First-Principles Calculation of Transport Properties of a Molecular Device

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We report first-principles calculations of the current-voltage (I-V) characteristics of a molecular device and compare with experiment. We find that the shape of the I-V curve is largely determined by the electronic structure of the molecule, while the presence of single atoms at the molecule-electrode interface play a key role in determining the absolute value of the current. The results show that such simulations would be useful for the design of future microelectronic devices for which the Boltzmann-equation approach is no longer applicable.

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Conventional Si-based microelectronics is likely to reach its limit of miniaturization in the next 10–15 years when feature lengths shrink below 100 nm. The main problem is the onset of quantum phenomena, e.g., tunneling, that would make scaled-down conventional devices inoperable. Successor technologies currently under development, such as tunneling field-effect transistors and single-electron transistors, are in fact based on quantum phenomena. For the ultimate miniaturization below nm, devices made from single molecules are currently attracting attention. Prototypes have already been fabricated. Reed *et al.* [1] reported I-V characteristics of single benzene-1,4-dithiolate molecules. Alivisatos and co-workers [2] reported similar I-V characteristics of semiconductor and metal nanoclusters between gold electrodes. Dekker and co-workers [3] reported transistorlike behavior in carbon nanotubes. Similar devices have been demonstrated by Avouris and co-workers using single-walled and multiwalled carbon nanotubes [4].

Theoretical modeling played a key role in the invention of the transistor and in the subsequent development of integrated circuits. Device modeling continues to provide indispensable input to circuit modeling for designing logic and memory chips and microprocessors. It is based on a “semiclassical approximation” that treats electrons and holes as classical particles, except that their kinetic energies are determined by the semiconductor energy bands, most commonly in the effective-mass approximation. In this scheme, transport is governed by Boltzmann’s equation. Most industrial modeling is done in the drift-diffusion approximation, to a lesser extent in the higher-order hydrodynamic approximation, and, at times, by solving Boltzmann’s equation directly by Monte Carlo techniques [5]. *For nanodevices, however, when quantum phenomena are dominant, the semiclassical Boltzmann’s equation does not apply.* Quantum mechanical simulations are needed. So far, only semiempirical approaches have been employed to investigate transport in molecular systems, providing useful insights into the fundamental mechanisms [6–9].

In this Letter we report first-principles calculations of the I-V characteristics of a molecule. In this method, the electrostatic potentials through the molecule and at the contacts are calculated self-consistently without empirical adjustments. We report calculations for the benzene-1,4-dithiolate molecule for which experimental data are available [1]. We find that, when the molecule is placed between two electrodes made of an ideal metal (homogeneous electron gas or jellium model [10]), the shape of the I-V characteristic is determined by the electronic structure of the molecule in contact with the electrodes and in the presence of the external electric field. The shape is essentially the same as that of the experimental curve. The absolute magnitude of the current, however, is more than 2 orders of magnitude larger than the experimental values. We investigated the origins of this discrepancy and found that insertion of a single gold atom at each metal-molecule contact, as suggested by the experimental setup, leaves the shape of the I-V characteristic globally unchanged, but reduces the absolute value of the current by more than an order of magnitude, reflecting reduced coupling between the s states of the gold and the p orbitals of the molecule, in the directions parallel to the electrode surfaces. Replacement of the single gold atoms by aluminum atoms, which have p_z orbitals in the relevant energy region, raises the value of the current by about 1 order of magnitude. Other factors that can affect the absolute value of the current are discussed later in this paper. These results show that such calculations can provide valuable quantitative information to help design molecular devices.

We begin with the study of the I-V characteristic of a single benzene-1,4-dithiol molecule between two ideal metallic contacts. It is well known that when the benzene-1,4-dithiol molecule is adsorbed on gold surfaces the H of the thiol terminations desorbs and the sulfur atoms at each end bond strongly to the Au(111) surfaces [11]. The remaining molecule (benzene-1,4-dithiolate) is then simply the one represented in Fig. 1, where we show the contour plot of the electronic density in the benzene ring plane. We

