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Application of systematic sequences of wave functions to the water dimer

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A systematic series of calculations encompassing a wide range of basis sets and correlated methods has been used to estimate the complete basis set, full CI hydrogen bond strength in the water dimer system. The largest basis set included up through h polarization functions on oxygen and g functions on hydrogen. The complete basis set limit for the self-consistent-field (SCF) interaction energy is estimated to be -3.55 kcal/mol with an accompanying correlation contribution of ~ -1.5 kcal/mol. This leads to an interaction energy of -5.1 kcal/mol, exclusive of vibrational zero-point considerations, and is in good agreement with experimental measurements of -5.4 ± 0.7 kcal/mol. Inclusion of an approximate adjustment for the basis set superposition error via the Boys/Bernardi counterpoise correction was found to substantially improve agreement with ΔE_∞ , our estimate of the complete basis set interaction energy, at the both the SCF and correlated levels for basis sets that were lacking in sufficient near-valence diffuse functions. For diffuse-function-augmented basis sets, application of the CP correction was found to sometimes worsen agreement with ΔE_∞ .

INTRODUCTION

Because of its fundamental importance in chemical and biological processes the water dimer has been the subject of numerous theoretical studies. As often happens when a variety of research groups examine the same molecular system using a wide assortment of *ab initio* techniques, the system evolves into a testbed for new methods. Among these systems relatively few generate sustained interest over a long enough period of time that it is possible to trace more than a decade's evolution in hardware and software merely by reading the associated literature. However, the $\text{H}_2\text{O}-\text{H}_2\text{O}$ system certainly falls into this category, with minimal basis set calculations appearing as early as 1979.¹

Both theoretical² and experimental³ studies have established the global minimum on the water dimer potential energy surface to possess C_s symmetry, as is seen in Fig. 1. Experimental estimates of the interaction energy place it at -5.4 kcal/mol,^{4,5} where vibrational effects and finite temperature effects have been subtracted. Among the many investigations of the water dimer found in the literature, some have been carried out with extended basis sets and highly correlated methods.⁶ Baum and Finney² used singles and doubles CI (SD-CI) to explore the dimer potential surface, relying on a reference energy obtained from water monomers at 500 Å plus the Davidson⁷ correction to partially offset the size extensivity problem. Frisch *et al.*^{8,9} reported the results of restricted Hartree-Fock (RHF) and second-order Møller-Plesset (MP2) geometry optimizations, which were followed by fourth-order (MP4) evaluations of the energy at the optimal structures. Interaction energies obtained with a range of basis sets, starting with the STO-3G minimal basis on up to the 6-311++G(3df,2dp) set with multiple polarization functions, were listed. Likewise, Szalewicz *et al.*¹⁰ used a wide range of basis sets with up to fourth-order many body perturbation theory and coupled cluster theory. The latter two studies both predicted

$\text{H}_2\text{O}-\text{H}_2\text{O}$ interaction energies in the vicinity of -4.7 kcal/mol. The correlation correction was estimated to contribute about -1 kcal/mol to this value. In a recent study of hydrogen bonding in ice, White and Davidson¹¹ computed the dimerization energy with multireference variational perturbation theory (MR-VARPT),¹² a method which yields a smaller size consistency error than conventional SD-CI. By employing a corresponding orbital transformation that maximized the similarity of the dimer orbitals to the monomer orbitals and using size extensive reference spaces, they minimized some of the drawbacks commonly associated with CI treatments.

By way of comparison, several monomer energies are also listed in Table I in order to establish the basis set limit. Feller *et al.*¹³ have reported energies and one-electron properties derived from large contracted, even-tempered Gaussian basis sets at both the self-consistent-field (SCF) and CI levels. To the best of our knowledge, Clementi and co-workers¹⁴ have reported the lowest SCF energy, a mere 0.0001 hartree (1 hartree = 627.51 kcal/mol) above the estimated HF limit,¹⁵ which they obtained with an extremely

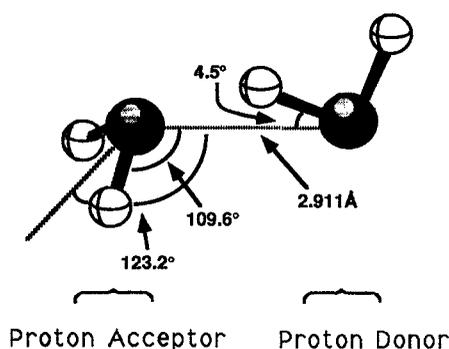


FIG. 1. The water dimer geometry used in the present work. Monomer fragments used $R_{\text{OH}} = 0.9571$ Å and an HOH bond angle of 104.34° .

TABLE I. Previous calculations of the water monomer and the water dimer interaction energy.^a

Basis set	#Funct.'s	SCF		Correlated			Ref.
		$E(\text{H}_2\text{O})$	$\Delta E_{\text{dimeriz}}$	Method	$E(\text{H}_2\text{O})$	$\Delta E_{\text{dimeriz}}$	
[3s,2p,1d/2s,1p]	24	-76.0630	-4.25 (-4.13)	SD-CI		+11.51 (+12.25)	11
				MP2		-1.63 (-0.50)	
				MRVARPT		+0.06 (+0.78)	
[4s,3p,1d/2s,1p]	29			MP4		-5.57 (-5.15)	18
[4s,3p,2d/2s,1p]	35		-3.79 (-3.64)	MP2		-5.48 (-4.22)	27
[5s,4p,1d/3s,1p]	35	-76.0520	-4.99 (-4.11)	SD-CI + Q	-76.2661	-6.00 (-4.37)	1
6-311 + + G(2df,2p)	47	-76.0494	-4.41 (-3.79)	MBPT(2)		-5.90 (-4.25)	10
				MBPT(4)		-5.90 (-4.30)	
				CCSD-T		-5.78 (-4.34)	
				MBPT		-5.08 (-4.42)	
6-311 + + G(3df,3pd)	75	-76.0587	-4.01 (-3.72)	MP2	-76.3243	-5.4 (-4.5)	9
6-311 + + G(3d2f,3p2d)	101	-76.0658	-3.78 (-3.73)	MP4	-76.3387	-5.3 (-4.6)	
6-311 + + G(3df,3pd)	75	-76.0587	-3.8 (-3.4)	MR SD-CI	-76.3366		
				MR SD-CI ^b	-76.3861		13
[14s,10p,4d,1f/6s,4p,1d]	120	-76.0672					
(28s,18p,8d,3f/18s,8p,3d)	143	-76.0674					14
Est. HF limit		-76.0675					15

^a Water energies are given in hartrees. The dimerization energies, $\Delta E_{\text{dimeriz}}$, are given in kcal/mol with the counterpoise-corrected values in parentheses. Unless otherwise noted, all correlated calculations were of the frozen core variety, i.e., the 1s pairs of electrons on the oxygen were not correlated.

^b All electrons were correlated.

big (28s,18p,4d,1f/18s,8p,3d) uncontracted set.

