

# CCSD[T] Describes Noncovalent Interactions Better than the CCSD(T), CCSD(TQ), and CCSDT Methods

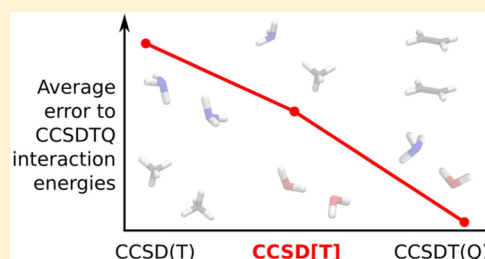
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## Supporting Information

**ABSTRACT:** The CCSD(T) method is often called the “gold standard” of computational chemistry, because it is one of the most accurate methods applicable to reasonably large molecules. It is particularly useful for the description of noncovalent interactions where the inclusion of triple excitations is necessary for achieving a satisfactory accuracy. While it is widely used as a benchmark, the accuracy of CCSD(T) interaction energies has not been reliably quantified yet against more accurate calculations. In this work, we compare the CCSD[T], CCSD(T), and CCSD(TQ) noniterative methods with full CCSDTQ and CCSDT(Q) calculations. We investigate various types of noncovalent complexes [hydrogen-bonded (water dimer, ammonia dimer, water ... ammonia), dispersion-bound (methane dimer, methane ... ammonia), and  $\pi$ - $\pi$  stacked (ethene dimer)] using various coupled-clusters schemes up to CCSDTQ in 6-31G\*(0.25), 6-31G\*\*(0.25, 0.15), and aug-cc-pVDZ basis sets. We show that CCSDT(Q) reproduces the CCSDTQ results almost exactly and can thus serve as a benchmark in the cases where CCSDTQ calculations are not feasible. Surprisingly, the CCSD[T] method provides better agreement with the benchmark values than the other noniterative analogs, CCSD(T) and CCSD(TQ), and even than the much more expensive iterative CCSDT scheme. The CCSD[T] interaction energies differ from the benchmark data by less than 5 cal/mol on average (for all complexes and all basis sets), whereas the error of CCSD(T) is 9 cal/mol. In larger systems, the difference between these two methods can grow by as much as 0.15 kcal/mol. While this effect can be explained only as an error compensation, the CCSD[T] method certainly deserves more attention in accurate calculations of noncovalent interactions.



## INTRODUCTION

The coupled-clusters (CC) theory, introduced to quantum chemistry almost half a century ago,<sup>1,2</sup> relies on the exponential formulation of the wave operator and its expansion into clusters-excitation operators. A very attractive feature of the CC theory is the fact that it is systematically improvable by the inclusion of higher excitation operators.<sup>3</sup> If a sufficiently large AO basis set is adopted, then the following sequence is (mostly) valid:

$$\text{CCSD} < \text{CCSD(T)} < \text{CCSDT} < \text{CCSDT(Q)} \\ < \text{CCSDTQ} < \text{fullCI}$$

Triple (T) excitations play an important role in the world of covalent as well as noncovalent interactions (see below), and thus the first truly accurate method in the series is the CCSD(T) scheme. The CCSD(T) method, characterized by iterative inclusion of single and double excitations with perturbative (4th-order and one term from the fifth order) inclusion of triple excitations, has been shown to be especially successful for ground-state energies and for the calculation of the properties of systems with single-reference character. As demonstrated in ref 4 and the references therein, the CCSD(T) one stands out among all CC-approximations as the “gold

standard” method for its excellent accuracy for the computational cost ratio.

