperature (that means that a conductor can be ohmic or not depending on temperature), magnetic field, etc... For this reason mesoscopic features were observed in a wide range of dimensions of conductors (see [39] for details). Mesoscopic conductors can present interesting features such as negative (differential) resistance, and so on.

There are mainly two approaches in modeling transport through mesoscopic systems and they are the transmission formalism or Landauer-Bütticker formalism (briefly introduced in the next section 4.3) and the Non-Equilibrium Green's Function formalism (NEGF). The first one has the advantage of being based on trivial concepts, but it has the disadvantage of holding essentially only for ballistic transport (i.e. only for coherent transport). The latter instead has the advantage of being very general and holding also for non-coherent transport. Actually the real power of NEGF can be appreciated when incoherent transport is considered (see later - section 5.18).

# 4.3 The transmission formalism

The purpose of this section is to provide a brief overview about the transmission formalism or the so called Landauer-Bütticker formalism. It is one of the two mainly used models for transport in mesoscopic systems. The other, namely the NEGF one, will be widely addressed in the next chapter.

In the transmission formalism the electrical current flowing through a mesoscopic conductor is expressed in terms of the probability that an electron can transmit through the conductor itself. For the moment let's assume zero temperature, so that the only energy states involved in conduction are only those with energy strictly in between the source and the drain Fermi levels. Moreover let's consider a conductor in between two large contacts. The probability of an electron of being transmitted from one contact (the source) to the other contact (the drain) passing through the conducting channel is indicated with T. The way in which it can be calculated depends on the nature of the considered device/channel, and will be briefly addressed in the next subsection. For the moment let's assume that it is known. Moreover it is assumed that the electrons can exit from the contacts with no reflections: "reflectionless" contacts. If a voltage  $V_{DS}$  is applied then the source and drain Fermi levels will be shifted of the amount  $qV_{DS}$ . Since the contacts are assumed reflectionless, the total incoming current of electrons from the source into the mesoscopic conductor can be evaluated considering the quantum conductance introduced in section 4.1.3. Indeed no reflections means unitary transmission, and with an applied bias  $V_{DS}$  the states in the source contact that are in between  $E_{FD}$  and  $E_{FS}$  see free states in the drain and try to go there such that the total energy of the system is lowered (they "try" to reach the equilibrium). The incoming current from the source is thus (notice the similarity -for zero kelvin- with the flow from source to dot of section 4.1):

$$I_{S,dot} = \frac{2q}{h} (E_{FS} - E_{FD}) = \frac{2q^2}{h} V_{DS}$$

The amount of electrons (or current) that reach(es) the drain, i.e. the outgoing current from the dot into the drain is thus given by the probability of transmission T through the dot that multiplies the incoming current  $I_{S,dot}$ :

$$I_{dot,D} = TI_{S,dot} = \frac{2q}{h}T(E_{FS} - E_{FD}) = \frac{2q^2}{h}TV_{DS}$$

The rest of the electron flux, or the incoming current, is instead reflected back to the source contact:  $(1 - T)I_{S,dot}$ . In conclusion the net current flowing in the device is:

$$I_{DS} = \frac{2q}{h}T(E_{FS} - E_{FD}) = \frac{2q^2}{h}TV_{DS}$$
(4.22)  
177

from which the conductance is:

$$G = \frac{2q^2}{h}T\tag{4.23}$$

That can be modified in:  $G = \frac{2q^2}{h}TM$ , if more modes/states within the quantum dot are considered, with M number of modes. In the previous treatment of a multi-level quantum dot (see section 4.1.2) M was "embedded" in T(E).

Equation (4.22) is called Landauer's equation for the electrical current, flowing in a mesoscopic ballistic conductor, and equation (4.23) is referred again as Landauer's equation for conductance. Notice that in this transmission standpoint conductance is essentially equivalent to transmission, indeed they are directly proportional. Sometimes one says that conductance is transmission [89]. Notice that equation (4.23) includes the contact conductance (or quantum conductance - see section 4.1.3).

So far the discussion neglected the effects of the contacts, that indeed were assumed to be reflectionless. A remark is due concerning this assumption. Very often it is reasonable assuming that the contacts are reflectionless for electrons coming from the dot and going into the contact, since the contact is huge and have many electron states, both occupied and available. Instead in general the reflection of electrons coming from the contact and going into the dot can be quite large, and cannot be neglected. Nevertheless the above formulae are correct since this reflection corresponds exactly to the contact conductance. In particular contact-dot reflections are accounted for by means of the contact conductance, that already considers them.

The extension of Landauer's equation to the case in which the temperature is no more zero kelvin is trivial. In particular instead of considering simply to take part to conduction the electron states between  $E_{FD}$  and  $E_{FS}$ , the Fermi-Dirac function "tails" should be considered. In particular equation (4.22) becomes:

$$I_{DS} = \frac{2q}{h} \int T(E) \left[ f_{FD}(E, E_{FS}) - f_{FD}(E, E_{FD}) \right] dE$$
(4.24)

that corresponds exactly to the previously found equations (4.6) for the single level quantum dot and (4.8) for the multi-level case. Indeed the aforementioned equations correspond to the Landauer's formula for a single or a multi-level quantum dot.

## **4.3.1** The transmission function T

While the model presented above is general and holds for each kind of small conductor or mesoscopic system, the particular expression for the transmission function T depends on the particular system that is considered. In general it is possible to estimate it by exploiting quantum mechanics, and in particular the transmission function T can be obtained from the Schrödinger's equation for the mesoscopic system. Indeed it is possible to define a transmission operator, that, once applied to the eigenfunctions of the quantum dot, provides the transmission probability for each energy level. This is not in principle much different from evaluating the transmission coefficient through a potential barrier (see section 2.3.7). In the transmission formalism all the complexity arising from the quantum mechanical treatment of the states in the dot is thus hidden within the transmission functions T. Notice that is also possible to calculate T starting from the NEGF formalism, indeed there exist a connection between the ballistic NEGF formalism and the transmission formalism (to this purpose see also section 5.15; while a good reference is e.g. [39]). Nevertheless it may have no much sense using the NEGF formalism only for evaluating Tand then using the more limiting transmission formalism (that remember holds essentially only for ballistic transport, while the NEGF is always holding in general).

A further remark is now provided relative to the transmission operator T. In section 2.4 it was illustrated a way of representing a differential operator in matrix form. It is thus intuitive that the above mentioned transmission operator can be expressed in matrix form. In this case the transmission function T becomes a matrix: the transmission matrix, that is indeed a representation of the transmission operator in a certain basis set. Moreover it is known from the electromagnetic fields courses that it is possible to define the so called scattering matrix S, that provides reflection and transmission coefficients for a multi-terminal (or multi-port) circuit among the various ports. Moreover it is known that there exist a connection between the scattering matrix S and the transmission one T, and it is possible to switch from one to the other by means of suitable transformation formulae. This holds true even in the case of transport through mesoscopic systems, such that the transmission formalism corresponds to the scattering formalism in which each mesoscopic system or sub-system is represented by means of scattering (or transmission) matrices, and a theory quite analogous to the high frequency electronic circuits one is used. In particular, a good choice for the basis set, can be the one of the energy eigenstates of the Hamiltonian operator of the mesoscopic system. In that case said M the number of allowed energy levels, i.e. eigenvalues, it follows that the basis set will have M eigenfunctions (if no degeneracy occur). In that case the transmission and the scattering matrices will be  $M \times M$  matrices. The transmission matrix element  $T_{i,j}$  will provide the probability of transmission between the j-th and the i-th proper modes, i.e. eigenstates. This point is further addressed in the next section.

### 4.3.2 Bütticker's formula

A simple and good discussion and introduction to the Bütticker formalism is provided in [39]. Here I will only mention that Bütticker extended the two terminal Landauer formula to the case of more terminal devices, by summing up the linear responses at each terminal (the responses must be linear to invoke the superposition of effects and sum them - see next section for a brief discussion of linear responses):

$$I_p = \frac{2q}{h} \sum_{q} \left[ T_{q,p} E_{Fp} - T_{p,q} E_{Fq} \right] = \sum_{q} \left[ G_{q,p} V_p - G_{p,q} V_q \right] \quad , \quad G_{q,p} = \frac{2q^2}{h} T_{p,q} \quad , \quad V_p = E_{Fp}/q$$

where the subscripts p and q refer to two terminals p and q, and  $T_{i,j}$  is the transmission function from terminal j to i. The electrical current must be zero when the applied voltages at all the terminals are equal, this fact implies that:

$$\sum_{p} G_{qp} = \sum_{q} G_{pq} \quad and \quad \sum_{p} T_{qp} = \sum_{q} T_{pq}$$
179

indeed it corresponds to charge conservation or matter conservation principle. Considering the last expressions it is possible to rewrite the current at terminal p as follows:

$$I_p = \sum_p G_{pq} \left[ V_p - V_q \right]$$

From basic circuit theory it is known that is possible to represent whatever linear network by means of an impedance matrix. If the network is resistive it corresponds to the resistance matrix, whose inverse matrix is the conductance matrix. Thus in the multi-terminal case the conductaces  $G_{p,q}$  can be seen as the elements of a conductance matrix. Moreover it is well known that a linear multi-port or multi-terminal (both lumped or distributed parameter) device admits also a representation in terms of scattering matrix, that is known being related to a transmission matrix. The transmission formalism allows to work with these matrices, and especially the scattering one is very used. Notice again that this is possible if the system is linear, topic briefly addressed in the next section. The usual approach is then to use quantum mechanics, and in particular the Schrödinger's equation, to evaluate the probability of transmission among states, i.e. the transmission rates among the different states. They are then collected within a matrix, that can be seen as a matrix representation for a transmission operator that provides the transmission probability between two different states (an initial and a final one). Then by means of algebraic transformation it is possible to get the scattering matrix, whose elements correspond to the scattering rates between the system states. Then, if a sequence of systems, or a complex mesoscopic system, is considered, it is possible to split it into simple parts or subsystems, recover the transmission or the scattering matrix and then suitably consider the total scattering/transmission matrix as a composition of the subsystem ones. This is analogous to what is done in conventional high frequency circuit. The transmission formalism rely on these few concepts, and "hides" the quantum mechanical complexity within the transmission (or scattering) function.

## 4.3.3 Linear response

The transmission formalism shows its full power in the moment in which a linear response is considered. This is the case of low-bias. In such conditions the transmission formalism framework allows to write and solve trivial equations, giving, at the same time, a quantitatively correct result in a fast way, and a physical insight in the description of the behaviors of the mesoscopic systems. These advantages arise from the fact that the transmission function can be written once at the beginning starting from quantum mechanical considerations on the system under study and then it is unchanged, and one works with the Landauer's formalism without handling quantum mechanics. Nevertheless in the moment in which a full current-voltage characteristics is considered things become suddenly more complicated and in particular a self-consistent iterative solutions of the involved equations must be considered. The aim of this section is to specify when a response can be considered linear and when instead it cannot. In the latter case the consequence will be that a self-consistent solution must be provided.

The response is linear whenever the transmission function is approximately constant over the considered bias window. This statement implies two assumptions: first, the transmission function is approximately constant over the considered bias window, but also: it is independent on the applied bias. The latter statement is not valid in general, since the applied bias can modify T(E), as already mentioned in section 4.1 (see final remarks). In the case of a constant T(E), that is:  $T(E) \sim T(E_F)$  where  $E_F$  is the Fermi level of the channel, and with a T(E) independent on the bias, the Landauer's formula can be rewritten as:

$$I_{DS} \sim \frac{2q}{h} T(E_F) \int [f_{FD}(E, E_{FS}) - f_{FD}(E, E_{FD})] dE \sim \frac{2q}{h} T(E_F) [E_{FS} - E_{FD}]$$

The last equality holds obviously for low temperature, but it is also possible to demonstrate that it holds true also for higher temperatures [39]. A linear response thus occurs if the conductance  $G(E) = \frac{2q}{h}T(E)$  is independent on energy in the bias window:  $G \sim \frac{2q}{h}T(E_F)$ . A sufficient condition for having a linear response is that the applied bias is small if compared to  $k_B T$ , where  $k_B$  is the Boltzmann's constant and T the temperature. Indeed in that case the Fermi levels difference is much less than  $k_BT$ , i.e.  $E_{FS} - E_{FD} \ll k_BT$ , and it is possible to show (by Taylor expanding the Landauer's formula for the electrical current), that the response is linear. Physically this is a consequence of the thermal broadening that affect the device. Due to temperature the electrons have extra kinetic energy w.r.t. to zero kelvin case, and as a result they can occupy higher energy levels (excited states) w.r.t. Fermi levels (ground state). Thus the Fermi functions have a longer tail and a slower exponential decay (in energy). Moreover the integral that defines the Landauer's electrical current can be seen as a correlation integral (a convolution integral in dE), noticing that the Fermi functions are dependent on E but also on Fermi level. This integral thus has the effect of "weighing" the transmission function T(E) over the thermal broadening  $k_B T$ . In other words, the greater is the temperature the smoother is the integral of the product between T(E) and the Fermi function difference. This appears very clear as soon as formulae are derived, see for example [39]. In summary, the response is linear if T(E) is almost constant in energy:  $T(E_F)$ , if it is bias independent and if the applied bias is much less than  $k_BT$ :  $E_{FS} - E_{FD} \ll k_BT$  (i.e. large thermal broadening w.r.t. applied bias). In such cases it is possible to formally write:

$$I_{DS} \sim \frac{2q}{h} T(E_F) [E_{FS} - E_{FD}] \quad and \quad I_p = \sum_p G_{pq} [V_p - V_q]$$

It is now addressed the question: "what happens if the applied bias is large?" In order to answer that question it must be said that in general when the bias is large (or not so small) an electric field develops within the channel. Such an electric field modifies in general the transmission functions thus leading to a non-linear response. It means that the transmission function T(E) is not only functions of the energy but also of the bias:  $T(E, E_{FS}, E_{FD})$  or  $T(E, qV_{DS})$ . In that case it is of extreme relevance including the effect of the applied electric field in order to get reliable quantitative results. In some easy cases it can be sufficient to consider a linear electric field inside the device, but in general one has to take into the electron density inside the channel and find the electric field by solving a suitable Poisson's equation (see SCF procedure - section 3.2). This corresponds in practice in implementing a self-consistent iterative solution, in which the electrostatic of the system is solved self-consistently with the evaluation of the transmission function. This is analogous to what already seen in section 4.1. This also means that the transmission function, that is obtained from the Schrödinger's equation, cannot be evaluated only once at the beginning and then assumed constant. This complicates the calculations with the Landauer's formalism, and each case should be addressed separately in order to understand if it is more convenient performing calculations with the transmission formalism or with the NEGF one. A good treatment is presented in [39].

## 4.3.4 Non-coherent transport

The previously introduced Landauer-Bütticker transmission formalism rigorously holds true only for ballistic transport, i.e. for coherent transport in which a single wave-function is supposed to "carry" the electron from the source to the drain.

For non-coherent transport a "vertical" flow of electrons occurs, where with "vertical flow" it is intended that incoherent scattering phenomena occur such that the electrons can dynamically change their energy state (i.e. wave-function or state) in consequence of such scattering phenomena, and thus undergo to momentum/energy relaxation.

Nevertheless if one calls "non-coherent elastic transport" the particular transport regime in which the electrons can undergo to phase-breaking phenomena but not to momentum relaxation processes, thus in this transport regime the Landauer-Bütticker's formalism still holds. In that case no vertical flow of electrons happens, since there is no net exchange of energy between the electrons and the surrounding channel, thus no dissipation of energy or relaxation (but only phase-breaking). In this case if an electron "enters" at source in a channel (e.g. a dot eigenstate) with a given energy, then it exits from the same channel at drain side with the same energy (no change of electron state occurs). Notice that another case is the one in which an electron with energy  $E_1$  scatters with an another electron at energy  $E_2$ . Again if no net energy is relaxed, i.e. if the scattering process is elastic in nature, at the end of the process the first electron will have energy  $E_2$  wile the second  $E_1$ . This means that there is always an electron in the channel  $E_1$  and one in the channel  $E_2$ , even if they are exchanged: i.e. a phase-breaking process occurred. It should be now clear the reason why in this "non-coherent elastic transport", in which phase-breaking occurs, the transmission formalism still holds. The picture of "no vertical flow" is sometimes represented by the fact that the electrons can travel in separated channels within the mesoscopic conductor, even if they can interact as mentioned above, by means of phase-breaking phenomena. Nevertheless after each phase-breaking phenomena one may think the electron continues flowing in the same channel (even if two electrons may be exchanged).

An interesting case is the one in which the transmission function is constant in the bias window. In this case the Landauer's formalism still holds. Because even if an incoherent scattering process occurs and a electron changes its energy during the propagation in the channel, since T(E) is constant in energy, its final transmission probability does not change relevantly. Thus the Landauer-Bütticker's formalism provide reasonable quantitatively results, and the committed error is small. Again this corresponds essentially to the linear case. Thus if the response is linear, then the error committed in neglecting incoherent transport is small and the transmission formalism can be used. If instead the transmission function T(E) has abrupt variations in the energy range included within the bias window, the Landauer-Bütticker's transmission formalism may lead to completely wrong results, if incoherent transport has relevant effects on the total transmission. An example can be the one of a potential barrier that is thick enough to lead small transmission probability. If the temperature is enough high that many highly energetic phonons are present, they can generate a relevant thermoionic current of electrons that classically overcome the barrier, thus leading to a much greater current w.r.t. the ballistic one. In this cases the transmission formalism is not reliable.

In summary it is possible to use the transmission formalism if:

- purely coherent transport is considered
- elastic non-coherent transport is considered (in which only phase-breaking phenomena occur but not energy relaxation ones)
- inelastic non-coherent linear transport is considered, i.e. the transmission function T(E) is approximately constant in the energy range within the bias window

Instead it must be carefully used in inelastic non-coherent and non-linear transport case, in which the transmission function T(E) varies abruptly within the bias window (e.g. because of localized states). In this last case the incoherent transport mechanisms can be so relevant that neglecting them can lead to completely wrong results.

Notice also that in the case of non-coherent transport it is possible to define an "effective transmission function"  $T_{eff}(E)$ , that embeds the scattering processes complexity, such that the Landauer's formula can be again be used. Nevertheless in order to derive  $T_{eff}(E)$  the NEGF formalism should be used, with the additional complexity of converting the NEGF equations into the Landauer's one with the term  $T_{eff}(E)$ . Thus usually it has no much sense this approach. A good and detailed treatment of these topics is provided in [39].

# 4.4 Molecular devices linear response and coherent transport

In section 4.1 it was introduced a simple model for transport through molecular quantum dots. In particular in sections 4.1.4 and 4.1.7 it was introduced a linear (or linearized) capacitive model for zero-extension quantum dots. A question that may arise is when these models hold, at least approximately. The answer comes from the discussion in the previous section regarding the linear response and the transmission formalism. Indeed if the transmission spectrum T(E) is approximately constant in the energy range within the bias window, the current-voltage characteristics will present a linear response, indeed the integral of a constant is a straight line. Notice that also the capacitances should be linearized w.r.t. the applied bias. This occurs if the applied bias is small, or if small variations occur such that they can be linearized around the working point. In order to get a linear response not only T(E) should be constant in the bias window, but also it should be independent on the applied voltage. The latter condition is usually true if the bias is much lesser than  $k_B T$  [39].

Nevertheless I would like to point out an important insight concerning the conditions under which T(E) is linear for a molecular device. In particular this happens if the molecular device is strongly coupled with the contacts. In that case indeed it was already mentioned that broadening occurs (section 4.1.1). If it is supposed to have an extremely strongly coupled molecular channel to the contacts, then the coupling factor  $\gamma$  will be very large, thus leading to a very broadened  $D_{ELi}(E)$  and consequently to a very broadened T(E). In this case it is easy to understand that T(E) is more constant than in the case of weak coupling. In conclusion, if strong coupling occurs, then a great delocalization of the wave-functions occur, leading to broadened transmission functions and thus a linear response. Otherwise if weak coupling occurs, then the localized states are responsible of a T(E) abruptly varying in energy, thus to a strongly non linear response. Another way of seeing the same concepts is in the current-voltage characteristics: the greater the broadening the more linear appears the current, the lower the broadening the steeper will appear the current variations in the *I-V* characteristics.

A last remark on incoherent transport is provided. From the discussion in the previous section it is known that a ballistic model for transport can be good if purely coherent transport is present, if elastic non-coherent transport is present, and if inelastic noncoherent transport is present but with a linear response. The latter case corresponds to the case of strong coupling with the contacts (see above). Thus the only case in which non-coherent transport can be relevant in molecular devices is when weak coupling case is present, and the incoherent contribution provides a large thermoionic current that the coherent picture is not capable of catching. This last case corresponds to the case in which a potential barrier arising from a localized (thus weakly coupled state), is enough big to make the thermoionic (classical) transmission probability comparable or greater to the coherent tunneling one. In this case, with incoherent transport models the calculated current can be very different from the coherently calculated one. Nevertheless one should also consider that molecules are small. A typical dimension is less than 1 nm (benzene ring is around 5 Å long while  $C_{60}$  has a diameter of the order of 7 Å). Thus the localized states that can prevent the coherent transport, can at most generate potential barrier of few Å, always less (or at most equal) to 1 nm. The coherent tunneling effect is thus not at all negligible through a barrier of that thickness. Moreover one should also consider the probability of interaction between electrons and molecular phonons (or molecular vibrations). Indeed in order to be in the case of relevant incoherent case the electrons should undergo to energy relaxation that is possible if they interact with phonons (or photons); since it was seen previously that the electron-electron interaction give rise to phase-breaking phenomena but not to energy relaxation, unless a third particle, like a phonon, is involved in the interaction.

In order to have an idea of the amount of incoherent transport through molecules (due to phonon interactions), the following reasoning is carried on. An electron at room temperature has a thermal velocity of the order of  $10^5$ m/s, and since the molecule is more or less 1 nm long, the electron transit time within the molecular channel is of the order of  $(10^{-9}\text{m})/(10^5\text{m/s})$  that is around  $10^{-14}$ s. A molecular vibration usually has a frequency of the order of  $10^{13}$ Hz, thus the vibration period will be of the order to  $10^{-13}$ s, ten times greater than the electron transit time. This could be an indication of the fact that the

incoherent transport is not in general negligible in molecular devices, but anyway the transit time is one order of magnitude lesser than the typical time required to accomplish a complete molecular vibration, thus making the resonance not exactly matched. In other words, the molecule can be considered essentially as a (quasi-)rigid environment, in which electrons travel, since, as mentioned, it requires one order of magnitude less to cross the entire molecule than to accomplish a complete oscillation. And since, as mentioned previously, rigid scatterers do not lead to phase-breaking processes, but only to phase mismatches, they are are accounted in a coherent transport framework by means of the transmission functions (that can be reduced by destructive interference of electron wave-functions). Actually this is true as long as molecules are very short. But there exist molecules that are even far longer than 1 nm. In such cases the transit time can be of the order of the molecular vibration period, or even longer, and consequently the molecule cannot be considered as rigid or static during the electron motion through it. In such cases the electron phase perturbation due to the molecular dynamics can be relevant and important, and it can leads to dynamic interference effects (phase-breaking). In this optics it should be now clear that the interaction probability of an electron traveling through the molecule and a molecular vibration or phonon depends on the time the electron spends inside the molecule. If the molecule is very short and the vibrational frequencies for that specific atomic/nuclear configuration are low (i.e. long vibrational periods), then the transport is in optimal approximation only coherent. Otherwise it may not be so. In section 4.1 it was introduced the concept of intrinsic time or escaping time  $\tau = \hbar/\gamma$ . It was said that it represents the time one electron on average spends inside the molecule before escaping into one contact. This time thus plays a role also in determining the amount of incoherent transport in the total transport balance [112]. Indeed, the longer is the time spent by an electron within the molecule, the larger the molecular vibrational interaction probability is. But since  $\tau$  is inversely proportional to the broadening  $\gamma$ , the smaller is the broadening (i.e. the weaker is the coupling of the molecular channel with the contacts) the longer is  $\tau$  and the higher is the probability of an electron to undergo incoherent scattering mechanics, that can be a phase-, momentum- or energy-relaxing process. In summary, if a short molecule is strongly coupled with contacts the transport the coherent transport will be essentially the only relevant mechanism of transport through it; if instead a long molecule weakly coupled with the contacts is considered, incoherent transport can be very important [112].

In this optics, [90] provides a discussion in which it concludes that incoherent transport is very improbable in devices shorter (smaller) than around 50 nm, like molecules are, because the transit time is much lesser than the scattering mean interaction time. Nevertheless this argument holds in general for crystalline semiconductor, while for molecules the previous considerations must be kept in mind. The level broadening plays a central role also in determining the amount of coherent transport, beside the more intuitive molecules length. In conclusion the point is that in many cases it may be accurate to completely neglect incoherent transport in molecular devices, especially if they are strongly coupled with contacts and the molecules are short, but there cases in which such a transport regime can be dominant, and by neglecting it quantitatively non-accurate results are obtained. These cases are often linked with a weak coupling of the molecular channel with the contacts, and with long molecules in which the orbital conjugation is broken. Indeed if

orbital conjugation is broken the molecular orbitals are not mixed together and thus they are localized, leading to an increase of the permanence time of electron in such part of the molecule, and within the molecule in general. The distance above which incoherent transport can be relevant can be also far below the limit of 50 nm mentioned above, and in particular in [113] it is found to be 2.5 nm while in [114] around 4 nm, both for conjugated molecules but with different properties. Thus the intrinsic geometry of the molecule can affect also the discriminating distance for transport features. These topics are again considered (under a slightly different perspective) in section 6.2.

# 4.5 The non-equilibrium Green's function formalism

Molecules are small and thus they obey to the laws of quantum mechanics. A purely quantum mechanical approach in modeling transport in molecular devices is the so called Non-Equilibrium Green's Function formalism (NEGF). For this reason it can do justice to all the complex phenomena that occur in such quantum systems.

In the previous sections of this chapter a "toy" model was presented, that despite its simplicity is capable of catching several physical insights of the transport through molecular channels. Nevertheless as already pointed out in section 4.1.9, it is not a general model and several issues are completely neglected, with the risk of getting totally unreliable quantitative results.

Moreover a brief introduction to the transmission formalism was also provided in section 4.3. The main advantage of the Landauer's approach is that the transmission function can be calculated with phenomenological (often simple) approaches, sometimes with semi-classical approaches, and in these cases the transmission formalism results extremely powerful since it easily provides accurate predictions on quantum mechanical systems in an easy way. Nevertheless it is not general and its application, especially for non-coherent transport should be carefully evaluated.

All these problems can be overcome once the NEGF model is considered. It is a rigorous way of treating the transport in mesoscopic systems that holds in general, with no restriction. In particular it holds also in the case of incoherent transport. Moreover by means of the NEGF formalism it is possible to evaluate also the dissipated power within a channel in which incoherent scattering mechanisms occur [39]. Actually the real power of the NEGF formalism is indeed in incoherent transport treatment. In general the NEGF formalism bridges the gap between the fully coherent picture of the Landauer's formalism and the fully incoherent picture of standard electronic devices modeling (that exploits average concepts like mobility, arising from the concepts of incoherent scattering processes). Moreover it is also a rigorous framework for the treatment of strongly non linear current-voltage characteristics, that are instead somehow difficult in conventional mesoscopic transmission based models. It will be addressed in the next chapter of this work.

# Chapter 5

# The Non-Equilibrium Green's Function formalism

The Non-Equilibrium Green's Function (NEGF) formalism is usually introduced in literature using the second quantization many-body perturbation formalism. In my opinion good references of these topics, that exploits such a formalism, are [115], [116]. Additionally, good introductions to second quantization and quantum field theory are provided in [92] and [117]. Nevertheless the part I of this work, i.e. the literature review about the theoretical models for molecular devices, is aimed to provide an introduction to these topics that is as much as possible accessible, fast, easy and clear to readers who have an electronic engineering background (like I am). In this optics, throughout this chapter, in reviewing and summarizing the main points of the NEGF formalism, I will follow the approach of [89] and [39]. This approach is an attempt of making accessible these topics also to readers who have never seen neither the second quantization formalism nor the many-body perturbation theory. This approach in thus suitable to be followed as reference for an introduction to NEGF suitable to be understood also to engineers. Indeed very often an electronic engineer working about molecular electronics has to set up atomistic simulations and handle their results, and the only way of doing it correctly is by having clear in mind the theory that is behind that processes, that is the NEGF theory for transport in mesoscopic systems. Having clear in mind the milestones of this rigorous theory concerning the transport in mesoscopic systems, one has not only the possibility of setting up and handling correct simulations but also to have clear the qualitative and quantitative explanation of the physics behind the obtained results. During the practical part of this work (part II). I will make a wide use of atomistic simulations, all based on the NEGF formalism.

# 5.1 The change of perspective

In order to understand the philosophy behind the NEGF formalism one has to consider the change of perspective w.r.t. traditional quantum mechanical problems, considered, for example, in chapter 2 and chapter 3. The purpose of this section is to exactly clarify it, in terms that are well established in an electronic engineer background.

In particular, standard quantum mechanical problems are aimed in finding what are the possible states of a quantum system. Indeed in solving the steady state Schrödinger's equation, the aim is to find the eigenvalues and eigenfunctions (or eigenstates) of a quantum mechanical system. These corresponds to the "allowed" or "permitted" states for that specific system. The procedure for doing so is to solve the steady state Schrödinger's equation under certain conditions, i.e. by enforcing suitable boundary conditions that represent the physical constraints arising from the specific physical nature of the system. Moreover this procedure is carried out assuming essentially no inputs, i.e. no stimuli that excite the considered system. An example could be a finite or infinite quantum well in which the steady states are the proper modes (i.e. eigenstates) for that specific geometry (width, height, etc...). Notice that, in order to point out exactly this, throughout all the previous chapters I always used interchangeably the following terms: eigenstates, proper modes, eigenfunctions, etc... So, standard quantum mechanical problems are problems in which the proper modes, i.e. the permitted states of the system are found. And in order to do that no stimulus is applied to the system, thus no input. In this optics, they all are free oscillation problems, in which it is studied the free response of the system, i.e. the response that arise from given initial/boundary conditions with no input. This is analogous of a free oscillation, or free response, of an electrical circuit/system in which it is assumed to have no input. The result in this case are the so called network poles, or oscillating frequencies, i.e. the proper modes of the system. Notice that the free response (the transient) of an electrical circuit is completely determined by the knowledge on the network poles, since it should be well known from circuit theory (or LTI system theory), that the free response (also called transient response) is a superposition of the proper modes of the network. In the analogy between electrical circuits and quantum mechanics one should only substitute the word "frequency", used in circuit theory, with the word "energy", used in quantum mechanics. Once this is done the conceptual correspondence is complete. For example, in the study of an LC resonator one is usually first of all interested in knowing the oscillation frequency, that is well known to be  $\omega_0 = 1/\sqrt{LC}$ . At this frequency the (ideal) LC circuit is able to sustain oscillations for an infinite time, even if no input is provided. In quantum mechanics an infinite height quantum well has some allowed energy values, that are the states in which a particle can exist for an infinite amount of time, even if no input and no interactions with external world are present.

It is also well known that beside a free oscillation study of the system, it is possible to perform a forced operation study of the system. In this case a continuous input (or in general an input) is provided as stimulus for the system and the output is evaluated, i.e. the system forced response is evaluated. An example can be the procedure of measuring the transfer function of an electrical circuit, e.g. an LC circuit. The input in that case is assumed to be a sinusoidal (harmonic) wave, and the output it is known to be again sinusoidal with same frequency but different amplitude (and phase). The ratio between

the output and the input provides the so called transfer function, that can be thus easily measured as just described by applying in input a series of sine signals at different frequencies. Notice that the transfer function is by definition the ration between the system output and its input, and it is rigorously defined in a forced operation study of the system. If this procedure is applied to the previously mentioned LC circuit it is well known that, considering increasing frequency, at low frequency (DC) essentially no output is present (no transmission occurs since the output is "filtered away"); then it increases until reaches a maximum, that is obtained for  $f_{input} = \frac{1}{2\pi\sqrt{LC}}$ , that is called the resonance frequency (notice that the term "resonance" is rigorously referred only to a forced operation, but the resonance frequency corresponds to the free oscillation frequency of the system). Then the transfer function modulus decreases again, until the output signal becomes negligible or null (again there is no more transmission through the filter). An important remark about this procedure is the following: in a free oscillation study the unknown is the oscillation frequency, thus the aim is to find a frequency value  $\omega_0$ . Instead in a forced operation study the frequency is supposed known, since it is the frequency of the input (sine) signals. In summary, a resonance peak occur when the input signal frequency is the resonance frequency, i.e. it is equal to the free oscillation frequency of the system.

Analogous facts happen also in a quantum system. In particular let's consider the single energy level quantum dot discussed in section 4.1. It is known that because of the presence of the contacts the level is broadened, e.g. with a Lorentzian distribution, and moreover it conducts only if is inside the bias window. Let's supposed that it is inside the bias window, but instead of calculating the current, let's supposed to be interested in evaluating the transmission function T(E), that was defined to be  $T(E) = 2\pi \frac{\gamma_S \gamma_D}{\gamma_S + \gamma_D} D_{EL}(E)$  in equation (4.5). If the geometry of the system is fixed then  $\gamma_S$  and  $\gamma_D$  are fixed and constant and thus  $T(E) \propto D_{EL}(E)$ , that is: the transmission coefficient trend w.r.t. energy E resembles the Lorentzian distribution shape. Now let's suppose to apply an analogous procedure to the one summarized above for the measurement of the transfer function. As said above the word "frequency" should be substituted with the word "energy", thus it is assumed to inject an electron with a known energy E from the source toward the quantum dot. Considering an electron of energy E has the only purpose of giving a physical picture to this procedure, the important fact is that one energy value E at a time is considered now, exactly like one frequency at a time was considered before relatively to the transfer function. When increasing energies are considered in input to the system the following happens. Since the shape of the transmission function resembles the shape of the Lorentzian distribution, the transmission coefficient will be small for energy well below the center value of the Lorentzian, that is the energy level  $E_L$  of the isolated quantum dot. Then for E approaching the value  $E_L$  the Lorentzian increases and for  $E = E_L$  the Lorentzian is maximum, i.e. for  $E = E_L$  a maximum in the transmission coefficient occurs. Then for larger energies the Lorentzian and the transmission decrease again until no transmission occur. At this point is clear that the transmitting behavior of the single level quantum dot is exactly analogous to the filtering behavior of the LC circuit. A resonance occurs for  $E = E_L$ , for which the transmission is maximum, where in fact  $E_L$  is an energy eigenvalues (free oscillation) of the quantum system.

Before completing the analogy let's summarize what said so far. In a free response operation study of the system the target is to find the system free oscillations, in terms of electrical circuits this means finding the oscillation frequencies, i.e. the free modes of the system, while in terms of quantum mechanical systems this means finding the permitted states, i.e. the eigenstates (and their energy eigenvalues and eigenfunctions) or proper modes of the system. The tasks are accomplished by setting to zero the inputs of the system, and by enforcing suitable boundary conditions. In a forced operation study of the system the target is to find the system response to a given stimulus. In terms of electrical circuits this means finding the frequency response (or analogously the transfer function) of the circuit, that indeed represents the response of the system to an input signal. In terms of quantum mechanical systems this means again finding the response of the system to an input stimulus, that in particular is an incoming electron (from the source contact) with a well defined (ad known) given energy E. Usually in forced operation study it is found that the system presents resonances at given frequencies or energies. In both electrical circuit and quantum mechanical terms the resonance corresponds to a maximum transmission. the difference is that in quantum mechanics the transmission corresponds indeed to the transmission of an electron.

The NEGF approach is conceptually different from the standard quantum mechanical one exactly in this: it corresponds to a forced operation study of the system instead of a free oscillation study of the system (like other quantum mechanical problems). Indeed throughout this chapter the energy will be no more the unknown to be found (the "allowed" energy eigenvalues), but instead it will be a parameter, characterizing the input electrons. Just to be very clear, another analogy can be the following: in standard quantum mechanics the task was finding the eigenenergies of an isolated channel, which is analogous in finding the resonant frequencies of a guitar string. Now with the NEGF approach the task is finding how the channel (or the string) responds when it is excited by an electron of any given energy from the contacts (or how the string responds when it is excited by a tuning fork at a given frequency).

In conclusion, it should be now clear the change of perspective of the NEGF framework w.r.t. to standard quantum mechanical problems: here the energy is considered known and a forced operation of the system is performed. Thus throughout this chapter E will be no more the unknown but a parameter, by means of which the results/solutions will be expressed.

#### Second quantization and quantum propagators

In general, with the second quantization formalism, the Green's function is seen as a so called "quantum propagator" [92], [115], [116]. In few words a quantum propagator is exactly a quantum mechanical operator that has the effect of propagating a stimulus that is supposed to be applied at a time t in the point  $\vec{r}$ , through the considered the system. The result is the knowledge of the system response to that specific stimulus, in any other point  $\vec{r'}$  at any other time t'. In this optics it is again clear that it corresponds in a forced operation of the system. Moreover that input stimulus in practice can be an incoming electron from the source, with a given energy. But more generally it can also be a photon, a phonon or any other quantum particle. Indeed the Green's function and NEGF (for the

out-of-equilibrium case) is a general perturbative theory that holds for any perturbation of the system under study. Nevertheless for the moment and in almost all practical cases, one is interested in the electrical current flowing through a (molecular) channel, thus it has sense of assuming the stimulus (equivalent, in the analogy of before, to a sine signal) to be an electron at a given energy.

## 5.1.1 The change of perspective in formulae

The above discussion is important from a conceptual point, because it is at the basis of the NEGF formalism. Nevertheless one may ask what are the practical implications of this "change of perspective". In this section I will try to give an answer to this question. A standard quantum mechanical problem very often reduces in solving the steady state Scrhödinger's equation, as it was discussed in chapter 2. Such an equation takes the form:

$$\widehat{H}\psi = E\psi$$

notice that is possible to rewrite it as:

$$\left[E - \widehat{H}\right]\psi = 0$$

From the previous treatment it is now clear that the last equation (that is always the steady state Schrödinger's equation for the system under study) corresponds to a free operation of the system study, in which no input is considered. The fact that is assumed to have no input leads to the zero at right-hand side (notice the correspondence with linear homogeneous systems of the kind  $[A]{x} = 0$ , especially if expressed in matrix form). In the moment in which an input, or a source (e.g. an electron that flows into the channel from a contact), is considered, the last equation is modified and an equation of the kind:

$$\left[E - \hat{H}\right]\psi = source \tag{5.1}$$

is obtained; in which the term "source" represents exactly the input stimulus (notice the correspondence with linear non-homogeneous systems). A full derivation of a general expression of the kind of eq. (5.1) is carried out in section 5.9. For the moment let's consider its physical meaning. The difference of eq. (5.1) w.r.t. standard quantum mechanical system is exactly in the source term, that usually does not appear. The meaning was already clarified previously and it is linked to the forced operation study of the system. Moreover it is of fundamental importance understand that assuming that a system can have an input, i.e. a source term, that can be an electron that flow from the a contact into the system, corresponds in assuming that the system can be open. By definition an open system is a system in which it is possible to have an exchange of matter between the system itself and the external world. Instead a closed system is a system in which it is not possible of having such exchange of matter. Standard quantum mechanical problems are thus referred to close systems, i.e. to system that are isolated from the rest of the world and do not exchange matter (particles or electrons) with the external world. Instead in a force operation study of the system, i.e. when the NEGF framework is considered, the

system is assumed to be open. This means that it can interact with the external world and in particular it can exchange electrons (i.e. matter) with the external world. This is represented by means of the source term in eq. (5.1). This topic regarding open and closed systems is further discussed in next sections, in particular in section 5.3.

Therefore eq. (5.1) can be derived when a non-isolated system is considered, and it is possible to embed in the term "source" the external interaction, i.e. the input stimulus. Equation (5.1) represents an open system, that is the case of interest in the moment in which a forced operation study of the system is performed, i.e. when an input stimulus is indeed considered. For the moment this is the main point or the main conceptual implication of the "change of perspective" widely discussed above. With this in mind it will be easier to address the topics treated in the next sections.

A last remark before going on: the general definition of Green's function, from a mathematical standpoint, is the following:

$$LG = \delta \tag{5.2}$$

where L indicates whatever mathematical linear operator,  $\delta$  is a delta-Dirac function and G is the Green's function. Notice that L can be e.g. a differential operator, like the Hamiltonian one, and it can also be a matrix representation of a linear operator (in that case eq. (5.2) is intended as algebraic -matrix- equation). More in general L can also be the entire Schrödinger's equation, indeed it is a linear equation/operator. Proceeding in this way, the  $\delta$  function can be intended as the input of the system described by the Schrödinger's equation L, and consequently G is the output of the system when the input is a delta-Dirac. In these terms the Green's function is in general an impulse response for a system whose input is indeed a delta-Dirac. In general it is called Green's function (instead of simply impulse response), if it is the output of the system when the delta-Dirac is not in time domain but in space domain. In that case it is a 3D delta Dirac, defined as:  $\delta(\vec{r} - \vec{r_0}) = \delta(x - x_0)\delta(y - y_0)\delta(z - z_0)$ . In the most general case it could also be 4D delta-Dirac (in the three space coordinates and in the time one). Notice that in order to have true eq. (5.2) it must hold:

$$G = L^{-1}$$

where  $L^{-1}$  is the inverse linear operator of L, that, if expressed in matrix form, corresponds exactly to the inverse matrix. In general it is possible to write the response R to the stimulus S of the system represented by the linear operator L as follows [39]:

$$LR = S \rightarrow R = L^{-1}S = GS$$
 ,  $G = L^{-1}$ 

where G is indeed the Green's function. This further clarify the point. Since the Green's function is the impulse response of the system described by L, each output of the system R can be written in function of the (known) input S by means of G. In other words, exactly like it happens for LTI systems (e.g. electrical circuits), the output of the system can be written in terms of the system impulse response. From which the knowledge concerning the system is complete in the moment in which it is known its Green's functions (impulse response). In particular during the next sections of this chapter it will be clear that it is

possible to derive each physical quantity of interest starting from the Green's function, and also the electrical current will be written in terms of Green's function. By putting together the last relation and eq. (5.1) it follows:

$$\left[E - \hat{H}\right]\psi = source \quad \rightarrow \quad \psi = \left[E - \hat{H}\right]^{-1} source$$

From which is clear that:

$$\psi = G \text{ source }, \quad G = \left[E - \widehat{H}\right]^{-1} \quad and \quad \left[E - \widehat{H}\right]G = \delta$$
 (5.3)

Thus once again, in terms of equation (5.1), the Green's function corresponds to the wave-function  $\psi$  that is the output of the system, in the moment in which the input term "source" is a delta-Dirac.

## 5.2 1D retarded and advanced Green's functions

In general the inverse of a differential operator is not uniquely determined until the boundary conditions are specified [39]. It is thus possible to define two Green's functions and not only one, corresponding to different boundary conditions [89], [39]. These Green's functions are called "retarded Green's function" and "advanced Green's functions", respectively. In order to introduce them I will follow the approach of [39], and the difference between the two Green's function will be addressed by means of a simple example.

Assume to have a 1D system (x-coordinate only), with a constant potential  $U_0$ . From the previous treatment of section 5.1.1 it is possible to write directly the Green's function as:

$$G = \left[ E - U_0 + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right]^{-1}$$

with:

$$\left[E - U_0 + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\right] G(x, x') = \delta(x - x')$$
(5.4)

Notice again that the last equation looks like the Schrödinger's equation but with a source term  $\delta(x - x')$  on right-hand side (instead of zero). Notice also that since  $U_0$  is constant and since the potential energy is defined up to an additive constant, it is always possible to choose such an additive constant such that it results  $U_0$ . This reasoning was already carried out in section 2.3.7, when the potential well was considered. In this optics it is possible to easily write the solution of the Schrödinger's equation as the solution for the free particle case (that indeed corresponds to the case  $U_0 = 0$ ), that is the sum of a forward propagating wave and a backward propagating wave. And notice that such a solution must hold in all the points in which it is assumed  $U_0$  constant or equivalently null. This is essentially what did in section 2.3.7 for writing the wave-function inside the quantum well, in which indeed the particle behaves as free. Here the situation is analogous, with the only differences that the potential is considered constant and equal to  $U_0$  in all x-axis points, and that instead of having zero at right-hand side there is a delta-Dirac. Nevertheless it is possible to write the solution of eq. (5.4) like a sum of a forward wave and a backward wave. At this point since the delta-Dirac  $\delta(x-x')$  is shifted at position x', then the Green's function G(x, x') can be interpreted as the wave-function at position x resulting from a unit excitation applied at x'. Physically it has thus sense that such an excitation give rise to two waves traveling outwards from the excitation point: a forward propagating wave in direction +x, and a backward one propagating in direction -x:

$$G(x, x') = \begin{cases} A^+ e^{ik(x-x')} &, & \text{if } x > x' \\ A^- e^{-ik(x-x')} &, & \text{if } x < x' \end{cases}$$

where  $k = \sqrt{\frac{2m}{\hbar^2}(E - U_0)}$ . It is possible to verify that this solution satisfies eq. (5.4) at all points other than x = x'. In order to satisfy eq. (5.4) also in x = x' the continuity of G(x, x') must be enforced in x = x', and this is pretty analogous to what was did in all the problems of section 2.3.7. Nevertheless a difference there exist on the first derivative boundary condition of G(x, x'). Indeed in section 2.3.7 it was always enforced that also the first derivative of the wave-function must have been continuous. But this fact was linked to the zero at right-hand side that is present in the Schrödinger's equation. Here instead there is a delta-Dirac, that corresponds to a first derivative of a step function. Consequently in order to satisfy eq. (5.4) the Green's function must have a discontinuous first derivative (think to a step-like discontinuity of the first derivative of G in x = x'), such that its second derivative can give rise to the delta-Dirac and thus eq. (5.4) is satisfied. Therefore it is possible to find suitable values for the two constants  $A^+$  and  $A^-$  by enforcing G(x, x') to be continuous in x = x' and its first derivative discontinuous in x = x'. The full procedure is illustrated in [39]. Here it is not important to carry out all the calculations, but only to understand them and the concepts arising from them.

With this procedure it is possible to find a Green's function G(x, x') that is solution of eq. (5.4). This solution includes only a forward wave for x > x' and only a backward wave for x < x', as one can imagine to be if the stimulus is applied in x'. Nevertheless there is another acceptable solution for eq. (5.4), that is the one that comprise a backward propagating wave for x > x' and a forward propagating wave for x < x'. Indeed in the above discussion it was mentioned that the solution of Schrödinger's equation with a constant potential  $U_0$  is given by the sum of a forward and a backward wave, that are defined in the entire region in which  $U_0$  is kept constant, that in this case is the whole x-axis. Here the situation (and the equation) is similar, and indeed also the Green's function:

$$G(x, x') = \begin{cases} B^{-}e^{-ik(x-x')} &, & \text{if } x > x' \\ B^{+}e^{+ik(x-x')} &, & \text{if } x < x' \end{cases}$$

is a solution of eq. (5.4). This solution includes the two waves that were excluded in the first solution, namely a backward wave for x > x' and a forward wave for x < x'. The two constants  $B^-$  and  $B^-$  can be determined by enforcing again the continuity on G at x = x' and the discontinuity of its first derivative in x = x'.

Beside the mathematics, the important fact is that both the solutions are acceptable. The first one corresponds to waves that are traveling outwards from x', i.e. from the excitation

point. It is called "retarded Green's function", and it is indicated with  $G^{R}(x, x')$ :

$$G^{R}(x, x') = \begin{cases} A^{+}e^{ik(x-x')} &, & \text{if } x > x' \\ A^{-}e^{-ik(x-x')} &, & \text{if } x < x' \end{cases}$$

The second instead corresponds to incoming waves that disappear at the excitation point x', and it is called "advanced Green's function". It is indicated with  $G^A(x, x')$ :

$$G^{A}(x, x') = \begin{cases} B^{-}e^{-ik(x-x')} &, & \text{if } x > x' \\ B^{+}e^{+ik(x-x')} &, & \text{if } x < x' \end{cases}$$

Both  $G^R(x, x')$  and  $G^A(x, x')$  satisfy eq. (5.4), but they correspond to different boundary conditions: the retarded corresponds to outgoing waves, while the advanced to incoming waves (far away from the source). What should be thus considered in a specific case is a matter of boundary conditions. This is the topic addressed in the next section.

# 5.3 Boundary conditions and open systems

In the previous section it was said that there are two solutions that equally satisfy eq. (5.4), namely the retarded and the advanced Green's functions. This holds in general, also for 3D systems. It was also said that the choice of the specific solution between the two, depends on the applied boundary conditions. In general the boundary conditions are a way of representing some physical constraints that exist in the real physical system that is modeled by means of the equations. Enforcing them corresponds in selecting the solution that is correct for a given specific application. A way to incorporate the boundary conditions directly within equation (5.4), is to add an infinitesimal imaginary part to the energy. Thus instead of eq. (5.4) one can write:

$$\left[E - U_0 + \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + i\eta\right]G^R(x, x') = \delta(x - x')$$
(5.5)

where  $\eta$  is assumed to be infinitesimal and strictly positive:  $\eta > 0$ . In this way the propagation constant is changed, and it becomes:

$$k' = \sqrt{\frac{2m}{\hbar^2} (E + i\eta - U_0)} = \sqrt{\frac{2m}{\hbar^2} (E - U_0)} \sqrt{1 + \frac{i\eta}{E - U_0}}$$

Notice that in this way  $k' = \operatorname{Re}(k') + i \operatorname{Im}(k')$  is complex, with a real part equal to k and with a small and positive imaginary part. In the previous section it was implicitly assumed that  $E > U_0$ , indeed for  $E < U_0$  there exists no state since  $U_0$  is infinitely extended in all the point of the domain (the solution would be null), such that  $E - U_0 > 0$  and the imaginary part is maintained positive. The positive imaginary part makes the advanced Green's function going to infinite for both  $x \to +\infty$  and  $x \to -\infty$ . Indeed:

$$G^{A}(x,x') = \begin{cases} B^{-}e^{-ik'(x-x')} = B^{-}e^{-i\operatorname{Re}(k')(x-x')}e^{+\operatorname{Im}(k')(x-x')} &, & \text{if } x > x' \\ B^{+}e^{+ik'(x-x')} = B^{+}e^{+i\operatorname{Re}(k')(x-x')}e^{-\operatorname{Im}(k')(x-x')} &, & \text{if } x < x' \end{cases}$$

and both the exponentials tends to infinite for  $x \to \pm \infty$  since k' has a positive imaginary part. Instead the retarded Green's function is still limited for each x, and also for  $x \to +\infty$ and  $x \to -\infty$ :

$$G^{R}(x,x') = \begin{cases} A^{+}e^{ik(x-x')} = A^{+}e^{+i\operatorname{Re}(k')(x-x')}e^{-\operatorname{Im}(k')(x-x')} &, & \text{if } x > x' \\ A^{-}e^{-ik(x-x')} = A^{-}e^{-i\operatorname{Re}(k')(x-x')}e^{+\operatorname{Im}(k')(x-x')} &, & \text{if } x < x' \end{cases}$$

Thus as indicated in eq. (5.5) if a small (infinitesimal) positive  $\eta$  is considered and if the imaginary term  $+i\eta$  is added to the energy, as in eq. (5.5), then the only acceptable solution is the retarded Green's function, since the response of the system must be bounded (otherwise it would be an unstable system, meaning that it is able to generate an infinite amount of energy in response to a finite stimulus, but this has no sense).

Analogously if a small (infinitesimal) term  $-i\eta$ , with  $\eta > 0$ , is added to the energy, eq. (5.4) becomes:

$$\left[E - U_0 + \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - i\eta\right]G^A(x, x') = \delta(x - x')$$
(5.6)

and the only acceptable solution becomes the advanced Green's function.

In general with reference to eq. (5.3), it is possible to define the retarded Green's function as:

$$G^{R} = \left[E - \hat{H} + i\eta\right]^{-1} \quad , \quad \eta \to 0^{+} \tag{5.7}$$

and the advanced Green's function as:

$$G^{A} = \left[E - \hat{H} - i\eta\right]^{-1} \quad , \quad \eta \to 0^{+} \tag{5.8}$$

Very often from hereon, if no misunderstanding is possible, I will refer to the retarded Greens' functions simply as Green's function.

Notice that adding an imaginary part to the energy is also a way of considering a system "open". It was already discussed that with the NEGF perspective a system is considered open, in the sense that it can exchange electrons with the external world (i.e. with the contacts), such that an input electron can be considered as stimulus for the system and a force operation study of the system is performed. In section 4.1.1, it was already said that an imaginary part of the energy is a way of considering exactly the fact that the system is not isolated, but it is open. Indeed if one wants to make calculations only considering the active part of the device, i.e. the channel, one should model the contact suitably, in order to consider the fact that the system is not isolated. A way for considering the contacts is to model them, and thus to write equations that not only involve the channel but also the contacts. Nevertheless the problem of this approach is that the contacts should have an enormous number of electrons and electron states, in order to be good contacts (see also section 4.1.3). This makes the previous approach unfeasible from a practical standpoint. Thus usually one prefers to write and solve equations relatively to the conductive channel only. In this latter approach nevertheless the contacts must be somehow modeled. The mathematical way of model them is by means of boundary conditions. And the correct boundary conditions for an open system are exactly the introduction of an imaginary part of the energy. Indeed in this way the exponential functions, that with a

real energy represent propagating waves, become real exponent (exponential) functions, i.e. decaying exponential. This holds true both for space and time variables. Indeed it was mentioned that the delta-Dirac pulse input can be in general both in space (3D) and in time (1D). If one considers time, then the same discussion already done in section 4.1.1 holds. In particular the states within the channel are no more infinite life-time states, but finite lifetime states, since an electron after a given amount escapes from the channel into the contacts. This is represented by a real exponent in the general solution of Schrödinger's equation. That can be obtained by means of an imaginary part of the energy. For space delta-Dirac the following remark can be done. If one considers an excitation in x' (delta-Dirac), it is reasonable thinking that this will propagate by means of outwards waves, like represented by the retarded Green's function. If the system is open, that is the electrons can escape from it (from the channel), then no reflections will occur at the channel boundaries. Consequently one will not have the advanced Green's function (that represents incoming waves, for example the reflected ones). This can be accounted for by means of the infinitesimal  $+i\eta$  term, as explained above. In conclusion, the infinitesimal parts of the energy are a way of representing the open system boundary conditions.

# 5.4 Eigenfunction expansion and matrix representation

It was shown in section 2.4 that is possible to represent a differential operator in matrix form, in particular it was demonstrated the way of rewriting the steady state Schrödinger's equation in matrix form as:

$$E[S]\{\psi\} = [H]\{\psi\}$$

where here the coefficient vector of the wave-function  $\psi$  is indicated with  $\{\psi\}$  (in section 2.4 it was instead indicated with  $\{c\}$ ); and where [S] is the so called overlap matrix and [H] is a possible matrix representation of the Hamiltonian operators. The elements of [S] and [H] are given by:

$$S_{nm} = \int u_n^*(\vec{r}) u_m(\vec{r}) d\vec{r} \quad , \quad H_{nm} = \int u_n^*(\vec{r}) \hat{H} u_m(\vec{r}) d\vec{r}$$

where  $\{u_m\}_m$  is the chosen basis set of basis functions for the particular representation. Notice that in electronic structure calculations of molecules it can be one of the basis sets introduced in chapter 3. Moreover it was said that if the basis set is orthonormal then the overlap matrix becomes the identity matrix [I], and the Schrödinger's equation assumes the form of a standard eigenvalues problem:

$$E\left[I\right]\left\{\psi\right\} = \left[H\right]\left\{\psi\right\} \quad \rightarrow \quad E\left\{\psi\right\} = \left[H\right]\left\{\psi\right\}$$

That can be again rewritten as:

$$\begin{bmatrix} E [I] - [H] \end{bmatrix} \{ \psi \} = 0 \tag{5.9}$$
197

It will be useful in the next of this chapter to represent in matrix form the Green's function. In particular it is useful and interesting to write it in the matrix representation of the eigenfunctions of the Hamiltonian operator. Indeed it was already discussed several times in chapter 2 that the set of eigenfunctions of an Hermitian operator is orthogonal (orthonormal after normalization) and complete, and thus it can be used as basis set for the Fourier series expansion/transform. Consequently it can be the basis set used for a representation of whatever linear (differential) operator, like the Green's function is (see eq. (5.7) and (5.8)). Notice that the eigenfunctions of the Hamiltonian operator (like any Hermitian operator eigenfunctions) are orthonormal and thus the overlap matrix reduces to the identity one as remembered above. From the general definition of Green's function it is clear that it is a linear operator (since it is the inverse of a linear operator L representing the system):  $G = L^{-1}$ , and thus it is expected to admit matrix representations (in an Hilbert space). In particular it is indeed possible to rewrite equations (5.7) and (5.8) in matrix form, and this is possible when eq. (5.4) is rewritten in matrix form. This is the purpose of this section. Notice that eq. (5.4) is a simplification for a 1D case, and in general in 3D it can be rewritten as:

$$\left[E - \hat{H} + i\eta\right] G^R(\vec{r}, \vec{r'}) = \delta(\vec{r}, \vec{r'})$$
(5.10)

The attempt now is to convince the reader that eq. (5.10) can be rewritten in matrix form as:

$$[(E+i\eta)[I] - [H]][G^R] = [I]$$
(5.11)

where the matrix representation is the one in the orthonormal basis set of the eigenfunctions of  $\hat{H}$ . Notice that E and  $+i\eta$  are scalars, thus they must be multiplied by the identity matrix in order to perform the matrix difference with [H], the identity matrix arise from the fact that the Hamiltonian eigenfunctions are orthonormal. Notice that  $[G^R]$  is a matrix, representing the retarded Green's function, and that the delta-Dirac becomes the identity matrix [I]. Notice the similarity between equations (5.9) and (5.11), corresponding to the already discussed similarity between the analogous equations with differential operators.

The task of rewriting eq. (5.10) like (5.11) will be achieved in two consecutive steps. Firstly a representation of the Green's function in the basis set of the Hamiltonian operator eigenfunctions will be provide. Then eq. (5.11) will be derived.

## 5.4.1 Eigenfunction expansion

In this section a general representation of  $G^R(\vec{r}, \vec{r'})$  in the basis of the Hamiltonian eigenfunctions is derived. The complete procedure is also detailed in [39]. The steady state Schrödinger's equation in differential form can be written as:

$$\dot{H}\psi_{\alpha} = \varepsilon_{\alpha}\psi_{\alpha} \tag{5.12}$$

where  $\psi_{\alpha}$  are the eigenfunctions and  $\varepsilon_{\alpha}$  the (energy) eigenvalues. Since the Hamiltonian eigenfunctions are orthonormal it holds:

$$\int \psi_{\beta}(\vec{r})\psi_{\alpha}(\vec{r})d\vec{r} = \delta_{\alpha\beta}$$
198

where  $\delta_{\alpha\beta}$  is the Kronecker delta. The retarded Green's function can be written as Fourier series in the eigenfunctions basis  $\{\psi_{\alpha}\}_{\alpha}$  like:

$$G^{R}(\vec{r},\vec{r'}) = \sum_{\alpha} C_{\alpha}(\vec{r'})\psi_{\alpha}(\vec{r})$$

where the coefficients must be determined. From the definition of Green's function (eq. (5.7)):

$$\left[E - \hat{H} + i\eta\right]G^R(\vec{r}, \vec{r'}) = \delta(\vec{r}, \vec{r'})$$

Making use of eq. (5.12) and considering that  $\hat{H}$  acts only on  $\vec{r}$  and not on  $\vec{r'}$ :

$$[E - \varepsilon_{\alpha} + i\eta] \sum_{\alpha} C_{\alpha}(\vec{r'})\psi_{\alpha}(\vec{r}) = \delta(\vec{r}, \vec{r'})$$

multiplying by  $\psi^*_{\alpha}(\vec{r})$  and integrating over  $\vec{r}$  (considering the orthonormality relation):

$$\sum_{\alpha} \int \left[ E - \varepsilon_{\alpha} + i\eta \right] C_{\alpha}(\vec{r'}) \psi_{\alpha}(\vec{r}) \psi_{\alpha}^{*}(\vec{r}) d\vec{r} = \int \delta(\vec{r}, \vec{r'}) \psi_{\alpha}^{*}(\vec{r}) d\vec{r}$$
  

$$\rightarrow \sum_{\alpha} \left[ E - \varepsilon_{\alpha} + i\eta \right] C_{\alpha}(\vec{r'}) = \psi_{\alpha}^{*}(\vec{r'})$$

From which:

$$C_{\alpha}(\vec{r'}) = \frac{\psi_{\alpha}^*(\vec{r'})}{E - \varepsilon_{\alpha} + i\eta}$$

In conclusion it is possible to express the retarded Green's functions on the basis of the eigenfunctions of the Hamiltonian operator as:

$$G^{R}(\vec{r},\vec{r'}) = \sum_{\alpha} C_{\alpha}(\vec{r'})\psi_{\alpha}(\vec{r}) = \sum_{\alpha} \frac{\psi_{\alpha}(\vec{r})\psi_{\alpha}^{*}(\vec{r'})}{E - \varepsilon_{\alpha} + i\eta}$$
(5.13)

An analogous procedure for the advanced Green's function leads to:

$$G^{A}(\vec{r},\vec{r'}) = \sum_{\alpha} \frac{\psi_{\alpha}(\vec{r})\psi_{\alpha}^{*}(\vec{r'})}{E - \varepsilon_{\alpha} - i\eta}$$
(5.14)

### 5.4.2 An important relation

From the last two equations (5.13) and (5.14), it is immediate to verify that:

$$G^{A}(\vec{r},\vec{r'}) = \left[G^{R}(\vec{r},\vec{r'})\right]^{*} \quad \rightarrow \quad G^{A} = \left[G^{R}\right]^{\dagger} \tag{5.15}$$

That is: the advanced Green's function is the Hermitian conjugate of the retarded one. If a matrix representation is used (see next section), it means that  $G^A$  is the transpose complex conjugate of  $G^R$ .

## 5.4.3 Matrix notation

Before rewriting eq. (5.10) in matrix form, it is necessary to write a representation for the delta-Dirac function in the same basis, i.e. the Hamiltonian operator eigenfunctions basis set. In order to do that, the definition of Fourier series expansion is used, indeed expanding a given function in a given basis set corresponds to provide its Fourier expansion in such basis set (see also chapter 2). In particular:

$$\delta(\vec{r} - \vec{r'}) = \sum_{\alpha} C_{\alpha} \psi_{\alpha}(\vec{r}) \quad , \quad C_{\alpha} = \left(\psi_{\alpha}(\vec{r}), \delta(\vec{r} - \vec{r'})\right) = \int_{-\infty}^{+\infty} \psi_{\alpha}^{*}(\vec{r})\delta(\vec{r} - \vec{r'})d\vec{r} = \psi_{\alpha}^{*}(\vec{r'})$$

From which:

$$\delta(\vec{r} - \vec{r'}) = \sum_{\alpha} \psi_{\alpha}^*(\vec{r'})\psi_{\alpha}(\vec{r})$$

In general also for the Green's functions  $G^R(\vec{r}, \vec{r'})$  and  $G^A(\vec{r}, \vec{r'})$  it is possible to apply directly the definition ad proceed as done for the delta-Dirac, nevertheless it was easier and interesting to achieve the result with the procedure used before.

At this point is possible to substitute in eq. (5.10) the representations of  $G^R(\vec{r}, \vec{r'})$ ,  $\delta(\vec{r} - \vec{r'})$ and  $\hat{H}$  in the Hamiltonian eigenfunctions basis set. Notice that each Hermitian operator in the basis set of its eigenfunctions become diagonal with its eigenvalues as diagonal elements, this is trivially verified from eq. (5.12), once it is written in matrix form. Thus eq. (5.10) becomes (remember the orthonormality of  $\{\psi_{\alpha}\}_{\alpha}$ ):

$$\left[E - \hat{H} + i\eta\right] G^{R}(\vec{r}, \vec{r'}) = \delta(\vec{r}, \vec{r'})$$

$$\rightarrow \quad \left[(E + i) \left[I\right] \eta - \left[H\right]\right] \sum_{\alpha} \frac{\psi_{\alpha}(\vec{r})\psi_{\alpha}^{*}(\vec{r'})}{E - \varepsilon_{\alpha} + i\eta} = \sum_{\alpha} \psi_{\alpha}^{*}(\vec{r'})\psi_{\alpha}(\vec{r})$$

$$\rightarrow \quad \left[(E + i) \left[I\right] \eta - \left[H\right]\right] \sum_{\alpha} \frac{1}{E - \varepsilon_{\alpha} + i\eta} = \sum_{\alpha} 1 = [I]$$

That is:

$$\left[ (E+i\eta) \left[ I \right] - \left[ H \right] \right] \left[ G^R \right] = \left[ I \right]$$

that corresponds to eq. (5.11) with  $[G^R]$  diagonal matrix, with diagonal elements:  $\frac{1}{E-\varepsilon_{\alpha}+i\eta}$ , that is:

$$[G^{R}] = \begin{bmatrix} \frac{1}{E-\varepsilon_{1}+i\eta} & 0 & \dots \\ 0 & \frac{1}{E-\varepsilon_{2}+i\eta} & \dots \\ 0 & 0 & \dots \end{bmatrix}$$
(5.16)

and where, as already mentioned:

$$\begin{bmatrix} H \end{bmatrix} = \begin{bmatrix} \varepsilon_1 & 0 & \dots \\ 0 & \varepsilon_2 & \dots \\ 0 & 0 & \dots \end{bmatrix}$$

Notice that  $[G^R]$  is exactly the inverse of the matrix  $[(E + i\eta)[I] - [H]]$ , indeed their product gives the identity matrix [I], that is:

$$[G^{R}] = [(E + i\eta) [I] - [H]]^{-1}$$
  
200

# 5.5 Green's function poles

From the treatment in the previous section it is clear that the Green's functions (both the retarded one and the advanced one) have poles. Indeed when the energy eigenstate representation is considered:

$$[G^{R}] = \begin{bmatrix} \frac{1}{E - \varepsilon_{1} + i\eta} & 0 & \dots \\ 0 & \frac{1}{E - \varepsilon_{2} + i\eta} & \dots \\ 0 & 0 & \dots \end{bmatrix}$$

it is clear the if the infinitesimal  $\eta$  would be exactly zero then the Green's function would be infinite at energy values  $E = \varepsilon_{\alpha}$ , i.e. for energies equal to the energy eigenvalues of the system. The infinitesimal  $\eta$  prevents the Green's function to blow to infinity. Notice that this behavior is quite analogous again to the behavior of the impulse response of an electrical circuit. Indeed the impulse response in frequency domain becomes the transfer function (by means of a Laplace or Fourier transform), and its poles corresponds exactly to the proper modes of the circuit. Here the situation is similar. The Green's function  $G^R(\vec{r},\vec{r'})$  is the impulse response of the system, and its representation in the energy eigenstates basis set corresponds to a Fourier transform of representation of  $G^R$ , indeed it corresponds to an its representation in the energy domain (the energy domain is isomorphous to frequency domain since E = hf, linked by a Fourier transform to time domain). And thus  $G^R$  presents poles in correspondence of the proper modes, i.e. the energy eigenvalues, of the system. The analogy is not at all complete since here there is the infinitesimal  $\eta$  that prevents  $G^R$  to blow to infinity. Nevertheless in analogy to circuit theory a maximum of transmission occurs for  $E = \varepsilon_{\alpha}$ , i.e. when the resonance condition occurs. This feature was already commented in the introductory section concerning the change of perspective.

## 5.6 Time domain impulse response

It was already discussed that the Green's function has the meaning of impulse response. Moreover it was said that this holds in general for time and space impulses, i.e. for time (3D) delta-Dirac  $\delta(\vec{r} - \vec{r'})$  and for time (1D) delta-Dirac  $\delta(t - t_0)$ . In this section is pointed out that the Green' function is indeed the impulse response in time domain for the time-dependent Schrödinger's equation. It is intuitive thinking that if a time impulse response is considered the system should be described by the time-dependent Schrödinger's equation and not by the steady state one. It will be considered a delta-Dirac centered in  $t_0 = 0$ , i.e.  $\delta(t)$ . In order to show that the Green's function is the time domain impulse response of the time-dependent Schrödinger's equation, let's start from the energy eigenfunctions representation of the Green's function  $[G^R(E)]$  derived in the previous section, notice that it if function of energy E:

$$[G^{R}] = \begin{bmatrix} \frac{1}{E - \varepsilon_{1} + i\eta} & 0 & \dots \\ 0 & \frac{1}{E - \varepsilon_{2} + i\eta} & \dots \\ 0 & 0 & \dots \end{bmatrix}$$
201

It is possible to show that its Fourier transform is (to this purpose see also appendix C.1):

$$\left[G^{R}(t)\right] = -\frac{i}{\hbar}\theta(t)e^{-\frac{\eta}{\hbar}t} \begin{bmatrix} e^{-\frac{i}{\hbar}\varepsilon_{1}t} & 0 & \dots \\ 0 & e^{-\frac{i}{\hbar}\varepsilon_{2}t} & \dots \\ 0 & 0 & \dots \end{bmatrix}$$

where  $\theta(t)$  is the Heaviside function. Notice that a representation of  $G^R$  in the system energy eigenstates is an its representation in energy domain, and the Fourier transform is a biunivocal application that allows to transform between energy (remember always that  $E = hf = \hbar\omega$ ) and time domain. Thus the last equation is the expression of  $G^R$  in time domain. Moreover it is possible to show that the diagonal elements of  $[G^R(t)]$ , namely the  $G^R_{\alpha,\alpha}(t)$ , are a solution for the following equation (to this purpose see appendix C.2):

$$\left(i\hbar\frac{\partial}{\partial t} - \varepsilon_{\alpha}\right)G^{R}_{\alpha,\alpha}(t) = \delta(t)$$

The last relation can be thus generalized in matrix form as follows:

$$\left(i\hbar\frac{\partial}{\partial t} - [H]\right)\left[G^{R}(t)\right] = \left[I\right]\delta(t)$$
(5.17)

From which is evident the interpretation of the Green's function (in time domain) as the (time) impulse response of the time-dependent Schrödinger's equation (eq. (2.17)) that indeed can be in general rewritten with all the terms at left side:

$$\left(i\hbar\frac{\partial}{\partial t} - [H]\right)\left\{\psi(t)\right\} = 0$$

In light of this the (n, m) elements of  $[G^R(t)]$ , namely  $G^R_{n,m}(t)$  provides the *n*-th component of the wave-function if the system is given an impulse excitation at its *m*-th component. Notice that  $[G^R(t)]$  is defined only for positive times t > 0 (it is multiplied by the Heaviside function  $\theta(t)$ ), i.e. it is causal, and indeed it provides the impulse response for positive times, successive to the time instant t = 0 at which the system is excited by means of the  $\delta(t)$ .

Nevertheless, there is another solution that mathematically is acceptable, and it is the advanced Green's function:

$$\left[G^A(t)\right] = \left[G^R(-t)\right]^*$$

with an analogous procedure it is possible to verify that it is solution of the same equation:

$$\left(i\hbar\frac{\partial}{\partial t} - [H]\right)\left[G^A(t)\right] = \left[I\right]\delta(t)$$

The difference is that  $[G^A(t)]$  is null for t > 0, and non-null for negative times. In energy domain the advanced and the retarded Green's function differ only for the infinitesimal  $\pm i\eta$  term:

$$[G^{R}(E)] = [(E + i\eta) [I] - [H]]^{-1} , \quad [G^{A}(E)] = [(E - i\eta) [I] - [H]]^{-1}$$
202

Instead in time domain they are very different, since the retarded one is causal and null for t < 0, while the advanced one is non-causal (or anti-causal) an null for t > 0. The retarded Green's function has thus the physical meaning of impulse response (to a impulse happening at t = 0), while the advanced one has no physical meaning (it is solution of the same equation but with unphysical initial conditions).

# 5.7 A remark on notation

In the following of this chapter I will simply indicates the matrix representation of a quantum mechanical operator with a capital letter, omitting the square brackets, for example:

$$\begin{bmatrix} S \end{bmatrix} \to S \\ \begin{bmatrix} H \end{bmatrix} \to H \\ \begin{bmatrix} I \end{bmatrix} \to I \\ \begin{bmatrix} G^R \end{bmatrix} \to G^R$$

The same holds for column vectors:

 $\{\psi\} \rightarrow \psi$ 

This notation will lighten and simplify a lot the reading of the formulae in matrix form. Of course whenever a misunderstanding will be possible I will specify the nature of the operators and the equations that I will write. If no misunderstanding is possible I will, for example, write the Schrödinger's equation:

$$E\left[S\right]\left\{\psi\right\} = \left[H\right]\left\{\psi\right\}$$

simply as:

 $ES\psi = H\psi$ 

while for example the equation:

$$\left[ \left( E+i\eta\right) \left[ I\right] -\left[ H\right] \right] \left[ G^{R}\right] =\left[ I\right]$$

becomes simply:

$$[(E + i\eta) I - H] G^R = I \quad with: \quad G^R = [(E + i\eta) I - H]^{-1}$$

# 5.8 "Contact-ing" the Schrödinger's equation: an intuitive introduction

The purpose of this section is to provide an easy introduction to what happens when a contact is connected to a channel. The purpose is to focus on the physical meaning of the general procedure that will be carried out in the next section. Even if in this section the procedure will not be so elegant, and also the equations will not be at all formally correct, they will be useful to get the point without getting lost in the mathematics. The same topic will be treated in a more rigorous and elegant manner in the next section.

It is possible to write the steady state Schrödinger's equation of the entire system that is considered. It takes, in matrix form, the expression:

$$ES\psi = H_{tot}\psi = \begin{bmatrix} H_R & H_{RD} \\ H_{DR} & H_D \end{bmatrix}\psi$$
(5.18)

where  $H_D$  is the isolated device Hamiltonian matrix,  $H_R$  is the isolated contact (or reservoir) Hamiltonian matrix,  $H_{DR}$  is the device-reservoir coupling Hamiltonian matrix and  $H_{RD}$  is the reservoir-device coupling Hamiltonian matrix. Notice that it is possible to show that:  $H_{RD} = H_{DR}^{\dagger}$ . It is intuitive that the contact-to-device coupling term will be the transpose (conjugate) of the device-to-contact one, indeed a sort of "symmetry" is expected. The total wave-function  $\psi$  of the system "contact + device" should satisfy simultaneously the device and reservoir Hamiltonians since it represents states that exist contemporary within the device and the contact. It can be split in the device only and the reservoir only wave-functions:  $\psi_D$  and  $\psi_R$  (see below). It is possible to rewrite the previous equation as a system of two matrix equations as follows (see also [105]):

$$E\begin{bmatrix}S_R & S_{RD}\\S_{DR} & S_D\end{bmatrix}\begin{cases}\psi_R\\\psi_D\end{cases} = \begin{bmatrix}H_R & H_{RD}\\H_{DR} & H_D\end{bmatrix}\begin{cases}\psi_R\\\psi_D\end{cases}$$
$$\Rightarrow \begin{bmatrix}ES_R - H_R & ES_{RD} - H_{RD}\\ES_{DR} - H_{DR} & ES_D - H_D\end{bmatrix}\begin{cases}\psi_R\\\psi_D\end{cases} = 0$$
$$\Rightarrow \begin{cases}(ES_R - H_R)\psi_R + (ES_{RD} - H_{RD})\psi_D = 0\\(ES_{DR} - H_{DR})\psi_R + (ES_D - H_D)\psi_D = 0\end{cases}$$

in which overlap matrices of suitable dimensions are introduced:  $S_D$ ,  $S_R$ ,  $S_{DR}$  and  $S_{RD}$ . If the chosen basis is orthonormal they become simply identity matrices of suitable dimensions:  $I_D$ ,  $I_R$ ,  $I_{DR}$  and  $I_{RD}$ . Then, from the first equation of the system:

$$\psi_R = -(ES_R - H_R)^{-1}(ES_{RD} - H_{RD})\psi_D$$

and substituting in the second one:

$$(ES_{DR} - H_{DR}) \left[ -(ES_R - H_R)^{-1} (ES_{RD} - H_{RD}) \right] \psi_D + (ES_D - H_D) \psi_D = 0$$
  
$$\Rightarrow \left[ ES_D - H_D - (ES_{DR} - H_{DR}) (ES_R - H_R)^{-1} (ES_{RD} - H_{RD}) \right] \psi_D = 0$$
(5.19)

Notice that eq. (5.19) involves the device wave-function  $\psi_D$  only, that can be known from a standard quantum mechanical study of the isolated molecule (see chapter 3), and the effects of the contacts are all included in the third term that is the only one involving the reservoir Hamiltonian  $H_R$ , and the coupling Hamiltonians  $H_{DR}$  and  $H_{RD}$ . It is thus possible to define a quantity, called "contact self-energy"  $\Sigma$ , that represents the effects of the contact on the channel, as:

$$\Sigma(E) = (ES_{DR} - H_{DR})(ES_R - H_R)^{-1}(ES_{RD} - H_{RD}) = \zeta G_R \zeta^{\dagger}$$
(5.20)

Remember that it was supposed to have a single contact at the beginning, but an analogous procedure to the one presented here, allows to write a self-energy matrix for each considered contact. More importantly they can simply be summed up to get the total self-energy matrix that represents the effect of all (usually two) the contacts connected to the device/channel. The important point of this procedure is that it is possible to "hide" the effects of the contact in a term  $\Sigma$  that is simply superimposed to the isolated device (isolated channel) Hamiltonian, giving rise to a modified Schrödinger's equation:

$$\Rightarrow \left[ES_D - H_D - \Sigma(E)\right]\psi_D = 0$$

that would correspond exactly to the isolated device/channel Schrödinger's equation if  $\Sigma$  would be null. Notice also that  $\Sigma$  depends on energy, thus it is not at all comparable to a conventional Hamiltonian.

The various terms within the self-energy matrix assume the following meanings:

•  $G_R = (ES_R - H_R)^{-1}$  is the so called "reservoir Green's function" of the isolated reservoir. Notice the similarity with the Green's functions defined previously. In this introductory treatment I have intentionally neglected to insert the term  $+i\eta$ , nevertheless as it will clarified in the next section the infinitesimal should be considered and thus it is present. Consequently  $G_R$  corresponds exactly to the retarded Green's function of the isolated reservoir. Here the subscript R is used to indicate that it is the (retarded) Green's function of the reservoir. It corresponds to an impulse response of the isolated contact, that is described by the contact (or reservoir) Hamiltonian  $H_R$  only. It can be evaluated from  $H_R$  (the overlap matrix  $S_R$  is fixed once the representation is chosen and the energy value E is supposed known). Usually  $H_R$  of a real contact would be too big to be actually used in evaluating  $G_R$ , thus only a portion of the contact is considered, namely the portion the interact with the channel. It may correspond to Green's function of the superficial atoms of the contacts that are involved in the chemical bonds with the channel. In this case instead of calling simply reservoir Green's function, it is indicated with  $g_R$  and it is called "Surface Green's function" (SGF) of the reservoir. This choice is motivated by the fact that only the contact interface (the portion that interact with the molecule) strongly influences the transport properties (e.g. originates the broadening).

- $\zeta = (ES_{DR} H_{DR})$  is related to the device-reservoir coupling matrix, it is the non-zero part of  $(ES_{DR} H_{DR})$  coupling the device to the SGF, and it represents the coupling factor. It represents the total Hamiltonian sub-matrix or block that represents the interaction strength between the reservoir Hamiltonian and the device one.
- $\zeta^{\dagger} = (ES_{RD} H_{RD})$  is related to the reservoir-device coupling matrix (notice that it can be shown that it is the transpose complex conjugate of  $\zeta$ ). Its physical meaning is analogous to the  $\zeta$  one and similar remarks can be done.

A pair of remark will be useful in the next section in order to understand the physical meaning of calculations and assumption:

a. In the next section the infinitesimal imaginary part of the energy  $+i\eta$  will be considered, such that the reservoir Green's function becomes exactly a retarded Green's function of the kind of those analyzed in the previous sections. What is the meaning of this infinitesimal imaginary part of energy? The answer can be easily found in the moment it is considered the open nature of the entire system "contact + device". It was said in section 5.3 that a way of representing the fact that the system is open is to introduce suitable boundary conditions to represent an open system in mathematical terms. It was also said that such a boundary condition consists in the introduction of the infinitesimal  $+i\eta$ . This because if the system is open there are two features. First, the lifetime of eigenstates is no more infinite but finite since electrons can escape the system, and this is accounted by a real exponential dependence in time, accordingly with the general solution of the Schrödinger's equation. Thus an imaginary part of energy can serve in representing the finite lifetime. Second, if an electron can escape from the system then it will be transmitted somewhere else. In the case of the contact, and thus in terms of the contact Green's function  $G_R$ , this means that an electron can escape the contact to go into the channel. It was said that this fact is again modeled by means of  $+i\eta$  such that no advanced Green's function is present (no reflections). Nevertheless now the point is why the imaginary part of energy is infinitesimal and not finite. The answer is in the nature of a good contact. Indeed by hypothesis (as also said in section 4.1.3), a contact in order to be considered a "good" contact, must contain a huge number of electrons or alternatively electron states. In this way it is possible to assume that the entire applied voltage drops across the device and that the contacts are in equilibrium. In this way the Fermi levels are pinned inside the contacts, and the interesting part of the physics is "played" only inside the channel, as one desires. In this optics thus the number of electrons that can escape from a contact is extremely small w.r.t. the total number

of electrons it can contain. Thus it is an open system, but the perturbation due to the fact that it is open is extremely small, because the large majority of electrons and electron states are unperturbed within the contact, such that it can be assumed in equilibrium. Thus the boundary condition that models the fact that the contact is open should be very small, let's say infinitesimal, and indeed it is exactly the infinitesimal  $+i\eta$ .

- b. The contacts are open systems, since electrons can escape to go into the channel. However also the channel must be open, because electrons can escape to go into the contacts. For a contact it is possible to represent the fact that it is open by inserting an infinitesimal perturbation in its Schrödinger's equation in order to account for that fact. Nevertheless the channel has a very small number of electron states, and the more it is small the more this statement is true. Thus it would be not reasonable assuming that the perturbation due to the fact that it is open is small, or infinitesimal. It is a completely wrong assumption. So the question can be how to represent the fact that also the channel is an open system. The answer is related to self-energy term introduced above. Indeed it was said that the introduction of  $\Sigma$  within the isolated channel Schrödinger's equation is a good way of representing the fact that the device is not isolated but it is connected to a contact. In this optics the self-energy is a suitable boundary condition to represent the contact. Thus if one writes the isolated channel Schrödinger's equation, and then wants to model the fact that the channel is not isolated, it is sufficient to modify the isolated channel Schrödinger's equation by inserting a suitable self-energy term aimed in modeling the effect of the contact on the channel. From the previous treatment it is clear that  $\Sigma$  represents indeed the coupling of the device with the contact. Notice that  $\Sigma$  is not infinitesimal, but it can be also large, let's say very important.
- c. When a device is connected to a contact neither the device nor the contact are no more closed systems: indeed they become open systems, and they can exchange electrons. This fact introduces a small perturbation in the contact, that can be accounted with the introduction of an infinitesimal imaginary part of the energy  $i\eta$ . Instead the perturbation of the channel due to the presence of the contact is very big, and a way of representing it is by means of the introduction of a contact self-energy. The way of calculating it is from the total system (i.e. contact + device) Schrödinger's equation. The procedure was briefly summarized above and is more formally introduced in the next section.
- d. Notice that the self-energy  $\Sigma$  is energy dependent (see above expression). Consequently the total energy eigenvalues of the open channel, i.e. of the system described no more by  $H_D$  but by means of  $[H_D + \Sigma]$ , are difficult to estimate since they are energy dependent, but they are energy levels. Consequently an iterative self-consistent loop would be necessary. Nevertheless if one thinks to the energy E as indicated in section 5.1, i.e. like a free parameter, the problem results extremely simplified (indeed if Eis a parameter that is e.g. the energy of an incoming electron there is no more the necessity of having an iterative loop).
e. Notice also that the contact self-energy depends on the contact Green's function  $G_R$ . As mentioned above, and as it will done in the next section,  $G_R$  contains a small imaginary part. This implies that also  $\Sigma$  has a real and imaginary part. Notice also that rarely its imaginary part will be very small, independently on the value of  $\eta$ , it will be finite, and eventually large. This means that  $\Sigma$  is non-Hermitian. It was mentioned several times in chapter 2 that quantum mechanical operators representing physical observables should be instead Hermitian. Nevertheless  $\Sigma$  does not represent a physical observable, but instead the boundary conditions that model the channel as open system. Thus no conceptual problem arises from this fact.

# 5.9 A more rigorous introduction: the contact selfenergy

The aim of this section is provide a method for representing the effect of a contact on a conductive channel. In this section a single contact will be considered. From the treatment of chapter 4, it is known that the way for having an electrical current is to have two contacts, that are kept out of equilibrium at a given potential difference (two distinct electrochemical potentials), such that the source contact keeps filling up the channel energy levels in an attempt to achieve the equilibrium, while the drain contact keeps emptying the channel energy levels in an attempt to achieve the equilibrium. The result is a current flow that involves the channel energy states in between the Fermi levels of the two contacts. Since now only a single contact is considered no current will flow. The generalization to the case of two contacts will be trivial by exploiting the superposition of effects, thus summing up the contribution related to the two contacts. The main result of this section was already pointed out in the previous section: it is in the introduction of a self-energy matrix  $\Sigma$  that represents the effect of the contact (i.e. the open system boundary condition) within a modified isolated channel Schrödinger's equation.

The isolated channel/device Schrödinger's equation has the following form (subscript D stands for device):

$$E\psi_D = H_D\psi_D \quad \rightarrow \quad [EI_D - H_D]\,\psi_D = 0$$

Where it is supposed of using an orthonormal basis set  $(I_D \text{ is the identity matrix of suitable dimensions})$ . The purpose of this section is to suitably modify it such that the effect of the contact, supposed connected to the channel, is embedded within an additional term  $\Sigma$  that is superimposed to the device Hamiltonian:

$$E\psi_D = [H_D + \Sigma]\psi_D + S \quad \rightarrow \quad [EI_D - H_D - \Sigma]\psi_D = S$$

where the term  $S = \{S\}$  is a column vector representing the source term that comes from the contact. In particular since the channel is an open system its energy eigenvalues, its electron states, are modified by means of  $\Sigma$ , and S represent the incoming electrons that escape from the contact to go into the channel. In this sense S is the source term. Notice that  $\psi_D$  are the wave-functions of the isolated device, and thus it is expected to have Srelated to wave-functions of the isolated reservoir (contact) instead. The last equation can be intended as a Schrödinger's equation for the open systems, i.e. for an open channel, of course different from the usual one (that is instead the Schrödinger's for an isolated and closed system). In this regard think again to the change of perspective.

Assuming again of employing an orthonormal basis set, the isolated contact Schrödinger's equation can be written as (subscript R stands for reservoir):

$$E\Phi_R = H_R\Phi_R \quad \to \quad [EI_R - H_R]\,\Phi_R = 0$$

Nevertheless if the contact is connected to the channel it is no more a closed system, and thus suitable boundary conditions must be used to represent the fact that it is an open system. As described in the previous section, since a contact is huge w.r.t. the channel, the latter introduces only a very small perturbation, that in mathematical terms can be represented by means of an infinitesimal imaginary part of the energy  $+i\eta$ . Thus the open system contact Schrödinger's equation becomes:

$$\left[EI_R + i\eta I_R - H_R\right]\Phi_R = S_R$$

The term  $i\eta I_R$  is a matrix representation of the infinitesimal  $i\eta$ , that represents the amount of electrons that escape from the contact to go into the channel. From the point of view of the contact they "disappear", so they have a finite lifetime (after which they annihilate). But since the number of electrons escaping into the channel is extremely small if compared to the total number of electrons of the contact, an infinitesimal perturbation is enough to represent it:  $\eta \to 0^+$  ( $\eta > 0$ ). Moreover it is also possible to have electrons going from the channel into the contact. From the standpoint of the contact this is a source term, that adds electrons, and it can be written in general as  $S_R$ . Notice that at steady state, one can think to set  $S_R$  equal to  $i\eta I_R$ , such that the number of electron leaving the contact equals the number of electrons entering in the contact. In that case  $S_R$  and  $i\eta I_R$  would simplify and the standard isolated contact Schrödinger's equation is recovered. Nevertheless this would be useless for the purpose of finding a self-energy, so for the moment it is considered the last equation in which both  $S_R$  and  $i\eta I_R$  appear.

In the moment in which a channel is connected to the contact, some electrons will go into the channel and vice versa. In particular the contact wave-functions  $\Phi_R$  will "spill over" giving rise to the wave-function  $\psi_D$  inside the device, that in turn will excite scattered waves  $\chi$  in the contact. The total wave-function will satisfy the total composite Schrödinger's equation for the entire system "contact + channel", that will be the following (it is the composition of the contact and the device blocks):

$$\begin{bmatrix} EI_R - H_R + i\eta I_R & -\zeta^{\dagger} \\ -\zeta & EI_D - H_D \end{bmatrix} \begin{pmatrix} \Phi_R + \chi \\ \psi_D \end{pmatrix} = \begin{cases} S_R \\ 0 \end{cases}$$
(5.21)

where  $\zeta$  is the coupling Hamiltonian, and where no imaginary energy term is considered in the device part since the purpose is to find a (finite and maybe large) self-energy that represents the contact (within the device Schrödinger's equation). Notice that the matrices relative to the reservoir are of dimension (R,R), that is huge when compared of the matrices relative to the device of dimension (d,d). The coupling Hamiltonian has dimensions (R,d). Noticing that  $S_R$  is unchanged w.r.t. the isolated contact Schrödinger's equation it is possible to rewrite the total wave-function as:

$$\begin{bmatrix} EI_R - H_R + i\eta I_R & -\zeta^{\dagger} \\ -\zeta & EI_D - H_D \end{bmatrix} \begin{pmatrix} \Phi_R + \chi \\ \psi_D \end{pmatrix} = \begin{cases} [EI_R - H_R + i\eta I_R] \{ \Phi_R \} \\ 0 \end{pmatrix} \\ \\ \Rightarrow \begin{cases} [EI_R - H_R + i\eta I_R] \{ \Phi_R + \chi \} - \zeta^{\dagger} \{ \psi_D \} = [EI_R - H_R + i\eta I_R] \{ \Phi_R \} \\ -\zeta \{ \Phi_R + \chi \} + [EI_D - H_D] \{ \psi_D \} = 0 \end{cases} \\ \\ \Rightarrow \begin{cases} [EI_R - H_R + i\eta I_R] \{ \chi \} - \zeta^{\dagger} \{ \psi_D \} = 0 \\ -\zeta \{ \Phi_R \} - \zeta \{ \chi \} + [EI_D - H_D] \{ \psi_D \} = 0 \end{cases} \\ \\ \Rightarrow \begin{cases} [EI_R - H_R + i\eta I_R] \{ \chi \} - \zeta^{\dagger} \{ \psi_D \} = 0 \\ -\zeta \{ \Phi_R \} - \zeta \{ \chi \} + [EI_D - H_D] \{ \psi_D \} = 0 \end{cases} \\ \\ \Rightarrow \begin{cases} [EI_R - H_R + i\eta I_R] \{ \chi \} - \zeta^{\dagger} \{ \psi_D \} = 0 \\ [EI_R - H_R + i\eta I_R] \{ \chi \} - \zeta^{\dagger} \{ \psi_D \} = 0 \end{cases} \end{cases}$$

From first equation:

$$\rightarrow \quad \{\chi\} = [EI_R - H_R + i\eta I_R]^{-1} \zeta^{\dagger} \{\psi_D\} = G_R \zeta^{\dagger} \{\psi_D\}$$

where:

$$G_R = [EI_R - H_R + i\eta I_R]^{-1} = [(E + i\eta) I_R - H_R]^{-1}$$

is the contact (reservoir) Green's function (R stands for reservoir, even if it is a retarded Green's function as well). By substituting  $\{\chi\}$  in the second equation:

$$[EI_D - H_D] \{\psi_D\} - \zeta G_R \zeta^{\dagger} \{\psi_D\} = \zeta \{\Phi_R\}$$

from which:

$$[EI_D - H_D - \Sigma] \{\psi_D\} = \{S\}$$
(5.22)

where it is defined the contact self-energy as:

$$\Sigma = \zeta G_R \zeta^\dagger \tag{5.23}$$

and the source term (relative to the device) S is defined as:

$$S = \zeta \left\{ \Phi_R \right\} \tag{5.24}$$

## 5.9.1 Evaluation of the contact self-energy $\Sigma$

From eq. (5.23) it is clear that evaluating  $\Sigma$  is not so trivial, especially from a computational standpoint, since the matrix  $G_R$  is of size (R,R), that is huge since theoretically a good reservoir should be infinite. Nevertheless the coupling Hamiltonian  $\zeta$ , that is expected to be of dimension (d,R), actually (in real space) only couples the r surface atoms/elements of the reservoir next to the channel. Indeed the chemical bond connecting the channel to the reservoir will involve only few atoms, and the reservoir atoms/element that interact

with the channel will be only few. Thus in practice it is possible to truncate  $\zeta$  to a matrix of size (d,r):

$$\Sigma = \zeta \quad g_R \quad \zeta^{\dagger}$$
  
(d, d) (d, r) (r, r) (r, d)

where  $g_R$  takes the name of Surface Green's Function (SGF) and represents an (r,r) subset of the full Green's function  $G_R$  involving just the r superficial elements. Consequently also  $\Phi_R$  results truncated to  $\phi_R$  of size (r,1).

In practice there are several methods, both analytical and numerical, to evaluate  $\Sigma$  and  $g_R$  and also S.

Often an analytical way of dealing with such quantities is in the eigenstate representation of the contact. In such representation  $H_R$  is diagonal and  $G_R$  is of the kind of the one of section 5.5, eq. (5.16). In such a representation unfortunately the coupling Hamiltonian cannot be truncated to smaller size and it is possible to show that  $\Sigma$  and S can be calculate by means of a (infinite) summation over the eigenstates of the reservoir. This summation can be carried out analytically and also analytically approximated or truncated. A simple introduction is provided in [89].

Another approach in evaluating  $\Sigma$  is by means of an analogous procedure of the one described in the previous section, in which the total Hamiltonian (including only the rsurface elements of the contact) is calculated by means of one of the methods illustrated in chapter 3. Since the contact is truncated some periodic boundary conditions can be enforced at boundaries of simulation domain such that the infinite extension of a crystalline contact is recovered (let's say "emulated" by means of such periodic boundary conditions). Then with a procedure analogous to the one reported in the previous section (that is simply an algebraic manipulation, simple to implement on a computer) the self-energy matrix is recovered and evaluated. This method is the one employed in [105].

As mentioned, several are the possible approaches and in literature many examples can be found. Here I would just like to mention other three possible methods for calculating  $\Sigma$ , that are the currently available methods in a widely spread commercial software called *Quantum-Wise Atomistic-Tool-Kit (ATK)* by *Synopsys*<sup>®</sup>. I will widely use this software in the practical part of this work. The three methods are the following:

• Direct Method: This method allows for the computation of total leads (i.e. active portion of contacts) Green's functions and then for the effective Hamiltonian  $H_{tot}$  directly in real space, without transforming in  $\vec{k}$  space or without performing contour integrals in energy domain (in energy domain the Green's function presents poles - see eq. (5.16) section 5.5). For this reason the name "Direct Method". Semi-infinite crystalline leads are considered, and their Hamiltonians are evaluated by means of tight-binding *spd* method (a semi-empirical method). A semi-analytical expression for the lead Green's function is found by starting from an infinite periodic crystalline lead and then by recovering the semi-infinite lead expression by applying suitable boundary conditions. The infinite lead Hamiltonian is built up by slicing the lead and by writing the Hamiltonian of each slice (diagonal elements of total Hamiltonian) and by coupling them by means of a "hopping" Hamiltonian. The Bloch's wave-functions of the infinite periodic structure are found. The total infinite lead Green's functions

are found analytically as superposition of Bloch's wave-functions (the wavepacket is represented by means of a summation of monochromatic -periodic- plane waves). The semi-infinite lead total Green's function is then found by enforcing suitable boundary conditions (that practically consist in reflection coefficients evaluated considering the reflection and transmission probability due to the end of the lead). Finally the total Hamiltonian  $H_{tot}$  (effective Hamiltonian) is found by means of a decimation algorithm (a recursive algorithm is used), from which it is finally possible to extract  $\Sigma$  and represent the effects of the contacts on the device. This method is presented in detail in [118].

- *Recursive Method*: The basic idea of this method is to employ a decimation recursive algorithm to speed up the computation of a crystalline lead Green's function. The approach in Hamiltonian and Green's function calculations is somehow comparable with the ones of Direct Method, but the original lattice is replaced by an effective lattice of twice the lattice constant of the original one. In the effective lattice each original layer plus the two neighbor layers are replaced by an effective layer. Effective layers interactions (before they were called them "hopping" Hamiltonians) are weaker w.r.t. the original ones. After n iterations one gets a chain of layers distant  $2^n$  times the original ones. The interactions among them are weaker and weaker such that at the end they are neglected and a great simplification in the Hamiltonian computation occurs (also because the effective Hamiltonian has a reduced dimension). Starting from the knowledge of the effective Hamiltonian  $H_{tot}$  is then possible to extract  $g_{R}$ ,  $\zeta$  and  $\Sigma$ . Notice that this algorithm allows for a significant speed up, especially w.r.t. to more conventional approaches. Notice that for a infinite contact the error would be null, otherwise a truncation error is present; moreover it is possible to evaluate both surface and bulk Green's functions. This method is presented in detail in [119].
- Krylov Method: In order to understand the basic idea behind this method it is better to clarify a possible interpretation of self-energy and broadening matrices. As mentioned in section 4.1.1 broadened states are finite life-time states, and they are subjected to an exponential decay in time. This point will be further clarified in section 5.12. As mentioned the origin of such finite lifetime and thus of the real exponent in the exponential is to be found in an imaginary part of the energy, that with the imaginary unit of the exponent makes it real and decaying. Moreover in section 5.3 it was also noticed that open systems have again the same exponential decaying behavior also in space, and again this was due an imaginary part of the energy, that causes the exponents to become reals. In particular it will be shown in section 5.12 that the self-energy  $\Sigma$  has a real and an imaginary part (intuitive since  $G_R$ contains the term  $i\eta$ ), and the latter causes an exponential decay in space. Therefore, broadened states not only have a finite life-time, but they are also confined states. Or better, they correspond to allowed states (or proper modes) that exist in the isolated contact itself (and thus they are solution for the steady state Schrödinger's equation of the isolated contact), that are not ideally confined into it (as it would be for an infinite potential barrier), but that "spill over" the contact boundary and go a bit into the device. This has physical sense if we think to a finite height potential well, considering that beyond the well boundary the wave-function exponentially decays

in space. Thus if we are interested in transport calculations, we are interested in propagating modes, that are propagating both in the contacts and in the channel, but since the device is a nanodevice, we are also interested in slowly spatial decaying states that can transmit the particle (i.e. the electron) from the source to the drain. Indeed these states contribute to conduction as well as the propagating ones.

The Krylov method is based on the evaluation of the self-energy matrices for a semi-infinite lead by starting from the solutions of a quadratic eigenvalue problem that arises for infinite periodic structures. Notice that evaluating the self-energy  $\Sigma(E)$ corresponds to the evaluation of bulk modes of a contact in a set of energy values (chemical potential), or k values, to which the contact could be forced to operate. As mentioned before, in practise only the propagating and the sufficiently slowly decaying evanescent modes of the bulk electrode contribute to transmission through the channel. These modes correspond to the solution of the quadratic eigenvalue problem with complex eigenvalues close to the unit circle in the complex plane (i.e. magnitude close to one). Keeping in mind what just mentioned, it is possible to generate the self-energy matrices with a reduced computational effort (and with a reasonable truncation error) by developing an algorithm that only computes the desired eigenvalues, which are supposed to be on, or inside, the unit circle (since other eigenstates would be decaying or growing too fast and can be neglected). The core is a particular algebraic transformation (the shift-and-invert spectral transformation) to Krylov subspace, that allows to easily find the target eigenvalues. This transformation to Krylov subspace is performed by means of an iterative algorithm, since the number of modes to be considered is not known a priori. Once the eigenvalues of interest are found, the non-iterative part of the algorithm evaluates the Bloch matrices and the self-energies from them by a direct method. This method is often employed with Hamiltonian operators found by means of DFT method, and it is presented in detail in [120] and [121].

### 5.9.2 The total system and the device Green's functions

Considering a system made of one contact (reservoir) connected to a small channel, it is possible to write the total Green's function of the entire system "contact + channel". The procedure is analogous to the one explained at the beginning of this section, and in particular it is straightforward starting from the definition of (retarded) Green's function (i.e. equation (5.7)):

$$G^R = \left[ \left( E + i\eta \right) I - H \right]^{-1}$$

in which the Hamiltonian is considered to be a block matrix (as did at the beginning of this section):

$$\begin{bmatrix} H_D & H_{DR} \\ H_{RD} & H_R \end{bmatrix} \rightarrow \begin{bmatrix} H_D & H_{DR} \\ H_{RD} & H_R \end{bmatrix} \psi = E\psi$$
$$\leftrightarrow \begin{bmatrix} EI_D - H_D & -\zeta \\ -\zeta^{\dagger} & EI_R - H_R \end{bmatrix} \psi = 0$$
213

where  $-\zeta = EI_{DR} - H_{DR}$ . It follows that the overall retarded Green's function of the entire system "reservoir + device" is thus:

$$G_{tot}^{R} = \begin{bmatrix} G_D & G_{DR} \\ G_{RD} & G_R \end{bmatrix} = \begin{bmatrix} (E+i\eta)I_D - H_D & -\zeta \\ -\zeta^{\dagger} & (E+i\eta)I_R - H_R \end{bmatrix}^{-1}$$

The power of the Green's function method comes from the fact that it is possible to evaluate the device Green's function block  $G_D$  exactly from the following relation:

$$G_D = [(E + i\eta)I_D - H_D - \Sigma(E)]^{-1}$$
(5.25)

Indeed it is possible to carry out a procedure similar to the one carried out at the beginning of the present section in which, starting from the overall Green's function  $G^R$  it is possible to write the device one  $G_D$ . In doing this the contact self-energy  $\Sigma$  is again used in order to represent the effect of the contact on the device. Consequently it is possible to evaluate the contact self-energy  $\Sigma$ , e.g. with one of the methods illustrated above, and then to write directly the retarded Green's function  $G_D$ , i.e. the impulse response, of the device connected to a contact by using eq. (5.25). The procedure that from the total Green's function  $G_{tot}^R$  leads to the device  $G_D$  is summarized in the following example from [89].

