A Quasimolecular Approach to the Field-effect Molecular Transistor: Theory and Application

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ABSTRACT

We report on a theoretical extension and computational implementation of a DFT-based quasimolecular approach to the description of molecular conductance, with consideration of gating effects in both metal - molecule and semiconductor - molecule junctions in a transistor-like device. A significant increase in the conductance at low bias has been found in the presence of a gate voltage. The origin of this transistor-diode behavior may be traced to a field-effect shift of a molecular frontier orbital.

Keywords: molecular conductance, gating, field-effect, computer modeling, Green's-function, *ab initio*

1 INTRODUCTION

Transistors are the basic building blocks of today's microelectronics industry. The current flowing through a transistor can be amplified or attenuated depending on the value of a second applied signal ("gating" voltage). Recently, using scanning tunneling microscopy (STM), Piva *et al.* have observed that the electrostatic field emanating from a fixed point-charge regulates the conductivity of nearby substrate-bound molecules at room temperature. [1] In this work, the current-voltage (I-V) behavior of a single molecular transistor was reproduced with an approximate conductance model based on *ab initio* electronic structure calculations.

2 THEORY

2.1 Background

A consistent theoretical methodology, based on a Landauer scattering formalism incorporating a nonequilibrium Green's function approach to transport theory, can provide physical insight into differential conductance. [2] Conductance g(V) at a bias voltage V is related to the current [I(V)] by,

$$g(V) = \frac{\partial I(V)}{\partial V}. \tag{1}$$

The conductance may be computed from the transmission matrix elements (T_{ij}) via,

$$g(V) = \frac{2e^2}{h} \sum_{ij} T_{ij}(E,V). \tag{2}$$

The calculation of $g(V)$ requires the computation of Green's functions, which for real molecules and electrodes is time-consuming.

2.2 Green's Function

We have developed a simplified model based on the following assumptions. [3]

(1) The molecule may be divided into fragments associated with electrodes. The extended model may consist of the bare molecule and a number of atoms representing the electrodes.
(2) Electrodes do not interact with the extended molecule except through a multiplicative spectral density.
(3) Green's functions may be constructed from the molecular orbital coefficients of the model.

Then, we can obtain:

$$T(E,V) = \Gamma_L(E)\Gamma_L(E)\left|G(E,\phi_V)\right|^2 \tag{3}$$

$$G(E,\phi_V) = \sum_{\mu=1}^{N_{orbs}} \frac{1}{E - e_\mu - is} \sum_{i=1}^{N_L} \sum_{j=1}^{N_R} c_{iu}^* c_{ju} \tag{4}$$

where s is an imaginary part added to the energy to simulate the interactions with the continuum of electronic states associated with the electrodes, e_μ is the energy of molecular orbital relative to work function or Fermi energy (we use the mean value of ε_{HOMO} and ε_{LUMO} herein), ϕ_V is molecular orbital under a certain bias electric field, N_L and N_R are the atomic orbital numbers of left and right fragments, N_{orbs} is the number of molecular orbitals, $G(E, \phi_V)$ is the Green's function, and Γ_L and Γ_R represent interaction between the molecule and electrodes (left and right).

2.3 Electrode Model

We consider two different models for molecule-electrode contacts: [4]
   (1) Metal-Molecule (Anderson-Newns chemisorptive model),

$$\Gamma(E) = \beta_0^2 / \beta \sqrt{1 - (E/2\beta)^2} , \qquad (5)$$

where β_0 and β are the molecule-electrode and metal-metal interactions, respectively.

   (2) In the case of semiconductor-molecule (Mujica-Ratner model)

$$\Gamma(E) = \frac{\beta_0^2}{\beta_1 \beta_2} \sqrt{1 - \left[\frac{E^2 - \beta_1^2 - \beta_2^2}{2\beta_1 \beta_2} \right]^2} , \qquad (6)$$

where β_0, β_1, and β_2 are the molecule-electrode and semiconductor site-site interactions, respectively.

This simple and computationally efficient model to compute I-V curves from molecular orbital has been coded by our group.

