POLITECNICO DI TORINO

Master's degree in
Electronic Engineering

Master Thesis

Investigation of molecular properties to perform nanocomputing

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Abstract

The need to have more performing electronics devices led the researches to scale down transistors more and more. However, when very small sizes are reached, some problems arise which led to exploration of new technologies in digital electronics. Among them, the most promising one seems to be Quantum-dot Cellular Automata (QCA), an approach in which the device is not used as a current-channel switch, but as a charge container where binary information can be represented. The basic unit of QCA device is a cell composed by four dots (seen as a vessels to host the charge) and the information is encoded depending on where the charge is localized. For the implementation of QCA paradigm, the molecular cell (Molecular Quantum dot Cellular Automata - MQCA) is the most promising trend: the molecules involved in this technology have redox centers (an atom or a group of atoms that can gain or loose an electron) acting as quantum dots.

In this work, for the study of the molecular properties, the MosQuiTo methodology has been used: for the computational chemistry analysis a series of *ab initio* simulations have been performed in different conditions and several figures of merit have been evaluated (Aggregated Charge, Electric field generated by molecule and so on). The aim is then to find the best molecules suitable for QCA purposes: in order to do that, a MATLAB tool interfacing with ORCA able to characterize the molecules has been used.

A characterization of the monostable Bis(trimethylsilyl) Sulfide and its others form (the molecule with thiol, long thiol ecc...) has been performed and the results have been studied: Aggregated Charge, Dipole moment and SCF Energy are some of the outputs of the tool. For having an idea of the impact of the clock on the system, even molecules with 3 DOT have been simulated. Bistable Diallyl butane has been taken as example for the study of the bistable molecules and methods.

The idea developed in this thesis is that to make a single phthalocyanine molecule as a full QCA cell. The phthalocyanines are organic compounds composed of four isoindole units linked by a ring of nitrogen atoms; the peculiarity of this class of molecules is that they lies in on a plane having a fourfold symmetry; the aim is then to make each isoindole group as a quantum dot of the QCA cell. In order to achieve this goal Hydrogenphthalocyanine (H_2Pc) molecule has been characterized and various disposition of charges around the molecule have been analyzed for emulate the presence of a driver or another molecule. From the simulations, it came out that the best charge disposition is with the charges along the two diagonals of the molecule: a relative good switching has been observed. In addition, an analysis on the polarizability on the most important phthalocyanines has been performed; more than 70 metal phthalocyanines have been prepared (substituting the two central hydrogen atoms with a metal atom, for example Cu, Zn, Co) and by stimulating the molecules with a proper electric field it has been studied their tendency to create a dipole moment. From the analysis carried out, it has been shown that in general the presence of metals improves the molecules polarizability, in particular the highest values of the isotropic polarizability have been encountered in the reduced forms of the molecules.

The overall results obtained in this work seems to be promising and renew the will to investigate further these aspects.

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Chi dice che è impossibile non dovrebbe
disturbare chi ce la sta facendo.
[A. EINSTEIN]

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Chapter 1

Introduction and background

1.1 CMOS limits

The need to have more performing electronic devices with high switching frequency led the researches to scale down transistors more and more [4].
In 1965 Gordon Moore, the Chief Founder of Intel Corporation, predicted that the number of transistors in an integrated circuit (IC) double every 18 months [10] and that the minimum dimension of these devices (calculated as the channel length) reduces of 30% every 3 years. Nowadays, the current dimension of a CMOS is of an order of few nanometers.
However, when such sizes are reached, some problems arise: the first is related to technology (lithography), the second regards quantum-mechanical effects and the third is related to power dissipation [5]. Focusing on this last point, scaling down devices led to an increase of leakage current making difficult to dissipate it and the consequence is the heating of the device.
To overcame these problems, new trends are explored in digital electronics: one of them is the so called Beyond CMOS. The International Roadmap for Devices and Systems (IRDS) refers to Beyond CMOS as the possible future digital logic technologies beyond the CMOS scaling limits; the aim is to introduce new devices with different physical behaviors with respect classical CMOS technology having low power application, high speed and high density characteristic. The new alternate devices includes Carbon Nanotube Transistors, Single Electron Transistors, Resonant Tunnelling Devices, Quantum Cellular Automata, spin transistors, superconducting electronics, and molecular electronics. Among them, the most promising one seems to be Quantum dot Cellular Automata (QCA), having high switching frequency associated to the reduced power dissipation [7] [14].

1.2 Quantum-dot Cellular Automata

The approach of Quantum-dot Cellular Automata (QCA) is to use device not as a current-channel switch but as a structured charge container where binary information can be represented.
The two main principles at the base of this technology are:
1) encode information depending on where the charge is localized;

2) use quantum dot as a "vessel" to host the charge.
The basic unit of a QCA device is a cell composed by four dots.

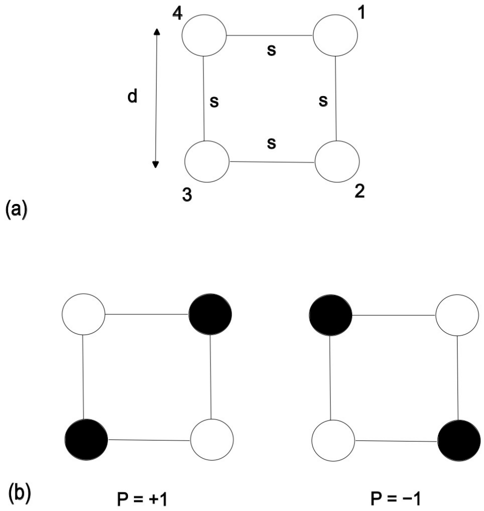

Figure 1.1. Basic four-site cell: (a) The geometry of the cell: s is the tunneling energy between two neighboring sites, while d is the near-neighbor distance. (b) Coulombic repulsion causes the electrons to occupy antipodal sites within the cell. The two bistable states result in cell polarization of P=+1 and P=-1.

In Figure 1.1 (a) it is shown the basic elementar element of a QCA device: d is the distance between two different dots, while s is the tunnelling energy between two neighboring sites. Two different configurations are possible when two electrons are introduced into the cell; they will occupy one dot each and due to Coulombic repulsion they will occupy one of the two diagonals [1]. There are two possible stable states depending on the position of the electrons and thanks to that it is possible to encode binary information: in Figure 1.1 (b) it can be seen the cell polarisation P = 1 (corresponding to the logic '1') and P = -1 (corresponding to the logic '0'). The two configurations are energetically equivalent.

1.2.1 Principle of information propagation

One of the advantages to use QCA technology is the ease to propagate information.

In Figure 1.2 it is shown a simple QCA wire in which the first cell is forced to stay in '1' logic state while the others are "free to move" in any others state. However, thanks to Coulomb repulsion, the electrons tend to stay as far as possible each others both inside each cell and between a cell and the other. Therefore the system reach the lowest energy state and then also the others cells will follow the same configuration of the first one. The cells influence each other and through coupling it is possible to propagate information along the wire [8].

It is important to underline some crucial aspects; there is no movement of the charges

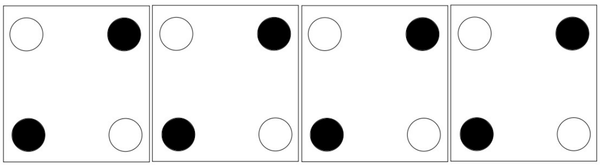

Figure 1.2. QCA wire.

between a cell and the others but the electrons move only inside the same cell through tunnel effect among the dots (between a diagonal and the other). Then, there is no power dissipation among the cells but the energy needed is the only required to switch the cells between the two configurations ('1' and '0'). Such energy is very small ($1 * 10^{-20}$J) if compared with that of a minimum size transistor switch ($1 * 10^{-18}$J), and this is one of the most important advantage of this technology which make QCA a low power technology trend.

1.2.2 QCA devices

By using different physical arrangements of the cells, one can construct different types of QCA devices [19]. In Figure 1.3 it is shown the fundamental QCA logic device, the three-input majority voter; the output encodes the majority of the input logic values and the central cell (also called "device cell") is where the computation takes place. In the device cell the position of the electrons is the one that has the minimum energy (the most stable state) and as a consequence also the output follow the same configuration.

In the example of Figure 1.3, input A = '1', input B = '1', input C = '1' and, as expected, also the logic value of the output cell is '1'.

A	B	C	OUT
0	0	0	0
0	0	1	0
0	1	0	0
0	1	1	1
1	0	0	0
1	0	1	1
1	1	0	1
1	1	1	1

Table 1.1. Majority voter Truth table

In Table 1.1 it is shown the entire Truth table of the Majority voter. By seeing these results, an important consideration can be done: if one input cell is forced to '0' logic

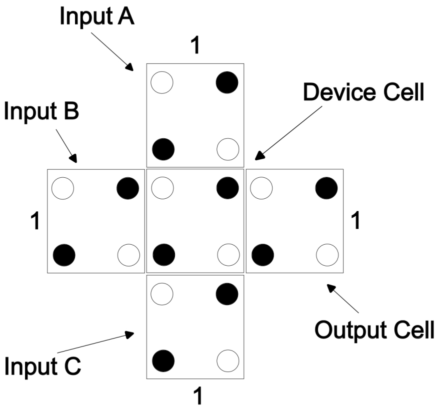

Figure 1.3. Three-input majority voter.

value (for example input A) the Majority voter become an AND gate, while if one input cell is forced to '1' logic value the Majority voter become an OR gate. In this sense, the Majority voter represents the fundamental device of the QCA logic. In Table 1.2 and 1.3 are represented, respectively, the Truth table of AND gate and OR gate.

B	C	OUT
0	0	0
0	1	0
1	0	0
1	1	1

Table 1.2. AND Truth table (with A=0)

Another important QCA device is the inverter (Figure 1.4); the antialignment of the input and output polarizations is a simple consequence of the mutual repulsion between electrons [19]. In the example, the input cell is forced to '1' logic value and, as expected, the output is '0'.

With Majority voter and inverter it is possible to have the full Boolean logic gate set and by starting from these components more complex logic can be designed, even simple microprocessor by using QCA paradigm [9].

B	C	OUT
0	0	0
0	1	1
1	0	1
1	1	1

Table 1.3. OR Truth table (with A=1)

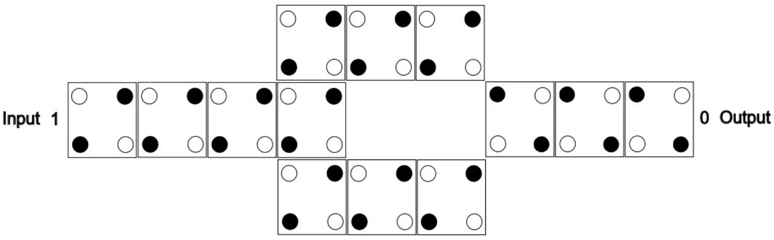

Figure 1.4. QCA inverter.

1.2.3 QCA clocking

In a QCA wire it is important to ensure the correct information propagation. For this purpose, it is convenient to enrich the cell with two further dots, as it can be seen in Figure 1.5.

In addition to '1' state and '0' state, a six-dot cell has also a "Null" state; here there is no information stored and it is possible to reach this state by applying a proper signal to the cell, called enable. The enable is an external signal (which can be for example an electric field) and when it is applied, forces the cell to "Null" state (or reset); the reset case is an unstable situation (due to the fact that the system does not have the minimum energy) and, indeed, when this signal is released, the cell goes in one of the two stable states ('1' or '0') depending on the configuration of the neighboring cells. In this last case the charges are trapped and there is an high potential barrier which prevents the electrons to overcame the tunnel energy to go in another state.

Another advantage to use six-dot cell regards energy consideration; to go from '1' state to '0' state (or viceversa) a certain energy is needed. There are two possible choices: the first is to go directly from '1' to '0', while the second is to pass first from an intermediate state ("Null" state). This last choice is the best, because the total energy needed is smaller than the direct case.

To properly propagate the information in a long wire a clocking system is needed for avoid

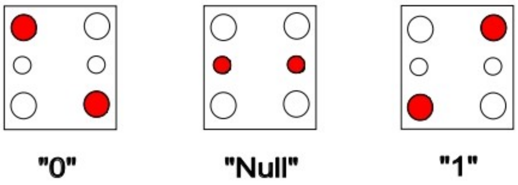

Figure 1.5. Schematic of six-dot QCA cells. A cell with six quantum dots (black circles) and two electrons (red discs) is shown in three electronic states: ’0’, “Null”, and ’1’.

possible mistake which can corrupt the information. In general, the clock changes the potential barrier among the dots, favouring or inhibiting the possibility for the electrons to move thanks to tunnel effect. The typical clock of a QCA system is composed by four phases, as shown in Figure 1.6.

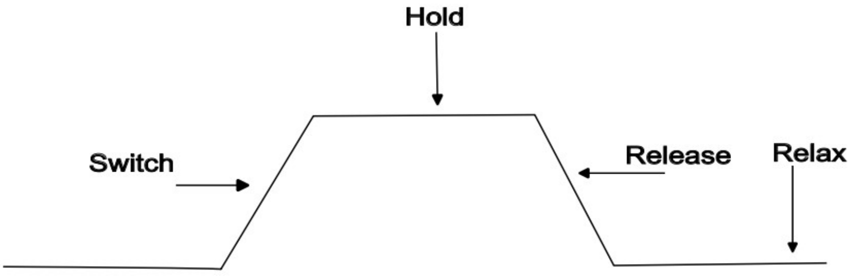

Figure 1.6. Clock Phases of QCA.

The first phase is Switch: the potential barrier is increased and the cell goes from the NULL state to one of the two stable state (’1’ or ’0’) depending on the neighboring cells.
The second phase is Hold: the potential barrier is kept high, in this way it is possible to preserve the logic state because the electrons can’t leave the dots.
The third phase is Release: the potential barrier decreases and the charges are forced to go in the NULL state.
The fourth phase is Relax: the potential barrier is kept low to avoid the possibility for electrons to escape from the dots and the NULL state is maintained.
In Figure 1.7 it is shown a simple clocked QCA wire.

In the example the driver is forced to stay in ’0’ logic state and when the clock is in

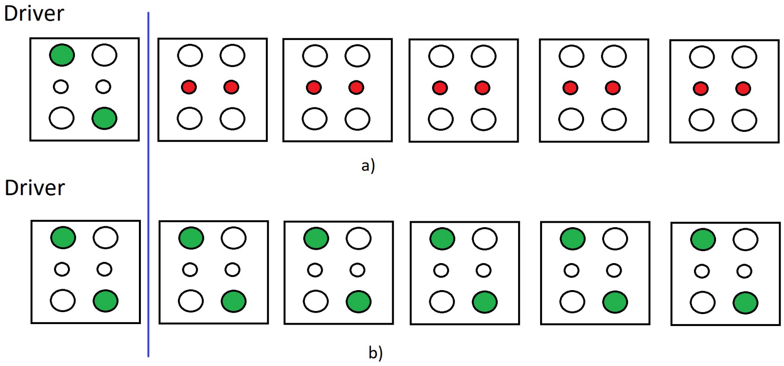

Figure 1.7. QCA wire. a) The clock is in the Relax phase and all the cells (except the driver) are in the NULL state. b) The clock is in the Hold phase and the charges are free to move among the dots. The cells follow the same configuration of the driver.

the Relax phase, all the cells are in the NULL state (Figure 1.7 (a)). If instead, the clock switches in the Hold phase the charges are free to move among the dots, and the cells follow the same configuration of the driver. This is the way with which the information is transmitted and the propagation direction is assumed to be from left to right, then the code stored in the driver passes to the right side of the wire.
With this configuration a problem can arise: if the wire is very long, when the clock switches from Relax to Hold, the last cells on the right can change their state before that the correct signal arrives, because the signal propagation is slower than the cells reaction. There is the possibility that they go in the opposite state and then the information at the end of the wire is wrong.
The solution used to avoid this problem is to organize the circuit in zone, in which each zone has a limited number of cells each of that having an independent enable (clock). In Figure 1.8 (a) it is shown a QCA wire divided in four clock zones composed by three cells each; having only few cells, there are no problems related to cells coupling and the information is properly transmitted. In figure 1.8 (b) it is shown the clock cycle (switch, hold, release and relax) in the four regions; as it can be seen in a wire composed by four clock zones, from a region to the next, the clock shifts by a quantity equal to $\pi/2$ and, by having this scheme, the information stored by the driver is then transmitted to the output in four time step (t1, t2, t3, t4). In Figure 1.8 (c) it is shown, at each time step, the propagation of the signal in the wire, pointing out the values assumed by the cells. After a clock cycle, at time t4, the information is transmitted to the end of the wire.
In this context it is also possible the implementation of the "concept of pipeline"; for example, in time step t4, the driver can eventually propagate another signal (clock region 1 in switch phase) because the previous information has already been transmitted. In this way the throughput of the device increases.

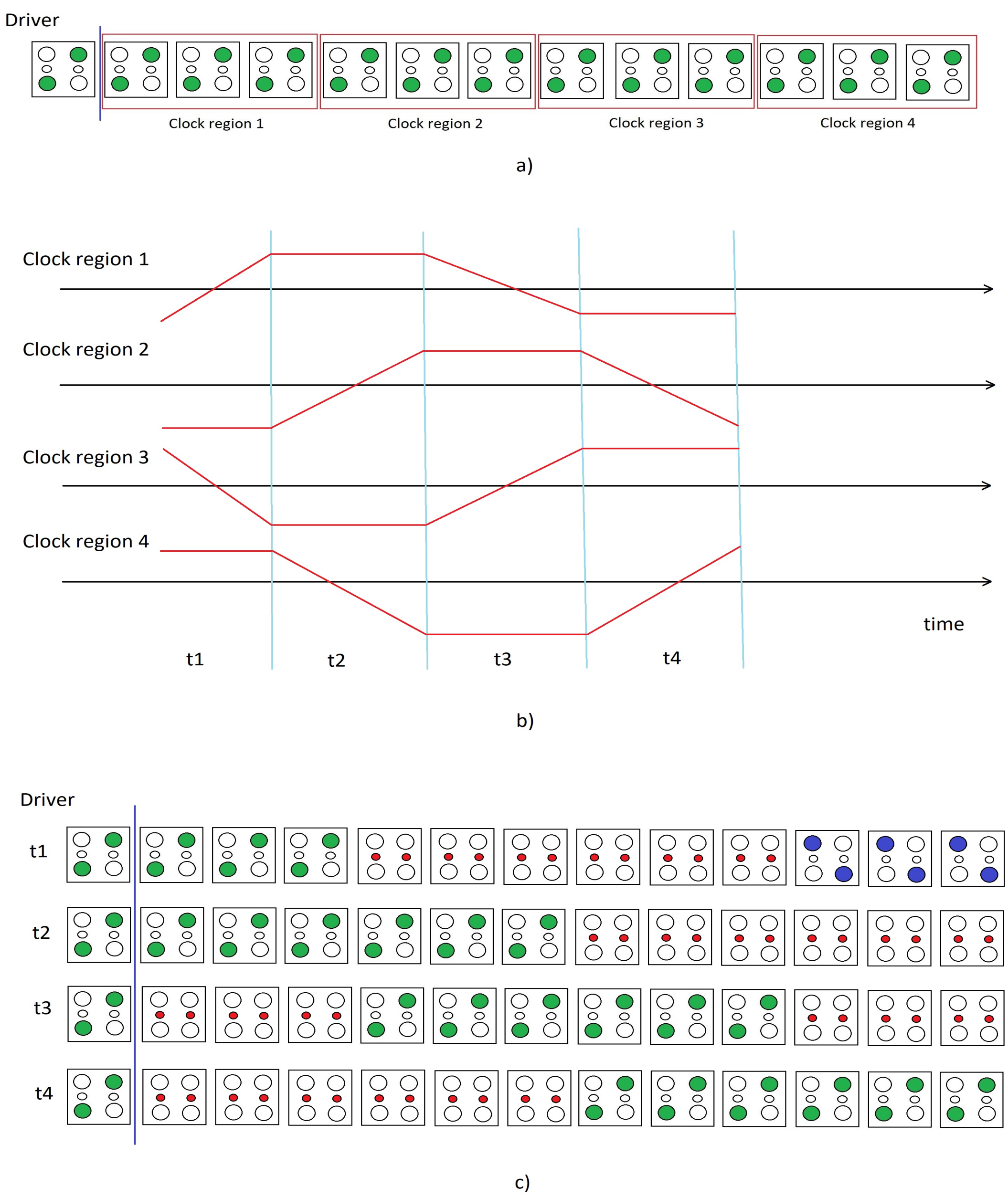

Figure 1.8. QCA clock scheme. a) QCA wire divided in four clock region each having an independent clock. b) The clock cycle. c) Propagation of the information in a clocked QCA wire.

To summarize the items seen so far:

- in QCA technology the aim is to switch a cell (from a stable state to another) spending the lowest energy possible, so assuming low potential barrier between the two configurations.
- On the other hand it is needed that the logic values stored by the cells are stable and then it is assumed high potential barrier between the two configurations for avoid undesirable switch.
- Direction of information propagation is assumed (for example from left to right).
- To assure correct information propagation the cell is enriched with two further dots (six-dots cell).
- The circuit is organized in zone (each of that with a certain number of cells).
- Each zone has a specific clock applied in a well defined sequence (information propagates in pipeline).

1.3 Molecular Quantum-dot Cellular Automata (MQCA)

For the implementation of QCA paradigm there are four possibilities: Metal-Island QCA, Semiconductor QCA, Molecular QCA and Magnetic QCA [7]. However, according to the Lent theory, the best implementation seems to be the molecular cell [3]; working with molecule, there are some advantages:

- it is possible to work at room temperature (while for example for the metallic implementation only very low temperatures are admitted).
- They are very small, the cell size is 20 to 30Åper side and predicted MQCA device densities are of order 10^{14} per cm^2 for $1nm^2$ devices [9].
- The molecules have self assembly characteristic which permits the production of uniformly sized devices.
- Power consumption is very low and the switching frequency is very high (>> 10 THz).

A standard MQCA device is represented by a group of molecules having redox centers acting as quantum dots [11]. A redox center is an atom or a group of atoms inside a molecule that can gain an electron or loose one without breaking the bonds [9]; the bridging ligands, instead, which connect one part of a molecule to another, act as tunneling paths.
The typical QCA six-dots cell is composed by two “V”-shaped three-dot molecules [18]; in Figure 1.9 it is shown a schematic representation of a molecule used for QCA purpose: the circles represent the dots while the straight lines represent the bonds.

In this example there are three redox centers and the logic encoding is obtained thanks to the localization of the oxidation/reduction charge on one of the molecule dots; in this way it is possible to encode ’1’, ’0’ or NULL logic value (Figure 1.10). The "V" shape of the molecule is important for clocking reason; in fact, by applying a proper electric field it

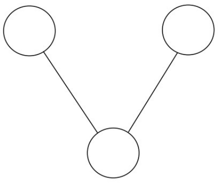

Figure 1.9. Schematic representation of generic molecule used for QCA. Each circle represents a dot.

