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Benchmark assessment of the accuracy of several van der Waals density functionals

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Abstract

The nonlocal correlation functional VV10, developed recently in our group, describes the whole range of dispersion interactions in a seamless and general fashion using only the electron density as input. The VV10 functional has a simple analytic form that can be adjusted for pairing with the exchange functional of choice. In this article, we use several benchmark datasets of weakly interacting molecular complexes to test the accuracy of two VV10 variants, differing in their treatment of the exchange component. For the sake of comparison, several other density functionals suitable for noncovalent interactions were also tested against the same benchmarks. We find that the “default” version of VV10 with semilocal exchange gives very accurate geometries and binding energies for most van der Waals complexes, but systematically overbinds hydrogen bonded complexes. The alternative variant of VV10 with long-range corrected hybrid exchange performs exceptionally well for all types of weak bonding sampled in this study, including hydrogen bonds.

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1 Introduction and description of tested methods

In typical density functional theory (DFT) approximations, the correlation energy is expressed as a local or semilocal functional of the electron density. Such (semi)local approximations cannot describe long-range van der Waals (dispersion) interactions.¹ It has become common practice to augment DFT functionals with an empirical dispersion correction. A variety of such corrections have been developed, but most of them assume a pairwise atom–atom additive form.^{1–4} To capture the proper physics of dispersion interactions within the formalism of Kohn–Sham DFT, the correlation energy must be expressed as a fully nonlocal functional of the density and/or orbitals.⁵ Among the most computationally tractable and affordable nonlocal correlation models is the family of van der Waals density functionals (vdW-DF) introduced by Langreth and coworkers.^{6–8} This family of functionals includes a few members developed in our group,^{9–11} with the most recent addition, denoted as VV10, having a particularly simple construction.¹⁰ VV10 is easy to implement, computationally efficient, and undemanding in terms of the basis set quality or the fineness of the numerical integration grid.¹⁰ In this article we assess the performance of VV10 for weakly interacting molecular systems and compare its accuracy to several other promising DFT models.

We test three density functionals with nonlocal correlation components: vdW-DF2 of Ref. 8, and VV10 and LC-VV10 of Ref. 10. In all three of these methods, the exchange–correlation (xc) energy is represented as a sum of three parts:

$$E_{xc} = E_x + E_c^0 + E_c^{nl},$$

where the terms on the right-hand side are exchange, (semi)local correlation, and nonlocal correlation respectively. In vdW-DF2, the refitted¹² version of Perdew–Wang–86 semilocal exchange¹³ functional (denoted as rPW86) is used for E_x and the local density approximation¹⁴ correlation functional is used for E_c^0 . In VV10 and LC-VV10, E_c^0 is described by the semilocal correlation functional of Perdew, Burke, and Ernzerhof (PBE).¹⁵ VV10 uses the semilocal rPW86 exchange,¹² while in LC-VV10 the exchange component is described by a long-range corrected

hybrid¹⁶ LC- ω PBE with the range-separation parameter $\omega = 0.45 \text{ bohr}^{-1}$. The two versions of VV10 use slightly different parameters¹⁰ in the nonlocal correlation component: the rPW86-based version of VV10 has $C = 0.0093$ and $b = 5.9$, whereas LC-VV10 has $C = 0.0089$ and $b = 6.3$. The parameter C was fitted to give accurate asymptotic dispersion C_6 coefficients, while b controls the short-range damping of nonlocal correlation.

All of the aforementioned nonlocal functionals have been implemented self-consistently^{10,17} into the Q-CHEM software package.¹⁸ Analytic energy gradients with respect to nuclear displacements are available,^{10,17} thus enabling efficient geometry optimizations.

