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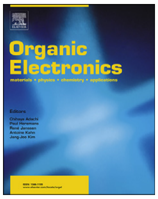

Transport properties through an aromatic molecular wire

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ABSTRACT

The quantum transport properties through a finite homogeneous chain of aromatic molecules composed by benzene rings connected to two semi-infinite leads are investigated. The study is based on the tight-binding approach using semi-analytic methods of Green's function techniques within a real space renormalization scheme. The transmission probability and the characteristic diagram $I-V$ of an aromatic molecular wire are calculated as a function of the molecule-leads coupling and the intra-rings coupling parameters. The obtained results show a good agreement with the previous reported DFT calculations.

1. Introduction

The issue of the dimensions of the electronic devices that have been used in molecular electronics has become an important subject of research in recent decades. This is due to the fact that the main components of microelectronic circuits are close to be in the regime of size of atoms or molecules. Such molecules or atoms which are somehow spatially confined can display a number of interactions arising from coupling such as electron-electron, electron-ion, or with molecular vibrations. They are related with the hopping between the electronic orbitals, and this may gives origin to low-dimensional devices with new physical phenomena. The possible applications of mono-molecular systems can be in transistors, in quantum wires, in rectifiers, in switches, or in storage devices, among others [1–9]. In fact, nanoscopic molecular-like devices have been widely studied both experimentally and theoretically to uncover properties such as electronic, magnetic or thermal, just to mention a few. It has been found that they can be altered by changing the positions of the different atoms or molecules in these systems [2,10–13].

Within this framework, we study the transport properties in a molecular-wire-like system called *Structure of a thiolated arylethynylene with a 9,10-dihydroanthracene (AH) core*, which is composed of individual molecules with a special configuration of benzene rings. This structure has attracted much interest because it has been used as a new nanoelectronic device designed to be employed as molecular electronic transistor. It is based on electron transfer, large negative differential conductance and among others principal properties [9]. The mechanism for the study of the electron transport through this aromatic molecule relies on placing it between metal contacts in such a way that it is possible to control the current through the molecular system which is, in general, a non-linear function of the bias voltage [14–17,19,21,22].

In the present manuscript, we propose a theoretical and analytical method to analyze the electronic properties when the molecular system can be renormalized. This method will be used to calculate the same properties reported by Perrin in the mentioned molecule [9]. Hence, the aim of this work is to compare our results for some transport properties obtained from the decimation process with those calculated by density functional theory (DFT). The system is modeled using a tight-binding Hamiltonian within a nearest-neighbor approximation described by Green's functions formalism, using a real space renormalization framework [12,16,21]. Then, by varying both the interaction between rings in the molecular system and the bias voltage, we investigate the electron transmission, the current, and the gap in the structure mentioned. As a result we find that the molecular system displays characteristics of electronic devices. The manuscript is organized as follows: In Section 2, the model based in a tight binding

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Hamiltonian for the molecule is introduced. In Section 3, the methodology is described. In Section 4, the results are presented and analyzed. Finally, the conclusions are given in Section 5.

2. Model

In order to describe the molecular system as an electronic device we have adopted a configuration with the (AH) molecule connected to the leads as it is shown in Fig. 1.

The full system is described by a tight-binding Hamiltonian:

$$H = H_{MS} + H_L + H_I. \tag{1}$$

Here H_{MS} corresponds to the Hamiltonian of the molecular system embedded between two electrodes, and is given by:

$$H_{MS} = \sum_i v_{i\pm1}\left(c_i^\dagger c_{(i+1)} + c_{(i+1)}^\dagger c_i\right) + \sum_i E_i c_i^\dagger c_i, \tag{2}$$

where $c_i^\dagger$ is the creation operator of an electron at site i, $v_{i\pm1}$ is hopping between atoms of molecular system (v_c, S and τ) and E_i is the energy of each atom of the molecule.

In addition, H_L and H_I represent the leads and their interaction with the molecule, respectively. Such that they are given by:

$$H_L = \sum_{k_L} \varepsilon_{k_L} d_{k_L}^\dagger d_{k_L} + \sum_{k_R} \varepsilon_{k_R} d_{k_R}^\dagger d_{k_R} \tag{3}$$

and

$$H_I = \sum_{k_L} \Gamma_S d_{k_L}^\dagger c_1 + \sum_{k_R} \Gamma_D d_{k_R}^\dagger c_N + h.c., \tag{4}$$

where the operator $d_{k_{L(R)}}^\dagger$ is the creation operator of an electron in a state $k_{L(R)}$ with energy $\varepsilon_{k_{L(R)}}$. Besides, $\Gamma_{S(D)}$ is the coupling between each lead (Source-Drain) with the aromatic molecule. In the following we will assume $\Gamma_{S(D)} = \Gamma_{L(R)}$.

