A first-principles density functional approach for charge transfer & transport

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Abstract:

We present a first-principles density functional theory (DFT) which is successful in classes of problems traditionally considered "too tough for DFT". The basic elements of this method are briefly reviewed (first principles tuning of the Baer-Neuhauser-Livshits range-separated hybrid), but the focus is on recent applications. Unlike most DFT approximations, our approach yields orbital energies that closely approximate the ionization potentials and electron affinity of atoms, molecules, clusters and solids. We demonstrate the success of the method in treating the breaking of 3 electron bonds and reaction barriers. The time-dependent version of the method falls within the Runge-Gross TDDFT framework, using generalized time-dependent Kohn-Sham equations. The method is capable of describing Rydberg and electron-transfer excitations. We give examples with comparison to experiment on coumarin dyes, aromatic molecular complexes and bipeptides. Finally, we discuss an application to molecular electronics, where a gate potential tunes the conductance level of a molecular junction. Concepts such as Coulomb blockade and exciton binding energy are clearly illustrated using the orbital energies of our first principles DFT method.

Literature:

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