Politecnico di Torino

Master of Science in Electronic Engineering

Master Thesis

Study of clocking system for molecular FCN

Supervisors
prof. Gianluca Piccinini
prof. Mariagrazia Graziano

Candidate
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Ringraziamenti

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Chapter 1

Introduction to QCA

1.1 Moore's law

In 1965 Gordon Earle Moore, co-founder and chairman of Intel Corporation, postulated that the number of components per square inch in an integrated circuit would have doubled every year for at least the following ten, relying on the observation of the technological improvements in the previous years. In 1975 he corrected his prediction estimating that the trend mentioned above would be every year and a half. Afterwards, this assumption was called *Moore's law*.
Mathematically it can be written as:

$$n_t = n_{t_0} \cdot 2^{\frac{t-t_0}{1.5}} \tag{1.1}$$

where n_{t_0} is the number of components in the instant t_0, while n_t is the number of components in a chosen instant t.
The Moore's law can be considered as the consequence of other two technological laws:

- Every three years the minimum dimension of the components decrease of the 30 percent.
- Every three years the maximum area of an integrated circuit doubles.

The consequence of these laws was that the costs of production decrease while the performance increase and their trends can be predicted. In 2012 for the first time since its postulation Moore's law was broken and the prevision was that in the following years the increase would have been every three years.
Nowadays the channel length of a standard CMOS is less than 10 nm and it is quite physically impossible to continue the scaling using a standard structure based on metal oxide and semiconductor due to atomic scale size. Moreover, others aspects that limit the scaling

are process variations, unsustainable power dissipation and the fact that the performance does not increase in a relevant way. So to continue with the technological progress different approaches must be found.
For these reasons in the last decade, the concept of *Beyond-CMOS* was born. It refers to the discovery and the development of new technologies, no more CMOS based, that can overcome the issues above mentioned.
Field-Coupled NanoComputing devices are among the most promising ones: the computation is performed without a current flow or exploiting voltage levels but via local interactions among single entities, so the power consumption can be drastically reduced. This group of devices includes Quantum-dot Cellular Automata logic [1, 2]. They can be implemented using nanomagnets, metallic junctions, semiconductors or molecules. The latter in particular called Molecular QCA will be analysed in this thesis.

1.2 Molecular Quantum Cellular Automata

In Molecular QCA the information is encoded in the charge distribution of oxidized molecules; in particular, the charge can be aggregated in two redox center called quantum dots, and it can pass from one dot to another one without leaving the molecule. In order to realize a molecular QCA cell, two near molecules are required and the four dots are placed as in the corners of a square.
In this way we can have only two possible configurations (showed in figure 1.1) one that is associated to the logic state '0' and one associated to '1', because the charge tends to move in order to minimize the total energy.

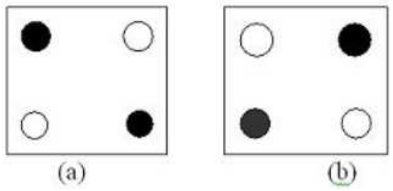


Figure 1.1: QCA cell possible configurations with black dot associated to a negative charge and white ones associated to a positive charge. (a) logic state '0' (b) logic state '1'.

In order to better control the cells, a third dot is required that is associated with the 'NULL' state. If the charge of the two molecules that form the molecular QCA cell is aggregated in the third dot no logic value can be obtained [2]. The charge can be forced in this dot exploiting an electric field. A complete overview is shown in figure 1.2 taken from [3].

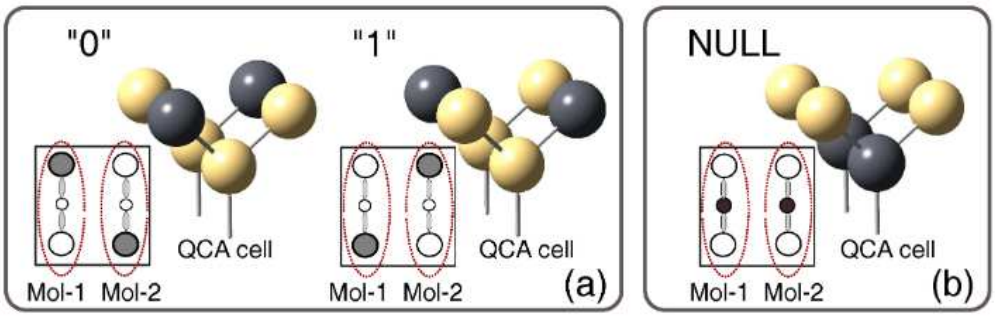


Figure 1.2: Six quantum dots molecular QCA cell scheme.(a) '0' and '1' logic state (b) 'NULL' state with charge in the third dots [3].

By arranging different mQCA cells many devices can be implemented such as a binary wire, majority voter and the inverter [4]. More complex devices such as the adder [5] or even μP have been proposed in the literature [6]. The molecules are so anchored on a gold substrate in order to obtain the requested structure. In the following figures are reported some examples.

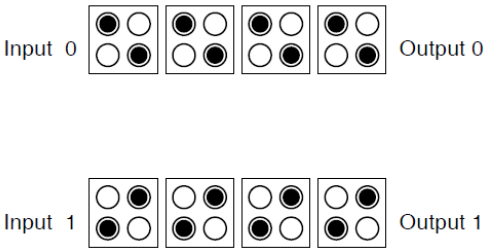


Figure 1.3: Cells placement for binary wire structure.

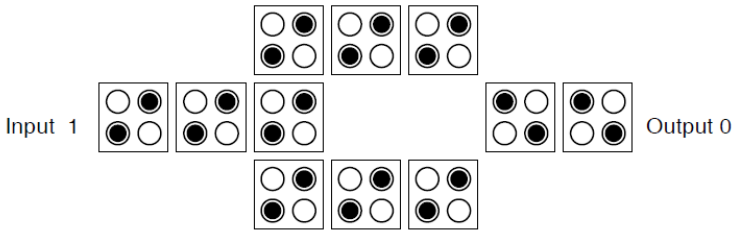


Figure 1.4: Cells placement for inverter structure.

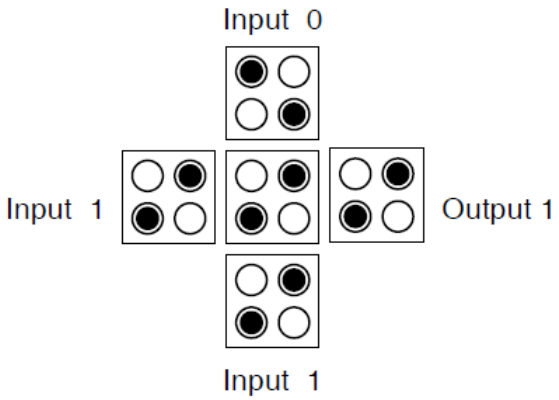


Figure 1.5: Cells placement for majority voter structure.

Ideally, in the case of the binary wire, the first molecule is strongly influenced by a driver that works as input, while all the others influence only the following one. In the real case, each molecule is influenced by all the others complicating the analysis.

1.3 The bis-ferrocene molecule

One of the problems linked to the realization of a molecular QCA cell is the research of a proper molecule that has to satisfy some fundamental characteristics: the molecule must have a functional group that allows the anchoring on a solid surface, and at least three dots where the charge can be aggregated [7].
A lot of molecules have been proposed (even if some of them have not been synthesized), but many of them can be used only in the gas phase or in solution and are not able to anchor on a surface due to their geometrical structure.
The one that attracted more attention is the bis-ferrocene, whose structure is shown in figure 1.6 [8].

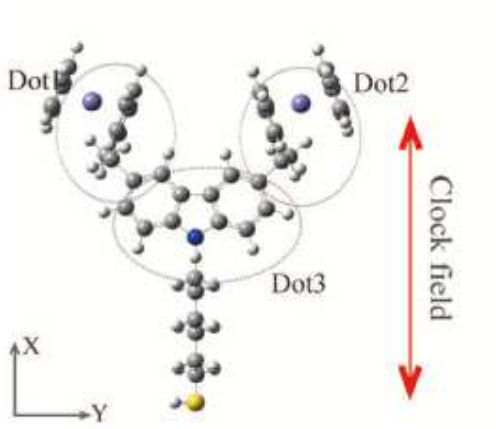


Figure 1.6: Bis-ferrocene molecule structure [8].

This molecule has been synthesized ad hoc for QCA computation purpose by a group of the chemistry department at the University of Bologna [9, 10]. As it can be it is formed by two ferrocene units, functioning as redox centres, and a carbazole, the third dot used for the 'NULL' state and to connect the two ferrocenes. An alkyl chain at the base is used to anchor the molecule to a gold substrate. One molecular QCA cell is so formed by positioning two bis-ferrocene molecules at a distance of 1 nm.
The choice of this molecule (besides for purely geometrical aspects) is based on the fact that when a positive electric field is applied (respect the x-axis in figure 1.6) the charge is free to move in the dot 1 and dot 2, while when a negative clock field is applied the charge is forced to stay in the dot 3 obtaining the 'NULL' state. In particular to obtain a complete inhibition of the molecules the value of electric field required is -2 V/nm; on the contrary with a value of +2V/nm, the molecule is completely activated. This is exactly the behaviour that is expected and that can be exploited for the realization of a molecular QCA cell.

1.4 The clock system

Due to quantum phenomena and thermodynamics mechanisms, there is a maximum number of molecules beyond which the information could not be propagated in the correct way; moreover, the abrupt switching of a molecular QCA cell state could lead to metastability problems along the circuits [11]. So even the simplest structure can not work without the use of a clock system that allows the propagation of the information.
As said applying an external electric field the molecules can be activated or inhibited, so the idea is to divide the circuit into different clock zones, each of them subject to a different value of the electric field. The clock signal applied has four phases that follow a precise sequence in order to ensure the correct propagation and are called: switch, hold, release and relax. In each phase different behaviours of the molecules can be observed:

- switch phase: the electric field slowly passes from a negative value to a positive one and the charges can leave the third dots associated to the 'NULL' state reaching the working dots encoding one of the two logical states;
- hold phase: the electric field remains positive and the logic state is kept stable to '1' or '0';
- release phase: the behaviour is opposite respect the switch phase, indeed the clock slowly passes from a positive value to a negative one forcing the molecule to the 'NULL' state.
- relax phase: the electric field is kept negative in order to maintain the molecule in the 'NULL' state.

This approach is called *adiabatic switching*, indeed varying slowly the electric field we ensure that the system is always in the ground state avoiding metastable or excited states. A system is in the ground state if it has the minimum possible energy.

In figure 1.7 is reported the definition of each clock phase with the correspondent effect on the molecular QCA cell.

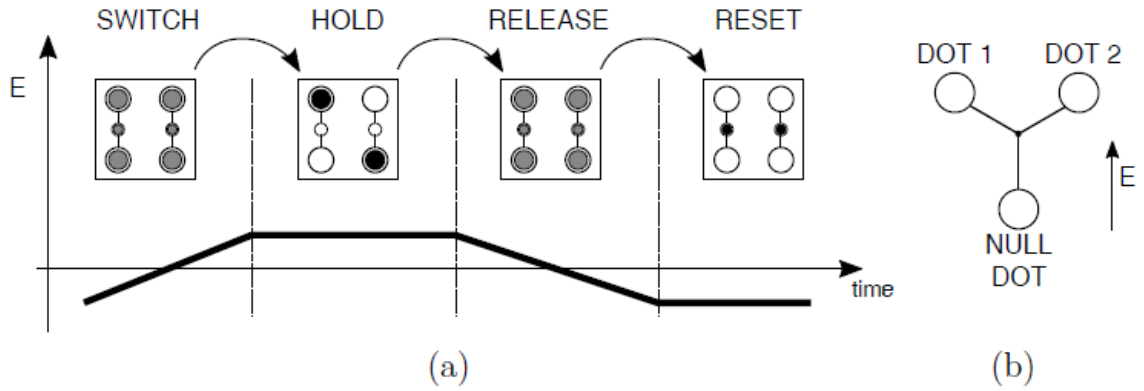


Figure 1.7: Clock phase definition and resulting effect on the molecular QCA cell. (a) Sequence of the phases in the various instants of time. (b) Representation of the bis-ferrocene molecule with electric field vector.

In a real case it reasonable that each clock zone can be formed by four cells, so eight molecules, in order to control in the optimal way the propagation and maximize the performance in terms of frequency.

1.5 Physical implementation of Molecular QCA

Among a lot of solutions the best physical implementation for the realization of molecular QCA structures is the following:

- A dielectric substrate is used to create a nanometric trench on which a gold nanowire is deposited. Gold is used because it is inert towards corrosion or oxidation, it is not toxic, can be studied with several experimental techniques and has a high sulphur affinity [12]. This last property is very interesting because the bis-ferrocene molecules (whose thiols end with a sulphur atom) can be disposed on the nanowire exploiting a self-assembly process.

- The clock system is obtained depositing metal electrodes on the substrate placed on the two sides of the trench. The gold nanowire is fixed to zero volt while to the others electrodes a voltage difference is applied in order to generate an electric field inside the trench.

A section of the described structure is reported in figure 1.8; the yellow zones are the nanowire and the metal electrodes golden facts, while the grey ones are the substrate made by *Silicon Nitride* (Si_3N_4). The four black points represent the position of the four dots of the bis-ferrocene.

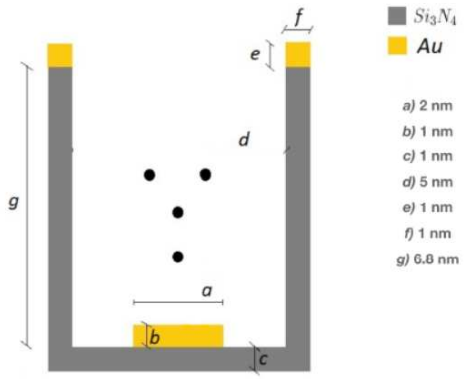
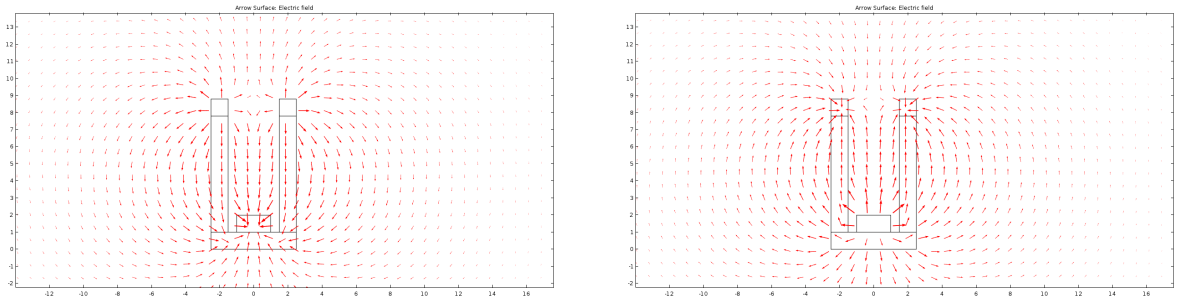


Figure 1.8: Section of the structure used for the realization of the trench in molecular QCA.

This is the optimal structure where the electric field generated by the electrodes is vertically oriented. Process variations related to the width and the height of the trenches have been analysed in order to find a Safe Operating Area in which the structure continues to work properly.
In order to realize the binary wire the idea is to have a certain amount of electrodes on the side of the trench each of them associated to a different clock zone; in this way, the propagation of the information can be controlled varying in each phase the voltage difference associated to the electrodes.

Others more complex structures required different solutions, so for example in the case of the majority voter in order to better control the central cell four smaller electrodes can be placed in the corners.

Considering the sign of the electric field it is negative inside the trench when a positive voltage difference is applied to the electrodes; so in order to inhibit the propagation in a clock zone forcing the molecules in the 'NULL' state a positive voltage difference must be applied (figure 1.9a). Differently when a negative voltage difference is applied the electric field inside the trench is positive and the propagation of the information in the corresponding clock zone can occur (figure 1.9b).



(a) (b)

Figure 1.9: Electric field lines inside the trench. (a) negative electric field generated applying a positive voltage difference to the electrodes. (b) positive electric field generated applying a negative voltage difference to the electrodes.

1.5.1 The Self-Assembly process

As said before the nanowire is golden fact and we can exploit its sulphur affinity to anchor the bis-ferrocene molecules on it through a self-assembly process. Self-assembled monolayers (SAM) are an organized layer of molecules obtained by the absorption of molecular constituents from solution on a solid surface (in this case the gold nanowire) [12]; the molecules organize spontaneously on crystalline (or semicrystalline) structures and tend to align and tilt with respect to the surface in order to minimize the Van Der Waals interactions [12, 13]. Self-assembled monolayers have a lot of applications such as catalysis [14], corrosion prevention [15, 16] and adhesion [17, 18], due to the fact that they are easy to prepare, stable and surface properties are easy to control.
A problem related to this process is that the exact position of the thiols on the gold surface is still not clear; some studies focused their attention on SAMs where alkanethiols are disposed on Au(111) that provides the lowest surface energy [19]. A proposed configuration is shown in figure 1.10 where the Au:S ratio is 3:1 when a perfect monolayer is formed.

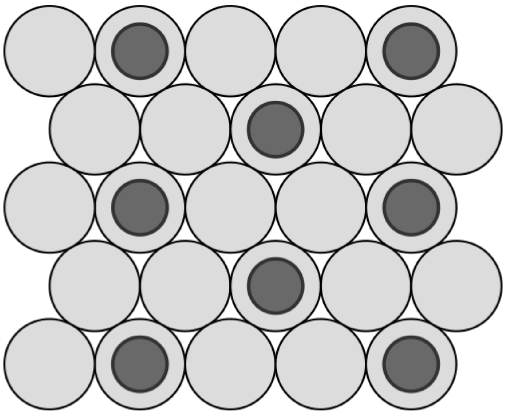


Figure 1.10: Organization of Sulphur atoms, in dark grey, on Au(111) in grey. The ratio between gold and sulphur atoms is 3:1.

Chapter 2

State of art

The QCA principle has been demonstrated by the physical implementation of metallic, magnetic and molecular solutions [20, 21]. The last one has been considered as the most promising because high working frequency (1 THz) [22] with very low power consumption can be reached [23]; moreover, it enables the production of uniformly sized devices [24].
In the molecular implementation, the encoding of the information is made possible by the aggregation of charge in the redox centres of the molecules acting as QCA dots. A redox centre can attract or release an electron generating respectively a negative or a positive charge. To improve the performance the molecules are chemically reduced or oxidised during the synthesis process using a counterion [25], in this way they are no more globally neutral and the charge in the redox centre can be equal to $\pm 1.60 \cdot 10^{19}$ Coulomb.
As said one molecular QCA cell is formed by two near molecules where the four redox centres are placed as in the corners of the resulting square; the charge tends to move in order to minimize the total energy obtaining only two possible configurations used to encode the two logic values "1" and "0". This is due to the fact that the charge of each molecule generates an electric field that influences the near one. In figure 2.1 the definition of electric field generated by a molecule and equivalent voltage on the receiver is shown.

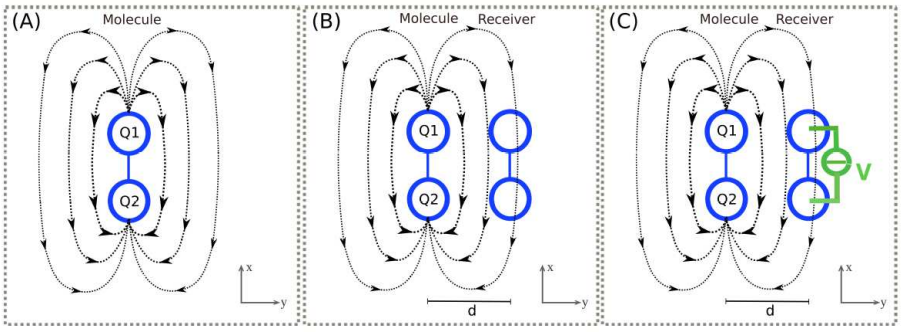


Figure 2.1: Definition of electric field generated by a molecule and obtained voltage at the receiver.

In depends on the sign of the electric field the charge of the near molecule can be aggregated in one of the two working dots.
So applying an external electric field parallel to the working dot axis, called *switching field*, the charge can be forced in one of the two active dots writing a logic state in the molecular QCA cell. In particular, for the bis-ferrocene the minimum electric field that can be used to write a logic state is $E_{sw} = \pm 0.5$ V/nm.

2.1 Generated electric field at the receier

The electric field generated by a molecule on a receiver can be calculated in equilibrium condition or in presence of a switching field that localizes the charge in one of the working dots. The component parallel to the dot axis of the electric field at the receiver placed at the distance of 1 nm has been calculated applying a switching field equal to +0.5 V/nm for the positive bias and -0.5 V/nm for the negative one; the obtained results are shown in figure 2.2. The vertical lines represent the position of the working dots of the receiver highlighting the range of interest for the evaluation [26].

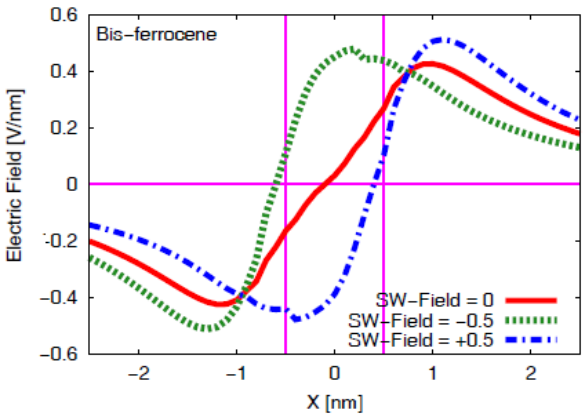


Figure 2.2: Electric field at the receiver calculated in equilibrium condition and with a positive and negative applied switching filed [26].

