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A systematic ab initio study of the water dimer in hierarchies of basis sets and correlation models

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Abstract. A systematic, high-level ab initio investigation of the water dimer has been performed. The oxygen-oxygen bond distance has been estimated to be around 2.90 Å, about 0.05 Å shorter than the experimentally estimated distance, challenging the accuracy of the latter. The interaction energy has been obtained at -5.0 ± 0.1 kcal/mol, which compares favourably with the experimentally estimated value of -5.4 ± 0.7 kcal/mol. The importance of employing basis sets that include diffuse functions in correlated calculations on hydrogen-bonded systems is confirmed. In correlated calculations on the water dimer and the hydrogen fluoride dimer, the counterpoise-corrected interaction energies converge considerably slower towards the basis set limit than do the uncorrected energies, provided that the correlation-consistent basis sets are augmented with diffuse functions.

Key words: Hierarchies – Basis sets – Basis set superposition error

1 Introduction

Several theoretical studies have been performed on the water dimer, focusing primarily on the determination of the equilibrium geometry and the interaction energy [1–14]. When calculating the interaction energy of the water dimer within the supermolecule approach, the basis set superposition error (BSSE) – a spurious contribution to the interaction energy because of the use of an incomplete set of basis functions – must be taken into account. Boys and Bernardi proposed an approximate way of accounting for BSSE known as the counterpoise-correction (CPC), in which the energies of the water monomers are calculated in the full basis of the dimer [15]. These counterpoise-corrected energies are then used instead of the energies of the isolated monomers in the calculation of the interaction energy. Although the CPC method is conceptually simple, it is computationally expensive since one must in general perform as many additional calculations in the full basis set of the dimer as there are non-equivalent fragments in the system.

A considerable amount of work concerning the accuracy of CPC for estimating BSSE has been reported in the literature – some favours it, some is against it, and some proposes extensions to it [16–24]. Nevertheless, there seems to be a consensus that CPC gives a correct order-of-magnitude estimate of BSSE. If one allows the monomer geometry to relax as the dimer is optimized, then the CPC monomer geometry becomes different from that of the isolated monomer, and the uncorrected and CPC-corrected interaction energies will not converge with each other in the limit of a complete basis unless the monomer deformation energy is taken into account. This point was investigated in detail for the water dimer by Xantheas [13]. However, if one freezes the monomer geometry in the optimization of the dimer, the pure electronic CPC due only to the incompleteness of the basis is obtained. This contribution will necessarily vanish in the limit of a complete basis.

When high accuracy is aimed for, it is insufficient to carry out a single calculation, using a single wave function and a single basis set. A more systematic approach is required and the calculations should preferably be carried out in hierarchies of basis sets and wave functions, making it possible to control and estimate errors. With regard to the one-electron basis sets, the hierarchies of the correlation-consistent sets of Dunning and co-workers cc-pVXZ and aug-cc-pVXZ (with X = D, T, Q, and 5) offer a systematic improvement to the description of the correlation energy with each increment in the cardinal number [25–28]. Concerning wave-function models, the sequence of functions self-consistent field (SCF), second-order Møller-Plesset perturbation theory (MP2), coupled cluster singles and doubles (CCSD), and CCSD augmented by a perturbative correction for triple excitations (CCSD(T)) has proved to be a useful hierarchy for the calculation of ground-state energies and equilibrium geometries [29].

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A systematic study of the water dimer using the Dunning basis sets at the SCF and MP2 levels was initiated by Feller [10]. Because of hardware and software limitations, Feller was not able to employ the largest basis sets in the series. His work was later completed by Feyereisen et al. [11] and by Xantheas et al. [12, 13], who performed the SCF and MP2 calculations for $2 \leq X \leq 5$, with and without augmented diffuse functions added. From these calculations, the MP2 basis set limit for the interaction energy was estimated at −4.9 kcal/mol, with an uncertainty smaller than 0.1 kcal/mol – in good agreement with the counterpoise-corrected value of Klopper et al., who obtained −4.94 kcal/mol using the R12-MP2 approach [30]. The MP2 estimate compares favourably with the experimentally measured value, provided the latter is corrected for vibrational and finite-temperature effects, giving an estimate of the electronic interaction energy of -5.4 ± 0.7 kcal/mol [31, 32]. Beyond the MP2 level, the correlation corrections are small: Feller found that the interaction energy increases by 0.02 kcal/mol and 0.05 kcal/mol, respectively, going from MP2 to MP4 and from MP2 to QCISD(T) [10]; Rybak et al. obtained MP2-to-MP4 shifts of 0.16 kcal/mol and 0.13 kcal/mol, respectively, in the uncorrected and CPC-corrected energies [8]. Mas and Szalewicz obtained MP2-to-MP4 and MP2-to-CCSD(T) shifts smaller than 0.02 kcal/mol [14]. The correlation effects beyond MP2 are thus of the order 0.1 kcal/mol, although we note that these corrections were all obtained in fairly small basis sets.

