Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections†

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We report re-optimization of a recently proposed long-range corrected (LC) hybrid density functional [J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2008, **128**, 084106] to include empirical atom–atom dispersion corrections. The resulting functional, ωB97X-D yields satisfactory accuracy for thermochemistry, kinetics, and non-covalent interactions. Tests show that for non-covalent systems, ωB97X-D shows slight improvement over other empirical dispersion-corrected density functionals, while for covalent systems and kinetics it performs noticeably better. Relative to our previous functionals, such as ωB97X, the new functional is significantly superior for non-bonded interactions, and very similar in performance for bonded interactions.

1. Introduction

Due to its favorable cost-to-performance ratio, Kohn–Sham density-functional theory (KS-DFT)[1,2] has become the most popular electronic structure theory for large-scale ground-state systems.[3–5] Its extension for treating excited-state systems,[6,7] time-dependent density functional theory (TDDFT), has also been developed to the stage where it is now very widely used.

The essential ingredient of KS-DFT, the exchange–correlation energy functional E_{xc}, remains unknown and needs to be approximated. Semi-local gradient-corrected density functionals, though successful in many applications, lead to qualitative failures in some circumstances where the accurate treatment of non-locality of exchange–correlation hole becomes crucial. These situations occur mostly in the asymptotic regions of molecular systems, such as spurious self-interaction effects upon dissociation[8,9] and dramatic failures for long-range charge-transfer excitations.[10–12] Widely used hybrid density functionals, like B3LYP,[13,14] do not qualitatively resolve these problems.

These self-interaction errors can be qualitatively resolved using the long-range corrected (LC) hybrid density functionals,[15,16,18] which employ 100% Hartree–Fock (HF) exchange for long-range electron–electron interactions. This is accomplished by a partition of unity, using $\mathrm{erf}(\omega r)/r$ for long-range (treated by HF exchange) and $\mathrm{erfc}(\omega r)/r$ for short-range (treated by an exchange functional), with the parameter ω controlling the partitioning of the interelectronic distance r. Over the past five years, the LC hybrid scheme has been attracting increasing attention[15] since its computational cost is comparable with standard hybrid functionals.[13] However, LC functionals have tended to be inferior to the best hybrids for properties such as thermochemistry.

Recently we have improved the overall accuracy attainable with the LC functionals by using a systematic optimization procedure.[18] One important conclusion is that optimizing LC and hybrid functionals with identical numbers of parameters in their GGA exchange and correlation terms leads to noticeably better results for *all* properties using the LC form. The resulting LC functional is called ωB97. Further statistically significant improvement results from re-optimizing the entire functional with one extra parameter corresponding to an adjustable fraction of short-range exact exchange, defining the ωB97X functional. Independent test sets covering thermochemistry and non-covalent interactions support these conclusions. However, problems associated with the lack of non-locality of the correlation hole, such as the lack of dispersion interactions (London forces), still remain, as the semi-local correlation functionals cannot capture long-range correlation effects.[19,20]

There have been significant efforts to develop a framework that can account for long-range dispersion effects within DFT. Zaremba and Kohn (ZK)[21] derived an exact expression for the second-order dispersion energy in terms of the exact density–density response functions of the two separate systems. To obtain a tractable non-local dispersion functional, Dobson and Dinite (DD)[22] made local density approximations to the ZK response functions. DD's non-local correlation functional was obtained independently[23] by modifying the effective density defined in the earlier work of Rapcewicz and Ashcroft.[24] By combining DD's non-local correlation functional with the LC functionals, Hirao and co-workers[25–27] have achieved impressive success in applications to various non-covalent systems.

Starting from the formally exact expression of KS-DFT, the adiabatic connection fluctuation–dissipation theorem (ACFDT), for the ground-state exchange–correlation energy, Langreth and coworkers[28] developed a so-called van der Waals density functional (vdW-DF) by making a series of reasonable approximations to yield a computationally tractable scheme.

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Recently, Becke and Johnson (BJ) developed a series of post-HF correlation models with a novel treatment for dispersion interactions based on the exchange-hole dipole moment.[29] The origin of dispersion claimed in the BJ models was recently questioned by Alonso and Mañanes,[30] and Ángyán[31] further showed that the BJ models effectively contain correlation effects. Nevertheless, the BJ models show promise for computing accurate interatomic and intermolecular C_6, C_8, and C_{10} dispersion coefficients with only a few empirical parameters. Furthermore, as a post-HF method, the BJ functional is intrinsically free of self-interaction errors.

Alternatively, one can add an empirical atom–atom dispersion potential to an existing density functional, to obtain a correction that is essentially of zero cost and zero complexity. Such an approach was used long ago to correct HF calculations,[32] and over the past 8 years has been incorporated into density functional theory.[33–46] These DFT-D (density functional theory with empirical dispersion corrections) schemes have shown generally satisfactory performance on a large set of non-covalent systems.[38,43] Currently available functionals of this type, such as B3LYP-D and B97-D appear to yield results for covalent systems that are at least comparable to their parent methods (*e.g.* B3LYP and B97).