As it can be seen, at the equilibrium the resulting electric field is null because the two dots are subject to an electric field with the same intensity but with opposite sign. So the molecule at the equilibrium is not able to influence the receiver.
In the others two cases, the sign of the electric field at the receiver in the range of interest is opposite respect to the sign of the switching field applied to the molecule. Considering the negative switching field the positive peaks is shifted towards the left and it is centred in the range of interest of the receiver. So at the receiver, the charge distribution will be opposite respect of the case of the molecule to which the switching filed has been applied. The same

phenomenon can be seen considering the positive switching field.

The result shown in figure 2.2 has been obtained by means of proper simulations, but in a more general way, the electric field generated by the charge distribution of a molecule can be computed through mathematical expression. In particular, it can be calculated considering a single charge $+q_1$ and a test charge q_t at the distance r_1 by the following equation:

$$E_1 = \frac{F_1}{q_t} = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_1}{r_1^2} \cdot \widehat{r_1} \tag{2.1}$$

Considering a system composed by N point charges their effects must be summarize on the test charge, obtaining this expression:

$$E_{tot}(x, y, z) = \frac{F_{tot}}{q_t} = \sum_{i=1}^{N} \frac{1}{4\pi\epsilon_0} \cdot \frac{q_i}{r_i^2} \cdot \widehat{r_i} \tag{2.2}$$

Following this procedure, the electric field can be calculated anywhere in the space around the molecule. The equivalent voltage at the receiver can be obtained integrating the component parallel to the molecule of the electric field along its width.

2.2 Simulation of a QCA wire

Once that one single molecule has been characterized, the working principle at the base of the simulation of a QCA wire can be described. An iterative method can be used as shown in figure 2.3: a switching field is applied to the first molecule of the wire imposing a logic state given by the obtained charge distribution. The charge distribution of the second molecule is obtained using the first one as a driver. In the following step the third molecule is influenced by the second one, and so on. The general rule is that during the step i the molecule i is in the neutral state and its charge is delocalized while the molecule *i-1* works as a driver.

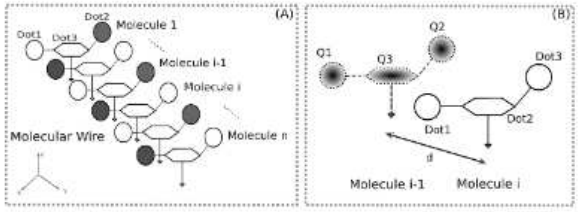


Figure 2.3: Molecular QCA wire simulation.

In a more realistic analysis all the molecules have an effect on the surrounding molecules; indeed once that a charge distribution has been obtained in the molecule i the electric field generated influence not only the molecule *i+1* but, even if a minimal way, also on all the others.

2.3 Effect of the clock signal on the molecules

To complete the overview on the propagation of the information between nearby molecules the effect of the clock signal is explained. As said the clock signal can be implemented with an electric field that crosses the molecule along the vertical axis. This one is generated by the electrodes,to which a potential difference is associated, positioned in such a way that only the vertical component can be considered inside the trench. The application of a negative electric field generates a charge displacement in which a negative charge is present in the two working dots, while in the third dot is present a positive charge. The opposite effect happens if the electric field is positive; indeed the charge in the working dots is positive and it is almost equal, while a negative charge is present in the third dot.
So the application of an electric field can be used to enhance or hinder the communication between the molecules present in the structure.

Chapter 3

Study of the clocking system

In this thesis, the clocking system for molecular QCA has been studied.
As said, the electric field used to control the molecules is generated by electrodes at which a voltage difference have been applied; ideally, the electrodes of a clock zone influence only the molecules belonging to that precise zone and the electric field generated is constant in it. Until now only this ideal case has been studied.
In reality, this is not the expected behaviour, indeed the electrodes influence also the molecules belonging to the adjacent clock zones, on which the resulting electric field is the sum of the various contributions. Considering that two nearby molecules belonging to different clock zones are placed at a distance of 1 nm, the variations are not so fast to ensure that they are subjected one to an electric field value equal to 2 V/nm and the other one to -2V/nm, or vice versa; the result is that the molecules anchored close to the next or the previous clock zone are subjected to intermediate values of electric field and they are not completely activated or inhibited. Furthermore, each molecule belonging to a clock zone is subject to a different value of the electric field because it is not constant it. In literature, this approach has not yet been dealt with in depth.

Considering the real values of the electric field allows finding the correct placement of the electrodes and which voltage values must be applied to ensure the correct operation of the fundamental elements that are used for the realization of the logic gate based on molecular QCA technology. Moreover, also possible implementations of these components that can be realized with the actual technology can be proposed. Indeed, as it can be seen in figure 1.8, the realization of the electrodes used required a resolution of 1 nm, now unachievable.

3.1 Objectives

Four fundamental components have been studied in depth paying attention to the problems of each of them:

- First of all the behaviour of a binary wire with three clock zones have been studied

considering the real values of the electric field generated by the electrodes. A further analysis has been performed on this structure: in the ideal case the gap between two near electrodes is equal to 1 nm so no molecules are anchored between two adjacent clock zones; the idea is to study what happens when the gap is higher finding the maximum one that allows the correct propagation of the information. For a more complete analysis, this studied has been done with three different molecule distance, in particular, 0.8 nm, 1 nm and 1.2 nm.

- The behaviour of the majority voter, in particular of the central cell that has to compute the operation, has been studied.
  Theoretically the three inputs are placed in a clock zone different respect the central cell; in this way when it is switched on it "sees" the three inputs (that are stable) and can elaborate the output. Even if the three inputs arrive in different moments no output is generated until the central cell remains in 'NULL' state.
  Unfortunately, this procedure is not so simple, indeed obtaining two well-defined zones limiting the effect of some electrodes only to the central cell, forcing the 'NULL' state, while the three inputs are switched on required an analysis on the correct placement of the electrodes and mostly on the applied voltages. If these one have not been chosen correctly could happen that if the inputs arrive staggered the output becomes function only of the first input generating a wrong result.
  At the beginning the optimal structure of the majority voter, that required a minimum resolution equal to 1 nm to be realized, has been studied trying to obtain the correct operation.
  Once that the correct behaviour of the of this component has been obtained in this case, an alternative structure that can be realized with the actual technology has been proposed; in this case the minimum resolution required for the realization of the electrodes is 3 nm instead 1 nm.

- A possible implementation of a structure able to split the information in two binary wires is proposed. The resulting structure will be called 'T structure' due to the fact that it reminds the letter of the alphabet. Also in this case the correct placement of the electrodes and applied voltages must be chosen properly in order to ensure the correct behaviour.
  Even if the obtained structure is similar to the previous one the working principles is different, indeed no operation must be performed by this component. In this case the information during the first phase reaches the centre of the structure, then in the following phases the two outputs are switched on and the information can be propagated in two separated wires.
  Moreover, a structure that can be realized with the actual technology has been proposed as in the previous case.

- The angle structure, that reminds the letter "L" of the alphabet, is proposed. This structure is a binary wire where the information must be propagated in the presence

of an angle of 90 degrees. It has been studied because to create complex circuits where a lot of elements are present this structure is fundamental to connect them.

The procedure used to analyse the different structures is always the same: they have been modelled using Comsol 5.2 in order to calculate the electric field generated by the electrodes along the molecules. Then these values are exported in text files and passed to a pre-existent Matlab algorithm [27] that has been enhanced in order to consider the real values of the electric field. This one, thanks to these values, calculates the propagation of the information in the structure.
The simulations made with Comsol are very useful because nowadays the realization of devices as small as mQCA is impossible, so exploiting them the behaviour, the functionalities, and any problems can be foreseen.

Chapter 4

Comsol Simulations

All the simulations made with this program follow the same procedure:

1. Model wizard selection: the first step consists in the selection of the number of dimensions used to realize the structure (3D, 2D or 1D). Physics, multi-physics, and studies can be selected in this preliminary phase or during the creation of the model.

2. Parameters input: a set of parameters can be defined manually or can be red by an external file.

3. Construction of the desired geometry: a lot of tools can be used for the construction of the geometry starting from the parameters defined previously. In order to simplify this step, it is important to exploit eventual symmetries present in the structure.

4. Selection of the materials: each domain, boundary or edge must be associated with a material and in depends on what kind of physics will be used different properties must be specified.

5. Physics and multi-physics settings: each physic provides different tools suitable for the analysis of a physical phenomenon. More than one physic can be used and moreover multi-physics allow to combine them adding new functionalities. In this step also the boundary and the initial conditions must be specified.

6. Generation of the computational grid: Comsol uses the Finite Element Method (FEM) so the geometry must be divided into sub-domains where the partial differential equations are solved. Depending on how thick the mesh is the obtained results will be more or less precise.

7. Execution of the simulation: different kind of studies can be performed, for example stationary, time-dependent or frequency domain.

8. Analysis of the results: at the end, a large variety of plots can be created, in order to show the trend of a particular variable in the space or on a plane.

In the following section, the realization of the Comsol models used are shown.

4.1 Binary Wire Comsol model

In this section, the model used for the simulation of the binary wire is described. At the beginning what kind of simulation will be performed must be selected. So a 3D structure is required, for the physics *Electrostatic (es)*, in the AC/DC section, has been chosen and a *Stationary* study will be done. Electrostatic has been chosen because among all the other physics it is the best for the computation of the electric fields. While a Stationary study has been selected because there are no parameters that change in time.
After that the simulation has been set in the *Global Definition* section a list of parameters (showed in figure 4.1) has been inserted. The used values for the realization of the trench are the same reported in figure 1.8.

Settings

Parameters

Name	Expression	Value
bottom_el...	5[nm]	5E-9 m
bottom_el...	top_el_length*3+zone_gap*2+2*spacing	2.5E-8 m
diel_depth	1[nm]	1E-9 m
diel_height	6.8[nm]	6.8E-9 m
diel_length	bottom_el_length	2.5E-8 m
domain_r...	20[nm]	2E-8 m
dot1_x	-bottom_el_length/2+spacing	-1.15E-8 m
dot1_y	-0.5061555[nm]	-5.0616E-10 m
dot1_z	4.3621776[nm]	4.3622E-9 m
dot2_x	-bottom_el_length/2+spacing	-1.15E-8 m
dot2_y	0.5082574[nm]	5.0826E-10 m
dot2_z	4.3621776[nm]	4.3622E-9 m
dot3_x	-bottom_el_length/2+spacing	-1.15E-8 m
dot3_y	-0.0011731[nm]	-1.1731E-12 m
dot3_z	3.686485[nm]	3.6865E-9 m
dot4_x	-bottom_el_length/2+spacing	-1.15E-8 m
dot4_y	-0.0053777[nm]	-5.3777E-12 m
dot4_z	2.8223702[nm]	2.8224E-9 m
el_depth	2[nm]	2E-9 m
el_height	1[nm]	1E-9 m
mol_diel_...	1.5[nm]	1.5E-9 m
mol_dist	1[nm]	1E-9 m
mol_el_dist	2[nm]	2E-9 m
spacing	1[nm]	1E-9 m
top_el_len...	7 [nm]	7E-9 m
V_bottom...	0[V]	0 V
V_zone1	-8[V]	-8 V
V_zone2	8[V]	8 V
V_zone3	8[V]	8 V
zone_gap	1[nm]	1E-9 m

Figure 4.1: Parameters used for the Comsol simulation of the binary wire.

These parameters are very useful because the geometry and the voltage values in the different clock zones can be simply modified varying them. The most significant are:

- *mol_dist* specifies the distance between two adjacent molecules. This parameter is used for the creation of the 3D lines in the Data sets section.
- *zone_gap* specifies the distance between two different electrodes. As said the scope is to analyse the behaviour of the component when this parameter increases. In figure 4.1 is equal to 1 nm that is the ideal case.
- *bottom_el_length* specifies the length of the bottom electrode that will be setted to 0 V, starting from the *zone_gap* and the length of the electrodes.
- *bottom_el_depth* and *diel_height* specify respectively the depth of the trench and the height of the side electrode. In this case, 5 nm and 6.8 nm are used and these values have been chosen in order to obtain an electric field oriented towards the bottom inside the trench, minimizing the other ones.
- *V_zone1, V_zone2, V_zone3* are used in the physics section in order to associate to the electrodes the proper values of voltage. The values are 8 V or -8 V in depends on the sign of the electric field that we want to obtain in each clock zone. These are the maximum ones that allow obtaining electric field values that do not exceed ± 2 V/nm.

Geometry

The Geometry has been realized starting from the dielectric and the electrode in the bottom, that compose the base of the structure, using the tool *Block*. The proper parameters must be inserted in order to specify the Width, the Depth and the Height. Analogously the side electrode on the left has been created using the same tool. Then the side dielectric on the right has been inserted exploiting the fact that it is exactly equal to the left one, so the function *Mirror* of Comsol has been exploited. For the realization of the electrodes, the same procedure has been performed using always the tool *Block*.
The representation of the molecules have been created inserting four points for each of them that indicates the four dots. For the simulation, these points have no role but they are used to better understand graphically their position. The first molecule is created specifying the position of the four dots manually, while the other ones are created exploiting the function *Array* of Comsol.
In order to perform the calculation of the electric field in the space the structure is positioned inside a sphere, whose radius must be sufficiently large (in this case 20 nm has been chosen). In the following figure the structure is reported hiding the sphere for a better vision (the reported greatness are in nanometers).

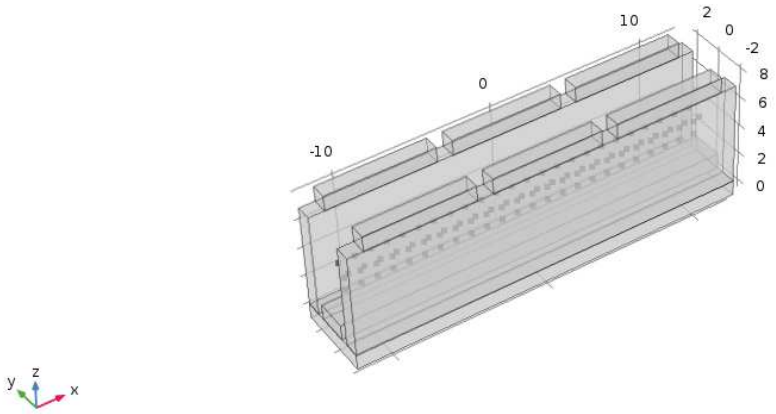


Figure 4.2: Geometry used for the Comsol simulation of the binary wire (prospective view).

Materials

The materials used in this simulation are:

- *Au - Gold*: as said the electrodes are made of gold so this material have been associated to them. For this kind simulation where the Electrostatics physics is used, for this material Comsol requires also the value of the relative permittivity that must be inserted manually; in these simulations the used value is 1.
- Si_3N_4 - *Silicon nitride*: all the other parts are dielectric made of Silicon nitride. This material has been chosen for its high relative permittivity (9.7).
- *Air*: it is associated to the domain inside the sphere.

Physics

As said before *Electrostatics* is the only physic used in this simulation. The values of the voltage are associated to the electrodes in order to have the three clock zones. To do this from all the possible tools that this physic allows to use *Terminal* must be selected, specifying Voltage as terminal type. For each clock zone a different *Terminal* must be used.

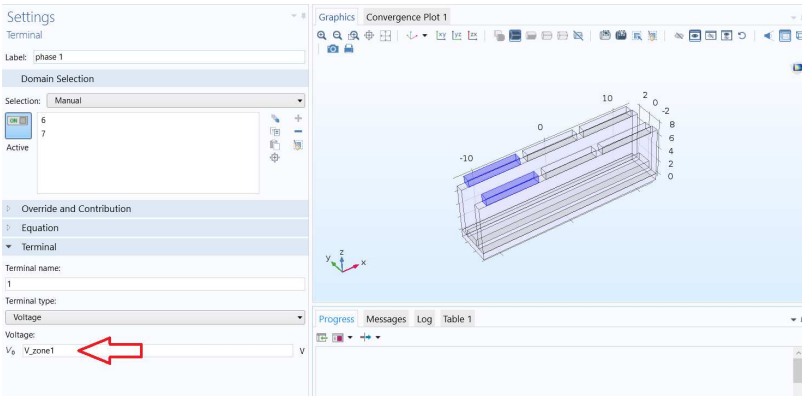


Figure 4.3: Physics and settings to associate to the first clock zone of the binary wire the correct voltage value. For the others two the same procedure has been followed changing the domain selected.

After this, in the Voltage section, the proper parameters can be inserted. In figure 4.3 is shown the case for the first clock zone. The same procedure can be applied for the other ones, while for the bottom electrode the value inserted is 0 V.

Mesh

For the realization of the mesh in the Setting window *Physics-controlled mesh* has been chosen setting *Element size* equal to *Finer*. Even if some edges are too small (indeed a Warning message can be seen) this choice is a good compromise between computational time and goodness of the results.

Study

As said a simple Stationary study is required for this simulation. The computational time depends on the thick of the mesh but it is in the order of a few tens of seconds.

Results

The aim is to calculate the electric field through all the molecules that are present in the wire. To obtain these values in the *Data Sets* section *Cut line 3D* must be selected; this tool allows the creation of a line in the space that in this case have to cross one molecule. So the starting point is between the dot 1 and dot 2 while the end is in correspondence of the dot 4. Exploiting the fact that all the molecules are positioned at the same distance a set of parallel lines passing through them can be created modifying only the coefficient that multiplies the *mol_dist* parameters in the column related to the x-axis. In figure 4.4 is reported the example for the ninth molecule.

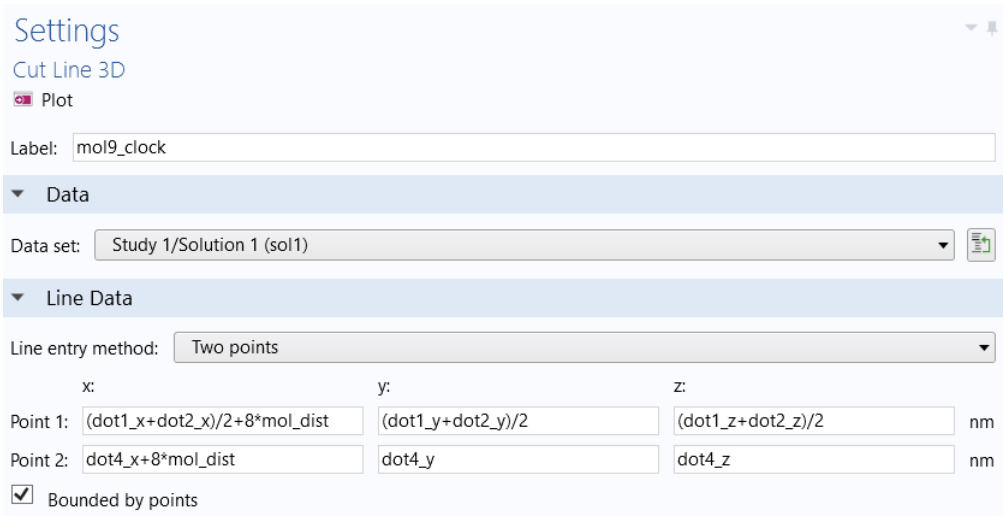


Figure 4.4: Example of 3D line passing through the ninth molecule

Once that all the lines have been created, in the *Derived Values* section line integration must be selected in order to calculate the electric field values in the z component; for each molecule, an integration must be performed so all the lines in the *Data set* section have been associated with one different line integration.

In order to see the trend inside the trench of the potential difference applied to the different molecules, another analysis has been done. In the *Data Sets* a 3D line has been selected in order to create a line that passes between the dots 1 and 2 of the various molecules, as it can be seen in figure 4.5.

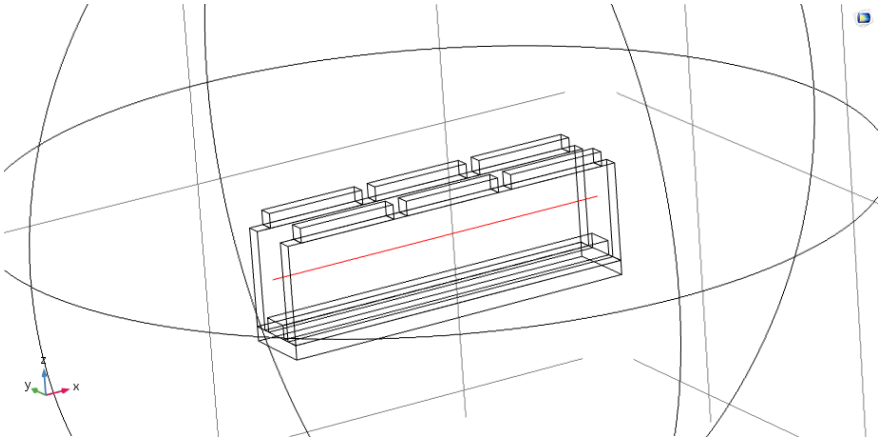


Figure 4.5: 3D line realized in the Data set passing through the dots 1 and 2 of the molecules in the wire.

Similarly, a 3D line passing through the dots four has been created.
At this point the function *Join* has been selected in the *Data Sets*: in this way, the difference between the results calculated along the two lines can be obtained. From the *Result* list *1D plot group* has been selected, so with a line graph associated to the *Join* line the trend of the electric field inside the trench can be evaluated.
In addition, Comsol generates others plots that are useful for the analysis of the electric field and the voltage inside the trench.

4.2 Majority voter Comsol model

In this section, the model used for the simulation of the majority voter is described. As before a 3D component is required and the same physics and study have been used.
The values used for the realization of the two trenches are almost the same as the previous case and are specified in the *Parameters* section. Different parameters have been inserted for the voltage values because a new configuration of the electrodes is used.
As said two versions of this structure have been analysed and the parameters that have been modified are reported in the following table:

Parameter name	Ideal structure	Modified structure	Description
bottom_el_h *top_el_h*	1nm	3nm	height of the bottom and top electrodes that generate the electric field
bottom_el_w	2nm	3nm	width of the bottom electrode
diel_depth	5nm	11nm	trench depth
diel_side_h	6.8 nm	8.8nm	height of the side dielectric
diel_side_w	1nm	3nm	width of the side dielectric
top_el_w	1nm	3nm	width of the top electrodes

Moreover the position of the dots must be adapted to the structure: due to the fact that the hight of the bottom electrode has been increased from 1 nm to 3 nm the position of the dots along the z-axis must be increased of 2 nm; this modification is not so relevant during the creation of the geometry but during the calculation of the electric field values in the *results* section.
As it can be noticed the parameters have been modified in order to increase the minimum resolution required to realize the electrodes from 1 nm to 3 nm; moreover, the width and the hight of the dielectric have been modified in order to obtain also in this case a vertically oriented electric field inside the trench.

