# Assessment of Coupled Cluster Theory and more Approximate Methods for Hydrogen Bonded Systems

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**S** Supporting Information

**ABSTRACT:** To assess the accuracy of post-Hartree−Fock methods like CCSD(T), MP3, MP2.5, MP2, SCS-MP2, SOS-MP2, and DFT-SAPT, we evaluated several effects going beyond valence-correlated CCSD(T). For 16 small hydrogen bonded systems, CCSD(T) achieves an RMS error of 0.17 kJ/mol in the dissociation energy compared to our best estimate, which is a composite method akin to W4 theory. The error of CCSD(T) is thus much lower than for atomization energies. MP2 is surprisingly accurate for these systems with an RMS error of 1.3 kJ/mol. MP2.5 yields a clear improvement over MP2 (RMS of 0.5 kJ/mol) but still has an error about 3 times as large as CCSD(T) for the absolute RMS and almost 10 times as large for the relative RMS error. Neither SCS-MP2, SOS-MP2, nor DFT-SAPT yield lower errors than MP2. With a ΔCCSD(T) correction to MP2, the basis set limit is readily achieved when employing diffuse functions—without these, the convergence is rather slow.

CCSD(T)
CCSD
DFT-SAPT
MP2
MP2.5
SCS-MP2
SOS-MP2
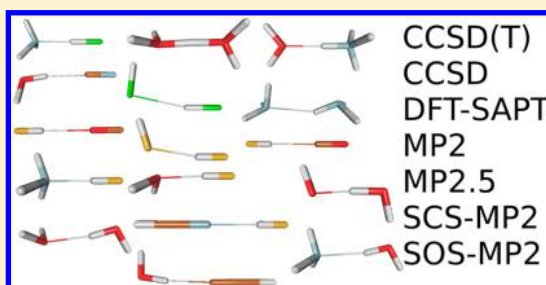
## 1. INTRODUCTION

Coupled-cluster theory with singles, doubles, and perturbative triple excitations [CCSD(T)] can be thought of as the "gold standard" in computational chemistry for single-reference systems. If affordable, it nowadays serves as a reference method in almost any computational approach. One common technique is to first test a method, either a density functional or post-Hartree−Fock scheme, on a small model system for which valence-correlated CCSD(T) can be computed. This best-performing method then usually serves as method of choice for the computation of the larger system, while the error in comparison to valence-correlated CCSD(T) is assumed to be constant.

The (root-mean-squared) RMS deviations of valence-correlated CCSD(T) to higher-order methods for atomization energies,[1−7] intramolecular bond lengths, and vibrational energies[8−11] are nowadays well established. This was done by both the HEAT project[1−3] as well as the various W$n$ methods[4−7] using either very accurate experimental reference values or post-Hartree−Fock methods beyond valence-correlated CCSD(T), like CCSDT(Q), CCSDTQ, and so on. The errors achieved by basis set limit valence-correlated CCSD(T) for atomization energies are on the order of about 3−4 kJ/mol (for sets of up to 100 small molecules),[1−7] those of intramolecular bond distances on the order of 0.33 pm, and vibrational energies on the order of 8 cm$^{-1}$ (for 30 diatomic species).[8]

For the computation of intermolecular interactions, valence-correlated CCSD(T) is considered to be very accurate, and estimates to its basis set limit (cbs) are frequently performed.[13−25] Those calculations then serve as test and/or fitting sets for new methods, such as MP2.5,[26,27] SCS-MP2,[28,29]

or new dispersion coefficients to add to density functional theory (DFT+D).[13,30−34] However, there are only very few studies on the accuracy of valence-correlated CCSD(T) for intermolecular interactions so far.[12,35,36] Intermolecular interactions, sometimes named noncovalent interactions, are commonly divided into hydrogen-bonded complexes, dispersion dominated systems, and mixed/other ones. The first category is dominated by induction, as dipole−dipole interactions are larger than dispersion for small molecules. $\pi$−$\pi$ interactions or interactions of rare gas dimers, for example, fall into the second category. In here, we will solely concentrate on hydrogen bonded systems, as we are interested in the largest errors we will attain with CCSD(T). Furthermore, hydrogen bonds have a paramount importance in biological systems like proteins and protein pockets,[37] and many chemical reactions take place in the liquid phase.

For comparison with experiment, zero-point energies need to be accurately estimated. This can be a rather challenging task because for low-frequency modes, a large part of the potential energy surface has to be computed.

We may expect that the CCSD(T) accuracy for intermolecular interactions is higher than for atomization energies. Most of the effects causing errors in valence-correlated CCSD(T) are of very short range: As a first example, core functions are very tight and short-range functions, and as such, core−valence effects are of very short range as well. Likewise, relativistic effects are connected to these tight core functions and to the contraction of orbitals near the nuclei. Furthermore, post-CCSD(T) valence-correlation effects can be thought of as

being associated with the multireference character of a molecule. Thus, only molecules of such a character will cause an effect for intermolecular interactions. Moreover, multi-reference interactions are of rather short range, as they can be mostly associated with bond-breaking of covalent bonds. However, in hydrogen-bonded systems, there is no covalent bond between the two monomers. Finally, effects beyond the Born−Oppenheimer approximation are mostly connected to hydrogen atoms and their short-range flexibility.

Thus, the publication outline is as follows: After presenting the computational details, we investigate the basis set convergence of Hartree−Fock for the dissociation energies. Next, the convergence of the MP2 and CCSD(T) correlation energies is evaluated, reaching the basis set limit of CCSD(T). Higher-order post-valence correlation energies are added using smaller basis sets as the absolute values of these effects decrease, together with the other effects which were neglected in valence-CCSD(T). With this benchmark reference data set, we evaluate the different W$n$ approximations, which either approximate basis set limit CCSD(T) or go beyond CCSD(T). Finally, we will address the more approximate post-Hartree−Fock methods and the composite schemes by investigating their accuracy by comparing it to the accuracy obtained by CCSD(T).

As a model systems, we used 16 hydrogen bonded systems tested in an earlier contribution:[22] $(ClH)\cdots(NH_3)$, $(CN)^-\cdots(H_2O)$, $(CO)\cdots(HF)$, $(FH)\cdots(NH_3)$, $(H_2O)\cdots(H_2O)$, $(H_2O)\cdots(NH_3)$, $(H_3O)^+\cdots(H_2O)$, $(HCC)^-\cdots(H_2O)$, $(HCl)\cdots(HCl)$, $(HF)\cdots(HF)$, $(HF)\cdots(H_2O)$, $(HF)\cdots(HCN)$, $(NH_3)\cdots(NH_3)$, $(NH_4)^+\cdots(H_2O)$, $(OC)\cdots(HF)$, and $(OH)^-\cdots(H_2O)$, thus comprising two cationic systems, three anionic systems, and 11 neutral hydrogen bonds. These are characterizing rather strong hydrogen bonds from about 7 to 150 kJ/mol, excluding only the weakest hydrogen bonds like CH···O bonds. The latter have a much larger dispersion character and can be thought of as in-between hydrogen bonded and van der Waals complexes.

## 2. COMPUTATIONAL DETAILS

All calculations have been performed with the TURBO-MOLE,[38] MOLPRO,[39] CFOUR,[40] and MRCC[41] program packages.

Overall, the following methods were used: The computationally least demanding method is MP2 (Møller−Plesset perturbation theory) with a scaling of $n^3N^2$, where $n$ is the number of correlated electrons and $N$ the number of virtual orbitals. (Although the computational time can be reduced by employing density-fitting or resolution-of-identity approximations, the MP2 scaling remains.) CCSD, DFT-SAPT (symmetry adapted perturbation theory), and MP3 have a formal scaling of $n^3N^3$. For DFT-SAPT, this can be reduced by density fitting to the same $n^3N^2$ scaling as MP2. CCSD(T) has an $n^3N^4$ scaling. It increases to $n^3N^5$ for CCSDT and $n^4N^5$ for CCSDT(Q), $n^4N^6$ for CCSDTQ, and so on. The electrons for all post-Hartree−Fock have been valence-correlated. The effects beyond core−valence correlation have been investigated with CCSD(T).

Fortunately, the amount of correlation recovered by each higher excitation also decreases, so that it is usually sufficient to calculate one of the less expensive methods with a very large basis set and add the contribution of a more expensive method with a smaller basis set. In this way, we are capable to approximate the basis set limit of a high-level method, whereas the same basis set effects are assumed for the high- and low-

level methods. Basically, this is akin to a simple subtractive scheme in a QM/QM calculation, where usually the molecular size is extended.