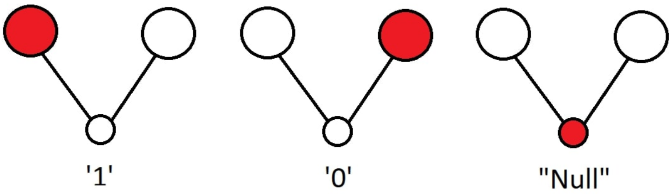

Figure 1.10. Schematic representations of the states. The three states correspond to occupation of each of the three dots by the excess negative charge (represented by red circle).

is possible to force the extra electron to go in the middle-lowest dot for encode the NULL state, which is used to synchronize the propagation of the signal.

By placing side by side two “V”-shaped three-dot molecules it is possible to create a standard MQCA cell, as depicted in Figure 1.11.

Also in this case some requirements are needed to permit the correct functioning of the system:

- the charges have to be localized into the DOTs.
- Low potential barrier is necessary to permit charge switching from one configuration to another.
- The information propagation happens through coupling thanks to Coulomb repulsion.
- The system has to be sensitive to clock.
- Anchoring of the molecule to the substrate has to be allowed.

An example of a candidate molecule for QCA purpose is the bis-ferrocene molecule; in Figure 1.12 it is shown its structure. Two ferrocene groups ($C_{10}H_{10}Fe$) are linked together

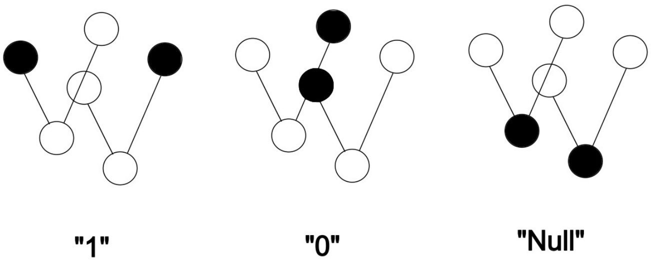

Figure 1.11. Schematic representations of the states in a standard MQCA cell.

by a central carbazole group ($C_{12}H_9N$); the first represent the two main dots for logic encoding, while the latter acts as a central dot for the NULL state. Attacked to the carbazole there is an alkyl-chain at whose end a thiol group (-SH) is responsible for the binding to the substrate (for example gold).

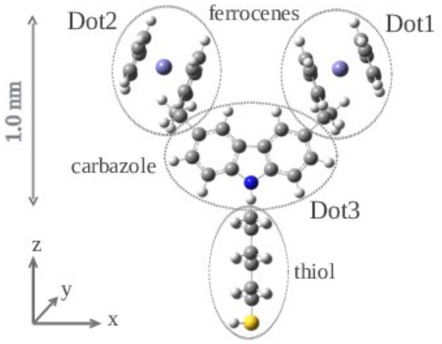

Figure 1.12. Bis-ferrocene molecule: two ferrocenes are linked together by means of a carbazole central group. These ferrocenes represent the two dots responsible for the logic state encoding, while the carbazole acts as the central third dot. An alkyl-chain provides the binding of the bis-ferrocene to the ending thiol (-SH) group. This end-group is responsible for the binding to the gold substrate. (Image from [13]).

1.3.1 Fabrication of organic thin films

As said in the previous section, one of the most important advantages to use molecules for QCA purpose regards their capability to self organize. Self-assembled monolayers (SAMs) are molecular layers that spontaneously assemble on a surface by adsorption, usually driven by specific noncovalent interactions, thus by realizing very patterned and organized organic thin films (OTF); this is possible thanks to the strong affinity of a particular functional

group for a substrate. Different materials have been investigated for SAMs, and the most promising one seems to be alkanethiolates with gold substrate [15].
Each molecule involved in SAMs process generally is composed by three parts: functional group, tail and head group. The functional group (for example the bis-ferrocene molecule) depends on the final application of the SAMs, the head (for example the thiol -SH) is a chemical group which strongly reacts with substrate (for example gold) favouring the adhesion of the molecule, while the tail (for example an alkyl-chain) is responsible for the bond between the head and the functional group. Figure 1.13 shows a schematic example of SAMs.

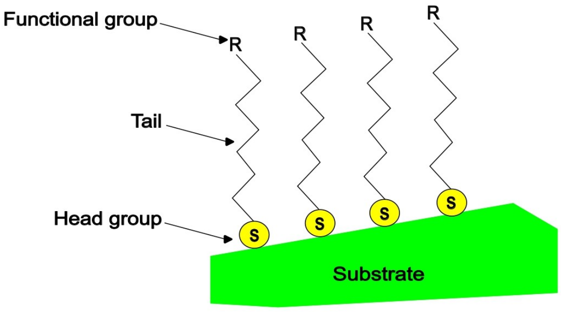

Figure 1.13. Schematic of a self-assembled monolayer (SAMs) showing the head group that is bound to the substrate. SAMs consist of a tail with a functional group at the terminal.

For the realization of organic thin films (OTFs) two main techniques are used; the first is the so called Langmuir-Blodgett. This method is classically known for preparing monolayers of molecules on solid substrates by transferring preorganized monolayers from air/water interface onto substrates [6]. The typical structure of the molecules used for Langmuir-Blodgett scope is formed by an hydrophobic tail and hydrophilic head. At first, molecules are deposited in a water bath with a certain concentration; at the ends of the bath there are two movable barrier which at a certain time are moved toward the center enhancing the creation of a dense film. This compact monolayer is formed at air-liquid interface due to the nature of the molecules (hydrophobic tail and hydrophilic head). In Figure 1.14 (a) are shown these first two steps.

Once the dense monolayer is created, a substrate is submerged into the bath and the thin film transfers from liquid surface to solid one; as a result, when the substrate is raised up the molecules are attached in a very regular and ordered structure (Figure 1.14 (b)).
The second technique used for the realization of OTFs is to immerse a substrate in a solution or in a recipe containing gas phase. The molecules composed by head groups and tails are immersed into the bath and the heads strongly react with substrates atoms allowing spontaneous adsorption of molecules on the surface via chemical bond creation. As a result, a very regular and self organized organic thin film is created.

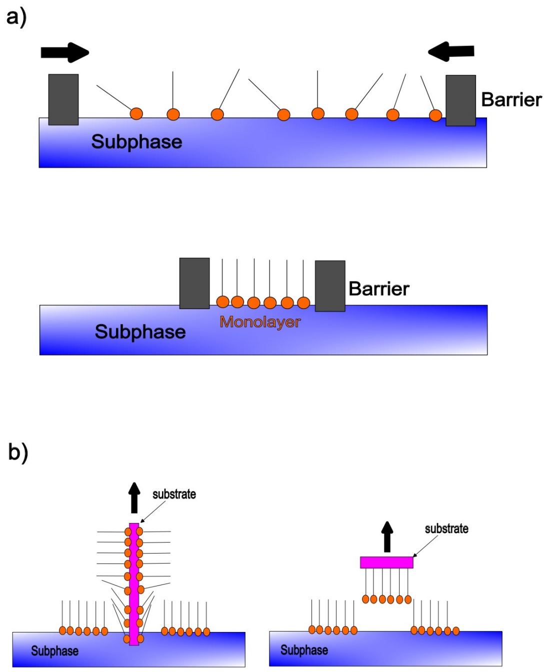

Figure 1.14. Schematic illustration of basic principles of Langmuir-Blodgett-type method. (a) Formation of dense monolayer at air-liquid interface (commonly using water as subphase) with molecules (orange, hydrophilic head; gray, hydrophobic tail) upon barrier compression. (b) Transfer of monolayer from liquid surface to substrate through vertical (left) or horizontal deposition (right).

With these techniques it is possible to create molecular wires and others more complex patterns by depositing molecules on them. It is important to underline that the organization of molecules on a substrate depends on several factors:

- substrates structure (lattice orientation).
- The position where head groups are attached.
- Molecules hindrance: for being energetically stable, molecules "need a certain space around them" and as a consequence not all the tails are linked to the functional groups.

In Figure 1.15 is depicted the deposition of a generic molecule on a gold substrate.

It is fundamental for the usability of a future eventual device to guarantee a clocking system to this structure. A first example is shown in Figure 1.16 (a) in which a molecule (in red) is inserted in a trench insulator; at the two top ends of the trench there are two electrodes (gold) connected to a different voltage values. As a consequence lines of electric field generates and it is possible to polarize the molecule aggregating the charges in one of the two top DOTs (encoding '1' or '0' logic value). In this way a driver can be generated.

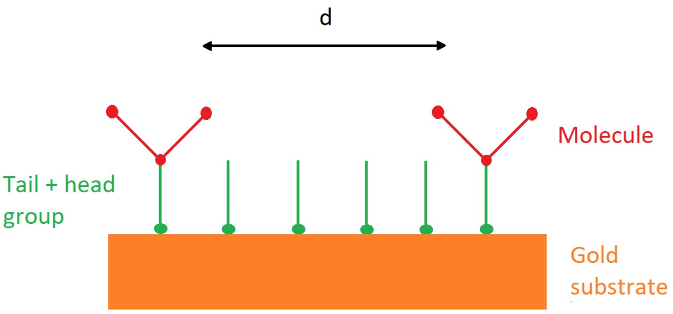

Figure 1.15. Molecular wire on a gold substrate. In red are depicted the functional groups, in green the tails plus the head groups while in orange the gold substrate. d is the distance between two molecules. Not all the tails are attached to the functional groups due to the molecules hindrance.

If instead the top electrodes are connected to the same voltage while the bottom one (what is under the molecule) has a different potential, the electric field lines become quasi-perpendicular to the molecule with the possibility to aggregate charges on the bottom DOT (providing the NULL state, Figure 1.16 (b)).

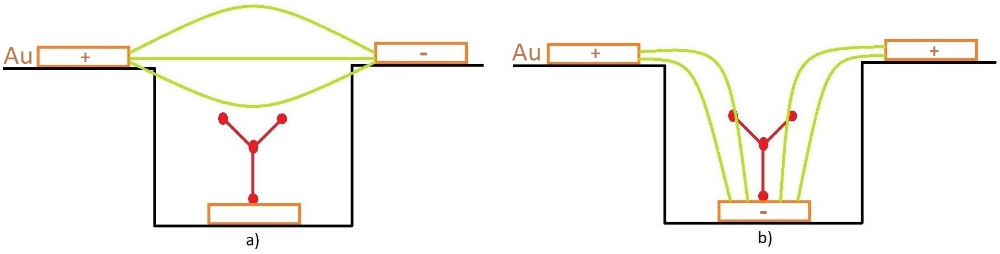

Figure 1.16. Possible structures for provide write-in and clocking system. (a) A molecule is inserted in a trench insulator in which the top electrodes are connected to different voltage values. Lines of electric field are generated and the molecule polarizes to ’1’ or ’0’ configuration. (b) The top electrodes are connected to the same voltage while the bottom one has different potential; the result is that the charges aggregate on the bottom molecular DOT encoding the NULL state.

Chapter 2

Methodology

In the previous chapter it has been discussed about QCA technology, introduced for overcame CMOS limits, having a focus above all on Molecular QCA paradigm. The next step is then to find methods and tools for analyse and simulate the molecules involved in these processes. Indeed, unlike standard CMOS technology, the simulation of molecular technology is still far from being mature to satisfy markets requirements; generally, the molecular properties are analyzed through *ab initio* calculation, which is a numerical method used to solve the Schröedinger equation of the molecules. However, this technique is very computational expensive, so it requires a lot of time: for having all the chemical/physical properties of simple molecules even weeks are required! Another disadvantage is the impossibility to launch dynamic simulation and only a single static electric field can be forced in a particular region (or emulate it with point charges). In addition, being a CPU intensive method, only systems composed by one or few molecules can be simulated.
The algorithm used in this thesis is the so-called MosQuiTo (Molecular Simulator Quantum-dot cellular automata Torino) methodology, introduced in [12] as a two-step procedure; the aim of this approach is to reduce the computational costs, so exploiting *ab initio* calculation minimally. Indeed, only for the first step *ab initio* simulation is used for characterization of the molecules, while for the post processing and the generation of the figures of merit, electrostatic equations are used.
In the following section, MosQuiTo methodology is deeper analysed, discussing also the third step, introduced in [3] and regarding the interactions among molecules and circuit simulation.

2.1 The MoSQuiTo methodology

The MoSQuiTo methodology is used to evaluate and simulate all the important parameters necessary for molecular QCA devices [12]. It is composed by three stages: *ab initio* simulation, post-processing evaluation of figures of merit and system-level analysis.

1. **Ab initio simulation**: computational chemistry analysis are performed to simulate electronic structure and physical properties of the molecules; in Figure 2.1 are shown the stages which lead to the output files starting by a molecular system. The molecule

is described using Z-matrix which is an input file containing the list of atoms and the relative position (distances and angles).

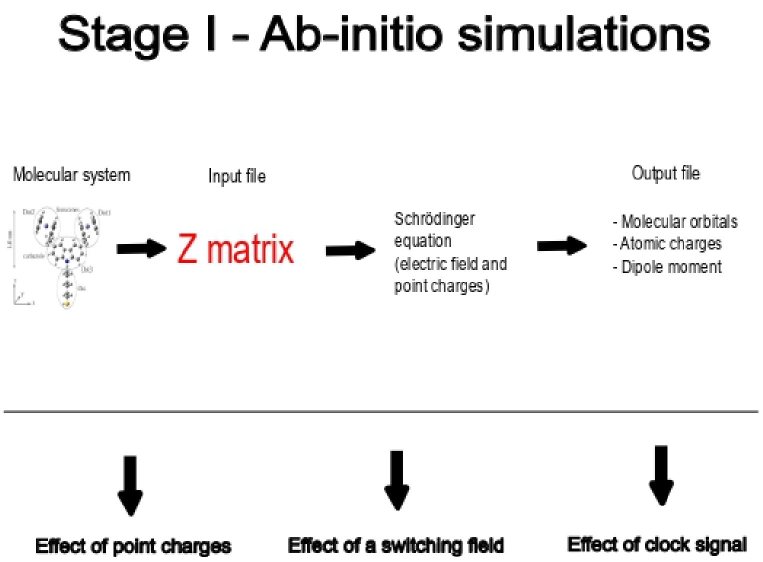

Figure 2.1. Ab-initio simulations: from molecular system to output file.

Afterwards, in order to have a complete characterization of the molecule, a set of *ab initio* simulations can be performed under different biasing conditions; the most typically used are:

- effect of a switching field: by applying an uniform electric field parallel to the two active dots (those which encode '1' or '0' logic value) the charges should be forced to localize in one of the two dots and by changing the sign of the field the charges should go in the opposite dot and then the molecule changes its logic state.
- Effect of point charges: it is possible to emulate the presence of a molecule (or a driver) by placing two point charges at a certain distance d from the molecule and located at the same position of the two working dots. In this way the system is considered as a complete QCA cell; for example, in the case of a neutral molecule, the point charges have values, respectively, $+1e$ and $-1e$. By swapping the position of the point charges it is possible to check if the molecule changes its state as well.
- Effect of clock signal: for assure correct information propagation it is fundamental a clocking system capable to enhance or inhibit communication among molecules. For this purpose, in the case of a three-dots molecule, an electric field is applied to the vertical axis of the molecule for testing its capability to go in the NULL state or exit from it.

Once have computed all these simulations, results are stored in look up tables and the behaviour of the molecule is extracted.

2. **Post-processing**: the outputs of *ab initio* calculations are post-processed in order to give an electronic description of the molecule and to provide to electronic engineers all the quantities necessary for the analysis of molecular circuits. For this purpose, through electrostatic equations and models, some figures of merit are generated:

   - aggregated charge (AC): the first analysed figure of merit is the so called aggregated charge. AC of the dots is simply defined by summing the charges of the atoms constituting the dot; then by grouping atomic charges into specific groups it is possible to imitate electrostatic behaviour of the molecule. In Figure 2.2 it is shown the bis-ferrocene molecule modeled with three charges (Q1, Q2 and Q3) corresponding, respectively, to the three dots (DOT1, DOT2 and DOT3).

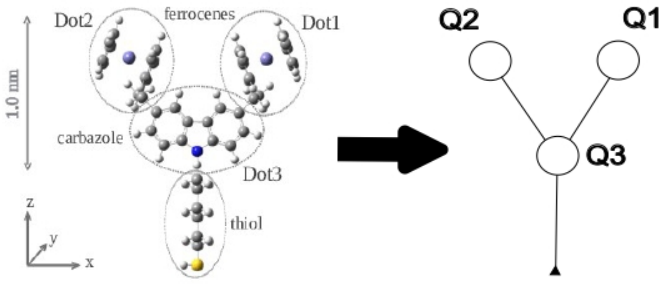

Figure 2.2. Definition of the aggregated charge for each dot.

   By calculating atomic charges with *ab initio* is then possible to group them into Aggregated Charges; AC demonstrates the charge distribution inside a molecule from a macroscopic point of view and it is used as the starting point for the definition of the other figures of merit which characterize the electrostatic properties of the molecules [3].

   - Electric field generated by molecule: a molecule with a certain charge distribution generates an electric field all around; in order to calculate the effect on a Molecule Under Test (MUT) a single charge $+q_1$ is considered to be placed at (x_0, y_0, z_0), and the electric field $E(x, y, z)$ can be evaluated by means of a positive test charge $+q_t$ positioned in (x, y, z). The distance r_1 between q_1 and q_t is defined as

$$r_1 = \sqrt{(x - x_0)^2 + (y - y_0)^2 + (z - z_0)^2}. \tag{2.1}$$

Applying the Gauss law, the Coulomb force $\vec{F_1}$ acting on the test charge is

$$\vec{F_1} = \frac{q_1 q_t}{4\pi\epsilon_0 r_1^2}\hat{r}. \tag{2.2}$$

Then, the electric field generated by q_1 and measured by q_t is

$$\vec{E_1} = \frac{\vec{F_1}}{q_t} = \frac{q_1}{4\pi\epsilon_0 r_1^2}\hat{r}. \tag{2.3}$$

Considering a system of N point charges, the total force affecting the test charge can be summarized as

$$\vec{F}_{tot} = \sum_{i=1}^{N} \frac{q_i q_t}{4\pi\epsilon_0 r_i^2}\hat{r} \tag{2.4}$$

and, as a consequence, the total electric field becomes

$$\vec{E}_{tot} = \frac{\vec{F}_{tot}}{q_t} = \sum_{i=1}^{N} \frac{q_i}{4\pi\epsilon_0 r_i^2}\hat{r}. \tag{2.5}$$

Then, by calculating the total electric field for all possible points in space where q_t could stay and by considering the generator q_i as the q_i of the aggregated charge of the molecule, the result is $\vec{E}_{tot}$ surrounding the molecule at any points. In Figure 2.3 it is shown a schematic representation of the generated electric field of the molecule.

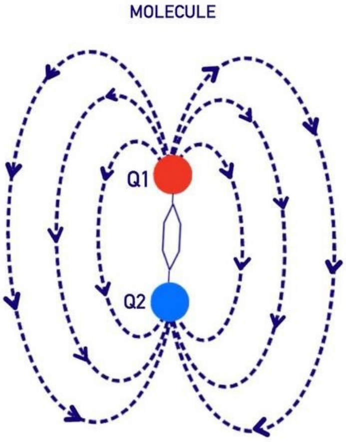

Figure 2.3. Definition of the generated electric field.

- Equivalent voltage at the receiver: the voltage at the MUT named input voltage or V_{in}, is evaluated by integrating the electric field (generated by the charge distribution of the molecule) that influences the molecule along the segment connecting the active dots of the MUT (Figure 2.4) [3].

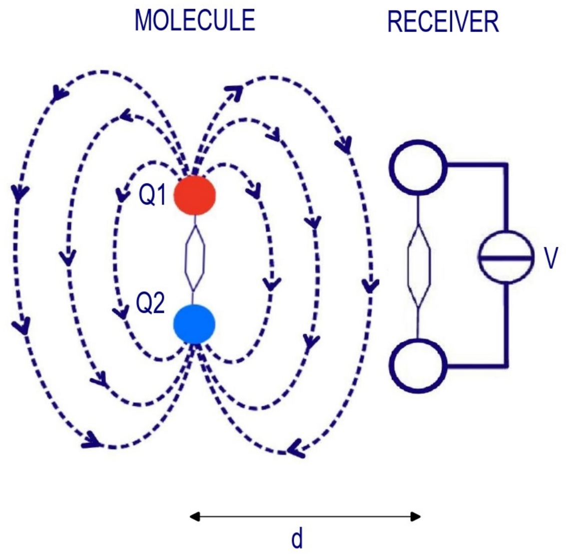

Figure 2.4. Equivalent voltage at the receiver.

- VACT: V_{in}–AC Transcharacteristics (VACT) is the relation between the input voltage and the Aggregated Charge.

3. **System-level analysis**: once the molecule has been fully characterized, the following step is to consider a molecular circuit composed by a group of interacting molecules. The information propagation in MQCA circuits can be evaluated considering parameters which are closer to the electronic engineering techniques and the study of molecular circuits is carried out from system level point of view [3]. The task is to find a model able to describe the interaction among the molecules.

2.2 Theoretical background

Having discussed MosQuiTo methodology, it is useful now to have a focus on the theory behind the computational chemistry in order to give a background necessary to understand all the concepts contained in this work. To this purpose an insight into the *ab initio* world is needed.
In the computational chemistry perspective, the molecule is seen as a group of atoms. Each atom of the molecule is composed by:

- Nuclei, composed by neutrons (mass $1{,}67 \cdot 10^{-27}$ kg - Charge $0e$) and protons (mass $1{,}67 \cdot 10^{-27}$ kg - Charge $+1e$);

- Electrons (mass $9{,}31 \cdot 10^{-31}$ kg - Charge $-1e$).

The molecule can be studied with Quantum Mechanics (QM) as a system of a set of N_N positive nuclei, with position $R_i = \{X_i, Y_i, Z_i\}$ and charge $Q_i \cdot e$, and a set of N_e electrons, with position $r_i = \{x_i, y_i, z_i\}$ and charge $-e$. The QM problem can be written as

$$\hat{H}\Psi = E\Psi \tag{2.6}$$

where Ψ is the so called molecular wavefunction:

$$\Psi = \Psi(R, r) = \Psi(X_1, Y_1, Z_1, ..., X_{N_N}, Y_{N_N}, Z_{N_N}, ..., x_{N_e}, y_{N_e}, z_{N_e}). \tag{2.7}$$

The quantity $|\Psi(R, r)|^2$ is the probability of finding the molecule in a precise status where the nuclei and the electrons have coordinates R and r respectively. Instead, $\hat{H}$ is the so called molecular Hamiltonian, and can be expressed as follow:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee} \tag{2.8}$$

where $\hat{T}_N$ and $\hat{T}_e$ are the kinetic contributions for nuclei and electrons respectively, whereas $\hat{V}_{NN}$, $\hat{V}_{Ne}$ and $\hat{V}_{ee}$ are the potential energies associated to nuclei-nuclei, nuclei-electrons and electrons-electrons interactions, respectively.

Due to the fact that the electron mass is much smaller than proton mass, the kinetic energy of nuclei is negligible, and it reasonable to imagine the electrons moving in an average potential generated by nuclei. This approximation leads to an equivalent QM problem related to the electron only:

$$[\hat{T}_N + \hat{V}_{Ne} + \hat{V}_{ee}]\Psi_{el}(r, R) = E\Psi_{el}(r, R). \tag{2.9}$$

The nuclei are considered frozen: the electron wavefunction Ψ_{el} still depends on nuclear coordinates, but not on the nuclear velocities. This concept is known as Born-Oppenheimer Approximation (BOA). So now, the quantity $|\Psi(R, r)|^2$ is the probability of finding the electrons in a precise position r considering the nuclei in frozen coordinates R. The nuclei, considered as point charges, generate an electrostatic potential: the electrons feel that electrostatic potential.

