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A long-range-corrected density functional that performs well for both ground-state properties and time-dependent density functional theory excitation energies, including charge-transfer excited states

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We introduce a hybrid density functional that asymptotically incorporates full Hartree–Fock exchange, based on the long-range-corrected exchange-hole model of Henderson *et al.* [J. Chem. Phys. **128**, 194105 (2008)]. The performance of this functional, for ground-state properties and for vertical excitation energies within time-dependent density functional theory, is systematically evaluated, and optimal values are determined for the range-separation parameter, ω, and for the fraction of short-range Hartree–Fock exchange. We denote the new functional as LRC-ωPBEh, since it reduces to the standard PBEh hybrid functional (also known as PBE0 or PBE1PBE) for a certain choice of its two parameters. Upon optimization of these parameters against a set of ground- and excited-state benchmarks, the LRC-ωPBEh functional fulfills three important requirements: (i) It outperforms the PBEh hybrid functional for ground-state atomization energies and reaction barrier heights; (ii) it yields statistical errors comparable to PBEh for valence excitation energies in both small and medium-sized molecules; and (iii) its performance for charge-transfer excitations is comparable to its performance for valence excitations. LRC-ωPBEh, with the parameters determined herein, is the first density functional that satisfies all three criteria. Notably, short-range Hartree–Fock exchange appears to be necessary in order to obtain accurate ground-state properties and vertical excitation energies using the same value of ω. [DOI: 10.1063/1.3073302]

I. THEORETICAL BACKGROUND

Generalized gradient approximations (GGAs) in density functional theory (DFT) are quite adept at describing properties that depend primarily upon short-range exchange and correlation effects (e.g., molecular geometries, bond enthalpies, and some valence excitation energies). These functionals, however, yield qualitatively incorrect asymptotic behavior for the exchange-correlation potential,[1–3] and thus fail miserably for properties such as charge-transfer (CT) excitation energies[4] or polarizabilities in conjugated systems[5] that are sensitive to the virtual orbitals and the long-range behavior of the exchange-correlation potential. Since the Hartree–Fock (HF) exchange interaction does exhibit the correct asymptotic decay,[4,6] one avenue toward improving DFT is to design exchange-correlation functionals that incorporate 100% HF exchange, as opposed to the far smaller fraction (~20%–25%) employed in popular hybrid functionals. Several functionals with 100% HF exchange have been introduced recently,[7–10] though few have been tested extensively for excited-state calculations within time-dependent (TD) DFT, and those that have been tested afford valence excitation energies that are inferior to those obtained with more traditional hybrid functionals.[11]

An alternative path to achieving correct asymptotic behavior is to preserve GGA exchange at short range while activating HF exchange asymptotically, via a range-separated Coulomb operator.[12–23] These long-range-corrected (LRC) functionals exhibit the correct asymptotic distance dependence for Rydberg and CT excitation energies, and thus generally improve the accuracy of both.[16,20,24,25] In particular, LRC functionals remove[23,26] the spurious, low-energy CT states that invariably contaminate TD-DFT calculations in large molecules,[27,28] clusters,[29,30] and liquids.[31] A variety of Coulomb attenuation schemes have been explored,[13,14,18,32–35] but the most common choice is a Ewald-style partition based on the error function:

$$\frac{1}{r_{12}} = \frac{1-\mathrm{erf}(\omega r_{12})}{r_{12}} + \frac{\mathrm{erf}(\omega r_{12})}{r_{12}}. \tag{1}$$

The first component, $[1-\mathrm{erf}(\omega r_{12})]/r_{12}$, is a short-range Coulomb-like potential that decays to zero on a length scale of $\sim 1/\omega$, where ω is taken to be an adjustable parameter. The second component, $\mathrm{erf}(\omega r_{12})/r_{12}$, is a nonsingular, long-range background potential.

Given a traditional exchange-correlation functional E_{xc}, which may be either a GGA or a hybrid functional, the corresponding LRC functional is

$$E_{\mathrm{xc}}^{\mathrm{LRC}} = E_c + (1 - C_{\mathrm{HF}})E_{x,\mathrm{GGA}}^{\mathrm{SR}} + C_{\mathrm{HF}}E_{x,\mathrm{HF}}^{\mathrm{SR}} + E_{x,\mathrm{HF}}^{\mathrm{LR}}. \tag{2}$$

The components labeled "LR" and "SR" are evaluated using the long-range and short-range Coulomb potentials, respectively, while C_{HF} denotes the coefficient of HF exchange ($E_{x,\mathrm{HF}}$) present in the original functional. Hybrid LRC functionals therefore contain some fraction of short-range HF exchange, but all LRC functionals contain full HF exchange in

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the long-range limit, by virtue of the final term in Eq. (2).