Other recent investigations of the dimer have examined the higher lying C_{2v} bifurcated transition state¹⁶ and numerous transition states for hydrogen interchange.¹⁷ Niesar *et al.*¹⁸ computed a large number of water dimer configurations with a polarized basis set at the MP4 level in order to improve the MCY two-body water-water potential. Some representative energies of the water monomer and the dimerization energy, taken from the literature, are listed in Table I.

Prior to beginning a series of calculations on novel hydrogen bonds in larger molecules we felt it necessary to calibrate our basis sets and computational models against the wealth of data on the prototype water-water system. This comparison was judged all the more important because the targeted hydrogen bonds were anticipated to be only half as strong as the typical 5-7 kcal/mol bond in hydrogen fluoride, water, or ammonia dimers. In the course of these calibration studies we have performed calculations of the $\text{H}_2\text{O}-\text{H}_2\text{O}$ bond strength using larger basis sets and more extensive correlation recovery than any in the existing chemical literature. Beyond calibrating new basis sets and computational methods, a secondary goal of the present work was to improve our estimate of the hydrogen bond strength in the water dimer as one approaches the complete basis set/full CI limit. The use of a systematic approach to basis set expansion and correlation recovery increases the likelihood of establishing accurate convergence trends and should improve our ability to refine the convergence limit.

PROCEDURE

Basis sets

Most of the calculations reported in the present work were carried out at the optimal O-O distance (2.911 Å) and bond angles found by Frisch *et al.*⁹ at the 6-

311 + + G(2d,2p)/MP2 level of theory. This structure is illustrated in Fig. 1. The individual monomer fragment geometries were frozen at the optimal 6-311 + + G(2d,2p)/MP2 level ($R_{\text{OH}} = 0.9571$ Å, HOH angle = 104.34°) in order to facilitate the basis set superposition (BSSE) analysis. The energy penalty incurred by not using relaxed monomer fragments in the dimer is quite small, amounting to only 5×10^{-5} hartree at the 6-311 + + G(2d,2p)/MP2 level. Trends established with smaller basis sets indicate that the potential surface becomes flatter as the basis set is enlarged. Thus with the very extended basis sets used in the present study any differences attributable to the use of a single geometry for all calculations, as opposed to reoptimizing the structure with each new basis set, should be minimal. Unless otherwise noted, all dimer calculations were performed with the cartesian coordinates listed in Table II.

Microwave spectral data have been interpreted by Odotola and Dyke¹⁹ as indicative of an O-O distance closer to 2.977 Å. MP2 calculations with a polarized basis set at the SCF optimized structure of Szalewicz *et al.*,¹⁰ which has similar OH bond lengths and HOH angles to the experimental structure plus an even longer O-O distance of 3.001 Å,

TABLE II. Cartesian coordinates (in bohr) for the water dimer.

Atom	X	Y	Z
O	0.0	0.0	0.0
H	-0.607 40	-0.928 21	1.428 53
H	-0.607 40	-0.928 21	-1.428 53
H	3.697 89	0.141 90	0.0
H	6.085 02	1.711 75	0.0
O	5.500 96	0.0	0.0

TABLE III. Basis sets used in the present work.

Name	# Funct.'s (Water)	Oxygen	Hydrogen
cc-pVDZ	24	(9s,4p,1d) → [3s,2p,1d]	(4s,1p) → [2s,1p]
aug-cc-pVDZ	41	above + diffuse (s,p,d)	Above + diffuse (s,p)
cc-pVTZ	58	(10s,5p,2d,1f) → [4s,3p,2d,1f]	(5s,2p,1d) → [3s,2p,1d]
aug-cc-pVTZ	92	above + diffuse (s,p,d,f)	Above + diffuse (s,p,d)
cc-pVQZ	115	(12s,6p,3d,2f,1g) → [5s,4p,3d,1g]	(6s,3p,2d,1f) → [4s,3p,2d,1f]
aug-cc-pVQZ	174	above + diffuse (s,p,d,f,g)	Above + diffuse (s,p,d,f)
cc-pV5Z	201	(14s,7p,4d,3f,2g,1h) → [6s,5p,4d,3f,2g,1h]	(8s,4p,3d,2f,1g) → [5s,4p,3d,1g]

shows a difference in energy relative to the geometry we have chosen to be < 0.0004 hartree. The differences between the *ab initio* and experimental estimates of the O–O distance have been attributed to large anharmonic corrections.

In order to have any hope of identifying basis set convergence patterns it is essential that one be able to perform a series of calculations in which the basis set is *systematically* improved until either the quantity in question has converged within acceptable tolerances or the basis set size needed to reach convergence becomes apparent. We have chosen the new Dunning²⁰ correlation consistent basis sets, labeled cc-pVxZ ($x = D, T, Q, 5$ for double, triple, etc.), and their extensions to include more diffuse functions, labeled aug-cc-pVxZ.²¹ The original correlation consistent basis sets were chosen so that all functions that contribute roughly equal amounts to the correlation energy of the atomic ground states are grouped together. This concept was expanded beyond a consideration of just the neutral atoms with the development of the augmented basis sets for anions.

Taken as a whole, these sets span a range of almost 2 orders of magnitude in size, with the largest containing over 200 functions when applied to the water monomer. Obviously, such sets are currently prohibitively expensive for use in bigger systems. We include them here primarily for the sake of establishing the degree to which smaller sets have approached the complete basis set limit.

The composition of the correlation consistent basis sets

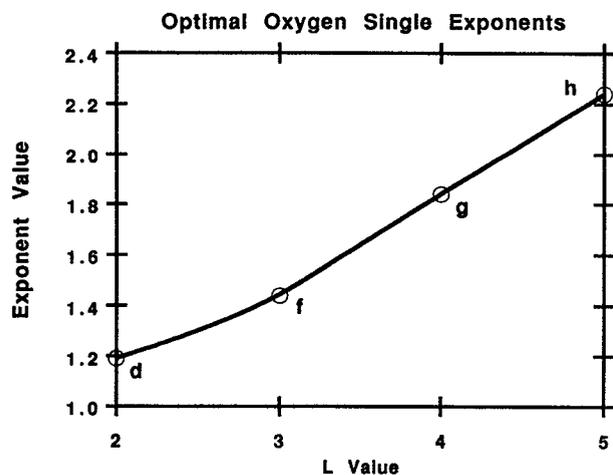


FIG. 2. Optimal exponent values for the first polarization function of each type added to the oxygen atom.

on oxygen and hydrogen are listed in Table III. The notation $(Ls, Mp, Nd) \rightarrow [ls, mp, nd]$ means that, for example, *Ls*-type Gaussian primitives were contracted to *ls*-type basis functions. Only the spherical components of the polarization functions are used (i.e., five component *d*'s, seven component *f*'s, etc.). Because the optimal *h*-function exponent on oxygen ($\zeta_h = 2.240$) and *g*-function exponent on hydrogen ($\zeta_g = 2.358$) for the cc-pV5Z were not available, we optimized their values at the MP2 and SD-CI (in H_2) levels, respectively. Previous exponent optimization for the correlation consistent basis sets was done at the SCF or SD-CI level. The choice of MP2 for the oxygen *h* function exponent was motivated because of a lack of availability of a flexible SD-CI package that supported high enough ℓ values. As seen in Fig. 2, the values of the optimal exponents for the first oxygen *d, f, g,* and *h* functions increase almost linearly with the ℓ quantum number, making it an easy matter to estimate the next member of the set.