*Example 5.1:* From [89]. It is possible to derive eq. (5.25) from  $G_{tot}^R$  by means of matrix algebra. In particular said:

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix}^{-1}$$

It follows (the following equation corresponds to  $[(E + i\eta)I - H]G^R = I$ ):

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} \begin{bmatrix} A & B \\ C & D \end{bmatrix}^{-1} = \begin{bmatrix} I & 0 \\ 0 & I \end{bmatrix} = I$$

so that (rows by columns products leads to) Aa + Bc = I and  $Ca + Dc = 0 \rightarrow c = -D^{-1}Ca$ and hence:  $a = [A - BD^{-1}C]^{-1}$ . With obvious replacements the last relation corresponds to:

$$G_D = \left[ (E + i\eta)I_D - H_D - \zeta G_R \zeta^{\dagger} \right]^{-1}$$

where  $G_R$  is the isolated reservoir Greens' function  $G_R = [(E + i\eta)I_R - H_R]^{-1}$  and where  $\Sigma = \zeta G_R \zeta^{\dagger}$ .  $\Box$ 

The advantage of writing the device Green's function as:

$$G_D = [(E + i\eta)I_D - H_D - \Sigma(E)]^{-1}$$

is that it is possible to obtain it by using matrices of dimension (d, d), (r, r) and (r, d), indeed the SGF  $g_R$  is used for evaluating  $\Sigma$  instead of the full  $G_R$ . This is important since R can be huge and assumed to be infinite.

#### 5.9.3 The Dyson's equation

Equation (5.25) is sometimes referred as Dyson's equation. Notice that at the beginning of this section it was said that it is not necessary to consider the infinitesimal  $+i\eta$  within  $G_D$ , but in eq. (5.25) it is present. Now I will clarify this statement. The purpose of the infinitesimal  $+i\eta$  is to represent the boundary conditions, i.e. the fact that the system is open and there is an exchange of electrons between the contact and the device. It was also said that since the contact should be enormous w.r.t. the channel (indeed it should be a reservoir of electrons), the effect of the channel on the contact is negligible or infinitesimal:  $+i\eta$ . Instead the effect of the contact on the channel is relevant and cannot be neglected. It is represented by  $\Sigma$ . In particular  $\Sigma$  is anything but negligible, and in general it has a real and an imaginary part (this is intuitive since  $\Sigma = \zeta G_R \zeta^{\dagger}$  and  $G_R$  has an imaginary part -infinitesimal  $+i\eta$ - that becomes relevant and finite in  $\Sigma$ ). Since the imaginary part of  $\Sigma$  is finite, it is always much greater than the infinitesimal  $+i\eta$ , and for this reason in equation (5.25) it is possible to neglect the infinitesimal without troubles. In conclusion the Dyson's equation (5.25) becomes simply:

$$G_D = [EI_D - H_D - \Sigma(E)]^{-1}$$
(5.26)

# **5.9.4** The impulse response $G_D$

So far it was considered a system of a channel connected with a reservoir. The features of a good reservoir were already mentioned few times and will be further discussed in the next section. The purpose of this section is to point out the results of what so far.

Starting from the total system "contact + device" Schrödinger's equation it is possible to find an equation for the device only, in which a term  $\Sigma$ , namely the self-energy, represents the effect of the contact on the channel, and thus its modification due to the presence of the contact. The following equation was demonstrated (see eq. (5.22)):

$$[EI_D - H_D - \Sigma] \{\psi_D\} = \{S\}$$

whose solution can be written in the form:

$$\{\psi_D\} = [G_D]\{S\}$$

where  $G_D$  is the retarded Green's function of the device only, modified with  $\Sigma$  in order to consider the effect of the contact:

$$G_D = \left[EI_D - H_D - \Sigma\right]^{-1}$$

 $G_D$  is thus the impulse response of the device, and indeed the general solution  $\{\psi_D\}$  can be written as the product of  $G_D$  by the source term  $\{S\}$ . Notice that if in eq. (5.22) the source term is a delta-Dirac the meaning of  $G_D$  is well understood. Indeed in that case equation (5.22) becomes:

$$[EI_D - H_D - \Sigma] \{\psi_D\} = [I]$$

since it is an equation in energy domain, i.e. in the energy eigenfunction representation, and it was shown in section 5.4 that the delta function becomes the identity matrix in

this representation. From the last equation it is obvious the meaning of  $G_D$ . Notice also that since the last equation is an energy domain representation, then  $G_D(E)$  corresponds more precisely to a transfer function, i.e. to a Fourier transform of the impulse response. Indeed in analogy with LTI systems it is the ratio between the output  $\{\psi_D\}$  of the system and its input  $\{S\}$ :  $\{\psi_D\} \{S\}^{-1} = [G_D]$ . In conclusion  $G_D$  has the meaning of impulse response of the entire system "contact + device", in its energy eigenstates representation (energy domain) it corresponds to a transfer function and the system output in response to a whatever stimulus  $\{S\}$  can be evaluated as described above. If its Fourier transform is considered  $G_D(t)$ , a representation in time domain is recovered. In this time domain representation  $G_D(t)$  still represents the impulse response, but the output in response to a given stimulus should be evaluated by means of a convolution operation (remembering the Fourier transform properties so a product in energy/frequency domain corresponds to a convolution in time domain).

# 5.9.5 A "good" contact

This section if aimed in definitively clarify the features of a good contact. In principle it is possible to carry on a procedure analogous to the one described at the beginning of this section, and treat the contact as of primary relevance and thus representing the channel effect on it through a self-energy. Mathematically indeed  $H_D$  and  $H_R$  are on the same footing. The only "asymmetry" comes from the terms  $+i\eta$  and S that were added "by hand" in order to account for the extraction and re-injection of electron from/into the contact by the channel. Usually the formal justification of  $i\eta$  from a mathematical standpoint is that it ensures the convergence of a Fourier transform [89], [116]. Nevertheless it assumes the meaning stated previously. In section 5.9.2 it was said that in general it is possible to introduce an infinitesimal term in the device Green's function, and it is formally correct, even if at practice it is neglected (see section 5.9.3) because of the presence of the more important  $\Sigma$  imaginary part. A good discussion of would happen if the contact and the channel roles are exchanged is provided in [89].

The point is that a good contact should be able to provide an electron escaping rate essentially constant. This happens only if it has a huge amount of electron states w.r.t. the channel ones. Indeed if the contact were small, with few electron states, then the escaping of one electron would empty the contact, that would be no more able to provide other electrons for a given amount of time. When an electron escapes from the contact into the channel it leaves an hole in the contact. If the contact had few electron states it would require a large amount of time to restore the hole with a new electron. This implies also that a large variation of the Fermi level would occur within the contact since few electron states are present and the presence or the absence of one electron is relevant and changes significantly the Fermi level. This is not what it is generally as a "good" contact. A contact is indeed by hypothesis a reservoir of electrons, able to provide a constant rate of electrons to the channel, and thus able to rapidly restoring the hole that is created by an electron flowing from the contact toward the channel, keeping the contact the Fermi level pinned. Again, the contact should be able to do that independently on the particular value of the infinitesimal  $\eta$ . This is possible only if many closely spaced energy levels are present in it, in the limit of an infinite number of atoms within the contact, a continuous energy

band is present in it. The contact should have a constant density of states independently on  $\eta$ . This is what typically happens in real world where the contact are huge macroscopic entities when compared to channel devices. This is the reason why only an infinitesimal perturbation of the contact is considered  $(+i\eta)$  and this is the foundation for neglecting  $\eta$ in the device Green's function, since the self-energy effect  $\Sigma$  is finite and relevant.

Practical remark: A last remark is due on the practical value of the infinitesimal  $\eta$  that must be set up in practical simulations (e.g. Quantum-Wise ATK allows to set it up). In numerical simulations it is important to always set up the infinitesimal  $\eta$  greater than the spacing  $\Delta \varepsilon$  between the energy levels on the contact. Indeed if the infinitesimal  $\eta$  is in excess of  $\Delta \varepsilon$ , the perturbation  $\eta$  is greater than the spacing  $\Delta \varepsilon$  making irrelevant the effect of  $\Delta \varepsilon$  and ensuring that the contacts behave like "good" reservoirs [89]. Moreover it must be ensured that the active part of the device has always much less electron states than the leads (the portion of the contacts connected to it). If it is not so, then the leads should be included in the device, and new leads (with a suitable dimension) should be considered. This has relevance in the choice of the geometry for simulations.

# 5.10 Density matrix, density of states and spectral function

The purpose of this section is collect few topics that will be useful in the next sections. For example the concepts of density of states and local density of states are introduced. The expression presented in this section will be e.g. useful in understanding the physical origin of broadening and the physical meaning of the contact self-energy  $\Sigma$  introduced in the previous section. In particular three quantities are introduced in this section: the density matrix, the density of states and the spectral function. In the treatment I will follow the approach of [89], that simplifies the topics by focusing on the physical meaning.

## 5.10.1 Density matrix

The electron density  $n(\vec{r})$  in a multi-electron system can be found by summing up the probability densities of each occupied eigenstate  $\alpha$ :

$$n(\vec{r}) = \sum_{\alpha} |\psi_{\alpha}|^2$$

Nevertheless this expression is true for closed systems (with no exchange of electron/matter with the external world) and at low temperature, because in that case there is a fixed number of electrons occupying the lowest available energy levels. In general states can be partially occupied and this can be account for by means of the Fermi-Dirac distribution function:

$$n(\vec{r}) = \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F) |\psi_{\alpha}|^2$$
(5.27)

where  $\{\varepsilon_{\alpha}\}_{\alpha}$  are the energy eigenvalues,  $E_F$  the Fermi level of the system and  $f_{FD}(E) = \left[1 + e^{E/k_BT}\right]^{-1}$ , being  $k_B$  the Boltzmann's constant and T the temperature.

In general in statistical mechanics it used the concept of "density matrix":  $[\rho]$ . The density matrix  $[\rho]$  of elements  $\rho(\alpha, \beta)$  "stores" the correlation  $C_{\alpha}C_{\beta}^{*}$  between each pair of coefficients of the wave-functions. Let me clarify better this crucial point. In general a multi-electron system will have a wave-function  $\Psi(\vec{r})$  representing the total state of the entire system, i.e. of all the electrons composing such a system. Thus  $\Psi(\vec{r})$  is the multi-electron total wave-function, representing the state of the whole system. Since the system eigenfunctions form a complete and orthonormal basis set, they can be used as basis for a Fourier expansion such that the generic state  $\Psi(\vec{r})$  can be expressed as superposition of the system eigenfunctions:

$$\Psi(\vec{r}) = \sum_{\alpha} C_{\alpha} \psi_{\alpha}(\vec{r}) \quad \rightarrow \quad |\Psi(\vec{r})|^2 = \sum_{\alpha} \sum_{\beta} C_{\alpha} C_{\beta}^* \psi_{\alpha}(\vec{r}) \psi_{\beta}^*(\vec{r})$$

The density matrix elements  $\rho(\alpha, \beta)$  indicates the correlation between every pair of coefficients  $C_{\alpha}C_{\beta}^*$ . It describes the statistical state of the entire quantum mechanical multi-electron system. If an eigenstate representation is used then (the eigenstates are orthonormal):

$$\rho(\alpha,\beta) = C_{\alpha}C_{\beta}^{*} = f_{FD}(\varepsilon_{\alpha} - E_{F})\delta_{\alpha\beta} = \begin{cases} 0 & \text{if } \alpha \neq \beta \\ f_{FD}(\varepsilon_{\alpha} - E_{F}) & \text{if } \alpha = \beta \end{cases}$$

Notice that if diagonal elements are considered:  $\alpha = \beta$ , then the coefficient squared modulus is:

$$\rho(\alpha, \alpha) = C_{\alpha} C_{\alpha}^* = |C_{\alpha}|^2 = f_{FD}(\varepsilon_{\alpha} - E_F) = f_{\alpha}$$

that is: the squared modulus of the coefficients is the Fermi-Dirac function, that provides the occupation probability of the eigenstate  $\psi_{\alpha}$ . Notice again that this holds true only if an eigenstates representation of the multi-electron system wave-function is used. In that case (since the eigenstates are orthonormal) there is no correlation between different eigenstates, i.e. out of diagonal elements are null, and the density matrix is diagonal, with diagonal elements given by  $\rho(\alpha, \alpha) = f_{FD}(\varepsilon_{\alpha} - E_F)$ . In the eigenstates representation:

$$[\rho] = \begin{bmatrix} f_{FD}(\varepsilon_1 - E_F) & 0 & 0 & \dots \\ 0 & f_{FD}(\varepsilon_2 - E_F) & 0 & \dots \\ 0 & 0 & f_{FD}(\varepsilon_3 - E_F) & \dots \end{bmatrix}$$
(5.28)

At this point it is possible to rewrite the electron density as:

$$n(\vec{r}) = \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F) |\psi_{\alpha}|^2 = \sum_{\alpha} \sum_{\beta} \rho(\alpha, \beta) \psi_{\alpha}(\vec{r}) \psi_{\beta}^*(\vec{r})$$

The last expression can be generalized to define (it is a definition):

$$\widetilde{\rho}(\vec{r},\vec{r'}) = \sum_{\alpha} \sum_{\beta} \rho(\alpha,\beta) \psi_{\alpha}(\vec{r}) \psi_{\beta}^{*}(\vec{r'})$$
(5.29)

that correlates the eigenstates in two different points  $\vec{r}$  and  $\vec{r'}$ . It follows that the electron density  $n(\vec{r})$  is thus given by its diagonal elements:

$$n(\vec{r}) = \left[\tilde{\rho}(\vec{r}, \vec{r'})\right]_{\vec{r'}=\vec{r}} = \sum_{\alpha} \sum_{\beta} \rho(\alpha, \beta) \psi_{\alpha}(\vec{r}) \psi_{\beta}^{*}(\vec{r})$$
(5.30)

Notice that equation (5.29) corresponds essentially to a transformation from the eigenstates representation to the real space representation of the density matrix of eq. (5.28). This is noticed considering that  $\rho(\alpha, \beta)$  in eq. (5.29) is the eigenstates representation of the density matrix, that the summations corresponds to matrix products (row by column) between the matrix  $\rho(\alpha, \beta)$  and the two matrices that have by columns the eigenstates  $\{\psi_{\alpha}(\vec{r})\}_{\alpha}$  and  $\{\psi_{\beta}(\vec{r'})\}_{\beta}$ , in the new basis of real space (they are the eigenstates in function of the position vector  $\vec{r}$ , i.e. the eigenstates in the real space representation - recall the change of basis in matrix algebra). A complete treatment is provided in [89], and a more formal (but still accessible) introduction is provided in [39].

A last remark: from equation (5.28) it follows that in the eigenstates representation it is possible to rewrite the equilibrium density matrix as:

$$\rho = f_{FD}(H - E_F I)$$

where H is the system Hamiltonian matrix and I the identity matrix. In the eigenstates representation this relation simplifies in eq. (5.28) since H is diagonal with its eigenvalues as elements. Nevertheless the lat expression  $\rho = f_{FD}(H - E_F I)$  holds true in any representation and not only in the eigenstates one. This is obvious if the transformation of eq. (5.29) is again considered.

#### Density matrix and total number of electrons

The density matrix can look very different depending on the specific representation. In the eigenstates representation (eq. (5.28)), it is diagonal because H is diagonal, but in real space it has also off-diagonal elements. Nevertheless in any basis set the diagonal elements  $\rho(m, m)$  provides the number of electrons occupying the state m. In real state the diagonal elements  $\rho(\vec{r}, \vec{r})$  provide the electron density  $n(\vec{r})$ . In general it is possible to show that the trace (the trace is the sum of diagonal elements of a matrix) of the density matrix is invariant in all representations and provides the total number of electrons of the system  $N_e$ :

$$N_e = Tr[\rho]$$

where Tr indicates the trace. In general only the diagonal elements of the density are needed to find the electron density.

#### Density matrix and DFT

In chapter 2 it was said that the in quantum mechanics to each physical observable F is associated an operator  $\hat{F}$ . Then in section 2.3.3 it was shown that the expectation value  $\langle F \rangle$  of the physical observable can be evaluated as:

$$\langle F \rangle = \int \psi^*(\vec{r}) \hat{F} \psi(\vec{r}) d\vec{r}$$
219

Substituting for the wave-function its Fourier expansion in terms of the chosen basis functions  $\{\phi_i\}_i$ :

$$\langle F \rangle = \int \sum_{j} C_{j}^{*} \phi_{j}^{*}(\vec{r}) \widehat{F} \sum_{i} C_{i} \phi_{i}(\vec{r}) d\vec{r} = \sum_{i} \sum_{j} C_{i} C_{j}^{*} \int \phi_{j}^{*}(\vec{r}) \widehat{F} \phi_{i}(\vec{r}) d\vec{r}$$

and noticing that  $\rho(i,j) = \rho_{ij} = C_i C_j^*$  are the elements of the density matrix in the basis set representation, and that:  $F_{ij} = \int \phi_j^*(\vec{r}) \hat{F} \phi_i(\vec{r}) d\vec{r}$  are the element of the matrix representation (see section 2.4) of the operator  $\hat{F}$  again in the chosen basis set, it follows that:

$$\langle F \rangle = \sum_{i} \sum_{j} \rho_{ij} F_{ij} = Tr \left[ \rho F \right]$$

where Tr indicates the trace,  $\rho$  the density matrix and F the matrix representation of  $\hat{F}$ . This is a general results and holds in any representation. Thus the expected value of any physical observable can be found by performing the trace of the (matrix) product of the density matrix with the matrix representation of the associated quantum mechanical operator F in that basis.

In general it is thus possible to derive each physical observable starting from the density matrix. This is intuitive if the physical meaning of density matrix is considered: it is the matrix that describes the statistical state (i.e. the state) of the many-body system, thus from the state it is intuitive thinking that is possible to derive each quantity of interest. In particular the link with electron density was already discussed. In chapter 3 it was said that the DFT methods express the system Hamiltonian in function of the electron density, this is true, but more often instead of using the electron density  $n(\vec{r})$  it is used the density matrix  $\rho$ . In general thus it is possible to talk about functionals of the density matrix  $\rho$ , that indeed is intimately linked with the electron density, and the density matrix is used instead of n in evaluating such functionals.

## 5.10.2 Density of states and local density of states

An isolated channel with a discrete set of eigenvalues  $\varepsilon_{\alpha}$  has a Density Of States (DOS) per unit energy given by:

$$D(E) = \sum_{\alpha} \delta(E - \varepsilon_{\alpha})$$

The problem of the above expression is that it does not consider the spatial distribution of states. Instead a quantity called the Local Density Of States (LDOS) defined as:

$$D(\vec{r}; E) = \sum_{\alpha} |\psi_{\alpha}(\vec{r})|^2 \,\delta(E - \varepsilon_{\alpha})$$
(5.31)

provides information about the spatial distribution of the states. In particular in eq. (5.31) each energy level (the DOS of each level) is weighted by multiplying its DOS by the its wave-function squared at location  $\vec{r}$ . This provide information about the space localization of states. In particular if d is the region of space of interest, e.g. the device region, then:

$$D(d; E) = \sum_{\alpha} |\psi_{\alpha}(d)|^2 \,\delta(E - \varepsilon_{\alpha})$$

will provide information about the amount of the eigenstate  $\alpha$  that is inside the device, and thus about the DOS portion of the total DOS of  $\alpha$  that resides within the device. The LDOS is a useful tool for understanding the physical origin of broadening - see next section.

## 5.10.3 Spectral function

In general it is possible to see the LDOS, defined in equation (5.31), as the diagonal elements divided by  $2\pi$  of a more general concept called the spectral function A:

$$A(\vec{r}, \vec{r'}; E) = 2\pi \sum_{\alpha} \psi_{\alpha}(\vec{r}) \delta(E - \varepsilon_{\alpha}) \psi_{\alpha}^{*}(\vec{r'})$$
(5.32)

in analogy to what seen in the previous section, concerning the electron density (eq. (5.27)):

$$n(\vec{r}) = \sum_{\alpha} |\psi_{\alpha}(\vec{r})|^2 f_{FD}(\varepsilon_{\alpha} - E_F)$$

that can be seen as the diagonal element of the density matrix (eq. (5.30)):

$$\rho(\vec{r},\vec{r'}) = \sum_{\alpha} \psi_{\alpha}(\vec{r}) f_{FD}(\varepsilon_{\alpha} - E_F) \psi_{\alpha}^{*}(\vec{r'})$$

notice the notation employed here slightly different from the one of before but with the same meaning [89]. In the previous section 5.10.1, it was said that the density matrix of last equation can be seen as real space representation of:

$$\rho = f_{FD}(H - E_F I)$$

that indeed corresponds to an eigenstate representation of the density matrix. Here in complete analogy (analogous considerations and calculation) allows to say that the spectral function  $A(\vec{r}, \vec{r'}; E)$  of eq. (5.32), can be viewed as the real space representation of the quantity:

$$[A(E)] = 2\pi\delta \left( E\left[I\right] - [H] \right)$$
(5.33)

that indeed corresponds to the general definition of spectral function in matrix form. Notice that the last equation holds true in any representation. Exactly like  $\rho = f_{FD}(H - E_F I)$ , and its particular representation depends on the specific representation used, indeed the Hamiltonian matrix changes with the representation. In particular in the eigenstate representation the Hamiltonian matrix is diagonal and thus:

$$H = \begin{bmatrix} \varepsilon_1 & 0 & 0 & \dots \\ 0 & \varepsilon_2 & 0 & \dots \\ 0 & 0 & \varepsilon_3 & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix} \rightarrow [A(E)] = 2\pi \begin{bmatrix} \delta(E - \varepsilon_1) & 0 & 0 & \dots \\ 0 & \delta(E - \varepsilon_2) & 0 & \dots \\ 0 & 0 & \delta(E - \varepsilon_3) & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix}$$

from which it is evident that the DOS is equal to its diagonal elements over  $2\pi$ . Notice again that in general the expression of [A(E)] changes with the specific representation used, i.e. with the specific basis set. In general anyway it is true that the LDOS is given by its diagonal elements divided  $2\pi$  (to this purpose see equation (5.31)).

In conclusion, the density matrix provides the correlation among the basis set functions and represents the quantum state of a many-body system. Its diagonal elements provide the electron density (per unit volume)  $n(\vec{r})$ , and its trace the total number of electrons of the system  $N_e$ . Here, analogously the spectral function A is a measure of the spectral DOS (i.e. states per unit energy), in particular its diagonal elements provide the LDOS  $D(\vec{r}; E)$ , while its trace (divided by  $2\pi$ ) provides the total density of states per unit energy (DOS):

$$D(E) = \frac{1}{2\pi} Tr \left[ A(E) \right] = \sum_{\alpha} \delta(E - \varepsilon_{\alpha})$$
(5.34)

## 5.10.4 Spectral function and density matrix

There exists a link between the density matrix and the spectral function. In particular:

$$[\rho] = f_{FD}(H - E_F I) = \int_{-\infty}^{\infty} f_{FD}(E - E_F) \delta([EI - H]) dE =$$
$$= \int_{-\infty}^{\infty} \frac{1}{2\pi} f_{FD}(E - E_F) [A(E)] dE$$

in which the definition of delta-Dirac, i.e.  $\int_{-\infty}^{\infty} f(x)\delta(x-x_0)dx = f(x_0)$ , is exploited (with x = EI and  $x_0 = H$ ). It has good sense since  $A(E)/2\pi$  is the matrix version of the density of states D(E), in the same way as the density matrix  $\rho$  is the matrix version of the total number of electrons  $N_e$ . Notice also that:

$$N_{e} = Tr[\rho] = Tr\left[\int_{-\infty}^{+\infty} \frac{1}{2\pi} f_{FD}(E - E_{F}) [A(E)] dE\right] = \int_{-\infty}^{+\infty} dE f_{FD}(E - E_{F}) Tr\left[\frac{[A(E)]}{2\pi}\right] = \int_{-\infty}^{+\infty} dE f_{FD}(E - E_{F}) D(E)$$

which simply states that the number of electrons is obtained by multiplying the DOS D(E) by the probability  $f_{FD}$  that they are occupied and adding (integrating) up the contributions from all the energies.

# 5.11 Summary of one contact system equations and some useful relations

The purpose of this section is to summarize the important set of equations introduced so far for the system "device + single contact". Moreover some useful relations are introduced. The full demonstrations of the formulae presented here is reported in appendix C.3, please refer to it for details; here only the important results are reported. The system can be described by the following equation:

$$\begin{bmatrix} EI_R - H_R + i\eta I_R & -\zeta^{\dagger} \\ -\zeta & EI_D - H_D \end{bmatrix} \begin{pmatrix} \Phi_R + \chi \\ \psi_D \end{pmatrix} = \begin{cases} S_R \\ 0 \end{cases}$$
(5.35)  
222

where:

$$\{\chi\} = G_R \zeta^{\dagger} \{\psi_D\}$$

$$G_R = [EI_R - H_R + i\eta]^{-1}$$

$$\{\psi_D\} = [G_D] \{S_R\}$$

$$G_D = [EI_D - H_D - \Sigma]^{-1}$$

$$\Sigma = \zeta G_R \zeta^{\dagger}$$

$$\{S_R\} = \zeta \{\Phi_R\}$$
(5.36)

The reservoir density matrix is:

$$\rho_R(\vec{r}, \vec{r'}) = \sum_{\alpha} \phi_{R\alpha}(\vec{r}) f_{FD}(\varepsilon_{\alpha} - E_F) \phi_{R\alpha}^*(\vec{r'})$$

that in matrix form becomes:

$$[\rho_R] = \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F) \{\phi_{R\alpha}\} \{\phi_{R\alpha}\}^{\dagger}$$
(5.37)

The device density matrix is:

$$[\rho_D] = \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F) \left\{ \psi_{D\alpha} \right\} \left\{ \psi_{D\alpha} \right\}^{\dagger} = \int \frac{dE}{2\pi} f_{FD}(E - E_F) G_D \zeta A_R \zeta^{\dagger} G_D^{\dagger}$$
(5.38)

where  $\{\psi_{D\alpha}\}\$  is the device wave-function (matrix representation, i.e. column vector), that from eq. (5.36) is:

$$\{\psi_{D\alpha}\} = G_D\{S_{R\alpha}\} = G_D\zeta\{\phi_{R\alpha}\} \quad , \quad \{S_{R\alpha}\} = \zeta\{\phi_{R\alpha}\}$$

Moreover it is defined the broadening function  $\Gamma$ , whose physical meaning will be discussed later in section 5.12:

$$\Gamma = i \left[ \Sigma - \Sigma^{\dagger} \right] = \zeta A_R \zeta^{\dagger}$$

in addition the following relations hold true:

$$A_D = i \left[ G_D - G_D^{\dagger} \right] = G_D \Gamma G_D^{\dagger} = G_D^{\dagger} \Gamma G_D$$
(5.39)

$$[G^n] = \left[G_D \Gamma G_D^{\dagger}\right] f_{FD}(E - E_F) = \left[A_D(E)\right] f_{FD}(E - E_F)$$
(5.40)

From which (see eq.(5.38)):

$$[\rho_D] = \int \frac{dE}{2\pi} f_{FD}(E - E_F) G_D \Gamma G_D^{\dagger} = = \int \frac{dE}{2\pi} f_{FD}(E - E_F) [A_D(E)] = \int \frac{dE}{2\pi} [G^n(E)]$$
(5.41)

Notice that a single contact is in equilibrium with the channel, and thus the previous relations holds at equilibrium:

$$[G^{n}(E)]_{equilibrium} = [A_{D}(E)] f_{FD}(E - E_{F})$$

and the density matrix  $[\rho_D]$  is intended at equilibrium. Notice that if two contacts are considered then the density matrix changes (non-equilibrium density matrix) and the same happens to  $[G^n]$  and  $[A_D(E)]$ . To this purpose see section 5.13. Notice again that the proof of all the above reported relations is provided in appendix C.3.

#### The correlation function $G^n$

In eq. (5.39) it was introduced the matrix  $[G^n(E)]$ , called "correlation function". Its physical meaning is clear when eq. (5.41) is considered: the correlation function is the matrix version of the electron density per unit energy. Indeed, in section 5.10.3, it was mentioned that the spectral function is the matrix version of the density of states per unit energy. Here, since  $[G^n(E)]_{equilibrium} = [A_D(E)] f_{FD}(E - E_F)$ , the correlation function gets the meaning of matrix representation of occupied density of states per unit energy. Thus integrating it over the energy, the matrix version of the electron density, i.e. the density matrix, is obtained.

Throughout this section I have followed the simple approach of [89]; a more formal (but equally accessible) introduction to these topics (and to the correlation function) is provided in [39].

# 5.12 Contact self-energy, levels broadening and finite lifetime

It was demonstrated ion section 5.9 that a channel connected to a contact can be described by a modified Schrödinger's equation of the form:

$$[EI_D - H_D - \Sigma] \{\psi_D\} = \{S\} \quad \rightarrow \quad E\{\psi_D\} = [H_D + \Sigma] \{\psi_D\} + \{S\}$$

Where  $\Sigma$  represents the effect of the contact on the channel. The matrix  $[H_D + \Sigma]$  has complex eigenvalues, that have the consequences of both broadening the channel density of states and give the eigenstates a finite lifetime. The purpose of this section is exactly to point out these two features.

## 5.12.1 The physical origin of broadening and the LDOS

As already pointed out in the previous section an isolated molecular channel has a density of states that is made of discrete energy levels, i.e. a DOS of the kind:

$$D(E) = \sum_{\alpha} \delta(E - \varepsilon_{\alpha})$$

In the moment in which the channel is coupled to the reservoir there is the creation of chemical bond (e.g. a covalent bond) between atoms in the contact and in the channel (usually with the so called anchoring group). There will thus be one energy level with its wave-function largely on the channel, that corresponds to a state that was already present in the isolated channel, but in addition there will be many other neighboring states with their wave-functions residing partially on the channel (states that originally were eigenstates of the isolated contact). This chemical interaction causes the DOS broadening, i.e. electrons from contact (eigenstates) that are no more well localized within the contact and can be localized also within the channel. The result in energy domain is a series of (very close or continuum) energy levels with varying heights, reflecting the percentage of the squared wave-function residing in the channel. This phenomenon is well represented by means of the LDOS already introduced with eq. (5.31):

$$D(\vec{r}; E) = \sum_{\alpha} |\psi_{\alpha}(\vec{r})|^2 \,\delta(E - \varepsilon_{\alpha})$$

In conclusion, the physical origin of DOS broadening is to be found in such contact eigenstates that "spill over" a bit in the channel, giving rise to a non-null  $D(\vec{r}; E)$  within the channel. In this regard notice that the broadened DOS will contain a mixture of the device and the contacts states (hybridization of wave-function), but if a state cannot exist within the contact it very likely will not be present also in the final DOS (unless particular cases occur during the hybridization procedure).

Notice that the following "sum rule" holds true: if a device with a single level is coupled to a contact, its DOS broadens into a series of levels, of varying strengths (weights), representing that the contact wave-functions contribute to different extents to the device DOS. But when a broadened DOS is integrated over the energy the same number of electrons of the original level is recovered. It is possible to provide a formal demonstration for this [89]. Nevertheless the point is quite intuitive: what a device loses from its one level due to wave-function hybridization with the contact ones, it gains back from the other levels, so that the broadened level in the device can accommodate exactly the same number of electrons that the discrete one could accommodate before it got coupled to the reservoir. See [89] for more details.

### 5.12.2 Finite lifetime of broadened states

In the introductory sections of this chapter it was highlighted the (space) impulse response meaning of the retarded and the advanced Green's function several times. Moreover in section 5.6 it was pointed out that the retarded Green's function has the physical meaning of time impulse response for the time-dependent Schrödinger's equation. Then in section 5.9.4 it was pointed out that the device retarded Green's function of the device/channel is:

$$G_D = [EI_D - H_D - \Sigma]^{-1}$$
(5.42)

and that it has again obviously the meaning of impulse response for the device, in the moment in which it is connected to a reservoir. In this section these concepts will be merged together and it will be proved that the effect of the contact on the device is to give a finite lifetime to its eigenstates. Intuitively this has sense, since the system "contact + channel" is an open system, in which electrons can escape (as already argued many times).

Considering the meaning of the (retarded) Green's function as time impulse response for the time-dependent Schrödinger's equation (section 5.6), it is possible to write the following equation (see equation (5.17) for comparison):

$$\left(i\hbar\frac{\partial}{\partial t} - [H_D] - [\Sigma]\right)[G_D(t)] = [I_D]\,\delta(t) \quad (wrong!) \tag{5.43}$$

that corresponds to a modified channel Schrödinger's equation to consider the contact effects, with time impulse response given by  $[G_D(t)]$  that is the Fourier anti-transform to

time domain of eq. (5.42), carried out as indicated in section 5.6. Nevertheless equation (5.43) is not generally correct. Indeed it corresponds to a Fourier anti-transform of the following equation:

$$[EI_D - H_D - \Sigma] [G_D(E)] = [I_D]$$
(5.44)

but since the self-energy  $\Sigma(E)$  is generally energy dependent the Fourier transform, from energy domain to time domain, of the product  $\Sigma(E)G_D(E)$  should include a convolution integral (indicated with "\*"):  $\Sigma(t) * G_D(t)$ . Thus resulting in the more correct expression:

$$\left(i\hbar\frac{\partial}{\partial t} - [H_D]\right)[G_D(t)] - [\Sigma(t)] * [G_D(t)] = [I_D]\,\delta(t)$$

Nevertheless for the purposes of this section it is much more convenient to get rid of this "detail", in order to focus on the physical insights of such equations. Thus the (wrong!) equation (5.43), is considered. In order to keep things simple, let's moreover consider only the case in which a single energy  $\varepsilon$  level is present. The Hamiltonian matrix and the self-energy becomes thus simple scalars (real and complex respectively). Under these hypotheses equation (5.43) reduces to:

$$\left(i\hbar\frac{\partial}{\partial t} - \varepsilon - \Sigma\right) [G_D(t)] = \delta(t) \quad (wrong!)$$

whose solution is (in this regard see also section 5.6):

$$G_D(t) = -\frac{i}{\hbar}\theta(t)e^{-i(\varepsilon+\Sigma)t/\hbar}$$

where  $\theta(t)$  is the Heaviside function. Notice that  $G_D(t)$  is the response to an impulse excitation of the device (connected to a contact) at time t = 0. Considering that  $\Sigma$  is complex:  $\Sigma = \text{Re}(\Sigma) + i \text{Im}(\Sigma)$ , the  $G_D(t)$  becomes:

$$G_D(t) = -\frac{i}{\hbar}\theta(t)e^{-i(\varepsilon + \operatorname{Re}(\Sigma) + i\operatorname{Im}(\Sigma))t/\hbar} = -\frac{i}{\hbar}\theta(t)e^{-i\varepsilon't/\hbar}e^{-\gamma t/2\hbar}$$
(5.45)

where:

$$\varepsilon' = \varepsilon + \operatorname{Re}(\Sigma) \quad , \quad \gamma = -2\operatorname{Im}(\Sigma)$$

The real part of the self-energy causes a shift in the device energy level from  $\varepsilon$  to  $\varepsilon'$ , while the imaginary part has the effect of giving rise to a finite lifetime (exponential decay in time) of the eigenstate lifetime. This is evident when the squared modulus of the  $G_D(t)$ wave-function is considered:

$$|G_D(t)|^2 = \frac{1}{\hbar^2} \theta(t) e^{-\gamma t/\hbar} = \frac{1}{\hbar^2} \theta(t) e^{-t/\tau\hbar}$$

The lifetime of the finite lifetime state is clearly linked to the imaginary part of the self-energy:

$$\tau = \frac{\hbar}{\gamma} = \frac{\hbar}{-2\operatorname{Im}(\Sigma)}$$
226

The last relation can be interpreted as the uncertainty relation between energy and time that was already discussed previously (see e.g. section 4.1.1). In this optics  $\tau$  corresponds to the escaping time or intrinsic time introduced in chapter 4 and  $\gamma$  is the coupling factor (or broadening of the Lorentzian distribution). In order to better visualize this, let's consider the Fourier transform of the impulse response of eq. (5.45), that is (see also appendix C.1):

$$G_D(E) = \frac{1}{E - \varepsilon' + i\gamma/2}$$

From equation (5.39) the spectral function is given by  $A_D = i \left[ G_D - G_D^{\dagger} \right]$ , and from equation (5.34), considering that in this example these quantities are all scalars:

$$\frac{A_D(E)}{2\pi} = D(E) = \frac{i}{2\pi} \left( G_D(E) - G_D^{\dagger}(E) \right) = \frac{i}{2\pi} \left( \frac{1}{E - \varepsilon' + i\gamma/2} - \frac{1}{E - \varepsilon' - i\gamma/2} \right) = \frac{\gamma/2\pi}{(E - \varepsilon')^2 + (\gamma/2)^2}$$

that is a Lorentzian distribution. The meaning is again that the channel LDOS is broadened into a Lorentzian of width  $\gamma$  equal to twice the imaginary part of the self-energy. Notice that in general it is not said that the shape is Lorentzian since this result was obtained by neglecting the energy dependence of the self-energy. In general a convolution should be considered and the shape can be also very different (depending of the kind of energy dependency of  $\Sigma$ ).

### 5.12.3 The broadening function

In the previous section it was clarified that the imaginary part of the self-energy provides the amount of broadening of channel energy levels and also the lifetime of the broadened states. Nevertheless, in general, the self-energy is a matrix if more energy levels are present, thus it is convenient to define a broadening matrix  $\Gamma(E)$  like the anti-Hermitian part of  $\Sigma$ :

$$\Gamma(E) = i \left[ \Sigma(E) - \Sigma^{\dagger}(E) \right]$$
(5.46)

 $\Gamma$  is responsible of the broadening of the energy levels. Instead the Hermitian component of  $\Sigma$ :

$$\Sigma_H(E) = \frac{1}{2} \left[ \Sigma(E) + \Sigma^{\dagger}(E) \right]$$

can be seen as a correction of the Hamiltonian  $H_D$ , responsible for the energy levels shift. Notice that since  $\Sigma(E)$  is dependent on energy also  $\Gamma$  and  $\Sigma_H$  are dependent on energy, and in particular all these quantities are also dependent on the applied bias. Thus the applied bias strongly modifies in general the transmission spectrum or transmission function (see section 4.3), and thus the general behavior of the device.

# 5.13 The two contacts case

In the case in which two contacts are considered, it is possible to exploit the linearity of the Hamiltonian operator and the Schrödinger's equation and write the total system "channel + 2 contacts" Schrödinger's equation by composing the three block:

$$\begin{bmatrix} EI_1 - H_1 + i\eta & -\zeta_1^{\dagger} & 0\\ -\zeta_1 & EI_D - H_D & -\zeta_2\\ 0 & -\zeta_2^{\dagger} & EI_2 - H_2 + i\eta \end{bmatrix} \begin{pmatrix} \Phi_1 + \chi_1\\ \psi_D\\ \Phi_2 + \chi_2 \end{pmatrix} = \begin{cases} S_1\\ 0\\ S_2 \end{cases}$$

where the notation is analogous to the one of section 5.9:  $H_1$ ,  $H_2$  are the Hamiltonians of the isolated contacts (e.g. subscript 1 refers to source and subscript 2 to drain),  $I_1$ ,  $I_2$ ,  $I_D$ are identity matrices of suitable dimensions,  $\zeta_1$ ,  $\zeta_2$  are the coupling Hamiltonians,  $H_D$  is the device Hamiltonian,  $\psi_D$  indicates the wave-function inside the channel/device,  $\Phi_1$ ,  $\Phi_2$ are the wave-functions inside the contacts,  $S_1$ ,  $S_2$  are the source terms that represent the amount of electrons going from the device to the contacts,  $+i\eta$  is the infinitesimal term that represents the electrons escaping from the contacts,  $\chi_1$ ,  $\chi_2$  are the two scattered term.

It is possible to carry out calculations analogous to the ones of section 5.9, and since the system is linear the following relations can be found (superposition of effects can also be invoked):

$$\{\chi_1\} = G_1 \zeta_1^{\dagger} \{\psi_D\} \quad , \quad \{\chi_2\} = G_2 \zeta_2^{\dagger} \{\psi_D\}$$

where  $G_1$  and  $G_2$  are the Green's functions of the two isolated reservoirs:

$$G_1 = [EI_1 - H_1 + i\eta]^{-1}$$
,  $G_2 = [EI_2 - H_2 + i\eta]^{-1}$ 

Moreover:

$$[EI_D - H_D - \Sigma_1 - \Sigma_2] \{\psi_D\} = [EI_D - H_D - \Sigma] \{\psi_D\} = \{S\}$$
(5.47)

where:

$$\Sigma_1 = \zeta_1 G_1 \zeta_1^{\dagger}$$
,  $\Sigma_2 = \zeta_2 G_2 \zeta_2^{\dagger}$ ,  $\Sigma = \Sigma_1 + \Sigma_2$ 

are the contacts self-energies, notice that the contributions from the two contacts can be summed to get the total effect:  $\Sigma = \Sigma_1 + \Sigma_2$ . The corresponding broadening matrices are:

$$\Gamma_1 = \zeta_1 A_1 \zeta_1^{\dagger} \quad , \quad \Gamma_2 = \zeta_2 A_2 \zeta_2^{\dagger} \quad , \quad \Gamma = \Gamma_1 + \Gamma_2$$

where  $A_1 = i \left[ G_1 - G_1^{\dagger} \right]$  and  $A_2 = i \left[ G_2 - G_2^{\dagger} \right]$  are the spectral functions of the two isolated contacts. The source term is:

$$\{S\} = \{S_1\} + \{S_2\} = \zeta_1 \{\Phi_1\} + \zeta_2 \{\Phi_2\}$$
(5.48)

is the sum of the source term  $({S_1})$  and the drain one  $({S_2})$ . Notice that (remember that the Hermitian conjugate of a product of two matrices is the product of the Hermitian conjugates of the two matrices taken in reverse order - see appendix C.3.1):

$$SS^{\dagger} = \zeta_1 \Phi_1 \Phi_1^{\dagger} \zeta_1^{\dagger} + \zeta_2 \Phi_2 \Phi_2^{\dagger} \zeta_2^{\dagger} + \zeta_1 \Phi_1 \Phi_2^{\dagger} \zeta_2^{\dagger} + \zeta_2 \Phi_2 \Phi_1^{\dagger} \zeta_1^{\dagger}$$

$$228$$

but since the wave-functions  $\Phi_1$  and  $\Phi_2$  are those of the two isolated contacts then the cross-terms are null and:

$$SS^{\dagger} = \zeta_1 \Phi_1 \Phi_1^{\dagger} \zeta_1^{\dagger} + \zeta_2 \Phi_2 \Phi_2^{\dagger} \zeta_2^{\dagger}$$

$$(5.49)$$

The device or channel (retarded) Green's function is:

$$G_D = [EI_D - H_D - \Sigma]^{-1} = [EI_D - H_D - \Sigma_1 - \Sigma_2]^{-1}$$
(5.50)

by means of which it is possible to write the total wave-function  $\psi_D$  inside the device, given by:

$$\{\psi_D\} = G_D\{S\} \rightarrow |\psi_D|^2 = \{\psi_D\}\{\psi_D\}^{\dagger} = G_D\{S\}\{S\}^{\dagger}G_D^{\dagger}$$

The total device density matrix of the system with two contacts can be written in matrix form as (see also the definition - equations (5.28) and (5.29)):

$$[\rho_D] = \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F) \{\psi_{D\alpha}\} \{\psi_{D\alpha}\}^{\dagger}$$

Noticing that the product  $\{\psi_{D\alpha}\} \{\psi_{D\alpha}\}^{\dagger}$  depends only on the product  $\{\psi_D\} \{\psi_D\}^{\dagger} = G_D \{S\} \{S\}^{\dagger} G_D^{\dagger}$  and that in  $\{S\}$  the cross products are null (see eq. (5.49)):

$$\begin{split} &[\rho_D] = \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F) \left\{ \psi_{D\alpha} \right\} \left\{ \psi_{D\alpha} \right\}^{\dagger} = \\ &= \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F) G_D \left[ \zeta_1 \Phi_{1\alpha} \Phi_{1\alpha}^{\dagger} \zeta_1^{\dagger} + \zeta_2 \Phi_{2\alpha} \Phi_{2\alpha}^{\dagger} \zeta_2^{\dagger} \right] G_D^{\dagger} = \\ &= \sum_{\alpha} f_{FD}(\varepsilon_{1\alpha} - E_{F1}) G_D \zeta_1 \Phi_{1\alpha} \Phi_{1\alpha}^{\dagger} \zeta_1^{\dagger} G_D^{\dagger} + \sum_{\alpha} f_{FD}(\varepsilon_{2\alpha} - E_{F2}) G_D \zeta_2 \Phi_{2\alpha} \Phi_{2\alpha}^{\dagger} \zeta_2^{\dagger} G_D^{\dagger} = \\ &= [\rho_D]_{due \ to \ 1} + [\rho_D]_{due \ to \ 2} \end{split}$$

From which it is evident that the non-equilibrium device density matrix is given by the superposition of the two device density matrices obtained considering separately the effects of the two contacts (this follows form the fact the source term  $\{S\}$  has null cross-terms). Exploiting the steps reported in appendix C.3.2 it is possible to rewrite each term in function of the relative contact spectral function:

$$\begin{aligned} [\rho_D] &= \int \frac{dE}{2\pi} f_{FD} (E - E_{F1}) G_D \zeta_1 A_1 \zeta_1^{\dagger} G_D^{\dagger} + \int \frac{dE}{2\pi} f_{FD} (E - E_{F2}) G_D \zeta_2 A_2 \zeta_2^{\dagger} G_D^{\dagger} = \\ &= \int \frac{dE}{2\pi} \left[ f_1 G_D \Gamma_1 G_D^{\dagger} + f_2 G_D \Gamma_2 G_D^{\dagger} \right] = \int \frac{dE}{2\pi} \left[ G_D f_1 \Gamma_1 G_D^{\dagger} + G_D f_2 \Gamma_2 G_D^{\dagger} \right] = \\ &= \int \frac{dE}{2\pi} G_D \left[ f_1 \Gamma_1 + f_2 \Gamma_2 \right] G_D^{\dagger} \end{aligned}$$
(5.51)

where the shortened notation  $f_1 = f_{FD}(E - E_{F1})$ ,  $f_2 = f_{FD}(E - E_{F2})$  is used, and where it is used also:  $\Gamma_1 = \zeta_1 A_1 \zeta_1^{\dagger}$  and  $\Gamma_2 = \zeta_2 A_2 \zeta_2^{\dagger}$ . By defining:

$$\Sigma^{in} = [\Gamma_1] f_1 + [\Gamma_2] f_2$$
229

It follows that:

$$G^{n} = G_{D} \Sigma^{in} G_{D}^{\dagger} =$$
  
=  $G_{D} [\Gamma_{1}] f_{1} G_{D}^{\dagger} + G_{D} [\Gamma_{2}] f_{2} G_{D}^{\dagger} = G_{D} [\Gamma_{1}] G_{D}^{\dagger} f_{1} + G_{D} [\Gamma_{2}] G_{D}^{\dagger} f_{2} =$  (5.52)  
=  $[A_{1}] f_{1} + [A_{2}] f_{2}$ 

where:  $[A_1] = G_D[\Gamma_1]G_D^{\dagger}$  and  $[A_2] = G_D[\Gamma_2]G_D^{\dagger}$ . This allows to rewrite the non-equilibrium density matrix as:

$$[\rho_D] = \int \frac{dE}{2\pi} G_D \Sigma^{in} G_D^{\dagger} = \int \frac{dE}{2\pi} \left[ G^n(E) \right]$$
(5.53)

The last equation holds in non-equilibrium with the assumption that  $[G^n(E)]$  is given by:  $[G^n(E)] = [A_1] f_1 + [A_2] f_2$ , that if compared to the equilibrium expression:

$$[G^{n}(E)]_{equilibrium} = [A(E)] f_{FD}(E - E_{F})$$

allows to think to the spectral function as consisting of two parts:  $[A_1(E)]$  arising from the spill-over (or propagation) of states in the contact 1, and  $[A_2(E)]$  arising from the spill-over (or propagation) of states in the contact 2. The former is filled according to  $f_1$  while the second accordingly to  $f_2$ . The device states are a superposition of the two contributions, and the device spectral function is:  $A_D = A_1 + A_2$ . This can be proved considering that  $\Sigma = \Sigma_1 + \Sigma_2$  and thus  $\Gamma = \Gamma_1 + \Gamma_2$  from which:  $A_D = G_D \Gamma G_D^{\dagger} = G_D [\Gamma_1 + \Gamma_2] G_D^{\dagger} = A_1 + A_2$ .

#### A remark on exclusion principle:

It was said and demonstrated that with two contacts superposition of the effects can be used. It may appear that by superimposing the two individual fluxes or wave-functions coming from the two distinct contacts, the Pauli's exclusion principle is violated. Nevertheless as long as the transport is coherent it is not so. Indeed in time domain it is very easy to see that. Consider two electrons in the device originated from two distinct eigenstates  $\Phi_1$  and  $\Phi_2$  in the two contacts. Initially there is no question of one blocking the other, since they are in two distinct contacts. Thus their wave-function are orthogonal (non-interacting):  $\{\Phi_1\}^{\dagger} \{\Phi_2\} = 0$ . At later times they propagate inside the device, thus the question can be if they interact or not, and if they are still orthogonal or not. The time evolution can be conveniently be evaluated by means of the time evolution operator (see section 2.5):

$$\{\psi_{D1}(t)\} = \widehat{S}(t, t_0 = 0) \{\Phi_1\} = e^{-\frac{i}{\hbar}Ht} \{\Phi_1\}$$
$$\{\psi_{D2}(t)\} = \widehat{S}(t, t_0 = 0) \{\Phi_2\} = e^{-\frac{i}{\hbar}\widehat{H}t} \{\Phi_2\}$$

It follows that their overlap at any time is:

$$\{\psi_{D1}(t)\}^{\dagger}\{\psi_{D2}(t)\} = \{\Phi_1\}^{\dagger} e^{+\frac{i}{\hbar}\widehat{H}t} e^{-\frac{i}{\hbar}\widehat{H}t} \{\Phi_2\} = \{\Phi_1\}^{\dagger}\{\Phi_2\} = 0$$

Thus wave-functions originating from orthogonal states remain orthogonal at all times and Pauli blocking never occurs. The situation is different if phase-breaking phenomena (e.g. electron-electron interactions) occur. If incoherent scattering phenomena occur then the phase is no more maintained, and this argument does not hold anymore. Notice that fixed scatterers (such as defect or fixed potential variations) are not phase-breaking phenomena (see also section 4.2). Instead mobile perturbation, like en electron-electron interaction are. Thus when incoherent scattering is considered it is possible to have forbidden transitions of states due to Pauli's exclusion principle. This topic will be further addressed in section 5.18.

# 5.14 Inflow, outflow and terminal current

After having discussed the case of two contacts connected to the device, and having derived an expression for the non-equilibrium density matrix, it is possible to consider the fluxes of electrons from contacts and then evaluating the electrical current flowing in the device. Again this task will be addressed by steps, starting from the single contact case.

A remark before starting: the current is given by the charge per unit time. It is thus:  $I = \frac{dQ}{dt} = (-q) \ electron \ flux$ , where the electron flux is given by the amount of electrons flowing within the device in the unit time. Thus if a single electron is in the state  $\psi_D$ , the flux of this electron will be the time derivative of the wave-function squared modulus:  $\frac{d}{dt} |\psi_D|^2 = \frac{d}{dt} \psi_D^{\dagger} \psi_D$ . This because of the wave-function squared modulus physical meaning of position probability density. The time variation (derivative) of  $\psi_D^{\dagger} \psi_D$  thus provides the time rate of change in the probability density inside the channel. Notice that if more electrons are considered then the total flow will be the sum of the single electron fluxes, thus they must be summed up. Since the interest is in the time derivative of the wave-function the time-dependent Schrödinger's equation will be considered, since it allows to estimate such a time derivative.

#### 5.14.1 One contact case

Consider again the case of one contact connected to the device. The Hamiltonian operator in matrix form is:

$$H_{tot} = \begin{bmatrix} H_D & \zeta \\ \zeta^{\dagger} & H_R + i\eta \end{bmatrix}$$

The corresponding time-dependent Schrödinger's equation in matrix form is:

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi \quad \leftrightarrow \quad i\hbar\frac{d}{dt} \begin{pmatrix} \psi_D \\ \Phi_{Rtot} \end{pmatrix} = \begin{bmatrix} H_D & \zeta \\ \zeta^{\dagger} & H_R + i\eta \end{bmatrix} \begin{pmatrix} \psi_D \\ \Phi_{Rtot} \end{pmatrix}$$
(5.54)

where  $\psi_D$  is the wave-function in the device and  $\Phi_{Rtot} = \Phi_R + \chi$  is the wave-function in the contact. This equation corresponds to the time-dependent version of eq. (5.21) in which the source term is dropped. Notice that since  $\psi_D$  is a scalar it is not a matter if the trace is taken or not, thus:

$$\psi_D^{\dagger}\psi_D = Tr\left[\psi_D^{\dagger}\psi_D\right] = Tr\left[\psi_D\psi_D^{\dagger}\right] = \psi_D\psi_D^{\dagger}$$
231

Its time derivative can be estimated from eq. (5.54), considering that such an equation can be rewritten as a system of two equations:

$$\begin{cases} i\hbar \frac{d}{dt}\psi_D = H_D\psi_D + \zeta \Phi_{Rtot} \\ i\hbar \frac{d}{dt}\Phi_{Rtot} = \zeta^{\dagger}\psi_D + (H_R + i\eta) \Phi_{Rtot} \end{cases}$$

Starting from first equation it is thus possible to find:

$$\frac{d}{dt}\psi_D^{\dagger}\psi_D = \frac{1}{i\hbar}Tr\left[\psi_D^{\dagger}\zeta\Phi_{Rtot} - \Phi_{Rtot}^{\dagger}\zeta^{\dagger}\psi_D\right]$$
(5.55)

The complete calculations are reported in appendix C.4. Then noticing that  $\Phi_{Rtot} = \Phi_R + \chi$  it is possible to rewrite eq. (5.55) as the sum of an inflow (i.e. from the contact to the device) and an outflow (i.e. from the device to the contact):

$$\frac{d}{dt}\psi_D^{\dagger}\psi_D = Inflow - Outflow \tag{5.56}$$

and after a bit of algebra it is possible to show that:

$$Inflow = \frac{1}{\hbar} \int \frac{dE}{2\pi} f_{FD}(E - E_F) Tr\left[\Gamma A_D\right]$$
(5.57)

$$Outflow = \frac{1}{\hbar} \int \frac{dE}{2\pi} Tr \left[ \Gamma G^n \right]$$
(5.58)

The full calculations are reported in appendix C.4. From the inflow and the outflow it is then possible to write the electric current, as it will be done in sections 5.14.3 and 5.15.

#### 5.14.2 Two contacts case

In the case of two contacts it is possible to proceed in an analogous manner to what did in section 5.13, for the non-equilibrium density matrix, and invoke the superposition of effects. In particular the important quantities are the inflow and the outflow at each contact. Noticing that the total source term is (eq. (5.48)):

$$\{S\} = \{S_1\} + \{S_2\} = \zeta_1 \{\Phi_1\} + \zeta_2 \{\Phi_2\}$$

and that  $S_1^{\dagger}S_2 = 0 = S_2^{\dagger}S_1$  (i.e. the cross-terms are null since no interaction there exists between wave-functions of the two contacts that are thus orthogonal), it is possible to decouple the effects of the two contacts and write directly the final inflow and outflow at each contact:

Inflow contact 
$$1 = \frac{1}{\hbar} \int \frac{dE}{2\pi} f_{FD}(E - E_F) Tr [\Gamma_1 A_D]$$
  
Outflow contact  $1 = \frac{1}{\hbar} \int \frac{dE}{2\pi} Tr [\Gamma_1 G^n]$   
Inflow contact  $2 = \frac{1}{\hbar} \int \frac{dE}{2\pi} f_{FD}(E - E_F) Tr [\Gamma_2 A_D]$   
Outflow contact  $2 = \frac{1}{\hbar} \int \frac{dE}{2\pi} Tr [\Gamma_2 G^n]$   
232

#### 5.14.3 Many contacts case and terminal current

The procedure illustrated in the previous section can be generalized to a whatever number of contacts, and in particular it is possible to write the i-th contact inflow and outflow like:

Inflow contact 
$$i = \frac{1}{\hbar} \int \frac{dE}{2\pi} f_{FD}(E - E_F) Tr [\Gamma_i A_D]$$
  
Outflow contact  $i = \frac{1}{\hbar} \int \frac{dE}{2\pi} Tr [\Gamma_i G^n]$ 

Considering again the *i*-th contact, the electric current can be derived from the above expressions for the inflow and the outflow at that contact. In particular the previous expressions are already comprehensive of the contributions from all the electrons (i.e. occupied states), as the integral in energy implies. To this purpose see also the full calculations in appendix C.4. Thus the total net flow of electrons is: Inflow - Outflow. This is the total flow of electrons entering the device from the contact *i*-th, i.e. the number of incoming electrons in the unit time. By multiplying it by the charge of one electron -q the net current at terminal *i*-th is obtained:

$$I_{i} = (-q) [Inflow - Outflow] = = \frac{(-q)}{\hbar} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} [Tr [\Gamma_{i}A_{D}] f_{FD}(E - E_{Fi}) - Tr [\Gamma_{i}G^{n}]]$$
(5.59)

Notice that by convention the electric current at terminal *i*-th should be positive if incoming and negative if outgoing (electric user sign convention). Indeed since the net flow: Inflow - Outflow is defined incoming, then, if incoming, it is positive, i.e. Inflow - Outflow > 0, otherwise the electric current is outgoing and it should be negative, exactly as it happens with eq. (5.59). Equation (5.59) provides a rule for computing the current with the NEGF formalism at terminal *i*-th, providing at the same the correct sign of such a current accordingly to the electric user sign convention.

In conclusion, it was finally obtained the crucial result of this chapter: the electric current with the NEGF formalism can be calculated by means of eq. (5.59). Nevertheless in the next section it will be provided an alternative expression for evaluating the current with the NEGF formalism that is also very used. Moreover such an expression gives rise to an interpretation in terms of transmission functions (i.e. Landauer formula), to the previous expression, providing thus a link between the NEGF formalism and the transmission one.

# 5.15 Transmission with NEGF

In the previous section it was derived an expression for the current at contact *i*-th, namely equation (5.59), that can in general be used to evaluate the current with the NEGF formalism. The purpose of this section is to provide a link with the transmission formalism (see chapter 4), and thus rewriting the current in terms of transmission function (or transmission spectrum), obtaining thus a Landauer's formula for the current.

Consider a two terminal device, with the source contact (contact 1) and the drain contact (contact 2). It is possible to show that the currents at the two terminals are:

$$I_{1} = \frac{(-q)}{\hbar} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \left[ Tr \left[ \Gamma_{1} A_{D} \right] f_{FD}(E - E_{F1}) - Tr \left[ \Gamma_{1} G^{n} \right] \right] =$$
  
$$= \frac{(-q)}{\hbar} \int_{-\infty}^{+\infty} \overline{T_{1}}(E) \left[ f_{FD}(E - E_{F1}) - f_{FD}(E - E_{F2}) \right] dE$$
(5.60)

$$I_{2} = \frac{(-q)}{\hbar} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \left[ Tr \left[ \Gamma_{2} A_{D} \right] f_{FD}(E - E_{F2}) - Tr \left[ \Gamma_{2} G^{n} \right] \right] =$$
  
$$= \frac{(-q)}{h} \int_{-\infty}^{+\infty} \overline{T_{2}}(E) \left[ f_{FD}(E - E_{F2}) - f_{FD}(E - E_{F1}) \right] dE$$
(5.61)

where:

$$T_1(E) = Tr \left[\Gamma_1 A_2\right]$$
  

$$\overline{T_2}(E) = Tr \left[\Gamma_2 A_1\right]$$
(5.62)

and where the  $2\pi$  is simplified with  $\hbar$  to give h. The proof of equation (5.60), (5.61) and (5.62) is provided in appendix C.5. In steady state the two terminal currents should be equal (and opposite in sign), and indeed it is possible to verify it, since it is possible to verify that:

$$Tr\left[\Gamma_1 A_2\right] = Tr\left[\Gamma_2 A_1\right] \tag{5.63}$$

a proof of equation (5.63) is again provided in appendix C.5. Therefore it follows that  $\overline{T_1}(E) = \overline{T_2}(E) = T(E)$ .

Consequently the total drain to source current can be written as:

$$I_{DS} = I_2 = -I_1 = = \frac{(-q)}{h} \int_{-\infty}^{+\infty} T(E) \left[ f_{FD}(E - E_{F2}) - f_{FD}(E - E_{F1}) \right] dE = = -\frac{(-q)}{h} \int_{-\infty}^{+\infty} T(E) \left[ f_{FD}(E - E_{F1}) - f_{FD}(E - E_{F2}) \right] dE = = \frac{q}{h} \int_{-\infty}^{+\infty} T(E) \left[ f_{FD}(E - E_{F1}) - f_{FD}(E - E_{F2}) \right] dE$$
(5.64)

where it is used:  $[f_{FD}(E - E_{F1}) - f_{FD}(E - E_{F2})] = -[f_{FD}(E - E_{F2}) - f_{FD}(E - E_{F1})]$ , and where the minus sign in front of  $I_1$  has the following meaning. If the electron fluxes from contacts to device are defined such that they are incoming positive, that is Net flux = Inflow - Outflow, it means that the current at source contact is assumed incoming positive (according to the user convention of sign). Nevertheless the drain to source current  $I_{DS}$  is assumed to be outgoing from the source (and incoming to the drain). Thus a minus sign is necessary, since:  $I_{DS} = -I_1$ . Instead for the drain contact the sign convention is already coherent with the sign definition in  $I_{DS}$ . In conclusion, by introducing the shortened notation:  $f_1(E) = f_{FD}(E - E_{F1})$  and  $f_2(E) = f_{FD}(E - E_{F2})$ , the total drain to source current is:

$$I_{DS} = \frac{q}{h} \int_{-\infty}^{+\infty} T(E) \left[ f_1(E) - f_2(E) \right] dE$$
(5.65)

where:

$$T(E) = Tr\left[\Gamma_1 A_2\right] = Tr\left[\Gamma_2 A_1\right] = Tr\left[\Gamma_1 G_D \Gamma_2 G_D^{\dagger}\right] = Tr\left[\Gamma_2 G_D \Gamma_1 G_D^{\dagger}\right]$$
(5.66)

where  $G_D = [EI_D - H_D - \Sigma]^{-1}$  is the device Green's function (with  $\Sigma = \Sigma_1 + \Sigma_2$ ), and  $G_D^{\dagger} = G_D^A$  is the device advanced Green's function. Notice that T(E) is called transmission function or transmission spectrum (since it provides the transmittivity in function of the energy E). Equation (5.65) is called "Landauer's equation" for the current and indeed it is analogous with the expression introduced in chapter 4 (see sections 4.1 and 4.3 - equations (4.4), (4.6), (4.8) and (4.24)); to this purpose see also the below reported remark concerning the spin degeneracy. The physical meaning of such equation (5.65), was already highlighted in chapter 4. Nevertheless the point is that  $I_{DS}$  can be viewed as the net difference between two counterpropagating fluxes, one from the source to the drain and the other from the drain to the source. The transmission function T(E) is a measure of the amount of electrons that can be transmitted from one side to the other through the channel. The energy states that contribute to the conduction are those for which the difference between the source and the drain Fermi functions is non-null, at zero kelvin it would reduce to the electron states between the two Fermi levels.

#### Spin degeneracy

The above reported calculations and results are referred to a net flux of electrons from source to drain. Nevertheless they are not accounting for the spin degeneracy. Indeed for each considered energy level E there exist two distinct electron states that are allowed accordingly with the Pauli exclusion principle (they have different sets of quantum numbers, considering the spin quantum number - see also section 2.5): the one with spin UP and the one with spin DOWN. Such a spin degeneracy can be considered simply by adding a factor two in front of the current expression:

$$I_{DS} = \frac{2q}{h} \int_{-\infty}^{+\infty} T(E) \left[ f_1(E) - f_2(E) \right] dE$$
(5.67)

where:

$$T(E) = Tr\left[\Gamma_1 A_2\right] = Tr\left[\Gamma_2 A_1\right] = Tr\left[\Gamma_1 G_D \Gamma_2 G_D^{\dagger}\right] = Tr\left[\Gamma_2 G_D \Gamma_1 G_D^{\dagger}\right]$$

This correction holds true if the transmission function T(E) is independent on spin. If for some reason the transmission functions for the spin UP and DOWN are different (e.g. the channel is a magnetic conductor/molecule or there is an applied magnetic field or again there occurs Coulomb blockade - see section 6.1), then they should be considered separately, and the total current is the superposition of the two. To be very clear a spin UP and a spin DOWN currents are found by means of eq. (5.65), with two different transmission functions, and then they are summed.

#### 5.15.1 Transmission formalism vs NEGF

The main results of the last sections are two equivalent formulae for the evaluation of the electric current, namely equation (5.59) and (5.65). By knowing the device Hamiltonian and its coupling to the contacts  $\Sigma_{1,2}$  it is possible to calculate the current using either (5.59) or (5.65). This is true as long as the transport is coherent, i.e. it does not suffer of energy relaxation. In particular this topic was already discussed in section 4.3.4, and for this reason here I only report the summary of situations in which a coherent transport model can be used to obtain quantitatively reasonable estimation of the current-voltage characteristics. In particular, equation (5.59) or (5.65) can be used to accurately calculate the current if:

- 1. Purely coherent transport is considered, i.e. non-interacting electrons/particles, that can be seen as proceeding from source to drain in completely separated and independent channels (each electron carried by a single plane wave).
- 2. A rigid defect or scatterer is present in the channel, i.e. if an anomalous or irregular potential shape is present in a point of the channel but it does not change in time. In this case the effect of the defect or scattering center can be incorporated through an appropriate defect potential in the Hamiltonian. Notice that instead if the scatterer is time-dependent (such as a phonon/vibration a photon than case (4.) should be considered).
- 3. Elastic non-coherent transport is considered (in which only phase-breaking phenomena occur but not energy relaxation ones): this could be case of interacting electrons, but with no energy dissipation (i.e. no other particles such as phonons are included in the interaction). Indeed in such a case the energy lost by one electron is entirely gained by the other, and since the two electrons are identical the final current is independent on state exchange of the two electron. The final situation is similar to the one depicted in point (1.). Indeed one could think to the two interacting electrons as moving on separated channels, at different energies. Then the consequence of the interaction (since no phonons/photons are involved: i.e. there is no energy dissipation from electrons to channel etc...) is that the two electrons are exchanged, but the final result is always of having one electron at a given energy and another at another energy. Thus the final transmission function does not change and it is the same of the case of coherent transport.
- 4. Inelastic non-coherent linear transport is considered. In general if energy dissipation occurs, then equations (5.59) and (5.65) cannot be applied. Nevertheless if small bias is considered, or if the transmission function T(E) is approximately constant in the energy range within the bias window, then the response will be linear. This means that T(E) can be approximated with its central value (or alternatively average value):  $T(E) \sim T(E_F) \sim T_{average}$ , and thus an electron that changes its states, e.g. by loosing energy under the form of a phonon, reaches the drain with (almost) the same probability of the case in which it is not scattered. In this case nevertheless the model should be applied with caution.

In general the transport through molecular channel is mainly coherent, and incoherent contribution is very marginal. To this purpose see also section 4.4. Nevertheless in some cases incoherent scattering could be important, and eventually incoherent transport corrections should be used. This case will be briefly addressed in section 5.18.

Very often in literature the coherent transport case is addressed by means of the transmission formalism (Landauer's formalism - section 4.3) instead of the NEGF one [89]. Nevertheless there are some advantages in using the NEGF formalism instead. In the words of [89] these advantages are:

- a. Generality of the NEGF formalism over the transmission formalism. The NEGF can be applied with no additional complexity to whatever shaped channels and contacts with no limitations. The partitioning between channel, described by [H], and contacts, described by  $[\Sigma_1]$ ,  $[\Sigma_2]$ , is very useful when dealing with complicated structures. It is also an important conceptual point that can be useful to change the perspective from classical transport and gain a physical intuition for the analysis and setting up of simulations in nano-devices. Moreover it has a practical implication: in many commercial softwares aimed in simulating nano-devices or molecular devices, it is required to set up the desired geometry by dividing the device in channel and leads, where the leads are the contact portions that interact with the channel. The above mentioned *forma mentis* that is created by the NEGF formalism can be thus very useful in correctly set up the geometry. The importance is that this step should be performed by the designer with no help from the employed CAD, since the computer cannot know what one desires to simulates today! Thus depending if ideal contacts or defecting contacts or what is the specific situation one wants to study, the geometry should be carefully set up in order to obtain reliable results.
- b. The NEGF approach allows to easily compute the density matrix (i.e. the electron density). This is very useful if the method for the electronic structure calculation is e.g. the DFT one, that is indeed based on the electron density (or density matrix) functionals. For this reason the couple NEGF + DFT is very popular in literature also for coherent transport calculations, even if NEGF would be not at all necessary for coherent transport. Within the transmission formalism framework it is also possible to evaluate the density matrix, but this is not so easy as in the NEGF one [89], [122].
- c. The NEGF formalism can handle incoherent transport as well, and as it will be described in section 5.18, it can do it with no much additional complexity. In transmission formalism instead phase-breaking processes can only be included phenomenologically [89], [123].

# 5.15.2 Landauer's formula, small bias and thermal broadening

As mentioned in chapter 4, section 4.3, the transmission formalism is often referred as Landauer's formalism, since Landauer pioneered the use of scattering theory of transport in mesoscopic systems [89], [39]. The main result was the fundamental connection between conductance and transmission function, indeed "conductance is transmission" in the Landauer's approach. This result was already pointed out in sections 4.1.3, 4.3; nevertheless it is now derived again starting from the last result of NEGF theory, i.e. equations (5.65) and (5.67), with the gain of the concept of thermal broadening. The electric current is identical zero when  $E_{FS} = E_{FD}$ , i.e. when  $f_1 = f_2$  in eqs. (5.65) and (5.67). If a small perturbative voltage  $\delta V$  is applied to the device (where  $\delta$  indicates the fact that it is small), then the current from eq. (5.67) becomes (the differential should be considered since both T(E) and the Fermi-Dirac's functions are function of the applied bias):

$$I_{DS} = \frac{2q}{h} \int_{-\infty}^{+\infty} T(E) \left[ f_1(E) - f_2(E) \right] dE$$
  

$$\to \quad I_{DS} \sim \frac{2q}{h} \left\{ \int_{-\infty}^{+\infty} \delta T(E) \left[ f_1(E) - f_2(E) \right] dE + \int_{-\infty}^{+\infty} T(E) \delta \left[ f_1(E) - f_2(E) \right] dE \right\}$$

The first term is null since  $f_1(E) - f_2(E)$  is unchanged w.r.t. equilibrium and leads to zero integral. The second term instead can be rewritten as:

$$I_{DS} \sim \frac{2q^2 V}{h} \int_{-\infty}^{+\infty} T(E) \left[ -\frac{\partial f_0(E)}{\partial E} \right]_{E=E_{Fdot}} dE$$

A full derivation of this formula can be found in [89], here I only notice that it is first order Taylor expansion of the kind:

$$\delta \left[ f_1(E) - f_2(E) \right] \sim \left. \frac{\partial f_0(E)}{\partial E} \right|_{E=E_{Fdot}} (E - E_{Fdot})$$

where  $E_{Fdot}$  is the Fermi level of the quantum dot and  $(E - E_{Fdot}) = -qV$ . By defining the thermal broadening function as (its explicit expression -out of the scope of this workis derived in [89]):

$$F_T(E) = -\frac{\partial f_0(E)}{\partial E}$$

The current becomes:

$$I_{DS} \sim GV$$
 ,  $G = \frac{2q^2}{h}T_0$  ,  $T_0 = \int_{-\infty}^{+\infty} T(E)F_T(E - E_{Fdot})dE$ 

The thermal broadening function represents the fact that at temperature above zero kelvin the Fermi-Dirac's functions is smooth with "tails" extending above the Fermi level, and thus there occurs a broadening of the energy levels of the order of  $k_BT$  (being  $k_B$  the Boltzmann's constant and T the temperature); while  $T_0$  represents the equilibrium transmission spectrum. The physical meaning of the last equation is that the conductance G is proportional to the transmittivity T(E), averaged over an energy range of a few  $k_BT$  around the equilibrium electrochemical potential  $E_{Fdot}$ , just as the quantum capacitance (see section 4.1.8) is proportional to the average DOS centered in  $E_{Fdot}$ . This is the linear response of the device (for small bias), indeed the transmission function is approximated as constant. Notice that the last expression for the conductance corresponds to the conductance expression previously introduced with the Landauer's transmission formalism (see section 4.3 equation 4.23).

#### 5.15.3 Channel proper modes and maximum conductance

In the case of more available modes (proper modes or energy levels for a quantum dot, or subbands for a quantum wire), the transmission  $T_0$  includes the transmission though each energy channel, if the number of modes is said to be M then one can rewrite the conductance (previous section 5.15.2) with:  $G = \frac{2q^2}{h} \widetilde{T}_0 M$ , where  $\widetilde{T}_0$  indicates the transmission per mode. In this optics it is obvious that not only the conductance is transmission, but also that it is directly proportional to the number of independent modes that there are within the channel. In particular the same considerations made about the quantum conductance in section 4.1.3 are still true. The interface resistance, or quantum limit of conductance, is thus a direct consequence of the fact that the maximum conductance, or equivalently the maximum transmission, is directly proportional to the number of modes in the narrowest portion of the device. This is usually the channel. Nevertheless an important remark is that if the channel has regions with more allowed modes (e.g. regions with more molecular orbitals) and regions with less allowed modes (e.g. regions with less orbitals, i.e. less allowed electron clouds), then the maximum will be always proportional to the number of electron states in the region in which there are less allowed states (this is intuitive since that regions will be like "bottlenecks" for the transport).

Notice also that in the case of a small molecule, short in the transport direction, if the coupling is large enough it is possible to have transmission from the source to the drain directly, even for energies not allowed in the molecular channel. This is a consequence of the fact that electrons are not exactly confined in the contacts, but there is a finite probability of finding them outside the contact (like in a finite height potential step). Mathematically this corresponds to the effect of the contact self-energy imaginary part (the broadened states or hybrid wave-functions), that causes a spatial exponential decay of the wave-function. For some values of  $\Gamma$  this exponential decay can be so large that the direct tunneling from source to drain is non-negligible. Instead in the case of a long molecule (in the direction of transport), or if the short molecule is weakly coupled with the contacts, this coherent transmission from source to drain is damped. In particular the contact self-energies cause always an exponential decay in space of the wave-function, but in that case the space interval separating source and drain can be too long to have relevant direct tunneling between source and drain. Again in such a case the maximum conductance will be proportional to the number of electron states in the region with less available states, most likely the central portion of the molecule (if the source and drain contacts are more or less equally coupled to the molecule).

This concepts were already pointed out in section 5.9.1, concerning the Krylov method for the contact self-energy computation.

# 5.16 Summary of NEGF transport equations

The purpose of this section is to summarize the main equations and quantities of the NEGF formalism for transport in mesoscopic systems. The physical meaning and the mathematical derivation were already provided in detail in the previous sections.

**Contact self-energies**  $\Sigma_1$ ,  $\Sigma_2$  of contact 1 and 2 (drain and source) respectively. They represent the effects of the contacts on the quantum dot (molecule), and they can be though as suitable boundary conditions that take into account the fact that the molecule is not isolated but connected to the contacts:

$$\Sigma_1 = \zeta_1 g_{R_1} \zeta_1^{\dagger} \qquad , \qquad \Sigma_2 = \zeta_2 g_{R_2} \zeta_2^{\dagger} \qquad (5.68)$$

where:

- $\zeta_1$  and  $\zeta_2$  are the contact coupling Hamiltonians which represent the strength of the coupling between the contacts and the quantum dot, i.e. the molecule. They are intimately linked to the quality of the chemical bonds between molecule (anchoring groups) and the contacts. They are related to the aptitude of moving electrons between contacts and molecule, and of course they are linked with the escaping rate or time  $\tau$ , i.e. the average time at which electrons escape from the device towards a contact or vice versa. From section 5.8, in which a single contact was considered, the coupling matrix is:  $\zeta = (ES_{DR} H_{DR})$  and its Hermitian conjugate was:  $\zeta^{\dagger} = (ES_{RD} H_{RD})$ . The extension to the case of two contacts is trivial.
- $g_{R_1}$  and  $g_{R_2}$  are the two surface Green's functions (SGF) of the two contacts. They are essentially the impulse responses of the borders of the contacts (they can be calculated starting from the knowledge on contact structures and only few surface atoms are usually involved in their estimation).

Linearity can be exploited and the effects of both the contacts can be considered together by summing up the two contacts self-energies obtaining:

$$\Sigma = \Sigma_1 + \Sigma_2 \tag{5.69}$$

**Broadening functions**  $\Gamma_1$ ,  $\Gamma_2$  are matrices defined as the anti-Hermitian parts of contact self-energies. They represent the effect of broadening of the isolated molecule energy levels due to the presence of contacts. They are linked to imaginary part of energy (finite life-time states) because the imaginary part of energy is the mathematical tool for describing the broadening:

$$\Gamma_1 = i[\Sigma_1 - \Sigma_1^{\dagger}] \qquad , \qquad \Gamma_2 = i[\Sigma_2 - \Sigma_2^{\dagger}] \qquad (5.70)$$

$$\Gamma = \Gamma_1 + \Gamma_2 \tag{5.71}$$

where i is the imaginary unit.

Dyson's equation:

$$G_D^R(E) = [EI_D - H_D - \Sigma]^{-1}$$
(5.72)

$$G_D^A = \left(G_D^R\right)^\dagger \tag{5.73}$$

where:

- $G_D^R$  is the retarded Green's function of the device
- $G_D^A$  is the advanced Green's function of the device
- $I_D$  indicates the identity matrix, in the case of non-orthogonal basis set it should be substituted with the overlap matrix  $S_D$
- $H_D$  is the device Hamiltonian operator (matrix form)
- *E* is the considered energy value

The Dyson's equation (5.72) can be considered as an operative definition of the retarded Green's function, i.e. of the device Schrödinger's equation impulse response; while equation (5.73) defines the advanced Green's function (it is just the transpose complex conjugate of the retarded one). It is useful to notice that all previously reported quantities are function of energy E, that actually can represent the energy of a "test" electron (or in general quantum particle) injected from contacts into the device, i.e. the energy of an input stimulus to the system. From this remark it should be clear that the NEGF formalism differentiates from conventional quantum mechanics since it corresponds to a forced study of the system (in which the input stimulus, of energy E, is supposed known), instead of a free oscillation study of the system as usually happens in quantum mechanics (see the change of perspective of section 5.1). The retarded Green's function has the physical meaning of impulse response of the device/channel in the moment in which it is connected to the contacts, thus it is the system output when the input stimulus is an impulse.

#### Transmission coefficient T(E):

$$T(E) = Tr[\Gamma_1 G_D^R \Gamma_2 G_D^A]$$
(5.74)

where:

- T(E) is the transmission coefficient at that energy value E
- "*Tr*" represents the trace of a matrix

Once the transmission coefficient is known for each energy value E of interest, the current can be evaluated by exploiting the **Landauer's equation** (term 2 for spin degeneracy):

$$I = \frac{2q}{h} \int T(E) [f_1(E) - f_2(E)] dE$$
(5.75)

where:

- q is the electron charge and h the Planck's constant
- $f_1(E)$  and  $f_2(E)$  are the Fermi-Dirac's distribution functions of the two contacts evaluated at energy value E (referred to  $E_{FS}$  and  $E_{FD}$  respectively)

Notice that the above reported Landauer's formula includes only ballistic transport, as discussed in section 5.15.1. Very often, considering the nanoscale dimension of a molecule, it is reasonable to neglect incoherent scattering [90]. Notice that the real power of NEGF formalism lays in the fact that is also possible to model incoherent scattering by means of an additional self-energy  $\Sigma_s$  [89], [124], that represents the incoherent terms, like they were adding or removing electrons from a fictitious contact (see section 5.18).

#### The single level case:

Notice that the previously reported NEGF formalism equations simplify in the corresponding equations introduced in chapter 4 (section 4.1 mainly) if a channel with a single energy level is considered. The complete demonstration of this correspondence is reported in [89], while here it is omitted for brevity. The reader is invited to have a look at that correspondence to gain confidence on the NEGF formalism.

# 5.17 The general procedure for the current calculation

Equation (5.75) can be used to evaluate the current flowing in the device of any coherent device (ballistic transport). This holds true for any device and for any applied voltage, and the complete *I-V* characteristics is obtained. A crucial point is that what just said is true if and only if it is known how the voltage drops across the device. In general to obtain quantitatively correct results a self-consistent loop must be implemented, providing the simultaneous and self-consistent solution of the transport equations, summarized in the previous sections, and also of the equation that provides the total voltage drop, i.e. potential energy shape, within the conductive channel. The latter equation is the Poisson's equation as described in a while. Before proceeding in the description of the general procedure for current calculations, a remark is provided about the special case in which it is not necessary to solve self-consistently the set of equations for transport. Indeed only in the special case in which a linear response is evaluated (i.e. with small applied bias), instead of solving self-consistently the set of NEGF equations for transport with the Poisson one, it is possible to simply assume a "reasonable" potential and solve only one time the NEGF equations. There is no unique way to estimate such a reasonable potential, and a detailed discussion is provided in [89]. For example if the applied bias is small, then one can assume that the electric field within the channel is more o less constant and thus the potential (energy) in the channel is linear decreasing from source to drain. This can be correct qualitatively and only if the applied bias is very small (less than the

thermal broadening, i.e. less than a few times  $k_BT$ ). In general, as mentioned above, the NEGF set of equations must be solved self-consistently with the Poisson's equation, that provides that potential shape within the channel. The principle is not so different from the one presented in sections 4.1.6 and 4.1.7, for the evaluation of the function U, with the difference that in general it is not sufficiently accurate considering the channel as having no physical extension; but instead it must considered the precise position of the atoms in order to evaluate the full 3D spatial variation of the potential energy from the Poisson's equation and thus solve the transport problem.

The self-consistent procedure for the evaluation of the electric current in a mesoscopic system is summarized in figure 5.1. Within the SCF approximation (see section 3.2), it is possible to evaluate a potential U embedding all the contributions, that represents the average total potential that an electron feels due to the change  $\delta n(\vec{r})$  in the electron density, or more generally in the density matrix:  $\delta[\rho]$ . This change can be due to an applied bias that forces the device working in a non-equilibrium condition, thus polarizing (or screening) the electron clouds/orbitals of the channel and varying the electron density. This variation of  $\rho$  leads to a variation of the potential U, accordingly with the (modified) Poisson's equation:

$$\nabla^2 V(\vec{r}) = -\frac{n(\vec{r})}{\varepsilon_0} \quad \leftrightarrow \quad \nabla^2 U(\vec{r}) = +q \frac{n(\vec{r})}{\varepsilon_0} \tag{5.76}$$

where n is the electron density, linked with the density matrix by equation (5.30), reported here for simplicity:

$$n(\vec{r}) = \left[\tilde{\rho}(\vec{r}, \vec{r'})\right]_{\vec{r'}=\vec{r}} = \sum_{\alpha} \sum_{\beta} \rho(\alpha, \beta) \psi_{\alpha}(\vec{r}) \psi_{\beta}^{*}(\vec{r})$$

Thus the Poisson's equation provides the Poisson's potential  $U(\vec{r})$  for a given electron density  $n(\vec{r})$ , that is easily recovered from the density matrix  $[\rho]$  by means of the above equation. The question now can be: "how is the density matrix evaluated?". The answer is simple: by means of equation (5.51) or analogously (5.53), derived previously in section 5.13, and reported here for simplicity:

$$[\rho] = \int \frac{dE}{2\pi} G_D \left[ f_1 \Gamma_1 + f_2 \Gamma_2 \right] G_D^{\dagger} = \int \frac{dE}{2\pi} G_D \Sigma^{in} G_D^{\dagger} = \int \frac{dE}{2\pi} \left[ G^n(E) \right]$$

From which it is evident that the evaluation of the density matrix  $[\rho]$  requires the knowledge about the potential energy U. Indeed U appears inside the device Hamiltonian  $H_D$ , that appears in the expression of the device Green's function  $G_D$ , highlighting again the necessity of the self-consistent approach.

In summary, the electron density is calculated from the density matrix. The new potential value is calculated from the electron density. The new density matrix is calculated from the broadening functions of the contacts and from the device Green's function, that depends on the potential energy through the device Hamiltonian. The procedure should be iteratively carried out until the convergence to a desired tolerance is obtained.


Figure 5.1: General Self-Consistent procedure for the solution of the NEGF transport and Poisson equations.

#### 5.17.1 A "toy" pseudocode

To get confidence about this procedure it may be useful considering the following ultrasimplified examples, before considering a real one.

First of all an equilibrium pseudocode, aimed to evaluate the equilibrium transmission spectrum, is reported. The equilibrium transmission spectrum is of fundamental general relevance in understanding conduction properties of molecules, and it is also the starting point for all the non-equilibrium calculations. Notice that a ultra-simplified non-equilibrium pseudocode can be simply derived from the one at equilibrium, by inserting it within two additional loops on the drain and gate voltage values (see below). Here a "toy" equilibrium pseudocode is reported:



In order to understand the principle behind this pseudocode, it is better to firstly recall the physical meaning of Green's function. The Green's function is the impulse response for Schrödinger's equation, i.e. the response of the system when the input is a delta-Dirac function (in general both in time and space) [89], [39], [92]. Moreover the formal introduction of Green's function as quantum propagator [92], even if not used here (and not reported for simplicity), is useful to clarify the physical meaning of Green's function under a slightly different perspective. In particular, as quantum propagator, the Green's function is something that creates a particle (I refer to this as "test electron") in a given spatial point and at a given time instant, then propagates it up to the moment in which it is annihilated in another point and at another time instant [115], [116]. All this under a possible perturbation of the equilibrium device Hamiltonian (e.g. under an external bias). Notice that in general the final goal is to simulate an isolated device by considering the effects of the external world; thus the creation or annihilation of an electron physically corresponds to an electron that flows from contacts to the device or from the device to the contacts respectively. By putting together the two aspects (impulse response of Schrödinger's equation and quantum propagator) it is clear that the NEGF formalism can be used to study a forced operation of the system (i.e. the device), in an analogous way to the forced operation study of a conventional LTI system (even if differences are of course present - in this regard see section 5.1). By carrying on this analogy, it is clear that injecting a test electron with a given (supposed known) energy E into the device and seeing what is the system response (in terms of transmittivity at that given energy value E), is conceptually similar to apply a sinusoidal signal of a given frequency to an LTI system and measuring the response of the system at that given frequency (in terms of transfer function). This explains the outer FOR loop on energy values that are chosen by user. They are all the energy values (of a test electron injected into the device) at which the system response, in terms of transimittivity, is tested. For each (user defined) energy value, the set of equations introduced in the previous section is exploited in order to find the transmission coefficient at that given energy value. In correspondence of molecular steady states (i.e. energy eigenvalues) transmission peaks will appear, anyway they will be naturally broadened thanks to the contributions of contact self-energies and broadening functions. Notice that in carrying on the analogy between LTI systems and NEGF, the concept of frequency is substituted by the concept of energy.

The output of this pseudocode is of course the transmittivity (or transmission spectrum) T(E), while its inputs are:

- the isolated molecule (equilibrium) Hamiltonian operator  $H_0$
- the contact self-energy matrices  $\Sigma_1$  and  $\Sigma_2$  (for each considered energy value E)

It is now reported another example, useful in understanding the "real world" example of the next section. It is an approximated and very simplified out-of-equilibrium pseudocode:

```
Evaluation of equilibrium isolated molecule Hamiltonian H_{0}
  FOR each (user defined) bias V_{GS}
      FOR each (user defined) bias V_{DS}
          Evaluation of perturbed H(bias)
          H_D = H_0 + H(bias)
         FOR each (user defined) energy value E
                  Evaluation of contact self-energies \Sigma_1 and \Sigma_2
                 \Sigma(E) = \Sigma_1 + \Sigma_2
                 G_D^R(E) = [EI_D - H_D - \Sigma]^{-1}
                 G_D^A = G_D^{R^{\dagger}}
                 \Gamma_1 = i[\Sigma_1 - \Sigma_1^{\dagger}]
                 \Gamma_2 = i [\Sigma_2 - \Sigma_2^{\dagger}]
                 \Gamma = \Gamma_1 + \Gamma_2

T(E) = Tr[\Gamma_1 G_D^R \Gamma_2 G_D^A]
         END FOR
         I(V_{GS}, V_{DS}) = \frac{2q}{h} \int_E T(E) [f_1(E) - f_2(E)] dE
      END FOR
  END FOR
```

The only difference w.r.t. equilibrium case is an outer loop on voltage bias points (eventually two loops if both  $V_{GS}$  and  $V_{DS}$  are simultaneously considered) and the evaluation of the perturbation of the Hamiltonian matrix due to the additional potential terms, that is summed up to the equilibrium one to get the total Hamiltonian of the system under bias.

Another difference is the integral of out-of-equilibrium spectra to get the value of current for a given bias point. Even if not represented in this simplified pseudocode a self-consistent procedure should be carried out, as described previously, to guarantee convergence of results. A complete example is reported in the next section.

Practical remark: With reference to the commercial tool Quantum-Wise ATK, in simulations it has no much sense choosing a very refined energy grid if the number of k-points is not so high. Indeed usually calculations are carried out in Fourier space, i.e. in k-space. Nevertheless the transmission spectrum in a given energy point is obtained summing up the contributions for different k values. A very refined energy grid evaluates T(E) in many points, but if the single T(E) values are not numerically precise (low number of k-points) the result can be not so much significant.

#### 5.17.2 The general procedure: a real example

In this section it is reported a real example of a self-consistent calculation, using the NEGF set of equations for transport and the Poisson's equation for evaluating the electron density. This example is very important to get confident not only with NEGF equations and the SCF approach in the solution of the transport problem, but also to explicitly point out how the gate electrode can affect the transport from the rigorous standpoint of the NEGF approach. The basic physical insights to this end were already introduced in chapter 4 (section 4.1.7), but now are considered under a different perspective. The example I briefly introduce here corresponds to the solution algorithm implemented in the free available and *MatLab*-based tool *Huckel-IV 3.0*, that allows for transport calculations in molecules (or in general in quantum dots) exploiting an EHT + NEGF approach, considering gating as well. It was developed mainly by prof. Ferdows Zahid with M. Paulsson, E. Polizzi under the supervision of prof. S. Datta at Purdue University (Indiana, USA) between 2003 and 2005; references are present in literature [105], [41], [24].

This software exploits EHT with CNDO (see also below Poisson's potential) to compute molecular (in general quantum dot) and contacts Hamiltonian operators and NEGF for transport calculations, along with a self-consistent description of electrostatics of the system. The molecular and the "molecule + contact leads" Hamiltonians are evaluated with EHT by means of a C code (a preliminary atom indexing Python code is used). The contact (gold FCC (111)) self-energies are evaluated in *MatLab* following the procedure explained in section 5.8 starting from the knowledge of the molecular and the contact leads Hamiltonians. The transport calculations employ the set of equations summarized in section 5.16. In the *Huckel-IV 3.0* version, a full 3D self-consistent description of the system electrostatics is performed. The molecule is supposed to be within a box with electrode plates as its sides (for two terminal calculations the dimension of the box is set to be 100 Å × 100 Å x L, being L the molecule length). Notice that up to four gate electrodes are possible, of which two in plane and two out of plane. A self-consistent procedure, comprising of two steps, is implemented to perform out of equilibrium analysis.

In this tool the device Hamiltonian (out of equilibrium) is divided into two parts: the core Hamiltonian  $H_0$  (i.e. the equilibrium Hamiltonian) and the self-consistent potential  $U_{SCF} = U(\rho)$ . Notice that H represents the total perturbed Hamiltonian. The density

matrix  $\rho$  is evaluated as described previously (and in section 5.13):

$$\rho = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left[ f_1 G_D^R \Gamma_1 G_D^A + f_2 G_D^R \Gamma_2 G_D^A \right] dE$$
(5.77)

where  $f_1$  and  $f_2$  are the Fermi-Dirac distribution functions of the two contacts (source and drain respectively):

$$f_{1,2} = \frac{1}{1 + e^{(E - E_{F1,2})/k_B T}}$$

Notice that a contour integral is needed to evaluate the integral of eq. (5.77) since the Green's functions have poles in energy domain (see section 5.5) that coincides more or less with the proper eigenvalues of the isolated molecule.

The self-consistent potential  $U(\rho)$  is dependent on the density matrix, and it represents the effects of the applied bias (both gate and drain electrodes) to the electrostatics of the system, due to any change of the density matrix. In particular it takes into account the charging effect (i.e. modification of molecule energy levels when a bias is applied due to variations in number of electrons in the system - see section 4.1.5) and for screening effect (essentially the molecule under bias is polarized, leading to variations of the spatial distribution of charge - i.e. molecular orbitals/wave-functions - and thus a variation of the density matrix the in real space representation).

In *Huckel-IV* the self-consistent potential is divided into three contributions as follows:

$$U(\Delta \rho) = U_{Laplace} + U_{Poisson}(\Delta \rho) + U_{image}(\Delta \rho)$$
(5.78)

where  $\Delta \rho$  represents the change in density matrix under bias:  $\rho - \rho_{equilibrium}$ . Since  $U(\Delta \rho)$  is a functional of  $\Delta \rho$  it describes only the change in the potential under bias and it is null at equilibrium. The spatial profile of the potential within the simulation domain (i.e. the above mentioned "box") is found, out of equilibrium, by means of eq. (5.78). The first term in eq. (5.78) represents the spatial distribution of the applied voltage, it is found by solving a standard Laplace's equation:

$$\nabla^2 U_{Laplace} = 0 \quad with \ boundary \ conditions: \quad U_{Laplace} = \begin{cases} -qV_S \ at \ source \\ -qV_D \ at \ drain \\ -qV_G \ at \ gate \end{cases}$$
(5.79)

In solving this equation the atomic sites are considered as points in free space (vacuum dielectric constant  $\varepsilon_0$ ). As mentioned, an applied potential (i.e. the presence of an external field) polarizes the molecule thus changing the spatial distribution of charge density (orbitals) in the molecule (screening effect), and moreover makes changing the number of electrons inside the device/molecule (charging effect). As a result of these two effects, a Poisson's potential arises. In principle it may be evaluated by solving the Poisson's equation (of the kind of 5.76) considering again the atoms like point charges in free space. Nevertheless in this way an infinite potential would arise in the points in which atoms are located, thus a different approach is followed in *Huckel-IV*. In particular the  $U_{Poisson}(\Delta \rho)$  in eq. (5.78) is evaluated by using CNDO method with Slater-type atomic orbitals (STO), considering only Hartree's potential (i.e. Coulomb interactions). The solution involves the

so called "gamma matrix" that stores the CNDO parameters. Details are provided in [24]. The last term  $U_{image}$  represents the image correction to the potential due to the presence of contacts surrounding the molecule, and it is evaluated by solving the following equation:

 $\nabla^2 U_{Image} = 0$  with boundary condition :  $U_{Image} = -U_{Poisson}(\vec{r})$  at the electrodes.

In this case atomic sites are again considered as point charges in free space. Notice that the electrodes are modeled as perfect electrical conductors (PEC) such that the image theorem is applied in order to evaluate the effect of the PEC on the resulting potential due to the charge distribution within the simulation domain. All these electrostatic calculations are performed by means of finite difference method (FEM). They are performed by a *Fortran* 90 program (using as preliminary Python and C programs) and by routines in *MatLab*. The gate oxide is considered in the continuum approximation as an homogeneous medium, thus characterized only with its dielectric permittivity and its thickness. This approximation holds as long as the oxide thickness is enough large.

The self-consistent loop consists of two steps:

- Step 1: Calculate the self-consistent potential given a density matrix using the functional relation of eq. (5.78) and thus get the total perturbed Hamiltonian H.
- Step 2: Calculate the density matrix  $\rho$  starting from NEGF quantities by means of eq. (5.77).

Hence the self-consistent field loop is built by using the density matrix as "checking variable". In general in a SCF loop the procedure is iterated up to when the difference between the new value and the old value of the "checking variable" is lesser than the desired convergence tolerance, or the maximum number of iterations is reached. Said A the "checking variable", the exit condition is:  $\Delta A = A_{new} - A_{old} < tolerance$ . Anyway in order to ensure convergence usually the "checking variable" is not simply updated, but the new value is found by updating the old one with a suitable weight, following a relation of the kind:

$$A_{new} = A_{old} + weight \cdot A_{re-evaluated} \tag{5.80}$$

This is an extreme simplification, but it is useful to understand the so called mixing schemes that are often used in SCF loops to ensure numerical convergence (indeed large variations of the quantity of interest could lead to numerical oscillating behaviours). Several possible mixing schemes are in general possible and well documented in literature, in *Huckel-IV* the famous Pulay's mixing scheme is used.

In Huckel-IV there is only one fitting parameter  $V_c$ , that is a number that somehow is aimed to consider the relative position between gold contacts Fermi levels and isolated molecule Fermi level. Indeed whenever a molecule is connected to the contacts a small amount of charge is transferred between molecule and contacts in order to align the equilibrium Fermi energy. Anyway the precise location of the equilibrium Fermi level depends very sensitively on many factors such as the nature of bonding between the anchoring group and the contact, the surface condition of the contact, geometrical fluctuations of the structure and environmental conditions. As a consequence in absence of detailed information on these factors the position of  $E_{Fdot}$  can be justifiably treated as a fitting parameter, to be set accordingly to experimental data or alternatively *ab initio* simulations. In *Huckel-IV* this is done by means of  $V_c$  parameter. Another possible approach could be to self-consistently evaluate it even at equilibrium (as for example did in *Quantum-Wise ATK*).

The inputs of *Huckel-IV* are just the molecule geometry file and the orthogonal distance between the anchoring atoms and the gold electrodes (it can be considered as an additional fitting parameter, eventually considering good or bad chemical bonds). Of course the fitting parameter  $V_c$  should be set suitably and information concerning the structure (such as number of gates and oxide dielectric constant, etc...) should be provided. Finally the bias has to be set to perform the desired simulation.

Its output are *MatLab* data structures and plots storing the current-voltage characteristics, the transmission spectrum, the variations of number of electrons and molecular energy levels with applied bias and all the other physical quantities of interest.

An operative description of such a tool is reported in appendix F. It will be used in the practical part of the present work (part II chapter 9), in order to estimate the sensor stray capacitances and other useful parameters to evaluate the sensor response time.

#### 5.17.3 Mixing schemes

In the previous section it was already presented the concept of mixing scheme for guaranteeing the convergence of a self-consistent procedure. The purpose of this section is to repeat it, in order to make it easily accessible when a fast consultation of this document is performed.

In general, in a SCF loop, the procedure is iterated up to when the difference between the new value and the old value of the "checking variable" is lesser than the desired convergence tolerance, or the maximum number of iterations is reached. Said A the "checking variable", the exit condition is:  $\Delta A = A_{new} - A_{old} < tolerance$ . Anyway in order to ensure convergence usually the "checking variable" is not simply updated, but the new value is found by updating the old one with a suitable weight, following a relation of the kind:

$$A_{new} = A_{old} + weight \cdot A_{re-evaluated} \tag{5.81}$$

This is an extreme simplification, but it is useful to understand the so called mixing schemes that are often used in SCF loops to ensure numerical convergence (indeed large variations of the quantity of interest could lead to numerical oscillating behaviours). Several possible mixing schemes are in general possible and well documented in literature, in *Huckel-IV* and also in *Quantum-Wise ATK* the default choice is the famous Pulay's mixing scheme. Notice that *Quantum-Wise ATK* allows the user to choose the mixing variable, that can be the Hamiltonian, the density matrix, etc...

#### 5.17.4 Poisson's solver in Quantum-Wise ATK

From the previous treatment it is evident that if the interest is in the entire shape of the current-voltage characteristics (I-V), then the potential profile obtained by solving the Poisson's equation is of crucial importance. The only case in which a non-self-consistent solution of the set of NEGF transport equations leads to approximate not so bad results is the case of linear response with small bias (much less than  $k_BT$ ). The self-consistent potential U can be calculated starting from the Poisson's equation. In general this could be a modified Poisson's equation such that it accounts for the electron-electron interaction (charging effect) by means of a correlation term (see section 3.2), in addition to standard electrostatic (i.e. Laplace) effects (like it happens in the Huckel-IV tool introduced previously). The purpose of this section is to highlight the methods and the correct setting up of the Poisson solver implemented in the commercial tool Quantum-Wise ATK (atomistic toolkit) by Synopsys<sup>®</sup> [125], [126]; that will be widely used in the practical part of this work.

Throughout this entire section I am referring to the *ATK* manual, version Q-2019.12, references: [125], [126].

In ATK there are four methods for the solution of the Poisson's equation, that is a second order differential equation. The methods are:

- *FFT/FFT2D*: In this method the Poisson's equation is solved in the Fourier domain (i.e. *k*-space), and not in real space. The Fast Fourier Transform algorithm (FFT) is used to perform numerical Fourier transformations. This method is very efficient and reliable for periodic systems, especially with periodic boundary conditions (see later for boundary conditions). It is not much suitable for molecular devices (in which there is no such periodicity) and it is not suitable if dielectric or metallic (non-atomistic PEC) regions are present. It exploits the *FastFourierSolver*, which is the most efficient FFT solver in the *QuantumATK* package.
- *MultiGrid* and *Direct*: For general systems, even non-periodic and with molecular channels, the Poisson's equation can be solved using an algebraic *MultiGridSolver* or *DirectSolver*. In that case the system is considered enclosed in a bounding box (the cell of the *Builder* tool), and the Hartree's potential (Laplace and Poisson potentials of the tool *Huckel-IV*) is defined on a regular grid inside the bounding box. The solution is addressed in real space. The *DirectSolver* is well suited for parallel computations and multi-process ones. Different boundary conditions can be imposed on the solution at the bounding box surface, see later.
- Conjugate Gradient: This is a method for solving linear systems belonging to the conjugate gradients family [127]. It solves again the Poisson's equation in real space. The differential equation must be discretized (by means of Finite Difference of Finite Elements method) and then the resulting algebraic system of n unknowns in n equations is solved by means of conjugate gradient method, that belongs to the family of Gauss elimination (or reduction) methods. It requires modest memory resources and exploits sparse matrices (with many zeros). It is very efficient for parallel computations and multi-process ones.