For all post-Hartree−Fock methods, Dunning's correlation consistent basis sets have been employed.[42−46] All of the variants, using diffuse functions (aug-cc-pVXZ), weighted core−valence basis sets (aug-cc-pwCVXZ), their Douglas Kroll variants (aug-cc-pVXZ-DK) for relativistic effects, and the standard cc-pVXZ basis sets have been utilized. A mixed scheme, in which we use diffuse functions on all atoms other than hydrogen is denoted aug′-cc-pVXZ.

When extrapolating the correlation energy (or in the case of DFT-SAPT, the dispersion), the standard $l^{-3}$ formula[47] and, when extrapolating Hartree−Fock, both the $l^{-5}$ [48,49] and $e^{-9\sqrt{l}}$ [50,51] formulas have been used. They will be abbreviated with cc-pV{X,Y}Z. The extrapolation is achieved by using the formulas:

$$E_{cbs} = E_{cc\text{-}pVYZ} + \frac{E_{cc\text{-}pVYZ} - E_{cc\text{-}pVXZ}}{\left(\frac{Y}{Y-1}\right)^{exp\,=\,3,5} - 1} \tag{1}$$

with $X = Y - 1$ and

$$E_{cbs} = E_{cc\text{-}pVYZ} + \frac{E_{cc\text{-}pVYZ} - E_{cc\text{-}pVXZ}}{\left(\frac{X \cdot e^{(9\sqrt{Y} - \sqrt{Y-1})}}{Y+1} - 1\right)} \tag{2}$$

Within the symmetry-adapted perturbation theory (DFT-SAPT)[52,53] framework, we used the asymptotically corrected PBE0 functional, PBE0-AC.[54] The underlying kernel for DFT-SAPT was the ALDA kernel, where by construction, all calculations were counterpoise-corrected.

We explicitly refrain from employing F12 theory because of the nonavailability of F12 to higher-order excitations. For DFT-SAPT and for example MP3, it is currently not possible to use F12, and we wish to keep the possibility to make comparisons between methods.

The dissociation energies are computed in the following way:

$$D_e^{unrelaxed} = E_{AB}(AB) - E_A(AB) - E_B(AB) \tag{3}$$

Here, the unrelaxed dissociation energy is calculated by subtracting the energy of the dimer from that of its monomers at the structure of the dimer.

$$D_e^{CPC,unrelaxed} = E_{AB}(AB) - E_A(AB) - E_B(AB) - BSSE \tag{4}$$

For the counterpoise-corrected energy of eq 4,[55] the BSSE is subtracted from the dissociation energy of eq 3, with the BSSE calculated from the energies of the monomers at the structures of the dimers, for with each a ghost calculation (using the basis set of the dimer) is performed:

$$BSSE = E_A^{ghost}(AB) + E_B^{ghost}(AB) - E_A(AB) - E_B(AB) \tag{5}$$

When using the BSSE calculations including extrapolation schemes, all energies are extrapolated separately.

In a similar manner, the relaxed dissociation energy is obtained:

**Table 1. Unrelaxed Hartree–Fock Counterpoise Corrected (eq 4) and Uncorrected Dissociation Energies (eq 3) of the Investigated Hydrogen Bonded Systems in kJ/mol**

| system | aug-cc-pV5Z | | aug-cc-pV6Z | | aug-cc-pV{5,6}Z | | | |
| | | | | | $e^{-9\sqrt{l}}$ | | | $l^{-5}$ |
| | $D_e^{CPC}$ | BSSE | $D_e^{CPC}$ | BSSE | $E_{relax}$ | $D_e^{CPC}$ | BSSE | BSSE |
|---|---|---|---|---|---|---|---|---|
| $(ClH)(NH_3)$ | −23.07 | 0.027 | −23.05 | 0.006 | 4.49 | −23.04 | −0.002 | −0.008 |
| $(CN)^-(H_2O)$ | −53.78 | 0.013 | −53.78 | 0.003 | 6.13 | −53.78 | 0.001 | −0.004 |
| $(CO)(HF)$ | −6.82 | 0.027 | −6.82 | 0.004 | 2.80 | −6.82 | −0.001 | −0.011 |
| $(FH)(NH_3)$ | −46.47 | 0.033 | −46.47 | 0.004 | 6.74 | −46.47 | −0.002 | −0.015 |
| $(H_2O)_2$ | −15.23 | 0.017 | −15.23 | 0.002 | 0.70 | −15.23 | −0.001 | −0.007 |
| $(H_2O)(NH_3)$ | −18.83 | 0.013 | −18.83 | 0.002 | 1.36 | −18.83 | −0.000 | −0.005 |
| $(H_3O)^+(H_2O)$ | −213.03 | 0.031 | −213.05 | 0.004 | 91.11 | −213.05 | −0.001 | −0.013 |
| $(HCC)^-(H_2O)$ | −65.69 | 0.018 | −65.69 | 0.003 | 9.12 | −65.69 | −0.000 | −0.006 |
| $(HCl)_2$ | −1.46 | 0.021 | −1.45 | 0.004 | 0.31 | −1.45 | 0.001 | −0.007 |
| $(HF)_2$ | −15.95 | 0.033 | −15.95 | 0.004 | 1.24 | −15.95 | 0.002 | −0.016 |
| $(HF)(H_2O)$ | −31.90 | 0.033 | −31.90 | 0.004 | 2.93 | −31.90 | −0.002 | −0.016 |
| $(HF)(HCN)$ | −25.05 | 0.036 | −25.05 | 0.005 | 0.61 | −25.05 | −0.001 | −0.016 |
| $(NH_3)_2$ | −6.59 | 0.008 | −6.59 | 0.001 | 0.29 | −6.59 | 0.000 | −0.003 |
| $(NH_4)^+(H_2O)$ | −79.16 | 0.018 | −79.16 | 0.003 | 3.69 | −79.17 | 0.000 | −0.007 |
| $(OC)(HF)$ | −7.02 | 0.033 | −7.02 | 0.004 | 1.63 | −7.02 | −0.002 | −0.015 |
| $(OH)^-(H_2O)$ | −368.10 | 0.039 | −368.10 | 0.010 | 276.21 | −368.10 | 0.004 | −0.009 |

$$D_e^{relaxed} = E_{AB}(AB) - E_A(A) - E_B(B)$$
$$= D_e^{unrelaxed} + E_{relax}$$
$$= D_e^{unrelaxed} + E_A(AB) + E_B(AB) - E_A(A)$$
$$- E_B(B) \quad (6)$$

with the counterpoise-corrected dissociation energy defined by

$$D_e^{CPC,relaxed} = E_{AB}(AB) - E_A(A) - E_B(B) - BSSE \quad (7)$$

Usually, counterpoise-corrected and uncorrected energies bracket the true basis set limit value. The uncorrected values overestimate the dissociation energy by monomer A imposing the basis functions on monomer B (and vice versa). The corrected values, on the other hand, underestimate the dissociation energy because the ghost functions on monomer A have greater flexibility (and are, in fact, not occupied) than the true basis functions of monomer A.

Composite methods like W1, W2,[48,49] and W4[5] theory consist of a series of approximations, estimating several components to get an estimate which is as good as possible.

W1, for example, extrapolates the SCF ($l^{-5}$) and CCSD ($l^{-3}$) energies with an aug′-cc-pV{T,Q}Z basis set, and the CCSD(T)-CCSD energy difference is added with an aug′-cc-pV{D,T}Z extrapolated basis set with an empirical exponent of 3.22 rather than 3. Both scalar relativistic effects as well as core–valence correlation effects are estimated with a basis set of small triple-$\zeta$ quality. For W2, the SCF and CCSD energies are extrapolated with the aug′-cc-pV{Q,5}Z basis, whereas the CCSD(T)-CCSD energy difference is added with an aug′-cc-pV{T,Q}Z extrapolated basis set. Finally, for W4 theory, SCF ($e^{-9\sqrt{l}}$) and CCSD are extrapolated with aug′-cc-pV{5,6}Z; the CCSD(T)-CCSD energy difference is added with an aug′-cc-pV{Q,5}Z. ΔCCSDT is added with cc-pV{D,T}Z, and ΔCCSDT(Q) is added with scaled cc-pVTZ, ΔCCSDTQ with a scaled cc-pVDZ basis set, and ΔCCSDTQPH with a VDZ basis. Core–valence correlations are estimated with aug-cc-pCV{T,Q}Z, scalar relativistic effects with aug-cc-pVQZ-DK, and DBOC with HF/aug-cc-pVDZ.