Much attention has been focused on the proper way to account for the so-called "basis set superposition error" (BSSE) when computing binding energies. This becomes especially important when dealing with bond strengths of 5 kcal/mol or less where the effect may be larger than the quantity to be measured. The BSSE manifests itself as an additional, artifactual energy lowering accrued by both molecular fragments when they approach within a short enough distance that each fragment finds it possible to offset their individual basis set inadequacies with functions from the other fragment. These functions are sometimes referred to as "ghost functions." If the BSSE is improperly handled, or ignored, it is possible to considerably overestimate the true strength of the interaction.

Boys and Bernardi²² proposed an approximate method for estimating the BSSE that involves replacing the energies of the isolated monomers with the energies of the monomers calculated in the full dimer basis set. This technique, known as the function counterpoise (CP) method, has been criticized for both overestimating and underestimating the true BSSE.²³ While some researchers have defended the counterpoise correction,²⁴ others have proposed their own variants. For example, Loushin *et al.*²⁵ argue that a better approach should include not only the ghost functions of the other monomer, but a "ghost field" due to the other center's electric field. They call their approach the "polarization counterpoise method." Gutowski *et al.*²⁶ formally argued that the entire set of ghost functions should be included in the CP correction. Similarly, Szczesniak and Scheiner²⁷ have ad-

vanced the argument that the full ghost set should be used at the MP2 level.

Latajka and Scheiner²⁸ point out that the “secondary” BSSE effect, first noticed by Karlstrom and Sadlej²⁹ in minimal basis set calculations on the water dimer, can be as large as the “primary” BSSE which the CP correction seeks to address. The secondary BSS is attributed to changes in the monomer’s electric moments induced by the ghost functions. For systems where the principal interaction is purely electrostatic, such as the H_3N-Li^+ complex studied by Latajka and Scheiner, the secondary BSSE is of varying sign depending upon the separation distance and can even exceed the primary BSSE. Such is *not* the case for the water dimer. A Morokuma analysis³⁰ of the water dimer interaction energy shows the electrostatic portion to only one of several contributions which are all of approximately equal size. Thus we expect the secondary BSSE to be much smaller in the water dimer than in the H_3N-Li^+ complex. Given the difficulty in correcting for it, the secondary BSSE is likely to remain unaccounted except in those cases where the bonding is largely electrostatics. Lacking a universally agreed upon definition of the BSSE, it is difficult to “prove” that any one particular technique is to be preferred over the others. We shall take a pragmatic approach and compare both uncorrected and CP corrected energies against our best estimates of the basis set limit interaction energies, denoted ΔE_∞ .

As will be seen, it is possible to employ basis sets with the proper size and composition such that the estimated BSSE is reduced to levels below 0.1 kcal/mol even at the correlated level of theory. This will be achieved using basis sets which were not specifically tailored for the water molecule. At the SCF level, White and Davidson¹¹ demonstrated that a small $[3s,2p,1/2s,1p]$ basis which was carefully constructed for the purpose of describing interaction between water molecules can achieve a BSSE of less than 0.1 kcal/mol.

Levels of theory

As already noted, a wide variety of computational techniques, ranging from RHF to perturbation theory and CI, have been used to evaluate the water dimer interaction energy. Experience has shown that RHF theory performed with large basis sets falls about 2 kcal/mol below the experimental value. Correlated methods improve on this, although some care must be exercised to ensure that the correlated method is “size extensive” (i.e., the energy of two noninteracting water molecules computed with the method in question should yield twice the energy of a single water molecule). Singles and doubles CI based on a one reference configuration is probably the most widely recognized example of a method that fails in this regard. However, various extensions to SD-CI, such as the use of size extensive reference spaces or the so-called quadratic CI methods, QCISD

TABLE IV. Total energies for the water molecule and computed interaction energies for the water dimer.

Theory	$E(H_2O)^a$	cc-pVDZ			$E(H_2O)$	aug-cc-pVDZ		
		$\Delta E_{dimeriz}$	Acceptor	Donor		$\Delta E_{dimeriz}$	Acceptor	Donor
SCF	-76.0268	-5.75 (-3.70)	-76.0297	-76.0272	-76.0414	-3.79 (-3.55)	-76.0417	-76.0415
MP2	-76.2284	-7.30 (-3.93)	-76.2332	-76.2291	-76.2608	-5.17 (-4.32)	-76.2617	-76.2612
SD-CI	-76.2300	+4.67 (+7.69)	-76.2342	-76.2305				
MP4	-76.2407	-7.10 (-3.73)	-76.2454	-76.2413	-76.2743	-5.20 (-4.27)	-76.2754	-76.2748
QCISD	-76.2381	-6.84 (-3.64)	-76.2426	-76.2387	-76.2691	-4.93 (-4.12)	-76.2700	-76.2695
QCISD(T)	-76.2411	-7.02 (-3.71)	-76.2457	-76.2417	-76.2740	-5.21 (-4.29)	-76.2750	-76.2744
Est. Full CI ^c	-76.2416	-6.0 (-2.5)	-76.2468	-76.2420				

Theory	$E(H_2O)$	cc-pVTZ			$E(H_2O)$	aug-cc-pVTZ		
		$\Delta E_{dimeriz}$	Acceptor	Donor		$\Delta E_{dimeriz}$	Acceptor	Donor
SCF	-76.0572	-4.37 (-3.55)	-76.0583	-76.0574	-76.0606	-3.61 (-3.54)	-76.0607	-76.0607
MP2	-76.3186	-6.04 (-4.40)	-76.3208	-76.3191	-76.3290	-5.10 (-4.64)	-76.3294	-76.3293
MP4	-76.3330	-5.95 (-4.32)	-76.3351	-76.3335	-76.3436	-5.14 (-4.66)	-76.3441	-76.3439
QCISD	-76.3249	-5.60 (-4.15)	-76.3268	-76.3253	-76.3425	-4.89 (-4.46)	-76.3346	-76.3345
QCISD(T)	-76.3324	-5.87 (-4.32)	-76.3344	-76.3328	-76.3425	-5.16 (-4.69)	-76.3430	-76.3428

Theory	$E(H_2O)$	cc-pVQZ			$E(H_2O)$	aug-cc-pVQZ		
		$\Delta E_{dimeriz}$	Acceptor	Donor		$\Delta E_{dimeriz}$	Acceptor	Donor
SCF	-76.0648	-3.90 (-3.57)	-76.0652	-76.0650	-76.0660	-3.60 (-3.56)	-76.0417	-76.0415
MP2	-76.3476	-5.45 (-4.67)	-76.3486	-76.3479	-76.3519	-5.05 (-4.81) ^b		

Theory	$E(H_2O)$	cc-pV5Z	
		$\Delta E_{dimeriz}$	
SCF	-76.0671	-3.66	
MP2	-76.3586		

^a Water energies are given in hartrees. The dimerization energies, $\Delta E_{dimeriz}$, are given in kcal/mol with the counterpoise-corrected values in parentheses. All correlated calculations were done within the frozen core approximation, i.e., the $1s$ pairs of electrons on the oxygen were not correlated.