#### **Boundary conditions**

Since the Poisson's equation is a second-order differential equation, boundary conditions are required in order to fix the solution. Molecular systems have the boundary condition that the potential goes asymptotically to zero, this is referred as Dirichlet boundary condition. In such a case the potential value is fixed at the simulation domain boundaries, i.e. the cell/box of the Builder tool. Instead in bulk systems, the boundary condition is that the potential is periodic, with period equal to the one of the crystal lattice; this conditions are called Periodic Boundary Conditions (PBC). In this case the potential value at one boundary facet of the simulation domain, is repeated identical in the facet that is on front the first one. Periodic boundary conditions only determine the Hartree's potential up to an additive constant, which reflects the physics that the bulk electrostatic potential does not have a fixed value relative to the vacuum level. Experimentally, this can be measured through the different work functions of different facets of a crystal. Finally a third boundary condition is possible in ATK, i.e. Neumann boundary condition. A Neumann boundary condition enforces the first derivative of the potential to be zero at the domain boundaries (i.e. the cell/box boundaries). Since the electric field is given by the first derivative of the potential, a Neumann boundary condition will set to zero the electric field in the faces to which it is enforced. For this reason it is particular suitable in modeling a PEC (Perfect Electrical Conductor) and thus it is the preferred choice where metallic (non-atomistic) regions are present (such as gates).

Notice that in the transport direction the user setting is ignored and the program always uses PBC for the electrodes and Dirichlet boundary conditions for the device. Indeed the *ATK* solver preliminary considers the contacts (well indicated in the *Builder* tool by vertical lines) as infinite and isolated, thus with PBC. Then, once their density of states (found with ideal crystal hypotheses) is known, it considers only the device and leads with at the two extremes the ideal contacts, that are no more considered as atomistic but like ideal crystalline unperturbed contacts. In the device/active portion of the system Dirichlet boundary conditions are used since they allow the potential to fluctuate and reach convergence without artifacts (like periodicity or null electric field) that would not correctly model it.

#### Solvent dielectric constant

In *Quantum-Wise ATK*, it is possible to perform calculations of solvents. In this case, the volume of the configuration is defined by inscribing each atom in a sphere with a size given by the van der Waals radius of the element. Inside the volume of the configuration, the dielectric constant is 1, and outside the volume of the configuration, the dielectric constant is equal to the value of the solvent dielectric constant. By contrast in *Huckel-IV* the Poisson solver solvent constant was fixed to the vacuum one (i.e. 1).

#### 5.17.5 Density matrix and contour integral

As mentioned previously in the SCF solution of transport equations it is required to evaluated the density matrix from the NEGF quantities. This can be done by means of equations (5.51) or analogously (5.53), or with reference with the practical example of

before, eq. (5.77). In all cases the density matrix calculation requires to integrate the Green's functions, that in energy domain presents poles (see section 5.5). Consequently an integral over a complex contour (remember that energy is complex, due to the infinitesimal  $\eta$ ), is required, analogously to what is done for evaluating e.g. the residues (e.g. for the time contacts calculations in electrical circuits). In *Quantum-Wise ATK* it is possible to set up the numerical method and few parameters in the "Contour Integral" section of the calculator tool. For references and details see the manual [125] and [126]; very often the default settings provide good result in terms of accuracy and computational cost.

# 5.18 The general self-energy concept and incoherent transport

So far only coherent transport was considered and all the dissipative/phase-breaking processes were assumed to happen only within the contacts, where they act to keep the electrons in local equilibrium. Indeed in the moment in which an electron "jumps" from the source to the channel, it leaves a hole in the source contact. Then there is an energy re-distribution of states such that the local equilibrium is again recovered, and in particular an electron at a higher energy will loose energy (under the form of heat/phonons) and will occupy the free state. Actually in general it is possible to have such processes also within the channel, and they are increasingly important as the channel length is increased. Incoherent scattering processes arise from electron-phonon, electron-photon and even electron-electron interactions. In the latter case, if only electrons are involved and the interaction is elastic (no dissipation of energy occurs under the form of phonons/photons) then a coherent model for transport is anyway correct (see e.g. the discussion in section 5.15.1).

The purpose of this section is to address the incoherent transport case, and how it is considered within the NEGF framework. Since in many practical applications the transport through molecules is with optimal approximation only ballistic, this topic is not covered in detail. Consequently the details about the microscopic processes giving rise to incoherent phenomena are not considered here, instead the focus will be on how to modify the NEGF transport set of equations in order to include the incoherent scattering. In order to do that, the matter will be addressed by steps, starting from the Bütticker theory and the extension to multi-contacts case. This is actually a topic slightly outside the purposes of this section (and of this work), nevertheless it is useful to understand why incoherent scattering can be though as an additional contact and consequently represented by means of a self-energy matrix as already done for the source and drain contacts. After that, the concept of "scattering probe" or "contact" is introduced, in which it is highlighted the analogy between the effects of scattering phenomena and a contact. Then the general approach is presented, indeed there are some issues preventing a full correspondence with the ballistic multi-probe case, and in conclusion few words about the dissipated power are said.

#### 5.18.1 Bütticker's probes and scattering

It is well known that conductance (or resistance) measurements are often performed using a four probe structure. Two terminals are dedicated to the injection of the test current, while the other two (kept separated from the previous two) are dedicated to the voltage drop measurement. Nevertheless in small structures, like mesoscopic conductors, this procedure had not a clear interpretation, until Bütticker in 1988 suggested an elegant interpretation for them [123]. Indeed he suggested that the Landauer's formula, see section 5.15.2 (and in chapter 4 section 4.3), that is (factor 2 for spin degeneracy):

$$G = \frac{2q^2}{h}\tilde{T} \quad , \quad I = \frac{2q}{h}\tilde{T}[E_{FS} - E_{FD}]$$

can be generalized in the case multiple terminals i, by writing:

$$I_i = \frac{2q}{h} \sum_j \widetilde{T}_{ij} [E_{Fi} - E_{Fj}]$$

where  $T_{ij}$  is the average transmission from terminal j to i. A full treatment is outside the purposes of this work, nevertheless it can be found in [89] and [39].

Now the point is another: it was mentioned in section 5.15 (and its subsections) that the Landauer's approach holds true only if the transport is coherent. But a voltage probe actually behaves like a phase-breaking scatterer [123]. This is clear if one considers the current flowing between two terminals with an additional third terminal acting as voltage probe in between (think again to the measurement set up for a four terminal conductance measurement). The voltage probe is aimed in measuring the voltage drop across the conductor and no current flows in principle through it (high impedance terminal - open circuit); and indeed it is left floating to an appropriate potential such that no current flows in it. A fraction of the electrons participating to the conduction goes directly from the source to drain terminal, bypassing entirely the probe. The remaining electrons from the source interact with the probe, and in particular they enter the probe and have their phases randomized before they reinjected into the device. Some of these electrons then reach the drain terminal, while others are reflected back to the source. The effect of the voltage probe is thus to introduce an incoherent component to the overall current, acting like a phase-breaking scatterer.

It is possible to reverse this argument and conclude that a phase-breaking scatterer can be emulated by means of a purely conceptual (voltage) probe, where none exist in the real structure. The idea is thus to use one or more fictitious probes or contacts to emulate and take into account the incoherent scattering phenomena; and then calculate the net current using the Bütticker's approach, that is general and can be applied to whatever number of terminals. With this approach the current at terminal i becomes [39] (factor 2 for spin degeneracy):

$$I_{i} = \frac{2q}{h} \int_{-\infty}^{+\infty} \left[ \sum_{j} T_{ij}(E) \left[ f_{i}(E) - f_{j}(E) \right] \right] dE = \frac{2q}{h} \sum_{j} \int_{-\infty}^{+\infty} \tilde{i}_{j}(E) dE$$
  
where:  
$$\tilde{i}_{j}(E) = T_{ij}(E) \left[ f_{i}(E) - f_{j}(E) \right]$$

Incoherent scattering processes take electrons out from one energy channel (or eigenstate) and reinject them at another energy value/channel (or eigenstate). Indeed they are inelastic processes in which electrons loose energy/momentum. As a consequence the "spectral current"  $\tilde{i}_j(E)$  that represents an incoherent scattering process is negative at some energies, representing the outscattering process, and positive at others, representing the inscattering. Nevertheless invoking the matter conservation (i.e. electrons does not disappear from the device even if they are scattered), it is clear that, if the *j*-th terminal is a conceptual probe representing an incoherent scattering phenomenon, then the spectral current  $\tilde{i}_j(E)$  associated to it must have an energy integral null:

$$\int_{-\infty}^{+\infty} \tilde{i}_j(E) dE = 0$$

Indeed the net outscattering must balance the net inscattering, and the net current flow in such a fictitious probe must be null, since conservation of matter holds true as explained above. Because of the scattering process the various channel energy eigenstates are coupled together, indeed the effect of the scatterer is exactly to take out an electron from a given energy and to reintroduce it at another energy. This fact extremely complicates the treatment, as better described in the next section.

The function  $i_j(E)$ , that has the dimensions of a current per unit energy, i.e. a spectral current, represents thus the "vertical flow" of electrons from one energy level to another due to an incoherent process. In general depending on the particular scattering process that is considered,  $\tilde{i}_j(E)$  has a different expression, and it can be evaluated starting from a microscopic theory of the scattering process. This usually requires the introduction of the so called "second quantization" formalism, that in this work is completely omitted. A simple treatment in this regard is for example provided in [89], in which the second quantization is avoided, and thus only the lowest order approximation is considered: the so called self-consistent Born approximation. Nevertheless this could be enough in many practical cases [89]. Another example of incoherent scattering process simple treatment is the one of [39].

Now, for the purposes of this work, the point is that it is possible to assimilate the incoherent scattering processes to a fictitious probe/contact, and applying the Bütticker's approach for evaluating their effect on the final current. The details concerning the microscopic treatment of the scattering process are not reported here while they are treated in a simple way in [89], but the conceptual point is that it is possible to derive an expression for the scattering process self-energy  $\Sigma_s$ . Once it is known  $\Sigma_s$  then superposition of effects can be in principle applied, the device Green's function is found and then the transmission is calculated by means of eq. (5.74):

$$T_{ij}(E) = Tr[\Gamma_i G_D^R \Gamma_j G_D^A]$$

This expression can be derived with a similar procedure to the one of section 5.15 (and 5.14). The total current can be then found as explained above.

#### Sum rule

This section reports an interesting topic, even if it is not necessary for the general treatment. An important result of the transmission formalism is that the sum of the rows or the sum of the columns of the transmission matrix, that provides the transmission coefficients between the terminals of the device, must equal the number of channel proper modes  $M_i$  (e.g. subbands in a quantum wire):

$$\sum_{j} T_{ij} = \sum_{j} T_{ji} = M_i$$

This formula can be demonstrated within the transmission formalism framework. This fact was already introduced in sections 4.3.2 and 5.15.3; nevertheless this is a more mathematical expression.

A similar expression can be recovered with the NEGF formalism:

$$\sum_{j} T_{ij} = \sum_{j} T_{ji} = Tr[\Gamma_i A_D]$$

In which the quantity  $Tr[\Gamma_i A_D]$  plays the role that the number of modes  $M_i$  plays in the scattering theory of transport (see section 5.15.3). The previous equation can be easily demonstrated as follows:

$$\sum_{j} T_{ij} = \sum_{j} Tr[\Gamma_i G_D \Gamma_j G_D^{\dagger}] = Tr[\Gamma_i G_D \sum_{j} \Gamma_j G_D^{\dagger}] = Tr[\Gamma_i G_D \Gamma G_D^{\dagger}] = Tr[\Gamma_i A_D]$$
$$\sum_{j} T_{ji} = \sum_{j} Tr[\Gamma_j G_D \Gamma_i G_D^{\dagger}] = Tr[\Gamma G_D \Gamma_i G_D^{\dagger}] = Tr[\Gamma_i G_D \Gamma G_D^{\dagger}] = Tr[\Gamma_i A_D]$$

where it is used:  $\Gamma = \sum_{j} \Gamma_{j}$ ; and that:  $A_{D} = G_{D} \Gamma G_{D}^{\dagger}$ ; and notice that the trace is invariant w.r.t. cyclic permutations.

#### 5.18.2 The general approach and the scattering self-energy

In general the electron-photon and electron-phonon interactions are a complicated matter, and no exact solution is generally possible. The standard way for considering them is by means of the second quantization formalism [116], [115], [92]. In [89] and [39] there are simple treatments of such interactions that do not require this formalism, but they are limited to the lowest-order approximation: the so called self-consistent Born approximation. Because of the reasoning reported in sections 4.4, 4.3.4, 5.15, the incoherent scattering mechanism are very often non-relevant in molecular devices and for this reason they are not considered in detail in the present work. I invite the reader to refer to the aforementioned references for details. The purpose here, as already pointed out, is only in describing how the scattering processes can be included within the NEGF framework. In the previous section it was introduced the idea of representing such incoherent processes by means of an additional contribution of self-energy  $\Sigma_s$ , and simply treat them as an additional and fictitious probe or contact that "shuffles" electrons among different energy eigenstates. Such a self-energy  $\Sigma_s$  explicit expression depends on the particular phenomenon considered and it can be evaluated starting from a microscopic treatment, as mentioned above usually with the second quantization formalism. Before going on a remark is due on the general concept of self-energy.

#### A remark on second quantization treatment and the general concept of selfenergy

So far it was introduced the so called "single-particle" Green's function. In this optics the so far considered Green's functions are all referred to a single electron, and the effects of the other electrons are accounted by means of as SCF potential. In general one may write a Schrödinger's equation involving more electrons and eventually also phonons and photons. This would be a many-body Schrödinger's equation for the entire system of electrons, phonons and photons. It is then possible to carry out a procedure similar to what did throughout this chapter and to define a many-body Green's function as its impulse response. With the second quantization treatment such many-body Green's function is called quantum propagator, indeed since it is an impulse response it propagates an input stimulus happening in a given point at a given time instant through the system, and provides information about the system response, in any point at any time instant. In general the dynamic equation that provides the time evolution of the system is a differential equation to be solved w.r.t. the total system many-body Green's function, somehow similarly to what reported in section 5.6. In general the problem with this procedure is that, even if one wants writing down only the single-particle Green's function, in the equation of motion for such single-particle Green's functions (i.e. essentially its time derivative), the two-particle Green's function appears. And analogously in recovering an expression for the two-particle Green's function the three-interacting-particle Green's function term appears, and so on. This procedure must thus be approximated at a given point, and for example if one wants to consider only the Green's function for a single particle, the two-, three-, four- etc.. particle terms will be cut away (similarly to what did in a Taylor's series). Nevertheless it is possible to consider them within an additional term, added starting from considerations about such interactions, and suitably approximating them such that the infinite recursion mentioned above does not occur. Such additional term is called "self-energy". The self-energy concept is a seminal concept of the many-body perturbation Green's function theory, and it is far more general than the one widely used so far for representing the contacts influence on the channel. In general any kind of interaction: electron-electron, electron-phonon, electron-photon, etc... can be represented by means of a suitable self-energy term. This term provides a sort of average effect for that specific interaction, and allows to write a single particle Green's function considering, e.g. the electron-electron interactions within it (similarly to what did in chapter 3 section 3.2). In conclusion, any interaction, and in particular any incoherent scattering process can be represented in terms of a suitable self-energy, whose explicit expression depends on the kind of considered interaction and the approximation adopted. Once it is known one can proceed as described in the following.

#### The general approach

In general it is unfortunately not possible to exploit the Landauer's transmission formula for evaluating the electric current in presence of incoherent scattering processes. This because for the contacts it was demonstrated the following relation (see section 5.13):

$$\Sigma^{in} = [\Gamma_1]f_1 + [\Gamma_2]f_2 = \Sigma_1^{in} + \Sigma_2^{in}$$
,  $\Sigma_1^{in} = [\Gamma_1]f_1$  and  $\Sigma_2^{in} = [\Gamma_2]f_2$   
257

that is not true in the case of scattering terms. Indeed from the microscopic theory it is possible to easily find an expression for  $\Sigma_s^{in}$ , but there is no simple connection between  $\Sigma_s^{in}$  and  $\Sigma_s$  or  $\Gamma_s$ :  $\Sigma_s^{in} \neq [\Gamma_s] f_s$ . So even if it is possible to simply add the scattering self energy  $\Sigma_s$  to the contact self-energies in order to get the total self-energy of the system:

$$\Sigma = \Sigma_1 + \Sigma_2 + \Sigma_s$$

and even if the same holds true for  $\Sigma^{in}$ :

$$\Sigma^{in} = \Sigma^{in}_1 + \Sigma^{in}_2 + \Sigma^{in}_s$$

in general the Landauer's formula, equation (5.65) or (5.75) does not hold. Nevertheless the general expression for the electric current in terminal *i* is still valid, i.e. equation (5.59), still holds with a small modification. This latter equation is reported now for clarity:

$$I_{i} = (-q) [Inflow - Outflow] =$$
  
=  $\frac{(-q)}{\hbar} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} [Tr [\Gamma_{i}A_{D}] f_{i}(E) - Tr [\Gamma_{i}G^{n}]]$ 

Notice that it is an expression for the net flow of electrons, multiplied by the electron charge. With the simple replacement  $\Sigma_i^{in} = [\Gamma_i] f_i$  the previous equation becomes:

$$I_{i} = (-q) [Inflow - Outflow] =$$
  
=  $\frac{(-q)}{\hbar} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} [Tr [\Sigma_{i}^{in}A_{D}] - Tr [\Gamma_{i}G^{n}]]$  (5.82)

And this last equation provides the terminal current, at terminal i, with i = 1, 2, s (where s indicates the fictitious scattering terminal), in the general case and it holds true even for the scattering case, and thus it holds in general.

In conclusion, starting from the physics of the incoherent scattering phenomena that are considered, it is possible to derive an expression for  $\Sigma_s$  and for  $\Sigma_s^{in}$ , even if the two are not simply connected. Then it is possible to write the general terminal current by means of equation (5.82), that is always correct and general. It is possible to demonstrated eq. (5.82) with a procedure similar to the one carried out in section 5.14. The concepts are summarized in the next section.

### 5.18.3 The general approach: a summary of transport equation with incoherent scattering

The purpose of this section is to summarize what explained in the previous ones. In particular once the scattering self-energy is known (to this purpose see [89] and [39] or for a more formal introduction [115], [116]), it is possible to write the following equations and recover the current by means of eq. (5.82):

$$\begin{split} G^n &= G_D \Sigma^{in} G_D^{\dagger} \\ G_D &= [EI_D - H_D - \Sigma]^{-1} \\ H_D &= H_{equi} + U_{SCF} \\ A_D &= i \left[ G_D - G_D^{\dagger} \right] \\ \Gamma &= i \left[ \Sigma - \Sigma^{\dagger} \right] \\ where : \\ \Sigma^{in} &= \Sigma_1^{in} + \Sigma_2^{in} + \Sigma_s^{in} \quad , \quad \Sigma_1^{in} &= \Gamma_1 f_1 \quad , \quad \Sigma_2^{in} &= \Gamma_2 f_2 \\ \Sigma &= \Sigma_1 + \Sigma_2 + \Sigma_s \quad , \quad \Sigma_{1,2} &= \zeta_{1,2} g_{1,2} \zeta_{1,2}^{\dagger} \quad , \quad \Gamma_{1,2} &= \zeta_{1,2} a_{1,2} \zeta_{1,2}^{\dagger} \end{split}$$

where  $g_{1,2}$  are the surface retarded Green's functions (of contacts 1 and 2 respectively, i.e. the source and the drain), and where  $a_{1,2}$  are the surface spectral functions of the two contacts. Moreover  $U_{SCf}$  is the potential energy U introduced in section 5.17, and  $H_{equi}$  the equilibrium Hamiltonian. From the above formulae it is possible to calculate the non-equilibrium density matrix and the current:

$$\rho = \frac{1}{2\pi} \int G^n(E) dE$$
$$I_i = \frac{(-q)}{h} \int_{-\infty}^{+\infty} \left[ Tr\left[ \Sigma_i^{in} A_D \right] - Tr\left[ \Gamma_i G^n \right] \right] dE$$
(5.83)

Notice that the terms  $Tr\left[\Sigma_i^{in}A_D\right]$  represent the inflows term, i.e. the electron fluxes toward the channel, while the terms  $Tr\left[\Gamma_i G^n\right]$  the outflows, from the channel toward the contacts (including the fictitious scattering contact). To this purpose see also figure 5.2. This was analytically already shown in section 5.14, but to get the point intuitively one may think that if, for example, a single physical contact, namely 1, is present, then  $\Sigma_1^{in} = \Gamma_1 f_1$  provides an indication of the incoming electron flux. In particular  $\Gamma_1$  represents the broadening, i.e. the wave-functions that "spill over" in the channel from such a contact, and  $f_1$  the probability of occupation of such states. Thus it is intuitive that  $Tr\left[\Sigma_i^{in}A_D\right]$ represents the inflow into the channel, since  $A_D$  represents the amount of free states in the channel (the spectral function is linked to the device DOS, i.e. allowed states) while  $\Sigma_1^{in}$ represents the inflow from the contact 1. Instead the correlation function  $G^n$  is a measure of the number of electrons inside the device/channel, and this is evident if it is considered that its integral in energy gives the density matrix. Thus the term  $-Tr\left[\Gamma_1 G^n\right]$  with minus sign is a measure of the flux of electrons leaving the channel, thus flowing toward the contact 1, represented by  $\Gamma_1$ , from the device, represented by  $G^n$ .



Figure 5.2: Schematic representation of the model for considering incoherent scattering within the NEGF framework. The various electron inflows and outflows are sketched.

#### Spin Degeneracy

Finally notice that if the spin degeneracy is considered, then a factor 2 should be considered in the current expression (if the inflows and outflows of electrons are not dependent on spin).

#### 5.18.4 Incoherent scattering and transmission

In the previous sections it was pointed out that there is no a general simple way of writing the total current flowing in a two-terminal device by means of a Landauer-like formula, i.e. with a transmission function, if incoherent scattering is taken into account. Indeed there is generally no simple way to link  $\Sigma_s^{in}$  and  $\Sigma_s$ , or analogously  $\Sigma_s^{in}$  with  $\Gamma_s$  unlike it happens for the contacts (this is clear if one thinks that it has no sense of talking about a Fermi-Dirac's function  $f_s$  of a fictitious contact representing actually a scattering phenomenon). Nevertheless the simplicity and the immediate physical interpretation of the Landauer's formula for the current is a tempting matter. For this reason it is sometimes defined an effective transmission function, by comparing equation (5.83) with the Landauer's formula of eq. (5.65) or (5.75). In particular this effective transmission is defined as:

$$T_{eff,i}(E) = \frac{Tr\left[\Sigma_i^{in} A_D\right] - Tr\left[\Gamma_i G^n\right]}{f_1(E) - f_2(E)}$$

where i = 1, 2, s with s representing the scattering term, and where  $f_1$  and  $f_2$  are the source and drain Fermi-Dirac's functions respectively. In this way equation (5.83) becomes:

$$I_i = \frac{(-q)}{h} \int_{-\infty}^{+\infty} T_{eff,i}(E) \left[ f_1(E) - f_2(E) \right] dE$$
(5.84)

assuming thus the form of a Landuaer's formula for the current in terminal i. For the sign convention please consider the discussion already reported in sections 5.14.3 and 5.15.

#### A remark on incoherent scattering enhanced current

One may think of simply writing the drain to source current as the sum of the coherent term plus the scattering term calculated by means of eq. (5.83) or (5.84) with i = s. Nevertheless in general it is not true because the electrons reinjected within the channel from the scatterer can be also reflected toward the source, and it is not said they are all transmitted toward the drain. Nevertheless if the applied bias is enough high, such that the band diagram of electrons is bent toward the drain (higher potential at source than at drain), and if the scattering processes are dissipative, e.g. phonon interactions (no absorption of photons), i.e. the electrons loose energy from source to drain due to scattering and they do not gain energy, then the amount of electron reflected back toward the scattered electrons go toward the drain. In such a case the current can be written as (factor 2 for spin degeneracy):

$$I_{DS} \sim \frac{(2q)}{h} \int_{-\infty}^{+\infty} T_{1,2}(E) \left[ f_1(E) - f_2(E) \right] dE + \frac{(2q)}{h} \int_{-\infty}^{+\infty} T_{eff,S}(E) \left[ f_1(E) - f_2(E) \right] dE$$

where the first term is the ballistic contribution (the Landauer's one) from source (contact 1) to drain (contact 2) and where  $T_{1,2}(E)$  is the source-to-drain transmission function evaluated neglecting incoherent scattering; while  $T_{eff,S}(E) = \frac{Tr[\Sigma_s^{in}A_D] - Tr[\Gamma_s G^n]}{f_1(E) - f_2(E)}$ is the effective transmission function of the scattering fictitious contact, representing the incoming electrons from the fictitious scattering probe. This expression highlight very well that incoherent dissipative scattering, i.e. scattering processes that diminish the scattered electron energies, can enhance the final drain-to-source current. This phenomenon is very useful in explaining e.g. the valley of current that follows the current peak in resonant tunneling diodes. In such devices indeed the coherent current predicts a much lower valley after the resonance conduction peak. Instead when incoherent scattering is considered then a more accurate result is obtained, and in particular the current is enhanced due to incoherent scattering processes. The intuitive reason of that is the one mentioned above: the scattering makes electron loosing their energy and thus enhancing the probability of transmission, since they have no enough energy to "come back" toward the higher energy source contact. This topic is very intuitively and clearly introduced in [89], while a great detail treatment is present in [39] (chapter about resonant tunneling devices).

#### A remark on the SCF procedure for current estimation

A final remark, if the general SCF procedure for the current calculation of section 5.17 is considered, it should be modified such that within the SCF loop also the scattering self-energy is evaluated. Indeed while the contacts self-energy are fixed once the applied bias and the energy value is fixed, the scattering self-energy can vary, indeed it can be dependent from the number of electrons within the channel (it affects the scattering rate or probability) and moreover it changes the average number of electrons at a given energy.

consequently it changes the density matrix and the electron density, that changes the SCF potential that changes the scattering terms. In conclusion, the evaluation of scattering terms must be included in the SCF loop to ensure correct convergence.

#### 5.18.5 Dissipated power

One great advantage of the NEGF approach w.r.t. the transmission one is that with the NEGF is possible to evaluated the dissipated power within the device. As long as the transport is coherent there occurs no dissipation in the device. Indeed the electrons starting at source with one energy value, reach the drain without loosing energy. The same holds true for phase-breaking processes originating by the interactions among electrons only, with elastic scattering processes and no dissipation of energy under the form of phonons. In such cases the dissipation (Joule effect) happens in the contacts but not in the device. In the contacts indeed inelastic processes are required to maintain the contacts in local equilibrium, as already explained. In small conductors an important fraction of the total dissipated power occurs in the contacts rather than in the conductor itself. In that case by knowing the resistance  $R_C$  of the contact the dissipated power is  $R_C I^2$ , where I is the current. There is concrete evidence that this is true, see for example [89] and references herein. This fact moreover allows to pump far more current through small conductors than what would enough to destroy them [39], [89].

In the moment in which incoherent scattering is instead considered, energy is dissipated and on average the electrons at drain side have less energy than the ones at source side. With this mind, and recalling the definition of spectral current  $\tilde{i}_i(E)$  at terminal i, it is possible to define the dissipated power within the device as follows [89]:

$$P_d = I_{E,source} - I_{E,drain} \quad , \quad where: \quad I_{E,i} = \frac{1}{h} \int_{-\infty}^{+\infty} E \ \tilde{i}_i(E) dE \tag{5.85}$$

where the term  $I_{E,i}$  is called "energy current". In order to interpret this definition notice that  $I_{E,i}$  would correspond to an electric current if the term E inside the integral were not present and if it were multiplied by the electron charge. Instead without multiplying the integral of the spectral current by the electron charge one gets only the net flow of electrons at terminal i, with i = source, drain. moreover by multiplying the spectral current inside the integral by E one gets a flow of electrons at terminal i (integral of the spectral current) weighted on energy E. Thus it corresponds to a flow of energy, i.e. to a power, that by definition is the energy in the unit time. In other words since the power is exactly the energy per unit time, and since the term:  $\frac{1}{h}\int_{-\infty}^{+\infty}\tilde{i}_i(E)dE$  is the total net flux of electrons (in the unit time), that flows through the terminal i, then by multiplying it by the energy E, the total (incoming) power in the terminal i, i = source, drain, is recovered. Moreover the dissipated power corresponds to the outgoing flux of energy, with minus sign. Indeed the fluxes by definition are defined positive if they are incoming into the device, thus an outgoing flux has negative sign, but with the user sign convention, the dissipated power should be positive in a user, like the device is. Therefore the dissipated power corresponds to the net outgoing power, with a minus sign in front. Since the above mentioned net fluxes are by definition incoming net fluxes, then the net outgoing power (from the device) is given simply by their difference (with no minus sign). Indeed the electrons at source have, on average, higher energy w.r.t. the ones at drain, thus the difference:  $I_{E,source} - I_{E,drain}$  (that is positive) provides the incoming power into the channel from the scattering fictitious contact. This because of the conservation of energy (or power), that implies that the energy lost from source (higher energy) to drain (lower energy) must flow in the scattering contact (is the amount of energy dissipated in the incoherent scattering processes). The incoming power from the scattering probe to the device, that as mentioned above corresponds to  $I_{E,source} - I_{E,drain}$ , is equal to minus the outgoing power from the channel to the scattering probe (again invoking energy/power conservation). And thus it is already the desired dissipated power. Notice that since the integral is linear the above definition can be rewritten like:

$$P_d = I_{E,source} - I_{E,drain} = \frac{1}{h} \int_{-\infty}^{+\infty} E\left[\tilde{i}_{source}(E) - \tilde{i}_{drain}(E)\right] dE$$

With these considerations in mind and with the previous formula for the dissipated power, the two cases of coherent and incoherent transport are now analyzed to highlight the physical meaning and the origin of the power dissipation. In the case of coherent scattering the electrons at source and at drain have the same energy, since no dissipation occurs. Thus the two spectral current will have the same distribution in energy, and since they will be the same the difference  $i_{source}(E) - i_{drain}(E)$  will be identically null, for each energy value. This does not mean that there is no power dissipated, but simply that it is dissipated within the contacts, and only the dissipated power within the device is null. Instead in the case in which incoherent processes are present, the spectral currents at drain will have the same (or similar) shape to the one at source, but shifted toward lower energies, since on average electrons at drain will have less energy that at drain. In such a case the difference  $i_{source}(E) - i_{drain}(E)$  will not be zero at all the energies, but in general it will different from zero. Then considering that such a difference is multiplied by the energy E and that at source the spectral current will be shifted toward higher energies, such a different is generally positive, leading to a positive dissipated power (as expected by the user sign convention). In conclusion, what makes the power to be dissipated within the device is a shift in the energy distribution of the current (i.e. in the spectral currents) between the two contacts, that finds its origin in the dissipative scattering processes. This happens even if matter conservation implies the integral over energy of the scattering probe spectral current  $\tilde{i}_{scattering}(E)$  component to be null (see the discussion of the previous sections).

A qualitative example is reported in figure 5.3.



Figure 5.3: Qualitative example of spectral currents at source (blue line) and at drain (orange/red line) for a device. The incoherent scattering phenomena lead to an energy shift between the two, and to a non-null dissipated power inside the device. The purple line represents the difference between the two, multiplied by the energy E, that is:  $E \cdot (\tilde{i}_{source}(E) - \tilde{i}_{drain}(E))$ . Always in purple it is highlighted the area below such a curve, that corresponds to its integral, i.e. to the dissipated power. Notice that there are a negative contribution and a positive contribution, but the positive one (right-side "hill") is greater, leading to a total positive dissipated power, i.e. to a net dissipated power (accordingly to the discussed sign convention).

### Chapter 6

## Transport regimes in nano-devices

The NEGF approach introduced in the previous chapter is a rigorous and powerful framework for the transport calculation in all kinds of nano-devices and not only in molecular devices. It holds in general, provided that the channel electronic structure, the SCF potential, and the various interactions (i.e. electron-electron, and if necessary incoherent ones such as electron-phonon and electron-photon interactions) are accurately described. The purpose of this chapter is to highlight the methods conventionally used for such calculations in different transport regimes. In general the couple DFT + NEGF is very common in literature, even if other solutions are possible and often used, such as the EHT + NEGF approach. Nevertheless in some cases these standard methods are not suitable to obtain accurate results. This happens especially when Coulomb blockade occurs. This phenomenon is introduced in section 6.1. It allows to discriminate between two modeling and transport regimes that require substantially different approaches. In order to appreciate these differences the various transport mechanisms that are possible in a molecular device are briefly summarized in section 6.2. While the possible and common simulation methods for the different transport regimes are briefly addressed in section 6.3, that is aimed in warning the user in selecting and judging the most suitable modeling technique for a specific case.

#### 6.1 Coulomb blockade

In this section the so called "Coulomb blockade" or "single-electron charging" regime of transport is addressed. In this transport regime the electrical current can be strongly affected by the charging effect that was introduced in chapter 4 (section 4.1.5) and in chapter 5 (e.g. section 5.17). In particular, energy levels within the conducting channel come in pairs, indeed due to spin degeneracy there is one up-spin and one down-spin electron state with same energy eigenvalue. In order to highlight the effects of the electron charging phenomenon let's consider a channel with a single energy level  $\varepsilon$  (two spin-degenerate levels), that for example contains only one electron when neutral:  $N_0 = 1$ 

(being  $N_0$  the number of electrons in  $\varepsilon$  at equilibrium). It is expected that if such a level, that is broadened for example in a Lorentzian-like DOS, is entirely included within the bias window, a current flows, accordingly to the transport model for a single-level quantum dot presented in chapter 4, section 4.1. Nevertheless in some cases, under certain conditions that will be clarified in while, the up-spin and the down-spin density of states splits into two distinct energy levels, separated by the single electron charging energy (see e.g. section 4.1.5). In other words the presence of a single electron causes the removal of the spin degeneracy, and the two electron states have different energies. As mentioned, the two levels are separated by an amount  $U_0 = q^2/C_E$ , where  $C_E$  is the total electrostatic capacitance of the system, and  $U_0$  is the potential energy that the channel gains because of the presence of the single electron (i.e.  $N_0 = 1$ ). This indeed corresponds to the charging potential energy associated to a transfer of a single-electron (see section 4.1.5). In this latter case if  $U_0$  is large, it can happen that the two levels are for example one above and one below the bias window, thus leading to a very small current flowing through the device (because in such a case only the Lorentzian "tails" fall in the bias window). In this case it is said that the device is in the "Coulomb blockade" regime of transport. The Coulomb blockade has been experimentally observed for systems in which the charging energy  $U_0$ exceeds the broadening  $\gamma$  of the energy level [89].

In the simple SCF picture (see section 3.2) there is no simple explanation for this phenomenon. Indeed it is expected the two levels to be degenerate as long as they "feel" the same SCF potential. Nevertheless this picture, that is the charging model based on the simple Poisson's equation, is a good-zero-order approximation. This is the Hartree's approximation for the SCF potential, as discussed in section 3.2, in which nevertheless the correlation is neglected. As already mentioned there, the point is that an electron does not "feel" any potential due to itself. Indeed assuming that the up-spin level is filled before, then the potential barrier to be overcome to put another electron there is equal to  $U_0$ , that indeed represent the energy to be spent in order to place another electron in the same level where an electron is already present (the work). In other words, the empty down-spin level, because of the presence of one electron in the up-spin level, is shifted up of  $U_0$ . Nevertheless the up-spin level is not shifted up of  $U_0$  because the electron does not "feel" any self-interaction. The same happens if the down-spin level is occupied before. In that case the up-spin level is shifted up of  $U_0$  while the down-spin one does not. In both cases if  $U_0$  is enough large, the two levels can fall outside the bias window, thus blocking the current.

In general the standard approach for describing the electric current in such a Coulomb blockade regime is based on a completely different theory from the one described so far (the NEGF but also the simple model of section 4.1). It is based on the so called "Master Equation" or "Orthodox Theory" [89]. Nevertheless there are attempts in literature of exploiting the NEGF approach (along with the DFT) to model the transport also in this regime, they are addressed in section 6.3.

Notice that in general there is no net distinction between the Coulomb blockade regime and the coherent regime of transport (the one widely discussed so far). Indeed, a gradual transition between the two and thus all the intermediate cases are in principle possible (between strong Coulomb blockade regime and fully coherent regime - in which no Coulomb blockade happen, i.e.  $U_0$  is very small). In particular, the following three regimes of transport occur [89]:

- SCF regime: if  $U_0 \approx k_B T$  and/or  $U_0 \approx \gamma$ , the SCF approach (section 3.2) can be used. Notice that the SCF method converges correctly if  $U_0$  is small, otherwise it can have convergence problems.
- Coulomb blockade regime: if  $U_0 \gg k_B T$  and  $U_0 \gg \gamma$ , the SCF approach is typically not adequate. In that case high accuracy in estimating the electron-electron correlation and in general the electron-electron interactions must be employed to get quantitatively correct results. In general the so called Master Equation is conventionally used for this case. Nevertheless it has the big drawback of neglecting completely the broadening (see section 6.3 and 6.3.2).
- Intermediate regime: if  $U_0$  is comparable to the larger between  $k_BT$  and  $\gamma$  (i.e. thermal or contact broadening), there is no simple approach in general. Indeed the SCF method fails in representing the strong charging effect, while the Master equation fails in representing the broadening. Notice that, as mentioned previously, in general it is possible to have all intermediate cases between the two above cases, thus this situation is not a minor importance case.

A last remark on the nature of  $U_0$  before proceeding. One may ask what determines  $U_0$ . The answer may be the extent of the electron wave-function. If one electron is smeared over the surface of a sphere of radius R then the potential of that sphere will be:  $\frac{q}{4\pi\varepsilon_0 R}$ , so that the energy needed to put another electron on the sphere will be  $\frac{q^2}{4\pi\varepsilon_0 R} \sim U_0$ . Welldelocalized wave-functions (large R) have a very small  $U_0$ , otherwise if R is small (i.e. the wave-function is highly localized)  $U_0$  can be large. Consequently when there are delocalized wave-functions the difference between the two energy levels (up-spin and down-spin) is smaller, since  $U_0$  is smaller. Thus the more the conductive molecular channel orbitals are delocalized, the better is the SCF approximation. This corresponds to the strong coupling between molecule and contacts, in which there is an high level of hybridization of the wave-function, i.e. the contact and the channel wave-functions mixed together. Instead the charging energy  $U_0$  can be large if there is weak coupling between the molecular channel and the contacts, i.e. if the states are localized and there is no (or small) hybridization of the electron orbitals. Moreover notice that since  $U_0$  is inversely proportional to the total electrostatic capacitance  $C_E$ , the charging energy  $U_0$  can be large also if  $C_E$  is very small. This is the case of small mescoscopic conductors. In some cases electronic devices/transistors are specifically designed to operate in the Coulomb blockade regime, and in that case they are called "Single Electron Transistors" (or SETs).

#### *I-V* characteristic and conductance

Notice that due to Coulomb blockade the current-voltage characteristics usually presents typical step-like shape. This because when the bias is increased (in modulus) from zero, for example a level that is empty in equilibrium enters the bias window originating an abrupt increment of the current, that from almost zero passes to a given finite value. After that, even if the bias is further increased, the current does not increase anymore due to Coulomb blockade. Only when the bias is increased of at least  $U_0$  (w.r.t. to the first conduction peak) a new electron can populate the energy level (with an opposite spin w.r.t. to the previous one). And thus only when the bias overcome  $U_0$  a new step arise in the current characteristics. Obviously the conductance will present peaks of conduction in correspondence of the bias values multiple of the charging potential (the differential conductance is the derivative of the current w.r.t. the voltage). These shapes of the current-voltage characteristics and of the conductance-voltage characteristics are typical of systems affected by Coulomb blockade.

#### 6.2 Transport mechanisms

The purpose of this section is to briefly illustrate the possible physical mechanisms behind the transport in molecular devices, with a particular reference to the review paper [10]. This is useful in understanding when and if the NEGF approach is more or less suitable for modeling transport in such devices. Notice that usually the NEGF approach provides much better and more accurate results than the simple fitting and idealized/simplified formulae presented below. Nevertheless to gain a physical intuition/insight of what happens in the molecular system, such formulae are sometimes used to fit the more precise NEGF results in order to identify the main transport mechanism in a specific system. This could be useful to derive design parameters and figure of merits, and thus to engineering the system in order to optimize some specific transport features, that are better highlighted with a simple intuitive model rather than with the more complete (and complex) NEGF.

In particular, the electron transport mechanisms in molecular junctions depend on the molecular size and structure, the temperature and the applied voltage. Moreover if not a single molecule but a self-assembled monolayer (SAM) connected to two metallic electrodes is considered, the intermolecular interactions like van der Waals interactions or polarization effects may be relevant. Concerning simulations, such effects can be considered within a DFT framework (SCF / mean field) by means of a supermolecular approach as described in section 3.7. However, in general, the following transport regimes are possible in molecular junctions:

a. Coherent non-resonant tunneling: for short molecules strongly coupled to contacts, without molecular energy levels in the bias window, the transport mechanism is direct non-resonant tunneling from the source to the drain contact. It can be idealized with a rectangular shaped barrier of finite height and small width (of the order of the molecule length), such that an exponential decay of the wave-function allows to get non-null probability of transmission through it (see section 2.3.7). This simplified model is referred in literature as Simmons' model. In this case the electron is coherently transmitted, but, since there is no energy match between the electron energy and an eigenstate within the molecule, an exponential decay with space occurs. In the Landauer's approximation the conductance can be written as [10]:

$$G = \frac{I}{V} = \frac{2q^2}{h} T_S T_D T_{mol} \quad , \quad G = G_{cont} T_{mol} \quad , \quad T_{mol} = e^{-\beta d}$$

Where  $T_S$  and  $T_D$  are the transmission coefficients relative to source-molecule and molecule-drain barriers,  $G_{cont} = \frac{2q^2}{h}T_ST_D$ , and the transmission through the molecule is fitted with an exponential decay. In such a regime of transport, sometimes, the experimental data or the more accurate simulation results (e.g. obtained with NEGF) are fitted with an exponential, and an equivalent  $\beta$  decay constant (measurement unit m<sup>-1</sup>) is derived. This procedure allows to a straightforward interpretation of the transport through the molecule that, as mentioned, is seen as a rectangular barrier. This transport regime is naturally accurately modeled by means of (coherent) NEGF approach. Usually this regime is relevant at low bias V ( $qV < E_0$ , being  $E_0$  the barrier height). Notice that this mechanism is independent on temperature and it is also independent on temperature.

- b. Coherent resonant tunneling: in this case there is matching between the incoming electron energy and a molecular eigenstate, thus there is high transmission probability and small reflection probability. As already commented in chapter 5, a peak in the transmission spectrum occurs (see also transparency of a potential barrier section 2.3.7). Such a transport regime is of course included within the NEGF modeling framework for coherent transport. Notice that this mechanism is essentially independent on temperature.
- c. Fowler–Nordheim tunneling: if the bias is large (say  $qV > E_0$ ) then the simple model for coherent non-resonant tunneling through the barrier (point (a.) above) is no more valid since the barrier distorts, and it becomes triangular. In such a case it is possible to have an enhancement of the tunneling transmission. Indeed for zero-bias it may happen that the barrier width is to large to allow significant tunneling, while with an enough high bias it tends to become triangular and thus thinner. Consequently the exponential decay of the wave-function can be no more enough to stop electron and a great improvement of the tunneling probability occurs. This is referred as Fowler–Nordheim tunneling. It is a well known process in electronics since there are many commercial memory devices based on this effect. In molecular devices such an effect leads to an enhancement of the tunneling via orbital-mediated tunneling. This transport regime is of course included within the NEGF modeling framework for coherent transport. Notice that this mechanism is essentially independent on temperature. Also in this case fitting parameters are sometimes extracted from experimental data to highlight the voltage enhancement of tunneling, analogously to what mentioned in point (a.).

These three transport mechanisms are coherent tunneling ones, independent on temperature. The NEGF is far more accurate than all these three, nevertheless it was mentioned the reason for introducing them, as conceptual tools to understand how to act in order to engineer the desired transport features. A trivial example is that if it appears that the transport mechanism is somehow essentially analogous to a Fowler–Nordheim tunneling, and for a given application it would be better to have more current, an increase of the voltage will trivially likely provide such an increased current, with an exponential relation. In [10] are summarized fitting formula for these transport mechanisms.

Higher order interactions (i.e. many body interactions), like the electron-electron, electronphonon and electron-photon interactions, can affect the transport through molecules. In such cases other transport mechanisms might be relevant in molecular devices. In particular, as discussed in section 4.4, in the strong coupling regime, the electronic states of the electrodes and the molecular orbitals are strongly hybridized, molecular charging effect (Coulomb blockade - see section 6.1) does not take place and elastic coherent tunneling dominates the transport. In this case it is expected to have a mix of transport mechanisms (a.), (b.), (c.). However, if a weak coupling occurs between the molecule and contacts, Coulomb blockade and charging effects may be relevant. In such a case the coherence between the motion of the electron from the left electrode to the molecule and that from the molecule to the right electrode can be completely lost. Indeed as mentioned in section 4.4, the longer is the time that an electron spends within the molecule, the higher is the probability that it interacts with molecular vibrations/phonons, etc... [112]. Indeed if the time an electron stays in the molecule is of the order (or even longer) than the molecular vibration period, the atomic positions cannot be assumed to be static, but instead they act as dynamic scatterers, thus breaking the phase coherence of electrons, leading to both interference among electrons and to inelastic/dissipative interactions (e.g. phonons). In such cases the dominant transport mechanism is the incoherent tunneling or alternatively the electron hopping mechanism (these transport mechanism will be introduced in a while - see below). Moreover, all the possible intermediate situations in between a full coherent picture (see above (a.), (b.), (c.) cases) and a full incoherent picture (see below) are possible. In the intermediate coupling regime a variety of novel phenomena related to electron–electron correlation effects (such as the Kondo effect and co-tunneling) are observed [10], [112], [89]. Coherent tunneling is effective for very short molecules, let's say of the order of 1 nm. In general depending on the nature of the molecule, on the nature of the contact-molecule coupling and on the applied bias range different transport behaviors are possible for different molecule lengths. For example in [113], it is found the limit molecular length for purely coherent transport in p-phenylenevinylene oligomers (conjugated molecules) is of the order of  $2.5\,\mathrm{nm}$ ; while in [114] the same is found to be around 4 nm for other conjugated molecules. Thus a wide variability is possible. The main incoherent transport mechanisms through molecules are:

d. Incoherent or Sequential tunneling: in this case the transport through a molecule is seen in terms of tunneling through multiple potential barriers/wells. This model applies quite well to conducting polymers [10]. The main different w.r.t. coherent tunneling is that the residence time of the electron in a potential well is long enough to affect the phase of the electron. Thus the electrons do not tunnel with same phase (or wavenumber) but each tunneling process, through each barrier, is independent from the previous one (and involves different states, different wave-functions). The whole electron transport process can be thus described as a series of discrete coherent tunneling steps through barriers. It is not temperature-dependent, like the other tunneling processes. This transport mechanism is again accurately modeled with the NEGF approach, even if incoherent scattering mechanism should be included to get accurate results. Indeed a strong electron-electron interaction or alternative dissipative processes can be extremely relevant to estimate the transition probability from one energy level to another while the electron is in transit within the molecule. And this is exactly what I called (with the notation of [39]) "vertical flow" of electrons within the channel, i.e. transitions/flow between different energy values (generally from an higher to a lower energetic channel/level but also vice versa). More details are also provided in the next section (see weak coupling / Coulomb blockade case).

- e. Hopping: in contrast to tunneling mechanisms (from (a.) to (d.)), hopping conduction involves electron motion over the barrier. In the sense that it corresponds to electron "jumps" from one molecular orbital to another. These jumps can occur if the electron gains energy (phonon/photon absorption) such that it temporarily overcome the barrier, or for example if the molecule is dynamically bent/twisted such that (in real space) two orbitals get closer allowing for a shorter barrier length and thus higher tunneling probability. In both the above mentioned cases it is noticeable that hopping is a thermally activated process, since high thermal energy is required to excite molecular vibrations such that an insurmountable barrier becomes instead easily crossed by electrons. Generally hopping follows the exponential empirical and classical Arrhenius relation. An explicit expression is provided for example in [10]:  $I \propto e^{-\frac{E_a}{k_B T}}$ , where  $E_a$  is the "activation energy", and the greater it is, the greater is the temperature required to activate that hopping phenomenon. In general it represents the barrier of potential energy that an electron should overcome to transit from a molecular orbital to another. For example in [113], molecular wires made by connecting together  $\pi$ -conjugated molecules are considered. In such a case it is demonstrated that the activation energy  $E_a$  fitting the experimental data, corresponds to the barrier for rotation of the  $\pi$ -conjugated aromatic rings, which transiently couples the conjugated aromatic sub-units (the rings). Thus torsional vibrations are responsible of the hopping, but only if they are enough wide. In particular it is verified that such collective torsional vibrations are associated to an energy of the order of  $E_a$ , that is thus the thermal energy necessary to stimulate such vibrations and activate the hopping among adjacent orbitals (that are the hopping sites). In general the activation energy is associated with the movements of nuclei. As mentioned above hopping electron transfer can only occur after a rearrangement of nuclei, that in the above example corresponds to a rotation of rings in a molecule into a coplanar conformation. Hopping involves, like incoherent tunneling, a series of transfers between different sites, but shows an inverse distance dependence. Hopping is probable at low bias high temperature. The NEGF approach can model accurately this transport mechanism but only if incoherent phenomena are considered. In particular molecular vibrations and electron-phonon interactions must be considered.
- f. Thermionic emission: the last transport mechanism in molecular device, discussed here, is the thermoionic emission. It is present also in classical electronic devices. In this case the electrons overcome the contact–molecule barrier by thermal agitation and the resulting current has a strong dependence on temperature. The barrier height is influenced by the local electric field which results in a nonlinear current dependence on applied voltage. Thermionic emission can be described using the classical Schottky–Richardson relation, that is conventionally introduced in electronic

devices courses. An expression referred to molecular devices is present in [10]. Thermoionic is relevant at high temperature and low contact-molecule barrier height. The NEGF approach intrinsically consider also this transport mechanism, especially when incoherent (phonons) scattering processes are accounted for. Notice that indeed electrons that are thermoionically emitted from source are those whose energy overcomes the barrier height. The barrier height is precisely calculated in NEGF thanks to the self-consistent loop by means of which the electrostatics of the system is taken into account, while the number of electrons with suitable energy are estimated by means of the Fermi-Dirac's distributions of contacts. Molecular phonons can enhance this transport mechanism.

In conclusion, even if conceptually very different, all the mentioned transport mechanisms (from (a.) to (f.)) are accurately modeled and considered by means of the NEGF approach. Obviously, if a relevant transport mechanism is non-coherent, the NEGF modeling should include the incoherent scattering mechanisms, and this is possible as described in section 5.18. The NEGF formalism results thus to be a completely general and accurate model for transport though molecules. As mentioned, the discussion reported in this section can be important to gain an intuition about what is happening in a given molecular system, and thus to correctly set up the desired simulations, such as, for example, incoherent features or corrections.

A critical issue that needs a more in-depth and careful discussion is the case of strong electron-electron interaction, that corresponds to large charging effect and Coulomb blockade regime (i.e. weak coupling with contacts). This is further addressed in the next section.

#### 6.3 Modeling approaches: strong vs weak coupling case and corrections

The purpose of this section is to provide a deeper insight in the NEGF modeling critical issues relative to the electron-electron interactions. The topic is addressed by steps, firstly summarizing the standard approach in transport modeling through systems in which it is possible to neglect electron-electron interactions (section 6.3.1) and then considering the possible corrections to such models, or directly alternative models to transport, for system in which the electron-electron interactions are important and cannot be neglected (section 6.3.2).

#### 6.3.1 Strong coupling case

It was already discussed (see section 4.4 and the previous sections in this chapter) that in the case of strong coupling between the molecular channel and the contacts the charging energy is small due to delocalization of molecular orbitals (hybridization). In such a case an SCF mean field approach (see section 3.2) is accurate, Coulomb blockade does not characterize the transport and no particular corrections should be performed. In this case (weak electron-electron interaction or strong coupling with contacts) the standard mean field DFT method can be used for calculating the molecular electronic structure while the standard (single-particle) NEGF, that was introduced in chapter 5, can be used to calculate the transport features and the full I-V characteristics. In literature it is very widely used the aforementioned couple DFT + NEGF, and this is also the approach considered e.g. in [89]. Another possible approach is to use a semi-empirical method instead of the DFT for the molecular electronic structure calculations. The most used one is the EHT method, and in this case the EHT + NEGF pair is used (usually with SCF self-consistent calculation in EHT). The differences between the two approaches are essentially only due to the differences between the EHT and DFT methods, described in chapter 3. Both the approaches are very accurate and successful as long as the electron charging energy and thus the electron-electron interactions are weak.

#### 6.3.2 Weak coupling case and the Single Electron Transistor

When the electron-electron interaction is strong and thus the electron charging energy is large, the fact that the electron correlation is ignored or not precisely modeled within an SCF framework can lead to confusion and inaccuracies [112]. Indeed the electron correlation is the key to suitably model the interactions among electrons and thus the charging effect (and consequently the Coulomb blockade). In fact it is because of the interactions between electrons that important energy shifts upon charging can happen [112], giving rise to the aforementioned phenomena. In general there is no unique way to overcome the problem. The various solutions can be classified in three wide groups:

- a. "Modified" DFT/Electronic structure calculations: the first approach can be to modify somehow the SCF mean field approach to consider also accurately the electron-electron interactions. In this case a "modified" DFT is employed along with a "non-modified" single-particle NEGF. Therefore the complexity and the corrections are included within the molecular electronic structure calculation method, i.e. the DFT, while the NEGF portion of the self-consistent loop (section 5.17) is unchanged w.r.t. the single-particle picture presented in chapter 5. This means that the effort is in finding an SCF potential that suitably models also the electron-electron interactions, while a single-particle picture is used for transport, considering a single-electron moving in an average potential representing accurately such interactions. It was mentioned in chapter 3 (section 3.4) that there exist electron correlation methods for the calculations of accurate electron correlation/interaction. Such approaches are not so used in literature, or better: some approaches (such as perturbation theories) leads actually to the same of the methods illustrated below in point (b.), while others are not usable as described above because of the excessive computational cost or analytical complexity.
- b. "Modified" NEGF: this approach moves the complexity within the NEGF/transport part, i.e. an unaltered standard (SCF mean field) DFT method (or EHT) is used for calculating the electronic structure while an "improved" NEGF is used for considering also the electron-electron interactions. This is not in principle a novel approach, since it simply correspond in the approach described throughout this work, simply with an additional self-energy aimed in modeling electron-electron interactions (accordingly to

what mentioned in section 5.18), indeed the self-energies (as said in section 5.18) are in general used to represent any kind of interaction, comprised the electron-electron one.

c. Completely novel approaches: the last approach can be the one of considering completely new methods aimed in accurately describing such systems.

These three groups of solutions are further discussed in the following subsections. Before going on a last remark on nomenclature. A transistor operating in the Coulomb blockade regime of transport is often referred as Single Electron Transistor (SET).

#### a. "Modified" DFT/Electronic structure calculations

In this approach, the complexity is added to the DFT such that the electron-electron strong interaction is considered within the SCF approach, i.e. by means of a potential that is solution of a Poisson's like equation. The critical point in using a mean field is indeed the electron correlation: it is difficult to find an accurate exchange-correlation potential (or exchange-correlation functional of the electron density / density matrix) that accurately provides and models the electron-electron interaction (see section 3.2), especially in the moment in which such an interaction is strong (as happens with weakly coupled molecular channels to contact and in the Coulomb blockade regime). If it were possible to find an enough accurate functional the problem will be easily overcome since it would be enough to use such a functional and then set up all the rest of the calculations as presented previously in this work (with single-particle NEGF, etc...).

As highlighted in [128], the problem with conventional exchange-correlation approximations (e.g. LDA, GGA, ...) is that their functionals are essentially "too smooth", and they are not able to accurately account for first derivative discontinuities that might occur in the total system energy eigenvalues. In particular, one may think the charging effect to be an abrupt variation of the charging potential. Indeed the charging energy  $U_0$  arises abruptly as soon as the number of electrons within a given energy value changes of one unity. In other words, consider an energy level weakly coupled with contacts and for this reason very localized and merely broadened, and consider an initial applied bias such that such a level is slightly outside the bias window. Assume also that this level is initially empty. As soon as the applied bias is increased a bit, the energy level enters abruptly in the bias window, since it is merely broadened, and starts conducting. For example in such conditions a single electron populate the level when it is in the bias window. At this point the charging energy is increased of  $U_0$ , that by hypothesis is large (see section 6.1). This means that, to put another electron in the same level, the barrier  $U_0$  should be overcome, or analogously that the mean field that is "felt" by a new incoming electron should be increased abruptly of the order of  $U_0$  at least in the region in which there is such localized orbital. This is possible if the exchange-correlation functional admits a discontinuous first derivative, such that it is possible to the potential energy to have abrupt variations. Nevertheless this is not the case of the standard LDA and GGA functionals, that instead have continuous first derivative [128], [129]. This fact prevent the system total energy and the electron density (or analogously the electron charge) within the channel to have abrupt variations, as it should be in the case of strong electron-electron interaction or strong charging effect. Moreover, the continuity of first derivative of the total energy functionals in standard approximations, is a consequence of the so called Self-Interaction Error (SIE), that is the interaction of an electron with the exchange-correlation potential generated by its own charge [128]. This spurious interaction is at the origin of the DFT failures in case of strong electron-electron interactions [129]. Indeed as mentioned in section 6.1, an electron does not "feel" any potential due to itself.

The simplest conceptual solution is the subtraction of such self-interaction contribution from the functional. In general there are more ways of practically doing it, and these corrections are called Self-Interaction Corrections (SIC) or Atomic Self-Interaction Correction (ASIC). In the commercial tool *Quantum-Wise ATK* it is possible to use a SIC for DFT calculations that is called "DFT-1/2" [125], [126], [130]; in which only one half of electron self-interaction is subtracted, for details [130]. Further details on the usage are provided within the user's manual [125], [126].

Another possible correction in *Quantum-Wise ATK* for considering the strong electronelectron interaction is the so called "Hubbard correction" [125], [126], [131], [132]. This is a semi-empirical correction of the exchange-correlation functional in LDA, GGA functionals. An additive term is added to such functionals, that is null if a molecular orbital is full or empty, but has a non-null value if an orbital is half-filled. This method improves on the deficiencies of the local exchange-correlation functionals discussed above. Further details on the usage are provided within the user's manual [125], [126].

A last approach of refining the electron-electron interaction and exchange-correlation potential within the DFT framework is by means of hybrid functionals (section 3.5), such as the famous B3LYP. Indeed such functionals allow to more accurately estimate the exchange-correlation. In literature there are several examples in which this approach is used also for simulating SETs. In *Quantum-Wise ATK* there is no wide choice for hybrid functionals, nevertheless the user's manual states that the functional TB09 (that is not hybrid but a meta-GGA functional) has performances that are often comparable to hybrid functionals ones [125], [126].

#### b. "Modified" NEGF

In this approach the complexity is moved inside the NEGF. In particular in section 5.18 it was mentioned that there several orders of approximation to model more o less accurately the many-body interactions such as the electron-electron, electron-phonon and electron-photon ones. In [89] the lowest order approximation is considered, i.e. the so called Born approximation. More refined approximations are possible in literature. One may think to these approximations as higher order terms in a Taylor expansion. In this optics it is clear that the higher order approximations lead to more accurate models. In particular in this specific case higher order approximations are considered. The ways of "embedding" such more refined approximations within the NEGF framework are essentially two: either by means of additional self-energy contributions aimed in modeling the specific interaction (i.e. the electron-electron one), or by means of a two-particle treatment (or in general n-particle treatment).

The first is for example the approach of [133]. The authors, starting from a general many-body Green's function (second order since two interacting electrons are considered), recover an expression for a single-particle (i.e. first order) Green's function of the system (analogous to the one presented in chapter 5), with an additional self-energy  $\Sigma_U$  that models the two-electron-interaction (two-electron interaction is a second order term - i.e. two particles). Notice that in this procedure there are approximations as well, indeed, as already mentioned in section 5.18, in the moment in which the second order Green's function is written (i.e. the one of two-interacting particles), it turns out that it is function of the third order one (three interacting particles), and so on... Thus the "recursion is cut" at a certain point. As one can intuitively think  $\Sigma_U$  is function of the number of electrons at equilibrium and of the number of electrons outside equilibrium.

The latter approach is for example the one used in [134]. In that case the difference w.r.t. the previous method is that the two-particles Green's function is maintained for doing the calculations. In deriving it the three-interacting-particle should be known, as mentioned above, but it is not considered (cut - like in a Taylor expansion), and thus approximations are introduced (the results are accurate for short range Coulomb blockade but for example not so suited for the Kondo effect).

#### c. Completely novel approaches

In general it is possible to proceed with completely novel approaches in modeling devices in which the transport is governed by Coulomb blockade, like in SETs. The standard approach, historically very used, for SET modeling is indeed the so called "Orthodox Theory" or "Master Equation" [116], [115]. The NEGF method is at the end a perturbative method, indeed as mentioned in section 5.18, in the second quantization formal introduction of NEGF, the Green's function is a quantum propagator that propagates a stimulus, i.e. a perturbation, through the system. The Master Equation approach is instead nonperturbative. The disadvantage of the NEGF is that the analytical and computational complexity increases fast if the one-particle picture is abandoned. Instead the Master Equation approach has he advantage of being relatively simple and general, even if, in the words of [116], it is a "quick and dirty" approach. In order to understand it notice that in general a Master Equation is an equation involving probability, or better probability rates or scattering rates. Thus the approach of the Master Equation is to use quantum mechanical laws to determine the transition probability, or scattering rates, among all the possible states of the multi-electron system. The Master Equation is the equation that collect all these transition probabilities, and that is thus able to predict the scattering rates among the different states. For this reason it is "quick"; because it does not requires many additional concepts to the ones of standard quantum mechanics. Moreover it is "dirty" compared with the extremely elegant Keldysh theory of the NEGF [116]. Nevertheless the drawbacks of such methods are far beyond the "elegance". There are mainly two extremely limiting disadvantages in the using the Master Equation. Firstly, since it involves transition probabilities among all the possible states, its complexity increases very fast with the number of electrons composing the multi-electron system. In particular with  $N_e$  electrons the Master Equation requires working with matrices of dimension  $2^{N_e} x 2^{N_e}$ . Second, there is no way of representing or introducing the broadening within the Master Equation

framework. Thus it is of course not suitable for the strong coupling case, but neither for all intermediate cases in which broadening is present, even if small. The above presented approaches instead have no limitations in these terms. For this reason in literature the Master Equation is usually employed for modeling simple SETs with few electron states and in strong Coulomb blockade and extremely weak coupling with contacts. Because of these disadvantages recent literature (last two/three years) seems to be oriented toward the approach (a.) or eventually (b.) for high accuracy.

Another modeling technique, possible for SETs, is the so called Quantum Monte Carlo. Analogously to its "classical" or "standard" counterpart, it is a statistical method in which random transitions among states are performed (considering quantum mechanical laws) and thanks to simulation of a huge number of transitions, accurate transition rates are found. This method is very effective in considering also a large number of electron states, and for this reason it is often used for circuit-level simulations of SET-based networks. A drawback is that, with this method, the physics is "hidden", and even if the final result can be accurate, the physical insight of the device is lost.

In literature several references are present about these topics, here I have chosen to avoid reporting them for conciseness, since I will never use these last two approaches in the rest of this work. A simplified introduction to Master Equation is moreover present in [89].

#### A remark on EHT and other approaches

In chapter 3 it was mentioned many times that semi-empirical methods are generally less accurate than *ab initio* ones, but the result might also be accurate. The correct general way of dealing with semi-empirical methods is thus to "validate" them by means of comparisons with experimental data or with *ab initio* calculations. Even in this case the approach is again this one. Indeed with the above mentioned methods and corrections, there is good confidence that calculations performed e.g. with NEGF or DFT + NEGF with the corrections of point (a.) are close to reality, even if there is no comparison with experimental data. Indeed in that cases the theory predicts it, and within a reasonable error range the results can be assumed reliable (with the limits of the considered approximations). With semi-empirical methods, and with EHT in particular, there is no *a priori* reason to assume that the result is wrong or inaccurate. Nevertheless, there is neither a theory behind that ensures the correctness (within certain limits). Thus in general one can use semi-empirical methods or the EHT method, but they should be somehow "validated" as explained above. In literature there are examples [33] [135] in which SETs, operating in the case of Coulomb blockade, are simulated with EHT + NEGF method; but in general no theoretical justification of the reason why the results are matched with experimental data or other methods is provided. Likely because such explanation does not exist, accordingly to what highlighted above. Sometimes in order to emulate weak contact coupling, the molecule is placed a little bit more far away from the contacts, again with no theoretical justification (also because in this case the geometry of the device is modified). Obviously if the molecule is taken away from contacts the coupling diminish, like does the orbital delocalization, thus the desired results can be obtained. In this optics one may think of treating the distance between molecule and contacts as a sort of additional fitting parameter (notice that there are already other fitting parameters in EHT and semi-empirical methods) for emulating the weak coupling with contacts. From this standpoint, if the final results are "validated" and enough accurate (for the purposes of the study) then there is no reason in my opinion of avoiding using such methods, that present the great advantage of being computationally inexpensive when compared with DFT or other approaches, being however aware of the above mentioned limits.

A final remark is provided about another approach, somehow similar in the principle to the one just described. In [136] the authors successfully perform simulation in the case of strong electron-electron interaction by proceeding as follows. They consider separately the up-spin and the down-spin states, and in particular they calculate the transmission spectra for up- and down-spin separately. At the end they sum the two spectra (obtained considering separated the up-spin and the down-spin), and the final result is somehow accurate. As the authors state this procedure allows to get good result but it is just a computational tool, with no theoretical foundation. Indeed they are considering a  $C_{60}$ molecule that has no magnetic properties, thus in general there is no reason to consider separated spins since electrons can in principle start at source with a given spin state and reach the drain with another spin state, i.e. spin mixing is possible in principle (the current is not spin-polarized). Nevertheless they neglect the spin mixing due to spin-orbit coupling (i.e. an electron can change spin state during propagation). Moreover they make another unphysical assumption: they neglect non-collinear spin densities (i.e. they assume that the electron cannot point in any direction but it can be only UP or DOWN belonging to the same plane). All these facts are non-physical, nevertheless the final result matches with other experimental and theoretical works. Notice that the transport regime that is considered is coherent (with separated spins). Since the final result is somehow accurate, this method can be used for simulations in the weak coupling regime; with the awareness of what just mentioned, and with some computational advantages. The reason why the final results is not totally wrong is because by considering separately the UP and the DOWN spin cases they are implicitly assuming that the electrons with different spins do not interact and thus they travel in completely separated channels. This corresponds somehow in emulating an high charging potential such that the presence of an electron in a state prevent another electron to transit in the same level (Coloumb blockade). This argument is not at all convincing, nevertheless such unphysical method works fine in some situations, and, aware of its assumptions, there is no reason to avoid using it.

### Part II

## Molecular electronic sensors
# Chapter 7 Molecular electronic sensors

Throughout the first part of this work I reviewed in detail the current state-of-the-art techniques for modeling molecular devices in general, and more specifically molecular electronic sensors (MES). The aim of this second part is twofold: firstly, to apply such models to novel (gas) molecular electronic sensors in order to verify their performances and effectiveness, and then to provide a practical methodology for the simulation and the design at device level of such MES. The molecular electronic sensors were already introduced in the introductory chapter in section 1.2, and table 1.2 summarizes their main distinct features. At the present, and to the best of my knowledge, in literature there are only few molecular electronic sensor examples (a dozen of papers in total - see bibliography). This is thus a pioneering field of electronics and sensing science and not much is already known, at least from the standpoint of practical implementations and MES performances. Nevertheless the physical phenomena and theory for transport that are behind the working principle of a MES are well known, and they are exactly the topics covered in the first part of this work. The purpose of this short chapter is to bridge the "abstract" modeling introduced in part I with the practice I am going to introduce in this part II of this work. In section 7.1 I will briefly review the working principle of MES, with the gain and in terms of the rigorous theoretical models introduced in the part I of this work. Moreover I will also cite literature examples of MES and briefly comment them. In section 7.2 I will introduce a possible methodology for proceeding in simulating and designing a MES gas sensor. In the next chapters of this work I will follow this methodology to set up the device geometry and verify its performances.

Notice that the SETs, and sometimes also molecular channel SETs, are often used and demonstrated to be effective charge sensor. Also the elementary single electron charge can be detected and moreover by exploiting the Coulomb blockade and injecting a spinpolarized current it is possible to perform spin detection. This application is useful is quantum computing memory reading operations, since the information is encoded by means of the electron spin. Nevertheless such applications are outside the purposes of this work, that instead is focused on molecular sensors, and since at moment in literature such applications are barely considering molecular channels, but semiconducting (or metal) quantum dots instead, they are not considered here.

## 7.1 Working principle

A molecular electronic gas sensor is a molecular wire or transistor in which the molecular channel conductivity is modulated such that it is possible to detect a given physical phenomenon or a specific chemical interaction aimed in identifying the presence, in the vicinity of the sensor, of a given chemical compound. In the rest of this work I will refer to gas sensors, nevertheless other sensors are in principle possible. In the following subsections I will considered them one by one, starting from the gas sensor one. In order to understand the principle behind a gas sensor, the concepts of physisorption and chemisorption are needed and for this reason they are preliminary introduced.

#### 7.1.1 Chemical adsorption: physisorption and chemisorption

In surface chemistry the "adsorption" is the process by means the binding of a molecule to a surface is performed [47], [104]. More generally the adhesion of atomic, ionic or molecular species to a surface (both in gases and liquids) is referred as adsorption. Notice that it is spelled different from "absorption", that has the conventional meaning (e.g. the absorption of a photon/phonon by an electron), and in macroscopic chemistry is instead referred to dissolution of a chemical species (the absorbate) by a liquid or solid (the absorbent). In the case of adsorption one talks about the adsorbate, that is the chemical species, adsorbed on the surface of the adsorbent. As aforementioned the adsorption is a surface phenomenon, while absorption involves the whole volume of the material [104]. In general the term sorption includes both the adsorption and the absorption, while the term desorption is used to indicate their reverse processes. Thus in the case of chemical adsorption, for example, a given molecule can be adsorbed on a metal or graphene surface, indicating that it is somehow bond to it (see below). After that, if an enough energy is provided to such molecule (i.e. the to the adsorbate), then a desorption chemical process can take place and make again free the molecule. The adsorption of a molecule to a surface can occur in two fundamentally different ways: by physisorption or by chemisorption. The first process is governed by van der Waals interactions, while in the latter a chemical bond (covalent or ionic) occurs [47], [104].

Physisorption, also called physical adsorption [47], is a process in which the attraction of a molecule to a surface occurs [104]. This might be due to an electric dipole in the adsorbate or to a van der Waals attraction. The interaction between the surface and the adsorbate is weak and typically is non-directional, i.e. little energy difference is expected between different binding sites and diffusion across the surface can occur and be rapid [104]. An important feature of physisorption is that no change to the chemical bonding structure occurs. In general there is also no (or small) overlap between the adsorbate and the adsorbent molecular orbitals. In a classical view (in the sense of Lewis theory for chemical bond) no chemical bond is created with physisorption between the adsorbate and the adsorbent. Since the van der Waals interactions are attractive, as the adsorbate moves closer to the surface, its electron wave-functions start to overlap with that of the surface atoms, leading, in turn, to a repulsive interaction (this is one of the so called steric effects [104]). Therefore in general (in system allowed to relax - e.g. because there is enough geometrical space) an equilibrium position or distance of the adsorbate from the surface is present. Such an equilibrium position is obviously the one that minimizes the total potential energy of the system.

Chemisorption, contrarily to physisorption, involves the creation of new chemical bindings between the adsorbate and the surface atoms. Consequently there can be a significant orbital interaction between the two, leading to high binding energies [104]. This means that a larger amount of energy should be provided to break the chemical bond and free the adsorbate w.r.t. the one needed in physisorption. The chemical bond between the adsorbate and adsorbent in chemisorption can be either ionic or covalent [47]. Notice also that chemisorption is a very specific process, i.e. the nature and the intensity of chemisorption can be greatly different depending on the considered chemical species. It is interesting to notice that corrosion is for example due to chemisorption. Another very interesting practical example of chemisorption is the formation of Self-Assembled Monolayers (SAMs), that are indeed formed by chemisorbing reactive reagents with metal surfaces. For example thiols (sulfur functional group S-H) adsorbing onto the surface of gold, allow the formation of strong chemical bonds with the release of  $H_2$  (such that at the end a molecule can be connected by means of a sulfur atom, called the anchoring group) [104]. This is a widely spread technique at basis of fabrication of several molecular devices [18], [15]. Notice that the chemisorption is also dependent on the initial kinetic energy of the adsorbate [104]. The adsorbate needs to be trapped onto the surface by not possessing enough energy to leave the gas-surface potential well. If it elastically collides with the surface, then it would return to the bulk gas. If instead it loses enough momentum through an inelastic collision, then it "sticks" onto the surface, forming a precursor state bonded to the surface by weak forces, similar to physisorption. Then the particle diffuses on the surface, indeed the physisorption interaction is not enough to keep it in a given position, until it finds a deep chemisorption potential well (i.e. a position onto the surface that is an equilibrium position by minimizing the total potential energy). Then it can react with the surface or simply desorb after enough energy and time.

The main differences between physisorption and chemisorption are:

- Physisorption is a general phenomenon and occurs in any solid/fluid or solid/gas system. Chemisorption is characterized by chemical specificity.
- In physisorption the forces at the basis of the interactions are the van der Waals forces (see section 3.7.2) such as London forces, dipole-dipole attractions, dipole-induced attraction and eventually hydrogen bonding. In chemisorption the creation of chemical bonds occur.
- In chemisorption the electronic configuration is changed by the creation of a chemical bond. In physisorption only small perturbation occurs (for example obitals deformations due to steric repulsion of electron clouds).
- In practice, the categorisation of a particular adsorption as physisorption or chemisorption depends principally on the binding energy of the adsorbate to the substrate, with physisorption being far weaker on a per-atom basis than any type of connection involving a chemical bond. Typical binding energies for physisorption are indeed of the order of 10÷300 meV and non-localized. Chemisorption usually forms bonding with energy of 1÷10 eV and localized.

Finally notice that despite the fact that there is an equilibrium position/distance in both physisorption and chemisorption (for chemisorption this is the bond length), there is no an abrupt transition from the two phenomena. Indeed it was experimentally demonstrated that it is possible a gradual transition between the two [137]. Namely the chemisorption can be obtained from physisorption if the distance between the adsorbate and the surface is forced to be reduced, with a gradual creation of the chemical bond (that it is not created abruptly). In general, if a system is allowed to relax, depending on the nature of the considered chemical species and also on the initial kinetic energy of the adsorbate (see above), it is possible to have physisorption or chemisorption, and they will occur at their equilibrium positions. This means that if a system is allowed to relax (there are no particular geometry constraints), the adsorbate will be find at a distance from the surface corresponding to the equilibrium distance of the physisisorption/chemisorption process. Otherwise if constraints are enforced, all the intermediate cases can occur, leading to a gradual transition between physisorption and chemisorption and more generally to a gradual creation of a chemical bond [137]. For example, in [137], the enforced constraint is exactly the distance between a CO molecule, attached to the tip of an atomic force microscope, by means of which such a distance is controlled. Then the interaction between the CO molecule and the adsorbent surface is measured and monitored, proving what mentioned above. The fact of having a "smooth" transition and creation of a chemical bond is in accordance with the quantum mechanical treatment of chemical bonds [104], that indeed justify the creation of chemical bonds by overlap of electron orbitals (due to electron attraction from both/all the involved positive nuclei). This is in principle slightly different from the classical Lewis theory of chemical bond, even if it is, in practice, a more satisfying explanation of it.

#### Metal-molecule interactions and molecular devices

In [10] is provided a good review of the possible situations characterizing a moleculemetal interface. In molecule-metal systems (such as molecular wires with metal contacts) the quality of the interface is an important factor influencing the transport through the entire system. Accordingly with the previous discussion, the molecule can generally be physisorbed or chemisorbed onto the metal contact, nevertheless also intermediate cases are possible. In general the following cases can be identified (with increasing interaction strength) [10]:

- Physisorption with no charge transfer between the metal and the molecule. This can be the case of saturated molecule, that are thus non-interacting (like noble gases are). In this case there is essentially no interaction.
- Physisorption with possible charge transfer between the metal and the molecule. In this case the molecule is still weakly coupled with the metal surface and an integer electron charge can be transferred. This of course corresponds to high charging energy case.
- Physisorption with rearrangement of electron density, i.e. molecule and metal surface polarization. This is possible for neutral and polarizable molecules or for molecules with an intrinsic dipole moment.

- Weak chemisorption with a possible charge transfer. This is the case of molecules with free electron pairs chemisorbed on metal surfaces. A small amount of charge is exchanged between the molecule and the metal to reach Fermi level alignment and thermodynamic equilibrium.
- Strong chemisorption with strong covalent bonds. In this case there is an high level of hybridization of the orbitals and a charge transfer is possible to reach the equilibrium. The presence of surface dipoles can arise due to the formation of covalent bonds between atoms with (in general) different electronegativity (the molecule anchoring group and the metal atoms). This case typically is the one in which a specific anchoring group is exploited to guarantee the creation of such chemical bonds during the fabrication process (see above the SAMs example).

In general, in the physisorption case, a weak coupling between the molecule and the contacts occurs. This leads to localization of electron states, small or absent broadening, high charging energy and Coulomb blockade. Usually no charge transfer is observed in physisorption case [10], and by biasing the structure an integer electron charge can be exchanged between the molecule and the metal. In the case of chemisorption a strong (covalent) bond is instead created between the molecule and the contact, and usually partial charge transfer occurs. This implies a strong interaction, with an high level of orbital delocalization and small charging energy with no Coulomb blockade. Notice that as mentioned above all intermediate cases are possible and there is no a net distinction between the two regimes, instead there is a gradual transition between the two [137]. In particular, to this purpose, notice that there will be two equilibrium distances between the contacts and the molecule, corresponding to the equilibrium distance for physisorption and for chemisorption respectively. Nevertheless if the system has constraints, it may happen that the geometry cannot relax, an intermediate situation occurs. For example, there can be a too short space in between the two electrodes to ensure physisorption relaxation to equilibrium, but at the same such distance between the contacts can be too large to ensure a creation of a strong chemical bond with wave-functions hybridization. In such a case, if the technological process is designed to have that the molecule has no enough kinetic energy to ensure being "caught" by the electrodes, then it will stay in between the two contacts, but with no optimal geometry, i.e. the most stable configuration will not be achieved. In that case the potential energy of the system will be higher than the equilibrium potential energy for physisorption, but lower than the same for chemisorption, and an external perturbation might easily (more easily than if equilibrium would reached) be enough to distort the geometry and cause variations or desorption.

#### 7.1.2 Gas molecular electronic sensors

In gas sensing applications the molecular channel is exploited as sensor of specific chemical compounds present in air or solution, and its conductivity is uniquely modulated by the presence of the target chemical species in proximity of the molecular channel. Examples in literature, based on single molecule conductive channels, are: [33], [34], [38], [138], [139]. In general the target molecule (sometimes referred as the analyte especially in biological applications [54]), will interact via van der Waals intermolecular interactions (see section

3.7.2) with the molecular channel, thus changing the electron states and the transmission function (thus the conductance - see Landauer sec. 4.3 and 5.15.2) of the channel. As a final effect the electrical current will change depending on the presence or not of the analyte. By detecting such a specific variation of current, it is possible to detect the presence of the target analyte and likely also its concentration. Accordingly with the treatment of section 7.1.1, the target molecule can be in general physisorbed or chemisorbed by the molecular channel. Even if, precisely, this would be an abuse of notation, since the two terms "physisorbed" and "chemisorbed" are strictly referred to an adsorbent that is a surface, while a single molecule is not. In general, anyway, if the channel molecule is very large w.r.t. the adsorbate then the process is quite similar. Even if it is not (i.e. the sensor molecule and the adsorbate one have similar dimensions), one can use the terms "physisorption" and "chemisorption" to highlight the nature of the chemical interaction [38], having in mind that they are not referred to a surface phenomenon. In addition, such (not precise) lexicon descend from a class of gas sensors that is very demonstrated in literature both by means of theoretical studies/simulations and from prototypes experimental data: namely the 2D FET-based gas sensors. In such sensors the working principle is analogous to the one of gas-MES, that indeed can be seen as the "novel generation", at moment at embryonic level, of the previous ones. For example a GNR-gas-sensor is a sensor in which a 2D sheet of graphene (i.e. the graphene nano-ribbon) is used adsconducting channel. Then the target molecule can be physisorbed or chemisorbed onto the GNR resulting in a modulated conductance. This class of devices, the 2D-FET-gas sensors, are well demonstrated in literature [49], [50], [50], [58], [57], [60], [63], [61], [62], [52], [30], (1D) nano-wire example with the same principle: [64]).

In [33], a  $C_{60}$  fullerene is used as molecular channel for a complete molecular transistor, and by means of simulations with EHT + NEGF methods, both at equilibrium and in nonequilibrium, the authors support its application as ammonia (NH<sub>3</sub>) gas sensor, providing also good results in terms of selectivity and response to different ammonia concentrations.

In [34], the authors prove the potential application of a modified/doped  $C_{70}$  fullerene as gas sensor for sulfur dioxide (SO<sub>2</sub>) and nitrogen dioxide (NO<sub>2</sub>), that are very toxic for humans [65]. In particular the study is focused only at equilibrium with no electrodes (thus the entire device is not studied), and the adsorption properties of SO<sub>2</sub> and NO<sub>2</sub> by the metal ion (Cr<sup>2+</sup> and Co<sup>2+</sup>)-prophyrin-induced C<sub>70</sub> is proved to be effective, thus making the latter promising candidate for gas nanosensors.

Similarly to the previous paper, in [38], the author prove the effective adsorption properties of  $C_{20}$  fullerene of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>). Again the study is carried out at equilibrium only and no complete device is proposed.

The two papers [138], [139] present other two gas sensors with analogous principles of the above mentioned ones.

#### Next in this work

In the next chapters of this work, inspired by the aforementioned papers, I will investigate the  $C_{60}$  molecular wire as gas sensor, and I will use it as an example of study to develop a general guiding methodology for the design at device level of a single-molecule gas sensor.

Indeed, to the best of my knowledge this is still lacking in literature, and it can be an important starting point toward a faster and critical analysis of such devices, that, as already mentioned, are at the moment only at embryonic level. My pioneering work can be useful in developing a standardized methodology of design of such devices toward a design by levels of abstraction. My choice of investigating the  $C_{60}$  has multiple reasons: firstly, it is a well known molecule, stable at room temperature, and since made of carbon only it is pretty interacting, indeed the hybridization of molecular orbitals is not complete in the sense that some valence electrons are not involved in chemical bonds and they are highly interacting, thus promising good interaction properties with target analytes. Moreover, its sensing properties were already investigated in recent years, especially in standard chemo-sensor architectures (see introductory section 1.2) as summarized in the review paper [37].

# 7.1.3 Single molecule event detection with molecular electronic sensors

Single molecule detection is a novel frontier of sensing science, in which the presence of a single molecule can be dynamically detected, making also possible the detection of intermediate (unstable) products of a complex chemical or bio-chemical reaction [27]. There are many ways of achieving such a task [27], [28], among which the novel molecular electronic sensor approach seems to be promising for a label-free real-time detection. For example in [23] a molecular wire is exploited for this task. The working principle is essentially identical to one presented previously for the gas sensors, with the exception that here the channel molecule is engineered to allow high specificity and thus high selectivity such that the sensor responds exclusively to the target analyte. In particular, for the first time, it was experimentally proved that a given theoretically predicted chemical reaction chain occurred, indeed the current flowing in the molecular wire resulted dynamically modulated by the presence of an unstable intermediate chemical species with a short life-time (of the order of ms) that results to be an intermediate product of the chemical reaction. This is in my knowledge the first prototype of its type, fabricated and tested. The presence of the target molecule is detected by means of a specific chemical interaction with the molecular channel, causing a modulation of the molecular wire current. The theoretical modeling is based on a DFT + NEGF approach: in particular it was used DFT with the hybrid functional B3LYP (Gaussian software) and equilibrium Green's function (Quantum-Wise ATK software) for evaluating equilibrium transmission spectra. The theoretical calculations matched the experimental data, thus being a literature prove of the effective modeling techniques introduced so far in this work.

#### 7.1.4 Light molecular electronic sensors

In principle light sensors are possible, even if at present in my knowledge there are no practical or complete device studies in literature. The basic principle is very easy: an incoming photon can be absorbed by the molecule thus exciting an electron to an higher energy level and modulating the current flowing through it. The principle is thus analogous to the working principle of conventional opto-electronic devices, also organic ones. The correct way for modeling the photon-channel interaction is by means of incoherent transport, with the addition of a suitable self-energy within the NEGF framework in order to account the photon-electron interaction, as already explained in section 5.18. The potential advantage of molecular device used as light sensors is that the molecular channel and the device can be optimized such that only specific transitions, involving only well defined energy levels and thus photon energy, are allowed and therefore detected. This allows to obtain great freedom at design level on the energy or wavelength of absorbed photons. Molecules can also emit photons, in such a case they are no more sensors or detectors but sources instead (analogously to Organic Light Emitting Diodes -OLED-).

#### 7.1.5 Humidity and temperature molecular electronic sensors

Humidity and temperature sensors can be also in principle realized. An example of trivial humidity sensor is provided in [32]. In this case a SET is used to detect the presence of  $H_2O$  in air. In particular an empty device, with ideal (PEC) contacts is supposed to have like a window in which air can circulating. If an  $H_2O$  molecule happens to be in between the source and the drain contacts, a variation of the (noise) current occurs, since it has in principle specific conduction properties, and the detection is possible. In principle it is also possible to have a molecular device (such as a  $C_{60}$ -based wire) and to study if (and in which way) the conductance changes if water molecule is present nearby the channel (in this case the principle becomes exactly the one presented previously for gas sensors).

In the case of temperature sensor it is obvious that it somehow affect the transport, since it influence the Fermi-Dirac's functions and also the number and the energy of phonons; thus it can be in principle be detected a temperature variation by detecting a current variation.

#### 7.1.6 DNA sequencing with molecular SETs

A thrilling application of SETs and molecular electronic sensors is the possibility of performing real-time DNA sequencing [35], [36], [85], [86], [84]. The working principle is the following. The DNA molecular chain is forced to flow through a nanopore to which a potential difference is applied. The nanopore can be an artificial graphene nanopore (e.g. [85], [86]) or a suitable enzyme and it works as contact (an all-around contact that surrounds the DNA nucleotides). By means of the applied electric field it is possible to force the flow of the DNA through the nanopore, and at the same time by measuring the electrical current it is possible to detect in real-time what nucleotide is in each moment present in the nanopore. Indeed DNA nucleotides are molecules, and by changing the molecule of the channel of the SET, it changes the electrical current flowing in it, thus making possible the recognition. The simulations techniques [35], [36] are generally in agreement with experimental data and prototypes were demonstrated to be functioning and effective as a fast and reliable method for DNA sequencing [85], [84].

### 7.2 Methodological approach: gas sensors

The purpose of this section is to summarize the logical steps I will follow in the next chapters to discuss the structure, design and performances of a  $C_{60}$  gas sensor. In this optics, it is a brief introduction to set the very practical part of this work, in order to avoid getting lost in the following.

In order to keep the treatment as much systematic as possible I will proceed by points:

- First of all a molecule that should be used as channel and the target molecule should be selected. In general there is no unique way of doing it, and the the channel can also be engineered to posses some specific physical-chemical properties such that the interaction with the target is enhanced and maximized, both from the standpoint of the sensibility/detectability and from the standpoint of selectivity/specificity. In the following I will consider a C<sub>60</sub> molecule as channel, and I will initially investigate its performances as ammonia (NH<sub>3</sub>) gas sensor, by following the approach of [33]. As mentioned in section 7.1.2, the choice of the C<sub>60</sub> has multiple reasons: it is a well known molecule stable at room temperature [140], and since made of carbon only it is pretty interacting [140], indeed some valence electrons are not involved in chemical bonds and they are highly interacting, thus promising good interaction properties with target analytes [140]. Moreover its sensing properties were already investigated in recent years, especially in standard chemo-sensor architectures as summarized in the review paper [37], besides that in [33]. By following what did in the same paper I will firstly investigate such device as gas sensor for ammonia.
- Once the channel molecule is chosen it should be chosen the device structure. In general mainly two architectures are possible: a molecular wire (two-terminal device) and a molecular transistor (with one or more gates). Since the fabrication process is more complex and thus expensive for molecular transistors than for the wires, I have chosen to start with studying and testing a molecular wire. Then, once the wire is characterized it is possible to add a gate in order to verify if a substantial performance improvement can be obtained. If not so, it has no sense using a transistor.
- At this point the contact material and eventually the presence of anchoring groups (i.e. functional groups aimed in anchoring the molecule to the contacts) should be selected. This is a crucial point since the contact-molecule interface strongly determines the quality and the regime of transport. In general in real cases it should be evaluated considering also the technological process and the production necessities. I have chosen to employ no anchoring group and metal electrodes of gold (Au), ideally FCC (111), i.e. Face-Centered-Cube crystalline cell, with orientation (111) please refer to the widely used Miller notation, see e.g. [141], [142]. The reason behind this choice is that the gold contact technology is already widely used and known for molecular junctions [18], [15]; and at the same time it is demonstrated in literature that carbon is capable of forming strong covalent bonds with gold, thus making an anchoring group redundant.
- The main parameter to be fixed in a molecular wire is the gap length between the two electrodes, in which the molecular channel will be host. In other words the distance

between the contacts and the  $C_{60}$  molecule should be fixed. In order to do that, it is advantageous choosing a distance that maximizes the sensitivity to the target, if there exists one. In this optics I have studied the sensitivity dependence in function of the contacts distance, resulting in higher sensitivity when the distance is smaller. The chosen distance was thus the one corresponding to the covalent gold-carbon bond length. This corresponds to the equilibrium distance in case of chemisorption, indeed notice that the gold electrode is essentially a gold surface with large dimensions w.r.t.  $C_{60}$  fullerene one, thus leading effectively to chemisorption. In order to choose and fix the geometry it is also reasonable to perform geometry relaxation simulations, to verify if the chosen geometry is actually a stable configuration, since it should be robust in time (and resist to energy/phonon absorption in order to avoid dynamical changes in the device geometry that would be highly undesired).

- In parallel to the geometry choice it should be also performed another kind of important analysis. Indeed it is convenient to preliminary check if the molecular channel is somehow sensitive to the target. This can be accomplished at equilibrium by verifying a change in the DOS or in the transmission spectrum. Moreover this analysis can be performed on the isolated C<sub>60</sub>, i.e. without the contacts, like for example done in [34], [38]. Nevertheless the disadvantage of doing so, especially in single molecules channels, is that the influence of contacts on the final DOS and transmission features can be relevant and can considerably change the attended results. For this reason I have chosen to perform a preliminary study on the equilibrium DOS and transmission spectrum of the entire device, i.e. with contacts. Such a study was performed with DFT calculations (considering the Grimme-D2 and Grimme-D3 correction for van der Waals interactions see section 3.7.3). A significant variation, in the case in which the target is present nearby the channel w.r.t. to the case in which it does not, either in the DOS or in the equilibrium transmission spectrum, is enough to verify the potentiality as sensor for that target.
- In general one may have time/resources requirements/constraints, such that it is not always possible to use the method known to be the most accurate for representing the physics/chemistry of interest. For example during my work I could not perform non-equilibrium simulations with DFT methods, because the server in which all computations were performed did not support it (the RAM was not enough to sustain such calculations, even with simulation settings to minimize memory usage). In that cases one may use other methods. For example I decided to use the EHT one, conscious of its limits. Nevertheless as mentioned several times EHT method should be validated. For this reason I have tried to reasonably validate it, for the non-equilibrium case, starting from the equilibrium more accurate DFT method simulations. The details are provided in the dedicated sections, nevertheless here the point is on the general methodology: when a method, generally expected to be not much accurate for the specific application, is used, then the obtained results should be somehow validated.
- At this point the device geometry should be fixed and the device is expected to be sensitive to some target. A crucial performance verification should be performed:

the selectivity of the sensor. Indeed the sensor in order to be able to detect the presence of a given target should respond in a unique way to the presence of such target, like it does not happen in response to other substances that can be present in the usage environment, such as air components (oxygen, nitrogen, humidity/water, etc...). This means that many simulations should be performed in order to verify such sensor selectivity. Moreover the sensor should provide a response to the various orientations of the target (especially if polar), and in this regard also a study of the equilibrium physisorption/chemisorption of the target onto the channel molecule should be performed.

- Once all the aforementioned tests are performed then a suitable bias point should be selected. The optimal one should maximize the sensitivity and selectivity, if those are the most important feature for a given application. Otherwise it may be chosen to maximize linearity and so no... Another criterion of choice can be the bias point for which there is maximum correspondence between the EHT and the DFT simulations (of course only if a method not at all suitable is used, as explained above).
- Sensor performances should also be checked, in order to highlight possible critical issues. To this purpose the response to different target concentrations should be studied, and for example the bias point with maximum linear response can be chosen if linearity is important in the sensor specifications. Moreover also the maximum distance above which no significant sensor response is obtained is a useful data for proceeding in the design. Another useful check can be on response time of the sensor and eventually dissipated power by it.
- Depending on the specifications several properties may be checked and verified. If not satisfied a study on the reason why it is so is always helpful in understanding if and how the device should be modified to satisfy the requirements. The actual device structure of MES is quite easy if compared to conventional nowadays electronic devices. Thus in order to keep the structure simple (since already in this way the technology is a big issue [18]), few parameters can be changed, unless the channel molecule is modified or changed. The latter solution is very effective and opens the way to an incredible variety of heterogeneous solutions. Nevertheless another solution can be to modify somehow the device; this could require a long time before converging to the desired solution.
- In order to improve performances the introduction of a gate electrode can be considered. This is a trivial solution that nevertheless can be potentially very effective in ameliorating the overall performances of the sensor.

By following more or less the above reported points it is possible to predict several features of the sensor and have thus a complete model, more or less refined, for the sensor, providing an idea on its behavior and response in different more or less realistic situations. In a real design process, depending also on the specifications and requirements, it is possible to have jumps among the above introduced points, and also it is possible to have a sort of feedback among them in order to optimize the device with the gain in knowledge of its performances, etc... This is indeed what I did and what I will try to present in the

next chapters. So the aforementioned steps are only indicative and can (and should!) be dynamically changed or ordered depending on several factors. Once the device is somehow characterized at least in terms of the above mentioned features it is possible to model it by means of a sort of "black-box" to be used for the design of the conditioning circuit or anyway at higher levels of abstraction. This step is not at all completed in this work. Of course operating by levels of abstraction has the advantage that the circuit-level or system-level designer is not required to have specific knowledge on modeling the MES, exactly as it happens for conventional electronic systems.

# Chapter 8 $C_{60}$ -based ammonia gas sensor

In this chapter the simulation results relative to a  $C_{60}$  molecular electronic sensor for ammonia gas detection are reported and discussed. In particular the main purpose is to verify the effectiveness of the methodology presented in the previous chapter 7 (section 7.2) in designing a MES device, and verifying its performances. Moreover the implemented procedure is an example of practical and real modeling of a complete MES. Indeed the methods presented in the theoretical part I of this work are now exploited in practice to simulate the sensor. In the presentation I will not always follow a chronological path, but instead I will try to prefer the natural logical exposure that follows the methodology conceived in section 7.2.

Throughout the present chapter I will investigate the  $C_{60}$  molecular wire as ammonia gas sensor, and as mentioned in the previous chapter 7, I will use it as an example of study to develop a general guiding methodology for the design at device level of a single-molecule gas sensor. Again as mentioned previously, to the best of my knowledge, this design methodology is still lacking in literature, while in my opinion it is important since it can be the starting point toward a faster and critical analysis and design of MES. In this optics the work presented here is a pioneering work, at least at Politecnico di Torino, where currently at the VLSI lab there is no such established methodology, simply because MES are novel devices conceived during the last few years only, and research in this field is still at embryonic level. Again as already discussed, my choice of investigating the  $C_{60}$ has multiple reasons: it is a well known molecule stable at room temperature [140], and since made of carbon only, it is pretty interacting [140], indeed some valence electrons are not involved in chemical bonds and they are highly interacting, thus promising good interaction properties with target analytes [140]. Moreover its sensing properties were already investigated in recent years, especially in standard chemo-sensor architectures as summarized in the review paper [37], besides that in [33].

All the simulations reported here were performed by means of *Quantum-Wise ATK* software by *Synopsys*<sup>®</sup>.

### 8.1 Device structure and geometry

First of all the contact material and eventually the presence of anchoring groups (i.e. functional groups aimed in anchoring the molecule to the contacts) should be selected. In general this choice should be done by considering also the technological processes and the production necessities. I have chosen to employ no anchoring group and metal electrodes of gold (Au), ideally FCC (111), i.e. Face-Centered-Cube crystalline cell, with orientation (111) (for Miller notation see e.g. [141], [142]). The reason behind this choice is that the gold contact technology is already widely used and known for molecular junctions [18], [15]; and at the same time it is demonstrated in literature that carbon is capable of forming strong covalent bonds with gold, thus making an anchoring group redundant [143], [144], [145], [146], [147]. At the beginning it was chosen no particular orientation of the C<sub>60</sub> molecule, placed in between the two gold contacts. Moreover the distance between the fullerene and the contacts was fixed to be of about 2.7 Å, similarly to the one used in [33]. This choice was no theoretically motivated, for the moment, since no preliminary study was performed in order to fix it. In the next sections, this point will be further discussed and the final geometry will result to be slightly different. With reference to a general methodology this initial choice can be intended to be a sort of "initial guess" for the geometry, in order to perform the preliminary analyses reported in the next section. The next two subsections summarize the  $C_{60}$  molecule properties and the initial geometry, respectively.

#### 8.1.1 The $C_{60}$ fullerene

The fullerenes are carbon allotropes, i.e. structurally different forms of the same element, in this case carbon [140]. The shape is somehow similar to the one of an empty sphere, with the surface composed by hexagons and pentagons with carbon atoms at vertices. In general the fullerene shape can be ellipsoidal or even tubular. The spheric and ellipsoidal fullerenes are called "buckyballs", while the tubular ones "buckytubes" (e.g. carbon nanotubes) [140]. The  $C_{60}$  fullerene is also called "buckminsterfullerene", and two pentagons do not share any side [140]. The presence of pentagons prevent the  $C_{60}$  fullerene geometry to be planar, and originate the aforementioned spherical shape. All fullerenes are very electronegative and with an high degree on unsaturation, i.e. all the carbon atoms are unsaturated. This means that they have valence electrons in the external shells not involved in chemical bonds and in this sense "free" of interacting with other chemical species [140]. Instead saturated (organic) molecules are such that all valence electrons are involved in chemical bonds and thus they are barely interacting molecules [140]. For this reason the  $C_{60}$  fullerene is expected to be interacting with other chemical species, among which an high interaction with the target molecule is desired. The  $C_{60}$  fullerene diameter is of around 7 Å, for this reason it can incorporate atoms or diatomic molecules, thus changing significantly its physical-chemical features [140], and also the transport [147].

#### 8.1.2 The initial geometry

As discussed and motivated at the beginning of the present section the initial geometry was fixed to be a molecular wire with a  $C_{60}$  molecule as conducting channel, gold Au FCC (111) electrodes at a distance of around 2.7 Å, compatible to one used in [33]. No gate was considered, since it has no sense of introducing such complex (and more expensive) solution in the device, at least if the performance specifications are already satisfied without it. In this the geometry used for the preliminary estimations of the next section is different from the one in [33]. It is depicted in figure 8.1.



Figure 8.1: Initial geometry of the  $C_{60}$  fullerene ammonia gas sensor. The  $C_{60}$ -contacts distances were fixed at around 2.7 Å, no special orientation of the  $C_{60}$  was considered. The figure was generated by ATK software [125], [126] (used for performing the simulations).

In order to investigate the device sensitivity to ammonia (NH<sub>3</sub>) other geometries were considered. In particular geometries with 1, 3 and 5 additional ammonia molecules were considered. Such ammonia molecules were positioned above the C<sub>60</sub>, centered on it, like it was the face of a die: one molecule at the center, three molecules in diagonal and five molecules with a center one and four around it like vertices of a square. All the molecules were positioned at a distance of about  $2.2 \div 2.3$  Å above the fullerene, in order to ensure van der Waals graphical spheres to be intersected. This should ensure an high level of interaction between the C<sub>60</sub> and the ammonia molecules. The distance of about  $2.2 \div 2.3$  Å is also justified from the fact that it is a sort of average distance for strong intermolecular interactions, in the sense that since intermolecular interactions are strongly inversely dependent on distance, above  $4 \div 5$  Å they decay rapidly and above few nm they are no more effective (see section 3.7). Thus such a chosen distance can be interpreted as an average short-distance strong intermolecular interaction distance. The distance from contacts was initial maintained to 2.7 Å. Images representing the three geometries with ammonia are reported in appendix D.1.

# 8.2 Preliminary equilibrium properties of the device

In order to perform a preliminary check of the potential of the  $C_{60}$  gas sensor the following equilibrium simulations were performed in *Quantum-Wise ATK* exploiting the geometries considered in the previous section. Both DFT and EHT methods were considered.

#### 8.2.1 DFT equilibrium simulations settings

The DFT simulations were performed at equilibrium with the GGA PBE functional and with a DZP basis set (FHI DZP). The complete list of the simulations settings are reported in tables 8.1, 8.2 and 8.3. Notice that the intermolecular van der Waals correction Grimme DFT-D2 was taken into account, essentially leading to no difference w.r.t. to uncorrected DFT. Moreover simulations with Grimm DFT-D3 simulations were also performed leading again to no significant variations. For the sake of completeness also electron-correlation corrections were considered. Hubbard correction (with default fitting parameters) did not lead again to any difference, while DFT-1/2 did. The results in terms of equilibrium DOS and transmission function T(E) are reported in appendix D.2. In the end, since no great charging effects was expected, the electron correlation correction DFT-1/2 was not considered in the rest of this work (indeed as it will be addressed in section 8.3 the molecular orbitals resulted well hybridized with contacts ones, thus leading to an expected small charging energy).

Notice that the parameter "Broadening" in "Numerical Accuracy" section of table 8.1 is measured in kelvin thus having the measuring unit of broadening temperature. Nevertheless this is not a physical temperature, but it is an artificial temperature to achieve the convergence of device self-consistent calculations in a smooth and faster way. The corresponding solution and derived physical quantities should not virtually depend on this temperature value within some user-set tolerance. Instead the device operating temperature is specified in "Electrode parameters", and since by default it is 300 K, it was not modified. Notice that the MES is thus supposed to work at room temperature.

