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Effect of a Clock System on Bis-ferrocene Molecular QCA

R. Wang, A. Pulimeno, M. Ruo Roch, G. Turvani, G. Piccinini and M. Graziano

***Abstract*—Molecular Quantum-dot Cellular Automata (mQCA) is found to be the most promising among all emerging technologies. It is expected to show remarkable operating frequencies (THz), high device densities, non-cryogenic working temperature and reduced power consumption. The computation relies on a new paradigm based on the interaction between nearby molecular QCA cells. This computation requires the aid of an external signal normally referred to as *clock* that enables/inhibits the molecular activity. The influence of clock on realistic molecules has never been deeply studied. In this paper, we performed a thorough analysis of the clock signal added to the molecular QCA cell based on an ad-hoc synthesized bis-ferrocene molecule.**

Ab-initio simulations and further post-processing of data have been used for characterizing the performance of bis-ferrocene molecule under the influence of a clock signal. Quantitative results on the molecule in terms of newly defined figures of merits, i.e., *aggregated charge*, *equivalent voltage* and *Vin-Vout trans-characteristic* have been shown. Meanwhile we demonstrate when and how much the presence of clock signal enhances or hinders the interactions between QCA molecules. These unprecedented data give a fundamental improvement to the knowledge on how information can be propagated through QCA devices. The results suggest directions to chemists, technologists and engineers on how to proceed in the next steps for this promising technology.

***Index Terms*—Quantum-dot Cellular Automata (QCA), molecular QCA (mQCA), ab-initio simulations, equivalent voltage, trans-characteristic.**

I. INTRODUCTION

QCA theory was first introduced as a new concept for digital computing in the early 90's [1]. According to this new paradigm a new device could be implemented by a cell with 6 dots containing two free charges, which is the simplest version of the theory proposed, as shown in Figure 1(B). The Coulomb interaction among free charges provides the digital communication between nearby QCA cells. The local field interaction determines the information transfer without involving charge transportation. The associated power consumption is then expected to be dramatically reduced [2].

Regarding the physical implementations envisaged for QCA technology, few proposed QCA devices involve metallic dots [3], nanomagnets [4] and molecules [5]. Here we focused on the molecular QCA which is considered the most promising for its high speed, high device density and low power dissipation. In particular, we analyzed a bis-ferrocene molecule (Figure 2(A)), a real molecule artificially synthesized for this purpose [6][7]. The interaction among free charges between the bis-ferrocene molecules provides the switching of logic states or digital communication through molecular QCA devices. An example of molecular wire has been depicted in Figure 1(C).

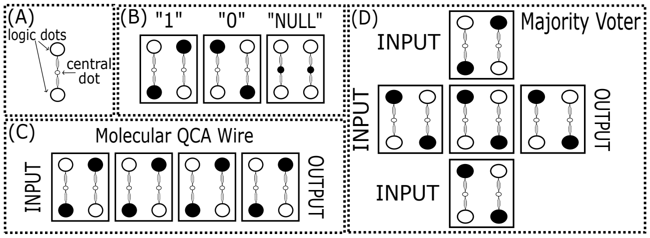

Fig. 1. QCA cells and basic logic blocks. (A) Logic dots and central dots in QCA; (B) Six dots QCA cell: two free charges, filled with black circles, are localized along one of the two diagonals, encoding the logic state 0 or 1; when charges are forced by an external signal into central dots of the cell, the *NULL* state is encoded. (C) A QCA wire: each cell along the line arranges its state according to its neighboring cell; when an external input forces a logic state on the first left cell as INPUT, the binary information propagates along the whole wire until reaching to the very right cell (as OUTPUT) in a domino-like style. (D) A majority voter: the output logic state depends on the state of the majority of three input cells. Moreover, another fundamental logic gate for QCA technology, the inverter has also been illustrated in [5].

According to a complete analysis of the quantum phenomena and thermodynamics mechanisms involved in a QCA circuits [1], a maximum number of consecutive QCA cells is allowed in a wire to warrant the proper QCA computation. This number increases with the decreasing size of the cell or with the lowering temperature. Moreover, the abrupt switching of the QCA cell state could lead to metastability problem along the circuits [8]. Hence a different mode of switching, called *Adiabatic Switching*, which is the quantum version of the adiabatic theorem, was proposed [8][9][10] to overcome these possible limits. It consists of three main steps: (i) lowering the inter-dot potential barriers in order to remove the old state of the QCA cell; (ii) applying a new input to the cell; then (iii) raising again the barriers in order to lock the cell in the new state.

From a technological point of view, the adiabatic switching could be implemented by means of a multi-phase clock system [9]. This implies the application of an external signal (*clock*) to help the logic state transition of the cells during each step of adiabatic switching. At the same time, clock signal is also necessary for guaranteeing the information propagation along

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QCA circuits. Authors in [11] exploited a clock signal to favor the electrostatic potential localization on one of the redox centers of ideal molecules for QCA technology encoding logic states 0 and 1. But no further analysis have been carried out on the feasibility and the application of a clock system to molecular QCA devices, especially based on real molecules.