In our recent review,<sup>5</sup> we demonstrated that the CCSD(T) in the complete basis set (CBS) limit represents the benchmark method for different types of noncovalent interactions, which is probably (at least) partially due to its compensation of higher-order excitations. This finding is supported by several earlier works<sup>6–8</sup> where model complexes were investigated. In the first paper,<sup>6</sup> published in our laboratory already in 2004, stacked (ethene dimer, formaldehyde dimer) and H-bonded complexes (formamide dimer, formamidinium dimer) were studied at the CCSDT level with various basis sets. The differences between the CCSD(T) and CCSDT schemes were small and became even smaller (below 100 cal/mol) when the aug-cc-pVDZ basis set was used. Hopkins and Tschumper<sup>7</sup> in the same year considered several dispersion-bound and stacked complexes (He dimer, N<sub>2</sub> dimer, ethyne dimer, butadiene dimer, NCCN dimer, furan dimer) and connected the passing from the CCSD(T) to CCSD(TQ) schemes with only small changes in the stabilization energy; they detected the largest effect (200 cal/mol) in the case of furan dimer. Finally, four years later

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again in our laboratory, the benzene dimer was studied at the CCSD(T) and CCSD(TQ) levels.<sup>8</sup> The contribution from connected quadruple excitations to stabilization energy calculated with the 6-31G\*(0.25) basis set differed for various benzene dimer structures between 21 and 40 cal/mol. Not all these conclusions can, however, be overestimated, because neither fully iterative CCSDT nor noniterative CCSD(TQ) provide the highest-accuracy correlation corrections (see later). A key question about the convergence of the CC series for noncovalent interactions thus still remains unanswered. Higher order methods have been applied only to small isolated molecules and, for noncovalent interactions, only to rare gas dimers,<sup>9–11</sup> but such evidence can not be applied directly to interactions in molecular complexes. The only exception is the recent work of Jankowski et al., who applied CCSDT(Q) in calculations of the infrared spectrum of the H<sub>2</sub>...CO complex (interaction energies have not been reported).<sup>12</sup>

Triple excitations play a decisive role in noncovalent interactions, and when they are not covered (e.g., in the CCSD scheme), the accuracy of the method strongly deteriorates (see e.g. Table 2 in ref 5.). The CC method was extended to non-iterative triples first by Urban et al.,<sup>13</sup> who originally used the abbreviation CCSD + T(CCSD); currently, the abbreviation CCSD[T] is utilized. A few years later, Raghavachari et al.<sup>14</sup> introduced an only slightly different scheme named CCSD(T). These methods differ in one-fifth-order term of the perturbation contribution to the energy, which CCSD(T) includes and CCSD[T] does not. The difference between the two methods was demonstrated by the calculation of the asymmetric stretching frequency of ozone, where the CCSD(T) method is able to reproduce the experiment while the CCSD[T] method yields an imaginary frequency. It was further shown<sup>15</sup> that the error of the CCSD[T] correlation energy when compared to CCSDT grows faster with the basis-set size than that of the CCSD(T) correlation energy. On the basis of these arguments, the CCSD(T) scheme was preferentially used over its earlier published competitor even in the realm of noncovalent interactions, where no evidence of their accuracy was available. In this paper, we quantify the accuracy of these methods against higher-order CC methods solely in the description of noncovalent interactions. In addition to the interaction energies, we also calculate the one-electron properties of the subsystems relevant to noncovalent interactions, the dipole moment and polarizability. The experience collected for isolated atoms and molecules<sup>15,16</sup> tells us that the inclusion of triples is not sufficient for obtaining the most accurate correlation energies; it is essential to cover the quadruple (Q) excitations (iteratively or noniteratively), whereas the inclusion of pentuples (P) brings only a much smaller improvement. The iterative CCSDTQ method, which includes the connected four-particle cluster T4, provides very accurate correlation energies, comparable to the full configuration interaction (FCI).

The aim of the present paper is to critically evaluate the performance of the CCSD[T] and CCSD(T) methods on the basis of a comparison with the results obtained at the CCSDTQ level. The performance of the two methods was tested on a wide range of noncovalent interactions. Consequently, various types of noncovalent complexes were considered, ranging from the strongest hydrogen-bonded complexes (water dimer, ammonia dimer, water ... ammonia), through weak dispersion-bound complexes (methane dimer,

methane ... ammonia) to a  $\pi$ - $\pi$  stacked complex (ethene dimer). All of these systems were calculated using a series of CC schemes (CCSD[T], CCSD(T), CCSD(TQ), CCSDT, CCSDT[Q], CCSDT(Q), and CCSDTQ) in three basis sets.