For the sake of comparison, we also included results obtained with two density functionals that contain no nonlocal correlation and therefore can be considered more “conventional”: M06-2X of Ref. 19 and ω B97X-D of Ref. 20. Both of these functionals contain a rather large number of empirical parameters that were fitted on training sets including weakly-interacting systems. ω B97X-D incorporates a force-field-like pairwise dispersion correction developed by Grimme.² M06-2X contains no long-range dispersion terms of any kind, but was parameterized to mimic short- and intermediate-range dispersion effects.¹⁹ The exchange component of ω B97X-D has the form of a long-range corrected hybrid, while in M06-2X the Hartree–Fock exchange is admixed in a “global hybrid” fashion.

For our benchmark test sets, we use highly accurate reference data published or updated within the last year.^{21–25} The errors reported in the tables are summarized with the help of mean signed errors (ME), mean absolute errors (MAE), mean signed percentage errors (MPE), and mean absolute percentage errors (MAPE). We define binding energies as positive, therefore a negative ME or MPE indicates an underbinding trend, while positive errors in interaction energies signify overbinding.

Table 1: Summary of deviations from the reference values (Ref. 22) of the binding energies for the S66 test set, computed at fixed equilibrium geometries from Ref. 21. All calculations were performed self-consistently with the aug-cc-pVTZ basis set and counterpoise corrected. MPE and MAPE are in percents, MAE is in kcal/mol.

	vdW-DF2	VV10	LC-VV10	ω B97X-D	M06-2X
<i>hydrogen bonds (23)</i>					
MPE (%)	-5.6	6.4	-0.4	-0.4	-3.3
MAPE (%)	5.8	6.4	2.3	2.2	3.9
MAE	0.62	0.53	0.20	0.16	0.32
<i>dispersion (23)</i>					
MPE (%)	-2.8	7.5	-2.1	17.0	-9.2
MAPE (%)	8.7	7.9	3.3	17.2	10.1
MAE	0.33	0.20	0.10	0.50	0.29
<i>others (20)</i>					
MPE (%)	-12.8	1.0	0.0	3.8	-4.6
MAPE (%)	13.1	4.3	4.5	5.6	7.3
MAE	0.49	0.15	0.17	0.20	0.26
<i>total (66)</i>					
MPE (%)	-6.8	5.1	-0.9	6.9	-5.8
MAPE (%)	9.0	6.3	3.3	8.5	7.1
MAE	0.48	0.30	0.15	0.29	0.29

2 Test results

2.1 S66 test set of equilibrium interaction energies

Standard test sets of accurate benchmark data serve an important purpose for calibration and comparative assessment of newly developed computational methods. The recently published S66 test set^{21,22} includes benchmark interaction energies for 66 weakly-bound molecular complexes that represent typical intermolecular interaction motifs found in biomolecular structures. The S66 set is divided into three subsets: 23 hydrogen bonded complexes, 23 dispersion-dominated complexes, and 20 others that exhibit some form of a mixed bonding character. The reference values of the binding energies were obtained at a high level of correlated wavefunction theory: the authors estimate²² the residual uncertainty in the reference values to be under 1%.

We have calculated the binding energies for all systems in the S66 set using five density functional methods described in the Introduction. The interaction energies are computed self-

consistently with the aug-cc-pVTZ basis set and counterpoise corrected. The unpruned Euler–Maclaurin–Lebedev (75,302) quadrature grid was used to evaluate all local and semilocal contributions and the (50,194) grid was used for the nonlocal components. Table 1 summarizes deviations from the reference values²² for binding energies computed at fixed equilibrium geometries from Ref. 21.

As can be seen by the sign of MPE in Table 1, vdW-DF2 tends to underbind on average. The underbinding tendency of vdW-DF2 is particularly pronounced for complexes where at least one of the monomers is aromatic. In terms of the average errors for the whole S66 set, vdW-DF2 is the worst performer among the five methods in Table 1.

