Propagation of a binary signal along a chain of triangular graphane nanoclusters

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Abstract

In this paper, we study the dynamic properties of a linear array of graphane triangular molecules that transmit a binary signal. The electronic properties of nanoclusters are studied using calculations based on first principles, with hybrid potentials. The dynamic of the system is studied by solving the time-dependent Schrodinger equation. Our results show that a linear array of these nanostructures under clock operations, allow to transmit binary information, with a efficiency close to unity.

Introduction

Currently, many research groups are conducting theoretical and experimental studies, in order to find materials for the new generation of computers. In this context, graphene is a simple bidimensional structure of carbon atoms. In 2004 the group of Kostya Novoselov [1] succeeded in isolating a simple layer of graphene using a technique by mechanical exfoliation of graphite. This work represented the beginning of many theoretical and experimental studies and their potential applications to systems derived from graphene [2 – 3]. A theoretical investigation in 2007 [4] predicted a new form of graphene totally saturated with hydrogen. The authors of this paper give the name "graphane" to this new form derived from the graphene. The shape of this new structure is similar to graphene, with the carbon atoms in a hexagonal lattice and alternately hydrogenated on each side of the lattice. In January 2009, the same group that isolated graphene in 2004 published a paper in Science magazine reporting the hydrogenation of graphene and the possible synthesis of graphane [5]. Since then there has been growing scientific interest in the study of hybrid graphene-graphane systems and their potential applications. Furthermore, has been attempted using cellular automata to develop classical computational processes with quantum entities. Important advances have been made with automata based on quantum dot arrays (QCA), the idea for which was proposed by C. Lent and collaborators [6]. The original idea was introduced as a system of quantum corrals with four quantum dots inside it and doped with two electrons. The electrons can tunnel through the quantum dots, but cannot get out of the corrals that form the cells of the automata. This architecture can propagate and process binary information with adequate control protocols [7]. The first experimental demonstration of the implementation of a QCA was published in 1997 [8]. A subsequent work also demonstrated an experimental method for the implementation of a logic gate [9], and a shift register was also reported [10]. These results provide good agreement between theoretical predictions and experimental outcomes at low temperatures. Implementation at room temperature requires working at the molecular level, and in the context of molecular cellular automata; there are also important contributions at the experimental level [11]. In the molecular case, the quantum dots correspond to oxide reduction centers, and as in the case of metallic quantum dots or semiconductors are operated with electrical polarization. The implementation of this cellular automata architecture is achieved with complex molecules, supported in a

chemically inert substrate. The implementation is achieved in an extremely small chain of molecules [11]. Another implementation at room temperature corresponds to an array of magnetic quantum dots that can propagate magnetic excitations to process digital information [12]. These systems use the magnetic dipolar interaction among particles whose size is at the submicrometer scale. A theoretical study was published about the behavior of cellular automata composed of an array of polycyclic aromatic molecules [13], using the polarization of electronic spin. In this work it is established that by increasing molecules in one of the directions of the plane, forming graphene nanoribbons, binary information can be transmitted at room temperature. In another work, we investigate the properties of a molecular array of graphane [14]. This study established that graphane nanoclusters, with two quantum dots, are eligible to transmit binary information. In this paper we investigate the dynamic behavior of a linear array of triangular graphane molecules, under clock operations to propagate binary information.

Triangular Graphane Molecules

We can consider a cell in the automaton that contains three quantum dots to provide an additional state. In this way, each cell would have the polarization state P = +1, if the hole (or electron) is found in one of the two active quantum dots, P = -1, if it is found in the other active dot and P = 0 if it is found in the null point [12]. This idea of a clocked cell has been studied with the theoretical model of the Aviram molecule [17]. This model poses the possibility of activating and deactivating each cell by using an electrical field. It is important to consider this type of cell in our structures, given that an appropriate line of clocked cells forms a shift register, a key component in QCA circuitry. A continuously varying clocking wave can move bits of information smoothly along the line. Power gain is essential for practical operations of systems that process information. A result of the dissipative effects, a part of the signal sent from one sector to another of a circuit is lost. In conventional electronics, the energy of the signal is reinforced with energy provided by the power source. In QCA technology devices, this energy is supplied by the clock. In this way, if the energy supplied to a particular cell falls below the operational threshold, the clock supplies additional energy so that the signal flows with a gain greater than one [18]. It has been theoretically and experimentally verified that this effect is automatic as a consequence