^b Estimated aug-cc-pVQZ basis set results. See the text.

^c Estimated by fitting MR SD-CI energies with an exponential form, as described in the text.

and QCISD(T), proposed by Pople and co-workers,^{31,32} can overcome the size extensivity problems. In the present work, we have combined the systematic correlation consistent basis sets with various orders of perturbation theory and several types of CI. All of the quadratic CI calculations and some of the smaller basis set Møller-Plesset calculations reported here were done with GAUSSIAN 90.³³ Larger basis set MP2 calculations were done with DISCO,³⁴ a direct SCF/MP2 program. Multireference single and double excitation CI's (MR SD-CI's) were done with MELDF-X.³⁵

RESULTS

RHF

The results of RHF calculations with the cc-pVxZ and aug-cc-pVxZ families of basis sets are tabulated in Table IV. Figure 3 shows the convergence of the water molecule's total energy and the corresponding water dimer BSSE's computed with all but the valence quintuple zeta basis. The latter results were not plotted for the sake of clarity, since they are indistinguishable from the aug-cc-pVQZ values.

The cc-pVDZ basis was found to possess a sizable 0.0033 hartree (2.1 kcal/mol) BSSE, which decreases by over an order of magnitude to only 0.0003 hartree (0.24 kcal/mol) when the diffuse (*s,p,d/s,p*) functions from the aug-cc-pVDZ basis set are included. Most of this decrease in the BSSE is a consequence of the improved description of the

oxygen lone pair electrons on the proton acceptor fragment. Of the remaining 0.0003 hartree BSSE the majority (~66%) is due to further inadequacies of the basis set in the valence region and not to shortcomings of the (1*s*,2*s*,2*p*) AO's. This was demonstrated by replacing the original cc-pVDZ 1*s*, 2*s*, and 2*p* AO's, which are expanded in terms of nine *s*-type Gaussians and four *p*-type Gaussians, with AO's defined in terms of (14*s*,9*p*). The resulting basis set, denoted aug-cc-pVDZ* in Fig. 3, produced a BSSE of 0.0002 hartree, only 33% less than the aug-cc-pVDZ set, thus suggesting that the source of the remaining BSSE must be outside the space of the oxygen AO's. Each of the unaugmented basis set's BSSE shows a substantial improvement when diffuse functions are added.

In spite of the size of the cc-pV5Z basis, the water monomer SCF energy listed in Table IV is still several tenths of a millihartree above two previously published values which appear at the bottom of Table I and 0.0004 hartree higher than the estimated HF limit. Thus the dimer's energy in this basis can be expected to be approximately 1 mhartree above the HF limit. Almost all of the observed deviation from the HF limit resides in the (*s,p,d/s,p*) portion of the basis set, as demonstrated by comparing the SCF energy obtained with the (*s,p,d/s,p*) portion of the cc-pV5Z basis with the (28*s*,18*p*,8*d*/18*s*,8*p*) results of Clementi *et al.*¹⁴

Figure 4 shows the convergence of the water-water interaction energy at the SCF level as a function of the basis set size. The raw cc-pVxZ basis set ΔE 's (i.e., those obtained without CP corrections) exhibit a very slow convergence to the apparent limiting value in the vicinity of -3.55 kcal/mol for the gas phase monomers. Even with a relatively large (*s,p*) set supplemented with up to *g* functions on oxygen and *f* functions on hydrogen, the cc-pVQZ basis yields an SCF interaction energy that is in error by >0.3 kcal/mol. Although, in an absolute sense, 0.3 kcal/mol is a small amount of energy it nonetheless represents more than 15% of the difference between the ΔE obtained with the smallest basis

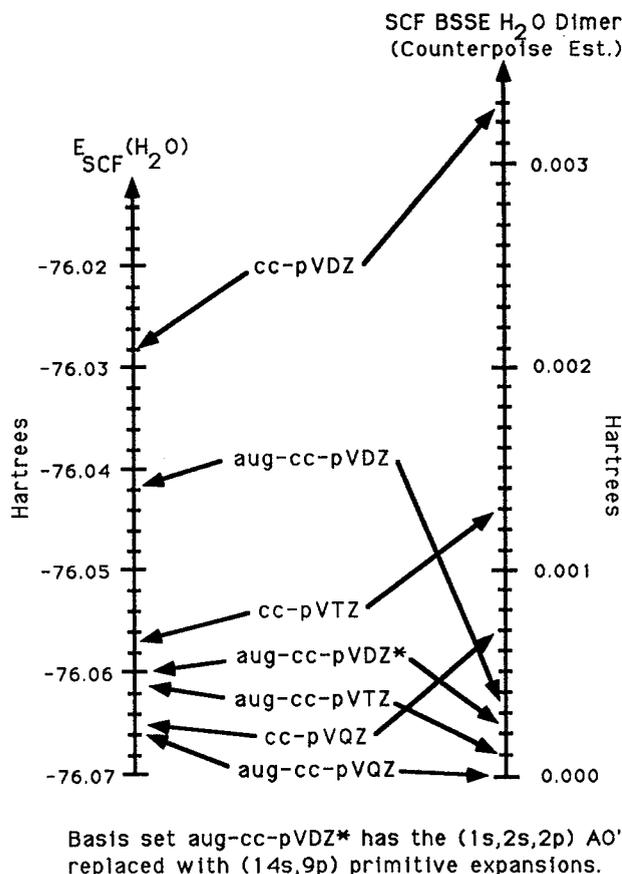


FIG. 3. SCF water energies and basis set superposition energies for the water dimer (in hartrees).

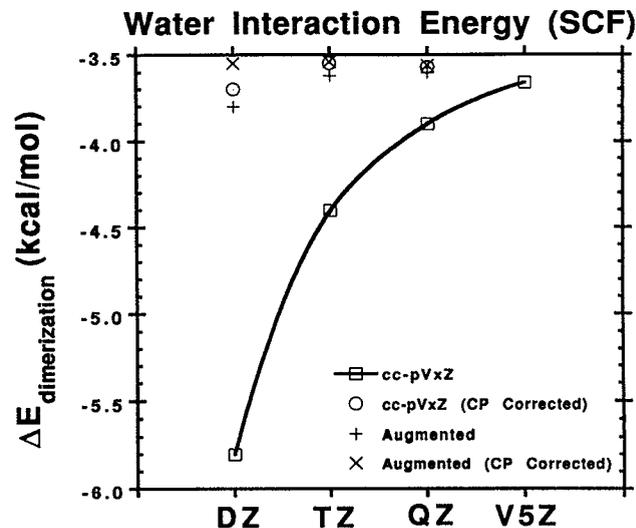


FIG. 4. Convergence of the SCF interaction energy with and without the counterpoise correction.

set and our best estimate of the HF limit. On the other hand, with the addition of diffuse functions to the double zeta basis, or the enlarging of the core set to the triple zeta level and beyond, the computed interaction energies converge quite rapidly to the limiting value. Because of the expense of the calculations, the CP correction was not applied to the results obtained with the (cc-pV5Z) basis set. We estimate that the uncorrected ΔE overestimates the basis set limit by ~ 0.1 kcal/mol in spite of the use of over 400 basis functions on the dimer.

