First-Principles Modeling of Molecular I-Vs and Calibration to Experiments

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There is much current interest in molecules as components in electronic devices due to their small size and myriad electrical, optical and chemical properties. Recently significant progress has been reported in experimentally measuring current flow through an individual or a group of molecule(s) connected to a metallic or a semiconducting substrate [1].

We present a rigorous yet computationally efficient method to analyze capacitance-voltage (C-V) and current-voltage (I-V) characteristics of molecules and molecular wires well-connected to contact(s). This regime of transport where the coupling to electrodes is comparable to or greater than the single-electron charging U, is the well-known self-consistent field regime. In earlier publications [2] we have presented I-Vs of quantum wires and molecules connected to metallic contacts using such a self-consistent field (SCF) calculation. The SCF I-V was obtained by modifying a standard quantum chemistry software Gaussian98 (G98) [3] and coupling it to a Non-equilibrium Green's Function (NEGF) formalism. G98 by itself is known to predict accurately the equilibrium properties of isolated molecules while NEGF allows one to calculate self-consistent charge density and transmission probability through small structures in the presence of semi-infinite contacts under an applied bias.

We point out two major challenges faced by any first-principles theory to explain experimental molecular I-Vs.
1) The precise location of the equilibrium Fermi energy of the electrode-molecule-electrode system i.e., the position of the Fermi energy with respect to the molecular levels. This, in turn critically affects various features of the I-V, including the onset of current and the overall shape of the I-V characteristics. Even in the semiconductor industry, in spite of thousands of man-hours worth of effort, threshold adjustment (equivalent to Fermi energy positioning) is a not-so-well-understood problem. Hence we would like to parametrically locate a reasonable equilibrium Fermi energy. In G98 we do so by placing image charges around the molecule that is equivalent to having a gate electrode. This in turn can shift the molecular levels with respect to the contacts allowing us to fix the equilibrium electrode-molecule-electrode Fermi energy.
2) The more reproducible experiments in molecular electronics involve a Scanning Tunneling Microscope (STM) tip as the second contact. In a typical STM experiment there is a sizeable

($\sim$5-15 $\overset{\circ}{A}$) vacuum gap between the tip and the molecule. The measured current level critically depends on the vacuum gap since it represents the least transmitting path. Hence obtaining an ab-initio description of vacuum is an important step in obtaining a match with experimental data. We use chargeless dummy atoms in G98 to represent vacuum. We calibrate the dummy atoms such that we obtain the precise conduction band-edge of vacuum which is at zero. With these two critical additions to our existing self-consistent ab-initio simulator we take a look at different experiments. In the talk we will present I-Vs obtained from our first-principles theory that correspond both in shape and magnitude with experimental data.

References: [1] T. Rakshit *et al.*, cond-mat 0305695, [2] P.S. Damle *et al.*, Phys. Rev. B 64, 201403®., [3] Gaussian 98 (Revision A.7), M.J. Frisch *et al.*.
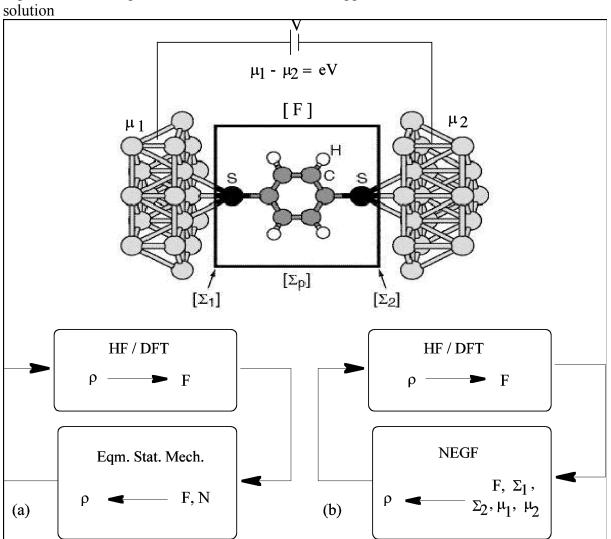
Figure 1: Coupled G98 and NEGF approach to obtain self-consistent solution