In this paper, our aim is to demonstrate the effectiveness of the clock signal for QCA logic states encoding and information propagation through devices focusing on a specific QCA molecule candidate, known as the bis-ferrocene [7], as a case study. The analysis flow started with ab-initio simulations of molecules [12]. Particularly, both half (single bis-ferrocene molecule) and complete QCA cell (two molecules aligned together) have been analyzed in presence of externally applied clock signal. The obtained results gave us the possibility to evaluate and quantify three key aspects: (i) We established the possibility to rearrange the charges inside the molecule. By applying a clock system, the capability of molecular QCA to encode a logic state was enhanced; (ii) We evaluated how much the interaction between molecular QCA cells could be controlled by the clock signal, favoring or hindering the information propagation through the QCA devices; (iii) We figured out the interaction between two nearby molecules, which were considered as a complete QCA cell or a part of QCA wire, by means of trans-characteristic functions under the influence of clock signal.

It is worth underlining that from a methodology point of view, we intended to work as much as possible near to the physical level in order to better understand the behavior of the device as much precisely as possible. This has the aim of compensating the immaturity of this technology from an experimental point of view. Hence we performed ab-initio simulations [12] and successive post-processing of the obtained data [13] to model these molecules as electronic devices.

II. BACKGROUND

A. Generic QCA working principle

The QCA paradigm allows the devices to be built by a cell with 6 dots containing two free charges inside. Depending on the positions of the free charges, three different states are possibly encoded (Figure 1(B)): when the two free charges stand along one of the two diagonals of the cell, the logic state 0 or 1 is encoded; if those two free charges are forced to occupy two central dots in the cell, such configuration of charge does not represent a real logic, but it is essential for realizing adiabatic switching issue, thus it is called *NULL* state [8]. Electrostatic repulsion is responsible for the interactions among QCA cells. In this way simple logic gates could be made by means of a specific layout of those QCA cells [14]. The basic QCA logic gates are wires, majority voters and inverters [5] as shown in Figure 1(C) and (D). Starting from these building blocks, many complex digital systems can be designed, like arithmetic circuits or even microprocessors [15][16].

B. Molecular QCA

In order to physically implement QCA devices many solutions have been proposed and, among all, the most performing one is based on molecular system [5][7][11][17][18]. Since the suitable molecules have nanometer sizes, room temperature operations of molecular QCA circuits are allowed; meanwhile the device density of the chip increases and its theoretical frequencies are estimated to be up to THz [5].

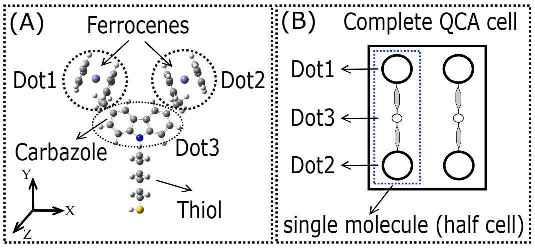


Fig. 2. (A) Bis-ferrocene molecule structure: two ferrocenes are linked together by means of a carbazole central group. An alkyl-chain provides the binding of the bis-ferrocene to the ending thiol (-SH) group. (B) Top view of a complete QCA cell in which single molecule acts as half of QCA cell.

Concerning the candidate molecule for realizing QCA device the authors in [7] synthesized a new molecule, named bis-ferrocene, ad-hoc for this purpose. The structure of bis-ferrocene is reported in Figure 2(A): it is constituted by two ferrocene units that represent two active (or logic) dots responsible for logic state encoding ($Dot1$ and $Dot2$); a central carbazole group acts as central dot ($Dot3$) used for *NULL* state. Moreover the carbazole group is terminated with an alkyl-chain to which a sulfur atom (a thiol, -SH) is attached. This end-group is responsible for binding bis-ferrocene to a gold substrate in terms of Self-Assembled-Monolayer (SAM) formation. Since the bis-ferrocene molecule has only three dots, it is considered as half QCA cell. A complete QCA cell is implemented aligning two molecules near each other with distance d obtaining a square cell with four ferrocenes localized at the corners, as sketched in Figure 2(B) [19]. In general, a molecule is always *neutral*, but its *oxidized* (or *reduced*) form can be obtained rendering a positive (or negative) free mobile charge to bis-ferrocene, resulting in a positive (or negative) net charge inside the molecule. Regarding the presence of the counterion of the molecule, a solid description is discussed by the authors of [20]. In this work neutral, oxidized and reduced forms of bis-ferrocene molecule have been taken into account for discussing clock effect. Moreover, we examined the clock effects in terms of enhancing or hindering the communication between two nearby molecules, as part of a QCA wire [21][22][23].

C. Clock system

For the purpose of accomplishing adiabatic switching, the clock system for a molecular QCA circuit could be made applying an external signal to emulate the multi-phase clock system [9]. The multi-phase clock system implies the partition of circuit in different clock zones and inside each clock zone, several molecules are located. Figure 3(A) depicts a multi-phase clock system for bis-ferrocene molecular QCA wire inherited by [24]. In particular, in presence of different clock signal values for each specific clock zone the free charge inside the molecules could be either forced to stand in central

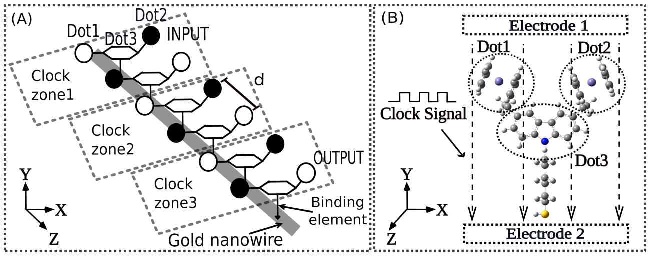


Fig. 3. (A) Bis-ferrocene molecules are aligned over a gold nanowire through the binding elements, meanwhile different clock zones are applied along the molecular wire; (B) In principle, clock signal can be realized adding an external electric signal to the tip of a scanning tunneling microscope (STM). These are principle sketches, depending on exact implementation technology there should be several molecules in each clock zone [11].