3 APPLICATIONS

The program "ivExplorer" is a Java program, designed with a user-friendly interface and for efficient operation. [5] A typical use of ivExplorer is shown in Figure 1.
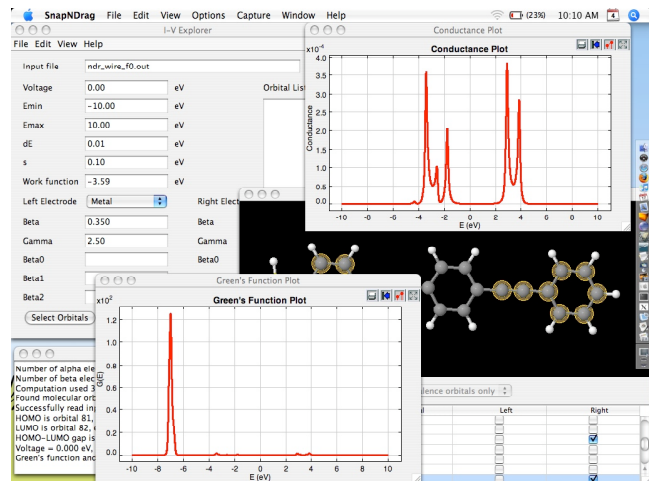

Figure 1. ivExplorer being used to compute I-V curves for a molecular wire.

3.1 Single molecule transistor

Now we examine the molecular conductance under the influence of a gating electric field. Rather than studying the molecule in vacuum, we introduce a layer of point charges to produce a gating voltage, mimicking the STM experiment (shown in Figure 2).
The model relaxes in the electric field formed by the bias voltage and point charges mimicking a gating voltage.

The AuSPhSAu systems were optimized at the B3LYP/LANL2DZ level of theory, with an applied field varying from 0-1 V. In order to mimic the gating field, a 10 x 10 grid of point charges (with charges of 0.01 a. u. each) was placed at a distance of 10 Å from the molecule (Figure 2). Kohn-Sham molecular orbitals under external fields were computed with Gaussian03 [6] and used in the I-V calculations with ivExplorer.
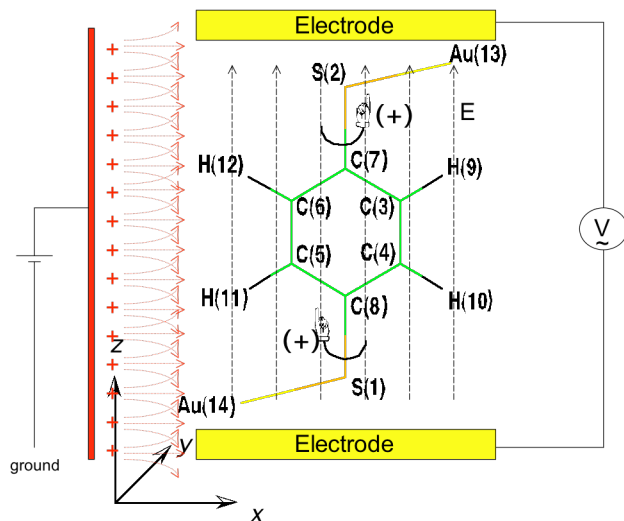

Figure 2. The computed AuS-Ph-SAu system under external fields that mimic the bias and gating voltages.

The potential energy surface with respect to the rotation of two C-S bonds of the model system in the gas phase is plotted in Figure 3. There are two minima on the surface (*cis* and *trans*), with the *cis* conformation more stable by 20-25 kJ/mol.
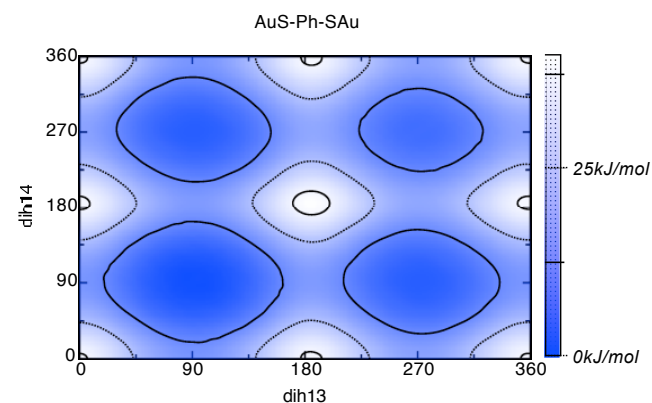

Figure 3. The rotational potential energy surface of AuS-Ph-SAu. [dih13 and dih14 are the two C-C-S-Au (Au13 and Au14) dihedral angles]

