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

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Abstract

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 configuration of the molecule as a function of a distance between the leads. We find that for the
distance long enough the energy of the system is minimized when the molecule is bonded asymmetricaly,
i.e. chemisorbed to one of the leads, whereas for the distance shorter than 12 Å the energy is minimized
for the molecule sitting 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 intensly studied recently both experimentally and theoretically as basic units in the systems of molecular electronics\(^1,2,3\). Unlike the traditional silicon based devices, the electronic transport through the molecular devices very much depend on subtle details of molecular configuration between the leads, due to importance of interference effects at the nanoscale. In several \textit{ab initio} works the influence of a 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\(^4,5,6\). Moreover the variability of the transport properties of the junctions with the change of width of the leads (being also the 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 change of the distance between the leads. We consider benzene dithiol (C\(_6\)H\(_4\)S\(_2\) 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 squares formed by 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.

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 total of 144 Au atoms (see Figure 1).

Such a lattice represents well enough the typical experimental setup as used in the mechanically controlled break junction (MCBJ) experiment\(^1\) which involves a single BDT molecule provided a number of molecular orbitals of BDT is small enough as compared to a number of Au atoms. Moreover, we have to avoid overlapping between the basis functions of BDT molecules from the neighbouring unit cells what means that the transverse size of the unit cell should be greater than the sum of the transverse size of the molecule and the maximal diameter of the basis function.

All the numerical results presented below are obtained using 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 correction (i.e. GGA) nor a spin-
FIG. 1: A perspective view of the optimized unit cell of the Au(100)-BDT-Au(100) molecular junction obtained from gOpenMol for $d_{\text{lead}}=11$ Å.

-dependent functional (LSDA) change the results substantially. We use the Troullier–Martin pseudopotential to represent potential of the atomic cores. Our function basis is restricted to single–zeta (SZ) functions and we checked some results using the DZP basis. The radii of all the pseudoorbitals were determined by the 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 2GB of a computer memory. We find the optimal configuration of the junction with the conjugated gradient method, relaxing also the positions of 4 Au 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 a small distance between the leads, $d_{\text{lead}} = 10$ Å, we find that the molecule centered at the middle between the leads 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 a small distance between the leads the central position represents the global minimum and there is no any other energetically stable configuration. The increase of $d_{\text{lead}}$ reduces the overlap of the S orbitals of BDT and Au orbitals from the leads surface and the energy of the system increases (see Figure 2). The central position remains the global energy minimum until a critical distance $d_{\text{lead}} = 12.25$ Å, where we find that the energy of the system can be reduced by shifting the molecule towards either one of
the leads.

FIG. 2: (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 lead surface was about 1.75 Å. $E_0 = -13100$ eV is a reference energy value. (b) Energy of the stable configuration of BDT molecule as a function of distance between the sulfur atom and the nearest Au atoms for $d_{\text{lead}} = 12.5$ Å. The solution for $d_{\text{S-Au}} = 3.3$ Å corresponds to the central position of the molecule. In the both figures circles show locally stable configurations.

For the lead distance 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 the nearest S-Au distance about 2.7 Å. The energy difference between the central position and the displaced one rises with increasing the distance between the leads and for a very large $d_{\text{lead}}$ reaches the value $2$ eV.

For the optimized junction configurations we computed transmission and I-V characteristics using the SMEAGOL package which is an overlay on the SIESTA to allow computations of the transport in nanostructures. The details of the applied method were described in a recent paper by Rocha and coworkers. The current $J$ was computed using the standard equation of the Landauer theory:

$$J = \frac{2e}{h} \int d\varepsilon T(\varepsilon;V) \left[ f_L(\varepsilon) - f_R(\varepsilon) \right]$$

where $T(\varepsilon;V)$ 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 computed using non-equilibrium Green
function method with the quasiparticle LDA Hamiltonian. For the small distance between the leads ($d_{\text{lead}} = 10.75$ Å) energy dependence of $T(E)$ exhibits a pseudogap region in the vicinity of the equilibrium Fermi level and initially the current shows a relatively slow linear increase with the voltage (see Figure 3). With increase of the voltage the source–drain voltage window extends first over the region of the HOMO level of the BDT, and next also the LUMO level, giving rise to a steep increase of the current and peaks in the differential conductance.

![Graphs of transmission and current](image)

FIG. 3: Transport properties of the junction with $d_{\text{lead}} = 10.75$ Å. (a) Transmission as the function of energy for $V = 0$ (thick black curve) and $V = 2V$ (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 the voltage (line) and the voltage derivative of the current (circles).

