

Dispersion-Weighted Explicitly Correlated Coupled-Cluster Theory [DW-CCSD(T**)-F12]

Michael S. Marshall and C. David Sherrill*

Center for Computational Molecular Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, United States

ABSTRACT: We propose a procedure denoted dispersion-weighted explicitly correlated coupled-cluster [DW-CCSD(T**)-F12] which mixes CCSD(T**)-F12a and CCSD(T**)-F12b so as to correct the small errors exhibited by each of the approximations in a small basis set, allowing for a black-box method that can provide high-quality interaction energies for a variety of nonbonded interactions. Relative to CCSD(T**)-F12a and CCSD(T**)-F12b, DW-CCSD(T**)-F12 reduces the mean absolute deviation by a factor of 2 and the maximum error by a factor of 3 (formic acid dimer) and 4 (stacked adenine–thymine) for the aug-cc-pVDZ basis set.

1. INTRODUCTION

Coupled-cluster with single, double, and perturbative triple excitations [CCSD(T)] has been referred to as the “gold standard” in computational chemistry.¹ This sophisticated description of dynamic electron correlation is often required to achieve benchmark quality results. In the context of noncovalent interactions, CCSD(T) can provide very accurate results,² but this typically requires very large basis sets, augmented with diffuse functions. Coupled with the steep computational scaling of CCSD(T), this significantly restricts the size of systems that may be studied at this level of accuracy. With the introduction of explicitly correlated wave functions, however, this computational cost is severely abated because accurate energies may be attained using relatively small basis sets.^{3–14} Applying these methods to noncovalent interactions, Marchetti et al.¹⁵ showed that CCSD(T**)-F12a/aug-cc-pVDZ can achieve an accuracy of better than 0.2 kcal mol^{−1} for all dimers in the S22 test set.¹⁶ They argued that this same accuracy would require at least an aug-cc-pVQZ basis set with traditional CCSD(T), which would be 1–2 orders of magnitude more expensive. More recently, de Lange et al.¹⁴ demonstrated that CCSD(T)-F12a/VDZ-F12 and CCSD(T)-F12b/VDZ-F12 achieve an average accuracy of 0.03 kcal mol^{−1} compared to CCSD(T)/CBS(a5Z,a6Z) for small molecules interacting with carbon dioxide. This accuracy is impressive considering the standard CCSD(T)/aug-cc-pVDZ has an average error of 0.4 kcal mol^{−1} for these complexes.

When employing explicitly correlated methods, the choice of ansatz and how to treat the triples correction are both very important. For coupled-cluster, the F12a and F12b approximations have become the most commonly used.^{9,12} Within the MOLPRO package¹⁷ used here, since there is no explicitly correlated triples correction, this quantity should be scaled to achieve highly accurate results. This work follows the approach of Werner and co-workers^{12,15} whereby the triples correction is scaled by the ratio of MP2 correlation energy and MP2-F12 correlation energy:

$$E_{(T^*)}^{\text{corr}} = E_{(T)}^{\text{corr}} \cdot \frac{E_{\text{MP2-F12}}}{E_{\text{MP2}}} \quad (1)$$

To retain size-consistency for interaction energies, one must use the same scale factor for all computations (the dimer, and both monomers). Because of this difference, we designate CCSD(T**)-F12 (2 asterisks) to refer to the size-consistent version (using the dimer scale factor for all three computations) and CCSD(T*)-F12 (1 asterisk) to refer to the independently scaled version.

In our recent study,¹⁸ CCSD(T**)-F12a/aug-cc-pVDZ is shown to yield a mean absolute deviation (MAD) of 0.09 kcal mol^{−1} against the newly revised interaction energies for the S22 test set¹⁶ (herein referred to as S22B).¹⁸ This accuracy is notable because standard CCSD(T) (in the absence of focal-point analysis) would require a much larger basis set, such as aug-cc-pVQZ, to reach this accuracy, and such computations would become prohibitively expensive for all but the smallest molecular systems. Notably, CCSD(T**)-F12a reproduces benchmark energies for hydrogen-bonded systems very accurately, while incurring small errors for dispersion-bound complexes, and CCSD(T**)-F12b reproduces benchmark energies for dispersion-bound complexes very accurately but degrades somewhat in quality for hydrogen bonding. A very similar problem has been investigated by Marchetti et al.¹⁵ in their studies of explicitly correlated spin-component-scaled Møller–Plesset perturbation theory (SCS-MP2-F12) and MP2-F12. In their work, they found MP2 significantly overbinds dispersion-bound complexes but does well for hydrogen bonding, while SCS-MP2-F12 can properly describe dispersion but underbinds hydrogen-bonding complexes. They proposed mixing the two approaches in a method known as dispersion-weighted MP2 (DW-MP2):