The water dimer is a weakly bound complex with a long interfragment distance, requiring a good description of the outer valence regions of each fragment and hence the inclusion of diffuse functions in the basis set. Accordingly, Feller [10], Feyereisen et al. [11] and Xantheas et al. [12, 13] observed large effects on the interaction energy when the cc-pVXZ basis set was augmented with a single set of diffuse functions (at the aug-cc-pVXZ level). The importance of a second set of diffuse functions was not investigated, however.

In this paper, we study the correlation effects in the water dimer, carrying out SCF, MP2, CCSD, and CCSD(T) calculations in the cc-pVXZ and aug-cc-pVXZ hierarchies with $X \leq 5$ as well as in the doubly augmented sets daug-cc-pVXZ [28] with $X \leq 4$. In particular, we address the question as to which of the three approaches is the best for a given cardinal number: (1) to carry out a CPC of the energy, (2) to augment the basis set with diffuse functions, or (3) to increase the cardinal number. In addition, we provide an accurate estimate of the interaction energy at levels of theory beyond MP2. The largest basis sets employed here require calculations that cannot be carried out with conventional (non-direct) programs. Instead, the calculations must be carried out using an integral-direct program, illustrating the usefulness of the integral-direct techniques introduced by Almlöf et al. [33] for SCF and later extended by Head-Gordon et al. [34] and Saebø and Almlöf [35] to the MP2 level and by Koch et al. [36–38] to the coupled-cluster models.

For an accurate determination of the interaction energy, an accurate geometry is needed for the water dimer. Theoretical [2, 4, 6, 9, 14] and experimental [39, 40] investigations agree that the global minimum of the water-dimer potential-energy surface (PES) possesses C_s symmetry as depicted in Fig. 1, with an oxygen-oxygen distance slightly shorter than 3 Å.

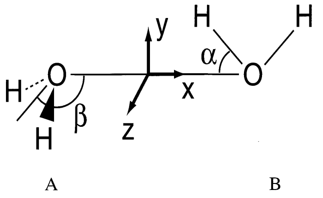

Fig. 1. The geometry of the water dimer. All the atoms in monomer B as well as the oxygen atom in monomer A lie in the plane of the paper (XY-plane), which constitute the mirror plane of the dimer complex

The experimental oxygen-oxygen distance R_o is 2.976 Å [39, 40], but large anharmonic vibrational corrections are present [10, 40]. These effects have been estimated in the experimental study by Odutola and Dyke, yielding an equilibrium oxygen-oxygen distance of 2.946 Å [40]. In agreement with this value, Mas and Szalewicz [14] obtained 2.953 Å, using symmetry-adapted perturbation theory. Likewise, van Duijneveldt-van de Rijdt and van Duijneveldt (vDs) [9] obtained 2.943 Å and 2.955 Å from the CPCPES at the MP2 and CEPA levels. Xantheas [13] obtained 2.907 Å (2.933 Å) in a full geometry optimization at the MP2/aug-cc-pVTZ level (correlating only valence electrons) and 2.905 Å (2.913 Å) in a restricted geometry optimization at the MP2/aug-cc-pV5Z level, where only the oxygen-oxygen distance was optimized with the remaining parameters fixed at the MP2/aug-cc-pVTZ geometry (the values in parentheses are obtained from the CPCPES). These values obtained by Xantheas [13] do not compare well with the experimental value. MP2 usually gives accurate geometries but has been found to fail in difficult cases [29]. The CCSD(T) model, in contrast, is robust and accurate for systems dominated by a single configuration. We have therefore performed a sequence of geometry optimizations at the MP2, CCSD and CCSD(T) levels, using the aug-cc-pVXZ series of basis sets to determine whether the oxygen-oxygen equilibrium distance is close to the experimental estimate or perhaps shorter.

2 Computational details

Currently there is no implementation that is capable of performing integral-direct geometry optimizations with the coupled-cluster wave functions, so we are only able to perform these optimizations with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. We used the ACESII program [41] freezing the water monomer geometry at the experimental monomer geometry [42] and correlating all the electrons. These constrained optimizations have three independent geometrical parameters: the oxygen-oxygen distance and the two angles α and β in Fig. 1. To investigate basis set effects further, we performed an optimization in the aug-cc-pVQZ basis set at the MP2 level, using the massively parallel program package described in Refs. [43–46]. The single-point energy calculations were carried out using the integral-direct coupled cluster program [36–38]. Since the valence basis sets do not contain any core-correlating orbitals, we have frozen the 1*s* orbital on the oxygen atoms in the post-SCF single-point calculations. In the largest basis set (aug-cc-pV5Z with 574 basis functions), the CCSD and CCSD(T) calculations are very time consuming. Therefore, only the CCSD calculation on the full dimer has been carried out in this basis sets.