Our best estimate is obtained using CCSD(T)/aug-cc-pV{Q,5}Z (cp-corrected) + ΔMP2/aug-cc-pV6Z (cp-corrected) + ΔCCSDT(Q)/cc-pV{D,T}Z [cc-pV{T,Q}Z where applicable] + ΔCCSDTQ/cc-pVDZ + DBOC(CCSD/aug-cc-pVDZ) + rel.(CCSD(T)/aug-cc-pV{T,Q}Z-DK) + core–valence(CCSD(T)/aug-cc-pwCV{T,Q}Z).

## 3. RESULTS AND DISCUSSION

**3.1. Accurate Reference Values Akin to W4 for Intermolecular Interactions.** For the accurate computation of the hydrogen-bonded dissociation energies, we used the geometries of a former contribution, namely CCSD(T)/aug′-cc-pVQZ structures.[22] Since the accurate computation of hydrogen-bonded geometries is not the focus of this investigation, we concentrate on the computation of energies.

*Hartree–Fock.* Hartree–Fock (HF) is the basis of all post-Hartree–Fock methods, and as such, the accurate description of the intermolecular interactions starts with this method. As has been noted before, the $l^{-5}$ extrapolation becomes less accurate with larger basis sets. A good extrapolation scheme does not only minimize the deviation between the basis set limit Hartree–Fock value and the respective basis set but minimizes also the BSSE exerted by it. Consequently, there is a direct correlation between Table 1 (the HF dissociation energies) of this paper and Table 1 of reference 50 (the total HF energies), which summarize the deviation from the basis set limit Hartree–Fock values for 10 model systems. The RMS values of the BSSE which for the QZ, 5Z, and 6Z basis sets are 0.1666, 0.0266, and 0.0045 kJ/mol, respectively, are compared to 2032 $\mu E_H$, 316 $\mu E_H$, and 57 $\mu E_H$ for the total energies in Table 1 of ref 50. For the $l^{-5}$ extrapolation, these values result in 0.0436 kJ/mol for aug-cc-pV{Q,5}Z and 0.0108 kJ/mol for aug-cc-pV{5,6}Z, compared to 574 $\mu E_H$ and 118 $\mu E_H$. Finally, the $e^{-9\sqrt{l}}$ extrapolation yields, not surprisingly, the most accurate description: 0.0031 kJ/mol for aug-cc-pV{Q,5}Z and 0.0016 kJ/mol for aug-cc-pV{5,6}Z for the BSSE and 129 $\mu E_H$ and 10 $\mu E_H$ for the deviation from the Hartree–Fock limit. The aug-cc-pV{5,6}Z extrapolation, on the other hand, does not decrease the BSSE by more than a factor of 3 in comparison to

**Table 2. Unrelaxed MP2 Counterpoise Corrected (eq 4) and Uncorrected Dissociation Energies (eq 3) of the Investigated Hydrogen Bonded Systems in kJ/mol**

| system | aug-cc-pV5Z $D_e^{CPC}$ | aug-cc-pV6Z $D_e^{CPC}$ | BSSE | $E_{relax}$ | aug-cc-pV{Q,5}Z $D_e^{CPC}$ | aug-cc-pV{5,6}Z $D_e^{CPC}$ | BSSE |
|---|---|---|---|---|---|---|---|
| (ClH)(NH$_3$) | −40.49 | −40.74 | 0.54 | 3.38 | −41.09 | −41.12 | −0.07 |
| (CN)$^-$(H$_2$O) | −69.25 | −69.42 | 0.56 | 3.13 | −69.64 | −69.66 | 0.19 |
| (CO)(HF) | −5.59 | −5.63 | 0.36 | −0.33 | −5.67 | −5.69 | 0.00 |
| (FH)(NH$_3$) | −54.98 | −55.2 | 0.52 | 2.59 | −55.45 | −55.49 | 0.03 |
| (H$_2$O)$_2$ | −20.67 | −20.76 | 0.33 | 0.15 | −20.88 | −20.89 | 0.06 |
| (H$_2$O)(NH$_3$) | −27.35 | −27.46 | 0.31 | 0.41 | −27.6 | −27.62 | 0.04 |
| (H$_3$O)$^+$(H$_2$O) | −218.28 | −218.69 | 0.94 | 76.31 | −219.22 | −219.24 | 0.20 |
| (HCC)$^-$(H$_2$O) | −83.09 | −83.31 | 0.56 | 5.28 | −83.58 | −83.61 | 0.26 |
| (HCl)$_2$ | −9.16 | −9.23 | 0.35 | 0.12 | −9.34 | −9.33 | −0.01 |
| (HF)$_2$ | −18.56 | −18.65 | 0.39 | 0.08 | −18.75 | −18.77 | 0.01 |
| (HF)(H$_2$O) | −36.68 | −36.84 | 0.51 | 0.75 | −37.03 | −37.06 | 0.05 |
| (HF)(HCN) | −32.11 | −32.22 | 0.50 | 0.62 | −32.36 | −32.37 | 0.08 |
| (NH$_3$)$_2$ | −13.16 | −13.22 | 0.15 | 0.10 | −13.29 | −13.29 | 0.01 |
| (NH$_4$)$^+$(H$_2$O) | −87.7 | −87.89 | 0.45 | 2.28 | −88.10 | −88.15 | 0.17 |
| (OC)(HF) | −16.08 | −16.14 | 0.39 | −0.08 | −16.22 | −16.22 | 0.00 |
| (OH)$^-$(H$_2$O) | −336.54 | −337.19 | 1.53 | 229.26 | −338.13 | −338.07 | 0.17 |

**Table 3. Unrelaxed CCSD(T) Counterpoise Corrected (eq 4) and Uncorrected Dissociation Energies (eq 3) of the Investigated Hydrogen Bonded Systems in kJ/mol**

| system | aug-cc-pVQZ $D_e^{CPC}$ | aug-cc-pV5Z $D_e^{CPC}$ | BSSE | $E_{relax}$ | aug-cc-pV{Q,5}Z $D_e^{CPC}$ | ΔMP2 [aug-cc-pV{5,6}Z] $D_e^{CPC}$ | CCSD(T) $D_e^{CPC}$ |
|---|---|---|---|---|---|---|---|
| (ClH)(NH$_3$) | −36.55 | −37.02 | 0.67 | 2.84 | −37.56 | −0.03 | −37.59 |
| (CN)$^-$(H$_2$O) | −67.54 | −67.86 | 0.52 | 3.01 | −68.19 | −0.01 | −68.2 |
| (CO)(HF) | −7.13 | −7.21 | 0.48 | −0.07 | −7.28 | −0.02 | −7.30 |
| (FH)(NH$_3$) | −54.17 | −54.55 | 0.64 | 2.81 | −54.96 | −0.04 | −54.99 |
| (H$_2$O)$_2$ | −20.66 | −20.83 | 0.37 | 0.14 | −21.01 | 0.00 | −21.01 |
| (H$_2$O)(NH$_3$) | −26.85 | −27.05 | 0.33 | 0.41 | −27.25 | −0.01 | −27.27 |
| (H$_3$O)$^+$(H$_2$O) | −216.29 | −217.26 | 1.01 | 76.96 | −218.17 | −0.01 | −218.18 |
| (HCC)$^-$(H$_2$O) | −80.72 | −81.12 | 0.49 | 5.23 | −81.52 | −0.03 | −81.55 |
| (HCl)$_2$ | −7.98 | −8.1 | 0.43 | 0.03 | −8.24 | 0.00 | −8.24 |
| (HF)$_2$ | −18.89 | −19.08 | 0.52 | 0.14 | −19.26 | −0.02 | −19.28 |
| (HF)(H$_2$O) | −36.61 | −36.9 | 0.63 | 0.84 | −37.21 | −0.03 | −37.24 |
| (HF)(HCN) | −31.05 | −31.24 | 0.61 | 0.44 | −31.43 | −0.01 | −31.45 |
| (NH$_3$)$_2$ | −13.01 | −13.11 | 0.16 | 0.07 | −13.21 | 0.00 | −13.21 |
| (NH$_4$)$^+$(H$_2$O) | −86.75 | −87.13 | 0.43 | 2.13 | −87.48 | −0.04 | −87.52 |
| (OC)(HF) | −14.65 | −14.76 | 0.51 | 0.03 | −14.86 | 0.00 | −14.86 |
| (OH)$^-$(H$_2$O) | −329.54 | −331.15 | 1.72 | 222.08 | −332.72 | 0.06 | −332.67 |

the aug-cc-pV6Z basis set alone and by more than a factor of 2 compared to the aug-cc-pV{Q,5}Z basis set, whereas the total energies of the molecules are improved by a larger amount.

