

Study of the transport properties of a molecular junction as a function of the distance between the leads

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We consider a model of a molecular junction made of BDT (benzene dithiol) molecule trapped between two Au(100) leads. Using the *ab initio* approach implemented in the SIESTA package we look for the optimal configurations of the molecule as a function of the distance between the leads. We find that for distances long enough the energy of the system is minimized when the molecule is bonded asymmetrically, i.e. chemisorbed to one of the leads, whereas for distances shorter than 12 Å the energy is minimized when the molecule sits in the middle between the leads. We discuss possible consequences of the above findings for the transport properties of the junction.

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Molecular junctions made of two leads bridged by a single molecule are intensely studied recently both experimentally and theoretically as basic units in the systems of molecular electronics [1–3]. Unlike the traditional silicon based devices, the electronic transport through molecular devices very much depend on subtle details of the molecular configuration between the leads, due to the importance of interference effects at the nanoscale. In several *ab initio* works the influence of the type of bonding between the metal surface and the bridging atom of the molecule (on-top, hollow place, bridge contact structures) on the current–voltage (I – V) characteristics was thoroughly studied for both Au(111) and Au(100) surfaces [4–6]. Moreover the variation of the transport properties of the junctions with the change of width of the leads (being also a kind of interference phenomenon) was demonstrated [4]. So far however a full understanding of the relation between the distance between the leads and the details of the I – V characteristics seems to be absent in the literature.

In this paper we study the evolution of electronic and transport properties of a molecular junction with the change of the distance between the leads. We consider a benzene dithiol ($C_6H_4S_2$ or BDT) molecule placed between the gold leads, with the sulfur atoms bound to the Au(100) surface at the hollow positions, i.e. at the centers of the squares formed by the surface Au atoms. We first look for the optimal configuration of the molecule between the leads and analyze how this configuration depends on the distance, and next we compute the transmission function and the I – V dependence for the optimized geometry of the junction.

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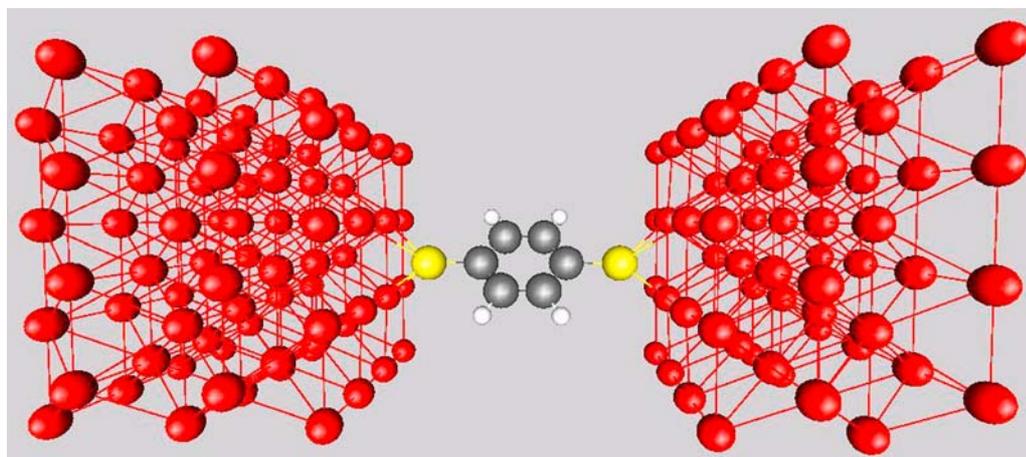


Fig. 1 (online-colour at: www.pss-b.com) A perspective view of the optimized unit cell of the Au(100)–BDT–Au(100) molecular junction obtained from gOpenMol for $d_{\text{lead}} = 11 \text{ \AA}$.

To find the optimal configuration of the Au(100)–BDT–Au(100) junction we apply the density functional approach as implemented in the SIESTA package [7]. In our SIESTA computation we consider a periodic 3D lattice with a unit cell consisting of BDT molecule and fragments of the opposite leads, which include a total of 144 Au atoms (see Fig. 1).

