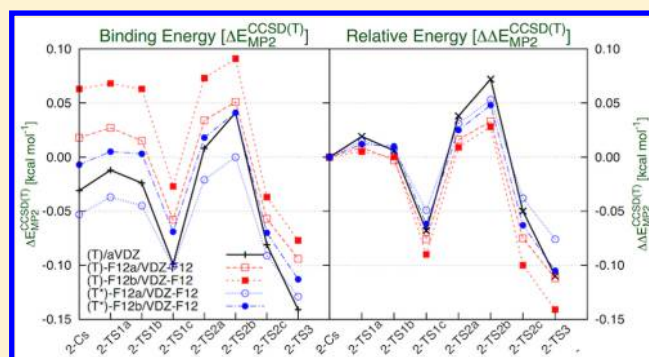


Importance and Reliability of Small Basis Set CCSD(T) Corrections to MP2 Binding and Relative Energies of Water Clusters

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Supporting Information

ABSTRACT: MP2 describes hydrogen-bonded systems well, yet a higher-order electron correlation correction in the form of a CCSD(T) calculation is usually necessary to achieve benchmark quality energies. We evaluated the importance and reliability of small basis set CCSD(T) corrections to MP2 ($\delta_{\text{MP2}}^{\text{CCSD(T)}}$) both on the binding (ΔE) and relative ($\Delta\Delta E$) energies for a large number of systems including four water dimer stationary points and 57 other clusters up to undecamers, $(\text{H}_2\text{O})_{11}$. By comparing the MP2 energies with CCSD(T) and the explicitly correlated MP2-F12 energies with variants of CCSD(T)-F12 using different basis sets, we were able to establish that the correction to the binding energy (ΔE) is sensitive to basis set size, especially for small double- ζ basis sets. On the other hand, the basis set sensitivity of the correction to the relative energy ($\Delta\Delta E$) within each cluster size is very small. While the $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ correction to the binding energy might vary in magnitude with basis set size, its effect on relative energy (and hence the stability of isomers) is remarkably consistent. Therefore, we recommend the inclusion of this correction to obtain the relative stability of closely spaced isomers using a double- ζ basis set with polarization and diffuse functions such as aug-cc-pVDZ.



1. INTRODUCTION

Hydrogen-bonding forces that bind water monomers into molecular clusters and dictate water's bulk properties have been the subject of many publications.^{1–6} Even though hydrogen-bonding interactions mainly result from electrostatics, induction and exchange repulsion, London dispersion forces also play a non-negligible role. According to localized molecular orbital energy decomposition analysis (LMO-EDA)⁷ of the binding energy of water clusters, the dispersion component amounts to as much as one-third of the total binding energy.⁸ Density functional theory (DFT) often fails to describe noncovalent interactions sufficiently,^{9,10} but the inclusion of empirical dispersion corrections (DFT-D)¹¹ generally improves its performance, even though some early implementations led to worse performance.¹² A quantitative description of water clusters using wave function methods requires the inclusion of electron correlation. Second-order Møller–Plesset theory (MP2)¹³ is the most affordable wave function method that includes electron correlation, and it has been shown to give reliable geometries and energies for hydrogen-bonded systems.^{14–19} Its cost scales as $O(N^5)$ with system size, and that is further reduced with approaches such as density-fitting (DF)^{20,21} and dual-basis (DB)²² without introducing large errors.²³ As a result, water clusters as large as $(\text{H}_2\text{O})_{20}$ ²⁴ and $(\text{H}_2\text{O})_{24}$ ²⁵ have been characterized using MP2. However, MP2 is known to significantly overbind systems dominated by

dispersion interactions such as the sandwich/stacked benzene dimer.^{26,27} Spin-component scaled MP2 (SCS-MP2)²⁸ in which the parallel- and antiparallel-spin components of the MP2 correlation energy are scaled separately, improves on MP2 for most systems and properties, but it actually leads to poorer results for hydrogen-bonded systems. Within hydrogen-bonded systems, MP2's performance varies based on the topology of the hydrogen bonds being described.²⁹ These deficiencies prompted the practice of adding a higher-order electron correlation correction to MP2 energies. Coupled-cluster theory with single, double, and perturbative triple excitations [CCSD(T)]³⁰ is a higher-level electron correlation method that provides benchmark quality binding energies for noncovalently bound systems. Much like MP2, it requires sufficiently large basis sets to give reliable energies. Unfortunately, its formal $O(N^7)$ scaling limits its use to small systems with large basis sets or moderate size systems with small basis sets. For most basis sets, the virtual (v) or unoccupied orbitals substantially outnumber occupied (o) ones, and the o^3v^4 scaling becomes difficult to overcome. As a result, a typical approach involves first extrapolating the MP2 energy to its complete basis set (CBS) limit and adding a CCSD(T) correction using a small basis set.

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$$E_{\text{CCSD(T)}}^{\text{CBS}} \approx E_{\text{MP2}}^{\text{CBS}} + \delta_{\text{MP2}}^{\text{CCSD(T)}} \quad (1)$$

where the correction is defined as

$$\delta_{\text{MP2}}^{\text{CCSD(T)}} = E_{\text{CCSD(T)}}^{\text{small_basis}} - E_{\text{MP2}}^{\text{small_basis}} \quad (2)$$

Combining CCSD(T) and MP2 is common for the study of water clusters. In our previous work,¹⁹ we calculated the binding energies of water clusters up to (H₂O)₁₀ using RI-MP2/CBS and incorporated CCSD(T) corrections using the aug-cc-pVDZ (aVDZ) basis set. We showed that this correction had a small but non-negligible effect on the binding energies of hydrogen-bonded systems and could significantly affect the relative stability of isomers. Bates and Tschumper²⁹ demonstrated the importance of CCSD(T) corrections to obtain accurate stabilities of water hexamers. The same correction has proven to be important in establishing the relative energies of (H₂O)₁₁³¹ and (H₂O)₁₆.³²

Significant computational work has been devoted to evaluating the CCSD(T) correction on various noncovalently bonded systems, including hydrogen-bonded systems, dispersion bound systems, and others exhibiting mixed interactions.^{33–38} The binding energies for both hydrogen-bonded and dispersion bound systems^{33–38} are extremely sensitive to the basis set used to include the CCSD(T) correction. It has been concluded that using double- ζ basis sets such as 6-31G*, 6-31G*(0.25), 6-31G**(0.25,0.15), cc-pVDZ, and aug-cc-pVDZ (aVDZ) yields inaccurate binding energies. That conclusion holds for both counterpoise (CP) corrected and uncorrected binding energies. In most cases, corrections calculated using double- ζ basis sets are not close to the extrapolated complete basis set (CBS) $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ values, and two-point extrapolations using a triple- ζ and larger basis sets would be needed to get the correction to converge to the right CBS limit. Marshall et al.³⁴ studied the effects of CCSD(T) correction on noncovalent interactions. Using a small basis set for the $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ correction to the binding energy of the S22 benchmark data set,³⁹ they showed that the CCSD(T) correction using double- ζ basis sets was unreliable and that larger basis sets resulted in corrections that are close to the extrapolated $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ CBS limit. Studies on other databases containing dimers yielded similar results when using double- ζ basis sets. For instance, using the double- ζ basis set (6-31G*) to correct formic acid dimer's binding energy is not recommended.³⁶ Platts et al.⁴⁰ examined the performance of composite post-MP2 *ab initio* methods for noncovalent interactions in the S66⁴¹ benchmark data set. For three complexes including water dimer, they found that explicitly correlated coupled cluster with scaled perturbative triples approximation [CCSD(T*)-F12a] with aVDZ basis set gives a root-mean-square error (RMSE) of 0.13 kcal mol^{−1} or 3% relative to the benchmark binding energies. Including a CCSD(T) correction with the small 6-31G*(0.25) basis set gave surprisingly good interaction energies (RMSE = 0.15 kcal/mol, or 4%). Employing spin component scaling (SCS) with CCSD(T*)-F12a yielded an even better performance (RMSE = 0.08 kcal mol^{−1}, or 2%) when the same- and opposite-spin scaling factors are optimized for the S66 data set.