## CALCULATIONS

**Geometries.** The geometries of all of the subsystems and complexes were determined by gradient optimization at the CCSD(T)/CBS level (using a numerical gradient of the composite scheme, where MP2 energy is extrapolated from the aug-cc-pVTZ and aug-cc-pVQZ basis sets and the CCSD(T) correction is calculated in the aug-cc-pVDZ basis set). In the case of the complexes, the counterpoise correction was used; for more details, see our previous paper.<sup>17</sup> The geometries of the complexes correspond to the known global minima. Ethene dimer is an exception; the stacked structure is not a minimum. Since it is a useful model for  $\pi$ - $\pi$  interaction, we have constructed the geometry by fixing two optimized monomers 3.5 Å apart in the most symmetric configuration.

**One-Electron Properties.** Electric dipole moments and the *zz* components of dipole polarizabilities were evaluated using finite-field perturbation theory.<sup>18</sup> In this approach, an external electric field of small intensity – a perturbation – is applied to a molecule, and the energy of the system is approximated by a Taylor expansion, where the first and second energy derivatives with respect to the electric field applied represent the dipole moment and dipole polarizability, respectively. The strength of the perturbing electric field used in our calculations was 0.001 au, 0.002 au, and 0.004 au. Numerical differentiations were carried out according to G. Maroulis.<sup>19</sup> These calculations were performed in the aug-cc-pVDZ basis set.

**Energies.** All-electron calculations were performed in three different basis sets: 6-31G\*(0.25), 6-31G\*\*(0.25, 0.15), and aug-cc-pVDZ. The first two basis sets are modified versions of the 6-31G\* and 6-31G\*\* basis sets in which the exponents of the polarization functions are changed from the original values to 0.25 (C, N, and O) or 0.15 (H), making them more diffuse.<sup>20</sup> These basis sets, developed specifically for the treatment of noncovalent complexes, have been used extensively in our laboratory for treating extended H-bonded and stacked complexes.<sup>21</sup> It has been shown that MP2 stabilization energies for stacked base pairs computed with these basis sets agree surprisingly well with CCSD(T)/complete basis-set (CBS) values<sup>22</sup> and that these basis sets are also useful for CCSD(T) calculations in the cases where larger basis sets are not applicable.

Stabilization energies were systematically calculated using the counterpoise method of Boys and Bernardi.<sup>23</sup> No orbitals were frozen in the CC calculations and very tight convergence limits (10<sup>−10</sup> a.u.) were used for both the SCF and CC iterative procedures.

Because of the steep scaling of the higher-order methods with the size of both the system and basis set, the CCSDTQ/aug-cc-pVDZ calculations could not be carried out on the available hardware. For the 6-31G\*\*(0.25, 0.15) split-valence basis set, the CCSDTQ calculations became too large in the case of ethene dimer and methane ... ammonia complex; it was also impossible to calculate the ethene dimer at the CCSDT(Q) level in this basis set.

To test the basis set dependence of the differences between the methods studied, we have calculated also the neon dimer in the aug-cc-pVTZ basis set. Here, the interaction energy (0.06 kcal/mol) is much smaller, and the differences between the

studied methods are practically negligible ( $<0.1$  cal/mol). For this reason, this system is not included among the results on molecular complexes but is discussed separately.

**Computational Details.** The CCSD(T) and CCSD[T] calculations have been carried out in Molpro version 2009.<sup>24</sup> The CCSD(TQ) calculations have been performed in ACES II.<sup>25</sup> The higher-order CC calculations have been performed using the MRCC program<sup>26</sup> coupled to the Cfour package.<sup>27</sup>

## RESULTS AND DISCUSSION

**Subsystems.** The optimized geometries of all the subsystems (water, ammonia, methane, ethene) are presented in the Supporting Information. Figure S1 therein shows the correlation energies of the studied methods relative to the corresponding CCSDT(Q)/aug-cc-pVDZ results.

