

# Basis set convergence of the interaction energy of hydrogen-bonded complexes

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The Hartree-Fock and correlation contributions to the interaction energy of the hydrogen-bonded complexes  $(\text{HF})_2$ ,  $(\text{HCl})_2$ ,  $\text{H}_2\text{OHF}$ ,  $\text{HCNHF}$ , and  $(\text{H}_2\text{O})_2$  are computed in conventional calculations employing the aug-cc-pVXZ series of basis sets at the levels of Hartree-Fock theory, second-order perturbation theory, and coupled-cluster theory with single and double excitations augmented by a perturbative triples correction. The basis set convergence of the interaction energy is examined by comparison with results obtained with an explicitly correlated wave function model. The counterpoise-corrected and uncorrected Hartree-Fock interaction energies both converge very unsystematically. The convergence of the uncorrected correlation contribution is also very unsystematic because the basis set superposition error and the error from the incomplete description of the electronic Coulomb cusp both are present. Once the former has been effectively removed by the counterpoise correction, the cusp dominates and the convergence of the counterpoise-corrected correlation contribution follows an  $X^{-3}$  form similar to the form for the correlation energy. Two-point extrapolated values obtained with this form are close to the basis set limit and represent a significant improvement on the unextrapolated results. © 1999 American Institute of Physics. [S0021-9606(99)30844-8]

## I. INTRODUCTION

The accurate determination of interaction energies of hydrogen-bonded complexes has been the subject of many theoretical studies<sup>1-21</sup> (the list should not be considered exhaustive) and represents an important issue of *ab initio* theory. When aiming at an accurate determination of the interaction energy of a hydrogen-bonded complex within the super-molecule approach, the basis set superposition error (BSSE) must be accounted for. BSSE is a spurious contribution to the interaction energy arising from the improved description of each fragment in the total basis of the complex compared to the fragment basis alone, and is thus ultimately a consequence of the incompleteness of the one-electron basis set. A conceptually simple way of accounting for BSSE is the counterpoise correction method,<sup>22</sup> in which the energies of the fragments are calculated in the full basis of the complex, and these counterpoise-corrected (CP) energies are used for the energies of the fragments when computing the interaction energy. The accuracy of the simple counterpoise

correction as a measure of BSSE has been the subject of some debate.<sup>23-30</sup> However, there appears to be a consensus that this method at least gives a correct estimate of BSSE, and as it furthermore is the procedure recommended to account for BSSE in a recent review on counterpoise theory,<sup>30</sup> we shall not dwell on this matter here and instead simply use the counterpoise-correction as our measure of BSSE.

Recognizing the incompleteness of the basis set as the origin of BSSE, the focus of the present study will be on the basis set convergence of the interaction energy toward the basis set limit, where BSSE vanishes. When studying basis set convergence, one must have a hierarchical sequence of basis sets with systematic improvements from level to level. The correlation-consistent polarized valence basis sets, denoted cc-pVXZ, and their singly and doubly diffusely augmented counterparts, denoted aug-cc-pVXZ and d-aug-cc-pVXZ, respectively, of Dunning and co-workers,<sup>31-34</sup> constitute such hierarchies and were used exclusively in our first investigation of the prototypical hydrogen-bonded complex  $(\text{H}_2\text{O})_2$ .<sup>17</sup> Hydrogen-bonded complexes are weakly bound and have rather long interfragment distances. An accurate description of the outer valence region of each frag-

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ment is therefore required, and the inclusion of diffuse functions in the basis set becomes important. Accordingly, Del Bene,<sup>7</sup> Feller *et al.*,<sup>8,13</sup> and Xantheas *et al.*<sup>9,14</sup> obtained major improvements in the interaction energy from the cc-pVXZ to the aug-cc-pVXZ basis sets, and in Ref. 17 the size of the counterpoise correction for (H<sub>2</sub>O)<sub>2</sub> was found to be reduced significantly from the cc-pVXZ to the aug-cc-pVXZ basis sets, whereas little happened when the next set of diffuse functions (in the d-aug-cc-pVXZ sets) was added. Besides confirming the importance of diffuse functions, it was found in Ref. 17 that the CP interaction energies ( $\Delta E^{\text{CP}}$ ) were closer to the basis set limit than the uncorrected ones ( $\Delta E$ ) for the Hartree-Fock self-consistent field (SCF) wave function model. It was also found that  $\Delta E^{\text{CP}}$  and  $\Delta E$  converged to the basis set limit from each side for all of the three correlated wave function models: second-order Møller–Plesset perturbation theory (MP2),<sup>35</sup> coupled-cluster singles and doubles (CCSD),<sup>36</sup> and CCSD augmented by a perturbational correction for connected triple excitations [CCSD(T)].<sup>37</sup> Furthermore, once diffuse functions were included in the basis set,  $\Delta E^{\text{CP}}$  displayed larger variations with the cardinal number  $X(D:2,T:3\dots)$  of the basis set than  $\Delta E$ , and  $\Delta E$  obtained with the small aug-cc-pVDZ basis set was remarkably close to the basis set limit. Finally, because  $\Delta E^{\text{CP}}$  and  $\Delta E$  for the correlated wave function models converged to the basis set limit from each side, the simple average of  $\Delta E^{\text{CP}}$  and  $\Delta E$  converged rapidly to the basis set limit.

In the present study, we investigate these matters in more detail for a broader sample of five hydrogen-bonded complexes, to establish whether our findings in Ref. 17 were specific for the water dimer or hold for hydrogen-bonded complexes in general. The systems under investigation (HF)<sub>2</sub>, (HCl)<sub>2</sub>, H<sub>2</sub>OHF, HCNHF, and (H<sub>2</sub>O)<sub>2</sub> contain hydrogen bonds involving N, O, F, and Cl, and thus cover most of the hydrogen bonds encountered in nature. In Ref. 17, the total interaction energy for the correlated wave function models was examined. In this study, we instead focus on each of the SCF and correlation contributions to the total interaction energy separately, as these contributions converge differently to the basis set limit.