Boese assessed the reliability of the correction to accurately define 16 different hydrogen-bonded systems.³⁸ The data reveals that the CCSD(T) correction does not improve the MP2 binding energies relative to benchmark numbers when double- ζ basis sets are used without diffuse functions. Including

diffuse functions to double- or triple- ζ basis sets improves the resulting binding energies, especially for dispersion bound systems.³⁸ Carrell et al.³⁷ found some basis set dependence in the higher-order correlation corrections for pi-type interactions on five dimers. For pi–pi systems such as the benzene dimer, using small basis sets yielded inaccurate binding energies.^{34,35,37} These studies showed that a triple- ζ basis set is needed to achieve benchmark binding energies and prompted the revision of the reference interaction energies reported for a group of databases of noncovalently bonded systems.³⁴

While many have studied the CCSD(T) correction to MP2 binding energies (ΔE) for weakly bound systems, none have focused on water clusters larger than the water dimer. Systematic work on the CCSD(T) correction to the MP2 binding (ΔE) and relative energies ($\Delta\Delta E$) for larger water clusters has not been reported in the literature. In this article, we assess the importance and reliability of small basis set higher-order electron correlation correction ($\delta_{\text{MP2}}^{\text{CCSD(T)}}$) to the binding (ΔE) and relative energies ($\Delta\Delta E$) of water clusters (H₂O)_{*n*=2–11}. We examine the correlation between this correction and the physical components of the binding energy in an attempt to explain the physical origins of $\delta_{\text{MP2}}^{\text{CCSD(T)}}$.

2. METHODS

Sixty-one water clusters ranging from water dimer (H₂O)₂ stationary points to water undecamers (H₂O)₁₁ were analyzed. These clusters included four water dimer stationary points, namely, the global minimum (2-C_s) and three first-order transition states (2-TS1, 2-TS2, 2-TS3), that were reported by Tschumper et al.³³ These previously reported structures were reoptimized using MP2/aug-cc-pVDZ to converge into their respective positions on the water dimer potential energy surfaces. The other structures for (H₂O)_{*n*=3–11} were RI-MP2/aug-cc-pVDZ optimized geometries reported in our previous papers.^{18,19,42,43} These were the RI-MP2/CBS low-energy structures based on the extrapolation of the RI-MP2/aug-cc-pVNZ (N = D, T, Q) basis sets^{44,45} with a 4–5 inverse polynomial extrapolation scheme.^{46,47} The binding energy (ΔE_i^n) of isomer *i* was defined as the energy difference between the cluster and *n* separated monomers:

$$\Delta E_i^n = E_i^n - n * E^1 \quad (3)$$

The relative energy ($\Delta\Delta E_i^n$) of cluster *i* was calculated using the global minimum of *N* clusters of the same size as a reference:

$$\Delta\Delta E_i^n = E_i^n - \min_{m=1\dots N} \{E_m^n\} \quad (4)$$

For hydrogen-bonded systems, the higher-order electron correlation correction ($\delta_{\text{MP2}}^{\text{CCSD(T)}}$) to the energy is small in magnitude, but it can affect the relative energies of isomers significantly.

$$\delta_{\text{MP2}}^{\text{CCSD(T)}} = E_{\text{CCSD(T)}}^{\text{aVDZ}} - E_{\text{MP2}}^{\text{aVDZ}} \quad (5)$$

Recent literature suggests that including this correction using a double- ζ basis set like aVDZ is not always reliable for noncovalently bound systems, especially hydrogen-bonded ones.^{34,37} One suggested alternative³⁴ is to perform this correction using explicitly correlated methods⁴⁸ because they improve the basis set convergence of energies by including explicit dependence of the correlation energy on interelectronic distances. Using MP2-F12 and CCSD(T)-F12 with a specially designed double- ζ basis, cc-pVDZ-F12 (VDZ-F12),⁴⁹ one can

calculate the F12 analog of the conventional electron correlation energy correction. There are many approximations to the CCSD-F12 energy, and two of them, namely, CCSD-F12a⁵⁰ and CCSD-F12b,⁵¹ are explored here. Since implementing an F12 analog of the triples correction is difficult, it is estimated by scaling the conventional (T) correction by the ratio of the MP2-F12 to MP2 correlation energies.

$$E_{(T)-F12} \approx E_{(T)} \cdot \frac{E_{MP2-F12}^{corr}}{E_{MP2}^{corr}} \quad (6)$$

To maintain the size consistency of the triples correction, Marchetti et al.⁵² recommend scaling the (T) correction uniformly with the dimer MP2-F12 to MP2 correlation energy ratio.⁵² Brauer et al.⁵³ scaled the (T) correction by the CCSD-F12 to CCSD correlation energy ratio but found no significant improvement. That approach will presumably work better in cases where MP2 itself may perform poorly because of substantial static correlation.⁵³ This method is designated with an asterisk next to the (T) as CCSD(T*)-F12, whereas the independently scaled approach is denoted CCSD(T)-F12.

$$\delta_{MP2-F12}^{CCSD(T)-F12} = E_{CCSD(T)-F12}^{VDZ-F12} - E_{MP2-F12}^{VDZ-F12} \quad (7)$$

$$\delta_{MP2-F12}^{CCSD(T^*)-F12} = E_{CCSD(T^*)-F12}^{VDZ-F12} - E_{MP2-F12}^{VDZ-F12} \quad (8)$$

Therefore, we report higher-order correlation corrections using conventional CCSD(T) with aVDZ basis as well as four variants of CCSD(T)-F12 theory with VDZ-F12 orbital basis. For each approach, we designate the correction to the binding energies as ΔE_X^Y and those to the relative energy as $\Delta\Delta E_X^Y$

$$\Delta E_X^Y = \Delta E_Y - \Delta E_X \quad (9)$$

$$\Delta\Delta E_X^Y = \Delta\Delta E_Y - \Delta\Delta E_X \quad (10)$$

where $X = MP2$ and $Y = CCSD(T)$ for conventional methods, and $X = MP2-F12$ and $Y = CCSD(T)-F12a$, $CCSD(T)-F12b$, $CCSD(T^*)-F12a$, or $CCSD(T^*)-F12b$ for explicitly correlated methods. For example, $\Delta E_{MP2}^{CCSD(T)}$ is the difference between the binding energy calculated using CCSD(T)/aVNZ and MP2/aVNZ, where $N = D, T$, or Q , at the RI-MP2/aVDZ geometry. Likewise, $\Delta\Delta E_{MP2}^{CCSD(T)}$ is the difference between the relative energy of a cluster computed using CCSD(T)/aVNZ and MP2/aVNZ, where $N = D, T$, or Q , at the RI-MP2/aVDZ geometry. All explicitly correlated calculations were performed using MOLPRO 2010⁵⁴ package, whereas conventional MP2 and CCSD(T) calculations utilized ORCA 3.0.2.⁵⁵ All the binding energies in this paper are not counterpoise corrected.