By evaluating the energy of the molecule as a function of the nuclei coordinates, we can define the so called Potential Energy Surface (PES), whose value may expressed as:

$$E_{PES}(R) = E(X_1, Y_1, Z_1, ..., X_{N_N}, Y_{N_N}, Z_{N_N}). \tag{2.10}$$

The Potential Energy Surface may show several local minima which represent the conformation geometry of the molecule. The procedure to find the geometry minimizing the PES value is known as "Geometry Optimization".

Considering the Born-Oppenheimer Approximation, the final QM problem for the only electrons becomes:

$$[\hat{T}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee}]\Psi_{el}(r, R) = E\Psi_{el}(r, R) \tag{2.11}$$

which can be expanded as

$$\begin{split}[-\sum_i \frac{\hbar^2}{2M_i}\nabla^2 r_i - \sum_i\sum_j \frac{Z_i e^2}{4\pi\epsilon_0|R_i - r_j|} + \frac{1}{2}\sum_i\sum_j \frac{e^2}{4\pi\epsilon_0|r_i - r_j|} + \\ + \sum_i\sum_j \frac{Z_i Z_j e^2}{4\pi\epsilon_0|R_i - R_j|}]\Psi_{el}(r, R) = E\Psi_{el}(r, R).\end{split} \tag{2.12}$$

2.2.1 The Hartree-Fock method

It is possible to imagine that the molecular wavefunction depends on the wavefunction of each electron. Each electron lies in a molecular orbital. Therefore, the electron wavefunction is considered to be a combination of the molecular orbital (MO) wavefunctions.

$$\Psi_{el} = \prod_i \Psi_i(x_i, y_i, z_i) = \Psi_1(x_1, y_1, z_1)....\Psi_{N_e}(x_{N_e}, y_{N_e}, z_{N_e}). \tag{2.13}$$

The previous expression is known as Hartree Product. In the simplest case of a two-MO molecule, Hartree product becomes

$$\Psi_{el} = \Psi_1(x_1, y_1, z_1) \cdot \Psi_2(x_2, y_2, z_2). \tag{2.14}$$

However, this procedure does not consider anti-symmetry principle. Indeed, if it is considered the case in which two electrons are in the same position, Ψ_{el} is generally non null, implicating that there is a probability of finding two electrons in the same position, which is physically impossible.
Another way to express the electron wavefunction is to exploit the so called Slater-Determinant, that is for two electrons:

$$\Psi_{el} = \Psi_1(x_1, y_1, z_1)\Psi_2(x_1, y_1, z_1) - \Psi_2(x_2, y_2, z_2)\Psi_1(x_2, y_2, z_2). \tag{2.15}$$

In this case, if the two electrons are in the same position, $\Psi_{el} = 0$, which means that the probability of finding them in the same position is null.
At this point, QM problem needs to be fixed and the expression of the MO wavefunctions has to be derived. In order to do that, Linear Combination of Atomic Orbitals (LCAO) is exploited, which expresses the molecular orbital Ψ_{MO} as a combination of atomic orbitals Ψ_{AO} centered on atoms:

$$\Psi_{MO}(x, y, z) = \sum_{i=1}^{N_e} c_i \Psi_{AO,i}(x - X_i, y - Y_i, z - Z_i). \tag{2.16}$$

Quantum Chemistry tools have to find the set of c_i minimizing the energy: this is the so-called Hartree-Fock method. It is possible to express the energy of the system by using the variational principle:

$$E = \frac{\int \Psi_{el} \hat{H}_{el} \Psi_{el}^* dV}{\int \Psi_{el} \Psi_{el}^* dV}. \tag{2.17}$$

The remaining unknown quantity is the expression of the atomic orbital. The physically bestmotivated orbital is the so called Slater-Type Orbital (STO) (it is a solution of the Schrödinger equation), but they are computationally challenging to treat since calculating integrals is not easy. For this reason, the atomic orbital of atom i is generally approximated as a sum of gaussian functions

$$\Psi_{AO,i}(x, y, z) = \sum_{j=1}^{N_e} k_j G_j(x, y, z) \tag{2.18}$$

where G is a Gaussian Type Orbital (GTO). The idea is to fit the STO orbital with a set n of GTO orbitals. Therefore, it is defined STO-nG basis set, that is, n Gaussian functions

fitting for the STO orbital (STO-3G, STO-4G, STO-5G, ..., STO-nG).
In some cases, the atomic orbitals may be stretched as a consequence of external stimuli. For example, an electric field may polarize the molecule, that means moving the electron cloud on a certain direction. Symmetrical Gaussian/Slater orbitals cannot account for this effect. At this purpose, "polarization functions" are introduced, that are functions modeling higher momentum orbitals (orbitals that should not be normally occupied).
A second important set of functions is the set of diffuse functions, that are GTOs with small exponent used to describe the regions far from nuclei. The most important orbitals playing a relevant role in the chemical reactions are the valence orbitals; therefore, it makes no sense to express all the orbitals with the same number of GTOs. For this purpose the Split-valence Basis sets are introduced, which have the following notation:

$$X - YZ_g \tag{2.19}$$

where X represents the number of STOs used for the core orbitals. The valence orbitals are represented with two atomic orbitals, one with Y GTOs, the second with Z GTOs. Some possible basis sets are:

- 3 - 21G - 3 GTOs for the core orbitals, valence orbitals are split into two orbitals, one composed of 2 GTOs, one with 1 orbital;
- 3 - 21$G*$ - Polarization functions on heavy atoms;
- 3 - 21$G**$ - Polarization functions on heavy atoms and hydrogen;
- 3 - 21 + G - Diffuse functions on heavy atoms;
- 3 - 21 + +G - Diffuse functions on heavy atoms and hydrogen;
- 3 - 21 + $G**$ - Polarization functions on heavy atoms and hydrogen, as well as diffuse functions on heavy atoms.

The most used basis sets are the Split-Valence "Ahlrichs basis sets" SV, SVP, DZ, TZV, TZVP, QZVP, and the "Karlsruhe basis sets", redefined from Ahlrichs basis sets, def2-SVP, def2-TZVP, def2-QZVP, def2-QZVPPD. In particular, def2-SVP splits the basis set into core and valence orbitals. The core and the valence orbitals are represented by a single set of functions (Gaussian orbitals). Def2-TZVP splits the basis set into core and valence orbitals. The valence orbitals are three sets of functions (Gaussian orbitals).

2.2.2 The Density Functional Theory

An alternative approach to the Hartree-Fock method is the so called Density Functional Theory (DFT) which is a computational technique based on the electron density. This quantity can be written as:

$$\rho(r) = \int ... \int |\Psi(r_1, r_2, ..., r_{N_e})|^2 dr_1 ... dr_{N_e}. \tag{2.20}$$

From the DFT theory, it comes out that the energy of the molecule can be written as a function of the electron density $E = E[\rho(r)]$. Mathematically, it can be expanded into two contributions

$$E = E'[\rho] + Functional \tag{2.21}$$

where $E'[\rho]$ is a closed-form equation describing the energy-density relation (for a set of N_e non interacting electrons). The second term (functional, partially empirical) incorporates the terms not (yet) included in the relationship. At this point, the problem becomes similar to the Hartree-Fock and can be solved by finding the electron density ρ that minimizes the energy of the molecule.

2.2.3 The Molecular Electrostatic Potential and the CHELPG charges

The molecule is composed of positive (nuclei) and negative (electrons) charges. Thus, the molecule generates an electrostatic potential equal to

$$V(r) = \frac{1}{4\pi\epsilon_0} \sum_{N_N} \frac{eQ_i}{|R_i - r|} - e \int \frac{\rho(r)}{|r' - r|} dr'. \tag{2.22}$$

This potential is named Molecular Electrostatic Potential (MEP).
Through a fitting, it is possible to evaluate a set of N charges generating the same potential; this technique is known as the CHELPG method (CHarges from ELectrostatic Potentials using a Grid-based method). The voltage generated by each point charge can be written with electrostatic equations:

$$V_C(r) = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N} \frac{q_i}{|r_j - r_i|}. \tag{2.23}$$

The error which should be minimized is the difference between the MEP potential and the voltage generated by the point charges:

$$\epsilon^2 = [V(r) - V_C(r)] = 0. \tag{2.24}$$

Chapter 3

Characterization of molecules

Having established a methodology for analyze and simulate the molecules properties, the focus is now to find the best molecules which can be used for QCA purposes. As said in the previous chapter, for simplicity and for simulation reasons, the molecules are modeled as a system of three charges (Q1, Q2 and Q3); Q1 and Q2 are named "active dots" (those which encode logic information: '1' or '0'), while Q3 is the NULL dot, which encodes the NULL state.
A first distinction among molecules can be done according to the stability:

- bistable molecules: at the thermal equilibrium, the charge naturally aggregates on one of the two dots (Q1 or Q2). So two stable states energetically equivalent exist. Some energy is needed to switch the molecule between the two states;
- monostable molecules: at the thermal equilibrium, the charge does not aggregate on Q1 or Q2. Some energy is needed to move and to keep the charge on one of the two dots.

It is possible to do a second distinction according to electrostatic behaviour of the molecules. It is important to remark that in chemistry the oxidation process is when a species undergoes a loss of electrons, while the reduction is the process in which a species gains one or more electrons. In this sense, three types of molecules can be defined (when encoding logic information):

- neutral molecules: the sum of the charges constituting the molecule is 0;
- oxidized molecules: the sum of the charges constituting the molecule is always +1;
- reduced molecules: the sum of the charges constituting the molecule is always -1.

In the case of oxidized or reduced form, a counterion is introduced in the solution; the aim of this element is to attract (or release) an electron from (or to) the molecule during the oxidation (or reduction) process, becoming negatively (or positively) charged. In this way, the molecule and the counterion form a neutral system [3]. In the analysis of the molecules, this can avoid possible disturbances in the intermolecular interaction.

3.1 Method for characterization

Some molecules have been proposed in literature to QCA purpose; however, it has not yet been found the best molecule able to satisfy all the requirements of this technology. For this purpose, a tool which automatically characterizes the molecule is needed. In this thesis a MATLAB interface communicating with ORCA (an *ab initio* quantum chemistry program having modern electronic methods) is used. The tool consists into three steps: molecule geometry optimization, molecule response evaluation and result analysis.

3.1.1 Molecule geometry optimization

The molecule is drawn by hand using Avogadro software, and a first optimization is carried out (using the "Auto Optimization Tool" in the Avogadro bar) in order to obtain the lowest energy conformation using Molecular Mechanics (MM) theory. MM considers molecules as a group of spheres (atoms) connected by springs (bonds). The optimization consists in minimizing the energy of the spring-sphere mechanical system and employs basic mechanics equations.
However, this is a model that allows only elementary calculations; it is necessary to analyze the molecule with higher precision by exploiting Quantum Mechanics, thus *ab initio* calculation. As said in the previous chapter, *ab initio* tool finds the minimum energy molecule conformation by solving the Schröedinger equation. In order to do that, an ORCA input file has to be written: it is possible to choose between Density Functional Theory (DFT) and Hartree-Fock (HF) methods. DFT functionals, basis sets, and additional corrections can also be selected. The user chooses the charge and the multiplicity of the molecule.

3.1.2 Molecule response

Once the molecule has been optimized, the tool applies an electric field to the system in order to characterize the molecule. In particular, it is possible to choose between FIELD system, where a uniform electric field is applied and SWITCH system, where the field is similar to the one generated by molecules. The field is generated by point charges.

3.1.3 Result analysis

The tool computes the VACT of the system; in particular, the V_{in} is automatically calculated by the script, while the Aggregated Charge is evaluated by grouping the atomic charges in a certain number of DOTS (generally two or three). In addition also the Dipole Moment and the *ab initio* Self-Consistent Field Energy of the molecule as a function of the input voltage are evaluated.

This work starts by analyzing the Bis(trimethylsilyl) Sulfide (in the following named for simplicity "SiSSi") molecule and its other forms.

3.2 General remarks

For all the molecules which will be taken into account in this section, the analysis starts by evaluating the geometry of the molecules and then by calculating the electrostatic characteristics in order to study its encoding capabilities.

In particular the Bis(trimethylsilyl) Sulfide is a monostable molecule and for the following treatment Density Functional Theory is used for its characterization. Unrestricted Kohn-Shann method, CAM-B3LYP functional, def2-TZVP basis set and D3 correction are the other parameters which are set. def2-TZVP (def2-Triple Zeta Valence Polarized) basis set splits the orbitals into valence and core orbitals and the valence orbitals are represented by three sets of functions.

For the characterization, an uniform electric field is applied to the system (FIELD case) generated by point charges, which assume different values in order to exploit a definite range of the input voltage V_{in}. The CHELPG method is applied to evaluate the atomic charges.

3.2.1 Bis(trimethylsilyl) Sulfide

The first analyzed molecule is the Bis(trimethylsilyl) Sulfide; this molecule is composed by a central Sulfur atom linked to two Silicon atoms (from here the name "SiSSi"). Each Si atom is connected to three methyl groups (CH_3); the chemical formula of the molecule is $((CH_3)_3Si)_2S$.

In Figure 3.1 it is shown a 3D representation of SiSSi obtained with Avogadro tool after the first optimization (with "Auto Optimization Tool"). In yellow it is represented the S atom, in light blue the two Si atoms, in grey the Carbons and in white the Hydrogens. The distance between the Silicon atoms is 3,354 Å.

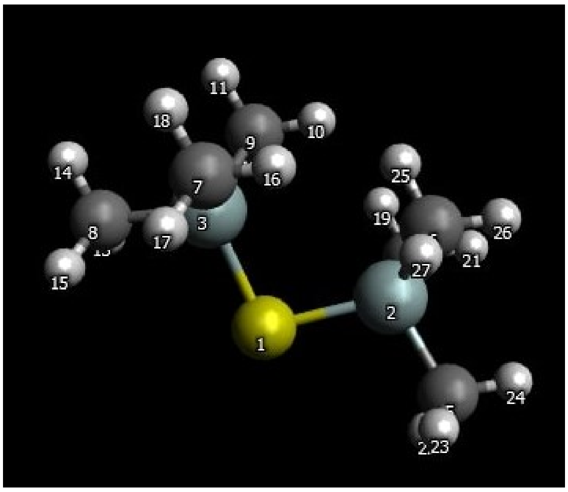

Figure 3.1. 3D representation of SiSSi obtained with Avogadro tool. In yellow the S atom, in light blue the two Si atoms, in grey the Carbons and in white the Hydrogens. The distance between the Silicon atoms is 3,354 Å.

Once this first optimization is performed, the second (more accurate) geometry optimization is computed with ORCA software, using the parameters shown before. The molecule is neutral (so the total charge is set to 0), and the multiplicity (the number of unpaired electrons that the molecule contains) is set to 1. The result is shown in Figure 3.2.

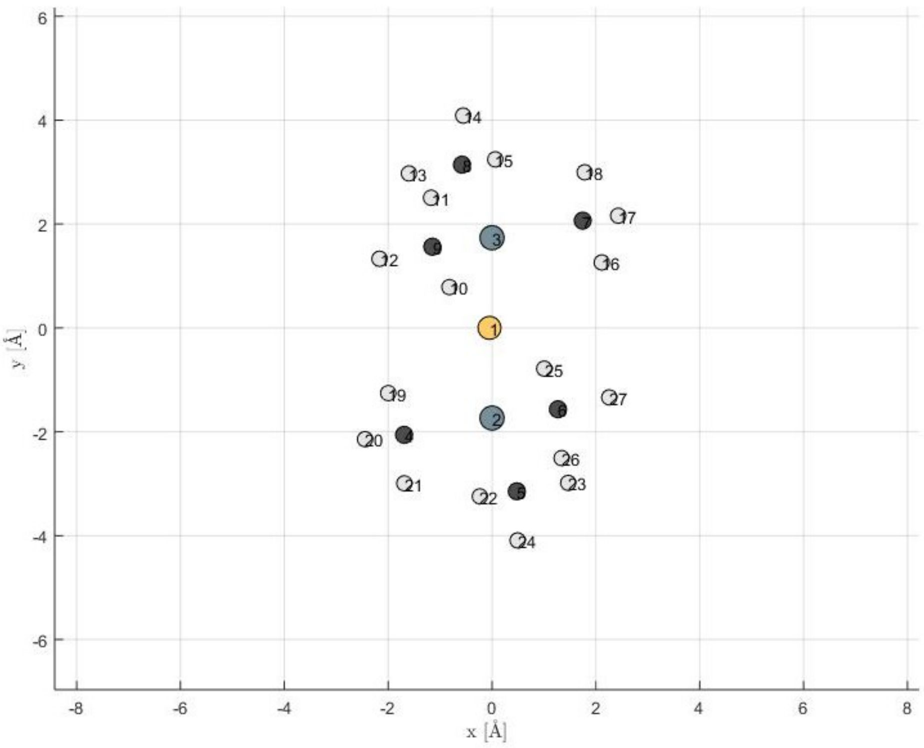

Figure 3.2. Optimized SiSSi molecule.

It is important to underline that the molecule has been then translated in order to align the two Silicon atoms to the point charges for maximize the effect of the electric field. The system composed by the molecule and the point charges is shown in Figure 3.3.

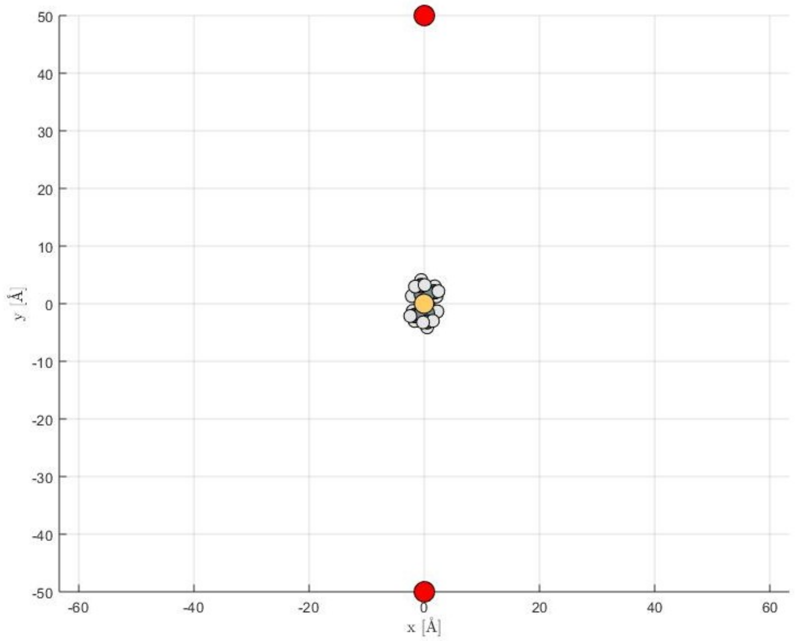

Figure 3.3. SiSSi molecule with point charges (in red).

The point charges are placed at a distance of 50Åeach from the center of the molecule. Different values of point charges are exploited in order to obtain a definite range of V_{in}; for this specific molecule, the potential difference is evaluated between the two Silicon atoms. For the evaluation of the Aggregated Charge, the molecule has been divided into three Dots according to the Figure 3.4 (top): in blue and in red are shown the atoms belonging to the active Dots, while in green is shown the Dot used for the NULL state (in this case composed by only the Sulfur atom). As it can be seen in Figure 3.4 (bottom), the AC of Dot1 and Dot2 does not have a significant variation when V_{in} changes (its value remains almost constant around 0,3 a.u.) and for this reason it is possible to say that this molecule is not good for QCA purposes (its switching capability is poor).

A possible idea is that to oxidize the molecule; however, only a shift in the transcharacteristics is seen and the total behaviour does not change (Figure 3.5).

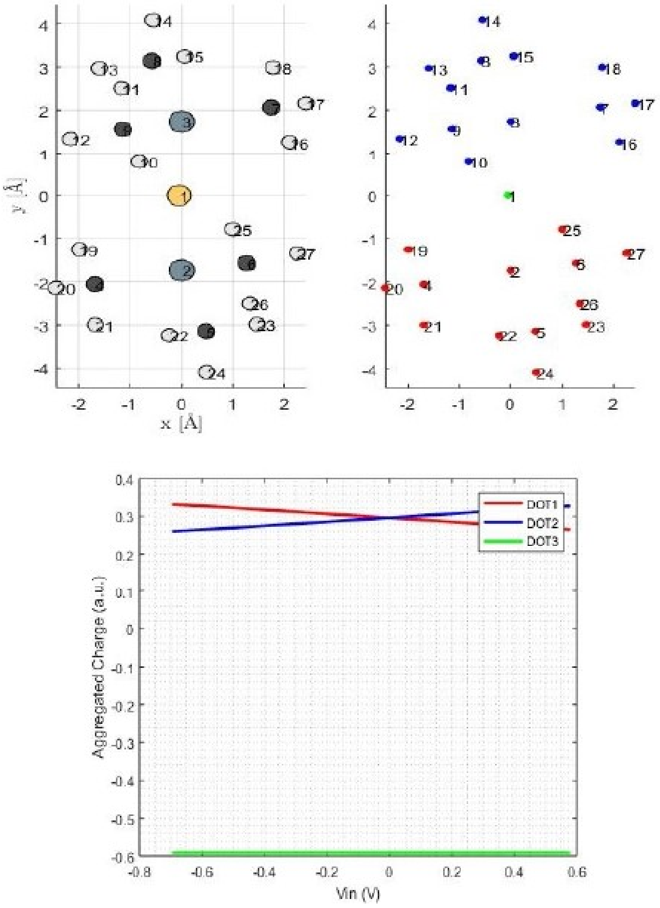

Figure 3.4. On top, SiSSi molecule and the division into three DOTS (blue, green and red). On the bottom, VACT transcharacteristics.

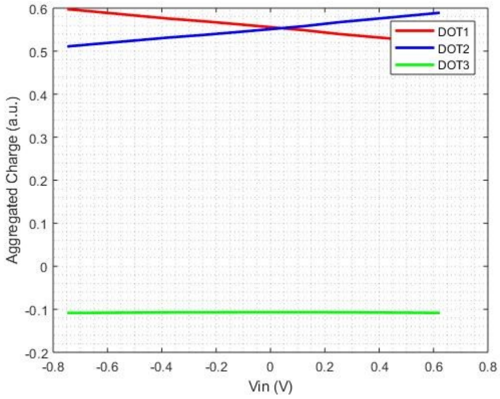

Figure 3.5. VACT of SiSSi molecule (oxidized).

3.2.2 Ethylenedithiobis(trimethylsilane)

For improve the switching capability of the molecule it has been tried to move the two Silicon atoms away. In order to achieve this purpose a thiol group is added at the center of the molecule; a thiol is any organosulfur compound of the form R-SH, where R represents an alkyl or other organic substituent. The optimized neutral molecule is shown in Figure 3.6. This molecule is called Ethylenedithiobis ("SiSSi thiol" for simplicity), having the chemical formula: $C_{12}H_{30}S_2Si_2$. Also in this case, for the characterization, two point charges are located at a distance of 50Åeach from the center of the molecule. As for the SiSSi molecule, they are placed perpendicular to the two Silicon atoms in order to maximize the effect of the electric field.
However, as it can be seen in Figure 3.7, the addition of the thiol has not improved the VACT of the molecule; there is still a low charge separation between the two active Dots (Dot1 and Dot2) varying V_{in}.