Application of the Boys and Bernardi²² counterpoise correction to the raw ΔE 's results in significantly better agreement with our estimate of the HF limit interaction energy, ΔE_{∞} (SCF) = -3.55 kcal/mol for those basis sets that lack extra diffuse functions. Moreover, even the diffuse-function-augmented sets show some improvement. In general, the CP corrected ΔE 's show remarkable stability as the size of the basis set is increased, in agreement with similar trends observed previously.²⁷

It has been argued that the CP correction does not provide quantitative improvements⁹ and is less efficient than merely recomputing ΔE with a larger basis set.³⁶ This conclusion has been questioned by Szalewicz *et al.*¹⁰ The present results suggest that the effectiveness of the CP correction at the SCF level is highly dependent on the nature of the basis set. As already mentioned, the CP correction produces significantly improved results when used in conjunction with basis sets that lack sufficient diffuse functions. When used with the larger aug-cc-pVxZ basis sets, the benefits are less clear, but in no case did the correction ever worsen agreement with the HF limiting value.

Popkie *et al.*³⁷ estimated the HF limit for the dimerization energy to be -3.90 ± 0.25 kcal/mol on the basis of large (*s,p,d,f*) basis set calculations. Subsequently, Szalewicz *et al.*¹⁰ proposed a downward revised estimate of -3.73 ± 0.05 kcal/mol, whereas our own -3.55 kcal/mol is still smaller and sits outside the error bars of both previous estimates. Since the geometry used by Szalewicz *et al.* differs slightly from the one we have chosen, we performed calculations using their geometries in order to ascertain the size of this effect. The resulting interaction energy was 0.03 kcal/mol less than our previous finding using the

geometry in Table II, thus *increasing* the disagreement between our two estimates of the HF limit. Other researchers, while avoiding a prediction of the HF limit, have nonetheless reported binding energies that are both larger and smaller than these. Using the 6-311 + + G(3*df*,3*pd*) basis set, Frisch *et al.*⁹ obtained a CP corrected SCF interaction energy of -3.4 kcal/mol, while White and Davidson¹¹ reported a value as large as -4.1 kcal/mol.

Correlated methods

Among the correlated methods that we chose to use, second-order Møller–Plesset perturbation theory (MP2) is computationally the fastest and, thus easiest to extend to larger basis sets. In spite of this, it proved impractical to directly compute the dimer's MP2 energy with the two largest basis sets listed in Table III. The aug-cc-pVQZ basis set would have required a dimer calculation with 348 basis functions in C_s symmetry and proved to be prohibitively large. Therefore, we investigated the possibility of estimating the dimer interaction energy at the aug-cc-pVQZ level by assuming that the effects of the diffuse higher angular momentum functions were additive. The accuracy of the additivity approximation was calibrated through a series of calculations with the triple zeta basis sets.

Base line energies are obtained using a cc-pVTZ basis augmented with a set of diffuse (*s,p*) primitives on the oxygens and a diffuse *s* primitive on the hydrogens. Next, a set of diffuse *d*'s was added to oxygen along with a set of *p*'s to hydrogen to give the energies shown in Table V. Up to this point no approximation has been invoked since we have rigorously evaluated the cc-pVTZ + (*spd/sp*) energies. The first approximation is introduced at the point where a final set of calculations was performed with the *d*'s and *p*'s replaced with *f*'s (on oxygen) and *d*'s (on hydrogen).

Table V shows that most of the effects of the extra diffuse functions have been accounted for at the cc-pVTZ + (*spd/sp*) level. The SCF interaction energy predicted by assuming additivity agrees within 0.03 kcal/mol with the aug-cc-pVTZ value which we are trying to estimate. However, at the correlated MP2 level the estimated ΔE and BSSE are in error by 0.14 and 0.07 kcal/mol, respectively. The net effect of the diffuse (*f/d*) set is being overestimated

TABLE V. Test of the MP2 energy additivity approximation for the diffuse functions in the aug-cc-pVTZ basis.^a

Basis	ΔE (SCF) ^b	ΔE (MP2) ^b	BSSE(MP2)
cc-pVTZ	-4.37	-6.04	1.64
cc-pVTZ + diffuse (<i>sp/s</i>)	-3.72	-5.05	0.60
Calc. contrib. of diffuse (<i>d/p</i>) set	0.14	+0.13	-0.19
Est. aug-cc-pVTZ ^c	-3.58	-4.92	0.41
Est. contrib. of diffuse (<i>f/d</i>) set ^d	-0.01 (-0.03) ^e	-0.32 (-0.18)	+0.12 (+0.05)
Est. aug-cc-pVTZ ^d	-3.59	-5.24	0.53
aug-cc-pVTZ	-3.61	-5.10	0.46

^a Energies are in kcal/mol.

^b Without counterpoise correction.

^c Based on calculations using the cc-pVTZ + diffuse (*spd/sp*) basis.

^d Based on calculations using the cc-pVTZ + diffuse (*spf/sd*) basis.

^e Actual contribution of the diffuse *f* set based on aug-cc-pVTZ calculations.

by roughly a factor of 2 because of an effect whereby neighboring atoms exploit the availability of the diffuse f and d functions so as to offset, to some extent, their own lack of diffuse d 's and p 's, in a manner reminiscent of the BSSE already discussed. Naturally when the complete aug-cc-pVTZ set is used, this phenomenon is prevented from happening, and the true effect of the (f/d) set is much reduced. It is expected that the amount by which the true contribution of a particular ($l + 1/l$) diffuse set to the binding energy is overestimated will increase with l simply because the number of functions involved increases.

Therefore, when attempting to estimate the aug-cc-pVQZ MP2 results we scaled the contributions of the (f/d) and (g/f) sets by a factor of 2. The impact of this scaling is less than might be expected from an examination of the triple zeta findings, because the total contribution of all diffuse sets is much less with the larger basis. For example, the diffuse (d/p) set contributed +0.13 kcal/mol to the cc-pVTZ MP2 interaction energy, but only 0.06 kcal/mol to the cc-pVQZ value. The *estimated* aug-cc-pVQZ MP2 interaction energy is -5.05 kcal/mol, whereas the cc-pVQZ + (spd/sp) interaction energy, which involved no approximation basis set treatment, is -4.98 kcal/mol.