Explicitly correlated linear R12-methods<sup>38–43</sup> give correlation energies close to the basis set limit, because they include terms in the wave function that are linear in the interelectronic distance  $r_{12}$  explicitly, as required by the electronic Coulomb cusp condition, and these methods have been successfully applied for hydrogen-bonded systems.<sup>12,19–21</sup> Guided by basis set limits established with the MP2-R12/A method, the basis set convergence of the MP2 correlation contribution to the interaction energy is investigated in detail in the present study. The convergence of  $\Delta E_{\text{corr}}$ ,  $\Delta E_{\text{corr}}^{\text{CP}}$ , and their simple average is examined for the aug-cc-pVXZ basis sets, and the performance of the recently advanced two-point  $X^{-3}$  extrapolation for acceleration of basis set convergence<sup>44–47</sup> is investigated. Finally, based on the experience obtained at the MP2 level, the basis set convergence of the CCSD(T) correlation contribution is investigated.

## II. COMPUTATIONAL DETAILS

For consistency with our previous work on the water dimer, the geometries of all the complexes have been optimized at the CCSD(T)/aug-cc-pVTZ level with the monomer fragments frozen at the experimental equilibrium geometry— $R_{\text{H-F}}=0.916\ 80$ ,<sup>48</sup>  $R_{\text{H-Cl}}=1.274\ 55$ ,<sup>48</sup>  $R_{\text{H-O}}=0.9572\ \text{\AA}$  and  $\angle_{\text{H-O-H}}=104.52^\circ$ ,<sup>49</sup> and  $R_{\text{H-C}}=1.062\ 55$  and  $R_{\text{C-N}}=1.152\ 87\ \text{\AA}$ .<sup>50</sup> All the electrons were correlated in the geometry optimizations, except for (HCl)<sub>2</sub>, where the ten lowest lying molecular orbitals—essentially the  $1s$ ,  $2s$ , and  $2p$  orbitals for the two chlorine—were kept uncorrelated, as the aug-cc-pVTZ basis set does not provide a sufficiently flexible description of the inner valence and core region around chlorine for correlating these orbitals. These calculations have been performed with the ACESII program.<sup>51,52</sup>

Conventional SCF, MP2, and CCSD(T) single-point energy calculations at the optimized geometries have been carried out for the aug-cc-pVXZ basis sets ( $X=D-5$ ) with only the valence electrons correlated. These calculations have been performed with a local version of the Dalton program<sup>53</sup> that contains the coupled-cluster code of Koch and co-workers.<sup>54–56</sup> The explicitly correlated MP2-R12/A single-point energy calculations have been carried out with the SORE program<sup>57</sup> correlating only the valence electrons. Large uncontracted basis sets of the form  $21s13p10d8f$  (Cl),  $15s9p7d5f$  (C, N, O, F), and  $9s7p5d$  (H) have been employed to satisfy completeness conditions related to the approximate evaluation of the many-electron integrals entering the MP2-R12 theory. These basis sets are constructed from the primitive *spdf* set of the cc-pV5Z basis set by addition of both diffuse and tight functions. The sets for H, N, O, and F are described in full detail in Ref. 58. For C, the primitive  $14s8p4d3f$  set in the cc-pV5Z basis set is augmented by a  $1s1p1d1f$  set of diffuse functions with exponents 0.0408 (*s*), 0.0308 (*p*), 0.075 (*d*), and 0.146 (*f*), and with a  $2d1f$  set of tight functions with exponents 20.25 (*d*), 7.966 (*d*), and 4.8 (*f*), and for Cl, the primitive  $20s12p4d3f$  set in the cc-pV5Z basis set is augmented by a  $1s1p1d1f$  set of diffuse functions with exponents 0.0537 (*s*), 0.0369 (*p*), 0.101 (*d*), and 0.156 (*f*), and with a  $5d4f$  set of tight functions with exponents 350.0 (*d*), 141.4 (*d*), 57.17 (*d*), 23.12 (*d*), 9.35 (*d*), 23.9 (*f*), 11.6 (*f*), 5.66 (*f*), and 2.76 (*f*).

From the calculated energies we obtain the uncorrected interaction energy as

$$\Delta E = E^{\text{comp}} - E^{\text{don}} - E^{\text{acc}}, \quad (1)$$

where  $E^{\text{comp}}$  is the energy of the complex, and  $E^{\text{don}}$  and  $E^{\text{acc}}$  are the energies of the isolated H donor and acceptor monomers, respectively. The CP interaction energy is obtained as

$$\Delta E^{\text{CP}} = E^{\text{comp}} - E^{\text{CP, don}} - E^{\text{CP, acc}}, \quad (2)$$

where  $E^{\text{CP, don}}$  and  $E^{\text{CP, acc}}$  are the energies of the two monomers in the full basis of the complex. The correlation contributions,  $\Delta E_{\text{corr}}$  and  $\Delta E_{\text{corr}}^{\text{CP}}$ , to the interaction energy are obtained from analogous expressions involving the corresponding correlation energies.

TABLE I. Cartesian coordinates for the CCSD(T)/aug-cc-pVTZ optimized equilibrium geometries of the complexes in atomic units.

Atom	X	Y	Z
(HF) <sub>2</sub>			
H	3.214 605 13	-1.496 401 78	0.000 000 00
F	2.511 286 53	0.086 918 66	0.000 000 00
H	-0.912 967 87	0.186 832 05	0.000 000 00
F	-2.633 383 52	-0.017 448 75	0.000 000 00
(HCl) <sub>2</sub>			
H	3.498 634 66	-2.343 865 35	0.000 000 00
Cl	3.548 559 49	0.064 168 10	0.000 000 00
H	-1.225 351 64	0.303 046 86	0.000 000 00
Cl	-3.614 076 98	-0.005 350 39	0.000 000 00
H <sub>2</sub> OHF			
H	0.712 704 86	-3.290 732 19	1.430 432 08
H	0.712 704 86	-3.290 732 19	-1.430 432 08
O	-0.101 818 48	-2.540 829 48	0.000 000 00
H	-0.068 203 40	0.719 544 76	0.000 000 00
F	0.013 724 89	2.450 107 80	0.000 000 00
HCNHF			
H	0.000 000 00	0.000 000 00	-5.722 109 90
C	0.000 000 00	0.000 000 00	-3.714 180 98
N	0.000 000 00	0.000 000 00	-1.535 571 97
H	0.000 000 00	0.000 000 00	1.945 645 75
F	0.000 000 00	0.000 000 00	3.678 147 03
(H <sub>2</sub> O) <sub>2</sub> <sup>a</sup>			
H	-3.302 569 70	-0.785 537 00	1.430 432 10
H	-3.302 569 70	-0.785 537 00	-1.430 432 10
O	-2.666 109 50	0.120 399 50	0.000 000 00
H	1.006 003 70	0.105 080 40	0.000 000 00
H	3.473 430 20	1.552 958 40	0.000 000 00
O	2.800 048 30	-0.125 879 10	0.000 000 00

<sup>a</sup>From Ref. 17.