The existence of an exchange-correlation functional of the form

$$E_{xc} = E_{xc}(\omega) + E_{x,\mathrm{HF}}^{\mathrm{LR}}, \tag{3}$$

in which $E_{xc}(\omega) \equiv E_{xc}(\omega)[\rho(\vec{r})]$ is some ω-dependent density functional, can be justified by introducing an electron-electron interaction of the form $[1-\mathrm{erf}(\omega r_{12})]/r_{12}$, then performing adiabatic connection with respect to variation of ω.[36,37] Such a derivation suggests, however, that ω should be a functional of the density, which has been demonstrated explicitly for the homogeneous electron gas.[12,38,39] Several approximations for the functional $\omega[\rho(\vec{r})]$ have been explored recently,[38,40] but these approximations fail to preserve the size consistency of E_{xc},[38,39] an important property that is preserved if ω is taken to be a system-independent constant. In the present work, we take ω to be a constant, opting to preserve size consistency at the expense introducing a functional that is not exact in the limit of a homogeneous electron gas. In view of this choice, the fixed-ω LRC scheme in Eq. (2) is perhaps best viewed as an *ansatz* designed to preserve desirable short-range features of GGA exchange, while incorporating the qualitatively correct asymptotic behavior of HF exchange.

Several schemes have been proposed for constructing the short-range GGA exchange functional, $E_{x,\mathrm{GGA}}^{\mathrm{SR}}$. Hirao and co-workers[15,17] describe a procedure, applicable to any GGA, which involves modifying the Fermi wave vector in the exchange enhancement factor. These authors have tested LRC versions of several different GGAs,[15–17] and their procedure was later adopted (using a somewhat different partition of the Coulomb potential) to develop the CAM-B3LYP functional,[18] where CAM stands for "Coulomb attenuation method." The Hirao formalism has an admirable simplicity and is straightforward to implement. We have recently shown, however, that functionals constructed in this way yield accurate TD-DFT excitation energies only for values of ω that afford very large errors in ground-state properties.[23] Conversely, values of ω that are acceptable in the ground state lead to excitation energies (in medium-size organic molecules) that are 0.5–1.0 eV too large.[23] Similar problems with CAM-B3LYP have been noted as well.[41]

An alternative LRC procedure has been proposed recently by Scuseria and co-workers,[19–21] based upon an earlier model for the Perdew–Burke–Ernzerhof (PBE) exchange hole.[42] The latest version of this short-range "ωPBE" exchange hole satisfies the exchange-hole normalization condition, for all values of ω, as well as several other exact constraints.[21] In this work, we use ωPBE for the short-range GGA exchange functional, $E_{x,\mathrm{GGA}}^{\mathrm{SR}}$.

We evaluate the performance of a hybrid LRC functional based upon ωPBE, in conjunction with the PBE correlation functional.[43] To the best of our knowledge, this represents the first attempt to use ωPBE in a hybrid functional with full long-range HF exchange, although hybrids with only short-range HF exchange,[44] or with "middle-range" HF exchange,[34,35,45] have been considered. The performance of this hybrid LRC functional is gauged, as a function of the parameters ω and C_{HF}, via a battery of ground-and excited-state tests similar to the ones employed in Ref. 23 to evaluate the performance of LRC functionals derived from the model of Hirao and co-workers.[15,17] Our goal is to find a set of parameters that yields acceptable results for both ground-state properties and TD-DFT excitation energies, and for which TD-DFT calculations are free of spurious, low-lying CT excited states. In what follows, we demonstrate that such a parameter set not only exists, but that the resulting functional performs reasonably well for both valence excitations and CT excitations, including excited states that are not in the training set.

II. COMPUTATIONAL DETAILS

We have implemented the ωPBE short-range exchange functional[21] within a locally modified, developers' version of Q-CHEM.[46] The combination of this short-range exchange functional with short-range HF exchange defines a two-parameter functional that we call LRC-ωPBEh, where the "h" indicates that the short-range functional is a hybrid.

We evaluate the performance of this functional, as a function of the parameters ω and C_{HF}, for ground-state atomization energies, reaction barrier heights, electron affinities, and ionization energies. Reference data for these properties are taken from the Minnesota Thermochemistry and Thermochemical Kinetics Database.[47–49] Ionization energies and electron affinities are calculated as the difference in energy between the neutral species and the ion. For all ground-state calculations, we use the same basis set (aug-cc-pVTZ) and molecular geometries as in our previous work.[23] Results are presented for $0 \leq C_{\mathrm{HF}} \leq 0.3$ and for $0 \leq \omega \leq 0.9 a_0^{-1}$, where a_0 denotes the Bohr radius. (Larger values of either parameter lead to unacceptable errors in one or more of the properties assessed here.)

An important conclusion from our previous study[23] is that standard TD-DFT benchmark molecules such as CO, N_2, and H_2CO are not always representative of the performance of TD-LRC-DFT for larger chromophores. It is therefore important to test LRC functionals for excitation energies in larger molecules, and in this work we employ an excitation energy database that is significantly expanded as compared to our previous work.[23] The new database is taken from Ref. 50, and provides best estimates (derived from correlated wave function calculations) of vertical excitation energies for a large set of molecules, and often for several excited states of each. We consider only singlet excited states in this work, and from the database in Ref. 50 we furthermore omit the $1\,^1B_{3g}$ state of *s*-tetrazine and the $2\,^1A_g$ states of the linear polyenes, as these states exhibit substantial double-excitation character[51,52] and are therefore absent from TD-DFT calculations performed within the adiabatic approximation.[52] Cyclopropene, cyclopentadiene, and norbornadiene are also omitted from our data set, as are several higher-lying excitations of the nucleic acid bases,[53] the latter owing to problems in assigning the states.