Since we have recently demonstrated that fully optimized LC functionals such as ωB97 and ωB97X[18] can yield better results for covalent systems than traditional hybrids or LC functionals that are not fully re-optimized, it seems natural to explore whether further improvements are possible by incorporating empirical atom–atom dispersion corrections. Although extending our LC functionals with DD's non-local correlation functional,[22,23] as suggested by Hirao and co-workers,[25–27] is also possible for obtaining dispersion corrections, its computational cost is, however, much higher than the DFT-D scheme due to the required double numerical integrations. Besides, its performance for non-covalent systems has been shown to be similar to the simpler DFT-D scheme.[27] In this work, we therefore introduce an empirical dispersion correction to the ωB97X functional, as this provides the missing pieces of the long-range vdW interactions without additional computational costs. It also emerges that optimization of the ωB97 functional with empirical dispersion corrections leads to essentially zero dispersion correction. Our results are compared with those by other DFT-D functionals as well as our previous LC hybrid functionals.

2. The DFT-D scheme

Following the general form of the DFT-D scheme,[33–46] our total energy

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}} \quad (1)$$

is computed as the sum of a KS-DFT part, using the ωB97X[18] functional, and an empirical atomic-pairwise dispersion correction. We choose to use an unscaled dispersion correction, given by

$$E_{\text{disp}} = -\sum_{i=1}^{N_{\text{at}}-1}\sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij}) \quad (2)$$

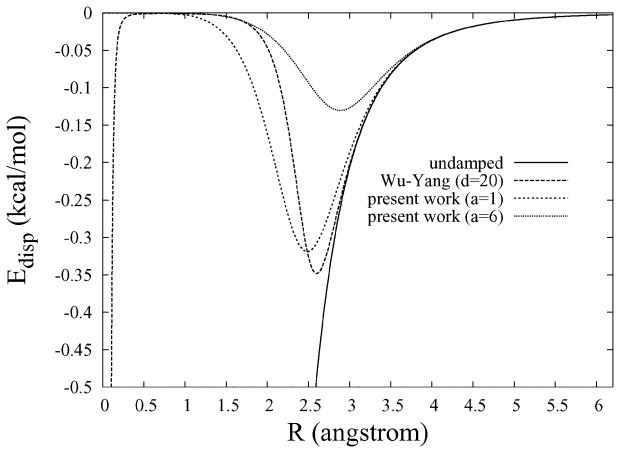

Fig. 1 Dispersion energy of the neon dimer with and without the damping functions. The damping function from Wu and Yang[34] $f_{\text{damp}}^{\text{Wu–Yang}}(R) = 1/(1 + \exp[-d(R/R_r - 1)])$ (R_r is the sum of vdW radii of the two neon atoms), and from the present work [see eqn (3)] are compared with the undamped function.

where N_{at} is the number of atoms in the system, C_6^{ij} is the dispersion coefficient for atom pair ij, and R_{ij} is an interatomic distance. The conditions of zero dispersion correction at short interatomic separations and correct asymptotic pairwise vdW potentials are enforced by introducing a damping function,

$$f_{\text{damp}}(R_{ij}) = \frac{1}{1 + a(R_{ij}/R_r)^{-12}} \quad (3)$$

which reduces to one at large R_{ij}, while vanishing fast enough to prevent divergence of the undamped vdW potentials at small R_{ij}. Here, R_r is the sum of vdW radii of the atomic pair ij,[37] and the only non-linear parameter, a, controls the strength of dispersion corrections. As shown in Fig. 1, our new damping function correctly fixes the undesirable divergence of dispersion correction at the small nuclear distance R of the neon dimer, while the Wu–Yang damping function,[34] widely used by many DFT-D functionals[37] does not completely remedy this problem (though this should not be a problem in practice).

To summarize, except for using our new damping function and constraining for the correct asymptotic pairwise vdW potentials (*i.e.* no overall scaling), we follow Grimme's work[37] for computing the empirical dispersion corrections, and denote this new functional as ωB97X-D.

