Electronic conduction through organic molecules

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In this paper, we present a method for computing the resistance of molecular wires and illustrate it with a systematic theoretical study of a particular class of organic molecules. These molecules consist of one or more benzene rings with a thiol(-SH) group at the ends. This end group can attach readily to metallic surfaces, thus allowing the molecule to function as a nanoelectronic interconnect. The conduction through these molecules at low bias occurs by tunneling, leading to resistances that are typically several tens of megaohms. The resistance goes up exponentially with the number of rings and is sensitive to the relative orientation of the rings and the bonding between them. The Green-function-based method presented here provides a powerful tool for accurate modeling of the semi-infinite contacts that are used to measure molecular resistance.

I. INTRODUCTION

The use of molecules for signal transmission in nanostructured materials is an area of significant current interest.[1,2] The synthesis of potential "molecular wires," based on oligomeric structures of conjugated molecules,[2,3] is proceeding at a rapid pace. Electronic conduction through a variety of different molecules has been studied experimentally.[4−6] However, the factors that control the electronic transport in these molecules is not well understood. For example, it is not clear how the resistance is affected by the internal structure of the molecule or by the nature of its coupling to the contacts used for measurement.

The purpose of this paper is to provide a general theoretical formulation that can be used to investigate these questions. We illustrate this with a systematic theoretical study of the resistance of a particular class of conjugated molecules as measured between a pair of gold contacts (see Fig. 1). These molecules consist of a chain of one or more parasubstituted benzene rings terminated by thiol(-SH) groups. This end group can attach readily to metal surfaces[7,8] allowing the molecule to function as a nanoelectronic interconnect. We show that the resistance of the molecule (a) increases exponentially with the number of benzene rings and (b) depends sensitively on the relative orientation of the rings and the bonding between them.

Our approach is based on the Landauer formula,[9,10]

$$R = \frac{h/2e^2}{T(E_f)} = \frac{12.9 \text{ k}\Omega}{T(E_f)}, \quad (1)$$

where $T(E_f)$ is the transmission function from one contact to another. This approach implicitly neglects inelastic scattering processes. However, in view of the strong coupling between the electrons and "phonons" (i.e., the molecular modes of vibration) this assumption may not be accurate. The theoretical model presented here is intended to provide a first-order estimate that can be compared with experimental data. The results can then be used to guide further refinement of the model. Also, the linear resistance given by Eq. (1) should be adequate as long as the voltage drop across the molecule is small in this energy scale.

A central factor in determining the resistance of molecular interconnects is the location of the Fermi energy of the metallic contact relative to the energy levels of the molecule. All the molecules we will be considering have a set of occupied levels separated by a gap of 2–3 eV from a set of unoccupied levels (Fig. 2). Clearly the resistance could be quite low if the Fermi level were to align with one of the
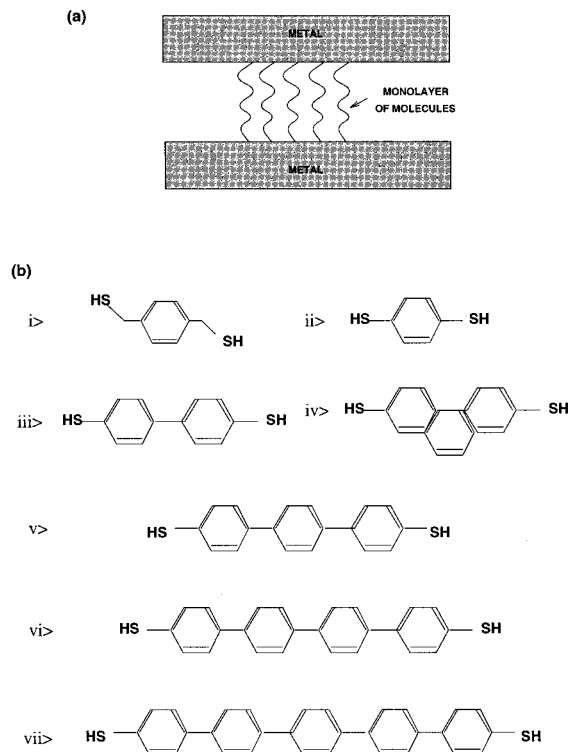