$Dot3$ keeping the molecule in *NULL* state, or released to the two active dots ($Dot1$ and $Dot2$) making the molecule ready to switch. In the case of molecular QCA wire, as seen in Figure 3(A), once the input signal (IN) is ready, the clock signal in $zone1$ allows the molecules in $zone1$ to arrange their logic states according to input signal. Meanwhile the clock signal in $zone2$ freezes the molecules in that zone in *NULL* state preventing them from the influence of molecules in $zone1$. When all molecules in $zone1$ stabilize their logic states, the clock signal then allows them to hold their states and to become new input signal for molecules in $zone2$. Thus, alternating clock zones along the molecular QCA wire or other QCA circuits ensures the proper information propagation as well as correct QCA computation.

In reality, for bis-ferrocene molecule the clock signal could be an electric field applied along the vertical Y-axis of the molecule. This Y-axis is perpendicular to the X-Z plane of the nanowire on which all the bis-ferrocene molecules are deposited (Figure 3(A)). This electric field might have different signs and intensities, according to the clock zone condition. In Figure 3(B) a principle possible scheme for the application of the clock signal to a bis-ferrocene molecule is illustrated: two metal electrodes generate a uniform electric field along the vertical axis of the molecule (Y-axis). The multi-phase clock signal could be done varying in time the values and sign of voltage applied to the electrodes. Specifically, here the clock system applied in simulations is an electric field, whose sign and intensity is analyzed to set-up the proper working conditions. In case more complex circuits should be designed, still the molecules would be placed on plane X-Z and connected to properly patterned nanowires.

It is worth underlying that in this work we analyze the behavior of a single bis-ferrocene molecule in presence of the clock signal, and such work has not been done before. In following work we will focus on the behavior of nearby bis-ferrocene molecules under the influence of the clock signal in the same clock phase.

III. METHODOLOGY

In this work, we focused on the evaluation of all the relevant parameters responsible for the performance of molecular QCA devices in presence of a clock signal. Furthermore, since our aim was to model the QCA molecules as electronic devices, we defined new figures of merits that allowed us to describe the state encoding of molecule as well as the interaction between nearby molecules [23]. To accomplish this, our analysis was then divided into two parts: (i) Ab-initio simulations were carried out on single bis-ferrocene molecule in presence of bias conditions, e.g. point charge driver and clock, to evaluate the charge distribution inside molecule. This is described in Section III.A. (ii) Electrostatic equations and models were established defining new figures of merits to compute the influence of a bis-ferrocene molecule to the other molecule located nearby, which is presented in Section III.B and Section III.C. On the basis of these acquired results it was possible to appraise the molecular interaction and to estimate the clock signal effect on the information propagation inside QCA cell.

A. Ab-initio simulations

For the purpose of exploring electronic structures and properties of molecular QCA technology, we performed computations and evaluations that were based on ab-initio simulations in *Gaussian 09* [12]. These simulations concentrate mainly on the laws of quantum mechanics and a set of physical constants. The analysis is extremely accurate but computationally intensive [23]. A quantum chemistry method called *UB3LYP* and a basis set named *LANL2DZ* have been chosen for the simulations since they are suitable for large molecular systems based on metal ions. In particular, as is known that HF calculations neglect electron correlation while DFT treats both exchange and correlation energies, albeit approximately. Therefore it is common to use the hybrid approach between these two, popular *UB3LYP* scheme is one such solution. Meanwhile, some biasing conditions were also allowed to be externally employed during the simulations.

First of all, the single bis-ferrocene molecule (neutral, oxidized or reduced) was simulated in presence of a clock signal. The clock signal was added introducing a uniform electric field with a vertical direction with respect to molecular axis (Y-axis), as depicted in Figure 3(B). The outputs of these simulations were charge distributions of molecule for specific working conditions with clock: given the atomic charges computed using the Merz-Singh-Kollman (MK) approximation scheme [25], it was possible to calculate the charge of each dot of bis-ferrocene molecule, defined as *aggregated charge* [18][23], simply summing all atomic charges that constituted that part of the molecule. The aggregated charge represents the charge distribution inside a molecule, meanwhile it is still a readable quantity for a possible read-out system. So the three states of the QCA molecule are possibly defined: when the charge localizes mainly on one of two active dots ($Dot1$ and $Dot2$) the molecule encodes the logic 0 or 1; if the charge is localized on central $Dot3$, the molecule is in the *NULL* state.

Depending on the sign and value of the electric field, the clock signal is able to force the charge of bis-ferrocene molecule to localize on two active dots or central $Dot3$. In the first case the presence of clock could enhance the total amount of charge available on the two active dots, thus increasing the charge difference between them while encoding different logic states. This makes those two logic states more easily recognizable by a read-out system and even more effective in molecule-molecule interaction. In the latter case, forcing molecules in *NULL* state allows to erase previous logic states or to hinder the communication between nearby molecules.

