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Electronic transport in single molecules

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Abstract

We present a review of recent results on the non-linear transport properties of single molecules using density-functional theory. In particular, we investigate the role of contact chemistry and geometry, current-induced forces, and polarization effects induced by a gate field on the current–voltage characteristics of molecules for which experiments are available. The results show that single molecules, if appropriately tailored, have physical properties that could be useful in electronic applications. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Using molecules or molecular wires as elements in electrical circuits is an appealing idea: molecules can have feature lengths smaller than 1 nm, so if we could assemble them onto a chip, as we do today with common transistors, we would gain orders of magnitude in integration levels. The idea was suggested more than two decades ago [1] but it is only recently that measurements of current–voltage (*I*–*V*) characteristics of molecular wires have been feasible [2–4]. The goal is to identify and synthesize molecules with specific conducting properties. In this respect, basic non-linear characteristics suitable for use in circuits have been already demonstrated [2–4]. Despite such demonstrations, however, we still lack a fundamental understanding of the basic mechanisms of the non-linear transport properties of molecular wires. If we reached such understanding, it would be possible to guide future experiments and reduce costly and time consuming trial-and-error procedures. For instance, molecules need to be connected to electron reservoirs in order to function as electrical conductors. However, unlike in mesoscopic samples, in molecular devices the contact region has feature lengths of the same order of magnitude as the sample. The atoms that bridge the molecules and the reservoirs can thus play an equally important role in the electron transport as the mol-

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ecules. We show in this paper that the contact chemistry and geometry can modify considerably the value of the current in molecular wires. This is an interesting result in view of the fact that, so far, molecular devices with conductances close to the quantum of conductance ($2e^2/h$) have not been realized in practice. Contact engineering is thus a promising avenue to design highly conducting molecular devices.

Another important issue in molecular electronics is the role of current-induced forces and their ability to weaken and break chemical bonds. The phenomenon of current-induced atom motion (also referred to as electromigration in the case of electron scattering off defects in solids) is still an important problem in microelectronics: the choice of the material making up the interconnects in silicon-based circuits is also dictated by the ability of the material to resist electromigration effects at large fields and current densities. Since molecular wires of nominal length 1 nm have been demonstrated to operate at voltages larger than 5 V (i.e., under a field larger than 5×10^7 V/cm), the question arises as to whether current-induced forces produce large structural transformations of the molecular wires and what is the resistance of molecular devices to electromigration effects. Referring to a prototype molecular device that has been recently investigated experimentally we show that (i) current-induced forces induce small structural transformations in this device and that, (ii) the shape of the I–V curve and the absolute value of the current are practically unchanged even for very large fields. At these high fields, these molecules can carry current densities larger than 10^9 A/cm^2. These results thus suggest that molecular devices are more resistant to electromigration than common metallization lines.

The most important element in electrical circuits is by far the field-effect transistor. The present authors have recently suggested that a single benzene-1,4-dithiolate molecule connected to external leads, and capacitatively to a gate field, can, in principle, show current modulation by field effect [5]. Very recently, Schön and coworkers [6–8] have realized a similar device by sandwiching self-assembled monolayers of thiol molecules between gold electrodes horizontally stacked next to vertical silicon gates. The gate field has to modulate the current flowing through the molecular wire and this modulation has to be done at reasonable field values. Since in these systems the modulation occurs by changing the relative position of the molecule–electrode states with respect to the right and left Fermi levels, the key ingredients in obtaining electric current modulation are the matrix elements of the field operator on all states. We show in this paper that, in systems with states that have zero dipole moment, the current modulation occurs via the anti-bonding states that enter in resonance with the Fermi levels. At resonant tunneling, conductances of the order of ($2e^2/h$) are found. However, since current modulation is induced by a second-order Stark effect, fields of the order of 1 V/Å are required to obtain modulation. This suggests that molecules with non-zero inversion symmetry with respect to the gate field direction could experience current modulation at much smaller fields [9].

The paper is organized as follows: in Section 2 we describe the theoretical method used to calculate the non-linear transport properties of molecular wires. In Section 3 we discuss the role of contact chemistry and geometry, and in Section 4 electromigration effects. Finally, in Section 5 we report results on the modulation effects induced by a gate field.

