The importance of middle-range Hartree-Fock-type exchange for hybrid density functionals

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Hybrid functionals are responsible for much of the utility of modern Kohn-Sham density functional theory. When rigorously applied to solid-state metallic and small band gap systems, however, the slow decay of their nonlocal Hartree-Fock-type exchange makes hybrids computationally challenging and introduces unphysical effects. This can be remedied by using a range-separated hybrid which only keeps short-range nonlocal exchange, as in the functional of Heyd *et al.* [J. Chem. Phys. **118**, 8207 (2003)]. On the other hand, many molecular properties require full *long-range* nonlocal exchange, which can also be included by means of a range-separated hybrid such as the recently introduced LC-ωPBE functional [O. A. Vydrov and G. E. Scuseria, J. Chem. Phys. **125**, 234109 (2006)]. In this paper, we show that a three-range hybrid which mainly includes middle-range Hartree-Fock-type exchange and neglects long- and short-range Hartree-Fock-type exchange yields excellent accuracy for thermochemistry, barrier heights, and band gaps, emphasizing that the middle-range part of the $1/r$ potential seems crucial to accurately model these properties. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2822021]

Due to its combination of relatively high accuracy and low computational cost, density functional theory[1,2] (DFT) has become the most popular method for electronic structure calculations in molecules and solids. The great successes of modern DFT owe much to the advent of hybrid functionals[3–7] which mix a fraction of nonlocal Hartree-Fock-type exchange with conventional local or semilocal exchange functionals, improving the accuracy of the method quite significantly. For example, the nonempirical hybrid PBEh (Refs. 6 and 7) reduces the errors in heats of formation and barrier heights by at least a factor of 2 compared to its parent, the semilocal PBE functional of Perdew *et al.*[8] Despite their improved accuracy, however, hybrid functionals have several drawbacks, two of which we discuss here.

One significant drawback of hybrid functionals in metallic systems is that the nonlocal exchange interaction has an unphysical and extremely slow spatial decay.[9] While hybrid functionals can be applied in systems with small or vanishing band gaps,[10–12] this slow decay makes the rigorous and numerically accurate application of hybrid functionals computationally challenging for such systems.

A second drawback of hybrid functionals is that the asymptotic decay of the exchange potential for atomic and molecular systems is incorrect. The exact exchange potential decays asymptotically as $-1/r$,[13,14] while that of a hybrid functional with a fraction c of nonlocal exchange decays as $-c/r$. This incorrect long-range decay is believed to be responsible for errors in describing charge transfer and Rydberg excitations[15] and polarizabilities of long chains.[16,17]

Either of these two drawbacks can be overcome by using a *range-separated* hybrid, which uses different fractions of nonlocal exchange at different interelectronic separations r_{12}.

The range-separated functional of Heyd, Scuseria, and Ernzerhof[18–20] (HSE) uses a fraction of nonlocal exchange only at short range (i.e., for small r_{12}), allowing it to rigorously include a portion of nonlocal exchange and treat metallic systems efficiently while still providing accuracy comparable to its parent PBEh hybrid for atomic and molecular systems.[18] However, since HSE cuts off the long-range nonlocal exchange, its exchange potential decays even faster than that of PBEh, and its performance for properties sensitive to the long-range exchange potential is on par with that of PBE.

On the other hand, there has been considerable effort invested in range-separated hybrid functionals which use full long-range nonlocal exchange to guarantee the proper asymptotic decay of the exchange potential.[15,16,21–24] Such a model can simultaneously deliver accurate barrier heights and, as recently shown, atomization energies.[21–23] Further, such models perform well for processes involving long-range charge transfer, Rydberg excitations, and other properties sampling the tail of the density.[15–17,25–29]

In this paper, we seek to reconcile these two seemingly different approaches; in doing so, we hope to increase the accuracy of the HSE functional so that it is comparable to that of long-range corrected functionals such as LC-ωPBE, while retaining broad applicability for periodic systems. The key to this goal is to note that the range scales in HSE and in LC-ωPBE are very different.