To understand what, exactly, $\delta_{MP2}^{CCSD(T)}$ is correcting, we attempted to find correlations between this correction and different components of the binding energy for each cluster. These electrostatic, exchange, polarization/induction, and dispersion components of the binding energy were calculated with symmetry-adapted perturbation theory (SAPT)⁵⁶ implemented in PSI4⁵⁷ for water dimer and localized molecular orbital energy decomposition analysis (LMO-EDA)⁷ of the MP2 binding energy using GAMESS-US⁵⁸ for larger clusters. For each cluster i , the relative interaction energy component ($\Delta\Delta E_{component}$) and the CCSD(T) correction ($\Delta\Delta E_{MP2}^{CCSD(T)}$) were calculated as follows.

$$\Delta\Delta E_{component,i} = [E_{component,i} - \min_{m=1\dots N} \{E_{component,m}\}] \quad (11)$$

$$\Delta\Delta E_{MP2,i}^{CCSD(T)} = [E_i^{CCSD(T)} - \min_{m=1\dots N} \{E_m^{CCSD(T)}\}] - [E_i^{MP2} - \min_{m=1\dots N} \{E_m^{MP2}\}] \quad (12)$$

Because SAPT is generally limited to dimers, we apply it to eight water dimer stationary points from Tschumper et al.'s work³³ that are reoptimized using MP2/aVDZ. This set of dimers consists of the C_s global minimum, and seven transition states: three first-order, three second-order, and one third-order. Their optimized coordinates are reported in Table S6. An efficient version of SAPT with up to third-order in intramolecular and intermolecular expansion is implemented in PSI4.⁵⁷ The definition of levels of SAPT and their performance for a large number of noncovalently bound systems is described in detail by Parker et al.⁵⁹ We chose the SAPT2+3 method, which has three, three, eight, and nine terms contributing to electrostatics, exchange, induction, and dispersion, respectively.

3. RESULTS

Hydrogen bonding results from attractive electrostatic, induction, and dispersion interactions largely counterbalanced by exchange-repulsion interactions. Because the dispersion component is not predominant, MP2 has been able to model hydrogen-bonded systems well. The CCSD(T) higher-order electron correlation correction to the MP2 binding energy is usually small in magnitude, but it can affect the relative energies of isomers significantly. The correction rarely exceeds 1% of the binding energy for any of the clusters investigated here. The basis set dependence of the $\Delta E_{MP2}^{CCSD(T)}$ of 23 water clusters including three transition states of water dimer (shown in Figure 1) are reported in Table 1, and the correction to the

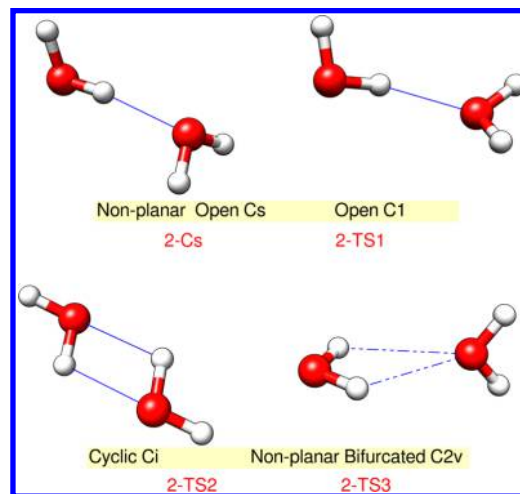


Figure 1. Three water dimer stationary points considered in this study. The original labels given to these clusters in ref 33 are highlighted in yellow, and the nomenclature used in the current study is shown in red.

relative energies ($\Delta\Delta E_{MP2}^{CCSD(T)}$) is shown in Table 2. As plotted in Figure 2, the conventional correction using aVDZ and aVTZ are very close for both the binding (top) and relative (bottom) energies, but the aVQZ binding energies already show substantial deviations from the aVDZ and aVTZ values. This is the first sign that the higher-order electron correlation corrections to binding and relative energies behave differently with increasing basis set size. Looking at the explicitly

Table 1. CCSD(T) Corrections to the MP2 Binding Energy (ΔE) for Water Clusters Using aVDZ, aVTZ, and aVQZ Basis Sets and Explicitly Correlated CCSD(T)-F12 Variants with VDZ-F12 Orbital Basis^a

	$\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$			$\Delta E_{\text{MP2-F12}}^{\text{CCSD(T/*)-F12[a/b]}}$				double-zeta statistics ^b	
	aVDZ	aVTZ	aVQZ	(T)-F12a	(T)-F12b	(T*)-F12a	(T*)-F12b	avg	SD
2-Cs	−0.03	−0.04	0.00	0.02	0.06	−0.05	−0.01	0.00	0.04
2-TS1	−0.01	−0.01	0.02	0.03	0.07	−0.04	0.00	0.01	0.04
2-TS2	−0.02	−0.05	−0.03	0.02	0.06	−0.04	0.00	0.00	0.04
2-TS3	−0.10	−0.11	−0.10	−0.06	−0.03	−0.10	−0.07	−0.07	0.03
3-UUD	0.04	0.02	0.09	0.19	0.34	−0.03	0.11	0.13	0.15
3-UUU	0.08	0.07	0.14	0.22	0.36	0.00	0.14	0.16	0.14
4-S4	0.21	0.16		0.42	0.66	0.03	0.27	0.32	0.23
4-Ci	0.22	0.18		0.42	0.66	0.04	0.28	0.32	0.23
5-CYC	0.37	0.30		0.60	0.90	0.10	0.41	0.48	0.30
5-CA-A	−0.08	−0.14		0.23	0.55	−0.30	0.02	0.09	0.32
5-CA-B	−0.17	−0.22		0.15	0.46	−0.38	−0.07	0.00	0.32
5-CA-C	−0.10	−0.17		0.20	0.51	−0.34	−0.02	0.05	0.32
5-FR-A	−0.02	−0.05		0.29	0.60	−0.22	0.08	0.15	0.31
5-FR-B	0.08	0.02		0.36	0.67	−0.15	0.16	0.22	0.31
5-FR-C	−0.02	−0.06		0.28	0.58	−0.23	0.07	0.14	0.31
6-PR	−0.13	−0.18		0.29	0.72	−0.42	0.00	0.09	0.43
6-CA	0.05	0.01		0.45	0.87	−0.26	0.16	0.25	0.43
6-BK-1	0.26	0.21		0.61	1.01	−0.05	0.35	0.44	0.40
6-CC	0.49	0.40		0.75	1.12	0.16	0.54	0.61	0.35
6-BAG	0.26	0.21		0.60	1.00	−0.07	0.33	0.42	0.40
6-BK-2	0.26	0.22		0.62	1.02	−0.05	0.35	0.44	0.40
6-CB-1	0.49	0.41		0.74	1.11	0.16	0.52	0.60	0.35
6-CB-2	0.48	0.39		0.73	1.09	0.15	0.51	0.59	0.35

^aAll units are in kcal mol^{−1}. The data for the larger clusters is available in Table S4. ^bThe average and standard deviation (SD) of $\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ with aVDZ basis set and four $\Delta E_{\text{MP2-F12}}^{\text{CCSD(T/*)-F12[a/b]}}$ with VDZ-F12 orbital basis.