To achieve an optimized functional for well-balanced performance across typical applications, we use the same diverse training set described in ref. 18, that contains 412 accurate experimental and accurate theoretical results, including the 18 atomic energies from the H atom to the Ar atom,[47] the atomization energies (AEs) of the G3/99 set[48–50] (223 molecules), the ionization potentials (IPs) of the G2-1 set[51] (40 molecules, excluding SH_2 ($^2A_1$) and N_2 ($^2\Pi$) cations due to the known convergence problems for semilocal density functionals[49]), the electron affinities (EAs) of the G2-1 set (25 molecules), the proton affinities (PAs) of the G2-1 set (8 molecules), the 76 barrier heights (BHs) of the NHTBH38/04 and HTBH38/04 sets,[52,53] and the 22 non-covalent interactions of the S22 set.[54] To prevent the double-counting of total

Table 1 Optimized parameters for ωB97X-D. Here, the non-linear parameter a is defined in eqn (3), and others are defined in eqn (28) of ref. 28

a	6.0
ω	0.2 Bohr^{-1}
$c_{x\sigma,0}$	7.77964×10^{-1}
$c_{c\sigma\sigma,0}$	1.00000×10^{0}
$c_{c\alpha\beta,0}$	1.00000×10^{0}
$c_{x\sigma,1}$	6.61160×10^{-1}
$c_{c\sigma\sigma,1}$	-6.90539×10^{0}
$c_{c\alpha\beta,1}$	1.79413×10^{0}
$c_{x\sigma,2}$	5.74541×10^{-1}
$c_{c\sigma\sigma,2}$	3.13343×10^{1}
$c_{c\alpha\beta,2}$	-1.20477×10^{1}
$c_{x\sigma,3}$	-5.25671×10^{0}
$c_{c\sigma\sigma,3}$	-5.10533×10^{1}
$c_{c\alpha\beta,3}$	1.40847×10^{1}
$c_{x\sigma,4}$	1.16386×10^{1}
$c_{c\sigma\sigma,4}$	2.64423×10^{1}
$c_{c\alpha\beta,4}$	-8.50809×10^{0}
c_{x}	2.22036×10^{-1}

energy from the KS-DFT and the dispersion corrections, all the parameters in ωB97X-D, are determined self-consistently by a least-squares fitting procedure described in ref. 18. For the non-linear parameter optimization, we focus on a range of possible ω values (0.0, 0.1, 0.2, 0.3, 0.4, and 0.5 Bohr^{-1}), and optimize the corresponding a values in steps of 0.1 for $a \leq 1$, in steps of 1 for $1 < a \leq 10$, in steps of 10 for $10 < a \leq 60$, and in steps of 20 for $a > 60$. The functional expansions employed in ωB97X-D are truncated at $m = 4$ with the uniform electron gas (UEG) limit being satisfied. The S22 data is weighted ten times more than the others. The optimized parameters of the ωB97X-D functional are given in Table 1.

In Fig. 2, the root-mean-square errors of the training set for ωB97X-D optimized at different values of ω are plotted. At $\omega = 0.2$ Bohr^{-1}, the optimization is done self-consistently, while at other values of ω, non-self-consistent orbitals are used for the linear least-squares fittings to reduce the computational difficulty. At $\omega = 0.0$ and 0.1 Bohr^{-1}, the corresponding RSHXLDA orbitals[17] are used, and at $\omega = 0.3$ and 0.4 Bohr^{-1}, the ωB97X and ωB97 orbitals[18] are used respectively. As previously demonstrated,[18] these results should only change insignificantly, when using self-consistent orbitals. As the root-mean-square errors at $\omega = 0.2$ and 0.3 Bohr^{-1} are very close to each other, the optimized ω value is finally chosen to be 0.2 Bohr^{-1} for the smaller mean absolute error.

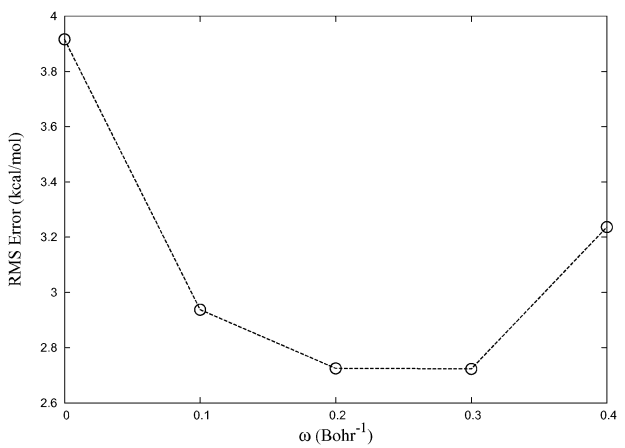

Fig. 2 The root-mean-square (RMS) errors of the training set for ωB97X-D optimized at different values of ω. At $\omega = 0.2$ Bohr^{-1}, the optimization is done self-consistently, while at other values of ω, non-self-consistent orbitals are used for the linear least-squares fittings (see text).