VV10 consistently overbinds all hydrogen bonded complexes in the S66 set. For the other two subsets of S66, VV10 also tends to overbind on average. Analysis of the errors for individual complexes reveals that the tendency of VV10 to overestimate equilibrium binding energies is more pronounced for systems of larger size. Among dispersion-dominated complexes, overbinding is quite strong for duplexes formed by two saturated hydrocarbons. The parameter b in VV10 was fitted¹⁰ to minimize the errors in equilibrium binding energies, but the training set was comprised of smaller (on average) systems than those in the S66 set. The main culprit of the uneven performance of VV10 for systems of different sizes is likely its semilocal rPW86 exchange component. The performance for S66 is substantially improved when a long-range corrected exchange functional is used: LC-VV10 yields the lowest total errors in Table 1 and exhibits a uniformly outstanding accuracy for all three subsets of S66.

Hujo and Grimme also recently applied VV10 to the S66 set.²⁶ For the standard version of VV10 (with rPW86 exchange and PBE correlation) they report MAE of 0.45 kcal/mol, which is considerably larger than MAE of 0.30 kcal/mol that we obtained for the same S66 test set. This substantial discrepancy cannot be explained solely by the difference in the adopted reference values (we used the numbers from Ref. 22, whereas Hujo and Grimme used the earlier values from Ref. 21) and must be in part due to the lack of self-consistency in the implementation of Hujo and Grimme²⁶ and differences in computational details.

As Table 1 shows, ω B97X-D yields rather low errors for hydrogen bonds, but performs poorly for the dispersion-dominated subset. ω B97X-D severely overbinds complexes of saturated hydrocarbons. For instance, the binding energy of cyclopentane-neopentane complex is overestimated by 40%. This overbinding tendency seems to stem from the dispersion correction included in ω B97X-D. The asymptotic C_6 coefficients used in ω B97X-D were adopted from the “second-generation” empirical dispersion correction scheme by Grimme,² which assigns $C_6 = 30.4$ a.u. (hartree·bohr⁶) for all types of carbon–carbon interactions. For the less-polarizable saturated sp^3 carbon atoms, this C_6 value is clearly too large. In fact, the more recent “third-generation” dispersion correction (denoted DFT-D3) by Grimme and coworkers³ uses a much smaller value of $C_6 = 18.1$ a.u. for interactions between saturated (sp^3 -hybrid) carbon atoms. It is not surprising that the more advanced DFT-D3 scheme performs rather well for the S66 test set.²⁷

For hydrogen-bonded complexes, the functionals with long-range corrected hybrid exchange components (LC-VV10 and ω B97X-D) perform particularly well. Thus, proper treatment of exchange interactions appears to be especially important for the description of hydrogen bonds. We note that M06-2X was applied to the S66 set in Ref. 27 and the results agree reasonably well with ours. M06-2X gives a rather uniform MAE of about 0.3 kcal/mol for each of the three subsets, as well as for the whole S66 set.

2.2 S66×1.25: out-of-equilibrium interaction energies

For the complexes in the S66 test set, reference binding energies are available not only at the equilibrium geometries, but also for a number of configurations deformed out of equilibrium.^{21,22} In this subsection we consider one such modified test set which we denote S66×1.25. The geometries of the systems in the S66×1.25 set are obtained from the equilibrium geometries by displacing the monomers away from each other, such that the minimum distance between them is 1.25 times the equilibrium value. The reference binding energies for the S66×1.25 complexes were calculated²¹ at a somewhat lower level of theory, but the estimated uncertainty in the reference values is still under 3%. In Table 2 we summarize the errors obtained with five density functionals using the

Table 2: Summary of deviations from the reference values of the binding energies for the $S66 \times 1.25$ test set. All calculations were performed self-consistently with the aug-cc-pVTZ basis set and counterpoise corrected. Geometries and reference binding energies are from Ref. 21. All numbers are in %.

	vdW-DF2	VV10	LC-VV10	ω B97X-D	M06-2X
<i>hydrogen bonds (23)</i>					
MPE	3.6	4.6	-0.3	-0.9	-4.8
MAPE	3.8	4.7	1.2	1.9	5.2
<i>dispersion (23)</i>					
MPE	16.1	6.5	-4.3	5.2	-36.0
MAPE	16.1	6.5	4.5	5.2	36.0
<i>others (20)</i>					
MPE	3.1	-0.9	-1.0	1.7	-16.8
MAPE	7.0	2.9	2.9	2.9	16.8
<i>total (66)</i>					
MPE	7.8	3.6	-1.9	2.0	-19.3
MAPE	9.1	4.8	2.9	3.4	19.4

same computational details as in the previous subsection.