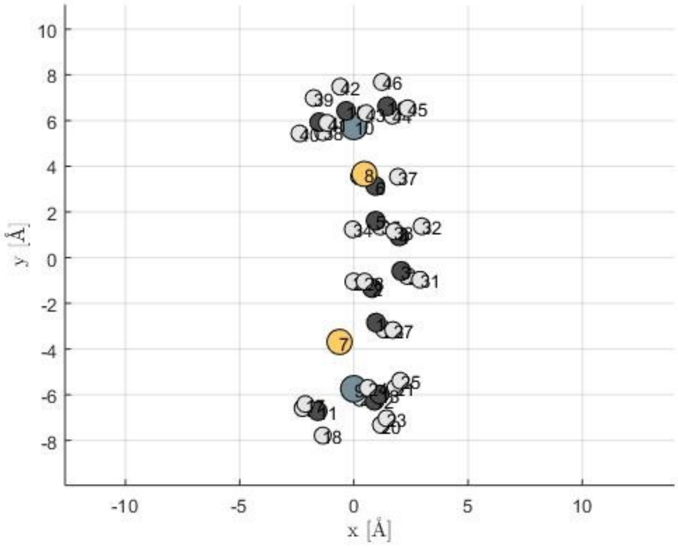

Figure 3.6. Optimized Ethylenedithiobis ("SiSSi thiol"). In orange are represented the Sulfur atoms, in white the Hydrogens, in black the Carbons and in grey the Silicons.

It is possible to have a better transcharacteristics by oxidizing the molecule; in the ORCA tool it is set the charge equal to 1 (meaning that the molecule has been privated of one electron and a net free positive charge arises), and the multiplicity equal to 2 (meaning that there is one unpaired electron).
The VACT of oxidized SiSSi thiol is shown in Figure 3.8; focusing on the active Dots, it is possible to see that when no potential is applied, the charge is delocalized (the value of AC for Dot1 and Dot2 is the same and is equal to 0,26 a.u.) and then no binary information can be represented. If instead V_{in} increases, the charges aggregate on Dot2 (while the AC of Dot1 tends to 0) and for $V_{in} = 2V$ a good charge separation it can be seen. In this way it is possible to encode a specific logic value (for example '1') and the molecule behaves as an half MQCA cell. The same considerations can be done when V_{in} decreases: the AC of

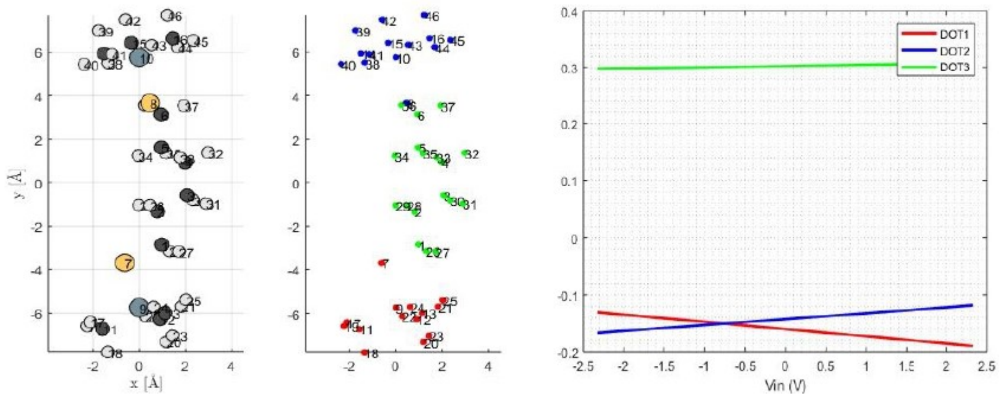

Figure 3.7. On the left, SiSSi thiol molecule and its division into three DOTS (blue, green and red). On the right, the VACT transcharacteristics.

Dot1 increases while the AC of Dot2 tends to 0 and, for example, '0' logic value can be encoded.

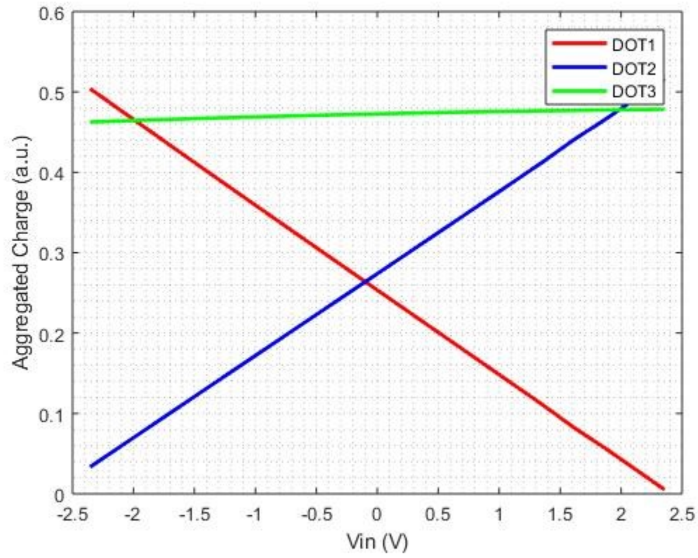

Figure 3.8. VACT of SiSSi thiol molecule (oxidized).

Another parameter which has been evaluated is the *ab initio* Self-Consistent Field (SCF) Energy of the molecule, shown in Figure 3.9. The energy profile is symmetric with respect to the zero voltage; this result is important because signs of asymmetries (in the case of monostable molecules) could mean the presence of unwanted bistable characteristics and a non-ground state situation. In general, the energy computation is also important in order to verify the correctness of the method used for characterize the molecule.

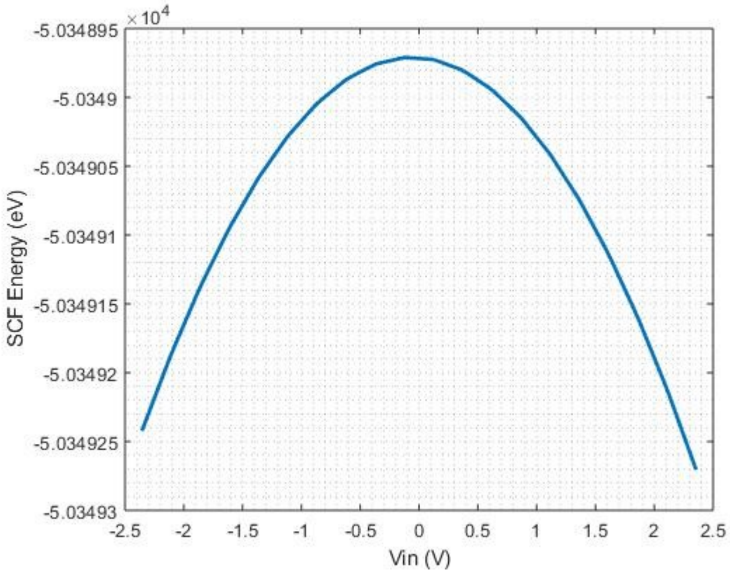

Figure 3.9. SCF Energy of SiSSi thiol molecule (oxidized).

3.2.3 SiSSi long thiol and SiSSi long odd thiol

To have more information about the switching capability of the molecule, it has been tried to lengthen the central atoms chain; the chemical formula of the molecule becomes $C_{18}H_{42}S_2Si_2$ and, for simplicity, it is called "SiSSi long thiol". The optimized neutral molecule it is shown in Figure 3.10.

The usual method is used for the characterization (two point charges located at 50 Åeach from the center of the molecule) and the resulting Aggregated Charge it is shown in Figure 3.11 (right). It is possible to deduce that the transcharacteristics is very similar to that of the Figure 3.7 (representing the VACT of SiSSi thiol molecule) showing that the adding of the thiol groups at the center of the chain has not affected the charge of the molecule. Then, in the case of neutral molecule, there is still a low charge separation between the active Dots varying V_{in}.

Also in this case, for improve the transcharacteristics it is necessary to oxidize the molecule. A better charge separation it is seen in Figure 3.12, where increasing or decreasing V_{in}, the charges aggregate on Dot2 and Dot1, respectively. In this way it is possible to encode binary information and the molecule behaves as an half MQCA cell. The downside of this molecule is that the VACT it is not perfectly symmetric; it is desirable to have a symmetrical transcharacteristics because, in this way, the same amount of energy is needed to lead the molecule in one of the two possible configurations ('1' or '0' logic value).

For achieve this purpose a possible idea is to make the molecule symmetric; in order to do that, another thiol group is added at the center of the atoms chain and the chemical

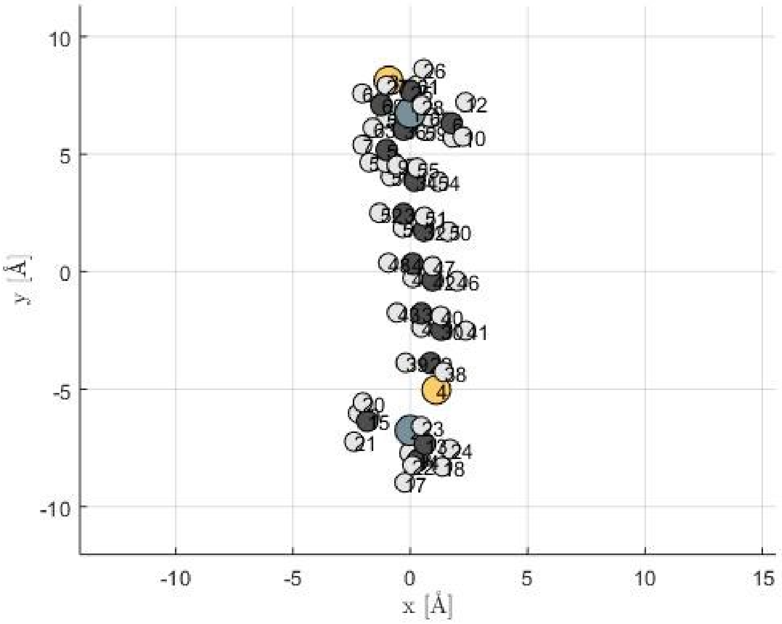

Figure 3.10. Optimized SiSSi long thiol molecule. In orange are represented the Sulfur atoms, in white the Hydrogens, in black the Carbons and in grey the Silicons.

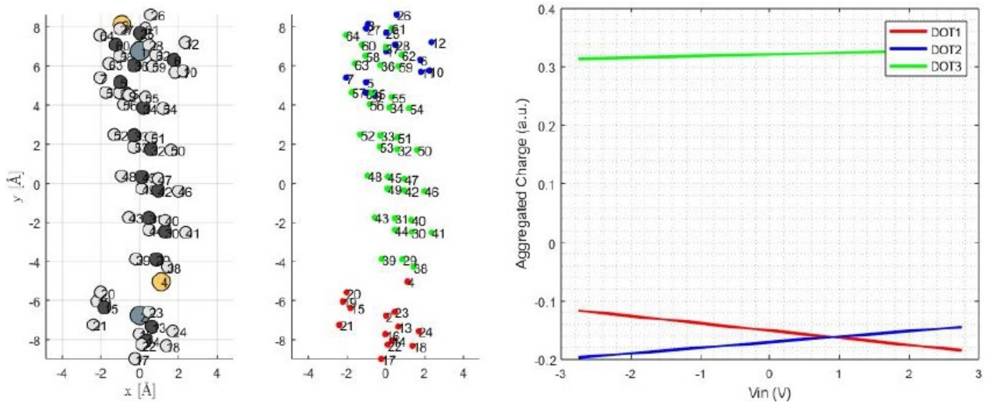

Figure 3.11. On the left, SiSSi long thiol molecule and its division into three DOTS (blue, green and red). On the right, the VACT transcharacteristics.

formula of the molecule becomes $C_{19}H_{44}S_2Si_2$; for simplicity it is called "SiSSi long odd thiol" for remark the presence of an odd number of thiol groups. The optimized molecule (oxidized) it is shown in Figure 3.13.

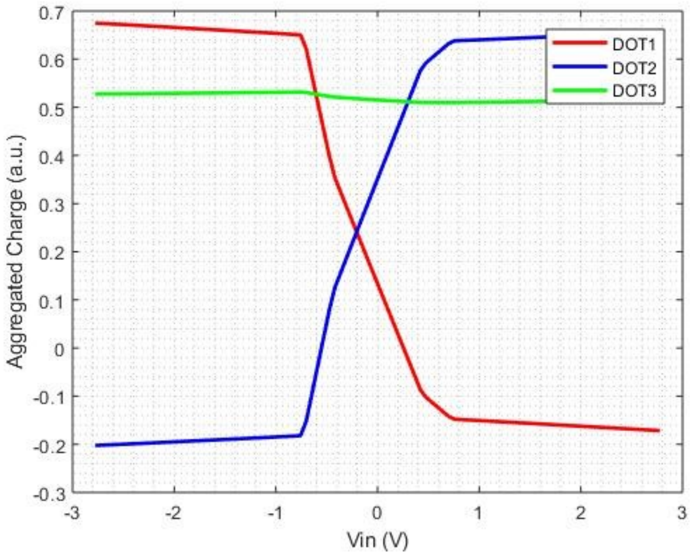

Figure 3.12. VACT of SiSSi long thiol molecule (oxidized).

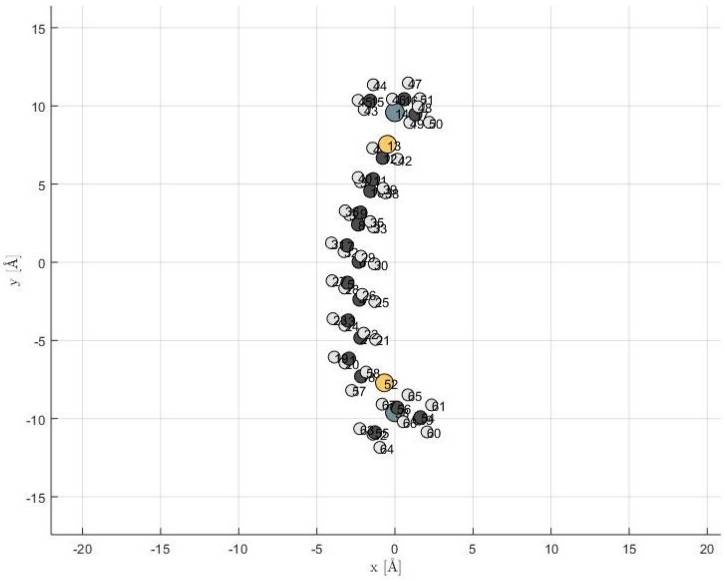

Figure 3.13. Optimized SiSSi long odd thiol molecule (oxidized). In orange are represented the Sulfur atoms, in white the Hydrogens, in black the Carbons and in grey the Silicons.

The Aggregated Charge it is shown in Figure 3.14 (right): the symmetry of the molecule has improved the symmetry of the VACT but it is still not equal for positive and negative voltages.

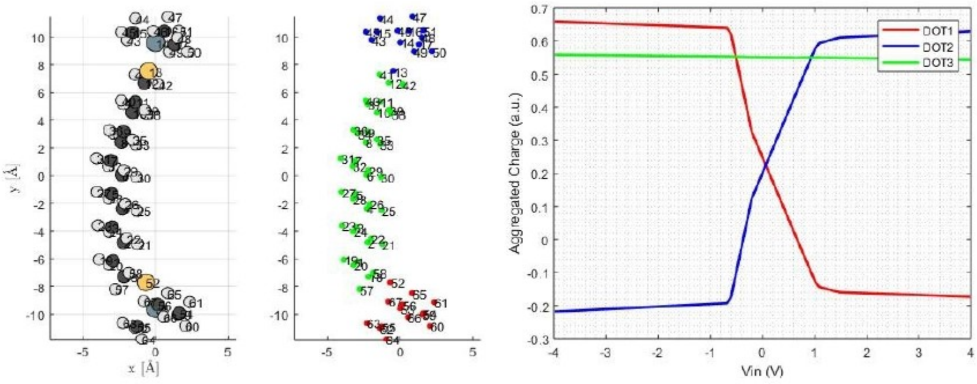

Figure 3.14. On the left, SiSSi long odd thiol molecule (oxidized) and its division into three DOTS (blue, green and red). On the right, the VACT transcharacteristics.

3.2.4 SiSSi benzenetrithiol

Up to now the focus of the treatment have been the active Dots of the molecules. Actually, all the investigated molecules have also a third Dot, but, as it can be seen in all the VACT transcharacteristics analyzed, the atoms composing this third Dot do not have an influence on the electrostatic behaviour of the molecules (the Aggregated Charge remains constant varying V_{in}).
As said in subsection 1.2.3, for ensure a correct information propagation in a QCA wire, it is convenient to have a cell in which there is a further Dot responsible for the "NULL" state.
In the following it will try to simulate the "SiSSi" molecule with the addition of a third chain for emulate the presence of a further Dot.
The first analyzed molecule is the so called "SiSSi benzenetrithiol"; this molecule has the structure of the Bis(trimethylsilyl) Sulfide with thiol groups and at the center of the atoms chain there is the benzenetrithiol which is a chemical compound composed by a benzene group at whose three vertices are linked three thiols unit (Figure 3.15).

The chemical formula of the molecule is $C_{24}H_{46}Si_2S_5$ and the optimized "SiSSi benzenetrithiol" (oxidized state) is shown in Figure 3.16. For the characterization, two point charges located at 50 Åeach from the center of molecule are used and, in order to exploit a definite range of V_{in}, different values of them are analyzed.

In Figure 3.17 (right) it is shown the VACT transcharacteristics of SiSSi benzenetrithiol; the Aggregated Charge is quite constant for all three Dots near $V_{in} = 0V$ but, unlike all other molecules previously studied, here Dot3 has an impact on the electrostatic behaviour of the system, because for higher and lower values of V_{in}, the AC is not constant. In

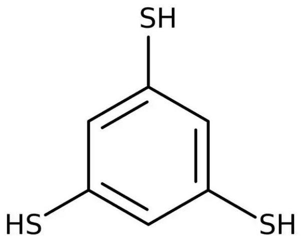

Figure 3.15. 1,3,5 - Benzenetrithiol.

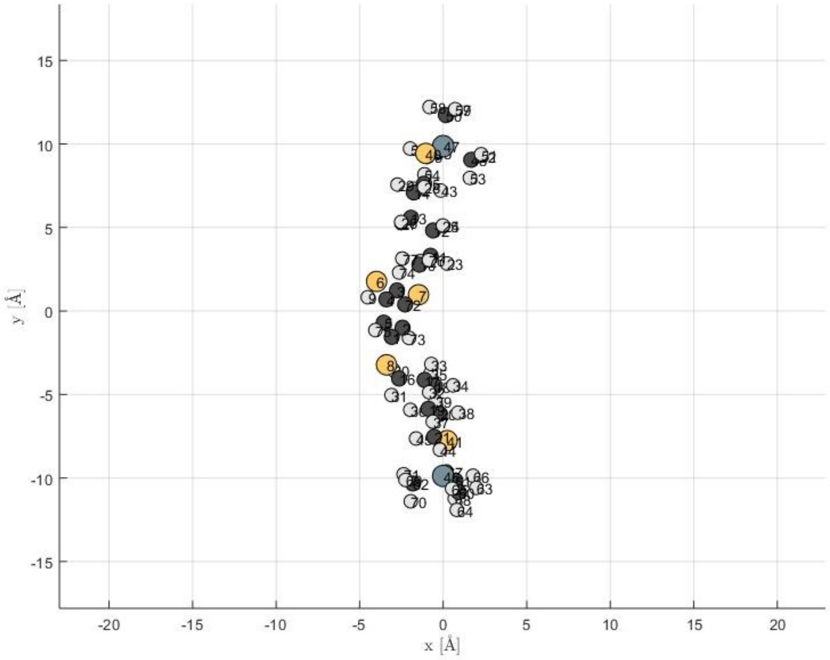

Figure 3.16. Optimized SiSSi benzenetrithiol molecule (oxidized). In orange are represented the Sulfur atoms, in white the Hydrogens, in black the Carbons and in grey the Silicons.

conclusion, by using always the same distribution of point charges, the atoms composing the benzenetrithiol functional group are not "indifferent" to the applied electric field. Regarding the active Dots (Dot1 and Dot2), for $V_{in} \simeq \pm 4V$ there is a relative good charge separation.

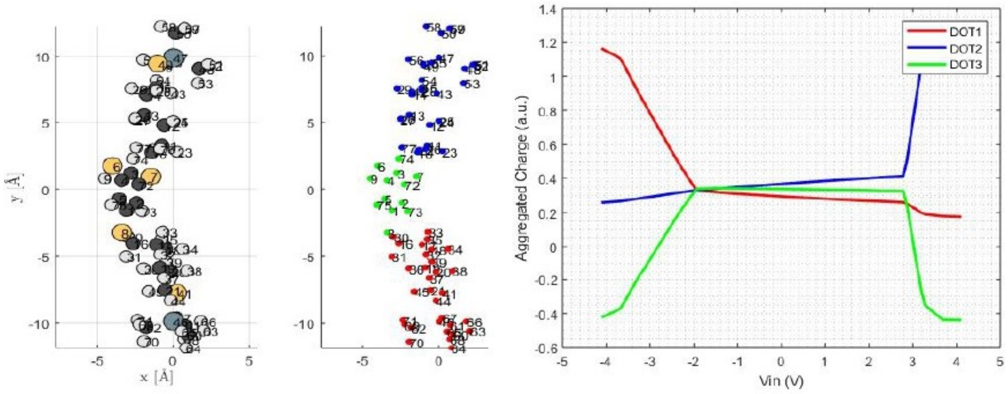

Figure 3.17. On the left, SiSSi benzenetrithiol molecule (oxidized) and its division into three DOTS (blue, green and red). On the right, the VACT transcharacteristics.

3.2.5 SiSSi trithiocyanuric acid

The second analyzed molecule is "SiSSi trithiocyanuric acid"; in this case, the functional group composing the third Dot is the so called Trithiocyanuric Acid (Figure 3.18), which is a chemical compound composed by the Cyanuric Acid to which three carbon atoms are linked as many thiol groups. The chemical formula of the entire molecule is $C_{21}H_{43}N_3Si_2S_5$ and the optimized molecule (oxidized state) it is shown in Figure 3.19.

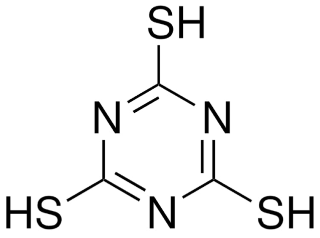

Figure 3.18. Trithiocyanuric Acid.

The VACT transcharacteristics is depicted in Figure 3.20 (right). As it can be seen, the AC of Dot3 is quite constant for the exploited V_{in} range and this means that the electric field does not influence the macroscopic behaviour of the charges composing the Trithiocyanuric Acid group. With the usual distribution of point charges, SiSSi trithiocyanuric acid behaves as a 2-Dot molecule with a good charges separation between the two active Dots. As for the SiSSi long thiol, also in this case the transcharacteristics is asymmetric, showing a lower charge separation between Dot1 and Dot2 for positive value of V_{in}.