Some aspects of the optimized parameters are interesting and deserve discussion. First, we observe that the optimized value of ω is reduced from $\omega = 0.3$ Bohr^{-1} in ωB97X to $\omega = 0.2$ Bohr^{-1} in ωB97X-D. At the same time, the fraction of short-range exact exchange increases by about 40% (from about 0.16 to about 0.22). Evidently the inclusion of long-range dispersion increases the optimal length scale on which we have 100% exact exchange, while at short distances we have increased the fraction of exact exchange. This increase of the fraction of short-range exact exchange in ωB97X-D is expected to compensate the reduction of the exact exchange using a smaller value of ω. The net effect is that ωB97X-D may have somewhat higher self-interaction errors. Second, regarding a possible ωB97-D functional, we find that the optimized value of ω occurs at 0.3 Bohr^{-1} with a rather large a value ($a = 80$). This implies that only very small dispersion corrections will be obtained (at long range only). Therefore we do not explore this possibility further here.

The limiting case where $\omega = 0$ for ωB97X-D is also very interesting, as it reduces to the existing B97 functional[55] with dispersion corrections. For comparisons within the training set, we denote this re-optimized functional as B97-D*. It should be noted that B97-D* contains a fraction of HF exchange, unlike Grimme's B97-D functional.[37] The overall performance of our new ωB97X-D will be compared with other DFT-D functionals, B97-D*, B97-D,[37] B3LYP-D,[37] and BLYP-D,[37] as well as our previous LC hybrid functionals, ωB97 and ωB97X.[18]

3. Results and discussion

3.1. The training set

All calculations are performed with a development version of Q-Chem 3.0.[56] Spin-restricted theory is used for singlet states and spin-unrestricted theory for others. For the binding energies of the weakly bound systems, the counterpoise correction[57] is employed to reduce basis set superposition error (BSSE).

Results for the training set are computed using the 6-311++G(3df,3pd) basis set with the SG-1 grid.[58] The error for each entry is defined as (error = theoretical value − reference value). The notation used for characterizing statistical errors is as follows: mean signed errors (MSEs), mean absolute errors (MAEs), root-mean-square (rms) errors, maximum negative errors (Max(−)), and maximum positive errors (Max(+)).

In Table 2, the first comparison (ωB97X-D *vs.* B97-D*) is quite significant because it indicates how much improvement is possible with the addition of a single extra parameter that makes long-range exchange exact and thus self-interaction free. Inspection of the training results shows significant improvement for both covalent and non-covalent interactions.

Table 2 Statistical errors (in kcal mol^{-1}) of the training set and the test sets. The B97-D* functional is defined in the text. The results for the ωB97X and ωB97 are taken from ref. 18

System	Error	ωB97X-D	B97-D*	B97-D	B3LYP-D	BLYP-D	ωB97X	ωB97
Training								
G3/99 (223)	MSE	−0.10	0.31	−1.71	−1.01	−0.83	−0.09	−0.20
	MAE	1.93	2.69	4.99	3.39	7.03	2.09	2.56
IP (40)	MSE	0.19	1.59	−0.88	2.16	−1.52	−0.15	−0.48
	MAE	2.74	3.35	3.58	3.68	4.43	2.69	2.65
EA (25)	MSE	0.10	1.02	−0.15	1.72	0.38	−0.43	−1.45
	MAE	1.92	2.33	2.08	2.41	2.58	2.05	2.67
PA (8)	MSE	1.49	0.35	2.27	−0.42	−1.07	0.60	0.68
	MAE	1.54	0.87	2.27	1.02	1.56	1.22	1.45
NHTBH (38)	MSE	−0.42	−2.29	−6.22	−5.13	−9.32	0.56	1.32
	MAE	1.51	2.66	6.46	5.24	9.34	1.75	2.31
HTBH (38)	MSE	−2.52	−3.20	−7.33	−5.39	−8.89	−1.51	−0.34
	MAE	2.64	3.20	7.41	5.39	8.89	2.24	2.24
S22 (22)	MSE	−0.08	−0.11	0.44	−0.28	0.22	0.53	0.16
	MAE	0.22	0.44	0.50	0.48	0.33	0.87	0.60
All (394)	MSE	−0.29	−0.13	−2.30	−1.28	−2.37	−0.15	−0.14
	MAE	1.94	2.62	4.73	3.52	6.40	2.05	2.39
Test								
G3/05 (48)	MSE	0.24		1.76	−2.62	1.88	0.76	1.28
	MAE	3.01		7.39	4.53	9.65	3.60	4.25
RE (30)	MSE	−0.21		−0.01	−0.29	0.73	−0.07	0.09
	MAE	1.66		2.70	1.92	3.01	1.74	1.97
Non-covalent (29)	MSE	−0.14		0.49	0.19	0.61	0.51	0.36
	MAE	0.43		0.77	0.73	0.90	0.73	0.65
All (107)	MSE	0.01		0.92	−1.21	1.21	0.46	0.69
	MAE	1.93		4.28	2.77	5.42	2.30	2.64

ωB97X-D shows a noticeable overall improvement (about 0.7 kcal mol^{-1}) relative to B97-D*, which we may infer is an indirect consequence of its asymptotically correct exchange potential.