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Typical range-separated hybrid functionals begin by writing[16,18,21,22,30,31]

$$\frac{1}{r_{12}} = \underbrace{\frac{\text{erfc}(\omega r_{12})}{r_{12}}}_{\text{SR}} + \underbrace{\frac{\text{erf}(\omega r_{12})}{r_{12}}}_{\text{LR}} \qquad (1)$$

and treating the two different components differently. The range-separation parameter ω governs the meaning of short range (SR) and long range (LR). In HSE, we have $\omega = 0.11\ a_0^{-1}$, while in LC-ωPBE, we instead have $\omega = 0.40 a_0^{-1}$. Both the short range in which HSE uses nonlocal exchange and the long range in which LC-ωPBE does so include a significant fraction of what we will here refer to as "middle range" (MR). Therefore, it seems interesting to explore the quality of results obtainable with an approach in which middle-range Hartree-Fock-type exchange is emphasized. For very small r_{12} the local density approximation to the exchange energy is exact,[32,33] so there would seem to be little need for short-range nonlocal exchange, while at very long range, as we have seen, nonlocal exchange can be computationally undesirable in systems with vanishing band gaps.

Range-separated hybrids can be rigorously justified through a model Hamiltonian formalism.[31,34] We begin by writing

$$H_0 = T + V_{\text{ext}} + \bar{V}_{\text{ee}}, \qquad (2)$$

where $\bar{V}_{\text{ee}}$ is some model electron-electron interaction operator. The ground state total energy can be obtained via a constrained search approach as follows:

$$E_0 = \min_{\Psi}(\langle\Psi|H_0|\Psi\rangle + \bar{F}[n_\Psi]), \qquad (3)$$

where $\bar{F}[n]$ is a universal functional of the density which can be written as

$$\bar{F}[n] = \frac{1}{2}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 n(\boldsymbol{r}_1)n(\boldsymbol{r}_2)(V_{\text{ee}} - \bar{V}_{\text{ee}}) + \bar{E}_{\text{xc}}[n]. \qquad (4)$$

Note that with this definition, the Coulomb energy is treated exactly, as is the external potential, while the majority of the kinetic energy is included in $\langle H_0 \rangle$. The unknown functional $\bar{E}_{\text{xc}}$ corrects the kinetic energy and accounts for electron exchange and correlation.

In the limit that $\bar{V}_{\text{ee}} = 0$, the foregoing scheme reduces to the usual Kohn-Sham approach. In this case, the minimization in Eq. (3) is simple since we may minimize over single determinants, but constructing accurate approximations to $\bar{E}_{\text{xc}}$ is not straightforward. In the limit that $\bar{V}_{\text{ee}} = V_{\text{ee}}$, this reduces to the usual wave function methodology, in which case $\bar{E}_{\text{xc}} = 0$ but the minimization of Eq. (3) is computationally intractable for all but the smallest systems. There is thus a trade-off between ease of minimization and ease of construction of $\bar{E}_{\text{xc}}$. Using nonzero $\bar{V}_{\text{ee}}$ but restricting the minimization to single determinants retains the computational simplicity of the Kohn-Sham scheme but is of course approximate. Conventional hybrids with a fraction c of exact exchange can

be seen as writing $\bar{V}_{\text{ee}} = cV_{\text{ee}}$, with the minimization restricted to single determinants only. Range-separated hybrids merely entail more elaborate forms for $\bar{V}_{\text{ee}}$.

