Molecular Electronics:

Simulation from Molecules to Circuits

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Background, Motivation, and Objectives:
The semiconductor industry is rapidly pushing the current technological approach to its limits and urgently needs new ideas to address the challenges beyond the end of its roadmap. The objective of this project is to bring experts from the chemistry of molecular electronics (Ratner, Mujica, Gonzalez, and Roitberg), the physics of electronic conduction at the molecular scale (Datta), electronic device and circuits technology (Lundstrom), and experimental research on new molecular devices (Reed) to address the challenges of electronics at the quantum scale. The goal is to speed the development of molecular electronics by combining chemical intuition (to relate molecular structure to energy levels and wavefunctions) and electrical engineering intuition (to relate energy levels and wavefunctions to device functionality and to large-scale circuits). The work involves modeling and simulation at multiple length scale, starting from atomic Hamiltonians and going to complex circuits. The project is organized into two interacting thrusts. The objective of the first thrust is to develop models that begin with a molecular Hamiltonian and simulate the current and charge vs. voltage characteristics of the device. The objective of the second thrust is to develop compact circuit models that describe the behavior of the device in terms of the voltages applied to its terminals and to use these models to explore new types of circuits. In the process we hope to explain recently observed experimental results on new molecular devices and to develop a general modeling and simulation methodology that begins with the molecular structure and ends with a circuit.

Approach:
Over the past few years, a basic understanding of conduction in molecules has emerged. Consider a molecule of phenyl dithiol sandwiched between two gold electrodes as shown in Fig. 1. The molecular energy levels consist of a set of occupied levels separated by a gap from a set of unoccupied levels. At equilibrium, the Fermi energy is typically located in the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital

(LUMO), but when a bias is applied, the Fermi energy in the right contact (μ_2) floats up by eV_D relative to the Fermi level in the left contact (μ_1). The molecule conducts when the bias is large enough that one or more of the molecular energy levels lie between μ_1 and μ_2.

We have developed this basic picture into a quantitative model by extending the standard methods of quantum chemistry [Tia98]. A molecular structure program is first used to obtain the self-consistent Fock matrix, [F] in a suitable basis whose eigenvalues give the energy levels of the isolated molecule. To this we add several terms. First, there is an applied potential between the two contacts, U_a. Second, there is a change in the self-consistent potential within the molecule, U_{scf}, due to the changes in the occupation of molecular orbitals under bias. Finally, there are self-energies, Σ_1 and Σ_2, which describe the effects of the macroscopic metallic contacts. Inelastic scattering can be described by an additional self-energy matrix. Once the matrices are known, the current is computed using the non-equilibrium Green's function (NEGF) method [Dat95]. Figure 1 compares the shape of the computed conductance spectrum with the measured results [Ree99]; good agreement is obtained without fitting parameters.

To describe electronic circuits with a large number of interconnected devices, a simple, analytically compact model is needed, but it should be physically based to provide insight for device and circuit engineers. For this work we adopt a scattering approach, which relates, for example, the near-equilibrium conductance of a molecule, G, to the current transmission coefficient at the Fermi energy, $T(E_f)$, according to the Landauer formula, $G = (2e^2/h)MT$, where M is the number of propagating modes. The NEGF method can be viewed as a rigorous approach for evaluating T. This approach can be generalized to treat incoherent transport under high bias, in which the transmission coefficient becomes a function of the bias applied across the device. Together, the two approaches are complementary, with the NEFG relating device function to molecular structure and the scattering approach capturing the essential physics of device operation in an analytically compact manner suitable for circuit models.

Project Status:

Interesting nonlinear I-V characteristics with potential circuit applications have been recently demonstrated using a molecule with a nitroamine redox center [Che99]. The mechanism responsible for the observed negative differential resistance is still unknown, so this problem provides us with a good model device for developing molecular scale models that predict device function. We have also recently developed a new compact model for the MOSFET that treats the device as a molecular transistor [Rah01]. Applying the methods of molecular electronics to a familiar device provides us with a starting point for the development of circuit models for unconventional devices.

