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# Optimal operators for Hartree–Fock exchange from long-range corrected hybrid density functionals

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ABSTRACT

The long-range operators for Hartree–Fock exchange from two recently proposed long-range corrected hybrid functionals, $\omega$B97 and $\omega$B97X [J.-D. Chai, M. Head-Gordon, J. Chem. Phys. 128 (2008) 084106], are discussed. A conserved property is found in the middle-range region of the operator from $\omega$B97X. We argue that the fine details of the Hartree–Fock exchange mixing in this region are responsible for the accuracy of the long-range corrected hybrid functionals in thermochemistry and barrier heights.

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In the last two decades, Kohn–Sham density-functional theory (KS-DFT) [1,2] has been the most popular quantum-chemical method for calculations on large-scale ground-state systems [3–5]. As a result, developing an accurate exchange-correlation energy functional $E_{xc}[\rho]$, continues being the subject of intense current interest.

Semi-local density functionals based on the local spin density approximation (LSDA) and generalized gradient approximations (GGAs) (commonly denoted as DFAs for density-functional approximations) are computationally favorable for large systems and have been shown to be successful in diverse quantum-chemical applications [3–5]. However, in circumstances where an accurate treatment of the non-locality of the exchange-correlation (XC) hole is crucial, DFAs can and do produce qualitatively incorrect results [6–15].

On the other hand, hybrid density functionals, combining density functionals with the exact Hartree–Fock (HF) exchange $E_x^{\mathrm{HF}}$, provide cost-effective ways of including the non-local effects of the XC hole. The concept of a hybrid scheme can be deduced from the adiabatic connection formalism for $E_{xc}$ [16]. The most widely used hybrid density functionals at present are *global* hybrids, which can be written as linear combinations of $E_x^{\mathrm{HF}}$ and $E_{xc}^{\mathrm{DFA}}$:

$$E_{xc} = c_x E_x^{\mathrm{HF}} + (1 - c_x) E_x^{\mathrm{DFA}} + E_c^{\mathrm{DFA}} \tag{1}$$

where $c_x$ is a small fractional number whose optimal value depends on the systems of interest [5].

Unlike the global hybrid functionals, the long-range corrected (LC) hybrid functionals [14,15,17–32] employ 100% HF exchange for a long-range (LR) part of the interelectron repulsion operator L(r)/r, DFA exchange for the complementary short-range (SR) operator [1 – L(r)]/r, and DFA correlation for the entire Coulomb operator 1/r:

$$E_{xc}^{\mathrm{LC}} = E_x^{\mathrm{LR\text{-}HF}} + E_x^{\mathrm{SR\text{-}DFA}} + E_c^{\mathrm{DFA}} \tag{2}$$

where L(r) is a fraction of HF exchange at r.

There are, however, two important issues relevant to the overall accuracy of the LC hybrid functionals. One is to develop accurate DFAs for the SR exchange and correlation, and the other is to seek optimal LR operators for the partition. For the first issue, an accurate DFA for SR exchange may be the main concern, as accurate DFAs for correlation are widely available [3–5]. Although the LSDA for SR exchange $E_x^{\mathrm{SR\text{-}LSDA}}$ has been available [24,25], the resulting LC hybrid LSDA functional is insufficiently accurate for typical quantum-chemical applications [26]. To make progress, Hirao and co-workers have proposed an *ansatz* for the generalization of any $E_x^{\mathrm{DFA}}$ to $E_x^{\mathrm{SR\text{-}DFA}}$ [27,28]. Although their LC hybrid GGA functionals outperform the LC hybrid LSDA functional, they are still inferior to global hybrid GGA functionals for properties such as thermochemistry.

Recently, we have also proposed a simple *ansatz* to extend any $E_x^{\mathrm{DFA}}$ to $E_x^{\mathrm{SR\text{-}DFA}}$, as long as the SR operator has considerable spatial extent [14]. With the use of flexible DFAs, our LC hybrid functionals outperform the corresponding global hybrid functionals, which must be attributed to the difference of the operators used for HF exchange in these functionals (i.e. the second issue). Note that the operator $c_x$/r is effectively used for the HF exchange mixing in the global hybrid functionals. This outcome seems quite puzzling, as the constraint of being LC was thought to be the main reason limiting the accuracy of the LC hybrid functionals, as the Coulomb tails have been shown to contribute insignificantly to relative energies, such as atomization energies [33].