Geometry

As before the starting point for the creation of the geometry are the bottom dielectric and the bottom electrode using the tool *Block*. In this case, they formed a sort of crossroad

so the structure has been created generating the horizontal base and rotating it of 90 degrees exploiting the function *Rotate* to create the second one. For the creation of the side dielectrics and the top electrodes the same principle has been exploited; due to the fact that the structure has been centred in the origin and that it is symmetric respect it, the function *Mirror* has been used specifying as the point of reflection always the centre of the axis. In figure 4.6 the sequence for the realization of the side dielectrics is shown.

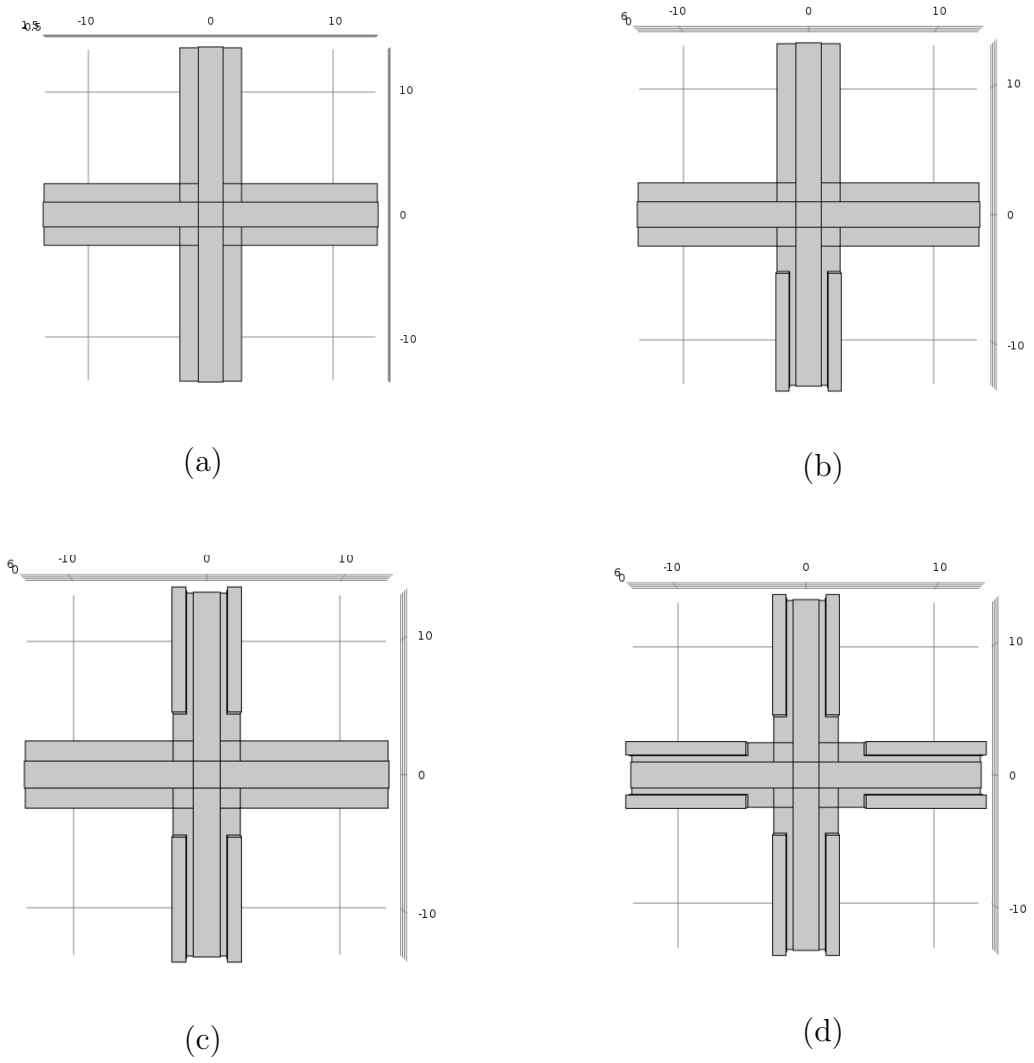


Figure 4.6: Steps for the creation of the side dielectrics (top views). (a) Crossroad formed by the bottom electrode and the bottom dielectric; (b) creation of two sides dielectric; (c) exploiting the function *Mirror* with the origin as point of reflection, the dielectric on the other side has been realized; (d) the function *Rotate* is used to generate the others two rotating the firsts of 90 degrees.

As said the scope is to have the three inputs in a clock zone and the central cell in another one. For this reason in the correspondence of the angle four electrodes have been inserted

in order to obtain an electric field that can influence almost exclusively the central cell. So to do this the dielectric and the electrode in the corners are formed by three blocks each. Exploiting the same principle used for the side dielectric only one corner has been realized, while the others have been created using the function *Mirror*.
For the positioning of the molecules (that as said before have no role for the simulation) the first molecule has been generated specifying the position of the four dots while all the others have been realized exploiting the function *Array*.
The final structure is reported in figure 4.7 and 4.8 (prospective and top view respectively).

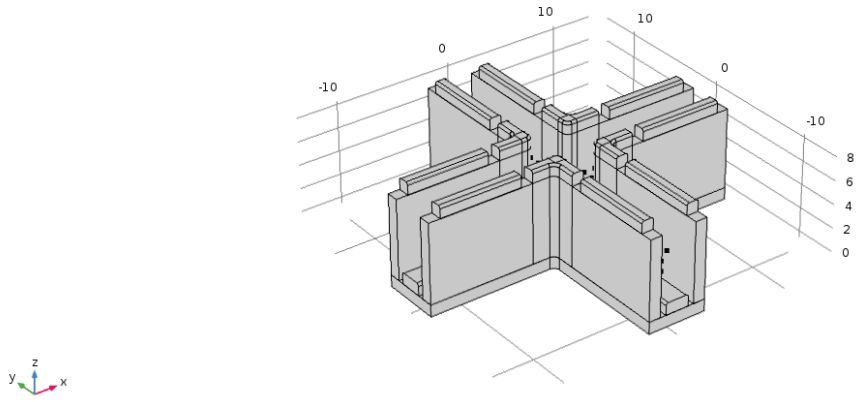


Figure 4.7: Geometry used for the Comsol simulation of the majority voter in the ideal case (prospective view).

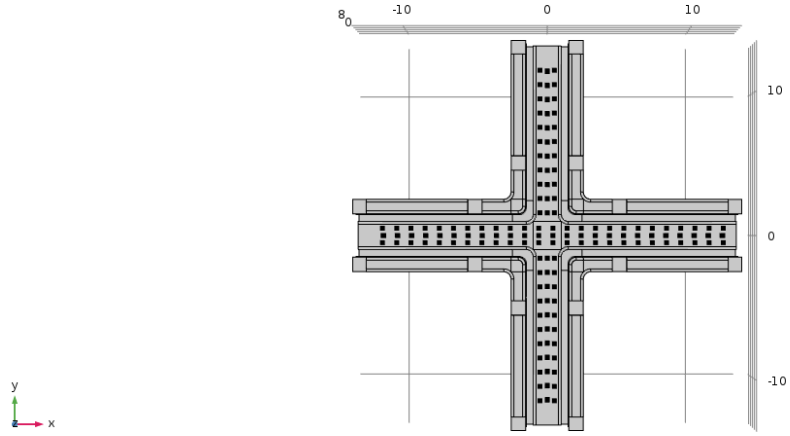


Figure 4.8: Geometry used for the Comsol simulation of the majority voter in the ideal case (top view).

Physics

The procedure is identical to the previous case of the binary wire. But in this case, also the voltage applied to the electrodes in the corners must be specified.

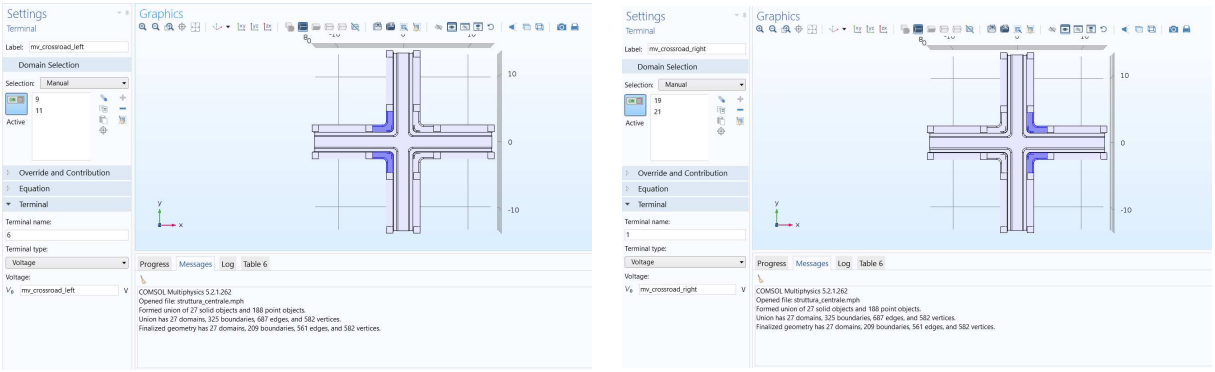


Figure 4.9: Association of voltage values to the electrodes in the crossroad.

As it can be seen in figure 4.9 in order to better control the central region different values of voltage can be associated with the terminals in the left part and in the right part.
The output is the wire on the right and a different value of voltage has been associated with respect to the others input wires.

Mesh

For the realization of the mesh in the Setting window *Physics-controlled mesh* has been chosen setting *Element size* equal to *Finer*. Even if some edges are too small (indeed a Warning message can be seen) this choice is a good compromise between computational time and goodness of the results.

Results

The procedure is equal to the previous case, so a set of lines is created in correspondence of the different molecules, then for each of them a line integration is performed in order to calculate the electric field (z component) along them.
The values are collected in a table and exported in a text file.

4.3 T structure Comsol model

This model is almost equal to the previous one and it has been realized with the same techniques so only the principal differences will be exposed. As said also a structure that required a minimum resolution equal to 3 nm has been realized.
The parameters that have been imported are the same of the previous case in order to create

a structure with the same sizes.

Geometry

The structure ,in this case, is a crossroads with one input wire and two output with opposite direction. To realize it the tool *Block* is used to generate the single elements and the symmetric part, such as the top electrodes of the two output, have been realized exploiting the function *Mirror* as before. The obtained structure is reported in figure 4.10 and 4.11 (prospective and top view respectively).

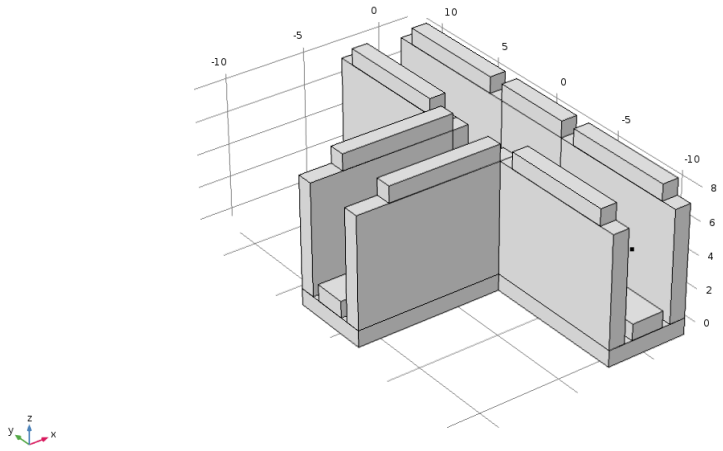


Figure 4.10: Geometry used for the Comsol simulation of the T structure (prospective view).

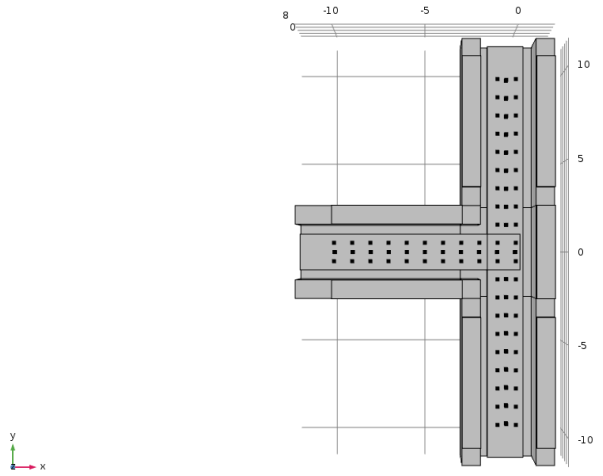


Figure 4.11: Geometry used for the Comsol simulation of the T structure (top view).

As it can be seen even if the structure is quite similar to the case of the majority voter the electrodes in the corners have been replaced with a single electrode at the bottom of the principal wire that will be called *front electrode*. This choice has been made because in this case the central cell can be considered in the same clock zone of the input. Furthermore, the electrodes in the corners are very difficult to realize so, in this case, a simpler solution has been found.

Physics

The used physic is as before *Electrostatics (es)*: using the tool *Terminal* the voltage values of the different clock zones can be associated with the electrodes. In particular, in this case, the wire that propagates the information along the x-axis is the input, while the others two along the y-axis are the two outputs. To the front electrode, a different value of voltage is associated so three terminals are used in this structure.

4.4 Angle structure Comsol model

Also for this simulation, the procedure and the techniques used are equal to the previous cases that are have been already described.

The parameters that have been imported are the same of the previous cases in order to create a structure with the same sizes.

Geometry

The structure must be able to allow the propagation of the information in presence of an angle of 90 degrees. The geometry used is reported in figure 4.12 and 4.13 (prospective and top view respectively).

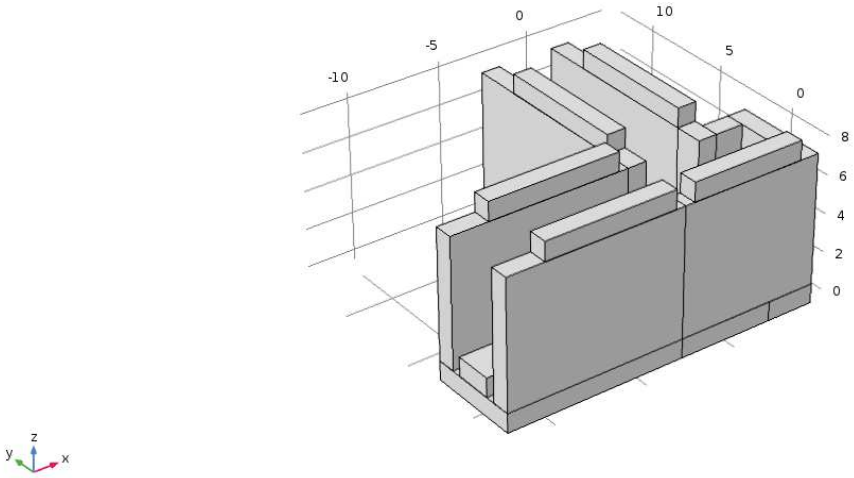


Figure 4.12: Geometry used for the Comsol simulation of the L structure (prospective view).

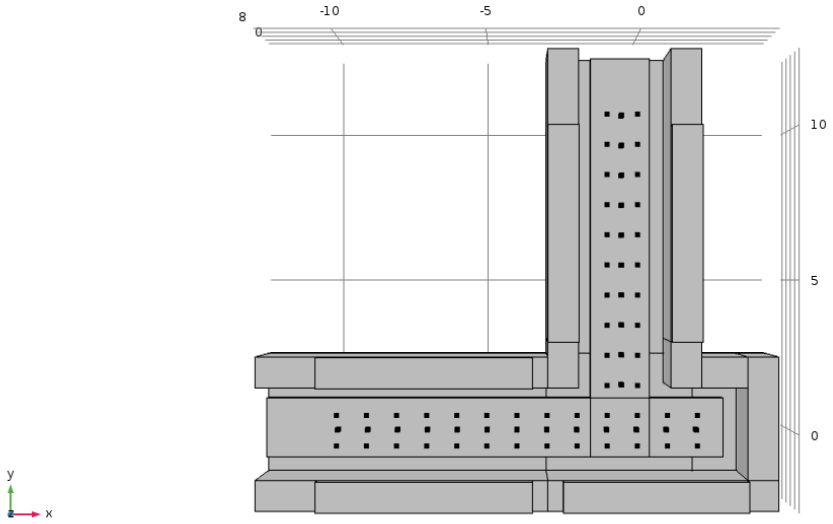


Figure 4.13: Geometry used for the Comsol simulation of the L structure (top view).

As it can be seen the structure has been created in order to have one more QCA cell at the end of the input wire.

Physics

The used physic is the *Electrostatics* one as the previous cases. Also in this case, an additional electrode has been inserted in order to control the propagation in the corners and,

in particular, in the cell in the centre. The input is the wire that propagates the information along the x-axis while the other one along the y-axis is the output. So three different *Terminals* are used in this simulation.

4.5 Comsol with Matlab

Once that the models have been created, to better control all the simulation and automatize the passages using *Comsol with Matlab* all the files have been saved as *Model File for Matlab(*.m)*. In this way, a script Matlab that reproduces the simulation is created obtaining a function and the voltage values of the different phases can be passed directly from the algorithm; after the computation of the electric field, these ones are immediately written in the text files. Others variable are passed to this function such as the folder name in which the text files must be saved, the number of molecules in the structure and the number of phases that allow a complete propagation.
In figure 4.14 is reported the example of the first part of the script for the function generated by the binary wire model.

```
7   function []=new_wire_3D(clock_zone1,clock_zone2,clock_zone3,num_mol,n_phase,folder_name)
8
9   str_num_mol=num2str(num_mol);
10
11  for phase=1:n_phase
12  string_zone1=[num2str(clock_zone1(phase)),'[V]']
13  string_zone2=[num2str(clock_zone2(phase)),'[V]']
14  string_zone3=[num2str(clock_zone3(phase)),'[V]']
15
16  import com.comsol.model.*
17  import com.comsol.model.util.*
18
19  model = ModelUtil.create('Model');
20
21  model.modelPath('C:\Users\giorg\Desktop\POLI\tesi\mio materiale\COMSOL');
22
23  model.comments(['Untitled\n\n']);
24
25  model.modelNode.create('comp1');
26
27  model.geom.create('geom1', 3);
28
29  model.mesh.create('mesh1', 'geom1');
30
31  model.physics.create('es', 'Electrostatics', 'geom1');
32
33  model.study.create('std1');
34  model.study('std1').create('stat', 'Stationary');
35  model.study('std1').feature('stat').activate('es', true);
```

Figure 4.14: First part of the .m file generated by the Comsol simulation of the binary wire.

As it can be seen the file is used as a function and the input value of the voltages are converted into string and used during the simulation. All the procedure is repeated in order to calculate the electric field values for each phases used to propagate the information.

The last part of the script that is automatically generated by Comsol has been modified: instead of creating a new 3D line in the Data set for each molecule and the consequential integration procedure a *for* cycle that automatically iterates this procedure for all the molecules has been used; in this way the code is much shorter and easier to use.
With the function *fprint* the calculated values are saved in the text files and the number of digits after the decimal point can be chosen. In figure 4.15 is reported the example for the binary wire function.

```
for i=1:num_mol
cln_string=['cln',num2str(i)];
mol_string=['mol_',num2str(i)];
point1=['(dot1_x+dot2_x)/2+mol_dist*',num2str(i-1)];
point2=['dot4_x+mol_dist*',num2str(i-1)];
int_str=['int',num2str(i)];
tbl_str=['tbl',num2str(i)];

model.result.dataset.create(cln_string, 'CutLine3D');
model.result.dataset(cln_string).label(mol_string);
model.result.dataset(cln_string).setIndex('genpoints', point1, 0, 0);
model.result.dataset(cln_string).setIndex('genpoints', '(dot1_y+dot2_y)/2', 0, 1);
model.result.dataset(cln_string).setIndex('genpoints', '(dot1_z+dot2_z)/2', 0, 2);
model.result.dataset(cln_string).setIndex('genpoints', point2, 1, 0);
model.result.dataset(cln_string).setIndex('genpoints', 'dot4_y', 1, 1);
model.result.dataset(cln_string).setIndex('genpoints', 'dot4_z', 1, 2);
model.result.dataset(cln_string).run;

model.result.numerical.create(int_str, 'IntLine');
model.result.numerical(int_str).set('data', cln_string);
model.result.numerical(int_str).setIndex('expr', 'es.Ez', 0);
model.result.table.create(tbl_str, 'Table');
model.result.table(tbl_str).comments('Line Integration 1 (es.Ez)');
model.result.numerical(int_str).set('table', tbl_str);
model.result.numerical(int_str').setResult;

fprintf ( nomefile , '%7.6g\n' , model.result.table(tbl_str).getReal);

end
```

Figure 4.15: Last part of the .m file generated by the Comsol simulation of the binary wire. For each molecule a 3D line crossing it is created and the integration is performed along it.

Chapter 5

Matlab algorithm

As said the electric field values obtained by the Comsol simulations are saved in text files that are read by a Matlab algorithm that, using them, computes the propagation of the information in the analysed structure. It is divided into two blocks (that will be further explained in the following sections):

- Layout: this part is used to create in Matlab the desired structure. Indeed its outputs files provide all the information about the molecules (position, shift, orientation and phase) and the drivers that will be used in the Main section. Moreover, the whole part concerning the calculation and saving of the electric field values is managed in this part.
- Main: this part is the core of the algorithm and it computes the effect that each molecule has on the others one, starting from their position and value of the electric field. The output is a 3D plot where the distribution of the charge in each molecule can be seen.