In total, our database of excitation energies contains 25 molecules and 84 transitions, consisting of 50 $\pi\pi^*$ states, 32 $n\pi^*$ states, and 2 $\pi\sigma^*$ states. Excited-state calculations

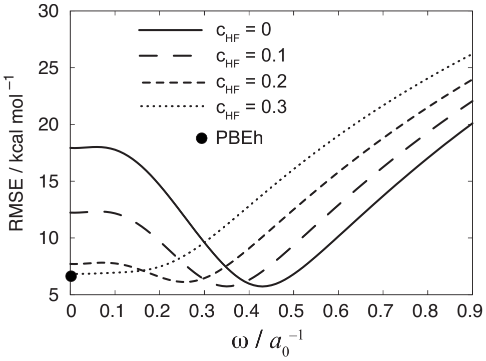

FIG. 1. Errors in atomization energies as a function of the range-separation parameter, ω.

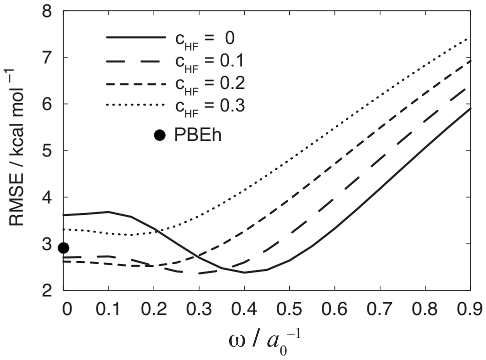

FIG. 3. Errors in electron affinities as a function of the range-separation parameter, ω.

for this database were performed using the aug-cc-pVDZ basis set and the SG-1 quadrature grid.[54] The Tamm–Dancoff approximation[55] is not used in this work.

CT excitation energies are known to be quite sensitive to the value of ω,[26] and an important goal of the LRC procedure (and an essential requirement, for application of TD-DFT to large systems) is the elimination of spurious, low-energy CT states. We therefore evaluate the performance of LRC-ωPBEh for the lowest CT excitation of the $C_2H_4-C_2F_4$ heterodimer,[4,16] using the cc-pVDZ basis set.

Finally, using the optimal values of ω and C_{HF} determined from the aforementioned benchmarks, we test the performance of TD-LRC-ωPBEh for vertical excitation energies in a different set of benchmark molecules. This set of five molecules, taken from Ref. 25, includes three polypeptides and two other molecules exhibiting intramolecular CT excitations. (Geometries corresponding to the ones used in Ref. 25 were obtained from Ref. 56.) These molecules are not part of the training set described above, and are chosen because they exhibit both CT excited states and localized (valence) excited states, at comparable energies. These TD-DFT calculations were performed using the cc-pVDZ basis and the SG-1 quadrature grid.[54]

III. RESULTS

A. Ground-state properties

Root-mean-square errors (RMSEs) for ground-state atomization energies, barrier heights, electron affinities, and ionization energies are shown in Figs. 1–4. (Analogous plots of the mean absolute errors can be found in the Supporting Information.[57]) In each figure, the RMSEs are plotted as a function of ω, for four different values of C_{HF}. Note that the choice $\omega=0=C_{\mathrm{HF}}$ yields the original PBE functional,[43] whereas the PBEh hybrid functional [also known as PBE1PBE (Ref. 58) or PBE0 (Ref. 59)] is realized with $\omega=0$ and $C_{\mathrm{HF}}=0.25$. For $C_{\mathrm{HF}}=0$, the functional examined here is identical to the LRC-ωPBE functional introduced by Henderson *et al.*[21]

The results for atomization energies (Fig. 1) differ qualitatively from what we reported previously[23] for LRC functionals constructed according to the prescription of Hirao and co-workers.[15,17] For the latter functionals, we observed that the RMSE for atomization energies increases rapidly as ω increases from zero, before eventually dropping at larger values of ω. As a result, the statistical error in atomization energies is only competitive with that of the "base" ($\omega=0$) functional for $\omega \approx 0.5a_0^{-1}-0.7a_0^{-1}$. This range of ω values, however, affords large errors in TD-DFT excitation energies.[23]

LRC-ωPBEh, in contrast, exhibits ω-dependent RMSE curves that are initially flat, as ω is increased from zero, but ultimately the error *decreases* as ω is increased, provided that $C_{\mathrm{HF}}<0.3$. The RMSE is minimized for $\omega \approx 0.25a_0^{-1}-0.45a_0^{-1}$, depending on C_{HF}. For $C_{\mathrm{HF}} \geq 0.3$, we observe a monotonic increase in the RMSE as a function of ω, meaning that the LRC always degrades the accuracy of

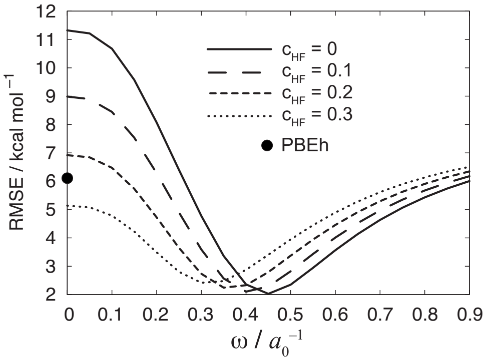

FIG. 2. Errors in barrier heights as a function of the range-separation parameter, ω.