Dipole moments and dipole polarizabilities were evaluated at the CCSD[T], CCSD(T), CCSDT, CCSDT[Q], and CCSDT(Q) levels of theory (see Table 1). For a water molecule, the

**Table 1. Dipole Polarizabilities (zz Component) of the Studied Subsystems Computed at Various Levels of Theory (a.u.) and the Electric Dipole Moment (Debye, Polar Molecules Only)<sup>a</sup>**

	CCSD[T]	CCSD(T)	CCSDT	CCSDT[Q]	CCSDT(Q)
Dipole polarizability:					
water	8.578	8.525	8.534	8.524	<b>8.546</b>
ammonia	14.882	14.785	14.797	14.793	<b>14.830</b>
ethene	21.824	21.820	21.820	21.786	<b>21.814</b>
methane	16.401	16.393	16.402	16.398	<b>16.408</b>
Dipole moment:					
water	1.768	1.771	1.770	1.771	<b>1.769</b>
ammonia	1.414	1.417	1.416	1.416	<b>1.415</b>

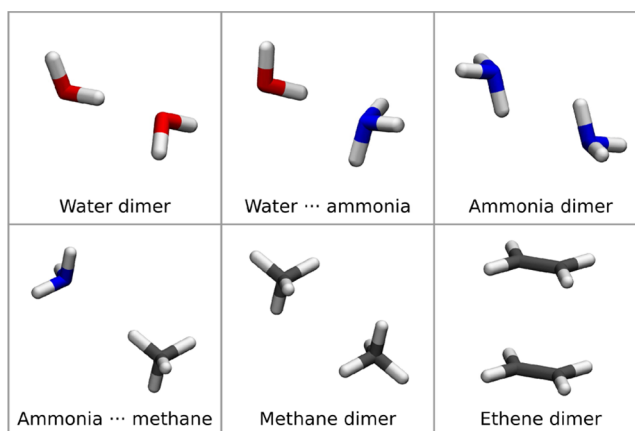
<sup>a</sup>The experimental values of the dipole moment of the ammonia and water molecules are 1.850 and 1.470 D, respectively.<sup>28</sup>

CCSDT(Q) dipole-moment value is the same as the one obtained at the CCSDTQ level of theory (1.769 D) and the difference in the zz component of dipole polarizability is only 0.004 au (CCSDTQ 8.542 vs CCSDT(Q) 8.546 au). As the CCSDT[Q] data deviate from the ones obtained with the iterative CCSDTQ method more significantly, the electric properties of the studied subsystems will be compared with the CCSDT(Q) results.

Of all the subsystems considered, only the ammonia and water molecules have an electric dipole moment. Since the current calculations have been carried out with a small basis set, our values are not very close to the experimental ones. There are very small differences in the dipole moments obtained with all of the coupled-clusters methods employed. On the basis of the zz components of dipole polarizabilities, it is possible to evaluate the performance of the two noniterative methods, CCSD(T) and CCSD[T]. In some cases, the CCSD[T] values are closer to the benchmark than the results obtained using the widely preferred CCSD(T) method. At the very least, there is no obvious pattern in our data of CCSD(T) outperforming the CCSD[T] variant.

**Complexes.** The optimized geometries of the complexes are presented in the Supporting Information and are visualized in Figure 1. The interaction energies in these complexes are provided in Table S1 in the Supporting Information.

As shown above, the CCSDTQ values can be considered as a benchmark for lower-order calculations. Unfortunately, we have



**Figure 1.** The six model noncovalent complexes for which we report interaction energies up to the CCSDTQ level.

not been able to determine CCSDTQ interaction energies systematically for all of the complexes and basis sets included in this study. However, the CCSDT(Q) values, which are available for all systems with the single exception of ethene dimer in the aug-cc-pVDZ basis set, reproduce the full CCSDTQ calculations with a negligible error (of max. 0.3 cal/mol); see Table 2. This only confirms previous results on correlation energy in small isolated molecules.<sup>15,16</sup> This error is an order of magnitude smaller than the differences between the methods studied here, and thus the CCSDT(Q) interaction energies can be safely used instead. The interaction energies in Table 2 and Figure 2 are listed and plotted relative to the CCSDT(Q) value. The errors in Table 2 are also calculated against this benchmark as a mean unsigned error (MUE). The CCSDTQ results are provided in the table and plots where available. Besides CCSDT(Q), we have tested also the similar CCSDT[Q] scheme. Apparently, the perturbative contribution here is not well balanced, and this method performs much worse than CCSDT(Q).