5.1 Layout section

In the first part of this script is present a section called *Settings* in which different variables are specified:

- *initial_charge*: the initial configuration of the charges in the four dots is set; three configurations can be selected in depends on the voltage applied to them in the starting point.
- *molecule_type*: with this string, the molecule used in the simulation can be specified. In this thesis, only one molecule has been considered but in the future, not only different configurations of the dots could be used but also different molecules. Indeed using only four quantum dots for the representation of the bis-ferrocene is a simplification, in a real case, it is composed of 91 dots. In this work the value used is always *bisfe4* that

means that the used molecule is bis-ferrocene considering only 4 quantum dots. The idea is that varying this string different configurations can be selected.

- *comsol_value*: with this variable, the user can choose to select the values calculated by Comsol, or use the values specified in the Layout script.

- *structure*: is used to select the structure that the users want to analysed; varying its value the variable *name_structure* changes. For example, setting *structure* equal to 1 the simulated structure will be a binary wire with three clock zones and 24 molecules.

- *dot_position*: this variable is used the specify the reference dot position. From these variables, the position of all the others molecules is calculated. This variable is a matrix with four rows and three columns, indeed each dot needs a coordinate for the x,y and z directions.

- *new_values_required*: as said the Comsol models have been converted into Matlab files and used as functions. So when this variable is set to 'yes' the function of the correspondent structure (previously choose) is call and the electric field values are calculated and saved in the text files. This is an easy way to automatize the calculation and saving procedure of the results.
  Due to the fact that these scripts are very long, the computation took some minutes and often the required values have already been calculated and saved in text files. So in order to avoid wasting of time when the values are already available, this variable can be set to 'no', in this way the algorithm does not recalculate the values but it uses those saved in the text files.

As said the structure is selected choosing the correspondent value of the variable *name_structure*; this one is passed to the function *select_structure* whose outputs are two matrices that represent the arrangement and the orientation of the molecular QCA cell; an example of them can be seen in figure 5.1.

```
if ( strcmp(name,'WIRE_24')==1)
dist_z = 10;
dist_y = (dist_z + abs(dot_position(1,2) - dot_position(2,2)));

QCA_circuit.structure = { 'Dr3' '1' '1' '1' '1' '1' '1' '1' '1' '2' '2' '2' '2' '2' '2' '2' '2' '3' '3' '3' '3' '3' '3' '3' '3'};

QCA_circuit.rotation =  {  '0'  '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0' '0'};
```

Figure 5.1: Example of matrices in the case of wire with 24 molecules.

The matrices are *QCA_circuit.structure* and *QCA_circuit.rotation* (in this case of a binary wire it is more correct to say that they are vectors due to the fact that the molecules are all on the same lines, but this is a special case): the first one specifies the position and the phase of each molecule, while the second one specifies the orientation of them; in this

case that the values are all equal to *'0'* the molecules are all parallel oriented in the same direction. Finally, *dist_z* specifies the distance between two molecules in Angstrom; this value must be equal to the constant *mol_dist* used in the Comsol simulation.

The two functions that have been added to the Layout section to consider the real values of the electric field calculated with Comsol are:

- *comsol*: this function as input receives all the information about the molecules, the drivers, their positions and the folder in which the text files must be saved or taken; for all the structures the voltage values for each clock zone in the different phases have been specified. As said in depends on the variable *new_values_required* the function calculates the new electric field values or reuses those saved in the text files. The output is a struct that for each molecule specifies the clock zone to which it belongs and the correspondent value of the electric field.
- *output_table*: this function generates as output a file that will be read by the Main section of the algorithm with the values of the electric filed taken from the text files for each molecule in the different phases. An example of this file is reported in figure 5.2.

	A	B	C	D	E	F
1	name	phase	time 0	time 1	time 2	time 3
2	Mol_1	1	1,5124	1,6751	-1,5124	-1,6751
3	Mol_2	1	1,6445	1,8062	-1,6445	-1,8062
4	Mol_3	1	1,6948	1,8774	-1,6948	-1,8774
5	Mol_4	1	1,6749	1,9249	-1,6749	-1,9249
6	Mol_5	1	1,5462	1,9258	-1,5462	-1,9258
7	Mol_6	1	1,3163	1,9325	-1,3163	-1,9325
8	Mol_7	1	0,9069	1,9288	-0,9069	-1,9288
9	Mol_8	1	0,313	1,9236	-0,313	-1,9236
10	Mol_9	2	-0,3502	1,9035	0,3502	-1,9035
11	Mol_10	2	-0,9531	1,8863	0,9531	-1,8863
12	Mol_11	2	-1,3693	1,8427	1,3693	-1,8427
13	Mol_12	2	-1,617	1,7643	1,617	-1,7643
14	Mol_13	2	-1,7719	1,6279	1,7719	-1,6279
15	Mol_14	2	-1,844	1,3742	1,844	-1,3742
16	Mol_15	2	-1,8871	0,9553	1,8871	-0,9553
17	Mol_16	2	-1,9042	0,3575	1,9042	-0,3575
18	Mol_17	3	-1,9255	-0,3152	1,9255	0,3152
19	Mol_18	3	-1,9365	-0,9089	1,9365	0,9089
20	Mol_19	3	-1,9436	-1,3162	1,9436	1,3162
21	Mol_20	3	-1,9335	-1,5528	1,9335	1,5528
22	Mol_21	3	-1,9134	-1,6673	1,9134	1,6673
23	Mol_22	3	-1,877	-1,6944	1,877	1,6944
24	Mol_23	3	-1,8167	-1,655	1,8167	1,655
25	Mol_24	3	-1,6808	-1,5216	1,6808	1,5216

Figure 5.2: Example of output table in the case of the binary wire with 24 molecules with values of the electric field calculated with Comsol.

In the first column, the name of the different molecules is reported while in the second one there is the clock zone of each of them.
In this case, in order to obtain the complete propagation of the information four phases have been used so the others four columns report the electric field values calculated with Comsol.

Thanks to the function *Plotting* a simple scheme of the structure is created in order to better understand it.
In figure 5.3 the case of the binary wire with 24 molecules divided in three clock zones is shown.

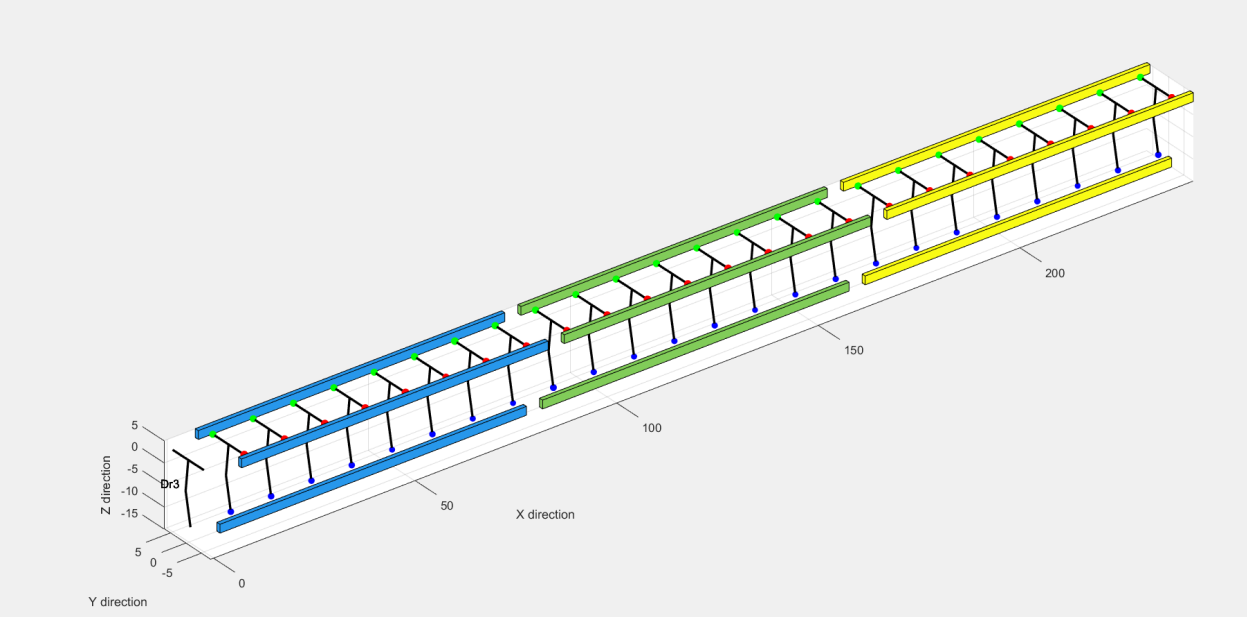


Figure 5.3: Example of the image generated by the layout script in the case of wire with 24 molecules.

As it can be seen the different clock zones of the molecules have been represented changing the colour of the stylized electrodes.

5.2 Main section

In the main script, the first operation is the reading of the files generated with the Layout script and to do this the function *Function_reader* is used.
A second function called *Settings* is used to prepare the simulation and some variables are specified; the most important are:

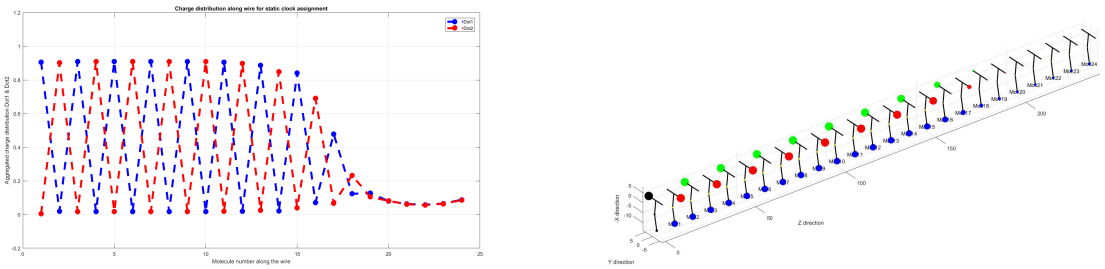
- *setting.max_step*: the algorithm exploits an iterative process and with this variable the maximum number of steps can be specified. Generally it executes a certain amount

of steps and it stops when the convergence has been reached. If, after the maximum number of steps, it is not reached the obtained result is shown anyway.

- *settings.fig_saver*: when it is set to 'yes' all the output figures are saved in a folder.
- *setting.solver*: it can be set equal to 'r' or 'y' and two different algorithms can be chosen. All the results obtained in this thesis have been obtained using the algorithm associated to the letter 'y'.
- *settings.conv_threshold_HP, settings.conv_threshold_LP* and *settings.conv_threshold_LLP* : the algorithm reaches the convergence when the difference between the results obtained in the two following steps is less than a threshold. Three different values of threshold have been used because during the first steps the smallest value is used by the algorithm; after a certain amount of them if the convergence has not been reached yet the one with an intermediate value is used, while in the final steps the higher is used in order to force the algorithm to reach the convergence.

After this two preliminary parts, the algorithm starts to work. The idea is that all the molecules have an effect on all the others so for each of them the sum of the effects is calculated. The most important function used to perform this operation are:

- *Clock_change*: this function is used to calculate the variation of the voltages and of the charges of a certain molecule when clock change occurs.
- *Drivers_effect*: this function is used to evaluate the effect that the drivers have on the molecules.
- Intersection: this function interpolates four point of the trans-characteristic of the molecule to calculate the charge in each dot.
- *MQCAWireCalCharge*: this function is used to implements the iterative procedure.
- *SearchValues*: this function starting from a voltage/clock combination calculate the four points of the trans-characteristic used for the interpolation.
- *Function_Plotting*: at the end for each phase used to evaluate the propagation two plots are created: a 2D graph that shows the distribution of the charge in the structure and a 3D picture that shows the charge in each dot of all the molecules present in the structure. An example of these two kinds of output figures is shown in figure 5.4.



(a) (b)

Figure 5.4: Example of output figures in the case of the wire with 24 molecules in the second phase. (a) distribution of the charge; (b) 3D plot that shows the charge in each dots to evaluate the correct propagation

Chapter 6

Results

6.1 Results obtained by the analysis of the binary wire

In this section, the analysis of the binary wire and the obtained results are shown.
In order to obtain the propagation of the information in a wire divided into three clock zones four phases have been used. The values of voltages associated with the electrodes of the three clock zones are reported in the following table.

	Clock zone 1	Clock zone 2	Clock zone 3
Time 1	-8 V	8 V	8 V
Time 2	-8 V	-8 V	8 V
Time 3	8 V	-8 V	-8 V
Time 4	8 V	8 V	-8 V

Table 6.1: Voltage values used for the simulation of the binary wire.

So for example in the 'Time 1' only the molecules in the first zone should be activated and can propagate the information, while all the others one should be in the 'NULL' state because a positive electric field is applied.
The chosen values are +8 V to generate a negative electric field and -8 V to generate a positive electric field, because these are the higher values that generate an electric field always between +2 V/nm and -2 V/nm inside the trench of the wire, that are the maximum and the minimum values allowed by the algorithm.

First of all the 3D distribution of the field is shown in order to qualitatively appreciate it. The two dielectrics on the sides concentrate the electric field inside the trench obtaining a vector vertically oriented, as it can be seen in figure 6.1 (front view). This is due to the fact that the electric field propagates in the air that has a low relative permittivity (1) rather than in the Silicon nitride that has a high value of it (9.7). The height and the width of the

trench are two fundamental parameters and must be properly selected.

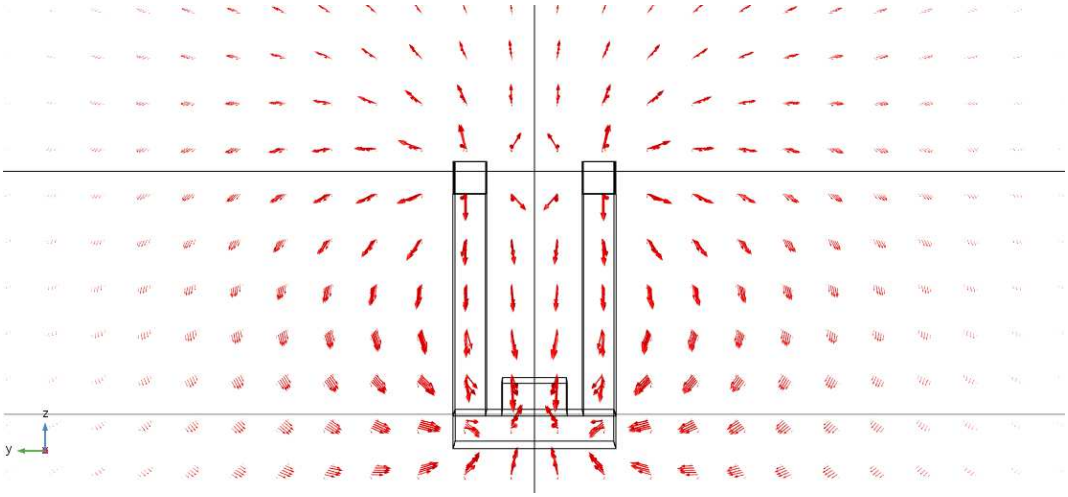


Figure 6.1: Field lines generated by the electrodes in the trench of a wire. The applied voltage in this case is positive so they are oriented towards the bottom.

As said in this thesis the real values of the electric field generated by the electrodes have been used to analyse the various structures. So the electrodes are no more considered ideal and they do not influence only the molecules of the correspondent clock zone. This phenomenon can be seen in figure 6.2 where the trend (ideal and real) of the electric field inside the trench during the first phase of the propagation is reported.

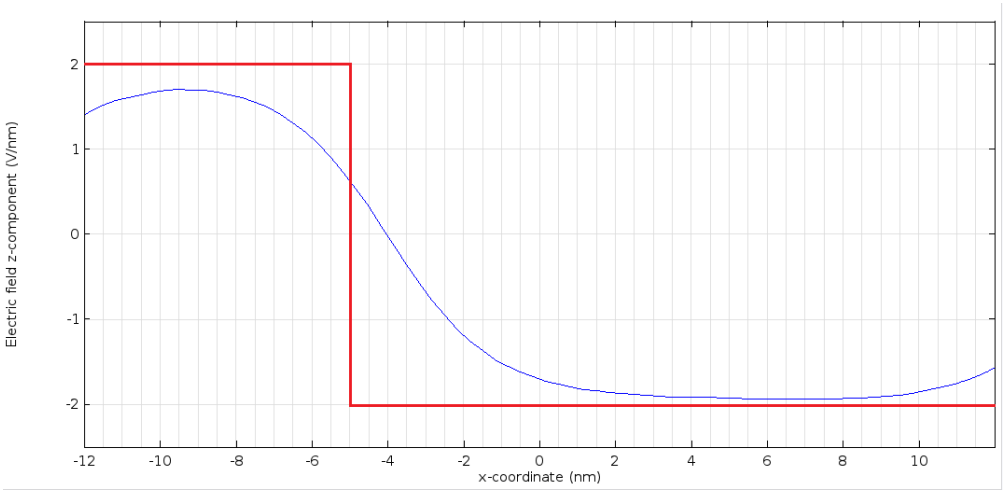


Figure 6.2: Trend of the obtained electric field inside the trench of the wire during the first phase (blue line). The red line represents the ideal behaviour in which all the molecules of a clock zone are subject to the same values of electric field.

The structure has been centred in the origin so 0 nm represent the centre. As it can be seen the obtained values are very different respect that of the ideal case in which the first eight molecules are all subject to an electric field equal to 2 V/nm.
A relevant difference is given by the fact that the electric field decreases very slowly and a lot of molecules are not completely activated or inhibited.
In the following figures is reported the complete propagation in the binary wire.

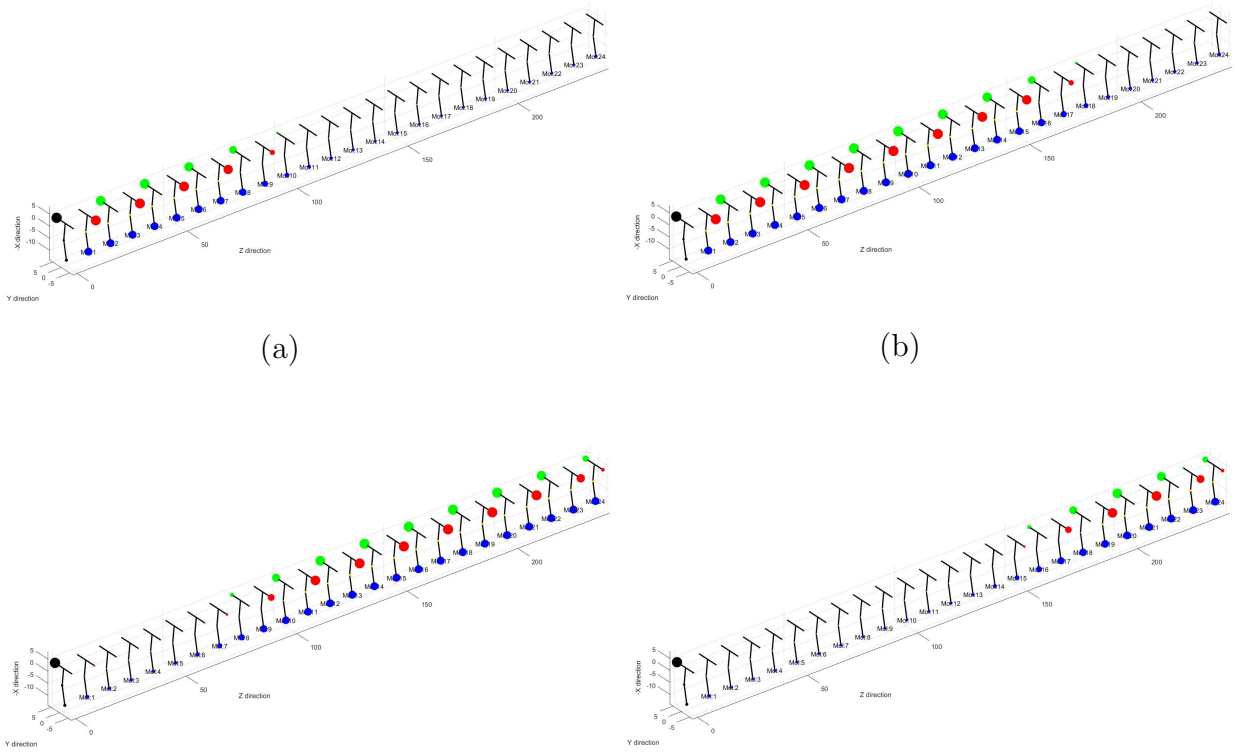
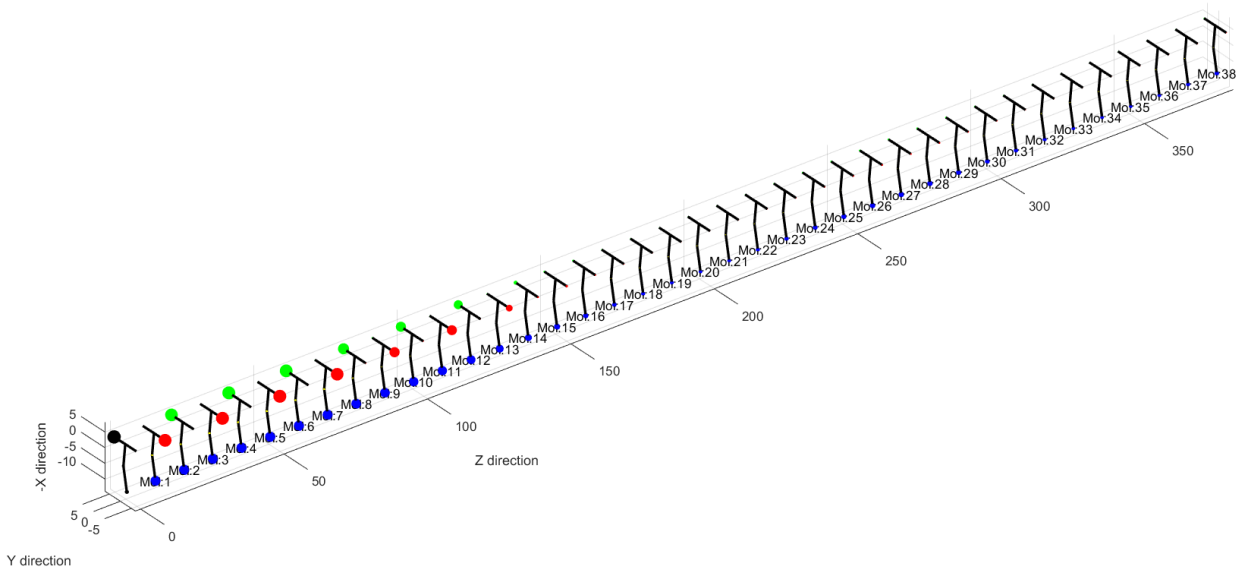


Figure 6.3: Complete propagation in the binary wire.