With respect to molecule-molecule interaction, the methodology discussed here implied the ab-initio simulations of a complete QCA cell as molecular system, as sketched in Figure 4(A). It contains an ideal *Driver* represented by a system of point charges located at the distance d from the Molecule-Under-Test (*MUT*) emulating the interaction between two nearby molecules. The point charges representing the driver correspond to aggregated charges ($D1$ and $D2$) of two active dots. Their values are set in such a way to simulate logic states 0 and 1, therefore localizing the entire charge in one of the two active dots of molecule. The values of charges on the driver depend on the form of the MUT. Therefore the sum of charges on the driver was $+1q$ ($-1q$) for representing an oxidized (reduced) bis-ferrocene molecule. However, regarding neutral form of molecule, the total charge on driver should be zero, e.g. $+1.0q$ and $-1.0q$ distributed on driver $D1$ and $D2$, respectively. Due to the low performance of neutral molecule, shown later in Section IV, we concentrated only on oxidized and reduced forms of bis-ferrocene molecule for molecule-molecule interaction analysis. In addition, the charge configuration of the driver, i.e., values of aggregated charges on two active dots were set in different conditions. These conditions are specified in the following. The starting point was the equilibrium state, in which two active dots had the same amount of charge, namely both dots had ideally $+0.5q$ ($-0.5q$) for the case of oxidized (reduced) form of the molecule. Starting from equilibrium state, charges on driver were gradually unbalanced until those charges were entirely localized on one of the two dots. In other words, in case of oxidized (reduced) form of molecule, the aggregated charge $D1$ of the driver was equal to $+1q$ ($-1q$) encoding logic state 1, oppositely logic state 0 implied the unit aggregated charge distributed only on $D2$ of the driver. This unbalance was obtained with a step of $0.1q$ changing between driver aggregated charges $D1$ and $D2$. Moreover, clock signal was also applied to improve or prohibit molecule-molecule interaction. Eventually each driver configuration together with applied clock represented a biasing condition for our analysis of molecules. In this way the MUT re-arranged its charge distribution $Q1$ and $Q2$, as sketched in Figure 4(A), according to both the point charge driver and clock signal.

B. Electrostatic analysis

Given the aggregated charges of bis-ferrocene molecule (e.g. MUT) under different bias conditions, we were able to compute the electric field generated by the charge distribution of the bis-ferrocene molecule at any specific point of the surrounding space through electrostatic equations implemented in Octave [13]. In particular, considering a generic charge q_i placed at the generic position (x_i, y_i, z_i) the generated electric field can be obtained computing the force acting on a test charge placed at the position (x, y, z). Thus, if a system of N point charges are given, the total force ($\overrightarrow{F_{tot}}$) acting on the test charge and then the total electric field $E_{tot}(x, y, z)$ can be calculated by Eq (1) and Eq (2). Meanwhile the three components E_x, E_y and E_z of $E_{tot}(x, y, z)$ are given by Eq (3), where c indicates one of the x, y or z axis.

$$\overrightarrow{F_{tot}} = \sum_{i=1}^{N} \frac{1}{4\pi\epsilon_0} \frac{q_i \cdot q_t}{r_i^2} \cdot \widehat{r} \tag{1}$$

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

$$E_c(x, y, z) = \sum_{i=1}^{N} E_{c,i}(x, y, z) \tag{3}$$

C. Trans-characteristic of QCA cell $V_{OUT}(V_{IN})$

As long as the electric field generated by MUT in a specific biasing condition was obtained, it continuously affected the molecule next to it, namely the *Receiver* shown in Figure 4(B). This impact urged the receiver to configure its charge distribution and was evaluated computing a new quantity defined as Equivalent-Output-Voltage (V_{OUT}). To be specific, as displayed in Figure 4(B), the electric field generated by test molecule (MUT) under the influence of a driver configuration ($D1$ and $D2$) is measured at the position where the receiver is located. According to QCA principle, there should be no charge transfer between nearby molecules, e.g. MUT and receiver, so only the electric field component parallel to the active dots axis of bis-ferrocene molecule have the influence of moving its internal charge from one active dot to the other. Hence such electric field component generated by the MUT is responsible for receiver to switch. In the case of bis-ferrocene molecule, those two active dots stand on the X-axis as sketched in Figure 2(A), therefore the corresponded V_{OUT}, shown in Figure 4(B), is computed integrating E_x along the width of the molecule. By the same logic, it is likewise possible to calculate the Equivalent-Input-Voltage (V_{IN}) integrating the proper electric field component E_x generated by driver at the position where the MUT is located, as depicted in Figure 4(A). Furthermore, with different driver configurations applied, we can obtain different input/output voltages.

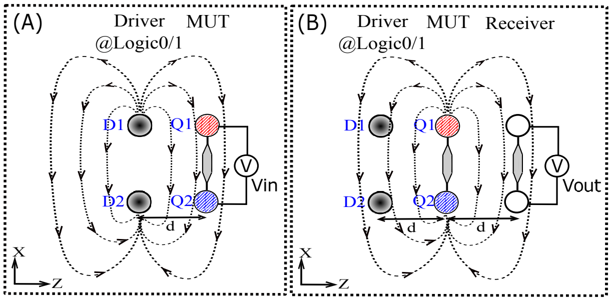


Fig. 4. Interaction between QCA molecules: (A) emulation of a driver molecule with a point charge system $D1$ and $D2$, and V_{in} computed at the Molecule-Under-Test (MUT); (B) V_{OUT} calculated at the receiver.