of the interactions among the systems. Power gains greater than 3 have been measured [19]. In this investigation we will study the properties and dynamic behavior of cells with three quantum dots to estimate power gain.

The dynamic properties of molecular array depend on the electronic properties of individual cells. The molecules studied in this work are triangular molecules of graphane (Figure 1), similar to triangular nanoclusters of graphene, saturated with hydrogen atoms, except at the corners (quantum dots). In those corners there are two unpaired electrons in each quantum dot and in the case of the molecular double cation (Figure 1b), there is an unpaired electron that can be located in a quantum dot or in the others. Our results obtained using methods based on First-principles calculations, shows that molecular double cation has a state of minimum energy with the electron located in one of the quantum dots (or superposition states in small molecules) and it has an excited state when the electron is positioned in any of the other quantum dots. In all our calculations the structure is relaxed by means of the method "Quasi-Newton Approach" [15] and we adopt Slater type orbitals and triple zeta polarized basis (TZP) wiht hybrids method B3LYP*, by using the ADF software [16]. In the previous work [14], we has established the best hybrid method, (First-principles calculation), for this type of the molecules, this method is B3LYP*.
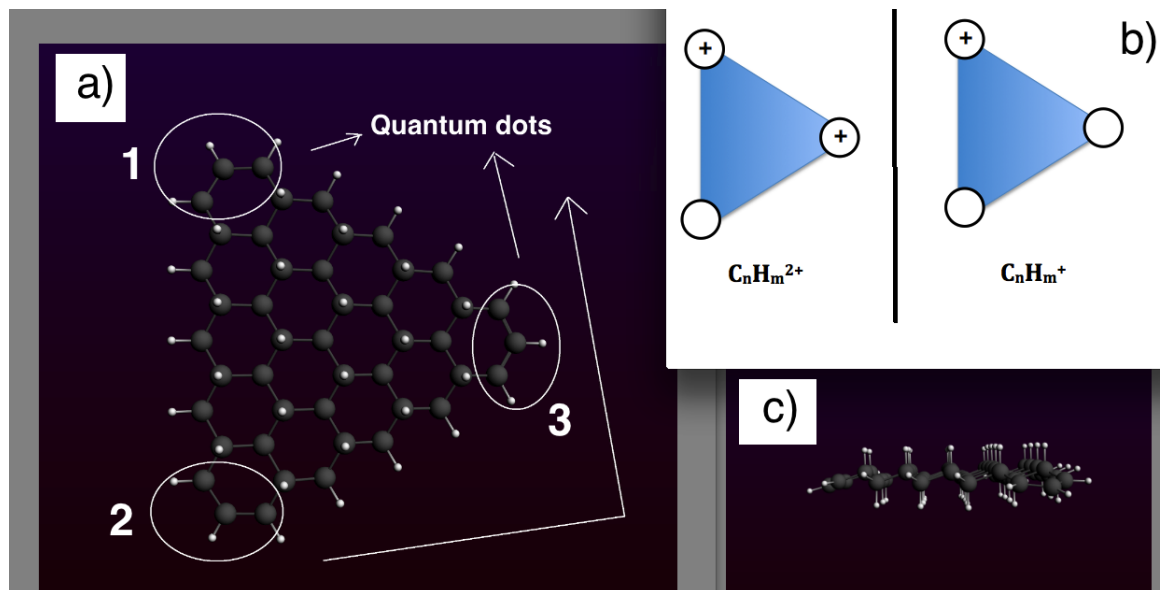

Figure 1: a) Triangular graphane molecule with three quantum dots. b) Scheme of the molecular double cation and molecular single cation. c) Scheme of the triangular graphane molecule in the plane.