### III. RESULTS AND DISCUSSION

The Cartesian coordinates of the CCSD(T)/aug-cc-pVTZ optimized equilibrium geometries of the complexes are listed in Table I, and in Tables II through V, the single-point energies and the interaction energies deduced from these are given for the SCF, MP2, and CCSD(T) wave function models.

#### A. Convergence in Hartree–Fock calculations

From the SCF results in Table II, we note that  $\Delta E$  and  $\Delta E^{\text{CP}}$  approach each other when  $X$  increases, as they should. Although  $\Delta E$  and  $\Delta E^{\text{CP}}$  approach each other, the basis set convergence of both is very unsystematic, and it is difficult to find features common to all five complexes. This is further illustrated in Figs. 1–5, where  $\Delta E$  and  $\Delta E^{\text{CP}}$  at the SCF level are plotted as a function of  $X$ . The convergence is very uneven and on several occasions it is nonmonotonic for  $\Delta E^{\text{CP}}$ . Furthermore,  $\Delta E^{\text{CP}}$  generally converges from above, except for (HCl)<sub>2</sub>, where  $\Delta E^{\text{CP}}$  is virtually constant with  $X$ , but the convergence differs significantly from complex to complex, with the largest reductions in the basis set error occurring at different  $X$ . By contrast,  $\Delta E$  converges from below in all five cases, but again the detailed convergence differs from complex to complex.

At the aug-cc-pV5Z level,  $\Delta E$  and  $\Delta E^{\text{CP}}$  differ only by about 0.01 mE<sub>h</sub>, and their average [ $\Delta E^{\text{ave}}(5)$ ] is therefore expected to be within a few hundredths of a mE<sub>h</sub> of the SCF basis set limit. For the comparisons to be made in the fol-

TABLE II. The SCF results obtained for the five complexes as a function of the cardinal number  $X$  of the aug-cc-pVXZ basis sets. The first column of results holds the energy of the complex, the second column the energy of the isolated H donor monomer, the third column the energy of the isolated H acceptor monomer, and in the next two columns follow the energy of these two monomers in the full basis set of the complex. The final three columns hold the uncorrected interaction energy, the CP interaction energy, and the simple average of these two. All the interaction energies are given in mE<sub>h</sub>, whereas the others are given in E<sub>h</sub>.

$X$	$E^{\text{comp}}$	$E^{\text{don}}$	$E^{\text{acc}}$	$E^{\text{CP,don}}$	$E^{\text{CP,acc}}$	$\Delta E$	$\Delta E^{\text{CP}}$	$\Delta E^{\text{ave}}$
(HF) <sub>2</sub>								
2	-200.073 147	-100.033 474	-100.033 474	-100.033 580	-100.033 768	-6.1991	-5.7991	-5.9991
3	-200.128 141	-100.061 078	-100.061 078	-100.061 125	-100.061 220	-5.9854	-5.7959	-5.8906
4	-200.143 143	-100.068 568	-100.068 568	-100.068 594	-100.068 630	-6.0059	-5.9181	-5.9620
5	-200.147 103	-100.070 583	-100.070 583	-100.070 589	-100.070 589	-5.9382	-5.9255	-5.9318
(HCl) <sub>2</sub>								
2	-920.185 955	-460.092 615	-460.092 615	-460.092 691	-460.092 845	-0.7245	-0.4193	-0.5719
3	-920.215 674	-460.107 600	-460.107 600	-460.107 624	-460.107 659	-0.4743	-0.3909	-0.4326
4	-920.223 209	-460.111 395	-460.111 395	-460.111 403	-460.111 414	-0.4192	-0.3923	-0.4057
5	-920.225 400	-460.112 504	-460.112 504	-460.112 508	-460.112 509	-0.3918	-0.3834	-0.3876
H <sub>2</sub> OHF								
2	-176.086 740	-100.033 474	-76.041 428	-100.033 612	-76.041 822	-11.8379	-11.3053	-11.5716
3	-176.133 307	-100.061 078	-76.060 613	-100.061 145	-76.060 708	-11.6163	-11.4542	-11.5353
4	-176.146 150	-100.068 568	-76.066 001	-100.068 612	-76.066 037	-11.5809	-11.5011	-11.5410
5	-176.149 415	-100.070 583	-76.067 320	-100.070 591	-76.067 324	-11.5121	-11.4994	-11.5057
HCNHF								
2	-192.930 371	-100.033 474	-92.887 498	-100.033 632	-92.887 888	-9.3986	-8.8509	-9.1248
3	-192.979 645	-100.061 078	-92.909 182	-100.061 160	-92.909 323	-9.3852	-9.1619	-9.2735
4	-192.992 434	-100.068 568	-92.914 635	-100.068 629	-92.914 661	-9.2311	-9.1448	-9.1879
5	-192.995 518	-100.070 583	-92.915 778	-100.070 593	-92.915 781	-9.1569	-9.1439	-9.1504
(H <sub>2</sub> O) <sub>2</sub>								
2 <sup>a</sup>	-152.088 835	-76.041 428	-76.041 428	-76.041 511	-76.041 747	-5.9797	-5.5776	-5.7787
3 <sup>a</sup>	-152.126 908	-76.060 613	-76.060 613	-76.060 660	-76.060 689	-5.6817	-5.5585	-5.6201
4 <sup>a</sup>	-152.137 667	-76.066 001	-76.066 001	-76.066 016	-76.066 033	-5.6657	-5.6175	-5.6416
5 <sup>a</sup>	-152.140 264	-76.067 320	-76.067 320	-76.067 323	-76.067 324	-5.6234	-5.6168	-5.6201

<sup>a</sup>From Ref. 17.