Since essentially all the other settings were already discussed in the previous chapters of this work, they are no commented here.

#### 8.2.2 A remark on transmission function T(E) in ATK

It was chosen to already analyze the full device " $C_{60}$  + gold contacts", indeed as mentioned in section 7.2, the final DOS and T(E) can be affected by the electrodes. Moreover by putting already in this phase the contacts the transmission spectrum T(E) can be evaluated (otherwise it does not since it has no sense talking about transmission if without electrodes).

Table 8.1:	ATK-DFT	equilibrium	calculator	settings.	If not	differently	stated,	all	the	DFT
	simulations	were perform	med with t	hese settin	ngs.					

	ATK-DFT: LCAO Calculator			
	Exchange correlation: GGA,			
LCAO	Functional: PBE,			
Basis	van der Waals correction: Grimme DFT-D2,			
Set	Pseudopotential: FHI,			
	Basis set: DZP			
	Density mesh cut-off: 75 Hartree,			
Numerical	Occupation method: Fermi-Dirac,			
Accuracy	Broadening: 1000 K,			
	k-points: Preset-Density: [4.0,4.0,150.0] Å			
	Tolerance: 0.0001 (default),			
	Maximum steps: 100,			
Iteration	Algorithm: Pulay Mixer,			
Control	Damping factor: 0.1,			
	History steps: 20,			
	Mixing variable: Hamiltonian			
	Initial density: (default)			
	Electrode constraint: off (default)			
Davias	Equilibrium Method: Green's functions,			
	Equilibrium Self-Energy: Recursion,			
algorithm	Non-equilibrium Method: Green's functions,			
	Non-equilibrium Self-Energy: Recursion,			
	Caching strategy: (default)			
Contour				
Integral	default settings			
parameter	_			
	Solver type: Conjugate gradient,			
Deigen	Boundary conditions:			
Folsson	(A) direction: PBC,			
Solver	(B) direction: Dirichlet,			
	(C) direction (transport): Dirichlet			
Electrode	default acttings			
parameters	default settings			

A remark on the Quantum-Wise ATK notation. The real total transmission coefficient is not actually T(E). Indeed one should perform an additional and separated transmission eigenstates and eigenvalues calculation to get the actual transmission probability, that is indeed provided by the so called transmission eigenvalues. These are the eigenvalues of the transmission quantum mechanical operator. Its eigenstates can be instead evaluated and projected in the real space as surfaces. These surfaces are the "transmission eigenchannels" of such an operator in real space, i.e. they correspond to the region of space in which

	Analysis: Device DOS		
Energy	$E_0 = -3.0 \text{ eV}, E_1 = 3 \text{ eV},$		
range	Points = 401		
k-point	Donsity: $n_1 = 7$ $n_2 = 7$		
sampling	Density. $n_a = 1, n_b = 1$		
Contributions	All		
Energy zero	Amora da Farmi laval		
parameter	Average Fermi lever		
Infinitesimal	1e-06 eV		
Self-energy	Pagurgion		
calculator	Recursion		

 Table 8.2: ATK-DFT equilibrium DOS calculator settings. If not differently stated, all the DOS simulations were performed with these settings.

 Table 8.3:
 ATK-DFT equilibrium transmission spectrum calculator settings. If not differently stated, all the transmission spectrum simulations were performed with these settings.

	Analysis: Transmission Spectrum			
Energy	$E_0 = -3.0 \text{ eV}, E_1 = 3 \text{ eV},$			
range	Points = 401			
k-point	Density: $n = 7$ $n = 7$			
sampling	Density. $n_a = 1, n_b = 1$			
Energy zero	Average Formi level			
parameter	Average Fermi level			
Infinitesimal	1e-06 eV			
Self-energy	Pagurgian			
calculator	necuision			

transmission occurs, or better they are the iso-surfaces of transmission, once a given value of transmission is chosen and fixed. Notice that if such surfaces are similar to molecular HOMO or LUMO levels it means that the main transmission channel for that given transmission value, or better the transmission eigenvalue, is indeed the HOMO or the LUMO. As said above the transmission eigenvalues are the actual transmission coefficients and they are indeed normalized to 1. This is clear when they are interpreted as the transmission operator eigenvalues, i.e. the results of a measurement on the transmission operator (see sections 2.3.6, 2.3.3), that provide a transmission coefficient (pure number no measuring unit).

Instead T(E) represents the transmission spectrum, i.e. the total transmittivity per unit energy ("spectrum" is indeed referred to Fourier transform in energy domain). As explained in the user's manual [125], [126], it may happen that several transmission eigenvalues (that are normalized to 1) can sum at a given energy, providing a total transmission spectrum, at that given energy, greater than unity. This corresponds to the situation in which, for that specific energy value, more transmission channel are available and sum to give T(E) > 1. In other words, in such a situation, the electrons can be transmitted from the source to the drain by means of different paths/states, i.e. different transmission channels/eigenstates. A single electron with a certain energy can thus travel from source to drain by means of different transmission channels/regions (of space), and the total transmission spectrum for that energy can be greater than unity.

In general ATK provides separated transmission spectra for different spins. In this work I am not considering spin-polarized currents or magnetic molecules such that the two T(E) for the two spins will always be equal. For this reason all the reported transmission spectra are intended to be single spin (UP or DOWN - they are equal), and the total one is obtained by summing them (double since they are equal). If not so I will declare clearly what the plot represents.

A last remark on the aforementioned transmission operator and the NEGF formalism. Within the NEGF framework the transmission function T(E), that provides the transmission in function of energy, i.e. the transmission spectrum, can be evaluated by means of equation (5.74) or analogously equation (5.66):

$$T(E) = Tr\left[\Gamma_1 A_2\right] = Tr\left[\Gamma_2 A_1\right] = Tr\left[\Gamma_1 G_D \Gamma_2 G_D^{\dagger}\right] = Tr\left[\Gamma_2 G_D \Gamma_1 G_D^{\dagger}\right]$$

This is a representation of the transmission quantum mechanical operator in the system energy eigenstates (and this is obvious, considering the procedure that led to such expression - sections 5.14.3 and 5.15). Nevertheless it is a quantum mechanical operator representing a physical observable, namely the transmission from source to drain. Therefore it is represented by an Hermitian quantum mechanical operator (see chapter 2), and there is a theorem stating that Hermitian matrices are always diagonalizable (see [87]). Thus it is always possible to diagonalize T and obtain a representation of T in its eigenstate representation, i.e. in the transmission eigenstates basis set. The latter representation for T is the representation mentioned previously. The diagonalization procedure will provide its eigenvalues, i.e. the transmission eigenvalues, normalized to 1; and also its eigenstates, i.e. the aforementioned transmission states/channels. If T is represented in energy domain, i.e. in the basis set of the system energy eigenstates, it is not said that it will be normalized to 1, and in general this does not happen. Indeed as mentioned above there may be more than one transmission eigenchannel that conduct for a specific energy, thus leading to a sum greater than 1. Finally notice that a real space representation of T corresponds to a projection in real space of T, that are surface of iso-transmission in space, as mentioned above.

#### 8.2.3 DFT equilibrium simulations results

The equilibrium simulations (with the settings of section 8.2.1) showed a significant variation in the device DOS depending on the concentration of ammonia  $(1, 3 \text{ or } 5 \text{ NH}_3 \text{ molecules})$ . The ammonia molecules were placed on top of the fullerene as described previously. The obtained DOS are reported in figure 8.2. Since the device DOS per unit energy is significantly different depending on the presence or not of ammonia nearby the fullerene, it is expected to have different non-equilibrium behaviors depending on the presence or not of ammonia molecule. Indeed the DOS is relevant in transport since it

determines the number of electron states that might participate to conduction. In order to have a better insight in the transmission properties also the equilibrium transmission spectra, again with no, 1, 3, and 5  $NH_3$  molecules were calculated and analyzed. The results are reported in figure 8.3. Notice that this is an equilibrium transmission spectrum, that has the physical meaning already pointed out in section 8.2.2, and notice that it is a quantity defined also at equilibrium. In non-equilibrium case the applied bias, the charging effect and the molecule screening can affect and modify the shape of the transmission spectrum, that plays the role of the transmission function discussed in chapters 4 and 5. Indeed it was mentioned that it is function also of the applied bias, also because the contact self-energies and the broadening functions are functions of the bias as well. Nevertheless the (converged) equilibrium spectrum is the starting point for the non-equilibrium spectra and thus the current. This both from a computational standpoint (in ATK the nonequilibrium calculations start always from a converged equilibrium one), and from a physical standpoint. Indeed it is reasonable thinking the applied bias as modifying the equilibrium properties among which the transmission probability plays a central role. This for justifying the fact that here an equilibrium transmission spectrum is used to make predictions about non-equilibrium properties, i.e. the electrical current. This is accurate if the applied bias is small (see sections 4.3, 4.4, 5.15.1, 5.15.2), that means considering energies nearby the zero in figure 8.3 (since it is shifted around the equilibrium Fermi level of the system). The more the applied bias is large, the greater are the differences between the equilibrium transmission spectrum and the non-equilibrium one. Nevertheless the important point here is that evident differences are present depending on the number of ammonia molecules around the fullerene, and since the transmission spectrum is changed, also changes in the electrical current are expected (Landauer's equation: (5.75)). This is evidently true at low bias, while rigorously it is not said at high bias, accordingly with the above discussion. Nevertheless it is reasonable thinking that even at high bias differences will occur, but they cannot be estimated considering the equilibrium spectrum; in other words the non-equilibrium transmission features can be very different from equilibrium ones.

In figure 8.4 the same equilibrium spectra are reported separately in order to make more clear the differences between the case of no ammonia molecule with the cases of 1, 3, 5 molecules. The bottom-right plot is the same of figure 8.3. Notice that important differences in the transmission spectra occur in the transmission peak at around  $-1.4 \,\mathrm{eV}$ , that not only changes its height but also its width/broadening. In general non-negligible differences occur in the HOSO-1, HOSO, LUSO, LUSO+1 levels. Where HOSO is the Highest Occupied System Orbital, and the LUSO is the Lowest Unoccupied System Orbital. They have analogous meaning to molecular HOMO and LUMO but they are referred to the entire system. No evident differences appear in the HOSO-LUSO-Gap (HLG), that is the energy range approximately between  $-1 \, \text{eV}$  and  $0 \, \text{eV}$ . This means that the presence of ammonia is not expected to relevantly change the (possible) conductance gap width, i.e. the sensor is not expected significantly conducting "before" (for lower bias) depending on the presence or not of the ammonia. Nevertheless with the fullerene  $C_{60}$  such a conductance gap is essentially null, i.e. it conducts or in other words the current is non-negligible, already for low biases close to zero. This can be deducted from the equilibrium spectrum around the zero bias condition (i.e. around 0 eV in the plot - that corresponds to the



Figure 8.2: Device equilibrium DOS with different ammonia molecule concentrations: 1, 3 and 5  $NH_3$  molecules were considered.



Figure 8.3: Device equilibrium transmission spectra with different ammonia molecule concentrations: 1, 3 and 5 NH<sub>3</sub> molecules were considered.

system Fermi level). If a bias is applied the bias window, under the hypothesis of having a symmetrical voltage division factor (see section 4.1.4), that is expected in this case since the device was built completely symmetrical w.r.t. to source and drain (in terms of distances etc..), is centered around the zero. And because of the presence of the small transmission peak for slightly positive energies, the current is expected flowing already at small bias.

In conclusion, the equilibrium analysis showed that the  $C_{60}$  MES can be potentially significantly sensitive to the presence of ammonia and thus it can potentially be used as ammonia sensor. In addition it showed sensitivity to different concentrations, since the DOS and T(E) were significantly changing depending on the considered number of ammonia molecules.



Figure 8.4: Device equilibrium transmission spectra with different ammonia molecule concentrations: 1, 3 and 5 NH<sub>3</sub> molecules were considered.

#### 8.2.4 EHT equilibrium simulations

The same analysis performed with the DFT method and described previously was repeated with the EHT one. The EHT method requires less computational effort, and for this reason if the simulations would be compatible with the DFT obtained ones, it can be used in place of the latter to speed up the analysis and design of the MES. In table 8.4 the settings for the performed EHT equilibrium simulations are reported. The settings for the equilibrium DOS and the equilibrium transmission spectrum are the same used for the DFT case, refer to tables 8.2 and 8.3.

The obtained results, DOS and T(E), are reported in figures 8.5, 8.6 and 8.7, respectively. The DOS estimates less electron states w.r.t. DFT one. Nevertheless it shows relevant differences depending on the number of molecules of ammonia. Analogously to the DFT case this is an important fact, implying the EHT method as well is capable of catching ammoniacarbon interaction in a significant manner, leading to DOS variations. The transmission spectrum also shows variations depending on the concentration of ammonia. In general it is less broadened than the DFT one, and the main transmission peaks are slightly shifted toward lower energy (this is a general feature of EHT method that tends to underestimate the energy levels w.r.t. DFT one [105]). Moreover, the EHT method estimate less transmission in the HLG w.r.t. to DFT, with a slightly large HLG. Nevertheless the important feature is that there occur clear variations depending if the ammonia molecule is present

Table 8.4:	ATK-SE (EHT) equilibrium calculator settings. If not differently stated, all	the	EHT
	simulations were performed with these settings.		

	ATK-SE: Extended Huckel Calculator			
	Parameterization: Extended Huckel,			
	Parameters (basis type): Hoffmann,			
Hamiltonian	Weighting scheme: Wolfsberg,			
	Spin: Unpolarized,			
	SCF iteration = $YES$			
	Density mesh cut-off: 10 Hartree,			
N 1	Interaction max range: 10 Ang,			
Numerical	Occupation method: Fermi-Dirac,			
Accuracy	Broadening: 300 K,			
	k-points: Preset-Density: [4.0,4.0,150.0] Å			
	Tolerance = 1e-05,			
	Maximum steps $= 100$ ,			
Iteration	Algorithm = PulayMixer			
control	Damping factor $= 0.1$			
parameter	History steps $= 20$ ,			
	Mixing variable: Hamiltonian,			
	Preconditioner: Off			
	Initial density: (default)			
	Electrode constraint: off (default)			
D :	Equilibrium Method: Green's functions,			
Device	Equilibrium Self-Energy: Recursion,			
algorithm	Non-equilibrium Method: Green's functions,			
	Non-equilibrium Self-Energy: Recursion,			
	Caching strategy: (default)			
Countour				
integral	default settings			
parameter				
	Solver type: Conjugate gradient,			
Deigan	Boundary conditions:			
POISSOI	(A) direction: PBC,			
Solver	(B) direction: Dirichlet,			
	(C) direction (transport): Dirichlet			
Electrode	defeult settings			
parameters	default settings			

or not and in what concentration (number of molecules). In particular relevant differences are present for slightly positive energies (LUSO) and for HOSO peak (between -1 eV and -1.5 eV). For what is concerning the HOSO, the EHT method estimates smaller variations, nevertheless this level will likely participate to transmission for bias windows of the order to 2 or 3 volts (if no large variations of T(E) occurs due to bias), thus make such a difference

not much relevant, at least at low bias. In conclusion to this preliminary analysis, it appears that the EHT can be potentially used to perform calculations on the considered MES.



Figure 8.5: Device equilibrium transmission spectra with different ammonia molecule concentrations: 1, 3 and 5 NH<sub>3</sub> molecules were considered (EHT method).



Figure 8.6: Device equilibrium transmission spectra with different ammonia molecule concentrations: 1, 3 and 5  $NH_3$  molecules were considered (EHT method).



Figure 8.7: Device equilibrium transmission spectra with different ammonia molecule concentrations: 1, 3 and 5 NH<sub>3</sub> molecules were considered (EHT method).

# 8.3 Device geometry engineering

According with the methodology presented in section 7.2, the first (and the main) design step consists in fixing the MES geometry. Since the chosen device structure is a molecular wire, the main things to be fixed are the distance between the  $C_{60}$  fullerene and the contacts, and the orientation of the  $C_{60}$  molecule. In this section I will consider both, starting from the first one. Notice that throughout the present section I will present only EHT method simulation results when in non-equilibrium conditions, the justification for doing so will be presented in section 8.5. I will start by considering the effect of the contact distance on the equilibrium DOS and transmission spectrum, and only then I will consider the non-equilibrium case. Only after these preliminary checks I will consider the presence of ammonia nearby the conducting channel and the sensitivity dependence with contact distance.

#### 8.3.1 Equilibrium DOS and T(E) and contact distance

In order to understand what was the optimal distance between the fullerene and the contacts, it was performed a preliminary equilibrium study on the DOS and transmission spectrum. These results will be useful to understand the trend in the current and in the sensitivity to ammonia presented later in this section. The various DOS and T(E) obtained at various distances between the C<sub>60</sub> and the contacts are reported in figures 8.8 and 8.9 respectively. In these two plots the initial distance of 2.7 Å was increased with a step of about 0.3 Å, the considered values were thus: 3.0 Å, 3.3 Å, 3.6 Å, 4.0 Å, 5.4 Å (the last value of 5.4 Å corresponds to roughly the double of the initial distance of 2.7 Å). The DOS in this case does not provide crucial information, instead the equilibrium transmission spectra (figure 8.9) show a very important fact: the equilibrium spectrum is more broadened if the molecule is closer to the contacts, and moreover it presents higher

transmission peaks if, again, the contacts are closer to the fullerene. This is obvious if one considers the physical origin of broadening (section 5.12), i.e. that it is intimately linked to the degree of hybridization of the electron wave-functions (of the channel with the ones of the contacts). Higher transmission peaks are moreover related to the higher transmission probability that occurs if the distance (i.e. the barrier thickness) is reduced. Notice that with 5.4 Å the transmission is essentially negligible, it oscillates between  $10^{-15}$ and  $10^{-11}$  (only slightly above the numerical noise), and the same is expected and it will be confirmed for the electrical current, making not possible to realize a sensor with such a tiny transmission/current. Thus to get an enough high current, in order to make possible to interface the MES with conventional electronics, it is necessary to choose an enough small contact-molecule distance. Nevertheless, in choosing such a distance, I followed also another important criterion: the MES sensitivity w.r.t. ammonia (see later).



**Figure 8.8:** Device equilibrium DOS with different molecule-contact distances: 2.7 Å, 3.0 Å, 3.3 Å, 3.6 Å, 4.0 Å, 5.4 Å (EHT method).

It is interesting to find the dependence relation of the transmission peaks w.r.t. distance of contacts. To this purpose the transmission peaks for different distances at around 1 eV were considered. Notice that such an interpolation is not at all significant, indeed the considered transmission peaks drift in energy as distance is changed. Indeed, as evident in figure 8.9, if the distance is increased then the transmission local maximum peak occurs at lower energies, thus making the comparison not at all justified. In spite of this the maximum peaks (as mentioned at around 1 eV) were interpolated with an exponential function of the kind:

$$g(x) = A - Be^{-Cx} \quad , \quad A, B, C \in \mathbb{R}$$

$$(8.1)$$

The result is plotted in figure 8.10. The graph and the fitting are generated with the MatLab code in appendix D.3. The exponential is a good fitting curve indicating that by increasing the distance the transmission exponentially decay, as expected from theory (see chapter 2, section 2.3.7). This corresponds to the Simmons' model introduced in section



**Figure 8.9:** Device equilibrium transmission spectra with different molecule-contact distances: 2.7 Å, 3.0 Å, 3.3 Å, 3.6 Å, 4.0 Å, 5.4 Å (EHT method).

6.2, i.e. the coherent-short-molecule transport case. Notice that since incoherent transport was not considered, it is obvious that only coherent transport appears, with the usual exponential decay with distance. Nevertheless here the point in subtle: since by increasing the contact distances the transmission peaks, at least around 1 eV, decay exponentially, it means that there is a potential barrier between the contacts and the fullerene, that approximately is square (Simmons' model), that prevent a full transmission. The physical origin of such a barrier will be investigated in the nest section and it corresponds in a less hybridization and thus delocalization of electron wave-functions between the contacts and the fullerene as distance increase. If the task were to design a SET thus a suitable and enough large distance with contacts should be chosen, such that localized states allow for having a relevant charging effect and possibly Coulomb blockade. Nevertheless here the task is slightly different: the final goal is indeed to design and optimize the geometry such that the molecular wire behaves like a MES. This implies that of extreme importance is the ability of the sensor of modulating the channel conductance depending on the presence or not of the target, i.e. the ammonia, and this is the property above all the others to be considered in the design. Moreover in the optics of exploiting conventional electronic devices (CMOS or FinFET devices) to implement the conditioning circuit, the electrical current flowing in it, and even its variations due to the ammonia, should be enough large to make detectable the ammonia presence. In this regard, a short distance between the contacts and the  $C_{60}$  is desired.

Notice also that the performed exponential fitting at around 1 eV is a special case, indeed if one looks at the other transmission peaks recognizes that not always this is the rule. For example at around 0.3 eV the transmission peak for 2.7 Å is less than the one for 3.0 Å, and a greater shift occurs for different distances. Moreover the peak for 2.7 Å is



Figure 8.10: Device equilibrium transmission spectrum peaks at around 1 eV values and their interpolation with an exponential fitting curve. The different considered molecule-contact distances are: 2.7 Å, 3.0 Å, 3.3 Å, 3.6 Å, 4.0 Å, 5.4 Å (EHT method). On abscissa axis the distance between the fullerene and the contacts, on ordinate axis the transmission peak value (at 1 eV).

more broadened than the one for 3.0 Å. This indicates, as expected, a greater level of delocalization/hybridization, and the total transmission peak integral (centered in 0.3 eV) is anyway greater for 2.7 Å than for 3.0 Å. Thus the matter is far more complicated than the simple Simmons' model, even if it was useful in understanding the fact that there are barriers between the contacts and the molecule, and they are more thick if the distance is increased.

#### 8.3.2 Device orbitals (MPSH) and contacts distance

The results obtained previously regarding the DOS and the T(E) are well explained in therms of system orbitals. In this section I consider the so called Molecular Projected Self-Consistent Hamiltonian (MPSH), that corresponds essentially to a projection in the real space (thus a real space representation) of the Hamiltonian of the system, that is evaluated self-consistently. Notice that the molecular Hamiltonian is the quantum mechanical operator representing the total energy of the system, and its eigenvalues are the possible energy levels of the system under study. Instead its eigenstates are corresponding, in real space (i.e. when "projected" in real space), to iso-energetic surfaces (once the energy is fixed), i.e. to the molecular orbitals; where "orbital" indicates the electron cloud in which it is highly probable to find the electron, i.e. the squared magnitude of the system electron wave-function. In other words the MPSH can be achieved by projecting the self-consistent Hamiltonian onto the Hilbert space spanned by the basis functions of the atoms in the central scattering region [148], i.e. the C<sub>60</sub> molecule, eventually with leads. Notice also that the eigenstates of the MPSH are associated with the poles of the Green's function (section 5.5) and roughly correspond to the transmission peaks in the transmission spectrum [148]. The equilibrium MPSH were inspected for all the considered distances. I report here only few interesting cases to be compared in order to have an insight of the physics of the device. For a distance of 5.4 Å, reported in figure 8.11, the HOSO and LUSO MPSH are both extremely localized, the first around the contact only, the second around the fullerene only. This means that an applied bias can cause a current flow only if the electron are transmitted through a barrier, that has a thickness of the order of the contact-fullerene distance (actually less since the wave-functions envelope the atomic nuclei). This explain the extremely small transmission probability, since no other possibility of exchange of electrons between the molecule and the contact is possible. This is a weakly coupled case.

Instead in figure 8.12 the HOSO for a distance of 4 Å and for a distance of 3 Å are reported, while in figure 8.13 the LUSO for the same two distances are reported. At a distance of 4 Å the situation is already very different for the HOSO if compared to the 5.4 Å case. It presents indeed a better delocalization. Nevertheless decreasing the distance at 3 Å the delocalization is far more accentuated, explaining the larger broadening in the equilibrium transmission spectrum, and the greater current (see next section). The same happens for the LUSO level, that at 4 Å is merely delocalized while at 3 Å it is very delocalized, creating possible transmission channels between the two contacts without the necessity of changing state.

The MPSH analysis carried out in this section confirm the reasonable and intuitive result already highlighted in the previous section and further confirmed in the next ones: the closer are the contacts, the greater the delocalization, thus the broadening and thus the current.

As mentioned previously the criterion for selecting the contact distances in the case of a MES can be to maximize the sensitivity to the target analyte. It can be now intuited that if the system are more delocalized, i.e. if the distance between the  $C_{60}$  and the contacts is reduced, then they are more interacting with the ammonia, simply because they occupy a larger space region, leading to a more probable interaction between the sensor and the ammonia orbitals. Remember that interaction between orbitals is a so called steric effect. Actually the functioning principle is more complicated than this since all intermolecular interactions must be considered (i.e. also dipole-dipole interactions), but the fact that a greater region of space is occupied by the sensor orbitals implies a (slightly) larger interacting region, from the standpoint of electron clouds repulsion (van der Waals interactions). The analyses carried on in the next sections will confirm that the sensor sensitivity is indeed increased when the contact distances are reduced.

The other advantage of using closer contacts is that, as mentioned previously, they lead to a larger current, thus more "handy" with pretty conventional circuits, and thus avoiding complicated and ingenious architectural solutions. This can be relevant in the total cost and complexity of the final sensor with its conditioning circuit.



(a) HOSO





Figure 8.11: MPSH of the HOSO (Highest Occupied System Orbital) and the LUSO (Lowest Unoccupied System Orbital) of the  $C_{60}$  molecular wire with molecule-contact distances of 5.4 Å. The two colors (teal and fuchsia) are referred to the phase (negative or positive) of the MPSH. The figure was generated by ATK software [125], [126] (used for performing the simulations).



(a) 4 Å





Figure 8.12: MPSH of the HOSO (Highest Occupied System Orbital) of the  $C_{60}$  molecular wire with molecule-contact distances of 4Å and 3Å, respectively. The two colors (teal and fuchsia) are referred to the phase (negative or positive) of the MPSH. The figure was generated by ATK software [125], [126] (used for performing the simulations).



(a) 4 Å





Figure 8.13: MPSH of the LUSO (Lowest Unoccupied System Orbital) of the  $C_{60}$  molecular wire with molecule-contact distances of 4Å and 3Å, respectively. The two colors (teal and fuchsia) are referred to the phase (negative or positive) of the MPSH. The figure was generated by ATK software [125], [126] (used for performing the simulations).

#### 8.3.3 Physisorption, chemisorption and equilibrium distances

In section 7.1.1 the concepts of physisorption and chemisorption were introduced. Considering that the electrodes are gold (111) surfaces, such concepts can be useful in understanding the anchoring of the  $C_{60}$  molecule to the contacts. In literature there are theoretical DFT calculations [144] and experimental data [143] showing that the  $C_{60}$  can be adsorbed onto a gold (111) surface, and in particular, when it is allowed to relax, it is adsorbed by chemisorption with the creation of covalent bonds between the carbon and the contact gold atoms with a bond length of 2.4 Å (that corresponds to a gold-carbon perpendicular distance of about 1.8 Å) [144], [143]. Moreover in [143], it was experimentally verified that there are two more favourable orientations of the  $C_{60}$  w.r.t. gold surface when the chemisorption is completed. These consist of a  $C_{60}$  molecule with a hexagon side toward the gold surface centered in a vacancy (at the center of the hexagon there is a vacancy and not a gold atom) and a  $C_{60}$  molecule with a pentagon, i.e. carbon-carbon 6:6 bond, toward the gold surface. Between the two orientations the most stable is the first one [143], i.e. the one with an hexagon toward the gold surface (centered on a vacancy); and at room temperature the 60% of the  $C_{60}$  fullerenes were experimentally found to be in such a configuration. This is confirmed by theoretical DFT calculations on adsorption of fullerene  $C_{60}$  on gold (111) surface [144]. Such a geometry is shown in figure 8.14. This means that it has no much sense forcing a lesser distance than 2.4 Å since it would lead the  $C_{60}$ -gold wire to operate in an non-equilibrium condition, thus making easier to have geometry drift in time. Indeed if the system is not at equilibrium, it has a potential energy that is greater than the minimum one (by definition of equilibrium geometry/situation), that implies that a smaller amount of energy is enough for example to accomplish the fullerene desorption, or anyway a modification in the geometry. For this reason the minimum distance between  $C_{60}$  and contacts was fixed to 2.4 Å, being as experimentally and theoretically verified, the equilibrium chemisorption distance. Actually, I decided to consider initially two geometries, both at 2.4 Å. The first was a geometry in which the same casual orientation of before (previous sections) was considered for the  $C_{60}$ ; the second, a geometry with the above mentioned most stable configuration for chemisorption, i.e. the one with hexagons toward the gold (111) face. This choice was motivated by the fact that previously no special orientation of the fullerene was considered, and thus the same (non-special) orientation was still considered with the reduced contact- $C_{60}$  distance at 2.4 Å, in order to be sure that possible differences in the current and in the sensor sensitivity (see later) were only due to the contact- $C_{60}$  distance. Then the special orientation with hexagons toward the gold surface was considered, in order to verify possible variations in the current and in the sensor sensitivity due to the fullerene orientations. It was verified that the latter geometry is the one providing the best performances for the sensor both concerning the current (it was generally higher) and the sensitivity (it was higher on average). These results are further considered and commented in the next sections.

In figure 8.15 is reported the equilibrium transmission spectrum at all distances considered previously and also at 2.4 Å with both the casual and the hexagon on gold surfaces orientations. The comments are similar to the one already did previously: decreasing the distance the broadening increases, and generally peaks are less high and sharp, nevertheless leading to greater transmission since they are broadened. An interesting feature is that

the hexagons on gold surfaces orientation presents more broaden peaks w.r.t. the casual orientation one. This can be explained considering that in such a configuration strong covalent bonds are created, and thus a greater hybridization/delocalization of the wavefunctions occurs, leading to greater broadening. Moreover a small transmission peaks shift toward lower energies is present. It is believed to be linked to a small shift toward lower energies of the system energy levels due to a more stable configuration.



Figure 8.14: Equilibrium geometry for chemisorption with gold-carbon bond length of 2.4 Å, and with the hexagons on the gold surfaces. Top-left (a): the  $C_{60}$  orientation. Lighted up atoms are the ones of the first contact layer, notice that the fullerene hexagon is centered on a vacancy. Top-right (b): the distance of 2.4 Å is measured. Bottom-left (c): side view. Bottom-right (d): top view. The figure was generated by ATK software [125], [126] (used for performing the simulations).

#### 8.3.4 C<sub>60</sub> orientation and geometry optimization

From the discussion of the previous section it is evident that since the distance of 2.4 Å corresponds to the creation of covalent bonds, higher distances, like the others already considered, corresponds to a transition between chemisorption and physisorption and to



Figure 8.15: Device equilibrium transmission spectra with different molecule-contact distances: 2.4 Å (both with casual/non-special orientation and with the hexagons on gold surfaces one), 2.7 Å, 3.0 Å, 3.3 Å, 3.6 Å, 4.0 Å, 5.4 Å (EHT method).

the physisorption cases. Moreover as mentioned in section 7.1.1 both the chemisorption and the physisorption have an equilibrium distance. In particular from theoretical and experimental data in literature, namely [144], [143], the chemisorption equilibrium distance is 2.4 Å. In order to fast verify that, and in order to understand the order of magnitude of the physisorption equilibrium distance, the following geometry optimization calculations were performed. First of all, since the literature data were already very clear and detailed, it was not necessary to carry out a complete and accurate geometry optimization, but instead only a fast check. To this purpose, even if usually one should perform geometry optimization calculations with the same electronic structure calculation methods that wants to use for performing the rest of the simulations, I decided to perform the geometry optimization with the force field method in ATK. My choice was justified by the fact that the aim was not to carry out a complete and accurate calculation, but instead a fast, immediate check, of the well documented literature results [144], [143]. The geometry potential energy minimization calculations were performed with the default settings, using force field and allowing to relax the fullerene (carbon atoms) and the first two gold layers (per contact). For brevity I will not report here the images and figures generated, since they would be many (a video was realized for each simulation by putting together the various frames). Nevertheless the results were the following:

• For the initial geometry with distance 2.4 Å and with hexagons toward of gold surfaces a small relaxation of the geometry occurred. The electrodes resulted essentially unmodified, with only few covalent bonds among some gold atoms missing. This was in agreement with other calculations in literature [144]. The explanation of such missing bonds is the following: since the carbon atoms nearby the contacts create covalent chemical bonds with the gold surface atoms, the gold atoms are less bond
together, because electrons are involved in the other bonds [144]. This leads to have gold atoms drift in time at room temperature, as detected in [143]. The fullerene resulted just slightly distorted and also slightly rotated on one side. This is again in agree with previous calculations [144] and experimental data [143]. In conclusion this geometry resulted to be stable, with a verification with force field method. Since the distortion of the fullerene was very small (let's say less than 10% of perturbation w.r.t. the initial geometry) I decided in the following to consider the initial ideal geometry. Indeed, in theory one should optimize the geometry using the same method that is used for the other calculations, and possibly with a good accuracy. Nevertheless on the VLSI server it was not possible to perform DFT geometry optimization due to RAM failure. For this reason I decided to do not rely on the force field method and considering the (ideal) initial geometry. Moreover also in [143] it was verified that such a geometry leads to just small distortions of the fullerene, and assuming it undistorted should not compromise the final results of this study.

- For the initial geometry with distance 2.4 Å and with casual orientation, the fullerene resulted very distorted. It rotated strongly and resulted deformed (like a rugby ball). Moreover on one side the molecule resulted closer to the contact while on the other side more distant, at around 3.0 Å. This is not expected to be an equilibrium geometry.
- For all the other distances the results were similar to the previous one, but less evident. In particular an important rotation of the fullerene always occurred. It resulted evidently distorted (like a rugby ball). Moreover it drifted toward one of the contacts leaving a greater distance on the other side. The more was the initial distance between the fullerene and the contacts the less evident was this fact. It seemed to be an equilibrium distance for physisorption of the fullerene on gold (111). Nevertheless more accurate calculations should be performed to confirm this.

In conclusion, the geometry optimization with the force field method confirmed that the most stable configuration, among the various considered in this work, was the one with chemisorption, bond length 2.4 Å, hexagons toward gold surface. All the other configurations resulted less stable. In particular a C<sub>60</sub>-contact distance of about 3.07 Å resulted to likely be another stable point, even if less stable than the above mentioned one (indeed major modifications occurred in the geometry in such a case). In the following sections, in addition to the previously considered distances also the 2.4 Å distance will be considered, and for that distance both the casual orientation of the fullerene and the one with hexagons on gold surfaces will be considered. The first one to verify that possible current/transmission variations and sensitivity variations were due to distance only (indeed this orientation is equal to the others considered previously); the latter to verify if any variation/amelioration occurs when the most stable orientations is considered.

### 8.3.5 *I-V* characteristic and contact distance

The current voltage characteristics with the different contact distances considered previously are reported in figure 8.16. Notice that in appendix D.4 it is reported also a plot with the I-V characteristic of the two orientations of the fullerene for 2.4 Å. They are evaluated using the EHT method, indeed it was not possible to carry out non-equilibrium calculations using DFT methods. In this regard see also section 8.5. The ATK settings used to perform these simulations are reported in table 8.5.

 Table 8.5: ATK-SE (EHT) non-equilibrium I-V characteristics calculator settings. If not differently stated, all the non-equilibrium I-V characteristic simulations were performed with these settings.

	Analysis: IV-curve
Voltage bias	$V_0 = 0 \text{ V}, V_1 = 2 \text{ V},$
range	Points = 11
Energy	$E_0 = -2 \text{ eV}, E_1 = 2 \text{ eV},$
range	Points=101
k-point	Grid type: Monkhorst-Pack
density	$n_a = 7, n_b = 7$
Energy zero	Avorago Formi lovol
parameter	Average Ferlin lever
Infinitesimal	1e-06 eV
Self-energy	Pogursion
calculator	Recuision

As expected, the current increases if the distance between the  $C_{60}$  and the contacts is decreased. This was already clear from the equilibrium analysis performed in the previous sections on the transmission spectra and the MPSH. The reason for that is expected to be in the barriers electrons have to overcome between the contacts and the fullerene.

In order to verify if the current dependence with the contact distances were exponential, as it could be for coherent tunneling through potential barriers (Simmons' model), the current values at fixed voltage values for the different considered distances were interpolated with the exponential function of eq. (8.1). Also the case of 2.4 Å was considered, nevertheless only the casual orientation was considered in order to compare it with the other distance cases (that indeed have casual/non-special orientation). The result for  $V_D = 1 \text{ V}$  is reported in figure 8.17, while the results for  $V_D = 0.4 \text{ V}$  and  $V_D = 1.6 \text{ V}$ are reported in appendix D.4. The calculations were performed (and the figures were generated) with a MatLab code analogous to the one of appendix D.3 (with just different numerical values to be interpolated). In all the three cases the current showed a clear exponential dependence on distances with contacts, thus confirming that in the coherent transport regime the main obstacles to conduction are the barriers between the contacts and the fullerene. This is reasonable by considering the great delocalization of fullerene orbitals (see also MPSH), that indeed allow electrons to move freely across the fullerene, thus being no a relevant obstacle to conduction. Of course depending on the considered molecules other situations are possible. The important point is that, since the exponential



**Figure 8.16:** Current-voltage (*I-V*) characteristics for the various considered distances between the contacts and the C<sub>60</sub> fullerene: 2.4 Å (both with casual/non-special orientation and with the hexagons on gold surfaces one), 2.7 Å, 3.0 Å, 3.3 Å, 3.6 Å, 4.0 Å, 5.4 Å (EHT method).

dependence of the current on the contact distance, the main design parameter for the  $C_{60}$ -based MES is exactly such a distance, because it is the "bottleneck" determining the main transport features. As long as the channel is a single  $C_{60}$  molecule, the main design degree of freedom strongly determining the transport is indeed such a distance. This justifies the great attention in fixing it.

For the sake of completeness the analysis was then extended to all the considered bias points from 0 V to 2 V, the result is reported in figure 8.18. If the bias point is fixed the independent variable is only one, namely the distance between the fullerene and the contacts. But since here the bias is made varying, the independent variables are two: the contacts distance and the bias voltage, thus leading to a surface plot in a 3D plot, like in figure 8.18. The red dots are the simulated points while the surface it created by merging the interpolating curves at all the considered bias. The general trend for all the voltages is again exponential, decaying fast as the contacts distance is increased. In appendix D.4, figure D.21, is reported the same graph of figure 8.18 with voltages only up to 0.8 V, in order to enlarge that region and highlight the good exponential trend for all the bias point. This is an additional confirmation of what stated above. The *MatLab* code generating such 3D plots is reported in appendix D.4.1.

#### 8.3.6 Geometry for maximum sensitivity

As mentioned in the previous sections an important criterion for the choice of the final geometry of the MES is the sensitivity to ammonia. In this optics, the distance that maximizes the sensor sensitivity to the target (ammonia), if there is one, should be preferred. Indeed it would be the best case, in which a larger current modulations occur





Figure 8.17: Dependence of current values on the distance between the fullerene and the contacts for a fixed voltage:  $V_D = 1$  V. The exponential fitting performs well. Top: linear scale, bottom: semilogarithm scale.

due to the presence (and possibly in which concentration) or not of the target. In order to check if there is and what is the geometry with maximum sensitivity to the ammonia, the *I-V* characteristics in presence of 1, 3 and 5 NH<sub>3</sub> molecules were calculated with EHT method (in section 8.5 is reported the reason of this choice - the settings are the same of table 8.5). By way of example, in figure 8.19 are reported the *I-V* characteristics for the case of a distance of 2.7 Å. It is noticeable a variation depending on the concentration of ammonia, i.e. on the number of ammonia molecules.

 $C_{60}$ -based ammonia gas sensor



Figure 8.18: Device current as a function of the applied voltage and the contacts distance. Red dots are the simulated points, while the surface corresponds to the exponential interpolation. Purple dots are those below the semi-transparent surface. A general good agreement is present (EHT method).



Figure 8.19: Current-voltage (I-V) characteristics for distances between the contacts and the C<sub>60</sub> fullerene of 2.7 Å; the cases with 0, 1, 3, and 5 NH<sub>3</sub> molecules are considered (EHT method).

In order to compare the various geometries/distances with contacts, the absolute variations  $|\Delta I_D|$  defined as:

$$|\Delta I_D(V_D)| = | (I_D(V_D)|_{ammonia} - I_D(V_D)|_{only fullerene}) |$$

were evaluated, for all the bias points  $V_D$ , for all the distances and for all the concentrations.

In figure 8.20 are reported the absolute variations in  $\mu$ A for the case of 2.7 Å of distance between the contacts and the fullerene. The other graphs for the other considered distances are reported in appendix D.4. In figure 8.21 the interpolated *I-V* characteristics and the interpolated absolute variation  $|\Delta I_D|$  are reported. They are obtained by spline (3<sup>rd</sup> order cubic) interpolation of the previous plots.



Figure 8.20: Absolute variations of current due to the presence of 1, 3, 5 NH<sub>3</sub> molecules, for distances between the contacts and the  $C_{60}$  fullerene of 2.7 Å (EHT method).

A good current variation and sensitivity is present, but it depends strongly on the considered bias point. For example at  $V_D = 0.8$  V, the variations of current in presence of ammonia are: 147 nA for 1 NH<sub>3</sub> molecule, 0.83 µA for 3 NH<sub>3</sub> molecules and 1.17 µA for 5 NH<sub>3</sub> molecules. It is thus possible to detect this variations with a suitable conditioning circuit. Instead for example at  $V_D = 1$  V the variations of current are very small, making very hard the detection. For  $V_D = 1.8$  V the variations are: 1.59 µA for 1 NH<sub>3</sub> molecule, 2.53 µA for 3 NH<sub>3</sub> molecules, and 3.28 µA for 5 NH<sub>3</sub>. These variations are detectable with quite conventional electronics, thus making possible a low-cost detection. In general for all the considered distances (see also plots in appendix D.4), there are bias points in which the current variations are greater, thus making easier the detection, and others in which this do not occur. Nevertheless the variations are not so abrupt, so it is possible to think of selecting a suitable bias point to get the desired current variation without having problems due to the bias point drift. This is important, indeed it is the first (non-equilibrium) confirmation that the ammonia C<sub>60</sub>-based sensor can potentially work, with a quite standard and low-cost conditioning circuit.

From the current modulation analysis it was clear that, in general, by decreasing the distance the sensitivity is increased, indeed greater absolute variations of currents occurred. This result is in contrast to what stated and assumed in [33], in which the authors assumed for grant that the sensor sensitivity was increased for increasing distances with contacts.





Figure 8.21: Top (a): Interpolated current-voltage (I-V) characteristics for distances between the contacts and the C<sub>60</sub> fullerene of 2.7 Å; the cases with 0, 1, 3, and 5 NH<sub>3</sub> molecules are considered (EHT method). Bottom (b): Interpolated absolute variations of current due to the presence of 1, 3, 5 NH<sub>3</sub> molecules, for distances between the contacts and the C<sub>60</sub> fullerene of 2.7 Å (EHT method).

Nevertheless they based their statement on literature studies that are performed on 1D/2D-FET devices used as gas sensor. In 2D devices it is intuitive thinking that by increasing the distance between the two contact the sensitivity increases, indeed in doing so it is increased the interaction surface with the target chemical species (think to a sheet that in lengthened,

its area increases). Nevertheless, it is not said that a molecular device undergoes to the same rule. And in particular in this case, the simulations performed showed the opposite trend: i.e. the absolute sensitivity decreased when the distance was increased. In order to have a concise and overall vision of the final result of this analysis the graph of figure 8.22 was conceived. In this plot the number of ammonia NH<sub>3</sub> molecules considered is on the abscissa axis, it is 1, 3, or 5. On the ordinate axis there is the overall absolute variation of current  $|\Delta I_D|$ , averaged over all the considered bias points in the range [0,2] V. It is evident that the more the distance is decreased the larger is the current variation, and thus the absolute sensor sensitivity is increased. A relevant improvement occurs between the 2.7 Å distance case and the 2.4 Å case, and a further unexpected improvement if the chemisorption orientation of the C<sub>60</sub> is considered (blue line). Indeed a significant and very important improvement of the absolute average sensitivity is obtained by simply rotating the fullerene in its favoured orientation.



Figure 8.22: Mean absolute variations of current, averaged over the range [0,2] V of applied voltage, due to the presence of 1, 3, 5 NH<sub>3</sub> molecules, for all the considered distances between the contacts and the C<sub>60</sub> fullerene (EHT method).

In order to have a deeper insight on how the sensitivity changes with the contact distances and with the  $C_{60}$  orientation the case of a single ammonia molecule was considered at all distances. In figure 8.23 are reported the various absolute variations of current for all the distances, and for the chemisorption equilibrium orientation of the fullerene. Even if the the differences among the various cases are well marked at high bias, above 1 V, this is not so at low bias, below 1 V. In the latter range of voltages there is still the trend of increasing sensitivity for decreasing the distance, but it is less evident and above all the case of chemisorbed  $C_{60}$  fullerene (black dashed curve) corresponds to an average less sensitivity w.r.t. the casual orientation. In addition at bias 0.4 V and 0.8 V it is less favourable than larger distances. Notice that analogous plots for the cases of 3 and 5 ammonia molecules are reported in appendix D.4, analogous considerations hold true, even if an amelioration of the chemisorbed geometry performances is present.



C60 wire sensor (EHT method):  $|\Delta I^{}_{\rm D}|$  in the case of 1 NH3 molecule

Figure 8.23: Absolute variations of current due to the presence of  $1 \text{ NH}_3$  molecule, for all the considered distances between the contacts and the C<sub>60</sub> fullerene (EHT method).

So, to check the "low-bias" sensitivity average variation w.r.t. contact distances and  $C_{60}$  orientation a graph similar to the one of figure 8.22 was conceived, in which the averages are considered only on the bias range [0,1] V. It is reported in figure 8.24. It shows again that in general the sensor sensitivity to ammonia is increased if the contact distances are reduced. Nevertheless in the bias rang [0,1] V the highest average sensitivity is obtained with a casual orientation of the fullerene, instead than with the chemisorption equilibrium orientation. An intuitive explanation for this (to be confirmed by calculations) can be the following: since in the chemisorption equilibrium position some electrons of the fullerene are involved in forming covalent bonds with the gold, they do not interact much with the ammonia, moreover the  $C_{60}$  orbital orientation can be relevant in determining the magnitude of interaction with the ammonia. These suppositions can only be confirmed by means of analysis of the transmission channels and the MPSH. Nevertheless for the moment this was not carried out (see later for an example of this kind of analysis).

The main point here is that decreasing the distance the absolute variation of current due to the presence of ammonia is increased. In the overall interval [0,2] V of applied voltages the maximum average sensitivity is obtained by means of the chemisorbed geometry at a distance of 2.4 Å and with hexagons toward gold surfaces. An extremely high improvement of the sensitivity occurs for that geometry especially at high bias, for  $V_D > 1$  V, as evident from the graph of figure 8.23. Instead in the range [0,1] V of applied bias the same geometry provides best sensitivity for  $V_D = 0.2$  V and for  $V_D = 0.6$  V (in the latter case comparable with the casual orientation at same contact distance). These two bias point are thus optimal bias points for doing a sensor working at low bias ( $V_D < 1$  V) with such a geometry, that has also the advantage of being the equilibrium one. The same geometry provides best sensitivity for  $V_D > 1$  V. Nevertheless it is lacking of performances in other bias values especially below 1 V, e.g. for  $V_D = 0.4$  V and  $V_D = 0.8$  V, where other geometries present better performances. In addition the configuration with casual orientation (and a distance of 2.4 Å) provides best average performances over all the others for  $V_D < 1$  V. Notice that analogous analysis carried on the 3 and 5 NH<sub>3</sub> molecule cases, showed an amelioration of the chemisorbed geometry sensitivity for  $V_D < 1$  V (see appendix D.4).



Figure 8.24: Mean absolute variations of current, averaged over the range [0,1] V of applied voltage, due to the presence of 1, 3, 5 NH<sub>3</sub> molecules, for all the considered distances between the contacts and the C<sub>60</sub> fullerene (EHT method).

An additional analysis was performed before choosing the final sensor geometry. It was said at the beginning of this section that the current exponentially decreases with contact distances, and the same trend was verified for the sensor sensitivity. For this reason the percentage variations of current were also considered. In particular a percentage variation was calculated as (in each bias point  $V_D$ ):

$$|\Delta I_D(V_D)| = \frac{|(I_D(V_D)|_{ammonia} - I_D(V_D)|_{only fullerene})|}{I_D(V_D)|_{only fullerene}} \cdot 100$$

The general and average trends (averaged over the entire bias range: [0,2] V) for the percentage variations of current are reported in figure 8.25. It is clear that beside the absolute variations of current due to ammonia increase by decreasing the contact distances, the percentage ones decrease. Therefore the percentage variation of current is greater for larger contact distances. The average percentage values are also reported in table 8.6. Notice that in this analysis, like in the previous one, the distances above 3.6 Å were not considered, since they would lead to a too small current to be reliably used with a conditioning circuit supposed to be implemented with conventional electronic devices. In order to have a significant improvement, i.e. greater than around 2%, of the percentage current variations, a contact distance greater than 3.0 Å should be considered. In the hypothesis of exploiting conventional electronic devices for the conditioning circuit the distances of 4 Å and 5.4 Å were not considered since they would lead to a too small current value. Thus the only two possible distance would be 3.3 Å and 3.6 Å. Nevertheless it must



Figure 8.25: Mean percentage variations of current, averaged over the range [0,2] V of applied voltage, due to the presence of 1, 3, 5 NH<sub>3</sub> molecules, for all the considered distances between the contacts and the C<sub>60</sub> fullerene (EHT method).

**Table 8.6:** Mean percentage current variation values, averaged over the range [0,2] V of applied voltage, due to the presence of 1, 3, 5 NH<sub>3</sub> molecules, for all the considered distances between the contacts and the C<sub>60</sub> fullerene (EHT method).

distance	$ \Delta I_D _{\%} (1 \text{ NH}_3)$	$ \Delta I_D _{\%} (3 \text{ NH}_3)$	$ \Delta I_D _{\%} (3 \text{ NH}_3)$
2.4 Å (hex)	7.85~%	9.56~%	9.99~%
2.4 Å (casual)	5.83~%	8.39~%	11.82~%
2.7 Å	7.94 %	11.52~%	16.44~%
3.0 Å	11.75~%	18.31~%	29.25~%
3.3 Å	32.11 %	41.39~%	45.34~%
3.6 Å	103.72~%	45.34~%	56.65~%

be considered that the current decreases exponentially with contact distance and thus such a large percentage variations corresponds to absolute variations of the current of the order of  $0.2 \,\mu\text{A} \div 0.4 \,\mu\text{A}$  (see figures 8.22 and 8.24), that are less than half the current variation at 2.4 Å (of the order of  $1 \,\mu\text{A} \div 2 \,\mu\text{A}$ ). The latter are thus much easily recognizable by a conditioning circuit. In addition to these considerations also what discussed in section 8.3.4 must be considered. It is indeed an enormous advantage to have an equilibrium geometry preventing the system to time drift due to relaxation. This means that if an energy exchange occurs for some reason, it is very unlikely that the device geometry is significantly perturbed. Moreover there is an higher probability of obtaining the desired geometry during the fabrication. Indeed as mentioned in the introductory chapter, process variations are at the moment the main limits in successful fabrication of such devices, since they are responsible of the low fabrication yield.

#### 8.3.7 The final $C_{60}$ -wire geometry

In conclusion, it was chosen to fix the sensor geometry to a contact-fullerene distance of 2.4 Å, with the fullerene hexagons on gold surfaces. This configuration, beside the above mentioned drawbacks has the advantage of maximizing the absolute (but not the percentage) sensitivity to ammonia and above all to be the most stable configuration, leading to higher expected reliability from technological standpoint. In addition it provides enough large current to be easily interfaced with conventional electronic devices supposed to implementing the conditioning circuit. This is not the only possible choice, and depending on the specifications, after the analysis performed in this section, one could choose another structure having better performances for that specific interest.

## 8.4 Equilibrium properties of the final $C_{60}$ -wire sensor

At the end of the previous section it was chosen the final  $C_{60}$ -based gas sensor geometry, and it corresponds to a distance between the contacts and the fullerene of 2.4 Å and to an orientation of the fullerene such that its hexagonal faces are pointed toward the electrodes surfaces and centered on a gold vacancy. This geometry is a good trade-off between stability and ammonia sensitivity as mentioned previously. In this section the equilibrium properties of such a system are considered and briefly analyzed. The equilibrium transmission spectrum for different ammonia concentrations is reported in figures 8.26 (DFT method) and 8.27 (EHT method). The two methods provide a compatible picture of the transmission properties of the sensor. With both the methods there are differences in the transmission peaks due to the presence of ammonia and also with different ammonia concentrations. This feature is expected to hold true also in non-equilibrium, i.e. for the *I-V* characteristics and their sensitivity to ammonia were already investigated for all the considered geometries, and in particular also for the selected one.

In appendix D.5 is reported also a comparison between equilibrium transmission spectra (without the ammonia) calculated with both the methods (DFT and EHT). The DOS are not reported for brevity, nevertheless they present differences, but as reported previously for the case of the initial 2.7 Å geometry, it is difficult to have precise insight by looking at them, while the aforementioned and commented equilibrium spectra provide. Notice also that, in the approximation of having a rigid T(E) independent on applied bias, from the equilibrium transmission spectrum of figure 8.27, it is possible to predict a good ammonia sensitivity due to significant transmission spectrum peak modulations at:

- low bias, slightly above the zero, due to zero-centered transmission peak modulation. In the next section it will be clear that this is the reason for the sensitivity local maximum at  $V_D = 0.2$  V.
- greater biases, sensitivity oscillations are probable since there is, at right-side of the zero, a sequence of peaks that are modulated and then spaced by low transmission values. In the next section it will be clear that this is the reason for the sensitivity

local maximums at  $V_D = 0.8 \text{ V}$  and  $V_D = 1.2 \text{ V}$ .

• bias around 2 V for which the left-side very modulated peaks at around -0.8 eV enter the bias window. This will be confirmed in the next section.



Figure 8.26: Equilibrium transmission spectra of the final ammonia sensor geometry, in the cases of 1, 3, 5 NH<sub>3</sub> molecules (DFT method).



Figure 8.27: Equilibrium transmission spectra of the final ammonia sensor geometry, in the cases of 1, 3, 5 NH<sub>3</sub> molecules (EHT method).

### 8.5 EHT non-equilibium calculations validation

It was said several times throughout the chapter 3 and also in highlighting the general methodology in section 7.2, that the usage of semi-empirical methods, such as EHT one, should be somehow validated. Unfortunately during this work it was not possible to carry out non-equilibrium simulations with the DFT method, due to a RAM failure on the VLSI laboratory server (at Politecnico di Torino) in which all simulations were performed (even with settings aimed in saving memory during execution). For this reason all the non-equilibrium simulations, such as the I-V characteristics, reported in the present work are performed by using the EHT methods. Nevertheless, in general, it not said such a method to be reliable, especially in presence of intermolecular interactions (see section 3.7). For this reason the non-equilibrium simulations with EHT method should be somehow validated, and this is the attempt of this section.

In general the transmission spectrum T(E) is a function of the applied bias, nevertheless if the applied bias is small it can be at first approximation assumed to be voltage-independent (sections 4.4, 5.15.1). In the reasoning carried out in this section the following assumption was made: the transmission spectrum T(E) does not undergo to substantial variation w.r.t. equilibrium when a bias is applied. As mentioned, the smaller the bias, the better this approximation is. Then, since only coherent transport is considered, the drain current can be calculated by means of the Landauer's formula eq. (5.75); that is: the current is proportional to the integral within the bias window of the transmission spectrum. Another assumption that was made is the following: the Fermi-Dirac's distribution "tails" are inessential and thus neglected; that is: the integrals are evaluated between the drain and the source Fermi levels without considering the thermal broadening/spreading over energy of the Fermi-Dirac's functions.

With these approximations in mind a measure of the accuracy of the non-equilibrium EHT simulations w.r.t. (expected) DFT ones can be estimated as follows. Different bias windows are considered, for example with a step of 0.1 V, i.e.  $V_D=0, 0.1, 0.2, 0.3, \dots$  (V). Then for each considered bias window the integrals, with and without ammonia molecules, and with both the DFT and the EHT methods were considered. Then the difference in such integrals were considered, i.e. the integral over the considered bias window of the DFT transmission spectrum without ammonia was subtracted to the integral over the same bias window of the DFT transmission spectrum with one  $NH_3$  molecule, and so on for each bias window. The same was did for the EHT method. The results of such a differences are reported in figure 8.28, for the case of  $1 \text{ NH}_3$  molecules. The cases of 3 and 5 ammonia molecules are reported in appendix D.6. On the abscissa axis, in this plots, there is the applied voltage, i.e. the bias window width. Instead on the ordinate axis the previously mentioned differences of the integrals over that bias window are reported. A curve (blue) is referred to DFT method, while the other (red/orange) is referred to EHT method. The integrals were performed with trapezoidal numerical method in MatLab, over the bias windows from  $0.1 \,\mathrm{V}$  to  $4 \,\mathrm{V}$  with a step of  $0.1 \,\mathrm{V}$ . The bias windows of interest (in the range [0,2] V) are highlighted with the black ellipsoid. In appendix D.6 is reported the used *MatLab* code.



Figure 8.28: Integral difference of the final ammonia sensor equilibrium transmission spectra in the cases of 1 NH<sub>3</sub> molecule. The results obtained with the two methods: DFT (blue curve) and EHT (red/orange curve) are compared. The ellipse is around the considered range of bias windows, i.e. up to 2 V. The integrals were performed with trapezoidal numerical method in *MatLab*, over the bias windows from 0.1 V to 4 V with a step of 0.1 V.

Two are the important results of this analysis:

- 1. The DFT spectrum differences (blue curve) are always greater than the EHT ones. This means that the non-equilibrium EHT simulations are expected to be all an underestimation of the real sensor sensitivity. This fact is likely intimately linked to the fact that EHT method does not explicitly account for intermolecular interaction, like the DFT instead does (remember that Grimme DFT-D2 correction was used). Despite of this also the EHT method is able to capable differences due to the presence of ammonia, but they are expected to be less evident than the actual ones.
- 2. There are some values of bias voltage for which the two methods are expected to provide very close non-equilibrium values. For example with reference to the figure 8.28 this happens for  $V_D$  of the order of 0.2 V, 1.4 V, and 1.8 V. This can be a good criterion of choice for the bias point. In particular if there is a bias point for which the sensor has a good sensitivity to ammonia, and moreover DFT non-equilibrium results are expected to be in agreement with the EHT ones, then it is expected the EHT previsions to be accurate, or close to reality. Notice that since this analysis was based on the assumption of having a bias independent T(E), and this is good only for small biases.

In conclusion, it is meaningful considering EHT simulations for the non-equilibrium case, with in mind the two important remarks (1.) and (2.) of above. In particular the aforementioned remarks are useful in determining an operating bias point for the MES.

## 8.6 Non-equilibrium properties and *I-V* characteristics

The *I-V* characteristics obtained for the final sensor geometry, with 0, 1, 3, 5 ammonia molecules, are plotted in figure 8.29 (a) together with their spline ( $3^{rd}$  order cubic) interpolations (b). The corresponding absolute differences in current, evaluated as previously explained, are instead reported in figure 8.30 (a), together with their spline ( $3^{rd}$  order cubic) interpolation (b).

Considering the previous remarks about the choice of bias point, see previous section 8.5, a very good candidate can be  $V_D = 0.2$  V. Indeed it is enough small to ensure as a first approximation a T(E) independent on the bias, and thus, accordingly to figure 8.28 a good correspondence between EHT and DFT method. Other possibilities, according to figure 8.30 can be voltages above 1.4 V, where, especially for the case of a single ammonia molecule there is an high sensitivity of the sensor to ammonia. Noticing that in the graph of figure 8.28 it is expected having an actual sensitivity (DFT) greater than the predicted one by the EHT, also other bias points could be very likely appropriate. Nevertheless from the EHT analysis it could be very hard quantifying exactly the actual entity of the real current variations. This is the reason why I mentioned that the 0.2 V can be instead a good choice.

In order to choose the bias point, also the sensor selectivity should be considered. Indeed in this way it is possible to choose a bias voltage such that the ammonia sensitivity is maximized and at the same time the sensor sensitivity to other atmospheric gases is minimized. This kind of analysis is carried out in the next sections. Nevertheless I anticipate since now that such a selectivity and specificity analysis will show a failure in the ammonia  $C_{60}$  sensor, revealing that it is equally sensitive to ammonia and other atmospheric gases.

 $C_{60}$ -based ammonia gas sensor





Figure 8.29: Top (a): Current-voltage characteristics for the final sensor geometry, the cases with 0, 1, 3, and 5 NH<sub>3</sub> molecules are considered (EHT method). Bottom (b): Interpolated (cubic spline) current-voltage characteristics for the final sensor geometry, the cases with 0, 1, 3, and 5 NH<sub>3</sub> molecules are considered (EHT method).





Figure 8.30: Top (a): Absolute current variations for the final sensor geometry, the cases with 0, 1, 3, and 5 NH<sub>3</sub> molecules are considered (EHT method). Bottom (b): Interpolated (cubic spline) absolute current variations for the final sensor geometry, the cases with 0, 1, 3, and 5 NH<sub>3</sub> molecules are considered (EHT method).

### 8.6.1 Sensitivity to different NH<sub>3</sub> orientations

Intermolecular interactions (see section 3.7) are supposed to be at the basis of the working principle of the considered MES. Nevertheless they are anisotropic interactions, i.e. they depend on the relative orientation of the two considered molecules, namely the  $C_{60}$  channel and the ammonia NH<sub>3</sub>. In order to verify this and to quantify (within the EHT method limits) such anisotropy, the following simulations were performed. The ammonia is a polar molecule, with the nitrogen more electronegative if compared to hydorgens. This implies an electron orbital/cloud shifted toward the nitrogen, that is: on average the electrons will

spend more time close to the nitrogen atom than close to hydrogen atoms [107], [108]. For this reason a small negative charge  $\delta^-$  arises nearby nitrogen and small positive charges  $\delta^+$ arise nearby the hydrogens. This makes the NH<sub>3</sub> molecule polar, and this fact can affect the transport through the sensor, since it will cause different electron orbitals interactions. In particular intermolecular and steric effects (arising from the repulsive forces between electron clouds/charges) can be significantly dependent on the orientation of ammonia molecule. This is exactly what happens leading to slightly different responses, as evident in figure 8.31, where the *I-V* characteristics of the sensor with two different ammonia orientations are reported in terms of current (a) and absolute current variations (b) . In this case the absolute variations were not assumed in magnitude, in order to highlight if the current is increased of decreased depending on the orientation of ammonia. The current variations are thus evaluated accordingly with the following formula:

$$\Delta I_D(V_D) = I_D(V_D)|_{ammonia} - I_D(V_D)|_{only\ fullerene}$$
(8.2)

thus a positive  $\Delta I_D$  indicates an increased current w.r.t. the case with no ammonia, and vice versa a negative  $\Delta I_D$  current indicates a decreased current. Notice that at low bias, i.e. for  $V_D < 1 \,\mathrm{V}$  the two orientations lead to different trends in the current. In particular in the case of nitrogen atom pointing down toward the fullerene the current is decreased, while in the case of hydrogens pointing down toward the fullerene it is increased. An intuitive explanation for this can be that due to the repulsive forces occurring in the first case (N down) the fullerene electron clouds are displaced (flattened), thus probably reducing the transmission due to transmission channel inhibition (like a bottleneck due to repulsive force between electrons and the negative N charge). Vice versa the hydrogen positive charge attract the fullerene orbitals thus making probable an enhancement of transmission channels. This hypothesis nevertheless is obviously too simple, indeed it does not explain at all the great increased of current obtained for high bias,  $V_d > 1$  V. Notice that it is not said a priori that for this range EHT simulations are accurate, indeed the bias is already enough large to possibly make non-valid the analysis of section 8.5. More precise DFT-based calculations can be thus necessary to have accurate result at high bias. Nevertheless the above reported intuition seems reasonable. But it necessitates of a more quantitative verification, for example by means of non-equilibrium MPSH analysis, carried out together with transmission eigenstates analysis, in order to identify the orbitals responsible of conduction and how the ammonia modifies the transmission channels thus changing the conductance. Nevertheless for the moment this analysis is not performed. The reason is that for the moment the interest is above all in determining the sensor performances in terms of selectivity and specificity, and not to gain physical insight/intuitions on the sensor behavior. The selectivity will be investigated in the next section.





Figure 8.31: Top (a): Current-voltage characteristics for the final sensor geometry, two different ammonia orientations are considered, namely the one with nitrogen N down pointing toward the fullerene, and the one in which the hydrogen atoms H are down pointing toward the fullerene (EHT method). Bottom (b): Absolute current variations with sign are considered for the same two cases (EHT method).

## 8.6.2 Selectivity to common atmospheric gases: the $C_{60}$ ammonia gas sensor failure

An extremely important feature for a MES is its selectivity or specificity, i.e. if it responds, at least in some conditions (e.g. for certain bias points) exclusively or in a well recognizable way only to the target chemical species. In order to verify the  $C_{60}$  fullerene gas sensor selectivity to ammonia, various non-equilibrium *I-V* characteristics were evaluated by placing around the sensor molecules composing the Earth atmosphere.

The main components of the Earth atmosphere are reported in table 8.7 along with their percentage [149] and indications concerning their polarity [107], [108]. In the following only  $N_2$ ,  $O_2$ , Ar,  $CO_2$  will be considered since representing the great majority of the total atmosphere. Table 8.7 considers dry air, in addition humidity (H<sub>2</sub>O) can be present and for this reason it is considered. Moreover other pollutants will be considered later in this work (CO, NO, NO<sub>2</sub>, C<sub>4</sub>H<sub>1</sub>0, PbO, PbCl<sub>2</sub>, PbSO<sub>4</sub>, etc...).

constituent	percentage	polar
N <sub>2</sub>	$\sim 78~\%$	no
$O_2$	$\sim 21 \%$	no
Ar	$\sim 1 \%$	no
$\rm CO_2$	$\sim 0.04~\%$	no
Ne	$\sim 0.001818~\%$	no
He	$\sim 0.000524~\%$	no
$CH_4$	$\sim 0.00018~\%$	no
Kr	$\sim 0.000114 \ \%$	no
H <sub>2</sub>	$\sim 0.000055~\%$	no
H <sub>2</sub> O	-	yes

 Table 8.7:
 Major atmosphere constituents.

Non-polar molecules present a uniform (or better isotropic) distribution of the electron clouds around their nuclei, so that they are neutral and no electric charge arise. For these molecules it not necessary (at least as first analysis) to perform simulations with different orientations, since they are, indeed, isotropic. Instead molecules like water (water vapor) are polar. In water the oxygen is more electronegative than hydrogen and thus a slightly negative charge appears close to it, since electrons will "spend" on average more time nearby it. Consequently a slightly positive charge arises around hydrogens. For polar molecule it is better to verify the changes in the I-V characteristics with different orientations, similarly to what did previously for the ammonia. Indeed in general convective motions of air particles can move the molecules and thus in different moments such molecules can be nearby the sensor with different orientations. It can be also possible to perform an adsorption study of such molecules, in order to understand what are the possible configurations of equilibrium, that will appear if attractive forces will start the adsorption process (see section 7.1.1). Nevertheless for the moment this analysis is not believed necessary, since as said before it may happen that various molecules in various time instants come close the sensor with casual orientation and with so high kinetic energy that no adsorption occur.

Before going on, notice that in general molecules made by atoms from different elements are polar, because the different elements will have different electronegativity. Nevertheless in practice some can be non-polar. For example the CO molecule is practically non-polar. Indeed even if oxygen attracts electrons more, there is a sort of compensation mechanism, leading to a negligible electric dipole. CO is a diatomic linear molecule, and a sigma bond ( $\sigma$ -bond) is present (lower energy level/orbital - see [107], [108]). This sigma orbital is polarized toward oxygen, thus leading to a slightly negative charge at oxygen side. Nevertheless there are still two valence electrons in oxygen that are not involved in such chemical bond. They both participate in creating a  $\pi$ -bond, that is more delocalized w.r.t. sigma one (that occupies the axis between the two nuclei mainly). Because of electrons repulsion (i.e. correlation) between the  $\sigma$ -bond electron cloud and the  $\pi$ -bond (it is a steric effect) the  $\pi$ -bond is shifted more toward the carbon, thus compensating for the dipole momentum, that in many practical applications is at all negligible [107], [108]. A similar mechanism occurs also in CO<sub>2</sub>, that again presents electric dipoles that cancel each other out, thus resulting in a non-polar CO<sub>2</sub> molecule. Notice again that CO<sub>2</sub> is linear, like CO, and for this reason the dipoles cancel out [107], [108].

The various considered atmospheric gas molecules were placed at a distance of around  $2.2 \div 2.4$  Å depending on the molecule and on the molecules size/shape. The range of distances was chosen so close to the fullerene in order to ensure consistent comparisons with the previously reported results for the ammonia, that indeed was placed at a distance of about 2.2 Å from the fullerene.

The *I-V* characteristics of the  $C_{60}$  sensor with ammonia (both orientations, namely with N down toward the fullerene and with H down toward the fullerene), along with various very common atmospheric gases are reported in figure 8.32 (a); while the absolute current variations (with sign, defined accordingly to eq.(8.2) - with the different chemical species instead of ammonia) are reported in figure 8.32 (b).

As evident from figure 8.32 the current variations due to the presence of ammonia cannot be clearly and uniquely detected, since in all the bias points such variations are too similar to variations due to other chemical species, making impossible the detection within certain reliability limits. This result is in net contrast with the result reported in [33], in which instead the authors find a good selectivity to ammonia, even in the case of other atmospheric components. This occurs even if in [33] the authors use Quantum-Wise ATK suite and EHT+NEGF method (as I did in this section), and if the I-V characteristics were compatible with the one I have reported previously. It must be said that there is an important difference between the device geometry I used in this work and the one in [33]: the authors indeed use a transistor configuration with a gate and a gate voltage of 1 V. Nevertheless considering that the ideal effect of the gate is only to suitably shift the transmission function T(E) in energy and thus centering the bias window, in my opinion this is not enough to justify such different results. In order to definitively clarify this point a gate should be considered and all the simulations should be performed again, but this is outside the purposes of this work (notice also that the distance at which chemical species are placed around the fullerene is important and can strongly affect the results - but in [33] such a distance is not declared making difficult a complete comparison).

Instead the main purpose of this work is to identify a general design methodology, starting with the cheaper molecular wire solution, and only then considering the gate solution for eventually improving the performances. In this optics, the main result of this chapter is the method accordingly with which it is possible to design the  $C_{60}$ -contact distances, the method for validating the EHT non-equilibrium simulations and the method for performing all the other secondary steps reported previously, that are anyway important to understand the device and thus gain control on the various design parameters.







Figure 8.32: Top (a): Current-voltage characteristics for the final sensor geometry, the two different ammonia orientations are considered along with various atmosphere constituents (EHT method). Bottom (b): Absolute current variations with sign are considered for the same chemical species (EHT method).

In appendix D.7 additional graphs concerning the sensor selectivity are reported, among which two zoomed in plots of the *I-V* characteristic of figure 8.32 at around 0.2 V and 1.4 V, two possible choice of bias accordingly with the discussion of the previous sections. From this plots it is evident that water, CO, CO<sub>2</sub> and N<sub>2</sub> curves are too close to the NH<sub>3</sub> ones. These are all very common constituents of atmosphere (a part CO), and again the detection is not feasible. In the next section other considerations are made, and in the next chapter the remaining steps of the general methodology of section 7.2 will be performed, no more relatively a C<sub>60</sub> ammonia gas sensor, but to a lead sulfate one.

#### 8.6.3 The $C_{60}$ lead sulfate gas sensor proposal

From the analysis of the previous section, it is clear that the selectivity of the MES to ammonia is inadequate. For the sake of completeness and in order to check if it would have been selective w.r.t. other pollutants the following non-equilibrium I-V characteristics and current variation analyses were carried out. All the mentioned analyses were performed following the same methods indicated previously, and the resulting graphs are reported in appendix D.7. In particular notice that all the chemical species were placed nearby the fullerene at around the same distance in order to make compatible the results for a comparison.

The sensitivity and selectivity to methane  $(CH_4)$  and butane  $(C_4H_{10})$  were verified to be extremely modest, thus proving that the MES was unable to reliably recognize the presence of such chemical species. The butane  $(C_4H_{10})$  is a bulky molecule w.r.t. ammonia, and thus it seemed that the molecular mass and above all the number of electron states was not a discriminating factor for what is concerning the MES operation. Moreover both these molecules are non-polar, thus increasing the suspect that the MES was able to well recognize strong polar molecules. For this reason it was supposed a strong correlation between the polarity of the target and the intensity of the intermolecular interactions at the basis of the conductance modulation. Consequently other polar pollutant molecules were take into account.

The MES sensitivity and selectivity to nitrogen oxide and dioxide (NO and  $NO_2$ ) were tested, see relative graphs in appendix D.7. Both the molecules are polar and thus different orientations were considered. It resulted that only in some bias points the current variations were enough large to allow a feasible and easy recognition of the target chemical species. Indeed whenever the  $\Delta I_D$  due to the target chemical species, in a given bias point, is enough "far away" from the other  $\Delta I_D$  due to other/common atmospheric constituents, it is in principle possible to reliably recognize the current variation  $\Delta I_D$  due to the target, and thus the presence of the target. For example, for the NO, it resulted that at  $V_D = 1$  V the  $\Delta I_D$  due to NO was clearly recognizable for all the main possible orientations of NO w.r.t. the fullerene (figure D.27). Indeed in such bias point the  $\Delta I_D$  due to all the orientations of NO were enough different from all the others. Notice that it is not necessary that such a current variation is larger (in magnitude) than all the others, but simply that it is, within a reasonable limit, different. Again with reference to figure D.27, the  $\Delta I_D$  due to NO oriented with oxygen pointing toward the  $C_{60}$  (O down) and in "flat" position are about  $3\,\mu\text{A}$  lower that the closest  $\Delta I_D$  due to other chemical species, namely the O<sub>2</sub>. In the same bias point the NO oriented with N down pointing toward the fullerene, provides a  $\Delta I_D$  that is different from those relative to other chemical species of at least  $0.94\,\mu\text{A}$ (referred to the closest curve, i.e. water - from argon the "distance" is of about  $1.7 \,\mu\text{A}$ ). In summary, the sensor is reasonably sensitive to NO, and with a  $\Delta I_D$  at least "distant" from all the others of about  $1 \mu A$ , it is possible to perform a recognition of the target (NO). Analogous considerations can be made relatively to  $NO_2$ . In such a case the sensor shows a recognizable  $\Delta I_D$  for example for  $V_D$  between 1.6 V and 1.8 V (see figure D.28). From the above analysis on NO and  $NO_2$  it seems that the  $C_{60}$  MES is able to recognize

From the above analysis on NO and NO<sub>2</sub> it seems that the  $C_{60}$  MES is able to recognize the presence of polar compounds, and it seems also there is a correlation between the atomic number of the atoms composing the polar chemical species and the sensitivity. An intuitive explanation for this is that the greater is the atomic number, and thus the number of electrons, the larger will be polar charges  $\delta^-$  and  $\delta^+$  and thus the stronger the (essentially electrostatic) intermolecular interaction. This reasoning seems to be confirmed also by noticing that the argon  $\Delta I_D$  for high bias (likely causing great polarization of argon atom) is very large when compared to all the others. And noticing that argon has the highest atomic number among the considered ones this intuitive reasoning seems confirmed (also considering that intermolecular forces are greater for greater molar mass and/or electric charge - like in ions, see section 3.7). In the next chapter a more quantitative analysis will be presented in this regard. Notice that the argon is a noble gas, i.e. it has a complete octect and accordingly to Lewis' chemical bond theory it should not be interacting. Nevertheless the interactions considered here are intermolecular van der Waals ones, thus regarding mainly (as supposed above) polarization, like temporary (London) or permanent dipoles of the molecules/orbitals. And in this regard it is useful recall that London discovered the "London forces" (induced dipole moment interactions) by experimental results on argon, thus making this hypothesis more sustained.

With this remark in mind it was decided to test the sensor sensitivity and selectivity to heavy metals compounds, that are involving both polar molecules and atoms with high atomic numbers (the heavy metals). If the intuition is correct, it is expected a good sensitivity and selectivity. Among the possibilities it was chosen to test the sensor with lead oxide (PbO), lead chloride (PbCl<sub>2</sub>) and lead sulfate (PbSO<sub>4</sub>), that correspond to the possible toxic volatile species involving lead in atmosphere [150]. More details on such molecules and a deeper investigation will be provided throughout the next chapter. For the moment the focus is again on sensor selectivity. Since such chemical species are polar then different possible orientations were considered. For PbCl<sub>2</sub>, at voltage  $V_D = 1.4$  V the current variations due to the target (PbCl<sub>2</sub>) are well recognizable w.r.t. the other atmospheric gases, presenting indeed enough separation w.r.t. them (see figure D.29). Similar considerations hold true for the PbO at again 1.4 V (see figure D.30).

The current variation plot relative to lead sulfate is instead reported in figure 8.33. Again due to PbSO<sub>4</sub> polarity, various molecule orientations were considered. They are better considered, explained and detailed in the next chapter. Nevertheless the legend "left-right" indicates a 180° rotation around a vertical rotation axis, such that the initial left-side becomes the right one and vice versa. Analogous for "up-down", while "SO down" and "Pb down" indicate that SO<sub>4</sub> group and Pb are pointing down toward the fullerene. At bias  $V_D = 0.8$  V the separation between the  $\Delta I_D$  of all the four orientations and the  $\Delta I_D$  due to other atmospheric gases is enough large to make likely possible a reliable recognition of the lead sulfate. Indeed the deviation between the "PbSO<sub>4</sub>-SO-down" and the closest chemical species, i.e. O<sub>2</sub>, is of about 0.81 µA, while the analogous between PbSO<sub>4</sub> and Ar is of the order of 1.7 µA. These deviations should be enough to ensure a reliable detection of the lead sulfate, whatever is the orientation. This remark, the above intuition relative to polarity of chemical species, atomic numbers and sensor sensitivity and selectivity are at the basis of the analysis carried out in the next chapter of this work, relative to the investigation of the C<sub>60</sub>-based MES for the detection of mainly PbSO<sub>4</sub>.



Figure 8.33: Absolute current variations (with sign) to lead sulfate  $(PbSO_4)$  and other common atmospheric gases. Different orientations of  $PbSO_4$  are considered (EHT method).

# Chapter 9 $C_{60}$ -based lead sulfate gas sensor

In the previous chapter it was considered the  $C_{60}$ -based MES as a gas sensor for ammonia. Accordingly the general methodology of section 7.2, the equilibrium properties were investigated, resulting in discrete variations depending if the ammonia was present or not and in which concentration. Then the device geometry was engineered (8.3) leading to the final geometry detailed in section 8.3.7 (see also section 8.3.3), that is the best compromise between maximum absolute sensitivity of the sensor to ammonia (the situation is different for the percentage sensitivity) and stability of the structure, since it corresponds to the expected equilibrium geometry for chemisorption of the fullerene onto the gold surfaces of the electrodes. Finally, different equilibrium and non-equilibrium properties of such a sensor were investigated in order to characterize it and perform a functional analysis of the device. This highlighted a failure of the  $C_{60}$  ammonia MES in selectively recognizing the presence of the target. Nevertheless additional sensitivity checks showed that it can potentially and selectively respond to other chemical species, among which the nitrogen oxide, nitrogen dioxide, lead chloride, lead oxide and lead sulfate (PbSO<sub>4</sub>).

introduced in section 7.2. In particular they are considered in order to carry out and complete the design at device level of a lead sulfate MES, based on the  $C_{60}$  molecular channel. Indeed, since the analysis reported in the previous chapter showed a failure in the case of ammonia regarding the sensor selectivity, it was not particularly interesting carry out the last steps of the design on it, while it could much more interesting doing that for the lead sulfate. In this optics, the attempt of the present chapter is to verify, by means of simulations, the various properties of a  $C_{60}$  lead sulfate gas sensor, and to perform a possible (ideal) design at device level of such a sensor. To this purpose the first sections are aimed in briefly summarize the same steps carried out in the previous chapter relatively to the  $C_{60}$  ammonia gas sensor for the PbSO<sub>4</sub> one, and then to apply the last steps of the general methodology (section 7.2) to it, in order to verify its main features and characterize it by gaining at the same time a deeper insight on its physical principles/behaviors, to be considered as general considerations true for all gas MES.

### 9.1 The $PbSO_4$ molecule

According with the World Health Organization report on "Health risks of heavy metals from long-range transboundary air pollution" [150] (2007), heavy metals cadmium, lead and mercury are still common air pollutants, being emitted mainly as a result of various industrial activities, even if their emission were strongly reduced in the last three decades. Although the atmospheric levels are low, they contribute to the deposition and build-up in soils of dangerous level of toxic agents, indeed heavy metals are persistent in the environment and are also subject to bio-accumulation in food-chains. In particular, lead is a well-known neurotoxin [150], and lead exposures have developmental and neurobehavioral effects on fetuses, infants and children, and elevate blood pressure in adults [150]. Even if food is the predominant source of lead uptake in the general population, inhalation exposure may be significant and lead emissions to the atmosphere should therefore be kept as low as possible [150]. Lead is released into the atmosphere from natural and anthropogenic sources, the latter because of combustion of fossil fuels from, for example, traffic, non-ferrous metal production, iron and steel production, cement production and waste disposal [150]. Lead concentration monitoring can be thus important already in industrial production processes. Generally atmospheric lead is bound to particulate matter (usually it is associated to large particles -  $0.2 \div 1\mu m$ ), but the main species upon emission are chlorides (PbCl<sub>2</sub>), oxides (PbO) and sulfates (PbSO<sub>4</sub>) [150]. In this chapter a MES for the single-molecule lead sulfate PbSO<sub>4</sub> is considered.

 $PbSO_4$  is an ionic compound in which sulphate ion,  $SO_4^{2-}$  is the anion (negatively charged). Since the charge on sulphate ion is -2q (being q the elementary charge), the charge on Pb ion is +2q (it is the cation - positively charged), and thus the oxidation state of Pb is +2q[107], [108]. Remember that the oxidation number, also called oxidation state, is the total number of electrons that an atom either gains or loses in order to form a chemical bond with another atom [107], [108]. In the case of PbSO<sub>4</sub> such chemical bond is an ionic bond, i.e. the electrostatic interaction between the two ions (namely  $Pb^{2+}$  and  $SO_4^{2-}$ ) is at the origin of the chemical bond. Usually the ionic compounds tend to form a crystalline structures. instead of single isolated molecule. As mentioned previously, in this chapter a  $C_{60}$ -based sensor of  $PbSO_4$  single molecules will be addressed, analogously to what did in the previous chapter for single molecules of ammonia. Independently on the real applications of such a device, the design procedure carried out here allows to gain important insights in the physics and engineering of a general MES, thus being significant for the methodology, main point of this work. In particular, studying such a structure is clarifying because of the chemical properties of the target chemical species, i.e. PbSO<sub>4</sub>, that allow to understand the general behavior of the  $C_{60}$  MES, thus providing explanation to the phenomena highlighted in the last sections of the previous chapter. In particular, the lead sulfate has the distinguishing features of being polar, indeed it is an ionic compound with strong charge localization (cation Pb is +2q while anion SO<sub>4</sub> is -2q), involving also an heavy metal (Pb) whose atomic number is high (82), and its investigation can be thus give answers to the question arose at the end of previous chapter, by confirming or not the hypotheses made.

### 9.2 Device structure and geometry

The first and maybe the most important step of the general methodology (section 7.2) is to fix the MES geometry. Since the considered MES is very simple, it corresponds essentially in determining the distances between the contacts and the C<sub>60</sub>. This corresponds, in practice, to the design of the device. As mentioned, two main features should be considered: first, the geometry stability and reliability, that from section 8.3 (also 8.3.4, 8.3.7) are known to be satisfied by the geometry with carbon-gold bonds of 2.4 Å and with hexagons toward gold surfaces, and then the sensor sensitivity to the target, in this case PbSO<sub>4</sub>. In order to verify how the MES sensitivity to lead sulfate varies with distances, an analogous procedure to the one already described in section 8.3 was carried out with the PbSO<sub>4</sub>. The following distances between contacts and fullerene were considered: 2.4 Å (both casual and general orientation), 2.7 Å, 3.0 Å, 3.3 Å, 3.6 Å. Moreover, for each of them, 0, 1, and 2 lead sulfate molecules were placed nearby (at around 2.25 Å) the fullerene, ensuring intersection of van der Waals spheres in *ATK* graphical interface and a strong intermolecular interactions.

### 9.2.1 The distance from contacts

First of all, it was verified if the optimal geometry found for the ammonia gas sensor case (section 8.3.7), were the optimal one also for the lead sulfate sensor. In order to do that an analogous procedure to the one presented in section 8.3.6 was carried out. It resulted an improvement of the total average sensor sensitivity if the distance between the fullerene and the contacts was reduced. To this purpose in figure 9.1 (a) is reported the average absolute current variation, evaluated as the arithmetic mean of the absolute current variations due to the presence of 1 and 2  $PbSO_4$ , averaging over the half voltage range: [0,1] V. The maximum current variation can be obtained with the minimum distance, i.e. 2.4 Å, confirming that to be the optimal geometry, for "low-bias" case. In the case in which the entire range of voltages [0,2] V is taken into account, then for a single PbSO<sub>4</sub> molecule the maximum average sensitivity is achieved again for 2.4 Å, while with two PbSO<sub>4</sub> molecules it does not. Nevertheless it is unlikely that two separated  $PbSO_4$  molecules are simultaneously present nearby the fullerene, if their dimensions are considered (they are bulky molecules w.r.t. ammonia for example, thus making less probable having much of them in proximity of the sensor). Considering also the great advantage of being 2.4 Å the chemisorption equilibrium distance, it was chosen it to be the final sensor geometry also in the case of PbSO<sub>4</sub>. In appendix E.1 additional figures are reported, with the absolute current variations (both in absolute value and with sign) in function of the applied voltage  $V_D$ . They show clearly that even though for the average variations it holds true what mentioned above, there are specific bias points in which the absolute variations for longer distances are greater than the ones for 2.4 Å. Nevertheless from the previous analysis on selectivity of section 8.6.3 it resulted convenient to use the sensor at 0.8 V. For that specific voltage value the best performances in terms of current variations are obtained with the above mentioned chosen geometry (2.4 Å hexagons pointing toward gold contacts).



Figure 9.1: Top (a): Average current variations in the case of 1 and 2 PbSO<sub>4</sub> molecules. The arithmetic mean is over the half voltage range: [0,1] V and considers absolute values of the current variations. Bottom (b): Average current current variations in the case of 1 and 2 PbSO<sub>4</sub> molecules. The arithmetic mean is over the full voltage range: [0,2] V and considers absolute values of the current variations.

For the sake of completeness also the percentage variations were evaluated. The average absolute and average variations are reported in table 9.1. As in the case of ammonia the percentage variation strongly decreases with decreasing the contact distances, resulting in the minimum percentage variation of current for 2.4 Å. Nevertheless, like done in

the case of ammonia, it was given more importance to the absolute current variations, since the percentage one are very favorable for large contact-fullerene distances, implying small currents and small absolute variations, likely difficult to be detected with standard electronic circuit/devices.

distance	$ \Delta I_D  (1 \text{ PbSO}_4)$	$ \Delta I_D _{\%} (1 \text{ PbSO}_4)$
2.4 Å	4.99 µA	28.72 %
$2.7\mathrm{\AA}$	$2.75\mu\mathrm{A}$	40.1 %
$3.0\mathrm{\AA}$	1.6 µA	81.8 %
$3.3\mathrm{\AA}$	3.1 µA	104.04~%
$3.6\mathrm{\AA}$	0.25 µA	476 %
distance	$ \Delta I_D $ (2 PbSO <sub>4</sub> )	$ \Delta I_D _{\%} (2 \text{ PbSO}_4)$
distance 2.4 Å	$\frac{ \Delta I_D  (2 \text{ PbSO}_4)}{3.9 \mu\text{A}}$	$\frac{ \Delta I_D _{\%} (2 \text{ PbSO}_4)}{30.05 \%}$
distance           2.4 Å           2.7 Å	$ \begin{array}{   }  \Delta I_D  & (2 \text{ PbSO}_4) \\\hline & 3.9 \mu\text{A} \\\hline & 4.96 \mu\text{A} \end{array} $	$\frac{ \Delta I_D _{\%} (2 \text{ PbSO}_4)}{30.05 \%}$ 73.68 %
distance           2.4 Å           2.7 Å           3.0 Å	$\begin{array}{c c}  \Delta I_D  & (2 \text{ PbSO}_4) \\\hline & 3.9 \mu\text{A} \\\hline & 4.96 \mu\text{A} \\\hline & 2.19 \mu\text{A} \end{array}$	$\frac{ \Delta I_D _{\%} (2 \text{ PbSO}_4)}{30.05 \%}$ $\frac{73.68 \%}{116.35 \%}$
distance           2.4 Å           2.7 Å           3.0 Å           3.3 Å	$\begin{array}{    }  \Delta I_D  & (2 \text{ PbSO}_4) \\\hline & 3.9 \mu\text{A} \\\hline & 4.96 \mu\text{A} \\\hline & 2.19 \mu\text{A} \\\hline & 2.86 \mu\text{A} \end{array}$	$\begin{array}{c}  \Delta I_D _{\%} \ (2 \ {\rm PbSO}_4) \\ \hline 30.05 \ \% \\ \hline 73.68 \ \% \\ \hline 116.35 \ \% \\ \hline 55.8 \ \% \end{array}$

**Table 9.1:** Mean absolute and percentage current variation values, averaged over the range [0,2] V of applied voltage, due to the presence of 1 and 2 PbSO<sub>4</sub> molecules, for all the considered distances between the contacts and the C<sub>60</sub> fullerene (EHT method).

Finally, the two different orientations of the  $C_{60}$  molecule were compared in terms of sensitivity to PbSO<sub>4</sub>, at the chosen distance of 2.4 Å. The result is reported in figure 9.2 in which the absolute current variations are reported for the two orientations in function of the applied voltage. Notice again that, even if in some bias points the casual orientation presents a larger sensitivity, at the above mentioned  $V_D = 0.8 \,\mathrm{V}$  the best performance is obtained with the geometry with hexagons toward gold surfaces, thus being an additional reason to choose it (considering again also the maximum selectivity to  $PbSO_4$  at that voltage - section 8.6.3). Moreover the geometry with hexagons toward gold surfaces presents an average better sensitivity, indeed the average current variation with such a geometry is of around 5 µA while with the casual orientation it is only of the order of  $3.8\,\mu\text{A}$ ; while the averages over only half range are  $2.6\,\mu\text{A}$  and  $1.94\,\mu\text{A}$ , respectively. In appendix E.1 is reported the same graph of figure 9.2 but with additional curves relative to current variations due to atmospheric constituents (figure E.1), from which the superior performances in terms of selectivity at  $V_D = 0.8 \text{ V}$  of the geometry with hexagons toward gold on the casual orientation are well highlighted, thus being an important reason to choose such a geometry.

### 9.2.2 The final geometry

In conclusion, the final geometry was the same of the ammonia case, i.e. 2.4 Å of distance between the contacts and the fullerene with the  $C_{60}$  hexagons pointing toward the gold surfaces. This is indeed the geometry maximizing the sensor absolute sensitivity to lead



Figure 9.2: Current variations in the case of  $1 \text{ PbSO}_4$  molecule for the casual orientation of the fullerene and for the special chemisorption equilibrium orientation (hexagons toward the gold surfaces). On average the latter presents better performances.

sulfate, at least in the range of voltage below 1 V. Moreover it is the most stable geometry for chemisorption thus ensuring long-term device reliability and likely less process variation issues. As mentioned above it is moreover the best configuration for maximizing all the sensor performances at  $V_D = 0.8$  V, being a possible choice of bias voltage also for the maximum sensor selectivity to lead sulfate, as already pointed out in section 8.6.3.

## 9.3 Preliminary equilibrium properties of the final $C_{60}$ -wire sensor

An analogous procedure to the one carried out in the previous chapter (section 8.4) was carried out also in the case of the PbSO<sub>4</sub> sensor. The DFT calculated transmission spectra are reported in figure 9.3 while the one evaluated with EHT method in figure 9.4. In both cases variations in the transmission properties are present depending on the presence or not of the target chemical species (PbSO<sub>4</sub>). Moreover these variations are dependent on the concentration of PbSO<sub>4</sub>, i.e. the number of molecules. From the equilibrium spectra it is expected a relevant variation of transmission properties, and thus of current, already at low bias, indeed with both the methods the transmission peaks around zero energy (i.e. around the system Fermi level since abscissa axis is the energy minus such a level) are modulated by the presence of PbSO<sub>4</sub>. Similarly to what noticed for the ammonia case, differences exist between the two methods. In particular the energy levels with EHT method are slightly shifted toward lower energies and with less transmission in the HLG, that moreover appears slightly overestimated w.r.t. DFT method one. The presence of two  $PbSO_4$  molecules nearby the channel give rise to additional transport states within the HLG in the EHT method while in the DFT one the number of peaks in the HLG are essentially unchanged. Other peaks are subjected to similar modifications with both the methods due to the presence of  $PbSO_4$ . In the next section a deeper analysis on integrals of such spectra will clarify differences between the two methods.



Figure 9.3: Equilibrium transmission spectra calculated with DFT method for the cases of 0, 1,  $2 \text{ PbSO}_4$  molecules.



Figure 9.4: Equilibrium transmission spectra calculated with EHT method for the cases of 0, 1,  $2 \text{ PbSO}_4$  molecules.

## 9.4 EHT non-equilibrium calculations validation

By carry out an analogous procedure to the one presented in section 8.5, and under the same hypotheses, the graph of figure 9.5 was obtained (the calculations and the plots are realized in *MatLab* with a code analogous to the one reported in appendix D.6). This graph can be useful in validating the EHT method non-equilibrium simulations on the basis of the non-equilibrium properties expected with the DFT method, analogously to what did in section 8.5. The EHT and DFT methods are expected to provide current variations of the same order of magnitude for low bias, let's say below 0.3 V, and for biases until 0.7 V. This is in contrast w.r.t. the ammonia case in which it always expected the EHT method to underestimate the current variations. Around  $0.8 \text{V} \div 1.2 \text{V}$ , the EHT method is expected to provide an underestimation of the current variations. This is positive since in that range, and especially for  $V_D = 0.8 \,\mathrm{V}$  the sensor is also expected to present good selectivity (see section 8.6.3, and successive sections of this chapter), i.e. to have larger current variations with  $PbSO_4$  than with all the other common atmospheric gases. In other words, for  $V_D = 0.8$  V the EHT curve (fig. 9.5) is below the DFT one, meaning that the EHT method can be considered as a "worst case", in which the current variations are underestimated. Therefore a design carried out with such a voltage value should be work as well even in the DFT case or better in the real case (the DFT is expected to be more accurate, since also the Grimme DFT-D2 correction was used - table 8.1). Finally, in between around 1.2 V and 1.7 V, the EHT method is again expected to overestimate the current variations and then, from 1.7 V to 2 V, again the vice versa occurs.



Figure 9.5: Integral difference of the final lead sulfate sensor equilibrium transmission spectra in the cases of 1 PbSO<sub>4</sub> molecule. The results obtained with the two methods: DFT (blue curve) and EHT (red/orange curve) are compared. The ellipsoid is around the considered range of bias windows, i.e. up to 2V. The integrals were performed with trapezoidal numerical method in *MatLab*, over the bias windows from 0.1 V to 4 V with a step of 0.1 V.

In appendix E.2 is reported an analogous graph for the case of two lead sulfate molecules. Analogous considerations are possible, and in particular also in this case there are bias points in which it is expected the EHT method to underestimate the current variations and others in which it is expected to overestimate them, and again others in which the EHT and DFT methods are expected to provide comparable current variations. Nevertheless in this case the EHT method generally underestimate more the current variations w.r.t. DFT if compared with the previous case (of a single PbSO<sub>4</sub> molecule).

In conclusion, on average, greater current variations are expected than the ones calculated with EHT method, even if in this case, depending on the bias point, the EHT method could also overestimated the current variations. The best solution would be performing non-equilibrium simulations with DFT method, but this was not feasible (for the same reasons explained in the previous chapter). EHT method is nevertheless expected to underestimate the current variations at 0.8 V that was previously noticed as possible bias point. If it would be chosen as the operating bias, it is thus expected the design to work in a worst case approximation w.r.t. the actual device.

## 9.5 Non-equilibrium properties and *I-V* characteristics

The non-equilibrium simulations were performed by means of EHT method, for the same reason already explained in the previous chapter. The warnings in using this method were already reported and commented in the previous section. In figure 9.6 (a) the *I-V* characteristics in the case of 0, 1, and 2 PbSO<sub>4</sub> molecules are reported. Evident differences are present depending if there is the target (PbSO<sub>4</sub>) chemical species is present or not, and in what concentration (1 or two molecules). This is a proof of the fact that the sensor can potentially be sensitive to PbSO<sub>4</sub>. In figure 9.6 (b) the interpolated (3<sup>rd</sup> order cubic spline) *I-V* characteristics are reported. A deeper look at the current variations is instead provided in figure 9.7, in which the absolute (in magnitude) current variations in the case of 1 and 2 lead sulfate molecules are reported. Notice that it is possible to distinguish between the concentrations in all bias points (a part for  $V_D = 0.9$  V and high biases near 2 V). It is highlighted the point at 0.8 V, being a possible operating bias point from section 8.6.3 and previous sections.

### 9.5.1 Sensitivity to different PbSO<sub>4</sub> orientations

Since the lead sulfate molecule is strongly polar it is interesting to study the changes in the *I-V* characteristic due to one molecule of  $PbSO_4$  positioned with different orientations. In order to make data comparable among them, the same distance of about 2.25 Å was assumed in all cases. The different orientations corresponds to the figures reported in appendix E.3. In particular "PbSO<sub>4</sub>" with no particular nomenclature/label refers to the a single PbSO<sub>4</sub> molecule placed horizontally with lead ion toward the source and the SO<sub>4</sub> group toward the drain (figure E.4). The "left-right" label refers to the same but with the




Figure 9.6: Top (a): I-V characteristics with 0, 1, and 2 PbSO<sub>4</sub> molecules (EHT method). Bottom (b): Interpolated (cubic spline) I-V characteristics with 0, 1, and 2 PbSO<sub>4</sub> molecules.

lead ion toward drain and the  $SO_4$  toward the source. The "up-down" refers to the PbSO<sub>4</sub> molecule rotated on its geometrical center of 180° degrees along a rotation axis parallel to transport direction. In this way the "top" becomes the bottom and vice versa, so the side pointing toward the fullerene (down) is now pointing upward. The "SO-down" refers to the orientation in which the SO<sub>4</sub> functional group is down-oriented pointing toward the fullerene, and the "Pb-down" refers to the orientation in which the Pb ion is down-oriented



Figure 9.7: Current variations in the case of 1 and 2 PbSO<sub>4</sub> molecules (EHT).

pointing toward the fullerene. The different I-V characteristics are reported in figure 9.8. The four orientations always provide an enough different current characteristics w.r.t. the case in which no lead sulfate molecule is present (blue curve). Nevertheless there is the drawback that the different orientations provide slightly different I-V shapes, thus making slightly more complex the detection. Nevertheless as already mentioned in section 8.6.3, and it will repeated in the next section 9.5.2, the current variations are always enough different from the one obtained with other common atmospheric gases, thus making possible the detection.

Notice that in general convective motion of air will move molecules and thus it is possible that dynamically they rotate and different  $PbSO_4$  molecules with different orientations interact with the channel. For this reason it is possible that the sensor must correctly detect the presence of  $PbSO_4$  with different orientations. It is also possible that a favoured configuration is present, corresponding to an equilibrium geometry for physisorption or for chemisorption, if the target molecules have enough low kinetic energy while approaching the sensor, when the transient (in which geometry modifications occur) is extinguished. A geometry optimization analysis can be performed to ascertain this. Nevertheless due to the lack of force fields (and also Slater-Koster parameters), relatively to lead mainly, it was not possible to perform such a study with such fast methods, while a DFT study would have required too much time and RAM resources, and for this reason it was not possible to consider it. Nevertheless in future for real applications it is suggested to perform such an analysis of geometry optimization in order to verify if and which orientation is the most stable one, and if corresponds to physisorption, chemisorption or other configurations.



Figure 9.8: *I-V* characteristics obtained with four different orientations of the lead sulfate molecule (EHT method).

# 9.5.2 Selectivity to common atmospheric gases: the $PbSO_4$ gas sensor proposal

In this section essentially the same analysis presented in section 8.6.3 is again proposed, with the gain of the knowledge of the previous sections. In figure 9.9 the current variation plot relative to the four above considered orientations of lead sulfate is reported, along with the current variations due to the other common atmospheric constituents. Among the possible different bias points, notice that at  $V_D = 0.8$  V the separation between the  $\Delta I_D$  of all the four orientations and the  $\Delta I_D$  due to other atmospheric gases is enough large to make likely possible a reliable recognition of the lead sulfate. Indeed the deviation between the "PbSO<sub>4</sub>-SO-down" and the closest chemical species, i.e. O<sub>2</sub>, is of about 0.81 µA, while the analogous between PbSO<sub>4</sub> and Ar is of the order of 1.7 µA. These deviations should be enough to ensure a reliable detection of the lead sulfate, whatever is the orientation, making  $V_D = 0.8$  V a possible choice for the DC operating bias point.

#### 9.5.3 Possible choice for the $PbSO_4$ gas sensor bias voltage

As mentioned in the previous section (and throughout the entire present chapter), a good candidate for a DC operating bias point is the  $V_D = 0.8$  V. For this voltage value indeed the C<sub>60</sub>-base lead sulfate sensor presents the following advantages (see previous sections for an explanation of all these features):

- maximum absolute sensitivity, i.e. absolute current variation to lead sulfate (w.r.t. all the other contact-fullerene distances and orientations of the fullerene).
- It is probable and expected that the real sensor has an even higher sensitivity than



Figure 9.9: Absolute current variations (with sign) to lead sulfate ( $PbSO_4$ ) and other common atmospheric gases. Different orientations of  $PbSO_4$  are considered (EHT method).

the one predicted with EHT method for such a bias voltage, making the design a "worst case" design and making in this optics the design likely robust and reliable.

- Different current values are expected with different concentrations of lead sulfate, thus making potentially possible the detection and the measurement of the  $PbSO_4$  concentration.
- The sensor presents reliable selectivity for such a bias point, for all the considered possible orientations of the lead sulfate, thus making the detection reliable in air in presence of the common atmospheric gases.