Under the bias and gating voltage, the *cis* conformer is slightly bent due to the external fields, as shown in Figure 4. This conformation change is dependent on the sign of the gating voltage.
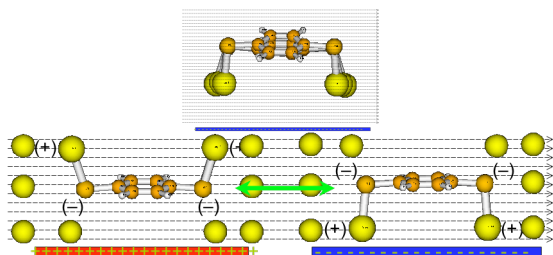
Figure 4. Illustration of conformational change produced by the applied fields.

Using structures optimized at different applied fields, I-V curves were computed using the ivExplorer software, with β_0 = 0.35 eV and β = 2.5 eV for the metal (Au) electrode case, and β_0 = 0.1 eV and β_1 = 1.27 eV and β_2 = 0.1 eV for the semiconductor (Si) electrode case. The calculated non-gated and gated I-V curves are plotted in Figure 5(a).

In order to facilitate comparison of our results with those of Piva *et al.* [1] We performed similar computations on the HS-PhC≡CPhC≡CPh system, which has been studied previously by our group. [3] The resulting I-V curves (Figure 5b) show similar behavior to the experiments reported by Piva *et al.* (Figure 5c).
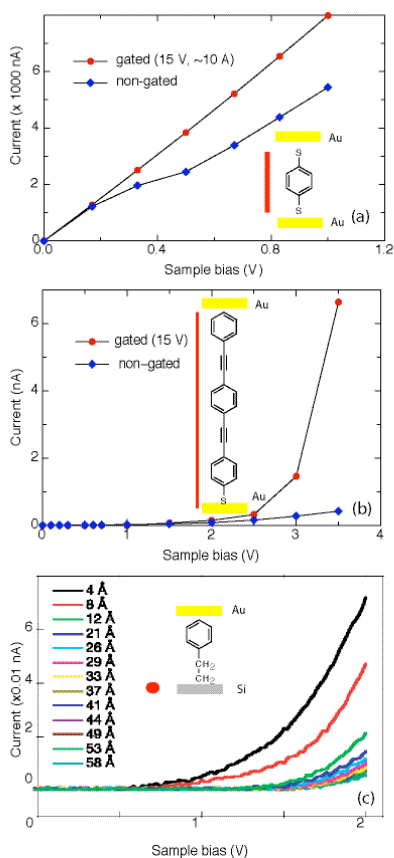

Figure 5. The computed I-V curves for the AuS-Ph-SAu model (a), the HS-PhC≡CPhC≡CPh model (b), and the STM experimental results of -CH$_2$CH$_2$Ph on silicon neighboring a point-charge (c), from ref. [1].

4   CONCLUSIONS

A simple conductance model based on a Green's function formalism based on molecular orbitals can reproduce the experimental I-V curve quite well, even in the case that the single molecule transistor is treated as a symmetric model for practical calculation and a metal-molecule-metal contact is used.

According to the computed results, it is likely that a molecular transistor is realized by applying a high electric field to the conductor molecules so as to generate a much larger current under a small bias voltage. The transistor behavior is related to field-shift of molecular frontier orbitals (Figure 6):

bias	non-gated			gated		
	0.00 V	0.35 V	0.70 V	0.00 V	0.35 V	0.70 V
LUMO	-0.14233	-0.14978	-0.15881	-0.20716	-0.21428	-0.22333
HOMO	-0.23983	-0.24384	-0.24674	-0.30898	-0.31383	-0.31674

Figure 6. Non-gated and gated LUMO and HOMO energy levels (in a.u.) of AuS-Ph-SAu under the bias potentials.

Conformational changes under external fields do not seem to be important in the absence of polar side-chains attached to the working molecules.

The approximate computational method is readily applied to the study of molecules that exhibit molecular rectification, switching effects, negative differential resistance, etc. Modeling of the semi-conductor-molecule-metal contact is currently under study.

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[5] To inquire about obtaining a copy of the ivExplorer software, contact carlos.gonzalez@nist.gov or thomas.allison@nist.gov.

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