

Molecular conduction using the parameter-free bond-pair model

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Available online 18 April 2005

Abstract

In this work we calculate transport properties in metallic contact–nanodevice–metallic contact systems. For this purpose we use the own-developed bond-pair (BP) model to calculate selfconsistently both the electronic structure of the central molecule and its coupling with the leads. The I – V curves for the Al–Al₄–Al system were evaluated and we have verified that the BP results are comparable with state-of-art calculations. Thus, the BP model, which offers a clear reading and interpretation of the relationship between the chemistry of the molecule and the I – V characteristics with an inexpensive computation effort, is a promissory approximation for the description and comprehension of experiments involving features of molecular electronic conduction of more complex devices.

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Keywords: Molecular conduction; Bond-pair model

1. Introduction

In transport through molecular wires the formation of pseudo-molecular orbitals critically defines the conduction channels and consequently the electronic transport properties. The own-developed bond-pair (BP) model [1,2] is a parameter-free proposal in which the whole system is built from the superposition of the elemental dimers that constitute it. In this work we implement the BP model to calculate selfconsistently the electronic structure of linear chains of atoms, and also the coupling with the leads. Then we evaluate I – V curves. We have verified that the BP model results comparable with state-of-art calculations [3–5] with the advantage of a transparent reading and interpretation of the relationship between the chemistry of the molecule and the I – V characteristics, besides a less expensive computation effort. Thus, the BP model is a promissory

approximation for the description and comprehension of experiments involving features of molecular electronic conduction of more complex devices.

2. Theory

The Hamiltonian of the junction can be decomposed as the sum of four terms

$$H = H_L + H_R + H_D + H_{\text{int}} \quad (1)$$

where $H_{L(R)}$ represents the Hamiltonian of the left (right) metallic contact, H_D describes the device (molecule, nanowire, etc.) and H_{int} is the coupling between the central cluster and the leads.

We use the BP model to calculate the electronic structure of the central molecule as well as the coupling elements between its molecular orbitals (MO) and the extended K -states of the electrodes. Briefly, the model is an effective Hamiltonian in which all the terms are evaluated from the atomic functions of each element of the system. The diagonal term of the BP Hamiltonian is (for a detailed description see Refs. [1,2])

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$$(H^{\text{BP}})_{jj}^{\sigma} = E_j^0 - \sum_{R_s} V_{jj}^{Z_s} + \tilde{U}_{jj} \langle n_{j-\sigma} \rangle + \sum_{i,R_s} (\tilde{J}_{ji} \langle n_{i-\sigma} \rangle + \tilde{G}_{ji} \langle n_{i\sigma} \rangle) - \sum_{i,R_s} S_{ji} T_{ji}^{\sigma \text{dim}} + \frac{1}{4} \sum_{i,R_s} S_{ji}^2 \Delta E_{ji}^{\sigma}, \quad (2)$$

where the indexes i and j means atomic states located at R_s . $(E_j^0 - \sum_{R_s} V_{jj}^{Z_s})$ accounts for one-electron contributions (kinetic energy and electron–nuclei interactions); \tilde{U}_{jj} is the intra-atomic coulomb repulsion, while \tilde{J}_{ji} and \tilde{G}_{ji} are, respectively, the direct and exchange coulomb integrals, all of them calculated in the non-orthogonal atomic basis set and corrected by terms of second-order in the overlap S . ΔE_{ji}^{σ} is the difference between j and i diagonal terms consistently with the overlap expansion.

The non-diagonal term is

$$(H^{\text{BP}})_{ji}^{\sigma} = T_{ji}^{\sigma \text{dim}} - \tilde{G}_{ji} \langle c_{i\sigma}^{\dagger} c_{j\sigma} \rangle. \quad (3)$$

The superindex dim indicates that the hopping is defined as a superposition of hoppings defined only with functions orthogonalized in each dimeric space. $T_{ji}^{\sigma \text{dim}}$ also includes the contributions due to two-electron terms within a mean-field approximation.

The current through the molecule for a bias voltage applied V between leads is calculated as in Ref. [3], i.e. by using the Landauer formula [6]

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} d\epsilon \text{Tr}(t t^{\dagger}) [f_L(\epsilon_-) - f_R(\epsilon_+)], \quad (4)$$

where f is the Fermi function, $\epsilon_{\mp} = \epsilon \mp eV$, and

$$t_{\alpha\alpha}(\epsilon, V) = 2\Delta_{\alpha,L}^{1/2}(\epsilon_-) G_{\alpha\alpha}^D \Delta_{\alpha,R}^{1/2}(\epsilon_+). \quad (5)$$

$G_{\alpha\alpha}^D$ being the Green function of the α -MO of the central cluster given by

$$G_{\alpha\alpha}^D(\epsilon, V) = [\epsilon - \Sigma_{\alpha} - \Sigma_{\alpha,L}(\epsilon_-) - \Sigma_{\alpha,R}(\epsilon_+)]^{-1}. \quad (6)$$

Σ_{α} are the MO energies of the molecule (self-consistent eigenvalues H^{BP}) and the self-energies $\Sigma_{L(R)}$ are related with the electronic structure of the leads and their coupling with the molecule in the following way

$$\Sigma_{\alpha,L(R)} = A_{\alpha,L(R)} + i\Delta_{\alpha,L(R)}, \quad (7)$$

where

$$\Delta_{\alpha,L(R)} = \pi \sum_{K_{L(R)}} |T_{\alpha,K_{L(R)}}|^2 \delta(\epsilon - E_{K_{L(R)}}), \quad (8)$$

and

$$A_{\alpha,L(R)} = P \sum_{K_{L(R)}} \frac{|T_{\alpha,K_{L(R)}}|^2}{(\epsilon - E_{K_{L(R)}})} \quad (9)$$