The selected bias point is highlighted in figure 9.10 (a) with an ellipse. In such a graph the various I-V characteristics obtained with all the four considered orientations of the lead sulfate and with the presence of the other common atmospheric gases are reported. Figure 9.10 (b) reports an enlargement around the bias point, highlighting the different curves and the fact that the separation among them is clearly visible, as already mentioned and discussed in the previous section (9.5.2), in which the current variations were considered.

#### 9.5.4 Sensitivity to different $PbSO_4$ distances

So far the distance between the sensor (the fullerene) and the target chemical species was maintained approximately fixed at around  $2.2 \text{ Å} \div 2.5 \text{ Å}$ . It might be interesting to check the dependence of the current value w.r.t. the above mentioned distance. The ideal case is the one in which no current variation occurs with such a distance in a given range of distances, but this is obviously impossible. Indeed the intermolecular interactions like van der Waals ones and London dispersion ones, are strongly dependent on the distance, thus



Figure 9.10: Top (a): *I-V* characteristics with different PbSO<sub>4</sub> molecule orientations, the possible bias choice is highlighted by means of an ellipse -  $V_D = 0.8$  V (EHT method). Bottom (b): Enlargement of the graph (a) around the chosen bias point.

influencing the current with distance. From the analysis it was clear that no general rule was present. In figure 9.11 is reported the plot of the current values in function of the distance between the PbSO<sub>4</sub> and the fullerene for a fixed voltage of 0.8 V, both simulated (black circles) and interpolated (blue line with cubic  $3^{rd}$  order spline and orange/red curve with linear polynomial of degree 1). There is no a well defined trend, neither increasing nor decreasing. With a distance in between 2.6 Å and 3.2 Å the deviation is small and thus it would be a good recognition range. For smaller and larger distances the deviation increases, leading to greater current fluctuations depending on the distance.



Figure 9.11: Current values for different  $PbSO_4$  distances at  $V_D = 0.8$  V. Black circles: simulated data. Blue line: cubic  $3^{rd}$  order spline interpolation. Red/Orange: linear interpolation.

The same kind of analysis can be repeated to all the considered bias points, leading to the surface plot of figure 9.12. In such a plot the red dots are simulated points, the surface is obtained by merging together the spline interpolating curves. In red it is highlighted the chosen bias point with  $V_D = 0.8 \text{ V}$ . In general by increasing the bias the fluctuations increase, providing an insight on the mechanism that give rise to them. For small bias very small variations occur, leading to good linearity of the sensor response w.r.t. the target analyte distance. This is very likely due to the small dependence at low bias of the transmission spectrum T(E) on the applied bias. Instead by increasing the bias the dependence of T(E) with the applied voltage (and electric field) increases, and transmission peaks undergo to greater variations and modifications due to the bias, accentuating eventual current variations. Moreover the greater current magnitude results in greater current absolute variations even in the case of fixed percentage oscillations, thus accentuating again this effect. Among the considered biases the chosen one at  $V_D = 0.8 \text{ V}$ is a good compromise in terms of current variations due to the target analyte distance (see red line in the graph of figure 9.12). Generally it is often more important the sensor linearity with the target concentration (see section 9.5.5), nevertheless if also the sensor linearity and/or current oscillations due to the target distance is relevant, the analysis carried out in this section can be useful to select a proper bias point to satisfy specification in such a direction.

In appendix E.4 a table and a graph summarizing the maximum error from linear response, for each bias point, are reported. The linear response is obtained by linear interpolation of the simulated current values in function of the target distance (analogously to figure 9.12). The chosen bias point presents the same "degree" of linearity w.r.t. the others below 1 V, thus resulting a good trade-off among them. Small deviations are present especially



Figure 9.12: Current values for different  $PbSO_4$  distances at different bias voltages. The chosen bias voltage (0.8 V) corresponds to the red line. Red dots are simulated values, the surface corresponds to cubic spline interpolation curves. Notice the greater variations/oscillations for larger bias points.

at 0.2 V and at 1 V. For voltages greater than 1 V strong non-linear behavior and large current variations w.r.t. target distance occur.

Notice again that a large current variation of the expected current w.r.t. target distance from sensor makes more difficult the detection since the conditioning circuit is required to recognize it properly. In practice, this can be a crucial point of the sensor specifications, and if necessary another bias point, with smaller variations, can be chosen. To this purpose the graph of figure 9.12 and the data in appendix E.4 can be useful tools.

#### 9.5.5 Sensitivity to different PbSO<sub>4</sub> concentrations

An important property for a sensor is its linearity in detecting different concentrations of the target substance. In order to verify it, different concentrations of PbSO<sub>4</sub> were considered: 0, 1, 2 PbSO<sub>4</sub> molecules were placed nearby the fullerene at a distance of 2.25 Å. At most two lead sulfate molecules were considered due to their large dimension when compared with fullerene, making impossible placing three or more molecules nearby the fullerene without atoms overlap. In figure 9.13 the resulting current values for the different numbers of PbSO<sub>4</sub> molecules and for the chosen bias point of 0.8 V are reported (black circles); moreover they are interpolated with cubic  $3^{rd}$  spline (blue curve) and with a linear straight line (red/orange). A good linearity is present. The maximum deviation from linearity, i.e. the maximum (absolute value) distance between the spline and the straight line resulted to be 1.35 µA. As mentioned previously the linearity of the sensor (w.r.t. the target concentration) is an important property, and thus it is useful verify the overall performances of the sensor for all the possible bias points, in order to have an idea of the general behavior of the sensor. Moreover, in the case in which "more linearity" is required, another bias point with a more linear, if there exist one, can be selected to this purpose.



Figure 9.13: Current values for different PbSO<sub>4</sub> concentrations and for  $V_D = 0.8$  V. Black circles: simulated values; blue curve: cubic  $3^{rd}$  order spline interpolation; red/orange: linear interpolation.

In figure 9.14 the current values for different sensors concentrations and for all the considered bias points are reported (red dots). They are interpolated with cubic splines, that all together give rise to the surface. The red line highlight the chosen bias point (0.8 V), for which notice that a good linearity is present. From this plot and from such an analysis it is evident that the best sensor linearity is obtained with a bias  $V_D = 0.4$  V, that indeed provides a maximum deviation from linearity of only  $0.3 \,\mu$ A. In table 9.2 all the maximum deviations from linearity are reported for all the considered bias points. Notice that the chosen bias point (0.8 V) is the second just after the aforementioned 0.4 V one, thus being a very good choice and trade-off for linearity of the sensor to different concentrations. In appendix E.5 a plot of such maximum deviations is reported, in function of the applied bias voltages. Notice again the good linearity for  $V_D = 0.8 \text{ V}$  (i.e. small deviation). Moreover, always in appendix E.5, a quadratic interpolation of the current values for the different concentrations of PbSO<sub>4</sub> and for  $V_D = 0.8 \,\mathrm{V}$  is reported. The quadratic curve (red/orange one) is perfectly overlapped with the spline one, thus proving that for  $V_D = 0.8 \,\mathrm{V}$  the sensor response to the  $PbSO_4$  concentration is of second order, i.e. quadratic, but with a small curvature, leading indeed to good linearity and small deviation error as mentioned above.

Finally as title of example in appendix E.5 two additional graphs are reported for  $V_D = 0.2 \text{ V}$ , showing bad linearity and strongly non-linear response, and for  $V_D = 0.4 \text{ V}$ , showing extremely good linearity. Such plots are essentially cuts at constant voltage of the plot of figure 9.14. In the case in which more linearity is needed the voltage can be set to 0.4 V, providing best linearity.



Figure 9.14: Current values for different  $PbSO_4$  concentrations at different bias voltages. The chosen bias voltage (0.8 V) corresponds to the red line. Red dots are simulated values, the surface corresponds to cubic spline interpolation curves. Notice the worse linearity for larger bias points.

**Table 9.2:** Maximum absolute deviation between the cubic spline interpolation and the linear interpolation of the current values in function of the  $PbSO_4$  concentration, for the various considered bias points.

$V_D$ (V)	Maximum deviation (µA)			
0.2	6.66			
0.4	0.3			
0.6	5.58			
0.8	1.35			
1	13.57			
1.2	13.33			
1.4	17.38			
1.6	34.41			
1.8	6.04			
2	19.05			

#### The case of two $PbSO_4$ molecules with opposite orientations

It is interesting to study the case in which two lead sulfate molecules are present nearby the fullerene, at the same distance, but with opposite orientations. The case of two PbSO<sub>4</sub> molecules considered so far, assumed the two lead sulfate molecules to be with same orientation, just shifted in the direction transverse to the transport and at the same distance w.r.t. fullerene, i.e. with both lead ions pointing toward the source. In this situation the two molecules are just shifted the one w.r.t. the other in x-direction, accordingly to figure E.5, but both with lead at left-side (according to fig. E.5). Instead in this subsection another case is considered. It is now supposed to have again two lead sulfate molecules placed at the same distance from the fullerene and shifted the one w.r.t. the other in x-direction; but now the two molecules are supposed to have the lead ions pointing in opposite directions, one toward the source and the other toward the drain. This geometry is identified in this work with the label "opposite direction". The obtained result is very interesting, and if considered together with the analysis on transport and transmission eigenstates that will be presented in the next section, is an extremely elucidating example concerning the physical working principle of single molecules gas sensors in general. In particular, in figure 9.15 the *I-V* characteristics with 0, 2, and "2 opposite direction" PbSO<sub>4</sub> molecules are reported. It is noticeable that in all the bias points the current is improved if two lead sulfate molecules, pointing toward opposite directions, are considered. Such an improvement is substantial also w.r.t. two lead sulfate molecules case. The same can be noticed concerning the equilibrium transmission spectrum, reported in appendix E.5. The spectrum results enhanced with more (in number) and also more pronounced transmission peaks in the case of two PbSO<sub>4</sub> "opposite direction" molecules. The final reason for these important features will be provided in the next section, that finally elucidate and clarifies the working principle of single-molecule gas sensors, explaining at the same the great majority of the gas sensors properties noticed so far.



Figure 9.15: Current-voltage characteristics in the case of 0, 2, and 2 with "opposite direction"  $PbSO_4$  molecules. Notice the current improvement in the latter case.

As it will be clarified later, the main point is that the positive charge around the lead ions enhance the transmission since it attracts electrons from contacts, thus lowering the potential barriers they have to overcome. If such ions are on the same side, only the barrier at that side is lowered (let's say the source contact one), with a certain amelioration in terms of current. If instead they are one at source side and the other at drain side, they lower both barriers, enhancing much more the transmission by creating conducting channels between the two contacts. Further details will be provided in the next section, along with more details on this fundamental mechanism.

### 9.5.6 Transmission eigenstates in real space: an insight in detection mechanism

The purpose of this section is to definitively clarify what is the physical principle behind the differences in transport properties in the different cases considered so far. In other words, the aim is to answer the question why the lead sulfate, placed at the same distance of the ammonia, provides much higher current variations w.r.t. the case of only  $C_{60}$ , than the ammonia. The task can be accomplished by having a deeper look in the electron transmission mechanism from source to drain in the different cases. In order to do that the transmission eigentstates must be considered. In section 8.2.2, it was already pointed out the difference between the transmission spectrum T(E) and the transmission operator eigenvalues and eigenstates. In particular the transmission at a given energy E, i.e. T(E), is the result of the sum of the transmission eigenvalues that cooperate in transmitting electron from source to drain at that specific energy. In other words, the transmission of an electron with energy E from source to drain, can be accomplished by means of different paths, all accessible to such an electron with such an energy. Each path, or transmission channel, is associated to a well defined transmission probability, or transmission coefficient, that is the transmission eigenvalue associated to such a transmission channel or eigenstate. Due to the physical meaning of transmission eigenvalues (i.e. transmission coefficients), they are indeed normalized to one. Nevertheless since more paths are possible in general for an electron with a given energy, their sum, i.e. T(E), can be greater than one. In this section the focus is on the transmission eigenstates in real space. They are the projection onto the real space basis set of the eigenstates (i.e. eigenvectors) of the transmission operator. They are thus surfaces of iso-transmission, i.e. surfaces in the 3D space, of equal transmission probability, and as such they corresponds to regions of space in which the transmission occurs. The simple visual inspection of the transmission eigenstates provides extremely useful and important information on the nature of the transport. Indeed if for example the transmission eigenstate of interest were very similar to a specific orbital, then one may conclude that the transmission for that specific energy value E, and by means of that specific transmission channel (generally cooperating with others to the total T(E)), is mainly due to such an orbital, providing thus important insights on the transport features. In Quantum-Wise ATK it is simple to perform a transmission eigenvalues and eigenstates analysis [125], [126]. Firstly, one should select a bias point to be investigated from this standpoint. In the case of the PbSO<sub>4</sub> it can be  $V_D = 0.8$  V, since it is the selected bias point for the potential lead sulfate sensor. Then for that bias point the transmission spectrum T(E) should be inspected, in order to select the main peaks of transmission within the bias window. In the case of the  $PbSO_4$  sensor, with the  $PbSO_4$  placed nearby the conductive channel, three main transmission peaks were present (see appendix E.6 figure E.6 that reports the computed transmission spectrum at  $V_D = 0.8 \text{ V}$ :

- a. at energy  $0.04 \,\mathrm{eV}$ , with a transmission peak of 0.587924
- b. at energy  $0.28 \,\mathrm{eV}$ , with a transmission peak of 1.05351
- c. at energy 0.4 eV (at the limit of the bias window), with a transmission peak of 1.08796

One the interesting and relevant transmission peaks are selected it is possible to calculate the transmission eigenvalues that cooperate (that sum) to give rise to such peaks. For the three selected peaks of above the transmission eigenvalues are reported in table 9.3. They are labeled with a quantum number (QN); the eigenvalue with QN = 0 is the highest one (highest transmission probability), then they are decreasing for increasing QN. In table 9.3 only the largest transmission eigenvalues are reported, in general for each energy value only few eigenvalues contribute significantly to transmission while the others are very small. Notice that the sum of the transmission eigenvalues for a fixed energy is equal to the transmission peak for the same energy (actually the sum is slightly lesser than the transmission peak simply because very small eigenvalues are neglected even if they also contribute to the transmission).

Table 9.3: Transmission eigenvalues for the three main transmission spectrum peaks within the bias window at  $V_D = 0.8$  V, for the sensor with a single PbSO<sub>4</sub> molecule nearby the fullerene.

Energy (eV)	Transmission eigenvalue	Quantum number $QN$
0.04	5.654839e-01	0
0.04	2.229667e-02	1
0.28	8.373195e-01	0
0.28	2.119902e-01	1
0.4	6.899972e-01	0
0.4	3.125305e-01	1
0.4	8.513583e-02	2

Once the eigenvalues are calculated it is possible to calculate the relative eigenstates in real space. The resulting plots are reported in appendix E.6. They are significant framings of the 3D plots generated in ATK. The main point that is present in all of them is the following. Since as mentioned in section 9.1 the lead donate two electrons to the  $SO_4$ , the first becomes a positive ion with charge +2q, the latter a negative ion with charge -2q. By inspection of the transmission eigenstates it is evident that in all the considered cases the positive charge of lead attracts electrons from the nearest contact, thus enhancing the transmission. Indeed a positive charge, will generate an attractive Coulombic potential, thus lowering the potential barrier between the contact and the  $C_{60}$ , allowing for the creation of transmission channel that easily can transmit electrons from (or toward) the contact to (or from) the  $C_{60}$ +Pb system. In the eigenstate plots, this corresponds to large transmission surfaces nearby the lead. Moreover, noticing that the lead has atomic number 82 (i.e. it has 82 electrons), and that its electronic configuration is thus:  $1s^2 2s^2 2p^6 3s^2$  $3p^{6} 3d^{10} 4s^{2} 4p^{6} 4d^{10} 5s^{2} 5p^{6} 4f^{14} 5d^{10} 6s^{2} 6p^{2}$ , the shape of such transmission surfaces is explained. Indeed the upper orbital is of *p*-type, thus leading to such a well known shape. The different colours correspond to different electron phases, and in particular the two lobes of the surface have indeed a phase shift of approximately  $\pi$ , corresponding exactly to atomic p-type orbitals phase (this is a consequence of the Pauli's exclusion principle and the fact that many body fermions wave-functions must be anti-symmetric - section 2.5). The effect of the  $Pb^{2+}$  ion is thus to lower the contact-fullerene barrier and enhancing the

transmission, due to Coulomb attraction, by creating new transmission channels that are not present without it. On the other hand the  $SO_4^{2^-}$  ion screens the electrons. Indeed it has a negative charge, thus a repulsive Coulombic force is acting on electrons nearby such an ion, and they undergo to an higher potential barrier. In all the analyzed transmission eigenstates there is always no transmission or very small transmission nearby the  $SO_4^{2^-}$ ion (a sort of "hole" with no iso-transmission surfaces is present). Nevertheless the final result is in an increase of the current. Indeed the electrons attracted by the lead ion easily overcome the first barrier between the source and the fullerene, then they can proceed to drain by means of transmission channels that are already present in the case of the C<sub>60</sub> without the PbSO<sub>4</sub>. This is evident in the transmission eigenstates plots since coherent (same color) surfaces are present, connecting the surfaces nearby the lead to the other contact (the drain), avoiding the  $SO_4^{2^-}$  ion.

In summary, the positively charged lead ion  $Pb^{2+}$ , by attracting electrons lowers the repulsive barrier between one contact and the fullerene, resulting in an improved transmission. On the other hand the  $SO_4^{2-}$  ion still repels electrons, that in spite of this can proceed toward the drain through other transmission channels. This mechanism also intuitively explain the presence of transmission peaks within the HLG that without the PbSO<sub>4</sub> are not present. For example, this is the case of the peak (*a*.) at energy 0.04 eV that was not present without the lead sulfate. The explanation is again simple: since the positive charge of lead enhances transmission, it allows electrons at that specific energy to be transmitted easily from the (source) contact to the fullerene (and then proceed toward the drain); fact that is not possible for such a low energy electrons without the lead ion. Finally notice that this entire analysis was performed for a constant bias  $V_D = 0.8$  V, and the improvement in transmission by the lead ion and the current is to be intended w.r.t. the same bias point without the PbSO<sub>4</sub> molecule (with only fullerene). Analogous analyses can be performed in all the other bias points, elucidating the transport mechanism and the transmission features for such specific bias points.

In conclusion, the important result of this section is the gain in the physical intuition and transport/transmission insights relative to the working principle of a single-molecule gas sensor. The important point is that a fullerene based sensor is able to well recognize polar molecules in proximity to its conductive channel. The stronger the polarization, i.e. the electric charge, present or induced (for temporary polarization) on the target molecule, the larger is the obtained current variation due to the presence of such chemical species. Thus the better is the recognition ability of the sensor for that chemical species, meaning that the sensitivity to such a molecule is larger and consequently the selectivity is improved (i.e. the current variations or sensitivity to the target compared with the ones due to other "spurius" chemical species). The lead sulfate molecule presents a very large permanent dipole, indeed it is an ionic compound maintained together by an ionic bond that allows the basic cell/molecule to have a charge equal to two times the electron charge on one side and minus such a quantity on the other side. The polarization charge is thus very large making possible great current variations and a good recognition.

For the ammonia the polarization involves smaller charges, thus making smaller also the current variations and the sensitivity and the selectivity. The proximity of the ammonia molecule to the fullerene is evidently moreover insufficient to temporary more polarize the molecule thus enhancing the recognition mechanism. Instead the argon is responsible of larger current variations for large biases because it has an high number of electrons (atomic number 18), and thus when temporary polarized it is responsible for larger positive charges nearby the fullerene, leading to an improvement of transport by lowering the barriers. The argon is considered more in details in appendix E.7. In the following subsections additional interesting cases of study are considered, to gain deeper understanding of the basic behavior explained above.

Before proceeding notice that this kind of analysis was not performed in the previous chapter in order to avoid repetitions and redundant topics. Indeed in the previous chapter the main topics were the first steps of the design methodology of section 7.2:

- fix geometry of the device (successfully done for maximizing the sensitivity)
- fix a method for validating the non-equilibrium EHT simulations (successfully achieved)
- verification of the gas sensor sensitivity to ammonia (successfully done)
- verification of the gas sensor selectivity to ammonia (successfully done, even if the result consists in a sensor failure)

While in this chapter the focus was mainly on the sensor features in terms of response to different concentrations and distances of the target, etc... comprising also the analysis of this section, aimed in clarify fundamental issues concerning the detection in single-molecule sensors. The analysis reported above confirmed the physical intuition mentioned at the end of the previous chapter, in section 8.6.3.

#### Two PbSO<sub>4</sub> molecules with opposite orientations

The analysis on the transmission eigenstates was repeated again at a bias voltage of  $0.8 \,\mathrm{V}$ , for the case in which two  $\mathrm{PbSO}_4$  molecules are placed nearby the fullerene with opposite directions such that their lead ions point toward the two opposite contacts. Three main transmission peaks were present within the considered bias wind at energies: -0.16 eV with transmission 0.887169; 0.04 eV with transmission 0.915297; and at 0.16 eV with transmission 0.849489. Their transmission eigenvalues were calculated and the relative transmission eigenstates, only for the highest eigenvalues, were evaluated and projected in real space. As a title of example the transmission eigenstate corresponding to the second eigenvalue (i.e. QN = 1) at energy 0.04 eV is reported in figure 9.5.6. In this case it is very well highlighted the role of the two Pb ions. They are in the middle of the two p-type orbitals with a blue lobe and a brown/orange lobe. In the picture it is well highlighted that the blue lobes of the two Pb ions are well delocalized and merged with the contacts wave-function, meaning an high coherent transmission from contacts to such an orbital nearby the lead atoms. The left Pb atom is not visible since hidden by the p-type lobes, while the right one is partially visible (dark grey color) in the middle of the blue and brown/orange lobe on the right. The role of the two lead ions is thus to lower both the barriers between the fullerene and the contacts. Instead very low transmission occurs nearby the  $SO_4$  groups, indeed no iso-transmission surface is present there. This again confirms that the negative charge of the  $SO_4^{2-}$  ions contributes in increasing the potential

barrier. Nevertheless once an electron is in the central region (fullerene plus lead sulfate) of the device, it can be transmitted to the other contacts by means of other transmission channels. For fully coherent paths an electron can follow the blue (or brown/orange) orbitals, otherwise if phase-breaking is possible, it can move across transmission surfaces of different colors (as mentioned in sections 4.4 and 5.15.1 phase-breaking processes are naturally included in a coherent picture since electrons are indistinguishable particles and if exchanged no difference occurs since the transmission in each channel/energy is the same). Additional pictures of transmission eigenstates for this specific geometry (and bias point) are reported in appendix E.6.1.



Figure 9.16: Transmission eigenstate (top view) corresponding to the transmission eigenvalue 3.540307e-1 with quantum number QN = 1, transmission peak at energy E = 0.04 eV, the geometry is the one with two PbSO<sub>4</sub> molecules with opposite directions, and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).

The point is that by means of the transmission eigenstates analysis carried out in this section it was possible to intuitively explain the result obtained at the end of the previous section, in which it was found that with such a geometry with two opposite  $PbSO_4$  a great current improvement occurred. The reason for that is exactly in the lowering of the contact-central region barriers thanks to the two positive lead ions. In the case of two  $PbSO_4$  parallel molecules the two lead ions are on the same side thus only lowering one of the barriers and providing a lesser current increase. This again confirm the intuition of section 8.3.5, in which it was stated that the main bottleneck for transport in a fullerene-based molecular wire are indeed the contact-fullerene barriers.

# The $PbSO_4$ molecule orientations with $SO_4$ group pointing down toward the fullerene

From the analysis performed in section 9.5.1 it was clear that at the chosen bias ( $V_D = 0.8$  V) the sensor had an improved current for three over four orientations. The one leading to a current decrease w.r.t. the case in which no PbSO<sub>4</sub> is present was the orientation with the SO<sub>4</sub> group pointing down toward the fullerene. A transmission eigenstates analysis for such a geometry and bias point can elucidate the reasons for that. For the selected bias point the transmission spectrum showed a peak entirely included in the bias window at energy 0.28 eV and two peaks at the two sides of the bias window. It was considered only the first peak and for it only the first transmission eigenvalue (with quantum number QN = 0, corresponding to the highest transmission coefficient for that transmission peak). The corresponding eigenstate is depicted in figure 9.17.



Figure 9.17: Transmission eigenstate (full view) corresponding to the transmission eigenvalue with quantum number QN = 0, transmission peak at energy E = 0.28 eV, the geometry is the one with a single PbSO<sub>4</sub> molecule, with the SO<sub>4</sub> group pointing down toward the fullerene with opposite direction, and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).

The negative charge at  $SO_4$  side contributes in decreasing the transmission due to repulsive Coulomb force and an enhancement of the potential barrier electrons have to overcome to be transmitted from source to drain. Indeed nearby the  $SO_4$  group no transmission occurs (the transmission eigenstates is not present there), and the Pb positive ion is too far for improving the transmission. As evident in figure 9.17 the transmission occurs exclusively through the fullerene and a clear transmission free region is present in the upper side of the device, closely to the  $SO_4$  group. This is the reason why a current decrease occurs for such a bias point for the considered geometry.

# 9.6 Sensor LUT-based circuit model

The aim of this section, and of the next two ones, is to build a MES model to be used in circuit behavioural and performance analysis. The task is split into two parts, firstly, in this section, a simple look-up-table model is implemented in *Cadence Virtuoso®* environment in order to allow performing behavioral and functional analyses at circuit level; then, in the next section, the sensor device stray capacitances are calculated along with some dynamic quantities that I will call "dynamic resistances", and finally in section 9.8 such parameters are exploited to estimate the order of magnitude of the sensor response time, by implementing a circuital model, for dynamic analyses that includes them.

As mentioned above, the focus in this section is on functional and static analyses of circuits including a MES, or generally a molecular wire or transistor (a molecular device). In order to evaluate the functionality and the behavior of circuits including a MES, the only needed information is the current-voltage characteristics of the considered MES. Notice that in principle this is also enough to estimate the static power performances of the circuit. In general, starting from previously simulated *I-V* characteristics, for example in an atomistic tool like *Quantum-Wise AKT*, as reported in the previous sections of this chapter, it is possible to obtain a sort of Look-Up-Table (LUT) in which the current value for a given input voltage  $V_{DS}$  is reported. This holds true if a molecular wire structure is used, instead if the device includes also a gate terminal (molecular transistor) such a LUT should store the current values for a given input voltage couple:  $(V_{GS}, V_{DS})$ . Moreover in the case of a MES the *I-V* characteristics are affected also by the presence of the target analyte, like PbSO<sub>4</sub>. In this regard the LUT should store the current values for each input voltage value/pair and for each considered number of target molecules (e.g. PbSO<sub>4</sub>).

For example, the MES considered previously in this chapter is a molecular wire, and thus it has no gate and no  $V_{GS}$ . So the LUT representing it should store the current values  $I_{DS}$ for each voltage value  $V_{DS}$  and for each number of PbSO<sub>4</sub> (target) molecules: namely 0 (no lead sulfate but only C<sub>60</sub> "alone"), 1, 2 PbSO<sub>4</sub> molecules. In order to account for the number of lead sulfate (target) molecules in proximity of the sensor, an additional input terminal can be used (besides the drain and the source ones), assuming that it is just a fictitious terminal able to select the correct *I-V* characteristics for the desired number of target molecules.

Once the output current  $I_{DS}$  is known for a set of input voltage values, it can be interpolated (in more or less refined way) to get a realistic quantitative previsions of the behaviour of the the considered device, placed within a given circuit (e.g. the conditioning circuit) under given operating conditions (i.e. specified  $V_{GS}$  and eventually  $V_{DS}$  values and number of target molecules nearby the MES). This is of course true at steady state, when all dynamic phenomena are extinguished, and the circuit DC operating point is stable. However, this model can also be used in performing some kinds of dynamic analyses. In particular if the interest is not in dynamic power nor in delay performances of the network, but just in quantitatively estimate the response of the circuit to a certain time-varying stimulus, this LUT-based simple model is effective as well. Indeed it is able to provide a good estimation of the output quantity values for a whatever time-varying input quantity. The obtained results are reliable if time-varying phenomena are slow enough to address a quasi-static regime of operation, in which all transients extinguish before a new variation of input voltages occur. Two main limitations are present in this approach: first, there is no delay in the response of the circuit (the simulator will instantaneously update the output when the input is changed); second, the output waveform shapes are ideal, in the sense that no stray capacitive or other stray effects are taken into consideration with this model, and as a result the response will neglect all waveform variations due to these effects.

The practical implementation of this model was performed directly in *Cadence Virtuoso*<sup>®</sup> as follows. Firstly a new symbol was created for the PbSO<sub>4</sub> MES, it is reported in figure 9.18. This means creating a new "cellview" of type symbol (eventually placed in a new library). Then another "cellview" of type verilogA (with the same name) for the PbSO<sub>4</sub> MES was created, in which a *verilogA* description of the device was provided. It consists in an interpolation  $(3^{rd}$  order spline polynomial function) of the LUT, that was built starting from simulated I-V characteristics of the sensor. More details and the *verilogA* code are provided in appendix G, section G.1. Notice that a fictitious terminal named "N\_PbSO4" is used to select the I-V characteristics for the desired number of  $PbSO_4$  molecules. For simplicity it was defined as an input voltage terminal assuming the user to be aware of the fact that it can assume only 0, 1, or 2 value, meaning that there 0, 1, or 2 PbSO<sub>4</sub> molecules nearby the sensor and selecting the correct I-V characteristics. Notice also that there is an advantage in treating such a fictitious contact like a continuum analog input voltage: by making varying for example from 0 to 1 (fictitiously "volts"), it can be emulated the approaching of the  $PbSO_4$  molecule to the sensor. Indeed the interpolation between the 0  $PbSO_4$  molecules and the 1  $PbSO_4$  molecule curves will provide a reasonable estimation of the real transient between the two I-V characteristics, that actually happens when the target dynamically approaches the sensor.



Figure 9.18: Circuit symbol for the PbSO<sub>4</sub> MES. Notice the drain terminal (D), source terminal (S), and the fictitious terminal "N\_PbSO4" that represents the number of lead sulfate molecules nearby the sensor. In yellow the instance name. The image is generated by *Cadence Virtuoso* software, used for performing circuit level simulations.

In conclusion, the simple LUT-based modeling approach can be used, in an effective way, for two main purposes:

• DC operating point or static analyses: steady state analyses require only the knowledge of the  $I_{DS}(V_{DS}, N\_PbSO4)$  for the two terminal device or  $I_{DS}(V_{GS}, V_{DS}, N\_PbSO4)$  for the gated one.

• Dynamic functional analyses (quasi-static regime): dynamic analyses can be performed if it is supposed to have enough slow variations of the inputs such that the outputs have always enough time to completely stabilize before a new variation is performed; keeping in mind that all dynamic effects (stray capacitances, etc...) are neglected and the device is thus considered as ideal.

Moreover if needed also static power analyses can be performed with such a trivial model: the static power for single device (i.e. the dissipated power when the network is in a given well-defined and stable state, to keep the network working in that state) can be simply and roughly estimated as  $I_{DS} \cdot V_{DS}$ .

In addition to above reported analyses, one may also be interested in performing dynamic power and transient duration analyses. In order to do that it is necessary to improve the LUT-based model as described in the following sections.

#### Functional verification of the LUT-based model

In order to verify if everything worked as expected the following functional verification of the LUT-based model was performed. The sensor symbol (i.e. the LUT) was connected to ideal voltage generators as depicted in figure 9.19 (a). The drain to source voltage (Vdd in the figure) was set to the chosen bias voltage for the PbSO<sub>4</sub> sensor, i.e. to 0.8 V. Then the fictitious voltage N\_PbSO4 was switched from 0 to 1, emulating the approaching of a single PbSO<sub>4</sub> molecule to the contact channel. The sensor current was verified to switch from 10.527 µA (corresponding to the current value with zero PbSO<sub>4</sub> molecules for an applied voltage of 0.8 V) to 13.573 µA (corresponding to the current value with one PbSO<sub>4</sub> molecules for an applied voltage of 0.8 V). The result is shown in figure 9.19 (b). A transient simulation was performed with the following settings (see figure 9.19 (a) for the defined quantities): Vdd = 0.8 V; Vn from 0 to 1 with linear transient, transient duration 100 ms centered around time instant 500 ms. Notice that the circuit behavior is ideal with no delay in the device response, as expected. Moreover additional tests were performed with different Vdd and Vn values, all leading to correct results and ideal results.

# 9.7 Sensor capacitances and "dynamic" resistances

In order to perform dynamic performance analyses at circuit level, it is necessary to estimate the electrostatic capacitances of the device. In particular, they are needed to estimate the dynamic power and the transient duration. The latter is in general particularly interesting for estimating the MES response time.

In order to correctly quantitatively estimate the device electrostatic capacitances, the quantum capacitance should also be considered and evaluated. It is an additional contribution of capacitance representing essentially the state filling within the molecular channel of the sensor. It was already introduced in section 4.1.8. Moreover, to estimate the time duration of transient phenomena (ad thus the MES response time), additional resistance contributions should be estimated as well, they are the source "dynamic" resistance  $R_s$ , and the drain "dynamic" resistance  $R_d$ . These two resistances do not model access resistances of the device, that are not present in a molecular wires or transistors. Indeed in a molecular



Figure 9.19: Left (a): LUT-based model testbench schematic. Right (b): Result of the transient simulation with the circuit in (a). The red line is the Vdd voltage, i.e. the DC voltage of the top DC generator in (a), DC voltage between ground and D. The yellow line is the fictitious voltage step applied to the N\_PbSO4 input terminal of the sensor (the bottom generator in (a)). The blue line is the sensor drain to source current, varying from 10.527 µA to 13.573 µA. The image is generated by Cadence Virtuoso software, used for performing circuit level simulations.

device the source and drain contacts are directly connected to the molecular channel, and thus the contact resistances are present (they are the resistances of the electrodes), while the access resistances, conventionally present in silicon devices, are not present. The above mentioned  $R_s$  and  $R_d$  contributions do not represent the contact resistances that will be neglected in the following, and that are very dependent on the specific technological process (since they depend on the contact dimensions). They instead represent the average amount of charge that, due to finite value of escaping rates (see coupling factors between channel and source/drain (S/D) contacts in section 4.1), can be exchanged between the molecular channel and the source and drain contacts in the unit time.  $R_s$  and  $R_d$  are useful in modeling the dynamics of the molecular device, and they are identically null in steady state case. Or better, source and drain intrinsic resistances themselves are of course already included in the  $I_{DS}(V_{DS})$  slope (i.e. they are the inverse of the conductance), and statically the channel conductance is known for each  $V_{DS}$  value as the tangent of the  $I_{DS}(V_{DS})$  curve in that point. But, here, the  $R_s$  and  $R_d$  values which I am referring to are not linked to the slope of  $I_{DS}(V_{DS})$  curve; their physical meaning is not the one of "conventional" resistances. They are just resistive contributions, to be considered in correctly modeling of source and drain electrostatic capacitances charging and discharging phenomena. In particular, they are just a way of modeling the amount of charge that (on average) can "pass" (or be exchanged) between the S/D contacts and the molecule in order to charge/discharge  $C_s$  and  $C_d$ . They are thus useful in transient duration analyses only (consider that in single-pole approximation the S/D time constants are approximated as  $R_sC_s$ ,  $R_dC_d$ ).

In the following these concepts will be further clarified and moreover a practical estimation of all these capacitive and resistive effects is performed. Notice that all the calculations I am referring to in this section were performed in *MatLab*, and the employed scripts are reported in appendix G (further details on methods and algorithms are explained directly in comments within the codes). In conclusion to this section also the gate capacitance and resistance are evaluated for completeness since they are useful if a third gate terminal is considered.

#### Practical implementation and the "Huckel-IV" tool

In chapter 5, section 5.17 (see in particular section 5.17.2), it was already introduced a free available *MatLab*-based tool called *Huckel-IV 3.0* and originally developed by prof. Ferdows Zahid with M. Paulsson, E. Polizzi under the supervision of prof. S. Datta at Purdue University (Indiana, USA) between 2003 and 2005 [105], [41], [24]. The general approach, method and algorithm behind this tool were already explained in detail in section 5.17.2. In appendix F is reported an operative description of such a tool, in the version I have modified (along with the precious contribution of Chiara Elfi Spano) during another project, the interdisciplinary workshop "Innovative Systems", a.y. 2018/2019 and 2019/2020. Such a version of the tool is obviously again free and available under request to me (or my colleague Chiara Elfi Spano). There are no substantial differences between the "our" version of the tool and the original one, only few changes in the system calls in order to ensure correct compiling on today's computers and few other things (such as the usage of the sign convention of voltage instead of the one of potential energies, etc...). All the operative details are well explained in our previous report about the workshop "Innovative Systems", and the main features are summarized in appendix F.

In the practical calculations of the quantities I am going to present in this section the simulated I-V characteristics were the ones obtained with such a tool (instead than the ones obtained with ATK). The main reason behind this choice is that the Huckel-IV 3.0 tool provides very useful data that are not easily accessible in ATK, and that are needed to perform the calculations I am presenting in a while. For example, in Huckel-IV 3.0 it is trivial to separate the Laplace potential contribution (the one directly due to the applied bias) from the Poisson one (that accounts for the screening and the charging of the molecular channel) - see section 5.17.2; that is a key information for doing all the calculations I need to introduce in the following.

In appendix G.2 is reported the MatLab code that was used to perform all the capacitance and resistances calculations reported in the following. The input data structure are the ones obtained with Huckel-IV 3.0 tool simulations and they are briefly presented in appendix F. Details on specific methods and algorithms are reported directly in the employed MatLab scripts.

#### Quantum capacitance $C_q$ calculation:

For an introduction to the quantum capacitance see section 4.1.8. It is an additional contribution of capacitance representing the state filling in the channel and to be considered in the total capacitive balance of the system. The calculation of the quantum capacitance becomes practically much complicated in the moment in which large variations occurs. In order to keep as simple as possible, I decided to proceed in a rough linearized approximated estimation of it, based on the following considerations. The equilibrium quantum capacitance value was determined exploiting the linearized definition:

$$C_q = q^2 DOS(E_F) \tag{9.1}$$

Then out-of-equilibrium values were determined exploiting again eq. (9.1), but with an average density of states  $DOS_{AV}$  value instead of  $DOS(E_F)$ . Such an average  $DOS_{AV}$  was evaluated as the average (arithmetic mean) of the molecule DOS, considering only the values within the bias window for each bias point. Moreover an additional average quantum capacitance  $C_{qAV}$  was then estimated as the average of all  $C_q$  values found in all bias points.

In appendix G.2.3 is reported the MatLab function that performs the quantum capacitance calculation.

#### Source and drain electrostatic capacitances $C_s$ , $C_d$ :

In addition to state filling (i.e.  $C_q$ ), conventional electrostatic capacitances should be considered. Indeed the movement of charges in response to the applied voltages would lead to capacitive effects. An introduction to electrostatic capacitances was already provided in chapter 4 (sections 4.1.4, 4.1.5, 4.1.7). Remember that in general the electrostatic effect and the charging effect are linked, and a self-consistent loop is necessary to ensure convergence (as for example implemented in *Huckel-IV* suite).

In order to correctly estimate the source and drain electrostatic capacitances in an easy way, the simple capacitive model of figure 4.6 can be considered. This is again a linear (or better linearized) model in which superposition of effects is used to find the total channel potential variation due to the different contributions, i.e. due to the applied voltages  $V_{GS}$ and  $V_{DS}$ , and the charging effect. In particular, it is possible to proceed in this simple way since the *Huckel-IV* suite outputs include:

- The Laplace potential within the channel in each considered bias point (in function of the *y*-coordinate, i.e. transport direction). It is the electrostatic effect (solution of Laplace's equation (5.79)).
- The total potential within the channel in each considered bias point, including also the charging effect (i.e. the Poisson's potential eq. (5.78)) and the image correction.

By exploiting the capacitive model of figure 4.6, by knowing the applied voltages  $V_{GS}$  and  $V_{DS}$  and the resulting channel potential, it is simple to derive the source and drain capacitances as follows. Exploiting as already mentioned the superposition of effects (linearized system hypothesis) the total average channel potential (this is the average

potential inside the quantum dot, that in this model is considered without physical dimensions) is given by (see also section 4.1.8, the only differences are due to a different notation):

$$U_{totAV} = U_{Laplace} + U_{charging} = U_{Vgs} + U_{Vds} + U_{charging}$$

$$\Rightarrow U_{totAV} = -q \frac{Cg}{C_{ES}} V_{GS} - q \frac{Cd}{C_{ES}} V_{DS} + q^2 \frac{\delta n}{C_{ES}}$$

where  $C_{ES} = C_s + C_d + C_g$  is the total electrostatic capacitance. Remembering the definition of quantum capacitance, it is possible to rewrite the last equation as follows:

$$U_{totAV} = -q \frac{Cg}{C_{ES}} V_{GS} - q \frac{Cd}{C_{ES}} V_{DS} - \frac{Cq}{C_{ES}} U_{totAV}$$

from which:

$$U_{totAV} = -q \frac{Cg}{C_{ES} + C_q} V_{GS} - q \frac{Cd}{C_{ES} + C_q} V_{DS}$$

that finally can be rewritten in terms of small (linearized) variations as:

$$\delta U_{totAV} = -q \frac{Cg}{C_{ES} + C_q} \delta V_{GS} - q \frac{Cd}{C_{ES} + C_q} \delta V_{DS}$$
(9.2)

At this point considering that the chosen bias points (i.e.  $V_{GS}$  and  $V_{DS}$ ) are of course known, the total channel potential  $U_{tot}$  is known from Huckel-IV simulations, the gate capacitance  $C_q$ , if present, can be evaluated from the device geometry as explained in the following and thus it is known, and the quantum capacitance (in each bias point) was already estimated (see above); the remaining only two unknowns are  $C_s$  and  $C_d$ . They can be easily estimated if it is assumed that  $C_s = C_d$ . This hypothesis is good in the ideal case in which the molecule is geometrically symmetric along the transport direction (as usually happens and like it happens for the  $C_{60}$  geometry chosen for the MES), and it is well (and symmetrically) anchored to the source and drain contacts. In particular this is often true if no dangling chemical bonds are present, and the source and drain contacts are made of same material (and same orientation). Under these hypotheses,  $C_s$  and  $C_d$ were estimated starting from the simple capacitive dividers of equation (9.2). In particular starting from the Huckel-IV outputs, it was possible to recover the space average (along the transport y-direction) channel potential  $U_{totAV}$  for each bias value. This was assumed the arithmetic mean of the total potential in each point along y. Then by fixing either  $V_{GS}$  or  $V_{DS}$  (i.e. considering an output characteristics only or a trans-characteristics only), it possible to consider only the relative term in eq. (9.2), thanks to the superposition of effects. Considering only small variations, that means considering the succession of simulated bias points starting from equilibrium and going up step-by-step up to the last one, and then starting again from equilibrium and going down step-by-step till the last one, it is possible to get the total capacitive ratios:

$$\frac{\delta U_{totAV}}{\delta V_{GS}}\Big|_{V_{DS}=0} = -q \frac{Cg}{C_{ES}+C_q} \quad \Rightarrow \quad \frac{Cg}{C_{ES}+C_q} \quad known$$

$$\frac{\delta U_{totAV}}{\delta V_{DS}}\Big|_{V_{GS}=0} = -q \frac{Cd}{C_{ES}+C_q} \quad \Rightarrow \quad \frac{Cd}{C_{ES}+C_q} \quad known$$

From which it is possible to find  $C_s$  and  $C_d$  values in function of the bias. In order to minimize the numerical error, source and drain capacitances were evaluated in the middle bias point between two consecutive simulated bias points, from which the variations  $\delta U_{totAV}$ ,  $\delta V_{GS}$  and  $\delta V_{DS}$  were evaluated. In the case of a molecular wire  $C_g$  was set to zero and  $V_{GS}$  was obviously not considered.

Notice that a different script was used to recover the equilibrium  $C_s$  and  $C_d$ . Equation (4.16) can be rewritten, by taking into account also the electrostatic effect, as follows ([90] - eq. (3.10) page 84):

$$\delta E_F = \frac{q^2}{C_q} \delta n + \frac{q^2}{C_{ES}} \delta n \tag{9.3}$$

where the first right-side term considers the state filling (i.e. quantum capacitance) and the second one the relative charging electrostatic effect (i.e. the fact that filling that states with charged electrons would lead to a shift in the molecule levels). This equation represents the charge transfer phenomenon to reach the equilibrium condition, and  $C_q$  and  $C_{ES}$  to be considered are the equilibrium values. The equilibrium quantum capacitance was already estimated (see above). The  $\delta n$  term is the difference in the number of electrons in the isolated molecule and the number of electrons in the molecule with contacts when the thermodynamic equilibrium is achieved. It is known from *Huckel-IV* simulations. The only unknown is then  $C_{ES}$ , that represents the total electrostatic capacitance at equilibrium. It was assumed that  $C_{ES}$  in equation (9.3) was given only by the sum of the source and the drain capacitances, since the charge transfer (electron transfer) to reach the thermodynamic equilibrium involves essentially only source and drain contacts and not the gate contact. Again, once  $C_{ES}$  is recovered (from eq. (9.3)), under the previous hypothesis and under the assumption of having  $C_s = C_d$  it is trivial to recover them at equilibrium.

Moreover the average  $Cs\_AV$  and  $Cd\_AV$  capacitances (simply obtained as the arithmetic mean over all bias point including equilibrium as well) were also estimated, in order to have single scalar values that immediately provide a fast estimation of the order of magnitude of the source and drain electrostatic capacitances for the considered molFET.

Finally another script was implemented in order to have a very fast, but also very rough, estimation of  $C_s$  and  $C_d$ . In this case they were evaluated using the parallel plate approximation, thus starting only from the molFET geometry, considering as source contribution half of the molecule in the transport direction, and for the drain contribution the other half. The dielectric constant of the molecule was simply approximated as the vacuum one. Even if this last approach is essentially wrong, it surprisingly led to estimated values that were not so different from the averaged ones.

All the developed *MatLab* scripts are reported in appendices G.2.2, G.2.4, and G.2.5.

#### Source and drain dynamic resistances $R_s$ , $R_d$ :

As mentioned above, in response to bias voltage variations, a variation in the channel free charges and thus in the device current occur too. This is modeled accordingly with eq. (4.20), by considering the electrostatic capacitances as proportionality factors between voltages and channel charge variations. However this is possible considering also the additional quantum capacitance contribution, i.e. the amount of available electron states (within the bias window), for which transitions between the contacts and the molecule are possible. For example, it is possible to have an electron transition from the source contact to the molecular channel only if in the molecule there is at least a free electron state at the considered energy eigenvalue. The amount of the exchanged charged is thus taken into consideration by means of the previously introduced capacitances.

In this section the focus is on how much time is required to accomplish a charge movement between the contacts and the molecule, in response to a (small) voltage variation. The answer must be of course linked to the quantum capacitance concept, that models the state availability in the channel, but also to the concept of escaping time that was introduced in section 4.1. In particular the total amount of charge that can be transferred between the contacts and the molecule is determined by  $C_q$  (i.e. by the DOS), while the time required to move that amount of charge is intimately linked with the escaping times of source and drain contacts  $\tau_s$ ,  $\tau_d$ . Here I follow the approach of [90] (see part 3). In particular I make the hypothesis of having only small variations, ideal source and drain ohmic contacts (and thus no contact resistances), and to be at zero kelvin. Under these assumptions it is possible to show (see [90] - part 3 for the detailed demonstration) that the current injected by the source contact into the molecule can be approximated as:

$$I_S = \frac{q}{\tau_S} \int_{-\infty}^{+\infty} DOS(E - U_{totAV}) \left[ f_{FD}(E, E_{FS}) - f_{FD}(E, E_{Fdot}) \right] dE \approx \frac{C_q}{\tau_S} \frac{E_{FS} - E_{Fdot}}{q}$$
(9.4)

where  $E_{FS}$  is the source Fermi level,  $E_{Fdot}$  is the molecule Fermi level,  $\tau_S$  the source to molecule escaping time and  $C_q$  the quantum capacitance. It follows that (even under the hypothesis of having ideal ohmic contacts) there is a source resistive contribution that, together with  $C_s$ , determines the amount of time required in transferring charges toward/from the molecule. This is the physical meaning of  $R_s$ . Moreover, this is of course only a dynamic quantity that plays a role only in the moment in which input voltages are varied. In particular from eq. (9.4) it is possible to define:

$$R_s = \frac{\tau_S}{C_q} \tag{9.5}$$

Proceeding analogously for the drain contact:

$$R_d = \frac{\tau_D}{C_q} \tag{9.6}$$

In practice,  $C_q$  is already known for each bias point. From the *Huckel-IV* output data it is possible to recover the coupling matrices (for source and drain contacts) in each bias point:

1

$$\zeta_S = ES_{SD} - H_{SD} \quad , \quad \zeta_D = ES_{DD} - H_{DD} \tag{9.7}$$

where E is the energy,  $S_{SD}$  is the source-to-device overlap matrix,  $H_{SD}$  is the source-todevice coupling Hamiltonian, and analogous notation is assumed for drain case. At this point by exploiting energy-time uncertainty relation it is possible to recover the escaping time matrices:

$$\tau_S = \frac{\hbar}{\zeta_S} \quad , \quad \tau_D = \frac{\hbar}{\zeta_D} \tag{9.8}$$

Then the  $R_s$  and  $R_d$  values for each considered bias point were evaluated by means of equations (9.5) and (9.6). Finally overall average scalar values of  $R_s$  and  $R_d$  (namely  $Rs\_AV$  and  $Rs\_AV$ ) were recovered by averaging over all bias points.

The developed MatLab scripts that evaluated such quantities are reported in appendix G.2.7.

#### Gate capacitance $C_q$ :

If the device has the structure of a molecular transistor a gate terminal is present. For completeness the gate capacitance and resistance are evaluated too. In this subsection the first is considered while the latter is considered in the next section.

The gate capacitance arises from the device structure, and it is a physical electrostatic capacitance. It is due to the fact that a gate oxide (or in general a gate dielectric insulating material) is in between the metal gate electrode and the channel, that is supposed to be populated by free carriers (at least in ON state) that originate the drain to source current. Since, in this work, the focus is not in an extremely accurate estimation of the capacitances, but more in their order of magnitude, I decided to evaluate the gate capacitance by using the parallel plate capacitor approximation. The gate capacitance was thus approximated as:

$$Cg = \frac{\epsilon_{ox}\epsilon_0}{t_{ox}} \cdot Area \tag{9.9}$$

where  $\epsilon_{ox}\epsilon_{0}$  is the gate oxide dielectric constant,  $t_{ox}$  the gate oxide thickness, and the gate contact area is evaluated as the molecule length in longitudinal direction L, multiplied by the total width  $W_{tot}$ , that consists in the molecule width plus 100 Å (i.e. the dimension of the simulation box in *Huckel-IV* suite).

The developed MatLab code used for estimating the gate capacitance (with the method explained above) is reported in appendix G.2.1.

#### Gate resistance $R_q$ :

The device gate resistance  $R_g$  arises from the device structure, and it is essentially the resistance of the gate oxide. Again in order to keep things easy, I decided to simply estimate  $R_g$  as the resistance of the gate piece of insulator. Thus, starting from the knowledge of the insulating material resistivity (in the following it will be always zirconium dioxide  $ZrO_2$ ) and the geometry of the gate structure (see also above the discussion concerning the gate capacitance),  $R_g$  was estimated as:

$$R_g = \frac{\rho_{ZrO2} \cdot t_{OX}}{Area} \tag{9.10}$$

where  $\rho_{ZrO2}$  is the ZrO<sub>2</sub> resistivity,  $t_{OX}$  is the gate insulator length, and the area is evaluated from the knowledge on the system geometry, similarly to what explained for the gate capacitance  $C_q$ .

The developed *MatLab* code used for evaluating the gate resistance is reported in appendix G.2.6.

#### 9.7.1 *Cadence* circuital dynamic model

Once all the dynamic contributions of interest are known (see previous section), it is possible to proceed in making more realistic dynamic previsions concerning circuits that include a MES. In particular, from the knowledge of  $C_g$  (if present),  $C_s$ ,  $C_d$  and of  $R_g$  (if present),  $R_s$  and  $R_d$  it is possible to estimate the transients duration (see next section) and thus the sensor response time. If necessary it is also possible to estimate the dissipated dynamic power, even if in this work it will be not considered.

In order to do that an equivalent circuit, that includes all these effects, can be derived, simply by placing each contribution next to the relative ideal S, D, (and eventually G) terminal. Depending on the purposes of the simulations different values for  $C_g$  (if present),  $C_s$ ,  $C_d$ ,  $R_g$  (if present),  $R_s$  and  $R_d$  can be employed: the average scalar ones, or the values at a fixed bias point, calculated as described previously.

In the next section the PbSO<sub>4</sub> MES response time will be estimated. The device structure is a molecular wire thus without the gate capacitance and resistance. A possible circuit schematic for such a device is reported in figure 9.20. Notice that this schematic is not suitable in estimating static or steady state properties of the network, but only for estimating transient properties such as the transient duration to perform a change of state of the network. Indeed at steady state the  $R_s$  and  $R_d$  are null, and should not considered (remember their physical meaning explained in the previous section). Moreover the current and voltages values obtained with that schematic are not significant, since, due to the fact that  $R_s$  and  $R_d$  disappear at steady state, they are not correctly estimated. Nevertheless, despite its limitations, the circuit of figure 9.20 can be used to estimated the response time of the sensor as follows. In the single-pole approximation the source and drain time constants, i.e. the time constants characterizing a transient from a steady state to another one, can be easily estimated as:  $R_sC_s$  and  $R_dC_d$ . Nevertheless the single-pole approximation is not bad if there is a well-dominant single-pole that mainly determines the cut-off frequency. In general this is not true since the source and the drain are interacting. From a circuit standpoint the source and drain capacitances generally can belong to the same closed loop in the network, thus leading to mixed frequency interaction since the two poles "will interact" giving rise to a novel frequency behavior. A more correct way of proceeding for the estimation of the transient duration is by means circuit simulation, for example performed in *Cadence Virtuoso*<sup>®</sup> environment. The circuit simulator accurately solves the network providing a more realistic information concerning the system cut-off frequency.

The exact procedure used to estimated the sensor response time is reported in the next section, it exploits the circuit of figure 9.20.



Figure 9.20: Circuit schematic for the sensor circuital model including  $C_s$ ,  $C_d$ ,  $R_s$  and  $R_d$ . The image is generated by *Cadence Virtuoso* software, used for performing circuit level simulations.

# 9.8 Sensor response time estimation

The previous two sections were dedicated in developing and implementing in a circuit level simulator, namely Cadence Virtuoso<sup>®</sup>, an equivalent circuit model for the molecular sensor aimed in detecting the lead sulfate. The sensor has two terminal, i.e. it is a molecular wire, and its model is derived from an ideal LUT-based model (section 9.6) by adding source and drain electrostatic capacitances and "dynamic" resistances (section 9.7). The final circuit model, implemented in *Cadence Virtuoso®*, that can be used for estimating the sensor response time is shown in figure 9.20. The fictitious input terminal called "N PbSO4" is aimed in selecting the number of lead sulfate molecules nearby the molecular channel of the sensor. The purpose of this section is to estimate the order of magnitude of the MES response time, intended as the time needed to the  $PbSO_4$  sensor to change the state and thus its current from the value of about  $10.527 \,\mu\text{A}$ , corresponding to the case in which no lead sulfate molecules are present close to the MES, to about  $13.573 \,\mu\text{A}$ , corresponding to the case in which one lead sulfate molecule is nearby the channel. The goal is not to precisely calculate such a response time but more to have an estimation of its order of magnitude. The interest in estimating it is because if such a time would be greater than the average time during which the lead sulfate is enough nearby the sensor, it would be not able to change the state due to the presence of  $PbSO_4$  before the latter leaves the significant interaction region, thus making impossible a reliable detection. In this section I will firstly address the sensor time response estimation and only then the comparison of it with the interaction time.

In order to estimate the sensor response time by means of the circuit model of figure 9.20, the source and drain electrostatic capacitances and "dynamic" resistances should be estimated. To do that the methods presented in the previous section can be used. Such methods exploits MatLab scripts for the calculation of  $C_s$ ,  $C_d$ ,  $R_s$  and  $R_d$ , starting from data structure obtained, in turn, by means of Huckel-IV simulations. So the first step to achieve, is to simulate the  $C_{60}$  molecular wire sensor by means of Huckel-IV tool and obtain I-V characteristics and the other needed (output) data structures. In figure 9.21 there are three I-V characteristics obtained with Huckel-IV tool for the following values of the fitting parameter  $V_c$ : 0.6, 0.625, 0.65. The other input parameter for obtaining these results are reported in appendix F, table F.1. The geometry file was generated in ATK, and corresponds to the sensor geometry already widely discussed previously in this chapter. Above 1.5 V there is a bad agreement between the *I-V* curves obtained with the two tools. Instead a good agreement is obtained for low bias voltage up to 1.2 V. In particular the obtained current shape is not well in agreement, and depending on what is the bias point of different  $V_c$  values provide good agreement between the results with the two tools. At around 0.8 V, i.e. for the sensor chosen bias point, a very good agreement is obtained with  $V_c = 0.65.$ 

The Huckel-IV simulation result with  $V_c = 0.65$  can be thus useful in estimating the sensor capacitances  $C_s$  and  $C_d$ , and the sensor "dynamic" resistances  $R_s$  and  $R_d$ . Starting from the Huckel-IV output data structures (see appendix F), and exploiting the MatLab scripts reported in appendix G.2, it was possible to estimate  $C_s$ ,  $C_d$ ,  $R_s$  and  $R_d$ . The estimated values at  $V_D = 0.8$  V together with average values are reported in table 9.4. Since it is supposed to use the PbSO<sub>4</sub> sensor at  $V_D = 0.8$  V the values obtained for that



Figure 9.21: *I-V* characteristics obtained with *ATK* and with *Huckel-IV 3.0* tool. The ellipse highlight the chosen bias point, i.e. 0.8 V. Notice the different values of the fitting parameter  $V_c$ . Depending on what is bias range of interest a different  $V_c$  values can be used. For  $V_D = 0.8$  V the best agreement is obtained with  $V_c = 0.65$ .

voltage value were considered and used for  $C_s$ ,  $C_d$ ,  $R_s$  and  $R_d$  in the Cadence Virtuoso circuit of figure 9.20. Notice that in order to minimize the numerical error on calculating the source and drain capacitances they are not directly evaluated in 0.8 V, but instead at 0.775 V and 0.825 V; for this reason their arithmetic average was considered and it was assumed:  $C_s = C_d = 2.7844 \cdot 10^{-21}$  F. Notice that this procedure implicitly implies the assumption that  $C_s$ ,  $C_d$ ,  $R_s$  and  $R_d$  are constant during all the sensing process. This is an approximation and in general it is not true. Indeed  $C_s$ ,  $C_d$ ,  $R_s$  and  $R_d$  are dependent from the bias point and in the moment in which a  $PbSO_4$  molecule approaches the sensor the current is obviously changed, thus changing, in general, also the  $C_s$ ,  $C_d$ ,  $R_s$  and  $R_d$ . Nevertheless this is neglected for simplicity, and the source and drain capaticances and "dynamic" resistances are assumed constant (like standard components are). This is a great simplification that makes very simple the estimation of the sensor response time, indeed all the parameters in the *Cadence* circuit of figure 9.20 are assumed constant. Notice once more that  $R_s$  and  $R_d$  are not the contact resitances that are now assumed null (i.e. ideal ohmic contacts), but they are, together with  $C_s$  and  $C_d$ , a way of measuring the time needed to move charges in/out the molecular channel of the sensor for achieving the state commutation that occurs in the moment in which a lead sulfate molecule approaches the MES. For this reason in the following analysis the steady state currents and voltages are not significant of the operation of the sensor. Indeed at steady state the source and drain "dynamic" resistances should be null to provide correct current (and voltage) values. Moreover, since their values, along with the electrostatic capacitances values, dynamically change, the sensor response time will be estimated with low accuracy, also because other stray elements, that actually influence the response time, are neglected (such as the contact resistances). The following analysis will thus provide only the order of magnitude of the sensor response time.

**Table 9.4:** Source and drain capacitance and "dynamic" resistance values calculated from the Huckel-IV current-voltage characteristic with  $V_c = 0.65$  for the fullerene molecular wire. The average values and the values at 0.8 V are reported. Notice that the approximated (parallel plates) source and drain capacitances resulted to be:  $C_s = C_d = 1.89516e$ -18 F. The  $C_s$  and  $C_d$  values at 0.8 V are the arithmetic mean of those at 0.775 V, that are:  $C_s = C_d = 2.171e$ -21 F, and those at 0.825 V, that are:  $C_s = C_d = 3.3978e$ -21 F.

$V_c = 0.65$ curve	Average	Value at $0.8\mathrm{V}$
Quantum capacitance $C_q$	5.77115e-19 F	3.875e-19 F
Source electrostatic capacitance $C_s$	4.51839e-20 F	2.7844e-21 F
Drain electrostatic capacitance $C_d$	4.51839e-20 F	2.7844e-21 F
Source dynamic resistance $R_s$	$250707~\Omega$	312600 $\Omega$
Drain dynamic resistance $R_d$	$1.00308e+06 \ \Omega$	1250710 $\Omega$

The simulation in *Cadence* environment was set up as follows. A transient simulation was performed. A sharp rising edge from 0 to 1 on the N\_PbSO4 terminal (fictitious) voltage was applied, emulating an extremely rapid appearance of a single lead sulfate molecule. Then the transient duration, i.e. the sensor intrinsic response time was estimated in *Cadence*. This procedure allows for estimating the intrinsic response time of the sensor for actuating the state transition between the  $C_{60}$  only current value to the  $C_{60}$  + PbSO<sub>4</sub> one. If the voltage at the fictitious N\_PbSO4 terminal were made varying too slowly there would be no possibility of appreciating the sensor response time. Instead by making it varying fast the sensor will respond with an exponential transient, allowing for the estimation of the response time. The delay after which the step on the N PbSO4 was occurring was set to 0.1 fs; the rise and fall times were assumed to be  $1 \times 10^{-20}$  s; the rising edge shape was assumed to be half-sine. The following quantities were monitored, with reference to figure 9.20. The "intrinsic" drain and source voltages, i.e. the voltages at the drain and source nodes close to the sensor symbol (between the sensor symbol and the RC groups), and the drain current flowing into the sensor drain terminal. The longest transient duration, among the three considered quantities, was assumed to be significant of the order of magnitude of the sensor response time. In Cadence environment it is possible to directly estimate the transient duration by means of the tool "Transient Measurements". It automatically detected the rise and fall edges (20% - 80%) occurring in the drain and source voltages, and in the drain current, and consequently the rise and fall times. The results are reported in table 9.5. The obtained waveforms in function of time are instead reported in figure 9.22. Notice again that the specific values of voltages and current are not of interest, but only the time require to perform the state transition and reach the steady state is of interest. Indeed such values are wrong since the voltage drops across  $R_s$ and  $R_d$  are actually a fictitious effect, since such resistances are not present in reality.

In addition to this analysis another "customized" analysis was carried out in *MatLab* environment starting from the *Cadence* simulated waveform. As already mentioned in the previous section, the source and drain capacitances are generally interacting, making necessary a precise calculation by means of a circuit simulator like *Cadence Virtuoso*. Once

**Table 9.5:** Rise and fall times for the drain and source voltages and the drain current of<br/>the sensor, evaluated by means of the "Transient Measurements" tool in *Cadence*<br/>environment. The quantities are defined with reference to figure 9.20. The undershoot<br/>and overshoot are provided in % w.r.t. the steady state (final) value.

Quantity	Rise time (s)	Fall time (s)	undershoot $(\%)$	overshoot $(\%)$
Drain voltage	560.7e-18	-	0.4	-
Source voltage	-	13.73e-18	-	0.943
Drain current	34.46e-18	3.623e-21	0.257	0.0966



Figure 9.22: Time dependent waveforms for the drain, the source voltages and the drain current of the circuit in figure 9.20. The analysis was carried out in *Cadence Virtuoso®* environment. The current and voltage values are not of interest in this analysis, so they are not considered (they are wrong); the transient duration is instead significant of the sensor response time.

the time dependence of the three quantities of interest (drain and source voltages and drain current) was obtained, a *MatLab* script was developed and used to estimate the transient duration my means of a graphical method. Indeed from basic circuit theory it is known that the time constant of a circuit is the exponential time constant of the time evolution waveform, and thus it can be estimated by evaluating the intercept of the exponential tangent straight line and the time axis. Then the transient can be estimated to be long  $3\div7$  times such a time constant. In the developed *MatLab* code it was assumed to be long 7 times the time constant, being this the worst case with largest margin. The developed

*MatLab* script is reported in appendix G.3, together with the plots that it generated (with the above mentioned interpolation). The estimated values for the transient duration are instead reported in table 9.6. Since it was aimed in estimating the worst case in order to have margin for the design, all the time constants and response times (i.e. 7 times the time constants) are longer than the ones estimated in *Cadence*. The longest one is the source voltage time constant, whose transient duration is of the order of  $10^{-14}$  s.

**Table 9.6:** *MatLab* estimated time constant and transient duration, defined as 7 times the relative time constants. The considered quantities are defined with reference to figure 9.20. The time constants are defined with a graphical method.

Quantity	Time constant: $\tau$ (s)	Transient duration: $7 \cdot \tau$ (s)
Drain voltage	1.16022e-16	8.12151e-16
Source voltage	1.66579e-15	1.16605e-14
Drain current	4.38149e-17	3.06704e-16

For the sake of completeness also the source and drain time constants in the single-pole approximation were evaluated. In this approximation the two terminals (source and drain one) are supposed to be non-interacting, with the capacitances belonging to different loops. This is not true in general. Despite the simplicity of this model the obtained values are similar, in their order of magnitude, to the previously reported ones:

source time constant :  $\tau_S(0.8 \text{ V}) = R_s \cdot C_s |_{V_D=0.8 \text{ V}} = 8.70403 \cdot 10^{-16} \text{ s}$ drain time constant :  $\tau_D(0.8 \text{ V}) = R_d \cdot C_d |_{V_D=0.8 \text{ V}} = 3.48248 \cdot 10^{-15} \text{ s}$ 

#### 9.8.1 Estimated interaction time and sensor response

So far the focus was in estimating the order of magnitude of the sensor response time, i.e. the time required to change its state, and thus its current, from the value corresponding to the  $C_{60}$  alone to the value obtained with the  $C_{60}$  molecular channel with a single molecule of lead sulfate in proximity. The purpose of this section is to estimate also the average expected interaction time, defined as the time interval in which a non-negligible and well detectable interaction of the PbSO<sub>4</sub> molecule with the sensor occurs, and to compare the latter with the sensor response time. Indeed if the sensor response time were too large when compared to the interaction time, the detection of the lead sulfate by the sensor would likely not be reliable, thus requiring additional precautions and expedients to ensure a reliable detection.

In general, accordingly with the kinetic theory of gases [151], [152], a gas can be described by a large number of particles or molecules which are in constant, rapid, random motion. In this simplified treatment the particles size is assumed to be much smaller than the average distance between them. Moreover the collisions are assumed to be elastic, and except during collisions, the interactions among molecules are assumed negligible (this last hypothesis ensure quantum mechanical effects to be negligible). In such a theory the average kinetic energy of the gas particles depends only on the absolute temperature T of the system. A detailed treatment is for example provided in [151].

One main result of this theory is that the single particle has a kinetic energy per degree of freedom that is given by  $E_d = \frac{1}{2}k_BT$ , where  $k_B$  is the Boltzmann's constant and T the temperature. Thus the kinetic energy of a single particle in the 3D space, with 3 degrees of freedom, is given by:  $E = \frac{3}{2}k_BT$ . And the kinetic energy of system of N particles, each with three degrees of freedom is  $\frac{3N}{2}k_BT$ . In the following the focus will be on the single particle (with 3 degrees of freedom) case, indeed the attempt is to estimate the average velocity of a single PbSO<sub>4</sub> molecule in air at room temperature, by means of which the average interaction time will be estimated.

If a single gas molecule is considered, its kinetic energy is  $E = \frac{3}{2}k_BT = \frac{1}{2}mv^2$ , where m is the mass of the molecule and v its velocity. In particular it is possible to define three different velocities for the gas molecules [151], and v corresponds to the root means square velocity (rms):  $v_{rms}$ . Thus the root mean square velocity of a molecule can be estimated as:

$$v_{rms} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3N_Ak_BT}{mN_A}} = \sqrt{\frac{3RT}{M}}$$

where  $N_A$  is the Avogadro's number ( $N_A = 6.02214076 \cdot 10^{23} \text{mol}^{-1}$ ), i.e. the number of particles (molecules) contained in a mole (that indeed is the substance quantity that contains exactly  $N_A$  elementary entities, e.g. molecules);  $R = N_A k_B$  is the so called (universal) gas constant; and  $M = mN_A$  is the molecular mass (i.e. the mass of a mole). As mentioned previously in addition to the root mean square velocity it is also possible to define the most probable velocity, that results to be [151]:

$$v_p = \sqrt{\frac{2}{3}} v_{rms}$$

and the arithmetic mean or average velocity [151]:

$$v_{av} = \sqrt{\frac{2}{\pi}} v_p$$

In the case of the PbSO<sub>4</sub> the molar mass M is 303.26 g/mol, and the at room temperature T = 300 K the three velocity result to be:

$$v_{rms} \sim 157 \,\mathrm{m/s}$$
 ,  $v_p \sim 128 \,\mathrm{m/s}$  ,  $v_{av} \sim 145 \,\mathrm{m/s}$ 

In order to estimate the time during which, on average, it is expected to have a PbSO<sub>4</sub> molecule nearby the channel such that a sufficiently large variation of current occurs and allows for its detection, the following reasoning is carried out. In section 7.1.1 it was mentioned that, in general, a molecule moves because of the kinetic thermal energy and the convective motion of air. It may approaching the sensor, and if its kinetic energy is enough large it can "collide" on it without being chemisorbed or physisorbed and then move away from it (elastic interaction). Now this situation is assumed to be the one happening, since it corresponds to a worst case situation in which the lead sulfate is not interacting with the sensor for a long time (as it would be it were chemisorbed or physisorbed). The kinetic theory of gases strictly holds under some assumptions that are not said to be satisfied in general (e.g. it strictly holds for gases made of same elementary particles, while in general

different particles with different masses and chemical/physical properties are present). Nevertheless such a theory is assumed to be valid. Moreover it is assumed that no other molecule is present for all the interaction time nearby the sensor, and thus the  $PbSO_4$  is unperturbed, and it moves with a straight trajectory perpendicular to the sensor and it moves away on a similar trajectory (this is not relevant since the focus is only on a order of magnitude estimation of the interaction time). With reference to the figure 9.11, the range of distance (between the PbSO<sub>4</sub> molecule and the fullerene) in which the interaction is assumed to be enough strong to allow a reliable detection of the lead sulfate by the sensor is assumed to be less than 3.9 Å (indeed the current variation for such a distance is still enough large). Moreover it is assumed the  $PbSO_4$  to do not reach the zero distance but to be "reflected" back at a distance of 1.5 Å (indeed electron clouds will already strongly interact at such a distance likely causing the reflection - if kinetic energy is enough high as supposed). Thus the useful region or distance in which the detection can occur is a region 3.9 - 1.5 = 2.4 Å long. In the moment in which the PbSO<sub>4</sub> is reflected it should again travel such a distance in order to move enough far away from the sensor to be no more detectable. By neglecting any change of velocity of the  $PbSO_4$  molecule in the whole process, it is thus possible to estimate the interaction time as the time needed by the lead sulfate molecule to travel toward the sensor for a distance of 2.4 Å and then to come back. The total distance is thus two times 2.4 Å. The interaction time can be finally estimated like:

# $Interaction \ time = \frac{total \ distance}{velocity}$

Since three velocity definitions are possible three interactions times can be defined. They were evaluated by means of a trivial *MatLab* code, that was also used to estimate the sensor response time in the single-pole approximation. It is reported in appendix G.4. The resulting interaction times are reported in table 9.7 . It is important their order of magnitude of  $10^{-12}$ s (i.e. ps). Notice that also with slightly shorter distances the interaction time order of magnitude is unchanged. It is two order of magnitude lesser than the longest (worst case) response time of the sensor, that, as estimated previously, was of the order of  $10^{-14}$ s.

In conclusion, from the analysis carried out, the expected interaction time (at room temperature) is of the order of 1 ps, and since it is two order of magnitude greater than the longest response time for the sensor (of the order of  $10^{-14}$ s) it is expected the sensor to respond fast to the presence of the target PbSO<sub>4</sub> molecule, thus allowing a reliable detection. Notice that an high speed conditioning circuit is required to detect the target analyte if a single event like the one described above happens.

Table 9.7:	MatLab estimated	interaction ti	ime accord	ingly with	the described	approximations
	and method.					

Velocity used for calculations	Interaction time (s)
root mean square velocity	3.0557e-12
most probable velocity	3.74245e-12
average velocity	3.31666e-12

# 9.9 Gating the sensor

It was mentioned in section 7.2 that it has no much sense considering since from the beginning a molecular transistor configuration for the sensor. Indeed such a device structure is more complicated and expensive since more technological steps are needed. Even if the fabrication steps are more in number they should not influence strongly the device reliability, indeed the transistor gate is usually built in a configuration like the one presented in the introductory section in figure 1.3, i.e. with the gate below the molecule. In such a device conventional and standardized technological steps can be used to build the metal gate and the insulator layers, thus with the high process reliability of conventional CMOS devices. The most critical part of the technological process is the realization of the molecular junction [18]. In the previous sections and also in the previous chapter the low cost and effective molecular wire device structure was used for the MES. Instead the purpose of this section is to briefly address the transistor configuration and in particular investigate if it can have potential performances w.r.t. the wire one.

# 9.9.1 Gate control and choice of the gate voltage

The gate terminal is not physically connected to the molecular channel (i.e. the fullerene), but instead it is only electrostatically coupled to it. The effect of a gate voltage was already introduced and discussed in section 4.1.7 and also, more formally, in section 5.17. The main point is that it changes the electrostatic of the system, thus it affects the energy levels and from the standpoint of the electrical current, in the Landauer's approximation of coherent transport, it modifies the transmission spectrum (and consequently the current). In an ideal case (see section 4.1.7) the effect of a gate voltage is to shift (up or down depending on its sign) the transmission spectrum T(E) rigidly. And in this simplified optics, it allows to work around at a specific energy value (i.e. it shifts the zero energy, i.e. the molecule Fermi level). Nevertheless from the detailed discussion of chapter 5, it is known that, actually, by applying a gate voltage, the transmission spectrum is modified in a more complex way, and its transmission peaks are shifted, merged or split, and modified in magnitude. In general there is no immediate and trivial way of predicting what will be the final T(E) with a given gate voltage, and a self-consistent algorithm should be used to make predictions on it.

These arguments make very difficult the choice of the optimal gate voltage for a given sensor. Indeed in a MES the gate voltage should improve the performances of the sensor (w.r.t. the wire configuration ones), but it is difficult actually predicting for which gate voltage value, and if, this occurs. In order to choose a gate that likely will improve the sensor performances the wire MES equilibrium transmission spectrum was analyzed. It is reported in figure 9.23 (a). In the approximation (this is an ideal non-realistic case) in which the transmission spectrum is not affected by the applied bias, and in which the gate voltage only shifts it around a given energy, it was chosen to try forcing the device working round the transmission peak at approximately  $1.8 \text{ eV} \div 2 \text{ eV}$ . Indeed for such an energy range the T(E) is well modulated by the presence or not of the target PbSO<sub>4</sub> molecule. If the effect of the gate voltage would be to shift rigidly the spectrum, a gate voltage  $V_G \sim 1.9 \text{ V}$  should be enough to make the device working around that transmission
peak. Nevertheless an additional non-ideality must be also considered. With reference to the treatment of section 4.1.7, the effect of the  $V_{GS}$ , can be considered by means of the potential energy term  $U_{Vgs}$ :

$$U_{Vgs} = -q \frac{C_G}{C_{ES}} V_{GS}$$

where  $C_{ES} = C_G + C_S + C_D$  is the total electrostatic capacitance. Thus it is evident that a gate voltage  $V_{GS}$  will ideally shift the transmission spectrum T(E) of a quantity  $U_{Vgs} = -qV_{GS}$  only if the capacitive ratio is almost unitary:  $\frac{C_G}{C_{ES}} \sim 1$ . This is possible only if the gate capacitance is very large if compared to the source and drain ones  $C_G \gg C_S, C_D$ , such that  $C_{ES} \sim C_G$ . This is again an ideal assumption, that usually in molecular devices is extremely wrong. Indeed molecular devices usually suffer of bad electrostatic control of the channel charge by the gate [12], [90]. This should not be a surprise since the standard electronic CMOS devices suffer of the same issue (short channel effects). In order to consider, at least to a small extent (let's say "to counteract a bit"), the latter non-ideal effect, it was chosen to fix the gate voltage to  $V_{GS} = 2.5$  V. In principle, at least if the gate capacitance is actually not too much small w.r.t. the source and drain ones, this should allow to work around the transmission peak at energy  $1.8 \text{ eV} \div 2 \text{ eV}$ , at least to benefit a bit of such large transmission modulation for some bias points in the bias window (i.e. for some applied  $V_{DS}$ ).

Moreover, if the insulator thickness is small and its dielectric constant is large, then the gate capacitance is larger, and the gate electrostatic control of the channel is better [2]. This is exactly analogous to what happens in conventional electronic CMOS devices. Indeed the MES transistor structure (refer again to figure 1.3) is quite similar to conventional electronic device ones. In order to make plausible calculations and quantitative estimations. a realistic gate insulator material and thickness should be chosen. It was chosen the zirconium dioxide material  $(ZrO_2)$ , that is a well known high-k material with relative dielectric constant  $\varepsilon_R = 25.0$  [153]. The gate insulator thickness was chose equal to a single-atomic layer of  $ZrO_2$ , i.e. 5.1 Å. Actually in [153] the lattice constant of  $ZrO_2$  is declared to be 5.07 Å, but since in [154] the experimentally measured one is  $(5.135 \pm 0.005)$ Å, it was chosen an intermediate thickness value of 5.1 Å. Notice that the simulations were performed in ATK, that allows the usage of gate terminals in the continuum approximation. This means that the gate insulator and metal regions are assumed to be continuum regions with ideal properties, and they are not treated as atomistic regions or contacts. This implies that the dielectric region is simply characterized by having a given dielectric constant, and insulator atom resolution is not considered. Moreover the metallic region is treated as an ideal metal region, i.e. like a PEC (Perfect Electrical Conductor), and indeed the used metal material should not be specified. The final geometry with the  $C_{60}$  fullerene is shown in figure 9.24.

As evident from figure 9.23, the gate effect is only barely the one of shifting the transmission spectrum toward higher energies, while the main effects are in modifying the shape and the height of the transmission peaks. The transmission peak around the zero is barely shifted to the left of approximately 0.06 eV, thus making evident that the ideal behavior is actually much different from reality in this specific case. In the next sections the gated MES performances are presented and discussed.





Figure 9.23: Equilibrium transmission spectra with and without the  $PbSO_4$  molecule for the wire configuration (a) and the transistor one (b).

The simulations were again performed in ATK software, and the settings were the same of the wire case (tables 8.1, 8.2, 8.3, 8.4, 8.5), except for the Poisson solver boundary condition in the face in which the gate is present, that was set up to Neumann boundary condition (i.e. null electric field - indeed a PEC is present).



Figure 9.24: MES structure with gate contact. The fullerene orientation and distance from source and gate contacts are unchanged. The gate terminal is added at the bottom. The purple region is the gate insulator, i.e.  $ZrO_2$  (dielectric constant 25.0) with thickness 5.1 Å. The white/light grey region is the metal contact. The figure was created with ATK software, used for performing the simulations.

#### 9.9.2 Sensor sensitivity and selectivity

In figure 9.25 is reported the I-V characteristics with and without PbSO<sub>4</sub> molecules nearby the conductive channel both for the wire MES and the transistor one (with  $V_{GS}$  fixed at 2.5 V). Notice that with the transistor configuration there is an increase of the current. Also in the case of the transistor configuration a significant current variation is present depending on the presence or not of the target PbSO<sub>4</sub> molecule.

The absolute and percentage average current variations are reported in table 9.8. With the gate, there is a significant improvement for the absolute variations (they are larger with the transistor than with the wire), for low biases, in the range [0,1] V; while the percentage current variation is essentially the same, even if it slightly decreased with the gate. Instead in the [0,2] V voltage range there is no improvement of performances but a slight decrease of the absolute variation and a significant decrease in the percentage one. In particular, depending on the considered bias point, there may be either a significant improvement in the absolute current variation or a worsening of the performances, since it can also be reduced w.r.t. the wire case. In appendix E.8, figure E.34, the absolute current variation for each bias point is reported. Notice that a good current variation improvement is present at 0.4 V and at 1 V, while at 0.8 V there is an improvement but less marked. Nevertheless such an improvement is of the order of 1 µA, thus being non-negligible, especially if the conditioning circuit for some reason needs more absolute current variation at 0.8 V is slightly reduced with the gate w.r.t. the wire case (see figure E.35 in appendix E.8).

In figure 9.26 the sensor current variations (with sign) to different  $PbSO_4$  orientations and to different common atmospheric gases are reported. It is important to notice that even in the case of sensor with the gate for 0.8 V the current variations due to  $PbSO_4$  (in all



Figure 9.25: Current-voltage characteristics with and without the PbSO<sub>4</sub> nearby the fullerene, both in the case of the wire sensor and in the transistor-based sensor one. For the transistor sensor the gate voltage was fixed at  $V_{GS} = 2.5$  V.

**Table 9.8:** Absolute average current variations  $|\Delta I_D|$  and percentage average current variations  $|\Delta I_D|_{\%}$  in the voltage ranges [0,1] V and [0,2] V; both in the case of the sensor wire and transistor structures.

Quantity	Wire	Transistor
$ \Delta I_D $ in the range [0,1] V	$2.252\mu\mathrm{A}$	3.767 μA
$ \Delta I_D $ in the range [0,2] V	4.799 μA	4.709 μA
$ \Delta I_D _{\%}$ in the range [0,1] V	30.78~%	29.55~%
$ \Delta I_D _{\%}$ in the range [0,2] V	28.72~%	23.02~%

the considered orientations) are enough distant from all the others, thus being again a potential DC working bias point also in this case. In the next section it will be verified that a very good linear response to different concentrations of  $PbSO_4$  will be possible at such bias voltage, thus making it more desirable as choice of bias point.

#### 9.9.3 Sensor response to PbSO<sub>4</sub> concentration

The same analysis of section 9.5.5 was carried out also in the case of the gated sensor. In particular, 0, 1, and 2 PbSO<sub>4</sub> molecules were considered, and the sensor response was analyzed in order to verify the linearity of the current variation w.r.t. the number of target molecules. By merging the spline (3<sup>rd</sup> order cubic) interpolating curves of the current-voltage characteristics for the above mentioned numbers of PbSO<sub>4</sub> molecules placed nearby the sensor, the surface plot of figure 9.27 was obtained. Notice that for  $V_D = 0.8$  V there is a very good linearity in the sensor response w.r.t. other bias points.



Figure 9.26: Current variations (with sign) to different  $PbSO_4$  orientations and to different common atmospheric gases are reported in the case of transistor-based sensor.



Current values in function of the PbSO4 concentration

Figure 9.27: Current flowing in the sensor with the gate structure in function of the applied drain-to-source bias  $V_D$  and of the number of PbSO<sub>4</sub> molecules nearby the molecular channel. Red points are simulated data, the surface is obtained by merging the spline (3<sup>rd</sup> order cubic) interpolating curves. The red line corresponds to the chosen bias point of 0.8 V; a good linearity is present.

In appendix E.8 the 1D graphs of the sensor current in function of the PbSO<sub>4</sub> concentration (i.e. number of molecules) are reported for  $V_D$  equal to 0.4 V, 0.8 V and 1 V. The most linear curve is the one for 0.8 V, while for 0.4 V and for 1 V the curves are extremely non-linear. For this reason, even if for 0.4 V and for 1 V the current variations are larger

both in absolute and percentage value (see previous section), a good choice for the bias point can be 0.8 V. Indeed, usually, the sensor linearity to target concentration is believed to be relevant, since it simplifies much the conditioning circuit and the detection process. Therefore, even in the gated device case, the 0.8 V can be a good choice for the sensor DC working point, due to its more linear behavior. This is also highlighted in figure E.42, in appendix E.8, in which the maximum error from linearity (i.e. maximum difference between interpolating straight line and spline  $3^{rd}$  order interpolation) is reported for each bias point. At 0.8 V such deviation from linearity is very low.

Even if the bias of 0.8 V leads to very good linearity w.r.t. PbSO<sub>4</sub> concentration, the best interpolating curve is obviously non-linear, but with a quadratic curve an extremely accurate interpolation is performed. To this purpose see e.g. figure E.40 in appendix E.8.

#### 9.9.4 Sensor response to PbSO<sub>4</sub> distance

In this section the different current-voltage characteristics for various distances of the target  $PbSO_4$  molecule w.r.t. fullerene  $C_{60}$  molecular channel are considered. In particular, the same analysis of section 9.5.4 (for the case of the wire sensor), was repeated in the gate device case, and a good linearity was found also in the latter case for a bias 0.8 V. In figure 9.28 is reported the interpolating surface, obtained by merging all the different cubic  $3^{rd}$  order spline interpolating curves for all the considered distances of the lead sulfate. The linearity is very good at 0.8 V, and this could be an additional reason to choose again such a voltage as the DC working voltage for the sensor even in the gate case. Notice also that in general a better linearity and less marked current variations are present in the case of the gate w.r.t. the wire case, indeed the ranges of current values with PbSO<sub>4</sub> distance are smaller than with the wire.

In appendix E.8, the plot at bias 0.8 V is reported and the linearity is again highlighted, even if w.r.t. the wire case it presents "slightly better linearity" and less current variations (absolute). Moreover in table 9.9 is reported the maximum error from linearity, i.e. the maximum difference between the spline and the straight line interpolating curves. Always in appendix E.8, the maximum errors are plotted w.r.t. the bias in figure E.44. Notice again that for 0.8 V the error is very low w.r.t. the other bias points and a good linear response to different lead sulfate distances is present.

#### 9.9.5 Sensor response time

In this section the sensor response time in the case of the gated device is considered. The starting point for estimating the sensor response time is to evaluate the sensor capacitances and "dynamic" resistances. In particular, the same methodology already used for the wire sensor was used also in this case, and the procedures illustrated in sections 9.6, 9.7, 9.8 were employed also in this case. The same *MatLab* scripts were used, i.e. the ones reported in appendix G.2, indeed they already included the gate case. The initial *Huckel-IV* simulations for the sensor parameters calculation in the case of the gated device were obtained by adding a gate (dielectric permittivity 25.0) at a voltage of 2.5 V, and by setting the fitting parameter  $V_c$  to 0.625 (to this purpose see figure E.45 in appendix E.8.1). No other modifications were present. A new symbol was defined for the static



Figure 9.28: Current flowing in the sensor with the gate structure in function of the applied drain-to-source bias  $V_D$  and of the distance of PbSO<sub>4</sub> molecule from the molecular channel. Red points are simulated data, the surface is obtained by merging the spline ( $3^{rd}$  order cubic) interpolating curves. The red line corresponds to the chosen bias point of 0.8 V; a good linearity is present.

Table 9.9:	Absolut	te maximum	errors from	linearity	for the	different	bias vo	ltages,	in t	the	case
	of the C	C <sub>60</sub> lead sulfa	te sensor w	ith gate.							

Bias voltage (V)	Error from linearity $(\mu A)$
0.2	1.92
0.4	1.69
0.6	15.43
0.8	4.74
1	11.12
1.2	17.11
1.4	7.54
1.6	28.8
1.8	77.33
2.0	68.82

model, with four terminals (an additional terminal for the gate). Its *VerilogA* description exploits the code reported in appendix G.5, and the *.txt* file storing the simulation data was structured as described in the *VerilogA* code comments.

The corresponding circuit symbol is reported in figure 9.29, that reports also the DC and transient generators used for verifying the LUT-based sensor model correct behavior. The correct current value was always obtained as expected (like reported in section 9.6 for the wire case).



Figure 9.29: LUT-based ideal model test-bench schematic. Notice the circuit symbol for the PbSO<sub>4</sub> MES. Notice the drain terminal (D), source terminal (S), and the fictitious terminal "N\_PbSO4" that represents the number of lead sulfate molecules nearby the sensor. In addition a gate terminal (G) is present. In yellow the instance name. The image is generated by *Cadence Virtuoso* software, used for performing circuit level simulations.

The same approximations already discussed in sections 9.7, 9.8 were used here. In particular it was assumed that all the capacitances  $(C_s, C_d \text{ and } C_g)$  were constant for all the transient duration. The same for the resistances  $(R_s, R_d, \text{ and } R_q)$ . Since, during the transient, the sensor DC working point was supposed to be fixed the used values were the ones obtained for  $V_{GS}$  fixed at 2.5 V and for  $V_{DS} = 0.8$  V. The used values are reported in table 9.10. Notice that the gate capacitance and gate resistance calculation were already discussed in section 9.7, since the MatLab scripts in appendix G.2 are general and consider automatically also the gate case. Nevertheless such a MatLab code estimates the gate capacitance and resistance assuming the device geometry of Huckel-IV tool, that has a fixed gate contact width (see section 5.17.2 and appendix F), slightly different from the one used for performing the ATK simulations. This is optimal if the LUT data are the ones obtained from *Huckel-IV* tool simulations. Nevertheless in this case the LUT data were those obtained with ATK simulations. For this reason the same approach and formulae (see equations (9.9) and (9.10)) were used to calculate  $C_q$  and  $R_q$ , but the device geometry (i.e. the gate area) was the one corresponding to the geometry of ATK simulations. Such values are reported are those reported in table 9.10 and used during time constant estimation. They are close to the ones obtained with Huckel-IV-based calculations, and in particular a very close single-pole approximation time constant is obtained:  $\tau_g = R_g C_g = 6.9950 \cdot 10^{-7} \text{s}$ , in the case of ATK geometry, and  $\tau_g = R_g C_g = 6.9948 \cdot 10^{-7}$ s, in the case of Huckel-IV geometry.

In order to estimate the sensor response time the circuit schematic of figure 9.30 was used. In addition to the LUT-based sensor model also the capacitances  $C_s$ ,  $C_d$ ,  $C_g$ , the gate resistance  $R_g$  (remember that this is a real resistance present in the device because of the gate structure), and the "dynamic" resistances  $R_s$ ,  $R_d$  were considered around it. With the same approximations, physical meaning and procedures already described in

**Table 9.10:** Source and drain capacitance and "dynamic" resistance values calculated from the Huckel-IV current-voltage characteristic with  $V_c = 0.625$  for the fullerene molecular transistor. The average values and the values at 0.8 V are reported. Notice that the approximated (parallel plates) source and drain capacitances resulted to be:  $C_s = C_d = 1.89516\text{e-}18$  F. The  $C_s$  and  $C_d$  values at 0.8 V are the arithmetic mean of those at 0.775 V, that are:  $C_s = C_d = 8.8539\text{e-}18$  F, and those at 0.825 V, that are:  $C_s = C_d = 8.2754\text{e-}18$  F. The gate capacitance and resistance were evaluated starting from the device geometry (parallel plate approximation); thus only one (average) value is reported.

$V_c = 0.625$ curve	Average	Value at $0.8\mathrm{V}$
Source electrostatic capacitance $C_s$	1.40895e-17 F	8.5647e-18 F
Drain electrostatic capacitance $C_d$	$1.40895e-17 \ F$	8.5647e-18 F
Source dynamic resistance $R_s$	179795 $\Omega$	220426 $\Omega$
Drain dynamic resistance $R_d$	719361 $\Omega$	881926 $\Omega$
Gate electrostatic capacitance $C_g$	2.2243e-18 F	-
Gate dynamic resistance $R_g$	3.1448e+11 $\Omega$	-

section 9.8, an estimation of the order of magnitude sensor response time was obtained. In particular, the fictitious voltage at terminal "N\_PbSO4" was made abruptly changing from 0 to 1 ("V"), emulating that suddenly a  $PbSO_4$  appears nearby the sensor. Then a transient occurred in order to make the current flowing in the sensor changing from the value corresponding to fullerene only case to the one corresponding to 1  $PbSO_4$  molecules nearby the channel. The transient duration was monitored for the source, drain voltages and for the drain current (see figure 9.30). The sensor time constants were estimated both in *Cadence* (transient measurements tool) and in *MatLab* (see appendix G.3). The resulting values are reported in table 9.11. Notice that the longest one corresponds to about 26 ps. If compared to the wire sensor case, in which the sensor response time was of the order of  $0.01 \,\mathrm{ps}$ , an important slowdown of the sensor response is present. This is due to the additional gate capacitance, that along with the gate resistance, gives rise to an additional time constant, thus slowing down the device. Moreover, the sensor interaction time can be evaluated as did in section 9.8 (see appendix G.4). Considering the previously reported analysis about the variation of the sensor current response for different  $PbSO_4$  molecule distances (see also figure E.44), a decreasing trend is present. Thus the "interaction" distance that determines the interaction time can be slightly reduced w.r.t. the wire sensor case, thus leading to a slightly smaller interaction time. This is obviously undesired, since it may be no more reliable the detection. Notice that the analyses carried out are rough estimations of the order of magnitude of such quantities, and moreover they are also worst case approximations. In light of this it is probable that the gate sensor is still able to detect the presence of  $PbSO_4$ , but as mentioned with less reliability, or better less robustness to all possible operating conditions. In particular, the interaction time analysis is a worst case since it is supposed to have the target moving at constant velocity with no collisions with other molecules that actually are present. Nevertheless it may happen that in some cases the gated  $PbSO_4$  is not able to quickly respond, making difficult the detection.



- Figure 9.30: Circuit schematic for the sensor circuital model (with gate) including  $C_s$ ,  $C_d$ ,  $C_g$ ,  $R_s$ ,  $R_d$  and  $R_g$ . The image is generated by *Cadence Virtuoso* software, used for performing circuit level simulations.
- **Table 9.11:** MatLab and Cadence estimated time constants and transient duration. The considered quantities are defined with reference to figure 9.30. The MatLab time constants  $\tau$  are estimated with a graphical method. Notice that Cadence failed in identifying correctly the rise/fall edges for the current.

Quantity	MatLab: $\tau$ (s)	MatLab: $7 \cdot \tau$ (s)	Cadence rise/fall time (s)
Drain voltage	3.72251e-12	2.60575e-11	1.788e-12
Source voltage	3.46648e-12	2.42654e-11	36.29 e-15
Drain current	1.79118e-13	1.25383e-12	-

# 9.10 Final remarks

In conclusion to this long chapter I would like to summarize the main practical results obtained throughout this chapter, in order to avoid to be lost in the big amount of information provided.

In the last two chapters the methods and the models presented in the part I of this work were applied to the study of ammonia and lead sulfate  $C_{60}$ -based molecular electronic sensors. The general methodology introduced in section 7.2 was followed to discover step by step the properties of these two sensors.

Chapter 8 was mainly focused on the methods and design figures of merit for choosing and fixing a device geometry, intended as distance between the fullerene and the contacts and the fullerene orientations. At the end of that chapter the selectivity verification showed a potential failure in the detection of ammonia when other common atmospheric gases are present. For this reason the present chapter collects the remaining steps of the general methodology of section 7.2 relatively to a lead sulfate gas sensor.

In the present chapter, once fixed the sensor geometry, the equilibrium properties were briefly analyzed, with methods consistent to the ones already widely used in the previous chapter, and then non-equilibrium properties were taken into consideration. In particular the sensor current sensitivity to lead sulfate, in its main orientations were considered (section 9.5.1), then the sensor sensitivity to different PbSO<sub>4</sub> concentrations and distances were analyzed along with the selectivity w.r.t. other common atmospheric gases (sections 9.5.2, 9.5.4, 9.5.5). These analyses allow to get familiar with the sensor properties and thus they are believed to be of help in the design process. They moreover allow to extract simple but meaningful figures of merit concerning different sensor features.

The choice of investigating the lead sulfate was not casual. Indeed, even if in practice it may have few applications (often a single  $PbSO_4$  molecule is rare, since lead sulfate tends to create conglomerates of small crystals that then are bond to large -of the order of the µm- particles), it was helpful to more deeply elucidating the functioning of MES gas sensors and of the mechanisms at the basis of their transport properties. In this regard, section 9.5.6 reports all the details. A potentially more practical (or market oriented) application will be investigated in the next chapter 10.

Moreover in sections 9.6, 9.7, and 9.8 useful device parameters were calculated and used to build an easy but effective, even if oversimplified, circuit equivalent model for the sensor. Starting from a simple LUT-based static model, more complete model for transient analyses was conceived. The developed model can be seen as a first (even if rough) step toward an equivalent "black-box" model of MES in general, in which the circuit-level designer does not care about the physical principles at the basis of the working of the sensor, but simply can exploit such a model to design the conditioning circuit, treating it as any other circuit component. This fancy "black-box" complete circuit level model is still far from the one developed in this chapter, nevertheless I believe an interested reader can find this helpful as a starting point for achieve the ambitious goal I have just mentioned.

In the last section 9.9, a slightly different device structure was considered, namely the transistor configuration with a gate terminal, in order to verify if a significant performance amelioration occurred or not. The purpose now is to comment the results and briefly compare them with the wire sensor case.

Introducing a gate terminal (ZrO<sub>2</sub>,  $V_{GS} = 2.5$  V) allows again to have a reliable sensitivity to lead sulfate and to reliably detect it, again for a drain-to-source working voltage of 0.8 V. The sensor absolute sensitivity is increased with the gate w.r.t. the wire case. This is more evident at low bias (below 1 V) while less marked at high bias (above 1 V). Nevertheless since the gate (at  $V_{GS} = 2.5$  V) enhances the current in the device the percentage sensitivity of the sensor to the target is decreased. Again the reduction is very small at low bias (below 1 V) while significant at high bias (above 1 V). Moreover by introducing a gate terminal, the sensor linearity is significantly enhanced w.r.t. the PbSO<sub>4</sub> molecule distance; and less current variations are present. For what is concerning the linearity to different PbSO<sub>4</sub> concentrations (or number of molecules), instead, the situation is the reverse: the gate slightly worsen the linearity and increases the current variations to different  $PbSO_4$  concentrations. From one side this allows for an easier recognition of the different concentration (if the trend is kept increasing -or decreasing- as it happens), from the other side a strongly non-linear sensor is undesirable. Nevertheless in both cases the deviation from linearity is contained.

In terms of sensor response time, the additional gate capacitance considerably increase the sensor response time w.r.t. the wire sensor. In particular it was estimated it to be longer of about three order of magnitude, thus making difficult a possible detection in case of fast interaction time (worst case).

Finally notice that in general it is not said that two lead sulfate molecules can be present nearby the channel, even for relatively high concentrations of PbSO<sub>4</sub>, that are anyway expressed in ppb thus meaning that the amount of lead sulfate is minimal w.r.t. common atmospheric gases. A possible solution can be to exploit an array of sensors displaced over a given area in order to improve the probability of interaction of the sensor with the target. In this case the concentration of lead sulfate (or whatever target) can be then measured starting from statistical analyses about the number and the frequency of PbSO<sub>4</sub> detection events happening in such a system.

Still a last remark is due relatively to sensor power. Indeed in general an important property for a sensor (and more generally for an electronic device characterization) is the dissipated power. Nevertheless, considering that the present work is a pioneering work on MES, that are still at embryonic phase of their development, and considering that likely several device optimizations and modifications will occur in order to optimize the performances and the fabrication of such devices, it is believed that at the moment it is poorly significant evaluating the dissipated power by the device. For this reason this topic is left to next studies on more realistic devices. For the moment, an indication can be obtained multiplying the applied bias voltage times the current flowing in it. At 0.8 V it means a dissipated static active power of the order of a dozen or a ten of  $\mu$ W, to this purpose see table 9.12. Nevertheless, a precise estimation of the power dissipated within the device (and within the contacts) requires more accurate analyses, as briefly mentioned in section 5.18 (e.g. eq. (5.85) can be used).

Table 9.12: Rough estimation of the static active dissipated power, for the wire and the gate $PbSO_4$  sensors.

Device	Power without $PbSO_4$ ( $\mu W$ )	Power with 1 $PbSO_4$ ( $\mu W$ )
Wire	14.3	17.6
Gate	8.42	10.9

# Chapter 10

# A glimpse on the $C_{60}$ -based nitric oxide gas sensor

This chapter is motivated by the analysis carried out in section 8.6.3, where it was verified a significant  $C_{60}$  wire sensor sensitivity to the nitric oxide (NO). The purpose is not to provide a detailed and complete analysis and design of an optimized sensor of nitric oxide, but instead to briefly investigate the main sensor properties and response to nitric oxide, in order to identify if a future additional work on a NO MES can be potentially profitable. Indeed in this entire work the focus is more on methods for modeling MES, both from a more theoretical standpoint (electronic structure, intermolecular interactions and transport), and from a practical standpoint (methodology for approaching the MES device-level modeling by atomistic simulations and extraction of relevant figures of merit). In this regard, in chapter 8 the basic  $C_{60}$  wire and basic equilibrium and non-equilibrium analyses were performed, supposing of being ammonia  $(NH_3)$  the target. In chapter 9 relevant analyses were developed mainly for the study of non-equilibrium (under bias) sensor properties, comprising dynamic features like the sensor response time. The important, even if conceptually simple, analyses carried out in chapter 9 allowed to characterize the sensor under few different important standpoints, and I believe they constitute a good set of analyses useful for the understanding and the design of MES aimed for gas analytes detection in general. Moreover a deeper insight on the basic physics behind the transport properties of such devices was given. This was possible supposing of being the lead sulfate the target of the sensor. In this chapter instead no novel analyses and methods will be proposed, but the already presented ones will be exploited to provide a brief and, even if incomplete under many aspects, satisfactory analysis of the  $C_{60}$  sensor for the detection of the nitric oxide. Because of the lack of time a complete analysis was not performed. For example it was assumed that the same geometries (wire and gate ones) already used for the ammonia and the lead sulfate were optimal also for the NO case, and thus only brief non-equilibrium analyses were carried out. Nevertheless it is believed the work to have anyway good consistency, since it summarizes in a concise way the steps for extracting the non-equilibrium figures of merit, presented in detail in the previous chapter. Moreover a series of significant analyses will be presented, showing the potentiality of the same sensor

to be able to detect both lead sulfate and nitric oxide, opening the way to multi-purpose potentially low-cost sensors. In this optics this chapter can be seen as a glimpse toward more practical consequences of the entire work, also considering the extreme importance of the detection (and purification) of air from nitric oxide (and all nitrogen oxides  $NO_x$  in general), as they are the collateral products of several motorized vehicles and industrial processes [65].