In this Letter, we try to unlock the above mystery by searching for a distinctive common feature of the optimized LR operators used for HF exchange mixing in $\omega$B97 and $\omega$B97X [14]. Upon uncovering such a feature, we then also compare to other proposed

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SR/LR partitions and comment on the prospects for future development of optimal LR operators.

By the SR/LR partition, Eq. (2) can be re-written as

$$E_{xc}^{\mathrm{LC}} = E_{xc}^{\text{SR-DFA}} + (E_{x}^{\text{LR-HF}} + E_{c}^{\text{LR-DFA}}). \tag{3}$$

A DFA XC hole is used for the SR operator, while the HF (exact) exchange hole and a DFA correlation hole are used for the LR operator. Due to its semi-local nature, a DFA XC hole is known to be reasonably accurate for small inter-electronic separations from the reference electron, but becomes inaccurate for large inter-electronic separations [34–37]. As a result, a DFA performs far better for the SR operator than does for the LR one. One thus expects only a small fraction of HF exchange is needed for the region where the DFA XC hole is already a good description of the exact XC hole. Therefore, L(r) should be small for the SR region, and it should approach unity asymptotically. The standard error function, erf($\omega r$), provides a smooth transition between these two extremes, and is the preferred L(r) in many LC hybrid functionals, such as $\omega$B97 [14], because it facilitates efficient evaluation of the exact exchange LR matrix elements over Gaussian basis functions [38].

Based on optimization over a large and diverse training set, the optimal parameter for the partition, $\omega$, is found to be 0.4 Bohr$^{-1}$ for $\omega$B97 [14], in agreement with the work of Vydrov et al. [29,30]. We thus expect that erf($\omega r$) is optimal at $\omega$ = 0.4 Bohr$^{-1}$ for the LC hybrid functionals with flexible and accurate GGAs.

To improve upon $\omega$B97, we have previously proposed to include a small fraction of $E_{x}^{\text{SR-HF}}$, as this should still be important for reducing the remaining self-interaction-error of $E_{xc}^{\text{SR-DFA}}$ [14]. Instead of using the erf operator, we effectively use the following LR operator (denoted as erfx) in Eq. (2)

$$\mathrm{erfx}(r;\omega,c_x) = \mathrm{erf}(\omega r) + c_x \mathrm{erfc}(\omega r) \tag{4}$$

where $c_x$ is a small fractional number.

This erfx operator has been shown to be superior to the erf operator [14], as the root-mean-square (RMS) errors of the training set for $\omega$B97X (with erfx) are significantly reduced (by 0.5 kcal/mol), when compared with $\omega$B97 (with erf). The RMS errors of the training set for $\omega$B97X optimized at different values of $\omega$ are plotted in Fig. 1. At $\omega$ = 0.3 Bohr$^{-1}$, the optimization is done self-consistently, while at other values of $\omega$, non-self-consistent orbitals are used. At $\omega$ = 0.0, 0.1, and 0.5 Bohr$^{-1}$, the corresponding RSHXLDA orbitals [26] are used, and at $\omega$ = 0.2 and 0.4 Bohr$^{-1}$, the $\omega$B97X-D [15] (a re-optimized $\omega$B97X with empirical atom–atom dispersion corrections) and $\omega$B97 orbitals [14] are used respectively. We have previously demonstrated that these results should only change insignificantly with the self-consistent orbitals [14]. Another type of operator that effectively includes short-range Hartree–Fock exchange has been developed with similar arguments [39,40].

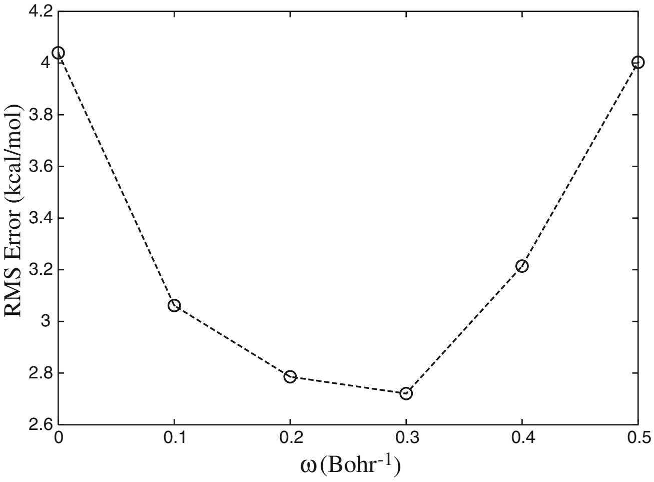

**Fig. 1.** The root-mean-square (RMS) errors of the training set for $\omega$B97X optimized at different values of $\omega$. At $\omega$ = 0.3 Bohr$^{-1}$, the optimization is done self-consistently, while at other values of $\omega$, non-self-consistent orbitals are used (see text).