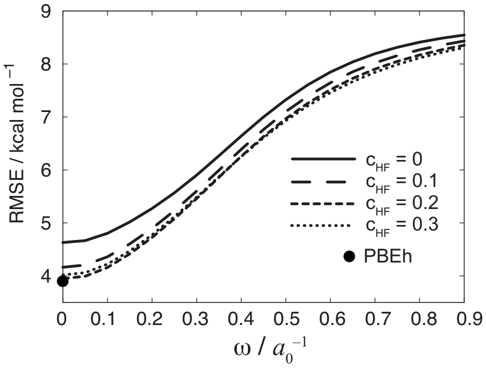

FIG. 4. Errors in ionization energies as a function of the range-separation parameter, ω.

atomization energies in these cases. For this reason, we consider only $C_{\mathrm{HF}} \leq 0.3$ in what follows.

For LRC-ωPBEh with $C_{\mathrm{HF}} < 0.3$, the error in atomization energies is minimized for values of $1/\omega$ in the range of 1.2–2.1 Å (depending on C_{HF}), or in other words, about the length scale of a chemical bond. This seems reasonable: in order to preserve the accuracy of the base functional for atomization energies, GGA exchange should be attenuated on a length scale not much shorter than a chemical bond. At the same time, we know that the most accurate non-LRC functionals for atomization energies are hybrids with $C_{\mathrm{HF}} \approx 0.20-0.25$ (e.g., B3LYP or PBEh), and for these values of C_{HF}, we observe that the LRC does not improve the accuracy of atomization energies by very much. RMSEs for C_{HF} values in this range tend to increase monotonically, or nearly monotonically, as a function of ω. We interpret this as evidence that, when C_{HF} is smaller than the optimal non-LRC value of ~ 0.2, the presence of short-range HF exchange (engendered by $\omega > 0$) compensates for some of the "missing" HF exchange on chemical-bond length scales, hence a nonzero value of ω outperforms the base functional. (This explanation is probably something of an oversimplification, as several recent studies indicate that it is the "middle-range" HF exchange that is most important for accurate atomization energies and barrier heights.[34,35,45])

The trends in RMSEs for barrier heights (Fig. 2) are qualitatively similar to the trends for atomization energies. The behavior of LRC-ωPBEh is superior to that of LRC functionals examined previously,[23] in the sense that the RMSEs initially decrease as ω is increased from zero, rather than showing an increase for small ω. This is an important consideration because, as we shall see below, the ideal ω values for excitation energies are less than $0.35 a_0^{-1}$. In the ground state, minimum-error values of ω lie in the range of $0.30 a_0^{-1}$–$0.45 a_0^{-1}$, only slightly larger than the minimum-error values for atomization energies.

For $C_{\mathrm{HF}} = 0$, the results above corroborate the findings of Henderson *et al.*,[21] although our data sets are much larger. Both studies find that $\omega \approx 0.45 a_0^{-1}$ is optimal for ground-state thermochemistry, which is comparable to the optimal value of $\omega = 0.4 a_0^{-1}$ determined recently for the ωB97 LRC functional,[22] again based largely on ground-state atomization energy and barrier height benchmarks.

With a properly optimized value of ω, incorporation of short-range HF exchange affords no statistical improvement whatsoever in either atomization energies or barrier heights, and actually degrades the latter, albeit very slightly. As shown in Sec. III B, however, inclusion of short-range HF exchange provides a functional that minimizes ground-state thermochemical errors at a value of ω that is also optimal, or nearly optimal, for excitation energies. It is also worth noting that when $C_{\mathrm{HF}} > 0$, errors in barriers heights and atomization energies exhibit a weaker dependence on ω than when $C_{\mathrm{HF}} = 0$, at least in the neighborhood of the optimal ω values.

Errors in electron affinities are shown in Fig. 3, and these errors also exhibit a much different ω-dependence than the LRC functionals that we examined previously.[23] In the present case, the error in electron affinities is minimized at much smaller values of ω than in previous cases. Addition of short-range HF exchange softens the ω-dependence of the RMSE, just as it does for atomization energies and barrier heights.

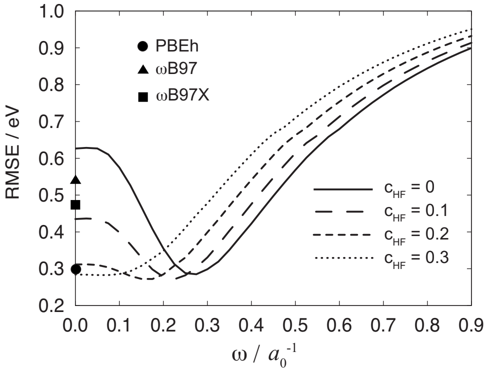

FIG. 5. Errors in TD-DFT vertical excitation energies as a function of the range-separation parameter, ω.