2. Theoretical method

Semiempirical methods for the calculation of current in small structures placed between two metal electrodes have been developed over the years [10]. For instance, semiempirical tight-binding models have been remarkably successful to provide a useful account of the linear transport properties of molecules and nanotubes [10]. On the other hand, charge redistribution in the molecules and at the contacts is an important issue to understand, for example, the role of current-induced forces or non-linear effects. In the case of current-induced forces, we will show in Section 4 that angular-dependent forces arise in molecular wires which are difficult to describe within a tight-binding approach. Also, local charge neutrality, often invoked in the tight-binding approximation is not strictly satisfied at very small biases, let alone in the non-linear regime. In this case a set of first-principles approaches is necessary.

We present in this section a parameter-free first-principles method to calculate the electronic and ionic dynamics under current flow based on density-functional theory [11]. To illustrate the method, we refer to Fig. 1 as an example of a typical system investigated. It consists of a molecule (or equivalently any set of atoms) between two bulk electrodes which are kept at a certain potential difference. The sample is part of an external circuit which, in first approximation is assumed to have zero impedance. Electrons are assumed to travel (say) from the right electrode without scattering until they reach a region in space close to the sample region (the molecule). Since the details of the electrodes are not important up to the interface with the sample, we represent them using a uniform-background (jellium) model [12,13]. The interface atoms and the molecule atoms are represented within a pseudopotential framework [14]. In previous work [16] we have shown that, in the case of gold electrodes, the jellium model correctly represents the scattering properties of molecular structures making contact with a flat surface. For other types of substrates the use of jellium is not a limitation either: the extra resistance between the jellium and the interface atoms, if any, can be easily determined, since it makes up for the difference between the current with and without the extra interface layers. The transport properties of the molecule are computed by means of the Lippmann–Schwinger equation [12,13]. Initially one calculates single-particle wavefunctions and self-consistent electron densities for the bare metallic electrodes in the presence of the bias within a density-functional formalism [12,13]. Then, the Lippmann–Schwinger equation is solved to obtain the steady-state self-consistent electron density and one-electron wave functions in the whole system, consisting of the molecule and the electrodes, which are maintained at distinct values of the electrostatic potential corresponding to the external voltages. The Lippmann–Schwinger equation to be solved is

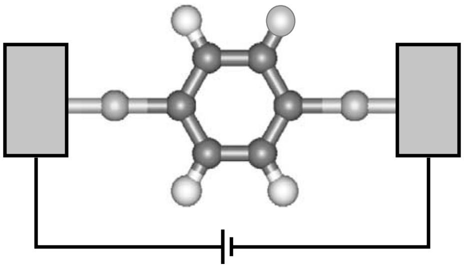

Fig. 1. Schematic of a benzene molecule connected to gold electrodes via sulfur atoms.

$$\Psi_{E\mathbf{K}_\parallel}(\mathbf{r}) = \Psi^0_{E\mathbf{K}_\parallel}(\mathbf{r}) + \int \mathrm{d}^3\mathbf{r}'\,\mathrm{d}^3\mathbf{r}''\,G^0_E(\mathbf{r},\mathbf{r}') \times V(\mathbf{r}'\mathbf{r}'')\Psi_{E\mathbf{K}_\parallel}(\mathbf{r}''), \tag{1}$$

where $\Psi_{E\mathbf{K}_\parallel}$ and $\Psi^0_{E\mathbf{K}_\parallel}$ refer to the wavefunctions of the complete system and to the pair of bare biased metal electrodes, respectively. $\mathbf{K}_\parallel$ is the component of the momentum parallel to the electrode surfaces and G^0_E is Green's function of the bare biased metal electrodes. The latter is evaluated with the standard definition involving the lesser and the greater functions [12,13]. $V(\mathbf{r}'\mathbf{r}'')$ is the scattering potential (in atomic units)

$$V(\mathbf{r},\mathbf{r}') = v_{\mathrm{ps}}(\mathbf{r},\mathbf{r}') + \left[v_{\mathrm{xc}}(n(\mathbf{r})) - v_{\mathrm{xc}}(n^0(\mathbf{r})) + \int \mathrm{d}^3\mathbf{r}''\,\frac{\delta n(\mathbf{r}'')}{|\mathbf{r}-\mathbf{r}''|}\right]\delta(\mathbf{r}-\mathbf{r}'). \tag{2}$$

