Electronic transport through benzene molecule: effect of gold contacts

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Abstract

As an example of a simple molecular device, we study electronic transport through a benzene molecule attached to two gold electrodes via sulfur clips. The conductance characteristics of the device is derived for two different atomistic models of the gold contacts: A chain model and part of Au(111) surface. The results show that the conductance characteristics strongly depends on the model used for the electrodes, therefore this factor should be taken into consideration while comparing different theoretical/experimental results.

Key words: Quantum transport; molecular devices; organic conductors

1. Introduction

Current trend of the miniaturization of electronic devices has resulted in intensive interest in molecular devices, which basically consist of a group of a few atoms, in contrast to the previous 'bulk' materials. The reason is that molecular devices possess two main characters which are important for probable applications: They are self-assembled and rather abundant.

As the molecules which are to be used as the main functional part of the device are typically a few angstroms in size, a natural question arises here, namely when these small building blocks are attached to the electrodes, how would their main characters of interest depend on the actual arrangement of the atoms in the electrode. This is an issue of concern for both experimentalists and theoreticians: In experiments, it should be known that which surface in general, and which part of the surface in particular, are more suited for to be used as the electrode. As for the theoretical calculations, it should be known that what model should be used in the description of the electrodes.

It is the purpose of the present study to investigate the above-mentioned issues for a typical case of a simple organic molecule, i.e., benzene, attached to two gold electrodes via sulfur clips.

2. Model and method

As the molecular part of the device, a benzene-1,4-dithiolate is considered. The sulfur atoms act like clips for attaching the benzene molecule to the gold contacts. As for the specific atomic arrangements of the gold contacts, we consider two different cases: In the first case a simple chain arrangement of the gold atoms is considered. In the second case, a particular arrangement of the gold atoms corresponding to part of an Au(111) substrate is considered. These two atomic configurations, together with the organic molecule, are depicted in Fig. 1.

We use *ab initio* modelling to describe the system, from which the Hamiltonian of the system is deduced. Moreover, as we use a non-orthogonal basis, the overlap matrix is also needed for our study. Using the Hamiltonian and the overlap matrices corresponding to the gold contacts, the surface Green's functions describing

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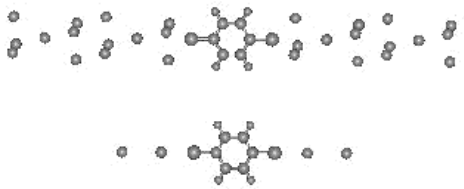

Fig. 1. Two different arrangements of the first two unit cells of the gold electrodes attached to the organic molecule used in our study: Top: the atomic arrangement extracted form the Au(111) surface. Bottom: simple chain arrangement of the gold electrodes, with inter-atomic distances set to 3 Å.

the two semi-infinite electrodes attached to the left and right of the molecule are derived. These surface Geen's functions, together with the Hamiltonian and overlap of the molecule, as well as the Hamiltonian and overlap of the molecule-electrode part, are then used in order to determine the conductance of the system [1–3]. More explicitly, the Green's function of the organic molecule including the effects of the two semi-infinite electrodes is given by:

$$G_{\rm OM} = (ES_{\rm OM} - H_{\rm OM} - \Sigma_1 - \Sigma_2)^{-1}, \quad (1)$$

where $G_{\rm OM}$ is the Green's function of the organic molecule attached to the electrodes, $H_{\rm OM}$ and $S_{\rm OM}$ are the Hamiltonian and overlap matrices of the organic molecule, and $\Sigma_{1(2)}$ indicate the surface terms that describe the effects of the gold contacts. The conductance of the system (in units of $2e^2/h$) is then determined using

$$\Gamma(E) = {\rm Tr}(\Gamma_2 G_{\rm OM} \Gamma_1 G^{\dagger}_{\rm OM}), \quad (2)$$

with

$$\Gamma_{1(2)} = {\rm i}(\Sigma_{1(2)} - \Sigma^{\dagger}_{1(2)}). \quad (3)$$

3. Results

The results of the calculations are depicted in Fig. 2. The Fermi energy of the whole system in equilibrium is assumed to be that of the semi-infinite gold electrodes. As is apparent from this figure, the conductance characteristics of the device strongly depend on the atomistic model used for the electrodes. As the configuration extracted from the Au(111) surface contains more gold atoms with closer inter-atomic distances, as compared to the chain gold electrodes, the band structure allows for more conducting channels at energies away from the Fermi energy. This is the reason for the higher conductance of this arrangement as compared to the conductance of the chain arrangement. The decisive dependence of the conductance on the actual atomic arrangement of the gold electrodes shows that although

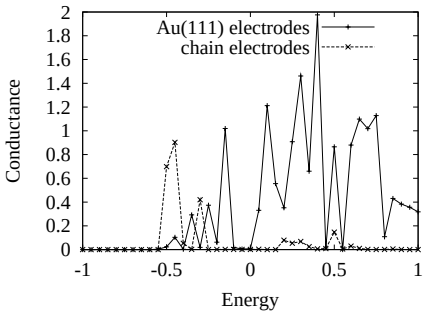

Fig. 2. Conductance (units of $2e^2/h$) vs energy for the two atomic arrangements of the gold electrodes.

the sulfur clips were thought to block the static charge transfer from the electrodes to the organic mlecule, the effects of the structure of the electrodes cannot be blocked by the sulfur clips.

Based on these results, we observe that the actual model used for the contacts of a molecular device plays an important role in transport calculations. This effect should be taken into account in order to be able to perform meaningful comparisons between different calculations/experiments based on the same organic molecule.

References

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