Using the CCSDT(Q) benchmark, we will first investigate the accuracy of the least expensive methods considered here, the CCSD[T] and CCSD(T) perturbative schemes. In all the basis sets considered, CCSD[T] performs better than CCSD(T). The difference (measured as a MUE) is especially large in the aug-cc-pVDZ basis sets, where the CCSD(T) error is twice as large as in CCSD[T]. The favorable behavior of CCSD[T] over CCSD(T) has been confirmed also in the larger basis set (aug-cc-pVTZ) in neon dimer, but the errors in comparison with CCSDT(Q) (0.2 and 0.8 cal/mol, respectively) are so small that should not be considered significant. Although there are some system and basis-set combinations where CCSD(T) is closer to the reference than CCSD[T], the differences in such cases are always small and do not affect the overall averages. In the largest basis set, this happens only in the case of water dimer and the difference is negligible (0.3 cal/mol). On the other hand, the largest difference in this basis set was found in the water – ammonia complex, where CCSD[T] is 10 cal/mol closer to the reference than CCSD(T). Averaged over all the systems and basis sets, the mean unsigned errors of CCSD[T] and CCSDT are 5.3 and 8.9 cal/mol. From these data, we can conclude that the CCSD[T] scheme describes noncovalent interactions better than CCSD(T).

The last comparable method based on iterative CCSD is the CCSD(TQ) scheme. Although it partially includes quadruple excitations, it does not perform better than CCSD(T) and

Table 2. Interaction Energies in the Studied Complexes in cal/mol, Relative to the CCSDT(Q) Values<sup>b</sup>

system	basis set	CCSD[T]	CCSD(T)	CCSD(TQ)	CCSDT	CCSDT[Q]	CCSDTQ
water dimer	6-31G*(0.25)	1.7	−14.2	5.1	2.0	8.3	−0.2
	6-31G**(0.25, 0.15)	6.0	−11.7	5.5	4.3	10.6	0.3
	aug-cc-pVDZ	2.7	2.4	2.4	9.2	18.4	−
water ... ammonia	6-31G*(0.25)	3.3	−8.4	16.7	3.9	11.2	−0.3
	6-31G**(0.25, 0.15)	−1.2	−0.8	30.7	5.1	18.0	0.2
	aug-cc-pVDZ	−1.6	12.0	12.0	14.7	28.3	−
ammonia dimer	6-31G*(0.25)	−3.1	−0.4	13.4	2.9	8.0	0.0
	6-31G**(0.25, 0.15)	−3.7	4.2	22.5	3.6	13.2	0.0
	aug-cc-pVDZ	4.6	11.9	11.9	10.9	19.3	−
methane ... ammonia	6-31G*(0.25)	1.2	3.3	6.1	2.0	3.8	0.0
	6-31G**(0.25, 0.15)	1.3	6.1	11.0	2.1	6.9	−
	aug-cc-pVDZ	6.7	10.2	10.2	5.1	9.4	−
methane dimer	6-31G*(0.25)	2.0	3.1	3.1	2.8	2.8	−0.1
	6-31G**(0.25, 0.15)	3.1	6.2	7.8	3.3	6.0	−0.1
	aug-cc-pVDZ	6.4	8.7	8.7	5.4	8.4	−
ethene dimer	6-31G*(0.25)	19.7	22.7	18.9	40.3	16.8	−
	6-31G**(0.25, 0.15)	22.1	25.2	24.7	43.6	21.4	−
	aug-cc-pVDZ <sup>a</sup>	−	−	−	−	−	−
mean unsigned error	6-31G*(0.25)	5.2	8.7	10.5	9.0	8.5	−
	6-31G**(0.25, 0.15)	6.2	9.0	17.0	10.3	12.7	−
	aug-cc-pVDZ <sup>a</sup>	4.4	9.0	9.0	9.1	16.8	−
	all basis sets	5.3	8.9	12.4	9.5	12.4	−

<sup>a</sup>The CCSDT(Q) calculation of ethene dimer in the aug-cc-pVDZ basis set was not performed because of its extreme computational demands. The average errors for this basis set have been calculated only for the first five complexes. <sup>b</sup>The CCSDTQ results are listed for the systems and basis sets where the calculation was possible. The average difference to the benchmark is listed as a mean unsigned error (MUE).