A three-range hybrid functional can be written as

$$E_x = (1 - c_{\text{SR}})E_x^{\text{SR-KS}} + c_{\text{SR}}E_x^{\text{SR-HF}} + (1 - c_{\text{MR}})E_x^{\text{MR-KS}}$$
$$+ c_{\text{MR}}E_x^{\text{MR-HF}} + (1 - c_{\text{LR}})E_x^{\text{LR-KS}} + c_{\text{LR}}E_x^{\text{LR-HF}}, \qquad (5)$$

where KS and HF, respectively, refer to semilocal exchange and nonlocal exchange. Note that nonlocal exchange here refers not only to the exchange energy but also to the exchange potential, both of which take the Hartree-Fock form. In other words, we are doing generalized Kohn-Sham in the sense of Seidl *et al.*[35] The short-, mid-, and long-range exchange energies are defined in terms of range-separation functions $\mathcal{F}_{\text{SR}}(r_{12})$, $\mathcal{F}_{\text{MR}}(r_{12})$, and $\mathcal{F}_{\text{LR}}(r_{12})$ by writing

$$\frac{1}{r_{12}} = \frac{\mathcal{F}_{\text{SR}}(r_{12})}{r_{12}} + \frac{\mathcal{F}_{\text{MR}}(r_{12})}{r_{12}} + \frac{\mathcal{F}_{\text{LR}}(r_{12})}{r_{12}}. \qquad (6)$$

For practical purposes, some constraints can be placed both on the coefficients c and the range-separation functions $\mathcal{F}$. If the exchange functional of Eq. (5) is to be generally applicable to metals, we wish to have $c_{\text{LR}} = 0$; we presumably want $c_{\text{MR}} \approx 1$ to aid in the description of quantities sensitive to the long-range potential, while we desire c_{SR} to be small. For small (large) r_{12} only $\mathcal{F}_{\text{SR}}$ ($\mathcal{F}_{\text{LR}}$) should be nonzero. The two-electron integrals needed to build the nonlocal exchange contributions at each range must be straightforward, and so too must be the integrals over the exchange hole needed to build the semilocal contributions. Linear combinations of error functions satisfy all of these criteria, and our range-separation functions are therefore chosen as

$$\mathcal{F}_{\text{LR}}(r_{12}) = \text{erf}(\omega_{\text{LR}}r_{12}), \qquad (7\text{a})$$

$$\mathcal{F}_{\text{SR}}(r_{12}) = \text{erfc}(\omega_{\text{SR}}r_{12}), \qquad (7\text{b})$$

$$\mathcal{F}_{\text{MR}}(r_{12}) = \text{erfc}(\omega_{\text{LR}}r_{12}) - \text{erfc}(\omega_{\text{SR}}r_{12}). \qquad (7\text{c})$$

Note that if $\omega_{\text{SR}} = \omega_{\text{LR}}$, then the middle range disappears. This is the case of HSE ($\omega_{\text{SR}} = \omega_{\text{LR}} = 0.11\ a_0^{-1}$) and LC-$\omega$PBE ($\omega_{\text{SR}} = \omega_{\text{LR}} = 0.40\ a_0^{-1}$). A distinction between ω_{SR} and ω_{LR} is not needed for two-range functionals but is needed for the three-range case.

In summary, the present work uses

$$E_x = (1 - c_{\text{SR}})E_x^{\text{SR-KS}} + c_{\text{SR}}E_x^{\text{SR-HF}} + (1 - c_{\text{MR}})E_x^{\text{MR-KS}}$$
$$+ c_{\text{MR}}E_x^{\text{MR-HF}} + E_x^{\text{LR-KS}} \qquad (8)$$