To investigate which part of the erfx operator is responsible for this improvement, the optimal erfx operators for $\omega$B97X [14] at different values of $\omega$ (0.2, 0.3, 0.4, and 0.5 Bohr$^{-1}$) are plotted in Fig. 2. Surprisingly, all of the operators almost intersect at one point ($r \simeq 0.8$ Bohr), which implies that the values of $c_x$ in this range of $\omega$ values are strongly dependent on $\omega$ (indeed $c_x$ becomes *negative* at $\omega$ = 0.5 Bohr$^{-1}$). This also indicates that these operators must not change significantly in the middle-range (MR) region in order to achieve good balanced performance for thermochemistry and barrier heights.

As the RMS errors still show strong $\omega$-dependence, the fine details of the MR region of the operators are clearly crucial. The diversity of behavior of these operators in the SR region ($r \lesssim 0.5$ Bohr) and in the LR region ($r \gtrsim 1.5$ Bohr) implies that exact exchange in these two regions is relatively insignificant for thermochemistry and barrier heights. Similar conclusions for the importance of MR region of operators have also been presented by Henderson et al. [41] using different arguments.

The exact exchange contribution from the SR region is expected to be unimportant for properties that do not involve changes in the core contributions to $E_{xc}$, such as thermochemistry and barrier heights, where their effects on relative energies nearly cancel. However, for properties sensitive to the core contributions, such as atomic energies and core excitation energies, the details of HF exchange mixing in the SR region could still be important.

The LR region of Coulomb operators contributes insignificantly to relative energies, like atomization energies, as demonstrated by Adamson et al. [33]. Of course, for the properties sensitive to these tail contributions, such as dissociation of cations with odd number of electrons [6–10,14,15] and long-range charge-transfer excitation energies [11–15], the details of exact exchange mixing in the LR region are crucial.

Finally, a GGA XC hole seem to be reasonably accurate even in the MR region (0.5 Bohr $\lesssim r \lesssim$ 1.5 Bohr), although less accurate than in the SR region. From the values of the optimal erfx operator used in $\omega$B97X, only 30% HF exchange is needed at $r$ = 0.5 Bohr, and 56% HF exchange is needed at $r$ = 1.5 Bohr, which reflects the decreasing appropriateness of the underlying GGA XC hole with inter-electronic distance. We infer that the constraint of having *zero*

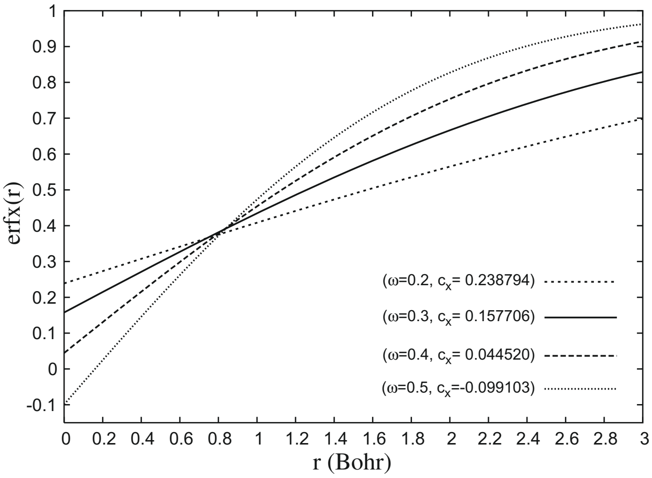

**Fig. 2.** The optimal erfx operators for $\omega$B97X [14] at different values of $\omega$.

slope in the operator used for the HF exchange mixing in a global hybrid functional results in its inferior performance to a corresponding LC hybrid functional.

