Optimally tuned range separated hybrid functionals

Thiago Branquinho de Queiroz
UFABC

Density functional theory (time independent, DFT, and time dependent, TDDFT) is one of the most attractive methods for describing the electronic structure of organic compounds, since it is, in principle, an exact quantum chemistry theory with a moderate computational cost. However, approximations need to be done to the unknown exchange-correlation energy and potential, which borders the accuracy of the method. Standard approximations as semi-local and global hybrid functionals can describe valence excitations for many molecular systems, but fail, even qualitatively, to describe charge transfer excitations or long range interactions (among other properties, as ionization potentials). There are many reasons for these fails, but the most visible is the wrong potential asymptotics (1/r at "far distances"). One interesting strategy is the range separated hybrid (RSH) functional, where the Coulomb-interaction is split into short and long range components with the help of the error function, \(\text{erf}[\omega r]\), which contains a range-separation parameter \(\omega\). In this way, the short component is composed by an local or semi-local approximation while the long range is represented by the Fock exchange potential. This strategy restablishes the asymptotics of the potential, but the free parameter (\(\omega\)), that determines the exchange distances between the short and long range, needs to be choosen. The best strategy so far is to adjust it by first principles, using the physical interpretation of the Kohn-Sham frontier orbitals (HOMO and LUMO), which should be equal to the ionization potentials (ionization energy and electron affinity). In the last years we have demonstrated that this strategy is imperative for the reliable description of solvated low bandgap oligomers, which show transitions with charge transfer character, and to note the effect of long range interactions.

In this talk I will briefly present the concept of the optimally tuned RSH and show some aspects on the aforementioned examples that could not be captured by regular functionals.

References