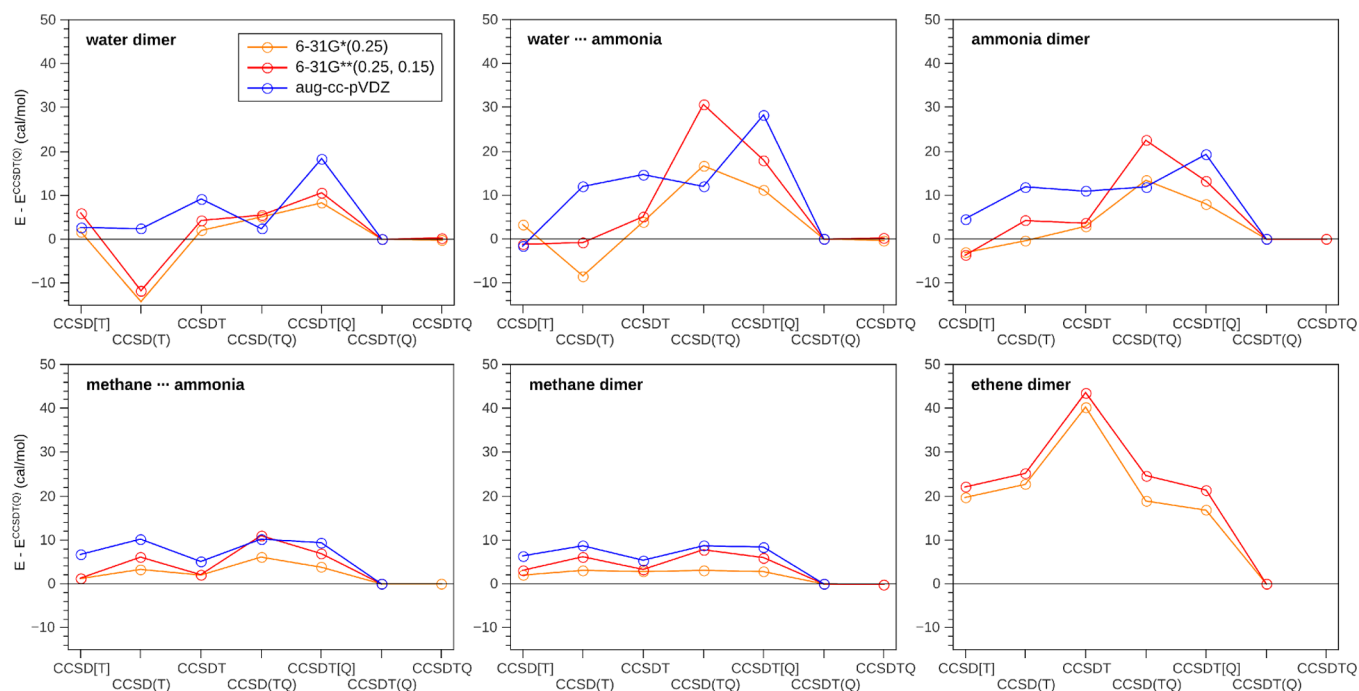


Figure 2. The plots of the coupled-clusters interaction energies in the studied noncovalent complexes, relative to the CCSDT(Q) value.

CCSD[T]. In the 6-31G\*(0.25) and 6-31G\*\*(0.25, 0.15) basis sets, it yields substantially larger errors, and in the aug-cc-pVDZ basis set (where ethene dimer is not included), it yields results practically identical to CCSD(T) (there is a difference only in the second or third decimal place, in cal/mol). From these results, it seems that CCSD(TQ) has no advantages over the simpler CCSD(T).