Table 2. CCSD(T) Corrections to the Relative Energy ($\Delta\Delta E$) for Water Clusters using aVDZ, aVTZ, and aVQZ Basis Sets and Explicitly Correlated CCSD(T)-F12 Variants with VDZ-F12 Orbital Basis^a

	$\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$			$\Delta\Delta E_{\text{MP2-F12}}^{\text{CCSD(T/*)-F12[a/b]}}$				double-zeta statistics ^b	
	aVDZ	aVTZ	aVQZ	(T)-F12a	(T)-F12b	(T*)-F12a	(T*)-F12b	avg	SD
2-Cs	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-TS1	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.00
2-TS2	0.01	−0.02	−0.03	0.00	0.00	0.01	0.01	0.00	0.01
2-TS3	−0.07	−0.08	−0.09	−0.08	−0.09	−0.05	−0.06	−0.07	0.01
3-UUD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-UUU	0.04	0.05	0.04	0.03	0.02	0.04	0.03	0.04	0.02
4-S4	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00
4-Ci	0.01	0.02		0.00	0.00	0.01	0.00	0.00	0.00
5-CYC	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00
5-CA-A	−0.45	−0.44		−0.36	−0.35	−0.40	−0.39	−0.39	0.04
5-CA-B	−0.54	−0.52		−0.45	−0.45	−0.49	−0.48	−0.48	0.04
5-CA-C	−0.47	−0.47		−0.40	−0.39	−0.44	−0.43	−0.43	0.03
5-FR-A	−0.39	−0.36		−0.30	−0.30	−0.33	−0.33	−0.33	0.04
5-FR-B	−0.29	−0.28		−0.24	−0.24	−0.25	−0.25	−0.25	0.02
5-FR-C	−0.39	−0.36		−0.32	−0.32	−0.33	−0.34	−0.34	0.03
6-PR	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00
6-CA	0.18	0.19		0.15	0.15	0.16	0.16	0.16	0.01
6-BK-1	0.39	0.40		0.31	0.29	0.37	0.35	0.34	0.04
6-CC	0.61	0.58		0.45	0.40	0.59	0.53	0.52	0.09
6-BAG	0.39	0.39		0.30	0.28	0.35	0.33	0.33	0.04
6-BK-2	0.39	0.40		0.32	0.30	0.37	0.35	0.35	0.04
6-CB-1	0.61	0.59		0.45	0.39	0.58	0.52	0.51	0.09
6-CB-2	0.60	0.57		0.43	0.37	0.57	0.51	0.50	0.10

^aAll units are in kcal mol^{−1}. The data for the larger clusters is available in Table S5. ^bThe average and standard deviation (SD) of $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ with aVDZ basis set and four $\Delta\Delta E_{\text{MP2-F12}}^{\text{CCSD(T/*)-F12[a/b]}}$ with VDZ-F12 orbital basis.

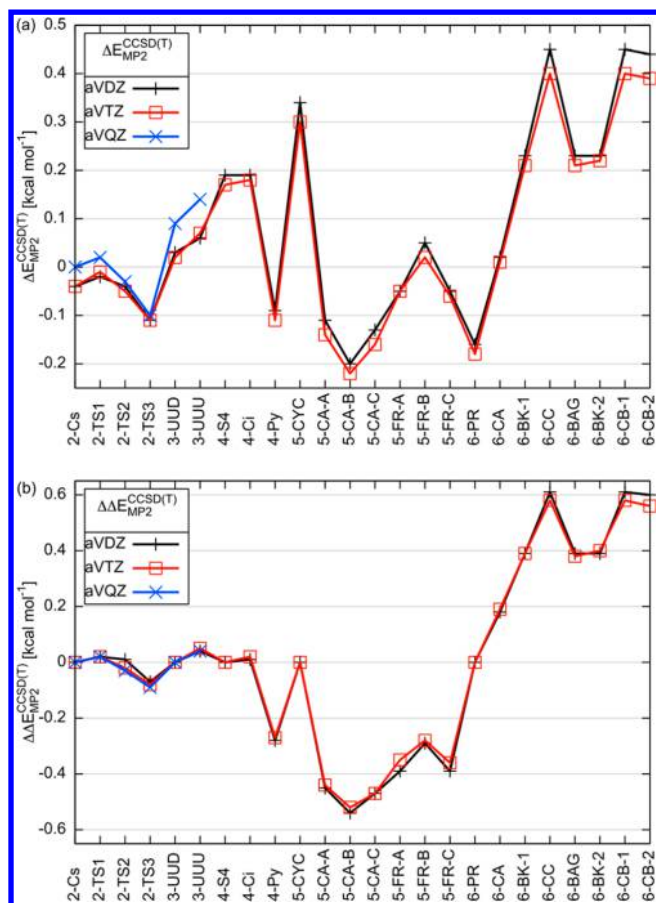


Figure 2. CCSD(T) correction to the MP2 binding energy (a) and relative energy (b) using aVDZ, aVTZ, and aVQZ basis sets at the RI-MP2/aVDZ optimized geometry.

correlated methods, the columns on the right side of Table 1 clearly differ from corrections from conventional methods shown on the left side for binding energies. For relative energies, however, the corrections from conventional and explicitly correlated methods are much closer, as reported in Table 2. Figure 3 further illustrates the disparity between binding energy (ΔE) corrections using conventional methods and explicitly correlated variants for $(\text{H}_2\text{O})_{n=2-10}$ at the top and $(\text{H}_2\text{O})_{11}$ at the bottom. A similar comparison for relative energies in Figure 4 indicates that the difference between corrections performed using conventional and explicitly correlated methods is small. It is not clear which variant of CCSD(T)-F12 is the most accurate, although Marshall and Sherrill^{34,60} have reported that the CCSD(T*)-F12a yields excellent results for the binding energy of hydrogen-bonded dimers. The basis set dependence that we see for the corrections to the binding energy increase rather uniformly with cluster size, suggesting that the error accumulates with increasing system size. The corrections to the relative energies are less predictable and smaller in magnitude. The average (avg) and standard deviation (SD) of $\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ and $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ calculated using double- ζ basis for each cluster is a good measure of the sensitivity of the two quantities. As reported in the last two columns of Table 1 ($\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$) and Table 2 ($\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$), the SD for $\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ is as large or larger than the avg, whereas the SD for $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ is much smaller than the avg. These findings are also obvious from the

