Molecular Electronics By The Numbers

S. T. Pantelides,[1,2] M. Di Ventra,[1,3] N. D. Lang,[4] and S. N. Rashkeev[1]

[1]Department of Physics and Astronomy, Nashville, TN 37235
[2]Oak Ridge National Laboratory, Oak Ridge, TN 37861
[3]Department of Physics, Virginia Polytechnic Institute and State University, Blacksburg, VA24061
[4]IBM T. J. Watson Research Center, Yorktown Heights, NY 10598

ABSTRACT

The paper gives an overview of recent work by the authors in first-principles, parameter-free calculations of electronic transport in molecules in the context of experimental measurements of current-voltage (I-V) characteristics of several molecules by Reed et al. The results show that the shape of I-V characteristics is determined by the electronic structure of the molecule 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 simulated, showing gain. Finally, recent data that show large negative differential resistance and a peak that shifts substantially as a function of temperature have been accounted for in terms of rotations of ligands attached to the main molecule, a phenomenon that is not present in semiconductor nanostructures .

1. 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,[1] 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,[2] 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.[3] The method has all the ingredients needed to compute current-voltage (I-V) characteristics of single molecules. We recently developed a suitable Hellmann-Feynman theorem for the calculation of current-induced forces on atoms that allows us to study the effect of current on relaxations and ultimately the breakdown of molecules.[4] 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.[5,6] 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.[7-10]

2. TRANSPORT IN A SINGLE BENZENE RING

Fig. 1 shows schematics of a single benzene ring bridging the gap between macroscopic gold electrodes. A sulfur atom at each end joins the benzene ring to the electrodes. The experimental I-V characteristic is shown in the top panel. The middle panel shows the theoretical results. We will discuss the third panel shortly.
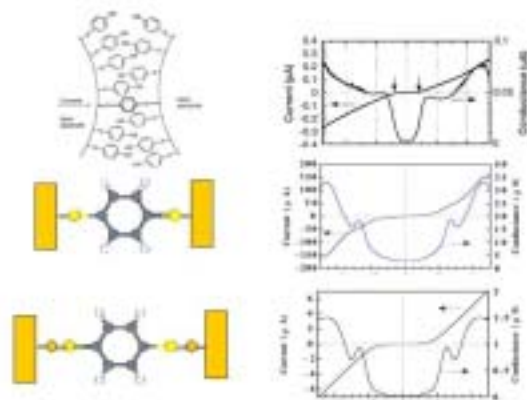

Fig. 1 Schematics of benzene ring configurations between electrodes and I-V characteristics. Top row: Experiment (Ref. 5). Middle row: Theory with S atoms only between benzene ring and macroscopic electrodes (Ref. 7). Lower row: Theory with Au atoms inserted between the S atoms and the macroscopic electrodes (Ref. 7).

It is clear from the figure that the theory reproduces the shape of the I-V curve quite well, but the absolute magnitude of the current is off by more than two orders of magnitude. We address each of these issues separately.

In Fig. 2 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 the 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 the 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.
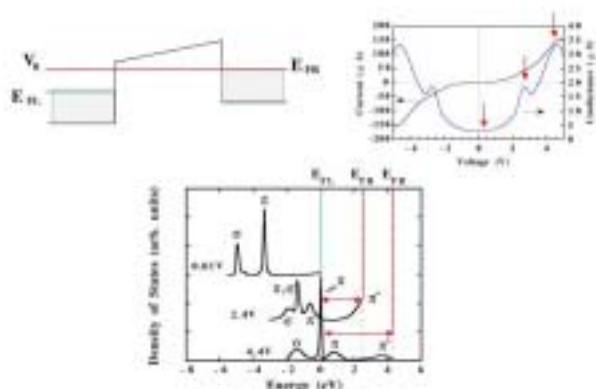

Fig. 2 Schematic of the setup showing the left and right quasi Fermi levels; the I-V characteristic as in Fig. 1, and the densities of states discussed in the text.

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 as shown in the lower part of Fig. 1. There was a dramatic decrease in the current, bringing its value much closer to the experimental value (lower panel in Fig. 1). 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. The gold atoms act as a quantum mechanical constriction. To test the idea we performed calculations by replacing the gold atoms with aluminum atoms. The latter have p electrons that should couple well with the π electrons of the molecule. Indeed, the current jumped to its initial value. 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 the apprpopriate linear combinations to produce sufficient coupling.

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".

3. A THREE-TERMINAL DEVICE

Transistor-like behavior in molecular three-terminal devices (molecular transistors) has been recently demonstrated in a single C_{60} bucky ball connected to gold electrodes,[10] in organic self-assembled monolayers,[11] and in single and multi-walled carbon nanotubes.[12,13] The source-drain current in these systems (three-terminal devices) is controlled by a gate voltage.