From the calculated energies, we obtain the uncorrected interaction energy as

$$\Delta E_{AB} = E_{AB} - E_A - E_B, \tag{1}$$

where E_{AB} is the energy of the dimer and E_A and E_B the energies of the isolated monomers A and B (see Fig. 1), which in our case are identical. The counterpoise-corrected interaction energy is calculated as

$$\Delta E_{AB}^{CP} = E_{AB} - E_A^{CP} - E_B^{CP}, \tag{2}$$

where E_A^{CP} is the counterpoise-corrected energy of monomer A in the full basis of the dimer and similarly for E_B^{CP}. Finally, the CPC to the interaction energy is obtained as the difference between the Eqs. (1) and (2)

$$\Delta E_{corr}^{CP} = (E_A - E_A^{CP}) + (E_B - E_B^{CP}), \tag{3}$$

which becomes the sum of the CPC of the two water monomers. The CPC of the water monomer is given as the average of the individual CPCs of the two monomers and is obtained by dividing Eq. (3) by two.

3 Results

3.1 Geometry of the water dimer

The results of the seven constrained optimizations are shown in Table 1. For all three models, we observe a contraction of the R_{O-O} bond distance of 0.02 to 0.025 Å from aug-cc-pVDZ to aug-cc-pVTZ. For MP2, we observe that as we go from aug-cc-pVTZ to aug-cc-pVQZ, the R_{O-O} bond distance increases by 0.004 Å. The shift from triple to quadruple zeta is thus about a factor of five smaller than the shift from double to triple zeta.

Table 1. Optimized values of the oxygen–oxygen bond distance (R_{O-O}) in angstroms and the angles α and β (see Fig. 1) in degrees in the water dimer

		MP2	CCSD	CCSD(T)	MP2/CPC
aug-cc-pVDZ	R_{O-O}	2.9120	2.9385	2.9194	2.977
	α	5.30	5.11	5.28	5.30
	β	124.7	124.9	123.6	124.7
aug-cc-pVTZ	R_{O-O}	2.8909	2.9148	2.8954	2.935
	α	4.75	4.45	4.76	4.75
	β	124.1	124.1	122.5	124.1
aug-cc-pVQZ	R_{O-O}	2.8953			2.915
	α	5.45	–	–	5.45
	β	124.3			124.3

From Table 1 we also note that the R_{O-O} distance calculated at the MP2 level is close to the distance obtained at the CCSD(T) level, both being 2 pm shorter than the CCSD distance. This behaviour – an appreciable shift from MP2 to CCSD and a shift in the opposite direction from CCSD to CCSD(T) – is also observed for normal bonds. However, for strongly bonded systems, the CCSD distances are usually shorter than both MP2 and CCSD(T) distances (see Ref. [29]).

From Table 1, we further note that the correlation effects beyond MP2 are comparable to the effects observed as we increase the basis set from aug-cc-pVTZ to aug-cc-pVQZ and that the R_{O-O} distances at the CCSD(T)/aug-cc-pVTZ and MP2/aug-cc-pVQZ levels are almost identical. Since CCSD(T) is usually superior to MP2 in predicting geometries, we believe the CCSD(T)/aug-cc-pVTZ geometry to be the most accurate discussed so far. The R_{O-O} distance at the CCSD(T)/aug-cc-pVTZ level (2.895 Å) compares well with the results of Xantheas [13] but is about 0.05 Å shorter than the experimental estimate.

The vDs [9] obtained a good agreement with the experimental estimate of the R_{O-O} distance using CPCPES. We have therefore investigated the CPCPES at the MP2 level, using the three basis sets of the standard geometry optimizations. For each basis set, we have fixed the angles to the values obtained in the corresponding standard optimization. The bond distance corresponding to the minimum of the CPC interaction energy was then determined.

The interaction energy is the difference between the absolute energy of the dimer complex and of the fragments. For an accurate calculation of the interaction energies, it is therefore essential to achieve a balanced description of the complex and the fragments, which is the reason for introducing the CPC correction. The geometry, however, is determined from the differential change of the energy of the complex. The demand for a balanced description is therefore not so strong in calculations of the geometry. Thus, in contrast to the situation for the interaction energy, there do not appear to be any strong theoretical arguments for using CPC in geometry optimizations. Of course, in the limit of a complete basis set, the CPC geometry and the ordinary geometry must converge with each other.

The MP2/CPC results are listed in Table 1. At the aug-cc-pVDZ level, the difference between the CPC and the standard geometries is rather large (0.065 Å), but it decreases steadily as we increase the basis set, with differences in the aug-cc-pVTZ and aug-cc-pVQZ sets of 0.044 Å and 0.020 Å, respectively. More importantly, the CPC geometries are more sensitive to changes in the basis set and the geometries obtained in the standard manner are closer to the basis set limit. As we shall shortly see, this situation is analogous to that for the interaction energy, where the uncorrected results in the augmented basis sets are also closer to the basis set limit than are the CPC-corrected ones.