In the molecular double cation, we define one active state and other inactive state. In the active state, we can define two logic states (0 and 1) and we can activate the molecule, with a electric field (clock field). Figure 2, shows the two logic states and inactive state. When the clock field is applied in the direction $-x$, the molecule has a state of minimum energy with the electron located in the quantum dot 3 (inactive state). The Figure 2c show the HOMO in the inactive state. When the clock field is applied in the direction x the molecule has a state of minimum energy with the electron located in the quantum dot 1, or located in the quantum dot 2. Figures 2a and 2b shows this situation.
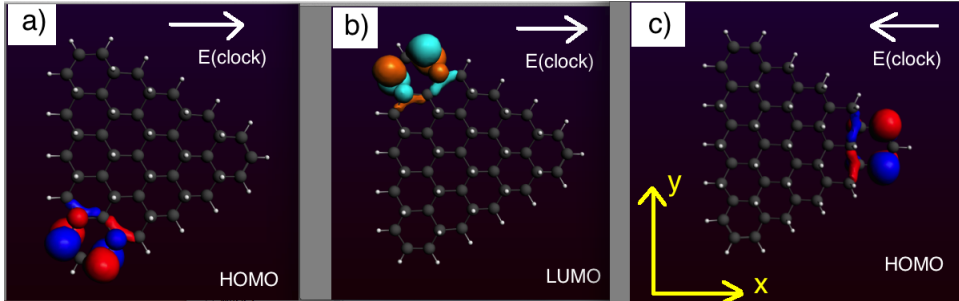

Figure 2. a) Logic state 0, b) logic state 1 and c) inactive state.

A very important parameter to determine the dynamic properties of molecular array, is the energy of tunneling between quantum dots of the molecule. For molecular double cation, in the active state, we can define this energy as $\gamma = \frac{E(LUMO)-E(HOMO)}{2}$. The table 1 show the γ values, for some triangular molecules. The L parameter correspond to the side of the equilateral triangule.

L (Å)	$E\,[Clock]\,\left(\frac{Hartree}{e\,Bohr}\right)$	$\gamma\,(mHartree)$
7.42	0.008	9.10
7.42	0.010	9.25
7.42	0.020	9.40
7.42	0.040	9.69
12.58	0.010	3.80
12.58	0.013	4.00

Table I: Energy of tunneling between quantum dots of the molecules, in the active state.

Our results shows that the γ parameter depend of the magnitude of the clock field and of

the molecular size. This result imply that we can dispose of a fine control on the dynamics property of the molecular array.

Propagation of binary signal

In this section we analyse the dynamic response of the molecular array when binary information is transmitted from one extreme to the other of the system. Let us consider a system consisting of N cells, as shown Figure 3. The first cell acts as a driver and its polarization is externally manipulated. For the remaining $N-1$ active cells, we solve the time-dependent Schrödinger equation using the occupation number Hamiltonian. Most of the work which exists in the literature on multiple quantum dot systems is based on occupation number (Hubbard-like) formalism [20–22]. This type of Hamiltonian is rather straightforward to implement and requires very limited computational resources. Each quantum dot and its interaction with the other dots are described by means of a few phenomenological parameters, such as the tunneling energy, the dot confinement energy, the onsite electrostatic interaction. Such descriptions are successful in capturing the overall behavior of the system, and in providing a qualitative understanding of the underlying physics. For the i-cell (in the active state) in the automaton, the Hamiltonian can be written:

$$H = V_1 \hat{n}_1 + V_2 \hat{n}_2 - \gamma \left(\hat{a}_1^\dagger \hat{a}_2 + \hat{a}_2^\dagger \hat{a}_1 \right) \tag{1}$$

