



The spectral adjustment in nanoscale transport combined with the density functional based tight binding method



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ARTICLE INFO

Article history:

Received 13 October 2016

Received in revised form 20 January 2017

Accepted 27 February 2017

Available online 16 March 2017

Keywords:

Density functional based tight-binding

Spectral adjustment

Single molecule

Transport properties

ABSTRACT

We present a study of coherent tunneling across rigid rod-like Oligo(phenylene-ethylene) molecules coupled to gold leads for different molecular lengths and anchoring groups. We employ a Density Functional Tight Binding (DFTB) Hamiltonian combined with Green's function formalism. We show that the correct decay β of the tunneling probability with respect to the molecular length is only recovered after a proper renormalization of the energy levels for the occupied and unoccupied molecular orbitals. To this end, we implement a density matrix based spectral adjustment. After correction a β independent of the anchoring group is obtained, in good quantitative agreement with available experiments and previous ab initio density functional calculations.

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1. Introduction

During the last decade, molecular electronics has raised a great deal of interest among researchers worldwide. Development of the electronic devices at the molecular scale involves study of the electronic level structure, response and charge transport at atomic scale [1]. These devices can be composed of single molecules, small groups of molecules, carbon nanotubes, nanoscale metallic or semiconductor wires [2] with emerging applications as transistors [3,4], switches [5,6], rectifiers [7,8], photovoltaics [9], memory units [10,11], and sensors [12,13]. After Aviram-Ratner's suggestion [14] to use a single molecule as an electronic component in 1974, molecular electronics has been rapidly developed due to advancements in the experimental techniques and theoretical models at molecular scale. Molecular wires offer a viable alternative to overcome difficulties associated with the continuing shrinking of common electronic devices [15]. A large variety of oligomers can also be contacted by nanoelectrodes, acting as an electronic molecular wire. Here the oligo(p-phenylene ethynylene) s (OPEs) are the molecules of interest. OPE derivatives have been widely studied in molecular electronics such as molecular diodes [16–18], molecular switches [19], and molecular memory devices [20]. Highly conjugated aromatic structure makes linear-type

OPE molecules good candidates for molecular wires to link different molecular components and metal contacts. Investigation of OPE molecules also helps to study the electron transport mechanism through a single molecule bridging two electrodes [21].

When molecules are bridging electrodes in molecular wires, resonances due to molecule's discrete orbitals coupled to continuum states of the electrode are recognized as the peaks in the transmission function. In a coherent transport regime, the shape and height of the peaks are determined by the symmetry of the junction and the coupling of the molecular orbitals to the electrodes, respectively [22]. In addition, transport properties of the molecule in this regime depend on the intrinsic properties of the molecule, including their length and conformation, the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the alignment of this gap to the metal Fermi level, the molecular bond characteristics, the chemical groups anchoring the molecule to the electrodes, and the contact geometry of the molecule-electrode interface. In non-resonant tunneling process, the conductance of molecular wires has a simple exponential length dependency as $G = G_c \exp(-\beta L)$, where G_c is the contact conductance, L is the length of the wire, and β is the decay constant. The 'chemical anchoring group' can be an atom, or a group of atoms, located at the ends of the molecule to bind it to the electrodes and affects strongly the contact conductance. On the other hand, the anchoring group affects weakly the decay constant and β is mainly deter-

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mined by the intrinsic properties of the molecule such as the energy gap between the HOMO and LUMO [23–25].

In this work, we will estimate the β numerically for molecular wires composed of OPE molecule of varying length and featuring different anchoring groups. We will apply the Density Functional based Tight Binding method (DFTB) [26–28], an approximate method based on reference Density Function (DFT) calculations, aimed at reaching an accuracy close to DFT with a much smaller computational footprint. DFTB can be employed for calculations of various physical properties including band structures, excitations, Raman spectra, geometries, polarizabilities, and conductances [29–33]. Compared to the Density Functional Theory (DFT) with semi-local functionals, the execution time of DFTB implementations is usually up to three orders of magnitude smaller for a system of similar size.