The CCSD(T)/aug-cc-pVTZ geometry optimized in the standard manner should therefore be the most accurate one and is consequently used in all single-point calculations on the dimer. The Cartesian coordinates of this geometry are listed in Table 2. At the MP2 level, we have observed a small elongation of the bond (0.004 Å) from aug-cc-pVTZ to aug-cc-pVQZ. Extending the basis set beyond aug-cc-pVTZ at the CCSD(T) level is therefore believed to result in an elongation of less than 0.005 Å. We have correlated all the electrons in a valence cc-pVXZ set. Helgaker et al. found that the error associated with the incomplete description of the core-correlation effects provided by the cc-pVXZ basis sets amounts to a few tenths of a pm (for first-row atoms) [29]. Finally, the effect of monomer relaxation on the $R_{O—O}$ distance was found by the vDs [9] to be about 0.1 pm. In conclusion, our results are therefore indicative of an $R_{O—O}$ distance of about 2.90 Å, questioning the experimentally estimated value of 2.946 Å.

Table 2. Cartesian coordinates for the (CCSD(T))/aug-cc-pVTZ optimized structure of the water dimer in atomic units in the center-of-mass coordinate system

Atom	X	Y	Z
O	−2.6661095	0.1203995	0.0000000
H	−3.3025697	−0.7855370	−1.4304321
H	−3.3025697	−0.7855370	1.4304321
O	2.8000483	−0.1258791	0.0000000
H	1.0060037	0.1050804	0.0000000
H	3.4734302	1.5529584	0.0000000

3.2 The basis set dependence of BSSE and CPC

The calculated single-point energies are listed with the calculated interaction energies, obtained from Eqs. (1) and (2), for the four different wave-function models in Tables 3–6. In Table 7, we have given the CPC to the interaction energy for all wave functions and basis sets. As expected, the CPC goes to zero as the basis set increases. We also observe that the CPC is smaller at the SCF level than at the correlated levels and that the CPCs are similar for the three correlated models. Furthermore, the CPC is reduced by about a factor of three when the cardinal number is increased by one at the SCF level and by a factor of two for the correlated models. This agrees well with the situation for the ground-state energy, where the convergence towards the basis set limit also is slower at the correlated levels than at the SCF level. The basis set errors are also larger at the correlated levels than at the SCF level (see Table 8) where we have listed the CPC of the monomer along with the basis set error. The basis set error is based on ground-state monomer calculations in the cc-pV6Z basis at the SCF level and MP2-R12 calculations [47]. From Table 8, we also note that, at the SCF level (but not at the MP2 level), the magnitude of CPC relative to the basis set error increases fast and monotonically with the cardinal number.

The most conspicuous feature of Tables 7 and 8 is the large difference in magnitude of CPC for sets with and without diffuse functions. Thus, when the standard cc-pVXZ set is augmented by a single set of diffuse functions, then the CPC is reduced by an order of magnitude at the SCF level and by a factor of three to four at the correlated levels. This reduction may be explained by the

Table 3. The SCF interaction energies (uncorrected and CP corrected) of the water dimer in E_h. Listed are also the energies of the monomers (uncorrected and CP corrected) and the energies of the dimer

	$E_A = E_B$	E_A^{CP}	E_B^{CP}	E_{AB}	ΔE_{AB}	ΔE_{AB}^{CP}
cc-pVDZ	−76.026799	−76.029772	−76.027154	−152.062705	−9.1077	−5.7794
cc-pVTZ	−76.057168	−76.058268	−76.057403	−152.121240	−6.9036	−5.5699
cc-pVQZ	−76.064835	−76.065252	−76.064975	−152.135833	−6.1624	−5.6057
cc-pV5Z	−76.067091	−76.067193	−76.067139	−152.139953	−5.7718	−5.6219
aug-cc-pVDZ	−76.041428	−76.041747	−76.041510	−152.088835	−5.9797	−5.5776
aug-cc-pVTZ	−76.060613	−76.060689	−76.060660	−152.126908	−5.6817	−5.5585
aug-cc-pVQZ	−76.066001	−76.066033	−76.066016	−152.137667	−5.6657	−5.6175
aug-cc-pV5Z	−76.067320	−76.067324	−76.067323	−152.140264	−5.6234	−5.6168
daug-cc-pVDZ	−76.041843	−76.042184	−76.041986	−152.089761	−6.0757	−5.5916
daug-cc-pVTZ	−76.060679	−76.060775	−76.060750	−152.127094	−5.7360	−5.5688
daug-cc-pVQZ	−76.066020	−76.066064	−76.066053	−152.137733	−5.6927	−5.6158

Table 4. The MP2 interaction energies (uncorrected and CP corrected) of the water dimer in E_h. Listed are also the energies of the monomers (uncorrected and CP corrected) and the energies of the dimers

	$E_A = E_B$	E_A^{CP}	E_B^{CP}	E_{AB}	ΔE_{AB}	ΔE_{AB}^{CP}
cc-pVDZ	−76.228420	−76.233256	−76.229043	−152.468489	−11.6488	−6.1894
cc-pVTZ	−76.318630	−76.320784	−76.319129	−152.646887	−9.6264	−6.9738
cc-pVQZ	−76.347633	−76.348605	−76.347943	−152.703971	−8.7039	−7.4230
cc-pV5Z	−76.358598	−76.358940	−76.358728	−152.725302	−8.1059	−7.6344
aug-cc-pVDZ	−76.260765	−76.261719	−76.261179	−152.529750	−8.2206	−6.8519
aug-cc-pVTZ	−76.328958	−76.329399	−76.329277	−152.666054	−8.1374	−7.3776
aug-cc-pVQZ	−76.351913	−76.352163	−76.352040	−152.711852	−8.0270	−7.6486
aug-cc-pV5Z	−76.360225	−76.360356	−76.360305	−152.728387	−7.9368	−7.7256
daug-cc-pVDZ	−76.261627	−76.262579	−76.262171	−152.531656	−8.4009	−6.9060
daug-cc-pVTZ	−76.329395	−76.329887	−76.329811	−152.667106	−8.3168	−7.4082
daug-cc-pVQZ	−76.352140	−76.352421	−76.352331	−152.712409	−8.1287	−7.6576