FIG. 1. (a) Model system with molecular "wires" connected to two metallic contacts. (b) Chemical structure of typical molecular "wires."
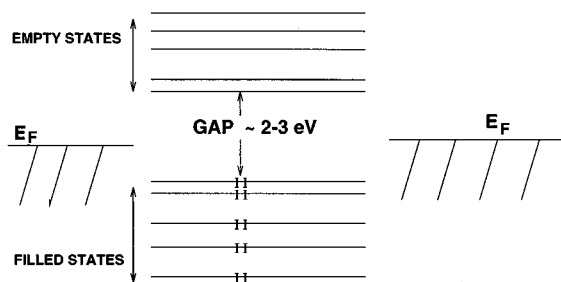
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FIG. 2. Schematic diagram showing the molecular energy levels and the Fermi level in the contacts.
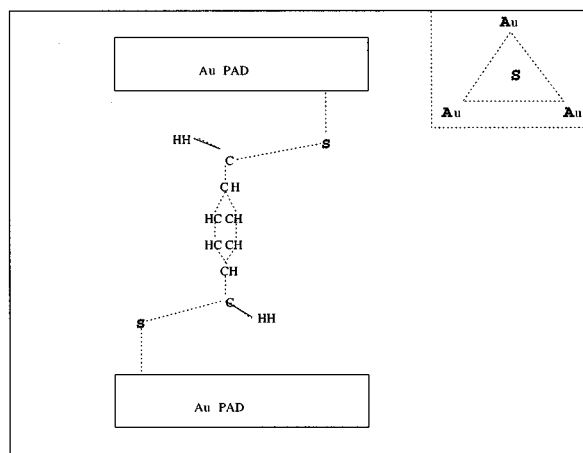

FIG. 3. Chemical structure of xylyl dithiol connecting two gold pads. [Inset shows the position of the S atom with respect to gold atoms on the (111) surface.]

energy levels of the molecule (either occupied or unoccupied). However, it seems fairly certain that under normal circumstances this will never be the case; the Fermi level will lie in the gap regardless of the nature of the molecule or the metal. This is exactly what one finds with metal-semiconductor contacts.[11] The Fermi energy always lies close to the charge neutrality level near the center of the gap; otherwise there would be too much excess charge in the semiconductor. One would expect a similar picture to hold for the metal-molecule contact as well.

This observation leads us to believe that conduction through the molecule will generally involve tunneling rather than propagation, at least at low voltages (with much less than ~ 1 V being dropped across the molecule). From this point of view we can estimate the transmission through a molecule of length L with an energy gap E_g as $T \sim e^{-2\sqrt{mE_g}L/\hbar}$, so that from Eq. (1) we can write resistance as

$$R \sim (12.9 \text{ k}\Omega) e^{0.7245\sqrt{E_g(eV)}L(A)}, \tag{2}$$

which for $E_g = 2$ eV yields $R \sim 2.1$ MΩ if $L = 5A$ and $R \sim 363$ MΩ if $L = 10A$. Equation (2) is of course far too simplistic to be taken seriously, but it does give an idea of the order of magnitude of the resistance that we can expect.

II. COMPUTATION OF TRANSMISSION FUNCTION OF THE MOLECULE

For a more accurate evaluation of the transmission function, we use the Green-function-based method described in Refs. 9 and 12. We generalize it to handle the nonorthogonal basis functions commonly used to describe the molecular orbitals. Our method is essentially equivalent to the scattering approach used[5,13] to model scanning tunneling microscopy studies of different surfaces and molecules. However, we feel that the Green-function method is more powerful and versatile in handling the open boundary condition associated with the semi-infinite contacts.

The Green function is given by

$$G = (ES - H - \Sigma_1 - \Sigma_2)^{-1}, \tag{3}$$

where H is the molecular Hamiltonian matrix and S is the overlap matrix (which would be equal to the identity matrix for orthogonal basis states). Σ_1 and Σ_2 are the self-energies resulting from the coupling of the molecule to the gold pads 1 and 2. These are given by

$$\Sigma_1 = \tau_1^\dagger g_1 \tau_1 \quad \text{and} \quad \Sigma_2 = \tau_2^\dagger g_2 \tau_2, \tag{4}$$

where τ_1 and τ_2 are matrices describing the coupling between the molecule and the gold, while g_1 and g_2 are the Green functions for the isolated gold pads. Once we have evaluated $[G]$ from Eq. (3), we can obtain the transmission function,[14]

$$T(E) = \text{Tr}[A_1 M A_2 M^\dagger]. \tag{5}$$

In Eq. (5), M is an effective matrix element given by $M = \tau_1 G \tau_2^\dagger$. A_1 and A_2 are the spectral functions for the isolated gold pads related to the respective Green functions by the relation $A = i(g - g^\dagger)$.

The calculation of the spectral functions A_1 and A_2 is relatively complicated and time consuming if we properly take into account all the s, p, and d levels that contribute to the band structure of gold.[15,16] However, one advantage of this method is that these functions are unaffected by the molecule. Consequently, A_1 and A_2 can be calculated once and for all, stored, and reused for different molecules.

