Electronic Transport in Molecular Devices from First Principles

M. Di Ventra[1], N.D. Lang[2] and S.T. Pantelides[3]

[1]Virginia Polytechnic Institute and State University,
Blacksburg, VA, 24061, diventra@vt.edu
[2]IBM Research Division, Thomas J. Watson Research Center,
Yorktown Heights, New York, LANG@watson.ibm.com
[3]Vanderbilt University, Nashville, TN 37235, pantelides@vanderbilt.edu

ABSTRACT

We present an overview of recent work by the authors in first-principles calculations of electronic transport in molecules for which experimental results are available. We find that the shape of the current-voltage characteristics is mostly determined by the electronic structure of the molecules in the presence of the external voltage whereas the absolute magnitude of the current is determined by the chemistry of individual atoms at the contacts. A three-terminal device has been modeled, showing gain. Current-induced forces have been found to induce collective oscillations of the benzene-1,4-dithiolate molecule at resonant-tunneling condition. Finally, recent data that show large negative differential resistance and a peak that shifts substantially as a function of temperature have been accounted for.

Keywords: Transport; first-principles calculations; molecular devices; resonant tunneling.

INTRODUCTION

Silicon-based microelectronics is reaching the level of miniaturization where quantum phenomena such as tunneling cannot be avoided and the control of doping in ultrasmall regions becomes problematical. Though it is likely that silicon-based technology will simply move to a different paradigm and continue taking advantage of the existing vast infrastructure and manufacturing capabilities, novel and alternative approaches may give new insights and ultimately may usher a new era in nanoelectronics. Molecules as individual active devices are obvious candidates for the ultimate ultrasmall components in nanoelectronics. Though the idea has been around for more than two decades, only recently measurements of current-voltage characteristics of individual molecules have been feasible.

Methods for the calculation of current in small structures placed between two metal electrodes have been developed over the years, but actual implementations have been scarce. For molecules, semiempirical methods have been used to study the dependence of current on various aspects of the problem, but quantitative predictions for direct comparison with data are not possible because values of parameters under current conditions cannot be determined independently.

In the 1980's, one of us (NDL) developed a practical method to calculate transport in the context of imaging atoms with scanning tunneling microscopy. The method has all the ingredients needed to compute current-voltage (I-V) characteristics of single molecules. [1] Recently, two of us (MDV and STP) developed a suitable Hellmann-Feynman theorem for the calculation of current-induced forces on atoms that allows studying the effect of current on atomic relaxations and ultimately the breakdown of molecules. [2] With these tools, we have carried out extensive studies of transport in molecules whose core is a single benzene ring. Such molecules have been synthesized and measured by Reed and coworkers. [3] In this paper we summarize the most important results of the recent work. The method of calculation and more details of the results can be found in the original papers.

1 TRANSPORT IN A SINGLE BENZENE RING

Fig. 1 shows a schematic of a benzene ring making contact to macroscopic gold electrodes via sulfur atoms at each end. The corresponding experimental I-V characteristic is shown in the top panel of Fig. 2. The middle panel of the same figure shows the theoretical results. We will discuss the third panel shortly.

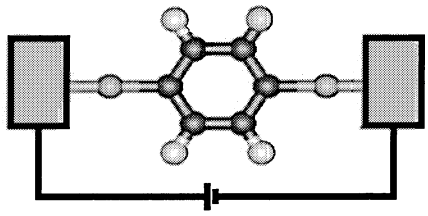

Figure 1: Schematic of a benzene molecule connected to gold electrodes via sulfur atoms.