Comparing MPEs in Table 1 to the MPEs in Table 2 for vdW-DF2 we observe a reversal of trends: from underbinding near equilibrium to overbinding at the $S66 \times 1.25$ geometries. This result is not unexpected, since vdW-DF2 is known to give shifted binding energy curves with minima at somewhat too large intermonomer separations.^{8,10}

Since the intermonomer distances in the $S66 \times 1.25$ set are increased, the overlap between the electronic densities of the monomers is diminished. Hence the local and semilocal components of the exchange-correlation functionals are expected to have a smaller contribution to interaction energies, while contributions of long-range nonlocal interactions become relatively more significant. In this regard, it is worth noting that the percentage errors of VV10 decrease from $S66$ to $S66 \times 1.25$. This may indicate that VV10 provides a satisfactory description of the long-range nonlocal correlations. A very different trend is exhibited by M06-2X: it performs reasonably well at equilibrium geometries (Table 1) but it strongly underbinds dispersion-dominated complexes in the $S66 \times 1.25$ set (Table 2). Thus the lack of long-range dispersion terms in M06-2X becomes clearly detrimental when intermonomer distances are just 25% larger than equilibrium.

As Table 2 shows, both long-range corrected functionals, LC-VV10 and ω B97X-D, perform

rather well for the $S66 \times 1.25$ set. $\omega B97X-D$ yields significantly lower total percentage errors for the nonequilibrium $S66 \times 1.25$ set (Table 2) as compared to the equilibrium geometries (Table 1).

2.3 Binding energy curves for benzene– H_2S and pyridine dimer

In Ref. 10 we computed interaction energy curves for several weakly-bound complexes using VV10 and vdW-DF2. In this subsection we report the binding energy curves of two systems that were not included in our previous¹⁰ study: the benzene– H_2S complex of C_{2v} symmetry and the pyridine dimer in the stacked sandwich-shaped configuration (C_{2h} symmetry group). For both of these systems, very accurate reference data have been tabulated recently.²³ We used the same set of five functionals and the same computational details as for the S66 set above. We used the molecular geometries provided in Ref. 23. Counterpoise corrections were applied at all intermonomer distances. The results are presented in Figures 1 and 2. In both of these figures, the left panel displays the binding energy curves computed with VV10 and vdW-DF2 — the two methods that incorporate the semilocal rPW86 exchange. The results shown in the right panel in Figures 1 and 2 correspond to the functionals with hybrid exchange components.

As Figure 1 shows, both VV10 and LC-VV10 yield very accurate interaction energies for benzene– H_2S at all sampled intermonomer distances. For the sandwich pyridine dimer (Figure 2), the equilibrium intermolecular separation is well reproduced by both VV10 and LC-VV10, but the interaction energy near equilibrium is slightly overestimated by VV10 and somewhat underestimated by LC-VV10.

As has been observed previously,^{8,10} vdW-DF2 yields binding energy curves that are much too repulsive at short range and with energy minima shifted to larger distances as compared to the reference curves. These effects are clearly seen in Figures 1 and 2. The equilibrium binding energy given by vdW-DF2 is underestimated for benzene– H_2S but overestimated for pyridine dimer.

For both systems shown in Figures 1 and 2, $\omega B97X-D$ reproduces the binding energy curves rather well at nearly all distances. For both complexes, the equilibrium intermonomer distance is predicted well by $\omega B97X-D$, but there is a slight overbinding near equilibrium.