For the calculation of $T_{\alpha,K_{L(R)}}$ we use the BP model adapted to molecule–surface interaction [2]. Thus, by performing a linear combination of atomic orbitals (LCAO) over the extended K -states and the α -MO of

the central molecule, we obtain the self-energy written in terms of the atom–atom interaction parameters. For example, the imaginary part Δ is

$$\Delta_{\alpha,L(R)} = \pi \sum_{i,R_{L(R)}} \rho_{i,R_{L(R)}}(\epsilon) \sum_{j,R_D} |c_{j,R_D}^{\alpha}|^2 |(H^{\text{BP}})_{ji}|^2 \quad (10)$$

with i representing atomic states of a contact atom located at $R_{L(R)}$ and j are atomic states of atoms located at R_D forming the central cluster. In this way we reduce the contact–molecule–contact interacting complex to an atom–atom-like system where the atomic coupling $(H^{\text{BP}})_{ji}$ is weighted by the partial and local density of states (DOS) of the leads, $\rho_{i,R_{L(R)}}$ and by the MO coefficients of the central cluster, c_{j,R_D}^{α} .

3. Results and discussion

As a zero-order attempt to implement the precedent equations, we calculate a system formed by a linear chain of four atoms of aluminium coupled to aluminium electrodes. We consider a semielliptical DOS at the leads and the MOs of the central cluster were solved for an AL4 linear chain isolated. A quantitative more reliable calculation requires a more accurate evaluation of the electrode DOS and the electronic structure of the central device, for instance, considering some contact atoms forming it and in presence of electrical field applied.

In Fig. 1, we plot the energy dependent transmission given by the trace of $t t^{\dagger}$ for each bias voltage considered. We also show the energy of the MOs of the AL4 system and we observe as the transmission roughly follows the MOs. However, because of the interaction its value is different to

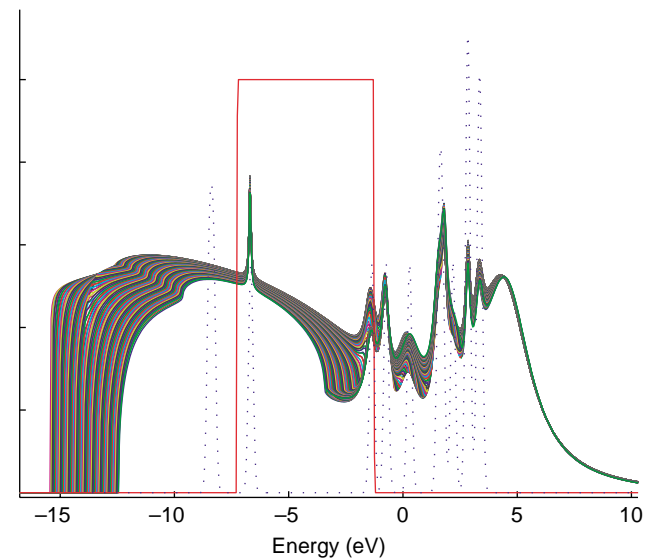


Fig. 1. Solid lines: transmission $[\text{Tr}(t t^{\dagger})(\epsilon)]$ for each bias voltage. Dotted line: BP-MO energies (enhanced by a gaussian function) for the AL4 cluster. Thick line is the difference between Fermi functions $f(\epsilon_-) - f(\epsilon_+)$ for $V = 3$ V. The Fermi level for AL is -4.25 eV.

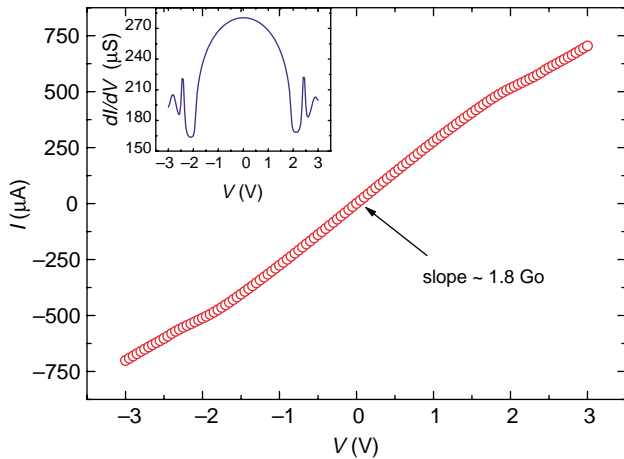


Fig. 2. I - V and dI/dV (inset) curves for Al-Al₁₄-Al system.

zero in the effective energy window given by the difference between Fermi functions of the contacts. Consequently, the I - V curve has an ohmic feature for small bias voltage as it is showed in Fig. 2. Besides, in this figure is seen as when a new conduction channel occur in the range of energies considered ($V \approx 2.5$ V), the dI/dV curve presents new peaks evidencing molecular-like conduction. We also calculate

the same system but reducing the coupling four times and we have checked a strong reduction of the current exhibiting a resonant feature in the conduction. These results are in good agreement with previous calculations [4,5] showing the correctness of our proposal.

In conclusion, we have implemented the BP model to calculate transport properties in molecular conduction obtaining good results which allow us to progress in this sense in order to describe more realistic systems. Work supported by Fundación Antorchas (14248-128), ANPCyT (PICT02 03-11769), CONICET and UNL (PE 213).

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