Such a lattice represents well enough the typical experimental setup as used in mechanically controlled break junction (MCBJ) experiments [1], which involves a single BDT molecule, provided the number of molecular orbitals of BDT is small enough as compared to the number of Au atoms. In order to avoid overlapping between the basis functions of BDT molecules from the neighboring unit cells, which is necessary to ensure that only one molecule is simulated, the transverse size of the unit cell should be greater than the sum of the transverse size of the molecule and two times the maximal diameter of the basis functions.

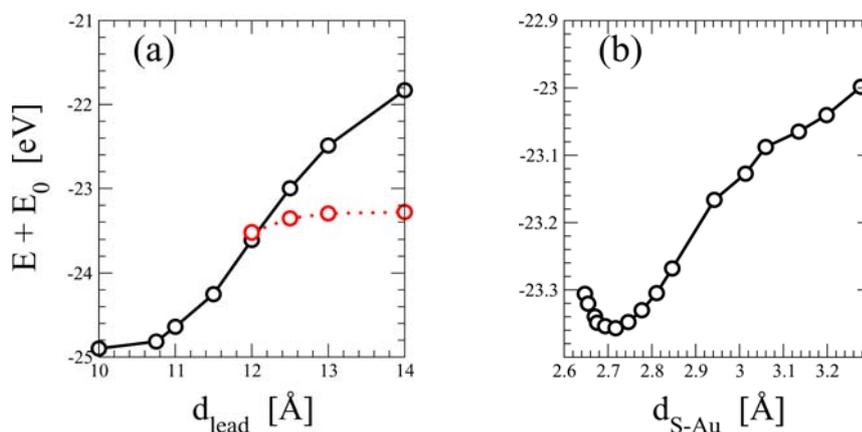


Fig. 2 (online-colour at: www.pss-b.com) (a) Dependence of the energy of the junction as a function of the distance between the Au leads. Solid line: BDT molecule at the central position, dotted line: BDT molecule shifted to one of the leads. For the shifted molecule the distance between the S atom and the closest lead surface was about 1.75 \AA . $E_0 = -13100 \text{ eV}$ is a reference energy value. (b) Energy of the stable configuration of the BDT molecule as a function of distance between the S atom and the nearest Au atoms for $d_{\text{lead}} = 12.5 \text{ \AA}$. The solution for $d_{\text{S-Au}} \sim 3.3 \text{ \AA}$ corresponds to the central position of the molecule. In both figures circles show locally stable configurations.

All the numerical results presented below are obtained using the local density approximation (LDA) for the exchange–correlation functional of the DFT method [9]. The results of other works as well as our own calculations show that neither nonlocal corrections (i.e. GGA) nor a spin-dependent functional (LSDA) change the results substantially. We use Troullier–Martins [8] pseudopotentials to represent the potentials of the atomic cores. Our basis functions are restricted to single-zeta (SZ) functions but we checked some results using a DZP basis. The radii of all the pseudoorbitals were determined by a pseudo-atomic orbital energy shift equal to 0.02 Ry. With the above restrictions all our electronic structure and transport computations (except the ones using the DZP basis) were possible using 2 GB of a computer memory. We found the optimal configuration of the junction with a conjugated gradient method, relaxing the molecular coordinates and also the positions of the 4Au atoms binding the molecule in each lead. A locally stable configuration is found numerically if the forces acting on each of the relaxed atoms are less than 0.1 eV/Å.

For small distances between the leads, $d_{\text{lead}} \sim 10$ Å, we find that if the molecule is centered in the middle between the leads it attains the local energy minimum. Computations with the molecule shifted uniformly out of the center lead to stable configurations with higher energy (or the molecule shifted back to the center by the minimization procedure). The energy increases steadily with displacement from the central position. We thus conclude that for small distances between the leads the central position represents the global minimum and there are no other energetically stable configurations.

The increase of d_{lead} reduces the overlap of the S-orbitals of the BDT and the Au orbitals from the leads surface and the energy of the system increases (see Fig. 2). The central position remains the global energy minimum until a critical distance $d_{\text{lead}} \sim 12.25$ Å, where the energy of the system can be reduced by shifting the molecule towards either one of the leads.