When taking a closer look at the Hartree−Fock dissociation energies, we observe that the cp-corrected energies converge much faster to the basis set limit than the noncorrected ones. For the aug-cc-pV6Z basis set, we also report the Hartree−Fock contribution to the relaxation energy from eq 6. The relaxation energy of the monomers at the reference geometries is especially large for the charged systems—for (OH)$^-$(H$_2$O), it is 276 kJ/mol, and for (H$_3$O)$^+$(H$_2$O), it is 91 kJ/mol.

The remaining BSSE is very small, with a maximum of 0.004 kJ/mol, which implies that the Hartree−Fock dissociation energy is basically converged to machine precision. The deviation between the cp-corrected aug-cc-pV6Z and the cp-corrected aug-cc-pV{5,6}Z is rather similar with 0.005 kJ/mol.

*Møller−Plesset Perturbation Theory.* For MP2, the BSSE is much larger, as shown in Table 2. Here, we detached the Hartree−Fock from the correlation energies and extrapolated

them separately: Hartree−Fock with $e^{-9\sqrt{l}}$ and the MP2 correlation with $l^{-3}$.

The RMS values of the BSSE for the MP2 energies are 1.00 kJ/mol for aug-cc-pV5Z, 0.61 kJ/mol for aug-cc-pV6Z, 0.30 kJ/mol for aug-cc-pV{Q,5}Z extrapolated, and 0.12 kJ/mol for the aug-cc-pV{5,6}Z extrapolated basis set. As for Hartree−Fock, the cp-corrected values converge much quicker to the basis set limit than the uncorrected ones—the RMS deviation between aug-cc-pV{Q,5}Z and aug-cc-pV{5,6}Z cp-corrected is 0.03 kJ/mol, and in comparison between the uncorrected aug-cc-pV{Q,5}Z and aug-cc-pV{5,6}Z values it is 0.26 kJ/mol. This implies, although the BSSE is still sizable, that the remaining basis set error is rather small and around 0.03 kJ/mol. This value is, however, still 1 order of magnitude larger than the BSSE of Hartree−Fock.

*Coupled-Cluster Theory with Singles, Doubles, and Perturbative Triples- CCSD(T).* For CCSD(T) (Table 3), the RMS value of the BSSE is smaller than for MP2 because the latter one has an overall larger correlation energy (by

**Table 4. Basis Set Convergence for the Difference between CCSDT and CCSD(T) Dissociation Energies in kJ/mol**

| | cc-pVDZ | aug-cc-pVDZ | cc-VTZ | cc-pV{D,T}Z | aug-cc-pVTZ | aug-cc-pV{D,T}Z | cc-pVQZ | cc-pV{T,Q}Z |
|---|---|---|---|---|---|---|---|---|
| $(ClH)(NH_3)$ | 0.033 | 0.063 | 0.162 | 0.217 | 0.143 | 0.177 | 0.191 | 0.212 |
| $(CN)^-(H_2O)$ | 0.089 | 0.014 | 0.148 | 0.173 | 0.057 | 0.076 | 0.149 | 0.150 |
| $(CO)(HF)$ | 0.048 | 0.048 | 0.043 | 0.041 | | | | |
| $(FH)(NH_3)$ | 0.021 | 0.020 | 0.063 | 0.080 | | | | |
| $(H_2O)_2$ | 0.010 | 0.044 | 0.038 | 0.050 | 0.029 | 0.023 | 0.046 | 0.052 |
| $(H_2O)(NH_3)$ | 0.010 | 0.025 | 0.055 | 0.073 | | | | |
| $(H_3O)^+(H_2O)$ | 0.033 | 0.099 | 0.131 | 0.172 | 0.113 | 0.119 | 0.150 | 0.165 |
| $(HCC)^-(H_2O)$ | 0.120 | 0.032 | 0.201 | 0.235 | 0.000 | −0.014 | | |
| $(HCl)_2$ | −0.013 | −0.060 | 0.041 | 0.064 | | | | |
| $(HF)_2$ | 0.004 | 0.055 | 0.024 | 0.032 | 0.016 | 0.000 | 0.027 | 0.029 |
| $(HF)(H_2O)$ | 0.025 | 0.067 | 0.051 | 0.062 | | | | |
| $(HF)(HCN)$ | 0.046 | 0.014 | 0.049 | 0.051 | | | | |
| $(NH_3)_2$ | −0.009 | 0.007 | 0.030 | 0.047 | 0.025 | 0.033 | 0.040 | 0.048 |
| $(NH_4)^+(H_2O)$ | −0.007 | 0.030 | 0.040 | 0.060 | | | | |
| $(OC)(HF)$ | −0.092 | −0.112 | −0.039 | −0.016 | | | | |
| $(OH)^-(H_2O)$ | 0.010 | 0.153 | 0.217 | 0.304 | 0.105 | 0.084 | 0.273 | 0.313 |

**Table 5. The Difference between CCSDT(Q) and CCSDT Dissociation Energies for Various Species and Basis Sets in kJ/mol[a]**

| system | cc-pVDZ | aug-cc-pVDZ | cc-pVTZ | cc-pV{D,T}Z | 1.1 × cc-pVTZ |
|---|---|---|---|---|---|
| $(ClH)(NH_3)$ | −0.155 | −0.149 | −0.223 | −0.251 | −0.245 |
| $(CN)^-(H_2O)$ | −0.395 | 0.153 | −0.423 | −0.435 | −0.465 |
| $(CO)(HF)$ | −0.025 | 0.001 | −0.053 | −0.064 | −0.058 |
| $(FH)(NH_3)$ | −0.103 | −0.033 | −0.115 | −0.120 | −0.126 |
| $(H_2O)_2$ | −0.059 | −0.013 | −0.074 | −0.080 | −0.081 |
| $(H_2O)(NH_3)$ | −0.082 | −0.050 | −0.109 | −0.121 | −0.120 |
| $(H_3O)^+(H_2O)$ | −0.208 | −0.078 | −0.188 | −0.179 | −0.207 |
| $(HCC)^-(H_2O)$ | −0.321 | −0.215 | −0.348 | −0.360 | −0.383 |
| $(HCl)_2$ | −0.039 | −0.059 | −0.077 | −0.092 | −0.084 |
| $(HF)_2$ | −0.026 | −0.011 | −0.046 | −0.054 | −0.050 |
| $(HF)(H_2O)$ | −0.073 | −0.002 | −0.82 | −0.085 | −0.090 |
| $(HF)(HCN)$ | −0.040 | −0.001 | 0.104 | 0.165 | 0.115 |
| $(NH_3)_2$ | −0.059 | −0.037 | −0.080 | −0.089 | −0.088 |
| $(NH_4)^+(H_2O)$ | −0.090 | 0.018 | −0.082 | −0.078 | −0.090 |
| $(OC)(HF)$ | −0.070 | −0.048 | −0.108 | −0.124 | −0.119 |
| $(OH)^-(H_2O)$ | −0.403 | −0.017 | −0.373 | −0.360 | −0.41 |

[a]In the last column, the cc-pVTZ difference value is scaled by 1.1.

comparing the MP2 energies of Table 2 with the CCSD(T) energies of Table 3)- the BSSE of MP2 for the aug-cc-pV{Q,5}Z extrapolated basis set is 0.30 kJ/mol, that of CCSD(T) is 0.13 kJ/mol in comparison.

The BSSE of the aug-cc-pV5Z basis set is 0.67 kJ/mol for CCSD(T), compared to 1.00 kJ/mol (MP2). The cp-corrected results of the aug-cc-pV5Z and the aug-cc-pV{Q,5}Z extrapolated basis sets differ by about the same amount. An RMS deviation of 0.56 kJ/mol for MP2 and 0.53 kJ/mol for CCSD(T) is found. Since this value is almost converged for MP2, we assume it is for CCSD(T) too, adding the difference between the aug-cc-pV{Q,5}Z and aug-cc-pV{5,6}Z extrapolated basis sets of MP2. This way, we suppose that the CCSD(T) cbs value is converged to at least 0.03 kJ/mol.