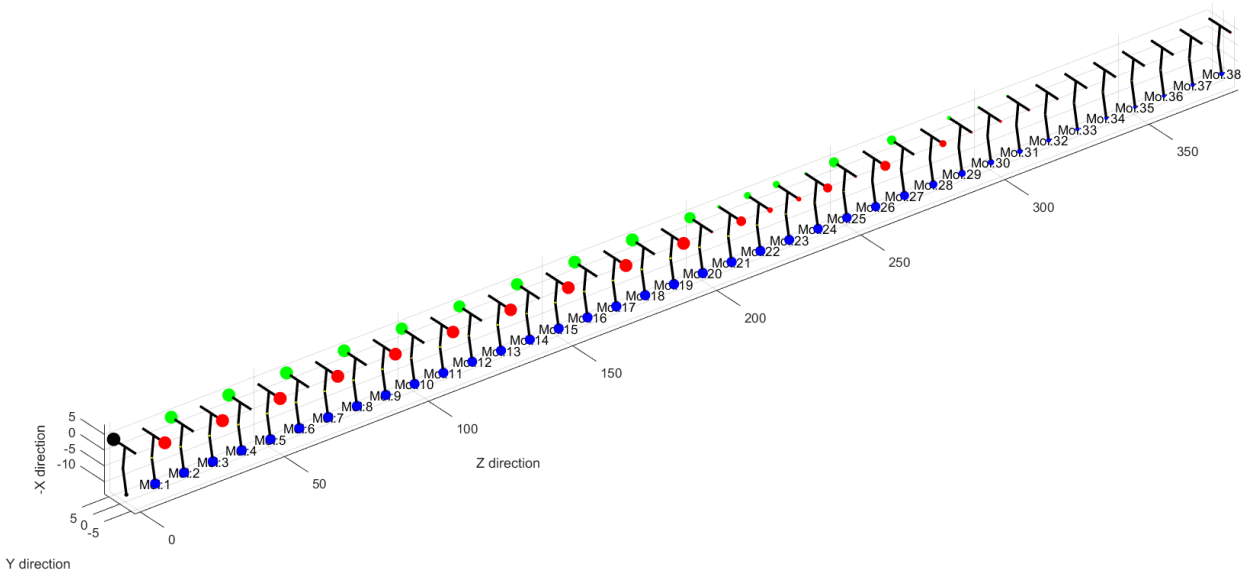
6.1.1 Electrode gap analysis

The metallization process could generate a gap between two adjacent electrodes higher respect 1 nm; so, due to the fact that the distance between two molecules is exactly 1 nm, increasing the gap there will be some molecules that will not belong in a well-defined way to a clock zone, therefore their behaviour will be uncertain.
So the operation of the binary wire has been tested with different values of the gap. To do this in the Matlab function obtained by the Comsol model of the wire the value of *zone_gap* has been varied in order to simulate the various cases. Moreover, due to the fact that a longer binary wire is obtained increasing the value of the gap, also the matrices *QCA_circui.structure* and *QCA_circui.rotation* in the Layout section have been modified in the different cases in order to consider a higher number of molecules.

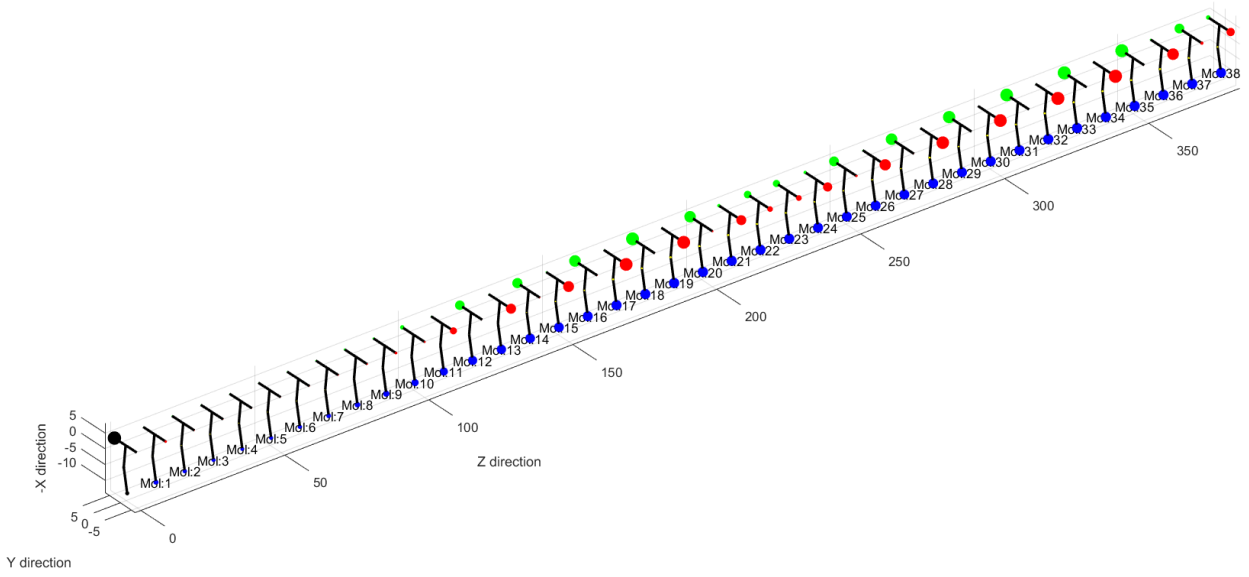
From the analysis has been discovered that if the distance between two adjacent electrodes is less or equal to 7 nm the propagation can occur correctly. For higher values the output information is wrong. This is due to the fact that the electric field halfway between two adjacent electrodes is too low to allow the correct propagation. Moreover, too many molecules are involved in the propagation so three clock zones are not sufficient to control them.
In the following figures, the propagation of the information in the case of gap equal to 8 nm is shown in order to put in evidence the origin of the error. Each line corresponds to a different phase.



(a)


Mol:1
Mol:2
Mol:3
Mol:4
Mol:5
Mol:6
Mol:7
Mol:8
Mol:9
Mol:10
Mol:11
Mol:12
Mol:13
Mol:14
Mol:15
Mol:16
Mol:17
Mol:18
Mol:19
Mol:20
Mol:21
Mol:22
Mol:23
Mol:24
Mol:25
Mol:26
Mol:27
Mol:28
Mol:29
Mol:30
Mol:31
Mol:32
Mol:33
Mol:34
Mol:35
Mol:36
Mol:37
Mol:38
-X direction
Z direction
Y direction
5
0
-5
-10
0
50
100
150
200
250
300
350

(b)


Mol:1
Mol:2
Mol:3
Mol:4
Mol:5
Mol:6
Mol:7
Mol:8
Mol:9
Mol:10
Mol:11
Mol:12
Mol:13
Mol:14
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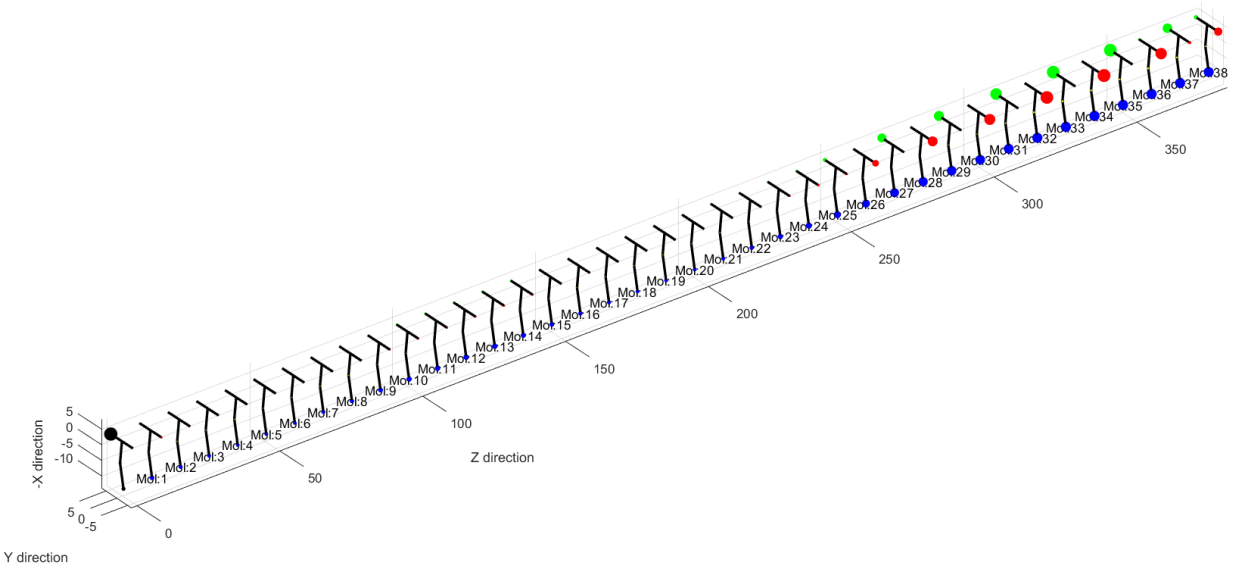
Mol:18
Mol:19
Mol:20
Mol:21
Mol:22
Mol:23
Mol:24
Mol:25
Mol:26
Mol:27
Mol:28
Mol:29
Mol:30
Mol:31
Mol:32
Mol:33
Mol:34
Mol:35
Mol:36
Mol:37
Mol:38
-X direction
Z direction
Y direction
5
0
-5
-10
0
50
100
150
200
250
300
350

(c)



(d)

Figure 6.4: Propagation of the information in the case of the binary wire with gap between electrodes equal to 8 nm.

As it can be seen during the second phase the propagation is not correct in correspondence of the molecules indicated with the numbers 22 and 23.
The error is caused by the fact that in the first phase the molecules placed between two adjacent electrodes are not totally switched off because the electric field is not strong enough; so the charge can move in the dot 1 and dot 2 baptizing erroneously one of the two logic value. So in the second phase, this molecule works as a driver for the near ones going into conflict with the correct information. In figure 6.5 the trend of the electric field is reported in this case of gap equal to 8 nm.

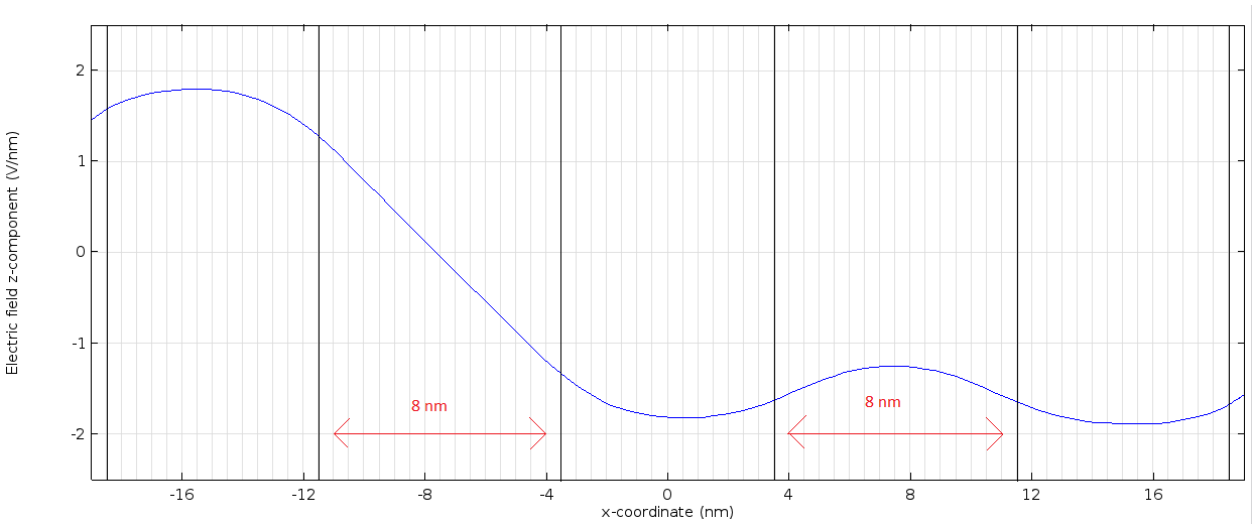


Figure 6.5: Trend of the electric field in the binary wire with the gap equal to 8 nm during the first phase of the propagation.

This analysis has been done also varying the distance between the molecules. All the previous results have been obtained with 1 nm of distance, now two different cases with 1.2 nm and 0.8 nm are presented.

Analysis with 1.2 nm of distance between the molecules

In this case, even with the gap between two electrodes equal to 1 nm, the propagation cannot occur because the distance between the molecules is too high. Indeed the electric field generated by the molecules is not strong enough to influence the surrounding molecules. In figure 6.6 the first phase of the propagation is reported. As it can be seen only the first molecule influenced by the driver has the correct charge distribution.

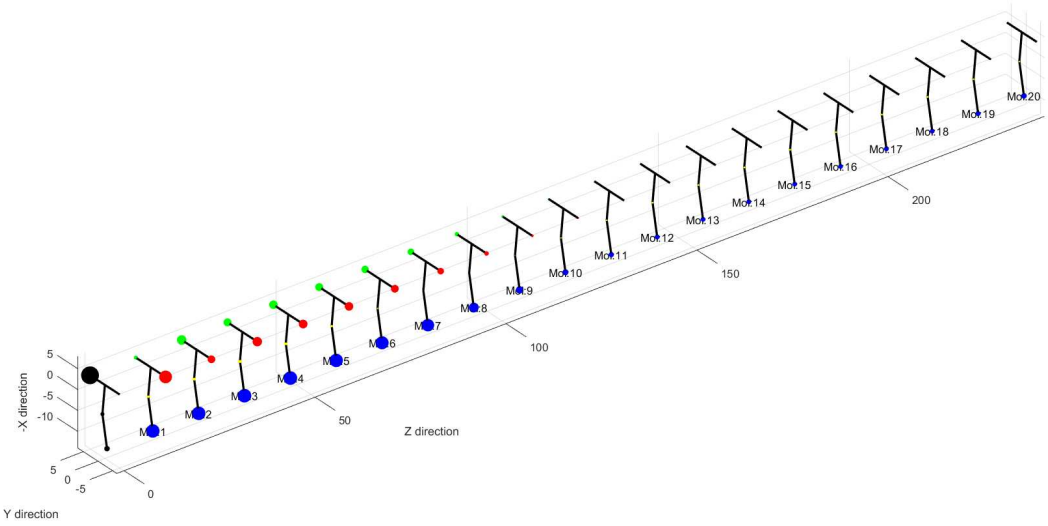


Figure 6.6: First phase of the propagation in the case of the wire with 1.2 of distance between the molecules.

Analysis with 0.8 nm of distance between the molecules

In this case, the opposite effect has been obtained: indeed the molecules are very close to each other and even with very low value of electric field they are able to propagate the information. The maximum value of the gap between electrodes that has been simulated is 17 nm and the resulting information obtained at the end of the wire is still correct. This is due to the fact the electric field obtained between two electrodes ($\simeq$ 0.3 V/nm) is enough to ensure the correct propagation.
This seems to be a possible solution to realized almost perfect molecular QCA cell, but unfortunately, it's impossible to anchor the molecules at such low distance.

6.2 Results obtained by the analysis of the majority voter

6.2.1 Ideal structure

In this section, the analysis of the majority voter and the obtained results are shown.
As said at the beginning the ideal structure has been analysed (reported in figure 4.7). In order to obtain a complete propagation of the information, three phases have been used, supposing in this case, that all the three inputs are available already during the first phase. Two different approaches have been analysed:

- The voltage values of the electrodes have been chosen in such a way that during the first phase, in which the inputs arrive, only the molecules anchored in the central cell of the majority voter and those in the output are subjected to a negative electric field. To obtain this effect, its value will not be so high in the centre and a certain amount of charge will be present even if the cell should be in the 'NULL' state.
  The voltage values used are reported in the following table.

	Inputs	Left corners	Right corners	Output
Time 1	-8 V	2 V	2 V	8 V
Time 2	-8 V	-2 V	-2 V	-8 V
Time 3	8 V	-2 V	-2 V	-8 V

Table 6.2: Voltage values used for the simulation of the majority voter (first approach).

- The voltage difference generated by the electrodes in the corners has been increased in order to generate a stronger electric field. In this case, also some molecules that should be in the inputs clock zones are subjected to a negative electric field and they remain switched off also in the first phase.
  The voltage values used are reported in the following table.

	Inputs	Left corners	Right corners	Output
Time 1	-8 V	5 V	3.5 V	8 V
Time 2	-8 V	-2 V	-3.5 V	-8 V
Time 3	8 V	-2 V	-2 V	-8 V

Table 6.3: Voltage values used for the simulation of the majority voter (second approach).

In figure 6.7 the trend of the electric field inside the structure is plotted. The plot has been obtained generating a 3D line inside the structure starting from the electrode of the top input until the electrode of the output along the y-axis.

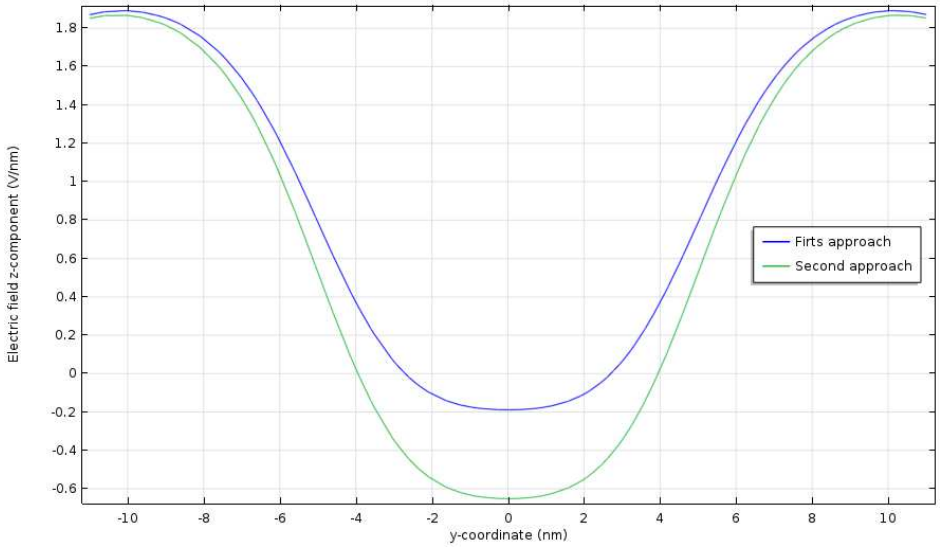
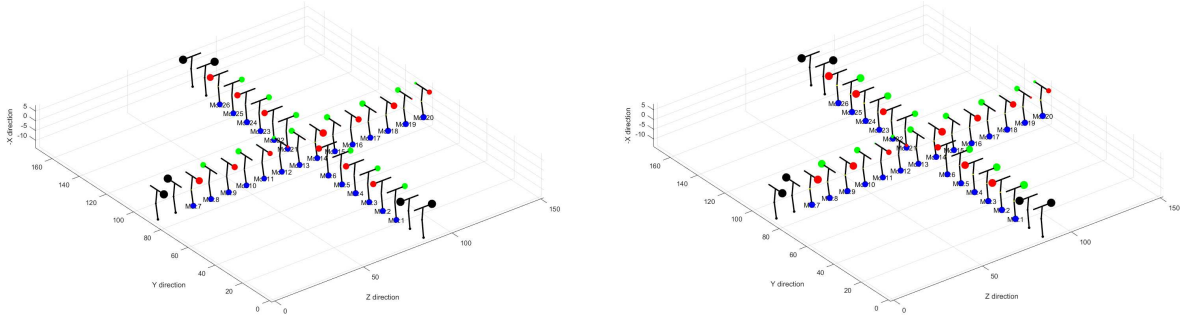


Figure 6.7: Trend of the electric field inside the trench of the majority voter in the two approaches described during the first phase in which the inputs are switched on; blue line first approach, green line second approach.

As it can be seen in the second approach the zone where the electric field remains negative is larger and its value is higher in correspondence of the centre where the cell that has to compute the operation is anchored.
These two approaches have been analysed with different configurations of the drivers; obviously, the structure must work for all the possible permutations of them.
In case the inputs all reach the central cell at the same time the two described approaches always generates the correct output and there are no differences between them; one of the possible cases is reported in figure 6.8.



(a) First approach (b) Second approach

Figure 6.8: Phase two of the propagation in the majority voter in the two approaches described. In this case the inputs that arrives from the top and from the bottom impose the logic value of the central cell.

In this case, the inputs that must impose the logic value to the central cell are the top and the bottom ones. On the contrary, the input coming from the centre has the opposite effect but being in the minority is not able to impose its logic value of the central cell.

A different behaviour can be seen if the inputs arrive in different moments. In order to simulate this case a higher number of phases is required: indeed in the first one of the input is switched off applying to the corresponding electrodes the same voltage value of the output. In the same way, two inputs can be delayed and the three inputs arrive in three different instants (five phases are required in this case).
Delaying one of the input the number of possible cases increases because different behaviours are expected in depends on which of them is delayed. In the following table are reported all the results obtained by the simulation of the majority voter using the first approach (the logic values have been associated as in the case reported in figure 1.1).