Thus, correlating all these output voltages V_{OUT} to input voltages V_{IN} defines the trans-characteristic of the molecular

QCA cell. This relationship between voltages enlightens the behavior of a complete QCA cell (Driver and MUT) and allows us to evaluate the capability of the bis-ferrocene molecule to forward the charges carried by the driver to the final receiver, like information propagated through a QCA wire. Additionally, with respect to the aim of this work, the trans-characteristic of the QCA cell is plotted in presence of various clock signals to thoroughly comprehend the enhancement or hindrance of the clock on such information propagation. It is noteworthy that in literature [2] the cell-cell response is normally used to characterize the interaction between two cells, however the trans-characteristic is here adopted in order to correlate the cell-cell response to quantities that can be physically measured when engineering the system, as output voltage resulting from an applied input voltage.

IV. RESULTS

In this section, the results based on ab-initio simulations and electrostatic analysis are recorded to demonstrate the behavior of molecular QCA device in presence of a clock signal. As is mentioned in Section III, the results presented here refer to: (i) analysis of single bis-ferrocene molecule when its neutral, oxidized and reduced forms are all taken into consideration; (ii) complete QCA cell which contains ideal driver and MUT, but similar analysis is focused only on the oxidized and reduced forms of molecule because of not satisfying performance of the neutral case. Additionally, the trans-characteristics of QCA cell are provided as is described in Section III in presence of the clock signal.

A. Single bis-ferrocene molecule

Following the foregoing methodological description, the first part of our result analysis centers on the influences of clock signal on a single bis-ferrocene molecule. Ab-initio simulations have been performed where the clock signal was emulated by uniform electric field with different signs and values. The resulting aggregated charges of bis-ferrocene molecule in such conditions are then computed and discussed in the following.

1) Neutral form of molecule: The trend of aggregated charges as function of the applied clock signal for neutral bis-ferrocene is shown in Figure 5(A). At equilibrium state, when the clock signal is $0V/nm$, the aggregated charges of bis-ferrocene molecule are almost zero for all its dots. Furthermore the charge configuration of the molecule remains almost steady with a wide range of clock signal values, because from $-5V/nm$ to $+5V/nm$ there are no significant variations on dot charges. Consequently, the molecule is considered in an undefined state. The application of a negative clock signal with a value smaller than $-5V/nm$ generates a displacement of charge inside bis-ferrocene molecule, therefore the two active dots become negatively charged, while the charge on central $Dot3$ becomes positive in order to maintain the neutrality of molecule. Oppositely, when a positive clock signal larger than $+5V/nm$ is applied, it leads to a dual configuration in which those two active dots both have a positive charge, almost equal, and the central $Dot3$ becomes negatively charged.

As displayed in the figure, exceeding the clock range from $-5V/nm$ to $+5V/nm$, when the clock value increases the charge begins to move internally. For a given clock signal value, the aggregated charges on two active dots could both reach to $+0.5q$ or $-0.5q$, depending on the sign of the clock, which are exactly the same charges of two active dots on an oxidized or reduced molecule at equilibrium state. In other words, it is possible to determine a minimum value of the clock signal to lead a neutral bis-ferrocene molecule into an electrically induced oxidized or reduced form of molecule, while still keeping the neutrality of the molecule. Such results are summarized in Table I(A): a clock signal equal to $+10V/nm$ leads the neutral molecule into an oxidized like configuration, i.e., behaving like a chemical oxidized molecule, while the reduced like configuration is obtained with a negative clock signal of $-10V/nm$. In both cases, the neutrality of bis-ferrocene molecule is preserved by the central $Dot3$ with a charge of $-1.03q$ and $+1.01q$, respectively.

TABLE I
CHARGE DISTRIBUTION [Q] OF THE BIS-FERROCENE MOLECULE IN PRESENCE OF CLOCK SIGNALS.

Clock signal	Dot1	Dot2	Dot3
(A) Neutral bis-ferrocene molecule			
Equilibrium (CK= 0 V/nm)	-0.002	-0.003	0.005
CK= +10 V/nm	0.52	0.51	-1.03
CK= -10 V/nm	-0.52	-0.49	1.01
(B) Oxidized bis-ferrocene molecule			
Equilibrium (CK= 0 V/nm)	0.37	0.35	0.28
CK= +2 V/nm	0.49	0.47	0.04
CK= -2 V/nm	0.04	0.04	0.92
(C) Reduced bis-ferrocene molecule			
Equilibrium (CK= 0 V/nm)	-0.20	-0.20	-0.60
CK= +2 V/nm	-0.06	-0.06	-0.88
CK= -2 V/nm	-0.45	-0.45	-0.10

2) Oxidized form of molecule: The charge distributions of oxidized molecule under the effect of various clock signal values are sketched in Figure 5(B). With the clock signal equal to $0V/nm$, the positive net charge of oxidized molecule distributes all around the molecule. Instead, the application of a positive clock signal on oxidized molecule has the effect of favoring a positive charge localization mainly on its two active dots ready to be switched. In particular, for clock signal values in the range from $+1V/nm$ to $+5V/nm$, the positive net charge of the molecule is almost equally located on the two active dots and there is barely no charge left on the central $Dot3$. Increasing the value of the clock signal over $+5V/nm$, the charges on the active dots increase and the charge on central $Dot3$ becomes more negative. On the contrary, a negative clock signal forces the positive net charge to localize on central $Dot3$, encoding thus the *NULL* state. Analysis concerning the stability and robustness of the bis-ferrocene molecule can be found in [7].