As an example of a three-terminal device we considered the same benzene ring as above but put a third "terminal" in the form of a capacitive gate: an external electric field across the molecule produces polarization that affects the current through the molecule. Figure 3 shows that at a very small (0.01 V) source-drain voltage, the current is a strong function of the gate voltage. In particular, we demonstrate substantial gain at the resonant peak.
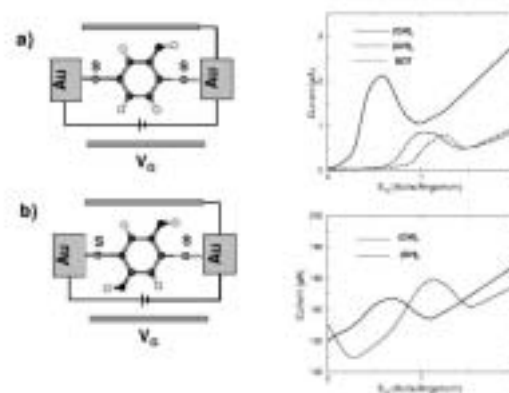

Fig. 3 Schematic of three-terminal devices using two different molecules as discussed in the text and the theoretical I-V characteristics as a function of the gate voltage for a small source-drain voltage.

Recently, we explored the effect of symmetry on the current-gate-field (I-E) characteristics of model molecular transistors. In particular, we investigated the role of intrinsic dipole moments on the current modulation in these structures. Figure 3 shows the two core molecules that have been constructed from the benzene-1,4-dithiolate molecule by substituting one of two hydrogen molecules by hydroxile groups (OH). The transport properties in these two molecules were found to be very different. The amplification of the current at the resonant tunneling regime is a few times larger in the asymmetric molecule which is a subject to a linear Stark effect in the gate electric field. At the same time, resonant tunneling occurs at much lower voltage than in the symmetric molecule.

The shape of the I-E characteristics depends on the value of the source-drain voltage in a nonlinear way, thus

manifesting a strong dependence between the source-drain current and the gate electric field. These results illustrate that substituents and symmetry considerations can provide considerable control of the behavior of molecular transistors. Further discussion of the results can be found in the original papers.[8,9]

4. A BENZENE RING WITH A LIGAND

Chen et al.[6] recently reported I-V characteristics of molecules consisting of chains of three benzene rings with ligands attached at various places. The most interesting result is 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.

Calculations for three-benzene-ring molecules are not practical, but we pursued the question by calculations for a single benzene ring with an NO_2 ligand replacing one of the hydrogen atoms. We found that the energy levels of the ligand move substantially with increasing voltage and push the π levels into the active window. Thus 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, in agreement with observations (Fig. 4). 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, even at the relatively low temperatures of the experiment, a large number of quanta are excited, making the ligand effectively a classical rotor that spends most of its time at the extrema of the amplitude. Ligand rotation is of course a unique phenomenon of the molecular world, explaining why large voltage shifts are not observed in semiconductor nanostructures.
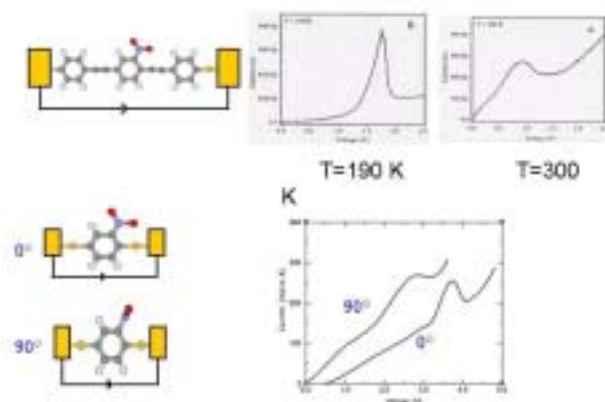

Fig. 4 Experimental data by Chen et al. (Ref. 6) at two temperatures and theoretical I-V curves for two different orientations of the ligand. See text for more details.

5. 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.

REFERENCES

[1] A. Aviram and M. A. Ratner, "*Molecular Rectifiers*", Chem. Phys. Lett. 29, 277 (1974). See also *Molecular Electronics*, edited by A. Aviram and M. A. Ratner (New York Academy of Sciences, New York, 1998).

[2] S. Datta, W. Tian, S. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, Phys. Rev. Lett. 79, 2530 (1997); S. N. Yaliraki, A. E. Roitberg, C. Gonzales, V. Mujica, and M. A. Ratner, J. Chem. Phys. 111, 6997 (1999); J. K. Gimzewski and C. Joachim, Science 283, 1683 (1999).

[3] See N. D. Lang, Phys. Rev. B 52, 5335 (1995); ibid. 49, 2067 (1994).

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

[5] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, Science 278, 252 (1997).

[6] J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour, Science 286, 1550 (1999).

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

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

[9] S. N. Rashkeev, M. Di Ventra, and S. T. Pantelides, Phys. Rev. Lett. (submitted).

[10] H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alvisatos, and E. P. McEuen, Nature 407, 57 (2000).

[11] J. H. Schon, H. Meng, and Z. Bao, Nature 413, 713 (2001).

[12] J. W. G. Wildoer, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, Nature (London) 391, 59 (1998).

[13] R. Martel, T. Schmidt, H. R. Shea, T. Herzel, and Ph. Avouris, Appl. Phys. Lett. 73, 2447 (1998).

[14] M. Di Ventra, S.-G. Kim, S. T. Pantelides and N. D. Lang, Phys. Rev. Lett. 86, 288 (2001)