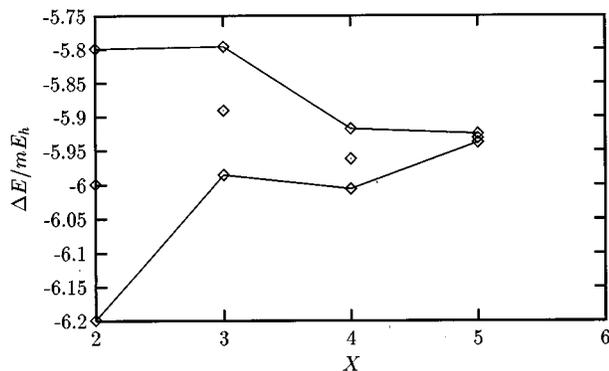


FIG. 1.  $\Delta E^{\text{CP}}$  (upper curve) and  $\Delta E$  (lower curve) for  $(\text{HF})_2$  at the SCF level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E^{\text{CP}}$  and  $\Delta E$  results.

lowing, this accuracy is sufficient, and we shall therefore adopt  $\Delta E^{\text{ave}}(5)$  as our estimate of the SCF basis set limit. We then observe that, at the aug-cc-pVQZ level,  $\Delta E^{\text{CP}}$  is always closer to the basis set limit than the corresponding  $\Delta E$  is, and except for two cases this also holds for the smaller basis sets. The simple average  $\Delta E^{\text{ave}}$  represents an improvement on the corresponding  $\Delta E$  for the double-, triple-, and quadruple-zeta basis sets, and in many cases the improvement is substantial. Compared to  $\Delta E^{\text{CP}}$ , however,  $\Delta E^{\text{ave}}$  does not always represent an improvement and it is not possible to recommend any one of these two in favor of the other. The largest basis set errors are observed for  $\Delta E$  at the aug-cc-pVDZ level, where the error is about  $0.3 \text{ mE}_h \approx 0.2 \text{ kcal/mol}$ . At the aug-cc-pVTZ level, both  $\Delta E^{\text{CP}}$  and  $\Delta E^{\text{ave}}$  are within  $0.1 \text{ kcal/mol}$  of the basis set limit, and at the aug-cc-pVQZ level,  $\Delta E^{\text{CP}}$  and  $\Delta E^{\text{ave}}$  are both within  $0.05 \text{ kcal/mol}$  of the basis set limit.

Because of the very unsystematic convergence it is not possible to find an analytical form for the convergence of  $\Delta E$  or  $\Delta E^{\text{CP}}$  at the SCF level, and reliable extrapolation schemes cannot be developed.

## B. Convergence of the MP2 correlation contribution

The MP2 correlation contributions in Table III show that  $\Delta E_{\text{corr}}$  and  $\Delta E_{\text{corr}}^{\text{CP}}$  also approach each other when  $X$  in-

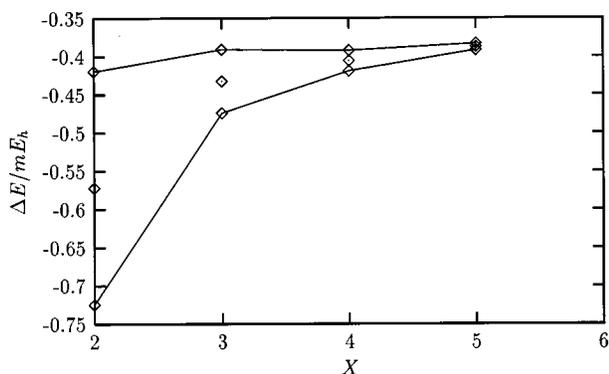


FIG. 2.  $\Delta E^{\text{CP}}$  (upper curve) and  $\Delta E$  (lower curve) for  $(\text{HCl})_2$  at the SCF level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E^{\text{CP}}$  and  $\Delta E$  results.

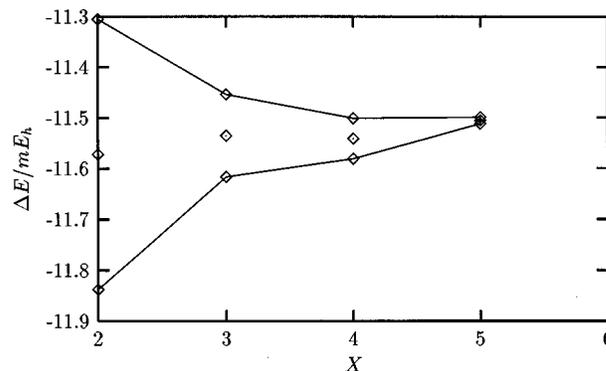


FIG. 3.  $\Delta E^{\text{CP}}$  (upper curve) and  $\Delta E$  (lower curve) for  $\text{H}_2\text{OHF}$  at the SCF level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E^{\text{CP}}$  and  $\Delta E$  results.

creases, as they should. However, for a given  $X$  the differences between the two results are much larger for the correlation part than for the SCF part (e.g., about  $0.2$  to  $0.3 \text{ mE}_h$  compared to about  $0.01 \text{ mE}_h$  at the aug-cc-pV5Z level). The R12 results for  $\Delta E_{\text{corr}}$  and  $\Delta E_{\text{corr}}^{\text{CP}}$  are much closer to each other, differing by more than  $0.04 \text{ mE}_h$  only for  $(\text{HCl})_2$ . The results are depicted in Fig. 6–10, where  $\Delta E_{\text{corr}}$  and  $\Delta E_{\text{corr}}^{\text{CP}}$  for the aug-cc-pVXZ basis sets are plotted as a function of  $X$  along with the two R12 results (CP and uncorrected interaction energies). The basis set limit is expected to lie close to these two R12 results, and their range indicates the uncertainty of its determination.

The convergence of  $\Delta E_{\text{corr}}^{\text{CP}}$  is more systematic than that of  $\Delta E^{\text{CP}}$  at the SCF level: the five curves for  $\Delta E_{\text{corr}}^{\text{CP}}$  look exactly alike, and the convergence of  $\Delta E_{\text{corr}}^{\text{CP}}$  is both monotonic, smooth, and invariably from above. The convergence of  $\Delta E_{\text{corr}}$ , however, is still unsystematic, although some common features are noted for all five complexes: The convergence is always nonmonotonic, as  $\Delta E_{\text{corr}}$  invariably decreases from aug-cc-pVDZ to aug-cc-pVTZ and increases from aug-cc-pVTZ to aug-cc-pV5Z, and  $\Delta E_{\text{corr}}$  thus converges from below, although not particularly smoothly. Especially, the decrease from aug-cc-pVDZ to aug-cc-pVTZ causes the aug-cc-pVTZ  $\Delta E_{\text{corr}}$  results to be *further away* from the basis set limit than the aug-cc-pVDZ  $\Delta E_{\text{corr}}$  results.