The term $v_{\mathrm{ps}}(\mathbf{r},\mathbf{r}')$ is the sum of the non-local pseudopotentials representing the atomic cores of the interface atoms and the molecule, $v_{\mathrm{xc}}(n(\mathbf{r}))$ is the exchange-correlation functional, $n^0(\mathbf{r})$ is the electron density for the pair of biased metal electrodes, $n(\mathbf{r})$ is the corresponding quantity for the total system, and $\delta n(\mathbf{r})$ is their difference. The exchange-correlation potential is assumed to be the one for electrons in the ground state, and we represent it in the local-density approximation [11]. The wavefunctions of the bare electrodes satisfy usual scattering boundary conditions. The self-consistent procedure starts with an initial guess for the electronic densities (e.g., atomic densities) which are used to calculate the potential V. The bound states Ψ_i, if any, are calculated by direct diagonalization of the total Hamiltonian. The new wavefunctions $\Psi_{E\mathbf{K}_\parallel}(\mathbf{r})$ and Ψ_i are then used to compute the new density, and the process is iterated until self-consistency is achieved in the density and/or potential V. All quantities are evaluated over a box in real space large enough to include the region where the potential is perturbed by the presence of the atoms. Finally, with the above self-consistent wavefunctions we calculate the electric current density

$$\mathbf{j}(\mathbf{r}) = -2\int_{E_{FL}}^{E_{FR}} \mathrm{d}E \int \mathrm{d}^2\mathbf{K}_\parallel \mathrm{Im}\Big\{[\Psi_{E\mathbf{K}_\parallel}(\mathbf{r})]^* \nabla \Psi_{E\mathbf{K}_\parallel}(\mathbf{r})\Big\}. \tag{3}$$

The equivalent quantity $\mathbf{j}^0$ for just the pair of biased electrodes is calculated. The total current of interest to us is

$$\delta J = \int \mathrm{d}^2\mathbf{R}\hat{z}\cdot[\mathbf{j}(\mathbf{r}) - \mathbf{j}^0] \tag{4}$$

which is a finite quantity independent of z. The vector $\hat{z}$ is the unit vector pointing towards the positive direction of the axis and perpendicular to the surfaces of the electrodes.

Once the self-consistent solution of the transport problem has been obtained at a given geometry, current-induced relaxation effects are taken into account by calculating forces according to the Hellmann–Feynman-like theorem developed by Di Ventra and Pantelides [15]. Its general formulation is as follows: let us consider the sample and the two electrodes. As described above, each of these systems can be treated separately by density-functional theory. In the total Hamiltonian only the potential V depends on the position of the atoms. For each energy E in the continuum we build square-integrable wavefunctions $\Psi_{E\mathbf{K}_\parallel\Delta}$ in an energy region $E < E' < E + \Delta$

$$\Psi_{E\mathbf{K}_\parallel\Delta} = A\int_E^{E+\Delta} \mathrm{d}E' \Psi_{E'\mathbf{K}_\parallel}, \tag{5}$$

where A is a normalization constant and the Ψ_Es are the continuum wavefunction solutions of the Lippmann–Schwinger equation (1). The force $\mathbf{F}$ acting on a given atom at position $\mathbf{R}_0$ due to the electron distribution as modified by the external bias can be shown to be [15]

$$\mathbf{F} = \sum_i \left\langle \Psi_i \left| \frac{\partial H}{\partial \mathbf{R}_0} \right| \Psi_i \right\rangle + \lim_{\Delta\to 0}\int_\sigma \mathrm{d}E \times \int \mathrm{d}^2\mathbf{K}_\parallel \left\langle \Psi_{E\mathbf{K}_\parallel\Delta} \left| \frac{\partial H}{\partial \mathbf{R}_0} \right| \Psi_{E\mathbf{K}_\parallel\Delta} \right\rangle. \tag{6}$$