for the exchange functional, with the range-separation functions $\mathcal{F}_{\text{SR}}$, $\mathcal{F}_{\text{MR}}$, and $\mathcal{F}_{\text{LR}}$ taking the form of Eq. (7). A plot of the short-range, middle-range, and long-range interactions $\mathcal{F}/r_{12}$ using our recommended values for the parameters ω_{SR} and ω_{LR} (*vide infra*) is given in Fig. 1. We use the PBE exchange hole model[36] to define the semilocal exchange contributions, and PBE correlation.[8] Both HSE and LC-ωPBE can be written as special cases of the general three-range functional of Eq. (5). In the case of HSE, one would write $c_{\text{SR}} = 0.25$ and $c_{\text{LR}} = 0$, while in the case of LC-ωPBE, we
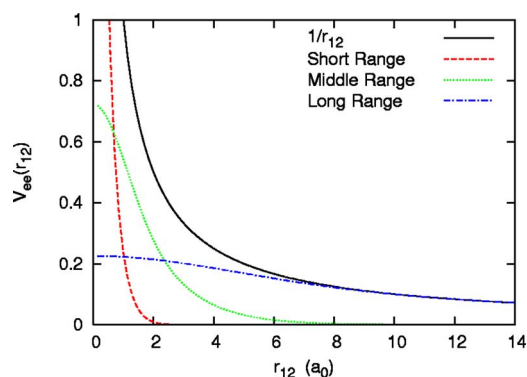
FIG. 1. (Color online) Range-separated electronic potentials $\mathcal{F}(r_{12})/r_{12}$ from the range-separation functions as defined in Eq. (7) with $\omega_{SR}=0.84\ a_0^{-1}$ and $\omega_{LR}=0.20\ a_0^{-1}$.

would write $c_{SR}=0$ and $c_{LR}=1$. Because in both cases $\omega_{SR}=\omega_{LR}$, the middle-range interaction of Eq. (7c) disappears.

All calculations are carried out self-consistently in the $6\text{-}311G++(3df,3pd)$ basis set, in a development version of the GAUSSIAN program.[37] We consider here the AE6 set of six atomization energies,[38] the BH6 set of six barrier heights,[38] the G3 set of heats of formation,[39,40] the HTBH38 set of proton-transfer barrier heights,[41] the NHTBH38 set of nonproton transfer barrier heights,[42,43] the total ground state energies of H through Ar,[44] and the band gaps of five solids (BN, BP, C, Si, and SiC) which we deem representative of those we used before to benchmark HSE.[20] Results are reported in Table I for two different sets of parameters. In both cases, we pick the values of c_{MR} and ω_{LR} and optimize ω_{SR} and c_{SR} non-self-consistently (i.e., using the PBE orbitals) to describe the AE6 and BH6 test sets. Barrier heights are weighted as three times more important than atomization energies (in line with the results from LC-ωPBE, for which errors in BH6 are three times smaller than errors in AE6). Notice that $c_{SR}=0$ in both cases—this is the optimal value, and is not imposed.

We begin with the column labeled "A," in which $\omega_{LR}=0.11\ a_0^{-1}$, chosen in analogy with HSE. We impose, however, $c_{MR}=1$, in analogy with LC-ωPBE. This combination of parameters gives quite excellent results for finite systems, being roughly equivalent to LC-ωPBE. This should not be too surprising. The long-range interaction turns on rather slowly, so is of limited energetic importance in these molecular systems. The crucial pieces are the short-range PBE and the mid-range nonlocal exchange, both of which are as used in LC-ωPBE. Moreover, the optimum value for ω_{SR} is $\sim\!0.40\ a_0^{-1}$, corresponding to that in LC-ωPBE. Performance for band gaps is unfortunately lacking, however, as they are overestimated substantially; evidently, the parameters which work for finite systems are not appropriate for extended systems.