$$\Delta E_{\text{DW-MP2}} = \omega \Delta E_{\text{MP2-F12}} + (1 - \omega) \Delta E_{\text{SCS-MP2-F12}} \quad (2)$$

$$\omega = \frac{1}{2} \left[1 + \tanh \left(\alpha + \beta \frac{\Delta E_{\text{SCF}}}{\Delta E_{\text{MP2-F12}}} \right) \right] \quad (3)$$

The chosen switching function (eq 3) is a hyperbolic tangent function with two fit parameters, and the switching metric between SCS-MP2-F12 and a MP2-F12 is the ratio of MP2-F12 and

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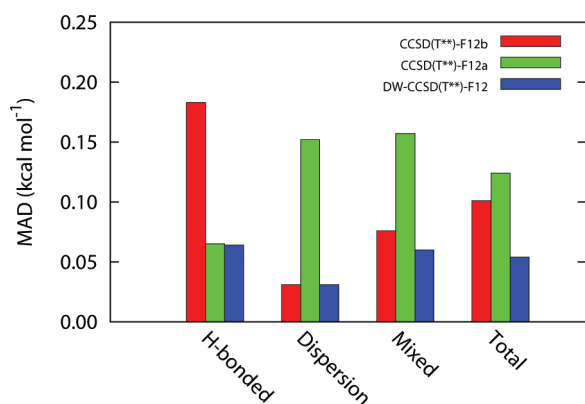


Figure 1. MAD of interaction energies versus S22B benchmark CCSD(T)/CBS values (ref 18) for explicitly correlated methods and DW-CCSD(T**)-F12 using the aug-cc-pVDZ basis.

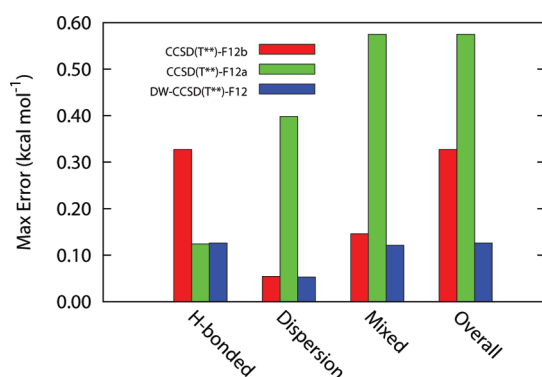


Figure 2. MAD of interaction energies versus S22B benchmark CCSD(T)/CBS (ref 18) values for explicitly correlated methods and DW-CCSD(T**)-F12 using the aug-cc-pVDZ basis.

self-consistent field (SCF) interaction energies. The underlying concept is that hydrogen-bonded complexes have a ratio near one because the interaction is predominantly electrostatic, which is properly captured by SCF, while dispersion-dominated systems should yield a ratio far from one, as SCF fails to model dispersion because of its lack of dynamic electron correlation. This mixing transforms MP2-F12 [root-mean-square error (RMSE) of 1.17 kcal mol^{−1} for the aug-cc-pVDZ basis] and SCS-MP2-F12 (1.08 kcal mol^{−1}) into DW-MP2 (0.24 kcal mol^{−1}) for the S22B test set. Inspired by this procedure, we explore analogous methods of combining CCSD(T**)-F12a and CCSD(T**)-F12b based on the character of the noncovalent interaction.

2. THEORETICAL METHODS

As demonstrated in Figures 1 and 2, direct computation of interaction energies by CCSD(T**)-F12, even when using the modest aug-cc-pVDZ basis set, yields surprisingly accurate values compared to the best available estimates. Here, we seek to correct the minor remaining deficiencies in explicitly correlated CCSD(T**)-F12a and CCSD(T**)-F12b with a scheme similar to the DW-MP2 approach of Marchetti et al.¹⁵

Using eqs 3 and 4, we fit α and β against the S22B test set. The SCF energy in eq 3 includes the complementary auxiliary orbital basis (CABS) correction.^{19,20} To test the transferability of these

fit parameters, we also consider another test set, HSG-A.^{18,21}

$$\Delta E_{\text{DW-CCSD(T**)-F12}} = \omega \Delta E_{\text{CCSD(T**)-F12a}} + (1 - \omega) \Delta E_{\text{CCSD(T**)-F12b}} \quad (4)$$