For improve the behaviour of the system, in the following it will try to study the SiSSi trithiocyanuric acid molecule with three chains of thiols group.

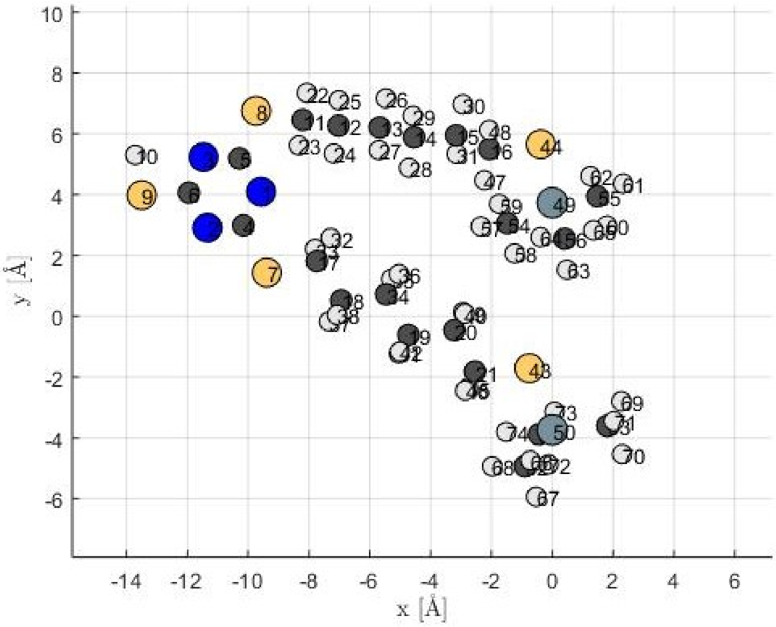

Figure 3.19. Optimized SiSSi trithiocyanuric acid molecule (oxidized). In orange are represented the Sulfur atoms, in white the Hydrogens, in black the Carbons, in grey the Silicons and in blue the Nitrogens.

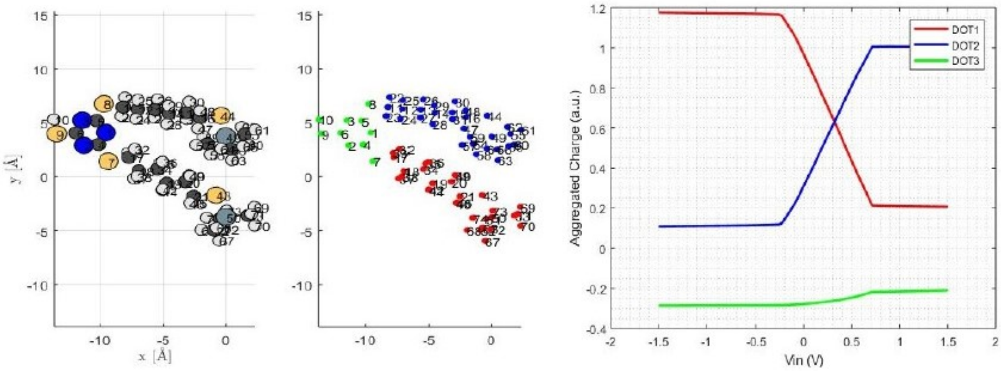

Figure 3.20. On the left, SiSSi trithiocyanuric acid molecule (oxidized) and its division into three DOTS (blue, green and red). On the right, the VACT transcharacteristics.

3.2.6 SiSSi trithiocyanuric acid with three chains

The molecule called "SiSSi trithiocyanuric acid with three chains" has the same structure of the SiSSi trithiocyanuric acid with the adding of a third chain of thiol groups. The chemical formula of the molecule is $C_{27}H_{55}N_3Si_2S_6$ and the optimized (oxidized) compound it is shown in Figure 3.21.

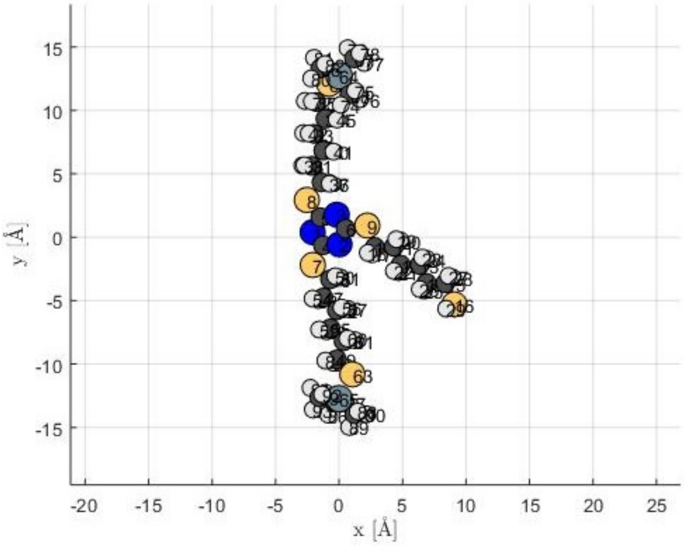

Figure 3.21. Optimized SiSSi trithiocyanuric acid with 3 chains molecule (oxidized). In orange are represented the Sulfur atoms, in white the Hydrogens, in black the Carbons, in grey the Silicons and in blue the Nitrogens.

In this work, this molecule is used as an example for simulate the presence of the clock in a MQCA system. The unit composed by the Trithiocyanuric Acid and the last added chain of thiol groups form Dot3, while the other two branches are the two active Dots. In Figure 3.22 it is represented the SiSSi trithiocyanuric acid with three chains molecule (oxidized) and its division into three DOTS (blue, green and red).

For the characterization, in addition to the usual two point charges located on the straight line intersecting the two active Dots (at 50 Åeach from the center of the molecule) responsible for the generation of the V_{in}, are placed two more charges for simulate the presence of the clock in the other direction (perpendicular to the atoms composing the third Dot). In Figure 3.23 it is represented the SiSSi trithiocyanuric acid with three chains molecule with the system of point charges.

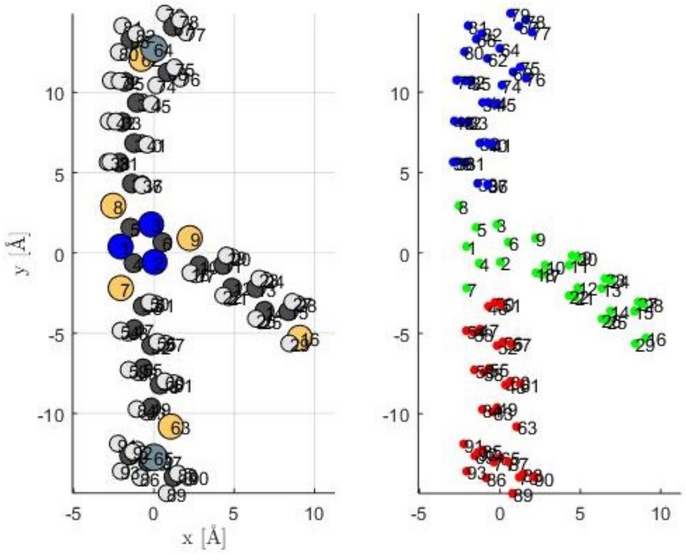

Figure 3.22. SiSSi trithiocyanuric acid with three chains molecule (oxidized) and its division into three DOTS (blue, green and red).

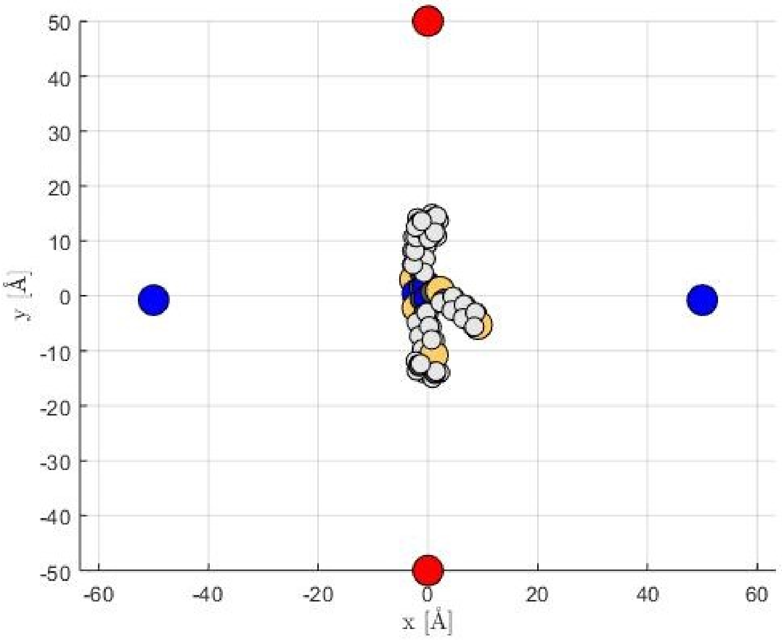

Figure 3.23. SiSSi trithiocyanuric acid with three chains molecule (oxidized) with a system of point charges (the red circles simulate the presence of V_{in} while the blue circles simulate the presence of the clock).

Two different cases are studied: the molecule subjected to a $Clock = +2V/nm$ and the molecule subjected to a $Clock = -2V/nm$. In Figure 3.24 (right), it is possible to see that when an electric field, pointing on the negative direction of the x-axis and corresponding to a $Clock = -2V/nm$, is applied to the compound, the system behaves as if it were in the Hold phase of the clock: depending on V_{in} value, the molecule can go in one of the two possible stable state ('1' or '0' logic value). In particular, there is a good charge separation between the active Dots and, even if the transcharacteristics still appears not perfectly symmetric, the behaviour is better than the SiSSi trithiocyanuric acid molecule without the third chain of thiols. The AC of Dot3 is constant and does not influence the electrostatic trend of the molecule.

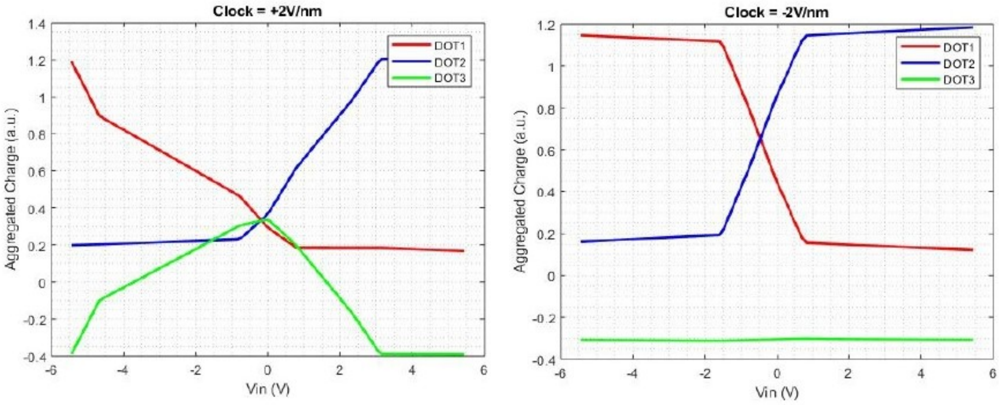

Figure 3.24. On the left, the VACT transcharacteristics of SiSSi trithiocyanuric acid with three chains molecule (oxidized) with $Clock = +2V/nm$. On the right, the VACT transcharacteristics of SiSSi trithiocyanuric acid with three chains molecule (oxidized) with $Clock = -2V/nm$.

In Figure 3.24 (left), instead, it is depicted the VACT transcharacteristics of the molecule when an electric field is applied in the positive direction of the x-axis (corresponding to a $Clock = +2V/nm$). For low values of V_{in}, the system behaves as if it were in the Relax phase of the clock: the molecule is forced to stay in the NULL state, the AC of all three Dots are quite similar and the charge is delocalized over the compound.
With this example, it has been established that by applying an electric field with lines in the same direction of the atoms composing the third Dots of a molecule, it is possible (by choosing the proper compound and the proper functional group) to switch the molecule between the Relax and the Hold phase and then to allow a correct information propagation in a MCQA wire.
Of course, it is possible to do better, to have a molecule with a better transcharacteristics, but this starting point is very significant.

3.3 Bistable diallyl-butane

Up to now the focus of this work has been the study of monostable molecules. However, in order to have a more complete view on the world of molecules, also the bistable characteristics and methodologies are useful to take into account.
For achieve this purpose, the bistable diallyl-butane is used as an example compound for demonstrate the modeling procedure of the bistable molecules; actually, recent studies have identified diallyl-butane with monostable characteristic, however for academic purposes, in the following this molecule will treated as bistable one.
The molecule is analyzed using Unrestricted Hartree-Fock method with basis sets STO-3G; for the characterization, an uniform electric field is applied to the system (FIELD case) generated by point charges and the CHELPG method is used to evaluate the atomic charges.
The diallyl-butane is a chemical compound composed by a butane group (C_4H_{10}) on whose two sides are linked two allyl groups ($-CH_2 - HC = CH_2$). The chemical formula of the molecule is $C_{10}H_{16}$. Being bi-stable, at the thermal equilibrium the charge should naturally aggregates on one of the two active Dots.
The first step for study this molecule is to optimize the geometry of the atoms; in Figure 3.25 it is represented the diallyl-butane (oxidized) in one of the two possible stable states. This configuration is called R_1.

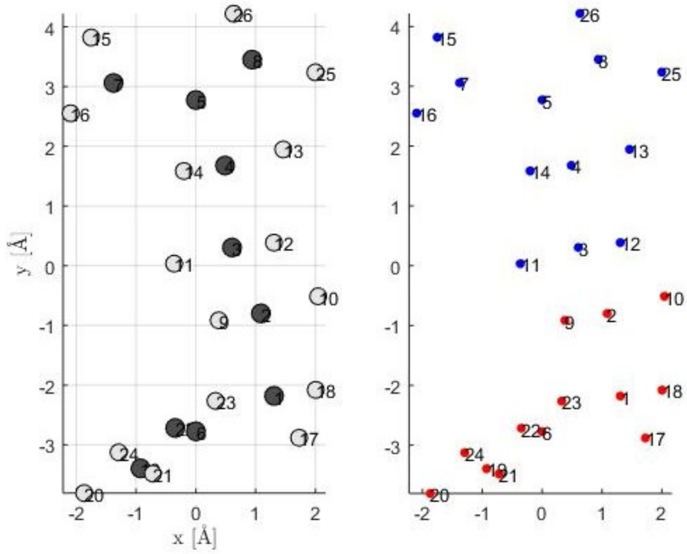

Figure 3.25. On the left, optimized diallyl-butane molecule (oxidized) in one of the two possible stable state (R_1). In white are represented the Hydrogens, in black the Carbon atoms. On the right, the division into two Dots of the molecule (blue and red).

For the characterization, two point charges are located at 50 Åeach from the center of the molecule; in Figure 3.26 it is shown the VACT transcharacteristics of R_1 configuration. In this analysis, the diallyl-butane is considered as a two-Dots molecule; at thermal equilibrium, the charge is located on Dot1 (composed by an allyl group and half butane molecule) and this confirms the bistable behaviour of the compound. The molecule is polar when there is no applied electric field. In addition, by increasing or decreasing V_{in}, there is a good charge separation between Dot1 and Dot2, whose trends alternates for opposite fields, demonstrating the capability to encode eventual information.

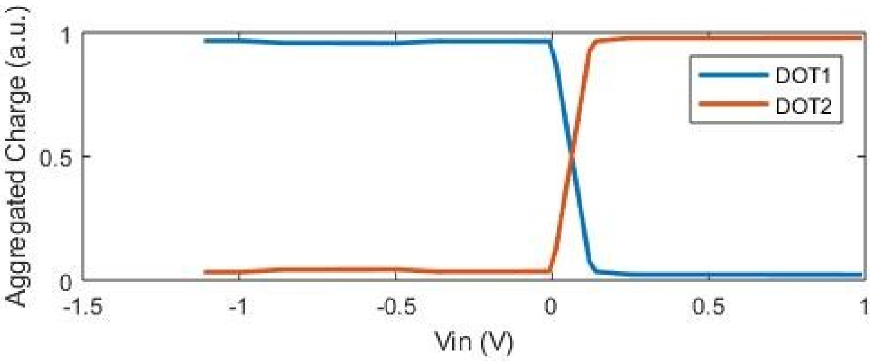

Figure 3.26. VACT transcharacteristics of oxidized diallyl-butane molecule (R_1 configuration).

For obtain the opposite state, it is necessary to make a mirror of molecule coordinates; in particular, denoting with R_2 the coordinate matrix of the other possible stable state of the system, it follows that:

$$R_2 = R_1 \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{3.1}$$

With this operation, the x-coordinate of the atoms has been inverted; in this way the atoms have moved a lot from their original position, for this reason it is necessary to reorder the rows of the coordinate matrix to ensure that the movement of each atoms is minimal. In Figure 3.27 it is shown the R_2 configuration of diallyl-butane molecule after the realignment process and its division into two Dots.

The VACT transcharacteristics of R_2 configuration is expected to be the opposite with respect to R_1 one. This is confirmed by the Figure 3.28, in which it can be seen that at the equilibrium the charge is localized on Dot2; also in this case there is a good charge separation between the two Dots by increasing or decreasing the V_{in} value.

The mean state of the molecule is derived by averaging the two configurations:

$$R_3 = \frac{1}{2}R_1 + \frac{1}{2}R_2 \tag{3.2}$$

with R_3 denoting the coordinate matrix of the averaged state.

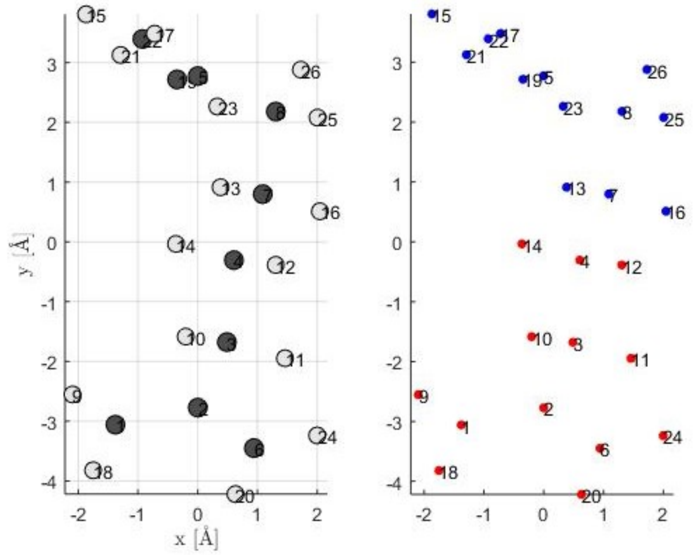

Figure 3.27. On the left, R_2 configuration of diallyl-butane molecule (oxidized). In white are represented the Hydrogens, in black the Carbon atoms. On the right, the division into two Dots of the molecule (blue and red).

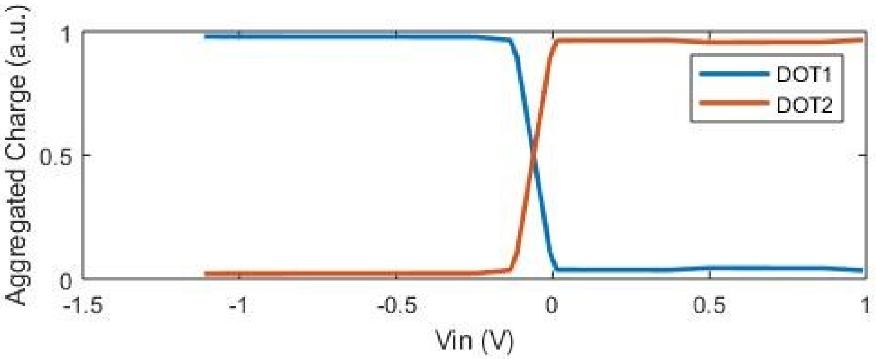

Figure 3.28. VACT transcharacteristics of oxidized diallyl-butane molecule (R_2 configuration).

In Figure 3.29 it is shown R_3 configuration of diallyl-butane molecule (oxidized) and its division into two Dots.

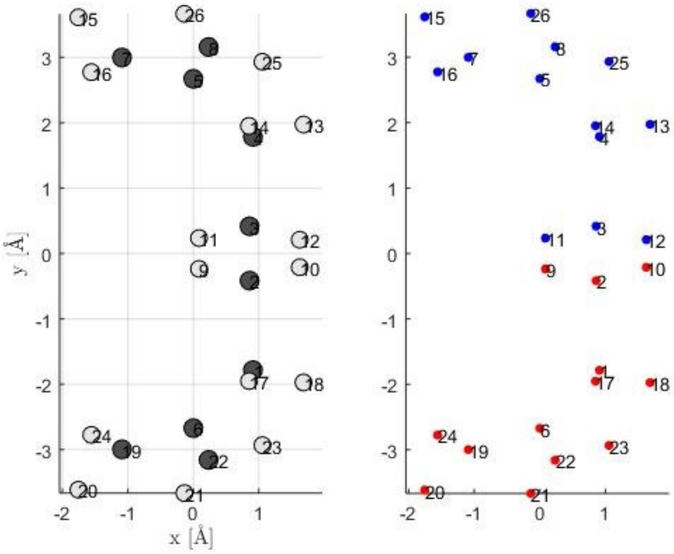

Figure 3.29. On the left, R_3 configuration of diallyl-butane molecule (oxidized). In white are represented the Hydrogens, in black the Carbon atoms. On the right, the division into two Dots of the molecule (blue and red).

From an energy perspective, it is interesting to compare the molecule energy obtained using bistable method with that obtained using monostable one. In order to do that, a single point analysis has been carried out; the bistable energy is obtained using Unrestricted Hartree-Fock (UHF) method with STO-3G basis sets and the energy of R_1 configuration results to be -383.050620740577 a.u. Instead, by optimizing and then by carrying out the single point analysis using monostable method (UKS CAM-B3LYP def2-SVP D3) the energy is -389.789343285559 a.u. The molecule, in this configuration, lies in a local minima and only when an external perturbation is applied to the system it is possible to change tha state of the diallyl-butane; a bistable behaviour it is observed.

In this Chapter have been studied the main methods and techniques for analyze monostable and bistable molecules; in particular, some of them show a good behaviour in terms of electrostatic characteristic for QCA purposes becoming possible candidates to be used for this technology. Of course, the way for the practical application is still long and the aim of this work it has been to give as general as possible methodologies in order to characterize the widest possible range of molecules.
In the following Chapter, a new class of molecules it will be investigated, the Phthalocyanines, showing interesting properties for nanocomputing applications.

Chapter 4

Phthalocyanines

The standard Molecular Quantum-dot Cellular Automata technology is composed by cells having two molecules with three dots each; in this way it is possible to have a six-dots cell able to encode logic information ('1' or '0' logic value) and, eventually, also the NULL state. Up to now, indeed, all the analyzed molecules in this work have these characteristics, having maximum three Dots and following the "original" MQCA trend.
The aim of this Chapter is to study and analyze a particular class of molecules able to constitute a single MQCA cell by only one molecule. These compounds are the Phthalocyanines; they have fourfold symmetry and for this reason in this thesis they are treated as four Dots units.
The methodologies for characterize them and the best charges distribution around these compounds will be studied in order to understand the possible information encoding. In addition, some figures of merit will be explored for having a more complete view on the electrostatic behaviour of these molecules.

