A case study of a metal/organic interface at the molecular level: a tip/C_{60} contact

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In this work, we analyze theoretically a Au/C_{60} interface based on the results obtained using DFT for a fully relaxed Au-tip/C_{60}/Au-tip geometry [1] with variable tip/tip distance, calculate the energy, forces, conductance and deformation, and discuss the organic/barrier formation at the molecular level comparing it with the full monolayer case [2]. We also analyze how this barrier formation at the molecular level can be related to the effective intrasite Coulomb interaction operating in the molecule (considered as a quantum dot). Finally, we also discuss how that Coulomb interaction allows us to obtain the transport energy gap of the molecule as a function of the tip-molecule distance.

The contact formation is analyzed by approaching each Au-tip in steps of 0.1 Å using a highly efficient MD-DFT code (FIREBALL[3]). After each step the atoms are relaxed to their corresponding minimum energy positions, excepting the atoms in the last Au-layer of both tips. We use the LDA exchange-correlation functional, and a basis set of short-range numerical atomic-like orbitals (NAOs). The electrical conductance of the system was calculated at each step of the deformation using a Keldish-Green´s function approach [4], together with the first-principles tight-binding hamiltonian of the system.

We have also calculated the density of states at several steps of the tip approach and analyzed them in terms of the Unified-IDIS model [6] For each case, the LUMO and HOMO levels, the molecule Charge Neutrality Level, the Fermi energy (zero energy) and the initial metal workfunction, Φ_M, are shown. The CNL is calculated integrating the C_{60}-DOS up to charge neutrality conditions; the tip/C_{60}/tip contact reacts creating a potential, V^t, that tries to align the organic CNL and the metal workfunction. Following the IDIS-description of MO interfaces [6], we can relate the total potential difference, V^t, created between the tips and $C_{60,}$ to the IDIS, V^{IDIS}, and to the "pillow" potential, V^{pillow}, in the following way:

$$V^t = V^{IDIS} + V^{pillow} \qquad (1)$$

where $V^{IDIS} = (1-S)(CNL - \Phi_M)$, and $V^{Pillow} = SV_0^{Pillow}$, S being the interface screening parameter and V_0^{Pillow} the bare "pillow" potential induced by the compression of the electron metal tails at the MO interface due to the Pauli repulsion [6].

Our calculation also provides us with a method to obtain the effective coulomb interaction, U^{eff}, associated with the injection of an electron in the molecule. This can be done by rewritting equation (1) as follows:

$$V^t = (1-S)(CNL - \Phi_M) + SV_0^{Pillow} = (1-S)(CNL - \Phi_M - V_0^{Pillow}) + V_0^{Pillow} \qquad (2)$$

then, U^{eff} is calculated dividing the charge transfer induced potential, $(1-S)(CNL-\Phi_M-V_0^{Pillow})$, by the charge transfer itself:

$$U^{eff}=(1-S)(CNL-\Phi_M-V_0^{Pillow})/\delta q \equiv \delta V^{charge}/\delta q \quad (3).$$

A similar equation for the LUMO and HOMO levels has also been found recently by Louie et al [7]. We have calculated the transport gap, as discussed in references [7,8]; this gap is the LDA-energy gap plus U^{eff}; this yields for cases A, B and C, E_{gap}^{trans}=3.5 eV(A); 3.1 eV(B) and 3.1 eV(C). It should be mentioned that the calculated DOS has been obtained using a scissor operator that fit the C_{60} –energy gap [2] to the values just mentioned.

Results for the case of a tip/C_{60}/surface geometry will be also shown and compared with the previous geometries

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Figures:

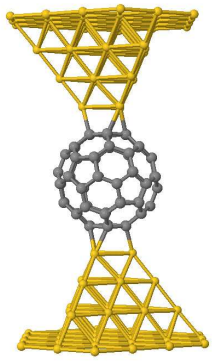

Fig. 1. Geometry of the C_{60} molecule between the gold tips