We can, however, adjust ω_{LR} and c_{MR}. Non-self-consistent investigations with $c_{MR}=1$ reveal that the error in the AE6 and BH6 training sets and the G1 test set of heats of formation[45,46] and the total atomic energies of H–Ar are weakly dependent on ω_{LR} for $\omega_{LR}\lesssim 0.20\ a_0^{-1}$. Evidently, at least for these sets, while finite systems benefit from the inclusion of middle-range exact exchange, the definition of middle range is somewhat loose. We can take advantage of this behavior to improve performance for solids. Further, we can adjust c_{MR}, and similar non-self-consistent investigations with $\omega_{LR}=0.20\ a_0^{-1}$ show that performance for finite systems is reasonable for $c_{MR}\gtrsim 0.5$. In the column of Table I labeled "B," we show self-consistent results with $\omega_{LR}=0.20\ a_0^{-1}$, $c_{MR}=0.60$, and c_{SR} and ω_{SR} optimized as previously described. Results for thermochemistry are still quite good, and while performance for barrier heights degrades slightly, performance for band gaps improves dramatically. Our recommended parameters are thus $c_{SR}=0$, $c_{MR}=0.60$, $\omega_{LR}=0.20\ a_0^{-1}$, and $\omega_{SR}=0.84\ a_0^{-1}$.

To get some sense of the physical content of the functional, we examine the fraction of nonlocal exchange used as a function of r_{12}, given by

TABLE I. Mean absolute errors and parameters for two different parametrizations of the functional of Eq. (8) and for several other functionals based on the PBE model. All results are in kcal/mol, except for atomic total energies (mhartree/electron) and band gaps (eV). Note that ω_{SR} and c_{MR} are optimized to describe the AE6 and BH6 sets with the other parameters fixed *a priori*, and that we do not fit to the other data sets at all.

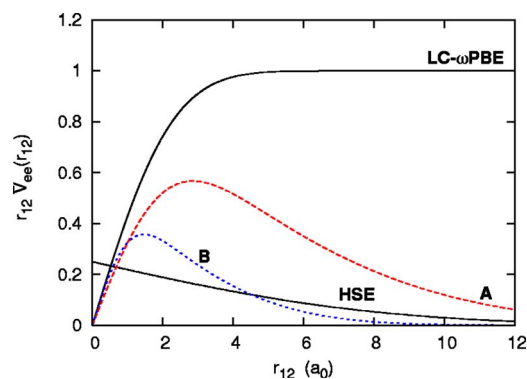|	PBE	PBEh	HSE	LC-ωPBE	This work	
					A	B
c_{SR}	0	0.25	0.25	0	0	0
c_{MR}	0	0.25	$\cdots$	$\cdots$	1	0.6
c_{LR}	0	0.25	0	1	0	0
$\omega_{LR}(a_0^{-1})$	$\cdots$	$\cdots$	0.11	0.40	0.11	0.20
$\omega_{SR}(a_0^{-1})$	$\cdots$	$\cdots$	0.11	0.40	0.42	0.84
AE6	15.1	6.1	4.7	4.9	4.6	5.9
G3	22.2	6.7	4.8	4.3	4.0	4.4
BH6	9.6	4.9	4.8	1.5	1.4	1.8
HTBH38	9.7	4.6	4.6	1.3	1.4	1.7
NHTBH38	8.6	3.6	6.7	2.4	2.1	1.8
Atomic energies	8.6	7.1	6.2	5.0	5.1	4.8
Band gaps	1.1	$\cdots$	0.1	$\cdots$	1.7	0.4

FIG. 2. (Color online) Fraction of nonlocal exchange as a function of electronic separation for a variety of range-separated hybrids. HSE and LC-ωPBE as defined in Refs. 18 and 22, respectively; A and B indicate the two parametrizations of the functional of Eq. (8) with parameters as in Table I.

$$r_{12}\bar{V}_{ee}(r_{12}) = c_{SR}\mathcal{F}_{SR}(r_{12}) + c_{MR}\mathcal{F}_{MR}(r_{12}). \qquad (9)$$

In Fig. 2 we show $r_{12}\bar{V}_{ee}(r_{12})$ for HSE, LC-ωPBE, and the present work for both sets of parameters. Parameter set A interpolates smoothly between HSE and LC-ωPBE, as one might expect, while our recommended parameter set B follows LC-ωPBE for small r_{12} before rapidly decaying below the HSE result.

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