The DFTB method is affected by the typical deficiencies of DFT itself. In molecular devices calculated currents can differ by orders of magnitudes from the experimental results, especially when looking at non-resonance transport. Since the current-voltage characteristics of such systems depend critically on the HOMO-LUMO gap, a major improvement is expected when GW quasiparticle energies would be used instead of DFT orbital energies [34,35]. Similar to DFT, GW calculations can also employ DFTB energies as zero-order approximations to the quasiparticle quantities [36,37]. But even with this improvement, the numerical complexity of the GW equations limits a first-principles evaluation to rather small system sizes of tens of atoms. The discrepancy caused by self-interaction error in standard (semi-) local exchange-correlation functionals in DFT has been also corrected to some extent by ad-hoc spectral adjustment methods such as DFT + Σ [38–40], atomic self interaction correction (ASIC) schemes [41,42], or spectral adjustment in nanoscale transport (SAINT) [43,44]. The DFT + Σ method improves on DFT-PBE and yields conductances within a factor 2 of the experimental results for certain positions of the image planes but it fails to capture the conductance trends in some studies [45]. ASIC is able to predict the correct ionization potential of molecules, and hence to describe relatively correct band alignment between the molecular orbitals and the Fermi level of the metallic electrodes. However ASIC doesn't consider the effect of renormalization of the molecular levels when image charges formed in the metallic electrodes when electrons are added to or removed from the molecule [39]. It is important to keep in mind that SIC calculations really affect the occupied states and shift them down in energy relative to the unoccupied conduction band states. Spectral adjustment methods are simply based on a shift of the HOMO and LUMO to correct the wrong DFT prediction of the HOMO-LUMO gap as a quasi-particle ground state quantity and the wrong alignment of the molecular orbitals with the leads, strongly affected by electron-electron interactions. As a result of the corrections, the gap is typically increased and the conductance reduced. It has been already shown that this method is in a very good qualitative agreement with GW method but faster and applicable to large systems with thousands of atoms [43].

We analyze in the present work the transport properties of gold (111) electrodes bridged by OPE derivatives with three different anchoring groups and molecular lengths. The backbone of these molecules has a varying number of units ranging from one to six. The DFTB is combined with a Green's function method [46] to calculate the transmission probability between the leads. The parameter-less SAINT method is implemented to properly renormalize the occupied and unoccupied states. The work is divided into two major parts: The first addresses the methodological and theoretical framework, while the second part focuses on the applications.

2. Materials and method

The relaxation of the molecular structures, total energy and electronic structure calculations have been done by using the charge density functional tight-binding (DFTB) method which is based on an expansion of the Kohn Sham total energy [47] around a properly chosen reference density $\rho_0(r)$ up to a second order in density fluctuation $\delta\rho(r)$. The reference density is usually chosen to be a superposition of atomic densities. The zeroth order approach is equivalent to a common standard non-self-consistent tight-binding scheme, while at second order a transparent and readily calculable expression for generalized Hamiltonian matrix elements can be derived. The resulting DFTB method provides accurate results comparable to the results obtained with *ab initio* DFT methods or first principles calculations, while requiring fewer computational resources.

2.1. SCC-DFTB formalism

SCC-DFTB takes the next step towards a better description, especially of highly inhomogeneous systems, with extending the DFTB approach in order to improve total energies, forces, and transferability in the presence of considerable long-range Coulomb interactions [48]. The SCC-DFTB total energy reads

$$E_{total} = E_{TB} + E_{2nd} + E_{rep}, \quad (1)$$

where E_{TB} is the usual tight-binding band energy, that is, the occupation weighted sum of the single particle eigenvalues of the zeroth-order DFTB Hamiltonian. E_{rep} and E_{2nd} are, respectively, a short-ranged repulsive interaction term and an electrostatic interaction term which takes into account charge fluctuations. Dividing the density fluctuations into atom-centered parts

$$E_{2nd} = \frac{1}{2} \sum_{\alpha,\beta}^N \Delta q_{\alpha} \Delta q_{\beta} \gamma_{\alpha\beta}, \quad (2)$$

where Δq_{α} is the net charge on the respective atom and $\gamma_{\alpha\beta}$ contains all quantities of the expansions excluding the net charges $\Delta q_{\alpha,\beta}$ [48]. The on-site terms $\gamma_{\alpha\alpha}$ can be approximated by the difference between the atomic ionization potential I_{α} and electron affinity A_{α} of the atom centered at α , which again can be well approximated by the so-called Hubbard parameter U_{α} . In order to get the net charges Δq , one calculates the Mulliken charges as an approximation to the atomic charge and subtracts the charge of the neutral atom.

The matrix elements of the zeroth-order Hamiltonian can be tabulated following the SK scheme under the usual approximations, for example, two-center and frozen core approximations. These matrix elements (parameter set) have to be known at the start of any calculation. The parametrization needed for this study has to be involved the Au-X (X = Au, H, C, N, O, S) interactions. We used a new Au parameters set which was developed for gold-thiolate compounds with atoms, including S, Au, N, C, and H [49]. The Au-Au and Au-X Hamiltonian and overlap integral values necessary for the DFTB scheme had been computed under the zeroth-order regular approximation (ZORA) Hamiltonian and using the PBE functional. For gold the 5d, 6s, and unoccupied 6p orbitals are treated explicitly in DFTB and the remaining electrons are included in a relativistic frozen core.

2.2. Calculation procedure

At first, we considered OPE molecule with three units connected to two gold electrodes via three different anchoring groups; (a) Sulfur, (b) Carbon, and (c) Amine. The left and the right bulk

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