For lead distances bigger than the critical one we find that the global energy minimum is obtained for the binding sulfur atom at about 1.75 Å from the nearest lead surface, corresponding to a S–Au distance of about 2.7 Å. The energy difference between the central position and the displaced position rises when the distance between the leads increases and for very large d_{lead} it reaches a value of ~ 2 eV.

For the optimized junction configurations we computed the transmission and the I – V characteristics using the *Smeagol* package [10] which is interfaced to SIESTA to allow computations of transport properties in nanostructures. The current J was computed using the standard equation of the Landauer theory [3]:

$$J = \frac{2e}{h} \int dE T(E, V) [f_L(E) - f_R(E)], \quad (1)$$

where $T(E)$ denotes the transmission function and f_L, f_R are the Fermi functions corresponding to the left and the right leads. The transmission function is calculated using the non-equilibrium Green function method with the quasiparticle LDA Hamiltonian. For small distances between the leads ($d_{\text{lead}} = 10.75$ Å) the energy dependence of $T(E)$ exhibits a pseudogap region in the vicinity of the equilibrium Fermi level. Initially the current shows a relatively slow linear increase with the voltage (see Fig. 3). When the voltage is increased the source–drain voltage window extends first over the region of the HOMO level of the BDT and next also over the LUMO level, giving rise to a steeper increase of the current and a series of peaks in the differential conductance.

The overall behavior of the transmission and the current are quite similar to the results obtained by Xue and Ratner [11], as well as Ke et al. [4]. As in the cited papers, the current at $V = 2$ V is greater than the experimental value by at least one order of magnitude which may be due to too a poor treatment of the electron correlations by the LDA functional. On the other hand, the equilibrium conductance obtained by us is several times smaller than the one computed in some other recent papers (see e.g. [5]) and also the shape of our differential conductance is more similar to the experimental one [1].

We verified our computation for several types of leads (3×3 , 4×3 and 5×5 atoms in the surface supercell) and found a clear tendency to reduce the value of $T(E_F)$ with increasing transverse size of the supercell. On this basis we suppose that quantitative differences with the other papers may be partly due

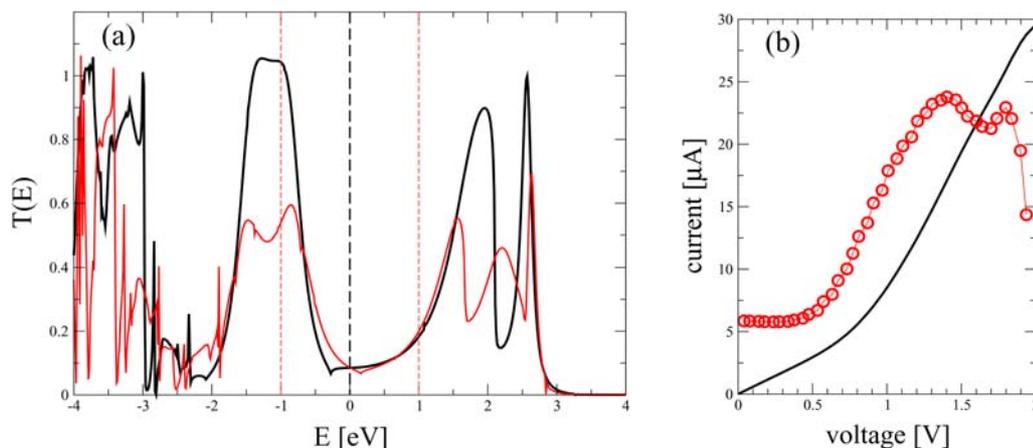


Fig. 3 (online-colour at: www.pss-b.com) Transport properties of the BDT junction with $d_{\text{lead}} = 10.75 \text{ \AA}$. (a) Transmission as a function of energy for $V=0$ (thick black curve) and $V=2$ V (thin curve, red in online edition). The broken lines show the corresponding voltage windows, with $E=0$ being the position of the equilibrium Fermi level. (b) Current as the function of voltage (line) and the voltage derivative of the current (circles).

to the greater transverse size of our Au leads (4×4 atoms, cf. Fig. 1). There are also other factors that can produce small differences: the size of the basis set, the exchange-correlation potential, and the slightly different contact geometry (4-atoms hollow position instead of 3-atoms hollow position in the Au(111) configuration).