4.1 Introduction to phthalocyanines

The phthalocyanines are organic compounds composed by four isoindole units linked by a ring of nitrogen atoms [20]; the isoindole group is an aromatic species consisting of a benzene ring fused with pyrrole. The typical structure of the phthalocyanine with two hydrogen atoms at the center of the molecule it is shown in Figure 4.1; in this work this molecule it will called "Hydrogen phthalocyanine" (or for brevity H_2Pc). The chemical formula of the compound is $(C_8H_4N_2)_4H_2$.

X-ray studies demonstrated that phthalocyanines form monociclic crystals and the entire molecule lies in on a plane (having a fourfold symmetry), except for the two central hydrogen atoms in the case of Hydrogen phthalocyanine compound [17].
The phthalocynines were discovered by happenstance. In 1907, Braun and Tchernian, at the South Metropolitan Gas Company in London, found a blue substance after heating *o*-cyanobenzamide: this substance probably was phthalocyanine [17].
One of the most important features of these compounds is that the two central hydrogen atoms can be replaced by metals belonging to every group of periodic table: the result

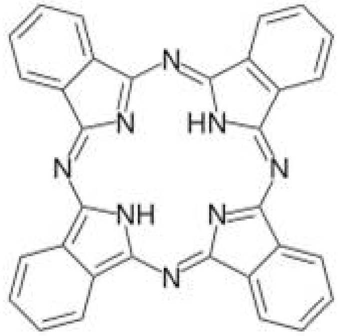

Figure 4.1. Hydrogen phthalocyanine.

is the formation of metal phthalocyanines. During the years, at least 70 metal phthalocyanines have been prepared with interesting and different chemical-physical properties. Thanks to their excellent tinctorial qualities, Copper phthalocyanine was accepted as an outstanding blue pigment. The aromaticity due to nitrogen and benzene structures may explain the high stability of these molecules; they are stable to acids, alkalies, moisture, heat, light and solvents. The phthalocyanines are thermally and chemically stable and can support intense electromagnetic radiations.

Among all the properties, certainly the one that is of greater interest for QCA application is the self-organization capability. It is possible to create long wires of phthalocyanine with various techniques; for example, to realize highly ordered 1D organic molecular chains, one possibility is to use a surface with regular step arrays whose step height is smaller than that of atomic steps [16]. In the case of Cobalt phthalocyanine (CoPc), Ag films grown on In/Si(111) satisfy this requirement; more in-depth studies have revealed that most of CoPc molecule adsorbed on this substrate have the same adsorbant angle. This is a "good news" in terms of information propagation, because, having the same molecular orientations, it is easier to create QCA wire (or, eventually, more complex logic architectures) and to study and predict the charge distribution among the atoms.

All the characteristics mentioned up to now may suggest that phthalocyanines (at least theoretically) could be interesting molecules for MQCA applications. In this way, in the following sections it will try to study their electrical properties for understanding how they behave under certain boundary conditions.

4.2 A new approach

Thanks to their interesting chemical and electrical properties, phthalocyanines are studied as possible QCA molecules candidate. As mentioned before, the particularity of this class of molecules is that they have a fourfold symmetry: the four isoindole groups form the vertices of a square.

The idea developed in this thesis is to try to make a single phthalocyanine molecule as a full QCA cell composed by four dots and then with the possibility to encode logic information. In Figure 4.2 it is shown a four dots cell with the corresponding phthalocyanine compound.

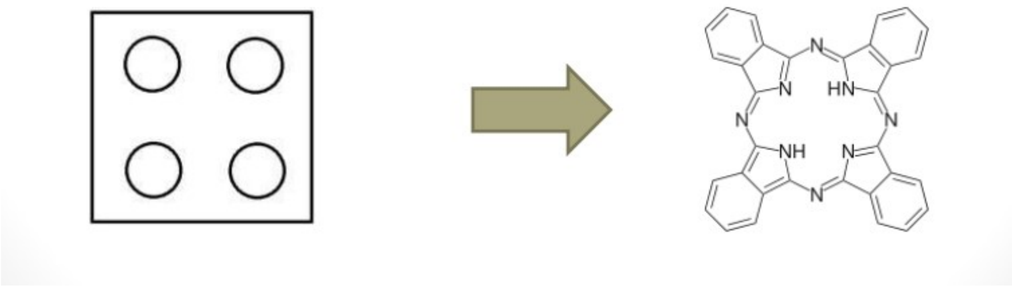

Figure 4.2. Four dots cell and the corresponding phthalocyanine compound.

In order to analyze and understand the possible charges distribution inside the molecules, the same methodology seen up to now it is used: molecule geometry optimization, molecule response evaluation and result analysis. The first compound which will be taken into account is Hydrogen phthalocyanine.

4.3 Hydrogen phthalocyanine

4.3.1 Molecule geometry optimization

The Hydrogen phthalocyanine is a monostable molecule and, for this reason, in order to optimize its geometry, Density Functional Theory is used; Unrestricted Kohn-Shann method, CAM-B3LYP functional, def2-TZVP basis set and D3 correction are the other parameters which are set. In Figure 4.3 it is shown the optimized compound (neutral) in the xy plane (top) and in the xz plane (down). From 4.3 (top) it is possible to see the fourfold symmetry of the molecule, with the four isoindole groups forming the vertices of a square. From 4.3 (down), instead, it can be observed that the entire molecule lies in on a plane.

4.3.2 Electrostatic characterization

The aim of this paragraph is to study the Hydrogen phthalocyanine response to electric fields. Point charges are used to emulate them and, in order to have a complete view on the molecule behaviour, several charges dispositions are analyzed for simulate the presence of electric fields in various directions. The studied configurations are:

1. charges on the right and left with respect the molecule;
2. charges above and below the molecule;
3. charges along z-axis;
4. charges along the main diagonal of the molecule;
5. charges along the secondary diagonal of the molecule.

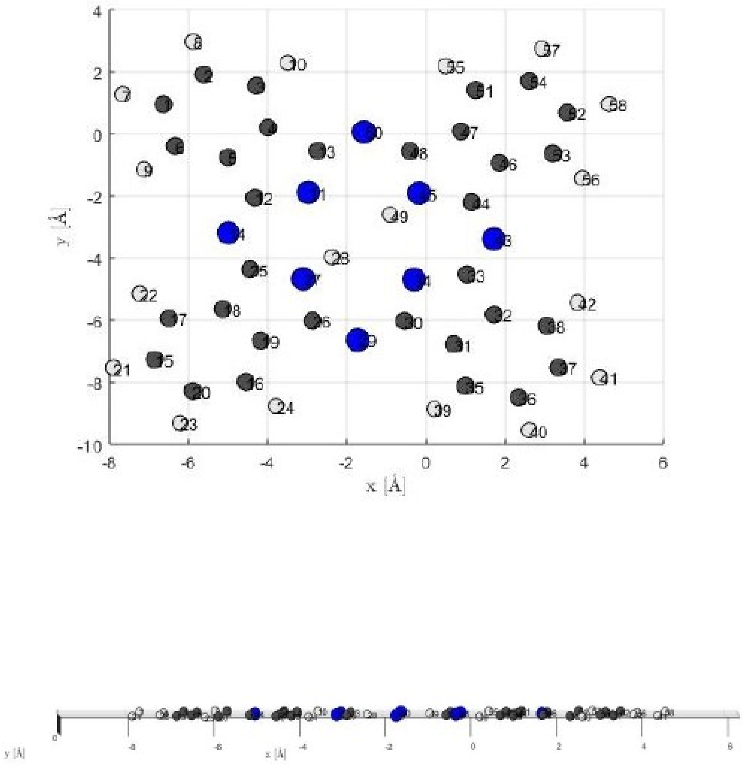

Figure 4.3. Optimized Hydrogen phthalocyanine molecule (neutral). On top it is shown the xy plane, down the xz plane. In white are represented the Hydrogen atoms, in black the Carbons and in blue the Nitrogens.

In Figure 4.4 it is shown the division into 4 Dots of H_2Pc. Each Dot is composed by one isoindole unit, except for the blue and green ones in which also the two central hydrogen atoms typical of this structure are included. The Nitrogens which act as binders of the isoindols do not belong to any Dot. For simplicity and greater clarity, for all the treatment the Dots will be indicated as follows:

- Blue dot = DOT1;
- Red dot = DOT2;
- Green dot = DOT3;
- Yellow dot = DOT4.

For the following analysis, CHELPG method is used to evaluate the atomic charges and the electric fields applied to the system are assumed to be uniform (FIELD case).

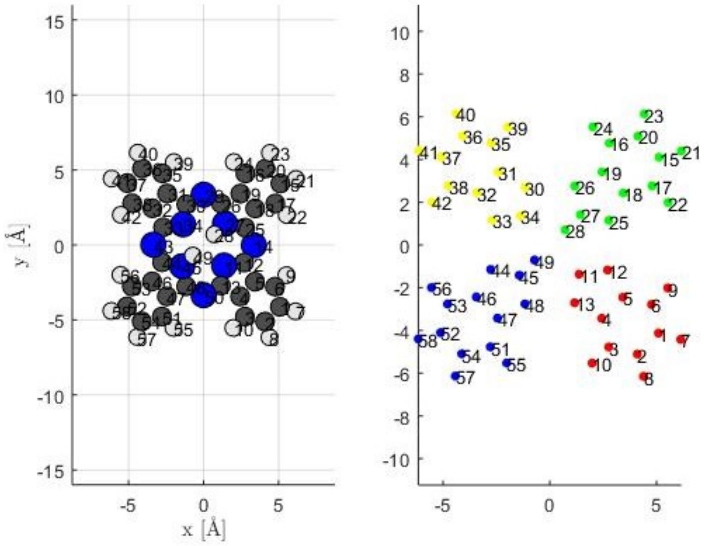

Figure 4.4. Hydrogen phthalocyanine molecule (left) and its division into 4 Dots (blue, red, green and yellow) (right).

1. **Charges on the right and left with respect the molecule**

   The first studied configuration sees the charges placed on the right and left with respect the molecule. In Figure 4.5 it is shown the xy-plane in which lies the Hydrogen phthalocyanine molecule and the two point charges (red circles) which are located on the x-axis at a distance of 50Åeach from the center of the molecule.

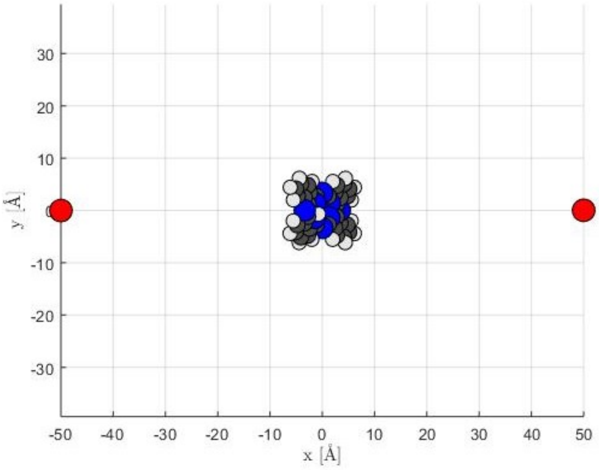

Figure 4.5. Hydrogen phthalocyanine molecule with two point charges (red circles).

The generated electric field has the lines parallel to x direction and it is evaluated in the point occupied by the Nitrogen atom n.43 (see Figure 4.4). The mathematical formula for calculate it is:

$$E_x = \begin{cases} \frac{kqQD1}{(-d-N)^2} + \frac{kq|QD2|}{(d-N)^2}; & \text{if } QD1 > 0 \\ -\frac{kq|QD1|}{(-d-N)^2} + \frac{kqQD2}{(d-N)^2}; & \text{if } QD1 < 0 \end{cases} \tag{4.1}$$

where:

- k: Coulomb constant;
- q: elementary charge;
- $QD1$ and $QD2$: point charges values;
- $d = 50$Å;
- N: x-coordinate of Nitrogen atom (n.43).

In order to analyze the molecule response in a definite range of E_x, sevaral values of point charges are exploited. In Figure 4.6 it is shown the AC of the Hydrogen phthalocyanine as a function of E_x.

It can be noted that when there is no applied electric field, Dot1 and Dot3 have the same AC as well as Dot2 and Dot4. In addition, due to the presence of the two central hydrogens, Dot1 and Dot3 have a greater total charge than Dot2 and Dot4. When E_x starts to increase (in the positive x-direction), the charges aggregate more on the left of the molecule; viceversa, if E_x decreases, they tend to go on the right side of H_2Pc.

From this first analysis, it can be deduced that by applying an even not too high field ($\pm 3V/nm$) it is possible to change the charges distribution inside the molecule. The AC separation between the Dots is quite low ($\sim$ 0,2$a.u.$), but this seems to be an interesting starting point for the characterization of others configurations.

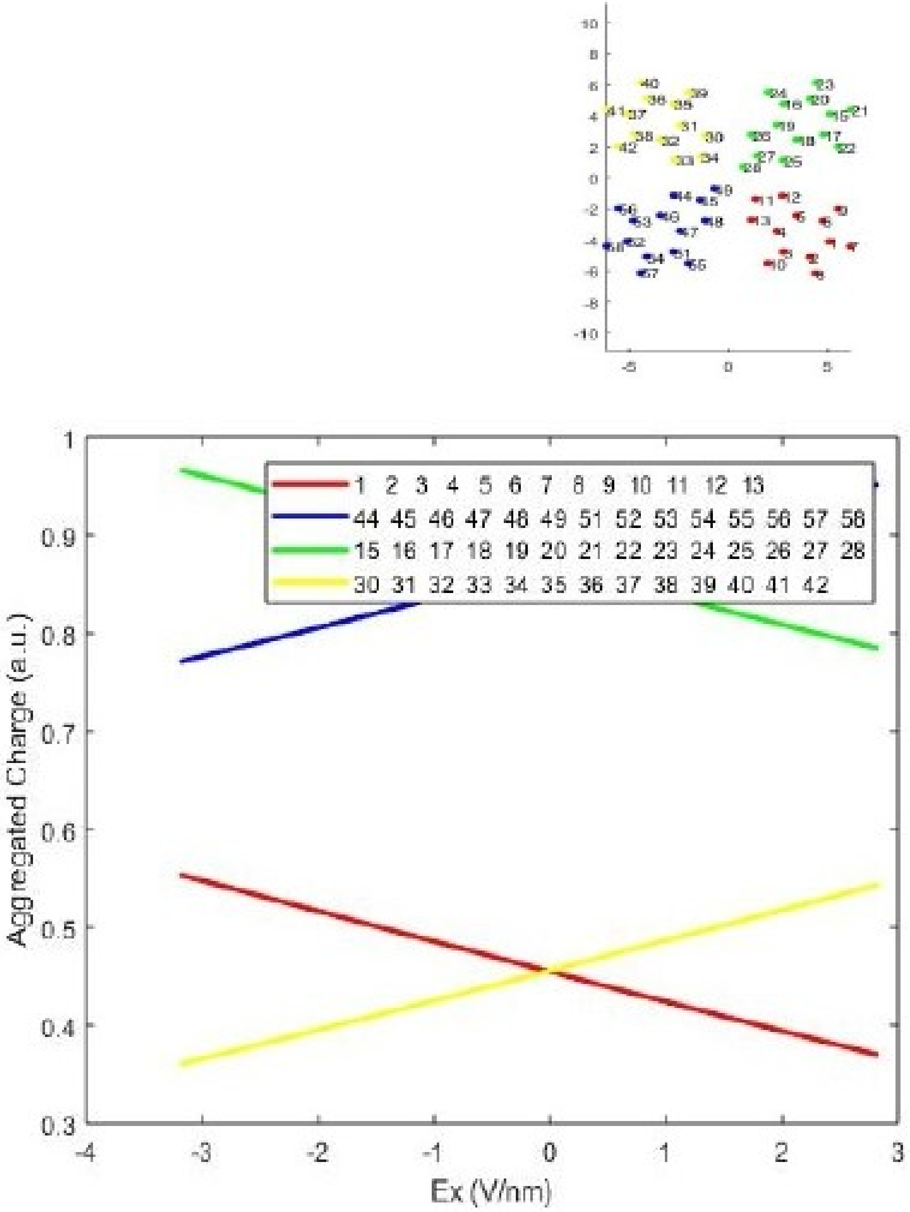

Figure 4.6. Aggregated Charge of Hydrogen phthalocyanine as a function of E_x with point charges placed on the left and right with respect the molecule. On top, the division into 4 Dots.

Also the *ab initio* Self-Consistent Field (SCF) Energy of the system is evaluated. As it can be seen from the Figure 4.7, the energy profile is symmetric with respect to the zero electric field; this means that there are no signs of bistability and, being the molecule monostable, the method used for analyze it, seems to be correct.

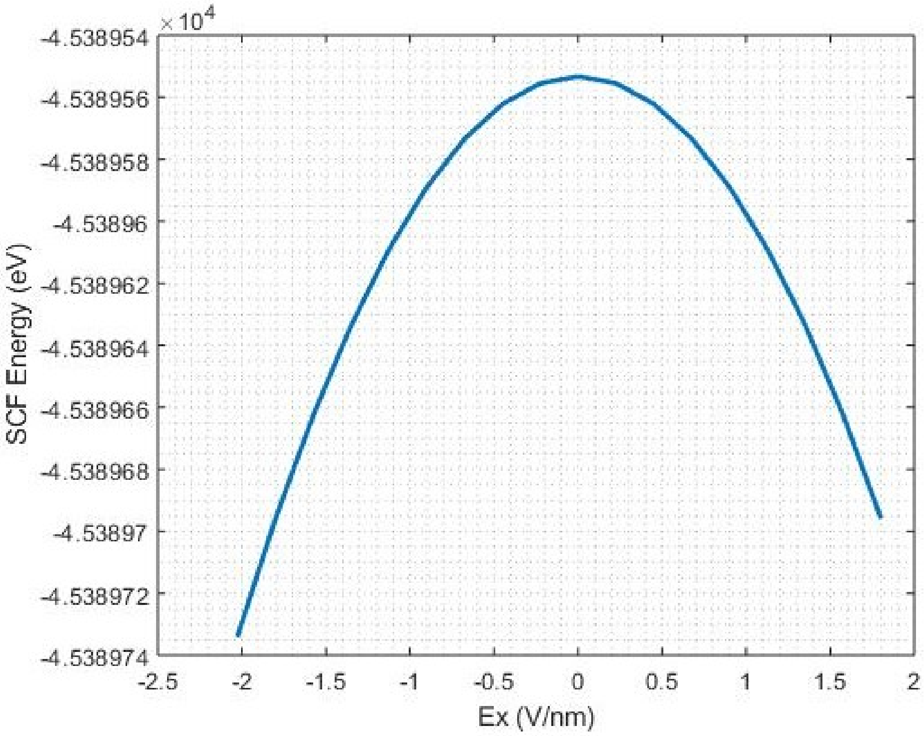

Figure 4.7. SCF Energy of Hydrogen phthalocyanine molecule.

2. **Charges above and below the molecule**

The second studied configuration sees the two point charges placed above and below with respect the molecule (Figure 4.8). In this case, the generated electric field is parallel to y-axis and it is evaluated in the point occupied by the Nitrogen atom n.29 (see Figure 4.4).

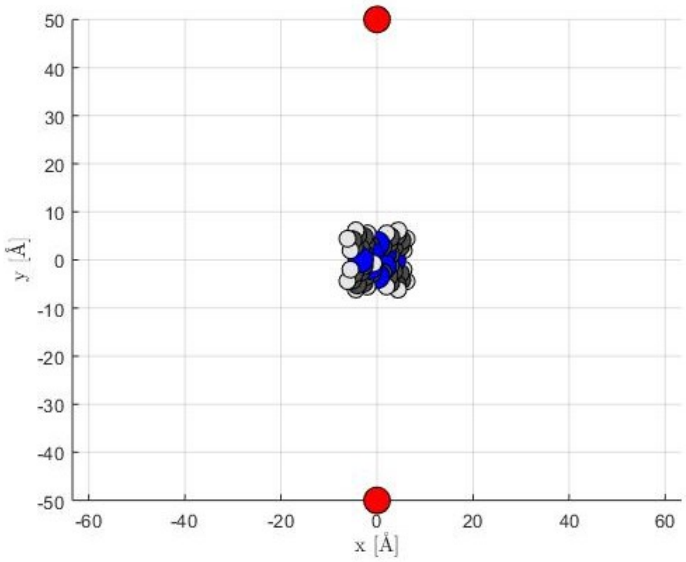

Figure 4.8. Hydrogen phthalocyanine molecule with two point charges (red circles).

The formula for calculate it is:

$$E_y = \begin{cases} -\frac{kqQD1}{(d-N)^2} + \frac{kq|QD2|}{(d-N)^2}; & \text{if } QD1 > 0 \\ \frac{kq|QD1|}{(d-N)^2} + \frac{kqQD2}{(-d-N)^2}; & \text{if } QD1 < 0 \end{cases} \tag{4.2}$$

where:

- k: Coulomb constant;
- q: elementary charge;
- $QD1$ and $QD2$: point charges values;
- $d = 50$Å;
- N: x-coordinate of Nitrogen atom (n.29).

The AC figure of merit is analyzed in order to study the molecule response to E_y. From Figure 4.9, it is possible to see that the trend is similar to the left-right point charges location: at the equilibrium the Aggregated Charge of Dot1 and Dot3 is greater than Dot2 and Dot4 due to the presence of the two central hydrogen atoms. If instead, E_y increases, the charges aggregate in the bottom part of the molecule;

viceversa, with E_y decreasing, the charge move towards the upper area. Also for this configuration the AC separation between the Dots is quite low (for $E_y \pm 3V/nm$, $AC \sim 0{,}2a.u.$).