Delayed input	Top	Center	Bottom	**Output**	
bottom	1	1	1	1	$\surd$
bottom	0	1	1	1	$\surd$
bottom	1	0	1	0	X
bottom	1	1	0	1	$\surd$
bottom	0	0	1	0	$\surd$
bottom	0	1	0	1	X
bottom	1	0	0	0	$\surd$
bottom	0	0	0	0	$\surd$

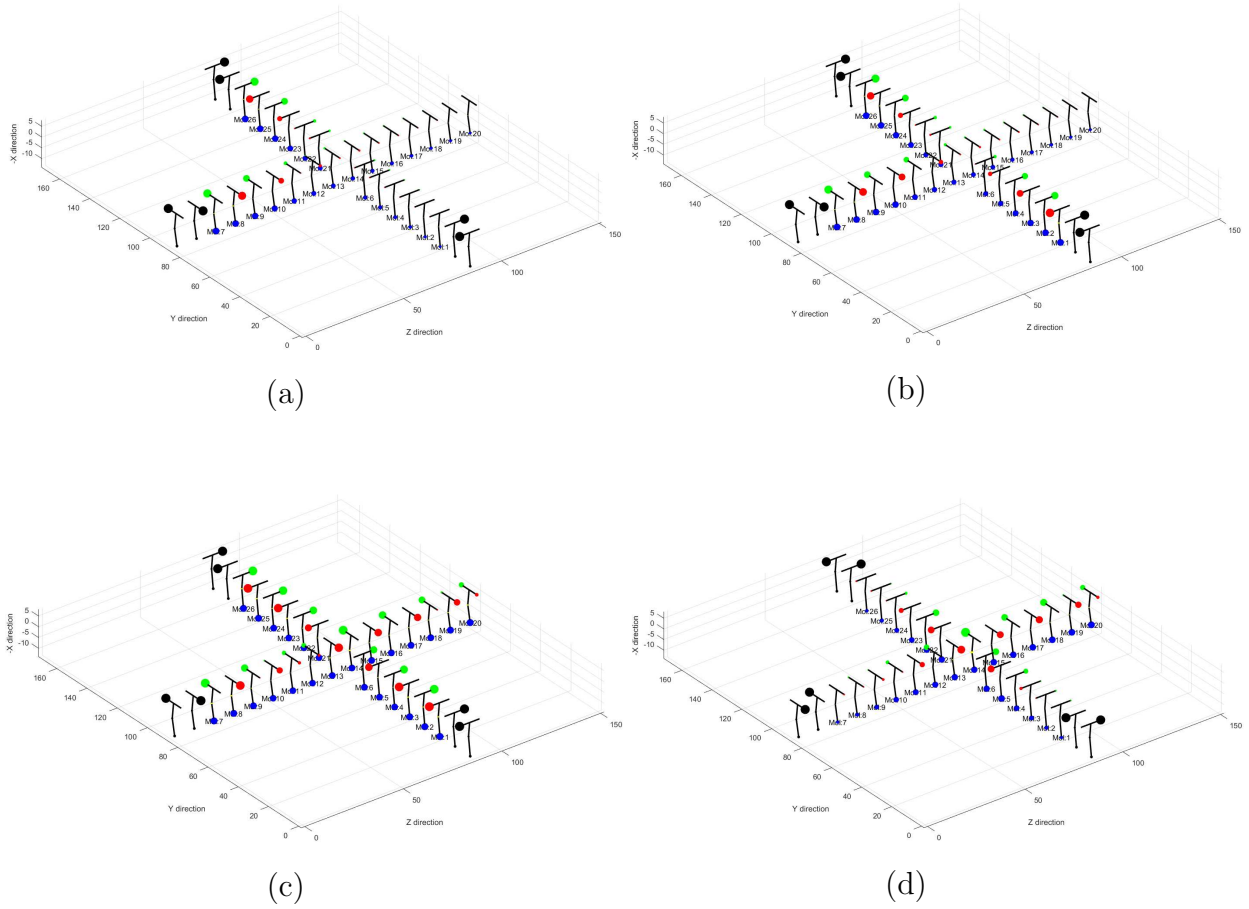
Delayed input	Top	Center	Bottom	**Output**	
center	1	1	1	1	$\surd$
center	0	1	1	1	$\surd$
center	1	0	1	1	$\surd$
center	1	1	0	0	X
center	0	0	1	1	X
center	0	1	0	0	$\surd$
center	1	0	0	0	$\surd$
center	0	0	0	0	$\surd$

Table 6.4: Output results of the majority voter (first approach).

As it can be seen in four cases the output is not correct. These ones show some similarities, indeed the two inputs that arrives in the first phase are different so the output value depends on the last one that has been delayed; the error comes from the fact that one of the

first two inputs slightly influence erroneously the central cell that is not completely switched off, so when all the inputs are available this one has already a stable logic value.

This phenomenon does not happen in the second approach because the electric field is stronger and the molecules could not propagate the information near the central cell during the first two phases, so it remains in the 'NULL' state. All the cases have been tested and the output results are always correct also in the case with one or two inputs delayed. In figure 6.9 is reported the propagation in the case of input top=1, center=0 and bottom=1 with the bottom input delayed (one of the combinations that generate an error in the previous case).



(a) (b)

(c) (d)

Figure 6.9: Complete propagation in the majority voter with one input delayed in the second approach. The input values are top=1, center=0, bottom=1. (a) the bottom input remains off while the others two are on, in order to simulate the delay. (b) all the inputs are switched on but no logic value is present in the central cell. (c) the central cell and the output are switched on and the computation is performed. (d) the inputs are switched off.

6.2.2 Larger structure

In this section, the results obtained by the analysis of the majority voter with a larger structure are shown. The voltage values used in this simulation are reported in the following table:

	Inputs	Left corners	Right corners	Output
Time 1	-8 V	5.5 V	4 V	8 V
Time 2	-8 V	-2 V	-3.5 V	-8 V
Time 3	8 V	-2 V	-2 V	-8 V

Table 6.5: Voltage values used for the simulation of the majority voter with larger structure.

The problem that derives from the fact that the structure is larger is that a higher number of molecules are anchored in correspondence of the electrodes placed in the corners that should influence only the central cell. Moreover, this one is further from the electrodes in the corners, so the used voltage values are higher respect the previous case in order to ensure that the molecules in the centre cell remain inhibited in the first phase. In figure 6.10 is reported a top view of the central region of the majority voter.

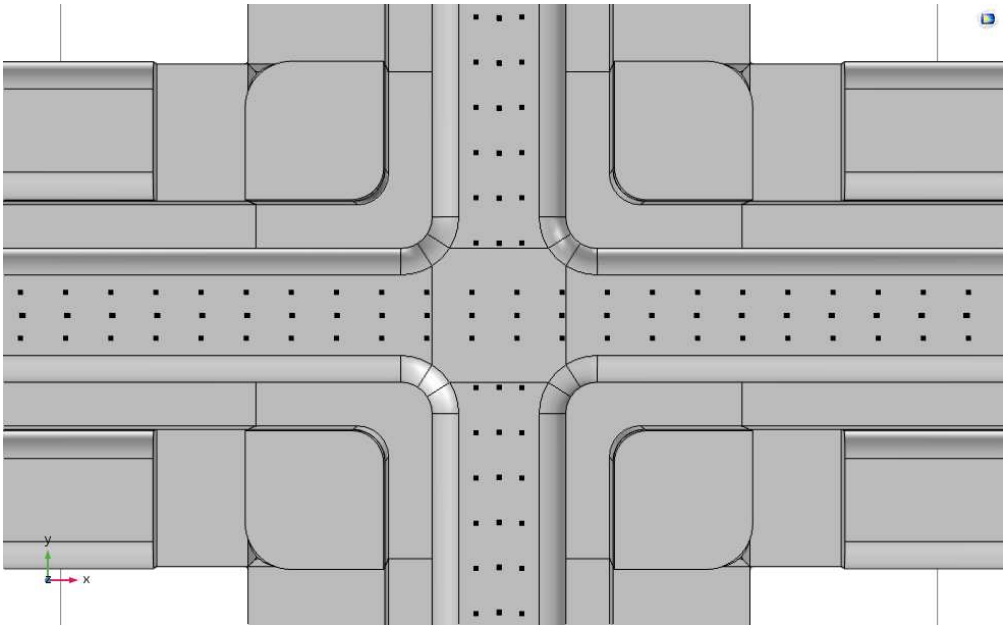


Figure 6.10: Top view of the majority voter central region in the structure where the realization of the electrodes required a resolution equal to 3 nm.

As it can be seen the electrodes in the corners in this case are cubic in shape and the side of the cube measure 3 nm. So five molecules for each input are anchored in correspondence

of these central electrodes. Moreover, other two molecules are placed in the gap between the central electrodes and the electrodes in the input. This is a limit case beyond which the structure could not work.
To confirm this in figure 6.11 is reported the trend of the electric field (calculated in the first phase where only the inputs should be switched on) inside the structure that has been obtained with a 3D line. The line goes from the electrode of the top input to the electrode of the bottom input, so a symmetric trend can be expected due to the fact that the same voltage values have been associated to the electrodes.

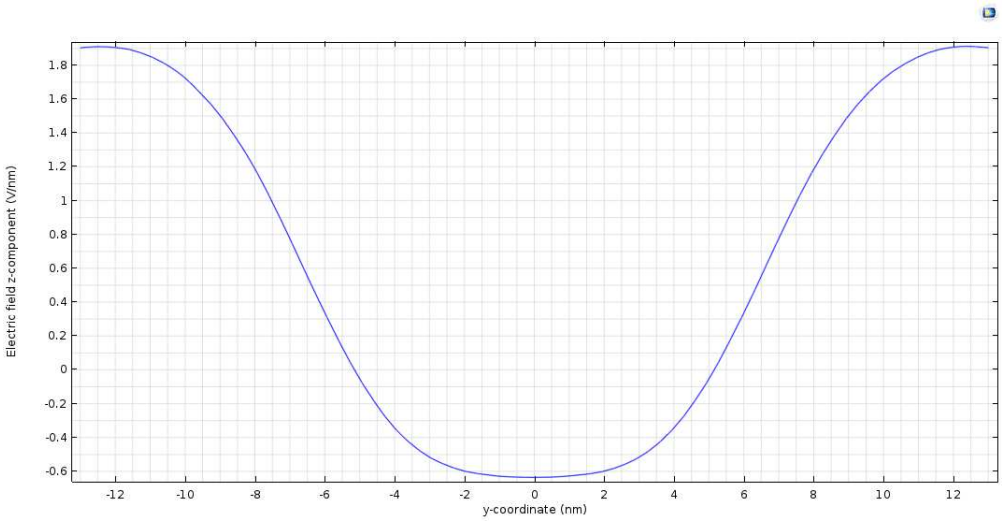
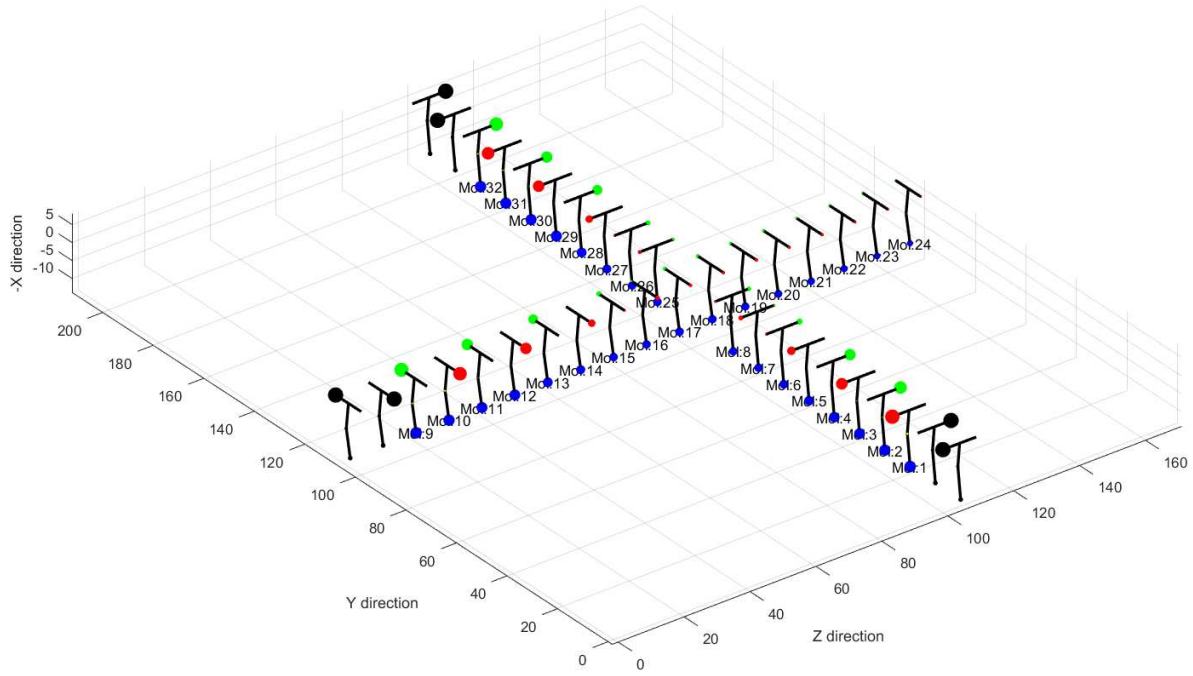
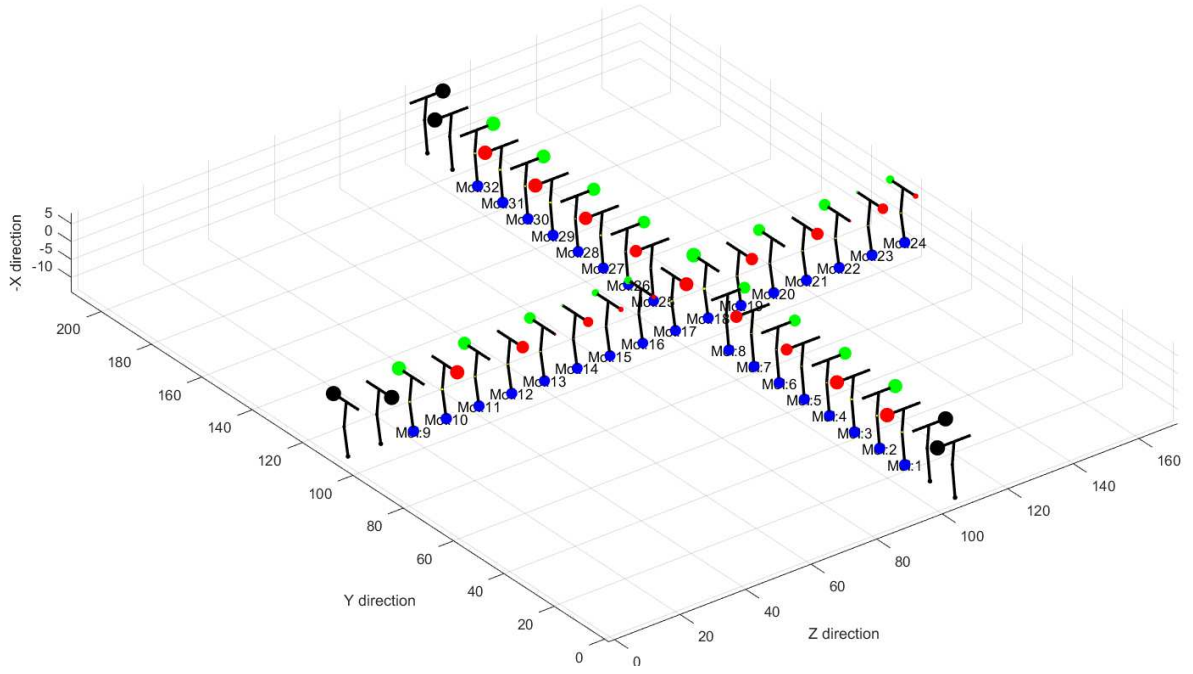


Figure 6.11: Trend of the electric field inside the trench of the majority voter with larger trench during the first phase when the inputs are switched on.

As it can be seen the electric field remains negative in the region between -5 nm and 5 nm (0 is the centre of the structure); in this region ten molecules are present but due to the fact that the value of electric field is not so high they are not completely inhibited. Decreasing the voltage value of the electrodes in the corners the value of the electric field that influences the molecules of the central cell become too small and they cannot be considered in the 'NULL' state.
In the following figures is reported the propagation in the three phases; the values of the input drivers are top=1, center=0 and bottom=1.


-X direction
5
0
-5
-10
Y direction
200
180
160
140
120
100
80
60
40
20
0
Z direction
0
20
40
60
80
100
120
140
160

(a)


-X direction
5
0
-5
-10
Y direction
200
180
160
140
120
100
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60
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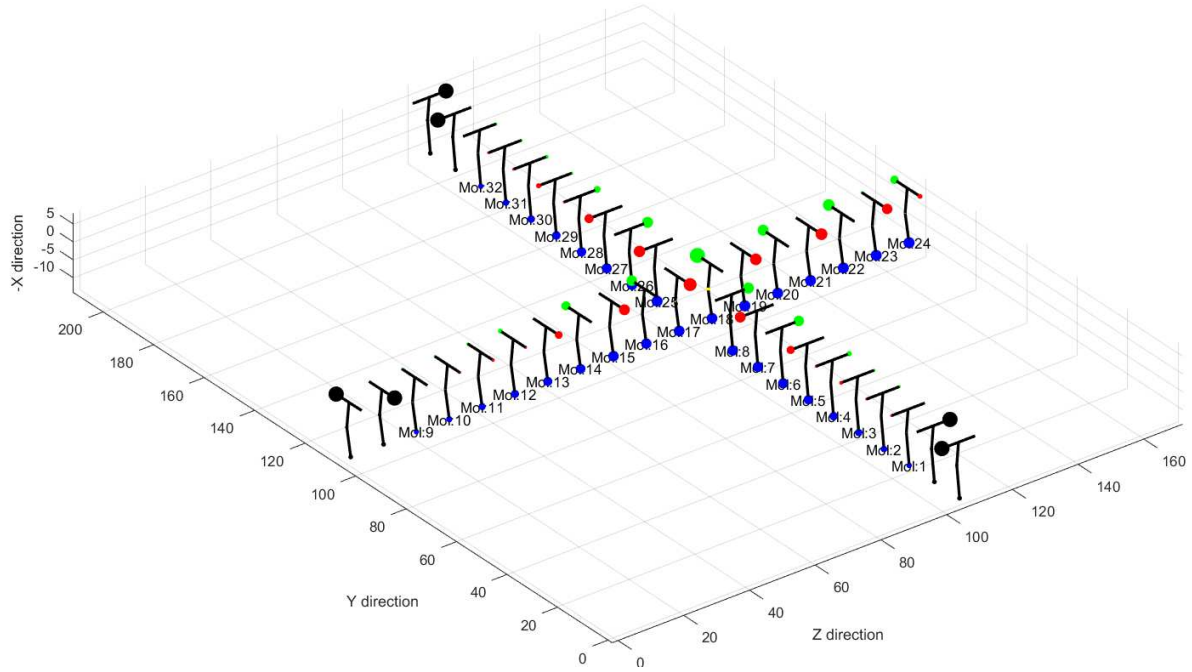
20
0
Z direction
0
20
40
60
80
100
120
140
160

(b)



(c)

Figure 6.12: Propagation in the majority voter with the larger structure; inputs logic values equal to top=1, center=0 and bottom=1 so the correct output values is equal to 1. (a) first phase, (b) second phase, (c) third phase.

In the first figure, it can be seen that not only the molecules in the centre but also the three near molecules of the inputs are completely switched off. Nevertheless, the structure is able to calculate the correct value in the centre cell and propagate it in the output during the second phase. On the contrary in the third instant of time not only the central cell remains switched on.
As before, in order to simulate a more realistic case, the propagation has been computed also in the case in which one input has a delay and reaches the centre cell in a different phase respect the others. The obtained output for all the permutation of the inputs is always correct.

6.3 Results obtained by the analysis of the T structure

6.3.1 Ideal structure

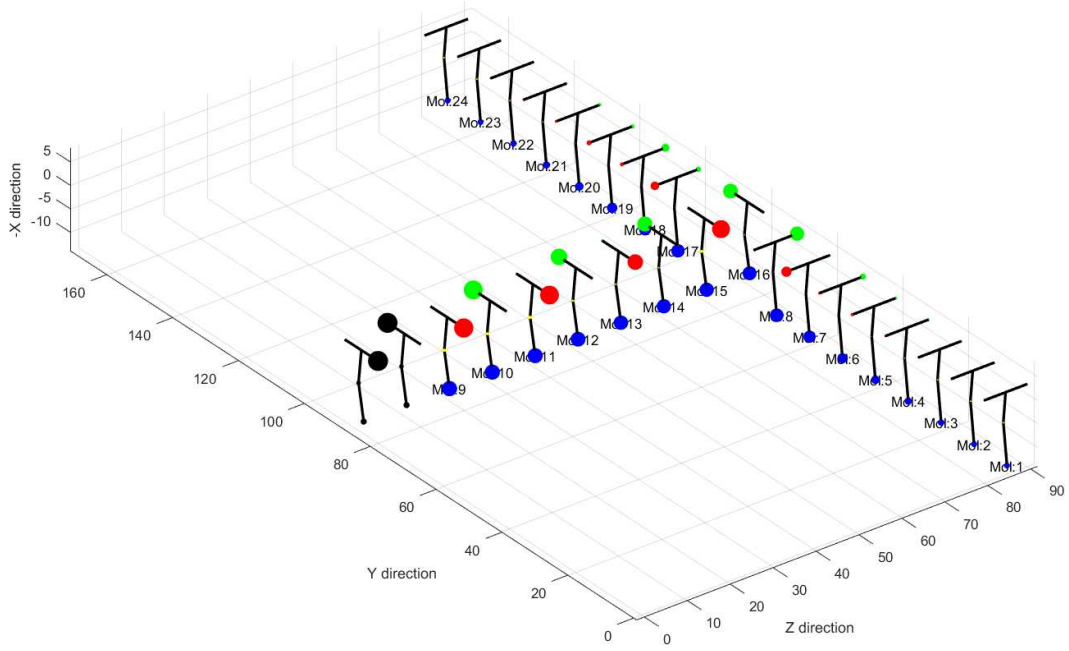
In this section, the results obtained from the study of the so-called T structure are shown. The role of this structure even if the geometry is quite similar to the majority voter is completely different. Indeed no operations have performed by the structure, simply the

information must be split into two wires; only three phases are required in this case. The voltage values that have been used are reported in the following table.