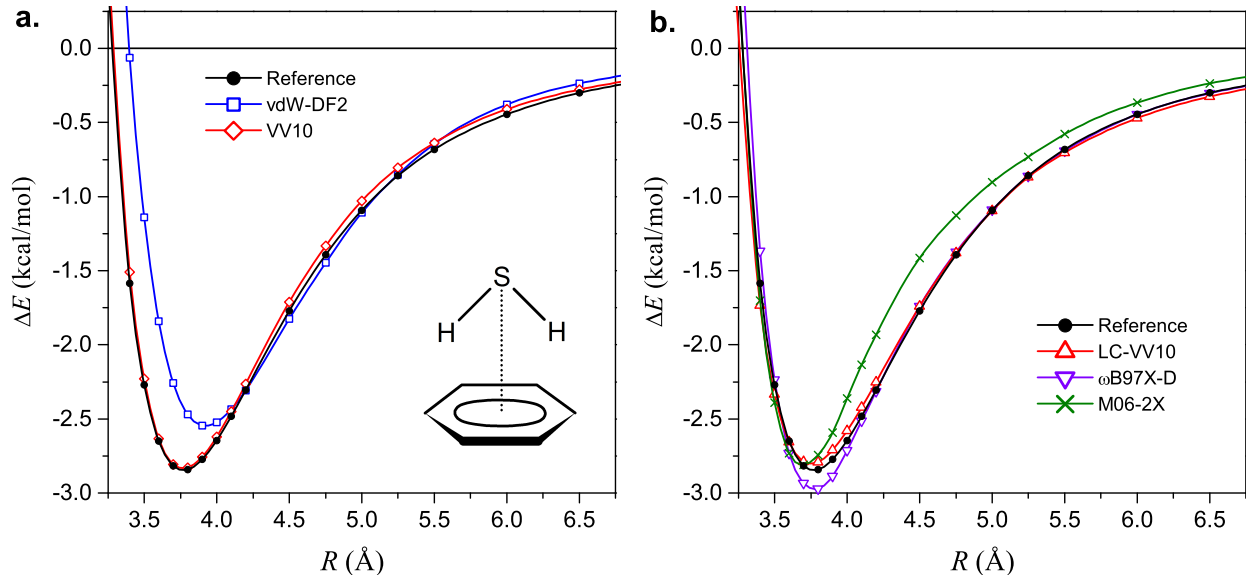


Figure 1: Interaction energy curves for the benzene-H₂S complex, computed self-consistently with the aug-cc-pVTZ basis set. R is the distance between the S atom and the benzene plane. Reference values are from Ref. 23.