III. RESULTS

We have used this formalism to compute the resistance of xylyl-dithiol [Fig. 1(b),(i)] connected between two gold (111) pads (Fig. 3). We assume there is no interaction between neighboring molecules, so that the resistance of N molecules in parallel is simply $(1/N)$ times that of a single molecule. The values quoted here correspond to a single molecule. This molecule has eight hydrogen atoms, eight carbon atoms, and two sulfur atoms. In our calculation we include $1s$ orbital for hydrogen, the $2s2p$ orbitals for carbon, and $3s3p3d$ orbitals for sulfur giving a (nonorthogonal) basis set of 58 orbitals describing the molecule. The structure of the molecule is obtained using a molecular mechanics method (HyperChem) (Ref. 17) and the 58×58 matrices (H) and (S) are obtained from the extended Hückel method.[18] The "-S" group at the end of the molecule is placed on top of the center of three gold atoms on the surface as shown in Fig. 3 with a sulfur to gold distance 1.905 Å.[8] For each gold atom we include nine orbitals ($5d6s6p$). The 9×58 cou-
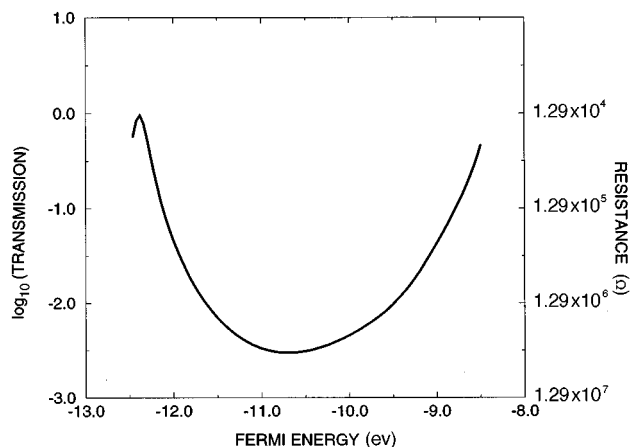
FIG. 4. Transmission function (and resistance) of xylyl dithiol vs Fermi energy in the contact. Log scale in the plot represents decimal log.

pling matrices (τ_1) and (τ_2) for each gold atom are obtained from the extended Hückel method.

Figure 4 shows the transmission function (on a logarithmic scale) vs position of the Fermi energy calculated from Eq. (5). The resistance at midgap is about 4 MΩ, in reasonable agreement with the experimentally reported value of 9 MΩ.[6] In view of the approximate nature of the extended Huckel parameters, this can be considered a fairly good agreement. Better accuracy could be achieved with sophisticated *ab initio* programs and might be desirable for accurate calculations once the basic physics has been clearly identified and understood.

From the simple reasoning leading to Eq. (2), we would

FIG. 6. Transmission function (and resistance) vs Fermi energy for molecules with successive benzene rings misaligned by different angles θ. As θ increases from 0° to 90°, transmission goes down (resistance goes up) due to decrease in overlap between the π orbitals in the rings. Log scale in the plot represents decimal log.

expect that for similar molecules with different chain lengths, the resistance should increase exponentially with length, if the band gap remains constant. Our detailed calculations for the set of molecules shown in Fig. 5 are consistent with this expectation.[19]
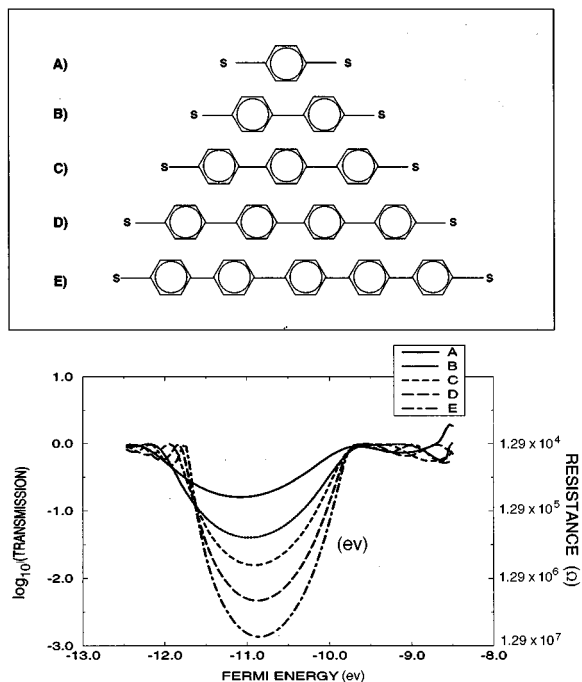