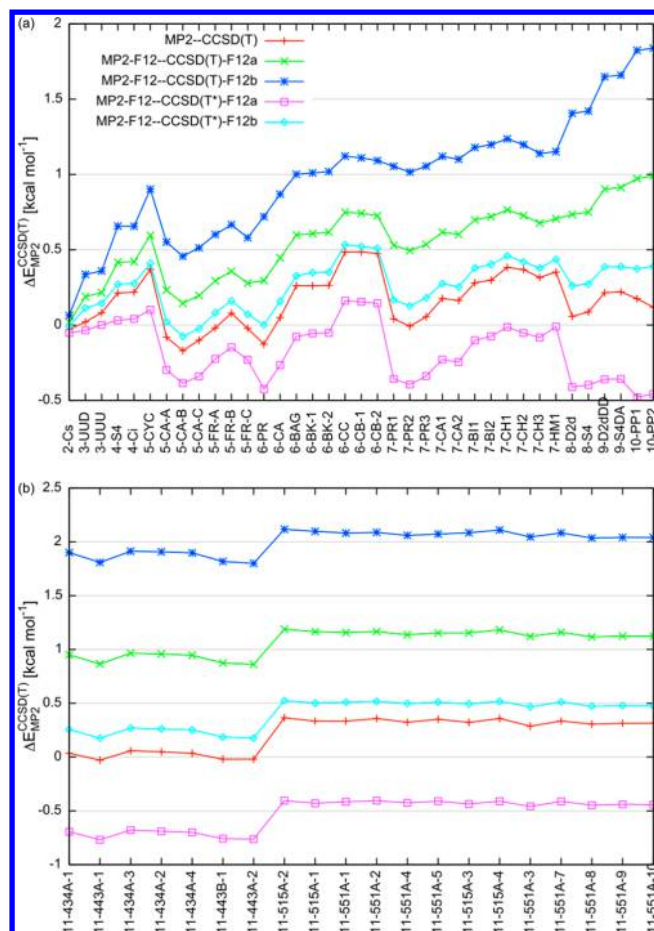


Figure 3. CCSD(T) corrections to MP2 binding energies (ΔE) using conventional [CCSD(T)/aVDZ] and explicitly correlated [CCSD(T)-F12/VDZ-F12] methods. The four variants of CCSD(T)-F12 depend on the F12a and F12b ansatz used for CCSD(T)-F12 calculation and the individual scaling factor (T) or uniformly scaling (T*) of the triples corrections with the water dimer factor.

large divergence of $\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ in Figure 3 and the tight convergence of $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ in Figure 4.

We explained the effect of higher-order electron correlation on the relative energy ($\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$) of isomers by examining its correlation with different binding energy components. For a set of eight water dimer stationary points from Tschumper et al.'s work,³³ the relative SAPT2+3 binding energy components ($\Delta\Delta E_{\text{component}}^{\text{component}}$) are plotted against the CCSD(T) correction ($\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$) for aVDZ, aVTZ, and aVQZ basis sets in Figure 5. None of the four components show significant correlation with $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ even though dispersion fares better than the others. We investigated similar correlations between $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ and energy components for larger clusters using LMO-EDA decomposition of the MP2/aVDZ binding energy. The correlation between $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ and relative LMO-EDA/MP2/aVDZ binding energy components of isomers of the water pentamer, hexamer, and heptamer is shown in Figure 6. The dispersion component exhibits reasonable correlation with $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ for all three cluster sizes, whereas the other components do not show consistent correlation. The dispersion component typically accounts for one-fifth to one-third of the total interaction energy for water clusters based on SAPT as well as other decomposition schemes such as LMO-EDA. Clusters with a greater dispersion component are typically

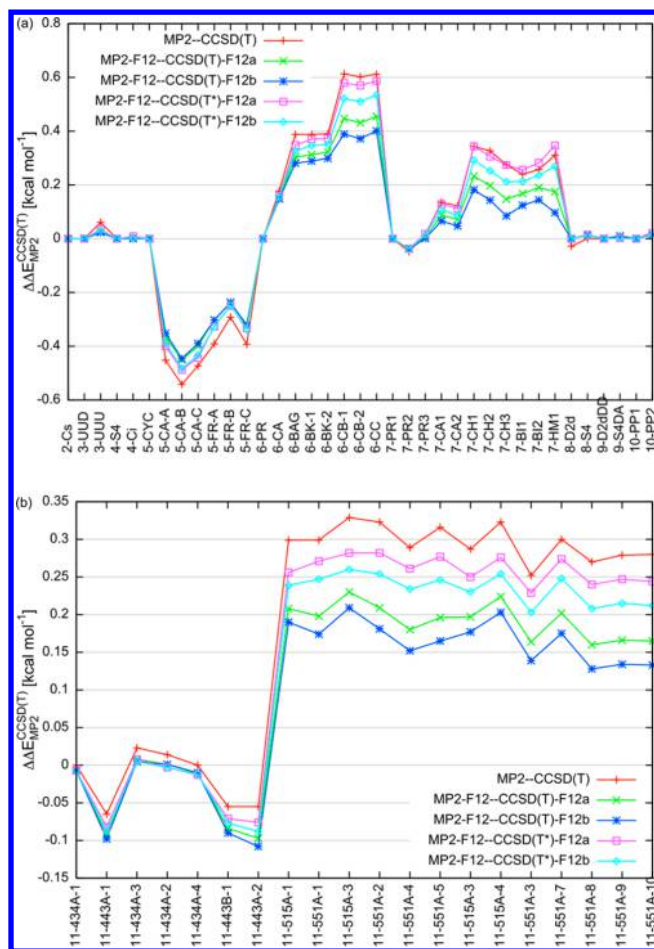


Figure 4. CCSD(T) corrections to MP2 relative energies ($\Delta\Delta E$) using conventional [CCSD(T)/aVDZ] and explicitly correlated [CCSD(T)-F12/VDZ-F12] methods. The four variants of CCSD(T)-F12 depend on the F12a and F12b ansatz used for CCSD-F12 calculation and the individual scaling factor (T) or uniformly scaling (T*) of the triples corrections with the water dimer factor.

stabilized by higher-order electron correlation corrections, whereas those with a lower dispersion contribution are destabilized by this correction in relative terms. In other words, there is a consistently positive correlation between $\Delta\Delta E_{\text{Disp}}$ and $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$. The CCSD(T) correction to MP2 relative energies most likely corrects for dispersion interactions that MP2 is not capturing fully, although its correction to other components cannot be ruled out.

4. DISCUSSION

The basis set dependence of the higher-order electron correlation on the binding ($\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$) and relative ($\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$) energies of water clusters and physical explanations for the observed patterns are discussed in detail below.