The final ground-state property that we examine is the ionization energy (Fig. 4). Unlike other ground-state properties, RMSEs for ionization energies increase monotonically as a function of ω, for all values of C_{HF}. Note, however, that the energy scale in Fig. 4 spans a much smaller range than that for either atomization energies (Fig. 1) or barrier heights (Fig. 2). For all values of ω, the functionals containing short-range HF exchange yield slightly smaller errors as compared to $C_{\mathrm{HF}} = 0$.

B. Vertical excitation energies

RMSEs for vertical excitation energies are shown in Fig. 5. To determine this statistical error, it was necessary to assign each of the 84 excited states in the database described in Sec. II, for each value of ω and C_{HF}. This process is mostly a straightforward (if tedious) exercise in group theory, although it is complicated by the fact that any plot of excitation energies versus ω (for a given molecule and a fixed value of C_{HF}) exhibit numerous avoided crossings. State assignments are further complicated by the appearance of a large number of low-energy Rydberg states when ω is small. As ω is varied, the diabatic curve corresponding to a given valence excitation therefore intersects a large number of diabatic curves corresponding to Rydberg states (and sometimes valence states as well). The valence excitation of interest is ultimately identified by examining the orbitals involved in the excitation, as well as the ω-dependent oscillator strengths, the latter being especially useful in cases where, for a given molecule, the database contains multiple excited states of the same symmetry. In many cases, Rydberg states can be identified (and subsequently ignored, for the purpose of our analysis) by comparison to ω-dependent excitation energy curves calculated in the absence of diffuse basis functions. (For the sake of correctness, we note that the RMSEs reported in Fig. 5 are calculated *with* diffuse functions, in the aug-cc-pVDZ basis set, although in reality the diffuse functions change the valence excitation energies very little but complicate the analysis quite a lot.) The ω-dependent vertical excitation energy profiles, for each C_{HF} value examined here, and for each molecule in our database, are available in the Supporting Information.[57]

According to Fig. 5, the optimal ω value for vertical excitation energies lies between $0.15a_0^{-1}$ and $0.25a_0^{-1}$ for $C_{\mathrm{HF}}<0.3$. As observed for ground-state properties, incorporation of short-range HF exchange leads to errors that are less strongly dependent on ω, as compared to results obtained with $C_{\mathrm{HF}}=0$. In general, we find that the ω-dependent excitation energy curves (for a given molecule and a given valence excited state) agree quite well with those obtained[23] using LRC functionals constructed according to the procedure of Hirao and co-workers.[15,17] The crucial difference is that, for the LRC-ωPBEh functional under consideration here, the range of ω values that affords good results for excitation energies overlaps the range that is acceptable for ground-state properties.

Recently, Chai and Head-Gordon[22] developed a pair of LRC functionals, denoted ωB97 and ωB97X, that provide excellent results (superior to most non-LRC functionals) for atomization energies, barrier heights, and other ground-state properties. For the set of vertical excitation energies considered here, these two functionals afford RMSEs of 0.54 and 0.48 eV, respectively, as indicated in Fig. 5, using the cc-pVDZ basis set. These RMSEs are significantly larger than those exhibited by the best functionals of the LRC-ωPBEh *ansatz*, including PBEh. Admittedly, the adjustable parameters in the ωB97 and ωB97X functionals (including not just ω and C_{HF} but also the 14 parameters in the B97 exchange functional[60]) were optimized exclusively using ground-state benchmarks, so the performance of these functionals for excitation energies could certainly be improved. This underscores the importance of simultaneous consideration of both ground-state properties and vertical excitation energies, when developing functionals that are intended to describe both.

C. Intermolecular charge transfer

One of the primary goals of the LRC procedure is the elimination of spurious, low-lying CT excited states in TD-DFT calculations. As such, we next examine long-range intermolecular CT excitation energies in the $C_2H_4-C_2F_4$ heterodimer, a standard benchmark system.[4,16] Figure 6 plots the lowest intermolecular CT excitation energy, $\Delta E_{\mathrm{CT}}(R)$, as a function of monomer separation R, for $C_{\mathrm{HF}}=0$ and $C_{\mathrm{HF}}=0.2$, and for several different values of ω in each case. (Analogous figures for other C_{HF} values are available in the Supporting Information.[57]) As is well known by now, traditional hybrid functionals with less than 100% HF exchange substantially underestimate the distance dependence of intermolecular CT excitations.[4] For small values of ω, LRC-ωPBEh also fails to reproduce the correct $-1/R$ distance dependence of $\Delta E_{\mathrm{CT}}(R)$, as judged in Fig. 6 by comparison to SAC-CI excitation energies.[16] This comparison indicates that we must demand that $\omega \geq 0.25a_0^{-1}$ (for $C_{\mathrm{HF}}=0$) or $\omega \geq 0.20a_0^{-1}$ (for $C_{\mathrm{HF}}=0.2$) in order to achieve the correct distance dependence. Short-range HF exchange is not necessary in order to obtain the correct distance dependence of $\Delta E_{\mathrm{CT}}(R)$, as the latter is a long-range property.