FIG. 5. Transmission function (and resistance) vs Fermi energy for molecules with different numbers of benzene rings. Transmission goes down exponentially (resistance goes up) as the number of benzene rings is increased. Log scale in the plot represents decimal log.
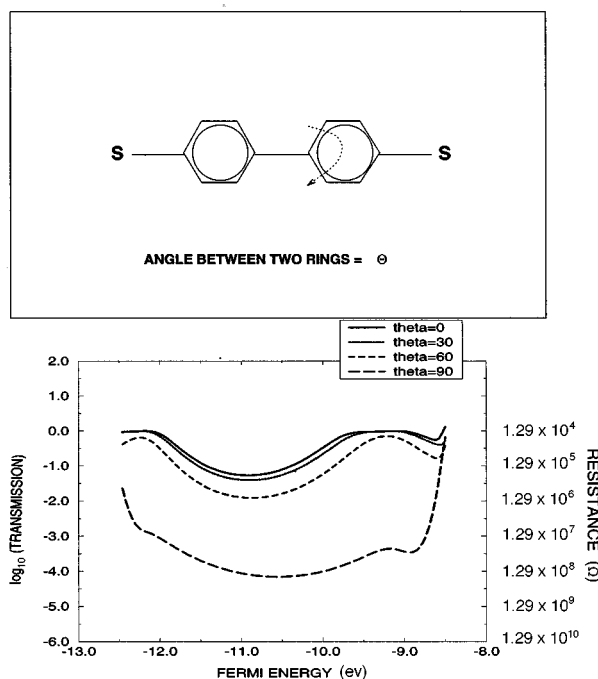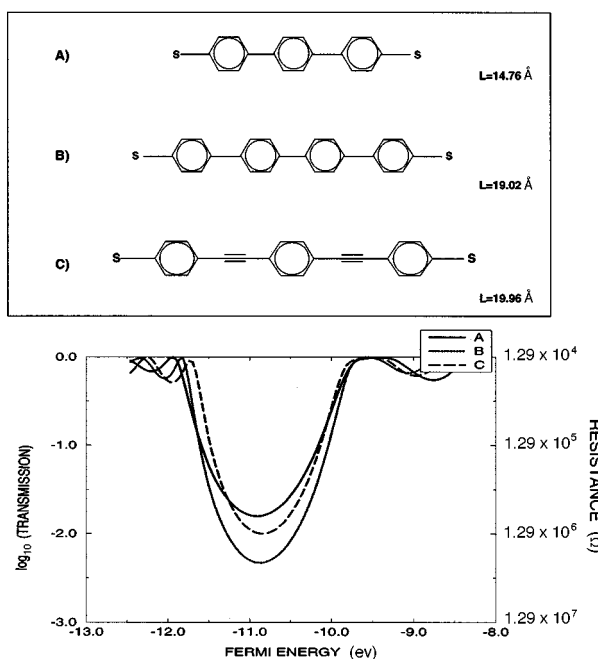

FIG. 7. Transmission function (and resistance) vs Fermi energy for a molecule with triple bonds (C) compared to molecules without triple bonds (A and B) shown earlier in Fig 5. Although C is longer than both A and B, its resistance is intermediate between them. Log scale in the plot represents decimal log.

Organic molecules are typically not very rigid. The bonds can flex and bend, thus changing the overlap between different orbitals. In order to assess the effect of such bending on the resistance, we have studied a set of similar molecules with different bond orientations (Fig. 6). Using our method we can easily show that the π orbitals are responsible for most of the current through these molecules. When two benzene rings in the molecule are in the same plane, the π orbitals have maximum overlap leading to lowest resistance. On the other hand, complete misalignment between the rings leads to highest resistance. The actual measured conductance of a molecule should correspond to an appropriate statistical average of different configurations. An even more complete study should also consider the other modes of vibrations of a molecule in the calculation.

By effectively tailoring the internal structure of the chain, it is possible to control the resistance of the molecule. In Fig. 7 we have considered a molecule C with a slightly different structure than those considered so far. This molecule has triple bonds in between the benzene rings. Although molecule C is longer than molecule B, it has a lower resistance because of the presence of triple bonds in the chain. The energy gaps of these two molecules are almost the same, so that we would not have expected this result from a naive application of Eq. (2).

In summary, we have presented a powerful computational method that can be used to calculate the resistance of molecules, taking proper account of the detailed electronic structure of the contact pads.

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[17] HyperChem™ Release 3 for Windows, Molecular Modeling System : © Hypercube, Inc. and Autodesk, Inc.

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