4.1. Correction to Binding Energies ($\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$). When one performs an additive CCSD(T) correction to MP2 energies using a small basis set, the implicit assumption is that the MP2 and CCSD(T) correlation energies converge to their respective CBS limits in a similar fashion. However, basis set incompleteness error (BSIE) and basis set superposition error (BSSE) affect MP2 and CCSD(T) differently. Marshall et al.³⁴ reported that the CCSD(T) correction to interaction energies of the S22 database can have different magnitudes and

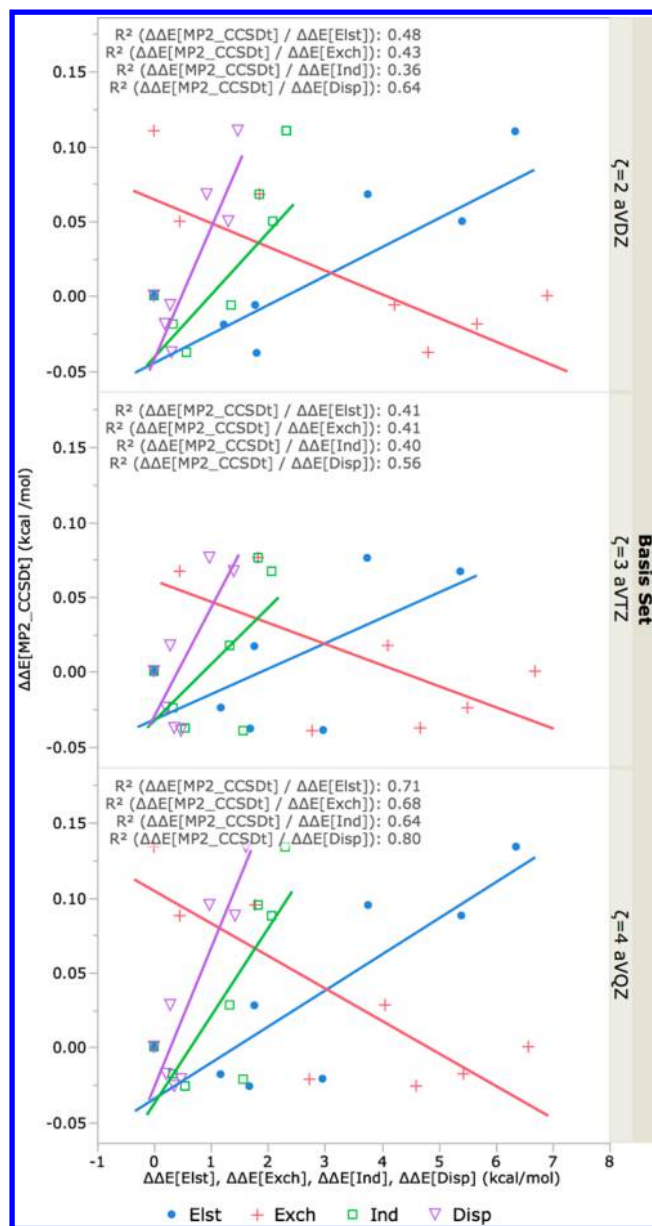


Figure 5. Correlation between relative SAPT2+3/aVDZ (top), SAPT2+3/aVTZ (middle), and SAPT2+3/aVQZ (bottom) binding energy components and $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ for eight water dimer stationary points. The correlations are generally poor, although dispersion correlates better than the other components. See Table S8 for coordinates of these eight water dimer stationary points.

signs depending on basis set as well as counterpoise correction. Taking corrections at two consecutive basis sets and extrapolating to the CBS limit can introduce errors if the basis sets are not large enough. This is especially true for the most relevant system in the S22 database, the water dimer. Because basis set errors make these corrections unreliable, explicitly correlated methods should be able to remove these errors and yield more consistent corrections. Explicitly correlated calculations using basis sets of cardinal number N usually perform equivalently to conventional calculations with basis set of cardinal number $N + 1$ or $N + 2$.⁶¹ Unfortunately, as indicated in Figure 3, it is unclear if the $\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ calculated using the explicitly correlated corrections is converged because it differs significantly from the conventional correction and

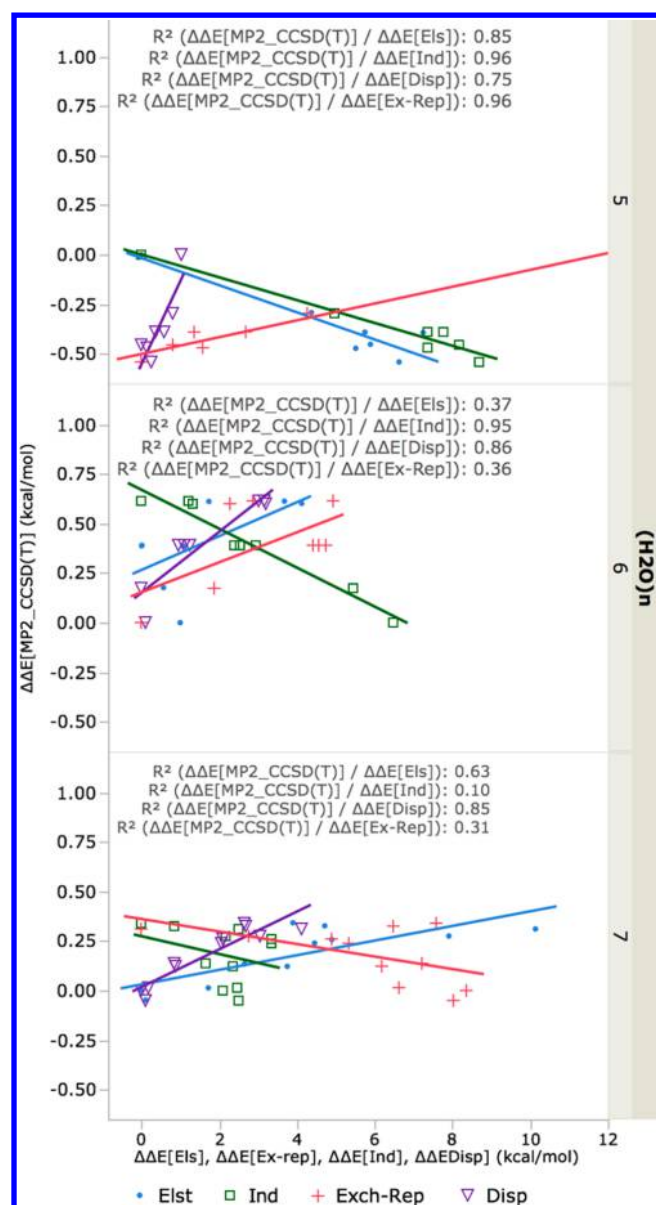


Figure 6. Correlation between $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ and relative LMO-EDA/MP2/aVDZ binding energy components of isomers of the water pentamer (top), hexamer (middle), and heptamer (bottom). The dispersion component shows reasonable correlation across all three clusters, whereas the other components are erratic.

among the different variants of CCSD(T)-F12. Looking at Figure 3, the magnitude of the conventional $\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ for the water clusters studied here is less than $0.5 \text{ kcal mol}^{-1}$, which is usually less than 1% of the total binding energy. Explicitly correlated methods predict corrections spanning a much larger range from $-0.7 \text{ kcal mol}^{-1}$ for CCSD(T*)-F12a of undecamers to about 2 kcal mol^{-1} for CCSD(T)-F12b correction for the same undecamers. For the water dimer, Marshall et al.³⁴ reported the CBS limit $\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ to be $-0.039 \text{ kcal mol}^{-1}$, which is closest to the corrections computed using conventional methods with aVDZ (-0.03) and aVTZ (-0.04) basis sets and explicitly correlated methods with CCSD(T*)-F12a/VDZ-F12 (-0.05) in Table 1. It would be unwise to make sweeping conclusions about the best approach for correcting binding energies based on the water dimer results alone. The clear takeaway message is that caution

should be used when correcting binding energies for higher-order electron correlation effects. Of the double-zeta basis sets, aVDZ performs the best for systems bound by dispersion and mixed interactions while 6-31G*(0.25) and 6-31G*(0.25,0.15) basis sets work best for hydrogen-bonded systems.³⁴