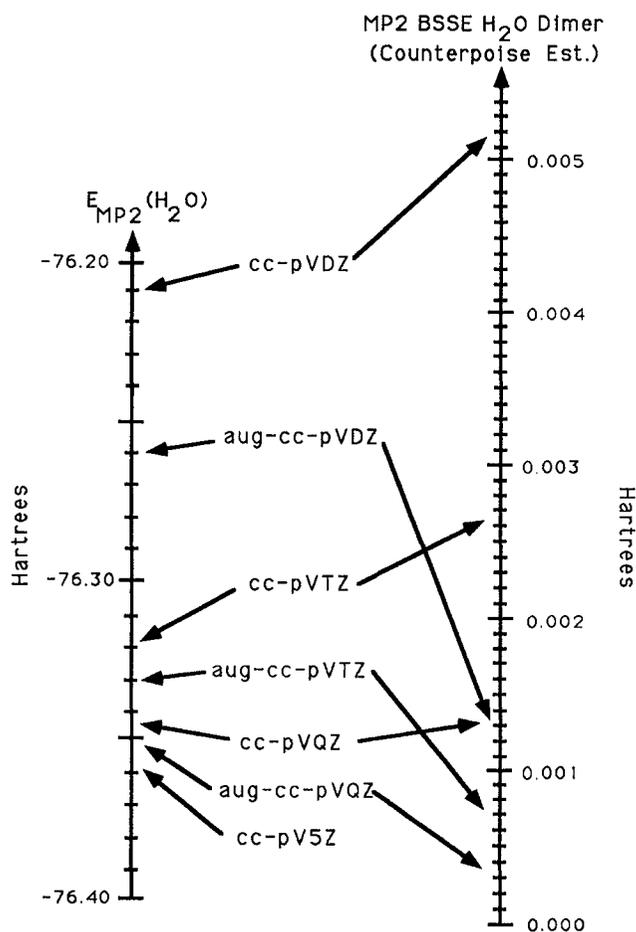


FIG. 5. MP2 water energies and basis set superposition energies for the water dimer (in hartrees).

TABLE VI. Contributions to the MP2 water energy and the water-water interaction energy from higher L functions in the aug-cc-pVTQ basis.^a

Functions		Water energy	non-CP Inter. contribution
Oxygen	Hydrogen		
d 's	p 's	89.24	2.95
f 's	d 's	17.97	0.03
g 's	f 's	5.07	0.01
$(h)^b$	$(g)^b$	1.50	

^a Water energy contributions and water-water interaction energies are in kcal/mol. The [$s,p/s$] portion of the aug-cc-pVQZ basis yielded MP2 energies of -76.172 97 and -152.358 57 for the monomer and dimer, respectively.

^b The aug-cc-pVQZ basis does not contain any h functions on oxygen or g functions on hydrogen. These estimates are based on adding the oxygen h and hydrogen g from the cc-pV5Z basis.

In analogy to the SCF results in Fig. 3, Fig. 5 shows the water energies and BSSE's computed at the MP2 level. As expected from the work of other groups, the BSSE is significantly larger at the correlated level. Likewise, the demands on the basis set in terms of numbers and types of functions required to reach the complete basis set limit are much greater. For example, while the water monomer's SCF energy essentially converges to within a millihartree at the (s,p,d,f) level, the inclusion of g and h functions on oxygen (plus f and g functions on hydrogen) contributes ~ 10 mhartree to the MP2 energy. Fortunately, as indicated by the data in Table VI, the effect on the dimer interaction energy is much less. At least at the MP2 level, functions beyond $l = 3$ (f 's) contribute a negligible amount to ΔE .

Figure 6 shows the convergence of the MP2 interaction energy with respect to basis set size and composition. Compared with the corresponding SCF curves, the MP2 results exhibit a much wider energy spread even with fairly large basis sets. The raw cc-pVxZ numbers and their CP corrected

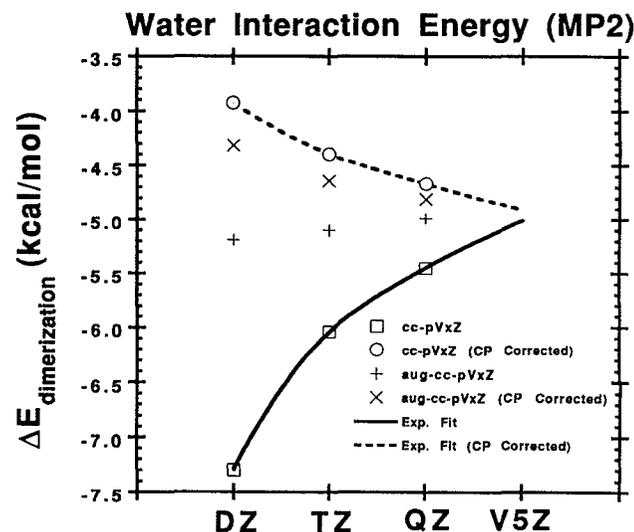


FIG. 6. Convergence of the MP2 interaction energy with and without the counterpoise correction.

counterparts form upper and lower bounds to the results obtained with diffuse function augmented sets. Exponential fits of the bounding values as well as the aug-cc-pVxZ findings suggest that the MP2 complete basis set limit of the water dimer interaction energy, ΔE_∞ (MP2), lies in the range of -4.95 ± 0.05 kcal/mol, somewhat larger than the -4.3 to -4.5 kcal/mol CP corrected values reported previously with (s,p,d,f) extended basis sets. Based on these results, the MP2 correlation correction to the binding energy is approximately -1.4 kcal/mol.

An interesting subtlety is observed in the variation of the MP2 correlation correction with basis set size. While the raw (i.e., non-CP corrected) MP2 corrections *decrease* slightly, from 1.55 (cc-pVDZ) to 1.45 kcal/mol (aug-cc-pVQZ), as one enlarges the basis, the CP corrected values *increase* substantially from 0.23 to 1.25 kcal/mol. Thus it is possible to arrive at diametrically opposing conclusions depending upon whether or not some adjustment is made for the BSSE.

As was found in the case of the SCF results, the CP corrected MP2 interaction energies for basis sets without added diffuse functions agree much better with ΔE_∞ (MP2) than the raw numbers. However, unlike the SCF case, when the CP correction is applied to the aug-cc-pVDZ and aug-cc-pVTZ basis sets the agreement gets worse. For the aug-cc-pVQZ basis the matter is too close to call, especially given the inherent uncertainties in our estimation of the MP2 results with this basis. This observation is in partial disagreement with the conclusions reached by Szczesniak and Scheiner²⁷ who argue in favor of the full CP correction for MP2 calculations. They based their conclusions on calculations done with smaller basis sets, ranging in size from 6–31G** to a $[4s,3p,2d/2s,1p]$ set. While it is true that the use of the CP correction at the MP2 level damps out much of the sensitivity to minor changes in the basis set, these authors were unable in 1986 to carry out calculations which approached the basis set limit as closely as the present set.

