Electronegativity and Electron Currents in Molecular Tunnel Junctions

I. Yeriskin[1], S. McDermott[1], R. J. Bartlett[2], G. Fagas[1], and J.C. Greer[1]

1Tyndall National Institute,

University College Cork, Ireland

[2]*Quantum Theory Project, University of Florida at Gainesville, FL, USA 32611*

Tyndall National Institute, Lee Maltings, Dyke Parade, Cork, Ireland

irene.yeriskin@tyndall.ie

Abstract:

Electronegativity directly regulates charge transfer and energy level alignments, and hence electron currents in single molecule tunnel junctions.

We discuss the impact of improving ionization Potentials (IPs) and electron affinities (EAs), and hence the electro-negativity, on prediction of currents across single molecules and relate these approximations to transport methods that rely on a direct determination of the reduced density matrix [1]. Correcting the Green's function through second order in the self-energy leads to improved prediction of iP's and EA's

Currents across molecules bonded between two metal electrodes are commonly treated as single electrons tunnelling through an effective potential barrier; this independent particle picture is well-known to describe many aspects of tunnelling. Examining quantum transport with explicit many-body treatments of the molecular region, we examine criteria for establishing effective single particle models to study tunnelling in metal-molecule-metal junctions. We find maximizing the overlap of the reduced density matrix derived from a single Slater determinant to the exact reduced density matrix defines the best single particle picture for transport [2].

Currents calculated from the one-electron reduced density matrix correct to second order in electron-electron correlation are identical to currents obtained from the one-electron Green∄fs function corrected to second order in electron self-energy.

A tight binding model of hexa-1,3,5-triene-1,6-dithiol (Figure below) bonded between metal electrodes is introduced, and the effect of analytically varying electron-electron correlation on electron currents and electronegativity is examined. The model analysis is compared to electronic structure descriptions of a gold-hexatriene (approximated by different exchange-correlation functionals) and Hartree-Fock states as zeroth-order approximations to the one-electron Green's function.

Comparison between the model calculations and the electronic structure treatment allows us to relate the ability to describe electronegativity within a single particle approximation to predictions of current-voltage characteristics for molecular tunnel junctions. [3]

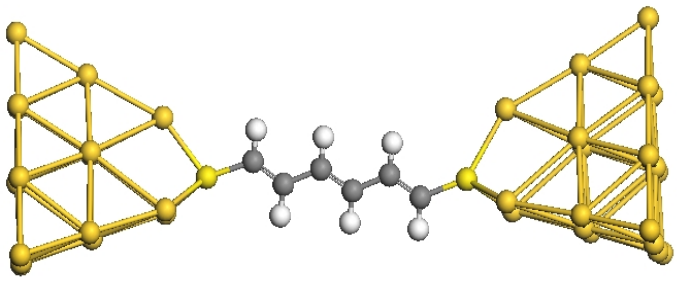

FIGURE: HEXA-1,3,5-TRIENE-1,6-DITHIOL BETWEEN TWO METAL CONTACTS

Bibliography:

[1] P. Delaney and J.C. Greer, *Phys. Rev. Lett.* **93**, 036805 (2004)

[2] G. Fagas, P. Delaney, and J.C. Greer, *Phys. Rev. B* **73**, 241314(R) (2006)

[3] I. Yeriskin, S. McDermott, R. J. Bartlett, G. Fagas, and J.C. Greer, *J. Phys. Chem. C,* **114**, 20564 (2010)