4.2. Correction to Relative Energies ($\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$). The correction to relative energies is much less sensitive to basis sets than the binding energy. This is evident in the small deviation between the different corrections plotted in Figure 2 (bottom) for the conventional ($\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$) and in Figure 4 for the explicitly correlated ($\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)-F12}}$) methods. The different basis set dependence of corrections to binding energies and relative energies can largely be attributed to the fact that binding energies factor in the energy of the constituent monomers, whereas relative energies do not. Basis set superposition error (BSSE) affects binding energies significantly, but intramolecular BSSE in one cluster largely cancels BSSE in another cluster, thereby having a minimal impact on relative energies. This property enables us to calculate the effect of higher-order electron correlation correction using a small basis set. Because the number of hydrogen-bonding configurations increases exponentially with the number of waters in a cluster,⁶² it is very important to sample many configurations and determine their relative energies accurately. As displayed in Figure 2a, the magnitude of the higher-order electron correlation correction to the binding energy does not exceed $0.6 \text{ kcal mol}^{-1}$ for any of these clusters. However, it can dictate the relative stability of isomers when there are many nearly degenerate isomers. A classic example of this is the water hexamer, where the Prism (PR), Cage (CA), and Book-1 (BK-1) isomers have relative energies of 0.00, 0.04, and $0.25 \text{ kcal mol}^{-1}$ at the RI-MP2/CBS level, respectively. Adding the harmonic zero-point vibrational energy (ZPVE) changes the relative energies of the Prism, Cage, and Book-1 to 0.35, 0.20, and $0.00 \text{ kcal mol}^{-1}$, respectively, at 0 K.¹⁹ Therefore, RI-MP2/CBS predicts that the Book-1 isomer should be the global minimum around 0 K, but we know from broadband rotational spectroscopy experiments that the Prism, Cage, and Book-1 isomers are present in population ratios of 4:4:1 at low temperatures.⁵ Adding a CCSD(T) correction using the aVDZ basis set changes the relative electronic energy of the Prism, Cage, and Book-1 to 0.00, 0.22, and $0.64 \text{ kcal mol}^{-1}$ and the ZPVE-corrected energy to 0.00, 0.02, and $0.04 \text{ kcal mol}^{-1}$, which is much more consistent with experimental observations.^{5,19} Other studies of the water hexamer using CCSD(T) report similar results.^{29,63,64} Another example of the importance of higher-order electron correlation is $(\text{H}_2\text{O})_{11}$, the water undecamer. As shown in Figure 7, the lowest energy members of its four most stable isomer classes are 11-515A-1, 11-43'4A-1, 11-55'1A-1, and 11-44'3'A-1, and their RI-MP2/CBS relative energies are 0.00, 0.03, 0.04, and $0.28 \text{ kcal mol}^{-1}$, respectively. Adding a CCSD(T) correction using the aVDZ basis set changes the relative energy of the four isomers to 0.22, 0.00, 0.27, and $0.17 \text{ kcal mol}^{-1}$, respectively. Therefore, including a CCSD(T) correction changes the predicted global minimum from 11-515A-1 to 11-43'4A-1. Likewise, Yoo et al. found the MP2/aVTZ global minimum of $(\text{H}_2\text{O})_{16}$ is a fused pentagonal prism called “boat-a”, whereas a CCSD(T) correction using aVTZ basis predicts a stacked-tetramer structure denoted 4444-a.³²

One notable conclusion about $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ is that it is largely dependent on the hydrogen-bonding topology of clusters. For example, Figure 4 shows that the correction for planar

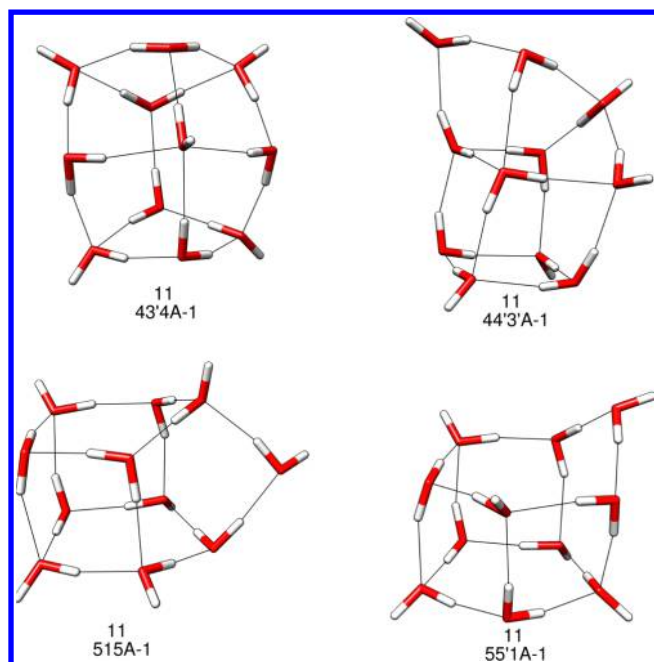


Figure 7. Lowest energy members of the water undecamer based on CCSD(T)/CBS calculations.

hexamers (6-CC, 6-CB-1, 6-CB-2) is distinctly different from that for quasi-planar (6-BK-1, 6-BK-2, 6-BAG) and three-dimensional (6-CA, 6-PR) hexamers. Similarly, the correction for prism hexamers (7-PR1, 7-PR2, 7-PR3) is markedly different from that for the other quasi-planar isomers. Examining $(\text{H}_2\text{O})_{11}$, the clusters made of stacks of tetramers and trimers such as 11-43'4A-1 and 11-44'3'A-1 have $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ values close to zero, whereas clusters based on stacked pentamers like 11-515A-1 and 11-55'1A-1 have corrections in the range of +0.15–0.30 kcal mol^{−1}. The dependence of the higher-order electron correlation correction to the binding energy on the hydrogen-bonding topology of clusters clearly suggests that MP2 and CCSD(T) capture components of the interaction energy differently. The most likely component is dispersion, and it is discussed in the next subsection.

4.3. Correlation between the Binding Energy Components and $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$. The physical significance of higher-order electron correlation on the relative energy ($\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$) of isomers can be studied by examining its correlation with physical components of the binding energy. We have used SAPT to get components (see Table S6) of the binding energy of eight water dimer (see Table S8 for coordinates) structures and LMO-EDA components (see Table S7) for all larger clusters up to water decamer, $(\text{H}_2\text{O})_{n=3-10}$. These binding energy components are named electrostatics, exchange (or exchange-repulsion), induction (or polarization), and dispersion. SAPT gives the more robust energy components since it computes them directly as a perturbation of isolated monomer wave functions. However, its application to anything larger than dimers has been reported only by Milet et al.,⁶⁵ who computed the pair- and three-body interaction energy components of cyclic trimers, tetramers, and pentamers. Therefore, we use it to study the water dimer structures exhaustively and also assess LMO-EDA binding energy components for the same systems. Much of that investigation is documented in Section 1 of the Supporting Information.