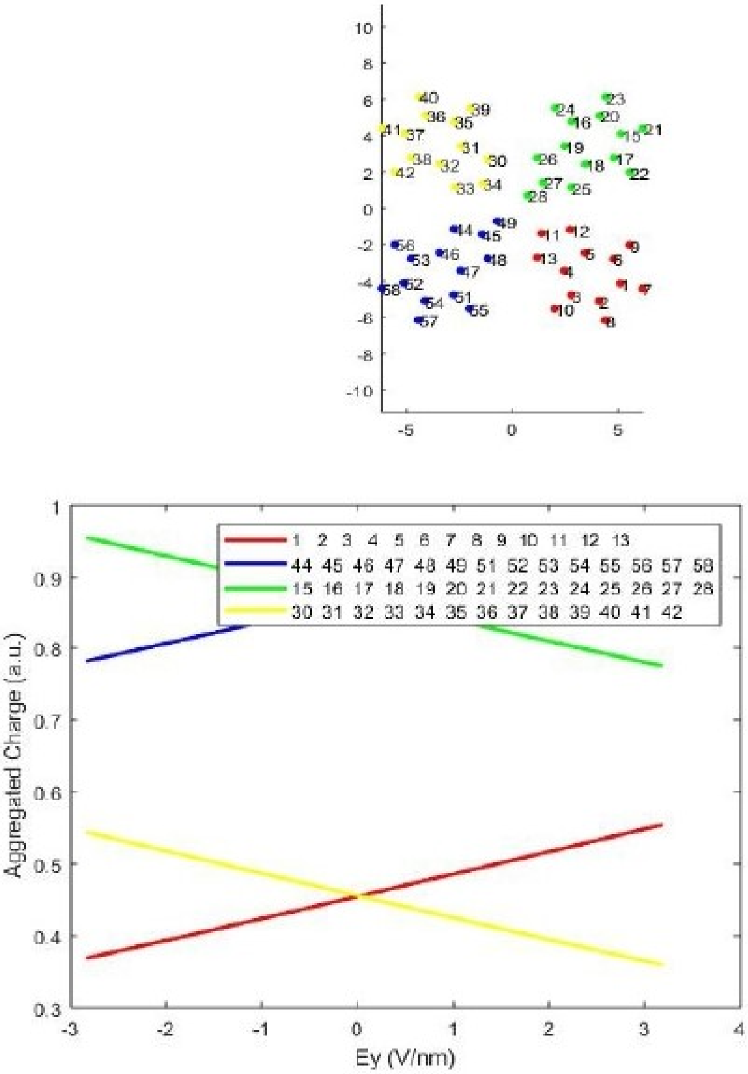

Figure 4.9. Aggregated Charge of Hydrogen phthalocyanine as a function of E_y with point charges placed above and below with respect the molecule. On top, the division into 4 Dots.

From these two first studied cases, it can be deduced that the charges move in the opposite direction with respect the positive electric field lines; however, the AC of the various Dots do not have a trend which might make it think to use these configurations as possible example of QCA cells.

3. **Charges along z-axis**

As already explained, the entire H_2Pc molecule lies in on a plane; this has been confirmed by optimizing its geometry (Figure 4.3). The third analyzed configuration sees the two point charges placed along the z-axis. The system composed by the Hydrogen phthalocyanine and the point charges it is shown in Figure 4.10; from this image it can be seen the molecule lying on the $z = 0$ plane.

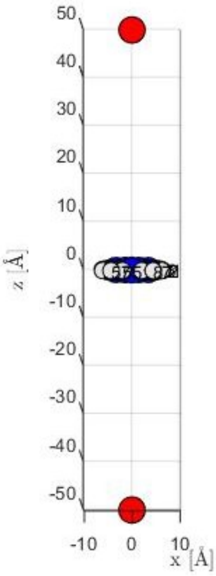

Figure 4.10. Hydrogen phthalocyanine molecule with two point charges (red circles).

In this case, the generated electric field is parallel to z-axis and it is evaluated in (0,0,0) point. The mathematical formula for calculate it is:

$$E_z = \begin{cases} -\frac{kqQD1}{d^2} + \frac{kq|QD2|}{d^2}; & \text{if } QD1 > 0 \\ \frac{kq|QD1|}{d^2} + \frac{kqQD2}{d^2}; & \text{if } QD1 < 0 \end{cases} \tag{4.3}$$

where:

- k: Coulomb constant;
- q: elementary charge;
- $QD1$ and $QD2$: point charges values;
- $d = 50Å$.

Being the electric field lines perpendicular to $z = 0$ plane, it is expected that the AC of the four Dots does not have a big variation. From Figure 4.11 it can be noted that the Aggregated Charge of Dot2 and Dot4 remains constant for the exploited E_z range ($\pm 3V/nm$). Dot1 and Dot3, instead, show a very low variation, but this is irrelevant for the task of the treatment. The result is that, when point charges are located perpendicular to the plane in which the molecule lies (for emulate the presence of a driver or another molecule), the generated electric field does not affect the electrical characteristics of H_2Pc.

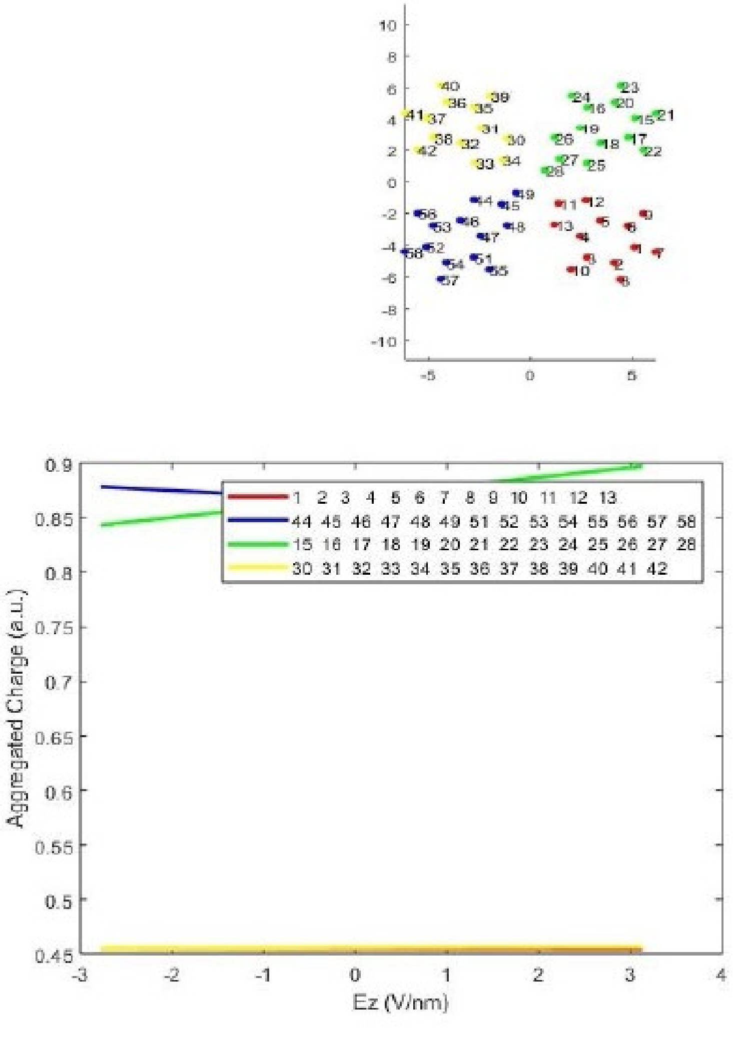

Figure 4.11. Aggregated Charge of Hydrogen phthalocyanine as a function of E_z with point charges along z-axis. On top, the division into 4 Dots.

4. **Charges along the main diagonal of the molecule**

The aim of this work is to "see" the Hydrogen phthalocyanine molecule as a 4-Dots cell; because of this, it is possible to identify inside the compound two diagonals which are typical of matrix theory. The main diagonal is composed by Dot2 and Dot4, the

secondary diagonal is composed by Dot1 and Dot3.
The fourth analyzed configuration sees the two point charges placed along the main diagonal of the molecule (Figure 4.12): considering the x-y plane, one point charge is located in (-40, 40) Å, while the other is located in (40, -40) Å. H_2Pc is optimized and then reallocated in such a way its center coincides with the origin of the axes.

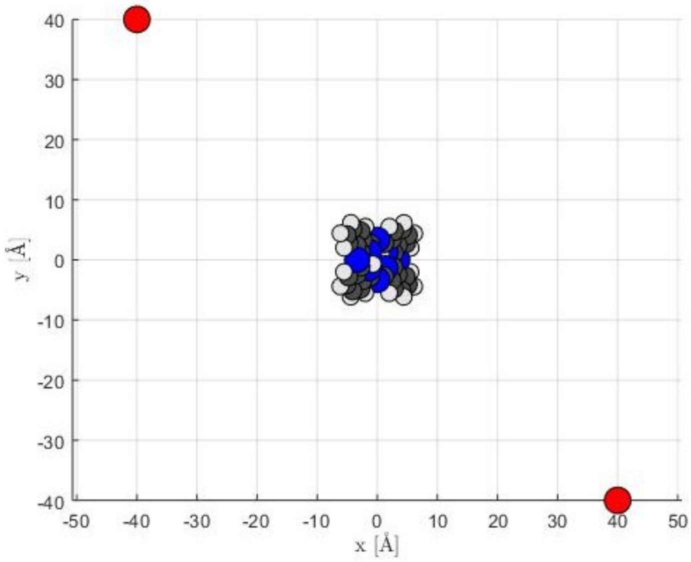

Figure 4.12. Hydrogen phthalocyanine molecule with two point charges (red circles).

Depending on the values of point charges, the generated electric field cross the main diagonal of the molecule, having the lines which begin and end in the two charges. In order to study the electrical response of the molecule, the AC of the various Dots are taken into account considering a field parallel to y-direction. The generated field is then decomposed into its three components and E_y is calculated as:

$$E_y = \begin{cases} -E_1cos(\frac{\pi}{4}) + E_2cos(\frac{\pi}{4}); & \text{if } QD1 > 0 \\ E_1cos(\frac{\pi}{4}) + E_2cos(\frac{\pi}{4}); & \text{if } QD1 < 0 \end{cases} \tag{4.4}$$

where:

- $E_1 = \frac{kq|QD1|}{a^2}$;
- $E_2 = \frac{kq|QD2|}{a^2}$;
- a: distance between the point charge and (0,0,0) coordinate;
- k: Coulomb constant;
- q: elementary charge;
- $QD1$ and $QD2$: point charges values.

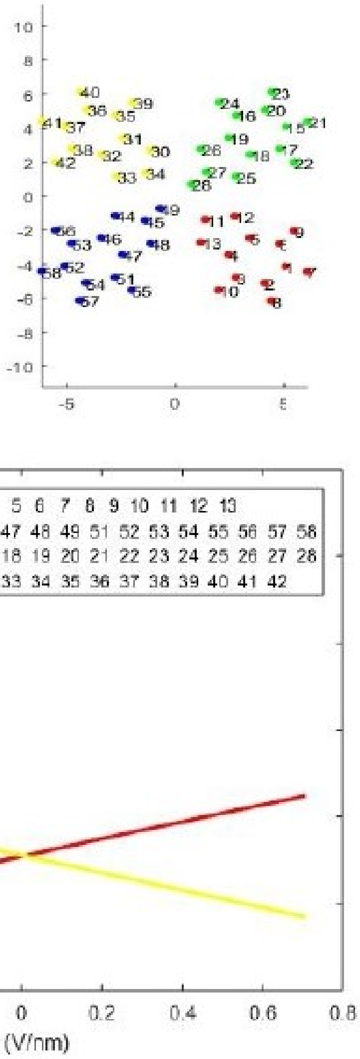

Figure 4.13. Aggregated Charge of Hydrogen phthalocyanine as a function of E_y with point charges located along the main diagonal of the molecule. On top, the division into 4 Dots.

In Figure 4.13 it is shown the Aggregated Charge characteristic as a function of E_y.

The AC of the Dots located on the secondary diagonal (Dot1 and Dot3) remains unchanged, while the Dots placed on the main diagonal are affected by the electric field. In particular, if E_y increases, the charges move on Dot2, while if E_y decreases, the charges aggregate more on Dot4. This is in agreement with what it has seen so far, with the movement of the charges which is opposite to the positive direction of field lines. Being the point charges located on the straight line intersecting the two Dots on the main diagonal, the resulting E_y component is lower than the case in

which the charges are placed above and below the molecule. In this configuration, the exploited E_y range is ±0,7V/nm and the charge separation between Dot2 and Dot4 is quite low ($\sim$ 0,12$a.u.$ at E_y value limits). However, by increasing the point charges values and as a consequence the exploited field range, the charge separation could be better.
For QCA purposes this configuration seems to be acceptable, in the sense that there are two Dots (secondary diagonal) which do not vary their amount of charge, while the others two, depending to the external influences, increase or decrease their AC. Two possible state can exist with the possibility to encode logic information. For sure, the way for the practical application is still long and hard, but these first simulative results make it think that the undertaken road could be the correct one.
Another interesting figure of merit are the isopotential surfaces of the molecule; in physics, an isopotential refers to a region in space where every point is at the same potential. In Figure 4.14 are represented the isopotential surfaces (evaluated at -0,4 V) of Hydrogen phthalocyanine.

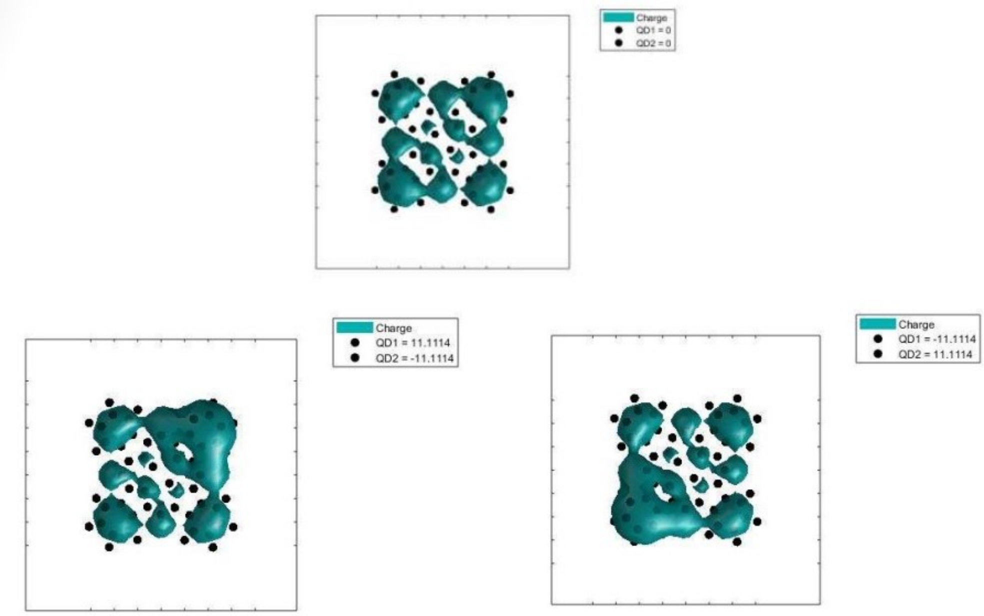

Figure 4.14. Isopotential surfaces (evaluated at -0,4 V) of Hydrogen phthalocyanine. On top it is shown the molecule in the absence of applied electric fields (QD1 = 0, QD2 = 0). On bottom, it is shown the molecule in which E_y lines go downwards (QD1 = 11,1114, QD2 = -11,1114) (left) and upwards (QD1 = -11,1114, QD2 = 11,1114) (right). QD1 and QD2 are the normalized values of the two point charges.

On top of the image, it can be seen the molecule in the absence of applied electric fields: the quasi-symmetric isopotential surfaces denotes the presence of a negligible dipole moment at the equilibrium and confirms the non-polar nature of H_2Pc. On bottom, instead, are shown the cases in which electric fields are applied to the molecule (on the left, E_y lines go downwards, on the right, E_y lines go upwards). In both cases, the electric field induces a displacement of the molecule charge center in the opposite direction of the field, inducing a non-zero dipole moment. Two opposite configurations arise and the molecule polarises. This confirms the monostable nature of Hydrogen phthalocyanine: some energy is needed to induce a polar behaviour in the compound.

5. **Charges along the secondary diagonal of the molecule**

The last analyzed configuration sees the two point charges located along the secondary diagonal of the molecule (Figure 4.15). One is placed in (40, 40) Å, the other in (-40, -40) Å.

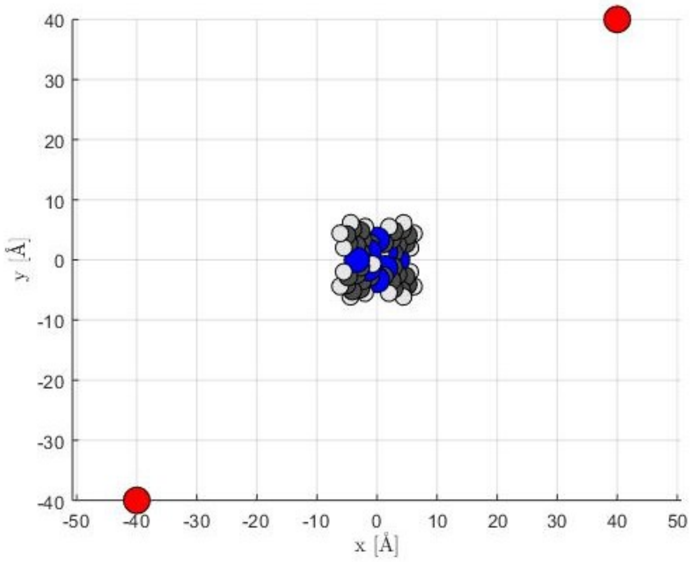

Figure 4.15. Hydrogen phthalocyanine molecule with two point charges (red circles).

Also in this case, for the characterization, the y-component of the electric field is taken into account. E_y is then calculated as:

$$E_y = \begin{cases} E_1 cos(\frac{\pi}{4}) + E_2 cos(\frac{\pi}{4}); & \text{if } QD1 > 0 \\ -E_1 cos(\frac{\pi}{4}) + E_2 cos(\frac{\pi}{4}); & \text{if } QD1 < 0 \end{cases} \tag{4.5}$$

where:

- $E_1 = \frac{kq|QD1|}{a^2}$;
- $E_2 = \frac{kq|QD2|}{a^2}$;
- a: distance between the point charge and (0,0,0) coordinate;
- k: Coulomb constant;
- q: elementary charge;
- $QD1$ and $QD2$: point charges values.

In Figure 4.16 it is shown the Aggregate Charge of Hydrogen phthalocyanine molecule as a function of E_y. In this case, the Dots placed on the main diagonal (Dot2 and Dot4) do not vary their amount of charges, while the others two (Dot1 and Dot3) are affected by E_y. In particular, for positive values of electric fields, the charges aggregate more on Dot1, while for negative values of electric fields, the charge move on Dot3.

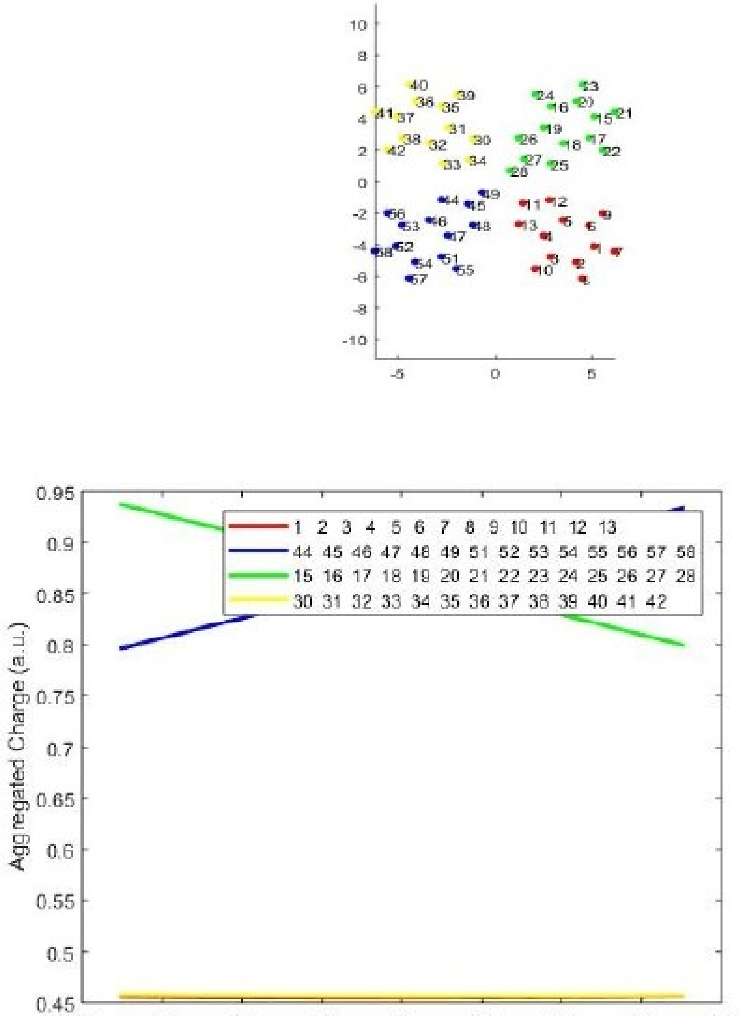

Figure 4.16. Aggregated Charge of Hydrogen phthalocyanine as a function of E_y with point charges located along the secondary diagonal of the molecule. On top, the division into 4 Dots.

As for the previous charges distribution, it is possible to identify two opposite configurations in which the molecule can lie. Being the Dots on the main diagonal "indifferent" to electric field, the molecule state depends on Dot1 and Dot3: they have opposite behaviour depending on the direction of E_y and logic information could be encoded.

From all analyzed charges configurations, the better results are given by placing the drivers along the two diagonals of the molecule. This is an interesting starting point for future studies on Hydrogen phthalocyanine, which has gave first informations on how drivers or others molecules could be positioned in the neighborhood of H_2Pc for making possible its application in QCA technology.

4.4 Polarizability

As said in 4.1, it is possible to replace the two central hydrogen atoms of H_2Pc with metals belonging to every group of periodic table; in this way metal phthalocyanines are created. In order to analyze their electrical characteristics, a "new" figure of merit is taken into account: the polarizability.
The polarizability is the tendency of a molecule to create a dipole moment when subjected to an electric field [2]. If the applied field is small, the induced dipole moment μ can be expressed as:

$$\mu = \alpha E \tag{4.6}$$

where α is the molecule polarizability and describes the linear response of the molecule to external electric fields. It is important to underline that the model used in this work applies only to monostable molecules; the phthalocyanines which will be studied show all monostable characteristics.
The polarizability of a molecule can be expressed as a 3×3 matrix:

$$\mu = \alpha E = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} E \tag{4.7}$$

The term α_{ij} represents the attitude of the molecule to create a dipole moment along the direction i as a response of a field along the direction j. If the molecules coordinates are properly chosen, the terms α_{ij} (with $i \neq j$) can be neglected. This means that any electric field induces a dipole along the same direction in which it is applied and neglecting molecule anisotropy; in this way it is possible to approximate the polarizability as a diagonal matrix:

$$\mu = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix} E \tag{4.8}$$

In order to study the polarizability of the phthalocyanines, DFT calculation is used; the molecules are stimulated with electric fields on the order of 0.001 a.u. (∼0.5 V/nm) using the function "elprop" of the ORCA package which enables to calculate some electrical properties of the compounds. In particular, numeric differentiation of dipole procedure is used.

4.4.1 Calculation of molecules polarizability

Hydrogen phthalocyanine

The first analyzed molecule is the well known Hydrogen phthalocyanine. The polarizability tensor is:

$$\alpha = \begin{pmatrix} 876{,}67951 & 12{,}14748 & 0{,}93054 \\ 12{,}14748 & 875{,}51084 & 2{,}40550 \\ 0{,}93054 & 2{,}40550 & 184{,}62904 \end{pmatrix} a.u. \tag{4.9}$$

It is possible to see that α_{ij} elements with $i \neq j$ are negligible with respect elements on the main diagonal. This confirms the statement that the electric field induces a dipole moment mainly on the direction in which it is applied. Another significant consideration is that α_{zz} value (184,62904 a.u.) is much lower than α_{xx} and α_{yy}; this is in agreement with the fact the the molecule lies on z = 0 plane and then any electric field applied on z direction does not have a great impact on the electrostatic properties of the molecule.
The polarizability tensor is symmetric and this reflects the fourfold symmetry of H_2Pc.
In the following it will be calculated the polarizability of some metal phthalocyanine molecules in order to compare their behaviour with the Hydrogen case.