In conclusion to this introduction, I would like to point out that an interested reader can perform the same procedures and design/analysis steps I have conceived and reported in the previous two chapters for the case of nitric oxide (or whatever other target analyte), obtaining a more accurate picture on such a sensor, and e.g. choosing an eventually more suitable geometry (or voltages) for maximizing the sensitivity and selectivity of the sensor to NO. It does not require much effort indeed to exploit the methods reported previously and carry out such a more complete analysis. As I will mention again in the next chapter, relatively to future works, I believe such analyses could be a big step in clarifying if the NO detection can be an actual potential application, thus confirming the brief analyses I am going to report in the following, or not.

## **10.1** Preliminaries

Nitric oxide (NO) is a toxic pollutants often found in air due to human activities; it is especially produced by combustion processes in motorized vehicles and industrial processes [65]. It is sometimes called nitrogen monoxide or nitrogen oxide, even if the latter is a generic term referred to all the NO<sub>x</sub> compounds (all toxic and emitted during several combustion processes). Due its relevant importance a novel NO sensor for NO detection in air can potentially appear as a market for a gas MES.

Nitric oxide is one of the principal oxides of nitrogen, it is an hetero-nuclear diatomic molecule and it is a free radical, i.e., it has an unpaired electron [107], [108]. Due to the slightly different electronegativity of N and O it is a polar molecule, and due to the unpaired electron it is very reactive and sensitive to electric fields and polarization. Accordingly to the analysis carried out in section 9.5.6, this seems to be, intuitively, the reason for the ample current variations already verified in section 8.6.3 (in this regard see also section 3.7).

In the next section the two device structures, namely the wire one and the gated one, are considered and a brief analysis on them is carried out. Since the purpose of this chapter is mainly to verify the potentiality of the  $C_{60}$  sensor in being effective not only in the lead sulfate detection but also in the NO one, only few of the many analyses and design steps of the previous two chapters (and section 7.2) will be carried out. In particular it will be assumed that the device structures for both the wire and the gate sensor are the same already analyzed and fixed in the previous two chapters. In particular the  $C_{60}$  fullerene is positioned at 2.4 Å from the contacts (chemisorption equilibrium distance) with the hexagons pointing toward the gold FCC (111) electrodes. In general it is not said this to be the device structure that maximizes the sensitivity to NO. In general the steps detailed at the beginning of chapter 8 can be performed again in the case of the NO sensor to verify what is the device structure (i.e. distances from contacts and  $C_{60}$  orientation) that maximizes the sensor sensitivity to NO. Nevertheless, since the chosen configuration was the most stable with the already discussed advantages in these terms, in this chapter it is chosen the same structure. Moreover, this chapter can be seen as an extension of the previous one, in the sense that it can be seen as an attempt of answering the question if the already developed and studied PbSO<sub>4</sub> sensor can also be used as well as for the NO detection or not. In this optics, if it would be verified that it can work also for the NO detection, the same device could be used as a multi-purpose device, thus potentially decreasing the cost.

Since the geometries are the same already discussed throughout this work they are no more reported here. Notice that the NO molecule was put at a distance of about 2.2 Å from the fullerene, as already done for all the others considered chemical compounds (in order to ensure meaningful comparisons). Since NO is a polar molecule three different orientations were considered, namely the one with N and O equidistant from the fullerene with the bond axis along the transport direction (flat); the one with N atom pointing down toward the fullerene (N down); and the one with the O atom down (O down).

Once the geometry is fixed (see above), the equilibrium properties of the sensor can be studied. This step is again omitted in this chapter. The reason is simply to speed up the analysis. It is in principle possible to perform the sensor equilibrium properties analysis as already done in chapters 8 and 9 (see sections 8.4 and 9.3). Nevertheless, from the non-equilibrium I-V characteristic analysis of section 8.6.3, it was already verified a significant sensor sensitivity to NO.

In principle it is not at all correct, in terms of results reliability, consider EHT method without having validated it (like done in sections 8.5 and 9.4). Nevertheless this step is again omitted in this chapter. Therefore in the next sections only few non-equilibrium analyses will be performed, such as the sensitivity and especially selectivity verification, and sensor response estimations.

# 10.2 The $C_{60}$ wire sensor

The purpose of this section is to answer the question if the wire  $C_{60}$ -based MES, already designed in chapters 8 and 9, is also capable of detecting the presence of nitric oxide nearby the channel or not. From the *I*-V characteristics with 0, 1, 2, and 3 NO molecules nearby the sensor (not reported here for brevity) significant variations of current were noticeable, depending if NO was present or not nearby the sensor and in what concentration (molecules number). Indeed the four above mentioned *I*-V characteristics were sufficiently different the one from the others. They were merged together to give rise to the surface of figure 10.1, generated with the same methods and scripts described in section 9.5.5. Notice that there is no much linearity, and the most linear current variations w.r.t. the number of NO molecules are obtained for 0.2 V and 1 V. Instead for the chosen bias point in the case of the PbSO<sub>4</sub> sensor, i.e. 0.8 V, a strongly non linear behavior is present. In general the sensor presents less linear trend w.r.t. the PbSO<sub>4</sub> one, concerning the target molecule concentration.



Figure 10.1: Current flowing in the wire NO sensor in function of the applied drain-to-source bias  $V_D$  and of the number of NO molecules nearby the molecular channel. Red points are simulated data, the surface is obtained by merging the spline ( $3^{rd}$  order cubic) interpolating curves. The red line corresponds to the PbSO<sub>4</sub> sensor operating bias point: 0.8 V.

The NO wire sensor selectivity was then tested. To this purpose see also the discussion of section 8.6.3. In appendix D.7, figure D.27 is reported the plot of the (signed) absolute current variations due to the NO, with the main three orientations already discussed in the previous section, and together with the current variations due to other common atmospheric chemical species. Only in some bias points the current variations were enough large to allow a reliable detection of the target substance, i.e. NO. It occurs essentially only for  $V_D = 1 \text{ V}$ , with large reliability margins, in which the NO is clearly recognizable for all its possible orientations. In particular the  $\Delta I_D$  due to NO oriented with oxygen pointing toward the C<sub>60</sub> (O down) and in "flat" position are about 3 µA lower that the closest  $\Delta I_D$  due to other chemical species, namely the O<sub>2</sub>. In the same bias point the NO oriented with N pointing down toward the fullerene, provides a  $\Delta I_D$  that is different from those relative to other chemical species of at least 0.94 µA (referred to the closest curve, i.e. water - from argon the "distance" is of about 1.7 µA). Therefore, the sensor is reasonably sensitive to NO, and with a  $\Delta I_D$  at least "distant" from all the others of about 1 µA it is possible to potentially perform a recognition of the target (NO).

Nevertheless this is true only for  $V_D = 1$  V, and not for  $V_D = 0.8$  V. This means that the same wire sensor, i.e. the same device, with different operating voltage can be used as PbSO<sub>4</sub> sensor (if  $V_D = 0.8$  V), and as NO sensor (if  $V_D = 1$  V). This can in principle be a limiting factor, even if I believe it is not a big issue in practical implementations. Indeed a series o many parallel C<sub>60</sub> MES can be fabricated on the same chip with the same technological process, and then some of them can be fed with a  $V_D = 0.8$  V, and connected to a conditioning circuit for the PbSO<sub>4</sub> detection, while the others can be fed with  $V_D = 1$  V and connected to a different conditioning circuit (or the same with suitable modifications where needed) aimed in the detection of NO. Another solution can be e.g. to dynamically change the voltage of the same sensor between 0.8 V and 1 V, in order to make possible the reliable detection of both the targets. Anyway, in both cases, this is obviously a drawback, since the cost and the chip complexity are unavoidably increased w.r.t. the case in which the sensor can work as both PbSO<sub>4</sub> and NO sensor with the same voltage (a solution can be to fix an intermediate voltage at 0.9 V accepting greater detection errors and less robustness).

In figure 10.2 the absolute current variations (with sign) obtained with PbSO<sub>4</sub> and NO in the case of the wire sensor are reported. In the two bias points of interest, i.e.  $V_D = 0.8$  V and  $V_D = 1$  V, such current variations are enough different (they differ of at least 1 µA), thus making possible a potential usage of the sensor for both the lead sulfate and nitric oxide detection, as described above.



Figure 10.2: Current variations (absolute with sign) obtained with  $PbSO_4$  and NO molecules nearby the wire  $C_{60}$  wire sensor.

In conclusion to this section, the NO wire sensor response time is considered. The same methods, approximations and calculations already used for the PbSO<sub>4</sub> wire sensor are used also in this case. The details were already illustrated in sections 9.6, 9.7, 9.8. The same *MatLab* scripts were used, i.e. the ones reported in appendix G.2, indeed they already included the gate case. The initial *Huckel-IV* simulations for the case of the NO sensor are again those for  $V_c = 0.65$ . Indeed, like in the case of PbSO<sub>4</sub>, it was supposed of having constant capacitances and "dynamic" resistances at source and drain, and they are determined without the target molecule, but with the fullerene alone, thus being unchanged also in the present case. The simulations were performed again in *Cadence* environment. In particular the used capacitance and resistance values are summarized in table 9.4. Moreover, a LUT model was developed in *Cadence*, exactly like already discussed in section 9.6. A new symbol analogous to the one of figure 9.18 was defined, with the

only difference that the third terminal (the fictitious one) was called "N\_NO" (instead of "N\_PbsO4"), and that the table (the *.txt* file) stored the NO simulation data. The LUT-based model correct behavior was verified by means of test-bench circuit analogous to the one of figure 9.19 and then the sensor response time to a step from 0 to 1 in the fictitious terminal N\_NO was calculated by means of a transient simulation, exploiting a circuit analogous to the one of figure 9.20. Then, both an analysis in *Cadence* (by means of the tool "transient measurements") and an analysis in *MatLab* (by means of the script reported in appendix G.3) were carried out. The final results are summarized in table 10.1.

Quantity	MatLab: $\tau$ (s)	MatLab: $7 \cdot \tau$ (s)	Cadence rise/fall time (s)
Drain voltage	1.18622e-16	8.30354e-16	2.037e-15
Source voltage	3.56136e-17	2.49295e-16	25.95e-18
Drain current	3.84138e-17	2.68897e-16	rise: 22.96e-18 fall: 1.426e-21

**Table 10.1:** MatLab and Cadence estimated time constants and transient duration. The MatLabtime constants  $\tau$  are estimated with a graphical method.

For brevity it was not performed an analysis of the current variations in function of the distance of the NO molecule, so it is unknown above which distance the interaction is so small that a negligible current variation occurs. Assuming the same interaction distance as the lead sulfate, see section 9.8, with the same procedure (and MatLab script) discussed in section 9.8, it was obtained an interaction time of the order of 1 ps (considering the NO molar mass of 30.01 g/mol). The worst case (longest) of the NO wire sensor response times is well below such a time, indeed it is of the order of 2 fs, thus three order of magnitude less. Nevertheless, from the detailed analysis about the transport mechanisms and the transmission eigenstates of section 9.5.6, it is supposed the lead sulfate to be more strongly interacting than the NO (because of the ionic bond that leads to strong polarization and the larger number of electrons in the molecule). For this reason the NO-fullerene interaction distance was also reduced. The minimum considered one was of the order of 1 Å, meaning, accordingly to the simple model based on kinetic gas theory of section 9.8, that the NO molecule is interacting with the sensor for 0.5 Å only and then it is reflected and interacts again only for 0.5 Å. This is a reasonable worst case. The resulting interaction time was of the order of 0.2 ps, that is still two order of magnitude greater than the sensor response time.

In summary, the NO wire sensor seems promising as potential sensor, also in the same device structure, of the already discussed PbSO<sub>4</sub> sensor. From the preliminary brief analyses carried out in this section it seems that the detection of NO can occur for  $V_D = 1 \text{ V}$ . A discrete sensor linearity to NO concentration is expected, and the sensor can potentially distinguish the PbSO<sub>4</sub> presence from the NO, at the chosen bias voltage (for 1 V). Moreover the sensor response time is estimated to be low enough if compared with the interaction time, to make the detection possible and likely reliable. Additional investigations, for example analogous to the other analyses reported in chapters 8 and 9, can elucidate more sensor properties and features, and point out possible ameliorations for the NO detection with a C<sub>60</sub> wire.

### 10.3 The sensor with gate

The purpose of this section is to answer the question if the C<sub>60</sub>-based MES with the gate terminal, already discussed in chapter 9, section 9.9, is also capable of detecting the presence of nitric oxide nearby the channel or not. Since the purpose is not to design an *ad hoc* sensor optimized for the NO detection, that can anyway be designed by following the methodology and procedures already presented in the previous chapters, the same device of section 9.9 is considered throughout the entire present section. In particular, w.r.t. the wire sensor treated in the previous section, a gate contact is added with a ZrO<sub>2</sub> gate insulator of thickness 5.1 Å and with a gate voltage fixed at  $V_{GS} = 2.5$  V. In principle it is not said that such a gate voltage is optimal for the NO detection. In this regard the equilibrium wire sensor spectra, with and without the NO molecule, can be of help in determining the first guess for the  $V_{GS}$  maximizing the detection performances of the sensor, as described for the lead sulfate at the beginning of section 9.9. Moreover the  $V_{GS}$  can be successively refined, by making it varying and considering the sensor I-V characteristics with and without the NO molecule and thus the sensor sensitivity to NO for various  $V_{GS}$ .

Nevertheless this is not the purpose of this section, that, again, is to check if the already designed sensor, with the geometry described in section 9.9, and with  $V_{GS} = 2.5 \text{ V}$ , is capable of simultaneously detecting, along with the lead sulfate, also the nitric oxide.

From the I-V characteristics with different NO orientations w.r.t. the fullerene channel, a potential detection capability is evident, indeed they are all significantly different from the C<sub>60</sub> alone I-V characteristic. They are reported in figure 10.3. Notice that for a drain voltage of 0.8 V, the various NO orientations lead all to different currents, leading to a potential usage of the device as NO sensor.

With the gate terminal at 2.5 V an increase of the current flowing in the device occurs, analogously to what described for the lead sulfate sensor (section 9.9). In particular the shape of the *I-V* characteristics is essentially unchanged but "translated" toward higher current values, see figure H.1 in appendix H. In both cases the punctual (i.e. in each bias voltage) current variations are not much changed (figure H.1), with a slight reduction in the gate device case. The average current variations both in the range of voltage [0,1] V and in the one [0,2] V and both absolute and percentage are reported in table 10.2. The whole absolute behavior over the entire range [0,2] V is essentially unchanged even if the percentage current variation is reduced with the gate case (due to the fact that the same current variations must be referred to a greater C<sub>60</sub> current reducing the percentage excursion). Instead in the range of voltages [0,1] V a significant reduction of the average values). Thus from this standpoint it seems, at the moment, that there is no advantage in using a gate terminal.

Although with the gate there is a decrease in the sensor average performances, and thus the wire allows for better detection properties, from a selectivity analysis (carried out in an analogous way of the one of sections 8.6.2 and 8.6.3) it turned out that it presents the great advantage of being potentially used for a reliable detection of NO, with all the three main possible orientations, at several bias points, also at low bias. In particular from figure 10.4, that reports the current variations due to the NO and other common



Figure 10.3: I-V characteristics obtained with the C<sub>60</sub> sensor with gate alone and with a single NO molecule with different relative orientations w.r.t. the fullerene. "Flat": the NO molecule is oriented with the bond axis parallel to transport direction, i.e. with N and O atoms at same distance from fullerene. "O down": the NO molecule is oriented with oxygen atom pointing down toward the fullerene. "N down": the NO molecule is oriented with nitrogen atom pointing down toward the fullerene.

**Table 10.2:** Absolute average current variations  $|\Delta I_D|$  and percentage average current variations  $|\Delta I_D|_{\%}$  in the voltage ranges [0,1] V and [0,2] V; both in the case of the sensor wire and transistor structures.

Quantity	Wire	Transistor
$ \Delta I_D $ in the range [0,1] V	1.228 µA	5.207 µA
$ \Delta I_D $ in the range [0,2] V	4.745 μΑ	4.741 μA
$ \Delta I_D _{\%}$ in the range [0,1] V	10.07~%	3.89~%
$ \Delta I_D _{\%}$ in the range [0,2] V	4.77 %	1.34~%

atmospheric gases, it appears that a reliable detection of NO can be performed at  $V_D$  equal to 0.4 V, 0.6 V, 0.8 V, 1.2 V, 1.4 V, 1.8 V. This is obviously a great advantage for the NO (gate) sensor.

So far it seems that in principle is possible to perform reliable detection of both PbSO<sub>4</sub> and NO at 0.8 V, since they both provide sufficiently different current variations w.r.t. other common atmospheric gases. In figure H.2, in appendix H, the current variations due to both lead sulfate and nitric oxide are reported for all the bias points. An issue is present at 0.8 V since the PbSO<sub>4</sub> with the SO<sub>4</sub> group pointing toward the C<sub>60</sub> fullerene and the NO with the N atom pointing toward the C<sub>60</sub> fullerene produce very similar current variations (and current value). Indeed they only differ for 0.27 µA, making the detection and the distinction between them very challenging and difficult. This is a big drawback, since a sensor that in principle should work as multi-purpose sensor for the



Figure 10.4: Current variations due to the different orientations of NO, and to other common atmospheric chemical species.

simultaneous detection of both the chemical species (i.e.  $PbSO_4$  and NO) should reliably distinguish between them. Smart solutions at conditioning circuit level are likely possible for overcome this issue, even if the cost would be likely increased. The simplest solutions are the following two. Firstly, supposing of using the sensor in a controlled environment, in which only one of the two chemical species is known can be present. In such a case the same sensor can be used for the detection either of  $PbSO_4$  only or NO only, and the issue is no more present. The second solution can be to avoid the detection for that current value corresponding to the NO (N down) and  $PbSO_4$  (SO down) ambiguity. In such a case the sensor is supposed to correctly detect both the presence of  $PbSO_4$  and NO simultaneously (and it works at a fixed  $0.8 \,\mathrm{V}$ ), but only if they are nearby the sensor with some specific orientations (namely not with N toward the sensor for the NO, and not with  $SO_4$  group toward the sensor for the  $PbSO_4$ ). In such a case, supposing that all the possible lead sulfate and nitric oxide orientations are equally probable, the sensor will detect NO with a reliability of the 66% (two cases over three), and the PbSO<sub>4</sub> with a reliability of the 80% (four cases over five possible are correctly detected). Of course these arguments are at the present only fantasy, since a real implementation is still far from now, and additional analyses (like the ones carried out in the previous sections and more accurate ones besides those) should be performed before making such kind of statements. Nevertheless the point is that unfortunately the  $PbSO_4$  and NO lead in some cases to an indistinguishable current variation in the sensor, but at the moment, with the information I have at the present, I believe solutions are possible, at different levels, for overcoming the issue toward a realization of a multi-purpose sensor.

The sensor current-voltage characteristics for different numbers of NO molecules placed nearby the channel were evaluated, and merged together in the surface of figure 10.5 (spline  $3^{rd}$  order interpolation is used). The main result is that at 0.8 V the sensor presents an extremely high linear response to different NO molecules concentrations (number). This is a great advantage of the NO sensor (with gate), indeed as mentioned several times the linearity to concentration is an important property of sensors. In appendix H is also reported the maximum error from linearity for the different bias points, confirming a very low error in the case of 0.8 V. Nevertheless it must be noted that such a linearity is only due to the fact that at 0.8 V the NO causes a very small current variation w.r.t. the case in which the fullerene alone is present and also among the different cases of 1, 2, and 3 NO molecules. Thus, considering also this, the sensor appears less attractive, since a difficult recognition can be an issue. In this regard consider also figure H.4 in appendix H, in which it is evident that the sensor is actually non-linear to NO concentrations at 0.8 V, and it presents small current variations. Further investigations can be carried out to this purpose, in order to elucidate more details concerning the issue.





Figure 10.5: Current flowing in the NO gate sensor in function of the applied drain-to-source bias  $V_D$  and of the number of NO molecules nearby the molecular channel. Red points are simulated data, the surface is obtained by merging the spline ( $3^{rd}$  order cubic) interpolating curves. The red line corresponds to the PbSO<sub>4</sub> sensor operating bias point: 0.8 V.

The current-voltage characteristics for different NO molecule distances from the sensor channel were evaluated, and merged together in the surface of figure 10.6 (spline  $3^{rd}$  order interpolation is used). The main result is that at 0.8 V the sensor presents good linearity w.r.t. the NO molecule distance, especially between 3.0 Å and 4.0 Å, in which the current value is very close to the one obtained for a distance of around 2.25 Å. This is better highlighted in figure H.5 in appendix H. The consequence is that, if it is possible to detect the NO molecule (with  $V_D = 0.8 \text{ V}$ ) at 2.25 Å (and from the analyses reported previously it seems to be so), it should be possible to detect it also for greater distances up to 4.0 Å. As already noticed in the previous chapter for the PbSO<sub>4</sub> case, the non-linear behavior increases when the voltage increases.



Figure 10.6: Current flowing in the sensor with the gate structure in function of the applied drain-to-source bias  $V_D$  and of the distance of the NO molecule from the molecular channel. Red points are simulated data, the surface is obtained by merging the spline ( $3^{rd}$  order cubic) interpolating curves. The red line corresponds to the chosen bias point of 0.8 V; a good linearity is present.

The above mentioned result can also be useful in estimating the interaction time of the NO molecule with the  $C_{60}$  sensor. Indeed since the current variation is almost constant up to 4.0 Å, it can assumed that the sensor successfully interacts with the NO from 2.25 Å to 4.0 Å (or slightly more), thus for a distance of about 2 Å (see interpolating curve - figure H.5). Considering the reflection a total interaction distance of about 4.0 Å is assumed, and by exploiting the already introduced (section 9.8) reasoning and method (and the practical implementation in *MatLab* - appendix G.4) an estimated interaction time in between 1.5 and 2 ps was evaluated. This can be thus compared with the sensor estimated response time to verify if a dynamic detection process can be reliable or not.

Before doing it, notice that this is consistent with the estimation performed previously for the wire case (an analogous procedure should definitively clarify this point); thus making reasonable the considerations made in the previous section.

The sensor (with gate) response time was estimated with the same procedure and methodology already discussed in the previous chapter (see section 9.9.5). Moreover, as did for the wire NO sensor in the previous section, the same capacitance and resistance values were used in a circuit schematic analogous to the one of figure 9.30 (with the only difference that the LUT stored simulation data obtained for the NO case). Indeed, as already commented in the previous section, in the hypothesis that such capacitances and resistances are fixed, they do not change during the sensor dynamic evolution from the state with no NO molecules to the one with 1 NO molecule, and they fixed to their initial values, i.e. those reported in table 9.10. The transients duration was then estimated both by means of the *Cadence* tool ("transient measurements") and in *MatLab* (appendix G.3), and their values are reported in table 10.3. The longest time (worst case) is 25.5 ps, and it is well above the estimated interaction time of the order of 1 or 2 ps. This can be a compromising drawback for this device structure, making extremely difficult the detection of NO by means of such a device. From this standpoint the wire sensor is believed to be much better.

**Table 10.3:** MatLab and Cadence estimated time constants and transient duration. The considered quantities are defined with reference to figure 9.30, suitably modified to model a NO molecule sensor (the LUT was modified with NO ATK simulated data). The MatLab time constants  $\tau$  are estimated with a graphical method. Notice that Cadence failed in identifying correctly the rise/fall edges for the current.

Quantity	MatLab: $\tau$ (s)	MatLab: $7 \cdot \tau$ (s)	Cadence rise/fall time (s)
Drain voltage	4.45146e-13	3.11602e-12	1.534e-12
Source voltage	3.6485e-12	2.55395e-11	110.3e-15
Drain current	1.79118e-13	1.25383e-12	-

# 10.4 Final remarks

In this chapter the previously analyzed lead sulfate sensors were briefly studied for the NO detection. Even if the illustrated analyses are incomplete, they show already significant results. More details can be extracted for example by implementing the analyses illustrated in the previous two chapters.

The C<sub>60</sub> fullerene molecular wire showed a discrete sensitivity to nitric oxide NO, and a good selectivity for a voltage  $V_D = 1$  V. It seems potentially and reliably usable as NO gas sensor for such a voltage value, with the drawback of requiring a different working voltage w.r.t. the C<sub>60</sub>-based PbSO<sub>4</sub> sensor. For such a bias points the current variations due to PbSO<sub>4</sub> and NO are sufficiently different. If compared with the gate device it shows generally greater both absolute and percentage current variations w.r.t. to the one obtained with the gated device, but at the same time it presents worse linear behavior w.r.t. NO concentration (i.e. number of molecules). From the fast estimations concerning the interaction and the sensor response times it seems to be able to reliably detect the NO presence, indeed the sensor response time is estimated to be three orders of magnitude less than the minimum interaction time of NO molecule with the sensor.

The C<sub>60</sub> fullerene molecular transistor (with the gate terminal) showed again a discrete sensitivity to nitric oxide NO, and a good selectivity for the following drain-to-source voltages:  $V_D = 0.4 \text{ V}, 0.6 \text{ V}, 0.8 \text{ V}, 1.2 \text{ V}, 1.4 \text{ V}, 1.8 \text{ V}$ . It seems potentially and reliably usable as NO gas sensor for such voltage values, with the advantage of being potentially able to correctly detect the NO presence at 0.8 V, i.e. the same working voltage of the PbSO<sub>4</sub> sensor. Nevertheless for such a bias points the current variations due to PbSO<sub>4</sub> and NO are too close for a given orientations (PbSO<sub>4</sub> with SO<sub>4</sub> group toward the fullerene and NO with N toward the fullerene). This makes difficult the distinction between the two chemical species. A different working voltage can be used for the NO detection, thus recovering the same drawback of the wire sensor. If compared with the wire device it shows generally smaller both absolute and percentage current variations w.r.t. to the one obtained with the wire device, but at the same it presents better linear behavior w.r.t. NO concentration (i.e. number of molecules). Moreover it presents a good linearity with small current variations (at 0.8 V) w.r.t. the NO distance. From the estimations concerning the interaction time and the sensor response time it seems to be not able to reliably detect the NO presence, since the sensor response time is estimated to be one order of magnitude greater than the interaction time. This could be an effective important drawback, that in the wire sensor is not present.

Considering the overall advantages and drawbacks of the two devices, the wire NO sensor seems to be more promising as effective and reliable low cost NO gas sensor. Further investigations should be carried out to confirm this, again starting e.g. from the analyses already presented in the previous chapters of this work.

# Chapter 11 Conclusions and future works

This entire work was mainly focused on the modeling of molecular electronic sensors (MES). The concept of MES was introduced in chapter 1, section 1.2, while the long way that led to them, passing through the beyond CMOS technologies and the molecular electronics, was briefly addressed again in the introductory chapter 1, section 1.1.

The first part of this work was essentially a literature review of the MES theoretical physical-chemical modeling techniques. Chapter 2 was aimed in reviewing quantum mechanics, i.e. the theory in which the MES models have their roots. All the needed topics to get a complete comprehension of the next chapters were introduced and discussed there. Chapter 3 was aimed in modeling the molecular channel electronic structure, i.e. the starting point for all the equilibrium and non-equilibrium modeling techniques of MES and transport through them. Moreover, intermolecular interactions and relative modeling techniques were discussed. They are of extreme importance for correctly modeling gas sensors, like those considered in the practical part (II) of this work. Chapters 4 and chapter 5 were dedicated to an deepened treatment of transport through MES. The first provided an intuitive introduction to the basic concepts, while the latter reported a formal and precise treatment. The attempt was always to keep the focus on the reasoning and the concepts behind the formalism. The detailed treatment of such topics is in general needed to understand and correctly setting up the atomistic simulations to be performed to practically make calculations on MES. Then, in chapter 6 additional transport-related topics were addressed, in order to mention also that cases that can practically happen and that are very important to be suitably modeled in order to avoid rough mistakes and wrong results. The information provided throughout the part I should be enough to perform an aware and correct setting up of atomistic simulations and to judiciously interpret the results.

The second part was instead focused on developing a general and complete methodology for the design and the analysis of a MES, by means of three cases of study that resulted to be very significant in order to develop such a methodological approach in MES simulations and design. At the moment, this crucial point is still lacking in the literature, even if it should be the first step toward the engineering and industrialization of the design process. In chapter 7 the methodology I followed during the work was briefly introduced, along with additional topics aimed in taking the step from the theory to the practice. In particular the MES working principles were reviewed with the gain of the part I theoretical treatment, and a focus on gas sensors was provided. In chapter 8, the  $C_{60}$  fullerene molecule was used as molecular channel for an ammonia MES. This practical application was the occasion to develop a method for the device geometry choice and optimization, to develop a simple approach for validating the EHT non-equilibrium simulations starting from DFT equilibrium ones and to quantitatively estimate the sensor sensitivity and selectivity. Unfortunately a failure in the ammonia selectivity occurred, and for this reason the next steps of the general methodology were carried out on a lead sulfate sensor, that was the subject of chapter 9. In such a chapter, after a brief repetition of the methodology steps already introduced, the main non-equilibrium properties of the lead sulfate MES were analyzed. In particular the sensor selectivity, sensitivity to different target orientations, concentrations and distances were analyzed and verified. These properties, all together, allow to gain a complete understanding of the sensor detection capabilities. Then a detailed analysis on transmission eigenstates of the MES under study was performed. Thanks to the strong lead sulfate polarization and the high atomic number of the lead (or high lead sulfate molecular mass), it was possible to clearly recognize the basic principles behind the transmission and the operation of the MES, providing, at the same time, an explanation of the reasons why the lead sulfate detection was reliable while the ammonia one was unreliable. An intermediate case between the ammonia and the lead sulfate was expected to be the nitric oxide case (as indeed it was confirmed in the chapter 10 analysis). In conclusion to chapter 9 an equivalent static and an equivalent dynamic circuit models of the sensor were proposed, aimed in evaluating the functionality of circuits including the MES (LUT-based model) and the sensor response time (dynamic model). A gate was also considered to verify the different performances in such a case. The last chapter of this work (chap. 10) was dedicated to a brief study of the nitric oxide detection by the same device structure already analyzed in the previous two chapters. Both the molecular wire and the molecular transistor device structures were considered and the same steps and methods, already introduced in the previous two chapters for the ammonia and the lead sulfate cases, were exploited to provide a brief characterization of the nitric oxide detection by the  $C_{60}$ -base MES.

This was, in short, what was did during this work. In the next section 11.1, the main obtained results are again considered, chapter by chapter, in order to succinctly collect all them together within a single paragraph. Then, in section 11.2, some ideas about what can be done next in this fascinating field are briefly illustrated.

# 11.1 Summary of the results

In this section the main points of this work, along with its main obtained results, are summarized. The treatment will be divided between part I and II and by chapters, such that an interested reader can easily refer to the parts of interest.

### 11.1.1 Part I

As mentioned previously, the part I of this work was aimed in providing a complete review of the theoretical modeling techniques of molecular devices generally, and of molecular electronic sensors specifically. The topics are quite well established in literature, and the main result of this part is to collect all the needed theoretical aspects, also belonging to very different fields, within the same document. In addition, since the only topics assumed for granted are the basic mathematical and physical knowledges, common to all engineering and scientific backgrounds, this document should be accessible without any extra requirement to electronic engineers. It was conceived to be a reference for understanding the meaning of the many input parameters of atomistic simulations that are usually required to be set up. Since very often the calculations are performed by means of commercial tools (like *Quantum-Wise ATK* used in this work), the task of setting up simulations may appear to be easy. Nevertheless a great amount of knowledge is actually required to avoid wrong settings and consequently unreliable results. This is the reason why this part resulted to be so long.

#### Chapter 2: "Brief review of quantum mechanics"

In this chapter the fundamentals of quantum mechanics were reviewed. This is a well established theory and the proposed treatment was not particularly novel. Nevertheless, since this work assumes the reader to have an electronic engineer background, the treated topics may or may not be already known, depending on the specific course of study, and for this reason also the very basics were recalled.

All the covered topics are important to have a full understanding of the following chapters, that in turn are important to correctly set up simulations and deal with MES. Basic quantum mechanics results (like confinement, electron wave-functions and orbitals, etc...) are indeed the starting point of chapters 3 and 4, and it was chosen to recall them in order to have an homogeneous notation and lexicon. The matrix notation for quantum mechanical operators, widely used in chapter 5, was also introduced.

#### Chapter 3: "Molecular electronic structure"

In this chapter the useful information for setting up molecular electronic structure calculations, geometry optimizations, and molecular device simulations was reported and discussed. In particular, the focus was on concepts and approximations behind the specific methods. Then, a more in-depth insight was provided relatively to the DFT (Density Functional Theory) and the EHT (Extended Hückel Theory) methods, since they were the ones used in the part II of this work. In addition, the advanced modeling techniques for weak interactions (like van der Waals ones) were briefly addressed with a focus on the recent supermolecular approach, suitable to correct DFT calculations. Such topics are the fundamentals for a correct setting up of atomistic simulation relatively to MES, especially for gas sensors or single molecule event detection, in which the working principle directly involves such kind of weak interactions.

#### Chapter 4: "An introduction to transport in molecular devices"

In this chapter the transport through molecular devices was introduced with an oversimplified model that allows to gain the physical intuition of what actually happens in such a kind of devices. All the main transport features of MES (and molecular devices in general) were introduced, along with a powerful and simple electrostatic treatment of the system. Moreover an introduction to transmission formalism was provided. This allowed to perform an interesting discussion about the molecular devices coherent transport framework limits of application, that in its features is at the present novel in literature (section 4.4). Actually, the concepts mentioned in such a discussion are not a news (see references therein), but their application and explication to molecular devices are.

#### Chapter 5: "The Non-Equilibrium Green's Function formalism"

In this chapter the transport through molecular devices was addressed by means the formal and general NEGF formalism, that allows not only to model transport in such devices in all their possible regimes of transport, but also to understand the meaning of the many simulation parameters to be set up in atomistic simulations and the way to correctly set up them. This was did in the relative short treatment of this chapter, that contains also purely qualitative sections, focused on concepts only. Moreover, a practical and complete example was provided, being the occasion to introduce an interesting free tool for EHT + NEGF transport calculations through molecular systems: Huckel-IV tool, that was also used in the practical part of this work for the sensor response time estimation.

#### Chapter 6: "Transport regimes in nano-devices"

In this chapter a brief review of the transport mechanisms through molecules was provided, and the way of accounting for them in the NEGF framework was presented. Moreover, the Coulomb blockade phenomenon was also addressed, and the possible modeling approaches in Coulomb blockade transport regime were explained, with reference to the methods that are increasingly becoming popular in literature in recent years (e.g. DFT corrections). Notice that every time there is suspect that Coulomb blockade regime can be present or dominant in the device under study, such corrections should be carefully considered to avoid completely wrong results.

#### 11.1.2 Part II

As mentioned previously, the part II of this work was aimed in developing a general method for analyzing and designing molecular electronic sensors by means of simulations. This was accomplished by considering three cases of study: a  $C_{60}$  gas sensor for ammonia detection, a  $C_{60}$  gas sensor for lead sulfate detection, and a  $C_{60}$  gas sensor for nitric oxide detection. In literature there is still very few about the topics covered in this part, and the great majority of the papers are still focusing on theoretical simulation studies rather than on prototypes. For this reason this part of the work is a pioneering attempt to "put order" in the large landscape of possible analyses and simulation one can perform on MES, in order to identify the analyses that are effective and useful to extract information and eventually figures of merit of such a kind of novel devices. The advantage of treating these topics by means of real cases of study was obviously the direct feedback about critical issues of such novel devices. In particular, first of all, an ammonia sensor was considered, inspired by a pair of the few papers that are present in literature relatively to MES. It allowed to fix many device parameters and to develop a way of doing it. The selectivity failure that occurred for the ammonia was of great help in having the intuition of the basic mechanisms at the basis of the detection process in gas MES. This was then confirmed from the lead sulfate study, that, even if likely of few practical interest, allowed, thanks to the particular properties of the lead sulfate single-molecule, to confirm the above mentioned intuition and to elucidate the detection working principle. Finally the nitric oxide was considered, being likely more interesting from a practical or a market standpoint.

#### Chapter 7: "Molecular electronic sensors"

In this chapter the working principles of different molecular electronic sensors were introduced, with the gain of the part I of this work. A focus was provided on the concepts of chemisorption and physisorption, that are very useful when gas sensors is considered, and also in the moment in which metal electrodes are used to contact the molecular channel. Moreover the general methodology, followed in the next chapters of this work, was introduced.

#### Chapter 8: "C<sub>60</sub>-based ammonia gas sensor"

In this chapter the  $C_{60}$  molecular wire (with gold electrodes) was studied as an ammonia gas sensor. The first result was an understanding of the equilibrium properties of such a sensor, from which it was confirmed that fast and simple analyses on equilibrium properties like the device DOS and transmission spectrum are enough to qualitatively understand if the device can be potentially able to detect the target. This depends on if significant variations in the above mentioned equilibrium properties occur or not. Then a method for designing and engineering the device geometry was developed and used to actually do it. During this analysis it was also obtained an insight on the transport mechanism through the fullerene. In particular, by analyzing the obtained I-V characteristics for different distances between the fullerene and the contacts, a clear exponential decreasing trend of the current with the fullerene-contact distance was identified. Accordingly with the Simmon's model, it was thus concluded that, due to the high delocalization of the fullerene orbitals, the main obstacles to electron transmission from source to drain in a  $C_{60}$  wire are the contact-fullerene barriers. Once the geometry was fixed, the main equilibrium properties of the sensor with the final geometry were again analyzed. In addition, a methodology for validating non-equilibrium EHT simulation results, starting from equilibrium DFT ones,

was conceived and presented. Then, the non-equilibrium properties and current-voltage characteristics were considered. The sensor sensitivity to ammonia and selectivity were estimated, considering also the sensor response to the most common atmospheric gases. The main result of this analysis was the failure of the sensor in reliably detecting ammonia if it is placed in an uncontrolled environment (in air). Nevertheless, it was obtained a potentially good sensor response to lead sulfate, nitric oxide and nitric dioxide. All these are polar molecules (like ammonia also is), and in particular lead sulfate contains the lead that is an heavy metal with high atomic number. At the same time considering that the sensor response to methane and butane was verified to be very poor, it was supposed the detection mechanism being related to the molecule polarity and the high atomic number of elements composing the target (high molecular mass), while it was supposed to be less dependent on the number of electron states of the target molecule. This intuition was confirmed in the next chapter.

#### Chapter 9: "C<sub>60</sub>-based lead sulfate gas sensor"

In this chapter the  $C_{60}$  molecular wire (with gold electrodes), already considered in the previous chapter, was studied as a lead sulfate gas sensor. Besides the likely poor applications (related to the fact that single lead sulfate molecule is very rare in air), this choice was motivated by the interest in better understanding the physical mechanisms at the basis of the detection process, in order to be, in future, able to more suitably select target and sensor molecules, and to address useful analyses to speed up the complete design. The same equilibrium and non-equilibrium analyses already presented in the previous chapter were carried out in this chapter relatively to lead sulfate detection, along with the device geometry choice and optimization for the best compromise between maximum sensitivity and most stable structure. Again, the EHT non-equilibrium simulation results were validated with the same method already used in the previous chapter. After that, the main non-equilibrium sensor properties like sensitivity to target and sensitivity to different orientations of the target (being a polar molecule and being the intermolecular interactions strongly anisotropic this should always be checked), along with the sensor selectivity. In addition the sensor response to different target concentrations and distances were analyzed. The main results of these analyses are that the sensor seemed to be promising as potential sensor for lead sulfate detection in air, or in controlled atmosphere. As already mentioned, a transmission eigenstates analysis was carried out confirming the intuitions reported at the end of the previous chapter to be true. The gas MES are thus very sensitive to polar molecules, the greater the target molecule electric dipole, the better the detection is. Moreover due to steric effects, the greater the atomic number of the target the better is expected to be the detection.

In order to estimate the sensor response time, a series of steps were performed, leading simultaneously to the construction of an equivalent MES circuit model. Firstly a simple static circuit model was conceived. This was a LUT-based model, aimed in performing static analyses and functional or behavioral verifications. Then the electrostatic capacitances of the sensor and other dynamic quantities having the dimensions of resistances, but with the only purpose of representing the fact that moving charges from/toward the sensor channel requires time, were estimated (I referred to such quantities as "dynamic" resistances). This led to another equivalent circuit model aimed in estimating the sensor transients duration and thus the sensor response time. By comparison with the estimated interaction time between the sensor and the target molecule, it was verified the potentiality of the sensor in performing real time detection of the target. Moreover the developed static and dynamic models were believed to be a useful starting point toward a general "black-box"-like circuit model of MES, to be used in designing conditioning circuits for the sensors and electronic systems including them.

In conclusion to this chapter, a different sensor device was considered, namely a sensor with an additional gate terminal. The gate structure and voltage were set to try enhancing the detection performances of the sensor, but at the same time to be realistic structure with the current technology. The analyses carried out for the wire sensor were all repeated for the gated sensor. A slightly greater sensor sensitivity was found with the gate w.r.t. the wire sensor, even if the percentage sensitivity was reduced (since there was an overall current increase with gate). In general no significant performance amelioration was found, and, in addition, the sensor response time resulted considerably longer (three order to magnitude greater), thus being a potential important drawback for a reliable real time detection of the target.

#### Chapter 10: "A glimpse on the $C_{60}$ -based nitric oxide gas sensor"

In this chapter the  $C_{60}$  molecular wire and transistor, already considered in the previous chapter, were studied as nitric oxide gas sensors. The already developed methodology was simply applied to the study of the nitric oxide detection properties of the same devices considered previously, with no differences in the devices structure. The wire sensor resulted capable of potentially recognize the presence of nitric oxide only for an applied voltage of 1 V, value different from the one employed for the lead sulfate detection in chapter 9. Apart from this, the sensor presented potential good response properties, including an enough fast response time, being thus suitable as nitric oxide sensor. The gate sensor did not reveal particular advantages w.r.t. the wire configuration, a part a wide range of voltages in which it resulted able to perform reliable detection of the target. Again, like for the lead sulfate, it also presented a significant increase in the sensor response time that resulted to be one order of magnitude longer than the interaction time between nitric oxide and the sensor, leading to an unreliable detection capability in an uncontrolled environment.

#### Final remarks

In conclusion, the MES modeling techniques were reviewed and used to investigate the detection properties of a  $C_{60}$ -based MES (with wire configuration and gated one). The ammonia, lead sulfate and nitric oxide detection capabilities of such devices were studied, and a general analysis and design methodology was developed. Few simple figures of merit were proposed to investigate the sensitivity and selectivity of such MES devices, allowing also to coherently compare them. The ammonia detection resulted unreliable because the low sensor selective response to ammonia if compared to the responses obtained with other common atmospheric chemical species. Instead the lead sulfate and nitric oxide detection resulted potentially possible. A simple circuit model for static and behavioral

analyses of circuits including MES was developed and implemented, and successively refined to get an equivalent circuit model able to estimate the sensor dynamic response time to concentration variations of the target chemical species. This model can be the starting point toward a more refined circuit equivalent "black-box"-like model to be used in designing circuits including MES. The MES devices with gates (i.e. molecular transistor configurations) analyzed in this work did not present significant advantages w.r.t. the (cheaper) wire ones, while all presented the drawback of an increased response time, thus potentially implying a non-reliable detection of target, that, instead, with the wire sensors resulted always possible.

There is still much to do in this fascinating field of research before achieving the design confidence to prototype and develop real devices; and then, there will be again much to do in order to achieve the confidence required to eventually put into production MES. During the long road still to go I believe much novel properties and discoveries will be achieved by studying MES, likely also in some transverse field of science and knowledge. In the next, and last, section of this work I will provide some suggestions on future topics to be investigated I had in mind during the development of this work, but that I had no time to address.

# 11.2 What is next?

In this section I would like to collect a set of ideas relative to future works in this field I conceived during the development of this work, but that I had no time to address. The section will be again divided into more theoretical or general topics, mainly related to part I of this work, and to more application-oriented topics, mainly related to part II of this work.

#### General methodology and modeling

The possible future works concerning the general modeling of molecular electronic sensors, and more in general of molecular electronic devices, can be divided into two groups: possible improvements and customization of the free tool *Huckel-IV*, and possible improvements of the MES equivalent circuit model. They are considered in the following:

- Possible improvements of the *Huckel-IV* suite:
  - a. inserting more contact materials (e.g. silicon or graphene contacts), that practically would mean to evaluate the surface Green's functions for the new contacts
  - b. eliminating the fitting parameter  $V_c$ , or better evaluating it, by means of a selfconsistent procedure for equilibrium calculations, starting from isolated contact and device geometries only
  - c. including also non-coherent scattering (on which electronic transport in weakly coupled devices is based)
  - d. improving it for simulating all kinds of quantum dots (such as nanocrystals, etc...) or even (short) quantum wires (always by means of atomistic simulations)

- e. improving it by including a DFT + NEGF method (along with EHT + NEGF)
- f. creating a graphical interface (or even an effective command line interface) in order to further ease the usage and the setting up of simulations by non-expert users
- Possible improvements of the equivalent circuit model:
  - a. more accurate estimations of the circuit model parameters:  $C_g, R_g, C_s, R_s, C_d, R_d$
  - b. inclusion of parasitic capacitive and resistive components, e.g. to account for contact resistances
  - c. development of a large and a small signal models, in order to treat the MES in the same way as conventional analog electronic devices

#### MES gas sensors

The possible future works concerning specifically MES for gas sensing applications can be:

- Further in-depth investigation of the nitric oxide and of other relevant chemical species (e.g. pollutants, etc...) detection capabilities, e.g. by following the same methodology of this work.
- Further investigation of the transistor device configuration for the detection of relevant chemical species.
- Investigation of different molecules for the sensor molecular channel in order to gain knowledge about the sensing properties of different classes of molecules, with a spetial consideration for the anchoring groups and their influence on sensing. For the molecular channel an example to be investigated can be the C<sub>20</sub> fullerene, that is the smallest fullerene, and presents greater chemical reactivity due to the smaller radius of curvature [140] w.r.t. the C<sub>60</sub> fullerene. Therefore it would be interesting, in my opinion, to investigate it as molecular channel to verify if, and in what terms, it can affect the sensing of target chemical species.
- Investigation of different contact materials, such as the graphene. Indeed the graphene is already used in 2D gas sensors due to its high reactivity and potential selectivity [50], [48], [49]. Therefore it would be interesting, in my opinion, to investigate it as contact material, considering also the recent development in graphene molecular junctions [21], [22], [23], to verify if, and in what terms, it can affect the sensing of target chemical species.
- Investigation of the sensor noise, and thus of noise in molecular electronic devices.
- Design and development of the conditioning circuit and of the entire measuring system.
## Bibliography

- [1] William Stallings. Computer Organization and Architecture. Designing for performance. Tenth Edition. Pearson Education, 2016 (cit. on p. 1).
- [2] Yuan Taur and Tak H. Ning. Fundamentals of Modern VLSI Devices. Second Edition. Cambridge University Press, 2013 (cit. on pp. 1, 2, 388).
- [3] G. Moore. «Cramming More Components Onto Integrated Circuits.» In: *Proceedings* of the IEEE, reprinted: January 1998 (originally: April 1965) (cit. on p. 2).
- [4] International Technology Roadmap for Semiconductors 2.0 Executive Report. 2015. URL: http://www.itrs2.net/ (cit. on pp. 2, 3, 9).
- [5] International Roadmap for Devices and Systems Executive Report. 2020. URL: https://irds.ieee.org/editions/2020 (cit. on pp. 2-5, 9).
- [6] International Roadmap for Devices and Systems Executive Report. 2018. URL: https://irds.ieee.org/editions/2018 (cit. on pp. 2, 3).
- [7] International Roadmap for Devices and Systems Executive Report. 2017. URL: https://irds.ieee.org/editions/2017 (cit. on pp. 2, 3).
- [8] TSMC 5 nm technological node. 2020. URL: https://www.tsmc.com/english/ dedicatedFoundry/technology/5nm.htm (cit. on p. 2).
- [9] Samsung Electronics 5 nm technological node. 2020. URL: https://news.samsung. com/global/samsung-electronics-expands-its-foundry-capacity-with-anew-production-line-in-pyeongtaek-korea (cit. on p. 2).
- Silvia Karthäuser. «Control of molecule-based transport for future molecular devices». In: Journal of Physics: Condensed Matter 23.1 (Nov. 2010), p. 013001. DOI: 10.1088/0953-8984/23/1/013001. URL: https://doi.org/10.1088%5C%2F0953-8984%5C%2F23%5C%2F1%5C%2F013001 (cit. on pp. 3, 9, 268-272, 284, 285).
- [11] Hyungsub Choi and Cyrus C.M. Mody. «The Long History of Molecular Electronics: Microelectronics Origins of Nanotechnology». In: Social Studies of Science 39.1 (2009), pp. 11–50. DOI: 10.1177/0306312708097288 (cit. on pp. 6–9, 19).
- [12] G. Cuniberti, G. Fagas, and K. Richter. *Introducing Molecular Electronics*. Springer, 2005 (cit. on pp. 6–8, 11, 388).
- [13] John Markoff. «Chip Industry Sets a Plan for Life after Silicon». In: NewYork Times 29 December (2005) (cit. on p. 6).

- Paven Thomas Mathew and Fengzhou Fang. «Advances in Molecular Electronics: A Brief Review». In: Engineering 4.6 (2018), pp. 760-771. ISSN: 2095-8099. DOI: https://doi.org/10.1016/j.eng.2018.11.001. URL: http://www.sciencedirect.com/science/article/pii/S2095809918306453 (cit. on pp. 6-8, 11).
- [15] James M. Tour. «Molecular Electronics. Synthesis and Testing of Components». In: Accounts of Chemical Research 33.11 (2000). PMID: 11087316, pp. 791-804.
   DOI: 10.1021/ar0000612. eprint: https://doi.org/10.1021/ar0000612. URL: https://doi.org/10.1021/ar0000612 (cit. on pp. 6-9, 11, 283, 289, 294).
- [16] Michael C. Petty, Takashi Nagase, Hitoshi Suzuki, and Hiroyoshi Naito. «Molecular Electronics». In: Springer Handbook of Electronic and Photonic Materials. Ed. by Safa Kasap and Peter Capper. Cham: Springer International Publishing, 2017, pp. 1–1. ISBN: 978-3-319-48933-9. DOI: 10.1007/978-3-319-48933-9\_51. URL: https://doi.org/10.1007/978-3-319-48933-9\_51 (cit. on p. 7).
- [17] Lanlan Sun, Yuri A. Diaz-Fernandez, Tina A. Gschneidtner, Fredrik Westerlund, Samuel Lara-Avila, and Kasper Moth-Poulsen. «Single-molecule electronics: from chemical design to functional devices». In: *Chem. Soc. Rev.* 43 (21 2014), pp. 7378– 7411. DOI: 10.1039/C4CS00143E. URL: http://dx.doi.org/10.1039/C4CS00143E (cit. on pp. 7, 11).
- [18] James M. Tour. Molecular Electronics. Commercial insights, chemistry, devices, architecture and programming. World Scientific publishing, 2003 (cit. on pp. 7, 8, 283, 289, 291, 294, 387).
- [19] Arieh Aviram and Mark A. Ratner. «Molecular rectifiers.» In: Chemical Physics Letters 29 (2 Nov. 1974), pp. 277–283 (cit. on p. 7).
- [20] Katharina Kaiser, Lorel M. Scriven, Fabian Schulz, Przemyslaw Gawel, Leo Gross, and Harry L. Anderson. «An sp-hybridized molecular carbon allotrope, cyclo[18]carbon». In: Science 365.6459 (2019), pp. 1299–1301. ISSN: 0036-8075. DOI: 10.1126/science.aay1914. eprint: https://science.sciencemag.org/content/365/6459/1299.full.pdf. URL: https://science.sciencemag.org/content/365/6459/1299 (cit. on p. 7).
- [21] Qizhi Xu, Giovanni Scuri, Carly Mathewson, Philip Kim, Colin Nuckolls, and Delphine Bouilly. «Single Electron Transistor with Single Aromatic Ring Molecule Covalently Connected to Graphene Nanogaps». In: Nano Letters 17.9 (2017). PMID: 28792226, pp. 5335-5341. DOI: 10.1021/acs.nanolett.7b01745. eprint: https: //doi.org/10.1021/acs.nanolett.7b01745. URL: https://doi.org/10.1021/ acs.nanolett.7b01745 (cit. on pp. 7, 10, 13, 423).
- [22] Chuancheng Jia, Bangjun Ma, Na Xin, and Xuefeng Guo. «Carbon Electrode– Molecule Junctions: A Reliable Platform for Molecular Electronics». In: Accounts of Chemical Research 48.9 (2015). PMID: 26190024, pp. 2565–2575. DOI: 10.1021/acs. accounts.5b00133. eprint: https://doi.org/10.1021/acs.accounts.5b00133. URL: https://doi.org/10.1021/acs.accounts.5b00133 (cit. on pp. 7, 9, 10, 12, 423).

- [23] Huimin Wen, Wengang Li, Jiewei Chen, Gen He, Longhua Li, Mark A. Olson, Andrew C. H. Sue, J. Fraser Stoddart, and Xuefeng Guo. «Complex formation dynamics in a single-molecule electronic device». In: *Science Advances* 2.11 (2016). DOI: 10.1126/sciadv.1601113 (cit. on pp. 7, 9–11, 287, 423).
- [24] F. Zahid, M. Paulsson, E. Polizzi, Ghosh A.E., Siddiqui L., and S. Datta. «A self-consistent transport model for molecular conduction based on extended Hückel theory with full three-dimensional electrostatics». In: *The Journal Of Chemical Physics* 123 (2005). DOI: 10.1063/1.1961289 (cit. on pp. 8, 11, 247, 249, 372, F1).
- [25] Chuancheng Jia et al. «Quantum interference mediated vertical molecular tunneling transistors». In: Science Advances 4.10 (2018). DOI: 10.1126/sciadv.aat8237. eprint: https://advances.sciencemag.org/content/4/10/eaat8237.full.pdf. URL: https://advances.sciencemag.org/content/4/10/eaat8237 (cit. on pp. 8, 11).
- [26] Angelika Balliou, Jiri Pfleger, George Skoulatakis, Samrana Kazim, Jan Rakusan, Stella Kennou, and Nikos Glezos. «Programmable Molecular-Nanoparticle Multi-Junction Networks for Logic Operations». In: Proceedings of the 14th IEEE/ACM International Symposium on Nanoscale Architectures. NANOARCH '18. Athens, Greece: Association for Computing Machinery, 2018, pp. 37–43. ISBN: 9781450358156. DOI: 10.1145/3232195.3232225. URL: https://doi.org/10.1145/3232195. 3232225 (cit. on p. 9).
- [27] Yu Li, Chen Yang, and Xuefeng Guo. «Single-Molecule Electrical Detection: A Promising Route toward the Fundamental Limits of Chemistry and Life Science». In: Accounts of Chemical Research 53.1 (2020). PMID: 31545589, pp. 159–169. DOI: 10.1021/acs.accounts.9b00347. eprint: https://doi.org/10.1021/acs.accounts.9b00347. uRL: https://doi.org/10.1021/acs.accounts.9b00347 (cit. on pp. 9, 10, 12, 15, 18, 287).
- Yu Li, Lihua Zhao, Yuan Yao, and Xuefeng Guo. «Single-Molecule Nanotechnologies: An Evolution in Biological Dynamics Detection». In: ACS Applied Bio Materials 3.1 (2020), pp. 68–85. DOI: 10.1021/acsabm.9b00840. eprint: https://doi.org/ 10.1021/acsabm.9b00840. URL: https://doi.org/10.1021/acsabm.9b00840 (cit. on pp. 9, 10, 12, 15, 18, 287).
- Wenwen Hu et al. «Electronic Noses: From Advanced Materials to Sensors Aided with Data Processing». In: Advanced Materials Technologies 4.2 (2019), p. 1800488. DOI: 10.1002/admt.201800488. eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/admt.201800488. URL: https://onlinelibrary.wiley.com/doi/abs/10.1002/admt.201800488 (cit. on pp. 9, 12, 15-17).
- [30] Matti Kaisti. «Detection principles of biological and chemical FET sensors». In: Biosensors and Bioelectronics 98 (2017), pp. 437-448. ISSN: 0956-5663. DOI: https: //doi.org/10.1016/j.bios.2017.07.010. URL: http://www.sciencedirect. com/science/article/pii/S0956566317304517 (cit. on pp. 9, 11, 12, 286).

- [31] Yoav Y. Broza, Xi Zhou, Miaomiao Yuan, Danyao Qu, Youbing Zheng, Rotem Vishinkin, Muhammad Khatib, Weiwei Wu, and Hossam Haick. «Disease Detection with Molecular Biomarkers: From Chemistry of Body Fluids to Nature-Inspired Chemical Sensors». In: *Chemical Reviews* 119.22 (2019). PMID: 31729868, pp. 11761–11817. DOI: 10.1021/acs.chemrev.9b00437. eprint: https://doi.org/10.1021/acs.chemrev.9b00437. URL: https://doi.org/10.1021/acs.chemrev.9b00437 (cit. on pp. 9, 12, 15, 17).
- [32] S. J. Ray. «Humidity sensor using a single molecular transistor». In: Journal of Applied Physics 118 (2015), p. 044307. DOI: 10.1063/1.4927296. eprint: http://dx.doi.org/10.1063/1.4927296 (cit. on pp. 9–11, 288).
- [33] A. Nasri, A. Boubaker, B. Hafsi, W. Khaldi, and A. Kalboussi. «High-Sensitivity Sensor Using C60-Single Molecule Transistor». In: *IEEE Sensors Journal* 18.1 (Jan. 2018), pp. 248–254. ISSN: 1558-1748. DOI: 10.1109/JSEN.2017.2769803 (cit. on pp. 10, 11, 277, 285, 286, 289, 293–295, 321, 337).
- [34] Sattar Arshadi and F. Anisheh. «Theoretical study of Cr and Co- porphyrininduced C70 fullerene: a request for a novel sensor of sulfur and nitrogen dioxide». In: Journal of Sulfur Chemistry 38.4 (2017), pp. 357–371. DOI: 10.1080/17415993. 2017.1298767. eprint: https://doi.org/10.1080/17415993.2017.1298767. URL: https://doi.org/10.1080/17415993.2017.1298767 (cit. on pp. 10, 11, 285, 286, 290).
- [35] Louis C. Brousseau. «Label-Free "Digital Detection" of Single-Molecule DNA Hybridization with a Single Electron Transistor». In: Journal of the American Chemical Society 128.35 (2006). PMID: 16939245, pp. 11346–11347. DOI: 10.1021/ja063022f. eprint: https://doi.org/10.1021/ja063022f. URL: https://doi.org/10.1021/ja063022f (cit. on pp. 10, 18, 288).
- [36] Yan-Dong Guo, Xiao-Hong Yan, and Yang Xiao. «Computational Investigation of DNA Detection Using Single-Electron Transistor-Based Nanopore». In: *The Journal* of Physical Chemistry C 116.40 (2012), pp. 21609–21614. DOI: 10.1021/jp305909p. eprint: https://doi.org/10.1021/jp305909p. URL: https://doi.org/10.1021/ jp305909p (cit. on pp. 10, 18, 288).
- S. Pilehvar and K. De Wael. «Recent Advances in Electrochemical Biosensors Based on Fullerene-C60 Nano-Structured Platforms». In: *Biosensors* 5 (2015), pp. 712–735.
   DOI: 10.3390/bios5040712 (cit. on pp. 10, 287, 289, 293).
- [38] Ahmed J. Hassan. «Computational study of adsorption of some gas molecules on the undoped and N-doped fullerenes C20 bowl as a gas sensor». In: *Iranian Journal* of Organic Chemistry 11.3 (2019), pp. 2659–2665 (cit. on pp. 10, 285, 286, 290).
- [39] Supriyo Datta. Electronic transport in mesoscopic systems. Cambridge University Press, 1995. ISBN: 9780511805776 (cit. on pp. 10, 115, 167, 176, 179, 181–184, 186, 187, 192–194, 198, 219, 224, 237, 245, 254–256, 259, 261, 262, 271).

- [40] Jie Bai et al. «Anti-resonance features of destructive quantum interference in single-molecule thiophene junctions achieved by electrochemical gating». In: *Nature Materials* 18.4 (2019), pp. 1476–4660. DOI: 10.1038/s41563-018-0265-4. URL: https://doi.org/10.1038/s41563-018-0265-4 (cit. on p. 11).
- [41] F. Zahid, Ghosh A.E., M. Paulsson, and S. Polizzi E. Datta. «Charging-induced asymmetry in molecular conductors». In: *Physical review B* 70.245317 (2004). DOI: 10.1103/PhysRevB.70.245317 (cit. on pp. 11, 247, 372, F1).
- [42] Zhi-Hao Zhao, Lin Wang, Shi Li, Wei-Dong Zhang, Gang He, Dong Wang, Shi-Min Hou, and Li-Jun Wan. «Single-Molecule Conductance through an Isoelectronic B–N Substituted Phenanthrene Junction». In: *Journal of the American Chemical Society* 142.18 (2020). PMID: 32321243, pp. 8068–8073. DOI: 10.1021/jacs.0c00879. eprint: https://doi.org/10.1021/jacs.0c00879. URL: https://doi.org/10.1021/jacs.0c00879 (cit. on p. 11).
- [43] Alexander V. Rudnev, Veerabhadrarao Kaliginedi, Andrea Droghetti, Hiroaki Ozawa, Akiyoshi Kuzume, Masa-aki Haga, Peter Broekmann, and Ivan Rungger. «Stable anchoring chemistry for room temperature charge transport through graphitemolecule contacts». In: Science Advances 3.6 (2017). DOI: 10.1126/sciadv.1602297 (cit. on p. 11).
- [44] Pascal Gehring et al. «Distinguishing Lead and Molecule States in Graphene-Based Single-Electron Transistors». In: ACS Nano 11.6 (2017). PMID: 28423272, pp. 5325– 5331. DOI: 10.1021/acsnano.7b00570. eprint: https://doi.org/10.1021/ acsnano.7b00570. URL: https://doi.org/10.1021/acsnano.7b00570 (cit. on p. 11).
- [45] Veronika Obersteiner, David A. Egger, and Egbert Zojer. «Impact of Anchoring Groups on Ballistic Transport: Single Molecule vs Monolayer Junctions». In: *The Journal of Physical Chemistry C* 119.36 (2015). PMID: 26401191, pp. 21198-21208. DOI: 10.1021/acs.jpcc.5b06110. eprint: https://doi.org/10.1021/acs.jpcc.5b06110. URL: https://doi.org/10.1021/acs.jpcc.5b06110 (cit. on p. 11).
- [46] Manabu Kiguchi. «Electrical conductance of single C60 and benzene molecules bridging between Pt electrode». In: *Applied Physics Letters* 95.073301 (2009). DOI: 10.1063/1.3204466 (cit. on p. 11).
- [47] K. Oura, V.G. Lifshits, A.A. Saranin, A.V. Zotov, and M. Katayama. Surface Science, An Introduction. Springer, 2003 (cit. on pp. 11, 12, 282, 283).
- [48] Muhammad H. Rashid, Ants Koel, and Toomas Rang. «Simulations of Graphene Nanoribbon Field Effect Transistor for the Detection of Propane and Butane Gases: A First Principles Study.» In: *Nanomaterials* 10.1:98 (2020). DOI: 10.3390/ nano10010098 (cit. on pp. 11, 423).
- [49] G. R. Ahmed Jamal, Mokter M. Chowdhury, Fahrin Rahman, M. Aminur Rahman, Sharika Shabnaz, and Umma Habiba. «Simulation of Graphene Nanoribbon Based Gas Sensor.» In: *Journal of Nanoscience and Nanoengineering* 1.2 (2015), pp. 66–73 (cit. on pp. 11, 286, 423).

- [50] Haroon Rashid, Ants Koel, and Toomas Rang. «Simulations of Propane and Butane Gas Sensor Based on Pristine Armchair Graphene Nanoribbon». In: *IOP Conference Series: Materials Science and Engineering* 362 (May 2018), p. 012001. DOI: 10. 1088/1757-899x/362/1/012001 (cit. on pp. 11, 286, 423).
- [51] David Harvey. Analytical Chemistry 2.0. DePauw University, 2009 (cit. on p. 11).
- [52] Hongliang Chen, Weining Zhang, Mingliang Li, Gen He, and Xuefeng Guo. «Interface Engineering in Organic Field-Effect Transistors: Principles, Applications, and Perspectives». In: *Chemical Reviews* 120.5 (2020). PMID: 32078296, pp. 2879–2949. DOI: 10.1021/acs.chemrev.9b00532. eprint: https://doi.org/10.1021/acs.chemrev.9b00532. URL: https://doi.org/10.1021/acs.chemrev.9b00532 (cit. on pp. 12, 286).
- [53] Pedro E. Martín Várguez, Frédéric Brunel, and Jean-Manuel Raimundo. «Recent Electrochemical/Electrical Microfabricated Sensor Devices for Ionic and Polyionic Analytes». In: ACS Omega 5.10 (2020), pp. 4733–4742. DOI: 10.1021/acsomega.9b04331. uRL: https://doi.org/10.1021/acsomega.9b04331. URL: https://doi.org/10.1021/acsomega.9b04331 (cit. on pp. 12, 15–17).
- [54] M.J. Schoening and A. Poghossian. Label-free biosensing: Advanced Materials, Devices and Applications. Elsevier, 2018 (cit. on pp. 12, 13, 15, 16, 285).
- [55] Matias Urdampilleta et al. «Molecule-based microelectromechanical sensors». In: *Scientific Reports* 8.1 (2018), pp. 2045–2322. DOI: 10.1038/s41598-018-26076-2. URL: https://doi.org/10.1038/s41598-018-26076-2 (cit. on p. 12).
- [56] Nishuang Liu, Guojia Fang, Wei Zeng, Hao Long, Longyan Yuan, and Xingzhong Zhao. «Novel ZnO Nanorod Flexible Strain Sensor and Strain Driving Transistor with an Ultrahigh 107 Scale "On""Off" Ratio Fabricated by a Single-Step Hydrothermal Reaction». In: *The Journal of Physical Chemistry C* 115.2 (2011), pp. 570–575. DOI: 10.1021/jp108352b. eprint: https://doi.org/10.1021/jp108352b. URL: https://doi.org/10.1021/jp108352b (cit. on p. 12).
- [57] Bingfang Wang, Yuanyuan Luo, Bo Liu, and Guotao Duan. «Field-Effect Transistor Based on an in Situ Grown Metal-Organic Framework Film as a Liquid-Gated Sensing Device». In: ACS Applied Materials & Interfaces 11.39 (2019). PMID: 31502434, pp. 35935-35940. DOI: 10.1021/acsami.9b14319. eprint: https://doi.org/10.1021/acsami.9b14319. URL: https://doi.org/10.1021/acsami.9b14319 (cit. on pp. 12, 286).
- [58] Óscar Leonardo Camargo Moreira et al. «High Selectivity Gas Sensing and Charge Transfer of SnSe2». In: ACS Sensors 4.9 (2019). PMID: 31456397, pp. 2546-2552. DOI: 10.1021/acssensors.9b01461. eprint: https://doi.org/10.1021/acssensors.9b01461. URL: https://doi.org/10.1021/acssensors.9b01461 (cit. on pp. 12, 286).

- [59] Hyunjin Park, Sungmi Yoo, Hyungju Ahn, Joohee Bang, Yuri Jeong, Mihye Yi, Jong Chan Won, Sungjune Jung, and Yun Ho Kim. «Low-Temperature Solution-Processed Soluble Polyimide Gate Dielectrics: From Molecular-Level Design to Electrically Stable and Flexible Organic Transistors». In: ACS Applied Materials & Interfaces 11.49 (2019). PMID: 31738047, pp. 45949–45958. DOI: 10.1021/acsami.9b14041. uRL: https://doi.org/10.1021/acsami.9b14041. URL: https://doi.org/10.1021/acsami.9b14041 (cit. on p. 12).
- [60] Saravanan Yuvaraja, Sandeep G Surya, Valeriya Chernikova, Mani Teja Vijjapu, Osama Shekhah, Prashant M. Bhatt, Suman Chandra, Mohamed Eddaoudi, and Khaled N. Salama. «Realization of an Ultrasensitive and Highly Selective OFET NO2 Sensor: The Synergistic Combination of PDVT-10 Polymer and Porphyrin-MOF». In: ACS Applied Materials & Interfaces 12.16 (2020). PMID: 32281789, pp. 18748–18760. DOI: 10.1021/acsami.0c00803. eprint: https://doi.org/10.1021/acsami.0c00803 (cit. on pp. 12, 286).
- [61] Yunpeng Zhang et al. «A Flexible Acetylcholinesterase-Modified Graphene for Chiral Pesticide Sensor». In: Journal of the American Chemical Society 141.37 (2019). PMID: 31448915, pp. 14643–14649. DOI: 10.1021/jacs.9b05724. eprint: https://doi.org/10.1021/jacs.9b05724. URL: https://doi.org/10.1021/ jacs.9b05724 (cit. on pp. 12, 286).
- [62] Yifan Wu, Yin Xiao, Xuepeng Wang, Xiaoxuan Li, and Yong Wang. «Chirality Discrimination at the Single Molecule Level by Using a Cationic Supermolecule Quasi-Gated Organic Field Effect Transistor». In: ACS Sensors 4.8 (2019). PMID: 31274289, pp. 2009–2017. DOI: 10.1021/acssensors.9b00270. eprint: https://doi.org/10.1021/acssensors.9b00270. URL: https://doi.org/10.1021/acssensors.9b00270 (cit. on pp. 12, 286).
- [63] Bin Wang et al. «A Highly Sensitive Diketopyrrolopyrrole-Based Ambipolar Transistor for Selective Detection and Discrimination of Xylene Isomers». In: Advanced Materials 28.21 (2016), pp. 4012-4018. DOI: 10.1002/adma.201505641. eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/adma.201505641. URL: https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201505641 (cit. on pp. 12, 286).
- [64] Seohyun Mun, Yoonkyung Park, Yong-Eun Koo Lee, and Myung Mo Sung. «Highly Sensitive Ammonia Gas Sensor Based on Single-Crystal Poly(3-hexylthiophene) (P3HT) Organic Field Effect Transistor». In: Langmuir 33.47 (2017). PMID: 29125766, pp. 13554–13560. DOI: 10.1021/acs.langmuir.7b02466. eprint: https://doi.org/10.1021/acs.langmuir.7b02466. URL: https://doi.org/10.1021/acs.langmuir.7b02466 (cit. on pp. 12, 286).
- [65] World Health Organization. Regional Office for Europe. WHO guidelines for indoor air quality: selected pollutants. World Health Organization, 2010. ISBN: 978 92 890 0213 4 (cit. on pp. 12, 16, 286, 402).

- [66] A. Bonanno, M. Crepaldi, I. Rattalino, P. Motto, D. Demarchi, and P. Civera. «A 0.13 μm CMOS Operational Schmitt Trigger R-to-F Converter for Nanogap-Based Nanosensors Read-Out». In: *IEEE Transactions on Circuits and Systems I: Regular Papers* 60.4 (Apr. 2013), pp. 975–988. ISSN: 1558-0806. DOI: 10.1109/TCSI.2012. 2220455 (cit. on p. 13).
- [67] G. Massicotte, S. Carrara, G. Di Micheli, and M. Sawan. «A CMOS Amperometric System for Multi-Neurotransmitter Detection». In: *IEEE Transactions on Biomedical Circuits and Systems* 10.3 (June 2016), pp. 731–741. ISSN: 1940-9990. DOI: 10.1109/TBCAS.2015.2490225 (cit. on p. 13).
- [68] S. S. Ghoreishizadeh, I. Taurino, G. De Micheli, S. Carrara, and P. Georgiou. «A Differential Electrochemical Readout ASIC With Heterogeneous Integration of Bio-Nano Sensors for Amperometric Sensing». In: *IEEE Transactions on Biomedical Circuits and Systems* 11.5 (Oct. 2017), pp. 1148–1159. ISSN: 1940-9990. DOI: 10. 1109/TBCAS.2017.2733624 (cit. on p. 13).
- [69] S. Naus, I. Tzouvadaki, P. Gaillardon, A. Biscontini, G. De Micheli, and S. Carrara. «An efficient electronic measurement interface for memristive biosensors». In: 2017 IEEE International Symposium on Circuits and Systems (ISCAS). May 2017, pp. 1– 4. DOI: 10.1109/ISCAS.2017.8050685 (cit. on p. 13).
- [70] A. Tuoheti, S. Aiassa, F. Criscuolo, F. Stradolini, I. Tzouvadaki, S. Carrara, and D. Demarchi. «New Approach for Making Standard the Development of Biosensing Devices by a Modular Multi-Purpose Design». In: *IEEE Transactions on NanoBioscience* 19.3 (July 2020), pp. 339–346. ISSN: 1558-2639. DOI: 10.1109/TNB.2020. 2995230 (cit. on p. 13).
- [71] I. N. Hanitra, F. Criscuolo, N. Pankratova, S. Carrara, and G. D. Micheli. «Multichannel Front-End for Electrochemical Sensing of Metabolites, Drugs, and Electrolytes». In: *IEEE Sensors Journal* 20.7 (Apr. 2020), pp. 3636–3645. ISSN: 1558-1748. DOI: 10.1109/JSEN.2019.2959885 (cit. on p. 13).
- [72] I. N. Hanitra, F. Criscuolo, S. Carrara, and G. De Micheli. «Multi-Target Electrolyte Sensing Front-End for Wearable Physical Monitoring». In: 2019 15th Conference on Ph.D Research in Microelectronics and Electronics (PRIME). July 2019, pp. 249–252.
   DOI: 10.1109/PRIME.2019.8787768 (cit. on p. 13).
- [73] Savannah Afsahi et al. «Novel graphene-based biosensor for early detection of Zika virus infection». In: *Biosensors and Bioelectronics* 100 (2018), pp. 85-88.
   ISSN: 0956-5663. DOI: https://doi.org/10.1016/j.bios.2017.08.051. URL: http://www.sciencedirect.com/science/article/pii/S0956566317305869 (cit. on pp. 15, 17).
- [74] Giwan Seo et al. «Rapid Detection of COVID-19 Causative Virus (SARS-CoV-2) in Human Nasopharyngeal Swab Specimens Using Field-Effect Transistor-Based Biosensor». In: ACS Nano 14.4 (2020). PMID: 32293168, pp. 5135-5142. DOI: 10. 1021/acsnano.0c02823. eprint: https://doi.org/10.1021/acsnano.0c02823. URL: https://doi.org/10.1021/acsnano.0c02823 (cit. on pp. 15, 17).

- Binghe Wang and Eric V. Anslyn. *Chemosensors*. John Wiley & Sons, Ltd, 2011.
   ISBN: 9781118019580. DOI: 10.1002/9781118019580. eprint: https://onlinelibraary.wiley.com/doi/pdf/10.1002/9781118019580. URL: https://onlinelibrary.wiley.com/doi/abs/10.1002/9781118019580 (cit. on p. 16).
- [76] Xiaoming Tao, ed. Wearable Electronics and Photonics. Woodhead Publishing, 2005.
   ISBN: 978-1-85573-605-4. DOI: https://doi.org/10.1016/B978-1-85573-605-4.50014-3 (cit. on p. 18).
- Jane McCann and David Bryson. Smart Clothes and Wearable Technology. Wood-head Publishing, 2009. ISBN: 978-1-84569-357-2. DOI: https://doi.org/10.1016/B978-1-84569-357-2.50023-X. URL: http://www.sciencedirect.com/science/article/pii/B978184569357250023X (cit. on p. 18).
- [78] I. Jones and G.K. Stylios. *Joining Textiles*. Woodhead Publishing, 2013. ISBN: 978-1-84569-627-6. DOI: https://doi.org/10.1533/9780857093967 (cit. on p. 18).
- [79] Vinod Kumar Khanna. Implantable Medical Electronics. Prosthetics, Drug Delivery, and Health Monitoring. Springer, 2016. ISBN: 978-3-319-25448-7. DOI: https://doi. org/10.1007/978-3-319-25448-7 (cit. on p. 18).
- [80] I. N. Hanitra, F. Criscuolo, S. Carrara, and G. De Micheli. «Multi-Target Electrolyte Sensing Front-End for Wearable Physical Monitoring». In: 2019 15th Conference on Ph.D Research in Microelectronics and Electronics (PRIME). July 2019, pp. 249–252. DOI: 10.1109/PRIME.2019.8787768 (cit. on p. 18).
- [81] M. Padash and S. Carrara. «A 3D printed wearable device for sweat analysis». In: 2020 IEEE International Symposium on Medical Measurements and Applications (MeMeA). June 2020, pp. 1–5. DOI: 10.1109/MeMeA49120.2020.9137273 (cit. on p. 18).
- [82] S. Shityakov, N. Roewer, C. Förster, and Croscheit J. A. «In Silico Modeling of Indigo and Tyrian Purple Single-Electron Nano-Transistors Using Density Functional Theory Approach.» In: *Nanoscale Res Lett* 12.439 (2017). DOI: https://doi.org/ 10.1186/s11671-017-2193-7 (cit. on p. 18).
- [83] Namik Akkilic, Stefan Geschwindner, and Fredrik Höök. «Single-molecule biosensors: Recent advances and applications». In: *Biosensors and Bioelectronics* 151 (2020), p. 111944. ISSN: 0956-5663. DOI: https://doi.org/10.1016/j.bios.2019.111944. URL: http://www.sciencedirect.com/science/article/pii/S0956566319310 22X (cit. on p. 18).
- [84] Yanxiao Feng, Yuechuan Zhang, Cuifeng Ying, Deqiang Wang, and Chunlei Du.
   «Nanopore-based Fourth-generation DNA Sequencing Technology». In: Genomics, Proteomics & Bioinformatics 13.1 (2015), pp. 4–16. ISSN: 1672-0229. DOI: https: //doi.org/10.1016/j.gpb.2015.01.009. URL: http://www.sciencedirect.com/science/article/pii/S1672022915000133 (cit. on pp. 18, 288).
- [85] S. Heerema and C. Dekker. «Graphene nanodevices for DNA sequencing.» In: Nature Nanotech 11 (2016), pp. 127–136. DOI: https://doi.org/10.1038/nnano.2015.
   307 (cit. on pp. 18, 288).

- [86] Henk W. Ch. Postma. «Rapid Sequencing of Individual DNA Molecules in Graphene Nanogaps». In: *Nano Letters* 10.2 (2010). PMID: 20044842, pp. 420-425. DOI: 10.1021/n19029237. eprint: https://doi.org/10.1021/n19029237. URL: https://doi.org/10.1021/n19029237 (cit. on pp. 18, 288).
- [87] Cesare Rossetti. Rudimenti di meccanica quantistica. Levrotto & Bella, 2008. ISBN: 9788882181321 (cit. on pp. 25, 37, 39, 41, 49, 52, 54, 56, 61, 70, 77, 79, 81, 95, 100, 104, 106, 111, 112, 125, 299, C3, C7).
- [88] Marcelo Alonso and Edward J. Finn. Fundamental University Physics III Quantum and Statistical Physics. Addison Wesley, 1968. ISBN: 978-0201002621 (cit. on pp. 25, 33, 34, 40, 43, 70, 77, 79, 90).
- [89] Supriyo Datta. Quantum transport: atom to transistor. Cambridge University Press, 2005. ISBN: 0521631459 (cit. on pp. 25, 93–95, 99, 100, 104, 115, 120, 121, 123, 137, 155, 156, 173, 178, 187, 193, 211, 214, 216, 217, 219, 221, 224, 225, 237, 238, 242, 245, 254–256, 259, 261, 262, 266, 267, 270, 273, 275, 277, B1, B5, C1, C3, C5).
- [90] Marc Baldo. Introduction to Nanoelectronics. MIT OpenCourseWare Publication, 2011 (cit. on pp. 25, 50, 156, 163, 172, 173, 185, 242, 375, 376, 388).
- [91] J. J. Sakurai. Modern quantum mechanics. Addison Wesley, 1994. ISBN: 0201539292 (cit. on pp. 25, 104).
- [92] Jun John Sakurai. Advanced quantum mechanics. Addison Wesley, 1967. ISBN: 0201067102 (cit. on pp. 25, 187, 190, 245, 256).
- [93] L. Schiff. Quantum Mechanics. 4th. Mc Graw-Hill, 2014. ISBN: 9781259062865 (cit. on p. 39).
- [94] Sheldon M. Ross. Introduction to probability and statistics for engineers and scientists. 3rd. Elsevier academic press, 2004. ISBN: 0-12-598057-4 (cit. on p. 46).
- [95] R. L. Allen and D. W. Mills. Signal analysis. Time, Frequency, Scale and Structure. IEEE Press - Wiley Interscience, 2004. ISBN: 8879920774 (cit. on pp. 58, 69, 96, 105).
- [96] L. Lo Presti and F. Neri. L'analisi dei segnali. 2nd. CLUT, 1992. ISBN: 8879920774 (cit. on pp. 58, 69, 96, 105).
- [97] Omar Manasreh. Semiconductor Heterojunctions and Nanostructures (Nanoscience and Technology). McGraw-Hill, 2005. ISBN: 0071452281 (cit. on p. 79).
- [98] Frank Jensen. Introduction to computational chemistry. 2nd. John Wiley & sons, 2007. ISBN: 0-470-01187-4 (cit. on pp. 117, 124–138, 140–145, 153).
- [99] M. Born and R. Oppenheimer. «Zur Quantentheorie der Molekeln». In: Annalen der Physik 389.20 (1927), pp. 457–484. DOI: 10.1002/andp.19273892002. eprint: https: //onlinelibrary.wiley.com/doi/pdf/10.1002/andp.19273892002. URL: https://onlinelibrary.wiley.com/doi/abs/10.1002/andp.19273892002 (cit. on p. 119).

- [100] Cohen E.R. et al. Quantities, Units and Symbols in Physical Chemistry IUPAC Green Book. 3rd. IUPAC & RSC Publishing, 2008. URL: https://web.archive. org/web/20161220125649/https://www.iupac.org/fileadmin/user\_uplo ad/publications/e-resources/ONLINE-IUPAC-GB3-2ndPrinting-Online-Sep2012.pdf (cit. on p. 119).
- [101] Chao Yang, Juan C. Meza, Byounghak Lee, and Lin-Wang Wang. «KSSOLV a MatLab toolbox for solving the Kohn–Sham equations». In: ACM Transactions on Mathematical Software 36.2 (2009). DOI: 10.1145/1499096.1499099 (cit. on pp. 120, 134, 135).
- [102] Jack Simons. An introduction to theoretical chemistry. Cambridge University Press, 2003. ISBN: 0521823609 (cit. on p. 120).
- [103] Lecture III : The Many-Body Hamiltonian and the Functional Derivative. http: //www.physics.metu.edu.tr/~hande/teaching/741-lectures/lecture-03.pdf (cit. on p. 126).
- [104] Thomas A. Albright, Jeremy K. Burdett, and Myung-Hwan Whangbo. Orbital interactions in chemistry. Ed. by John Wiley & sons. 2nd. 2013. ISBN: 9780471080398 (cit. on pp. 126–128, 130, 132, 133, 135, 143, 282–284).
- [105] Ferdows Zahid, Magnus Paulsson, and Supriyo Datta. «Electrical Conduction through Molecules». In: Advanced Semiconductors and Organic NanoTechniques. Academic Press, 2003 (cit. on pp. 145, 204, 211, 247, 302, 372, F1).
- [106] Kurt Stokbro, Dan Erik Petersen, Søren Smidstrup, Anders Blom, and Mads Ipsen.
   «Semiempirical model for nanoscale device simulations». In: *Physical review B* 82.075420 (2010). DOI: 10.1103/PhysRevB.82.075420 (cit. on p. 145).
- [107] Theodore L. Brown, Jr. LeMay Eugene H., Bruce E. Bursten, Catherine J. Murphy, and Patrick M. Woodward. *Chemistry: The Central Science*. 14th. Pearson College Div, 2018. ISBN: 9780134414232 (cit. on pp. 146, 149, 334, 336, 337, 344, 402).
- [108] Tro Nivaldo. Chemistry: A Molecular Approach. 4th. Pearson Education, 2017. ISBN: 1292152389 (cit. on pp. 146, 149, 334, 336, 337, 344, 402).
- [109] Ilya G. Kaplan. Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials. Ed. by John Wiley & sons. 2006. ISBN: 978-0-470-86332-9 (cit. on pp. 150, 151).
- [110] Mark Waller and Stefan Grimme. «Weak Intermolecular Interactions: A Supermolecular Approach». In: *Handbook of Computational Chemistry*. Ed. by Jerzy Leszczynski. Dordrecht: Springer Netherlands, 2016, pp. 1–27. ISBN: 978-94-007-6169-8. DOI: 10.1007/978-94-007-6169-8\_12-2. URL: https://doi.org/10.1007/978-94-007-6169-8\_12-2 (cit. on pp. 151, 152, 154).
- [111] Sujay B. Desai, Hossain M. Fahad, Theodor Lundberg, Gregory Pitner, Hyungjin Kim, Daryl Chrzan, H.-S. Philip Wong, and Ali Javey. «Gate Quantum Capacitance Effects in Nanoscale Transistors». In: *Nano Letters* 19.10 (2019). PMID: 31532995, pp. 7130-7137. DOI: 10.1021/acs.nanolett.9b02660. eprint: https://doi. org/10.1021/acs.nanolett.9b02660. URL: https://doi.org/10.1021/acs. nanolett.9b02660 (cit. on p. 174).

- [112] Michael Galperin, Mark A. Ratner, Abraham Nitzan, and Alessandro Troisi. «Nuclear Coupling and Polarization in Molecular Transport Junctions: Beyond Tunneling to Function». In: Science 319.5866 (2008), pp. 1056-1060. ISSN: 0036-8075. DOI: 10.1126/science.1146556. eprint: https://science.sciencemag.org/content/319/5866/1056.full.pdf. URL: https://science.sciencemag.org/content/319/5866/1056 (cit. on pp. 185, 270, 273).
- [113] William B. Davis, Walter A. Svec, Mark A. Ratner, and Michael R. Wasielewski.
   «Molecular-wire behaviour in p-phenylenevinylene oligomers». In: *Nature* 396 (1998), p. 6706 (cit. on pp. 186, 270, 271).
- Seong Ho Choi, BongSoo Kim, and C. Daniel Frisbie. «Electrical Resistance of Long Conjugated Molecular Wires». In: Science 320.5882 (2008), pp. 1482-1486.
   ISSN: 0036-8075. DOI: 10.1126/science.1156538. eprint: https://science.sciencemag.org/content/320/5882/1482.full.pdf. URL: https://science.sciencemag.org/content/320/5882/1482 (cit. on pp. 186, 270).
- [115] Henrik Bruus and Karsten Flensberg. Many-Body Quantum Theory in Condensed Matter Physics: An Introduction. OUP Oxford, 2004. ISBN: 0198566336 (cit. on pp. 187, 190, 245, 256, 259, 276).
- [116] Alexander Altland and Ben Simons. Condensed matter field theory. Cambridge University Press, 2010. ISBN: 9780511789281 (cit. on pp. 187, 190, 216, 245, 256, 259, 276).
- [117] Mark Srednicki. Quantum field theory. Cambridge University Press, 2007. ISBN: 9780521864497 (cit. on p. 187).
- [118] S. Sanvito, C. J. Lambert, J. H. Jefferson, and Bratkosvky A.M. «General Green'sfunction formalism for transport calculations with spd Hamiltonians and giant magnetoresistance in Co- and Ni-based magnetic multilayers». In: *Physical review* B 59.18 (1999) (cit. on p. 212).
- [119] M. P. López Sancho, J. M. López Sancho, and J. Rubio. «Highly convergent schemes for the calculation of bulk and surface Green functions». In: *Journal of Physics F: Metal Physics* 15 851-858 (1985) (cit. on p. 212).
- [120] Hans Henrik B. Sørensen, Per Christian Hansen, Dan Erik Petersen, Stig Skelboe, and Kurt Stokbro. «Krylov subspace method for evaluating the self-energy matrices in electron transport calculations». In: *Physical review B* 77.155301 (2008). DOI: 10.1103/PhysRevB.77.155301 (cit. on p. 213).
- [121] Daniele Stradi, Umberto Martinez, Anders Blom, Mads Brandbyge, and Kurt Stokbro. «General atomistic approach for modeling metal-semiconductor interfaces using density functional theory and nonequilibrium Green's function». In: *Physical review B* 93.155302 (2016) (cit. on p. 213).
- M. Cahay, M. McLennan, S. Datta, and M. S. Lundstrom. «Importance of spacecharge effects in resonant tunneling devices». In: *Applied Physics Letters* 50.10 (1987), pp. 612–614. DOI: 10.1063/1.98097. eprint: https://doi.org/10.1063/1.98097. URL: https://doi.org/10.1063/1.98097 (cit. on p. 237).

- [123] M. Buttiker. «Symmetry of electrical conduction». In: IBM Journal of Research and Development 32.3 (1988), pp. 317–334 (cit. on pp. 237, 254).
- [124] Supriyo Datta. «Nanoscale device modeling: the Green's function method». In: Superlattices and Microstructures 28.4 (2000). DOI: 10.1006/spmi.2000.0920 (cit. on p. 242).
- Søren Smidstrup et al. «QuantumATK: An integrated platform of electronic and atomic-scale modelling tools». In: J. Phys: Condens. Matter 32 (2020), p. 015901 (cit. on pp. 251, 253, 275, 295, 298, 310–312, 314, 362, 366, 367, D1, D2, D3, E4, E5, E6, E10, E11, E12, E13, E14, E15, E16, E18, E19, E20).
- [126] QuantumATK version Q-2019.12, Synopsys QuantumATK
   www.synopsys.com/silicon/quantumatk.html (cit. on pp. 251, 253, 275, 295, 298, 310–312, 314, 362, 366, 367, D1, D2, D3, E4, E5, E6, E10, E11, E12, E13, E14, E15, E16, E18, E19, E20).
- M. R. Hestenes and Stiefel E. «Methods of Conjugate Gradients for Solving Linear Systems». In: Journal of Research of The National Bureau of Standards 49.6 (1952), p. 2379 (cit. on p. 251).
- [128] C. Toher, A. Filippetti, S. Sanvito, and Kieron Burke. «Self-Interaction Errors in Density-Functional Calculations of Electronic Transport». In: *Phys. Rev. Lett.* 95 (14 Sept. 2005), p. 146402. DOI: 10.1103/PhysRevLett.95.146402. URL: https://link.aps.org/doi/10.1103/PhysRevLett.95.146402 (cit. on pp. 274, 275).
- Stephan Kümmel, Leeor Kronik, and John P. Perdew. «Electrical Response of Molecular Chains from Density Functional Theory». In: *Phys. Rev. Lett.* 93 (21 Nov. 2004), p. 213002. DOI: 10.1103/PhysRevLett.93.213002. URL: https: //link.aps.org/doi/10.1103/PhysRevLett.93.213002 (cit. on pp. 274, 275).
- [130] Luiz G. Ferreira, Marcelo Marques, and Lara K. Teles. «Approximation to density functional theory for the calculation of band gaps of semiconductors». In: *Phys. Rev. B* 78 (12 Sept. 2008), p. 125116. DOI: 10.1103/PhysRevB.78.125116. URL: https://link.aps.org/doi/10.1103/PhysRevB.78.125116 (cit. on p. 275).
- S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton. «Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study». In: *Phys. Rev. B* 57 (3 Jan. 1998), pp. 1505–1509. DOI: 10.1103/PhysRevB.57.1505. URL: https://link.aps.org/doi/10.1103/ PhysRevB.57.1505 (cit. on p. 275).
- [132] Matteo Cococcioni and Stefano de Gironcoli. «Linear response approach to the calculation of the effective interaction parameters in the LDA + U method». In: *Phys. Rev. B* 71 (3 Jan. 2005), p. 035105. DOI: 10.1103/PhysRevB.71.035105. URL: https://link.aps.org/doi/10.1103/PhysRevB.71.035105 (cit. on p. 275).

- [133] Zhizhou Yu, Jian Chen, Lei Zhang, and Jian Wang. «First-principles investigation of quantum transport through an endohedral N@C60in the Coulomb blockade regime». In: Journal of Physics: Condensed Matter 25.49 (Nov. 2013), p. 495302. DOI: 10.1088/0953-8984/25/49/495302. URL: https://doi.org/10.1088%2F0953-8984%2F25%2F49%2F495302 (cit. on p. 276).
- [134] Antonio Martinez, John R Barker, and Riccardo Di Pietro. «Dissipative non-equilibrium Green function methodology to treat short range Coulomb interaction: current through a 1D nanostructure». In: Journal of Physics: Condensed Matter 30.29 (June 2018), p. 294003. DOI: 10.1088/1361-648x/aacc49. URL: https://doi.org/10.1088%2F1361-648x%2Faacc49 (cit. on p. 276).
- [135] A. Nasri, A. Boubaker, W. Khaldi, B. Hafsi, and A. Kalboussi. «Transport propreties of organic single electron transistor; dependence on acene length». In: 2017 International Conference on Engineering MIS (ICEMIS). 2017, pp. 1–7 (cit. on p. 277).
- J. J. Palacios. «Coulomb blockade in electron transport through a C<sub>60</sub> molecule from first principles». In: *Phys. Rev. B* 72 (12 Sept. 2005), p. 125424. DOI: 10.1103/ PhysRevB.72.125424. URL: https://link.aps.org/doi/10.1103/PhysRevB.72. 125424 (cit. on p. 278).
- [137] Ferdinand Huber, Julian Berwanger, Svitlana Polesya, Sergiy Mankovsky, Hubert Ebert, and Franz J. Giessibl. «Chemical bond formation showing a transition from physisorption to chemisorption». In: Science 366.6462 (2019), pp. 235-238. ISSN: 0036-8075. DOI: 10.1126/science.aay3444. eprint: https://science.sciencemag.org/content/366/6462/235.full.pdf. URL: https://science.sciencemag.org/content/366/6462/235 (cit. on pp. 284, 285).
- S. J. Ray. «Single molecular transistor as a superior gas sensor». In: Journal of Applied Physics 118.3 (2015), p. 034303. DOI: 10.1063/1.4926853. eprint: https: //doi.org/10.1063/1.4926853. URL: https://doi.org/10.1063/1.4926853
   (cit. on pp. 285, 286).
- Barsha Jain, K. Vinod Kumar, B. SanthiBhushan, Kumar Gaurav, Manisha Pattanaik, and Anurag Srivastava. «A tetracene-based single-electron transistor as a chlorine sensor». In: *Journal of Computational Electronics* 17.4 (Dec. 2018), pp. 1515–1520. ISSN: 1572-8137. DOI: 10.1007/s10825-018-1214-9. URL: https://doi.org/10.1007/s10825-018-1214-9 (cit. on pp. 285, 286).
- [140] Klaus Sattler. Handbook of Nanophysics, Clusters and Fullerenes. Ed. by Taylor & Francis group CRC press. Nov. 2010. ISBN: 9781138115101 (cit. on pp. 289, 293, 294, 423).
- [141] S. M. Sze and M. K. Lee. Semiconductor Devices: Physics and Technology 3rd ed. John Wiley & Sons Inc, 2012. ISBN: 978-0470537947 (cit. on pp. 289, 294).
- [142] G. Ghione. Semiconductor Device for High-Speed Optoelectronics. Cambridge University Press, 2009. ISBN: 978-0521763448 (cit. on pp. 289, 294).

- [143] Heekeun Shin et al. «Structure and dynamics of C<sub>60</sub> molecules on Au(111)». In: *Phys. Rev. B* 89 (24 June 2014), p. 245428. DOI: 10.1103/PhysRevB.89.245428. URL: https://link.aps.org/doi/10.1103/PhysRevB.89.245428 (cit. on pp. 294, 313, 315, 316).
- [144] Reinhard J. Maurer, Victor G. Ruiz, Javier Camarillo-Cisneros, Wei Liu, Nicola Ferri, Karsten Reuter, and Alexandre Tkatchenko. «Adsorption structures and energetics of molecules on metal surfaces: Bridging experiment and theory». In: *Progress in Surface Science* 91.2 (2016), pp. 72–100. ISSN: 0079-6816. DOI: https:// doi.org/10.1016/j.progsurf.2016.05.001. URL: http://www.sciencedirect. com/science/article/pii/S0079681616300089 (cit. on pp. 294, 313, 315, 316).
- K. Xu, T. Yang, Y. Feng, X. Ruan, Z. Liu, G. Liang, and X. Wang. «Endohedral Fullerene Fe@C<sub>28</sub> Adsorbed on Au(111) Surface as a High-Efficiency Spin Filter: A Theoretical Study.» In: *Nanomaterials* 9 (2019), p. 1068. DOI: 10.3390/nano90810 68 (cit. on p. 294).
- [146] Xiaoliang Zhong, Ravindra Pandey, Alexandre Reily Rocha, and Shashi P. Karna.
  «Can Single-Atom Change Affect Electron Transport Properties of Molecular Nanostructures such as C60 Fullerene?» In: *The Journal of Physical Chemistry Letters* 1.10 (2010), pp. 1584–1589. DOI: 10.1021/jz100360t. eprint: https://doi.org/ 10.1021/jz100360t. URL: https://doi.org/10.1021/jz100360t (cit. on p. 294).
- [147] Adam Jaroš, Esmaeil Farajpour Bonab, Michal Straka, and Cina Foroutan-Nejad.
   «Fullerene-Based Switching Molecular Diodes Controlled by Oriented External Electric Fields». In: Journal of the American Chemical Society 141.50 (2019). PMID: 31744293, pp. 19644–19654. DOI: 10.1021/jacs.9b07215. eprint: https://doi.org/10.1021/jacs.9b07215. URL: https://doi.org/10.1021/jacs.9b07215 (cit. on p. 294).
- Jiuxu Song, Yintang Yang, Hongxia Liu, Lixin Guo, and Zhiyong Zhang. «Electronic transport properties of the armchair silicon carbide nanotube». In: Journal of Semiconductors 31.11 (Nov. 2010), p. 114003. DOI: 10.1088/1674-4926/31/11/114003. URL: https://doi.org/10.1088%5C%2F1674-4926%5C%2F31%5C%2F11%5C%2F114003 (cit. on pp. 308, 309).
- [149] Robin McIlveen. Fundamentals of weather and climate. Oxford University Press, 2010. ISBN: 978-0199215423 (cit. on p. 336).
- [150] World Health Organization. Regional Office for Europe. Health risks of heavy metals from long-range transboundary air pollution. World Health Organization, 2007. ISBN: 978 92 890 7179 6 (cit. on pp. 340, 344).
- [151] F.W. Sears and G.L. Salinger. Thermodynamics, Kinetic Theory, and Statistical Thermodynamics. Third Edition. Addison-Wesley Publishing Company, 1975. ISBN: 978-0201068948 (cit. on pp. 384, 385).
- [152] 5.62 Physical Chemistry II. MIT OpenCourseWare, 2008. URL: https://ocw. mit.edu/courses/chemistry/5-62-physical-chemistry-ii-spring-2008/ lecture-notes/29\_5621n08.pdf (cit. on p. 384).

- [153] Robertson, J. «High dielectric constant oxides». In: Eur. Phys. J. Appl. Phys. 28.3 (2004), pp. 265–291. DOI: 10.1051/epjap:2004206. URL: https://doi.org/10.1051/epjap:2004206 (cit. on p. 388).
- [154] R.A. Ploc. «The lattice parameter of cubic ZrO2 formed on zirconium». In: Journal of Nuclear Materials 99.1 (1981), pp. 124–128. ISSN: 0022-3115. DOI: https://doi. org/10.1016/0022-3115(81)90146-X. URL: http://www.sciencedirect.com/ science/article/pii/002231158190146X (cit. on p. 388).