The sum and integral in Eq. (6) include spin variables also and σ is the part of the continuous spectrum occupied by the electrons at a given bias. For convenience, we choose plane waves to represent the Hilbert space. In this case, Pulay-like terms in the forces are identically zero [15]. Starting from a given atomic configuration (e.g., the atoms at the equilibrium experimental atomic positions for the molecule and interface atoms), we calculate the forces acting on each atom. We then move the atoms according to the gradient of these forces until the force on each atom is zero (generally lower than a defined precision).

The method of calculation and more details of the results can be found in [12,13,15–18].

3. The role of contact chemistry and geometry

We discuss in this section transport across a single molecule sandwiched between two bulk electrodes. Different contact configurations are investigated to obtain information on the role of contact chemistry and geometry on the electronic transport. We study the benzene-1,4-dithiolate molecule that has been investigated experimentally (see Fig. 1) [2]. The experimental I–V characteristic of such molecular device is shown in the top panel of Fig. 2 as measured by Reed et al. [2]. Due to the lack of any specific experimental information, we assume that a single molecule makes contact to both the right and left leads as shown in Fig. 1, even though this configuration might not be the actual experimental one [19].

The contact geometry is not known a priori, so we assume, to begin with, that the S atoms of the benzene-1,4-dithiolate molecule make contact with a flat surface (assuming a (1 1 1) gold surface where the sulfur atom makes contact with three gold atoms – see below). In the lower panel of Fig. 2 we report the theoretical results for this contact geometry. It is clear from Fig. 2 that the shape of the

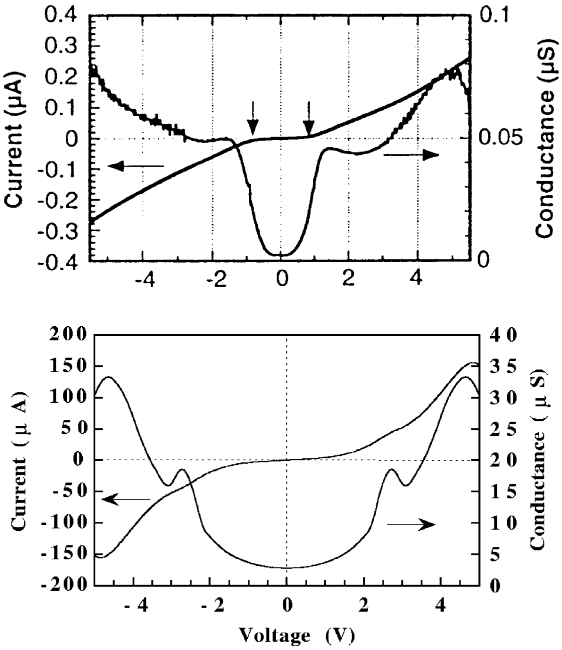

Fig. 2. Top panel: experimental *I–V* characteristics of the benzene-1,4-dithiolate molecule [2]. Bottom panel: theoretical *I–V* characteristics of the molecule of Fig. 1 [16]. (Reproduced with permission from reference [16]. Copyright 2000 American Physical Society.)

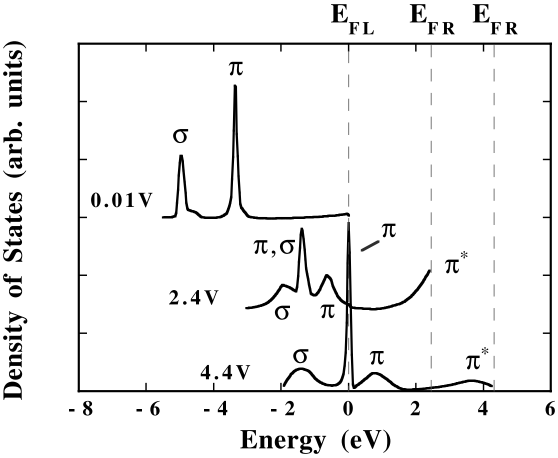

Fig. 3. Difference between the density of states of the two semi-infinite electrodes with and without the benzene-1,4-dithiolate molecule in between, for three different voltages. The left Fermi level EFL has been chosen as the zero of energy. The labels EFR correspond to the energy position of the right Fermi levels. The three curves correspond to the bias voltages indicated. (Reproduced with permission from reference [16]. Copyright 2000 American Physical Society.)