A second significant comparison is between ωB97X-D and ωB97X, to assess how significant the empirical dispersion corrections are. We observe generally very modest changes in relative energies associated with covalent interactions, but a significant improvement in the results for non-covalent interactions (the S22 data). This indicates the limited scope of chemical improvement that is attainable with the fixed functionality of atom-atom dispersion interactions. Nevertheless, this essentially zero-cost correction does correct one clear physical limitation of ωB97X.

3.2. The test sets

To test the performance of ωB97X-D outside its training set, we also evaluate its performance on various test sets involving the additional 48 atomization energies in the G3/05 test set[59] (other than the 223 atomization energies in the G3/99 test set[48–50]), 30 chemical reaction energies taken from the NHTBH38/04 and HTBH38/04 databases,[52,53] 29 non-covalent interactions,[60,54] 166 optimized geometry properties of covalent systems,[61] 12 intermolecular bond lengths[54] and one long-range charge transfer excitation curve of two well-separated molecules. There are a total of 286 pieces of data in the test sets. The detailed information of the test sets as well as the basis sets, and numerical grids used is given in ref. 18.

The results for the test sets are summarized in Tables 2 and 3. As can be seen in Table 2, ωB97X-D performs the best with an overall accuracy of 2 kcal mol^{-1}. The ωB97X, ωB97, and B3LYP-D functionals also perform reasonably well, with overall accuracies of about 2.5 kcal mol^{-1}. The semi-local DFT-D functionals, B97-D and BLYP-D, produce enormously large mean absolute errors for the atomization energies, which shows the important role played by mixing of the exact HF exchange for reducing self-interaction errors.

Satisfactory predictions of molecular geometries of covalent and non-covalent systems by density functionals are necessary for practical use. For covalent systems, we perform geometry optimizations for each functional on the equilibrium experimental test set (EXTS),[61] while for non-covalent systems, we compute the intermolecular bond lengths of 12 weakly bound complexes taken from the S22 set,[54] using 6-311++G(3df,3pd) basis set with the fine grid, EML(75,302), consisting of 75 Euler–Maclaurin radial grid points[62] and 302 Lebedev angular grid points.[63] For non-covalent systems, we compare our results with the second-order Møller–Plesset perturbation theory (MP2).[64] The resolution-of-identity (RI) approximation[65] is used for the MP2 calculations using the aug-cc-pvqz auxiliary basis set. As shown in Table 3, performance of all of the hybrid functionals in predicting optimized geometries of EXTS is similar, and clearly better than that of the semi-local DFT-D functionals, B97-D and BLYP-D. Their performance in predicting intermolecular bond lengths is similar to MP2 theory.

In our previous work,[18] we have showed that our LC hybrid functionals resolve the qualitative failure of semi-local density functional in describing long-range charge-transfer (CT) excitations between a donor and an acceptor.[10–12] In this work, we perform TDDFT calculations for the lowest CT excitations on the same system with the same optimized geometries.[66] The high-level SAC-CI results, taken from ref. 16, are used for comparison.

As shown in Fig. 3, all of our LC hybrid functionals, ωB97X-D, ωB97X and ωB97, predict CT excitation curves

Table 3 Statistical errors (in Å) of EXTS[61] and bond lengths of 12 weakly bound complexes from the S22 set.[54] The EXTS results for the ωB97X and ωB97 are taken from ref. 18

System	Error	MP2	ωB97X-D	B97-D	B3LYP-D	BLYP-D	ωB97X	ωB97
EXTS (166)	MSE		−0.002	0.014	0.004	0.019	−0.003	−0.002
	MAE		0.009	0.015	0.009	0.020	0.009	0.010
	rms		0.013	0.021	0.013	0.025	0.014	0.015
	Max(−)		−0.078	−0.062	−0.078	−0.064	−0.084	−0.085
	Max(+)		0.055	0.107	0.065	0.103	0.055	0.059
Weak (12)	MSE	−0.087	−0.044	−0.021	−0.100	−0.076	−0.031	−0.092
	MAE	0.093	0.064	0.058	0.107	0.090	0.072	0.111
	rms	0.121	0.085	0.071	0.136	0.111	0.100	0.145
	Max(−)	−0.231	−0.198	−0.114	−0.267	−0.200	−0.231	−0.362
	Max(+)	0.024	0.056	0.125	0.043	0.079	0.177	0.077

