The role of middle-range Hartree-Fock-type exchange in hybrid functionals

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While hybrid functionals are responsible for many of the successes of modern Kohn-Sham theory, they have several drawbacks as well. The slow decay of nonlocal exchange makes hybrids computationally demanding in extended systems with small bandgaps, while in finite systems the rapid decay of semilocal exchange causes errors in describing such phenomena as charge transfer and Rydberg excitations, polarizabilities of long chains, and so forth. In addition, different amounts of nonlocal exchange seem to be optimal for the description of different quantities - reaction barriers, for example, appear to require a substantially larger fraction of nonlocal exchange than do heats of formation. These problems can all be addressed by range-separated hybrids which include different amounts of nonlocal exchange at different values of the interelectronic separation. Excluding long-range nonlocal exchange in extended systems improves computational efficiency without loss of accuracy, while including full long-range nonlocal exchange in finite systems improves accuracy in quantities sensitive to the long-range potential, and makes it possible to treat both reaction barriers and thermochemistry with one simple functional. Both approaches use a significant fraction of nonlocal exchange for intermediate electronic separations. We show that a hybrid functional that uses nonlocal exchange only for this middle range has many advantages, properly describing thermochemistry, reaction barriers, and bandgaps in the same framework.