It is clear from figure 2 that the shape of the I-V curve is reproduced quite well, but the absolute magnitude of the

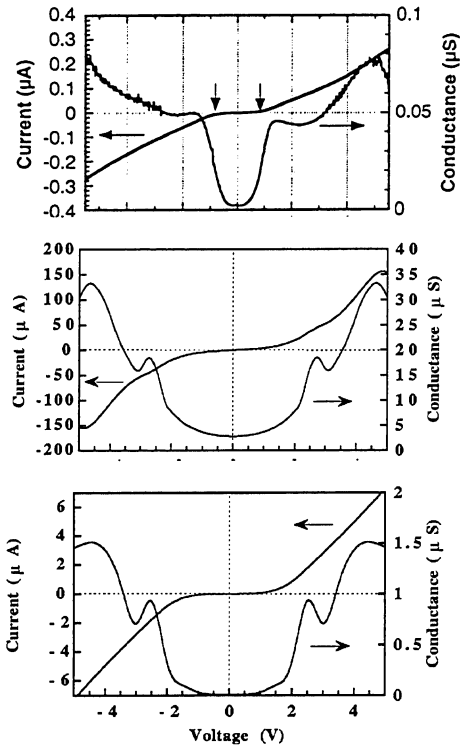

Figure 2: Top panel: experimental I-V characteristics of the benzene-1,4-dithiolate molecule (Ref. [3]). Middle panel: theoretical I-V characteristics of the molecule of Fig. 1. Bottom panel: theoretical I-V characteristics of the molecule of Fig. 1 with one extra gold atom between S and gold electrode at each end (Ref. [4]).

current is off by more than two orders of magnitude. We address each of these issues separately.

In Fig. 3 we show the density of states of the molecule for three different voltages: 0.01 V, 2.4 V and 4.4 V and mark out the energy window between the left and right quasi Fermi levels. States within this window contribute to transport. We see that there is virtually no density of states in the small window at small voltages, in agreement with the slow initial rise of I-V curve. At 2.4 V, the π^* states of the molecule enter the transport window and give rise to the first peak in the spectrum. At 4.4 V, the π states of the molecule enter the window while π^* continue to participate, giving rise to the second peak in the spectrum. The peak at 2.4 V is somewhat more pronounced in the theoretical curve. The observed smoothing is likely to be caused by interactions between the electrons and vibrational modes.

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 at each end of the molecule. There was a dramatic decrease in the current, bringing its value much closer to the experimental value (see bottom panel of Fig. 2). The decrease is attributed to the fact that gold atoms have only one *s* electron available for transport and *s* electrons do not couple with the π electrons of the molecule, thus breaking the channel for electronic transport. To test the idea we performed calculations by replacing the gold atoms with aluminum atoms.

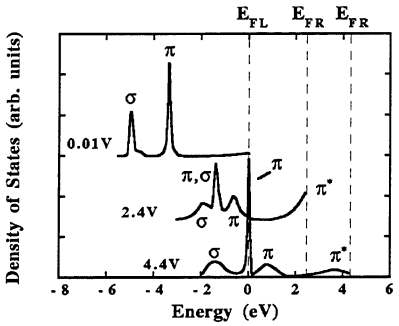

Figure 3: Difference between the density of states of the two semi-infinite electrodes with and without the benzene-1,4-dithiolate molecule in between, for three different voltages. The left Fermi level E_{FL} has been chosen as the zero of energy. The labels E_{FR} correspond to the energy position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

The latter have *p* electrons that should couple well with the *p* electrons of the molecule. Indeed, the current increased by about an order of magnitude. An additional test was carried out with three gold atoms instead of a single gold atom. The current was again at its full value because the three *s* orbitals on the three gold atoms can form enough linear combinations to produce sufficient coupling.

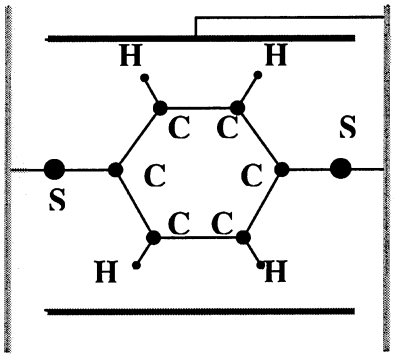

Figure 4: Scheme of the three-terminal geometry used in the present study. The molecule is sandwiched between source and drain electrodes along the direction of electronic transport. The gate electrodes are placed perpendicular to the molecule plane.

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. The results illustrate the power of theory to contribute to device design, especially "contact engineering".

Computational Nanoscience 2001, (www.cr.org), ISBN 0-9708275-3-9.