Finally, we compare the iterative CCSDT method against the higher-order benchmark. The difference to CCSDT and CCSDT(Q) clearly demonstrates the error in the description of noncovalent interactions when quadruple excitations are omitted. Surprisingly, CCSDT systematically performs slightly worse than CCSD(T), which can be caused only by an error compensation in the perturbative treatment of the triples. This error compensation is even stronger in CCSD[T], which is

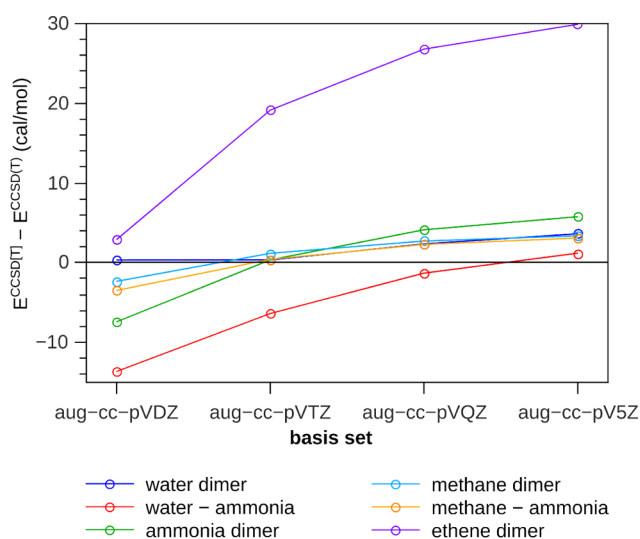


always closer to the higher-order reference than the more rigorous CCSDT approach.

To conclude, we have found that the CCSD[T] approach yields the best results among the tested methods when compared to the CCSDT(Q) benchmark. Due to an error cancellation, it outperforms not only the more common CCSD(T) but also the more computationally demanding CCSD(TQ) and CCSDT methods. This effect has been demonstrated in small basis set up to aug-cc-pVDZ and is yet to be confirmed in the larger basis sets, although the results for neon dimer suggest that the behavior is similar.

**The Basis-Set Dependence of the CCSD(T) and CCSD[T] Errors.** One of the objections against the use of CCSD[T] is the fact that the error of CCSD[T] as compared to CCSDT was reported<sup>15</sup> to grow faster with the basis-set size than the error of CCSD(T). However, we have shown here that CCSD(T) and especially CCSD[T] yield results closer to the CCSDT(Q) benchmark than CCSDT, which makes CCSDT a questionable reference if the best results are sought.

Because it is not possible to calculate CCSDT(Q) in larger basis sets, we can only compare the magnitude of the effect of the basis set to the basis-set dependence of the difference between CCSD[T] and CCSD(T) shown in Figure 3. The



**Figure 3.** The basis-set dependence of the difference between the CCSD[T] and CCSD(T) interaction energies.

differences are larger in the case of ethene dimer because the complex is larger and so is the absolute correlation interaction energy. The difference converges to a more positive value in the complete basis-set limit, but the behavior is different in different complexes, because the starting point of the series is different (in some cases the absolute difference increases, in others it decreases). This smooth convergence indicates that in terms of interaction energies, both methods behave similarly when the size of the basis set is increased, in contrary to ref 15. The largest differences between these two methods observed for any basis in the series are approximately as large as the error of these methods as compared to the CCSDT(Q) reference.

In the aug-cc-pVDZ basis set for which the CCSDT(Q) results are available, the CCSD[T] interaction energy exhibits larger stabilization, which is the correct trend toward the higher-order reference. In this (and smaller) basis set, CCSD[T] should be preferred over CCSD(T). In aug-cc-

pVTZ, the difference between CCSD(T) and CCSD[T] is close to zero on average. In larger basis sets, CCSD[T] yields less stabilization than CCSD(T); higher-order calculations in these basis sets would be needed for the assessment of the accuracy of these two schemes. To conclude, CCSD[T] can be recommended for calculations using up to triple- $\zeta$  basis sets; calculations beyond our current capabilities are needed to quantify the relation between CCSD[T] and CCSD(T) in larger basis sets.