As is shown in Table I(B) we selected optimum values of the clock signal to improve charge distribution of oxidized bis-ferrocene molecule or lead it into *NULL* state. Specifically, the optimal charge distribution for a further logic state encoding is obtained with clock signal equal to $+2V/nm$, as a consequence the positive net charge is equally distributed on two active dots leaving almost zero charge on the central $Dot3$ $(+0.04q)$ ensuring proper logic switching between nearby molecules. However, with clock signal greater than $+2V/nm$, similar charge distribution can be achieved as well (Figure 5(B)), but it requires higher power consumption. If the clock signal keeps increasing, for example, if it becomes larger than $+5V/nm$, the amount of positive charge on two logic dots is even larger, but such huge available charge on the logic dots is unnecessary for logic switching. Furthermore, a negative clock field of $-2V/nm$ forces almost all the positive charge on the central $Dot3$ $(+0.92q)$ leaving the two active dots almost empty. These results illustrate the effectiveness of clock signal on a single oxidized bis-ferrocene molecule. Concerning the selected values of clock signal, they are equal in absolute values but with opposite sign thus facilitates the physical realization of a clock system in a real QCA circuit for adiabatic switching, like the one proposed in Figure 3(B).

3) Reduced form of molecule: The analysis performed on reduced bis-ferrocene molecule reveals a dual molecular behavior with respect to oxidized case, as sketched in Figure 5(C). Similarly, when the clock signal is not applied $(0V/nm)$, the negative net charge localizes around the whole molecule. But if a negative clock signal in the range from $-5V/nm$ to $-1V/nm$ is applied, the negative net charge is then mainly distributed on two active dots and almost no charge left on the central $Dot3$. A further increase of negative clock value (lower than $-5V/nm$) increases the negative charge on both $Dot1$ and $Dot2$, meanwhile leaving the central $Dot3$ becoming positive so as to keep the total amount of unit negative charge. On the contrary, a positive clock signal compels the molecule in the *NULL* state, since the two active dots are almost empty and the negative net charge is mainly on the central $Dot3$.

The optimal values for the clock signal in reduced molecule case are summarized in Table I(C): the best charge distribution for a further logic state switching can be obtained with a clock signal of $-2V/nm$. The clock signal value required to realize the *NULL* state of reduced molecule is $+2V/nm$. It means that the optimal clock signals of the reduced case for adiabatic switching have also the same value but opposite signs.

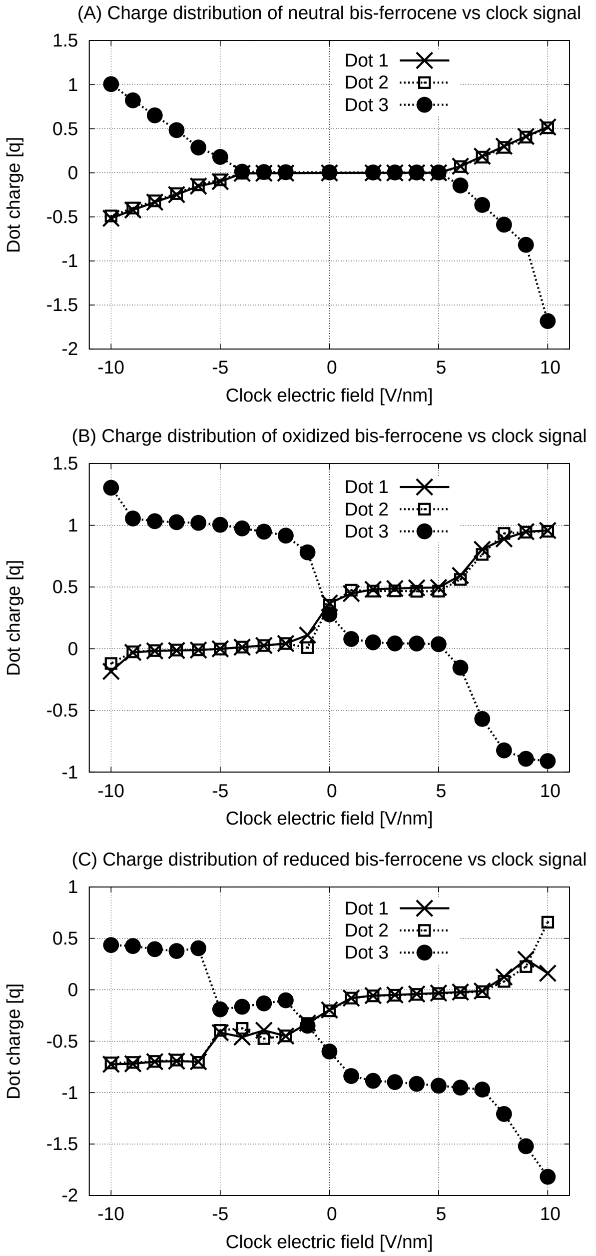


Fig. 5. Charge distributed on bis-ferrocene molecule as function of applied clock signal values, both three forms of molecule are present: (A) Neutral; (B) Oxidized; (C) Reduced.

B. Interaction within a complete QCA cell

For the sake of completely appraising the effects of clock signal during molecule-molecule interactions, ab-initio simulations concerning two bis-ferrocene molecules aligned together (complete QCA cell) with a distance d of $1.0nm$ have been carried out. As shown in Figure 4(A), these two aligning molecules are the driver and the MUT. The driver was emulated by a system of point charges with specific values to encode the logic state 0 or 1. The values of point charges depend on the exact form of the molecule under evaluation, and neutral, oxidized and reduced case were all considered. Regarding the application of clock signal, its values were chosen according to the results reported in Table I.

