

# Electron Transport at the Nanoscale from First-Principles

Giorgos Fagas<sup>\*</sup>, Tom Henderson, Paul Delaney, and Jim Greer  
*Tyndall National Institute, Lee Maltings, Prospect Row, Cork, Ireland*

---

Modelling quantum transport from first-principles has proven to be a challenging task; debate continues as to the proper theoretical approach for treating electron currents across metal-molecule-metal junctions [1]. Compared to their mesoscopic counterparts based on artificially tailored heterostructures, the precise atomic arrangement and chemical synthesis must be realistically described. This means that common electronic structure theory needs to be modified so that it enables the description of the electron dynamics under electric fields in systems with open boundary conditions. Much attention has been drawn on transport schemes based on single electron scattering or non-equilibrium 1-body Green functions (NEGF) approaches with stationary a priori implementations of the electronic structure. The latter include Extended Hückel (EH), ab initio or semiempirical Self-Consistent-Field (SCF) and Density Functional Theory (DFT) methods. A common feature is the treatment of independent electrons moving in the mean-field of the others. In fact though, there is no established criterion for selecting a single-particle Hamiltonian to be used in transport calculations.

Here, we review an alternative physical scheme for transport at the many-body level and its implementation leading to calculation of IV curves for molecular scale systems [2]. To treat electron correlations, a method allowing open system boundary conditions to be applied to configuration interaction calculations is presented. Systematic approximations can be derived from this higher-level theoretical treatment. Difficulties associated with generalizing single particle ideas to a quantum mechanical many-electron system are outlined [3], and then constraints capable of mimicking electron reservoirs in a many-electron picture are specified.

The resulting computational scheme is applied to electron transport across several well-studied single molecules like benzene dithiol and short oligomer chains [4]. All lead to results that compare well to the best experimental data available. The explicit treatment of electron-electron interactions allows us to investigate the extent of correlations beyond the single-particle picture and identify conditions for defining a “best” independent particle model for the tunnelling currents observed. We find that the most suitable single particle effective potential is not one commonly in use by electronic structure methods, such as the Hartree-Fock or Kohn-Sham approximations.

## References:

- [1] *Introducing Molecular Electronics*, G. Cuniberti, G. Fagas, K. Richter (Eds), Lecture Notes in Physics **680** (Springer, Berlin and Heidelberg 2005), ISBN: 3540279946
- [2] P. Delaney and J. C. Greer, Phys. Rev. Lett. **93**, 036805 (2004)
- [3] T. Henderson, G. Fagas, E. Hyde, and J.C. Greer, submitted to J. Chem. Phys. (2006)
- [4] G. Fagas, P. Delaney, and J.C. Greer, Phys. Rev. B **73**, 241314(R) (2006)

---

<sup>\*</sup> Email: gfagas@tyndall.ie