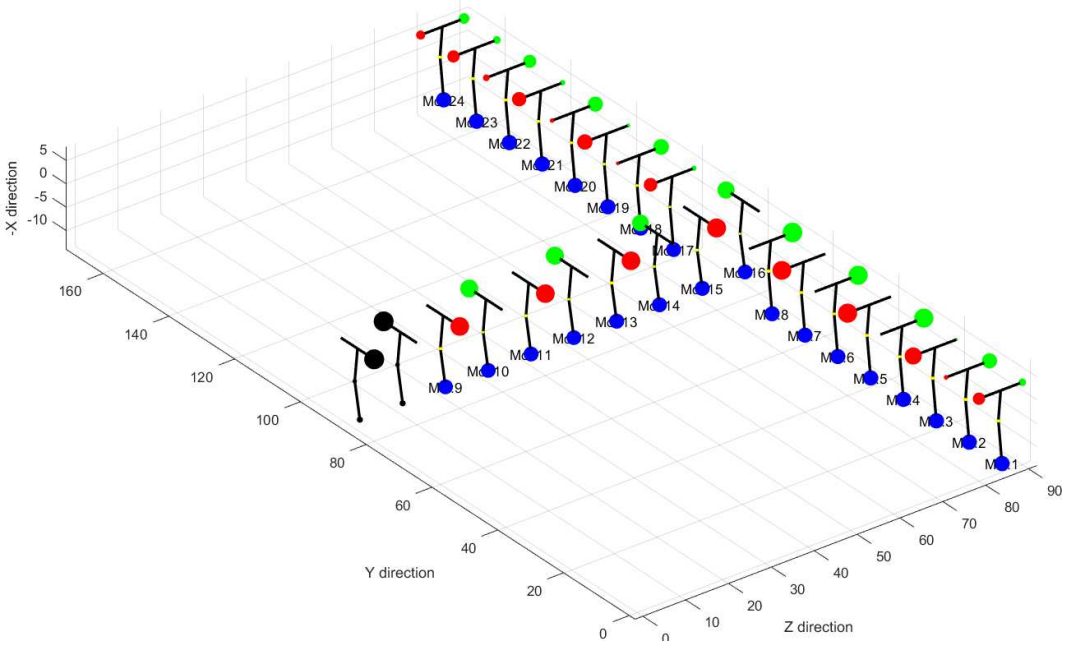
	Input	Front electrode	Outputs
Time 1	-8 V	-3.5 V	8 V
Time 2	-5 V	-5 V	-8 V
Time 3	8 V	-5 V	-8 V

Table 6.6: Voltage values used for the simulation of the T structure.

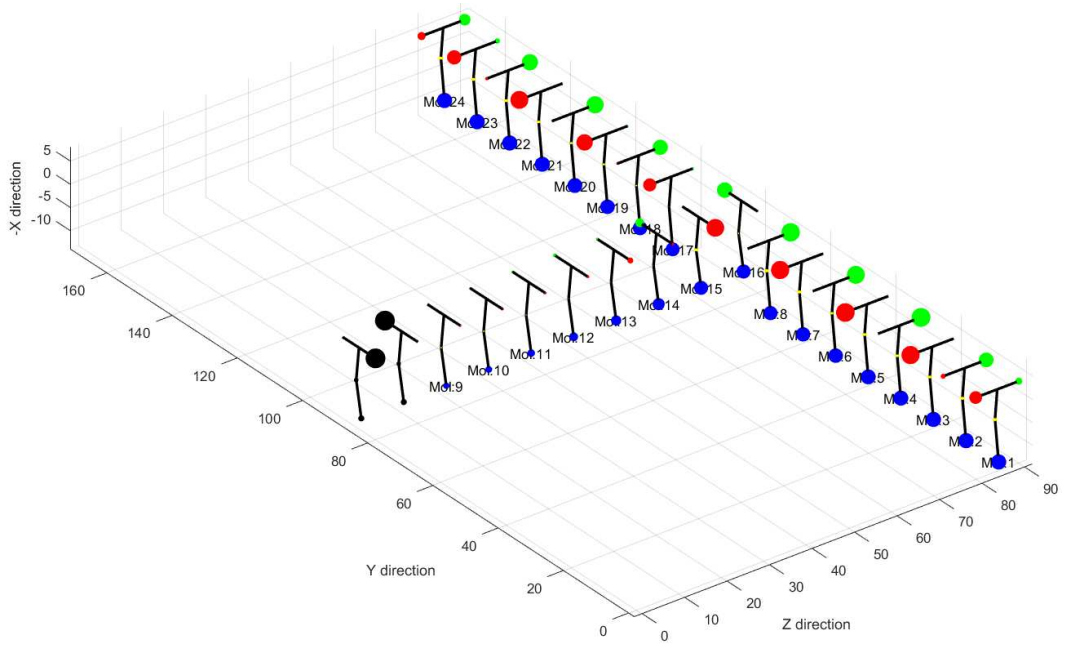
This is not the only possible solution but among all the others this maintains the logic value in the centre cell stable during all the steps without conditioning the outputs in the first phase and the input in the last one.
In the following figures is reported the propagation in the case of input equal to 0.



(a)



(b)



(c)

Figure 6.13: Propagation in the T structure with '0' as input. (a) first phase, (b) second phase, (c) third phase.

As it can be seen in the second figure the charges present in the molecules of the bottom wire is higher than that in the top one, even if the structure is perfectly symmetric and the voltage values applied to the electrodes of two wires are the same. This is due to the fact that the molecule indicated in the figure with the number 14 influences the charge distribution of the first molecule in the top wire because the distance is slightly higher of 1 nm; on the contrary, it has no effect on the first molecule in the bottom one. In figure 6.14 this phenomenon can be better observed.

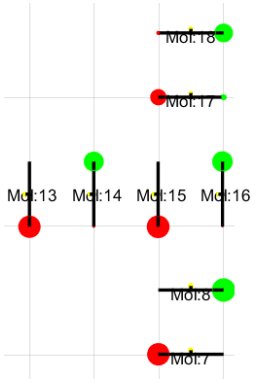


Figure 6.14: Top view of the central cell in the T structure during the second phase. The figure highlights the different behaviour of the two outputs.

The result is that the charge in the working dot of the molecule number 17 is limited by the fact that two adverse effects act on it and the resulting propagation in the wire is not perfect. Obviously changing the input value this phenomenon can be seen in the bottom wire.
The used voltage values in the second phase have been chosen in order to minimize this effect: indeed -5 V has been used in order to maintain the input switched on with a positive electric field but limiting the effect on the output.
The voltage value of the front electrode is modulated during the different phases in order to influence almost exclusively the two molecules of the central cell.

6.3.2 Larger structure

As in the case of the majority voter the ideal structure has been studied also in a larger version. The parameters that have been modified are the same of before so the minimum required resolution to realize the structure is 3 nm instead of 1 nm.
The obtained structure are reported in figures 6.15 and 6.16 (prospective and top view respectively).

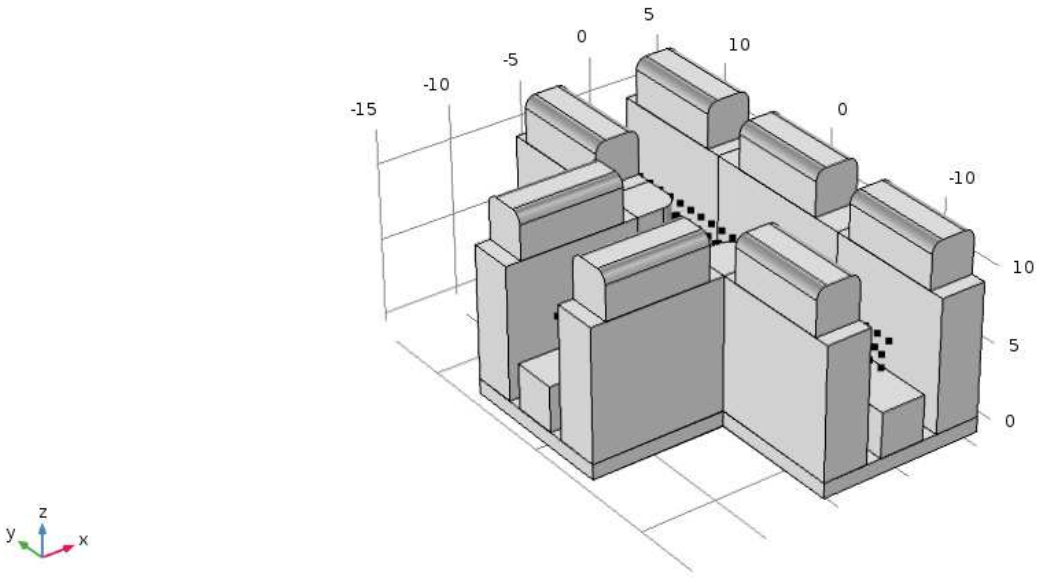


Figure 6.15: T structure with larger dimensions (prospective view).

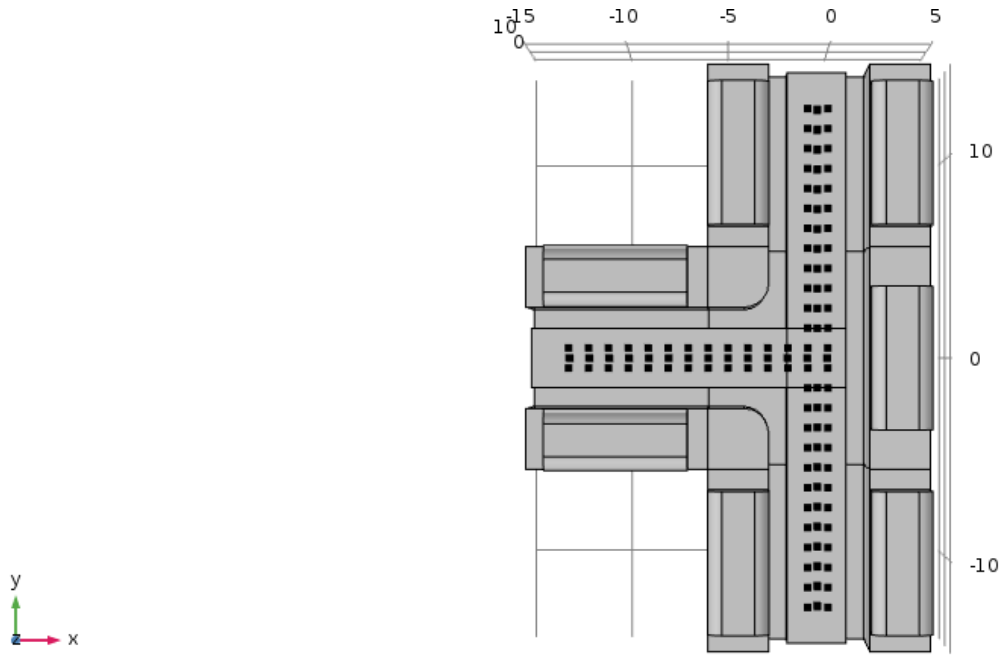


Figure 6.16: T structure with larger dimensions (top view).

The voltage values used in this case are reported in the following table.

	Inputs	Front electrode	Output
Time 1	-8 V	5 V	8 V
Time 2	-8 V	-5 V	8 V
Time 3	-5 V	-5 V	-8 V
Time 4	8 V	-4 V	-8 V

Table 6.7: Voltage values used for the simulation of the T structure with larger structure.

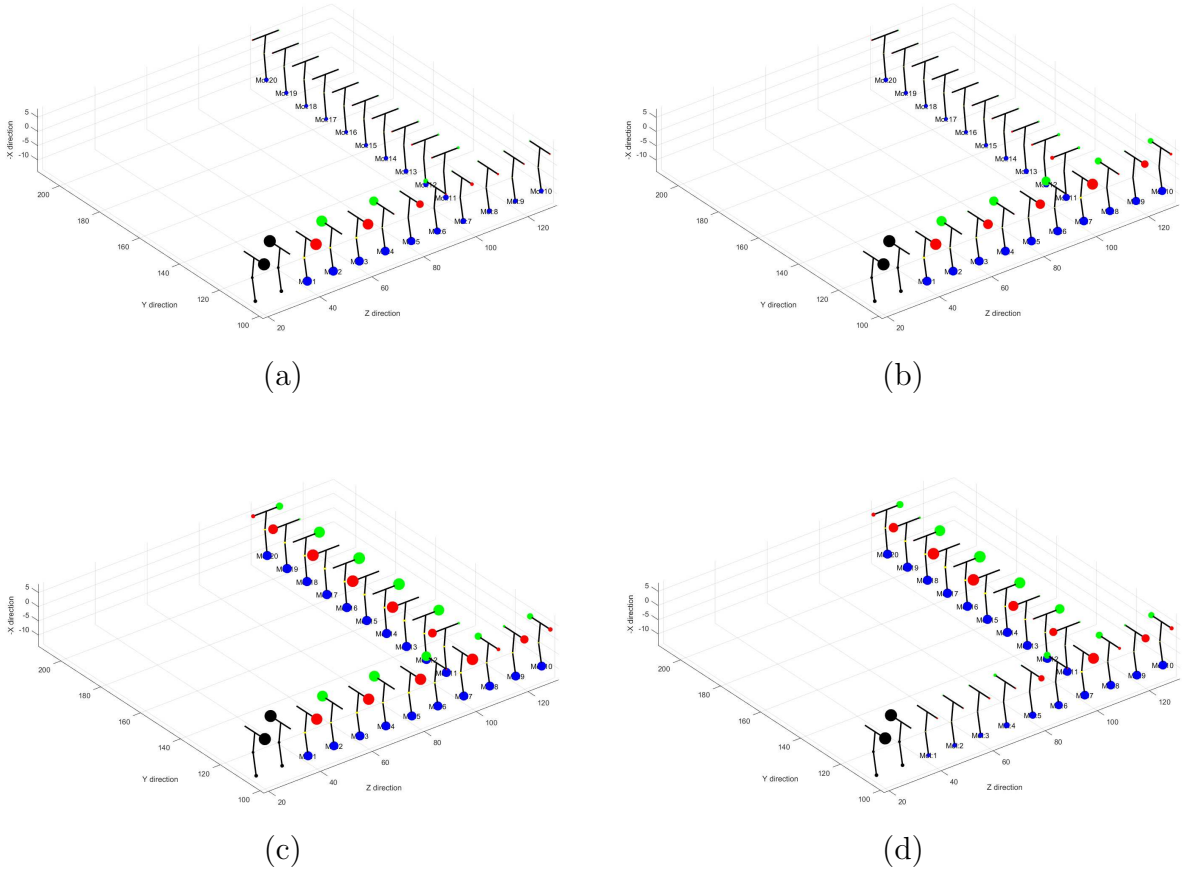
The propagation requires one more phase because a larger number of molecules is present in the structure and in this way they can be better controlled, but is very similar to the previous case so it is not reported.

6.4 Results obtained by the analysis of the angle structure

In this section, the results obtained by the analysis of the angle structure are shown, also motivating the choices made during the construction of the structure.
Four phases are used in this case in order to better control the propagation and the used values of voltage are reported in the following table.

	Inputs	Front electrode	Output
Time 1	-8 V	8 V	8 V
Time 2	-5 V	-5 V	8 V
Time 3	-5 V	-5 V	-8 V
Time 4	8 V	-5 V	-8 V

In the case of the T structure one of the two wire propagates the information better because it is not influenced by the molecule before the cell in the centre; changing the logic value in input this phenomenon can be seen on the other output wire. In this case, that only one output is present, one of the two logic values generates the same problem during the propagation while the other one is propagated perfectly.
So in order to sustain the cell in the corner one more molecular QCA cell is inserted at the end of the input wire. The two cases, with and without the additional cell, are reported in the following figures in order to put in evidence the two different behaviours.

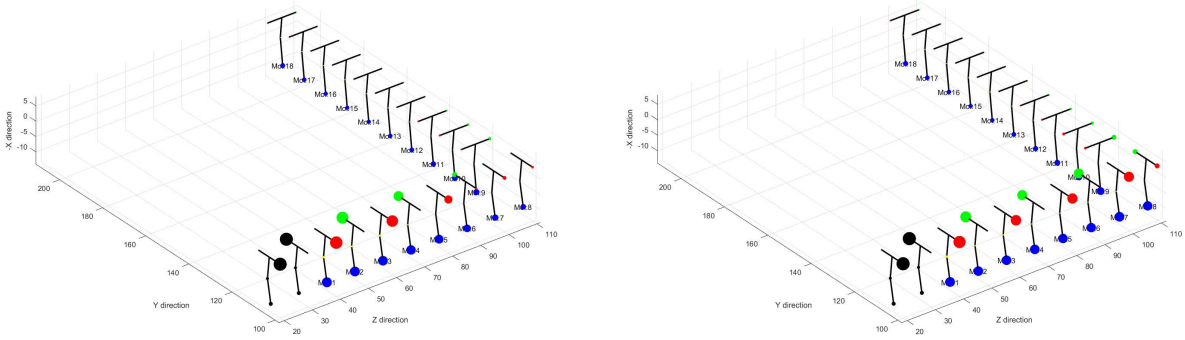


(a) (b)

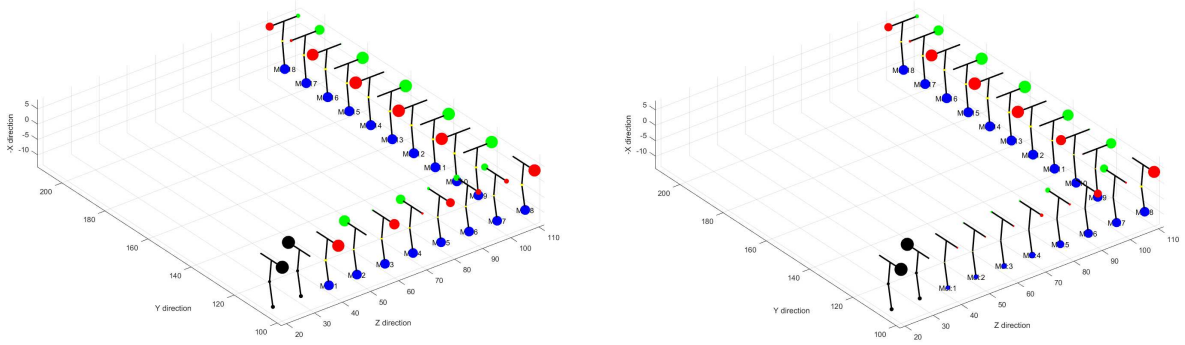
(c) (d)

Figure 6.17: Propagation of the information in the angle structure with one more molecular QCA cell at the end of the input binary wire.

In the case reported the input logic value is the one that can generate problems on the output. As it can be seen it can be generated correctly thanks to the additional cell that maintains the previous one stable.



(a) (b)



(c) (d)

Figure 6.18: Propagation of the information in the angle structure without the molecular QCA cell at the end of the input binary wire.

As it can be seen in figure 6.18(c) and 6.18(d) the output logic value is not correct; this is due to the fact that the last molecule of the input wire is influenced only by the previous one when the output is still switched off, so the charge aggregated in the working dot is not sufficiently high. The result is that in the following phase the first cell of the output generates a wrong logic value because it is not influenced by the correct molecules.

In this analysis the case in which the input information is propagated horizontally by the input, the angle is towards the left and then is vertically propagated by the output has been shown but a lot of other situations are possible; however it is foreseeable that in all of them always the same values of the electric field are generated by the electrodes so those calculated in this analysis can be reused.

Chapter 7

Simulation of a small circuit

Once that all the fundamental elements have been analysed they can be combined in order to simulate a small circuit with the real values of electric field. To do this, the *Layout* section of the Matlab algorithm has been enhanced in order to combine the elements and associate to the molecules the correct values of the electric field in the various phases. A further function called *merge* has been implemented for this scope.
This analysis validates all the previous work and demonstrates that once that all the fundamental elements have been studied complex structures can be implemented without the realization of the Comsol model which would require a long time to be realized otherwise. Indeed all the values of the electric field have already been saved and can be used during the simulation.

A circuit composed of a majority voter, a binary wire and a T structure has been created merging the three correspondent matrices in the Layout section of the algorithm. Arranging the matrices in a different order other circuits can be simulated. Obviously increasing the number of the molecules and of the phases the computational time required by the algorithm to calculate the propagation increases in consequences; in this case, with 74 molecules, the simulation took 30 minutes.
The obtained structure is reported in figure 7.1 and in order to obtain the complete propagation of the information nine phases has been used.
.

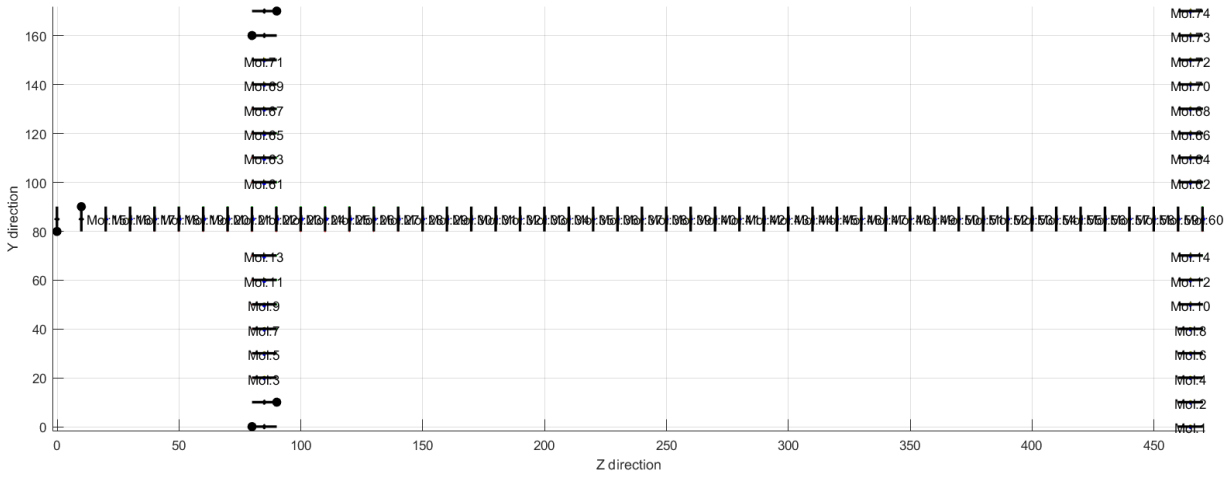


Figure 7.1: Scheme of the circuit generated with Matlab. On the left the majority voter, centre the binary wire, on the right the T structure.