In Fig. 4 we show the equilibrium transmission functions in the lowest energy configurations for several values of the distance between the leads. Until $d_{\text{lead}} \sim 12.5 \text{ \AA}$ the transmission changes gradually with the distance. For small d_{lead} the maximum of $T(E)$ at the HOMO peak is smaller than unity ($T \sim 0.9$) and is separated from E_F by about ~ 1.5 eV. When d_{lead} increases, the peak shifts towards E_F , and finally splits into two peaks. For such distances $T(E)$ is very close to unity. This resembles the behavior of a simple tight-binding model of a two-atom molecule. There, for a coupling between the molecule and the leads stronger than some critical value (depending on the interatomic hopping), the two peak structure merges into a single peak, which decreases with further increase of the coupling [12]. This suggests that the transmission of BDT can be partly understood in terms of the two-atom model, in which the internal

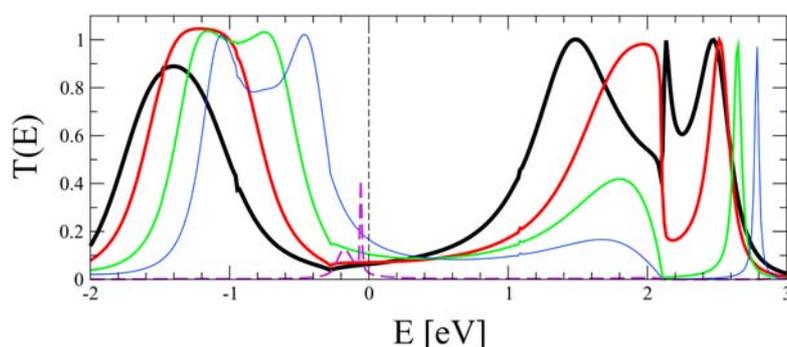


Fig. 4 (online-colour at: www.pss-b.com) Transmission as the function of energy for $V=0$ and variable distance between the leads: $d_{\text{lead}} = 10, 10.75, 11.5,$ and 12 \AA (the line thickness decreases with the distance). The broken line near $E=0$ shows the transmission for $d_{\text{lead}} = 12.5 \text{ \AA}$, with the BDT molecule attached asymmetrically to one of the leads in the lowest energy configuration of Fig. 2(b).

part of BDT (all the atoms except the sulfur ones) can be approximately represented by a small and weakly energy dependent hopping between the external atoms binding the molecule to the leads.

As a consequence of the upward shift of the HOMO peak, the transmission at E_F steadily increases with the distance between the leads from $T(E_F) \sim 0.05$ at $d_{\text{lead}} = 10 \text{ \AA}$ to $T(E_F) \sim 0.15$ at $d_{\text{lead}} = 12 \text{ \AA}$. When the distance crosses the critical value the central position of BDT molecule between the leads is no longer energetically favored. The transmission in the asymmetric position is considerably smaller (see the broken curve in Fig. 4), since it is limited by a very weak coupling with the more distant lead. As a result, the current in the asymmetric position is smaller than $\sim 0.2 \mu\text{A}$ for any voltage.

In relation to experiments the last results suggest that with a carefully controlled increase of the distance between the leads one would observe first a steady rise of the transmission. At a distance slightly larger than 12.25 \AA the current measured at some constant voltage would suddenly drop. On the other hand, a large value of the current observed for large distances would suggest that a significant reorganization of the junction takes place. In fact on the basis of the molecular dynamical simulation of Krüger et al. [13] pulling of a string of Au atoms by a molecule chemisorbed to an Au(111) lead can be expected.

Finally a general comment is in order concerning the value of the computed current, which greatly overestimates the currents observed experimentally. So far this seems to be the common deficiency of all the DFT and Hartree–Fock [14] based approaches, at least for a weak coupling or relatively small molecules. It remains to be seen if a full self-consistent implementation of a better treatment of the electron correlations (e.g. SIC [15]) will bring a substantial progress here. Our results indicate also that a better understanding of the role of electron correlations in the transport through a simple two-atom molecule can be very helpful in this respect.

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