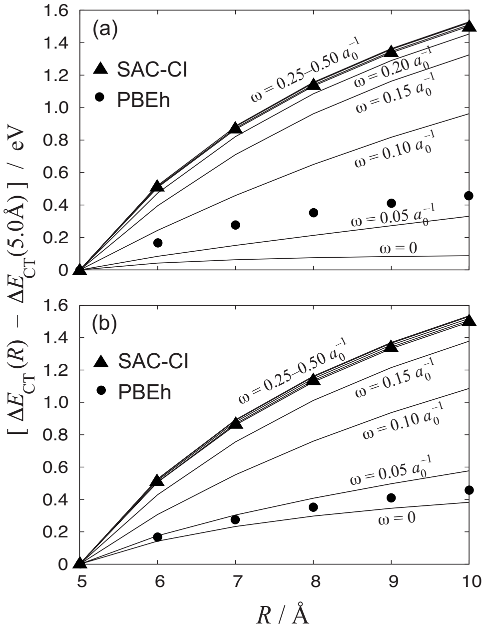

FIG. 6. Lowest intermolecular CT excitation energy, ΔE_{CT}, as a function of the monomer separation R, for the $C_2H_4-C_2F_4$ heterodimer with (a) $C_{\mathrm{HF}}=0$ and (b) $C_{\mathrm{HF}}=0.2$. To emphasize the distance dependence, excitation energies at each value of ω are shifted to a common origin at $R=5.0$ Å. The SAC–CI values are taken from Ref. 16.

IV. DISCUSSION

Based on the data examined above, the values $C_{\mathrm{HF}}=0.2$ and $\omega=0.2a_0^{-1}$ represent the best compromise that affords accuracy comparable to—or better than—the PBEh functional, both for ground-state properties as well as vertical excitation energies, while simultaneously achieving the correct distance dependence for intermolecular CT excitations. These values, or something very close to them, are the only ones that simultaneously achieve all three of these goals. In fact, this parameter set is very nearly optimal for most of the individual properties considered here, including atomization energies, electron affinities, vertical excitation energies, and the ΔE_{CT} distance dependence in the $C_2H_4-C_2F_4$ system. Statistical errors obtained using this preferred parameter set are summarized in Table I.

For ionization energies, all values of $\omega>0$ degrade the

TABLE I. Mean absolute error (MAE) and RMSE in various properties, computed using the LRC-ωPBEh functional with the optimal parameter set ($C_{\mathrm{HF}}=0.2$, $\omega=0.2a_0^{-1}$) determined in this work.

Property	Units	MAE	RMSE
Atomization energies[a]	kcal/mol	4.6	6.6
Barrier heights[b]	kcal/mol	3.6	4.7
Electron affinities[c]	kcal/mol	2.0	2.5
Ionization energies[d]	kcal/mol	4.1	4.7
Ex. energies (localized)[e]	eV	0.22	0.28
Ex. energies (CT)[f]	eV	0.26	0.31

[a] Based on 109 atomization energies taken from Ref. 47.
[b] Based on 44 barrier heights taken from Ref. 47.
[c] Based on 13 electron affinities taken from Ref. 47.
[d] Based on 13 ionization energies taken from Ref. 47.
[e] Based on 84 $^1n\pi^*$, $^1\pi\pi^*$, and $^1\pi\sigma^*$ excitation energies taken from Ref. 50.
[f] Based on 13 intramolecular CT excitation energies taken from Ref. 25.

TABLE II. Vertical excitation energies (in eV) for a set of localized (L) and CT excitations. Results for LRC-ωPBEh are given both for our recommended parameter set ($C_{\mathrm{HF}}=0.2$, $\omega=0.2a_0^{-1}$) and for an alternative set of parameters ($C_{\mathrm{HF}}=0.2$, $\omega=0.3a_0^{-1}$) that performs better for barrier heights. Results for the LRC-ωPBE functional ($C_{\mathrm{HF}}=0$, $\omega=0.45a_0^{-1}$) are also shown. The notation for the polypeptide excited states is the same as that used in Ref. 25.