The electric field values have been calculated for each component by the correspondent function applying the proper values of voltages for each phase and subsequently, they have been saved in the same folder. In this way, using the function *comsol*, when the *name_structure* "MERGE" is selected, these files can be opened and the correct values of the electric field can be associated to the correspondent molecule.
The values of voltage for each component used in this simulation are reported in the following table:

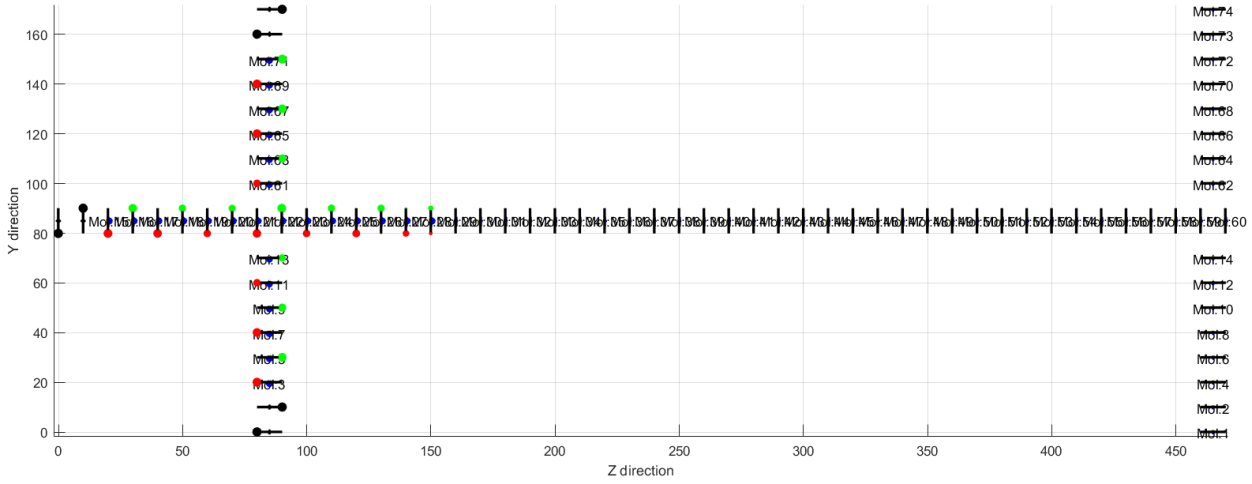
Majority voter				
	Inputs	Left corners	Right corners	Output
Time 1	-8 V	5 V	3.5 V	8 V
Time 2	-8 V	-2 V	-3.5 V	-8 V
Time 3	8 V	-2 V	-2 V	-8 V
Time 4	8 V	-2 V	-2 V	-8 V
Time 5	8 V	5 V	5 V	8 V
Time 6	8 V	5 V	5 V	8 V
Time 7	8 V	5 V	5 V	8 V
Time 8	8 V	5 V	5 V	8 V
Time 9	8 V	5 V	5 V	8 V

Binary wire			
	Clock zone 1	Clock zone 2	Clock zone 3
Time 1	8 V	8 V	8 V
Time 2	8 V	8 V	8 V
Time 3	8 V	8 V	8 V
Time 4	-8 V	8 V	8 V
Time 5	-8 V	-8 V	8 V
Time 6	8 V	-8 V	-8 V
Time 7	8 V	8 V	-8 V
Time 8	8 V	8 V	8 V
Time 9	8 V	8 V	8 V
T structure			
	Input	Front electrode	Output
Time 1	8 V	5 V	8 V
Time 2	8 V	5 V	8 V
Time 3	8 V	5 V	8 V
Time 4	8 V	5 V	8 V
Time 5	8 V	5 V	8 V
Time 6	8 V	5 V	8 V
Time 7	-8 V	-5 V	8 V
Time 8	-5 V	-5 V	-8 V
Time 9	8 V	-5 V	-8 V

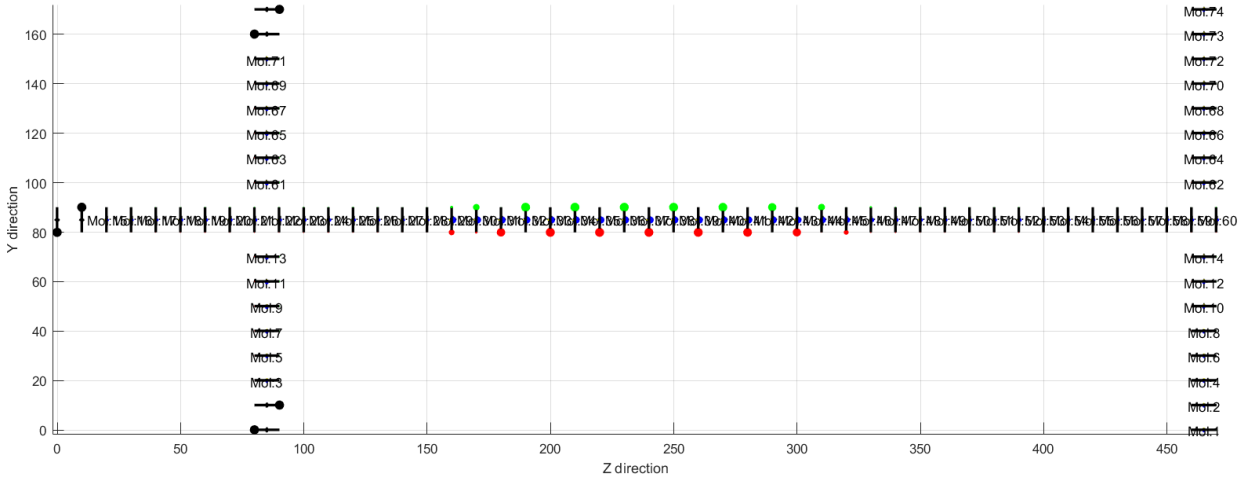
Table 7.1: Voltage values used for the simulation of the circuit divided for each component.

The voltage values for the majority voter are equal to the case in which the single component has been studied when it has to propagate the information during the first four phases; in the following phases, when the propagation occurs in the binary wire and in the T structure, it has to remain switched off and the voltage values have been chosen to obtain this condition. The same procedure has been done for the binary wire, indeed during the first and the last two phases it is completely switched off.
The general idea is to have always two adjacent clock zones switched on so each molecule remains active only for two phases.

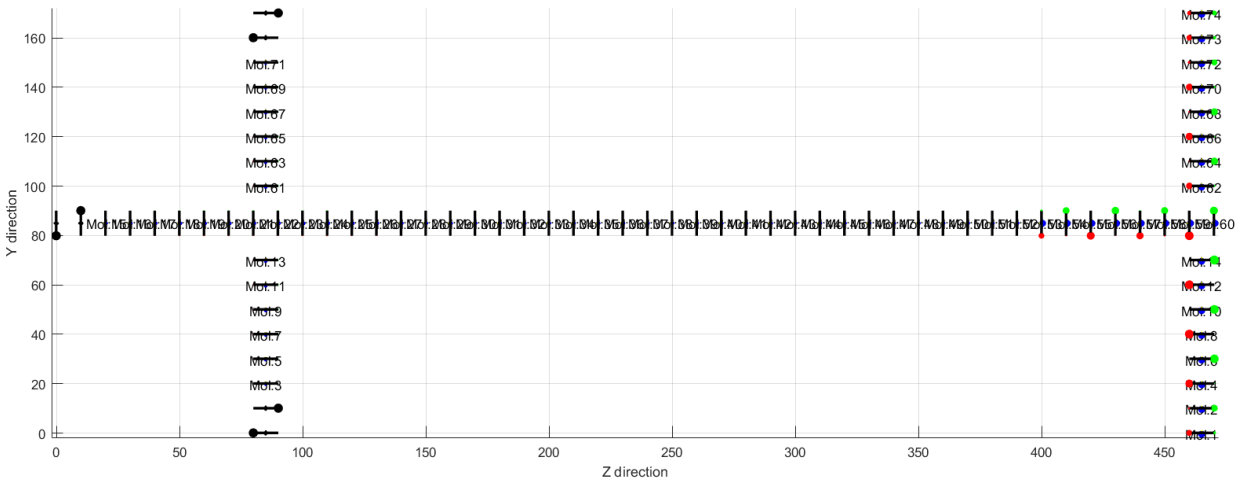
Three of the principal steps of the propagation of the information in this structure are reported in the figure 7.2. In order to provide a complete overview of the propagation, these three phases have been chosen because in each of them a different component has been switched on.



(a)



(b)



(c)

Figure 7.2: Propagation of the information in the simulated circuit. (a) second phase in which the majority voter is switched on. (b) fifth phase in which the propagation occurs in the binary wire. (c) eighth phase with the T structure switched on.

In this case, in which the aim was to highlight the correct functioning of the various elements when they are combined, once that the information has been transmitted by the first component to the second one it remains switched off and does not compute other computations until the end of the simulation. In a further analysis this aspect can be improved; indeed during the fifth phases the majority voter could be switched on again changing the input logic values of the drivers starting a new simulation.

Chapter 8

SAM simulation performed with GROMACS

In the first chapter has been introduced the concept of Self-Assembly process: it refers to the spontaneous adsorption and assembly of molecules (in this case bis-ferrocene) on a surface in a well-defined structure. The way in which the molecules are anchored to the gold nanowire is not yet clear. For this scope, an analysis using *GROMACS* (GROningen MAchine for Chemical Simulations) can be performed. It is an open-source molecular dynamics package developed in the Biophysical Chemistry department of the University of Groningen. Once that a configuration file has been created where several molecules (possibly including solvent) used by the simulation have been specified, the simulation can be run producing at the end a trajectory file, which describes the movements of the atoms over time.
More in details a complete simulation follows some precise steps:

1. Generation of the *PDB* file: these kinds of files can be downloaded by the Protein Data Bank, or can be created ad hoc using *Avogadro* when complex structures are required as in this case of the Self-Assembly monolayer.

2. Generation of a GROMACS topology file: The topology file contains all the information on the atoms present in the structure used during the simulation. For example the charge of each atom, the mass, the bonds and the angles formed between them. This kind of file can be created using functions made available by GROMACS or using the function written ad hoc for a precise force field or molecule.

3. Creation of the box: the structure must be inserted inside a box in which the molecules can move. The size and the shape of the box strongly influenced the obtained result and the computational time.

4. Solvent insertion: GROMACS has been used principally for the simulation of proteins, lipids and nucleic acids that required a solvent during the simulation. The specified solvent is inserted inside the box previously created.

5. Run the simulation: the simulation can be launched after that an MDP file has been created; it contains all the parameters of the simulation such as the steps required, the temperature, the solver and the tolerance.

6. Analysis of the results: two kinds of output files are generated, one is a trajectory file used to see how the molecules move upon time, and another one that used to make an energy analysis of the system.

In this thesis, a first approach to a simulation of this kind has been done.

8.1 Creation of the PDB file with Avogadro

As said the first step is the creation of a PDB file that contains information about the atoms in the structure. Due to the fact that this is a complex system where different kind of atoms are present this file has been created with Avogadro. In this simulation, an Au(111) slab has been created and one thiol composed of five atoms of carbon has been inserted in order to study how it reacts with the slab.
For the creation of the slab these steps have been done:

1. The structure of the crystal has been imported from the Avogadro crystal library choosing: File>Import>Crystal.

2. Due to the fact that a gold slab is required from the list elements>Au-Gold.cif has been selected. The structure reported in figure 8.1 has been created where the unit cell of the slab is present.

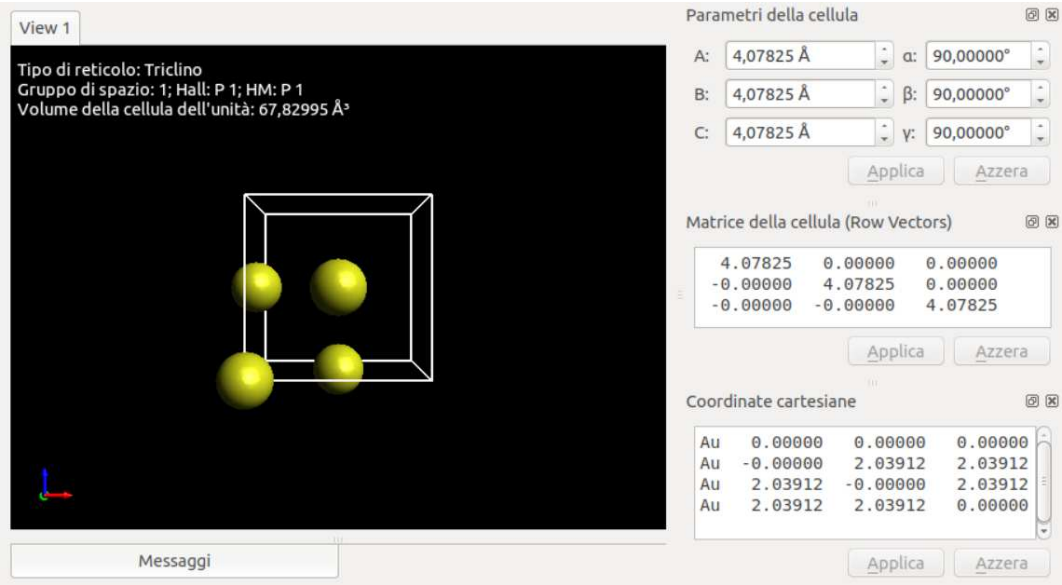


Figure 8.1: Unit cell of the Au slab created with Avogadro.

3. From the tools above the graphic window e Crystallography>Build>Slab... has been selected. A window appears on the right where the Miller indices and the dimension of the slab can be selected. For the indices, 1 1 1 has been inserted.

4. After the computation, the resulting structure is the complete slab. An example is reported in figure 8.2.

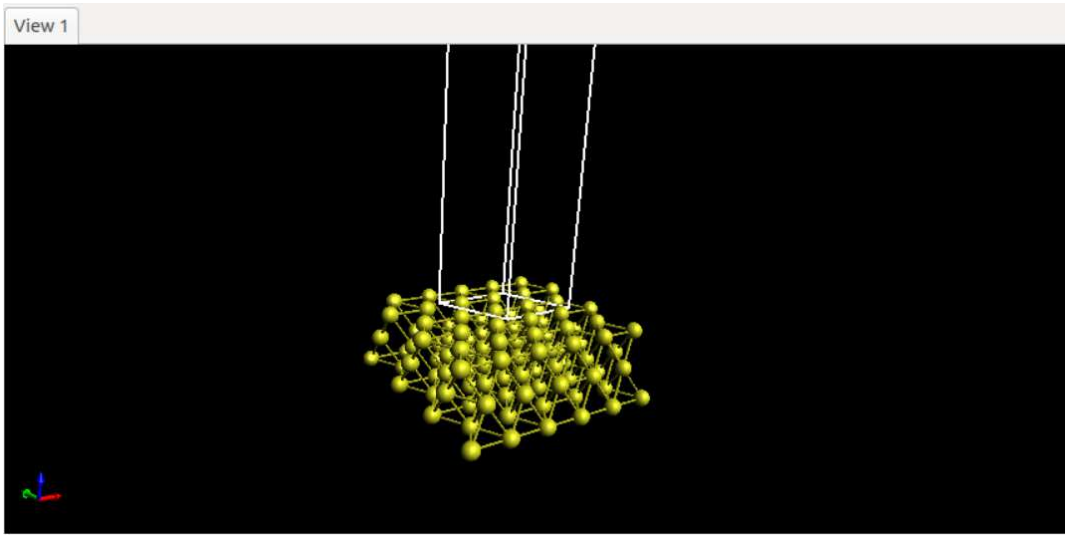


Figure 8.2: The Au(111) slab used during the simulation created with Avogadro.

The white lines put in evidence the unit cell of the structure.

After that the slab has been created the thiol can be inserted: from the toolbar, select Compile>Insert>Fragment>thiols. A list containing some of the possible thiols that can be inserted appears at this point.
Selecting from the toolbar *Cartesian editor* the position of all the atoms present in the structure can be seen; a precise atom can be moved or removed just modifying the correspondent values in this section.
Saving the file as .pdb a text file containing all the information concerning the molecules is created automatically and can be elaborated in GROMACS.

8.2 Topology file

The topology file contains information about molecule types and the number of molecules in the analysed system; it can be created using the function *gmx x2top* of GROMACS or using a function written ad hoc. In this work, a topology file generator has been used because a complex system has to be analysed. the first part of the topology file used can be seen in figure 8.3.

```
#include "oplsaa.ff/forcefield.itp"

[ moleculetype ];

PRO          1

[ atoms ]
;   nr           type      resnr residue   atom   cgnr     charge      mass      typeB    chargeB      massB
     1          opls_135      1     PRO      AU      1      0.000    196.96657
     2          opls_135      1     PRO      AU      1      0.000    196.96657
     3          opls_135      1     PRO      AU      1      0.000    196.96657
     4          opls_135      1     PRO      AU      1      0.000    196.96657
     5          opls_135      1     PRO      AU      1      0.000    196.96657
     6          opls_135      1     PRO      AU      1      0.000    196.96657
     7          opls_135      1     PRO      AU      1      0.000    196.96657
     8          opls_135      1     PRO      AU      1      0.000    196.96657
     9          opls_135      1     PRO      AU      1      0.000    196.96657
    10          opls_135      1     PRO      AU      1      0.000    196.96657
    11          opls_135      1     PRO      AU      1      0.000    196.96657
    12          opls_135      1     PRO      AU      1      0.000    196.96657
    13          opls_135      1     PRO      AU      1      0.000    196.96657
    14          opls_135      1     PRO      AU      1      0.000    196.96657
    15          opls_135      1     PRO      AU      1      0.000    196.96657
    16          opls_135      1     PRO      AU      1      0.000    196.96657
    17          opls_135      1     PRO      AU      1      0.000    196.96657
    18          opls_135      1     PRO      AU      1      0.000    196.96657
    19          opls_135      1     PRO      AU      1      0.000    196.96657
```

Figure 8.3: First part of the topology file generated with GROMACS where the parameters of the atoms are specified.

As it can be seen some parameters must be specified such as the force field, the kind of residue, the name, the charge and the mass of the atoms.

8.3 MDP file

This kind of file contains all the information regarding what kind of simulation the user wants to perform. In particular, due to the fact that the idea is to obtain the trajectory of the thiols upon time two important parameters must be specified:*nsteps* that is the number of steps used in the simulation and *dt* that is the time interval between two of them.
Others parameters specify the options for the generation of the output files, the temperature, the pressure and the electrostatic setting.

8.4 Trajectory file

After that the simulation is complete a trajectory file (.trr) is created; using this file same physical aspects can be analysed such as the radial distribution function that describes how density varies as a function of distance from a reference point and the root mean square fluctuations that capture, for each atom, the fluctuation about its average position. The

result of the analysis can be seen using *Grace ("GRaphing, Advanced Computation and Exploration of data")* that is one of the most prominent 2D plotting tool for Linux.

Chapter 9

Conclusion and future perspectives

In this thesis, a study made with Matlab and Comsol of the clocking system of four fundamental components realized with molecular QCA has been proposed. In particular, for the first time, they have been studied using the real values of the electric field generated by the electrodes, instead of using ideal values; a possible physical implementation of these structures has been also proposed, finding the maximum sizes that continue to guarantee the correct behaviour.
This allows to understand the correct placements of the electrodes and which voltage values must be applied in order to obtain the correct propagation in the different structures. The fact that at the end of the work, the simulation of a small circuit using the same methodology gives good results validates the analysis made on the single fundamental components, and this can be considered a first step for the simulation of complex circuits in real conditions.
One of the principal aspects is that the Layout section of the Matlab algorithm has been enhanced in order to create an initial section where the user, modifying just a list of variables, can performed all the possible simulations that have been shown; indeed the calculation, saving and elaboration procedure of the electric field values is completely automatized and do not require any intervention of the user.
Furthermore, due to the fact that the calculated values are saved in text files, they can be calculated just the first time and reused during the subsequent simulations where the only difference could be the input logic values.

Several are the possible future perspectives. First of all the layout part of the Matlab algorithm can be further enhanced in order to facilitate the creation of bigger and more complex circuit because the merging procedure of the different matrices is not convenient when a lot of components must be combined. Also the Main section can be enhanced in terms of computational time that is too high when the number of molecules and phases increases.
An important aspect is that the calculation of the electric field values is made by the functions generated with Comsol that exploit its libraries; a possible improvement could be the creation of a Matlab function that, knowing the position of the molecules and those of the electrodes, is able to calculate the electric field replacing the function generated with Comsol.

Finally, a further step in the analysis of the clock system is to replace the concept of clock zone in which different signals control different electrodes: the new idea is to have one sinusoidal signal that is propagated on a single electrode. The propagation, especially in a binary wire, can be better controlled in terms of frequency because it will depend on the frequency of the applied signal.

The molecular QCA technology offers a lot of advantages but several are the critical aspects. First of all the physical realization of electrodes that required a minimum resolution of at least 3 nm and trenches with sufficiently high values of aspect ratio required to obtain a vertically oriented electric field inside them.
Secondly, the molecules are anchored on the gold substrate with a self-assembly process so it has to be well prepared in order to ensure the correct position and orientation. In this thesis, the position of the molecules has been considered ideal so they are all at the same distance and oriented in the optimal direction. A more thorough analysis of the self-assembly process with GROMACS could provide a better comprehension of this phenomenon.

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