For neutral bis-ferrocene molecule the results of interaction between driver and MUT are reported in Table II(A): without clock $(0V/nm)$, both driver configurations of logic 0 and 1 induce a variation of charge on the MUT, but the charge difference between $Dot1$ and $Dot2$ of the MUT is so weak that the MUT state encoding is hard to be recognized by read-out system. When the clock, either positive or negative, is applied, the driver induces an unbalance of charge between two active dots of the MUT. In particular, the charge localization of the MUT is opposite with respect to the driver in terms of charge quantity on each active dot, ergo the MUT encodes a logic state opposite to the one of the driver because of Coulomb repulsion. However, although clock is present, such charge difference between two active dots of the MUT is still not large enough. This would make the read-out difficult or

TABLE II

CHARGE DISTRIBUTION [Q] OF THE BIS-FERROCENE MOLECULE IN PRESENCE OF THE DRIVER AND DIFFERENT CLOCK SIGNALS.

(A) Neutral molecule	Driver @ 1 D1=+1q, D2=-1q			Driver @ 0 D1=-1q, D2=+1q		
Clock	Dot1	Dot2	Dot3	Dot1	Dot2	Dot3
0 V/nm	0.006	0.022	-0.028	0.019	0.012	-0.031
+10 V/nm	0.45	0.60	-1.05	0.63	0.40	-1.03
-10 V/nm	-0.68	-0.32	1.00	-0.34	-0.65	0.99
(B) Oxidized molecule	Driver @ 1 D1=+1q, D2=0q			Driver @ 0 D1=0q, D2=+1q		
Clock	Dot1	Dot2	Dot3	Dot1	Dot2	Dot3
0 V/nm	0.03	0.71	0.26	0.70	0.03	0.27
+2 V/nm	0.19	0.74	0.07	0.76	0.17	0.07
-2 V/nm	0.02	0.03	0.95	0.03	0.02	0.95
(C) Reduced molecule	Driver @ 1 D1=-1q, D2=0q			Driver @ 0 D1=0q, D2=-1q		
Clock	Dot1	Dot2	Dot3	Dot1	Dot2	Dot3
0 V/nm	-0.04	-0.32	-0.64	-0.31	-0.04	-0.65
+2 V/nm	-0.04	-0.05	-0.91	-0.05	-0.04	-0.91
-2 V/nm	-0.16	-0.69	-0.15	-0.69	-0.16	-0.15

even make the interaction with successive molecule very weak causing an interrupt of the information propagation. These results confirm the poor effectiveness of neutral bis-ferrocene for QCA computation, as is demonstrated in [26].

In case of oxidized bis-ferrocene molecule, the effects of the driver on MUT with clock signal applied are reported in Table II(B). Without clock ($0V/nm$) the molecule is naturally induced by the driver configuration to encode an opposite logic state, since now the net positive charge is mainly localized on one of the two active dots. The charge difference between two active dots is so evident that the two logic states encoded by MUT are well identified. This is true also for a positive clock ($+2V/nm$) applied, nevertheless the dot charge values are very close to that without clock applied. This implies that this optimum clock signal value does not improve much the logic state encoding of oxidized molecule. Considering the application of negative clock signal ($-2V/nm$), the results in terms of driver-molecule interaction are very fascinating: the MUT is not influenced by the driver for both the logic states, since the positive net charge is mainly confined on the central $Dot3$. This indicates that the clock signal can be used to prohibit the communication between QCA devices, in the meantime it also confirms the feasibility of adiabatic switching in molecular circuits made by bis-ferrocene molecules.

Finally, the results of reduced bis-ferrocene molecule are recorded in Table II(C). Without clock applied, the MUT reacts to the driver with a small charge localization on one of the two active dots depending on driver logic state, while keeping the rest huge amount of charge in the central $Dot3$. The application of a negative clock ($-2V/nm$) enhances the charge difference between $Dot1$ and $Dot2$ moving the negative charge from the carbazole to the ferrocenes. Therefore, the negative net charge is mainly localized on one of the two active dots and the MUT can encode properly the logic states. Oppositely, a positive clock ($+2V/nm$) forces the MUT in *NULL* state and inhibits its interaction with the driver. As a matter of fact, the active dot charges are almost zero and all negative net charge is trapped on central $Dot3$, even if the driver is present next to it. These results verify again the effectiveness of clock signal for adiabatic switching and information propagation along QCA devices.

C. Trans-characteristic of QCA cell

As is described in Section III, the last part of our analysis is the definition of trans-characteristic for QCA cell. The aim is to assess the behavior of complete QCA cell and the capability of bis-ferrocene to propagate information on driver to successive molecules. The results reported here are for the oxidized and reduced forms of the molecule.

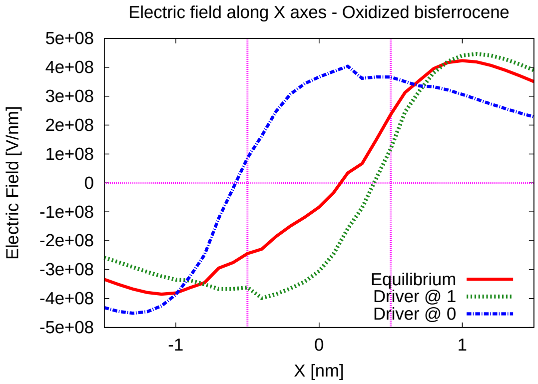
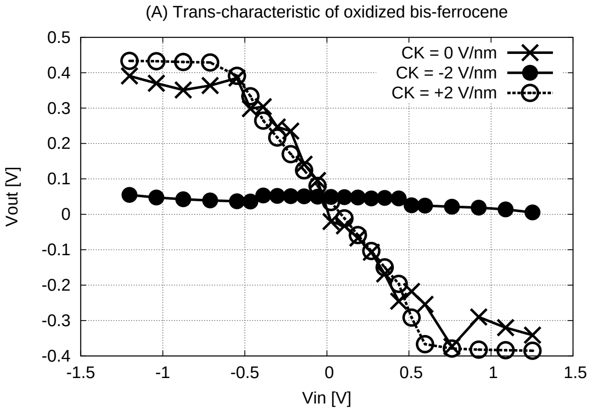


Fig. 6. Electric field at the ideal receiver for different bias conditions of oxidized bis-ferrocene.