**Larger Systems.** The higher-order CC methods are not applicable to larger complexes, but it is possible to analyze the difference between CCSD(T) and CCSD[T] applying our knowledge from small models. We have used the S66 data set,<sup>29</sup> for which CCSD(T) and CCSD[T] interaction energies were calculated<sup>30</sup> in the heavy-augmented cc-pVTZ basis set (the diffuse function on all atoms but hydrogens). The average absolute difference between CCSD(T) and CCSD[T] is 0.02 kcal/mol (what is 0.4% of the average interaction energy in the set), which is negligible in the context of other errors in the calculations, such as the incompleteness of the basis set. On the other hand, the difference could be rather large in some cases. The largest differences have been found in the stacked complexes; in the stacked uracil dimer, the difference amounts to 0.15 kcal/mol (1.25%). This value is about the same as the accuracy with which the CCSD(T)/CBS scheme used approaches the exact CBS limit. In line with our model calculations, the CCSD[T] interaction is more stabilizing, and we can thus expect it to be closer to the higher-order calculations.

The other geometry of the uracil dimer present in the set, a hydrogen-bonded base pair, exhibits a smaller difference (of 0.04 kcal/mol, 0.23%) with the opposite sign. Again, this agrees well with our model calculations, where CCSD(T) overestimates the strength of the hydrogen bond in water dimer, while CCSD[T] is close to the CCSDTQ reference. In total, the relative stability of the two structures of uracil (stacked and H-bonded) changes by 0.19 kcal/mol when passing from CCSD(T) to CCSD[T] because of the opposite signs of the differences between these methods for these two complexes. While it does not matter in this case, such a large difference can change the order of energetically close minima in some complexes (e.g., benzene dimer).

## CONCLUSIONS

CCSDTQ and CCSDT(Q) calculations, applied for the first time to a set of complexes featuring different types of noncovalent interactions, allowed us to compare more approximate CC methods to a reliable benchmark. We have studied six noncovalent complexes that represent the smallest models of interactions in larger systems.

1) We have found that the CCSDT(Q) interaction energies reproduce full CCSDTQ results with only a negligible error, which makes it possible to use the more efficient CCSDT(Q) method as a benchmark for lower-order methods.

2) All of the studied methods describe unimolecular properties (the dipole moment and polarizability) similarly and are in good agreement with the CCSDT(Q) benchmark. It is the intermolecular correlation that makes the difference in the noncovalent interactions.

3) The inclusion of quadruple excitations when passing from CCSDT to CCSDT(Q) changes the interaction energies by about 10 cal/mol on average when the aug-cc-pVDZ basis set is used. This difference in small model complexes will become

more substantial in larger systems. We estimate the error of CCSDT interaction energies with respect to higher-order calculations to be below 0.1 kcal/mol in the commonly studied systems consisting of tens of atoms.

4) Both CCSD(T) and CCSD[T] yield interaction energies closer to the higher-order reference than the more expensive CCSDT method. This error compensation is stronger in CCSD[T], at least in basis sets up to aug-cc-pVDZ for which the accurate reference exists. The results presented here suggest that CCSD[T] should be preferred in most applications to noncovalent interactions where CCSD(T) is now commonly used. This is especially true in the composite schemes where the complete basis set limit is estimated from extrapolation at the lower level and the CC calculation in a small basis set.

To extend these conclusions to larger basis sets, further calculations possible only with cutting-edge hardware and software are needed. Also, more systems should be examined to make more general conclusions. We will continue working in this direction with the overall goal of characterizing the accuracy of benchmark methods for noncovalent interactions.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Optimized geometries of the complexes and their subsystems are provided along with table of the coupled clusters interaction energies discussed in this paper. We also provide a plot of correlation energies in the subsystems calculated by the methods discussed here for comparison with interaction energies plotted in Figure 2. 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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## ■ DEDICATION

This paper is dedicated to our distinguished colleague and friend Miro Urban on the occasion of his 70th birthday.

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