### Appendix A

## Additional quantum mechanics related topics

#### A.1 Solution of second order homogeneous differential equations

The steady state Schrödinger's equation can always be written as:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + U(x)\psi(x) = E\psi(x) \quad , \quad U(x) = 0 \quad \forall x \in \mathbb{R}$$

$$\rightarrow \frac{d^2}{dx^2}\psi(x) + k^2\psi(x) = 0 \quad , \quad k = \sqrt{\frac{2m}{\hbar^2}(E - U(x))}$$

Usually in practical cases a piece-wise constant potential energy is recovered. Let's call the potential constant value in the interval of interest with  $U_0$ . Thus:

$$\frac{d^2}{dx^2}\psi(x) + k^2\psi(x) = 0 \quad , \quad k = \sqrt{\frac{2m}{\hbar^2}(E - U_0)}$$

This is an homogeneous ordinary differential equation of second order with constant coefficients. Depending if  $E > U_0$  or  $E < U_0$  two different solutions are possible. In general, a second order homogeneous equation can be written as:

$$\frac{d^2}{dx^2}y(x) + a\frac{d}{dx}y(x) + by(x) = 0 \quad with \ a, b \in \mathbb{R}$$

and its solution depends on the discriminant of the characteristic polynomial:

$$\lambda^2 + a\lambda + b = 0 \quad \rightarrow \quad \lambda_{1,2} = \frac{-a \pm \sqrt{\Delta}}{2} \quad , \quad where: \quad \Delta = a^2 - 4b$$

In the Schrödinger's equation case a = 0 and  $b = k^2$ :

$$\lambda^2 + k^2 = 0 \quad \rightarrow \quad \lambda_{1,2} = \pm \sqrt{-k^2} = \pm ik \quad and \quad \Delta = -4k^2$$

The following cases are generally possible:

•  $\Delta > 0$ : the characteristic polynomial roots are real and distinct. In the Schrödinger's equation case this corresponds to a purely imaginary k. This is the case in which  $E < U_0$  such that:

$$k = i\beta_k \in \mathbb{C}$$
,  $\beta_k = \sqrt{\frac{2m}{\hbar^2} (U_0 - E)} \in \mathbb{R}^+$ 

Indeed  $\Delta = -4k^2 = +4\beta_k^2 > 0$ . The general solution is:

$$y(x) = Ae^{\lambda_1 x} + Be^{\lambda_2 x} \quad A, B \in \mathbb{R}$$

that in the Schrödinger's equation case becomes:

$$\lambda_{1,2} = \pm ik = \mp \beta_k \in \mathbb{R} \quad and \ thus: \quad \psi(x) = Ae^{+\beta_k x} + Be^{-\beta_k x} \quad , \quad A, B \in \mathbb{R}$$

- $\Delta = 0$ : in this case the two roots of the characteristic polynomial are real and equal. Nevertheless this case cannot appear in the solution of the Schrödinger's equation since it would correspond to k = 0, that means no state (trivial solution - not of interest).
- $\Delta < 0$ : in this case the two roots of the characteristic polynomial are complex conjugate. This is the case in which  $E > U_0$  such that:

$$k = \sqrt{\frac{2m}{\hbar^2} \left( E - U_0 \right)} \quad \in \mathbb{R}^+$$

In this case  $\Delta = -4k^2 < 0$ . The complex conjugate solutions of the characteristic polynomial are indicated as:  $\lambda_{1,2} = \sigma \pm i\varepsilon$ . The general solution is:

 $y(x) = C_1 e^{\sigma x} cos(\varepsilon x) + C_2 e^{\sigma x} sin(\varepsilon x) \quad , \quad C_1, C_2 \in \mathbb{R}$ 

that in the Schrödinger's equation case becomes:

$$\begin{split} \lambda_{1,2} &= \pm ik \quad , \quad with: \quad \sigma = 0 \quad and \quad \varepsilon = k \\ and \ thus: \quad \psi(x) &= C_1 e^{\sigma x} cos(\varepsilon x) + C_2 e^{\sigma x} sin(\varepsilon x) \quad , \quad C_1, C_2 \in \mathbb{R} \end{split}$$

Noticing that  $\sigma = 0$  and thus  $e^{\sigma x} = 1$ , that  $\varepsilon = k$  and remembering that is possible to express cosine and sine functions in term of complex exponentials:

$$\psi(x) = C_1 \cdot 1 \cdot \frac{e^{ikx} + e^{-ikx}}{2} + C_2 \cdot 1 \cdot \frac{e^{ikx} - e^{-ikx}}{2i} =$$
  
=  $\frac{C_1}{2} \left( e^{ikx} + e^{-ikx} \right) + \frac{C_1}{2i} \left( e^{ikx} - e^{-ikx} \right)$   
 $\rightarrow \quad \psi(x) = \left( \frac{C_1}{2} - \frac{C_2}{2}i \right) e^{ikx} + \left( \frac{C_1}{2} + \frac{C_2}{2}i \right) e^{-ikx}$ 

and said:  $A = \frac{C_1}{2} - \frac{C_2}{2}i$  and  $B = \frac{C_1}{2} + \frac{C_2}{2}i$  it becomes:

$$\psi(x) = Ae^{+ikx} + Be^{-ikx} \quad , \quad A, B \in \mathbb{C}$$
  
A2

In summary, the two cases of interest that is possible to encounter in the solution of the steady state Scrhödinger's equation are the following:

•  $E < U_0$ : for which:

$$k = i\beta_k \in \mathbb{C}$$
,  $\beta_k = \sqrt{\frac{2m}{\hbar^2}(U_0 - E)} \in \mathbb{R}^+$ 

and the general solution is:

$$\psi(x) = Ae^{+\beta_k x} + Be^{-\beta_k x} \quad , \quad A, B \in \mathbb{R}$$

•  $E > U_0$ : for which:

$$k = \sqrt{\frac{2m}{\hbar^2} \left( E - U_0 \right)} \quad \in \mathbb{R}^+$$

and the general solution is:

$$\psi(x) = Ae^{+ikx} + Be^{-ikx} \quad , \quad A, B \in \mathbb{C}$$

It is possible summarize the results by saying that the general solution is always:

$$\psi(x) = Ae^{+\lambda_1 x} + Be^{+\lambda_2 x}$$

with  $\lambda_{1,2} = \pm ik$  solutions of the characteristic polynomial. Then if  $E < U_0$ , thus k is purely imaginary, by writing it as  $k = i\beta_k$  (where  $\beta_k$  is real positive) one gets:  $\lambda_{1,2} = \pm \beta_k$  and the solution becomes:

$$\psi(x) = Ae^{+\beta_k x} + Be^{-\beta_k x}$$
, remembering that:  $A, B \in \mathbb{R}$ 

Otherwise if  $E > U_0$ , thus k is real (positive), then:  $\lambda_{1,2} = \pm ik$  and the solution becomes:

$$\psi(x) = Ae^{+ikx} + Be^{-ikx} \quad , \quad remembering \ that: \ A, B \in \mathbb{C}$$

#### A.2 Another method for the 1D finite height quantum well

In section 2.3.7 it was addressed the solution of the steady state Schrödinger's equation in the case of a finite height 1D quantum well. It was pointed out that no full analytical solution is possible, but also that another procedure, less involved of the one briefly discussed there, is possible. In this appendix this way of proceeding is briefly presented. The same result obtained in section 2.3.7, can also be obtained in an another way by noting that the potential U(x) has an even symmetry. It is possible to verify that in this case the solutions  $\psi(x)$  can be symmetric or anti-symmetric. In the first case  $\psi(x)$  is even, while in the second it is odd. Within the Schrödinger's equation:  $\hat{H}\psi = E\psi$ , the wave-function is multiplied by a second order derivative and by the potential energy at left hand side  $(\hat{H})$ , and by a real scalar E on right hand side. Thus an even wave-function can be a solution for that equation if the application of the Hamiltonian operator on it (left hand term) does not change its symmetry (that on the right hand side is not changed by the multiplication with the real scalar E). Fortunately a second order derivative of an even function is even and the multiplication of an even function U(x) by an even function  $\psi(x)$  is still even. Thus an even wave-function can be solution of the Schrödinger's equation. Analogously an odd wave-function can be a solution of the Schrödinger's equation, since a second order derivative of an odd function is odd and the multiplication of an even function U(x) by an odd one  $\psi(x)$  is again odd. Notice instead that a wave-function that is given by the sum of an even and an odd functions cannot be a solution. Consequently there are two types (even or odd wave-function) of independent solutions. They will be addressed separately.

The results that are the starting points for what is presented now (see section 2.3.7 for their derivation) are the wave-function general expressions:

$$\psi(x) = \begin{cases} \psi_I(x) = K_1 e^{+\beta_k x} & \text{if } x < -\frac{L}{2} & (\text{region } I) \\ \psi_{II}(x) = K_2 \cos(kx) + K_3 \sin(kx) & \text{if } -\frac{L}{2} \le x \le +\frac{L}{2} & (\text{region } II) \\ \psi_{III}(x) = K_4 e^{-\beta_k x} & \text{if } x > +\frac{L}{2} & (\text{region } III) \end{cases}$$

and the continuity conditions on it and its first derivatives:

$$\begin{cases} \psi_{I}(-\frac{L}{2}) = \psi_{II}(-\frac{L}{2}) & (cond. \ 1) \\ \psi_{II}(+\frac{L}{2}) = \psi_{III}(+\frac{L}{2}) & (cond. \ 2) \\ \frac{d}{dx}\psi_{I}(x)|_{x=-\frac{L}{2}} = \frac{d}{dx}\psi_{II}(x)|_{x=-\frac{L}{2}} & (cond. \ 3) \\ \frac{d}{dx}\psi_{II}(x)|_{x=+\frac{L}{2}} = \frac{d}{dx}\psi_{III}(x)|_{x=+\frac{L}{2}} & (cond. \ 4) \end{cases}$$

Case of  $\psi(x)$  even: From the general solution of  $\psi(x)$  in order to have an even solution it is possible to set  $K_1 = K_4$  and  $K_3 = 0$ , such that:

$$\psi(x) = \begin{cases} \psi_I(x) = K_1 e^{+\beta_k x} & \text{if } x < -\frac{L}{2} & (region \ I) \\ \psi_{II}(x) = K_2 cos(kx) & \text{if } -\frac{L}{2} \le x \le +\frac{L}{2} & (region \ II) \\ \psi_{III}(x) = K_1 e^{-\beta_k x} & \text{if } x > +\frac{L}{2} & (region \ III) \end{cases}$$

From the continuity condition (cond. 1) one gets:

$$K_1 e^{-\beta_k \frac{L}{2}} = K_2 cos(-k \frac{L}{2}) = K_2 cos(k \frac{L}{2})$$
 (A.1)

From the continuity condition (cond. 3) one gets:

$$K_1 \beta_k e^{-\beta_k \frac{L}{2}} = -K_2 \ k \ \sin(-k\frac{L}{2}) = +K_2 \ k \ \sin(k\frac{L}{2}) \tag{A.2}$$

The equations (A.1) and (A.2) constitute an homogeneous linear system of two equations in two unknowns (namely  $K_1$  and  $K_2$ ). The system is:

$$\begin{cases} K_1 e^{-\beta_k \frac{L}{2}} - K_2 cos(k \frac{L}{2}) = 0\\ K_1 \beta_k e^{-\beta_k \frac{L}{2}} - K_2 \ k \ sin(k \frac{L}{2}) = 0 \end{cases}$$

Its determinant should be enforced to be null such that only non-trivial solutions can be found:

$$\begin{vmatrix} e^{-\beta_k \frac{L}{2}} & -\cos(k\frac{L}{2}) \\ \\ \beta_k e^{-\beta_k \frac{L}{2}} & -k\sin(k\frac{L}{2}) \end{vmatrix} = 0$$

From which:

$$e^{-\beta_k \frac{L}{2}} k \sin(k\frac{L}{2}) + \beta_k e^{-\beta_k \frac{L}{2}} \cos(k\frac{L}{2}) = 0$$
  
$$\rightarrow \beta_k = k \tan\left(k\frac{L}{2}\right)$$
(A.3)

This last equation represents a constraint on the possible energy values that are permitted for the quantum well (in the sense that they are the proper energy values for that structure). Indeed both k and  $\beta_k$  are function of energy E, and thus the equation leads to possible values of E, i.e. of energy eigenvalues for the quantum well.

Case of  $\psi(x)$  odd: By proceeding in an analogous way for an odd solution it is possible to recover a similar expression, that is again a constraints on the possible energy values E, coming from the odd solutions of the Schrödinger's equation. The wave-function can be made odd by assuming  $K_1 = -K_4$  and  $K_2 = 0$ , such that:

$$\psi(x) = \begin{cases} \psi_I(x) = K_1 e^{+\beta_k x} & \text{if } x < -\frac{L}{2} & (region \ I) \\ \psi_{II}(x) = K_3 sin(kx) & \text{if } -\frac{L}{2} \le x \le +\frac{L}{2} & (region \ II) \\ \psi_{III}(x) = -K_1 e^{-\beta_k x} & \text{if } x > +\frac{L}{2} & (region \ III) \end{cases}$$

From the continuity condition (cond. 1) one gets:

$$K_1 e^{-\beta_k \frac{L}{2}} = K_3 sin(-k \frac{L}{2}) = -K_3 sin(k \frac{L}{2})$$

From the continuity condition (cond. 3) one gets:

$$K_1 \ \beta_k \ e^{-\beta_k \frac{L}{2}} = K_3 \ k \ \cos(k \frac{L}{2})$$

The last two equations constitute an homogeneous linear system of two equations in two unknowns (namely  $K_1$  and  $K_3$ ). The system is:

$$\begin{cases} K_1 e^{-\beta_k \frac{L}{2}} + K_3 \sin(k\frac{L}{2}) = 0\\ K_1 \beta_k e^{-\beta_k \frac{L}{2}} - K_3 \ k \ \cos(k\frac{L}{2}) = 0\\ A5 \end{cases}$$

Its determinant should be enforced to be null such that only non-trivial solutions can be found:

From which:

$$-e^{-\beta_k \frac{L}{2}} k \cos(k\frac{L}{2}) - \beta_k e^{-\beta_k \frac{L}{2}} \sin(k\frac{L}{2}) = 0$$
$$\rightarrow \beta_k = -k \cot\left(k\frac{L}{2}\right)$$
(A.4)

This last equation represents a constraint on the possible energy values that are permitted for the quantum well (in the sense that they are the proper energy values for that structure). Indeed both k and  $\beta_k$  are function of energy E, and thus the equation leads to possible values of E, i.e. of energy eigenvalues for the quantum well.

The two equations (A.3) and (A.4) must hold simultaneously, thus they constitute a system of two equations to be satisfied in order to have acceptable solutions of the Schrödinger's equation for the quantum well. Equation (A.3) must hold for the even wave-functions, while equation (A.4) for the odd ones. Nevertheless the solutions must be merged, indeed they are simultaneous solutions of the same equation, even if they were recovered independently the one from the other. A full analytical solution of the system of equations (A.3) and (A.4) is not possible. Numerical or graphical procedures are needed, usually the graphical procedure is preferred because it allows to understand better the concept of "binding power" introduced in section 2.3.7. In order to do that the functions  $k \tan\left(k\frac{L}{2}\right)$  and  $-k \cot\left(k\frac{L}{2}\right)$  can be plotted with kL on abscissa axis, see figure A.1. The solutions are given by the intersections of these curves with the  $\beta_k(k)$  ones (since they must be equal). Notice that  $\beta_k$  is function of k (and thus of E):

$$\beta_k(k) = \sqrt{\frac{2m}{\hbar^2} \left( U_0 - E \right)} = \sqrt{\frac{2m}{\hbar^2} U_0 - \frac{2m}{\hbar^2} E} = \sqrt{k_0^2 - k^2}$$

where  $k_0^2 = \frac{2m}{\hbar^2} U_0$  and  $k^2 = \frac{2m}{\hbar^2} E$ . The intersections between the curve  $\sqrt{k_0^2 - k^2}$  and the above mentioned  $k \tan\left(k\frac{L}{2}\right)$  (even modes) and  $-k \cot\left(k\frac{L}{2}\right)$  (odd modes) corresponds to the only possible k values for the quantum well. From figure A.1 it is evident that these values are quantized (indeed there is no a continuous range of values but only discrete points), and consequently the permitted energy eigenvalues for the quantum well are discretized, indeed:

$$E = \frac{\hbar^2 k^2}{2m}$$
 , k is quantized.



Figure A.1: Graphic solution of the system of the two equations (A.3) and (A.4). In blue:  $k \tan\left(k\frac{L}{2}\right)$ ; in orange:  $-k \cot\left(k\frac{L}{2}\right)$ ; in black: the functions  $\beta_k = \sqrt{k_0^2 - k^2}$  for various  $k_0$ . The only possible solutions are the intersection points, highlighted with red circles, between  $\beta_k = \sqrt{k_0^2 - k^2}$  and the functions  $k \tan\left(k\frac{L}{2}\right)$  and  $-k \cot\left(k\frac{L}{2}\right)$ . These intersection points correspond to discrete values of k and thus of energy E.

#### A.3 *MatLab* implementation of the finite difference method for the 1D finite height quantum well

In this section is reported a *MatLab* code that solves the steady state Schrödinger's equation in the case of a quantum well. The quantum well is supposed to be tall  $U_0$  and long L. The well can also have an internal barrier of thickness W and height  $U_1$ . The electron mass is assumed to be the free electron mass (effective mass set to 1). The code was developed during the course "Micro & Nano systems" (a.y. 2018/2019) as an exercise. Instructions and remarks on its usage are directly provided within the code comments.

```
%% Micro&Nano discretized Quantum Well Hamiltonian exercise.

clear all

close all

clc

string_to_be_displayed = sprintf('Potential well exercise.\n');

disp(string_to_be_displayed);

%% Useful constants: (do NOT modify please! =) )

m0 = 9.10938291e-31; % electron mass, kg

q = 1.6021766208e-019; % elementary charge, C

h = 6.626070040e-34; % Planck constant, J*s

hbar = h/(2*pi); % J*s

hbar_eV = h/q; % Planck constant, eV*s

bhar_eV = h_eV/(2*pi); % eV*s
```

```
16
17 \% input data: (set them properly! =) )
_{18} L = 10e-9; %try: 22e-9; % width of the well, m
19 N = 100; % number of nodes
_{\rm 20} \left| \, U0 \, = \, 1 \, ; \, \, \% \right. height of the well, eV
21 % central portion of the well:
  U1 = 0.8; % height of central portion of the well, eV (it should be
22
       lesser than UO!)
_{23} W = 5e-9; % central well width, m (it should be lesser than L!!)
24 % electron effective mass in considered material:
m = 1 * m0; % by default it is set equal to free electron mass: m = 1 * m0
      m0;
26 %
27
28 7 Hamiltonian operator construction:
29 %
_{30} % set the mesh grid (it is created a mesh 2L long):
|_{31}| space = linspace(-L, L, 2*N);
32 % Create the potential shape:
_{33}|U = linspace(-L, L, 2*N);
_{34}|U(1:end) = U0; \% eV, initialization to U0
35 % index and correct potential shape generation:
_{36} well = find (abs(space) < L/2);
|\text{small\_well} = \text{find}(\text{abs}(\text{space}) < W/2);
_{38} U(well) = 0; % eV
_{39}| U(small_well) = U1; % eV
_{40} %
41
  % Kinetic energy operator term:
_{42}|_{a} = \operatorname{space}(2) - \operatorname{space}(1); \% elementary interval (linspace is used so each
      intervals are all equal)
  t0 = hbar_eV^2/(2*m*a^2);
43
44 %
45 % H diagonal elements:
46 diag_elements = 2 * t0 * ones (1, length (U));
47 diag_elements = diag_elements + U/q; % here U is expressed in J
_{48}|_{\rm H} = {\rm diag}({\rm diag\_elements});
49 % H upper/lower diag elements:
<sup>50</sup> up low diag elements = -t0 * ones(1, length(U) - 1);
_{51} H = H + diag(up_low_diag_elements, 1);
_{52} H = H + diag(up_low_diag_elements, -1);
53 %
54
55 % Eigenvectors and Eigenvalues calculation:
_{56}|\% Function "eig" evaluates the first 2N eigenvalues and eigenvectors
      where N
_{57} % is the H dimensione (2Nx2N, with N set in input data section).
_{58} % Bounded states (i.e. states of interest in this code/problem)
_{59} \% are then found by selecting the eigenvalues (and corresponding
60 % eigenfunctions) with energy below U0.
61
  [EigenVect, EigenValues] = eig(H);
62
  EigenValues_eV = EigenValues*q; % eV
63
_{64} %
```

```
65 % copy eigenvalues in an suitable output data-structure:
66 Energy_Values = zeros(1, length(U));
_{67} Energy_Values = diag(EigenValues_eV);
68 %
69 % Bounded states selection: states with energy below U0.
   Confined Energy Values = find (Energy Values < U0);
70
  %
71
  % % IN THE CASE IN WHICH U1>U0 AND YOU WANT TO PLOT ALSO THE
72
      EIGENFUNCTIONS
_{73} % WITH EIGENVALUES IN BETWEEN U0 AND U1: PLEASE COMMENT THE INSTRUCTION
_{74}|\% % ABOVE AND USE THE FOLLOWING (uncomment it):
_{75} % Umax = max(U0, U1);
<sup>76</sup> % Confined_Energy_Values = find (Energy_Values < Umax);
77
78 % PLOT RESULTS:
79 %
80 % CONFINED EIGENVALUES:
| figure (1)
82 hold on
83 grid on
84 plot (space *1e9, U, 'k', 'LineWidth', 2);
85 % well abscissa axis definition:
|abscissa = linspace(-L/2, L/2, N);
87 for i=1:Confined_Energy_Values(end)
  EigenValue_to_be_plotted = Energy_Values(i);
88
  EigenPLOT = EigenValue\_to\_be\_plotted * ones(1,N);
89
   plot(abscissa*1e9, EigenPLOT, 'LineWidth', 2);
90
   end
91
   xlabel('space-axis (nm)');
92
   ylabel ('Energy (eV)');
93
   title ('Eigenvalues of confined states in the well');
94
   set(gca, 'fontsize', 15);
95
  %
96
  % NUMBER OF CONFINED EIGENVALUES IS PRINTED in command window:
97
   string_to_be_displayed = sprintf('Number of confined eigenvalues: <math>\%g.\n',
98
        Confined_Energy_Values(end));
   disp(string_to_be_displayed);
99
100 %
101 string_to_be_displayed = sprintf('
                                                  '); % just for appearance
      reasons
   disp(string_to_be_displayed);
103 %
104 % WAVEFUNCTIONS PLOTS:
   string_to_be_displayed = sprintf('Press any key to continue (as many
105
      times as the number of confined eigenvalues) - figure (2) \cdot (n');
   disp(string_to_be_displayed);
106
   %
107
   figure(2)
108
   aesthetic_factor = 2;
109
   for i=1:Confined_Energy_Values(end)
110
       hold on
       grid on
112
```

```
xlabel('space-axis (nm)');
113
       ylabel('Wavefunctions (eV)');
114
       Umax = max(U0, U1);
115
       ylim([-Umax/2 \ Umax]);
116
       title ('Bounded wavefunctions in function of space');
       set(gca, 'fontsize', 15);
plot(space*1e9, U, 'k-', 'LineWidth', 2);
118
119
       plot(space*1e9, aesthetic_factor*EigenVect(:,i), 'LineWidth', 2);
120
       legend_string_well = sprintf('quantum well shape');
121
       legend_string = sprintf('wavefunction %g', i);
       legend(legend_string_well, legend_string, 'Location', 'best');
123
       pause
124
            if(i ~= Confined_Energy_Values(end))
125
            clf
126
            end
   end
128
  %
   string_to_be_displayed = sprintf('Press any key to continue (as many
130
       times as the number of confined eigenvalues) - figure (3) \cdot n';
   disp(string_to_be_displayed);
131
  %
  figure (3)
   aesthetic_factor = 0.4;
134
   hold on
   grid on
136
   xlabel('space-axis (nm)');
137
   ylabel ('Wavefunctions (eV)');
138
   title('Bounded wavefunctions in the well');
139
  set(gca, 'fontsize', 15);
plot(space*1e9, U, 'k', 'LineWidth', 2);
140
141
   for i=1:Confined_Energy_Values(end)
142
       plot(space*le9, Energy_Values(i) + aesthetic_factor*EigenVect(:,i), '
143
       LineWidth', 2);
144
       pause
  end
145
  %
146
   string_to_be_displayed = sprintf('Press any key to continue (as many
147
       times as the number of confined eigenvalues) - figure (4).\langle n' \rangle;
   disp(string_to_be_displayed);
148
149 %
  string_to_be_displayed = sprintf('
150
                                                     '); % just for appearance
       reasons
   disp(string_to_be_displayed);
_{152} %
  figure (4)
153
   aesthetic_factor = 2;
  hold on
155
   grid on
156
   xlabel('space-axis (nm)');
157
   ylabel ('Wavefunctions (eV)');
158
   title('Squared modulus of bounded wavefunctions in the well');
159
160 set (gca, 'fontsize', 15);
```

```
plot(space*1e9, U, 'k', 'LineWidth', 2);
161
   for i=1:Confined_Energy_Values(end)
       plot(space*1e9, Energy_Values(i) + aesthetic_factor*abs(EigenVect(:, i
       )).<sup>2</sup>, 'LineWidth', 2);
       pause
164
   end
165
   %
166
   string_to_be_displayed = sprintf('Execution Terminated.\n <math>\rightarrow If a graph
167
       is not clear, please modify the relative aesthetic factor in plot
       functions ! = (n');
   disp(string_to_be_displayed);
   %
169
```

### A.4 *MatLab* implementation of the finite difference method for the 1D potential barrier (and step)

In this section is reported a *MatLab* code that solves the steady state Schrödinger's equation in the case of a potential step, barrier or double barrier. It was derived from the code reported in the previous section A.3. Notice that in this exercise the energy of the incoming electron should be arbitrary. Nevertheless in order to speed up and simplify the solution, only proper eigenstates of the space domain are considered, and they were evaluated with no boundary conditions. This means that the space is considered limited instead of unlimited, with a total extension equal to L (that is the input domain). Consequently discretization occurs and only wave-functions that are proper eigenmodes of the structure (that is long L) are considered. In a real world potential step/barrier the space is considered unbounded and infinite to both left and right sides. Consequently the Hamiltonian spectrum is continue and not discrete, like it happens here. Among the calculated (discrete) eigenfunctions, the plotted ones (see section 2.3.7) are the so-called "considered" ones, i.e. those with energy lesser than  $E_{max}$  (see input parameters). They are anyway significant of the main physical insights of this class of problems. Depending on the particular case it is left to the user the physical interpretation of the plotted wave-functions. They may correspond to incoming electrons from left or from right, or even from any intermediate region. All the solutions are anyway solutions of the steady state Schrödinger's equation for the considered shape of the potential. This code should be refined such that suitable boundary conditions are enforced and only interesting cases, namely corresponding to incoming electrons from left, are found.

Instructions and remarks on its usage are directly provide within the code comments.

 <sup>1 %%</sup> Micro&Nano discretized Quantum Well Hamiltonian exercise. By Fabbro.
 2 clear all

<sup>3</sup> close all

<sup>4</sup> clc

string\_to\_be\_displayed = sprintf('Potential step/barrier exercise.\n');

<sup>6</sup> disp(string\_to\_be\_displayed);

```
8 % Useful constants: (do NOT modify please! =) )
m0 = 9.10938291e - 31; % electron mass, kg
|_{10}|_{q} = 1.6021766208e - 019; \% elementary charge, C
11 h = 6.626070040e - 34; \% Planck constant, J*s
12 hbar = h/(2*pi); % J*s
13 h_eV = h/q; % Planck constant, eV*s
  hbar_eV = h_eV/(2*pi); \% eV*s
15
_{16} model matrix (set them properly! =) )
_{17} L = 10e-9; % total space length of region of interest, m
18 N = 1000; % number of nodes for numeric solution
_{19} %
_{20} U0 = 2; % height of the FIRST barrier, eV
21 W0 = 5e - 9; % width of the FIRST barrier, m (it should be lesser than L!!)
_{22} sp0 = 0e-9; % x-coordinate at which the FIRST barrier starts, in m
23 %
_{24} U1 = 0; % height of the SECOND barrier, eV
_{25}|W1 = 0e-9; % width of the SECOND barrier, m (it should be lesser than L
      !!)
  sp1 = 7e-9; % x-coordinate at which the SECOND barrier starts, in m
26
_{27} %
_{28} % Set the max energy level you desire to consider in solving the problem,
_{29} % the eigenstate with E < Emax will be plotted:
_{30} Umax = max(U0, U1);
_{31} Emax = 1.25 * Umax; % default is: Umax
32 % electron effective mass in considered material:
m = 1 * m0; \% by default it is set equal to free electron mass: m = 1 * m0; \%
      m0:
  %
34
35
_{36} %% Mesh and potential shape U(x):
37 %
_{38} % set the mesh grid (it is created a mesh long L):
space = linspace(-L/2, L/2, N);
40 % Create the potential shape:
_{41}|_{U} = linspace(-L/2, L/2, N);
_{42} %
_{43} potential shape generation, at most two barriers are built:
  for i = 1:N
44
       if (\text{space}(i) \ge \text{sp0}) & (\text{space}(i) \le \text{sp0+W0}) % only if \text{space}(i) is a
45
      point in the FIRST well then U(\,i\,) is set to U0
           U(i) = U0; \% eV
46
       elseif (space(i) >= sp1) && (space(i) <= sp1+W1) % only if space(i)</pre>
47
      is a point in the FIRST well then U(i) is set to U1
            U(i) = U0; \% eV
48
       else U(i)=0; % eV, otherwise U(i) is initialized at zero
49
      end
50
  end
  %% Hamiltonian operator construction:
54 % Kinetic energy operator term:
```

```
_{55}|a = \text{space}(2) - \text{space}(1); \% elementary interval (linspace is used so each
      intervals are all equal)
  t0 = hbar_eV^2/(2*m*a^2);
56
57 %
58 % H diagonal elements:
_{59} diag_elements = 2*t0*ones(1, length(U));
60 diag elements = diag elements + U/q; % here U is expressed in J
_{61} | H = diag (diag_elements);
62 % H upper/lower diag elements:
_{63} | up\_low\_diag\_elements = -t0*ones(1, length(U)-1);
_{64} H = H + diag(up_low_diag_elements, 1);
_{65} H = H + diag (up_low_diag_elements, -1);
66 %
67
  %% Eigenvectors and Eigenvalues calculation:
68
<sup>69</sup> % Function "eig" evaluates the first 2N eigenvalues and eigenvectors
      where N
_{70} % is the H dimensione (2Nx2N, with N set in input data section).
_{71} 8 Bounded states (i.e. states of interest in this code/problem)
_{72} % are then found by selecting the eigenvalues (and corresponding
_{73} (% eigenfunctions) with energy below Emax to be considered !!
74
 7878787878787
              the maximum between U0 and U1.
75
76
  [EigenVect, EigenValues] = eig(H);
77
  EigenValues_eV = EigenValues*q; \% eV
79
  % copy eigenvalues in an suitable output data-structure:
80
  Energy_Values = zeros(1, length(U));
81
82
  Energy_Values = diag(EigenValues_eV);
83
  %
  % Eigenstates selection: only eigenstates with energy below Umax
84
  \% decomment if desired to set Emax = Umax (max between U0 and U1): Emax =
85
       Umax:
  Considered_Energy_Values = find (Energy_Values < Emax);
86
87
  % Remark:
88
_{89} % The following theoretical remark is printed in the command window:
  string_to_be_displayed = sprintf('In this exercise the energy of the
90
      incoming electron should be arbitrary.\nNevertheless in order to
      simplify the solution only proper eigenstates of the space domain are
      considered.\nThis means that the space is considered LIMITED instead
      of unlimited, with a total extension equal to L \setminus n (that is the input
      domain)... Consequently discretization occurs and only wave-functions
      that are proper eigenmodes\nof the structure (that is long L) are
      considered.\nIn a real world potential step/barrier the space is
      considered unbounded and infinite to both left and right sides.
      nConsequently the Hamiltonian spectrum is continue and NOT discrete,
      like it happens here.\nAmong the calculated (discrete) eigenfunctions,
      the plotted ones are the so-called "considered" ones, \ni.e. those
      with energy lesser than Emax (see input parameters).\nThey are anyway
      significant of the main physical insights of this class of problems.\n
      \langle n' \rangle;
```

```
91 disp(string_to_be_displayed);
92
  %% PLOT RESULTS:
93
94 %
  % CONSIDERED EIGENVALUES:
95
   figure(1)
96
   hold on
97
   grid on
98
   plot(space*1e9, U, 'k', 'LineWidth', 2);
99
   for i=1:Considered_Energy_Values(end)
100
  EigenValue_to_be_plotted = Energy_Values(i);
101
102 | EigenPLOT = EigenValue_to_be_plotted * ones(1,N);
   plot(space*1e9, EigenPLOT, 'LineWidth', 2);
  end
104
  xlabel('space axis x (nm)');
  ylabel('Energy (eV)');
106
  title('Considered steady state energy values');
107
   set(gca, 'fontsize', 16);
108
109 %
110 % NUMBER OF CONSIDERED EIGENVALUES IS PRINTED in command window:
   string_to_be_displayed = sprintf('Number of considered eigenvalues: %g.\n
111
       ', Considered_Energy_Values(end));
   disp(string_to_be_displayed);
112
  %
113
   string_to_be_displayed = sprintf('
114
                                                     '); % just for appearance
       reasons
   disp(string_to_be_displayed);
  %
116
  % WAVEFUNCTIONS PLOTS:
117
   string_to_be_displayed = sprintf('Press any key to continue (as many
118
       times as the number of confined eigenvalues) - figure (2) \cdot n';
   disp(string_to_be_displayed);
119
  %
120
121 figure (2)
   aesthetic_factor = 10;
   for i=1:Considered_Energy_Values(end)
       hold on
124
       grid on
       xlabel('space axis x (nm)');
126
       ylabel(' \ psi(x)');
       Umax = max(U0, U1);
128
       \operatorname{ylim}([-\operatorname{Umax}/2 \mod(\operatorname{Umax}, \operatorname{Emax})]);
       title('Considered wave-functions');
130
       set(gca, 'fontsize', 16);
plot(space*1e9, U, 'k—', 'LineWidth', 2);
131
132
       plot(space*1e9, aesthetic_factor*EigenVect(:,i), 'LineWidth', 2);
       legend_string_well = sprintf('potential energy shape (eV)');
134
       legend_string = sprintf('wavefunction %g', i);
       legend(legend_string_well, legend_string, 'Location', 'best');
136
       pause
137
            if(i ~= Considered_Energy_Values(end))
138
            clf
139
```

```
end
140
   end
141
_{142} %
   string_to_be_displayed = sprintf('Press any key to continue (as many
143
       times as the number of confined eigenvalues) - figure (3) \cdot n';
   disp(string_to_be_displayed);
144
   %
145
   figure(3)
146
   aesthetic_factor = 1;
147
   hold on
148
   grid on
149
   xlabel('space-axis x (nm)');
150
   ylabel(' \ psi(x)');
151
   title('Considered wave-functions');
   set(gca, 'fontsize', 16);
plot(space*1e9, U, 'k', 'LineWidth', 2);
153
154
   for i=1:Considered Energy Values(end)
155
       plot(space*1e9, Energy_Values(i) + aesthetic_factor*EigenVect(:,i), '
156
       LineWidth', 2);
       pause
157
   end
158
  %
159
   string_to_be_displayed = sprintf('Press any key to continue (as many
160
       times as the number of confined eigenvalues) - figure (4) \cdot n';
   disp(string_to_be_displayed);
161
   %
162
   figure (4)
163
   aesthetic_factor = 400;
164
   for i=1:Considered_Energy_Values(end)
       hold on
166
167
        grid on
        xlabel('space axis x
                                  (nm)');
168
        ylabel('||psi(x)|^2');
169
       Umax = max(U0, U1);
170
       \operatorname{ylim}([-\operatorname{Umax}/2 \mod(\operatorname{Umax}, \operatorname{Emax})]);
        title('Squared modulus of wave-functions');
       set(gca, 'fontsize', 16);
plot(space*1e9, U, 'k-', 'LineWidth', 2);
174
        plot(space*1e9, aesthetic_factor*abs(EigenVect(:,i)).^2, 'LineWidth',
        2);
        legend_string_well = sprintf('potential energy shape (eV)');
       legend_string = sprintf('wavefunction %g', i);
177
       legend(legend_string_well, legend_string, 'Location', 'best');
178
179
        pause
            if (i ~= Considered_Energy_Values(end))
180
            clf
181
            end
182
   end
183
   %
184
   string_to_be_displayed = sprintf('Press any key to continue (as many
185
       times as the number of confined eigenvalues) - figure (5) \cdot n';
   disp(string_to_be_displayed);
186
187 %
```

```
188 figure (5)
   aesthetic_factor = 50;
189
   hold on
190
   grid on
191
   xlabel('space axis x (nm)');
ylabel('|  psi(x)|^2');
192
193
   title('Squared modulus of wave-functions');
194
   set(gca, 'fontsize', 16);
plot(space*1e9, U, 'k', 'LineWidth', 2);
for i=1:Considered_Energy_Values(end)
195
196
197
        plot(space*1e9, Energy_Values(i) + aesthetic_factor*abs(EigenVect(:, i
198
        )).^2, 'LineWidth', 2);
        pause
199
   end
200
   %
201
   string_to_be_displayed = sprintf('
202
                                                       ____'); % just for appearance
       reasons
   disp(string_to_be_displayed);
203
   %
204
   %
205
   %
206
   %
207
   string_to_be_displayed = sprintf('Execution Terminated.\n \rightarrow>> If a graph
208
        is not clear, please modify the relative aesthetic factor in plot
        functions ! = ) \setminus n');
   disp(string_to_be_displayed);
209
210 %
```

### Appendix B

# Additional molecular electronic structure related topics

#### **B.1** Hartree approximation and electron correlation

The purpose of this section is to provide an oversimplified quantitative treatment of the Hartree approximation widely used in Hartree-Fock and Hartree-Fock derived methods and in the Density Functional Theory (DFT) method. The treatment is not rigorous and has to be intended as an introduction to these topic to non-expert readers. Essentially the classical physics is used to convince the non-expert reader of the rationality of the equations written in sections 3.2 and 3.3. In this section I will follow the approach of [89], that despite its simplicity is capable of catching the main physical insights. The topics presented in sections 3.1 and 3.2 are given as known here, the notation will be analogous.

#### Hartree approximation

Consider a many-body system with  $N_e$  electrons, and with a total electron-electron interaction equal to  $U_{ee}(N_e)$ . If the average potential energy for the case of a single electron interacting with another single electron (1 electron - 1 electron interaction) is called  $U_0$ , then the total electron-electron interaction energy of a collection of  $N_e$  electrons is proportional to the number of distinct pairs:

$$U_{ee}(N_e) = U_0 N_e (N_e - 1)/2 \tag{B.1}$$

where  $N_e/2$  is the number of distinct pairs of electrons; each pair of electron has an average interaction energy  $U_0$ , thus  $U_0N_e/2$  is the average interaction energy of the  $N_e$  electrons in the system (in other words each electron has an average interaction energy  $U_0/2$  and there are  $N_e$  electrons); and since a single electron in the system interacts with the other  $N_e - 1$  ones the total interaction energy in the system of  $N_e$  electrons is  $U_0N_e(N_e - 1)/2$ . Notice that if two electrons are exchanged of state no variation occurs because they are identical particles.

In general it is possible to have ionization of the system, that is an electron is excited for some reason (it is provided enough thermal energy -phonon- or it absorb a photon of enough large energy) and has enough energy to break the chemical bond and "escape" from the system. This correspond to provide enough energy to an occupied electron state in the system such that the electron can overcome the vacuum level and be released. This amount of energy is called ionization potential. In a molecule it corresponds to the difference between the vacuum level and the highest occupied energy level in the molecule: the Highest Occupied Molecular Orbital (HOMO). Analogously it is possible for the system to gain an extra electron. In this case a free available electron state is occupied by a new electron. In order to make this happening the electron should loose a given amount of energy, corresponding to the difference between the vacuum level and the energy level it is going to occupy. This amount of energy is called electron affinity. In a molecule it corresponds to the difference between the vacuum level and the lowest free energy level in the molecule: the Lowest Unoccupied Molecular Orbital (LUMO). Figure B.1 summarizes these concepts.



Figure B.1: IP is the Ionization Potential while EA is the Electron Affinity. The ionization potential includes the repulsive potential from  $N_e - 1$  electrons while the electron affinity that of  $N_e$  electrons, thus the latter is higher in energy by the single electron charging energy  $U_0$ .

By solving exactly the steady state Schrödinger's equation, one is in principle able to calculate exactly the energy eigenvalues of the system and consequently the ionization potential and the electron affinity. Nevertheless as mentioned previously this is possible only if the number of electrons in the system  $N_e$  is very small. If not so an SCF potential can be considered instead in the Schrödinger's equation in order to simplify the problem. Now the question can be how to choose the SCF potential to correctly estimate the ionization potential and the electron affinity. In the case of the ionization potential the system that previously has  $N_e$  electrons looses one electron, thus it is reasonable to estimate its SCF potential as (considering also the previous expression for  $U_{ee}(N_e)$ ):

$$U_{SCF \ ionization} = U_{ee}(N_e) - U_{ee}(N_e - 1) = \frac{U_0}{2} N_e(N_e - 1) - \frac{U_0}{2} (N_e - 1)(N_e - 2) = U_0(N_e - 1)$$
B2

Analogously for the electron affinity it can be choosen a SCF potential given by:

$$U_{SCF\ affinity} = U_{ee}(N_e+1) - U_{ee}(N_e) = \frac{U_0}{2}N_e(N_e+1) - \frac{U_0}{2}N_e(N_e-1) = U_0N_e$$

In general it is chosen only one SCF potential, because otherwise a new set of single-electron steady state Schrödinger's equations is needed for each energy level (in this case two systems of equations: one for the ionization and the other for the affinity). A reasonable choice can be the (arithmetic) average betwen the two (indeed the SCF potential is already a mean field). Thus:

$$U_{SCF} = \frac{1}{2} \left( U_{SCF \ ionization} + U_{SCF \ affinity} \right) = \frac{1}{2} \left( U_0 (N_e - 1) + U_0 N_e \right) = U_0 N_e - \frac{U_0}{2}$$

Notice that this corresponds in taking the derivative w.r.t.  $N_e$  of  $U_{ee}(N_e)$ :

$$\frac{\partial}{\partial N_e} U_{ee}(N_e) = \frac{\partial}{\partial N_e} \left[ \frac{1}{2} U_0 N_e(N_e - 1) \right] = \frac{\partial}{\partial N_e} \left[ \frac{U_0 N_e^2}{2} - \frac{U_0 N_e}{2} \right] = U_0 N_e - \frac{U_0}{2}$$

This is the general assumption that is made in a general case. Notice that it has sense since it corresponds to a linearization of the electron-electron interaction term  $U_{ee}$ , that can be seen indeed as a mean field  $U_{SCF}$  of electron-electron interaction.

Before going on a remark on the nature of  $U_0$ . One may ask what determines  $U_0$ . The answer may be the extent of the electron wave-function. If one electron is smeared over the surface of a sphere of radius R then the potential of that sphere will be:  $\frac{q}{4\pi\varepsilon_0 R}$ , so that the energy needed to put another electron on the sphere will be  $\frac{q^2}{4\pi\varepsilon_0 R} \sim U_0$ . Well-delocalized wave-functions (large R) have a very small  $U_0$ , otherwise if R is small (i.e. the wave-function is highly localized)  $U_0$  can be large. Consequently when there are delocalized wave-functions the difference between the ionization SCF potential and the affinity SCF potential (and in general the difference between the SCF potentials relative to different energy levels in the conductor) are smaller, since  $U_0$  is smaller. Thus the more the conductive channel (in this work molecule) orbitals are delocalized, the better is the approximation:

$$U_{SCF} \cong \frac{\partial}{\partial N_e} U_{ee}(N_e) \tag{B.2}$$

since the difference between the SCF potentials relative to different energy levels (ionization or affinity in the aforementioned example) is lesser. Indeed if  $U_0$  is very small and  $N_e$  is very large it is true that:  $U_{SCF \ ionization} = U_0(N_e - 1) \sim U_{SCF \ affinity} = U_0N_e$ . Notice that such a delocalization often occurs whenever strong chemical bonds are created between the molecule and the contact, because the molecular orbitals are subjected to hybridization with the (metal) contact orbitals (that generally are well delocalized).

Under this hypothesis the distinction between the different SCF potentials for the different energy levels can be neglected and the previous (first order - i.e. first derivative) approximation of equation (B.2) can be generalized as follows:

$$U_{SCF}(\vec{r}) \cong \frac{\partial}{\partial [n(\vec{r})]} U_{ee}(n(\vec{r}))$$
(B.3)
This last expression is the one used also in the density functional theory (see later, section 3.5). The meaning of eq. (B.3) is the following: the self consistent potential at any point  $\vec{r}$  is assumed to be equal to the change in the electron-electron interaction energy due to an infinitesimal change in the number of electrons at the same point.

From classical electrostatics it is possible to get an expression for  $U_{ee}$ . From equation (B.1) if it is assumed  $N_e$  enough large that  $N_e \sim N_e - 1$  (reasonable for large conductors), one has:

$$U_{ee} = \frac{1}{2}U_0 N_e (N_e - 1) \cong \frac{1}{2}U_0 N_e^2$$

from which:

$$U_{ee} = \frac{1}{2} \int \frac{-qQn(\vec{r'})}{4\pi\varepsilon_0 |\vec{r} - \vec{r'}|} d\vec{r'} = \frac{1}{2} \int \int \frac{q^2 n(\vec{r}) n(\vec{r'})}{4\pi\varepsilon_0 |\vec{r} - \vec{r'}|} d\vec{r'} d\vec{r}$$
(B.4)

where  $V_{Ne} = \int \frac{-qn(\vec{r})}{4\pi\varepsilon_0|\vec{r}-\vec{r'}|} d\vec{r'}$  is the electrostatic potential of  $N_e$  electrons, given by integrating the charge density  $-qn(\vec{r})$ ; Q is the charge due to  $N_e$  electrons and it is given by integrating the charge density  $-qn(\vec{r})$  and 1/2 arises from the count on distinct pairs of electrons. Notice that the double  $U_{ee}$  of eq. (B.4) corresponds to the energy (work) that must be provided to put in the same volume, in which there are  $N_e$  electrons (which generate an electrostatic potential  $V_{Ne}$ ), other  $N_e$  electrons (charge Q). Notice also that if  $N_e = 2$  (the minimum number of electrons in order to have an electron-electron interaction is 2) from equation (B.1)  $U_{ee} = U_0$ , and  $U_{ee}$  can be again written as:

$$U_{ee} = \frac{1}{2} \int \int \frac{q^2 n(\vec{r}) n(\vec{r'})}{4\pi\varepsilon_0 |\vec{r} - \vec{r'}|} d\vec{r'} d\vec{r}$$

where the integrals over the entire volume in which the two electrons are localized give 2, thus:

$$U_{ee} = \frac{1}{2} \int \int \frac{q^2 n(\vec{r}) n(\vec{r'})}{4\pi\varepsilon_0 |\vec{r} - \vec{r'}|} d\vec{r'} d\vec{r} = \frac{1}{2} \frac{2q^2}{4\pi\varepsilon_0 D} = \frac{q^2}{4\pi\varepsilon_0 D}$$

that is exactly the expression for the energy required to put a (point) charge -q at a distance  $D = |\vec{r} - \vec{r'}|$  from the (point) charge -q that gives rise to the potential:  $\frac{-q}{4\pi\varepsilon_0 D}$ . From equation (B.3) the SCF potential is obtained by differentiating  $U_{ee}$  w.r.t. the

From equation (B.3) the SCF potential is obtained by differentiating  $U_{ee}$  w.r.t. the electron density n, this is essentially the so called Hartree approximation. Thus from equation (B.4) one has:

$$U_{SCF \ Hartree}(\vec{r}) = \int \frac{q^2 n(\vec{r'})}{4\pi\varepsilon_0 |\vec{r} - \vec{r'}|} d\vec{r'}$$
(B.5)

This last expression is the SCF potential in the Hartree approximation. Notice that if  $N_e$  is not so big to assume it to be equal to  $N_e$  then equation (B.4) can be corrected by multiplying it by a corrective term  $(N_e - 1)/N_e$ , similarly to what done in eq. (3.5). This is possible since the electrons are identical particles and thus by exchanging them (their states) the final electron-electron interaction is always the same. In this case the Hartree SCF potential becomes:

$$U_{SCF \ Hartree}(\vec{r}) = \frac{N_e - 1}{N_e} \int \frac{q^2 n(\vec{r'})}{4\pi\varepsilon_0 |\vec{r} - \vec{r'}|} d\vec{r'}$$

that indeed corresponds exactly to the expression of eq. (3.5).

The Hartree SCF potential can be seen as the solution of the following Poisson's equation (written here directly for the potential energy):

$$-\nabla^2 U_{SCF \ Hartree}(\vec{r}) = -\frac{q^2 n(\vec{r})}{\varepsilon_0}$$

where an homogeneous medium with dielectric permittivity  $\varepsilon_0$  (vacuum) is assumed. If another medium should be considered (among the nuclei and electrons of the molecule), a proper dielectric constant should be considered instead of  $\varepsilon_0$ .

The previous discussion was aimed on convincing non-expert readers of the rationality of the important equations (B.3), (B.4) and (B.5). Nevertheless the concept here is quite simple: the Hartree approximation consists in writing the electron-electron interaction by means of a mean field, i.e. the SCF potential (eq. (B.5)), that is the first order derivative (i.e. variation - see eq. (B.3)) of the classical electron-electron interaction (eq. (B.4)) derived from classical electrostatics. This approximation is at the basis of the Hartree method that will be further discussed in section 3.3. The main problem of the mean field based methods (namely the electron correlation) is presented in the next subsection.

#### The correlation energy

The problem in the treatment presented so far is that the actual interaction energy is less than the one predicted in equation (B.4), essentially because electrons can correlate their motion (around the atomic nuclei composing the molecule) so as to avoid each other. This correlation comes out naturally in a many-body picture, but it is missed in the mean field approximation (Hartree approximation) in which the many-body problem is written as a set of single-electron ones. A simple way to include the aforementioned correlation is by means of the introduction of a correlation function g in equation (B.4), that can be rewritten as:

$$U_{ee} = \frac{1}{2} \int \int \frac{q^2 n(\vec{r}) n(\vec{r'}) [1 - g(\vec{r}, \vec{r'})]}{4\pi\varepsilon_0 |\vec{r} - \vec{r'}|} d\vec{r'} d\vec{r}$$
(B.6)

The correlation function g accounts for the fact that the probability of finding two electrons simultaneously ilat  $\vec{r}$  and  $\vec{r'}$  is not just proportional to  $n(\vec{r'})n(\vec{r'})$ , but is somewhat reduced because electrons "try to avoid each other" [89]. The real picture is more complicated than this one, indeed g is also spin-dependent, but to keep the treatment minimal the approach of [89] is followed and the spin-dependence is ignored.

By deriving eq. (B.6) w.r.t. *n* the SCF potential is found to be:

$$U_{SCF} = \int \frac{q^2 n(\vec{r'}) [1 - g(\vec{r}, \vec{r'})]}{4\pi\varepsilon_0 |\vec{r} - \vec{r'}|} d\vec{r'} = \int \frac{q^2 n(\vec{r'})}{4\pi\varepsilon_0 |\vec{r} - \vec{r'}|} d\vec{r'} - \int \frac{q^2 n(\vec{r'}) g(\vec{r}, \vec{r'})}{4\pi\varepsilon_0 |\vec{r} - \vec{r'}|} d\vec{r'} =$$
(B.7)  
=  $U_{Hartree}(\vec{r}) + U_{XC}(\vec{r})$ 

The first term in equation (B.7) corresponds to the Hartree SCF potential of eq. (B.5), while the second term depends on g and is usually called "exchange-correlation" potential. Thus the effect of the electron correlation is to add a (negative) potential energy term

 $U_{XC}(\vec{r})$  to the Hartree term. Notice that the within the Hartree approximation the exchange-correlation potential is neglected. Much research effort has gone (and is still going on) in accurately estimating g.

# Appendix C NEGF useful calculations

#### C.1 Fourier transform of Green's function

First of all notice that the Green's functions in the energy eigenfunction (energy domain) representation is diagonal. The Fourier transform of a diagonal matrix can be defined as the diagonal matrix that has the Fourier transform of the diagonal elements of the original matrix for elements (in general it is well defined the analytical function of matrix and it is the analytical function of all its elements - otherwise the functions of matrices are defined as series expansions). Moreover the Fourier transform of the matrix  $[G^R(E)]$  is not trivial because it requires contour integration on a complex plane since  $[G^R(E)]$  presents poles in energy eigenstates representation (and energy is complex due to  $i\eta$ ):

$$[G^{R}] = \begin{bmatrix} \frac{1}{E - \varepsilon_{1} + i\eta} & 0 & \dots \\ 0 & \frac{1}{E - \varepsilon_{2} + i\eta} & \dots \\ 0 & 0 & \dots \end{bmatrix}$$

A possible simplified treatment is the one of [89]. Here I will follow another way, starting from the fact that for stable system the Fourier transform is trivially linked with the Laplacian one. Notice that  $i\eta$  prevents the Green's functions to go to infinity at  $E = \varepsilon_{\alpha}$ , thus the system is stable. Then for stable system it is possible to switch between the unilateral (causal) Laplace transform and the Fourier one with the substitution:

$$s \leftrightarrow j\omega$$

where s is the complex variable of Laplace's transform:  $s = \sigma + j\omega$  and  $j\omega$  (j is the imaginary unit) is the Fourier transform variable. The above relation holds if the Fourier transform is defined with the sign convention typical of engineering problems. Usually physicists use another sign convention such that (the exponent sign in the Fourier transform is opposite):

$$s \leftrightarrow -i\omega$$

With this correspondence in mind, the (unilateral) Laplace transform pair:

$$\theta(t)e^{-at} \stackrel{\mathcal{L}}{\longleftrightarrow} \frac{1}{s+a}$$
C1

becomes:

$$\theta(t)e^{-at} \stackrel{\mathcal{L}}{\longleftrightarrow} \frac{1}{s+a} \quad \leftrightarrow \quad \frac{1}{-i\omega+a} = \frac{1}{-i\frac{E}{\hbar}+a}$$

where  $\theta(t)$  is the Heaviside function. Thus the diagonal elements of  $[G^{R}(E)]$  are:

$$\frac{1}{E - \varepsilon_{\alpha} + i\eta} = \frac{-i/\hbar}{-i/\hbar(E - \varepsilon_{\alpha} + i\eta)} = \frac{-i/\hbar}{-iE/\hbar + i\varepsilon_{\alpha}/\hbar + \eta/\hbar}$$

The numerator is simply a multiplicative constant, the denominator corresponds to the Laplace/Fourier transform of  $\theta(t)e^{-at}$  with  $a = +i\varepsilon_{\alpha}/\hbar + \eta/\hbar$ , and thus:

$$-\frac{i}{\hbar}\theta(t)e^{-\frac{i}{\hbar}\varepsilon_{\alpha}t}e^{-\frac{\eta}{\hbar}t}$$

corresponds to the Fourier transform of the diagonal elements of  $[G^{R}(E)]$ , from which:

$$\left[G^{R}(t)\right] = -\frac{i}{\hbar}\theta(t)e^{-\frac{\eta}{\hbar}t} \begin{bmatrix} e^{-\frac{i}{\hbar}\varepsilon_{1}t} & 0 & \dots \\ 0 & e^{-\frac{i}{\hbar}\varepsilon_{2}t} & \dots \\ 0 & 0 & \dots \end{bmatrix}$$

#### C.2 Impulse response of time dependent Schrödinger equation

In this section is provided a guideline for the verification that the diagonal elements of the time-domain retarded Green's function  $[G^R(t)]$  are a solution for the following equation:

$$\left(i\hbar\frac{\partial}{\partial t}-\varepsilon_{\alpha}\right)G^{R}_{\alpha,\alpha}(t)=\delta(t)$$

Substituting the generic diagonal element of  $[G^{R}(t)]$  (evaluated in the appendix C.1) into the previous equation:

$$\left(i\hbar\frac{\partial}{\partial t}-\varepsilon_{\alpha}\right)-\frac{i}{\hbar}\theta(t)e^{-\frac{i}{\hbar}\varepsilon_{\alpha}t}e^{-\frac{\eta}{\hbar}t}=\delta(t)$$

from which:

$$\rightarrow \quad i\hbar \frac{\partial}{\partial t} \left[ \frac{1}{i\hbar} \theta(t) e^{-\frac{i}{\hbar} \varepsilon_{\alpha} t} e^{-\frac{\eta}{\hbar} t} \right] - \varepsilon_{\alpha} \frac{1}{i\hbar} \theta(t) e^{-\frac{i}{\hbar} \varepsilon_{\alpha} t} e^{-\frac{\eta}{\hbar} t} = \delta(t)$$

Notice that the time derivative should be intended as the distributional derivative, i.e. in the sense of distributions and not of conventional functions, since the delta-Dirac and the Heaviside function  $\theta(t)$  are formally distributions. Remember also that the distributional derivative of the Heaviside distribution is a delta-Dirac distribution. In the following I will not adopt the standard formal notation, but I will use a "shortened and dirty" notation. The final result do not change, please keep in mind what said above:

$$\rightarrow \ \delta(t)e^{-\frac{i}{\hbar}\varepsilon_{\alpha}0}e^{-\frac{\eta}{\hbar}0} - \frac{i}{\hbar}\varepsilon_{\alpha}\theta(t)e^{-\frac{i}{\hbar}\varepsilon_{\alpha}t}e^{-\frac{\eta}{\hbar}t} - \frac{i}{\hbar}\eta\theta(t)e^{-\frac{i}{\hbar}\varepsilon_{\alpha}t}e^{-\frac{\eta}{\hbar}t} + \varepsilon_{\alpha}\frac{i}{\hbar}\theta(t)e^{-\frac{i}{\hbar}\varepsilon_{\alpha}t}e^{-\frac{\eta}{\hbar}t} = \delta(t)e^{-\frac{i}{\hbar}\varepsilon_{\alpha}t}e^{-\frac{\eta}{\hbar}t} = \delta(t)e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t} = \delta(t)e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t} = \delta(t)e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t} = \delta(t)e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t} = \delta(t)e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t} = \delta(t)e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t} = \delta(t)e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t} = \delta(t)e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t} = \delta(t)e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}t}e^{-\frac{\eta}{\hbar}$$

where in doing the distributional derivative the first term is evaluated in t = 0 and where in the limit of  $\eta \to 0$  the third term is null, thus:

$$\rightarrow \quad \delta(t) = \delta(t)$$

#### C.3 Some useful relations

In this sections some useful relations are demonstrated, a good treatment in this regard is in [89].

#### Review of some useful linear algebra results

Before proceeding a review of some properties and theorems of linear algebra is provided. In the following sections these results will be very useful to understand the various steps.

1: Two matrices A and B that are simultaneously diagonalizable are always commutative: AB = BA, where simultaneously diagonalizable means that the eigenvector representation of the first matrix is also an eigenvector representation for the second one.

2: The trace of a square matrix A, indicated with Tr[A], is defined as the sum of its diagonal elements. *Properties:* 

- 2a: The trace is invariant with respect to a change of basis.
- 2b: The trace is a linear mapping: Tr[A + B] = Tr[A] + Tr[B] and cTr[A] = Tr[cA], with c scalar.
- 2c: A matrix and its transpose have the same trace:  $Tr[A] = Tr[A^T]$ .
- 2d: The matrices in a trace of a product can be switched without changing the result: Tr[AB] = Tr[BA].
- 2e: More generally the trace is invariant under cyclic permutations, i.e. : Tr[ABCD] = Tr[DABC] = Tr[CDAB] = Tr[BCDA]. Instead arbitrary permutations are not allowed.
- 2f: The trace of a square matrix equals the sum of the eigenvalues counted with multiplicities.

#### C.3.1 A useful theorem

A theorem states that the Hermitian conjugate (i.e. transpose and complex conjugate) of the product of two matrices is equal to the the product of their Hermitian conjugates taken in reverse order:  $(AB)^{\dagger} = B^{\dagger}A^{\dagger}$ . For a proof and details see [87].

#### C.3.2 Equation 5.38: device density matrix $[\rho_D]$

From the definition of density matrix (eqs. (5.28) and (5.29)):

$$\rho_D(\vec{r}, \vec{r'}) = \sum_{\alpha} \psi_{D\alpha}(\vec{r}) f_{FD}(\varepsilon_{\alpha} - E_F) \psi_{D\alpha}^*(\vec{r'})$$

where  $\{\psi_{D\alpha}\}_{\alpha}$  are the device eigenstates. The previous expression in matrix form becomes:

$$[\rho_D] = \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F) \{\psi_{D\alpha}\} \{\psi_{D\alpha}\}^{\dagger} =$$
$$= \int dE f_{FD}(E - E_F) \sum_{\alpha} \delta(E - \varepsilon_{\alpha}) \{\psi_{D\alpha}\} \{\psi_{D\alpha}\}^{\dagger}$$

where the definition of delta-Dirac is used:

$$\int_{-\infty}^{+\infty} dE f_{FD}(E - E_F) \sum_{\alpha} \delta(E - \varepsilon_{\alpha}) = \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F)$$

Since  $\{\psi_{D\alpha}\} = G_D \zeta\{\phi_\alpha\}$  and  $\{S_\alpha\} = \zeta\{\phi_\alpha\}$  (see equation 5.36), it follows that:  $\{\psi_{D\alpha}\}^{\dagger} = \{\phi_\alpha\}^{\dagger} \zeta^{\dagger} G_D^{\dagger}$ , where the theorem of section C.3.1 was used. Thus the density matrix becomes:

$$\begin{aligned} [\rho_D] &= \int dE f_{FD} (E - E_F) G_D \zeta \left[ \sum_{\alpha} \delta(E - \varepsilon_{\alpha}) \left\{ \phi_{\alpha} \right\} \left\{ \phi_{\alpha} \right\}^{\dagger} \right] \zeta^{\dagger} G_D^{\dagger} = \\ &= \int \frac{dE}{2\pi} f_{FD} (E - E_F) G_D \zeta A_R \zeta^{\dagger} G_D^{\dagger} \end{aligned}$$

where eq. (5.32) is used:

$$A_R(E) = 2\pi \sum_{\alpha} \{\phi_{\alpha}\} \,\delta(E - \varepsilon_{\alpha}) \,\{\phi_{\alpha}\}^{\dagger} \qquad \Box$$

### **C.3.3** Equation 5.39: $A(E) = i \left[ G(E) - G^{\dagger}(E) \right]$

From equation (5.33) the spectral function is:

$$[A(E)] = 2\pi\delta \left( E\left[I\right] - \left[H\right] \right)$$

Notice that a possible definition for the delta-Dirac distribution is the following:

$$\delta_{\eta}(x) = \left. \frac{1}{\pi} \frac{\eta}{\eta^2 + x^2} \right|_{\eta \to 0}$$

that is the limit  $\eta \to 0$  of the Lorentzian (or Cauchy) distribution. It follows:

$$\pi\delta_0(x) = \pi\delta(x) = \left.\frac{\eta}{\eta^2 + x^2}\right|_{\eta \to 0} \quad and: \quad 2\pi\delta(E - \varepsilon_\alpha) = \left.\frac{2\eta}{(E - \varepsilon_\alpha)^2 + \eta^2}\right|_{\eta \to 0}$$

Moreover:

$$i\left[\frac{1}{E-\varepsilon_{\alpha}+i\eta}-\frac{1}{E-\varepsilon_{\alpha}-i\eta}\right] = i\left[\frac{-i\eta-(+i\eta)}{(E-\varepsilon_{\alpha}+i\eta)(E-\varepsilon_{\alpha}-i\eta)}\right] = i\frac{-2i\eta}{(E-\varepsilon_{\alpha})^{2}-(i\eta)^{2}} = \frac{2\eta}{(E-\varepsilon_{\alpha})^{2}+\eta^{2}}$$
C4

In the end:

$$A(E) = 2\pi\delta \left( E\left[I\right] - \left[H\right] \right)$$

in the energy eigenstate representation is:

$$\begin{split} A(E) &= 2\pi \sum_{\alpha} \delta\left(E - \varepsilon_{\alpha}\right) \\ with: \quad \delta\left(E - \varepsilon_{\alpha}\right) &= \frac{2\eta}{(E - \varepsilon_{\alpha})^2 + \eta^2} \Big|_{\eta \to 0} = i \left[\frac{1}{E - \varepsilon_{\alpha} + i\eta} - \frac{1}{E - \varepsilon_{\alpha} - i\eta}\right] \\ \to \quad A(E) &= i \left[G(E) - G^{\dagger}(E)\right] \end{split}$$

and generalizing to whatever representation (a relation holding in eigenstate representation should also be true in any other representation - see [89]):

$$A(E) = 2\pi\delta \left( E\left[I\right] - \left[H\right] \right) = i \left\{ \left[ (E + i\eta)I - H \right]^{-1} - \left[ (E - i\eta)I - H \right]^{-1} \right\}$$

That corresponds to:

$$A(E) = A(E) = i \left[ G(E) - G^{\dagger}(E) \right] \qquad \Box$$

### C.3.4 Broadening function equation: $\Gamma = i \left[ \Sigma - \Sigma^{\dagger} \right] = \zeta A_R \zeta^{\dagger}$

The broadening function is defined as the anti-Hermitian part of the self energy:

$$\Gamma = i \left[ \Sigma - \Sigma^{\dagger} \right]$$

and the self energy is (eq (5.36)):  $\Sigma = \zeta G_R \zeta^{\dagger}$ . From which:

$$\Gamma = i \left[ \Sigma - \Sigma^{\dagger} \right] = i \left[ \zeta G_R \zeta^{\dagger} - \left( \zeta G_R \zeta^{\dagger} \right)^{\dagger} \right] = i \zeta G_R \zeta^{\dagger} - i \zeta G_R^{\dagger} \zeta^{\dagger} = \zeta i \left[ G_R - G_R^{\dagger} \right] \zeta^{\dagger} = \zeta A_R \zeta^{\dagger}$$

where it is used that  $A_R = i \left[ G_R - G_R^{\dagger} \right]$  (see section C.3.3) and the theorem of section C.3.1 is used.  $\Box$ 

#### C.3.5 Equation 5.39: $A_D = G_D \Gamma G_D^{\dagger} = G_D^{\dagger} \Gamma G_D$

First of all notice that:

$$\left[G_{D}^{\dagger}\right]^{-1} - \left[G_{D}\right]^{-1} = \left[EI_{D} - H_{D} - \Sigma^{\dagger}\right]^{-1} - \left[EI_{D} - H_{D} - \Sigma\right]^{-1} = \Sigma - \Sigma^{\dagger} = -i\Gamma$$

where it is used that the Hermitian conjugate of a sum is the Hermitian conjugate of all the terms (it is a linear operator), and that  $EI_D$  and  $H_D$  are Hermitian operators:

 $EI_D^{\dagger} = EI_D$  and  $H_D^{\dagger} = H_D$ . By definition  $\Gamma = i [\Sigma - \Sigma^{\dagger}]$  from which:  $-i\Gamma = \Sigma - \Sigma^{\dagger}$ . Then noticing that:

$$G_D(-i\Gamma)G_D^{\dagger} = G_D \left[ \left[ G_D^{\dagger} \right]^{-1} - \left[ G_D \right]^{-1} \right] G_D^{\dagger} = G_D \left[ G_D^{\dagger} \right]^{-1} G_D^{\dagger} - G_D G_D^{-1} G_D^{\dagger} = G_D - G_D^{\dagger} = \frac{A_D}{i} = -iA_D$$

From which (see section C.3.3):

$$A_D = i \left[ G_D - G_D^{\dagger} \right] = i G_D (-i\Gamma) G_D^{\dagger} = i G_D \left( \frac{\Gamma}{i} \right) G_D^{\dagger} = G_D \Gamma G_D^{\dagger}$$

An analogous procedure leads to:

$$\begin{aligned} G_D^{\dagger}(-i\Gamma)G_D &= G_D^{\dagger} \left[ \left[ G_D^{\dagger} \right]^{-1} - \left[ G_D \right]^{-1} \right] G_D = G_D^{\dagger} \left[ G_D^{\dagger} \right]^{-1} G_D - G_D^{\dagger} G_D^{-1} G_D = \\ &= G_D - G_D^{\dagger} = \frac{A_D}{i} = -iA_D \end{aligned}$$

that leads to:

$$A_D = i \left[ G_D - G_D^{\dagger} \right] = G_D^{\dagger} \Gamma G_D \qquad \Box$$

**C.3.6 Equation 5.40:**  $[G^n] = \left[G_D \Gamma G_D^{\dagger}\right] f_{FD} = [A_D] f_{FD}$ 

Equation (5.40) can be viewed as a definition. Nevertheless from section C.3.2, the density matrix is:

$$[\rho_D] = \int \frac{dE}{2\pi} f_{FD}(E - E_F) G_D \zeta A_R \zeta^{\dagger} G_D^{\dagger}$$

from section C.3.4 it follows:

$$[\rho_D] = \int \frac{dE}{2\pi} f_{FD}(E - E_F) G_D \Gamma G_D^{\dagger}$$

from sectionC.3.5 it follows:

$$[\rho_D] = \int \frac{dE}{2\pi} f_{FD}(E - E_F) \left[ A(E) \right]$$

from which:

$$[\rho_D] = \int \frac{dE}{2\pi} \left[ G^n(E) \right]$$

that corresponds to equation (5.41).  $\Box$ 

#### C.4 One contact inflow and outflow

The overall "contact + device" time-dependent Schrödinger's equation in matrix form is (eq. (5.54)):

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi \quad \leftrightarrow \quad i\hbar\frac{d}{dt} \begin{pmatrix} \psi_D \\ \Phi_{Rtot} \end{pmatrix} = \begin{bmatrix} H_D & \zeta \\ \zeta^{\dagger} & H_R + i\eta \end{bmatrix} \begin{pmatrix} \psi_D \\ \Phi_{Rtot} \end{pmatrix}$$

where  $\psi_D$  is the wave-function in the device and  $\Phi_{Rtot} = \Phi_R + \chi$  is the wave-function in the contact. This equation corresponds to the time-dependent version of eq. (5.21) in which the source term is dropped. Notice that since  $\psi_D$  is a scalar it is not a matter if the trace is taken or not, thus:

$$\psi_D^{\dagger}\psi_D = Tr\left[\psi_D^{\dagger}\psi_D\right] = Tr\left[\psi_D\psi_D^{\dagger}\right] = \psi_D\psi_D^{\dagger}$$

(property 2d - section C.3 - is used).

Its time derivative can be estimated from eq. (5.54), considering that such an equation can be rewritten as a system of two equations:

$$\begin{cases} i\hbar \frac{d}{dt}\psi_D = H_D\psi_D + \zeta \Phi_{Rtot} \\ i\hbar \frac{d}{dt}\Phi_{Rtot} = \zeta^{\dagger}\psi_D + (H_R + i\eta)\Phi_{Rtot} \end{cases}$$

The equation of interest is the first one:

$$i\hbar \frac{d}{dt}\psi_D = H_D\psi_D + \zeta \Phi_{Rtot} \tag{C.1}$$

There is theorem stating that the Hermitian conjugate of the time-dependent Schrödinger's equation is given by [87]:

$$\left[i\hbar\frac{\partial}{\partial t}\psi=\widehat{H}\psi\right]^{\dagger}\quad\rightarrow\quad i\hbar\frac{\partial}{\partial t}\psi^{\dagger}=-\widehat{H}\psi^{\dagger}$$

indeed in quantum mechanics the time is a parameter and there is no quantum mechanical operator associated to it. Thus the time derivative operator is not said to be Hermitian, and indeed from the above result it is not Hermitian. Instead the Hamiltonian operator is Hermitian since it represents a physical observable in quantum mechanics (i.e. the total energy of the system). From equation (C.1) exploiting the above reported theorem one has:

$$i\hbar\frac{d}{dt}\psi_D^{\dagger} = -\psi_D^{\dagger}H_D^{\dagger} - \Phi_{Rtot}^{\dagger}\zeta^{\dagger} = -\psi_D^{\dagger}H_D - \Phi_{Rtot}^{\dagger}\zeta^{\dagger}$$

where the theorem C.3.1 is used:  $(AB)^{\dagger} = B^{\dagger}A^{\dagger}$ . With these relations in mind, and remembering that the derivative of a product of two functions is the derivative of the first

times the second plus the first times the derivative of the second, one gets:

$$\begin{split} i\hbar \frac{d}{dt} |\psi_D|^2 &= i\hbar \frac{d}{dt} \left[ \psi_D^{\dagger} \psi_D \right] = i\hbar \frac{d}{dt} \left[ Tr \left[ \psi_D^{\dagger} \psi_D \right] \right] = \\ &= Tr \left[ \left[ i\hbar \frac{d\psi_D^{\dagger}}{dt} \right] \psi_D + \psi_D^{\dagger} \left[ i\hbar \frac{d\psi_D}{dt} \right] \right] = \\ &= Tr \left[ -\psi_D^{\dagger} H_D \psi_D - \Phi_{Rtot}^{\dagger} \zeta^{\dagger} \psi_D + \psi_D^{\dagger} H_D \psi_D + \psi_D^{\dagger} \zeta \Phi_{Rtot} \right] = \\ &= Tr \left[ \psi_D^{\dagger} \zeta \Phi_{Rtot} - \Phi_{Rtot}^{\dagger} \zeta^{\dagger} \psi_D \right] \\ &\to \quad \frac{d}{dt} \left[ \psi_D^{\dagger} \psi_D \right] = \frac{1}{i\hbar} Tr \left[ \psi_D^{\dagger} \zeta \Phi_{Rtot} - \Phi_{Rtot}^{\dagger} \zeta^{\dagger} \psi_D \right] \end{split}$$

At this point noticing that the wave-function within the contact  $\Phi_{Rtot}$  is constituted by superposition of two contributions:  $\Phi_{Rtot} = \Phi_R + \chi$ , where  $\Phi_R$  represents an "incident" wave and  $\chi$  a "scattered" wave the previous expression becomes:

$$\frac{d}{dt}\left[\psi_D^{\dagger}\psi_D\right] = \frac{1}{i\hbar}Tr\left[\psi_D^{\dagger}\zeta\Phi_R + \psi_D^{\dagger}\zeta\chi - \Phi_R^{\dagger}\zeta^{\dagger}\psi_D - \chi^{\dagger}\zeta^{\dagger}\psi_D\right]$$

that can be split into two contributions: an inflow from the contact to the channel (involving the terms with  $\Phi_R$ ) and an outflow from the channel to the contact (involving the terms with  $\chi$ ):

$$\frac{d}{dt}\left[\psi_D^{\dagger}\psi_D\right] = \frac{1}{i\hbar}Tr\left[\psi_D^{\dagger}\zeta\Phi_R - \Phi_R^{\dagger}\zeta^{\dagger}\psi_D\right] - \frac{1}{i\hbar}Tr\left[\chi^{\dagger}\zeta^{\dagger}\psi_D - \psi_D^{\dagger}\zeta\chi\right] = Inflow - Outflow$$

noticing that  $\psi_D = G_D S_R$ ,  $\psi_D^{\dagger} = S_R^{\dagger} G_D^{\dagger}$  and that  $S_R = \zeta \Phi_R$ ,  $S_R^{\dagger} = \Phi_R^{\dagger} \zeta^{\dagger}$  the inflow becomes:

$$Inflow = \frac{1}{i\hbar}Tr\left[\psi_D^{\dagger}\zeta\Phi_R - \Phi_R^{\dagger}\zeta^{\dagger}\psi_D\right] = \frac{1}{i\hbar}Tr\left[S_R^{\dagger}G_D^{\dagger}S_R - S_R^{\dagger}G_DS_R\right] = \\ = \frac{1}{i\hbar}Tr\left[S_R^{\dagger}\left[G_D^{\dagger} - G_D\right]S_R\right] = \frac{1}{i\hbar}Tr\left[S_R^{\dagger}\frac{A_D}{(-i)}S_R\right] = \frac{1}{\hbar}Tr\left[S_R^{\dagger}A_DS_R\right]$$

in which it is used (eq. (5.39) - section C.3.3):  $A_D = i \left[ G_D - G_D^{\dagger} \right] = -i \left[ G_D^{\dagger} - G_D \right]$  and the property:  $\frac{1}{i} = -i$ .

The last expression corresponds to the inflow for a single wave-function/electron in the channel. The total inflow from the contact to the channel is given by summing over all the

channel electrons (i.e. occupied states) the previous expression:

$$Total \ Inflow = \sum_{occupied \alpha} \frac{1}{\hbar} Tr \left[ S_{R\alpha}^{\dagger} A_D S_{R\alpha} \right] =$$

$$= \frac{1}{\hbar} Tr \left[ \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F) \Phi_{R\alpha}^{\dagger} \zeta^{\dagger} A_D \zeta \Phi_{R\alpha} \right] = \frac{1}{\hbar} Tr \left[ \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_F) \Phi_{R\alpha} \Phi_{R\alpha}^{\dagger} \zeta^{\dagger} A_D \zeta \right] =$$

$$= \frac{1}{\hbar} Tr \left[ \int_{-\infty}^{+\infty} dE \sum_{\alpha} f_{FD}(E - E_F) \delta(E - \varepsilon_{\alpha}) \Phi_{R\alpha} \Phi_{R\alpha}^{\dagger} \zeta^{\dagger} A_D \zeta \right] =$$

$$= \frac{1}{\hbar} Tr \left[ \int_{-\infty}^{+\infty} \frac{dE}{2\pi} f_{FD}(E - E_F) A_R \zeta^{\dagger} A_D \zeta \right] =$$

$$= \frac{1}{\hbar} Tr \left[ \int_{-\infty}^{+\infty} \frac{dE}{2\pi} f_{FD}(E - E_F) \zeta A_R \zeta^{\dagger} A_D \zeta \right] =$$

where the definition of delta-Dirac is used (see also section C.3.2), the definition of the isolated reservoir spectral function (eq. (5.32)):  $A_R = 2\pi \sum_{\alpha} \delta(E - \varepsilon_{\alpha}) \Phi_{R\alpha} \Phi_{R\alpha}^{\dagger}$ , the fact that  $\Gamma = \zeta A_R \zeta^{\dagger}$  (see section C.3.4), and the property 2e (section C.3). Since the Fermi-Dirac is not a matrix:

Inflow = 
$$\frac{1}{\hbar} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} f_{FD}(E - E_F) Tr [\Gamma A_D]$$

that corresponds to eq. (5.57). Instead the outflow is:

$$Outflow = \frac{1}{i\hbar} Tr \left[ \chi^{\dagger} \zeta^{\dagger} \psi_D - \psi_D^{\dagger} \zeta \chi \right]$$

noticing that:  $\chi = G_R \zeta^{\dagger} \psi_D$  and  $\chi^{\dagger} = \psi_D^{\dagger} \zeta G_R^{\dagger}$ , it follows:

$$\begin{aligned} Outflow &= \frac{1}{i\hbar} Tr \left[ \psi_D^{\dagger} \zeta G_R^{\dagger} \zeta^{\dagger} \psi_D - \psi_D^{\dagger} \zeta G_R \zeta^{\dagger} \psi_D \right] = \frac{1}{i\hbar} Tr \left[ \psi_D^{\dagger} \zeta \left[ G_R^{\dagger} - G_R \right] \zeta^{\dagger} \psi_D \right] = \\ &= \frac{1}{i\hbar} Tr \left[ \psi_D^{\dagger} \zeta \left( iA_R \right) \zeta^{\dagger} \psi_D \right] = \frac{1}{\hbar} Tr \left[ \psi_D^{\dagger} \Gamma \psi_D \right] \end{aligned}$$

where it is again used eq. (5.39) - section C.3.3:  $A_D = i \left[ G_D - G_D^{\dagger} \right] = -i \left[ G_D^{\dagger} - G_D \right]$ , the property:  $\frac{1}{i} = -i$  and  $\Gamma = \zeta A_R \zeta^{\dagger}$  (see section C.3.4).

This is again an outflow for a single wave-function/electron in the channel. The total inflow from the contact to the channel is given by summing over all the channel electrons (i.e. occupied states) the previous expression:

$$Total \ Outflow = \sum_{occupied \alpha} \frac{1}{\hbar} Tr \left[ \psi_{D\alpha}^{\dagger} \Gamma \psi_{D\alpha} \right] =$$

$$= \frac{1}{\hbar} Tr \left[ \sum_{\alpha} f_{FD}(\varepsilon_{\alpha} - E_{F}) \psi_{D\alpha} \psi_{D\alpha}^{\dagger} \Gamma \right] =$$

$$= \frac{1}{\hbar} Tr \left[ \sum_{\alpha} \int_{-\infty}^{+\infty} dE f_{FD}(E - E_{F}) \delta(E - \varepsilon_{\alpha}) G_{D} \zeta \Phi_{R\alpha} \Phi_{R\alpha}^{\dagger} \zeta^{\dagger} G_{D}^{\dagger} \Gamma \right] =$$

$$= \frac{1}{\hbar} Tr \left[ \int_{-\infty}^{+\infty} \frac{dE}{2\pi} f_{FD}(E - E_{F}) G_{D} \zeta A_{R} \zeta^{\dagger} G_{D}^{\dagger} \Gamma \right] =$$

$$= \frac{1}{\hbar} Tr \left[ \int_{-\infty}^{+\infty} \frac{dE}{2\pi} f_{FD}(E - E_{F}) G_{D} \Gamma G_{D}^{\dagger} \Gamma \right] = \frac{1}{\hbar} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} Tr \left[ \Gamma G^{n} \right]$$

where it is used that  $\psi_D = G_D S_R = G_D \zeta \Phi_R$ , the property 2e (section C.3), the definition of delta-Dirac (see also section C.3.2), the definition of the isolated reservoir spectral function (eq. (5.32)):  $A_R = 2\pi \sum_{\alpha} \delta(E - \varepsilon_{\alpha}) \Phi_{R\alpha} \Phi^{\dagger}_{R\alpha}$ , and the expression for the correlation function in non-equilibrium:  $G^n = f_{FD}(E - E_F)G_D\Gamma G^{\dagger}_D$  (eq. (5.40)). The last expression corresponds to eq. (5.58).

#### C.5 Transmission function calculations

Consider a two terminal device, with the source contact (contact 1) and the drain contact (contact 2). From equation (5.59) it is known that the current at terminal i is given by:

$$I_i = \frac{(-q)}{\hbar} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \tilde{i}_i(E) \quad , \ with: \quad \tilde{i}_i(E) = Tr\left[\Gamma_i A_D\right] f_i - Tr\left[\Gamma_i G^n\right] \tag{C.2}$$

where  $f_i$  indicates:  $f_i = f_{FD}(E - E_{Fi})$ .

Notice that in the case of two contacts  $\Gamma = \Gamma_1 + \Gamma_2$ , from which:  $A_D = G_D \Gamma G_D^{\dagger} = G_D [\Gamma_1 + \Gamma_2] G_D^{\dagger} = A_1 + A_2$ , and moreover from equation (5.52), the correlation function is:  $G^n = [A_1] f_1 + [A_2] f_2$ . In the case of two contacts it is thus possible to rewrite  $\tilde{i}_i(E)$ , for the two contacts, as follows. For contact 1 (property 2b - section C.3 is used):

$$\begin{split} i_1(E) &= Tr \left[ \Gamma_1 A_D \right] f_1 - Tr \left[ \Gamma_1 G^n \right] = \\ &= Tr \left[ \Gamma_1 A_1 \right] f_1 + Tr \left[ \Gamma_1 A_2 \right] f_1 - Tr \left[ \Gamma_1 A_1 \right] f_1 - Tr \left[ \Gamma_1 A_2 \right] f_2 = \\ &= Tr \left[ \Gamma_1 A_2 \right] f_1 - Tr \left[ \Gamma_1 A_2 \right] f_2 = Tr \left[ \Gamma_1 A_2 \right] (f_1 - f_2) \end{split}$$

Analogously for contact 2:

$$\widetilde{i_2}(E) = Tr [\Gamma_2 A_D] f_2 - Tr [\Gamma_2 G^n] = = Tr [\Gamma_2 A_1] f_2 + Tr [\Gamma_2 A_2] f_2 - Tr [\Gamma_2 A_1] f_1 - Tr [\Gamma_2 A_2] f_2 = = Tr [\Gamma_2 A_1] f_2 - Tr [\Gamma_2 A_1] f_1 = Tr [\Gamma_2 A_1] (f_2 - f_1)$$

Substituting in equation (C.2), one gets:

$$I_1 = \frac{(-q)}{h} \int_{-\infty}^{+\infty} Tr\left[\Gamma_1 A_2\right] (f_1 - f_2) dE$$
$$I_2 = \frac{(-q)}{h} \int_{-\infty}^{+\infty} Tr\left[\Gamma_2 A_1\right] (f_2 - f_1) dE$$

That correspond to equations (5.60) and (5.61), respectively (considering eq. (5.62) for the transmission functions), in which the  $2\pi$  is simplified with  $\hbar$  and h is obtained.

Then, considering that (with  $A_D = G_D \Gamma G_D^{\dagger} = G_D^{\dagger} \Gamma G_D$  - see section C.3.5 and equation 5.39):

$$Tr\left[\Gamma_{1}A_{D}\right] = Tr\left[\Gamma_{1}G_{D}\Gamma G_{D}^{\dagger}\right] = Tr\left[\Gamma G_{D}^{\dagger}\Gamma_{1}G_{D}\right] = Tr\left[\Gamma A_{1}\right]$$

(where property 2e section C.3 is used) and subtracting the  $Tr[\Gamma_1A_1]$  from both sides:

$$Tr [\Gamma_1 A_D] - Tr [\Gamma_1 A_1] = Tr [\Gamma A_1] - Tr [\Gamma_1 A_1]$$

$$\rightarrow Tr [\Gamma_1 A_D] - Tr [\Gamma_1 A_1] = Tr [\Gamma_1 A_D - \Gamma_1 A_1] = Tr [\Gamma_1 [A_1 + A_2] - \Gamma_1 A_1] = Tr [\Gamma_1 A_1 + \Gamma_1 A_2 - \Gamma_1 A_1] = Tr [\Gamma_1 A_2]$$

$$\rightarrow Tr [\Gamma A_1] - Tr [\Gamma_1 A_1] = Tr [\Gamma_1 A_1 + \Gamma_2 A_1 - \Gamma_1 A_1] =$$
  
= Tr [\Gamma\_2 A\_1]

where it is used that  $A_D = A_1 + A_2$ , and property 2b - section C.3. In conclusion:  $Tr [\Gamma_1 A_2] = Tr [\Gamma_2 A_1]$ 

In steady state the two terminal currents should be equal (and opposite in sign), and indeed, since  $Tr[\Gamma_1 A_2] = Tr[\Gamma_2 A_1]$  they are so:

$$I_{1} = \frac{(-q)}{h} \int_{-\infty}^{+\infty} Tr\left[\Gamma_{1}A_{2}\right] (f_{1} - f_{2})dE = \frac{(-q)}{h} \int_{-\infty}^{+\infty} Tr\left[\Gamma_{2}A_{1}\right] (f_{1} - f_{2})dE =$$
$$= -I_{2} = -\frac{(-q)}{h} \int_{-\infty}^{+\infty} Tr\left[\Gamma_{2}A_{1}\right] (f_{2} - f_{1})dE = \frac{(-q)}{h} \int_{-\infty}^{+\infty} Tr\left[\Gamma_{2}A_{1}\right] (f_{1} - f_{2})dE$$

where it used:  $[f_1 - f_2] = -[f_2 - f_1]$ .

Finally the total drain to source current can be written as:

$$I_{DS} = I_2 = -I_1 = = \frac{(-q)}{h} \int_{-\infty}^{+\infty} T(E) [f_2 - f_1] dE = = -\frac{(-q)}{h} \int_{-\infty}^{+\infty} T(E) [f_1 - f_2] dE = = \frac{q}{h} \int_{-\infty}^{+\infty} T(E) [f_1 - f_2] dE$$
(C.3)

where the minus sign in front of  $I_1$  has the following meaning. If the electron fluxes from contacts to device are defined such that they are incoming positive, that is Net flux = Inflow - Outflow, it means that the current at source contact is assumed incoming positive (according to the user convention of sign). Nevertheless the drain to source current  $I_{DS}$  is assumed to be outgoing from the source (and incoming to the drain). Thus a minus sign is necessary, since:  $I_{DS} = -I_1$ . Instead for the drain contact the sign convention is already coherent with the sign definition in  $I_{DS}$ .

In conclusion the total drain to source current is:

$$I_{DS} = \frac{q}{h} \int_{-\infty}^{+\infty} T(E) \left[ f_1(E) - f_2(E) \right] dE$$

that corresponds with eq. (5.65); where:

$$T(E) = Tr\left[\Gamma_1 A_2\right] = Tr\left[\Gamma_2 A_1\right] = Tr\left[\Gamma_1 G_D \Gamma_2 G_D^{\dagger}\right] = Tr\left[\Gamma_2 G_D \Gamma_1 G_D^{\dagger}\right]$$
(C.4)

where  $G_D = [EI_D - H_D - \Sigma]^{-1}$  is the device Green's function (with  $\Sigma = \Sigma_1 + \Sigma_2$ ), and  $G_D^{\dagger} = G_D^A$  is the device advanced Green's function. Notice that T(E) is called transmission function or transmission spectrum.

### Appendix D

# Chapter 8 - Additional images, graphs and material

Details are provided directly in the captions.

D.1 Additional images and graphs relative to section 8.1



Figure D.1: Initial geometry of the  $C_{60}$  fullerene ammonia gas sensor, with a single NH<sub>3</sub> molecule. The  $C_{60}$ -contacts distances were fixed at around 2.7 Å, no special orientation of the  $C_{60}$  was considered. The figure was generated by *ATK* software [125], [126] (used for performing the simulations).



Figure D.2: Initial geometry of the  $C_{60}$  fullerene ammonia gas sensor, with a single NH<sub>3</sub> molecule. van der Waals spheres are shown. Since they are intersected, the interaction should be strong. The  $C_{60}$ -contacts distances were fixed at around 2.7 Å, no special orientation of the  $C_{60}$  was considered. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure D.3: Initial geometry of the  $C_{60}$  fullerene ammonia gas sensor, with a single  $NH_3$  molecule. The ammonia  $C_{60}$  distance is of about 2.2 Å The  $C_{60}$ -contacts distances were fixed at around 2.7 Å, no special orientation of the  $C_{60}$  was considered. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure D.4: Initial geometry of the  $C_{60}$  fullerene ammonia gas sensor, with three NH<sub>3</sub> molecule. The  $C_{60}$ -contacts distances were fixed at around 2.7 Å, no special orientation of the  $C_{60}$  was considered. The figure was generated by *ATK* software [125], [126] (used for performing the simulations).



Figure D.5: Initial geometry of the  $C_{60}$  fullerene ammonia gas sensor, with five NH<sub>3</sub> molecule. The  $C_{60}$ -contacts distances were fixed at around 2.7 Å, no special orientation of the  $C_{60}$  was considered. The figure was generated by *ATK* software [125], [126] (used for performing the simulations).

# D.2 Additional images and graphs relative to section 8.2



**Figure D.6:** Equilibrium DOS per unit energy obtained with various DFT-based method. All curves are overlapped apart for the DFT-1/2 correction that is different.



**Figure D.7:** Equilibrium transmission spectrum obtained with various DFT-based method. All curves are overlapped apart for the DFT-1/2 correction that is different.

## D.3 MatLab code used for exponential fitting of the transmission spectrum peaks at 1 eV

```
clear all
 close all
2
3 clc
_4|\% exp fitting of the transmission peak @ around 1 eV for a casual
     oriented
 % C60 fullerene in between two contacts.
5
6
  Tx_{peaks} = [2.825e-6, 0.03647, 0.6774, 1.013, 1.538, 1.63].'; \% 1 eV Tx
     peaks
  distances = [5.4, 4, 3.6, 3.3, 3, 2.7] '; % corresponding distances
8
9
  g = fittype('A-B*exp(-C*x)'); \% exponential fitting type
10
 11
  distances_interp = linspace (2.7, 6, 1000); % smooth x-axis definition
12
13
_{14} % PLOT the result:
_{15} Ang = char (197);
16 figure
17 hold on
18 grid on
19 plot (distances, Tx_peaks, '*', distances_interp, f0 (distances_interp), '
     LineWidth', 3);
  title('C60 wire sensor (EHT method): interpolated transmission peak (@1eV
20
     ) in function of distance');
21 lgnd1 = strcat("Simulated values");
22 | lgnd2 = strcat("Exponential interpolating curve");
23 legend(lgnd1, lgnd2, 'location', 'best');
24 xstring = strcat('Distance between the C60 and the contacts (', Ang,')');
25 xlabel(xstring);
26 ylabel('Transmission peak value');
27
  set(gca, 'fontsize', 16);
```

# D.4 Additional images and graphs relative to section 8.3



Figure D.8: Current-voltage (I-V) characteristics for 2.4 Å of distance between the contacts and the C<sub>60</sub> fullerene. The two orientations casual/non-special and with the hexagons on gold surfaces one are considered.





Figure D.9: Dependence of current values on the distance between the fullerene and the contacts for a fixed voltage:  $V_D = 0.4$  V. The exponential fitting performs well. Top: linear scale, bottom: semilogarithm scale.





Figure D.10: Dependence of current values on the distance between the fullerene and the contacts for a fixed voltage:  $V_D = 1.6$  V. The exponential fitting performs well. Top: linear scale, bottom: semilogarithm scale.



Figure D.11: Absolute variations of current due to the presence of 1, 3, 5 NH<sub>3</sub> molecules, for distances between the contacts and the  $C_{60}$  fullerene of 2.4 Å (EHT method).



Figure D.12: Absolute variations of current due to the presence of 1, 3, 5 NH<sub>3</sub> molecules, for distances between the contacts and the  $C_{60}$  fullerene of 3.0 Å (EHT method).



Figure D.13: Absolute variations of current due to the presence of 1, 3, 5 NH<sub>3</sub> molecules, for distances between the contacts and the  $C_{60}$  fullerene of 3.3 Å (EHT method).



Figure D.14: Absolute variations of current due to the presence of 1, 3, 5 NH<sub>3</sub> molecules, for distances between the contacts and the  $C_{60}$  fullerene of 3.6 Å (EHT method).



Figure D.15: Absolute variations of current due to the presence of  $3 \text{ NH}_3$  molecules, all the considered distances between the fullerene and the contacts are compared (EHT method).



Figure D.16: Absolute variations of current due to the presence of  $5 \text{ NH}_3$  molecules, all the considered distances between the fullerene and the contacts are compared (EHT method).



Figure D.17: Percentage variations of current due to the presence of  $1 \text{ NH}_3$  molecules, all the considered distances between the fullerene and the contacts are compared (EHT method).



Figure D.18: Percentage variations of current due to the presence of 1 NH<sub>3</sub> molecules, only the distances 2.4 Å (both with the chemisorbed and the casual orientations), 2.7 Å and 3.0 Å are compared for clarity (EHT method). All the curves are instead reported in figure D.17.



Figure D.19: Percentage variations of current due to the presence of  $3 \text{ NH}_3$  molecules, all the considered distances between the fullerene and the contacts are compared (EHT method).



Figure D.20: Percentage variations of current due to the presence of 5  $NH_3$  molecules, all the considered distances between the fullerene and the contacts are compared (EHT method).



Figure D.21: Device current as a function of the applied voltage and the contacts distance. Red dots are the simulated points, while the surface corresponds to the exponential interpolation. Purple dots are those below the semi-transparent surface. A general good agreement is present (EHT method). Voltage up to 0.8 V only are considered.

#### D.4.1 MatLab code for exponential interpolation with 3D plots

```
%% importing simulation data
   [....]
   % Distances array:
 3
   distances = [5.4, 4, 3.6, 3.3, 3, 2.7, 2.4] '; % corresponding distances
   %% CURRENT ARRAY:
   Vd_bias = linspace(0, 2, 11);
   % all distances all currents merged together
9
   Id\_all = [IV\_C60\_11biasEHT\_5d4A(:,2), IV\_C60\_11biasEHT\_4A(:,2),
         \begin{array}{ll} \mathrm{IV}\_\mathrm{C60}\_\mathrm{11biasEHT}\_\mathrm{3d6A}\left(:\,,2\right)\,,&\ldots\\ \mathrm{IV}\_\mathrm{C60}\_\mathrm{11biasEHT}\_\mathrm{3d3A}\left(:\,,2\right)\,,&\mathrm{IV}\_\mathrm{C60}\_\mathrm{11biasEHT}\_\mathrm{3A}\left(:\,,2\right)\,, \end{array} 
11
        IV_C60_11biasEHT(:,2), IV_C60_11biasEHT_2d4A(:,2)];
12
  %% Exp fitting of the current:
13
   Npoints_interp = 120;
14
   DATA\_interp = zeros(11, Npoints\_interp);
15
16
   for i=1:11 % number of bias points
17
18
        Id = Id\_all(i,:);
19
        Id = Id';
20
|\mathbf{g}| = \text{fittype}(|A-B*\exp(-C*x)|); \% exponential fitting type
```

```
22 f0 = fit (distances, Id, g, 'StartPoint', [[ones(size(distances)), -exp(-
      distances)]\Id; 1]); %fitting the point
  distances_interp = linspace(2,6, Npoints_interp); % smooth x-axis
23
      definition
24
  % PLOT the result: (1D plots)
25
_{26} Ang = char (197);
  figure
27
  hold on
28
  grid on
29
  plot(distances, Id*1e6, 'O', distances_interp, f0(distances_interp)*1e6,
30
      'LineWidth', 2.5);
  title_stringazza = sprintf('C60 wire sensor (EHT method): interpolated
31
     I_D value for V_D = \% V in function of distance', Vd_bias(i));
  title(title_stringazza);
32
33 lgnd1 = strcat("Simulated values");
<sup>34</sup> lgnd2 = strcat ("Exponential interpolating curve");
35 legend(lgnd1, lgnd2, 'location', 'best');
_{36} xstring = strcat('Distance between the C60 and the contacts (', Ang, ')')
  xlabel(xstring);
37
  ylabel('Drain current value I_D (\muA)');
38
  set(gca, 'fontsize', 16);
39
40
<sup>41</sup> DATA_interp(i,:) = f0(distances_interp);
  end
42
43
44 % 3D plot / surface plot:
45 figure
46
  hold on
47
  grid on
  surf(Vd_bias, distances_interp, 1e6.*DATA_interp');
48
49
  colorbar
  alpha 0.7
  distances = distances ';
52
  for i = 1:11
      hold on
54
      Vbias_now = ones(1,7) * Vd_bias(i);
      Id_now = Id_all(i, :);
56
      plot3(Vbias_now, distances, Id_now*1e6, 'o', 'Color', 'r', 'MarkerSize'
57
      ,6, 'MarkerFaceColor', 'r');
58
  end
  titlestringazza = sprintf("Current values in function of the contact
59
      distance");
  title(titlestringazza);
60
  ylabelstringazza = strcat('Distance between the contacts and the
61
      fullerene (', Ang, ')');
  ylabel(ylabelstringazza);
62
  xlabel('V_D (V)');
63
  zlabel('Current (\muA)');
64
  set(gca, 'fontsize', 16);
65
```

## D.5 Additional images and graphs relative to section 8.4



Figure D.22: Equilibrium transmission spectrum of the  $C_{60}$  molecular wire with the final sensor geometry; the DFT and EHT methods are compared.

## D.6 Additional images, graphs and material relative to section 8.5

### D.6.1 MatLab code for implementing trapezoidal integration of equilibrium transmission spectra

```
clear all
  close all
2
  clc
3
  %
  \% In this code the comparison between the DFT and EHT equilibrium
     transmission spectra
  %
     for the final/definitive chosen geometry (hexagons toward Au(111)
     faces)
 %
    is performed. The method is to compare the difference (delta) in the
 %
    transmission spectra between the case in which a molcule of NH3 is
9
  %
     present and the case in which it isn't. The cases: no NH3 molecules, 1
 %
    NH3 molecules, 3 NH3 molecules, 5 NH3 molecules are considered.
11
 %% Simulated data loading:
14
```

```
_{15} Tx_C60_equiDFT = [ -3.000000e+00
                                     6.948648e - 01
   -2.985000e+00 8.874635e-01
16
17
   2.985000\,\mathrm{e}{+00} \qquad 3.808501\,\mathrm{e}{-01}
18
    3.000000e+00
                  3.009928e - 01 ];
19
20
  Tx C60 1NH3 equiDFT = [-3.000000e+00]
                                          1.144230e+00
21
   -2.985000e+00 7.631720e-01
22
   23
    2.985000e+00 3.515896e-01
24
    3.000000e+00 2.581333e-01 ];
25
26
  Tx_C60_3NH3_equiDFT = [ -3.000000e+00]
                                         8.109276e - 01
27
   -2.985000e+00 8.434297e-01
28
    29
    2.985000e+00 4.671696e-01
30
    3.000000e+00 3.809816e-01 ];
31
32
  Tx_C60_5NH3_equiDFT = [ -3.000000e+00]
                                          7.364717 e - 01
33
   -2.985000e+00 6.733038e-01
34
35
   2.985000\,\mathrm{e}{+00} \qquad 5.122041\,\mathrm{e}{-01}
36
    3.000000e+00 4.469724e-01 ];
37
38
  Tx_C60_equiEHT = [ -3.000000e+00]
                                     3.703120 e - 02
39
   -2.985000 \,\mathrm{e}{+00}
                  7.349435e - 02
40
41
   2.985000e+00
                  5.252394e - 01
42
43
    3.000000e+00
                  3.438951e - 01 ];
44
  Tx_C60_1NH3_equiEHT = [-3.000000e+00]
                                          3.978667 e - 02
45
   -2.985000e+00 3.878050e-02
46
47
    2.985000e+00
                  5.071415e - 01
48
    3.000000e+00 3.419053e-01 ];
49
50
  Tx_C60_3NH3_equiEHT = [-3.000000e+00]
                                          4.864458e - 02
   -2.985000e+00 4.444041e-02
52
53
    2.985000e+00 5.011339e-01
54
    3.000000e+00
                  3.581258e - 01 ];
55
56
  Tx_C60_5NH3_equiEHT = [ -3.000000e+00
57
                                         5.007842 e - 02
   -2.985000e+00 4.544048e-02
58
59
   2.985000e+00 5.226207e-01
60
    3.000000e+00
                  3.864298e - 01 ];
61
62
 %% COMPARISON OF DELTA T(E) BETWEEN EHT and DFT:
63
 % trapezoidal integration is used: https://www.mathworks.com/help/matlab/
64
     ref/trapz.html?s_tid=srchtitle
_{66} \% "for" loop is used to get the various integrals in the various bias
```

```
_{67} windows –BW– (in eV), the step is 0.1 eV:
_{68} BW_step = 0.1; % eV
69 max_Vds=2; % V , max Voltage value considered in the wire (e.g. 2V)
_{70} max_BW = 2*max_Vds; % eV - it can be at most 6 (indeed -3eV < E <+3eV); in
        the I-V curve it is used BW=max_Vds
   number of integrals = max BW/BW step; % total number of performed
71
       integrals
   BW_width = linspace (BW_step, max_BW, number_of_integrals); % considered
72
       bias windows, it starts from BW_step
                                                                       % since it is
73
       the first non null bias window value
   Energy = Tx_C60_equiDFT(:, 1); % it is always the same since all the data
74
       have 401 points in energy between -3 and +3 eV
  % output integrals data structures are initialized:
75
   Tx_C60_equiDFT_integrals = zeros(1, number_of_integrals);
76
   Tx_C60_1NH3_equiDFT_integrals = zeros(1, number_of_integrals);
77
   Tx C60 3NH3 equiDFT integrals = zeros(1, number of integrals);
78
   Tx_C60_5NH3_equiDFT_integrals = zeros(1, number_of_integrals);
79
   Tx_C60_equiEHT_integrals = zeros(1, number_of_integrals);
80
   Tx_C60_1NH3_equiEHT_integrals = zeros(1, number_of_integrals);
81
   Tx_C60_3NH3_equiEHT_integrals = zeros(1,number_of_integrals);
82
   Tx_C60_5NH3_equiEHT_integrals = zeros(1, number_of_integrals);
83
  % output Delta (see below) integrals data structures are initialized:
84
   Delta\_Tx\_C60\_1NH3\_equiDFT\_integrals = zeros(1, number\_of\_integrals);
85
   Delta_Tx_C60_3NH3_equiDFT_integrals = zeros(1,number_of_integrals);
86
   Delta_Tx_C60_5NH3_equiDFT_integrals = zeros(1,number_of_integrals);
Delta_Tx_C60_1NH3_equiEHT_integrals = zeros(1,number_of_integrals);
Delta_Tx_C60_3NH3_equiEHT_integrals = zeros(1,number_of_integrals);
Delta_Tx_C60_5NH3_equiEHT_integrals = zeros(1,number_of_integrals);
87
88
89
90
91
   for i = 1:number_of_integrals
92
       current_BW = BW_width(i);
93
       positive_part_of_current_BW = current_BW/2;
94
       current_indeces_for_integration = find( abs(Energy) <=</pre>
95
       positive_part_of_current_BW );
       % then integrals are performed:
96
       X = Energy(current_indeces_for_integration);
97
       %
98
       Y = Tx_C60_equiDFT(current_indeces_for_integration, 2);
99
       Tx_C60_equiDFT_integrals(i) = trapz(X,Y);
100
       %
       Y = Tx_C60_1NH3_equiDFT(current_indeces_for_integration, 2);
       Tx_C60_1NH3_equiDFT_integrals(i) = trapz(X,Y);
103
       %
104
       Y = Tx_C60_3NH3_equiDFT(current_indeces_for_integration,2);
       Tx_C60_3NH3_equiDFT_integrals(i) = trapz(X,Y);
106
       %
       Y = Tx_C60_5NH3_equiDFT(current_indeces_for_integration,2);
108
       Tx_C60_5NH3_equiDFT_integrals(i) = trapz(X,Y);
       Y = Tx_C60_equiEHT(current_indeces_for_integration, 2);
111
       Tx\_C60\_equiEHT\_integrals(i) = trapz(X,Y);
       %
113
```

```
Y = Tx_C60_1NH3_equiEHT(current_indeces_for_integration,2);
114
       Tx_C60_1NH3_equiEHT_integrals(i) = trapz(X,Y);
      %
       Y = Tx_C60_3NH3_equiEHT(current_indeces_for_integration,2);
       Tx_C60_3NH3_equiEHT_integrals(i) = trapz(X,Y);
       %
       Y = Tx \ C60 \ 5NH3 \ equiEHT(current indeces for integration, 2);
120
       Tx_C60_5NH3_equiEHT_integrals(i) = trapz(X,Y);
      \% then the differences (DELTA) between the xNH3 cases and the C60
123
      with no
      \% NH3 molecules case are evaluated for each considered BW (bias
124
      window):
       Delta_Tx_C60_1NH3_equiDFT_integrals(i) = abs(
      Tx C60 1NH3 = quiDFT integrals(i) - Tx C60 = quiDFT integrals(i));
       Delta_Tx_C60_3NH3_equiDFT_integrals(i) = abs(
126
      Tx C60 3NH3 equiDFT integrals(i) - Tx C60 equiDFT integrals(i));
       Delta_Tx_C60_5NH3_equiDFT_integrals(i) = abs(
      Tx_C60_5NH3_equiDFT_integrals(i) - Tx_C60_equiDFT_integrals(i));
      %
128
       Delta_Tx_C60_1NH3_equiEHT_integrals(i) = abs(
129
      Tx_C60_1NH3_equiEHT_integrals(i) - Tx_C60_equiEHT_integrals(i));
       Delta_Tx_C60_3NH3_equiEHT_integrals(i) = abs(
130
      Tx_C60_3NH3_equiEHT_integrals(i) - Tx_C60_equiEHT_integrals(i));
       Delta_Tx_C60_5NH3_equiEHT_integrals(i) = abs(
      Tx_C60_5NH3_equiEHT_integrals(i) - Tx_C60_equiEHT_integrals(i));
   end
134
135
  %PLOTs:
136
137
  figure
  hold on
138
   grid on
139
   plot (BW_width, Delta_Tx_C60_1NH3_equiDFT_integrals, BW_width,
140
      Delta_Tx_C60_1NH3_equiEHT_integrals, 'LineWidth', 2);
   title ('C60 wire sensor: DFT vs EHT methods (integrals differences)');
141
   legend ('\Delta \int T(E) with DFT (1NH3)', '\Delta \int T(E) with EHT (1
142
      NH3)', 'location', 'best');
   xlabel('Applied Voltage (V) or Bias window width (eV) - i.e. Domain of
143
      integration width (centered around 0 \text{ eV});
  ylabel('\Delta of T(E) integral (average Transmission)');
144
145 set (gca, 'fontsize', 16);
146 % plot ellipse around the region interested for low bias (less that 2V of
       Vds)
  px = 0; % the ellipse start in the origin (it is inside a rectangle
147
      starting in origin: px, py starting bottom left corner)
  py = 0;% the ellipse start in the origin (it is inside a rectangle
148
      starting in origin: px\,,\ py starting bottom left corner)
  dx = 2; %since in the I-V curve it will be Vds = (0,2)V then the max bias
149
                 \% window will be 2eV \rightarrow ractangle width is 2
150
  dy = 0.055; % see the graph to choose it properly !!
```

```
152 rectangle('Position',[px py dx dy],'Curvature',[0.75,0.75]); % '--k', '
153
154
[ .....]
```

#### D.6.2 Graphs for the case of 3 and 5 ammonia molecules



Figure D.23: Integral difference of the final ammonia sensor equilibrium transmission spectra in the cases of 3 NH<sub>3</sub> molecule. The results obtained with the two methods: DFT (blue curve) and EHT (red/orange curve) are compared. The ellipse is around the considered range of bias windows, i.e. up to 2 V.