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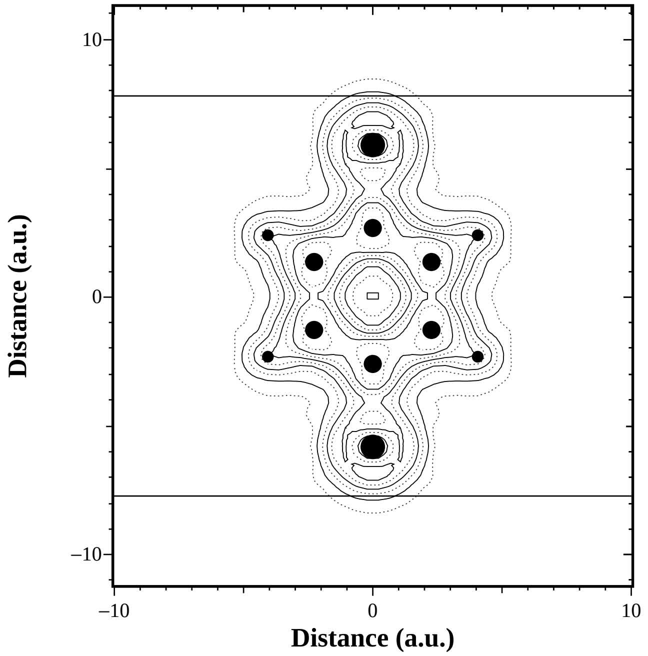

FIG. 1. Contour plot of the electron density of the molecule described in the text. The dots represent the positions of the atoms. The lines represent the position of the model metal surfaces.

assume that the molecule stands perpendicular to the metal surfaces. The molecule has π bonding and π^* antibonding orbitals formed by the carbon and sulfur p orbitals perpendicular to the ring plane and σ bonds due to the in-plane orbitals of the atoms.

We computed the I-V characteristic using the method developed in Ref. [12]. The electron density of the jellium electrodes is taken equal to the value for metallic gold ($r_s \approx 3$). The electron wave functions are computed by solving the Lippman-Schwinger equation iteratively to self-consistency in steady state. Exchange and correlation are included in the density-functional formalism within the local-density approximation [13]. All atomic positions are kept fixed at their equilibrium values in the free molecule. The current is computed from the wave functions of the electrode-molecule system. The differential conductance is then calculated as the derivative of the current with respect to the external bias. Small variations in the atomic positions (of the order of 0.1 Å) change the current by less than 1%.

The calculated I-V characteristic is shown in the bottom panel of Fig. 2. The experimental curve is also shown for comparison in Fig. 2. It is clear that the shapes of the two curves are similar, but the absolute magnitude of the current and conductance is quite different. We will first discuss the origins of the shape and then address the question of absolute values.

We focus on three distinct regions in the calculated conductance curve: the initial rise (from zero bias to about 1 V), the first peak at 2.4 V, and the second peak at 4.4 V.

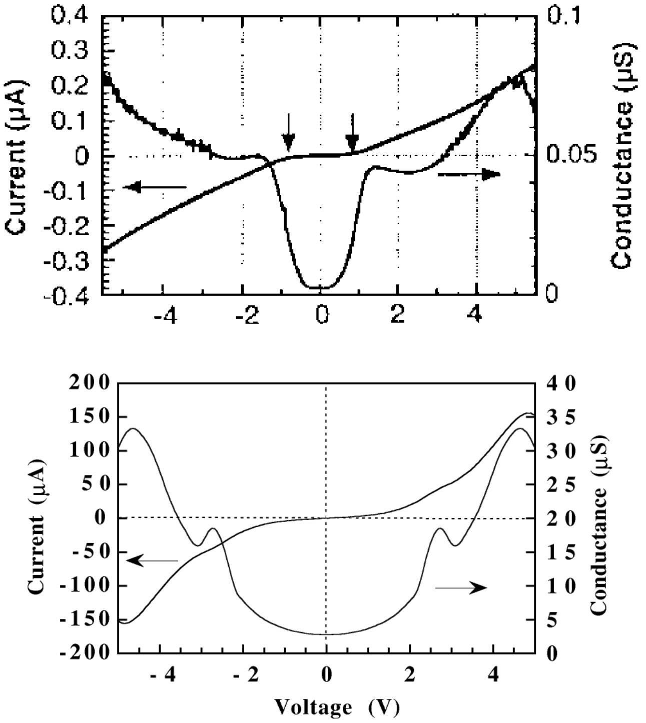

FIG. 2. Top: Experimental I-V characteristic of a benzene-1,4-dithiolate molecule measured by Reed *et al.* [1]. Bottom: Conductance of the molecule of Fig. 1 as a function of the external bias applied to the metallic contacts.