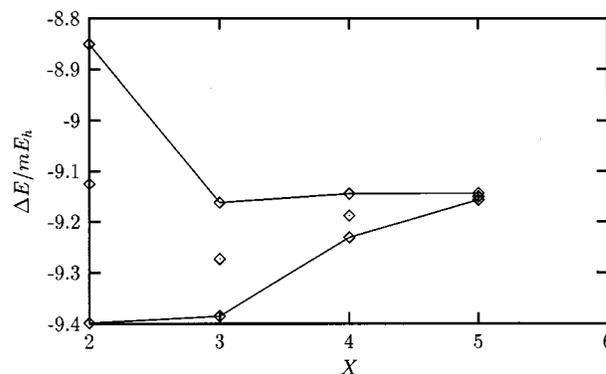


FIG. 4.  $\Delta E^{\text{CP}}$  (upper curve) and  $\Delta E$  (lower curve) for  $\text{HCNHF}$  at the SCF level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E^{\text{CP}}$  and  $\Delta E$  results.

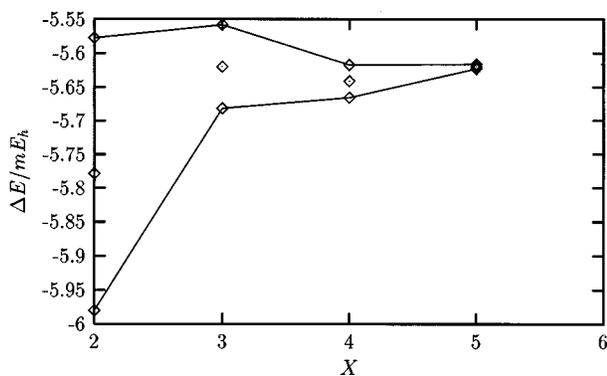


FIG. 5.  $\Delta E^{\text{CP}}$  (upper curve) and  $\Delta E$  (lower curve) for  $(\text{H}_2\text{O})_2$  at the SCF level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E^{\text{CP}}$  and  $\Delta E$  results.

This behavior may be attributed to the remarkably good performance of the aug-cc-pVDZ basis set, which must arise from a fortuitous cancellation of errors between BSSE and the other (ordinary) basis set errors (e.g., those arising from the incomplete description of the electronic Coulomb cusp). The  $\Delta E_{\text{corr}}^{\text{CP}}$  results for the aug-cc-pVDZ and aug-cc-pVTZ basis sets have larger basis set errors than the corresponding  $\Delta E_{\text{corr}}$  results. Especially the  $\Delta E_{\text{corr}}^{\text{CP}}$  aug-cc-pVDZ results are

very poor, with basis set errors from 0.8 to  $1.3 mE_h \approx 0.5$  to 0.8 kcal/mol, while the errors of the  $\Delta E_{\text{corr}}^{\text{CP}}$  aug-cc-pVTZ results are between 0.2 and 0.4 kcal/mol. As  $\Delta E_{\text{corr}}$  and  $\Delta E_{\text{corr}}^{\text{CP}}$ , beyond the double-zeta level, converge toward the basis set limit from each side, their average is close to the basis set limit. At the aug-cc-pVTZ level, the average is within 0.15 kcal/mol of the basis set limit, whereas at both the aug-cc-pVQZ and aug-cc-pV5Z levels it is within 0.05 kcal/mol of this limit. However, it should be noted that in three cases,  $\Delta E_{\text{corr}}^{\text{ave}}$  at the aug-cc-pV5Z level is slightly farther from the basis set limit than the  $\Delta E_{\text{corr}}^{\text{ave}}$  aug-cc-pVQZ result is, and in all these cases the aug-cc-pV5Z average result is slightly too low.

### C. Extrapolations of the MP2 correlation contribution

The basis set convergence of the correlation energy for the correlation-consistent basis sets has recently been found to follow the form<sup>44,45</sup>

$$E_{\text{corr},X} = E_{\text{corr,lim}} + AX^{-3}, \quad (3)$$

where  $E_{\text{corr},X}$  is the correlation energy obtained with the correlation-consistent basis set with cardinal number  $X$ , and  $E_{\text{corr,lim}}$  is the basis set limit value of the correlation energy. For large  $X$ , Eq. (3) displays the correct asymptotic behavior of the correlation energy<sup>44–46</sup> compared with the theoretical

TABLE III. The MP2 correlation contribution to the different results obtained for the five complexes as a function of the cardinal number  $X$  of the aug-cc-pVXZ basis sets. The ordering of the columns of results is the same as the one in Table II, and the rows with R12 for  $X$  give the MP2-R12 results. All the interaction energy contributions are given in  $mE_h$ , whereas the others are given in  $E_h$ .