The main conclusion is that clusters whose binding energy has a larger dispersion component are typically stabilized by higher-order electron correlation corrections, whereas those with a lower dispersion contribution are destabilized by this correction in relative terms. Even though the correlations are weak, Figure 5 shows that the dispersion component is positively correlated with $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ for eight dimers studied using SAPT2+3/aVNZ, where N = D, T, Q. Likewise, Figure 6 demonstrates a similar correlation for water pentamers, hexamers, and heptamers whose energies were decomposed using LMO-EDA/MP2/aVDZ. Counterpoise (CP) corrected LMO-EDA/MP2/aVDZ analogs of these correlations are reported in Figure S4, and they lead to similar conclusions. In general, the more compact structures have a greater dispersion contribution, and they are stabilized by a CCSD(T) correction relative to more planar structures. For the water dimer, the contribution of dispersion has been shown through SAPT calculations to be strongly dependent on orientation.⁶⁶ The improved correlation between the dispersion component and $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ for systems studied with LMO-EDA compared to that with SAPT can be attributed to the definition of dispersion in each case. In LMO-EDA, the electrostatic, exchange, and repulsion terms are derived at the Hartree–Fock (HF) level, whereas the polarization or induction term arises from HF orbital relaxation upon going from isolated monomers to supermolecules. All post-HF contributions to the binding energy are attributed to dispersion.⁶⁷ In contrast, SAPT's dispersion component is calculated directly from many contributing terms based on the monomer (intramolecular) wave function and perturbation (intermolecular) order. The definition of levels of SAPT and their performance for a large number of noncovalently bound systems is described in detail by Parker et al.⁵⁹ As shown in Table S1 (Supporting Information), some of these are cross-terms that are somewhat arbitrarily assigned to one of the four physically motivated interaction energy components. Therefore, comparing interaction energy components from SAPT and LMO-EDA is difficult.

The good correlation between the importance of dispersion and the size of the CCSD(T) correction suggests that CCSD(T) is partly correcting for MP2's incomplete account of dispersion interactions. Decompositions of the interaction energy at higher orders of the SAPT perturbation theory show that the electrostatic, induction, and exchange components are mostly converged at the MP3 level.^{59,68} All corrections in the perturbation order past that using MP4 or CCD or other higher-order correlation methods are attributed to dispersion. Our SAPT2+3/aVDZ calculations on the water dimer potential energy surface along the hydrogen-bond distance and angle (see Figure S6) suggest that a combination of higher-order dispersion terms combine to give the $\Delta\Delta E_{\text{MP2}}^{\text{CCSD(T)}}$ surface. These results are included in the Supporting Information.

Presumably, approaches like dispersion-corrected MP2 (MP2+ ΔvdW)⁶⁹ can improve on MP2's performance and remove the need for expensive CCSD(T) corrections. However, Tkatchenko's results for water dimer and ammonia dimer show that while MP2+ ΔvdW is better for dispersion bound systems it actually performs worse than MP2 for hydrogen-bonded systems.⁶⁹ Cybulski and Lytle attributed MP2's success in describing hydrogen-bonded nucleic acid bases and failure in modeling stacked configurations of the same complex to the uncoupled Hartree–Fock dispersion energy component and suggested a modification to reproduce

CCSD(T) interaction energies.⁷⁰ Hesselmann⁷¹ suggested improving interaction energies computed using MP2 by replacing the uncoupled second-order dispersion contribution in the interaction energy with coupled dispersion energy from time-dependent density functional theory (TD-DFT). Apparently, MP2 is so delicately balanced that all of these empirical methods to correct it do not yield a universal improvement for all systems and properties.

Despite concerns about the basis set dependence of the CCSD(T) correction to MP2 binding energies, QM:QM methods combining MP2 and CCSD(T)⁷² have been quite successful for water clusters. In this approach, the two- and three-body interactions are calculated using CCSD(T), and the larger many-body interactions are computed using MP2. The binding energies from this approach reproduce CCSD(T) interaction energies within 0.07 kcal mol⁻¹ for (H₂O)_n, *n* = 3–10.^{6,73} Szalewicz and co-workers⁶⁴ “stratified approximation” many-body approach (SAMBA) has similarly been successful in combining high-level methods for two- and three-body interaction energies with lower level methods for larger *N*-body interactions to yield CCSD(T)/CBS quality interaction energies for (H₂O)_n, *n* = 6, 16, 24.

Ultimately, even CCSD(T) relies on some error cancellation to reach chemical (1 kcal mol⁻¹) or subchemical accuracy. To achieve more accurate binding energies rigorously, post-CCSD(T) corrections are necessary. As recently demonstrated by Smith et al.,⁷⁴ the same basis set dependence problems reported for CCSD(T) corrections to MP2 binding energies persist for CCSDT corrections to CCSD(T) and CCSDT(Q) corrections to CCSDT. In each case, the convergence of these corrections to their respective CBS limits was slow. Also, smaller basis sets like 6-31G*(0.25) and 6-31G**(0.25,0.15) that performed sufficiently in some cases^{75,76} proved to be unsuitable for these post-CCSD(T) corrections. Using larger aug-cc-pVDZ and aug-cc-pVTZ basis sets yields marked improvement, but the cost is prohibitive due to the steep scaling of these methods.

5. CONCLUSIONS

We evaluated the validity of including a small basis set higher-order electron correlation correction ($\delta_{\text{MP2}}^{\text{CCSD(T)}}$) to the binding (ΔE) and relative ($\Delta\Delta E$) energies of water clusters by comparing CCSD(T) and variants of CCSD(T)-F12 with MP2 and MP2-F12, respectively. The results indicate that the correction to the binding (ΔE) and relative ($\Delta\Delta E$) energies for (H₂O)_{n=2–11} have different sensitivities. While this correction to the binding energy varies substantially with basis set size, its affect on relative energy (and hence stability of isomers) is remarkably consistent. Therefore, we recommend including this correction to estimate the relative stabilities of isomers of water clusters. Even using a double- ζ basis set such as aug-cc-pVDZ (aVDZ) for a $\delta_{\text{MP2}}^{\text{CCSD(T)}}$ correction to the MP2 CBS energies has real value in correctly identifying the ordering of water cluster isomers. The good correlation between the importance of dispersion and the size of the CCSD(T) correction suggests that CCSD(T) is largely correcting for MP2’s incomplete account of dispersion interactions.

■ ASSOCIATED CONTENT

Supporting Information

Efforts to understand CCSD(T) correction to MP2 using energy decomposition analysis; RI-MP2/aVDZ optimized Cartesian coordinates; MP2/aVDZ, CCSD(T)/aVDZ, MP2-

F12/VDZ-F12, CCSD(T)-F12a/VDZ-F12, CCSD(T)-F12b/VDZ-F12, CCSD(T*)-F12a/VDZ-F12, and CCSD(T*)-F12b/VDZ-F12 absolute energies; SAPT binding energy and its components for 8 stationary points of water dimer; and LMO-EDA/MP2/aVDZ binding energy components for (H₂O)_n, *n* = 5–7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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