We also regard this interdisciplinary project as an opportunity for education and outreach. For example, a new course that brings the methods of computational chemistry to beginning electrical engineering students is being developed, and the simulation tools being developed in this effort are being disseminated through a unique computational infrastructure known as The Nanotechnology Simulation Hub (www.nanohub.purdue.edu)

[Che99]   J. Chen, et al., *Science*, **286**, 1550 (1999)
[Dat95]   S. Datta, *Electronic Transport in Mesoscopic Systems*, Cambridge Univ. Press (1995)
[Rah01]   A. Rahman, et al., Modeling and Simulation of Microsystems, xxx, March xxx, 2001
[Ree99]   M.A. Reed, *Proc. IEEE*, **87**, 652 (1999)
[Tia98]   W. Tian, et al., *J. Chem. Phys*., **109**, 2874 (1998)

(a)

(b)

LUMO

HUMO
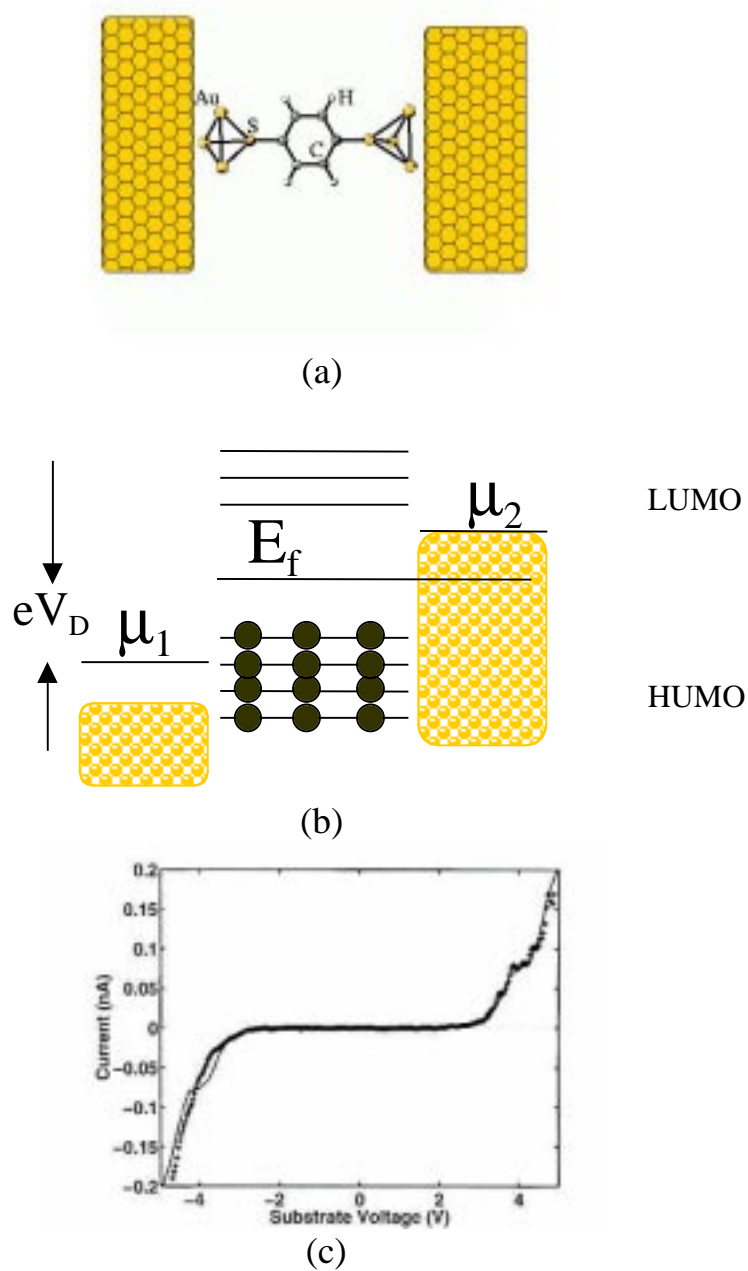
E_f

μ_2

μ_1

eV_D

(c)

Fig. 1 (1) A molecule of phenyl dithiol attached to two gold electrodes. (b) Schematic illustration of the molecular energy levels and the location of the energies levels under bias. (c) Current vs. applied voltage, V for the xylyl dithiol molecule attached to two gold electrodes. Solid line is theory and the points are the data.