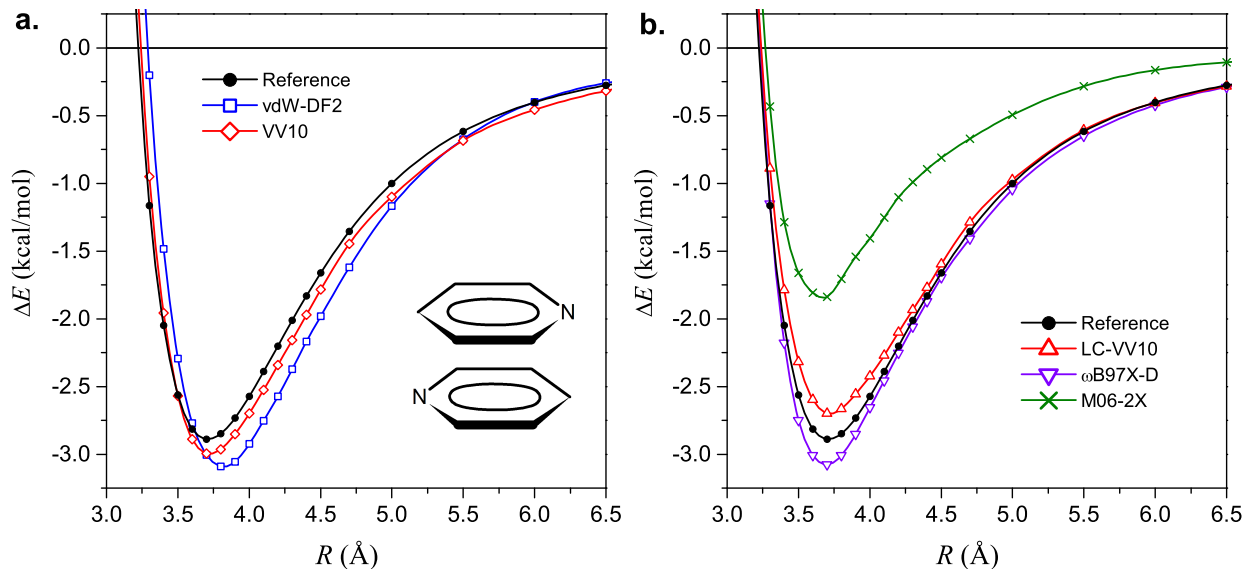


Figure 2: Interaction energy curves for the pyridine dimer in sandwich configuration, computed self-consistently with the aug-cc-pVTZ basis set. R is the separation between the monomer planes. Reference values are from Ref. 23.

Table 3: Counterpoise-corrected dissociation energies (in kcal/mol) for $\text{CO}_2\text{-X}$ complexes computed with the aug-cc-pVQZ basis set. Molecular geometries are fully optimized in each method. Reference values are from Refs. 24 and 25.

Complex	Symm.	Ref.	vdW-DF2	VV10	LC-VV10	ω B97X-D	M06-2X
$\text{CO}_2\text{-Ar}$	C_{2v}	0.57	0.69	0.60	0.41	0.27	0.36
$\text{CO}_2\text{-N}_2$	C_{2v}	0.94	1.06	0.97	0.78	0.51	0.71
$\text{CO}_2\text{-CO}$	C_{2v}	1.16	1.29	1.31	1.06	0.79	1.03
$\text{CO}_2\text{-H}_2\text{O}$	C_{2v}	2.92	2.83	2.84	2.81	2.17	3.13
$\text{CO}_2\text{-NH}_3$	C_s	3.04	3.06	3.33	3.02	2.71	3.32
$(\text{CO}_2)_2$ T	C_{2v}	1.23	1.26	1.11	1.03	0.63	0.96
$(\text{CO}_2)_2$ PD	C_{2h}	1.49	1.50	1.39	1.23	0.83	1.34
MPE (%)			6.6	1.7	-13.0	-37.0	-12.6
MAPE (%)			7.4	7.2	13.0	37.0	17.3

M06-2X gives reasonable equilibrium binding energy for benzene- H_2S , although the minimum is at a shorter distance as compared to the reference. As seen in Figure 1, M06-2X underestimates the interaction energies for $R > 3.7 \text{ \AA}$, but the underestimation is not very strong in this case, because the asymptotic interactions in benzene- H_2S are dominated by electrostatic and induction contributions. Binding energy curves for benzene- H_2S obtained with M06-2X and a few other density functionals were previously reported in Ref. 28. M06-2X performs notably worse for the pyridine dimer: as Figure 2 shows, M06-2X strongly underbinds this sandwich-shaped complex at all intermonomer distances. This indicates that long-range dispersion interactions (missing in M06-2X) are crucial for the proper description of $\pi\text{-}\pi$ stacking in the pyridine dimer.

2.4 Complexes of CO_2 with small molecules

In this subsection, we consider a set of weakly bound complexes containing carbon dioxide. For all of these complexes, given in Table 3, very accurate equilibrium geometries and interaction energies are available, obtained at a high level of correlated wavefunction theory.^{24,25} The test set in Table 3 includes two different configurations of the CO_2 dimer: T-shaped and parallel-displaced (PD). The set also includes five complexes of CO_2 with other molecules. All of these $\text{CO}_2\text{-X}$ complexes have a T-shaped form with a nonhydrogen atom of the X molecule positioned on top of the carbon atom of CO_2 . We have fully optimized the geometries of all the complexes and their

Table 4: Intermolecular distances for CO₂-X complexes. Computational details as in Table 3.

