ELECTRONIC TRANSPORT THROUGH MOLECULAR BRIDGES WITHIN AB-INITIO METHODOLOGIES

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Theoretical control of electron flow at the nanoscale will be only supported by a description at the quantum level, since atomic- and molecular-level information on structures in nanosized regions is needed[1–3]. Presumably, these basic informations will be attained within *ab-initio* methodologies[4]. This work is intended to shed light in the *ab-initio* methodology used in our group to describe quantum transport[5].

The discussion will be centered on three points:

- Electronic structure of Molecular Bridges. The electronic problems derived from the Shrödinger equation for the infinite system must be simplified in order to compute a numerical solution.

  It is currently admitted that a Density-Functional Theory (DFT) is the only manageable tool in this respect, regarding a compromise between accuracy and computational cost. The DFT success is based, for the most part, on the existence of manageable approximations to the local- exchange and correlation- potentials, local-v_{xc}, within Kohn-Sham formalism (DFT-KS methods)[6]. Concerning atomic-structure calculations, which relies on total-force-calculations, the DFT-KS success relies on the existence of manageable approximations to the exact local-v_{xc}. Concerning electronic-response calculations, which are supported on the calculation of the Green's functions[7], the applicability of DFT-KS is not well supported *a priori* [8]. In this respect, Todorov and di Ventra[9], showed that attempts to improve the DFT-KS description of an electronic transport problem could be done within Time-Dependent DFT. In this line, some recent theoretical works, formally establishes the non-existence of an exact Time-Dependent DFT-KS, (TDDFT-KS), for the characterization of electrical response [10, 11]. In addition, they formally stated, that the addition of non-local corrections to v_{xc} in the TDDFT-KS methodology is a necessity, for an exact formulation of electrical response, (**TDCDFT**).

  With all these premises, we propose a route to correct DFT-KS methodologies but remaining within mean-field methods. Numerically, we suggested that a DFT formulation of electronic response must be managed with the introduction on non-local dependences in v_{xc}. The influence of these non-local dependences is studied updating the spirit of Becke's works labeled as **Hybrid-DFT** [12]. The amount of the non-local corrections to v_{xc} is proposed through a parameter-free route[13]. Remarkably, our numerical **Hybrid-DFT** results, are closer to the experimental measurements of electronic conductance in molecular bridges than those reported within DFT-KS methodologies. The same level of agreement is being notice when comparison between **TDCDFT** and TDDFT-KS are performed at the zero-frequency limit[11].

- Chemistry-based Molecular Electronics. There are no doubts that the electronic transport measurements through molecular bridges strongly depends on the atomic arrangements in the region which connect this *finite* system to the *infinite* metallic nanocontacts. These nanojuntions exhibit radically new properties that cannot be anticipated from the behavior as finite clusters or in the bulk. These changes open up the possibility of exploring novel ideas. Nevertheless, to place this capacity in perspective, research is needed in a new field labeled Chemistry-Based Molecular Electronics. So far, we are *transporting* the capabilities of the traditional Molecular Chemistry and Condensed Matter, to this novel field. Therefore, to characterize the molecular bridges chemically, we start using standard topographical concepts like reaction bonds, self-assembly, and atomic configurations. Besides, we are assuming the existence of energetically well-defined molecular orbitals which are employed throughout the analysis of the density of states in the zone to be chemically studied[14].

- Statistical analysis of Conductance measurements.

  The characterization of Molecular Bridges is necessarily carried out through a statistical analysis of the low-bias conductance with what is called conductance histograms[2, 3]. Within this work we approach this statistical description, based on the existence of a distribution function for the electronic conductance measurements $f \equiv f(G)$. The parameters needed in the model for $f(G)$ such as, the number of the accessible microstates, the value of the conductance in those positions, and the estimation of deviations is done within the *ab-initio* methods describe in the two sections above.