I–V curve is reproduced quite well, but the absolute magnitude of the current is off by more than two orders of magnitude. It is worth noting here that recent experiments by Schön et al. on single benzene-1,4-dithiolate molecules show a remarkable agreement with our theoretical results in both the shape of the *I–V* curve *and* absolute value of the current [8]. We first discuss the origin of the shape of the *I–V* curve, and then address the issue related to the absolute value of the current. In Fig. 3 we show the density of states of the molecule for three different bias voltages: 0.01, 2.4 and 4.4 V. The density of states for the 0.01 V case above the right quasi-Fermi level is shown in Fig. 8. We also indicate the energy window between the left and right quasi-Fermi levels where electronic transport occurs. We see that there is virtually no density of states in the small energy window at small voltages: the molecule behaves like a large resistor at these voltages. The π^* states are closer to the Fermi levels than the π states, in agreement with the transfer of about $0.1e$ from the electrodes to the molecule. At about 2.4 V, the π^* anti-bonding states of the molecule enter the energy window for transport and give rise to the first peak in the conductance spectrum. At about 4.4 V, even though the π^* states continue to participate to transport, the π bonding states of the molecule enter the energy window for transport with relatively larger density of states, and generate the second peak in the conductance. At both 2.4 and 4.4 V, the molecule thus behaves as a resonant-tunneling device.

Several effects can be responsible for the difference in the value of the current between theory and experiment. We discuss here the effects due to the contacts and in the next section the ones due to current-induced forces. In order to explore the mechanism that controls the absolute magnitude of the current we performed calculations by inserting an extra gold atom between the sulfur atom and the macroscopic electrode (the single gold atom assumed to face the hollow site of a (1 1 1) surface) at each end of the molecule. This study was motivated by the fact that the molecular device investigated has been realized experimentally using break–junction contacts which are generally assumed to be atomically terminated [2]. We found a dramatic decrease in the current with the sulfur atoms attached to single gold atoms, bringing the theoretical value much closer to the experimental one (see Fig. 4). The decrease is attributed to the fact that gold atoms have only s orbitals available for transport at the Fermi level. However, the gold s orbitals do not couple with the p orbitals of the sulfur atom parallel to the metal surface, while those perpendicular to the metal surface form σ bonds with the gold s orbitals. The latter bonds are, however, located at a much lower energy than the Fermi level, and, therefore, do not contribute directly to transport. The single-gold-atom–sulfur bond thus forms an additional barrier for electrons to tunnel from the electrodes into the molecule. The idea is appealing, since it provides a way to engineer molecular devices by selectively choosing the correct geometry and chemistry of the molecule–lead contacts. To further test this idea we performed calculations by replacing the single gold atoms at each contact with aluminum atoms. The latter have p electrons that should couple well with the p electrons of the molecule. Indeed, the current increases by about an order of magnitude with aluminum atoms replacing the gold atoms. An additional test was carried out with each sulfur atom in front of the center of a triangular pad of three gold atoms on each electrode surface. The current is again at its full value because the three s orbitals on the three gold atoms can form enough linear combinations to produce sufficient coupling [16]. It is clear from the above that molecules determine the shape of the *I–V* characteristic, but the nature of individual atoms at the molecule–electrode contact determines the absolute magnitude of the current. Further work has to be done to address the remaining difference in the absolute value of the current between theory and experiment (still about an order of magnitude). This difference is certainly not due to current-induced forces (see following section) but it could be due to temperature effects, electron–electron scattering or even a different structural configuration of the device involving transport across several interacting molecules [19].