Table 5. The CCSD interaction energies (uncorrected and CP corrected) of the water dimer in E_h. Listed are also the energies of the monomers (uncorrected and CP corrected) and the energies of the dimers

	$E_A = E_B$	E_A^{CP}	E_B^{CP}	E_{AB}	ΔE_{AB}	ΔE_{AB}^{CP}
cc-pVDZ	−76.237987	−76.242509	−76.238583	−152.486804	−10.8310	−5.7122
cc-pVTZ	−76.324546	−76.326421	−76.324986	−152.657993	−8.8997	−6.5856
cc-pVQZ	−76.350804	−76.351589	−76.351058	−152.709739	−8.1309	−7.0924
cc-pV5Z	−76.359522	−76.359777	−76.359624	−152.726718	−7.6732	−7.3176
aug-cc-pVDZ	−76.268534	−76.269461	−76.268925	−152.544908	−7.8400	−6.5218
aug-cc-pVTZ	−76.333665	−76.334078	−76.333967	−152.675128	−7.7971	−7.0830
aug-cc-pVQZ	−76.354214	−76.354406	−76.354317	−152.716070	−7.6416	−7.3468
aug-cc-pV5Z	−76.360648			−152.728841	−7.5448	
daug-cc-pVDZ	−76.269374	−76.270298	−76.269894	−152.546779	−8.0311	−6.5874
daug-cc-pVTZ	−76.334069	−76.334536	−76.334462	−152.676112	−7.9738	−7.1135
daug-cc-pVQZ	−76.354376	−76.354600	−76.354534	−152.716488	−7.7357	−7.3543

Table 6. The CCSD(T) interaction energies (uncorrected and CP corrected) of the water dimer in E_h. Listed are also the energies of the monomers (uncorrected and CP corrected) and the energies of the dimers

	$E_A = E_B$	E_A^{CP}	E_B^{CP}	E_{AB}	ΔE_{AB}	ΔE_{AB}^{CP}
cc-pVDZ	−76.241020	−76.245739	−76.241649	−152.493210	−11.1694	−5.8215
cc-pVTZ	−76.332189	−76.334223	−76.332664	−152.673731	−9.3526	−6.8442
cc-pVQZ	−76.359793	−76.360667	−76.360071	−152.728165	−8.5781	−7.4257
cc-pV5Z	−76.369040	−76.369332	−76.369154	−152.746176	−8.0952	−7.6900
aug-cc-pVDZ	−76.273740	−76.274779	−76.274187	−152.555769	−8.2880	−6.8038
aug-cc-pVTZ	−76.342289	−76.342730	−76.342609	−152.692790	−8.2112	−7.4504
aug-cc-pVQZ	−76.363582	−76.363788	−76.363691	−152.735217	−8.0538	−7.7388
aug-cc-pV5Z	−76.370293					
daug-cc-pVDZ	−76.274667	−76.275690	−76.275252	−152.557823	−8.4885	−6.8801
daug-cc-pVTZ	−76.342725	−76.343215	−76.343138	−152.693838	−8.3882	−7.4856
daug-cc-pVQZ	−76.363758	−76.363994	−76.363924	−152.735664	−8.1484	−7.7466

Table 7. Averaged counterpoise-corrections (mE_h) for the water dimer

		D	T	Q	5
SCF	cc-pVXZ	3.3283	1.3337	0.5567	0.1499
	aug-cc-pVXZ	0.4021	0.1232	0.0482	0.0066
	daug-cc-pVXZ	0.4841	0.1672	0.0769	
MP2	cc-pVXZ	5.4594	2.6526	1.2809	0.4715
	aug-cc-pVXZ	1.3687	0.7598	0.3784	0.2112
	daug-cc-pVXZ	1.4949	0.9086	0.4711	
CCSD	cc-pVXZ	5.1188	2.3141	1.0385	0.3556
	aug-cc-pVXZ	1.3182	0.7141	0.2948	
	daug-cc-pVXZ	1.4437	0.8603	0.3814	
CCSD(T)	cc-pVXZ	5.3479	2.5084	1.1524	0.4052
	aug-cc-pVXZ	1.4842	0.7608	0.3150	
	daug-cc-pVXZ	1.6084	0.9026	0.4018	

Table 8. The SCF and MP2 basis set errors in the water monomer energies and counterpoise-corrections in mE_h

