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GW Corrections of Energy Bandgaps for Coherent Transport Across Molecular Junctions

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ABSTRACT

Despite its mathematical complexity, the non-equilibrium Green's function method has gained a great popularity in recent years in the computation of transport across molecular junctions, mostly because of the elegant way in which, at least in principle, electron-phonon and electron-electron interactions can be treated in a unified and systematic way [1], [2], [3].

In most cases the system Hamiltonian is described within a single particle DFT approach. The advantage is the possibility to include several hundreds of atoms which are normally necessary in order to describe both contacts and molecule. The main problem of DFT is related to the description of the unkown exchange-correlation potential, usually approximated as that of a free electron gas. This tends to overestimate the metallic characteristics of the molecular states, producing among the others, an underestimation of the HOMO-LUMO gap, with relevant consequences to transport.

Therefore a batter correlation potential is a central issue in order to achieve not only quantitative predictions of tunneling currents, but also correct qualitative trends. In order to improve this aspect many groups have tried to improve the DFT formalisms either using hybrid functionals, or including correlated transport [4], [5] and self-interaction corrections [6].

In this paper we present a different approach based on the GW approximation technique, related to Green's function theory [7], [8]. The system Hamiltonian is obtained within the spirit of a DFT-based tight-binding approach called DFTB [9]. The implementation of the GW method over DFTB in the plasmon-pole approximation is a fast and flexible scheme [10]. This scheme is quite accurate in predicting correction to HOMO and LUMO states, in good agreement with the experimental workfunction and affinities. Unfortunately the quasiparticle energies degrade for energy levels of the molecule far from the gap. This is due to the approximations of our GW implementation and the use of a minimal basis set. However this lack of accuracy becomes problematic in transport calculations. Numerical artifacts have been observed, producing large broadering of the energy levels tailing in the energy gap considerably enlarging the transmission. We expect however the off-resonant transmission to be dominated by the position and broadening of the HOMO and the LUMO energies only, with little effect of the other levels. For these reasons we have worked around the problem by using the GW correction as a first step for the energy gap correction and implemented a simple scissor operator which rigidly shifts the valence and conduction set of molecular orbitals according to the GW prediction. This scheme was applied to calculations of various polymeric chains. Here we show results relative to poly-phenylene molecules represented in Figure 1.

Figure 2 shows the complex band structure calculated for an infinite poly-phenylene chain. The imaginary part of the complex bandstructure represents the tunneling decay for vanishing states and is related to off-resonant tunneling. The plot shows the difference between the full GW renormalization in comparison to the shissor operator.

Figure 3 shows the coherent tunneling across phenylene chains of varying lengths. The figure shows a significant increase of the HOMO-LUMO gap with a consequent decrease of tunneling probability at the Fermi level of the Cu-Molecule-Cu system used in our calculations.

REFERENCES

[1] S. Datta, *Electronic Transport in Mesoscopic System*. -: Cambridge University Press, 1995.

[2] M. Galperin, M. Ratner, and A. Nitzan, *Nano Lett.*, vol. 4, p. 1605, 2004.

[3] S. V. Faleev and M. I. Stockman, *Phys. Rev. B*, vol. 66, p. 085318, 2002.

[4] A. Ferretti, A. Calzolari, R. D. Felice, F. Manghi, M. J. Caldas, M. B. Nardelli, and E. Molinari, *Phys. Rev. Lett.*, vol. 94, p. 116802, 2005.

[5] N. Sai, M. Zwolak, G. Vignale, and M. Di Ventra, *Phys. Rev. Lett.*, vol. 94, p. 186810, 2005.

[6] C. Toher, A. Filippetti, S. Sanvito, and K. Burke, *Phys. Rev. Lett.*, vol. 95, p. 146402, 2005.

[7] F. Aryasetiawan and O. Gunnarsson, *Rep. Prog. Phys*, vol. 61, pp. 237–312, 1998.

[8] G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys*, vol. 74, p. 601, 2002.

[9] T. Frauenheim, G. Seifert, M. Elstner, T. Niehaus, C. Kohler, M. Amkreutz, M. Sternberg, Z. Hajnal, A. Di Carlo, and S. Suhai, *J. Phys.: Condensed Matter*, vol. 14, p. 3015, 2002.

[10] T. A. Niehaus, M. Rohlfing, F. Della Sala, A. Di Carlo, and T. Frauenheim, *Phys. Rev. A*, vol. 71, p. 022508, 2004.

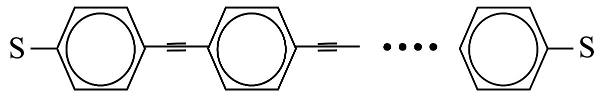

Fig. 1. Schematic representation of a poly-phenylene-dithiol molecule.

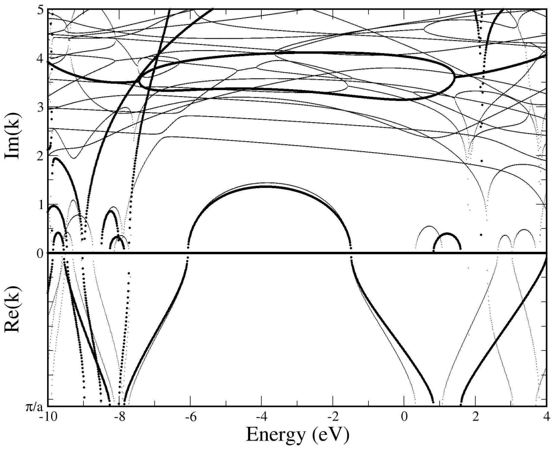

Fig. 2. Complex bandstructure of poly-phenylene. Thin curves correspond to a complete GW calculation, thick curves to the cut-shift operator based on the GW gap renormalization.

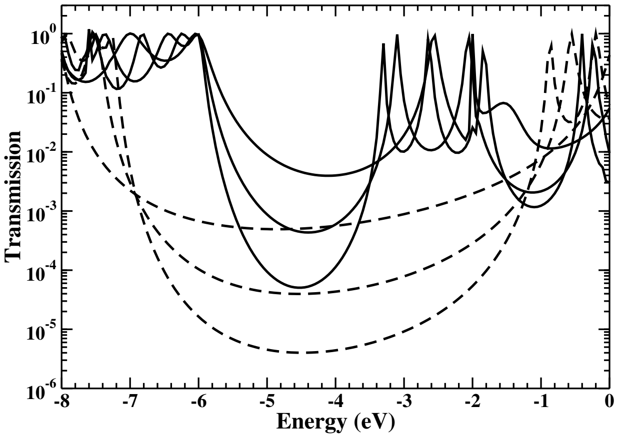

Fig. 3. Transmission across thio-phenylenes of increasing lengths (1 to 3 benzene rings). Solid lines correspond to DFT calculations, dashed lines to GW corrected results.