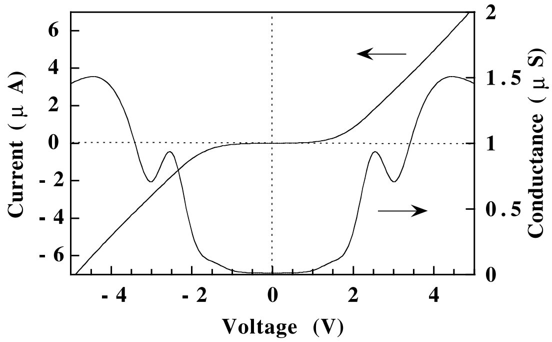

Fig. 4. Conductance of the molecule of Fig. 1 with one Au atom between the metal surface and the sulfur for each contact as a function of the external bias applied to the metallic contacts. (Reproduced with permission from reference [16]. Copyright 2000 American Physical Society.)

We conclude this section by briefly discussing the effect of different anchoring groups on the transport properties of molecular devices. It was suggested by Yaliraki et al. [20] that molecules with Se anchoring groups show a larger conductance than molecules with S (by a factor of 25). On the other hand, density-functional calculations without the inclusion of an external bias have suggested that S provides the best (in terms of conductance) contact [21]. We find, in agreement with Yaliraki et al. [20], that Se contacts provide a larger conductance than S contacts (even though by only a factor of three). The increase in conductance is due to a charge transfer from the molecule to the electrodes that brings the HOMO level close to the Fermi levels. This study confirms the importance of determining self-consistently the local field produced by the electrons upon scattering [13].

4. How much current can a molecular wire sustain?

Assuming that the current in the molecular device discussed above flows mainly across a typical surface of 10×10 Å^2 [22], then such device carries current densities larger than 10^7 Å/cm^2. The theoretical predictions show current-carrying capacities of one or two orders of magnitude larger. Similar values of current densities have been observed in nanotubes [23]. In normal metals such large current densities produce substantial current-induced displacement of atoms leading to break-up of electric circuits [24]. Such an effect is more pronounced the smaller the material dimensions as, e.g., in the case of metallization lines in conventional circuits. The question thus arises as to whether molecular wires undergo structural transformations under current flow and how much current they can sustain before break-up. We addressed this issue by studying the effect of current-induced forces on the two-terminal molecular device depicted in Fig. 1 using the Hellmann–Feynman-like theorem discussed in Section 2. For each external bias we calculated the current-induced forces on each atom and relaxed the atomic positions until the force on each atom was negligible [18]. We find that current flow has essentially two effects on the atomic structure: (i) the structure at 0 V has been found to be unstable under current flow: with increasing bias, the mirror symmetry with respect to a plane perpendicular to both the benzene ring plane and the surface of the electrodes can be easily broken, leading to a twisting of the molecule around the axis perpendicular to its plane, (ii) the molecule expands at the bias for which the first resonant tunneling condition occurs, then contracts at about 2.8 V corresponding to approximately the valley of Fig. 2, lower panel. The first effect increases with increasing bias even though the global current is not substantially altered. The second effect is due to the depletion of charge between the central C atoms at the first resonance peak due to resonant tunneling into anti-bonding states. The charge is again recovered in the central C bonds when the resonant-tunneling condition is lost and the molecule contracts back to nearly its original bond-length distances. This "breathing" effect as a function of bias is not observed at the second peak bias because resonant tunneling in that case is mainly due to π bonding orbitals. Apart from these structural transformations, however, current-induced forces do not substantially affect the absolute value of the current up to biases as high as 5 V, i.e., fields as high as 5×10^7 V/cm (see Fig. 5). At external voltages larger than 5 V, the contact that is depleted of electrons during current flow weakens considerably with a consequent dramatic reduction of the current. This suggests that molecular wires can operate at very large fields without current-induced breakdown. Also, the molecular device at hand can carry current densities larger than 10^9 A/cm^2, i.e., much larger than those allowed in conventional interconnects. Since, on the other hand, atomic gold wires have been found to break at biases of 1–2 V [25] we deduce that the origin of this resistance to electromigration can be attributed to the strong C–C bonds of the carbon-based molecule. Similar conclusions have been reached in the case of nanotubes, where the strength of the carbon sp^2 bonds has been invoked to justify the large resistance to electromigration in these systems [24]. Further details on the effect of current-induced forces can be found in [18].