		SCF				MP2			
		D	T	Q	5	D	T	Q	5
cc-pVXZ	error	40.60	10.23	2.57	0.31	140.98	50.77	21.77	10.80
	CPC	1.66	0.67	0.28	0.07	2.73	1.33	0.64	0.24
aug-cc-pVXZ	error	25.97	6.79	1.4	0.08	108.64	40.44	17.49	9.18
	CPC	0.20	0.06	0.02	0	0.68	0.38	0.19	0.11
daug-cc-pVXZ	error	25.56	6.72	1.38		107.77	40.01	17.26	
	CPC	0.24	0.08	0.04		0.75	0.45	0.24	

observation that, since the augmented basis sets already provide a good description of the outer valence regions, the new orbitals that are introduced in this region when calculating the CPC energy have a smaller effect than they have in calculations with the standard basis sets, which provide a cruder description of the outer regions. We also note that the effect on both CPC and the ground-state energy when going from an augmented to a doubly augmented basis set is small, especially compared with the effect of the single augmentation. We are thus approaching saturation with respect to diffuse functions with the singly augmented basis sets.

In Figs. 2–5, we have plotted the calculated interaction energies – both counterpoise-corrected and uncor-

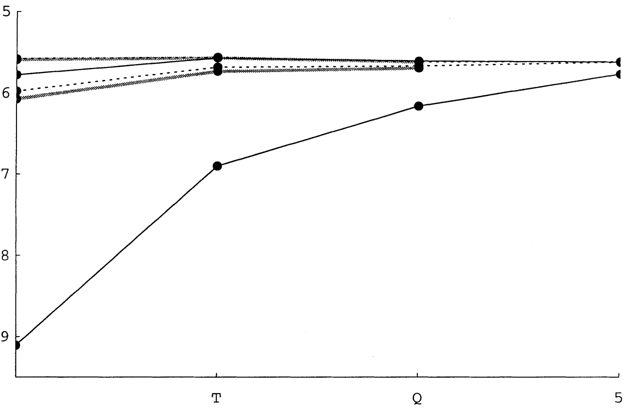

Fig. 2. The SCF interaction energy of the water dimer (in mE_h) plotted against the cardinal number X. The *solid lines* are the uncorrected (*lower curve*) and CP corrected (*upper curve*) for the cc-pVXZ basis. The *dashed* and *grey curves* are used for the aug-cc-pVXZ and daug-cc-p VXZ energies, respectively

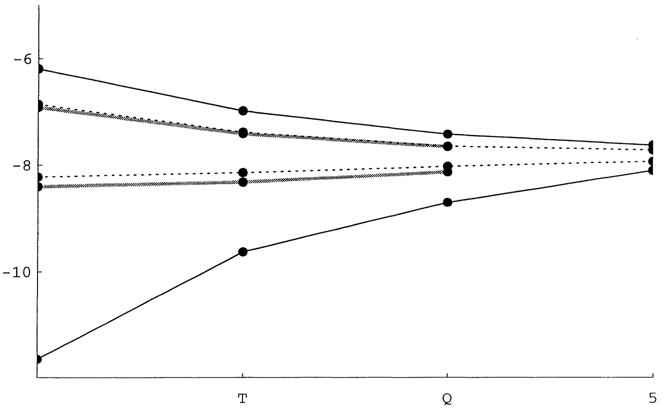

Fig. 3. The MP2 interaction energy of the waer dimer (in mE_h) plotted against the cardinal number X. The *solid lines* are the uncorrected (*lower curve*) and CP corrected (*upper curve*) for the cc-pVXZ basis. The *dashed* and *grey curves* are used for the aug-cc-pVXZ and daug-cc-pVXZ energies, respectively

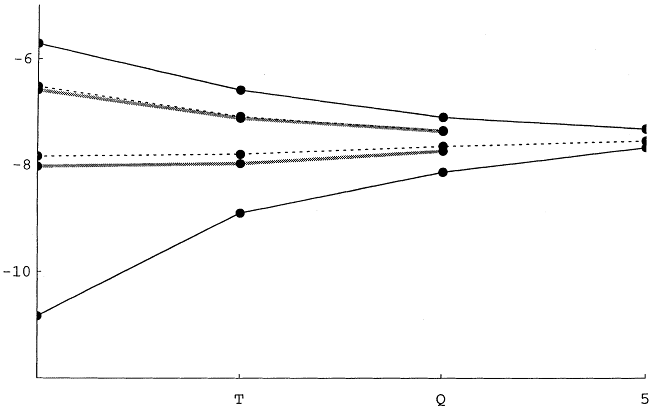

Fig. 4. The CCSD interaction energy of the water dimer (in mE_h) plotted against the cardinal number X. The *solid lines* are the uncorrected (*lower curve*) and CP corrected (*upper curve*) for the cc-pVXZ basis. The *dashed* and *grey curves* are used for the aug-cc-pVXZ and daug-cc-pVXZ energies, respectively