				LRC-ωPBEh				
Molecule	Excitation	Type	Benchmark[a]	Recommended[b]	Alternate[c]	$C_{\mathrm{HF}}=0$ [d]	ωB97	ωB97X
Dipeptide	$n_1\to\pi_2^*$	CT	8.07	7.75	8.89	9.54	9.17	8.74
	$\pi_1\to\pi_2^*$	CT	7.18	6.93	7.49	8.45	8.24	7.42
	$n_1\to\pi_1^*$	L	5.62	5.65	5.74	5.76	5.77	5.73
	$n_2\to\pi_2^*$	L	5.79	5.91	5.99	6.01	6.02	5.98
β-dipeptide	$n_1\to\pi_2^*$	CT	9.13	8.45	9.68	10.11	9.94	9.53
	$\pi_1\to\pi_2^*$	CT	7.99	8.01	8.94	9.54	9.26	8.83
	$n_1\to\pi_1^*$	L	5.40	5.64	5.73	5.74	5.76	5.72
	$n_2\to\pi_2^*$	L	5.10	5.77	5.85	5.86	5.88	5.84
Tripeptide	$\pi_1\to\pi_2^*$	CT	7.01	6.92	7.47	8.44	8.24	7.40
	$\pi_2\to\pi_3^*$	CT	7.39	7.15	7.63	8.66	8.44	7.57
	$\pi_1\to\pi_3^*$	CT	8.74	8.72	9.94	10.64	10.32	9.82
	$n_1\to\pi_3^*$	CT	9.30	8.88	10.24	10.95	10.58	10.07
	$n_2\to\pi_3^*$	CT	8.33	8.22	9.36	10.01	9.65	9.21
	$n_1\to\pi_2^*$	CT	8.12	7.69	8.83	9.48	9.12	8.68
	$n_1\to\pi_1^*$	L	5.74	5.67	5.77	5.79	5.80	5.75
	$n_2\to\pi_2^*$	L	5.61	5.91	6.01	6.03	6.04	6.00
	$n_3\to\pi_3^*$	L	5.91	6.00	6.09	6.10	6.11	6.07
PP	$1\,^1B_2$	L	4.85	5.14	5.29	5.35	5.29	5.25
	$2\,^1A_1$	L	5.13	5.25	5.41	5.48	5.42	5.37
	$2\,^1B_2$	CT	5.47	5.36	5.71	5.89	5.81	5.67
	$3\,^1A_1$	CT	5.94	6.05	6.79	7.19	7.01	6.72
DMABN	^1B	L	4.25	4.75	4.94	5.03	5.09	5.02
	^1A	CT	4.56	4.99	5.14	5.20	5.38	5.33
RMSE for L excitations				0.31	0.41	0.44	0.45	0.41
RMSE for CT excitations				0.31	0.75	1.36	1.11	0.66

[a] From Ref. 25.

[b] $C_{\mathrm{HF}}=0.2$, $\omega=0.2a_0^{-1}$.

[c] $C_{\mathrm{HF}}=0.2$, $\omega=0.3a_0^{-1}$.

[d] $\omega=0.45a_0^{-1}$ (optimized for ground-state properties).

performance of the functional; however, our recommended parameter set achieves a RMSE that is only about 0.6 kcal/mol higher than that of PBEh, which achieves the best performance of any parameter set, for this particular property. We do not regard this as a serious problem.

Reaction barrier heights are the one property considered here for which one might quarrel with our choice of parameters. Using our preferred parameters ($C_{\mathrm{HF}}=0.2$, $\omega=0.2a_0^{-1}$), we obtain an RMSE of 4.7 kcal/mol for barrier heights, significantly smaller than the RMSE of 6.1 kcal/mol that is obtained using PBEh. However, by increasing ω to something in the range of $0.35a_0^{-1}$–$0.45a_0^{-1}$, the RMSE for barrier heights could be reduced to as low as 2 kcal/mol, at the expense of an increase of ~0.1 eV in the RMSE for vertical excitation energies, if C_{HF} were reduced somewhat. Errors in the other properties considered here are altered very little by this change. As demonstrated below, however, this alternate set of parameters yields large errors for CT excitation energies, and therefore does not afford a balanced description of both localized and CT excitations.

In order to evaluate the performance of LRC-ωPBEh for excitation energies that are not contained in the training set used in Sec. III B, we next consider a different set of molecules and excited states. The new data set is taken from Ref. 25 and consists of two dipeptides, a tripeptide, and the molecules *N*-phenylpyrrole (PP) and 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN). These molecules are a subset of those used by Peach *et al.*[25] to evaluate the performance of CAM-B3LYP, and we have selected this particular subset because, for each of the aforementioned molecules, Peach *et al.* provide benchmark excitation energies for both "localized" $n\pi^*$ and $\pi\pi^*$ excitations, as well as intramolecular CT excitations. (These benchmarks come from CC2 and CASPT2 calculations, as well as gas-phase experiments; see Ref. 25 for details.)

Table II compares these benchmarks to the excitation energies obtained using LRC-ωPBEh, for both our preferred parameter set ($C_{\mathrm{HF}}=0.2$, $\omega=0.2a_0^{-1}$) as well as the alternative parameters $C_{\mathrm{HF}}=0.2$ and $\omega=0.3a_0^{-1}$ that reduce the overall error for barrier heights. As a point of additional comparison, we also consider the parameter set ($C_{\mathrm{HF}}=0$, $\omega=0.45a_0^{-1}$), which corresponds to the LRC-ωPBE functional originally developed by Henderson *et al.*[21] (In Ref. 21, ω is optimized using only atomization energies and barrier heights. Consistent with our own results, these authors find that $\omega=0.45a_0^{-1}$ affords the smallest RMSEs for these two properties, when C_{HF} is constrained to be zero.) The ωB97 and ωB97X functionals[22] are also considered in Table II.

Using our recommended parameter set, the LRC-ωPBEh functional affords the same RMSE, 0.31 eV, for both the localized excitations and the intramolecular CT excitations. (RMSEs for these two types of excitations are computed separately in Table II.) This is practically identical to the RMSE obtained for the much larger set of valence excitation energies considered in Sec. III B (cf. Fig. 5). For comparison, the PBEh functional also yields an RMSE of 0.31 eV for the localized excitations, but the RMSE for the CT excitations is 3.01 eV for PBEh,[25] due to this functional's well-known inability to describe CT excitation energies.