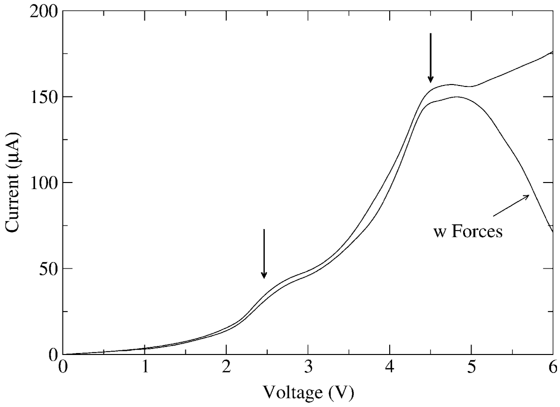

Fig. 5. Theoretical *I–V* curve of the molecular structure of Fig. 1 with and without the effect of current-induced forces. The vertical arrows indicate the onset of resonant tunneling via anti-bonding (at ~ 2.4 V) and bonding (at ~ 4.4 V) states. (Reproduced with permission from [18]. Copyright 2002 American Physical Society.)

5. Molecular transistors

Since field-effect transistors are the most important elements in present electronics, it would be desirable to realize similar devices using single molecules. Schön et al. [6–8] have realized prototype molecular transistors using self-assembled monolayers of thiol molecules between gold electrodes horizontally stacked next to vertical silicon gates. We investigate in this section a mechanism that could lead to field-effect modulation of the

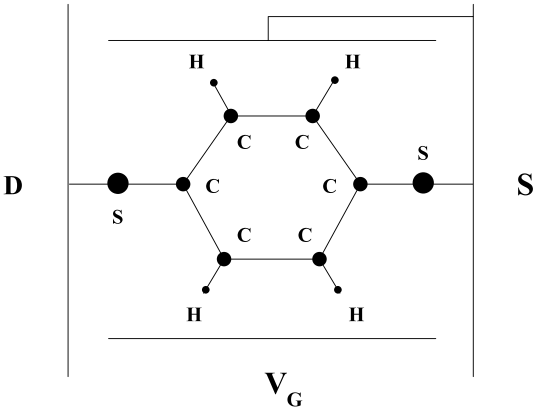

Fig. 6. Scheme of the three-terminal geometry used in the present study. The molecule is sandwiched between source and drain electrodes along the direction of electronic transport. The gate electrodes are placed perpendicular to the molecule plane. (Reproduced with permission from [5]. Copyright 2000 American Institute of Physics.)

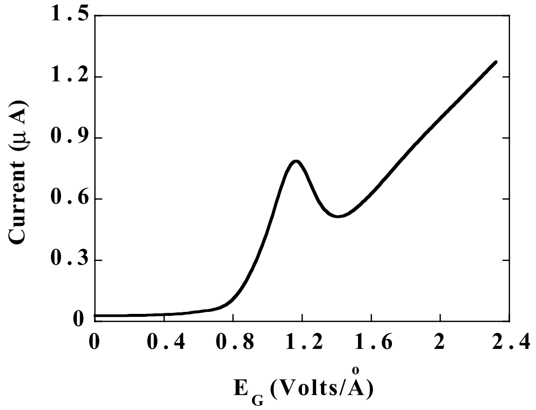

Fig. 7. Conductance of the molecule of Fig. 6 as a function of the external gate field. (Reproduced with permission from [5]. Copyright 2000 American Institute of Physics.)