To test the transferability of the above observations and arguments, and demonstrate the importance of the MR region of the operator used for exact exchange, we consider another LR operator, the erfgau operator [32,42]:

$$\mathrm{erfgau}(r;\omega,k,a) = \mathrm{erf}(\omega r) - k\frac{2\omega r}{\sqrt{\pi}}e^{-(1/a)\omega^2 r^2} \tag{5}$$

The erfgau operator has a sharper separation (with positive $k$ and $a$) between the LR and SR region than the erf operator. In the work of Toulouse et al. [32], $k = 1$ and $a = 3$ are chosen to ensure the value of erfgau(r)/r and its first derivative vanish at $r = 0$. Recently, Song et al. have found that this operator gives poor results for atomization energies and barrier heights [31], with an optimized $\omega$ (=2.6 Bohr$^{-1}$). Their results are greatly improved by optimizing all the three parameters ($\omega$, $k$, and $a$) of the erfgau operator. They have found that a *negative k* is essential for good atomization energies and barrier heights. To see the significance of their findings, the three optimal erfgau operators in their work are plotted in Fig. 3, and are compared with the optimal erf operator used for $\omega$B97, as well as the optimal erfx operators used for $\omega$B97X [14], and for the corresponding global hybrid (at $\omega = 0.0$ Bohr$^{-1}$).

As can be seen, the original erfgau($\omega = 2.60$ Bohr$^{-1}$, $k = 1.00$, $a = 3.00$) has a very sharp transition in the MR region, while their newly proposed erfgau($\omega = 0.39$ Bohr$^{-1}$, $k = -16.4$, and $a = 0.013$) and erfgau($\omega = 0.42$ Bohr$^{-1}$, $k = -18.0$, and $a = 0.011$) resemble the optimal erf operator of $\omega$B97 [14] in that region, which should be responsible for their improvements upon the original erfgau operator. In the SR and LR regions, all operators differ significantly, which supports our arguments that these are relatively unimportant regions for thermochemistry and barrier heights.

Of course, functionals modeled on other types of LR operators can also be considered [43], and we believe that the MR region of operators is the most important. Interestingly, it has been previously suggested that Coulomb-attenuated functionals cannot be simultaneously optimized for good thermochemistry and charge-transfer excitation energies [44]. Since we have shown that the former is controlled by the MR region, and the latter is likely controlled by the LR region, it seems worthwhile to revisit this question in the future.

In conclusion, we have found a conserved feature of the optimal erfx operators for $\omega$B97X at different values of $\omega$. On this basis, we argue that the MR region ($r = 0.5$ to 1.5 Bohr) of the partitioning operators seems to be crucial for thermochemistry and barrier heights. The fine details of the MR region of the operators for the HF exchange mixing in the LC hybrid functionals are responsible for their improved performance over the corresponding global hybrid functionals. The MR regions of the optimal LR operators of $\omega$B97 and $\omega$B97X [14], erf($\omega = 0.4$ Bohr$^{-1}$) and erfx($\omega = 0.3$ Bohr$^{-1}$, $c_x = 0.157706$) respectively, can be used an initial criterion for devising new and improved LR operators. As the LR region is found to be unimportant for thermochemistry and barrier heights, one may devise new LR operators that approach to unity faster (better for the LR properties) than the optimal erf and erfx operators, without reducing the accuracy in thermochemistry and barrier heights. We are now investigating this possibility.

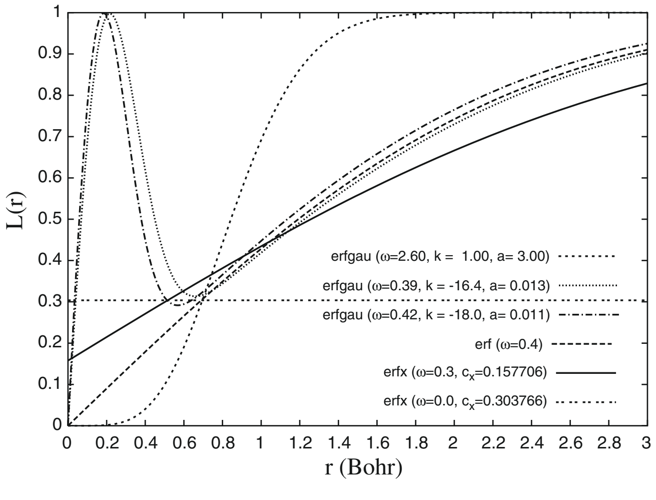

**Fig. 3.** The three optimal erfgau operators in Ref. [31] are compared with the optimal erf operator used for $\omega$B97, as well as the optimal erfx operators used for $\omega$B97X [14], and for the corresponding global hybrid (at $\omega = 0.0$ Bohr$^{-1}$).

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