In this equation the subscripts 1 and 2 denote the upper and lower quantum dot respectively (Fig. 1a). The terms $\hat{n}$, $\hat{a}^\dagger$ and $\hat{a}$ correspond to the number, creation and annihilation operators, respectively. The parameter γ corresponds to the tunneling energy between the quantum dots of the molecule and it was defined in the previous section. The terms V_1 and V_2 represent the Coulomb interaction between the charge in the dot 1 or 2 and the other cells. These terms take into account the interaction with neighboring. The vector representing the state of the i-cell is written as:

$$|\psi(t)\rangle = c_1(t) |1\rangle + c_2(t) |2\rangle \tag{2}$$

where $|1\rangle$ and $|2\rangle$ are the charge wave functions as it is in the upper quantum dot and in the lower, respectively. Using the Hamiltonian given by Eq. (1), the dynamics is obtained from the equation:

$$i\frac{\partial \left|\psi\left(t\right)\right\rangle}{\partial t} = H\left|\psi\left(t\right)\right\rangle \tag{3}$$

By replacing the wave vector (2) in the Schrödinger equation (3), a system of differential equations for the coefficients are obtained which we solve numerically with given initial conditions. In our study, the value of polarization P = +1 (in atomic units) means the hole (positive charge) is in the upper quantum dot and P = −1, means it is on the lower quantum dot.
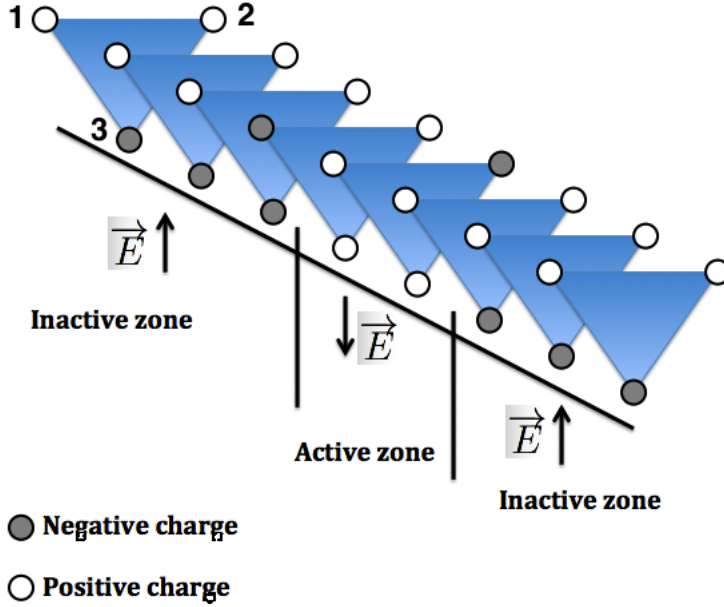

Figure 3: Scheme of the molecular array with the actives zones and inactives zones.

Results and conclusions

Clock operation is defined as follows: In a time period Ω, only two cells are in the active state, the rest of the system is in the idle state. Each cell remains in the active state for a time equal to 2Ω. When a period ends and the next begins, the electric field causes it to disable one of the cells and activate the next. This situation is depicted in Figure 4. We define the time parameter as: $\Omega = \frac{8\pi}{\triangle\gamma}$, where $\triangle$ corresponds to the step of the algorithm used to solve the system of equations and γ parameter was defined above. The study of the properties of the molecule, shows us that we can modulate the γ parameter with the electric field (clock). During clock operation, we change the magnitude of the electric field on a time interval of (t_{clock}), to modify the γ parameter.
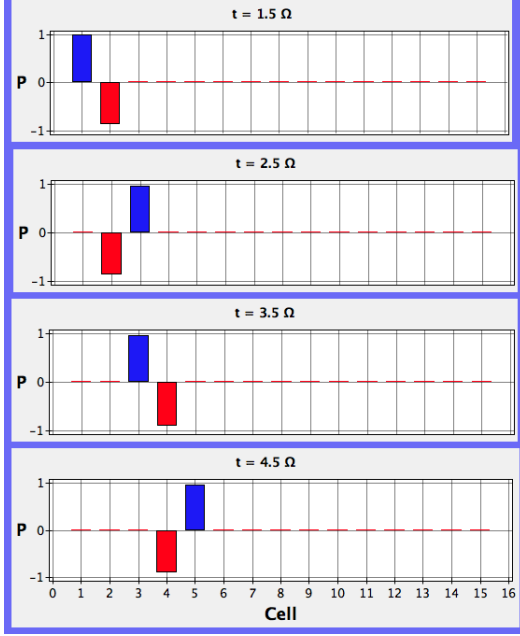
Figure 4. Scheme clock operation of molecular array with 15 cells. In the x axis, the cells that form the array are presented. In the y axis, the polarization of each of the cells (in atomic units) is represented.