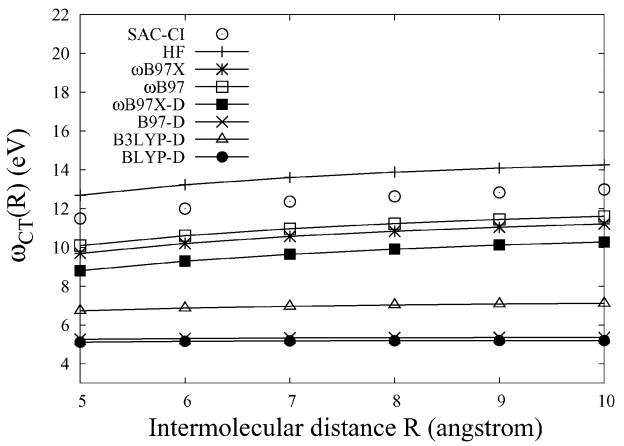

Fig. 3 The lowest CT excitation energy of $C_2H_4\cdots C_2F_4$ dimer along the intermolecular distances R (in Å). The results for the HF, ωB97X, and ωB97 are taken from ref. 18, while the results for the SAC-CI are taken from ref. 16.

that are in qualitative agreement with the high-level SAC-CI results, while B97-D, B3LYP-D and BLYP-D predict qualitatively incorrect CT excitation curves. This emphasizes the important role of the LC hybrid functionals in TDDFT, especially for CT excited states. Finally we note that the remaining short-range self-interaction error is somewhat larger for ωB97X-D than for ωB97X than for ωB97. This reflects their relative ω values, and suggests that ωB97 will be preferred for TDDFT applications. We intend to investigate this question further in a future study.

4. Conclusions

We have developed a new LC hybrid DFT-D functional based on our previous work.[18] This functional, called ωB97X-D, includes 100% long-range exact exchange, a small fraction (about 22%) of short-range exact exchange, a modified B97 exchange density functional for short-range interaction, the B97 correlation density functional,[55] and empirical dispersion corrections. When the constraint of $\omega = 0$ is applied, ωB97X-D reduces to the existing B97 functional form[55] with the same empirical dispersion corrections. The constrained form ($\omega = 0$), when re-optimized on the same training set, provides poorer fits to training data, indicating that the single extra degree of freedom corresponding to long-range exchange is physically important. Relative to our previous functional, ωB97X, ωB97X-D provides significant improvement only for non-covalent interactions.

Since ωB97X-D is a parametrized functional, we test it against three well-established existing DFT-D functionals (B97-D,[37] B3LYP-D,[37] and BLYP-D[37]) as well as our previous LC hybrid functionals (ωB97X and ωB97) on a separate independent test set of data, which includes further atomization energies, reaction energies, non-covalent interaction energies, equilibrium geometries, and a charge-transfer excited state. The results indicate that this new long-range corrected DFT-D functional is generally somewhat superior in overall performance. Relative to ωB97X, we recommend ωB97X-D for applications where non-covalent interactions are expected to be significant.

ωB97X-D does have some limitations that are appropriate to summarize as we conclude. Like other LC functions, it is free of long-range self-interaction, but still suffers from some self-interaction at short-range. The optimized parameters we have obtained are such that this effect is slightly larger for ωB97X-D than for ωB97X, which in turn was slightly larger than for ωB97. We also note that long-range correlation effects are solely treated by the empirical dispersion corrections in ωB97X-D, and therefore the KS orbitals themselves are not directly influenced by dispersion effects.

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References

1 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.
2 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133.
3 R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
4 R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many Body Problem*, Springer-Verlag, Berlin, 1990.
5 W. Kohn, A. D. Becke and R. G. Parr, *J. Phys. Chem.*, 1996, **100**, 12974.
6 M. E. Casida, *Recent Advances in Density Functional Methods, Part I*, World Scientific, Singapore, 1995.
7 E. K. U. Gross, J. F. Dobson and M. Petersilka, *Density Functional Theory II*, Springer, Heidelberg, 1996.
8 T. Bally and G. N. Sastry, *J. Phys. Chem. A*, 1997, **101**, 7923; B. Braïda, P. C. Hiberty and A. Savin, *J. Phys. Chem. A*, 1998, **102**,