In Fig. 3 we show the calculated density of states of the molecule for three different voltages, namely, 0.01, 2.4, and 4.4 V (the density of states shown is the difference between that of the molecule-electrode system and that of the electrodes without the molecule). The zero of energy is the left Fermi level so that the right Fermi level is equal

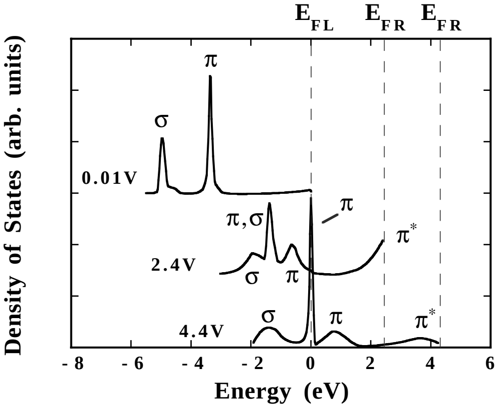

FIG. 3. Difference between the density of states of the two semi-infinite electrodes with and without the benzene-1,4-dithiolate molecule in between, for three different voltages. The left Fermi level (E_{FL}) has been chosen as the zero of energy. The labels E_{FR} correspond to the energy position of the right Fermi levels. The three curves correspond to the bias voltages indicated.

to the external bias (in Fig. 3 the labels E_{FR} correspond to the 2.4 and 4.4 V values of the bias).

The initial slow rise of the conductance, which is also present in the experimental data, represents basically Ohmic behavior. Figure 3 (top curve) shows that the molecule has a small but relatively smooth density of states through which current can flow. The σ and π bonding states lie several eV below the Fermi energy so that a considerable bias is needed to produce nonlinear behavior.

After the initial increase of the current with increasing bias, a first conductance peak and subsequent valley are observed. This is also observed experimentally, though at somewhat lower voltages and with a smaller peak-to-valley ratio. The peak and the valley are due to *resonant tunneling* through π^* *antibonding* states, which are the first to appear in the window of energy between the right and left Fermi levels (see Fig. 3, middle curve). Inclusion of the vibrational coupling would smear out the peak and generate a lower peak-to-valley ratio in the I-V characteristic, bringing closer the agreement between theory and experiment. Note also that the bonding σ and π states are altered significantly by the bias simply because the different atoms of the benzene ring are at different potentials.

Increasing the bias further, a second I-V peak is found due to resonant tunneling with π *bonding* states. From Fig. 3 it is evident that the π^* antibonding states are still present in the energy region between the right and left Fermi levels but with a lower peak ratio with respect to the π bonding states. The discrepancy between the theoretical and experimental peak positions is consistent with known limitations of the local-density approximation [14].

The different scattering processes that occur for different biases can be studied in more detail by looking at the local density of states along the direction of current flow. The local density of states integrated between the left and right Fermi levels for small bias is plotted in Fig. 4(A). As in the case of the total density of states, we plot here the difference between the local density of states of the molecule-electrode system and that of the electrodes without the molecule. It is evident that the sulfur-to-metal contact has a very low density of states, in effect constituting a barrier through which electrons must tunnel. After tunneling through this barrier, the electrons encounter a region of relatively smooth, higher density of states corresponding to the states of the molecule. For biases in the neighborhood of 2.5 V [Fig. 4(B)], the electrons find a much larger density of states originating from the π^* antibonding states of the molecule (resonant tunneling condition). The antibonding region is between the middle carbons of the molecule. Finally, with a further increase of the bias, to the range of 5 V, resonant tunneling occurs through bonding states of the molecule [see Fig. 4(C)].