$X$	$E_{\text{corr}}^{\text{comp}}$	$E_{\text{corr}}^{\text{don}}$	$E_{\text{corr}}^{\text{acc}}$	$E_{\text{corr}}^{\text{CP,don}}$	$E_{\text{corr}}^{\text{CP,acc}}$	$\Delta E_{\text{corr}}$	$\Delta E_{\text{corr}}^{\text{CP}}$	$\Delta E_{\text{corr}}^{\text{ave}}$
(HF) <sub>2</sub>								
2	-0.445 563	-0.222 260	-0.222 260	-0.222 569	-0.222 676	-1.0440	-0.3186	-0.6813
3	-0.560 927	-0.279 785	-0.279 785	-0.280 028	-0.280 138	-1.3568	-0.7604	-1.0586
4	-0.603 657	-0.301 189	-0.301 189	-0.301 318	-0.301 391	-1.2802	-0.9482	-1.1142
5	-0.621 218	-0.309 974	-0.309 974	-0.310 086	-0.310 115	-1.2703	-1.0170	-1.1436
R12	-0.642 992	-0.320 947	-0.320 947	-0.320 962	-0.320 918	-1.0990	-1.1124	-1.1057
(HCl) <sub>2</sub>								
2	-0.321 260	-0.159 096	-0.159 096	-0.159 391	-0.159 659	-3.0666	-2.2088	-2.6377
3	-0.418 444	-0.207 530	-0.207 530	-0.207 721	-0.207 901	-3.3829	-2.8217	-3.1023
4	-0.452 737	-0.224 704	-0.224 704	-0.224 812	-0.224 918	-3.3303	-3.0077	-3.1690
5	-0.467 861	-0.232 273	-0.232 273	-0.232 357	-0.232 428	-3.3154	-3.0758	-3.1956
R12	-0.493 075	-0.244 997	-0.244 997	-0.245 001	-0.244 884	-3.0803	-3.1894	-3.1349
H <sub>2</sub> OHF								
2	-0.443 550	-0.222 260	-0.219 337	-0.222 729	-0.220 197	-1.9531	-0.6233	-1.2882
3	-0.550 285	-0.279 785	-0.268 345	-0.280 121	-0.268 802	-2.1546	-1.3617	-1.7581
4	-0.589 290	-0.301 189	-0.285 912	-0.301 407	-0.286 191	-2.1893	-1.6919	-1.9406
5	-0.605 007	-0.309 974	-0.292 905	-0.310 132	-0.293 062	-2.1280	-1.8129	-1.9704
R12	-0.624 219	-0.320 947	-0.301 323	-0.320 967	-0.301 277	-1.9491	-1.9754	-1.9622
HCNHF								
2	-0.519 571	-0.222 260	-0.294 213	-0.222 758	-0.294 904	-3.0989	-1.9095	-2.5042
3	-0.633 111	-0.279 785	-0.350 167	-0.280 144	-0.350 557	-3.1591	-2.4098	-2.7845
4	-0.674 288	-0.301 189	-0.369 877	-0.301 444	-0.370 188	-3.2224	-2.6553	-2.9389
5	-0.690 684	-0.309 974	-0.377 664	-0.310 142	-0.377 799	-3.0461	-2.7419	-2.8940
R12	-0.711 878	-0.320 947	-0.388 044	-0.320 969	-0.388 053	-2.8878	-2.8568	-2.8723
(H <sub>2</sub> O) <sub>2</sub>								
2 <sup>a</sup>	-0.440 914	-0.219 337	-0.219 337	-0.219 668	-0.219 972	-2.2409	-1.2743	-1.7576
3 <sup>a</sup>	-0.539 146	-0.268 345	-0.268 345	-0.268 617	-0.268 710	-2.4557	-1.8191	-2.1374
4 <sup>a</sup>	-0.574 185	-0.285 912	-0.285 912	-0.286 024	-0.286 130	-2.3613	-2.0311	-2.1962
5 <sup>a</sup>	-0.588 123	-0.292 905	-0.292 905	-0.292 982	-0.293 032	-2.3134	-2.1088	-2.2111
R12 <sup>b</sup>	-0.604 844	-0.301 323	-0.301 323	-0.301 335	-0.301 307	-2.1974	-2.2019	-2.1997

<sup>a</sup>From Ref. 17.

<sup>b</sup>From Ref. 21.

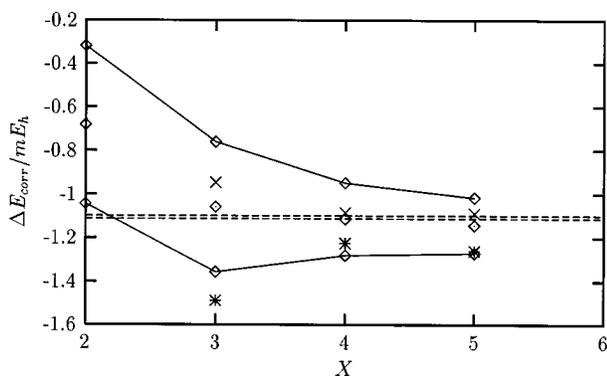


FIG. 6.  $\Delta E_{\text{corr}}^{\text{CP}}$  (upper curve) and  $\Delta E_{\text{corr}}$  (lower curve) for  $(\text{HF})_2$  at the MP2 level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E_{\text{corr}}^{\text{CP}}$  and  $\Delta E_{\text{corr}}$  results, the unconnected crosses ( $\times$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, the asterisks (\*) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}$  results, and the two horizontal dashed lines are the two R12 results.

analysis of the partial-wave expansion of the helium atom.<sup>59</sup> The form in Eq. (3) is therefore theoretically motivated, and extrapolations based upon Eq. (3) yield correlation energies in good agreement with those obtained from large R12 calculations.<sup>44,45</sup> The fewer results obtained with basis sets of low  $X$  that are included in the extrapolations, the better the extrapolated basis set limits agree with the R12 results. Indeed, the most accurate extrapolated results beyond a given  $X$  are obtained by using only the results for  $X$  and  $X-1$ , for which the extrapolation may be cast in the following simple closed form:<sup>45</sup>

$$E_{\text{corr,lim}} = \frac{X^3}{X^3 - (X-1)^3} E_{\text{corr},X} - \frac{(X-1)^3}{X^3 - (X-1)^3} E_{\text{corr},X-1}. \quad (4)$$

As the correlation contribution to the interaction energy is a simple linear combination of correlation energies, a form similar to Eq. (3) is expected for the correlation contribution

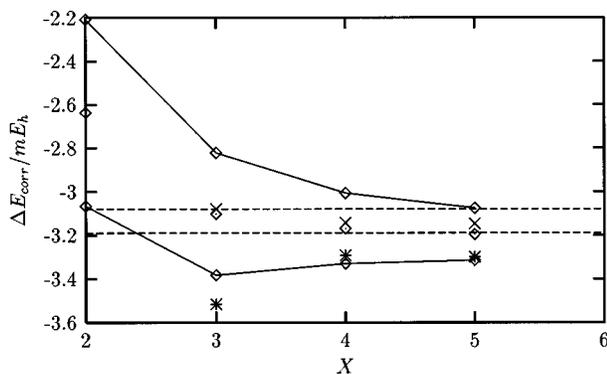


FIG. 7.  $\Delta E_{\text{corr}}^{\text{CP}}$  (upper curve) and  $\Delta E_{\text{corr}}$  (lower curve) for  $(\text{HCl})_2$  at the MP2 level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E_{\text{corr}}^{\text{CP}}$  and  $\Delta E_{\text{corr}}$  results, the unconnected crosses ( $\times$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, the asterisks (\*) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}$  results, and the two horizontal dashed lines are the two R12 results.