7872; P. Mori-Sánchez, A. J. Cohen and W. Yang, *J. Chem. Phys.*, 2006, **125**, 201102; A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov and G. E. Scuseria, *J. Chem. Phys.*, 2007, **126**, 104102.
9 A. D. Dutoi and M. Head-Gordon, *Chem. Phys. Lett.*, 2006, **422**, 230.
10 A. Dreuw, J. L. Weisman and M. Head-Gordon, *J. Phys. Chem.*, 2003, **119**, 2943.
11 A. Dreuw and M. Head-Gordon, *J. Am. Chem. Soc.*, 2004, **126**, 4007.
12 A. Dreuw and M. Head-Gordon, *Chem. Rev.*, 2005, **105**, 4009.
13 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
14 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
15 H. Stoll and A. Savin, in *Density Functional Methods in Physics*, eds. R. M. Dreizler and J. D. Providencia, Plenum, New York, 1985, p. 177; A. Savin, in *Recent Developments and Applications of Modern Density Functional Theory*, ed. J. M. Seminario, Elsevier, Amsterdam, 1996, pp. 327–357; P. M. W. Gill, R. D. Adamson and J. A. Pople, *Mol. Phys.*, 1996, **88**, 1005; T. Leininger, H. Stoll, H. -J. Werner and A. Savin, *Chem. Phys. Lett.*, 1997, **275**, 151; H. Iikura, T. Tsuneda, T. Yanai and K. Hirao, *J. Chem. Phys.*, 2001, **115**, 3540; J. Toulouse, F. Colonna and A. Savin, *J. Chem. Phys.*, 2005, **122**, 014110; J. G. Ángyán, I. C. Gerber, A. Savin and J. Toulouse, *Phys. Rev. A*, 2005, **72**, 012510; E. Goll, H.-J. Werner and H. Stoll, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3917; E. Goll, H. -J. Werner, H. Stoll, T. Leininger, P. Gori-Giorgi and A. Savin, *Chem. Phys.*, 2006, **329**, 276; O. A. Vydrov, J. Heyd, A. V. Krukau and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 074106; O. A. Vydrov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 234109; I. C. Gerber, J. G. Ángyán, M. Marsman and G. Kresse, *J. Chem. Phys.*, 2007, **127**, 054101; J.-W. Song, T. Hirosawa, T. Tsuneda and K. Hirao, *J. Chem. Phys.*, 2007, **126**, 154105; A. J. Cohen, P. Mori-Sánchez and W. Yang, *J. Chem. Phys.*, 2007, **126**, 191109.
16 Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai and K. Hirao, *J. Chem. Phys.*, 2004, **120**, 8425.
17 I. C. Gerber and J. G. Ángyán, *Chem. Phys. Lett.*, 2005, **415**, 100.
18 J. -D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2008, **128**, 084106.
19 J. F. Dobson, K. McLennan, A. Rubio, J. Wang, T. Gould, H. M. Le and B. P. Dinte, *Aust. J. Chem.*, 2001, **54**, 513.
20 S. Kristyan and P. Pulay, *Chem. Phys. Lett.*, 1994, **229**, 175.
21 E. Zaremba and W. Kohn, *Phys. Rev. B*, 1976, **13**, 2270.
22 J. F. Dobson and B. P. Dinte, *Phys. Rev. Lett.*, 1996, **76**, 1780.
23 Y. Andersson, D. C. Langreth and B. I. Lundqvist, *Phys. Rev. Lett.*, 1996, **76**, 102.
24 K. Rapcewicz and N. W. Ashcroft, *Phys. Rev. B*, 1991, **44**, 4032.
25 M. Kamiya, T. Tsuneda and K. Hirao, *J. Chem. Phys.*, 2002, **117**, 6010.
26 T. Sato, T. Tsuneda and K. Hirao, *J. Chem. Phys.*, 2005, **123**, 104307.
27 T. Sato, T. Tsuneda and K. Hirao, *J. Chem. Phys.*, 2007, **126**, 234114.
28 H. Rydberg, B. I. Lundqvist, D. C. Langreth and M. Dion, *Phys. Rev. B*, 2000, **62**, 6997; H. Rydberg, M. Dion, N. Jacobson, E. Schröder, P. Hyldgaard, S. I. Simak, D. C. Langreth and B. I. Lundqvist, *Phys. Rev. Lett.*, 2003, **91**, 126402; M. Dion, H. Rydberg, E. Schröder, D. C. Langreth and B. I. Lundqvist, *Phys. Rev. Lett.*, 2004, **92**, 246401; D. C. Langreth, M. Dion, H. Rydberg, E. Schröder, P. Hyldgaard and B. I. Lundqvist, *Int. J. Quantum Chem.*, 2005, **101**, 599; S. D. Chakarova-Käck, E. Schröder, B. I. Lundqvist and D. C. Langreth, *Phys. Rev. Lett.*, 2006, **96**, 146107; A. Puzder, M. Dion and D. C. Langreth, *J. Chem. Phys.*, 2006, **124**, 164105; T. Thonhauser, A. Puzder and D. C. Langreth, *J. Chem. Phys.*, 2006, **124**, 164106; T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard and D. C. Langreth, *Phys. Rev. B*, 2007, **76**, 125112.