The two test sets considered here, S22 and HSG, were chosen for their small size, convenient separation into hydrogen-bonded, dispersion-dominated, and mixed bonding classes and quality of available benchmark interaction energies. S22 is an established test set with systems ranging from water dimer to adenine–thymine complexes. Its reference values have recently been revised (S22B) to be of MP2/CBS(aug-cc-pVTZ, aug-cc-pVQZ) + $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ /aug-cc-pVTZ quality or better. For the 10 smallest complexes in the S22 test set, at least MP2/CBS(aug-cc-pVQZ, aug-cc-pV5Z) + $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ /aug-cc-pVQZ quality is achieved to ensure that we can reliably benchmark both DW-CCSD(T**)-F12/aug-cc-pVDZ (against the entire S22 test set) and DW-CCSD(T**)-F12/aug-cc-pVTZ (against the ten smallest complexes in the S22 test set). The HSG test set was formed by dissecting the binding site of a bound protein–drug complex (HIV-II protease/indinavir) into 21 pairs of chemical fragments (each of which is not necessarily at its individual equilibrium geometry).²¹ We recently revised¹⁸ the HSG benchmark energies replacing the previous extrapolated heavy-aug-cc-pVDZ/heavy-aug-cc-pVTZ $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ corrections with the bare heavy-aug-cc-pVTZ $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ corrections to avoid overestimating the coupled-cluster correction for hydrogen-bonded systems [here heavy-aug-cc-pVXZ refers to the aug-cc-pVXZ basis where diffuse functions are added only to heavy (nonhydrogen) atoms]. This revision results from the recent systematic study of the nonmonotonic convergence of $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ for various members of the S22 test set.¹⁸ The revised HSG-A values are thus similar in accuracy to the S22B values. All interaction energies were counterpoise corrected for basis set superposition error (BSSE) using the scheme outlined by Boys and Bernardi.²²

3. RESULTS AND DISCUSSION

Using eqs 3 and 4, we smoothly combine the F12a to F12b ansatz according to the relative difference in ΔE_{SCF} and $\Delta E_{\text{MP2-F12}}$ interaction energies. Figure 1 and Table 1 illustrate the errors associated with each ansatz independently, and it is clear that some combination of the two should result in a method that captures both types of interactions accurately on average. We find fitted parameters of $\alpha = -1$ and $\beta = 4$ for the S22B set, which results in a MAD of 0.06, 0.03, 0.07, and 0.05 kcal mol^{−1}, respectively, for hydrogen-bonding, dispersion-dominated, and mixed interactions and overall. The complexes were assigned to these categories according to the SAPT2+(3)/aug-cc-pVTZ results of Hohenstein and Sherrill.²³ The most substantial gain of this approach is in the reduction of maximum errors for each subset, as shown in Figure 2. The maximum errors for F12a and F12b are 0.58 and 0.33 kcal mol^{−1}, respectively, whereas the largest error incurred by DW-CCSD(T**)-F12 is 0.13 kcal mol^{−1} for formamide dimer. This is a factor of 3–4 reduction in the maximum error and a factor of 2 reduction in the MAD. Figure 3 shows the error for each complex in the S22B test set for CCSD(T**)-F12a, CCSD(T**)-F12b, and DW-CCSD(T**)-F12. In this figure, one can clearly see how DW-CCSD(T**)-F12 switches between CCSD(T**)-F12a and CCSD(T**)-F12b as appropriate to avoid the largest maximum errors.

Table 1. Counterpoise Corrected Interaction Energies (kcal mol^{−1}) for the CCSD(T^{**})-F12a, CCSD(T^{**})-F12b, and DW-CCSD(T^{**})-F12 Methods Compared to S22B Benchmark Values (ref 18)^a