In general, the use of more sophisticated correlation recovery methods tends to diminish ΔE with smaller basis sets and increase it with larger basis sets. For example, fourth-order Møller–Plesset (MP4) perturbation theory reduces the interaction energy by 0.2 kcal/mol with the cc-pVDZ basis, but increases it very slightly (by 0.02 kcal/mol) with the aug-cc-pVTZ basis. Unfortunately, because we lacked access to an MP4 program that supported nine component g functions, calculations beyond the aug-cc-pVTZ level were not possible. Even if such a program were available, the amount of disk storage required for all widely available MP4 implementations would make the calculations very difficult.

Singles and doubles CI applied to the dimer and isolated water molecule shows the consequences of the lack of size extensivity in the method as it predicts the dimer to be nearly 8 kcal/mol higher in energy than the infinitely separated monomers. Application of the Davidson⁷ correction for unlinked cluster contributions reverses the ordering and predicts the dimer to be bound by -6.5 kcal/mol. In spite of this poor showing, the CI method is very flexible, and, as mentioned earlier, by applying it intelligently these limitations can largely be ameliorated.

The quadratic CI methods can be viewed as falling

somewhere between conventional CI and coupled cluster methods. In the quadratic CI methods the normal CI linear equations are modified so as to include terms that are quadratic in the expansion coefficients. QCISD and QCISD(T) are both size extensive methods,³⁸ but the latter method includes an approximate perturbative correction for triple excitations. The QCISD method yields somewhat smaller interaction energies than MP2, whereas QCISD(T) yields energies that are close to, but slightly larger than MP4. Due to a combination of factors the small cc-pVDZ basis set, CP-corrected QCISD(T) estimate of the binding energy is coincidentally within 0.01 kcal/mol of the SCF value. It should not be concluded from this result that correlation effects are negligible. With the aug-cc-pVTZ basis the corresponding difference is > 1 kcal/mol.

It would have been of interest to compare all available methods against a set of full CI (FCI) results, but the software and hardware for correlating 16 electrons among the 46 valence orbitals associated with even the smallest basis was unavailable. Instead, we have derived estimates of the cc-pVDZ full CI energies using a recently developed technique that extrapolates the results of a systematic sequence of CI wave functions to the full CI limit.³⁹

The first step in constructing the estimates is to identify a list of reference configurations capable of qualitatively describing the system. Then a CI wave function consisting of all single and double excitations from each configuration in this list is generated. For the case of the water dimer the HF configuration dominates the wave function so the initial wave functions for the monomer and dimer were HF SD-CI's. The configuration expansion coefficients are ordered on their magnitude and a small number of the most important configurations are chosen to serve as the next reference space out of which all single and double excitations are taken in order to form the CI wave function in the sequence. The new wave function, in turn, serves as a pool out of which the reference space is again augmented and all single and double excitations are again generated. The entire process is continued until the desired convergence is achieved or the calculations become intractable.

As the reference space grows there may come a point at which a variational calculation including all the singles and doubles would be prohibitive. In fact, this did occur with the largest three references of the water dimer where between 3–12 million configuration state functions (CSF's) were generated. On the 4 MFLOP workstation used for most of the calculations presented in this paper, the largest variational calculation which could be run contained just over 1.2 million configurations. To proceed further, second-order perturbation theory was used to select those double excitations whose energy contribution exceeded a threshold of on the order of 10^{-9} hartree. The small amount of energy corresponding to configurations which were not selected was estimated as described previously.³⁹ All single excitations are automatically kept. The virtual orbital space was transformed to a set of orbitals known as K orbitals⁴⁰ so as to improve the rate of convergence of the CI expansion.

Once the CI energies are obtained they are fit with an exponential function of the form

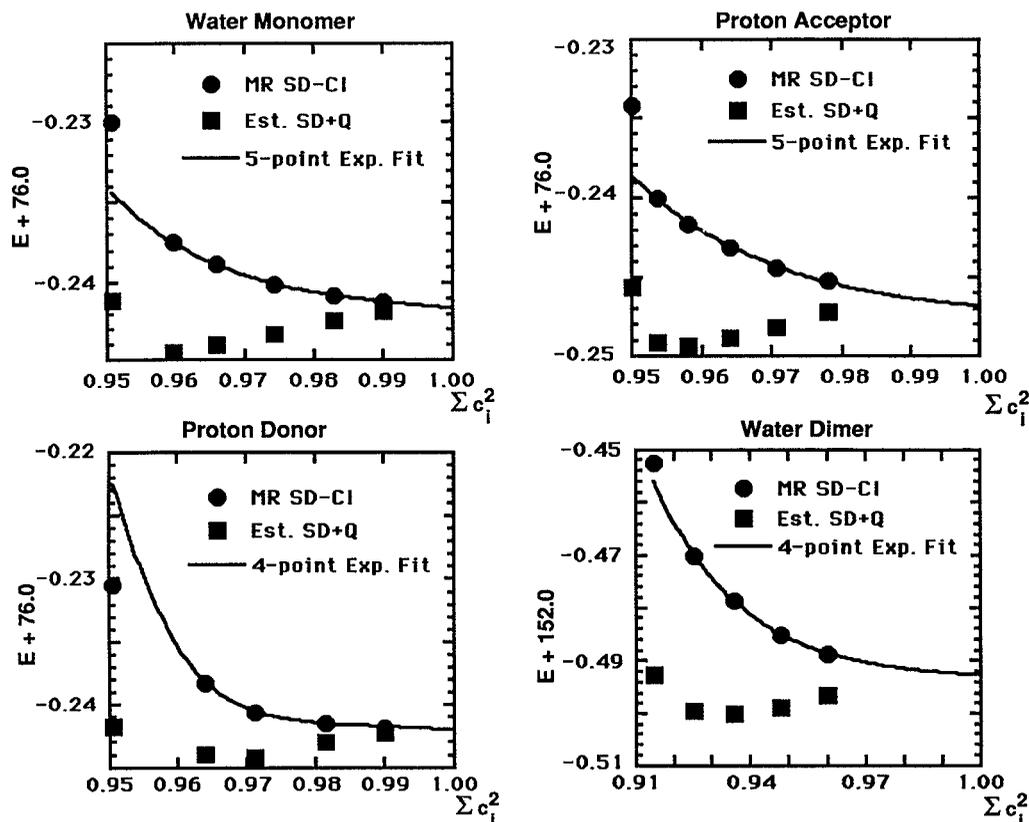


FIG. 7. MR SD-CI energies for water, the monomer fragments, and the water dimer as a function of the weight of the reference space in the final CI wave function.

$$f\left(\sum c_i^2\right) = a + b \cdot \exp\left[c \cdot \left(1 - \sum c_i^2\right)\right],$$

where $\sum c_i^2$ is the sum of the squares of the reference configuration's CI expansion coefficients. The full CI result, E_{FCI} , is approached in the limit that $\sum c_i^2 \rightarrow 1$. While this is an admittedly *ad hoc* approach, in previous tests it has demonstrated remarkable predictive accuracy. For example, with a $[4s, 2p, 1d / 2s, 1p]$ DZP basis set, this procedure was able to estimate the true 6.7 million CSF full CI energy to within 0.0001 hartree. Additional tests run on N_2 with a similar basis set yielded errors on the order of 0.0004 hartree.