The first system studied, is formed by 15 triangular molecules of size 1.26 nm (Figure 1a). The separation distance between the molecules is 1.00 nm. Figure 4 shows results, for $t_{clock} = 0.9\Omega$, $\Omega = 3.04\ ps$, $\gamma_{max} = 0.020\ Hartree$ and $\gamma_{min} = 0.001\ Hartree$. Figure 4a shows γ parameter for each cell (The colors in the figure correspond to the γ parameter of the cells). Figure 4b shows polarization of each cell over time and Figure 4c shows the polarization of molecular array for some moment. We see that the digital signal arrives slightly degraded at the other end of the lineal molecular array. We define $\eta = \frac{P_{out}}{P_{in}}$ as a measure of efficient, where P_{in} is the polarization of the cell 1 and P_{out} is the polarization of last cell. By definition, the polarization of first cell is equal to one. We calculate the polarization of last cell using:

$$P = \frac{1}{\Omega} \int\limits_{N\Omega}^{(N+1)\Omega} P(t)\, dt \qquad (4)$$

where $P(t)$ is polarization over time of last cell and N is the cells number.
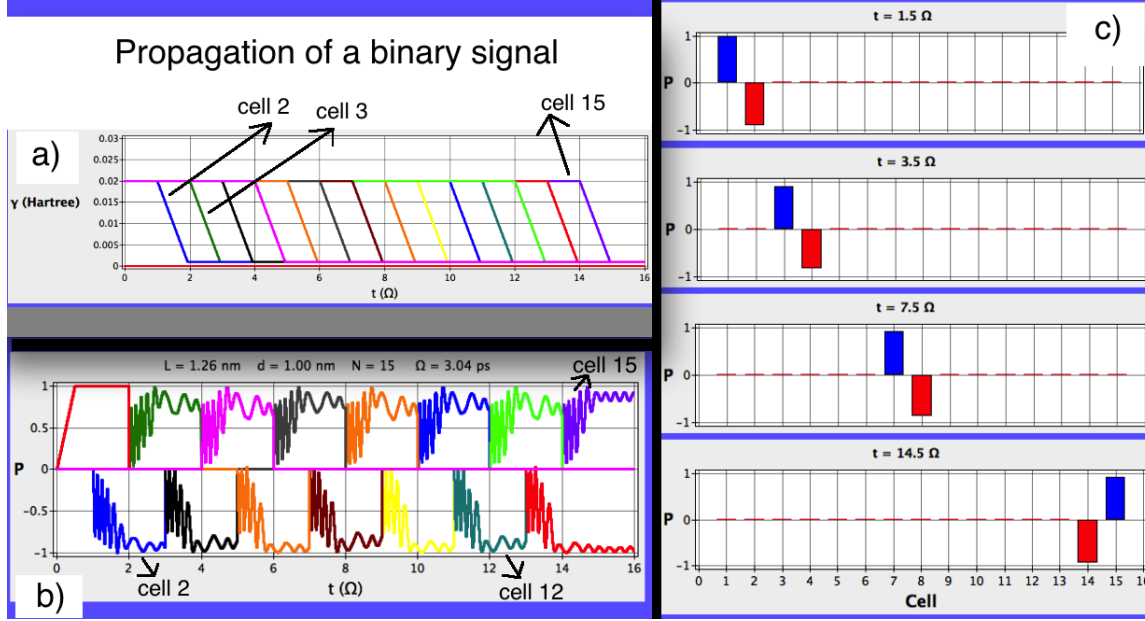
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Figure 5: a) Scheme of γ parameter's change over time. b) Polarization of the molecular array over time. c) Propagation of a bit information.