	complex	reference IE	F12a	F12b	DW-F12
1	HB ammonia dimer, C _{2h}	−3.133	−3.11	−3.05	−3.10
2	HB water dimer, C _s	−4.989	−4.92	−4.86	−4.92
3	HB formic acid dimer, C _{2h}	−18.753	−18.63	−18.43	−18.63
4	HB formamide dimer, C _{2h}	−16.062	−15.94	−15.80	−15.94
5	HB hydrogen-bonded uracil dimer, C _{2h}	−20.641	−20.63	−20.45	−20.63
6	HB 2-pyridone–2-aminopyridine, C ₁	−16.934	−16.98	−16.79	−16.97
7	HB adenine–thymine WC, C ₁	−16.660	−16.72	−16.51	−16.71
8	DD methane dimer, D _{3d}	−0.527	−0.53	−0.51	−0.51
9	DD ethene dimer, D _{2d}	−1.472	−1.50	−1.44	−1.44
10	DD benzene–methane, C ₃	−1.448	−1.47	−1.40	−1.40
11	DD parallel displaced benzene dimer, C _{2h}	−2.654	−2.90	−2.64	−2.64
12	DD pyrazine dimer, C _s	−4.255	−4.54	−4.26	−4.26
13	MX stacked uracil dimer, C ₂	−9.805	−10.17	−9.84	−9.88
14	DD stacked indole–benzene, C ₁	−4.524	−4.92	−4.57	−4.57
15	MX stacked adenine–thymine, C ₁	−11.730	−12.30	−11.84	−11.85
16	MX ethene–ethine, C _{2v}	−1.496	−1.51	−1.47	−1.49
17	MX benzene–water, C _s	−3.275	−3.23	−3.13	−3.19
18	MX benzene–ammonia, C _s	−2.312	−2.31	−2.23	−2.23
19	MX benzene–hydrogen cyanide, C _s	−4.541	−4.49	−4.39	−4.47
20	DD T-shaped benzene dimer, C _{2v}	−2.717	−2.78	−2.66	−2.66
21	MX T-shaped indole–benzene, C ₁	−5.627	−5.73	−5.56	−5.58
22	MX phenol dimer, C ₁	−7.097	−7.15	−6.99	−7.07
Hydrogen Bonded					
	maximal deviation		0.12	0.33	0.13
	mean signed deviation		0.03	0.18	0.04
	MAD		0.06	0.18	0.06
	RMSD		0.08	0.20	0.08
Mixed Influence					
	Maximal Deviation		−0.57	0.15	−0.12
	Mean Signed Deviation		−0.13	0.05	0.02
	MAD		0.15	0.09	0.07
	RMSD		0.25	0.10	0.07
Dispersion Bound					
	Maximal Deviation		−0.01	0.05	0.05
	Mean Signed Deviation		−0.40	0.02	0.02
	MAD		0.15	0.03	0.03
	RMSD		0.21	0.04	0.04
Full Set					
	Maximal Deviation		−0.57	0.33	0.13
	Mean Signed Deviation		−0.08	0.08	0.02
	MAD		0.12	0.10	0.05
	RMSD		0.19	0.13	0.07

^a Fit parameters are $\alpha = -1$ and $\beta = 4$. Computations use the aug-cc-pVDZ basis set. The errors and mixing in the DW approach can be seen graphically in Figure 3.

To evaluate the transferability of fitting parameters, DW-CCSD(T^{**})-F12/aug-cc-pVDZ was applied to the HSG-A test set using the parameters fit against the S22B test set; it achieves a MAD of 0.04 kcal mol^{−1} for overall interaction energies. This is a significant achievement, especially because the diverse, nonequilibrium nature of the complexes found in the HSG-A set is often challenging for computational methods. The maximum

error across this test set is 0.10 kcal mol^{−1}. These impressive results compare to a MAD of 0.42 kcal mol^{−1} and a maximum error of 1.53 kcal mol^{−1} for conventional CCSD(T)/heavy-aug-cc-pVDZ.

DW-CCSD(T^{**})-F12 was also tested using an aug-cc-pVTZ basis set against the 10 smallest complexes in the S22B benchmark set Figure 4 and Table 2. With fit parameters $\alpha = 0.4$ and