rected – for each wave function model in the three series of basis sets as a function of the cardinal number. In agreement with the above statements, we first note that the plots for the three correlated wave functions look alike and differ significantly from the SCF plot. From Table 3 and Fig. 2, we see that, for the standard basis sets at the SCF level, the CPC gives a significant improvement in the interaction energy; even for the small basis sets, the counterpoise-corrected interaction energy is close to the basis set limit. The same is true for the smaller sets in the two augmented series in contrast to the situation at the correlated levels. From the correlated results in Figs. 3–5, we see that diffuse functions reduce the basis set error significantly and should therefore always be used. With augmented basis sets, the CPC interaction energies are more sensitive to the size of the basis set than are the uncorrected energies. Interestingly, the uncorrected interaction energies are close to the basis set limit even at the augmented double-zeta level. It is of some interest to examine whether this behaviour holds not only for the water dimer, but for hydrogen-bonded systems in general. We have therefore also examined the hydrogen fluoride dimer. As for the water dimer, we optimized the geometry at the CCSD(T)/aug-cc-pVTZ level with the monomer geometry fixed at the experimental geometry [48]. The results are given in Tables 9 (coordinates) and 10 (bond length and angles). In Table 10 we have also given the geometry estimated from experiments [49]. The agreement with experimental data is excellent – all parameters are well within the experimental uncertainties. With this agreement in mind, we find it hard to believe that the oxygen-oxygen distance in the water dimer should be as much as 5 pm too short.

To compare the CPC and uncorrected energies in $(HF)_2$, we have plotted the interaction energies in the aug-cc-pVXZ basis sets for $X \leq 4$ in Fig. 6 using the geometry of Table 9. Although the uncorrected curve is not as straight as for the water dimer, the overall picture is the same. The CPC energies are much more sensitive to the size of the basis set than are the uncorrected en-

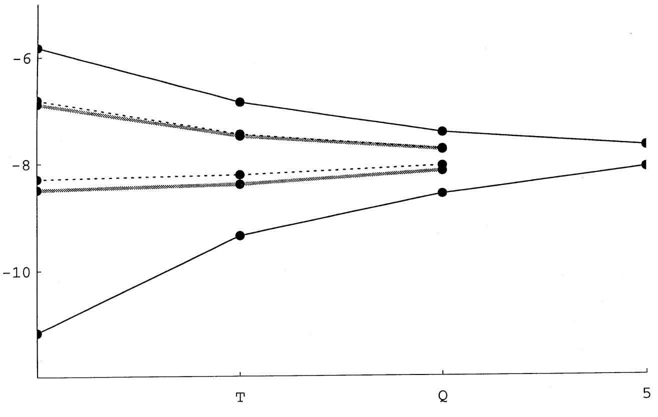

Fig. 5. The CCSD(T) interaction energy of the water dimer (in mE_h) plotted against the cardinal number X. The *solid lines* are the uncorrected (*lower curve*) and CP corrected (*upper curve*) for the cc-pVXZ basis. The *dashed* and *grey curves* are used for the aug-cc-pVXZ and daug-cc-pVXZ energies, respectively

Tabel 9. Cartesian coordinates for the CCSD(T)/aug-cc-pVTZ optimized structure of the hydrogen flouride dimer in atomic units in the center-of-mass coordinate system

Atom	X	Y	Z
H_1	−0.91294702	0.18717624	0.0000000
F_1	−2.63369928	−0.01747484	0.0000000
F_2	2.51153392	0.08692408	0.0000000
H_2	3.21587296	−1.49635635	0.0000000

Table 10. Comparison of calculated and experimental equilibrium geometrical parameters for the hydrogen flouride dimer. The F—F bond distance is in angstroms and the angles are in degrees

	$R_{F—F}$	$<H_1—F_1—F_2$	$<F_1—F_2—H_2$
Calculated	2.7233	5.62	112.82
Experimental	2.72 ± 0.03	10 ± 6	117 ± 6

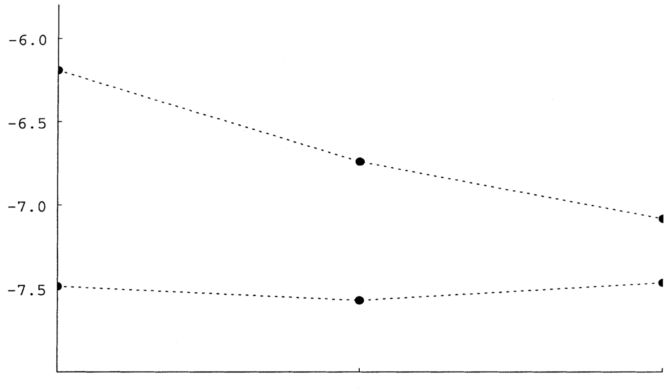

Fig. 6. The CCSD(T) interaction energy of the hydrogen flouride dimer (in $\mathrm{mE_h}$) plotted against the cardinal number X. The upper is the uncorrected and the lower the CP corrected curve for the aug-cc-pVXZ basis

ergies and the uncorrected energies are closer to the basis set limit. It thus appears that this behaviour may be common to hydrogen-bonded dimers.