We calculated the electric fields generated by the MUT in different driver configurations and in presence of clock. Then only the electric field component parallel to the active dot axis (E_x) was considered. After we evaluated it at the position where another molecule is located, known as the receiver next to MUT, as shown in Figure 4(B). Thus effects of the MUT on the receiver were identified in terms of the output voltage (V_{OUT}). For sake of brevity, we reported in Figure 6 only the results for an oxidized bis-ferrocene molecule at the equilibrium state and in presence of driver with both logic states. At the equilibrium condition the electric field generated at the receiver location shows a negative and a positive peak. Two vertical dashed lines in the figure indicate the spatial edge of the receiver. It makes sense to observe the electric field only between these two lines. Thus integrating the electric field along the width of the receiver gives us an almost zero output voltage, since the positive area is compensated by the negative one. When the driver is in logic 0, the electric field generated by the molecule is almost positive along the receiver width, accordingly the equivalent output voltage is positive. By the same logic, when the driver is at logic 1 the output voltage of the molecule will be negative.

As is mentioned in Section III, by computing firstly the equivalent input voltage V_{IN} generated by the driver configuration and then the output voltage V_{OUT} caused by MUT at the position of a receiver, it is possible to define the trans-characteristic of QCA cell in presence of clock signal.

Figure 7(A) displays the trans-characteristic of oxidized bis-ferrocene molecular QCA cell as function of the applied clock signals. In case of no applied clock or a positive clock signal ($0V/nm$ or $+2V/nm$, respectively) the curves are almost overlapped, confirming that this positive clock does not alter molecular switching. They also show an inverted behavior which indicates that the two molecules in a complete QCA cell have opposite logic states. From the figure, it can be observed that the trans-characteristic has a wide linearity range, i.e., from $-0.5V$ to $0.5V$, where the charge on MUT localizes gradually in one of its two active dots, and two saturated regions, i.e., $V_{IN} < -0.5V$ and $V_{IN} > +0.5V$, which correspond to a complete localization of the positive net charge on only one active dot. In case of a negative clock ($-2V/nm$) applied, the trans-characteristic is almost flat and the voltage values are nearly zero meaning that the communication is hindered by the clock.


(A) Trans-characteristic of oxidized bis-ferrocene

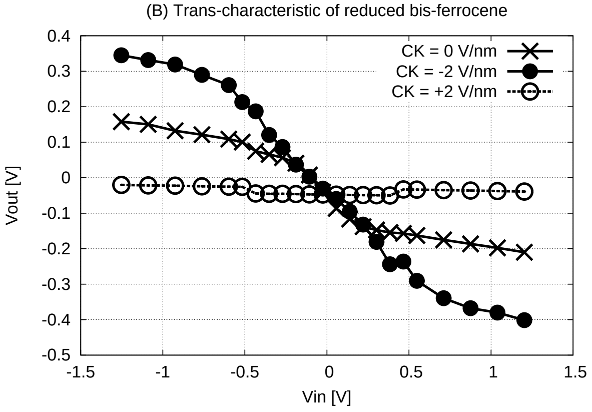

(B) Trans-characteristic of reduced bis-ferrocene

Fig. 7. Trans-characteristic of oxidized (A) and reduced (B) molecular QCA cell at equilibrium and in presence with clock signals.

The trans-characteristic of reduced case is sketched in Figure 7(B). With respect to oxidized case, when the clock signal is equal to $0V/nm$ or $-2V/nm$, the trends of the trans-characteristics are almost identical. Both of them have a central linear region and two saturated ones. However, the negative clock has the effect of improving V_{OUT} computed at the position of receiver and, as a consequence the molecular interaction between MUT and receiver is enhanced. In case of a positive clock ($+2V/nm$) applied, the trans-characteristic is almost flat with zero output voltage values, ensuring the effectiveness of the positive clock to prohibit the information propagation through QCA cell.

V. CONCLUSION

This paper focused on demonstrating the effectiveness of clock signal applied on the bis-ferrocene molecules as QCA device. It has been illustrated that the bis-ferrocene molecule is a good candidate for realizing circuits based on QCA technology. We characterized the performance of QCA devices in presence of a clock signal by means of ab-initio simulations and defining new figures of merits.

Both the results concerning single molecule and complete QCA cell have been analyzed thoroughly. Moreover, we evaluated the trans-characteristic of complete QCA cell in presence of different clock signals. The results are fundamental and extremely convincing, as they are profoundly essential to comprehend the effectiveness of clock signal in terms of either enhancing or hindering the interactions between nearby QCA cells. In addition, these quantitative results eventually give hints on how to control the information propagation through QCA devices and show the implementation of multiple clock zones making adiabatic switching in QCA circuits possible.

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