current via a gate field in a molecular resonant-tunneling device [5]. In particular, we want to identify the main properties a molecular structure needs to have in order to show current modulation at low gate fields. To this aim, a third terminal is introduced in the form of a capacitor field generated by two circular charged disks at a certain distance from each other placed perpendicular to the transport direction. The disks are kept at a certain potential difference, with one of the two disks at the same potential energy as the source Fermi level (see Fig. 6). As a prototype device we investigate the benzene-1,4-dithiolate molecule investigated in the two previous sections. The axis of the cylindrical capacitor is on the plane of the benzene ring. Since in practical realizations of this device the gate could be of different form and size we discuss the results in terms of the applied gate field along the axis of the capacitor. The calculated *I–V* characteristic as a function of the gate bias is shown in Fig. 7. The source–drain voltage difference has been fixed at 10 mV. We observe an increase of the current with the gate field, after a region of nearly constant current. The current reaches a maximum value at 1.1 V/Å, then decreases till about 1.5 V/Å, to increase further afterwards linearly. The different features of the *I–V* curve can be understood by looking at the density of states for different gate voltages. The initial slow rise of the conductance represents basically ohmic behavior. It is also observed experimentally for the two-terminal geometry. The top curve of Fig. 8 shows the small density of states through which current can flow. The s and p bonding states are several eV below the Fermi levels while the π^* antibonding states are nearly 1 eV above the Fermi levels. A peak and subsequent valley in the current–voltage characteristic are observed at about

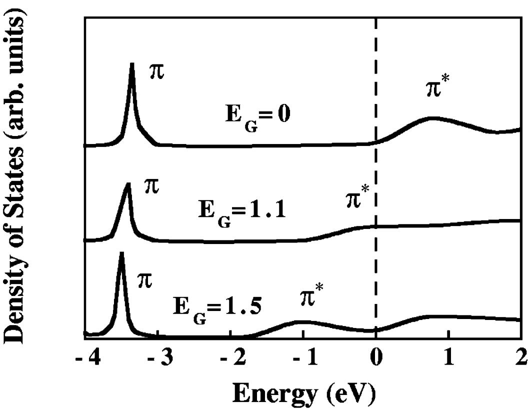

Fig. 8. Difference between the density of states of the two semi-infinite electrodes with and without the benzene-1,4-dithiolate molecule in between, for three different gate voltages. The left Fermi level has been chosen as the zero of energy. (Reproduced with permission from [5]. Copyright 2000 American Institute of Physics.)

1.1 V/Å. From Fig. 8 (middle curve) it is evident that the peak and the valley are due to resonant tunneling through π^* anti-bonding states. The anti-bonding states shift in energy with increasing gate bias, and eventually enter into resonance with the states between the right and left Fermi levels, separated by 10 meV (see Fig. 8). The π states are less affected by the gate bias than the π^* states due to a lower density of continuum states in their proximity. Therefore the gap between the π states and π^* states decreases about 1 eV at resonance. Increasing the bias further (bottom curve of Fig. 8), the resonant-tunneling condition is lost and a valley in the *I–V* characteristic is observed. Finally, as the gate bias is increased further the current starts to increase with the gate bias.

The value of the gate field at which resonant tunneling occurs (≈ 1 V/Å) seems slightly high for a molecule of nominal length of 8 Å. We have seen in the previous section, however, that molecular wires can sustain very large current densities and very large fields. On the other hand, for practical applications, current modulation at smaller fields is desirable. We suggest that this can be achieved by breaking the inversion symmetry of the molecule with respect to the gate field direction. In this case states with non-zero dipole moment appear that can have energy position close to the Fermi levels and shift with the gate field via a linear Stark effect [9]. At a fixed gate field, the larger the dipole moment the larger is the shift of the state to lower energy values. Molecular structures that could, in principle, show large dipole moments, and thus current modulation at relatively low gate fields, are the ones investigated by Chen et al. [4] (see also [17]) where a single H atom of the benzene-1,4-dithiolate molecules is replaced by an NO_2 ligand.

6. Conclusions

Controlling transport properties in nanoscale structures "by design" is the ultimate goal of the technology that will use molecules as electronic components. The calculations summarized above show that molecular wires, if appropriately tailored, can have physical properties that could be used in electric circuits. Among these properties, important ones are: (1) the possibility to vary considerably the absolute value of the current via contact engineering, (2) large resistance of molecular wires to electromigration, and (3) current modulation via a gate field. These calculations, based on density-functional theory, are thus seen to be extremely valuable in guiding and complementing experimental efforts in the development of Molecular Electronics.

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