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Range-separated Hybrid Functionals for Molecules and Interfaces

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Density functional theory (DFT) and its time-dependent extension (TD-DFT) are powerful tools enabling the theoretical prediction of the ground- and excited-state properties of many-electron systems with reasonable accuracy at affordable computational costs. The DFT treatment of particular electronic and structural properties, however, reveals severe qualitative failures of standard out-of-the-box functionals. Important examples include the wrong level alignment and spurious charge-transfer at organic-organic interfaces as well as the underestimation of bond-length alternations and excited-state energies in polymers. These failures can be traced back to the delocalization error inherent to semilocal and global hybrid functionals. In this talk, I will discuss recent efforts to reduce the delocalization error by using range-separated hybrid functionals combined with a non-empirical tuning procedure for the range-separation parameter [1-3]. The benefits and drawbacks of using range-separated hybrid functionals for the description of the ground and excited states of molecules and interfaces will be discussed. It will be demonstrated that this approach provides for robust and efficient means of calculating ionization potentials and electron affinities, for characterizing the electronic couplings in organic mixed-valence systems, for the calculation level alignment at organic/organic interfaces, and for the reliable prediction of the optical band-gap of low band-gap polymers. I will further motivate why RSH functionals provide for a superior starting point for non-self-consistent *GW* calculations as compared to standard semilocal or global hybrid functionals.

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[3] T. Körzdörfer, R. M. Parrish, J. S. Sears, C. D. Sherrill, and J.-L. Brédas, *J. Chem. Phys.* **137**, 124305 (2012).