Figure D.24: Integral difference of the final ammonia sensor equilibrium transmission spectra in the cases of 5 NH<sub>3</sub> molecule. The results obtained with the two methods: DFT (blue curve) and EHT (red/orange curve) are compared. The ellipse is around the considered range of bias windows, i.e. up to 2 V.
# D.7 Additional images and graphs relative to section 8.6

D.7.1 Zoom in of figure 8.32 for  $V_D = 0.2 \text{ V}$  and  $V_D = 1.4 \text{ V}$ 



Figure D.25: Zoom-in of the current-voltage characteristics for the final sensor geometry. The two different ammonia orientations are considered along with various atmosphere constituents (EHT method). Top (a): curves at  $V_D = 0.2$  V; bottom (b): curves at  $V_D = 1.4$  V.

#### D.7.2 Sensitivity of the $C_{60}$ wire to additional pollutants



Figure D.26: Top (a): Absolute current variations with sign for methane  $CH_4$  and butane  $C_4H_{10}$  (EHT method). Bottom (b): Absolute current variations with sign for methane  $CH_4$  and butane  $C_4H_{10}$  along with common atmosphere constituents (EHT method).

D23



Figure D.27: Absolute current variations with sign for NO along with other common atmospheric chemical species (EHT method).



Figure D.28: Absolute current variations with sign for  $NO_2$  along with other common atmospheric chemical species (EHT method).



Figure D.29: Absolute current variations with sign for  $PbCl_2$  along with other common atmospheric chemical species (EHT method).



C60 wire sensor (EHT method):  $\Delta \mathbf{I}_{\mathbf{D}}$  in various cases

Figure D.30: Absolute current variations with sign for PbO along with other common atmospheric chemical species (EHT method).

D26

## Appendix E

## Chapter 9 - Additional images, graphs and material

Details are provided directly in the captions.

## E.1 Additional images and graphs relative to section 9.2



Figure E.1: Absolute current variations for various atmospheric gases and for  $PbSO_4$  with the two fullerene orientations: the casual one and the equilibrium chemisorption one, with hexagons toward gold (EHT method).



C60 wire sensor (EHT method):  $|\Delta I_D|$  at different contact distances



Figure E.2: Top (a): Absolute current variations (magnitude) due to lead sulfate single-molecule, for the different considered distances between the fullerene and contacts. Bottom (b): Absolute current variations (with sign) due to lead sulfate single-molecule, for the different considered distances between the fullerene and contacts (EHT method).

# E.2 Additional images and graphs relative to section 9.4



Figure E.3: Integral difference of the final lead sulfate sensor equilibrium transmission spectra in the cases of 2 PbSO<sub>4</sub> molecule. The results obtained with the two methods: DFT (blue curve) and EHT (red/orange curve) are compared. The ellipsoid is around the considered range of bias windows, i.e. up to 2 V. The integrals were performed with trapezoidal numerical method in *MatLab*, over the bias windows from 0.1 V to 4 V with a step of 0.1 V.

### E.3 Additional images and graphs relative to section 9.5



E.3.1 Different PbSO<sub>4</sub> orientation geometries

Figure E.4: Geometry labeled as "PbSO<sub>4</sub>" simply. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.5: Geometry labeled as  $PbSO_4$  "left-right". It corresponds to a rotation w.r.t. a vertical rotation axis. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.6: Geometry labeled as  $PbSO_4$  "up-down". It corresponds to a rotation w.r.t. a rotation axis parallel to the transport direction. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.7: Geometry labeled as  $PbSO_4$  "SO-down". The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.8: Geometry labeled as  $PbSO_4$  "Pb-down". The figure was generated by ATK software [125], [126] (used for performing the simulations).

#### E.4 Additional material relative to section 9.5.4

**Table E.1:** Maximum absolute deviation between the cubic spline interpolation and the linear interpolation of the current values in function of the target-fullerene distance, for the various considered bias points.

$V_D$ (V)	Maximum deviation $(\mu A)$
0.2	2.34
0.4	20.63
0.6	25.24
0.8	22.57
1	9.1
1.2	72.32
1.4	77.69
1.6	69.35
1.8	156.84
2	165.46



Figure E.9: Maximum absolute deviation between the cubic spline interpolation and the linear interpolation of the current values in function of the target-fullerene distance, for the various considered bias points. Notice the chosen bias point at  $V_D = 0.8 \text{ V}$ ; it is a good compromise among the possible choices. For  $V_D$  grater than 1 V the current variations/oscillations are much more marked.

#### E.5 Additional material relative to section 9.5.5



Figure E.10: Maximum absolute deviation between the cubic spline interpolation and the linear interpolation of the current values in function of the PbSO<sub>4</sub> concentration, for the various considered bias points. Notice the chosen bias point at  $V_D = 0.8$  V; it is a good compromise among the possible choices.



Figure E.11: Current values for different PbSO<sub>4</sub> concentrations and for  $V_D = 0.8$  V. Black circles: simulated values; blue curve: cubic  $3^{rd}$  order spline interpolation; red/orange: quadratic interpolation. The latter is exactly overlapped to the cubic interpolation thus meaning a perfect agreement and a quadratic sensor response for  $V_D = 0.8$  V.



Figure E.12: Current values for different PbSO<sub>4</sub> concentrations and for  $V_D = 0.2$  V. Black circles: simulated values; blue curve: cubic  $3^{rd}$  order spline interpolation; red/orange: linear interpolation. Strongly non linear sensor response is present for  $V_D = 0.2$  V.



Figure E.13: Current values for different PbSO<sub>4</sub> concentrations and for  $V_D = 0.4$  V. Black circles: simulated values; blue curve: cubic  $3^{rd}$  order spline interpolation; red/orange: linear interpolation. The sensor response for  $V_D = 0.4$  V is very linear.



Figure E.14: Equilibrium transmission spectra in the case of 2  $PbSO_4$  molecules and in the case of 2  $PbSO_4$  molecules oriented in opposite directions.

#### E.6 Additional material relative to section 9.5.6



Figure E.15: Transmission spectrum with a PbSO<sub>4</sub> molecule for a bias  $V_D = 0.8$  V. Abscissa axis: transmission; ordinate axis: energy (eV);  $\varepsilon_{L,R}$  are the two contacts Fermi levels, and the energy values in between them correspond to the one within the bias window. The red arrows highlight the three main transmission peaks within the bias window, at energy 0.04 eV, 0.28 eV and 0.4 eV. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.16: Transmission eigenstate (full view) corresponding to the transmission eigenvalue 5.654839e-1 with quantum number QN = 0, transmission peak at energy E = 0.04 eV, the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.17: Transmission eigenstate (top view) corresponding to the transmission eigenvalue 5.654839e-1 with quantum number QN = 0, transmission peak at energy E = 0.04 eV, the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface (smaller transmission value w.r.t. the one of figure E.6), the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.18: Transmission eigenstate (full view) corresponding to the transmission eigenvalue 2.229667e-2 with quantum number QN = 1, transmission peak at energy E = 0.04 eV, the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.19: Transmission eigenstate (top view) corresponding to the transmission eigenvalue 2.229667e-2 with quantum number QN = 1, transmission peak at energy E = 0.04 eV, the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface (smaller transmission value w.r.t. the one of figure E.6), the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.20: Transmission eigenstate (side view) corresponding to the transmission eigenvalue 8.373195e-1 with quantum number QN = 0, transmission peak at energy E = 0.28 eV, the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.21: Transmission eigenstate (full view) corresponding to the transmission eigenvalue 2.119902e-1 with quantum number QN = 1, transmission peak at energy E = 0.28 eV, the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.22: Transmission eigenstate (full view) corresponding to the transmission eigenvalue 6.899972e-1 with quantum number QN = 0, transmission peak at energy E = 0.4 eV, the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.23: Transmission eigenstate (side view) corresponding to the transmission eigenvalue 3.125305e-1 with quantum number QN = 1, transmission peak at energy E = 0.4 eV, the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.24: Transmission eigenstate (full view) corresponding to the transmission eigenvalue 8.513583e-2 with quantum number QN = 2, transmission peak at energy E = 0.4 eV, the geometry is the one with a single PbSO<sub>4</sub> molecule and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).

## E.6.1 Additional material relative to section 9.5.6: two opposite oriented $PbSO_4$ molecules



Figure E.25: Transmission eigenstate (top view) corresponding to the transmission eigenvalue 5.594843e-1 with quantum number QN = 0, transmission peak at energy E = 0.04 eV, the geometry is the one with two opposite oriented PbSO<sub>4</sub> molecules and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.26: Transmission eigenstate (top view) corresponding to the transmission eigenvalue 8.684692e-1 with quantum number QN = 0, transmission peak at energy E = -0.16 eV, the geometry is the one with two opposite oriented PbSO<sub>4</sub> molecules and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.27: Transmission eigenstate (top view) corresponding to the transmission eigenvalue 7.872365e-1 with quantum number QN = 0, transmission peak at energy E = 0.16 eV, the geometry is the one with two opposite oriented PbSO<sub>4</sub> molecules and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.28: Transmission eigenstate (top view) corresponding to the transmission eigenvalue 6.032937e-2 with quantum number QN = 1, transmission peak at energy E = 0.16 eV, the geometry is the one with two opposite oriented PbSO<sub>4</sub> molecules and with a bias voltage  $V_D = 0.8 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).

#### E.7 Argon transmission eigenstates analysis

In section 8.6.2 it was considered also the sensor sensitivity to argon since it is a common atmospheric gas, and it was verified that the argon is responsible of large current variations for large biases. The reason was supposed to be in its high atomic number that is 18, meaning that it has 18 electrons. It was supposed that a such large number of electrons leads to a strong (if compared with ammonia and the other considered molecules with lower atomic number and thus less electrons) polarization charge, that was supposed to be at the basis of the strong current variation induced in the sensor. This is confirmed in the analysis carried out in this section. In particular in figure E.29 is shown the MPSH for the system HOSO level, in a side view (zoomed in), for bias  $V_D = 1.6$  V (being a bias point with large current deviation and sensitivity to argon). It is noticeable that there is no symmetry of the argon orbitals. The argon atomic number is 18 leading to the following electronic configuration:  $1s^2 2s^2 2p^6 3s^2 3p^6$ . Notice that argon is a noble gas with a complete octet and that in atmosphere it is found as single atoms. The HOSO and LUSO orbitals, nearby the argon, are thus expected to be somehow derived from the upper occupied orbitals of argon, i.e. *p*-type orbitals; and indeed it is recognizable the typical "8" shaped figure centered at the argon atom (onto the fullerene in the middle). In the case of the HOSO, evidently, the argon orbitals cooperating in the HOSO formation are the  $p_y$  ones (vertical "8"). Nevertheless it is expected to have a deformation of them, due to the steric effect of repulsion of electron clouds. This is again confirmed in figure E.29, since the upper lobe is longer in y-direction while the lower one is squashed. This is indeed the result of the electron-electron repulsion, but the point here is that this geometry induces a (temporary) polarization of the argon atom. The polarization involves up to 18 electrons, thus originating an electric charge relatively large, in particular with a slightly positive region nearby the fullerene. This positive region is suppose to somehow lower the contact-fullerene barriers, and enhancing the transport by attracting electrons from contacts. Nevertheless, due to the spatial position of the argon, such a transmission improvement occurs only for sufficiently high biases (in practice for voltages above 1 V). because a certain amount of electric field is needed to overcome the barriers, already present, between the two contacts and the fullerene. This mechanism can be understood by looking at the transmission eigenstates in real space. In figure E.30 is reported a view of the main transmission eigenstate (the one corresponding to the highest transmission eigenvalue) for energy 0.32 eV, that is the main transmission peak within the bias window, for an applied bias of 1.6 V. It is evident the existence of transmission paths nearby the argon, and moreover the great transmission is due to the existence of an almost unique phase coherent path that connects the source and the drain by means of the argon (the blue path). Actually it is not at all coherent since in few point the phase coherence is broken, but in such regions the barriers are so small that the electron is transmitted almost without attenuation. Another important feature is that such transmission eigenchannel corresponds essentially to transmission through the HOSO level. This is clear when figure E.30 and E.29 are compared, by noticing that great similarity in the shape and phases between the two. This similarity is less marked with the LUSO, that is instead reported in figure E.31, thus clarifying that for such a bias point the transmission occurs mainly thanks to the HOSO level. For comparison a pair of transmission eigenstates for a lower bias,

namely 0.4 V, for which indeed there is no great current variation w.r.t. the case without the argon (i.e.  $C_{60}$  alone), are reported in figures E.32 and E.33. It has to be noted that in such a case the transmission is less evident between the contacts and the fullerene, due to the presence of the contact-fullerene barriers that cannot be easily overcome for that bias (with such an applied electric field). In addition phase decoherence occurs between the lower argon lobe and the fullerene one. These results essentially confirm the intuition of section 8.6.2, that can be an intuitive explanation for these behaviors, leading also to a selecting criterion for target molecules, for high sensitivity sensors.



Figure E.29: MPSH (zoomed in) for the HOSO level of the system  $C_{60}$  + Ar (side view). The considered bias point is 1.6 V. The figure was generated by *ATK* software [125], [126] (used for performing the simulations).



Figure E.30: Transmission eigenstate (full view) corresponding to the main transmission eigenvalue with quantum number QN = 0 for the transmission peak at energy E = 0.32 eV, and with a bias voltage  $V_D = 1.6 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.31: MPSH for the LUSO level of the system  $C_{60} + Ar$  (side view). Notice again the argon orbitals polarization. the considered bias point is 1.6 V. The figure was generated by *ATK* software [125], [126] (used for performing the simulations).



Figure E.32: Transmission eigenstate (side view) corresponding to the main transmission eigenvalue with quantum number QN = 0 for the transmission peak at energy E = 0.2 eV, and with a bias voltage  $V_D = 0.4 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).



Figure E.33: Transmission eigenstate (side view) corresponding to the second transmission eigenvalue with quantum number QN = 1 for the transmission peak at energy E = 0.2 eV, and with a bias voltage  $V_D = 0.4 \text{ V}$ . The surface corresponds to an iso-transmission surface, the colors correspond to different phases. The figure was generated by ATK software [125], [126] (used for performing the simulations).

### E.8 Additional images and graphs relative to section 9.9



Figure E.34: Absolute current variations due to the presence of the  $PbSO_4$  molecule for the case of the wire sensor and the transistor-based one.



Figure E.35: Percentage current variations due to the presence of the  $PbSO_4$  molecule for the case of the wire sensor and the transistor-based one.



Figure E.36: Current-voltage characteristics for 0, 1, and 2  $PbSO_4$  molecules nearby the conducting channel, in the case of the gated sensor. Notice that a good variation occurs among them and thus it is expected the sensor to be able to detect also the concentration.



Figure E.37: Current variations due to 1 and  $2 \text{ PbSO}_4$  molecules nearby the conducting channel, in the case of the gated sensor.



Figure E.38: Sensor current in function of the number of  $PbSO_4$  molecules for  $V_D = 0.4$  V. Black circles: simulated data; blue line: spline interpolation; red/orange line: straight line interpolation.



Figure E.39: Sensor current in function of the number of  $PbSO_4$  molecules for  $V_D = 0.8$  V. Black circles: simulated data; blue line: spline interpolation; red/orange line: straight line interpolation.



Figure E.40: Sensor current in function of the number of  $PbSO_4$  molecules for  $V_D = 0.8$  V. Black circles: simulated data; blue line: spline interpolation; red/orange line: second order polynomial interpolation.



Figure E.41: Sensor current in function of the number of  $PbSO_4$  molecules for  $V_D = 1$  V. Black circles: simulated data; blue line: spline interpolation; red/orange line: straight line interpolation.



Figure E.42: Sensor maximum deviation from linearity in function of the applied bias, for different  $PbSO_4$  concentrations. It is the maximum difference between the straight line interpolating curve and the spline  $3^{rd}$  order interpolating curve. Notice the low error at 0.8 V.



Figure E.43: Sensor current in function of the  $PbSO_4$  molecule distance from the sensor for  $V_D = 0.8$  V. Black circles: simulated data; blue line: spline interpolation; red/orange line: straight line interpolation.



Figure E.44: Sensor maximum deviation from linearity in function of the applied bias, for different  $PbSO_4$  distances. It is the maximum difference between the straight line interpolating curve and the spline  $3^{rd}$  order interpolating curve. Notice the low error at 0.8 V.

#### E.8.1 Sensor response time (gate case): section 9.9.5



Figure E.45: *I-V* characteristics obtained with *ATK* and with *Huckel-IV 3.0* tool. The ellipse highlight the chosen bias point, i.e. 0.8V. Notice the different values of the fitting parameter  $V_c$ . For  $V_D = 0.8$  V the best agreement is obtained with  $V_c = 0.625$ .

### Appendix F

## An operative introduction to the free available tool *Huckel-IV 3.0*

In chapter 5, section 5.17 (see in particular section 5.17.2), it was already introduced a free available MatLab-based tool called Huckel-IV 3.0 and originally developed by prof. Ferdows Zahid with M. Paulsson, E. Polizzi under the supervision of prof. S. Datta at Purdue University (Indiana, USA) between 2003 and 2005 [105], [41], [24]. The general approach, method and algorithm behind this tool were already explained in detail in section 5.17.2. The purpose of this section is to provide an operative description to the usage of such a tool in the current version I have used during the present work. This version was modified and used by my colleague Chiara Elfi Spano and I during the workshop "Innovative systems" a.y. 2018/2019 and 2019/2020. The treatment in this section is entirely taken from our final report about the aforementioned work. I have decided to do not modify it in order to make justice to that work and to make clear the separation between the present work and the previous one. Moreover in the present thesis work I have used exactly such a version of the tool, so no modifications were needed. The version of the tool I have used is accessible under request, alternatively the original version of the tool is accessible on the website www.nanohub.org (checked in 2019, March) or with a request to prof. Ferdows Zahid [105], [41], [24]. In the following the operative description of such a tool (in the "our" version), taken from the "Innovative system" workshop final report is reported.

Once we got access to Huckel-IV 3.0 suite we needed some time in order to make it working and correctly compiling on today's computer, since it was developed more than fifteen years ago exploiting softwares that are nowadays obsolete (such as Fortran 90 or Hamlet environment). In order to do that we needed to suitably modify the system calls and perform some other updating operations (indeed even though Huckel-IV is mainly developed in MatLab it performs system calls to compile and execute Python, Fortran 90 and C language programs). At the end of this phase we got an updated version of *Huckel-IV* able to correctly work on nowadays both Windows and Linux environments. After that we decided to create a unique *MatLab* main script, well commented and complete of explanations and instructions on how to set up all the input parameters, in order to ease an eventual inexpert user. In the actual version we are using, this is essentially the only script to be executed from users, and it performs all the operations and needed routine/system calls. Moreover we wrote a "readme" file with all detailed operative instructions on how to use the "our" version of *Huckel-IV 3.0*.

The next phase was to become familiar with the usage of Huckel-IV, and above all to verify the correctness of operation of the modified tool we had in our hands. In order to do that we performed many simulations changing all the possible input parameters and we compared results with the commercial (that we assumed reliable) tool *QuantumWise ATK* by Synopsys<sup>®</sup>, obtaining consistent results.

#### **Operative description**

The aim of this section is to provide and operative description of the way of using the Huckel-IV tool presented in section 5.17.2. Many of the following material is directly extracted from the «readme» file we wrote.

The sequence of operations performed by *Huckel-IV* is briefly summarized in the following:

- 1. Input or empirical parameters should be set by the user.
- 2. Isolated molecular energy levels and valence electron number are computed.
- 3. The molecule is suitably rotated such as it is aligned with y-axis, i.e. transport direction.
- 4. Atom indexes id and kd are generated
- 5. Hamiltonian and overlap matrices of the device plus leads are generated.
- 6. Coupling and Gamma (CNDO parameters) matrices are generated (isolated device is considered).
- 7. Laplace and image potentials are calculated for device only.
- 8. Surface Green's function are imported in main script for the selected energy range. If the energy range is modified, SGF calculations must be performed again separately (and before running the main script). See the "readme" file and relative scripts for instructions on how to practically doing it.
- 9. Charge neutrality and density matrix calculations are performed at equilibrium.
- 10. Transport (and self-energy) calculations are then performed for the selected bias and energy ranges.
- 11. Plots, figures and graphs are then generated and stored in the output folder.

In order to perform molecular wire and molecular transistor simulations the following steps should be performed:

- 1. Generate geometry files and save them into *input\_data* folder. Two input geometry files should be generated (e.g. starting from *.xyz* files from *ATK*, or *Avogadro*, etc...):
  - "device" file (no extension): xyz description of the isolated molecule.
  - "isolated" file (no extension): xyz description of the isolated molecule with initial and ending hydrogen atoms.

For file structures see example files (and remarks below). Notice that the names should be exactly "device" and "isolated" (without double quotation marks) in order to make it working correctly. Moreover the transport direction is assumed to be the y-direction.

- 2. Set input parameters and paths and run the main *MatLab* script "*MAIN\_script.m*". Instructions are provided directly into the code. Please read all the comments.
- 3. Outputs: once the computation is completed, output data are available in *output\_data* folder (suggested path). In particular:
  - *HS.mat* stores the device + leads Hamiltonian and overlap matrices and other related useful data.
  - *Hrho.mat* stores the Hamiltonian and density matrices at every bias points and other related useful data.
  - IV.mat stores  $I_D(V_D)$  for two terminal system and other related useful data.
  - IDVD.mat stores the output characteristic  $I_D(V_D)$  at a given  $V_G$  (for three terminal system) and other related useful data.
  - IDVG.mat stores the trans-characteristic  $I_D(V_G)$  at a given  $V_D$  (for three terminal system) and other related useful data.
  - *TEV.mat* stores transmission spectrum and density of states as a function of energy and drain bias and other related useful data.
  - *NEcnl.mat* stores the number electrons as a function of chemical potential and other related useful data.
  - In *energy\_level\_outputs* folder there is a file *Ne* that stores the number of valence electrons for that molecule, and a *MatLab* figure of isolated molecular energy levels.
  - In *figures* folder there are the output *MatLab* graphs.
  - *VdVgVimage.mat* stores image and Laplace potential value (output of *laplace3d\_solver* module).
  - *id* and *kd* are useful atom indexes to be used for creating some output graphs (or to perform post processing computations).
  - gamma.mat stores the gamma (CNDO parameters) matrix for the molecule.

• File *device* and *extended\_device* are modified (rotated) geometry files of the device without and with gold leads respectively.

Important remarks:

- (a) If the energy grid in the main script is modified, it is also necessary to modify the energy grid in HkSk\_SGF\_Calculator\_main.m script (that is located in HkSk\_SGF\_Calculator folder) and then execute the SGF (surface Green's Functions) calculator for the two contacts, i.e. execute HkSk\_SGF\_Calculator\_main.m (further instructions are provided in comments). This operation must be performed before running the main script.
- (b) In order to correctly complete calculations the following tools are necessary (system calls are performed to execute other programs):
  - *Python* 2.7.15*rc*1 (successive versions are not ensured to work correctly)
  - GCC (suggested) compiler (alternatively: other C language compilers if not GCC please modify system calls in main script and *Elevel.m* script)
  - g95 Fortran compiler (alternatively: other .f90 compilers, Fortran 90 compatibility must be ensured if not g95 please modify system calls in the main script)

Be sure that above mentioned tools and programs work correctly from command line (environment variables etc...). Useful links (updated on April 2019): https://www.python.org/downloads/release/python-2715rc1/ https://gcc.gnu.org/ https://www.g95.org/

(c) *device* and *isolated* file structure:

- $1^{st}$  column: atomic number of that atomic
- 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup> columns: x, y, z position of that atom (y-direction is transport direction)
- it is suggested to set up the geometry such that z column is identically zero (if possible, like e.g. in planar molecules that should be in xy plane only) to get a symmetric I-V characteristic

Here a list of folders and a brief explanation of main routines used in "our" version of *Huckel-IV* is reported. Users simply need to store input geometry files in folder *input\_data* and get calculation results in *output\_data* folder. For input and output brief description see above. It follows a very brief description of other folders (and routines):

- energy\_level: stores a MatLab function that is able to compute isolated molecular energy levels at equilibrium. It exploits also huckel.c (that is huckel.exe in windows environment after compilation) and Ne.py programs to evaluate the molecular Hamiltonian (with EHT method) and number of valence electrons respectively.
- $gamma\_parameters$ : stores a MatLab function that is able to compute CNDO parameters (starting from CNDO database in the same folder) for the considered device. The result of computation is used for the Poisson's potential  $U_{Poisson}$  evaluation, during transport calculations.

- *HkSk\_SGF\_Calculator*: stores *MatLab* functions aimed to calculation of gold contacts (13 Au atoms each) Hamiltonian and overlap matrices in k-space with a given number of k-points, and of contacts SGF.
- huckel\_hamiltonian: stores all what is needed to evaluate the Hamiltonian (HH) of the extended device (that is molecule + contact leads) and relative overlap matrix (S). From HH and S is then possible to get Hd and Sd (of device only). Moreover function coupling\_3au\_111.m evaluates the coupling matrices  $\zeta_1$  and  $\zeta_2$  between gold electrodes and molecule.
- *index\_atoms*: stores a python program that is able to evaluate *id* and *kd* indices (on the basis of molecular structure) widely used in transport calculations (for further detail see the code).
- *input\_data*: already described. It stores the user input data for calculations.
- *input\_generator*: useful *MatLab* data structure that stores SGF for 9 or 17 k-points. The ones used during calculations are in the sub-folder *contact\_input*.
- *laplace3d\_solver*: stores all what is needed to solve Laplace's equation and evaluate the Laplace and image potentials within the device. Results are stored in suitable data structures and are used during transport calculation to get the effective Laplace and image potential contributions.
- *output\_data*: stores the output data produced by *Huckel-IV*. For a brief description see above.
- *plotting*: stores *MatLab* functions used to produce figures and graphs (that are stored in *output\_data/figures* folder).
- rotation: stores a *MatLab* function able to suitably rotate the molecule (used in preliminary computations to correctly align the molecule with electrodes in transport direction). If the input files are constructed accordingly to what said above (and in the "readme" file) this rotation should not be necessary.
- *transport*: stores the *MatLab* functions that perform all the transport computations. The most important *MatLab* functions are the following:
  - Ulaplace.m is used to evaluate the actual Laplace's potential  $U_{Laplace}$  for the given bias point.
  - $scf\_30.m$  is aimed in performing the SCF loop presented in section 5.17.2. It calls  $poisson\_image.m$  that perform Poisson's and image ( $U_{Poisson}$  and  $U_{image}$ ) potential calculations (starting from the "gamma matrix" and "image potential" data structures previously evaluated) and provides the Hamiltonian starting from the density matrix. It calls also  $cal\_density.m$  that performs contour integral of eq. (5.77) to get the density matrix starting from NEGF quantities. Moreover it calls  $pulay\_mix.m$  that performs the Pulay's mixing procedure to update the density matrix to the new guess.
- -iv.m performs the integration of transmission spectrum to get the current value for that given bias point. It implements Landauer's equation (eq. (5.75)).
- -TE.m and TDE.m: they perform the transmission spectrum calculations and the transmission spectrum and density of states calculations, respectively. They essentially implement the set of equations presented in section 5.16. They are called within a loop on the energy grid, in a similar manner to what presented in section 5.17.1.

#### Main differences between Huckel-IV and QuantumWise ATK

The scope of this section is to highlight the main differences between Huckel-IV 3.0 tool and the commercial one QuantumWise ATK by Synopsys<sup>®</sup>. Indeed in the following we are going to compare simulations performed with both these softwares, in order to validate "our" version of Huckel-IV. Even though in QuantumWise ATK there is the possibility to perform NEGF based transport calculations starting from the EHT Hamiltonian, there are mainly two differences between Huckel-IV and QuantumWise ATK that must kept in mind in comparing the results. In particular:

- 1. In *Huckel-IV* the charge transfer that leads to Fermi energy alignment when molecularmetal contacts are created, is considered by means of the fitting parameter  $V_c$ , while in *ATK* a self-consistent equilibrium calculation is performed to evaluate the relative positions of Fermi energies.
- 2. Even if *Huckel-IV* uses a recursive method to evaluate the SGF and the self-energies (similar to what explained in section 5.8), this method is different from all the selectable methods in *ATK*. As a consequence, since each method will have a different error or different approximations, very likely the final result will be slightly different. It is expected that this will imply small differences in positions and broadening of molecular energy levels in the density of states or in the transmission spectrum (thus with small consequences also on the current).

Finally notice that even if both the tools use EHT method, it is not said that the starting semi-empirical potentials are exactly the same, and, more important, it is not said that the two methods use exactly the same weight to perform the needed linear combinations for the construction of the Hamiltonian. Indeed several variations are possible, and since we have no access to the ATK code we cannot know the exact formulae and algorithms that it employs.

#### Huckel-IV simulations

In this section we briefly summarize the procedure to be followed in order to perform molecular wire simulations. The steps are the following:

1. Generate geometry files and save them into *input\_data* folder. Two input geometry files should be generated (e.g. starting from *.xyz* files from *ATK*, or *Avogadro*, etc...):

- "device" file (no extension): xyz description of the isolated molecule.
- "isolated" file (no extension): xyz description of the isolated molecule with initial and ending hydrogen atoms.

For file structures see example files (and remarks below). Notice that the names should be exactly *device* and *isolated* in order to make it working correctly. Notice that in order to get a symmetric I-V curve the molecule should be centered in its geometrical center. This task could be difficult if geometry is generated in tools such as *Avogadro*, in which e.g. is very easily instead to center it around its mass center. For small molecule this is a good compromise, for complex geometries the error is more evident. From a theoretical point of view a possible reason for an asymmetric I-V characteristic is an asymmetric potential shape in space (especially in the transport direction). This is obviously related to molecule geometry and to what mentioned above.

- 2. Set input parameters and paths and run the main MatLab script. Instructions and explanations about them are provided directly into the main code  $MAIN\_script.m$ . In particular for all the simulations below the parameters reported in table F.1 were used. Notice that the chosen dl and dr values corresponds to a bonding distance of 2.4 Å, the employed values of  $V_c$  are reported below, no differences were noticeable if T would be set to 300 K, no gates were used so gx = gz = 0, and grid in expressed in Å.
- 3. Outputs: once the computation is completed, output data are available in *output\_data* folder (suggested path).

dl	1.8	vertical distance from the left contact in Å
dr	1.8	vertical distance from the right contact in Å
pl	1	row position in the "device" file for the most left atom
pr	60	row position in the "device" file for the most right atom
Vc	0.6; 0.625; 0.65	fitting parameter Vc
Т	0	Temperature in K
kp	9	number of k-points considered in SGF calculations
image	1	(if 1 the image correction is activated)
gx	0	number of gates in x-direction (no gates are present)
gz	0	number of gates in z-direction (no gates are present)
tox	0	gate oxide thickness (not used)
eox	0	gate oxide dielectric constant (not used)
grid	0.6	spatial grid step (in Å)
Idv	0	0 means two terminal calculations (molecular wire)
Vmin	0.0	minimum applied voltage in V
Vmax	+2.0	maximum applied voltage in V
NV	41	number of bias points between Vmin and Vmax
V	0	for two terminal calculations it must be 0
Emin	-14	minimum energy value considered in eV
Emax	-5	maximum energy value considered in eV
NE	9001	number of energy grid points between Emin and Emax
pulay_weight	5	Pulay mixing is used, this is the weight
damping	0.25	damping factor
iteration	50	max number of iterations
tolerance	1e-4	convergence tolerance of scf

**Table F.1:** Huckel-IV parameters used for the  $C_{60}$  molecular wire simulations. First column:<br/>parameter. Second column: set value. Third column: brief explanation.

## Appendix G

# Chapter 9 - Molecular electronic sensor circuit level parameters and modeling

### G.1 LUT-based model: *verilogA* code

In the following is reported the *verilogA* code for defining the three terminal sensor by means of LUT-based model. The data are stored in the *.txt* file named: "C60 PbSO4 sensor ATK.txt" that is reported in the next section.

```
VerilogA for SensorResponseTime, PbSO4 Sensor LUTdevice, veriloga
  `include "disciplines.h"
  `include "constants.h"
  module PbSO4_Sensor_LUTdevice(D, S, N_PbSO4);
  // "N_PbSO4" is a fake input contact, 0 means no PbSO4 molecule, 1 means
     that there is 1 PbSO4 molecule nearby the channel, 2 means that there
     are 2 PbSO4 and so on \ldots
  // the LUT data are simulated in Quantum-Wise ATK and the curves with
     different "N_PbSO4" are previously obtained in ATK
  input N_PbSO4;
11
  electrical N_PbSO4;
  // input type "electrical" is chosen for convenience, to perform easily
13
     transient analyses
14
  // Drain
15
16 inout D;
17 electrical D;
18
```

```
// Source
19
  inout S;
20
  electrical S;
21
22
  // Description:
23
  analog
24
      begin
25
26
  // 3rd order polynomial spline interpolation (3L)
27
  // Data are stored in C60_PbSO4_sensor_ATK.txt file
28
  // first row is V(N_{PbSO4,S}), second is V(D,S) and third is I(D,S)
29
30
  I(D,S) <+ $table_model(V(N_PbSO4,S), V(D,S), "C60_PbSO4_sensor_ATK.txt",
31
      "3L,3L");
  //1st order interpolation is not used: I(D,S) <+  $table_model(V(G,S), V(D))
      ,S), "bio_dati.txt", "1,1");
      end
35
  endmodule
36
```

#### G.1.1 LUT data: the "C60\_PbSO4\_sensor\_ATK.txt" file

In this section the content of the "C60\_PbSO4\_sensor\_ATK.txt" file is reported; it defines the LUT, storing the current values in function of the voltage  $V_{DS}$  values and the number of molecules: N\_PbSO4. The first column corresponds to the number of PbSO<sub>4</sub> molecules, i.e. the value of N\_PbSO4 variable; the second is the applied  $V_{DS}$ , and the third the current  $I_{DS}$ .

```
0.000000e + 000 0.000000 0.000000e + 00
  0.000000e + 000 0.200000 6.071283e - 06
  0.000000e + 000 0.400000 6.374918e - 06
3
  0.000000e + 000 0.600000 9.715714e - 06
  0.000000e + 000 0.800000 1.052677e - 05
  0.000000e + 000 1.000000 1.902070e - 05
6
  0.000000\,\mathrm{e}{+}000\ 1.200000\ 2.277715\,\mathrm{e}{-}05
  0.000000e + 000 1.400000
                             3.132946e - 05
  0.000000e+000
                  1.600000
                             3.034601 e - 05
Q
  0.000000e+000
                   1.800000
                             3.197763 e - 05
  0.000000e + 000 2.000000
                             3.259942e - 05
11
  1.000000e+000
                  0.000000
                             0.000000e+00
  1.000000e + 000 0.200000
                             5.019747 e - 06
13
  1.000000e + 000 0.400000 9.077101e - 06
14
  1.000000e + 000 0.600000 1.347075e - 05
  1.000000e + 000 0.800000 1.357319e - 05
  1.000000e + 000 1.000000 2.407807e - 05
  1.000000e + 000 1.200000 2.986192e - 05
18
  1.000000e + 000 1.400000 3.690916e - 05
19
  1.000000e + 000 1.600000 4.117528e - 05
20
  1.000000e + 000 1.800000 3.748752e - 05
```

22	1.000000e+000	2.000000	$4.287889 \mathrm{e}{-05}$
23	2.000000e+000	0.000000	0.000000e+00
24	2.000000e+000	0.200000	7.966706e-06
25	2.000000e+000	0.400000	$1.159848 \mathrm{e}{-05}$
26	2.000000e+000	0.600000	$1.387970\mathrm{e}{-05}$
27	2.000000e+000	0.800000	$1.580951\mathrm{e}{-05}$
28	$2.000000 \mathrm{e}{+}000$	1.000000	2.099119e - 05
29	2.000000e+000	1.200000	2.894659e - 05
30	2.000000e+000	1.400000	3.206264e-05
31	2.000000e+000	1.600000	$3.136089 \mathrm{e}{-05}$
32	2.000000e+000	1.800000	$3.937469 \mathrm{e}{-05}$
33	2.000000e+000	2.000000	4.172977 e - 05

# G.2 Device capacitances and "dynamic" resistances calculations

In this section it is reported the *MatLab* script used for evaluating the quantum and the electrostatic capacitances and the "dynamic" resistances of the sensor. In the following sub-sections the various functions called by the main script are also reported. Details on the methods and algorithms are directly provided within the codes in the comments.

```
%% The aim of this script is to provide a quantitative estimation of
     molFET
 %
     capacitances Cg, Cs, Cd and resistances Rg, Rs, Rd.
2
3
  % PAY ATTENTION !!11
 % !! At the moment the only possible device structures are:
 %
     1) no gate: molecular wire: gx=0 and gz=0
7 %
    2) a single gate molFET: gx=1, gz=0
|\%|  1 At the present this code works only for voltage division factors
9\% eta=0.5, thus if Cs=Cd (where Cs and Cd are assumed to be the average
10 % source and drain capacitances) !!!
  clear all
  close all
  clc
14
  % welcome:
16
  disp('Welcome in molFET parameters calculator program!');
17
18
 %% Load data:
19
 % Firstly the needed data are loaded, in order to do that the user should
20
 % correctly set the following path:
21
 % path of the output_data folder you want to use (PLEASE SET IT CORRECTLY
23
     1):
24 % (IT SHOULD BE AN OUTPUT CHARACTERISTIC FOR FIXED Vgs if the gate is
     present, if a molecular wire is considered it should be an I-V char)
25
```

```
26 % Vc=0.6 eV
 \%output_data_folder = 'C:\ [...] \C60_dldr1d8_Vc0d6';
27
28
 % Vc = 0.625 eV
29
  \%output_data_folder = 'C:\ [...] \C60_dldr1d8_Vc0d625';
30
  % Vc=0.65 eV
32
  output_data_folder = 'C: \ [...] \ C60_dldr1d8_Vc0d65';
33
34
  78787%
          NO MORE USER INPUTS %%%%
35
36
  \% If no variations to output data storage are made the following paths
37
      are
 % automatically found (DO NOT MODIFY!):
38
39
40 % "Hrho.mat" structure path:
41 Hrho_path = strcat(output_data_folder, '\Hrho.mat');
42 % "device" file path:
43 device_path = strcat(output_data_folder, '\device');
44 % "TEV.mat" structure path:
<sup>45</sup> TEV_path = strcat(output_data_folder, '\TEV.mat');
46 % "HS.mat" structure path:
47 HS_path = strcat(output_data_folder, '\HS.mat');
48 % "id" file path:
49 id_path = strcat(output_data_folder, '\id');
50
51 % correct data import:
<sup>52</sup> disp('Data are correctly imported from:');
<sup>53</sup> disp (output_data_folder);
  string_to_be_displayed = sprintf('-
                                                             - - - - - - - \langle n' \rangle;
54
<sup>55</sup> disp(string_to_be_displayed);
56
57 97% Check the device structure: molecular wire or transistor
  [gate] = check_if_gate(Hrho_path);
58
 % gate variable is 1 if a gate is present otherwise (molecular wire) it
59
      is 0
60 % Display it:
  if gate = 0 \% molecular wire:
61
      string_to_be_displayed = sprintf('The device is a molecular wire\n');
62
      disp(string_to_be_displayed);
63
  elseif gate == 1 % molecular transistor:
64
      string_to_be_displayed = sprintf('The device is a molecular
65
      transistor \langle n' \rangle;
      disp(string_to_be_displayed);
66
67
  else
      string_to_be_displayed = sprintf('The device is not recognized!\n');
68
      disp(string_to_be_displayed);
69
  end
70
71
  %% Cg gate capacitance (assumed to be constant):
72
73
_{74} % by default in Huckel-IV 3.0 the molecule is supposed to be inside a box
75 % of dimensions 100x100xL (angstrom) L=length of the molecule,
```

```
_{76} % so the width W of the gate is W = box_length = 100 angstrom.
77 \% Simulation domain dimension (DO NOT MODIFY!):
78 box_length = 100; % angstrom
79 % gate width in angstrom:
_{80}|W = box_length; \% angstrom
81
  \% if it is a molecular wire the gate capacitance is not evaluated, if it
82
      is
  \% a molFET with the gate it is evaluated:
83
84
   if gate == 1 % only if a gate is present the gate capacitance is
85
      estimated:
86
      \% The following function performs the Cg calculation:
87
       [Cg] = Cg_calculator (Hrho_path, device_path, W);
88
89
      % Display it:
90
       string_to_be_displayed = sprintf('The electrostatic gate capacitance
91
      resulted to be:
                           Cg = \%g F', Cg;
       disp(string_to_be_displayed);
92
93
   else \% otherwise, if it is a wire, Cg is not calculated:
94
      \% Nevertheless , the variable Cg is anyway defined and set to zero ,
95
      \% since it will be useful later:
96
       Cg=0;
97
   end
98
99
  % Approximated estimation of Cs and Cd from parallel plane approximation
100
  \% details on the method are provided directly as comments inside the
  % function:
104
105|H = W; % contact height is the same of the width
106
   [Cs_approx, Cd_approx] = Csd_calculatorAPPROX(Hrho_path, device_path, W,
      H);
108
   string_to_be_displayed = sprintf('The approximated (parallel plates)
109
      source and drain capacitances resulted to be:
                                                          Cs = Cd = \%g F',
      Cs_approx);
  disp(string_to_be_displayed);
110
112 7% Quantum capacitance in function of applied Vds (fixed Vgs):
113
114 % The following function evaluates the quantum capacitance Cq(Vds) in
|_{115}|_{\%} function of the applied bias Vds, it is an approximate expression based
  \% on linearized approximation of Cd in the considered bias window.
116
      Details
  % on employed method are in Cq_calulator.m
118
  [Vg, Vds, Cq] = Cq_calculator(TEV_path, Hrho_path);
119
120
```

```
|121| Cq = Cq *2; % SPIN DEGENERACY: DOS=DOS*2 !!
_{123} \% Since Cq is evaluated in each Vds bias point, the returned array Vds is
_{124} % exactly the aaplied bias Vds array (used in ouput char estimation).
_{125} % Also Vg is exactly the same used for finding the current output char.
126
  \% Plot Cq(Vds):
                        two cases are considered in order to correctly set up
127
  %
128
                        the title and legends:
  %
       1) molecular wire: (gx=0, gz=0):
129
     gate = 0 % molecular wire, Vg does not exist (no gate is present!):
130
   i f
       figure
       hold on
       grid on
       plot (Vds,Cq, 'LineWidth',2.0);
134
       title_string = sprintf('Average linearized quantum capacitance in
      function of Vds');
       title (title string);
136
       xlabel('Vds(V)');
       ylabel('Approximated Cq (F)');
138
       set (gca, 'LineWidth', 2.0, 'FontSize', 15.0);
139
   elseif gate = 1 % molecular transistor, Vg is fixed to a given value
140
      since output char are considered:
       figure
141
       hold on
142
       grid on
143
       plot (Vds,Cq, 'LineWidth',2.0);
       title_string = sprintf('Average linearized quantum capacitance in
145
       function of Vds for Vgs = \%g V', Vg;
       title(title_string);
147
       xlabel('Vds(V)');
       ylabel('Approximated Cq (F)');
148
       set(gca, 'LineWidth', 2.0, 'FontSize', 15.0);
149
  end
  % Euilibrium Cq(Vds=0) is now extracted:
152
  equilibrium_index = find ( Vds==0 );
  Cq_equi = Cq(equilibrium_index);
155
  %% Ceq_0 equivalent electrostatic capacitance at equilibrium:
156
157
158 % Ceq_0 is the equivalent electrostatic capacitance of molFET at
159 % thermodynamic equilibrium (i.e. when contacts and molecule Fermi energy
160 % levels are aligned). It is the sum of:
_{161} %
    > Cg (IF PRESENT!!), already evaluated from MOm physical geometry,
      thus indipendent from Vgs
     > Cd_0, drain capacitance at equilibrium (i.e. Vds=0 V). Indeed it is
_{162} %
      a
  %
     non linear capacitance dependent on the applied bias.
163
     > Cs_0, source capacitance at equilibrium (i.e. Vds=0 V). Indeed it is
164 %
       a
165 %
     non linear capacitance dependent on the applied bias.
  \% Notice that if dl=dr then the electrode-molecule coupling is the same
166
      for drain
```

```
_{167} % and source, thus the assumption Cd=Cs holds, and Ceq_0 = 2*Cd_0 + Cg.
168 % (IF THE GATE IS PRESENT, otherwise Cg does not exist)
169
  % The following function performs the Ceq_0 calculation:
   [Ceq_0] = Ceq_0_calculator (Hrho_path, Cq_equi);
174
  % Display it:
   string_to_be_displayed = sprintf('The equivalent electrostatic
176
                                                        Ceq_0 = \%g F', Ceq_0;
      capacitance at equilibrium resulted to be:
   disp(string_to_be_displayed);
177
178
_{179} % equilibrium drain capacitance calculation (the same holds for Cs_0):
180 Cd_0 = (Ceq_0) / 2;
_{181} % OR MAYBE:
                    (only IF the gate is present)
_{182} %Cd_0 = (Ceq_0 - Cg) /2;
183 % OR MAYBE:
                   (only IF the gate is present)
184 | \% Cd_0 = abs( (Ceq_0 - Cg)/2);
185
  Cs_0 = Cd_0; % true if voltage division factor eta is 0.5 (i.e. if dl=dr
186
      and same contact material -and surface orientation - is used for S and
      D)
187
  % Display it:
188
   string_to_be_displayed = sprintf('The electrostatic drain/source
189
      capacitance at equilibrium resulted to be:
                                                     Cd \ 0 = Cs \ 0 = \%g \ F',
      Cd_{0};
   disp(string_to_be_displayed);
190
191
  %% Source and Drain Cs, Cd eletrostatic capacitances in function of
      applied Vds (fixed Vgs):
193
  % The following function evaluates the source and drain capacitances
194
|_{195}| % Cs(Vds) and Cd(Vds) in function of the applied bias Vds, supposing Vgs
_{196} % fixed (IF a gate is present): thus the variations wrt Vgs are not
      considered and the channel
  % potential variations due to Vds variations are supposed to be given by
197
  % capacitive divider: Cd/(Ces+Cq) where Ces=Cs+Cd+Cg. (IF Cg is present)
198
199
   [Vg_Csd, Vds_Csd, Cs, Cd] = Csd_calculator(Hrho_path, HS_path,
200
      device\_path\ ,\ id\_path\ ,\ Cd\_0\ ,\ Cs\_0\ ,\ Cg\ ,\ Cq)\ ;
201
  % Since Cs and Cd are evaluated as differential capacitances (exploiting
202
  \% sequence of small Vds variations) they are evaluated in different Vds
203
  % bias points: Vds_Cds is different from Vds !!!
204
  % In particular in Vds_Cds there are halfway values of Vds wrt to Vds
205
      array
  % ones !! Thus in plotting Cd and Cs Vds_Csd should be used !!
206
207
208 % Plot Cs and Cd: two cases are considered in order to correctly set up
```

```
209 %
                         the title and legends:
  %
       1) molecular wire: (gx=0, gz=0):
210
   i f
      gate = 0 % molecular wire, Vg does not exist (no gate is present!):
211
       figure
212
       hold on
       grid on
214
       plot(Vds_Csd,Cs, Vds_Csd,Cd, 'LineWidth',2.0);
215
       title_string = sprintf('Source and Drain capacitances in function of
216
       Vds');
       title(title_string);
217
218
       ylim=get(gca, 'ylim');
219
       xlim=get(gca, 'xlim');
220
       text(xlim(1)+0.1,ylim(2)-0.2e-19,'since voltage division factor is
221
       assumed to be 0.5 they are equal');
222
       legend('Cs', 'Cd');
223
       xlabel('Vds (V)');
224
       ylabel('Approximated Cs and Cd (F)');
225
       set(gca, 'LineWidth', 2.0, 'FontSize', 15.0);
226
227
   elseif gate = 1 % molecular transistor, Vg is fixed to a given value
228
       since output char are considered:
229
       figure
230
       hold on
       grid on
232
       plot (Vds_Csd, Cs, Vds_Csd, Cd, 'LineWidth', 2.0);
233
       title_string = sprintf('Source and Drain capacitances in function of
234
       Vds for Vgs = \%g V', Vg\_Csd);
       title(title_string);
235
236
       ylim=get(gca, 'ylim');
237
       xlim=get(gca, 'xlim');
238
       text(xlim(1)+0.1,ylim(2)-0.2e-19,'since voltage division factor is
239
       assumed to be 0.5 they are equal');
240
       legend('Cs', 'Cd');
241
       xlabel('Vds(V)');
242
       ylabel('Approximated Cs and Cd (F)');
243
       set(gca, 'LineWidth', 2.0, 'FontSize', 15.0);
244
   end
245
246
  %% Gate resistance Rg estimation (ONLY IF THE GATE IS PRESENT !! ):
247
248
   if gate == 1 % ONLY IF A GATE IS PRESENT Rg IS EVALUATED:
249
250
       \% details on the method are provided directly as comments inside the
251
       % function:
252
253
       % choose the dielectric material to be used as oxide layer (uncomment
254
       the
       % desired one):
255
```

```
oxide = 'ZrO2';
256
       \%oxide='SiO2';
257
       % The following function performs the Rg calculation:
       [Rg] = Rg_calculator(Hrho_path, device_path, W, oxide);
260
261
       % Display it:
262
       string_to_be_displayed = sprintf('The approximated gate resistance
263
                           Rg = \%g \text{ ohm}', Rg;
       resulted to be:
       disp(string_to_be_displayed);
264
265
266
   end
267
  % Source and Drain Rs, Rd resistances in function of applied Vds (fixed
268
      Vgs):
269
270 % The following function evaluates the source and drain resistances
271 % Rs(Vds) and Rd(Vds) in function of the applied bias Vds, supposing Vgs
272 % (IF present) fixed.
273 % Further details on method are provided directly in the function
274 % code. It returns also the average coupling factors tauS, tauD (again in
_{275} % function of the applied bias).
276
   [Vgs_fixed, Vds, Rs, Rd, tauS, tauD] = Rsd_calculator(Hrho_path, HS_path,
277
       TEV_path, Cq);
   \% Plot Rs(Vds) and Rd(Vds):
                                     two cases are considered in order to
279
      correctly set up
   %
                                     the title and legends:
280
       1) molecular wire: (gx=0, gz=0):
281
   %
   if gate == 0 \% molecular wire, Vg does not exist (no gate is present!):
282
       figure
283
       hold on
284
       grid on
285
       plot(Vds,Rs, Vds,Rd, 'LineWidth',2.0);
286
       title_string = sprintf('Source and Drain resistances in function of
287
       Vds ');
       title(title_string);
288
       legend('Rs', 'Rd');
289
       xlabel('Vds(V)');
290
       ylabel('Approximated average Rs and Rd (\Omega)');
291
       set(gca, 'LineWidth', 2.0, 'FontSize', 15.0);
292
293
       figure
294
       hold on
295
       grid on
296
       plot(Vds,tauS, Vds,tauD, 'LineWidth',2.0);
297
       title_string = sprintf('Source and Drain coupling factors in function
298
       of Vds');
       title(title_string);
299
       legend('tauS', 'tauD');
300
       xlabel('Vds(V)');
301
       ylabel ('Approximated average tauS and tauS (s)');
302
```

```
set(gca, 'LineWidth', 2.0, 'FontSize', 15.0);
303
304
   elseif gate = 1 % molecular transistor, Vg is fixed to a given value
305
       since output char are considered:
306
       figure
307
       hold on
308
       grid on
309
       plot(Vds,Rs, Vds,Rd, 'LineWidth',2.0);
310
       title_string = sprintf('Source and Drain resistances in function of
311
       Vds for Vgs = \%g V', Vgs_fixed;
       title(title_string);
312
       legend('Rs', 'Rd');
313
       xlabel('Vds(V)');
314
       ylabel('Approximated average Rs and Rd (\Omega)');
315
       set(gca, 'LineWidth', 2.0, 'FontSize', 15.0);
316
317
       figure
318
       hold on
319
       grid on
320
       plot (Vds, tauS, Vds, tauD, 'LineWidth', 2.0);
321
        title_string = sprintf('Source and Drain coupling factors in function
322
        of Vds for Vgs = %g V', Vgs_fixed);
        title(title_string);
323
       legend('tauS', 'tauD');
324
       xlabel('Vds (V)');
325
       ylabel('Approximated average tauS and tauS (s)');
326
       set(gca, 'LineWidth', 2.0, 'FontSize', 15.0);
327
328
   end
329
330
331 7% Average Cs, Cd, Rs, Rd, Cq, tauS, tauD, are now evaluated:
332 % the Cs, Cd, Rs, Rd, Cq, tauS, tauD are evaluated in function of the
333 % applied bias Vds, now they are averaged over the considered bias values
334
_{335} Cq_AV = mean(Cq);
_{336} Cs AV = mean (Cs);
_{337} Cd_AV = mean(Cd);
|\operatorname{Rs}_{AV} = \operatorname{mean}(\operatorname{Rs});
_{339} Rd_AV = mean(Rd);
  tauS_AV = mean(tauS);
340
  tauD_AV = mean(tauD);
341
342
343 % Display them:
   string_to_be_displayed = sprintf('Averages values: ');
344
   disp(string_to_be_displayed);
345
   string_to_be_displayed = sprintf('The averaged (over bias Vds) Cq is:
346
        Cq_AV = \% g F', Cq_AV ;
   disp(string_to_be_displayed);
347
   string_to_be_displayed = sprintf('The averaged (over bias Vds) Cs is:
348
        \label{eq:cs_AV} Cs\_AV \,=\, \%g \ F \ \ , \ \ Cs\_AV) \ ;
349 disp(string_to_be_displayed);
```

```
string_to_be_displayed = sprintf('The averaged (over bias Vds) Cd is:
350
       Cd\_AV = \%g \ F', \ Cd\_AV);
   disp(string_to_be_displayed);
351
   string_to_be_displayed = sprintf('The averaged (over bias Vds) Rs is:
352
       Rs_AV = \% g \text{ ohm}', Rs_AV);
   disp(string_to_be_displayed);
353
   string_to_be_displayed = sprintf('The averaged (over bias Vds) Rd is:
354
       Rd_AV = \% g \text{ ohm '}, Rd_AV);
   disp(string_to_be_displayed);
355
   string_to_be_displayed = sprintf('The averaged (over bias Vds) tauS is:
356
          tauS_AV = \% g s', tauS_AV;
   disp(string_to_be_displayed);
357
   string_to_be_displayed = sprintf('The averaged (over bias Vds) tauD is:
358
         tauD_AV = \% g s', tauD_AV);
   disp(string_to_be_displayed);
359
   string_to_be_displayed = sprintf('-
360
                  - - - |n'|;
   disp(string_to_be_displayed);
```

#### G.2.1 Gate capacitance calculation

```
%% This function calculates the gate capacitance Cg of a molFET:
  function [Cg] = Cg_calculator(Hrho_path, device_path, W);
  % Input Data:
5
  load(Hrho_path); % it stores eox, tox, dl, dr
6
\sqrt{\mathbf{xyz}=\mathbf{load}(\mathbf{device}_{\mathbf{path}})}; \% it stores the geometry of the molecule
9 % in vacuo dielectric permettivity:
10 eps0 = 8.8542e - 12; \% F/m
12 % Findind the molecule length L:
_{13}|Y=xyz(:,3);
14 Y1=min(Y)-d1; Y2=max(Y)+dr;
_{15}|Y=[Y1;Y;Y2]; \% Y-axis is the transport axis
_{16} L=Y(end) - Y(1); % (angstrom) molecule total length,
_{17} \% L includes also anchoring groups and space from gold contacts to
_{18} methods and methods and methods are source to drain total length (from gold methods).
_{19} (so contact to gold contact). L is in angstrom, but now it is converted in
      m:
_{20} L = L*1e-10; % m, in meters
22 % Findind the molecule width Wmol:
23 Z=xyz(:,4); % Z-axis is the transverse axis
_{24} Wmol= max(Z) - min(Z); % (angstrom) molecule total max width
25
_{26} total gate width (as evaluated in laplace solver fortran90 code):
_{27} Wtot = W + Wmol; % angstrom
28 % Wtot is converted to m:
```

```
Wtot = Wtot*1e-10; \%m, in meters
29
30
  \% tox is known in angstrom, so it is converted to m:
31
  tox = tox*1e-10; % m, in meters
32
  % Gate electrode area in (squared) meters:
34
  Area = Wtot*L; \% m<sup>2</sup>
35
36
  % Gate capacitance:
37
  Cg = ((eox*eps0)/tox)*Area; \% F, it is in farad
38
39
  end
40
```

# G.2.2 Source and drain electrostatic capacitance calculation, by means of the parallel plate approximation

1 1 1 2 Electrostatic capcitances in parallel plane approx (uniform Electric field and linear Utot channel potential):  $_{3}$  % This function implements a simple estimation of the S and D capacitances  $_4 
vert \%$  based on the parallel plate capacitor approximation, presented in Baldo 5 % page 84-85 eqs. 3.13-3.14. This approximation holds under the hypotheses:  $_{6}|\%$  1) uniform electric field inside the whole channel (i.e. contant 7 % electric field in each point of the molecule)  $_8$  % and  $_{9}$  % 2) the contact area much greater than the distance between the plates.  $_{10}$  % The second hypothesis is (almost) always true if we assume that the 11 contact leads (13 gold atoms – added to device Hamiltonian) are just a  $_{12}$  % small portion of the entire contact that has same extension of the 13 simulation domain bos: i.e.  $100 \times 100 \times L$  angstrom (L=molecule length),  $_{14}|_{\%}$  leading to a contact area of 100x100 angstrom. External parameters W,H  $_{15}|\%$  are used to indicate the S/D contact width and heigth respectively  $_{16}$  (defualt are 100 angstrom each). For coherence with the laplace solver 17 (frotran90 code) total width and height Wtot and Htot are found by adding  $_{18}\left|\%\right.$  molecule dimensions to W,H. The source capacitive effect is then  $_{19}$  % considered to be the charge variation in response to an applied voltage  $_{20}|$ % of the first half of the molecule, while the drain one is considered to % involve the second half only, thus spacing between capacitor plates is 21  $_{22}$  % in both cases simply L/2 (L=molecule length), and Cs=Cd. 23 % Finally it is supposed to have vacuum dielectric contant inside the  $_{24}$  % channel/molecule (i.e. empty space or air between atoms of the molecule  $_{25}|_{\infty}$  that are ju neglected in this estimation while considered as puntual  $_{26}$   $\infty$  charges -value depending on the atomic number- in the laplace solver that 27 % estimates the Poisson and image potential). 28

```
<sup>29</sup> function [Cs, Cd] = Csd_calculatorAPPROX(Hrho_path, device_path, W, H);
30
31 % Input Data:
32 load (Hrho_path); % it stores eox, tox, dl, dr
  xyz=load(device_path); % it stores the geometry of the molecule
33
34
  % in vacuo dielectric permettivity:
35
  eps0 = 8.8542e - 12; \% F/m
36
37
 % Finding the molecule length L:
38
^{39} Y=xyz (:,3);
_{40} Y1=min(Y)-d1; Y2=max(Y)+dr;
41 Y=[Y1;Y;Y2]; % Y-axis is the transport axis
_{42} L=Y(end) - Y(1); % (angstrom) molecule total length,
_{43} \% L includes also anchoring groups and space from gold contacts to
_{44} anchoring groups: it is the source to drain total length (from gold
_{45} (\% contact to gold contact). L is in angstrom, but now it is converted in
     m:
_{46}|L = L*1e-10; \% m, in meters
47
_{48}\left|\%\right. Now it assumed that the Cs includes the capacitive effects in the first
_{49} half of the molecule (d=L/2, d=distance between the capacitor plates)
      and
_{50}\left|\%\right. Cd the second half (d=L/2):
_{51} d = L/2; % distance between the plates of the capacitor, m
52
53 % Finding the molecule width Wmol:
54 Z=xyz(:,4); % Z-axis is the transverse axis
_{55} Wmo\models max(Z) - min(Z); % (angstrom) molecule total max width
56
 \% total S or D contact width (as evaluated in laplace solver fortran90
57
      code):
58 Wtot = W + Wmol; \% angstrom
59 % Wtot is converted to m:
_{60} Wtot = Wtot *1e - 10; %m, in meters
61
62 % Findind the molecule height Hmol:
63 X=xyz(:,2); % X-axis is the transverse (height) axis
_{64} | Hmol= max(Z) - min(Z); % (angstrom) molecule total max height
65
_{66} % total S or D contact height (as evaluated in laplace solver fortran90
      code):
_{67} Htot = H + Hmol; % angstrom
68 % Htot is converted to m:
69 Htot = Htot *1e - 10; \%m, in meters
70
_{71} % S/D electrode area in (squared) meters:
  Area = Wtot * Htot; \% m<sup>2</sup>
73
  % S/D capacitance:
74
  Cs = ((eps0)/d) * Area; \% F, it is in farad
75
_{76} Cd = Cs;
  end
77
```

#### G.2.3 Quantum capacitance calculation

```
1 1 7 This function calculates the quantum capacitance Cq of a molFET:
_3 % For each Vds value a quantum capacitance value is found, it is the
_4 % average quantum capacitance over the considered bias window, under the
_{5} /% hypothesis of having a voltage division factor equal to 0.5, i.e. equal
_{6} source and drain capacitances, the returned data structure Cq is a
     vector
_{7} % that store average Cq values for each Vds value.
  function [Vgs_fixed, Vds, Cq] = Cq_calculator(TEV_path, Hrho_path);
11 % electron charge:
_{12} q = 1.60217662e-19; % electron charge, C
14 % Input Data:
<sup>15</sup> load (Hrho_path); % it stores Ef = equilibrium Fermi level
  load (TEV_path); % it stores the Vds bias and DOS(Vds)
16
17
  \% converting the polarity in order to get the applied voltage (voltage
18
     polarity convention):
19
  Vds = -fliplr (Vd_bias);
                           % V
  Vgs\_fixed = - Vg; \% V
20
21
22 % output data structure allocation:
_{23} Cq = zeros(1, NVd); % NVd is the number of Vds bias points
24
25 % For each bias point
                             % they are considered sequentially (convention
  for bias_point = 1:NVd
26
      of potential energy as in Vd_bias array !!)
                             \% -> at the end Rs and Rd are flipped !!
27
28
      bias_window = Vd_bias(bias_point); % this is the bias window width in
29
      eV
      % The bias window is assumed to be centered around equilibrium Fermi
30
      % level of contacts Ef plus Vc value, i.e. from Datta eq. 7.3.11 p
      .174
      % Cq = q^2 * DOS(E=Ef), where Ef=equilibrium Fermi level,
      % approximated with contact Fermi level: gold (111) is -9.5 eV
34
      % Contact Fermi Levels for the current bias point:
35
      36
37
38
      \% Minimum between muS and muD:
39
      \min\_bias\_window = \min(muS, muD);
40
      % Maximum between muS and muD:
41
      \max\_bias\_window = \max(muS, muD);
42
43
      \% Cq in this bias point is then proportional the average of the DOS
44
     in
```

```
\% the considered bias window:
45
      considered_E_indeces = find ( min_bias_window <= E & E <=
46
     max_bias_window); % considered_E_indeces stores the indeces of
      interest
      % The considered DOS (for the average) in this bias window is:
      considered_DOS = Dev(considered_E_indeces, bias_point);
48
      % average DOS in the considered range (mean is arithmetic mean):
49
      DOS\_av = mean(considered\_DOS);
50
      % linearized average Cq (eq. 7.3.11 p.174 Datta):
      Cq(bias_point) = q*DOS_av;
      % remark: q is simply used in above expression for Cq (instead of q
     ^2)
      % since the energy was in eV, thus in Datta p.174 in eq. 7.3.5 and
      \% 7.3.6 it should be simply used q (if U is in joule then U/q is in
     eV)
      % instead of q^2 and as consequence also in eq. 7.3.11 it should be
56
      % used simply q.
58
  end
60
 % The calculated Cq array corresponds actually to (average) Cq values as
61
_{62} % function of the applied potential energy: Vd_bias was indeed used.
_{63} Now it is flipped to make it corresponding to applied voltage instead:
_{64} % Vds array define above (voltage convention). Thus it is simply flipped:
65
 Cq = fliplr(Cq); % such that Cd(Vds) and not Cq(Vd_bias) !!
66
67
 % Thus Cq can be plotted in function of the returned Vds voltage
68
69
70
  end
```

#### G.2.4 Equilibrium total electrostatic capacitance calculation

```
%% This function calculates the equivalent electrostatic capacitance at
equilibrium of a molFET:
function [Ceq_0] = Ceq_0_calculator(Hrho_path, Cq_0);
% Input Data:
load(Hrho_path); % it stores Vc, Neq, Ne
q=1.6021773e-19; % elementary charge [C]
% MolFET charging energy at equilibrium Uch_0 is equal to Vc.
% Vc is the difference between Fermi level of the isolated molecule
% (geometry described in 'isolated ' file) and Fermi level of the
electrode.
% Notice it is expressed in eV.
Uch_0 = Vc; %[eV]
```

```
15
_{16} \Big|\% deltaN_0 is the difference between the number of electrons in the the
_{17} molecule when the molecular junction is created and no bias is applied
      (Neq)
 \% and the number of electrons in the isolated molecule (Ne).
18
  deltaN 0 = Ne - Neq;
19
20
  % electrostatic equivalent capacitance at equilibrium
21
  \% (eq. 3.21 Baldo, with energy expressed in eV thus simply q should be
22
      used)
 \% Ceq_0 = q*deltaN_0/Uch_0; % F, it is in farad
23
24
  % total electrostatic capacitance at equilibrium (eq. 3.10 page 84 Baldo)
25
  Ceq_0_powerm1 = Uch_0/(q*deltaN_0) - 1/Cq_0; \% Cq_0 is the (equilibrium E)
26
     =Ef) quantum capacitance, Ceq_0_powerm1 is the reverse of Ceq_0 \!
  Ceq_0 = abs (Ceq_0_powerm1^-1); % F, This is the equilibrium
      electrostatic capacitance
28
  end
29
```

#### G.2.5 Source and drain capacitances calculation

```
\% This function calculates the source and drain capacitances Cs, Cd of a
      molFET
<sup>3</sup> % For each Vds value a Cs, Cd value is found. Vgs (IF present) is
     supposed fixed, thus
_4 % the variations wrt Vgs are not considered and the channel potential
5 % variations are supposed due to Vds variations only.
6 \% A simple capacitive divider (i.e. Cd/(Ces+Cq) where Ces=Cs+Cd+Cg) is
_{7}|_{\%} considered as proportionality factor between variations in the channel
8 % potential wrt Vds variations.
  , device_path, id_path, Cd_0, Cs_0, Cg, Cq);
11
 % electron charge:
  q = 1.60217662e - 19; \% electron charge, C
14
 % Input Data are loaded:
15
  load(Hrho_path);
16
  load (HS_path);
17
  xyz=load(device_path); % it stores the geometry of the molecule
18
  id=load (id_path); % load "id" file (atom indeces)
19
20
21 Nd=size(id,2); % number of atoms in the molecule
23 % transport y-axis is recovered from xyz geom file:
24 Y=xyz(:,3); % molecule y-axis selection
```

```
_{25} Y1=min(Y)-d1; Y2=max(Y)+dr;
26 Y=[Y1;Y;Y2]; % Y stores the full y-axis from gold S contact to D gold
      contact (it includes the distances between gold and sulfur atoms)
  \% converting the polarity in order to get the applied voltage (voltage
28
      polarity convention):
  Vds = -fliplr(Vd_bias); \% V
29
  Vgs\_fixed = - Vg; \% V
30
31
 % Average channel potential data structure allocation:
32
  Utot\_av = zeros(1, NVd); \% NVd is the number of Vds bias points
33
34
35 % output data structures allocation:
_{36} Cs = zeros(1, NVd); % NVd is the number of Vds bias points
_{37} Cd = zeros(1, NVd); % NVd is the number of Vds bias points
38 Vds_Csd = zeros(1, NVd); % NVd is the number of Vds bias points
39
_{40} % First, for each bias point, the total channel potential is recovered:
_{41} [% It is found in function of Y and then it is simply averaged over the
_{42} whole molecule length in order to find the channel average potential
43 % energy. This is performed with the first "for" loop.
44
_{45}\left|\%\right. Second, this average value is then used in evaluating the source and
_{46} |\% drain average capacitances in that given bias point. Anyway this is
_{47} \% performed starting from equilibrium Vds=0 and proceeding considering
_{48}|\% sequential bias point in order to ensure small variations wrt previous
 \% bias point and thus linearized ss model is used. This is performed with
49
 % the second "for" loop.
50
  for bias_point = 1:NVd % First loop on -q*Vds potentials
      % The total channel potential energy is recovered for the considered
54
      % bias point in function of Y:
      U=diag(HM(:,:,bias_point)-Hd); % Hamiltonian potential energy for the
56
      considered Vds bias point
      j = 1;
      for i=1:Nd
58
           Utot(i)=U(j);
           if id (i)==0
60
               j = j + 1;
           end
           if id (i)==1
64
               j=j+4;
           end
           if id (i)==2
66
               j=j+9;
67
           end
68
      end
      V = Vd\_bias(bias\_point); \% this is the potential energy -q*Vds
70
      associated to the considered Vds
      %Utot=[-0.5*V Utot 0.5*V]; % total channel potential energy in
71
      function of Y
      Utot_av(bias_point) = mean(Utot); % arithmetic mean is performed
72
```

```
73
  end
74
75
_{76} Since the Utot_av evaluation is performed by using potential energy
  \% convention for signs, then it should be flipped to get its elements in
77
  % the correct order, accordingly with Vds array:
78
  Utot_av = fliplr(Utot_av); % it is still a potential energy (sign +
79
      instead of -)
80
  \% The index for which Vds=0 (equilibrium) is found and used in
81
      calculating
82 % the channel potential over applied potential ratio:
  equi_idex = find(Vds==0);
83
_{84} Since Vds array was already ordered and adjusted in sign to perform the
_{85} potential energy to electrostatic potential convertion, it stores
      negative Vds
_{86} values (lesser that Vds=0) in its left part, and positive Vds values (
      greater
  % than Vds=0) in its right part.
87
88
89 % Limit cases: a. equi_index=1 -> Vds>0 only
                  b. equi_index=NVd -> Vds<0 only
  %
90
91
92 % Set-up Vds=0 into Vds_Csd array at right index position:
93 Vds_Csd(equi_index) = 0; \% V
_{94}|% Set-up equilibrium values into Cs and Cd arrays at right index position
  Cs(equi\_index) = Cd_0; \% F
95
  Cd(equi\_index) = Cs_0; \% F
96
97
  \% Second loop on Vds electrostatic potentials: it is splitetd into two
98
      loops.
  % one on positive and one on negative Vds:
99
100
  % Positive voltage values:
101
  if equi_index ~= NVd % it is exectued only if there are positive Vds
      values:
       for bias_point = equi_index:1:(NVd-1)
103
           delta_Uch = abs(Utot_av(bias_point+1) - Utot_av(bias_point)); %
      in eV, it can be considered divided by -q thus in volts
           delta_Vds = abs(Vds(bias_point+1) - Vds(bias_point)); \% in V
105
           cap_ratio = delta_Uch/delta_Vds; \% this ratio equals the
106
      capacitive divider: Cd/(Ces+Cq) where Ces=Cs+Cd+Cg
           \% It is assumed a voltage division factor eta=0.5 such that
           % Cs=Cd
108
           \% An average quantum capacitance Cq value (between the two bias
109
           % points) is used for the calculation:
           Cq_av = abs(Cq(bias_point+1) - Cq(bias_point))/2; \% average Cq in
111
       \mathbf{F}
           Cd(bias\_point+1) = ((Cg+Cq\_av)*cap\_ratio)/(1-2*cap\_ratio); \% Cd
      for the current {\tt bias\_point}\,, in F since Cg and Cq are in F
           Cs(bias_point+1) = Cd(bias_point+1); % Cs for the current
      bias_point, in F since Cg and Cq are in F
```

```
114
           % Finally Vds_Csd is correctly updated using halway values of Vds
115
        array:
           Vds_Csd(bias_point+1) = (Vds(bias_point) + Vds(bias_point+1))/2;
       end
   end
118
   % Negative voltage values:
120
   if equi_index \sim = 1 \% it is exectued only if there are negative Vds values
       for bias_point = equi_index: -1:(1+1)
           delta\_Uch = abs(Utot\_av(bias\_point-1) - Utot\_av(bias\_point)); \%
123
       in eV, it can be considered divided by -q thus in volts
           delta_Vds = abs(Vds(bias_point - 1) - Vds(bias_point)); \% in V
           cap_ratio = delta_Uch/delta_Vds; \% this ratio equals the
       capacitive divider: Cd/(Ces+Cq) where Ces=Cs+Cd+Cg
           \% It is assumed a voltage division factor eta=0.5 such that
126
           % Cs=Cd
           \% An average quantum capacitance Cq value (between the two bias
128
           % points) is used for the calculation:
129
           Cq_av = abs(Cq(bias_point - 1) - Cq(bias_point))/2; \% average Cq in
130
       F
           Cd(bias\_point-1) = ((Cg+Cq\_av)*cap\_ratio)/(1-2*cap\_ratio); \% Cd
          the current {\tt bias\_point}\,, in F since Cg and Cq are in F
       for
           Cs(bias_point - 1) = Cd(bias_point - 1); % Cs for the current
132
      bias_point, in F since Cg and Cq are in F
133
           % Finally Vds_Csd is correctly updated using halway values of Vds
134
        array:
           Vds\_Csd(bias\_point-1) = (Vds(bias\_point) + Vds(bias\_point-1))/2;
135
136
       end
137
   end
138
   end
```

#### G.2.6 Gate resistance calculation

```
%% This function estimates the gate resistance Rg of a molFET:
% This function estimates the Rg value of the Metal-Oxide-Molecule (MOM)
% simply evaluating the electrical resistance of the dielectric layer
% material as R=(rho*L)/(W*H), where rho is the resistivity of the
% dielectric material chosen as oxide.
function [Rg] = Rg_calculator(Hrho_path, device_path, W, oxide);
% Input Data:
load(Hrho_path); % it stores tox, eox
xyz=load(device_path); % it stores the geometry of the molecule
```

```
_{15} if (oxide='ZrO2')
      \% ZrO2 resistivity min, max, avarege values expressed in Ohm*m
16
      rho_ZrO2_min = 3.16 e3;
17
      rho_ZrO2_max = 3.16 e10;
18
      rho_ZrO2_av = (rho_ZrO2_min + rho_ZrO2_max)/2;
19
  elseif(oxide='SiO2')
20
      % SiO2 resistivity min, max, avarege values expressed in Ohm*m
21
      rho_SiO2_min = 1e15;
      rho_SiO2_max = 1e19;
23
      rho_SiO2_av = (rho_SiO2_min + rho_SiO2_max)/2;
24
25
  end
26
  \% Findind the molecule length L which corresponds to the width of the
27
      oxide
28 % cross-section:
29 Y = xyz(:,3);
_{30} Y1=min(Y)-d1; Y2=max(Y)+dr;
31 Y=[Y1;Y;Y2]; % Y-axis is the transport axis
_{32} Lmol= Y(end) - Y(1); % (angstrom) molecule total length,
_{33} \% L includes also anchoring groups and space from gold contacts to
_{34} (% anchoring groups: it is the source to drain total length (from gold
_{35} \% contact to gold contact). L is in angstrom, but now it is converted in
     m:
  W_oxide = Lmol*1e-10; \% m, in meters
36
 % Findind the molecule width Wmol which correspond to the height of the
38
      oxide
39 % cross-section:
40 Z=xyz(:,4); % Z-axis is the transverse axis
_{41} Wmo\models max(Z) - min(Z); % (angstrom) molecule total max width
_{42} \% total dielectric layer width (as evaluated in laplace solver fortran90
      code):
  Wtot = Wmol + W; \% angstrom
43
  \% Wtot is converted to m:
44
45 H_oxide = Wtot*1e-10; \%m, in meters
46
47
 % dielectric layer area in (squared) meters:
48
49 Area = H_oxide*W_oxide; % m^2
50
_{51} % dielectric material length is the oxide thickness since it extends
_{52} |\% along the direction through which the current, although very small,
53 % should flow
_{54} L_oxide = tox*1e-10; %m, in meters
56 % Rg approximated estimation:
57 Rg = (rho_ZrO2_min*L_oxide)/Area; % Ohm
  end
```

#### G.2.7 Source and drain "dynamic" resistances calculation

```
1 % Source and Drain access resistances evaluation:
_{3} % This function evaluates the average Rs(Vds) and Rd(Vds) values for each
4 % considered Vds bias point. Small variations from equilibrium Vds=0 to
_{5} % first bias point (and so on for all the sequence of Vds value) are
_{6} (% considered, thus a linearized approximate model (Baldo page 99) is used
_{7} % Moreover the estimation is performed neglecting completely the
8 % temperature effects, and thus the thermal broadening and Fermi-Dirac
9 % functions, as explained in Baldo p.99.
_{10} % The first performed task is the estimation of average coupling factors.
_{11}|\% For each bias point an average coupling factor tau is considered for
     both
_{12} \% source and drain contacts. This tau_av value is the average of coupling
_{13} % factors for the energy values inside the considered bias window Vds (i.
     е.
 \% with energies between (Ef_equilibrium - muS) and (Ef_equilibrium + muD)
14
_{15} |% supposing a voltage division factor eta=0.5).
16
17
  function [Vgs_fixed, Vds, Rs, Rd, tauS_avVds, tauD_avVds] =
      Rsd_calculator(Hrho_path, HS_path, TEV_path, Cq);
18
 % electron charge:
19
  q = 1.60217662e - 19; % electron charge, C
20
 % Input Data:
22
  load(Hrho_path); % it stores Ef (equilibrium Fermi level of molecule-
23
      contacts system) and the energy array E
                   % and the Vds bias array Vd bias
24
  load (HS_path); % it stores the matrices taoHl, taoHr used to evaluate the
25
       total coupling matrices tauS, tauR
                 \% and the overlap matrix of device Sd and contact leads Sl
26
        Sr
  load (TEV_path); % it stores the energy values array E
27
28
  \% converting the polarity in order to get the applied voltage (voltage
29
     polarity convention):
  Vds = -fliplr(Vd_bias); \% V
30
  Vgs\_fixed = - Vg; \% V
31
32
 % output data structures allocation:
33
  tauS_avVds = zeros(1, NVd); \% NVd is the number of Vds bias points
34
  tauD_avVds = zeros(1, NVd); % NVd is the number of Vds bias points
35
_{36}| Rs = zeros(1, NVd); % NVd is the number of Vds bias points
_{37} Rd = zeros(1, NVd); % NVd is the number of Vds bias points
38
39 % For each bias point
40 for bias_point = 1:NVd % they are considered sequentially (convention of
       potential energy as in Vd_bias array !!)
                           \% -> at the end Rs and Rd are flipped !!
41
```

42	
43	bias window = Vd bias(bias point): % this is the bias window width in
10	
44	% The bias window is assumed to be centered around equilibrium Fermi
44	% level of contacts Ef plus Vc value i e from Datta eq. 7.3.11 p
40	174
	$\mathcal{V}_{c} = a^{2} + DOS(E - Ef)$ where Ef-acuilibrium Earmi level
46	70  Cd = q 2  z-bos(E-E1), where Elecquinibrium Fermi level,
47	% approximated with contact Fermi level: gold (111) is -9.5 ev
48	
49	% Contact Fermi Levels for the current bias point:
50	$muS = Ef + (bias_window./2); % Source Fermi Level$
51	$muD = Ef - (bias_window./2); \%$ Drain Fermi Level
52	
53	% Minimum and Maximum energy value to be considered in this bias
	point:
54	$\operatorname{Emin} = \min(\operatorname{muS}, \operatorname{muD});$
55	Emax = max(muS, muD);
56	
57	% the considered bias window:
58	considered E indeces = find (Emin $\leq E \& E \leq Emax$ ); %
	considered E indeces stores the indeces of interest
59	
60	% allocation of temporary variables:
61	tauS avE = zeros (1, length (considered E indeces)): % length (
01	considered E indeces) is the number of considered energy points in
	this biss window
60	tauD ave $= 2 \cos(1 - \log t) (\cos s) dered E indeces)$ (% length (
02	considered E indeces) is the number of considered energy points in
	this biss window
0.2	this bras window
64	for energy point $-1$ : length (considered E indeces)
65	for energy_point = 1. rengen (compacted_ii_indeces)
00	opergy index - considered E indeces(energy point); % current
00	index to be used in operative and F
	and to be used in energy array by a compart value of energy
67	energy_value = E(energy_index), % current value of energy
68	
69	$taus = (energy_value * s1) - taohi;$
70	tauD=(energy_value*sr)-taonr;
71	
72	% tauS, tauD are the source and drain coupling matrices for the
73	% considered energy value. They are expressed in function of
74	% contact leads overlapping matrices SI, Sr.
75	% taoS, taoD are matrices of dimension 27xdim where 27 is the
76	% number of basis functions (i.e. eigenvalues/eigenstates)
77	% considered for the gold FCC (111) 13 atoms contact leads, while
78	% dim is the number of basis fuctions (i.e. eigenvalues/
	eigenstates)
79	% considered for the device. The device Hamiltonian e.g. is of
80	% dimensione dimxdim while the contact lead Hamiltonian is of
81	% dimensione 27x27. The two coupling matrices tau are of course
	of
82	% dimension 27xdim. For describing the contact leads ths are used
83	% 27 energy levels (energy eigenvalues and thus 27 eigenstates)
~~	$\cdots$

% combined together following the EHT method. Analogously the 84 % device employs dim energy levels (energy eigenvalues and thus 85 % dim eigenstates). 86 % For each couple of contact lead - molecule/device states there 87 i s % a scalar value of tau, thus in total there are 27xdim numbers, 88 % stored within a molecule. 89 90 % In the following the average of ALL these 27xdim different tau 91 i s % considered, it is the average tauS\_avE or tauD\_avE (for the 92 current energy point):  $tauS_avE(energy_point) = mean(tauS, 'all');$ 93  $tauD_avE(energy_point) = mean(tauD, 'all');$ 92 end 95 96 % At this point a further average is considered: 97 % The average tauS\_avVds and tauD\_avVds for the current bias point 98 are % then evaluated (they are the average of all tauS\_avE and tauD\_avE 99 % elements respectively): 100  $tauS_avVds(bias_point) = mean(tauS_avE); \%$  averaging wrt to energy values (inside the current bias window) tauD\_avVds(bias\_point) = mean(tauD\_avE); % averaging wrt to energy values (inside the current bias window) end 104 % The calculated tauS\_avVds and tauD\_avVds arrays correspond actually to 106 % (average) coupling factors in function of the applied potential energy: 107 % Vd\_bias was indeed used. 108 109 % Now they are flipped to make them corresponding to applied voltage instead:  $_{110}|\%$  Vds array define above (voltage convention). Thus they are simply flipped: tauS\_avVds = fliplr(tauS\_avVds); % such that Cd(Vds) and not Cq(Vd\_bias) 11211  $tauD_avVds = fliplr(tauD_avVds);$ 113 114 12% Up to now tauS\_avVds, tauD\_avVds are coupling factors expressed in eV, i.e. they are energies 116 % indeed they are part of the total devire-reservoir Hamiltonian. Now thev % are converted in coupling times (escaping rates): 117 118 h\_bar = 6.58211928e-16; % eV\*s, reduced Plank's constant 119  $tauS_avVds = h_bar./abs(tauS_avVds); \% s$ , absolute value because of the 120 physical meaning of time interval  $tauD_avVds = h_bar./abs(tauD_avVds); \% s$ , absolute value because of the physical meaning of time interval  $_{123}$  % Finally the Rs(Vds) and Rd(Vds) values for the all the considered bias

```
124 % point are evaluated (Baldo p.99):
125 Rs = tauS_avVds ./ Cq; % element-wise division is performed
126 Rd = tauD_avVds ./ Cq;
127 end
```

### G.3 Sensor time constant and response time estimation

#### G.3.1 MatLab code for the time constant estimation

```
%% This script estimates the time constant (step response) of a molecular
       device:
  clear all
3
  close all
4
  clc
5
  \% Once the simulations on Cadence Virtuoso are conluded, please export
      data
 % in .csv format file (since ".matlab" format is not recognized here).
8
     Then
 % follow the instructions provided in the command window... =)
9
 DataTable = readtable('DATA_Vd_Vs_Ids_simTrans_AV3curves.csv');
 %DataTable = readtable('Vd_Vs_Ids_DATA_Vc0d65.csv');
12
13
14
  %%%%
           NO MORE USER'S INPUTS %%%%
16
17
  DataNames = DataTable. Properties. VariableNames;
  Data = table2array(DataTable);
18
  DataSize = size(Data);
19
20
  %% Plot data and choice of curve:
21
  string_to_be_displayed = sprintf('\nPlots are generated automatically.\n'
23
      );
  disp(string_to_be_displayed);
24
25
  for index = 1:2: DataSize(2)
26
  figure
27
28 hold on
  grid on
29
  plot(Data(:,index),Data(:,index+1),'LineWidth',2.0);
30
  VariableName = char(DataNames(index));
31
<sup>32</sup> VariableName = VariableName (1: end - 1);
33 title_string = sprintf('Imported data: %s', VariableName);
```

```
34
35 |%XaxisString = string(DataNames(index));
_{36} %YaxisString = string (DataNames(index+1));
37 % title_string = sprintf('Imported data: % vs % s', XaxisString,
      YaxisString);
38
  title(title_string);
39
  xlabel('time (s)');
40
  ylabel ('Voltages (V) or Currents (A)');
41
  set(gca, 'LineWidth', 2.0, 'FontSize', 15.0);
42
43
  string_to_be_displayed = sprintf('Press "%g" to proceed in time constant
44
      estimation for the "%s" quantity.', index, VariableName);
  disp(string_to_be_displayed);
45
  end
46
47
  %%%%%%% INPUT INDEX AND PROCEED WITH TIME CONSTANT ESTIMATION:
48
49
  index = input('>> ');
50
  if (index > DataSize(2)) % wrong value
52
      string_to_be_displayed = sprintf('Value "%g" is NOT allowed. Please
53
      restart.(n', index);
      disp(string_to_be_displayed);
54
  elseif (rem(index, 2) = 0) % wrong value, since introduced index is even
56
      string_to_be_displayed = sprintf('Value "%g" is NOT allowed. Please
      restart.\n', index);
      disp(string_to_be_displayed);
58
  elseif (rem(index, 2) == 1)
      VariableName = char(DataNames(index));
61
      VariableName = VariableName (1: end - 1);
62
      string_to_be_displayed = sprintf('You have chosen: %s', VariableName)
      disp(string_to_be_displayed);
64
      string_to_be_displayed = sprintf('Time constant is now found by means
      of a linear interpolation.');
      disp(string_to_be_displayed);
66
      string_to_be_displayed = sprintf('Now a suitable time interval, for
67
      exponential transient linear interpolation, should be selected.');
      disp(string_to_be_displayed);
      string_to_be_displayed = sprintf('Please insert an initial time
69
      instant for interpolation of transient: ');
      disp(string_to_be_displayed);
      InitialTimeTrans = input('>> ');
71
      string\_to\_be\_displayed = sprintf('Now insert a final time instant for
      interpolation of transient: ');
      disp(string_to_be_displayed);
      FinalTimeTrans = input('>> ');
74
      string_to_be_displayed = sprintf('Now insert an initial time instant
      for interpolation of regime steady state region: ');
      disp(string_to_be_displayed);
76
```

```
InitialTimeSS = input('>> ');
77
       string_to_be_displayed = sprintf('Now insert a final time instant for
78
       interpolation of regime steady state region: ');
       disp(string_to_be_displayed);
79
       FinalTimeSS = input( >> ');
80
81
       if (FinalTimeTrans < InitialTimeTrans | FinalTimeSS < InitialTimeSS)
82
      % error
       string_to_be_displayed = sprintf('Input error: Usually a final time
83
      instant should be greater than an initial one. =)');
       disp(string_to_be_displayed);
84
       elseif (InitialTimeSS < FinalTimeTrans) % error</pre>
85
       string_to_be_displayed = sprintf('Input error: Usually the steady
86
      state is achieved after a transient. =)');
       disp(string_to_be_displayed);
87
       else
88
           NewTimeAxis = linspace(Data(1, index), Data(end, index), 10000);
89
           timeindex = find ( InitialTimeTrans < Data(:, index) & Data(:, index
90
      ) < FinalTimeTrans );
           \% first order polynomial fit (least-squares is used) for
91
      exponential transient:
           Pexp = polyfit (Data(timeindex, index), Data(timeindex, index+1), 1)
92
           \% Evaluate the fitted polynomial Pexp in the whole time interval:
93
           StraightLine = polyval(Pexp, NewTimeAxis);
94
95
           SSindex = find (InitialTimeSS < Data(:,index) & Data(:,index) <
96
      FinalTimeSS );
           \% first order polynomial fit (least-squares is used) for SS=
97
      steady state:
           Pss = polyfit (Data(SSindex, index), Data(SSindex, index+1), 1);
98
           % Evaluate the fitted polynomial Pss in the whole time interval:
99
           StraightLineSS = polyval(Pss, NewTimeAxis);
100
           %find the intersection point (i.e. time constant) between the
102
      straight lines:
           error = abs(StraightLine - StraightLineSS); % error array
           minimum_error = \min(\text{error}); % minimum error corresponds to
104
      interstection point
           TimeConstIndex = find(error == minimum_error); \% the value for
105
      which the error is minimum is the intersection point, i.e. time
      constant
106
           % The found time value is saved and then displayed:
           TimeConstant = NewTimeAxis(TimeConstIndex) - InitialTimeTrans; %
108
      given by the difference the time value in intersection point and
      transient initial time instant
           string\_to\_be\_diplayed = sprintf('\nFound time constant value:
      Tconst=%g s', TimeConstant);
           disp(string_to_be_diplayed);
           string_to_be_diplayed = sprintf('Conventional transient duration:
111
       7*Tconst = \% g s', 7*TimeConstant);
           disp(string_to_be_diplayed);
112
```

```
string_to_be_diplayed = sprintf('Minimum period: 2*7*Tconst = 14*
113
      Tconst = \%g s', 14*TimeConstant);
           disp(string_to_be_diplayed);
           string_to_be_diplayed = sprintf('Maximum operating frequency:
      (14*Tconst)^{-1} = \% Hz', (14*TimeConstant)^{-1});
           disp(string_to_be_diplayed);
           % Plot:
           figure
           grid on
120
           hold on
121
           plot (Data (:, index), Data (:, index+1), 'LineWidth', 2.0);
           plot (NewTimeAxis, StraightLine, 'Color', [0 0 0]/255, 'LineWidth'
        1.25); % black curve
           plot (NewTimeAxis, StraightLineSS, 'Color', [130 130 130]/255, '
      LineWidth', 1.25); %gray curve
           plot(NewTimeAxis(TimeConstIndex), StraightLine(TimeConstIndex), '
      or', 'MarkerSize', 10); % plot the intersection point
           VariableName = char(DataNames(index));
126
           VariableName = VariableName(1:end-1);
127
           title_string = sprintf('Time constant evaluation: %s(t)',
128
      VariableName);
           title(title_string);
           xlabel('time (s)');
130
           ylabel ('Voltage (V) or Current (A)');
           egend('I_{OS})', 'subthreshold linear interpolation', '
      above threshold linear interpolation ', 'Location', 'Best');
           set(gca, 'fontsize', 14);
133
       end
134
135
136
   else
       string_to_be_displayed = sprintf('Something went wrong during input
137
      acquisition. Please restart.(n');
       disp(string_to_be_displayed);
138
139
  end
140
```

#### G.3.2 MatLab output figures for time constant estimations

In this section the figures generated with the *MatLab* code for the time constant estimation reported in the previous section are reported. The input data are the *Cadence* simulated curves reported and discussed in section 9.8. Such curves are the same plotted in these figures, in which there are also the interpolating straight lines. The time constant are determined by means of a graphical approach, the red circles highlight the intersection points between the exponential interpolating straight line and the time axis (or the steady state region/value).



Figure G.1: Drain voltage in function of time for the circuit of figure 9.20. The interpolating straight lines are also shown, and the red circle highlight their intersection point, useful to determined graphically the time constant.



Figure G.2: Source voltage in function of time for the circuit of figure 9.20. The interpolating straight lines are also shown, and the red circle highlight their intersection point, useful to determined graphically the time constant.



Figure G.3: Drain current in function of time for the circuit of figure 9.20. The interpolating straight lines are also shown, and the red circle highlight their intersection point, useful to determined graphically the time constant.

## G.4 MatLab code for the interaction time estimation

In the following is reported a *MatLab* code for the interaction time estimation and also for the sensor time constant calculations in the single-pole approximation.

```
clear all
  close all
2
3
  clc
  %
4
  %% Time constant estimation and velocity particle estimation:
  % constants:
9
_{10}\left|\mathrm{M}=~303.26\,\mathrm{e}-3
ight; % kg/mol , lead sulfate molecular mass (the mass of one
      mole of lead sulfate)
 R = 8.31446261815324; \% J/(mol*K), (universal) gas constant, it is: R =
      Na*kB where Na = Avogadro's number and kB = Boltzmann's constant
  T = 300; \% K , temperature in kelvin
13
  % Root Mean Square velocity:
14
  v_{rms} = sqrt( 3*R*T/M ); \% m/s
15
16
 % Most probable (or mode) speed:
17
|v_p = sqrt(2/3) * v_rms; \% m/s
19
20 % Arithmetic mean or average velocity:
```

G29

```
v_{av} = (2/(sqrt(pi))) * v_p; \% m/s
 % INTERACTION SPACE:
23
  space_of_interaction = 2*0.24e-9; % m , factor 2 because it moves closer
24
     and then it moves away
25
  % Interaction times:
26
  Time_interact_rms = space_of_interaction/v_rms;
27
  Time_interact_p = space_of_interaction/v_p;
28
  Time_interact_av = space_of_interaction/v_av;
29
 \% From other scripts:
31
 Cs_Vc0d65_0d8V = 2.7844e - 21; \% F
32
 Cd Vc0d65 0d8V = Cs Vc0d65 0d8V;
33
 Rd Vc0d65 0d8V = 1250710; % ohms
34
  Rs Vc0d65_0d8V = 312600; \% ohms
35
36
 \% in single pole approximation (i.e. non-interacting S,D):
37
  tau_Vc0d65_D = Rd_Vc0d65_0d8V*Cd_Vc0d65_0d8V;
38
  tau_Vc0d65_S = Rs_Vc0d65_0d8V*Cs_Vc0d65_0d8V;
39
40
 % DATA OUTPUT & DISPLAY:
41
  string_to_be_displayed = sprintf("The time interval during which the
42
     PbSO4 interacts with the sensor is estimated to be:");
  disp(string_to_be_displayed);
43
  string_to_be_displayed = sprintf("(from root mean square velocity)
44
      Interaction time = %g s\n", Time_interact_rms);
  disp(string_to_be_displayed);
45
  string_to_be_displayed = sprintf("(from most probable velocity))
46
      Interaction time = \%g s\n", Time_interact_p);
  disp(string_to_be_displayed);
47
  string_to_be_displayed = sprintf("(from average velocity) Interaction
48
     time = %g s \ r, Time_interact_av);
  disp(string_to_be_displayed);
49
  string_to_be_displayed = sprintf("----");
50
  disp(string_to_be_displayed);
  string_to_be_displayed = sprintf("The time constant of the source side of
       the sensor, in the single pole approximation, is estimated to be:");
  disp(string_to_be_displayed);
53
  string_to_be_displayed = sprintf("tau @ Source = %g s\n", tau_Vc0d65_S);
<sup>55</sup> disp(string_to_be_displayed);
  string_to_be_displayed = sprintf("The time constant of the drain side of
56
      the sensor, in the single pole approximation, is estimated to be:");
57
  disp(string_to_be_displayed);
  string_to_be_displayed = sprintf("tau @ Drain = %g s\n", tau_Vc0d65_D);
58
  disp(string_to_be_displayed);
59
```

### G.5 LUT-based model (gate case): verilogA code

In the following is reported the *verilogA* code for defining the foure terminal sensor by means of LUT-based model, the gate is also considered. The data are stored in the *.txt* 

file named: "C60\_PbSO4\_Gate\_sensor\_ATK.txt" that is reported in the next section. Within the code the description of the *.txt* data file is reported; the file is omitted for brevity.

```
// VerilogA for SensorResponseTime, PbSO4_Gate_Sensor_LUTdevice, veriloga
2
3
  `include "disciplines.h"
  `include "constants.h"
6
  module PbSO4_Sensor_LUTdevice(G,D,S,N_PbSO4);
7
8
  // "N_PbSO4" is a fake input contact, 0 means no PbSO4 molecule, 1 means
9
      that there is 1 PbSO4 molecule nearby the channel, 2 means that there
      are 2 PbSO4 and so on...
  // the LUT data are simulated in Quantum-Wise ATK and the curves with
10
      different "N_PbSO4" are previously obtained in ATK
  input N_PbSO4;
  electrical N_PbSO4; // input type "electrical" is chosen for convenience
13
      , to perform easily transient analyses
14
15 input G;
  electrical G; // Gate
16
17
18 inout D;
  electrical D; // Drain
19
20
  inout S;
21
  electrical S; // Source
22
23
24
     analog
25
        begin
26
  // 3rd order polynomial spline interpolation // first row is V(N_PbSO4, S)
      , second is V(G,S)\,, third is V(D,S) and fourth is I\,(D,S)
28
      I(D,S) \ll  table model(V(N PbSO4,S), V(G,S), V(D,S), "
29
      C60_PbSO4_Gate_sensor_ATK.txt", "3L,3L");
//I(D,S) <+ $table_model(V(G,S), V(D,S), "bio_dati.txt", "1,1");
30
31
      end
32
33
  endmodule
34
```

G32

# Appendix H Chapter 10 - Additional images, graphs and material

Details are provided directly in the captions.



**Figure H.1:** *I-V* characteristics with and without the NO molecule both in the case of the wire sensor and in the case of gated one (EHT method).


Figure H.2: Current variations in the gate sensor with both the lead sulfate  $PbSO_4$  and the nitric oxide NO, for all the (main) possible orientations of such molecules. Notice the behavior at 0.8 V.



Figure H.3: Sensor maximum deviation from linearity in function of the applied bias, for different NO concentrations. It is the maximum difference between the straight line interpolating curve and the spline  $3^{rd}$  order interpolating curve. Notice the low error at 0.8 V.



Figure H.4: Current values for different NO concentrations and for  $V_D = 0.8$  V. Black circles: simulated values; blue curve: cubic  $3^{rd}$  order spline interpolation; red/orange: linear interpolation.



Figure H.5: Current values for different NO distances from the sensor and for  $V_D = 0.8$  V. Black circles: simulated values; blue curve: cubic  $3^{rd}$  order spline interpolation; red/orange: linear interpolation.