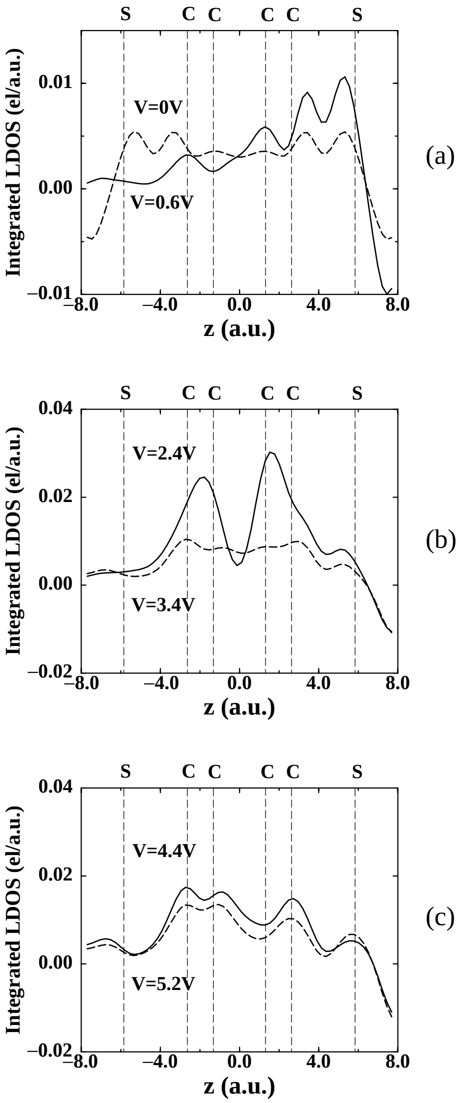

FIG. 4. Local density of states difference between that of the molecule-electrode system and that of the electrodes without the molecule, integrated between left and right Fermi levels. Voltage region (A) corresponds to the linear response regime. Region (B) corresponds to the first resonant tunneling. Region (C) corresponds to the second resonant tunneling bias conditions.

We now turn to the absolute value of the current which differs by more than 2 orders of magnitude from the experimental value. We attribute part of this discrepancy to the contact geometry and chemistry. The experiment by Reed *et al.* [1] suggests that the contacts are atomically terminated, which means that the sulfur atoms are attached to *single* Au atoms. We investigated the effect of such a possibility on the I-V characteristic by introducing a single gold atom between the sulfur and the model metal surface at each contact. The shape of the I-V characteristic (Fig. 5) remains essentially the same, but the absolute value of the conductance *decreases* by almost 2 orders of magnitude. This reduction is partly due to the constriction resistance generated by the *geometry* of the contact and partly due to the *chemistry* of the contact between the gold and the sulfur atoms. The Au atoms contribute s states at the Fermi level while the sulfur atoms that attach to them

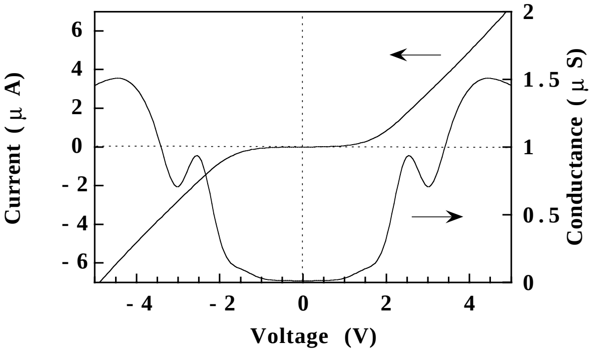

FIG. 5. Conductance of the molecule of Fig. 1 with one Au atom between the model metal surface and the sulfur for each contact as a function of the external bias applied to the metallic contacts.

contribute *p* states. Only the *p* states that are perpendicular to the electrode surfaces can couple, by symmetry, to the *s* states of the gold atoms, forming σ bonds. The *p* states of the sulfur atoms that are parallel to the metal surfaces do not couple to the gold *s* states, thus breaking the π scattering channel that connects the electrode to the main benzene ring. The gain in resistance is thus mainly due to the type of contacts. This conclusion is confirmed by a calculation where the single gold atoms at the contacts are replaced by aluminum atoms. For a bias of 0.01 V the resistance changes from 96 to 2.9 MΩ. The Al atoms can now contribute with *p* orbitals at the Fermi level that are parallel to the electrode surface and form π states with the *p* orbitals of the sulfur atoms similarly oriented. Finally, we performed a test calculation by positioning the S atom in front of the center of a triangular pad of three gold atoms on each electrode surface. This simulates a S atom on top of a Au(111) surface. The calculated resistance is nearly the same as the one for the sulfur attached to the model metal. The reason for this is that the *s* states of each Au atom in the pad form a state of *s* symmetry and two states of *p* symmetry parallel to the surface of the electrodes that can couple to the corresponding sulfur *p* state.

The above calculations show that the absolute magnitude of the current is an extremely sensitive function of the contact geometry and chemistry. For the case at hand, the discrepancy with experiment is still about an order of magnitude. There are of course additional effects that can alter the value of the current, such as temperature (hot electrons and vibrational coupling) or local disorder in the Au metal near the contacts that can produce electron localization [15]. The latter effect may arise from the breaking of the gold wire when contacts to the molecule are made [1]. We further note that the experimental measurements have an uncertainty of at least a factor of 2 [1]. Additional theoretical and experimental work is clearly needed to further clarify these issues.

In conclusion, we have simulated from first-principles the *I*-*V* characteristics of a molecular device and found that the atomic-scale contact geometry and chemistry play a critical role in the absolute value of the conductance. This result sheds new light on the transport properties of molecular devices and shows that such calculations would be useful in designing devices and engineering contacts for future nanotechnology.

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