2 THREE-TERMINAL DEVICES

We investigate now the effects of a polarization field in the direction perpendicular to the current flow. [5] To do this, 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. 4). 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 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. 5.

The source-drain voltage difference has been fixed at 10 mV. After a region of nearly constant current, the current increases with the gate field, 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. [3] Fig. 6 (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 are several eV below the Fermi levels while the π^* antibonding states are nearly 1 eV above the Fermi levels.

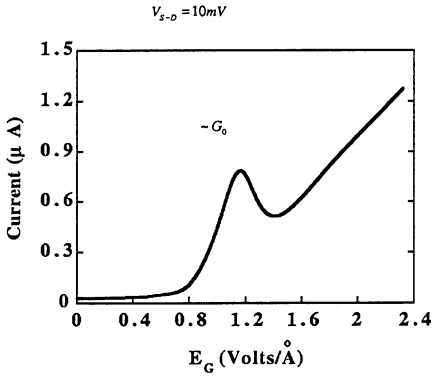

Figure 5: Conductance of the molecule of Fig. 4 as a function of the external gate field.

After the initial increase of the current with increasing gate bias, a first conductance peak and subsequent valley are observed. The peak and the valley are due to resonant tunneling through π^* antibonding states. The antibonding states thus shift in energy and eventually enter into resonance with the states between the right and left Fermi levels, separated by 10 meV (middle curve of Fig. 6). The gap between the π and π^* states decreases about 1 eV at resonance. Increasing the bias further (bottom curve of Fig. 6), 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 peak-to-valley ratio of the present system is however 1.4, that is probably so small that it would be washed out by the vibrational coupling with the modes of the molecule and leads. This has already been argued in the two-terminal geometry case [4]: the peak-to-valley ratios observed experimentally in the present system for the two-terminal geometry are considerably smaller than theoretically predicted (see discussion above).

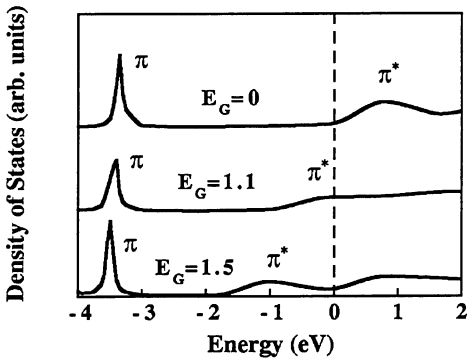

Figure 6: Difference between the density of states of the two semi-infinite electrodes with and without the benzene-1,4-dithiolate molecule in between, for three different gate voltages. The left Fermi level has been chosen as the zero of energy.

The value of the gate field at which resonant tunneling occurs (1V/Å) seems slightly high for a molecule of nominal length of 8 Å. Two observations are however in order: i) we have previously shown [4] that the theoretical peak of transmission due to antibonding states occurs at higher external bias than the experimental one. ii) In a practical realization of the device the capacitance field would certainly leak into the source and drain electrodes, providing a pocket of electrons with higher kinetic energy to tunnel, thus reducing the gate bias value at which the resonance occurs. Both above remarks give us confidence that resonant tunneling and amplification can occur at lower gate field.

3 CURRENT-INDUCED FORCES

The effect of forces on the two-terminal molecular device have been investigated in the case of the molecule connected to two bare electrode metals. The current flow has essentially two effects on the atomic structure: i) the molecule twists 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 2.8V corresponding to the valley of Fig. 2, middle panel. The first effect increases with increasing bias even though the global current is not substantially altered. The second effect is due to the deplation of charge between the central C atoms at the first resonance peak due to resonant

tunneling with antibonding 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 is not observed at the second peak bias, because resonant tunneling in that case is mainly due to bonding π orbitals. Further details on current-induced forces will be given elsewhere. [6]

4 LIGAND AND TEMPERATURE EFFECTS

Chen et al. recently reported I-V characteristics of molecules consisting of chains of three benzene rings with ligands attached at various places. [3] The most interesting result is the large negative differential resistance evinced by a relatively sharp spike in the I-V characteristic. The spike is found to broaden and shift on the voltage axis with increasing temperature. The shift, by about 1 V, is very unusual. In semiconductor nanostructures resonant peaks have been found to broaden (by standard electron-phonon interactions) but they never shift appreciably. We found, by means of ground-state density-functional calculations on the three-ring molecule, that rotation of the middle ring produces no perceptible change in the electronic structure of the molecule in the vicinity of the highest-occupied molecular orbital (HOMO)-LUMO states whereas rotation of the ligand does.