The overall behaviour of the transmission and the current are quite similar to the results of the papers of Xue and Ratner as well as the Ke et al. As in the cited papers, the current at $V = 2V$ is greater than the experimental value by at least order of magnitude which may be due to too poor treatment of electron correlations by the LDA method. On the other hand, the equilibrium conductance obtained here is several times smaller than the one computed in some other recent papers (see e.g.) and also the shape of our differential conductance is more similar to the experimental one. We speculate that the difference may be due to the greater transverse size of the Au leads in our paper.

In Figure 4 we show the equilibrium transmission functions in the lowest energy configurations for several values of the distance between the leads. Until $d_{\text{lead}} = 12.5$ Å the transmission changes gradually with the distance. For a small $d_{\text{lead}}$ the maximum of $T(E)$ at the HOMO peak is smaller than unity ($T < 0.9$) and separated from $E_F$ by about 1.5 eV. With increase of $d_{\text{lead}}$,
the peak shifts towards $E_F$, and finally it splits into two peaks, where $T(E)$ is very close to unity. This behaviour resembles the corresponding one 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 an interatom hopping), the two peak structure merges into a single peak, which decreases with further increase of the coupling. This suggests that the transmission of BDT can be partly understood in terms of the two-atom model, in which the internal 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.

![Graph](image)

**FIG. 4**: Transmission as the function of energy for $V = 0$ for variable distance between the leads: $d_{\text{lead}} = 10 \, \text{Å}, 10.75 \, \text{Å}, 11.5 \, \text{Å},$ and $12 \, \text{Å}$ (the line thickness decreases with the distance). The broken line near $E = 0$ shows the transmission for $d_{\text{lead}} = 12.5 \, \text{Å}$, with the BDT molecule attached asymmetrically to one of the leads in the lowest energy configuration from the Figure 2(b).

As a result of the upward shift of the HOMO peak, the transmission at $E_F$ steadily increases with the distance between the leads from $T(E_F) \approx 0.05$ at $d_{\text{lead}} = 10 \, \text{Å}$ to $T(E_F) \approx 0.15$ at $d_{\text{lead}} = 12 \, \text{Å}$. When the distance crosses the critical value the central position of BDT molecule between the leads is no longer energetically favoured. The transmission in the asymmetric position is considerably smaller (see the broken curve in Figure 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 0.2 A for any voltage.

In relation to an experiment 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 bigger than 12.25 Å the current measured at some constant voltage would
suddenly drop. On the other hand, a large value of current observed for a bigger distance would suggest that a significant reorganisation of the junction takes place. In fact on the basis of the molecular dynamical simulation of Krüger et al. pulling of a string of Au atoms by a molecule chemisorbed to an Au(111) lead can be expected.

Finally the general comment is in order concerning the value of the computed current, which greatly overestimates the ones observed experimentally. So far this seems to be the common deficiency of all the DFT and Hartree-Fock based approaches, at least for a weak coupling or relatively small molecules. It remains to be seen if a full selfconsistent implementation of a better treatment of the electron correlation (e.g. SIC) 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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1 M. A. Reed C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, Science 278, 252 (1997).
2 R. L. McCreery, Chem. Mater. 16, 4477 (2004).
3 A. Nitzan and M. A. Ratner, Science 300, 1384 (2003).
4 S. H. Ke, H.U. Baranger, and W. Yang, J. Chem. Phys. 123, 114701 (2005).
5 H. Kondo, H. Kino, J. Nara, T. Ozaki, and T. Ohno, Phys. Rev. B 73, 235323 (2006).
6 A. Grigoriev, J. Sköldberg, G. Wendin, and Z. Crljen, Phys. Rev. B 74, 045401 (2006).
7 P. Ordejón, E. Artacho and J. M. Soler, Phys. Rev. B 53, R10441-R10443 (1996); J.M. Soler, E. Artacho, J.D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal J. Phys. Condens. Matter 14, 2745 (2002).
8 N. Troullier and J.L. Martins, Phys. Rev. B 43, 1993 (1991).
9 J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
10 A. R. Rocha, I V. M. García-Suárez, S. Bailey, C. Lambert, J. Ferrer, and S. Sanvito, Phys. Rev. B 73, 085414 (2006).
11 Y. Xue and M. A. Ratner, Phys. Rev. B 68, 115406 (2003).
12 T. Kostyrko, J. Phys. Condens. Matter 14, 4393 (2002).

13 D. Krüger, H. Fuchs, R. Rousseau, D. Marx, and M. Parrinello, Phys. Rev. Lett. 89, 186402 (2002).

14 T. Shimazaki, Y. Xue, M.A. Ratner, and K. Yamashita, J. Chem. Phys. 124, 114708 (2006).

15 C. Toher, A. Filippetti, S. Sanvito, and K. Burke, Phys. Rev. Lett. 95, 146402 (2005).