Exchange functionals with local range-separation

Hilke Bahmann

Physical and Theoretical Chemistry,University of Wuppertal, Gaussstr. 20, 42119 Wuppertal, Germany
bahmann@uni-wuppertal.de

ABSTRACT

Among the persisting short-comings of existing exchange-correlation functionals are limitations of hybrid schemes due to fixed system-wide parameters. One example is the parameter that steers the transition from short to long-range exchange in range-separated functionals. For spectroscopic properties, this parameter is often tuned to a given system. The optimal RS parameter is, however, highly system dependent and this mismatch is particulary pronounced in semiconductor-organic interfaces where traditional range-separated functionals overestimate the semiconductor band gaps considerably.

By replacing the constant RS parameter with a density-dependent function, a more versatile hybrid functional with local range separation is obtained. These functionals can be implemented efficiently and have been shown to be superior to their counterparts with a global RS paramter for basic chemical properties[1]. They are further assessed for ionization energies, electron afinities and band gaps of TiO_2 clusters, as well as the energy levels in representative systems with an interface between an organic dye and TiO_2.

An accurate description of the electronic structure at such interfaces is crucial for models of energy conversion materials and understanding the underlying charge-transfer processes. For larger model systems with a sizeable TiO_2-cluster, local hybrid functionals with a real-space admixture of the exact and (semi)local energy densities, have been studied as well. They provide the best compromise so far for the description of the separate systems and the interface[2].

References

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