In this first simulation the value of η is 0.874, close to the unit value. Our study verified that the efficiency η increases if t_{clock} decreases, for this physical configuration of the molecules. Figure 6 shows the results for the same system of Figure 5, but with $t_{clock} = 0.09\Omega$. We can observe that the polarization of each cell is higher (in magnitude) than in the previous case and the value of the efficiency in this case is 0.933.
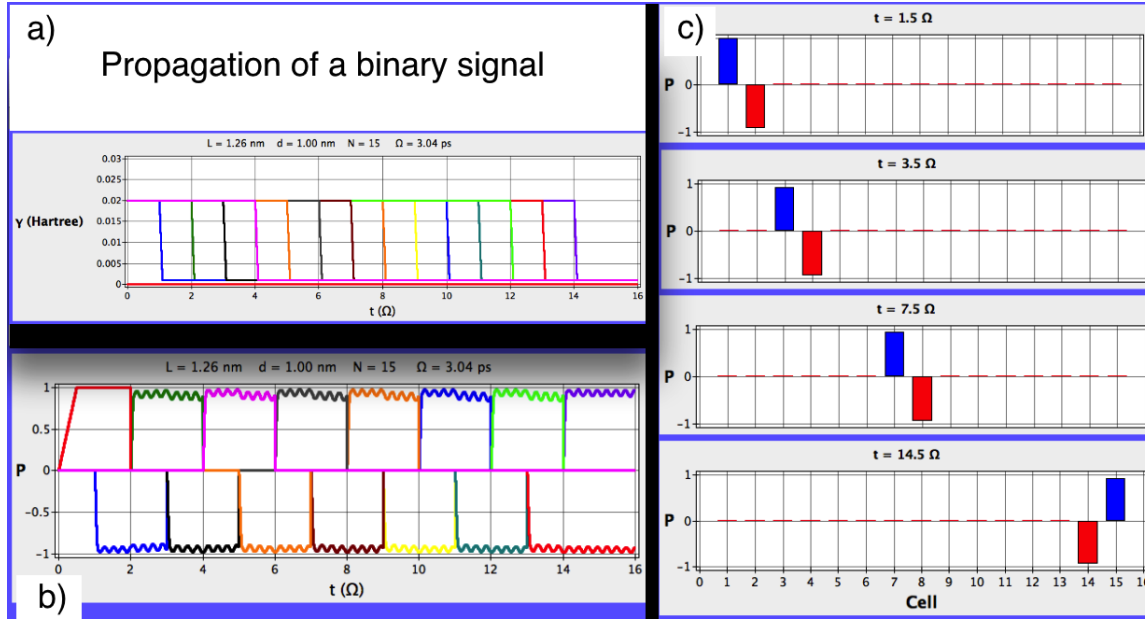
Figure 6: a) a) Scheme of γ parameter's change over time. b) Polarization of the molecular array over time. c) Propagation of a bit information.

We perform simulations for different molecule sizes, separation distances, tunneling energy and duration of the operation clock. We were able to verify that the efficiency depends on all these parameters and for chains whose length is greater than 15 cells, the value of the efficiency is close to unity (greater than 90%). We conclude that a linear array of triangular graphane molecules, with three quantum dots, digital information can be transmitted long distances without damaging the bit of information, as long as we make a proper clock operation.

In this work we developed a proof of concept to show that a linear arrangement of graphane nanoclusters efficiently transmits one bit of information an appreciable distance. From this theoretical study, one could design an experimental protocol to demonstrate the behavior of graphane in such applications.

Acknowledgment

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