*Higher-Order Post-Correlation Effects beyond CCSD(T).* Having obtained an estimate for Hartree−Fock, valence-correlated MP2 and CCSD(T) at the basis set limit, we can evaluate all post-CCSD(T) correlation effects on the dissociation energy.

Since only rather small basis sets can be utilized when going beyond CCSD(T), the higher order correlation effects are estimated without counterpoise corrections: In fact, for small basis sets and MP2, the RMS deviation from the basis set limit is much larger for corrected than for uncorrected energies.[22]

For all species except OCHF, the binding energy is reduced when going from CCSD(T) to CCSDT, as shown in Table 4.

While the $\Delta[CCSDT-CCSD(T)]$ difference between the cc-pV{D,T}Z and cc-pV{T,Q}Z extrapolated basis sets is very similar in all cases, the employment of diffuse functions (aug-cc-pV{D,T}Z) yields somewhat different values, especially for the anions. Since all basis sets which do not include diffuse functions are close to each other, and even differences between aug-cc-pVDZ and aug-cc-pVTZ are very large, we assume that for the calculation of the differences in the dissociation energies, the standard basis sets without diffuse functions yield the best values. In fact, the same was observed when developing W3 theory. Probably, basis sets with diffuse functions are not as well suited for basis set extrapolations, especially when employing very small basis sets as in this case. Besides these observations, the CCSDT-CCSD(T) difference for the dissociation energies between cc-pV{D,T}Z and cc-pV{T,Q}Z extrapolated basis set is very small: For the seven species where the cc-pV{T,Q}Z has been calculated, the RMS difference is 0.010 kJ/mol. In comparison, the RMS deviation

between aug-cc-pV{D,T}Z and cc-pV{T,Q}Z is almost 10 times as large—0.095 kJ/mol.

The next, obvious step is to investigate the CCSDT(Q)−CCSDT difference in Table 5. As for the atomization energies,[4,5] almost all contributions (exceptions are HFHCN and OCHF) have the opposite sign of the CCSDT−CCSD(T) difference, and thus both contributions (going from CCSD(T) to CCSDT and CCSDT(Q)) cancel in most cases. The dissociation energies are reduced for every hydrogen-bonded system investigated except for the HFHCN system. Hence, as reported before,[4,5] CCSD(T) relies on a good error cancellation between the higher-order post-Hartree−Fock effects. To check the cc-pV{D,T}Z extrapolated value of the CN−H2O, we additionally performed a cc-pVQZ calculation with CCSDT(Q), which is lower than the CCSDT(Q)-CCSDT difference value (with −0.397 kJ/mol), yielding the cc-pV{T,Q}Z extrapolated value of −0.379 kJ/mol. This indicates that the maximum error for this contribution is probably around 0.06 kJ/mol, since $(CN)^-(H_2O)$ also shows the largest absolute contribution. This is not surprising, as $CN^-$ has a certain amount of multireference character (and a rather short hydrogen bond length since it is charged), which is capable of contributing to the dissociation energy.

The CCSDT(Q)-CCSDT difference (with an RMS value of 0.20 kJ/mol) is somewhat larger than the CCSDT-CCSD(T) difference (RMS 0.13 kJ/mol), which implies that the overall CCSDT(Q) value will be lowered in comparison to CCSD(T).

This effect, however, is rather small, as CCSDTQ-CCSDT-(Q) raises the dissociation energy with an RMS deviation of 0.03 kJ/mol with the cc-pVDZ basis set (Table 6). Even higher

**Table 6. Higher Order CCSDTQ, CCSDTQPH, and Sum of All Post-CCSD(T) Valence-Correlation Effects in kJ/mol**

| | Δ(CCSDTQ-CCSDT(Q)) | | Δ(CCSDTQPH−CCSDTQ) | sum |
|---|---|---|---|---|
| | cc-pVDZ | 1.1 × cc-pVDZ | VDZ | post-CCSD(T) |
| $(ClH)(NH_3)$ | 0.021 | 0.023 | | −0.018 |
| $(CN)^-(H_2O)$ | 0.067 | 0.074 | −0.043 | −0.261 |
| $(CO)(HF)$ | 0.021 | 0.023 | | 0.000 |
| $(FH)(NH_3)$ | 0.016 | 0.028 | | −0.022 |
| $(H_2O)_2$ | 0.012 | 0.013 | | −0.016 |
| $(H_2O)(NH_3)$ | 0.011 | 0.012 | | −0.035 |
| $(H_3O)^+(H_2O)$ | 0.035 | 0.038 | −0.016 | 0.004 |
| $(HCC)^-(H_2O)$ | 0.043 | 0.048 | | −0.077 |
| $(HCl)_2$ | 0.004 | 0.004 | | 0.024 |
| $(HF)_2$ | 0.008 | 0.009 | | −0.016 |
| $(HF)(H_2O)$ | 0.016 | 0.018 | | −0.006 |
| $(HF)(HCN)$ | 0.031 | 0.034 | | 0.249 |
| $(NH_3)_2$ | 0.008 | 0.009 | | −0.033 |
| $(NH_4)^+(H_2O)$ | 0.010 | 0.016 | | −0.003 |
| $(OC)(HF)$ | 0.010 | 0.012 | | −0.129 |
| $(OH)^-(H_2O)$ | 0.077 | 0.085 | | 0.030 |

contributions (CCSDTQPH−CCSDTQ) lower the energy by 0.043 kJ/mol for $(CN)^-(H_2O)$ and 0.016 kJ/mol for $(H_3O)^+(H_2O)$. This brings us to the final value of the post-CCSD(T) valence-correlation, where we sum up all effects: It is, perhaps not surprisingly, the largest for $(CN)^-(H_2O)$ (−0.261 kJ/mol) and (HF)(HCN) (+0.249 kJ/mol). These are the two complexes where we expect the largest contribution because of the nondynamic (static) correlation of the HCN/

CN− molecule. Aside from these two complexes, the largest postvalence correlation CCSD(T) effect of −0.13 kJ/mol is observed for (OC)(HF), which is almost negligible when comparing it to effects on atomization energies: For molecules like ozone, the effect can extend to about 12 kJ/mol. The average RMS over all these effects in the atomization energies is 2.6 kJ/mol; for the intermolecular dissociation energies it is 0.10 kJ/mol. We can thus expect that the post-CCSD(T) valence correlation effects are rather small in comparison.

*Diagonal Born−Oppenheimer Corrections, Core−Valence Correlation, and Scalar Relativistic Effects.* These are not the only effects to be considered: For W4 theory,[5] diagonal Born−Oppenheimer corrections (DBOC), core−valence CCSD(T) effects, and scalar relativistic effects are taken into account (Table 7), whereas for W3 theory, DBOC is neglected.[4,5]

The effects of the DBOC correction on the atomization energies are 1 order of magnitude lower than those of the post-CCSD(T) valence correlation with an RMS contribution of 0.28 kJ/mol.

Since DBOC corrections are associated with the floppiness of the nuclei on the potential energy surface, their relative contribution might be somewhat larger for dissociation energies in comparison to atomization energies. However, since the absolute contribution to atomization energies is already very small, any further decrease will make it insignificant. The RMS deviation (Table 7) is thus 0.075 kJ/mol, which is comparable to the 0.10 kJ/mol for the post-CCSD(T) valence correlation effects. In all cases, it is smaller than 0.125 kJ/mol and lower than the dissociation energy; the largest deviation can be found for $(NH_4)^+(H_2O)$ and $(H_3O)^+(H_2O)$. For the DBOC contribution, the basis set as well as the method does not change the results by much—the two methods, HF/aug-cc-pVTZ and CCSD/aug-cc-pVDZ differ by a RMS deviation of 0.013 kJ/mol only.

The core−valence effects are, as for the atomization energies (RMS deviation of 4.3 kJ/mol), the largest effects encountered and are probably causing the largest errors for the system. Nevertheless, their contribution is an order of magnitude less than for the atomization energies (RMS deviation of 0.261 kJ/mol) and with the exception of (CO)(HF), all of them raise the dissociation energy (thus have a negative contribution). The largest contribution is found for $(H_3O)^+(H_2O)$ with 0.42 kJ/mol.