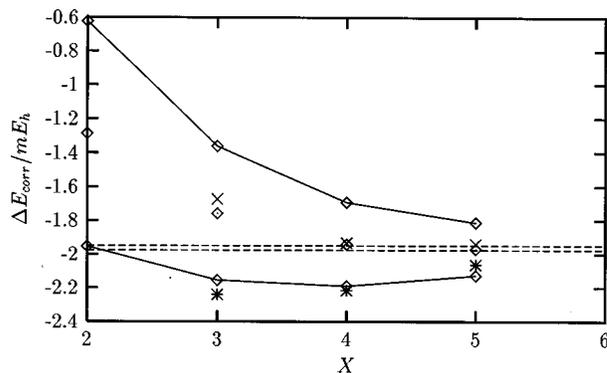


FIG. 8.  $\Delta E_{\text{corr}}^{\text{CP}}$  (upper curve) and  $\Delta E_{\text{corr}}$  (lower curve) for  $\text{H}_2\text{OHF}$  at the MP2 level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E_{\text{corr}}^{\text{CP}}$  and  $\Delta E_{\text{corr}}$  results, the unconnected crosses ( $\times$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, the asterisks (\*) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}$  results, and the two horizontal dashed lines are the two R12 results.

to the interaction energy. In the following, we therefore consider two-point extrapolations for two consecutive  $X$  of the form (4).

The basis set convergence of  $\Delta E_{\text{corr}}^{\text{CP}}$  is, as opposed to that of  $\Delta E_{\text{corr}}$ , systematic. Furthermore, the convergence of  $\Delta E_{\text{corr}}^{\text{CP}}$  is both monotonic and slow; closely resembling the basis set convergence of the correlation energy. The CP interaction energies therefore appear better suited for extrapolations than the uncorrected interaction energies. This is confirmed by the results in Table IV and in Fig. 6–10. As the aug-cc-pVTZ  $\Delta E_{\text{corr}}$  results are further away from the basis set limit than the corresponding aug-cc-pVDZ results are, the 2–3 extrapolated  $\Delta E_{\text{corr}}$  results are poorer than the original aug-cc-pVTZ  $\Delta E_{\text{corr}}$  results. Likewise, the 3–4 extrapolated  $\Delta E_{\text{corr}}$  results do not represent much of an improvement on the original aug-cc-pVQZ  $\Delta E_{\text{corr}}$  results (for  $\text{H}_2\text{OHF}$  and  $\text{HCNHF}$  they are in fact worse). Finally, except for  $\text{HCNHF}$ , the 4–5 extrapolated  $\Delta E_{\text{corr}}$  results are not significantly better than the original aug-cc-pV5Z  $\Delta E_{\text{corr}}$  results. This behav-

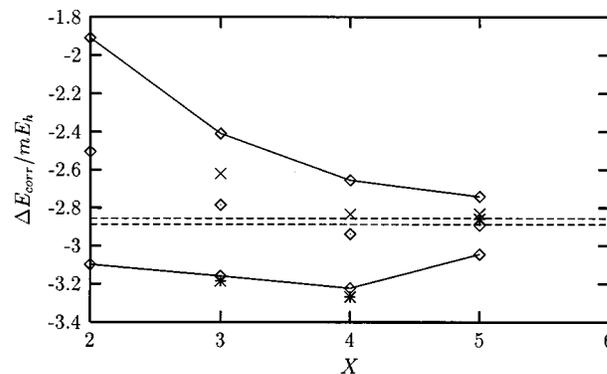


FIG. 9.  $\Delta E_{\text{corr}}^{\text{CP}}$  (upper curve) and  $\Delta E_{\text{corr}}$  (lower curve) for  $\text{HCNHF}$  at the MP2 level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E_{\text{corr}}^{\text{CP}}$  and  $\Delta E_{\text{corr}}$  results, the unconnected crosses ( $\times$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, the asterisks (\*) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}$  results, and the two horizontal dashed lines are the two R12 results.

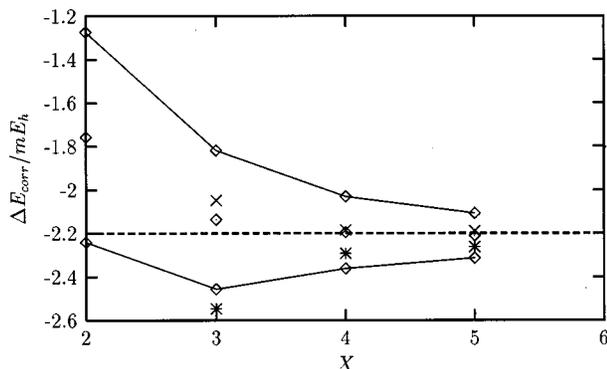


FIG. 10.  $\Delta E_{\text{corr}}^{\text{CP}}$  (upper curve) and  $\Delta E_{\text{corr}}$  (lower curve) for  $(\text{H}_2\text{O})_2$  at the MP2 level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E_{\text{corr}}^{\text{CP}}$  and  $\Delta E_{\text{corr}}$  results, the unconnected crosses ( $\times$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, the asterisks ( $*$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}$  results, and the two horizontal dashed lines are the two R12 results.

ior, however, does not imply that the two-point  $X^{-3}$  extrapolation is in any way deficient. Instead, it mirrors the unsystematic convergence of  $\Delta E_{\text{corr}}$ , which is a consequence of the combination of the basis set incompleteness errors arising from the incomplete description of the electronic Coulomb cusp and the BSSE. The  $X^{-3}$  extrapolation, by construction, remedies only the former, and as long as a substantial BSSE persists, the extrapolated values will be contaminated by this. Indeed, once the BSSE has been effectively removed by the counterpoise correction, the convergence of the correlation contribution to the interaction

energy resembles that of the correlation energy itself, and the  $X^{-3}$  extrapolation gives solid improvements on the original unextrapolated  $\Delta E_{\text{corr}}^{\text{CP}}$  results. The 2–3 extrapolated  $\Delta E_{\text{corr}}^{\text{CP}}$  results are thus within 0.2 kcal/mol of the basis set limit, and the 3–4 extrapolated  $\Delta E_{\text{corr}}^{\text{CP}}$  results are within 0.05 kcal/mol of the basis set limit. The 4–5 extrapolated  $\Delta E_{\text{corr}}^{\text{CP}}$  results are also within 0.05 kcal/mol of the basis set limit, and, if anything, slightly above the basis set limit.

