Effects of Gold Contacts on Transport through Benzene Molecule

A. A. Farajian*, R. V. Belosludov*, H. Mizuseki* and Y. Kawazoe*

* Institute for Materials Research,
Tohoku University, Sendai 980-8577, Japan, amir@imr.edu

ABSTRACT

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 depend on the model used for the electrodes, therefore this factor should be taken into consideration while comparing different theoretical/experimental results. The relevance of the accurate determination of the relative position of sulfur clips and surface gold atoms are clarified.

Keywords: molecular device, electronic transport, conductance, gold electrodes

1 INTRODUCTION

Individual molecules in general, and organic compounds in particular, have been assigned the possible role of the basic building blocks of the next generation of electronic devices, for quite some time. 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. Among others, we may mention two reasons for this attention toward devices based on individual molecules: They are self-assembled and rather abundant.

As the size of the molecules which are to be used as the main functional part of the device are typically a few angstroms, 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 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. Two different coupling regimes can be considered while studying transport through individual molecules attached to metallic (e.g., gold) contacts: weak and strong. In the weak coupling regime, the functional part of the device, i.e., the molecule, is separated from the electrodes by a 'spacer' which can be as small as the functional molecule itself. The role of the spacer is to screen the effect of the details of the electrode structure, such as surface roughness, so as to prevent them from influencing the main characters of interest of the device. In the strong coupling regime, on the other hand, the functional part of the device is usually attached to the electrodes via chemical bonds. This makes the coupling between the functional molecule and the atomic arrangement of the electrodes in the vicinity of the contact point strong enough to affect the transport characteristics of the device. In a sense, discarding the details of the spacer characters, one may correspond the weak coupling regime to physisorption, i.e., van der Waals coupling, while the strong coupling may be corresponded to chemical bonding.

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. Due to the presence of chemical bonds in attaching the functional part to the gold contacts, the coupling can be considered to be strong. As we shall see shortly, this strong coupling indeed results in the dependence of the transport characteristics, i.e., conductance, on the atomistic model of the electrodes.

2 *AB INITIO* MODEL

Taking nto account that in order to calculate transport properties, we need to know the description of the system in a localized basis, and considering the relatively small number of atoms involved in this study, we choose *ab initio* modeling for both the functional part of the device and the electrodes. As the functional 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

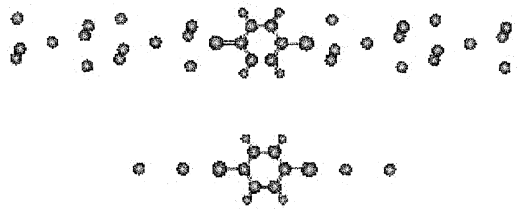

Figure 1: Two different arrangements of the first two unit cells of the gold electrodes attached to the organic molecule used in our study: Top: the atomic arrangement extracted form the Au(111) surface. Bottom: simple chain arrangement of the gold electrodes, with inter-atomic distances set to 3 Å.

atomic configurations, together with the organic molecule, are depicted in Fig. 1.

We use *ab initio* modeling 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. The necessary data corresponding to the Hamiltonian and overlap matrices are obtained using the Gaussian 98 program [1]. The basis set corresponds to choosing 13 vectors for Au (s&s&p&p&d), 5 vectors for C (s&sp), 4 vectors for S (s&p), and 1 vector for H (s).

3 TRANSPORT

In order to calculate transport properties, we adopt the Green's function approach, which is quite general and capable of handling a wide category of systems. In this general approach the system under consideration is devided into three parts: A semi-infinite part to the left, a finite part in the middle, and a semi-infinite part to the right. The semi-infinite parts resemble the 'leads' which are used to connect the middle finite part, i.e., functional part, to the external bias. Using the Hamiltonian and the overlap matrices corresponding to the gold contacts, the surface Green's functions describing 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 [2]–[4]. More explicitly, the Green's function of the organic molecule including the effects of the two semi-infinite electrodes is given by:

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

where G_{OM} is the Green's function of the organic molecule attached to the electrodes, H_{OM} and S_{OM} are the Hamiltonian and overlap matrices of the organic molecule, and $\Sigma_{1(2)}$ indicate the surface terms that describe

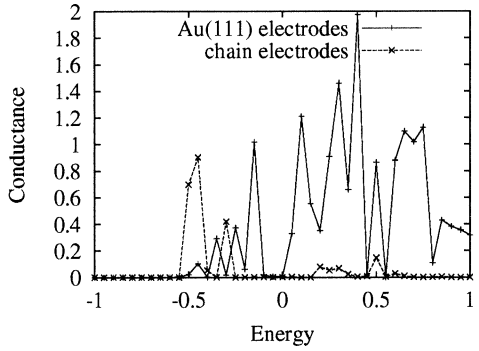

Figure 2: Conductance (units of $2e^2/h$) vs energy for the two atomic arrangements of the gold electrodes.

the effects of the gold contacts. The conductance of the system (in units of $2e^2/h$) is then determined using

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

with

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

In order to calculate the surface Green's functions $\Sigma_{1(2)}$, we make use of a recursive approach [5] which is suitable for calculating the right and left surface Green's functions, as well as that of the bulk.

4 RESULTS

In the strong coupling regime considered here, the atomistic model of gold contacts resemble the local environment in the vicinity of the position of the sulfur clips. The results of the calculations are depicted in Fig. 2. As is apparent from this figure, the conductance characteristics of the device strongly depend on the atomistic model used for the electrodes. More specifically, the inter-atomic distances within the gold electrodes, and the relative position of the gold atoms, that enter the transport calculation via the surface Green's function strongly affect the conductance characteristics. The decisive dependence of the conductance on the actual atomic arrangement of the gold electrodes shows that although 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.

5 CONCLUSIONS

In summary, we have investigated the effects of the gold-contact modeling in strong coupling with the funcional molecule part of the device. This resemble the atomic arrangement of the electrodes in the vicinity of the chemical bonds which attach the functional part to the conducting electrodes. We observe that the local configuration of the electrode atoms indeed influence the conductance characteristics of the molecular device.

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