This effect is somewhat canceled by the computed scalar relativistic effects, which all lower the dissociation energy. This effect is—with the exception of both HCl containing species—rather small, with an RMS deviation of 0.082 kJ/mol (including the HCl containing species, it is 0.151 kJ/mol). Since higher-order effects (e.g., spin−orbit effects) are even an order of magnitude smaller (we considered only closed-shell species), we can probably neglect those.

*Best Estimates.* In Tables 8 and 9, we display the dissociation energies computed by various W*n* theories in comparison to our best estimate in which we sum up all previous contributions. W1 and W2 theories use various approximations to obtain the CCSD(T) basis set limit and add relativistic corrections with a Darwin-mass-velocity approximation and core−valence correlation effects with smaller basis sets. For W3 and W4, post CCSD(T)-valence-correlation effects are calculated as well as a better description of the relativistic, core−valence correlation effects together with the DBOC correction.

**Table 7. Diagonal Born−Oppenheimer Correction (DBOC), Core−Valence CCSD(T), and Scalar Relativistic Effects for the Intermolecular Interactions in kJ/mol**

| | DBOC | | core−valence CCSD(T) | | | scalar relativistic effects | | |
|---|---|---|---|---|---|---|---|---|
| | HF/ATZ | CCSD/ADZ | ACTZ | ACQZ | AC(T,Q)Z | ATZ-DK | AQZ-DK | A(T,Q)Z-DK |
| $(ClH)(NH_3)$ | −0.120 | −0.112 | −0.244 | −0.327 | −0.388 | 0.808 | 0.494 | 0.402 |
| $(CN)^-(H_2O)$ | −0.063 | −0.051 | −0.250 | −0.277 | −0.296 | 0.069 | 0.034 | 0.023 |
| $(CO)(HF)$ | −0.023 | −0.021 | 0.198 | 0.137 | 0.093 | 0.103 | 0.068 | 0.057 |
| $(FH)(NH_3)$ | −0.116 | −0.107 | −0.244 | −0.327 | −0.388 | 0.117 | 0.097 | 0.090 |
| $(H_2O)_2$ | −0.065 | −0.063 | −0.111 | −0.124 | −0.133 | 0.081 | 0.061 | 0.054 |
| $(H_2O)(NH_3)$ | −0.076 | −0.070 | −0.135 | −0.145 | −0.152 | 0.067 | 0.048 | 0.041 |
| $(H_3O)^+(H_2O)$ | −0.122 | −0.123 | −0.429 | −0.423 | −0.419 | 0.180 | 0.159 | 0.152 |
| $(HCC)^-(H_2O)$ | −0.072 | −0.055 | −0.362 | −0.379 | −0.391 | 0.058 | 0.059 | 0.068 |
| $(HCl)_2$ | −0.025 | −0.024 | −0.094 | −0.187 | −0.255 | 0.640 | 0.400 | 0.328 |
| $(HF)_2$ | −0.054 | −0.052 | −0.074 | −0.054 | −0.040 | 0.095 | 0.070 | 0.060 |
| $(HF)(H_2O)$ | −0.096 | −0.093 | −0.176 | −0.184 | −0.189 | 0.144 | 0.120 | 0.111 |
| $(HF)(HCN)$ | −0.064 | −0.061 | −0.208 | −0.228 | −0.243 | 0.148 | 0.113 | 0.101 |
| $(NH_3)_2$ | −0.042 | −0.039 | −0.066 | −0.077 | −0.085 | 0.024 | 0.016 | 0.013 |
| $(NH_4)^+(H_2O)$ | −0.103 | −0.123 | −0.317 | −0.313 | −0.310 | 0.157 | 0.138 | 0.131 |
| $(OC)(HF)$ | −0.036 | −0.033 | −0.039 | −0.085 | −0.119 | 0.084 | 0.051 | 0.040 |
| $(OH)^-(H_2O)$ | −0.099 | −0.061 | −0.181 | −0.193 | −0.202 | 0.092 | 0.074 | 0.069 |

**Table 8. W1 and W2 Theories in Comparison to the CCSD(T) Basis Set Limit with the Best Description of Relativistic and Core−Valence Effects Possible As Well As Our Best Estimate (All Values in kJ/mol)**

| | W1 | W1(cp) | W2 | W2 (aug') | Aug-aug' (W2) | W2(cp) | CCSD(T)/cbs +rel+cv |
|---|---|---|---|---|---|---|---|
| $(ClH)(NH_3)$ | −35.34 | −35.07 | −34.95 | −35.02 | 0.07 | −34.73 | −34.81 |
| $(CN)^-(H_2O)$ | −65.35 | −65.05 | −65.07 | −64.55 | −0.52 | −65.11 | −65.15 |
| $(CO)(HF)$ | −7.58 | −7.22 | −7.21 | −7.08 | −0.13 | −7.19 | −7.26 |
| $(FH)(NH_3)$ | −52.91 | −52.17 | −52.09 | −52.11 | 0.02 | −52.23 | −52.30 |
| $(H_2O)_2$ | −21.08 | −20.96 | −20.88 | −20.84 | −0.04 | −20.90 | −20.91 |
| $(H_2O)(NH_3)$ | −27.06 | −26.95 | −26.84 | −26.82 | −0.02 | −26.91 | −26.93 |
| $(H_3O)^+(H_2O)$ | −141.90 | −141.11 | −141.08 | −141.16 | 0.08 | −141.34 | −141.46 |
| $(HCC)^-(H_2O)$ | −76.73 | −76.47 | −76.53 | −76.37 | −0.16 | −76.54 | −76.59 |
| $(HCl)_2$ | −8.39 | −8.30 | −8.37 | −8.26 | 0.11 | −8.23 | −8.24 |
| $(HF)_2$ | −19.46 | −19.16 | −19.23 | −19.10 | −0.13 | −19.11 | −19.13 |
| $(HF)(H_2O)$ | −36.96 | −36.39 | −36.39 | −36.35 | −0.04 | −36.39 | −36.44 |
| $(HF)(HCN)$ | −31.96 | −31.08 | −30.94 | −30.93 | −0.01 | −31.09 | −31.08 |
| $(NH_3)_2$ | −15.70 | −15.74 | −13.11 | −13.15 | 0.04 | −13.17 | −13.17 |
| $(NH_4)^+(H_2O)$ | −85.76 | −85.54 | −85.41 | −85.43 | 0.02 | −85.49 | −85.55 |
| $(OC)(HF)$ | −15.19 | −14.91 | −14.99 | −14.77 | −0.22 | −14.95 | −14.97 |
| $(OH)^-(H_2O)$ | −111.58 | −110.15 | −110.27 | −110.32 | 0.05 | −110.26 | −110.66 |
| RMS error CCSD(T) limit | 0.774 | 0.667 | 0.168 | 0.228 | | 0.112 | |
| RMS error best estimate | 0.722 | 0.695 | 0.328 | 0.417 | | 0.266 | 0.206 |

For W1 (using the standard aug'-cc-pVXZ basis sets), we observe the problems associated with a rather small basis set: The RMS deviation is 0.72 kJ/mol or 4.9% for the 16 investigated systems. Employing the cp-corrected results improves the errors by a small amount to 0.70 kJ/mol or 4.7%. Even though one could argue that 0.7 kJ/mol is already a very good accuracy, increasing the basis set as it is done here in W2 theory leads to much better results: Standard W2 theory with an aug'-cc-pVXZ basis set (uncorrected) yields a deviation about 2 to 4 times smaller with about 0.42 kJ/mol or 1.0%. For those calculations, it even pays off to add diffuse functions on the hydrogen atoms, as the RMS deviation between W2(aug') and W2(aug) is comparably large with 0.09 kJ/mol. Especially the strongly bound systems in Table 8 are described better when using diffuse functions on the hydrogen atoms, decreasing the RMS error to 0.33 kJ/mol. Finally, the cp-corrected W2 method has a remaining RMS error of 0.27 kJ/mol and 0.66%, which can be decreased by using even larger

basis sets to 0.21 kJ/mol when moving to the CCSD(T) limit value.

W3 (RMS % error: 0.95), W3.2 (0.93%), and W4 (noncp-corrected, 1.14%) have a similar accuracy compared to our best values when compared to W2. Only W4lite has a certain amount of error compensation (0.55%), while our best estimate basically agrees with the cp-corrected W4 value.