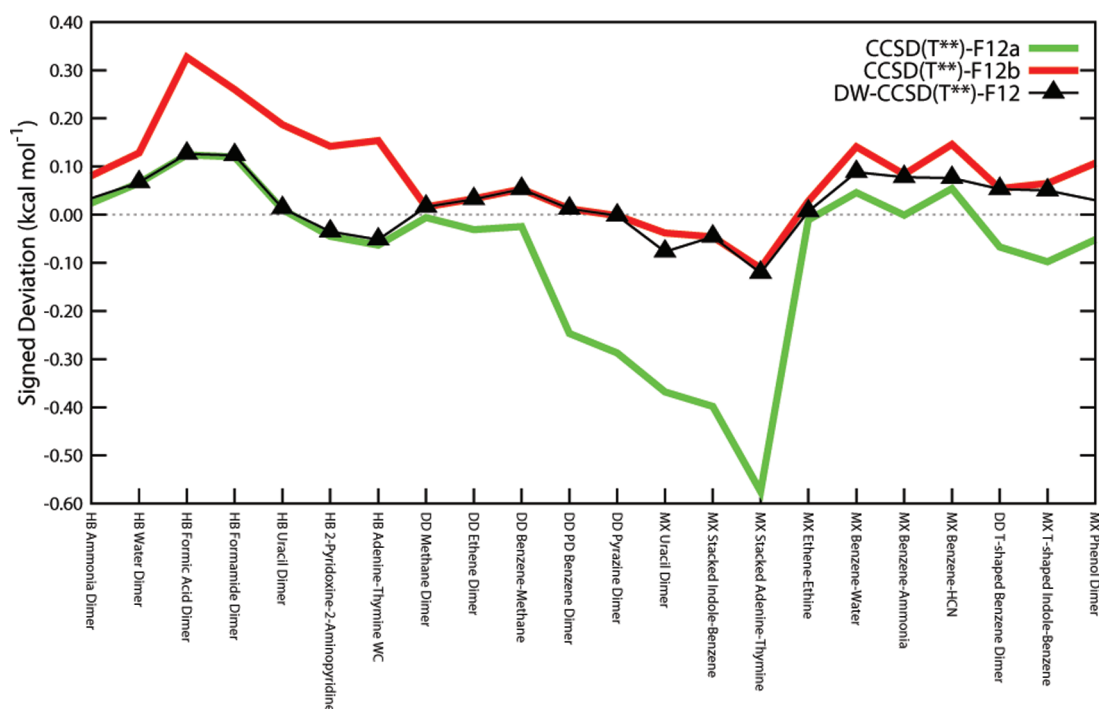


Figure 3. For the aug-cc-pVDZ basis set, interaction energy errors for CCSD(T**)F12a, CCSD(T**)F12b, and DW-CCSD(T**)F12 methods for each complex in the S22 test set. All errors in kcal mol⁻¹, relative to S22B CCSD(T)/CBS benchmarks (ref 18). Individual errors and statistics can be found in Table 1.