Cobalt phthalocyanine

By substituting the two central hydrogen atoms with the Cobalt metal, the result is the formation of the Cobalt phthalocyanine molecule ($CoPc$). The optimized compound it is shown in Figure 4.17 and the chemical formula of the molecule is: $C_{32}H_{16}CoN_8$.

Also in this case, the polarizability matrix is evaluated:

$$\alpha = \begin{pmatrix} 735{,}82736 & 9{,}06479 & 12{,}94713 \\ 9{,}06479 & 735{,}25501 & -2{,}56235 \\ 12{,}94713 & -2{,}56235 & 188{,}29990 \end{pmatrix} a.u. \tag{4.10}$$

As for the Hydrogen phthalocyanine, even for $CoPc$ the α tensor shows isotropic behaviour: the dipole moment is significant only in the direction in which the field is applied. α_{xx} (735,82736 a.u.) and α_{yy} (735,25501 a.u.) are lower then H_2Pc molecule (α_{xx} = 876,67951 a.u. and α_{yy} = 875,51084 a.u.) pointing a less tendency to polarize of Cobalt phthalocyanine in x and y directions.
As depicted in Figure 4.17, CoPc shows symmetric geometry and this is confirmed by the symmetry of α matrix.

Fluorinated Cobalt phthalocyanine

A method used for trying to improve the polarizability of the molecules is the so called "fluorination" process. In the case of Cobalt phthalocyanine, it consists in the replacement of the sixteen hydrogen atoms composing the four benzene groups with as many fluorine atoms. The result is a molecule named Fluorinated Cobalt phthalocyanine (Figure 4.18). The chemical formula of the compound is: $C_{32}F_{16}CoN_8$.

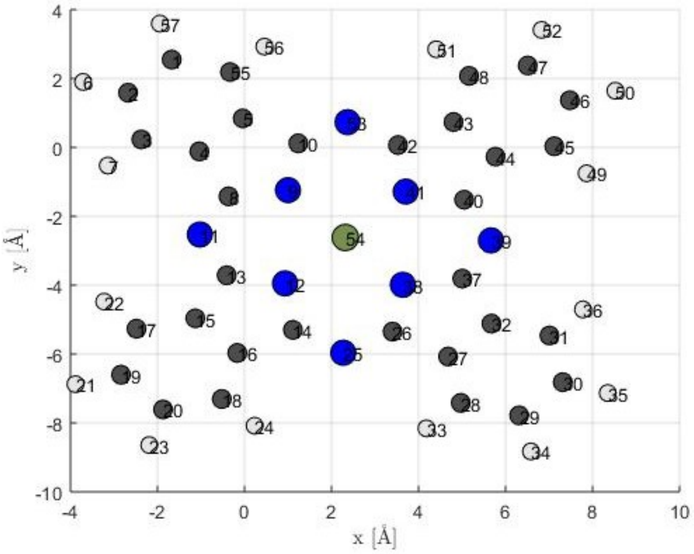

Figure 4.17. Optimized Cobalt phthalocyanine molecule (neutral). In white are represented the Hydrogen atoms, in black the Carbons, in blue the Nitrogens and in dark green the Cobalt metal.

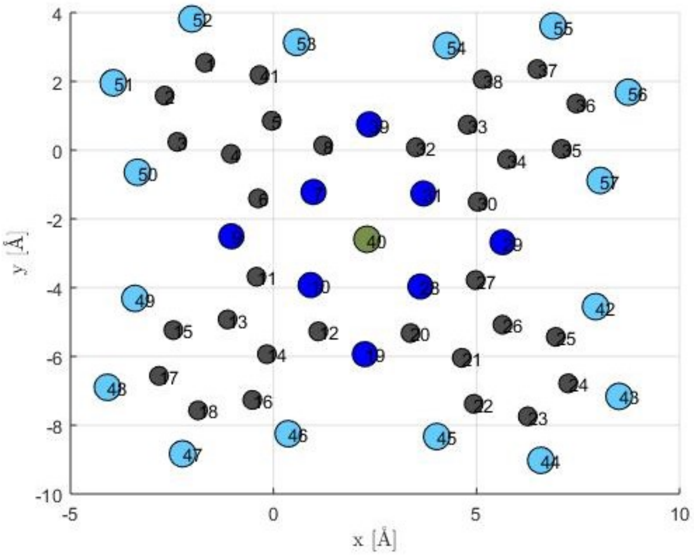

Figure 4.18. Optimized Fluorinated Cobalt phthalocyanine molecule (neutral). In light blue are represented the Fluorine atoms, in black the Carbons, in blue the Nitrogens and in dark green the Cobalt metal.

The polarizability tensor is:

$$\alpha = \begin{pmatrix} 771{,}21585 & 9{,}74411 & 14{,}56064 \\ 9{,}74411 & 770{,}52066 & -3{,}09412 \\ 14{,}56064 & -3{,}09412 & 195{,}39630 \end{pmatrix} a.u. \tag{4.11}$$

As it can be seen from 4.11, the values on the main diagonal are bigger then Cobalt phthalocyanine coefficients; this means that fluorinated molecule shows a greater tendency to create a dipole moment on x, y and z directions with respect CoPc compound.

Magnesium phthalocyanine

Another molecule which has been analyzed is the Magnesium phthalocyanine; the optimized compound it is shown in Figure 4.19 in which it can be seen the Magnesium metal (purple circle) at the center of the phthalocyanine structure. The chemical formula of the molecule is: $C_{32}H_{16}MgN_8$.

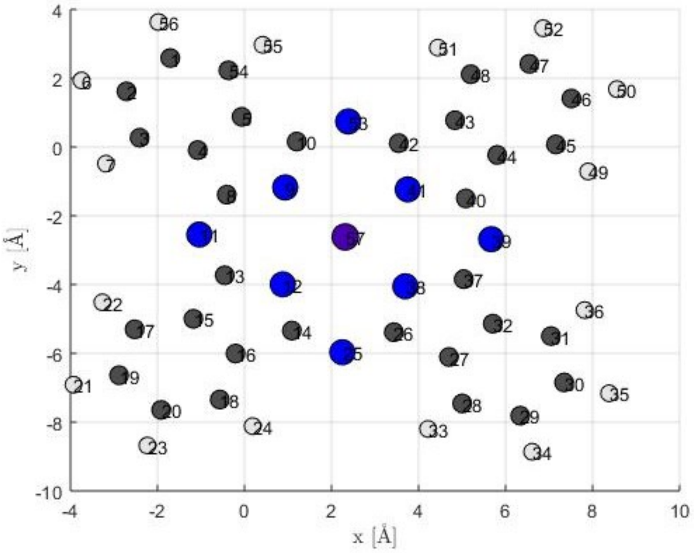

Figure 4.19. Optimized Magnesium phthalocyanine molecule (neutral). In white are represented the Hydrogen atoms, in black the Carbons, in blue the Nitrogens and in purple the Magnesium metal.

The polarizability tensor is:

$$\alpha = \begin{pmatrix} 883{,}31942 & 0{,}06324 & 16{,}02557 \\ 0{,}06324 & 883{,}61899 & -2{,}89717 \\ 16{,}02557 & -2{,}89717 & 189{,}41130 \end{pmatrix} a.u. \tag{4.12}$$

The Magnesium metal has improved the polarizability of the molecule; α_{xx} (883,31942 a.u.) and α_{yy} (883,61899 a.u.) are slightly bigger than H_2Pc coefficients, pointing that the presence of the "right" metal can improve the tendency of the molecule to create a dipole

moment.
Also in this case the matrix is symmetric showing an isotropic behaviour; α_{zz} is small indicating that the molecule lies on z = 0 plane.

Fluorinated Zinc phthalocyanine

In order to find the "best" molecule in terms of polarizability behaviour, a certain number of metal phthalocyanines have been studied. The larger polarizability matrix appears to be that of the Fluorinated Zinc phthalocyanine compound. The optimized molecule it is shown in Figure 4.20, in which it can be noted the substitution of the hydrogen atoms with fluorines (light blue circles) and the presence of the zinc metal (green circle) at the center of the structure. The chemical formula of the compound is: $C_{32}F_{16}ZnN_8$.

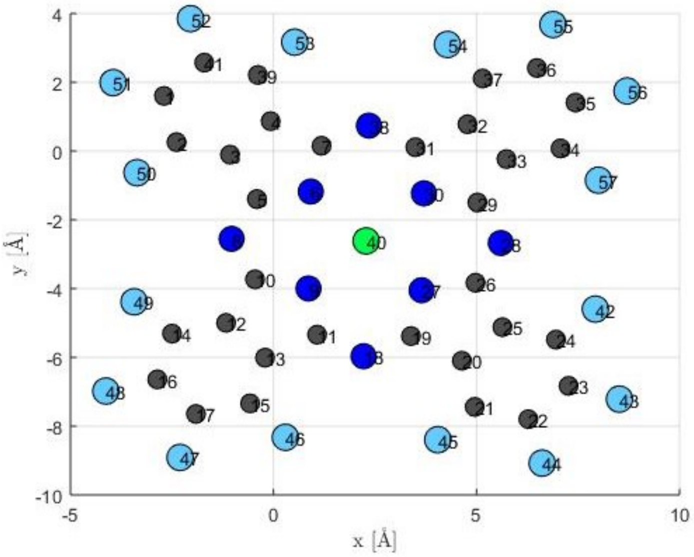

Figure 4.20. Optimized Fluorinated Zinc phthalocyanine molecule (neutral). In light blue are represented the Fluorine atoms, in black the Carbons, in blue the Nitrogens and in green the Zinc metal.

The polarizability matrix is:

$$\alpha = \begin{pmatrix} 905{,}36169 & 1{,}32053 & -104{,}75227 \\ 1{,}32053 & 918{,}81689 & 9{,}53477 \\ -104{,}75227 & 9{,}53477 & 202{,}38509 \end{pmatrix} a.u. \tag{4.13}$$

α_{xx} (905,36169 a.u.) and α_{yy} (918,81689 a.u.) are quite large and the matrix is symmetric. From 4.13 it can be noted that α_{xz} and α_{zx} are not negligible; this means that the molecule does not perfectly lie on z = 0 plane, but the atoms have also z coordinates which have to be taken into account. In Figure 4.21 it is shown the Fluorinated Zinc phthalocyanine on xz plane; the presence of the Zinc metal made a shift of the atoms coordinates along the z-axis and the molecule is tilted. If an electric field is applied on x (or z) direction there is the creation of a low (but not negligible) dipole moment on z (or x) direction.

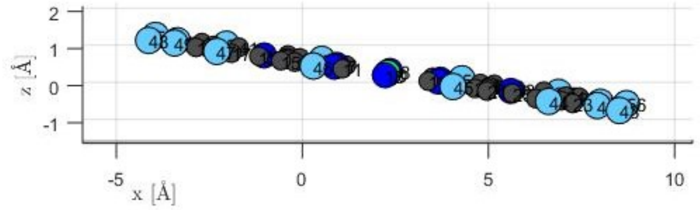

Figure 4.21. Optimized Fluorinated Zinc phthalocyanine molecule (neutral) - xz plane.

The "elprop" function of ORCA package returns also the isotropic polarizability of the analyzed molecule. In particular, the isotropic polarizability is defined as the average value of the main diagonal coefficients of the polarizabilty tensor. It gives an idea on the "capability" of a determined compound to create a dipole moment on x, y and z directions when an electric field is applied in the same direction. In addition, it points out the isotropic behaviour of the molecule giving informations on how negligible are the terms α_{ij} with $i \neq j$.

In this work, several metal phthalocyanines are studied and in Table 4.1 it is shown the isotropic polarizability of some analyzed molecules.

The first visible result is that in general the presence of metals increase the tendency of the molecules to create dipole moment; only Copper and Cobalt make their behaviour worse. In addition, the "fluorination" process increases the polarizability of the compounds, showing that the substitution of the hydrogen atoms with fluorines could be a "good" practice for enhance the electrostatic behaviour of the phthalocyanines.

In contrast with what has been seen in Chapter 3, oxidize a phthalocyanine molecule decrease the polarizability value. Indeed, by the analysis carried out on SiSSi compound (and its derivatives) and diallyl-butane, the oxidation process, in general, increased the charges separation in the VACT transcharacteristics making it a necessary reaction in order to exploit these molecules for QCA purposes.

In the case of phthalocyanine compounds, the trend is opposite. It has been tried to *reduce* the Hydrogen phthalocyanine and Copper phthalocyanine for studying their electrical response. The reduction consists in a gain of one or more electrons by a chemical species; the studied molecules have the sum of the charges equal to -1. Both H_2Pc and $CuPc$ show a better isotropic polarizability in the reduced form (663,235 a.u. and 651,596 a.u., respectively) demonstrating their greater attitude to create a dipole moment.

The analysis of molecules polarizability is dealt as a preliminary step for understanding

Molecule	Isotropic polarizability [a.u.]
$C_{32}F_{16}ZnN_8$	675,521
$C_{32}H_{16}FeN_8$	664,612
$C_{32}H_{16}CuN_8(reduced)$	663,235
$C_{32}H_{16}PbN_8$	661,532
$C_{32}H_{16}OTiN_8$	656,524
$C_{32}H_{16}AlClN_8$	656,182
$C_{32}H_{16}MgN_8$	652,116
$C_{32}H_{18}N_8(reduced)$	651,596
$C_{32}H_{16}ZnN_8$	647,900
$C_{32}H_{18}N_8(neutral)$	645,606
$C_{32}H_{16}CuN_8(neutral)$	642,561
$C_{32}H_{18}N_8(oxidized)$	618,206
$C_{32}H_{16}CuN_8(oxidized)$	610,134
$C_{32}F_{16}CoN_8$	579,044
$C_{32}H_{16}CoN_8$	553,127

Table 4.1. Isotropic polarizability of some phthalocyanine molecules.

if a compound can be considered as a possible candidate for QCA purposes. Indeed, before starting with the electrostatic characterization and with the study of the figures of merit (VACT transcharacteristic, Energy, Isopotential surfaces, ecc...) it is convenient to have an idea if the molecule has the intrinsic tendency to create a dipole moment and then to have a non uniform charges distribution under the effect of electric fields. In this work it has been concentrated on phthalocyanines, but the used methodology works for all the molecules which show monostable behaviour.

4.4.2 Rotated molecules

In Figure 4.22 it is shown the Hydrogen phthalocyanine molecule after the geometry optimization process.

In order to maximize the polarizability, a possible idea is to rotate the molecule by 45° in the xy plane for having two dots parallel to x-axis and the others two parallel to y-axis. In Figure 4.23 it is shown the Hydrogen phthalocyanine rotated by 45° clockwise; in this way, when an electric field is applied on the x or y direction, the Dots should be affected more by this external stimulus and as a consequence also the polarizability value should be greater.

However, after the application of an electric field on the order of 0,001 a.u., the polarizability tensor is:

$$\alpha = \begin{pmatrix} 886{,}46194 & -3{,}68544 & -0{,}57301 \\ -3{,}68544 & 861{,}56765 & -0{,}68277 \\ -0{,}57301 & -0{,}68277 & 184{,}35515 \end{pmatrix} a.u. \tag{4.14}$$

Comparing 4.14 and 4.9 expressions, it is possible to see that the main diagonal coefficients of the matrices are very similar indicating that the rotation of the molecule has not

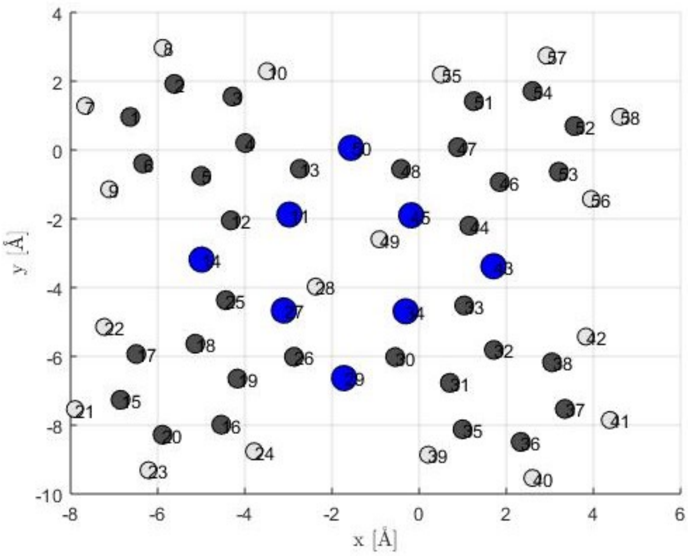

Figure 4.22. Hydrogen phthalocyanine molecule.

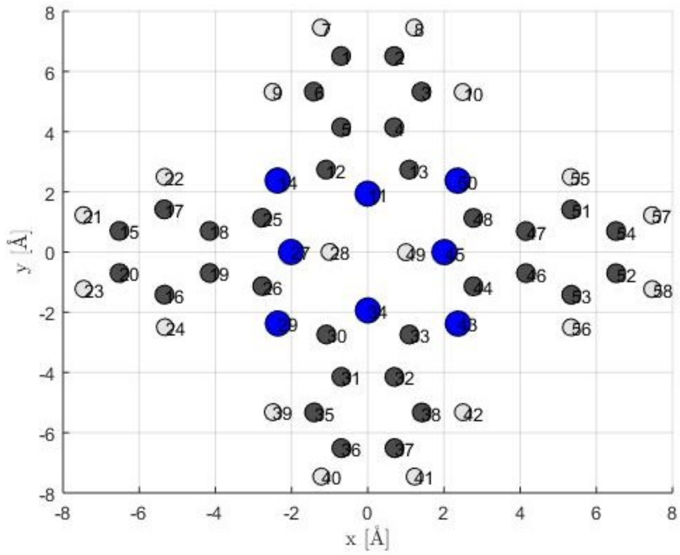

Figure 4.23. Hydrogen phthalocyanine molecule rotated by 45° clockwise in the xy plane.

got a significant impact on the polarizability of the compound.
An explanation of this phenomenon could be the fact that if the molecule is aligned with the axis (x and y), only one branch contributes to the polarizability in that direction; when the molecule starts to rotate, the branch previously involved loses partially its effectiveness but the other branch begins to be "active" and then the two contributions add up. The results is that the polarizability is almost the same in both cases as well as the dipole moment.
Mathematically, if the molecule if perfectly aligned with the axis and an electric field is applied along x direction (E_x), the resulting dipole moment (along x-axis) is defined as:

$$\mu_x = \alpha_x E_x \tag{4.15}$$

If the molecule starts to rotate of a generic θ angle, the dipole moments along the two branches of the compound are so defined:

$$\mu_1 = \alpha_x E_x cos(90° - \theta) = \alpha_x E_x sen(\theta) \tag{4.16}$$

$$\mu_2 = \alpha_y E_x cos(\theta) \tag{4.17}$$

As a consequence, the absolute value of the x component of μ is:

$$|\mu_x| = \sqrt{\mu_1^2 + \mu_2^2} = \sqrt{(\alpha_x E_x sen(\theta))^2 + (\alpha_y E_x cos(\theta))^2} \tag{4.18}$$

By the analysis of the polarizability matrices of the studied phthalocyanines, it is possible to approximate $\alpha_x = \alpha_y$. Then:

$$|\mu_x| = \alpha_x E_x \tag{4.19}$$

So, the modulus of the dipole seems to be the same as that of the original molecule. This result is interesting, because it say that the polarizability of H_2Pc does not depend on the rotation angle which the molecule can be subjected on the lying plane.

In Figure 4.24 it is represented H_2Pc compound (on top) and the schematic representations of the original and rotated molecules when an electric field (E_x) is applied to the system (on bottom).

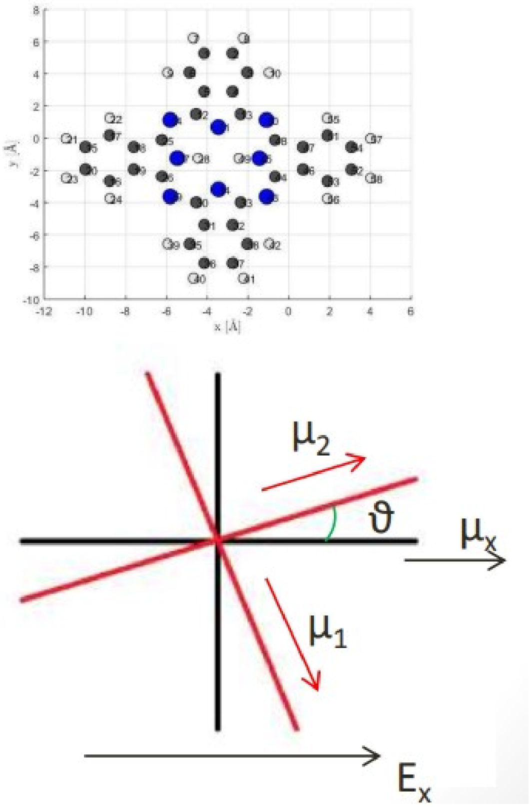

Figure 4.24. On top, Hydrogen phthalocyanine molecule. On bottom, schematic representation of two H_2Pc compounds. The black cross represents the original molecule. The red cross represents the molecule rotated by a generic θ angle. The Figure shows the dipole moment components when E_x is applied to the system.

In this work, only Hydrogen phthalocyanine has been rotated. Of course, interesting results could be derived in case this procedure it also applies to molecules with metal atoms.

Chapter 5

Conclusion and future perspectives

This work demonstrates a methodological approach to fill the gap between molecular perspective and electronic world. First of all, a general methodology has been studied for having a tool able to characterize the widest possible range of molecules in a way that aims to be the most universal and automated one. In particular, it has been demonstrated that molecules can be well-characterized using the so-called Vin-Aggregated Charge Transcharacteristics (VACT), giving to the compound an electronic perspective, with proper input (electric field) and proper output (Aggregated Charge).

A new approach has been tried to study, in order to have a single QCA cell constituted by only one molecule. The Phthalocyanines have the geometry suitable for this purpose (four-fold symmetry) and by positioning the point charges in a well defined way, it is possible to have a relative good switching between the two configurations. The charges separation between the Dots is not too high in case of Hydrogen Phthalocyanine, but the obtained results seems to be interesting for future analysis.

The use of metal atoms in the Phthalocyanine structure, in general, improves the electrostatic behaviour of the compound; in particular an in-depth analysis on polarizability of some molecules has shown that they have a quite good tendency to create a dipole moment when an electric field is applied to the system. The fluorination process as well as the reduction of the molecules, increase their isotropic polarizability.

The obtained results seems to be significant because show that the Phthalocyanines have the tendency to create a non uniform charges distribution under the effect of electric fields. For sure, the study of polarizability is intended as a preliminary step before starting with the evaluation of the various figures of merit (Aggregated Charge, Dipole Moment, Energy, ecc...).

Possible future works could be the electrostatic characterization of metal phthalocyanines by following the same point charges distribution used for H_2Pc.

Another interesting perspectives is to make molecules communicate with each others; it would be relevant to study how a molecule influences the charges distribution of a neighboring phthalocyanine in order to create QCA wires or more complex logic circuits. Indeed, a working molecular circuit prototype has not been realized yet, and one of the main problems is the necessity of realizing nanopatterned devices with sub-nm precision.

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