29 A. D. Becke and E. R. Johnson, *J. Chem. Phys.*, 2005, **122**, 154104; E. R. Johnson and A. D. Becke, *J. Chem. Phys.*, 2005, **123**, 024101; A. D. Becke and E. R. Johnson, *J. Chem. Phys.*, 2005, **123**, 154101; A. D. Becke and E. R. Johnson, *J. Chem. Phys.*, 2006, **124**, 014104; E. R. Johnson and A. D. Becke, *J. Chem. Phys.*, 2006, **124**, 174104; E. R. Johnson and A. D. Becke, *Chem. Phys. Lett.*, 2006, **432**, 600; A. D. Becke and E. R. Johnson, *J. Chem. Phys.*, 2007, **127**, 124108; A. D. Becke and E. R. Johnson, *J. Chem. Phys.*, 2007, **127**, 154108; E. R. Johnson and A. D. Becke, *J. Chem. Phys.*, 2008, **128**, 124105.
30 J. A. Alonso and A. Mañanes, *Theor. Chem. Acc.*, 2007, **117**, 467.
31 J. G. Ángyán, *J. Chem. Phys.*, 2007, **127**, 024108.
32 R. Ahlrichs, R. Penco and G. Scoles, *Chem. Phys.*, 1977, **19**, 119.
33 X. Wu, M. C. Vargas, S. Nayak, V. Lotrich and G. Scoles, *J. Chem. Phys.*, 2001, **115**, 8748.
34 Q. Wu and W. Yang, *J. Chem. Phys.*, 2002, **116**, 515.
35 U. Zimmerli, M. Parrinello and P. Koumoutsakos, *J. Chem. Phys.*, 2004, **120**, 2693.
36 S. Grimme, *J. Comput. Chem.*, 2004, **25**, 1463.
37 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787.
38 J. Antony and S. Grimme, *Phys. Chem. Chem. Phys.*, 2006, **8**, 5287.
39 P. Jurečka, J. Černý, P. Hobza and D. R. Salahub, *J. Comput. Chem.*, 2006, **28**, 555.
40 A. Goursot, T. Mineva, R. Kevorkyants and D. Talbi, *J. Chem. Theory Comput.*, 2007, **3**, 755.
41 S. Grimme, J. Antony, T. Schwabe and C. Mück-Lichtenfeld, *Org. Biomol. Chem.*, 2007, **5**, 741.
42 J. Černý, P. Jurečka, P. Hobza and H. Valdés, *J. Phys. Chem. A*, 2007, **111**, 1146.
43 C. Morgado, M. A. Vincent, I. H. Hillier and X. Shan, *Phys. Chem. Chem. Phys.*, 2007, **9**, 448.
44 T. Schwabe and S. Grimme, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3397.
45 M. Kabeláč, H. Valdés, E. C. Sherer, C. J. Cramer and P. Hobza, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5000.
46 J. Černý and P. Hobza, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5291.
47 S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia and C. F. Fischer, *Phys. Rev. A*, 1993, **47**, 3649.
48 L. A. Curtiss, K. Raghavachari, P. C. Redfern and J. A. Pople, *J. Chem. Phys.*, 1997, **106**, 1063.
49 L. A. Curtiss, P. C. Redfern, K. Raghavachari and J. A. Pople, *J. Chem. Phys.*, 1998, **109**, 42.
50 L. A. Curtiss, K. Raghavachari, P. C. Redfern and J. A. Pople, *J. Chem. Phys.*, 2000, **112**, 7374.
51 J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari and L. A. Curtiss, *J. Chem. Phys.*, 1989, **90**, 5622.
52 Y. Zhao, B. J. Lynch and D. G. Truhlar, *J. Phys. Chem. A*, 2004, **108**, 2715.
53 Y. Zhao, N. González-García and D. G. Truhlar, *J. Phys. Chem. A*, 2005, **109**, 2012; Y. Zhao, N. González-García and D. G. Truhlar, *J. Phys. Chem. A*, 2006, **110**, 4942 (erratum).
54 P. Jurečka, J. Šponer, J. Černý and P. Hobza, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1985.
55 A. D. Becke, *J. Chem. Phys.*, 1997, **107**, 8554.
56 Y. Shao, L. Fusti-Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. Distasio Jr., R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. Van Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer III, J. Kong, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3172.
57 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.
58 P. M. W. Gill, B. G. Johnson and J. A. Pople, *Chem. Phys. Lett.*, 1993, **209**, 506.
59 L. A. Curtiss, P. C. Redfern and K. Raghavachari, *J. Chem. Phys.*, 2005, **123**, 124107.
60 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2005, **109**, 5656.
61 R. A. DiStasio Jr., R. P. Steele, Y. M. Rhee, Y. Shao and M. Head-Gordon, *J. Comput. Chem.*, 2007, **28**, 839.
62 C. W. Murray, N. C. Handy and G. J. Laming, *Mol. Phys.*, 1993, **78**, 997.
63 V. I. Lebedev, *Zh. Vychisl. Mat. Mat. Fiz.*, 1975, **15**, 48; V. I. Lebedev, *Zh. Vychisl. Mat. Mat. Fiz.*, 1976, **16**, 293; V. I. Lebedev, *Sibirsk. Mat. Zh.*, 1977, **18**, 132.
64 C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.
65 R. A. Kendall and H. A. Früchtl, *Theor. Chem. Acc.*, 1997, **97**, 158.
66 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2006, **110**, 13126.