For the localized excitations, the two other parameter sets considered in Table II afford RMSEs of about 0.4 eV, only slightly larger than that obtained with our "optimal" functional. However, the RMSEs for the CT excitations are much larger: 0.75 eV for the alternative short-range hybrid functional, and 1.36 eV for the LRC-ωPBE functional with $C_{\mathrm{HF}}=0$. As such, these two functionals do not appear to provide a balanced description of both localized and CT excitation energies, and this is why we prefer the parameter set ($C_{\mathrm{HF}}=0.2$, $\omega=0.2a_0^{-1}$), despite its somewhat larger error for barrier heights. The performance of the LRC-ωPBE ($C_{\mathrm{HF}}=0$) functional for CT excitations could be improved by reducing the value of ω, but any significant reduction will result in substantially larger errors for ground-state properties. Within the LRC-ωPBEh *ansatz*, short-range HF exchange appears to be necessary in order to describe all of the properties considered here with reasonable accuracy.

The ωB97 functional lacks short-range HF exchange, and this functional fails to provide a balanced description of both localized and CT excitations. Note that $\omega=0.4a_0^{-1}$ for ωB97,[22] and localized excitation energies predicted by this functional are virtually identical to those obtained using the LRC-ωPBE functional with $C_{\mathrm{HF}}=0$ and $\omega=0.45a_0^{-1}$. Both functionals significantly overestimate the CT excitation energies, although CT excitation energies are, on average, about 0.2 eV lower (and therefore more accurate) for ωB97. Notably, the only case in which LRC-ωPBE predicts a CT excitation energy lower than that of ωB97 is for the ^1A state of DMABN, a nominal CT state that, in the gas phase, exhibits only a small degree of CT at the ground-state geometry.[25] Based upon these observations, and the fact that CT excitation energies generally decrease as ω decreases,[26] we conclude that both of these functionals utilize an ω value that is too large to predict accurate CT excitation energies.

Unlike ωB97, the ωB97X functional does contain short-range HF exchange ($C_{\mathrm{HF}}=0.157\,706$, $\omega=0.3a_0^{-1}$).[22] For the localized excitations in Table II, this functional affords excitation energies that are virtually identical to those obtained from LRC-ωPBEh using our "alternative" parameter set ($C_{\mathrm{HF}}=0.2$, $\omega=0.3a_0^{-1}$). This similarity is notable since, in both cases, the parameters in these functionals are optimized for ground-state properties. Both functionals significantly overestimate the CT excitation energies, although to a lesser extent that the functionals considered above.

Finally, we note that Peach *et al.* considered the data set in Table II using the CAM-B3LYP functional, reporting RMSEs of 0.34 eV for the localized excitations and 0.30 eV for the CT excitations.[25] Although these errors are essentially the same as those obtained using LRC-ωPBEh with our optimized parameters, for CAM-B3LYP the optimal parameters for vertical excitation energies are known to afford large errors in ground-state properties.[41]

Based upon this survey of the latest LRC functionals, in conjunction with our previous study of earlier LRC functionals,[23] we conclude that LRC-ωPBEh with our optimal parameter set is the only existing LRC functional that provides accurate ground-state properties, localized excitation energies, and CT excitation energies. Reoptimization of the ωB97X parameters, using a training set that includes vertical excitation energies, might significantly improve this functional's performance for excitation energies, but we have not attempted such an optimization here.

V. CONCLUSIONS

Using a range-separation parameter of $\omega=0.2a_0^{-1}$ in conjunction with 20% short-range HF exchange, the LRC-ωPBEh functional examined here provides reasonable accuracy for both ground-state properties as well as for TD-DFT vertical excitation energies, both for localized excitations and for CT excitations. (Statistical errors in various properties are summarized in Table I.) Compared to the popular PBEh hybrid functional,[58,59] the LRC-ωPBEh functional with the aforementioned parameters provides the same accuracy for atomization energies and is only slightly inferior for ionization energies, but is clearly superior to PBEh for barrier heights and electron affinities. The RMSE for localized excitation energies (evaluated over a large set of medium-sized molecules) is 0.3 eV, comparable to the performance of the best non-LRC functionals, when evaluated over a similar set of excitations.[61] Perhaps most importantly, the statistical error for intramolecular CT excitations is no larger than that determined for localized excitations. To the best of our knowledge, this represents the first density functional to provide reasonable accuracy for both ground-state properties and TD-DFT excitation energies, while affording a balanced description of both localized and CT excitation energies.

Consistent with a growing body of data for various LRC functionals,[15,17,19–22,34,35,45] we find that short-range HF exchange is not necessary in order to obtain accurate values for ground-state atomization energies or barrier heights, nor is it necessary in order to obtain accurate TD-DFT excitation energies. Our results demonstrate, however, that short-range

HF exchange does appear to be necessary in order to obtain statistically accurate values for all of these properties simultaneously.

Note added in proof: We have recently determined that the parameters ($C_{\mathrm{HF}}=0,\ \omega=0.3a_0^{-1}$) also provide RMSEs of 0.3 eV for both localized and CT excitations, though the performance for atomization energies is degraded relative to ($C_{\mathrm{HF}}=0.2,\ \omega=0.2a_0^{-1}$).

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