

Single Molecule Conductivity: The role of junction-orbital degeneracy in the artificially high currents predicted by *ab initio* approaches

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A priori evaluations, using Hartree-Fock self-consistent-field (SCF) theory or density-functional theory (DFT), of the current passing between two electrodes through a single bridging molecule result in predicted conductivities that may be up to 1-2 orders of magnitude larger than observed ones. We demonstrate that this can arise due to the improper application of the computational methods. Conductivity is shown to arise from tunneling between junction states of the electrodes through the molecule; these states are inherently either quasi 2-fold or 4-fold degenerate and *always* comprise the HOMO band at the Fermi energy of the system. Frequently, in previous cluster based molecular conduction calculations, closed-shell SCF or Kohn-Sham DFT methods have been applied to systems that we demonstrate to be intrinsically open-shell in nature. Such calculations are shown to induce artificial HOMO-LUMO band splittings that Landauer-based formalisms for steady-state conduction interpret as arising from extremely rapid through-molecule tunneling at the Fermi energy, hence, overestimating the low-voltage conductivity.

It is demonstrated that these shortcomings can be eliminated, reducing calculated current magnitudes, through the alternate use of electronic-structure calculations based on the spin-restricted open-shell (ROHF) formalism and related multi-configurational SCF or DFT approaches. Further, we demonstrate that most anomalies arising in DFT implementations arise through the use of hybrid density functionals such as B3LYP. While the enhanced band-gap properties of these functionals have made them the defacto standard in molecular conductivity calculations, we demonstrate that it also makes them particularly susceptible to open-shell anomalies.

Finally, with the spurious effects of open shell anomalies removed subtle fluctuations in the current are evident with changes in the geometry of the system. Consequently, the implications of different binding geometries can be examined and it is shown that whilst these will have an impact, in the cases studied it has not proved to be a dramatic effect. This is a positive result for molecular electronics as it means that the binding site of a molecule may not have to be controlled with atomic precision for a device to function with the desired properties.