3.3 The interaction energy of the water dimer

From Table 3, the SCF basis set limit of the interaction energy for the water dimer is found to be −5.62 $\mathrm{mE_h}$ (i.e. −3.53 kcal/mol). This result compares well with the value of −3.55 kcal/mol estimated by Feller, who used a different geometry, with an $R_{O—O}$ distance of 2.911 Å [10].

Since the two series of calculations CPC and uncorrected in the singly augmented basis sets converge towards the same interaction energy, we may estimate the MP2 basis set limit of the interaction energy to be −7.83 ± 0.10 $\mathrm{mE_h}$. This value is obtained as the average of the uncorrected and corrected interaction energies in the aug-cc-pV5Z basis set: −7.83 $\mathrm{mE_h}$; and the uncertainty is (conservatively) estimated as half of the difference between the uncorrected and corrected interaction energies in the same basis. Our MP2 estimate equals −4.91 ± 0.07 kcal/mol and it compares well with the values of −4.9 kcal/mol of Feyereisen et al. [11] and Xantheas et al. [12, 13] and −4.94 kcal/mol of Klopper et al. [30].

At the CCSD level, we estimate the basis set limit of the interaction energy to be −7.50 $\mathrm{mE_h}$ from the average value of the uncorrected and corrected interaction energies, obtained in the aug-cc-pVQZ basis set. This estimate is in good agreement with the converging trend of the uncorrected interaction energy, where we also have determined the aug-cc-pV5Z value. The uncertainty in the CCSD estimate is slightly larger than the uncertainty of the MP2 estimate since not all the CCSD calculations were carried out at the aug-cc-pV5Z level.

At the CCSD(T) level, we obtain an estimate of the basis set limit of the interaction energy of −7.90 $\mathrm{mE_h}$ using the same procedure as for CCSD, which at first yields an uncertainty of 0.16 $\mathrm{mE_h}$. However, by comparing Tables 4 and 6, we note some similarities in the MP2 and CCSD(T) results: the interaction energies calculated as the average of the corrected and uncorrected energies in the aug-cc-pVXZ series display very similar convergence in the two models. Thus, going from aug-cc-pVDZ to aug-cc-pV5Z, the MP2 results are −7.58 ± 0.68, −7.76 ± 0.38, −7.84 ± 0.19 and −7.83 ± 0.10 $\mathrm{mE_h}$, whereas the corresponding CCSD(T) results are −7.55 ± 0.74, −7.83 ± 0.38 and −7.90 ± 0.16 $\mathrm{mE_h}$. We therefore expect the calculated interaction energy of −7.90 $\mathrm{mE_h}$ to be a good estimate of the CCSD(T) basis set limit and that the uncertainty may be narrowed down to at least 0.10 $\mathrm{mE_h}$, yielding an estimate of −4.96 ± 0.06 kcal/mol. The change from the MP2 to CCSD(T) is seen to be about 0.05 kcal/mol in good agreement with our expectations from earlier studies.

At the 6-311++G(2*d*,2*p*)/MP2 level, Feller found that the energy penalty incurred by not relaxing the monomer geometry amounted to 0.03 kcal/mol [10]. Adding this correction to our estimated CCSD(T) basis set limit and to the uncertainty, we finally arrive at −5.0 ± 0.1 kcal/mol for the interaction energy at the CCSD(T) level, taking monomer relaxation into account. This value compares favourably with the experimentally estimated value of −5.4 ± 0.7 kcal/mol, i.e. it is well within the error bars of the experimental estimate and has a precision that is significantly higher.

4 Conclusion

An ab initio investigation of the water dimer has been carried out. We have calculated the equilibrium geometry at the MP2 level (uncorrected and CPC corrected) using basis sets up to aug-cc-pVQZ and at the CCSD(T) level using basis sets up to aug-cc-pVTZ. Based on these calculations, the $R_{O—O}$ equilibrium distance is estimated to be 2.90 Å, challenging the experimentally estimated value of 2.946 Å. The CCSD(T) basis set limit of the interaction energy is estimated to be equal to −5.0 ± 0.1 kcal/mol, confirming previous estimates of the correlation effects beyond MP2 and narrowing down the uncertainty in the experimentally estimated value of −5.4 ± 0.7 kcal/mol.

The calculations carried out on the water dimer have demonstrated and confirmed the importance of diffuse functions for the reliable calculation of interaction energies of hydrogen-bonded systems. More surprisingly, our calculations on the water and hydrogen-fluoride dimers have demonstrated that, for the correlated models and for the augmented correlation-consistent basis sets, the CPC interactions energies are considerably more sensitive to the size of basis set than are the uncorrected energies. Moreover, in the uncorrected calculations, even the small aug-cc-pVDZ basis set gives results close to the basis set limit. It would be interesting to investigate whether this behaviour holds for hydrogen-bonded systems in general.

Our calculations show that in order to establish the basis set limit of interaction energies unambiguously, there is no substitute for a series of calculations carried out in a hierarchical set of basis sets that include diffuse basis functions. CPC can never serve as a remedy for an inadequate basis set. However, together with the uncorrected interaction energies, the CPC energies make error estimation easier and more reliable.

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