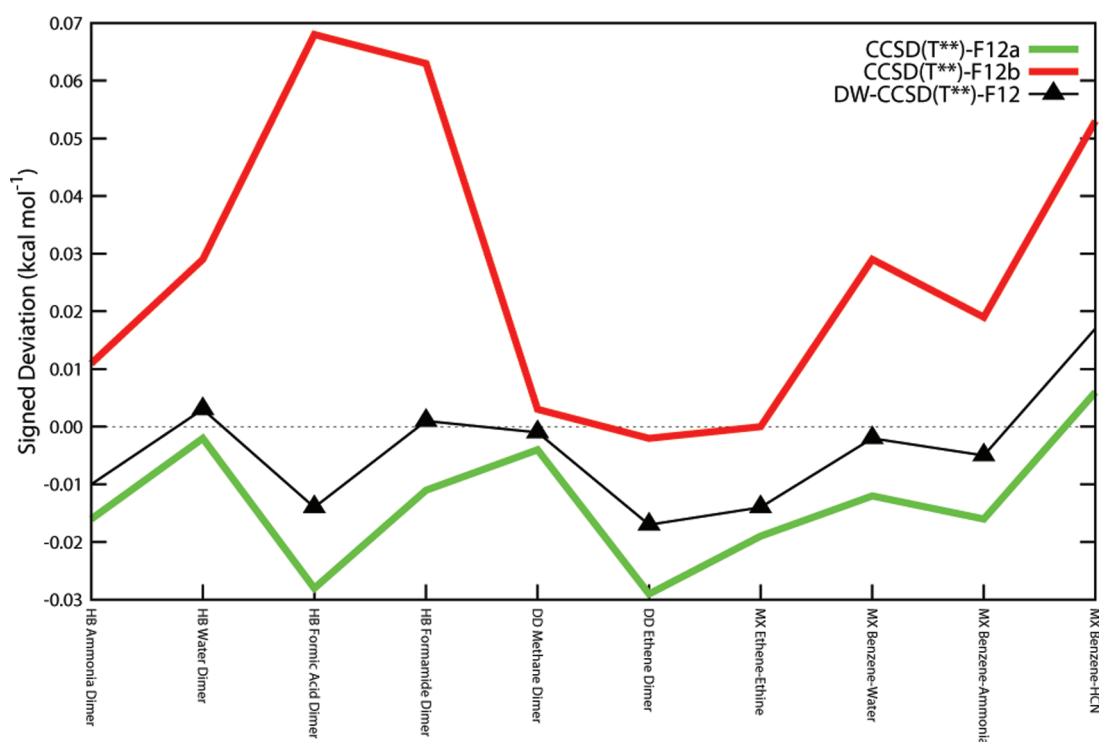


Figure 4. For the aug-cc-pVTZ basis set, interaction energy errors for CCSD(T**)F12a, CCSD(T**)F12b, and DW-CCSD(T**)F12 methods for each complex in the S22 test set. All errors in kcal mol⁻¹, relative to a subset of the S22B CCSD(T)/CBS benchmarks (ref 18).

$\beta = 0.6$, we find MADs of 0.028, 0.014, and 0.008 kcal mol⁻¹ and maximum errors of 0.029, 0.068, and 0.017 kcal mol⁻¹ for CCSD(T**)F12a, CCSD(T**)F12b, and DW-CCSD(T**)F12,

respectively. When using the aug-cc-pVDZ fit parameters of $\alpha = -1$ and $\beta = 4$, DW-CCSD(T**)F12 still achieves an overall MAD of 0.011 kcal mol⁻¹ and a maximum error of 0.027 kcal mol⁻¹

Table 2. Counterpoise Corrected Interaction Energies (kcal mol⁻¹) for the CCSD(T)-F12a, CCSD(T**)-F12b, and DW-CCSD(T**)-F12 Methods Compared to S22B Benchmark Values (ref 18)^a**

complex	reference IE	F12a	F12b	DW-F12
1 HB ammonia dimer, C _{2h}	-3.133	-3.15	-3.12	-3.14
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3 HB formic acid dimer, C _{2h}	-18.753	-18.78	-18.69	-18.77
4 HB formamide dimer, C _{2h}	-16.062	-16.07	-16.00	-16.06
8 DD methane dimer, D _{3d}	-0.527	-0.53	-0.52	-0.53
9 DD ethene dimer, D _{2d}	-1.472	-1.50	-1.47	-1.49
16 MX ethene-ethine, C _{2v}	-1.496	-1.52	-1.50	-1.51
17 MX benzene-water, C _s	-3.275	-3.29	-3.25	-3.28
18 MX benzene-ammonia, C _s	-2.312	-2.33	-2.29	-2.32
19 MX benzene-hydrogen cyanide, C _s	-4.541	-4.54	-4.49	-4.53
maximal deviation		0.029	0.068	0.017
MAD		0.014	0.028	0.008

^a Fit parameters are $\alpha = 0.4$ and $\beta = 0.6$. Computations use the aug-cc-pVTZ basis set. The errors and mixing in the DW approach can be seen graphically in Figure 4.

(formic acid dimer). DW-CCSD(T**)-F12 was also tested using the heavy-aug-cc-pVDZ basis set, which is aug-cc-pVDZ on the nonhydrogen atoms and cc-pVDZ on the hydrogens. DW-CCSD(T**)-F12/heavy-aug-cc-pVDZ achieves an MAD of 0.131 kcal mol⁻¹ for the S10 subset (compared to 0.065 kcal mol⁻¹ for this subset when using the aug-cc-pVDZ basis).

4. CONCLUSION

A new “dispersion-weighted” approach is proposed for explicitly correlated coupled-cluster studies of weakly bound systems that accurately describes both hydrogen-bonding and dispersion-bound complexes through a black-box admixture of CCSD(T**)-F12a and CCSD(T**)-F12b. This technique achieves MAD values of 0.05 and 0.04 kcal mol⁻¹ for the S22B and HSG-A test sets (using S22B-fit parameters), corresponding to a factor of 2 reduction of the MAD and a factor of 3 and 4 reduction in maximum error relative to F12a and F12b methods, respectively. Explicitly correlated CCSD-F12 computations are more expensive than canonical CCSD, but the extra cost is usually negligible with the inclusion of perturbative triples. This suggests that CCSD(T**)-F12, and perhaps the dispersion-weighted variant proposed here, should become a preferred approach for obtaining accurate benchmarks for noncovalent interactions.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sherrill@gatech.edu.

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