  To conclude, we present numerical results for some well-know samples in the context of Theoretical Molecular Electronics and in close relation to recent experimental measurements[2, 3]. The systems selected range from a single Hydrogen to carbon-based molecules like benzene dithiolate, placed between Platinum and Gold nanocontacts (see Figure 1).
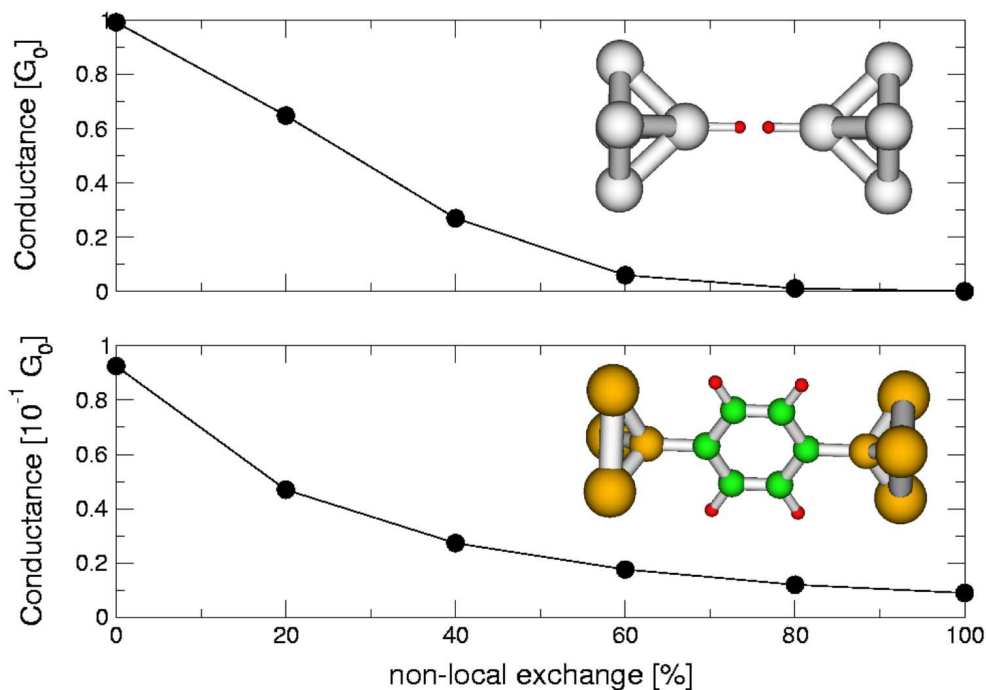
FIG. 1: **Reduction of the conductance** due to the progressive substitution of the local DFT-KS potential by a non-local contribution, Hybrid-DFT ($G_0 = 2\frac{e^2}{h}$).
Up: Hydrogen bridging Pt nanocontacts.
Down: Benzene dithiolate bridging Gold nanocontacts.

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[1] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).
[2] R. H. M. Smit, Y. Noat, C. Untiedt, N. D. Lang, M. C. van Hemert, and J. M. van Ruitenbeek, Nature (London) **419**, 906 (2002).
[3] X. Xiao, B. Xu, and N. J.Tao, Nanoletters **4**, 267 (2002).
[4] A. W. Ghosh and S. Datta, J. Comp. El. **1**, 515 (2002).
[5] E. Louis, J. A. Vergés, J. J. Palacios, A. J. Pérez-Jiménez, and E. SanFabián, Phys. Rev. B **67**, 155321 (2003).
[6] W. Kohn, Reviews of Modern Physics **71**, 50 (1999).
[7] S. Datta, *Electronic transport in mesoscopic systems* (Cambridge University Press, Cambridge, 1995).
[8] R. M. Martin, *Electronic Structure. Basic Theory and Practical Methods* (Cambridge University Press, 2004).
[9] M. D. Ventra and T. N. Todorov, Journal of Physics: Condensed Matter **16**, 8025 (2004).
[10] G. Vignale and W. Kohn, Phys. Rev. Lett. **77**, 2037 (1996).
[11] N. Sai, M. Zwolak, G. Vignale, and M. D. Ventra, Phys. Rev. Lett. **94**, 186810 (2005).
[12] A. D. Becke, J. Chem. Phys. **98**, 5648 (1992).
[13] Y. García, J. Sancho-García, E. SanFabián, J. A. Vergés, E. Louis, and J. J. Palacios (to be published).
[14] J. J. Palacios, A. J. Pérez-Jiménez, E. Louis, E. SanFabián, J. A. Vergés, and Y. García, in *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczynski (World Scientific, Singapore-New Jersey-London-Hong Kong, 2005), vol. 9, in press.