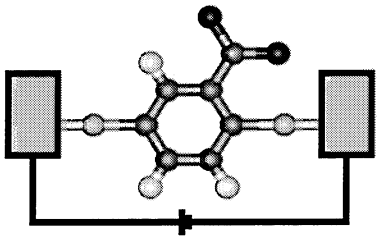

Figure 7: Scheme of the molecular structure investigated. The structure is the benzene-1,4-dithiolate molecule where a H atom is replaced by a NO_2 group. All atoms lie on the plane defined by the carbon ring. The sulfurs attach to ideal metallic leads.

We thus pursued the question by calculations for a single benzene ring with an NO_2 ligand replacing one of the hydrogen atoms (see Fig. 7). We found that the energy levels of the ligand move substantially with increasing voltage and push the π levels into the active window for transport. Therefore the main peak in the current arises primarily from π electrons instead of π^* electrons. We then explored the effect of rotating the ligand. We found that a rotation by 90° shifts the peak to lower voltage by almost 1 V (see Fig. 8), in agreement with the observations. The interpretation is that higher temperatures excite the rotational modes of the ligand. Calculations of the total energy of the molecule as a function of ligand rotation show that the effective rotational quantum of energy is only 3 meV. Thus the ligand group can easily rotate at room temperature, practically as a classical rigid rotator and the system will spend most of the time at the highest degree of rotation possible at a given temperature. Ligand rotation is of course a unique phenomenon of the molecular world, explaining why large voltage shifts are not observed in semiconductor nanostructures.

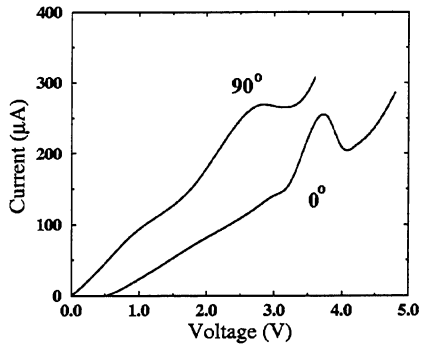

Figure 8: Theoretical I-V curve of the benzene-1,4-dithiolate molecule with a ligand substitution for zero and 90 degrees of rotation of the ligand group with respect to the carbon-ring plane (Ref. [7]).

CONCLUSIONS

The calculations summarized above show that theory has now advanced to the point where quantitative predictions can be made about transport in single molecules. Such calculations are expected to play a major role in the evolution of molecular electronics, the way that simple drift-diffusion calculations of current in semiconductor structures have played in the evolution of silicon-based microelectronics.

Acknowledgement: This work was supported in part by a grant from DARPA/ONR, by the National Science Foundation and by the William A. and Nancy F. McMinn Endowment at Vanderbilt University.

REFERENCES

[1] N.D. Lang, Phys. Rev. B **52**, 5335 (1995).

[2] M. Di Ventra and S.T. Pantelides, Phys. Rev. B **61**, 16207 (2000)

[3] M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, J.M. Tour, Science **278**, 252 (1997); J. Chen, M.A. Reed, A.M. Rawlett, and J.M. Tour, Science **286**, 1550 (1999).

[4] M. Di Ventra, S.T. Pantelides, and N.D. Lang, Phys. Rev. Lett. **84**, 979 (2000).

[5] M. Di Ventra, S.T. Pantelides, and N.D. Lang, Appl. Phys. Lett. **76**, 3448 (2000).

[6] M. Di Ventra, S.T. Pantelides, and N.D. Lang, in preparation.

[7] M. Di Ventra, S.G. Kim, S.T. Pantelides, and N.D. Lang, Phys. Rev. Lett. (in press).