Since we have a many-body problem where an electron passes through the molecular system and interacts electronically with the components of the molecule, it could be represented by Huckel-Hubbard-Ohno model [18]. Due to the complexity of our problem, we can perform the approximation in which the electron-electron interaction is not explicitly taken into account. This assumption leads the many-body problem into a scattering problem of a single-electron in a multichannel system, where the molecular states of the system (Contact-molecule-Contact) are expanded into a linear combination of atomic orbitals (LCAO) [19]. In the specific case of the AH molecular system, the states correspond to the p orbitals or π-electron. This approximation is known as the Hückel molecular orbital method (HMO) [20]. In fact, these states are defined by $\phi_i = \sum c_i \psi_j$, where i represents the electronic site in the leads or in the molecular system.

After the elimination of the degrees of freedom in the source, drain, leads and transforming the system in an effective one-body model, we can rewrite the Hamiltonian of molecular system in the form:

$$H_{MS} = \sum_i v_{i,i+1} |i\rangle\langle i+1| + v_{i+1,i} |i+1\rangle\langle i| + \sum_i E_i |i\rangle\langle i|. \tag{5}$$

In this approach, all the elements of the Hamiltonian that represent the AH molecular system are assigned using experimental values which makes this method a semi-empirical orbital one.

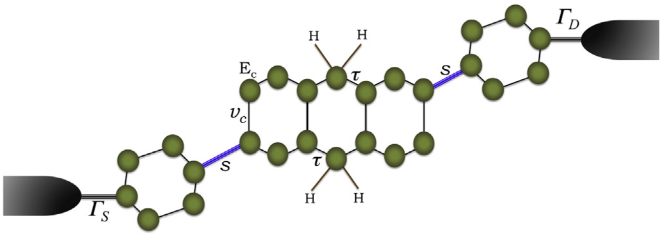

Fig. 1. Representation of the structure of a thiolated arylethynylene with a 9,10-dihydroanthracene (AH) core.

3. Method

We study the transport properties through molecular systems by using the Landauer-Büttiker formalism [19,21,22], based on Green's function techniques within a real-space renormalization approach (decimation procedure) [23–27].

The Green's function of the molecular system coupled to the leads is calculated by using the Dyson equation

$$G = G^0 + G^0(\Sigma_L + \Sigma_R)G, \tag{6}$$

where G^0 is the bare Green's function of the isolated molecular system and Σ_L and Σ_R are the self-energies of the left and right lead, respectively. The transmission probability can be obtained by using the Fischer-Lee relationship [19], which is given by

$$T(E) = Tr\left[\Gamma^L G^r \Gamma^R G^a\right], \tag{7}$$

where $\Gamma^{L(R)} = i(\Sigma^{L(R)} - \Sigma^{L(R)\dagger})$ is the spectral matrix density of the left (right) lead. In what follows, we will take $\Sigma^L = \Sigma^R = -i\Gamma/2$. As it can be seen in Fig. 2, we transform the molecular system representation into a 1D heterogeneous effective chain of N sites, obtaining renormalized Green's functions with effective inter-site couplings, which contains all the information of the planar aromatic molecule.

Then, the transmission probability can be written as:

$$T(E) = \Gamma_{11}^L \Gamma_{NN}^R \left|G_{1N}^r\right|^2, \tag{8}$$

where G_{1N}^r is given by:

$$G_{1N}^r = \frac{G_{1N}^0}{\left[1 - \left(\frac{\Gamma}{2}\right)^2 \triangle G_1\right] + i\left(\frac{\Gamma}{2}\right)^2 \left(G_{11}^0 + G_{NN}^0\right)}, \tag{9}$$

where $\triangle G_1 = G_{11}^0 G_{NN}^0 - (G_{1N}^0)^2$. The Green's function G_{1N}^0, G_{NN}^0 and G_{11}^0 can be analytically determined by using the renormalization techniques, where N represents the effective atomic site.

Once we have obtained the normalized effective systems, which contains all the information of their respective atomic sites and coupling, we take into account a new molecular quantum system with Green's function (as we have mentioned above) that will be analyzed.

The corresponding Green's functions G_{1N}^0, G_{NN}^0 and G_{11}^0 are given by:

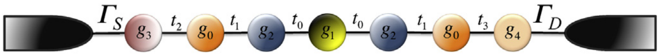

Fig. 2. Representation of the AH effective molecule coupled with the contacts.

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