For the electronic dissociation energy excluding zero-point correction, we only neglected two effects: relativistic effects beyond scalar relativity (for closed-shell molecules, usually an order of magnitude less than scalar relativistic effects) and the difference in the geometries beyond CCSD(T)/aug'-cc-pVQZ. Since the potential energy surface is rather flat with respect to the intermolecular orientation, however, we do not expect the energy differences caused by the geometry to change by much.

Of course, for comparison to experiments, both the zero-point contribution and especially thermal effects would introduce the largest errors, while for the accurate computation

**Table 9. W3 and W4 Methods in Comparison to Our Best Estimate for the Dissociation Energy in kJ/mol**

| | CCSD(T)/cbs | W3 | W3.2 | W4lite | W4[a] | W4[a](cp) | best estimate | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | | | | overall | w/o rel., DBOC |
| (ClH)(NH₃) | −34.75 | −34.90 | −35.00 | −35.08 | −34.38 | −34.77 | −34.77 | −35.15 |
| (CN)⁻(H₂O) | −65.18 | −65.31 | −65.36 | −65.77 | −65.66 | −65.73 | −65.75 | −65.73 |
| (CO)(HF) | −7.37 | −7.17 | −7.22 | −7.21 | −7.03 | −7.23 | −7.23 | −7.28 |
| (FH)(NH₃) | −52.18 | −52.12 | −52.23 | −52.63 | −52.41 | −52.62 | −52.68 | −52.67 |
| (H₂O)₂ | −20.87 | −20.89 | −20.96 | −21.12 | −20.92 | −21.03 | −21.02 | −21.02 |
| (H₂O)(NH₃) | −26.86 | −26.85 | −26.92 | −27.11 | −26.98 | −27.07 | −27.07 | −27.04 |
| (H₃O)⁺(H₂O) | −141.23 | −141.12 | −141.24 | −141.51 | −141.44 | −141.60 | −141.58 | −141.62 |
| (HCC)⁻(H₂O) | −76.32 | −76.65 | −76.69 | −76.90 | −76.84 | −76.83 | −76.79 | −76.79 |
| (HCl)₂ | −8.21 | −8.35 | −8.37 | −8.24 | −7.90 | −8.10 | −8.11 | −8.49 |
| (HF)₂ | −19.14 | −19.22 | −19.27 | −19.36 | −18.96 | −19.17 | −19.18 | −19.19 |
| (HF)(H₂O) | −36.40 | −36.39 | −36.49 | −36.71 | −36.38 | −36.58 | −36.57 | −36.6 |
| (HF)(HCN) | −31.00 | −30.90 | −30.99 | −31.17 | −30.86 | −31.00 | −31.15 | −31.2 |
| (NH₃)₂ | −13.14 | −13.12 | −13.16 | −13.28 | −13.23 | −13.28 | −13.28 | −13.26 |
| (NH₄)⁺(H₂O) | −85.40 | −85.45 | −85.55 | −85.78 | −85.68 | −85.69 | −85.71 | −85.72 |
| (OC)(HF) | −14.83 | −15.08 | −15.11 | −15.11 | −14.85 | −15.06 | −15.06 | −15.08 |
| (OH)⁻(H₂O) | −110.59 | −110.37 | −110.47 | −110.72 | −110.35 | −110.78 | −110.74 | −110.75 |
| RMS Error | 0.206 | 0.275 | 0.223 | 0.114 | 0.213 | 0.044 | | |

[a]Excluding the (CCSDTQ56-CCSDTQ) energy difference and estimating the aug-cc-pV{5,6}Z correlation energy with MP2 rather than CCSD.

of these two effects a treatment beyond the harmonic approximation would be necessary, probably not only including anharmonic corrections but also the consideration of the full potential energy surface.

We can conclude that CCSD(T) at the basis set limit is of very high accuracy for intermolecular interactions with an RMS error 0.3 kJ/mol, well below 1 kJ/mol or 1% in relative numbers: Except both HCl-containing species, all relativistic errors are less than 0.16 kJ/mol; the core−valence correlation effects are somewhat larger, but still less than 0.42 kJ/mol, DBOC less than 0.13 kJ/mol, basis set effects (when looking at the change of the cp-corrected, extrapolated aug-cc-pV{Q,5} and aug-cc-pV{5,6}Z values) less than 0.06 kJ/mol, and the post-CCSD(T) valence correlation effects less than 0.13 kJ/mol when disregarding the two cyanide-containing dimers. Even if there would be no error cancellation, all individual maximum errors sum up to about 1 kJ/mol only.

Since hydrogen bonded systems are some of the strongest intermolecular interactions, this can serve as a reference value for the accuracy of this method for such interactions.

**3.2. Accuracy of CCSD, MP3, MP2.5, MP2, SOS-MP2, SCS-MP2, and DFT-SAPT.** Having obtained high-accuracy values for the 16 dimers, we can also look at the accuracy of more approximate methods like CCSD, MP3, MP2.5,[26,27] MP2, SOS-MP2,[56] SCS-MP2,[28,29] and DFT-SAPT.[52,53] In many cases, they have been compared to CCSD(T) values already, whereas it might be interesting to see if the error changes when comparing it to our best estimate and to this set of hydrogen bonded systems in general. In all cases, we extrapolate the energies to the basis set limit, applying at least aug-cc-pV{Q,5}Z extrapolations.

Their RMS errors of total binding energies in kJ/mol, which weigh the strongly bound systems more, compared to our best estimates are displayed in Figure 1. Their RMS relative percentage errors in the binding energies, which weigh the weakly bound systems more, are shown in Figure 2. For MP2, SCS-MP2, and SOS-MP2 we used a cp-corrected aug-cc-p{5,6}Z extrapolation; for MP2.5, MP3, DFT-SAPT, CCSD, and CCSD(T), we used the cp-corrected aug-cc-p{Q,5}Z values to obtain the basis set limit.
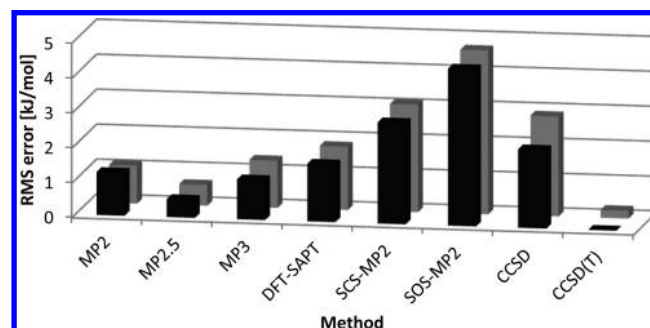


**Figure 1.** RMS error in kJ/mol for several post-Hartree−Fock methods (including DFT-SAPT), compared to the best estimate for the 16 hydrogen-bonded systems. For DFT-SAPT, (H₃O)⁺(H₂O) and (OH)⁻(H₂O) had to be excluded. The first, black bars display the RMS error to CCSD(T) at the basis set limit, and the gray bars, that to our best estimate.
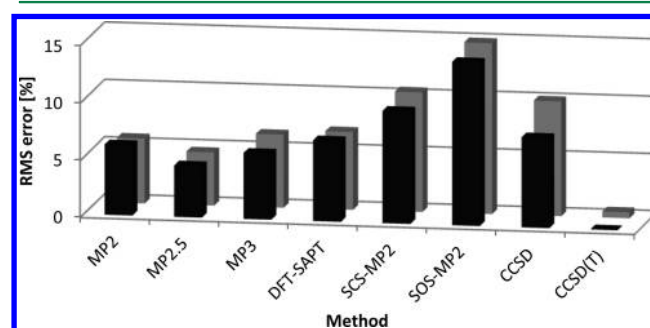


**Figure 2.** Percentage RMS error of several post-Hartree−Fock methods (including DFT-SAPT), compared to the best estimate for the 16 hydrogen-bonded systems. For DFT-SAPT, (H₃O)⁺(H₂O) and (OH)⁻(H₂O) had to be excluded. The first, black bars display the RMS error to CCSD(T) at the basis set limit, the gray bars, that to our best estimate.

CCSD has the worst scaling of all the compared methods (except CCSD(T)) and is sometimes reported to be rather accurate for hydrogen bonds. Its performance, however, is rather poor, especially when compared to MP2—the RMS

error to its best estimate (2.88 kJ/mol) is about twice the RMS error of MP2 (1.26 kJ/mol) for our systems.