Complex	R^a	Ref.	vdW-DF2	VV10	LC-VV10	ω B97X-D	M06-2X
CO ₂ -Ar	C...Ar	3.42	3.49	3.40	3.50	3.89	3.42
CO ₂ -N ₂	C...N	3.13	3.17	3.10	3.18	3.40	3.06
CO ₂ -CO	C...C	3.22	3.29	3.16	3.23	3.32	3.13
CO ₂ -H ₂ O	C...O	2.76	2.84	2.76	2.77	2.83	2.68
CO ₂ -NH ₃	C...N	2.92	3.01	2.88	2.91	2.95	2.84
(CO ₂) ₂ T	C...O	2.96	3.02	2.98	3.02	3.32	2.92
(CO ₂) ₂ PD	C...C	3.51	3.65	3.54	3.58	3.79	3.37
(CO ₂) ₂ PD	\angle CCO	58.9°	57.6°	58.8°	58.4°	57.8°	59.3°
	ME (Å) ^b		0.08	-0.01	0.04	0.23	-0.07
	MAE (Å) ^b		0.08	0.03	0.04	0.23	0.07

^a Interatomic distances (in Å) at the equilibrium, plus the CCO angle in the PD dimer.

^b Include only the distances and exclude the CCO angle in (CO₂)₂ PD.

constituent monomers using the aug-cc-pVQZ basis set. The (99,590) grid was used for semilocal xc components, while (75,302) was used for nonlocal correlation.

As Table 3 shows, the equilibrium binding energies of CO₂-containing duplexes are predicted quite accurately by vdW-DF2 and VV10, but systematically underestimated with LC-VV10 and ω B97X-D. The underbinding in ω B97X-D is not only systematic but also quite severe. M06-2X underestimates dissociation energies of most (but not all) complexes in Table 3.

Table 4 shows equilibrium intermonomer distances as predicted by each of the five tested functionals. It also includes the C-C-O angle in the parallel-displaced CO₂ dimer. VV10 yields very accurate geometries for all the complexes, and LC-VV10 performs almost equally well. Equilibrium intermolecular distances are systematically overestimated by both vdW-DF2 and ω B97X-D, but the errors are much larger in ω B97X-D. M06-2X yields intermonomer separations that are moderately but systematically underestimated.

The large systematic errors of ω B97X-D for CO₂-containing complexes render it the worst performer among the methods included in Tables 3 and 4. The best performer for these systems is clearly VV10.

3 Conclusions

Among the five methods tested in this study, only M06-2X does not incorporate any long-range dispersion terms. However, M06-2X was fitted to mimic the effects of dispersion correlations at intermediate range, and in this respect it is among the best of its kind. Indeed, M06-2X often gives reasonably good interaction energies for van der Waals complexes near equilibrium geometries, where the monomer densities overlap substantially. At the same time, M06-2X gives large errors for complexes out of equilibrium, where the density overlap is diminished.

The inclusion of an explicit dispersion correction (as in ω B97X-D) does not necessarily lead to improved performance for weakly bound complexes at equilibrium. In fact, in many of our tests we found ω B97X-D to be inferior to M06-2X for near-equilibrium geometries. The parameterization of the empirical dispersion correction in ω B97X-D may not be optimal and there is certainly room for improvement. Development of dispersion corrections is an active area of research and more flexible and elaborate models have already been proposed^{3,4} and shown to perform rather well.²⁷

The main focus of this article was on the latest generation of seamless nonlocal correlation functionals. We have demonstrated that these van der Waals density functionals (vdW-DF2, VV10, and LC-VV10) provide the predictive power on par with the most accurate methods of comparable computational cost. In most of our benchmark assessments, VV10 and LC-VV10 emerged as best performers among the tested methods. The accuracy of VV10 for hydrogen bonds is not fully satisfactory, but the culprit appears to be the semilocal rPW86 exchange incorporated therein. The version with the long-range corrected hybrid exchange — LC-VV10 — exhibits outstanding performance for all types of intermolecular interactions considered in this study; although the better overall accuracy of LC-VV10 is attained at a higher computational cost associated with the inclusion of exact long-range exchange terms.

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