First-principles studies of electrical transport in nanoscale molecular junctions

J. B. NEATON, Molecular Foundry, Lawrence Berkeley National Laboratory

Understanding the conductance of individual molecular junctions is a forefront topic in theoretical nanoscience. The development of a general, efficient atomistic approach for treating an open system out of equilibrium with good accuracy, and then using it to inform experiment, is a significant open challenge in the field. Here I will describe studies where first-principles techniques, based on density functional theory (DFT) and beyond, are used to investigate some of the fundamental issues associated with single-molecule transport measurements. After a brief summary of previous work, a DFT-based scattering-state approach is presented and applied to H$_2$ and amine-Au linked molecular junctions [1], two systems for which there exist reliable data [2]. Similar to most ab initio studies, we rely on a Landauer approach within DFT for junction conductance. Using this framework, which has proven relatively accurate for metallic point contacts, good agreement with experiment is obtained for the H$_2$ conductance. For amine-Au linked junctions, however, the computed conductance is significantly larger than that measured, although structural trends are reproduced by the calculations. To explore this further, we draw on GW calculations of a prototypical metal-molecule contact, benzene on graphite, where interfacial polarization effects are found to drastically modify frontier orbital energies [3]. A physically motivated model self-energy correction is developed from our GW calculations, applied to the amine case, and shown to quantitatively explain the discrepancy with experiment. The importance of many-electron corrections beyond DFT for accurately computing molecular conductance and understanding experiments is thoroughly discussed. [1] S. Y. Quek et al., Nano Lett 7, 3482 (2007); K. H. Khoo et al., submitted (2007). [2] R. Smit et al., Nature 419, 906 (2002); L. Venkataraman et al., Nature 442, 904 (2006). [3] J. B. Neaton et al., Phys. Rev. Lett. 97, 216405 (2006).

1This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.