The RMS error of MP3 (1.18 kJ/mol) is only slightly below that of MP2. As Hobza and co-workers noted,[26] MP2 overestimates most dissociation energies, while MP3 underestimates them. Taking an average of the two (MP2.5) produces much improved interaction energies—not only for the S22 set, but also for our set of hydrogen bonded dissociation energies (Figures 1, 2, and 3).
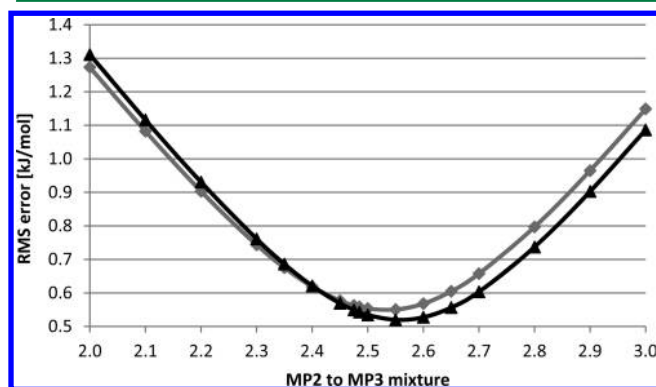


**Figure 3.** RMS error in kJ/mol compared to CCSD(T) (black) as well as the best estimate (gray) for different mixtures of MP2 and MP3.

In Figure 3, the RMS error of the MP2 to MP3 method is displayed, and indeed there is a minimum in the RMS error around 2.5. For our rather strongly bound hydrogen bonded systems, it is shifted toward somewhat larger values around 2.55—for other systems, it is slightly smaller. Nevertheless, it might be an alternative method to be used when CCSD(T) is too expensive. The main improvement to MP2 is for the stronger bound hydrogen bonded systems, as the percent error only decreases from 6.5% (MP2) to 5.0% (MP2.5).

DFT-SAPT, as another method which has come of more frequent use recently, does not perform as well as MP2 with an RMS error of 1.65 kJ/mol (absolute error) and 7.5% (relative error)—the use of a hybrid (0.25% Hartree−Fock and 75% ALDA) rather than the full ALDA kernel changes the result to 1.55 kJ/mol and 9.7%. Here, $(H_3O)^+(H_2O)$ and $(OH)^-(H_2O)$ had to be excluded, as latter two dimers exhibit very large dissociation energies and cannot be treated by intermolecular perturbation theory. Like SCS-MP2 (with an RMS error of 2.88 kJ/mol), DFT-SAPT is known to give much better results for more weakly bound systems. As the RMS error is still rather close to MP2, it is probably preferable over the latter. Finally,

SOS-MP2 has the lowest scaling and the largest RMS errors (4.48 kJ/mol and 14.6%), more than an order of magnitude larger than the error of CCSD(T).

Thus, MP2.5 might provide a useful alternative to MP2 when calculating hydrogen bonded systems, although its absolute error is still about twice as large as CCSD(T).

**3.3. MP2 + ΔCCSD(T).** Another way to approximate CCSD(T) is to calculate it with a small basis set and to estimate the basis set limit with MP2,[20,21,57−59] the same way we have used the additive scheme to get to our best estimate. This is akin to QM/QM methods, where the extension of the cluster size is calculated with a more approximate method. However, too small basis sets of double-$\zeta$ quality barely yield any improvement, as can be seen from Table 10. Here, it is especially important to use diffuse functions. For example, the employment of a ΔCCSD(T) correction with a simple cc-pVDZ basis set does not improve the RMS error of MP2 at all. Thus, in such cases, the expensive CCSD(T) calculation does not yield any improvement. Most of the CCSD(T) corrections are overestimated with these small basis sets (with an RMS deviation of 2.9 kJ/mol for the 6-31G* and cc-pVDZ basis sets, and 2.3 kJ/mol using a cc-pVTZ basis set), and the difference between CCSD(T) is much smaller at the basis set limit (1.4 kJ/mol with aug′-cc-pV5Z).

This is especially important, since various reference sets use either cc-pVDZ or cc-pVTZ as corrections, claiming CCSD-(T)/cbs values. It might be worthwhile recomputing some of these reference data in order to ensure that the ΔCCSD(T) correction yielded even an improvement in the dissociation energies.

Using diffuse functions, the values change completely, and using an aug′-cc-pVDZ basis set for the ΔCCSD(T) correction, values are comparable to the cc-pVQZ basis set (without diffuse functions; see Table 10). The accuracy of CCSD(T) is already obtained with the aug-cc-pVTZ basis set.

The smallest basis set which yields some improvement is actually the 6-31G*(0.25) basis set, yielding an even better performance than cc-pVTZ. For the 6-31G*(0.25) basis set, the standard d polarization functions have been replaced by more diffuse ones.[60]

Only when starting to extrapolate the aug′-cc-pV{T,Q}Z basis set or using an aug′-cc-pVQZ basis set for MP2 can we see an improvement in the combined MP2/CCSD(T) energy. For MP2 alone, a basis set of aug′-cc-pVTZ quality is probably enough because of the intrinsic error of MP2.

**Table 10. Basis Set Dependence of the MP2 Basis Set (Columns) and CCSD(T) Basis Set (Rows) for which the Additive Scheme Was Assessed**

| | | MP2 basis set | | | | |
|---|---|---|---|---|---|---|
| | | a′pVTZ | a′pV{D,T}Z | a′pVQZ | a′pV{T,Q}Z | a′pV5Z |
| | | 1.04 | 1.36 | 1.03 | 1.27 | 1.02 |
| | 6-31G* | 1.25 | 1.05 | 1.28 | 1.20 | 1.38 |
| | cc-pVDZ | 1.45 | 1.23 | 1.44 | 1.32 | 1.53 |
| | 6-31G*(0.25) | 0.76 | 1.00 | 0.57 | 0.71 | 0.48 |
| ΔCCSD(T) basis set | cc-pVTZ | 1.04 | 0.85 | 0.95 | 0.81 | 1.03 |
| | aug′-cc-pVDZ | 0.90 | 0.77 | 0.67 | 0.43 | 0.70 |
| | cc-pVQZ | 0.66 | 0.60 | 0.58 | 0.47 | 0.66 |
| | aug′-cc-pVTZ | 0.73 | 0.60 | 0.45 | 0.21 | 0.45 |
| | aug′-cc-pVQZ | | | 0.35 | 0.19 | 0.37 |

## 4. CONCLUSIONS

A thorough assessment of the accuracy of CCSD(T) and more approximate methods was done for 16 hydrogen bonded species. For this purpose, the effects going beyond valence-correlated CCSD(T) were investigated, namely scalar relativistic effects using the Douglas–Kroll–Hess method, effects of the Born–Oppenheimer diagonal correction, valence-correlated post-Hartree–Fock, and core–valence CCSD(T). Of all these effects, the core–valence correlation contributes the largest remaining error, up to 0.4 kJ/mol.

The accuracy of CCSD(T) is rather high, with a RMS error of 0.17 kJ/mol and a relative RMS error of 0.6%. These errors are surprisingly low, as the best estimates of the bonds range between 7 and 142 kJ/mol. The dissociation energy of the strongest hydrogen bond between charged species is for example close to the atomization energy of the fluorine molecule.[5]

MP2.5 yields RMS errors of around 0.5 kJ/mol or 5%, and MP2 of around 1.3 kJ/mol or 6.5%, while the other tested methods (such as DFT-SAPT, SCS-MP2, SOS-MP2, and CCSD) yield larger errors. When using MP2 in a combined scheme to estimate the basis set limit of CCSD(T), it is important to use diffuse functions when calculating CCSD(T) corrections with a triple-$\zeta$ or smaller basis set or smaller. A double-$\zeta$ basis set without diffuse functions does not yield any improvement. With a basis set of aug'-cc-pVTZ quality for the correction, the accuracy of CCSD(T) is basically achieved for these systems with an error of 0.21 kJ/mol.

These two approximate methods (MP2.5 and MP2+$\Delta$CCSD(T)) are thus alternatives to improve the accuracy of MP2 for describing hydrogen bonds. Especially the latter method turns out to be very accurate when hydrogen bonds are dominant for intermolecular interactions.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The full material, including all individual energies (in excel), is available. This information 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.

## ■ ACKNOWLEDGMENTS

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