Figure 7 shows the variational CI energies for the water monomer, the dimer and the two fragments in the dimer basis as a function of $\sum c_i^2$. A simple estimate of the contribution from higher order excitations not explicitly included in either the perturbation theory analysis or the variational CI leads to the curve labeled "est. SD + Q". It was obtained by augmenting the CI energies with an additional term based on one form of the "Davidson quadruples correction"

$$\Delta E_Q = \Delta E_{SD} \left(1 - \sum c_i^2\right) / \left(2 \sum c_i^2 - 1\right),$$

where ΔE_{SD} is the energy lowering for the unselected CI relative to the zeroth-order energy, E_0 , the eigenvalue associated with Ψ_0 , the eigenvector corresponding to the lowest energy root of the reference space. In all of the systems to which this method has been applied the est. SD + Q energies approach the E_{FCI} from below. To the extent this observation is true in general the Davidson-corrected energies pro-

vide a crude lower bound to our estimate of the limiting energy.

As can be seen in Fig. 7, the weight of the HF configuration in an HF SD-CI, indicated by the smallest value of $\sum c_i^2$ in each of the graphs, varies considerably between the monomer (or the monomer fragments) and the dimer, falling from 0.95 to around 0.91. This is another manifestation of the size extensivity problem inherent with the singles and doubles CI method. Nonetheless, for the extrapolation to succeed, the sequence of MR SD-CI wave functions need only converge smoothly as the reference space is enlarged. The largest CI performed on the monomer contained approximately 100 000 CSF's generated from a reference space of 245 CSF's. The largest CI on the dimer contained approximately 1.2 million CSF's selected from 12 million, with a reference space of 323 CSF's.

When fitting the four sequences of CI energies, it was found that excluding the HF SD-CI points resulted in much improved fitting for the remaining data points. Root mean square (rms) deviations of the exponential fit with respect to the actual MR SD-CI points were less than 0.0001 hartree. Since there is no formal proof that fits of this sort should be capable of predicting the full CI energy (to within specific error bars), all that can be done in the way of establishing or refuting the utility of the method is to examine its behavior in a wide variety of cases. In that sense, the small rms errors lend support to our estimates, since for the estimated E_{FCI} to be substantially in error the functional form that has shown itself capable of accurately fitting the computed CI energies

over a range of Σc_i^2 values in the vicinity of the full CI must suddenly fail as it closes in on the full CI limit. While such a catastrophic turn of events cannot be entirely ruled out, it seems improbable and has so far not been observed where the actual full CI energy is available for comparison.

The estimated full CI binding energy using the cc-pVDZ basis is -6.0 kcal/mol (-2.5 with the CP correction). Of the other methods whose results are shown in Table IV, QCISD(T) appears to come the closest in terms of its total energies and size of the BSSE; BSSE = $+3.3$ kcal/mol for QCISD(T) vs $+3.5$ kcal/mol for the est. full CI. However, there is a substantial 1.7 mhartree (1 kcal/mol) difference in the predicted binding energies. It may well be that, because we were prevented from performing CI calculations on the dimer with large enough reference spaces to achieve values of Σc_i^2 as large as the largest used the monomer and the donor/acceptor fragments (0.98 – 0.99), we are underestimating the dimer's energy and, thus underestimating the binding.

The Davidson-corrected CI energy for the dimer in the largest CI (1.2 million CSF, $\Sigma c_i^2 = 0.96$) is -152.497 compared to -152.493 , which is predicted by the four-point fit. Even if we were to assume that the Davidson-corrected value represents a lower bound to the true E_{FCI} , the 4 mhartree difference is too large to provide too much guidance in deciding if favor of the QCISD(T) value or the estimated full CI value. To the extent the binding energy estimate based on fitting the MR SD-CI energies is correct, the magnitude of correlation corrections beyond the MP2 level is larger than what is found with QCISD(T).

Szalewicz *et al.*¹⁰ predicted a correlation contribution to the binding energy of -1.0 ± 0.3 kcal/mol. On the basis of our projection of -1.4 kcal/mol for the limiting MP2 contribution to ΔE and the trend observed in Table IV for the combination of higher order correlation effects and very large basis sets to slightly increase ΔE , we would predict a correlation contribution, in the complete basis set limit, of ~ 1.5 kcal/mol.

CONCLUSION

A systematic series of calculations encompassing a wide range of basis sets and levels of correlation recovery have been carried out on the water dimer system. The complete basis set limit for the SCF interaction energy is estimated to be -3.55 kcal/mol and the correlation contribution is estimated to be ~ 1.5 kcal/mol. This leads to an interaction energy of -5.1 kcal/mol, exclusive of vibrational zero-point considerations. If we had chosen to perform our dimer calculations at the experimental O–O distance we estimate that the dimer's energy would have been increased by ~ 0.2 kcal/mol, with the binding energy decreased by the same amount, to -4.9 kcal/mol. The experimental work most often cited for the binding energy of the water dimer is the thermal conduction work done of Curtiss *et al.*⁴ They report a standard enthalpy of formation of -3.59 kcal/mol and include an estimate of the contributions from translational, rotational, and vibrational degrees of freedom (1.85 kcal/mol) for a $\Delta E_{\text{electronic}} = -5.4$ kcal/mol.

Frisch *et al.*⁸ computed the additional terms needed to

convert their $\Delta E_{\text{electronic}}$ into ΔH_f^{298} using MP2 vibrational frequencies and found a correction of 1.7 kcal/mol. It should be noted that there appears to be a 0.6 kcal/mol discrepancy between the frequencies reported in their Table VIII and the zero-point correction listed in Table IX.

Nonetheless, if we apply the same 1.7 kcal/mol correction to our best estimate of the electronic interaction energy we arrive at a value of $\Delta H_f^{298} = 3.4$ kcal/mol, which is within 0.3 kcal/mol of the experimental result. By comparison, Frisch *et al.* report in their Table IX nearly exact agreement with experiment at the MP4/6-311 + G(3df,3pd) level, but no accounting of the BSSE has been made. If the CP correction is included, their ΔH_f^{298} decreases to -2.9 kcal/mol.

The counterpoise correction was found to substantially improve the computed interaction energies agreement with ΔE_{∞} when used at either the SCF or MP2 levels in conjunction with basis sets lacking in diffuse functions. However, with diffuse-function-augmented basis sets of double or triple zeta quality, the CP correction actually worsens the MP2 interaction energies. The MP2 correction to the bond energy increases with the size of the basis. Qualitatively different conclusions can be drawn about the impact of extended basis sets on ΔE depending upon the use or nonuse of the CP correction.

To the extent that the present findings are representative of other hydrogen bonding situations involving water, the aug-cc-pVDZ basis set without the CP correction appears to be a reasonable choice for calculations on larger systems. When used with second-order Møller–Plesset perturbation theory, it was within 0.2 kcal/mol of results obtained with much larger basis sets and higher levels of correlation recovery.

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