The performance of the two-point  $X^{-3}$  extrapolation for interaction energies is analogous to what has recently been observed for electric dipole moments.<sup>47</sup> Because of the linear dependence of the electric dipole operator on the electronic coordinates, an accurate description of the outer valence region is needed for the dipole moment, and the absence of diffuse functions in the basis set may lead to large basis set errors not related to the incomplete description of the electronic Coulomb cusp.<sup>47,60</sup> Such errors are not recovered by the two-point  $X^{-3}$  extrapolation. Accordingly, when applied to the cc-pVXZ basis sets, which do not include diffuse functions, the extrapolation gave results of varying quality for the dipole moment.<sup>47</sup> However, when applied to the aug-cc-pVXZ basis sets, dipole moments in very good agreement with basis set limits determined by R12 methods were obtained. Thus, once the significant basis set errors other than those originating from the description of the electronic Coulomb cusp have been addressed, the cusp dominates and the  $X^{-3}$  form for the basis set convergence is observed. In essence the same is seen here: once the errors arising from BSSE have been effectively removed by the counterpoise

TABLE IV. The MP2 correlation contribution to the different results obtained for the five complexes at the 2-3, 3-4, and 4-5  $X^{-3}$  extrapolated levels and at the MP2-R12 level. The ordering of the columns of results is the same as the one in Table II. All the interaction energy contributions are given in  $mE_h$ , whereas the others are given in  $E_h$ .

$X$	$E_{\text{corr}}^{\text{comp}}$	$E_{\text{corr}}^{\text{don}}$	$E_{\text{corr}}^{\text{acc}}$	$E_{\text{corr}}^{\text{CP,don}}$	$E_{\text{corr}}^{\text{CP,acc}}$	$\Delta E_{\text{corr}}$	$\Delta E_{\text{corr}}^{\text{CP}}$	$\Delta E_{\text{corr}}^{\text{ave}}$
(HF) <sub>2</sub>								
2-3	-0.609 501	-0.304 006	-0.304 006	-0.304 222	-0.304 332	-1.4885	-0.9464	-1.2175
3-4	-0.634 839	-0.316 807	-0.316 807	-0.316 854	-0.316 900	-1.2244	-1.0851	-1.1548
4-5	-0.639 643	-0.319 191	-0.319 191	-0.319 285	-0.319 268	-1.2599	-1.0892	-1.1745
R12	-0.642 992	-0.320 947	-0.320 947	-0.320 962	-0.320 918	-1.0990	-1.1124	-1.1057
(HCl) <sub>2</sub>								
2-3	-0.459 363	-0.227 924	-0.227 924	-0.228 070	-0.228 213	-3.5160	-3.0798	-3.2979
3-4	-0.477 763	-0.237 235	-0.237 235	-0.237 284	-0.237 335	-3.2920	-3.1434	-3.2177
4-5	-0.483 729	-0.240 214	-0.240 214	-0.240 273	-0.240 309	-3.2998	-3.1472	-3.2235
R12	-0.493 075	-0.244 997	-0.244 997	-0.245 001	-0.244 884	-3.0803	-3.1894	-3.1349
H <sub>2</sub> OHF								
2-3	-0.595 226	-0.304 006	-0.288 980	-0.304 286	-0.289 268	-2.2394	-1.6726	-1.9560
3-4	-0.617 753	-0.316 807	-0.298 731	-0.316 940	-0.298 880	-2.2146	-1.9329	-2.0738
4-5	-0.621 497	-0.319 191	-0.300 242	-0.319 287	-0.300 270	-2.0637	-1.9398	-2.0017
R12	-0.624 219	-0.320 947	-0.301 323	-0.320 967	-0.301 277	-1.9491	-1.9754	-1.9622
HCNHF								
2-3	-0.680 917	-0.304 006	-0.373 726	-0.304 306	-0.373 990	-3.1845	-2.6204	-2.9025
3-4	-0.704 336	-0.316 807	-0.384 260	-0.316 987	-0.384 514	-3.2685	-2.8345	-3.0515
4-5	-0.707 886	-0.319 191	-0.385 833	-0.319 268	-0.385 785	-2.8612	-2.8327	-2.8470
R12	-0.711 878	-0.320 947	-0.388 044	-0.320 969	-0.388 053	-2.8878	-2.8568	-2.8723
(H <sub>2</sub> O) <sub>2</sub>								
2-3	-0.580 507	-0.288 980	-0.288 980	-0.289 231	-0.289 227	-2.5461	-2.0485	-2.2973
3-4	-0.599 754	-0.298 731	-0.298 731	-0.298 727	-0.298 842	-2.2924	-2.1858	-2.2391
4-5	-0.602 747	-0.300 242	-0.300 242	-0.300 283	-0.300 273	-2.2631	-2.1903	-2.2267
R12 <sup>a</sup>	-0.604 844	-0.301 323	-0.301 323	-0.301 335	-0.301 307	-2.1974	-2.2019	-2.1997

<sup>a</sup>From Ref. 21.

TABLE V. The CCSD(T) correlation contribution to the different results obtained for the five complexes as a function of the cardinal number  $X$  of the aug-cc-pVXZ basis sets. The ordering of the columns of results is the same as the one in Table II. The rows with 4–5, 3–4, and 2–3 for  $X$  give the results obtained at the 4–5, 3–4, and 2–3  $X^{-3}$  extrapolated levels, respectively. All the interaction energy contributions are given in  $mE_h$ , whereas the others are given in  $E_h$ .

$X$	$E_{\text{corr}}^{\text{comp}}$	$E_{\text{corr}}^{\text{don}}$	$E_{\text{corr}}^{\text{acc}}$	$E_{\text{corr}}^{\text{CP,don}}$	$E_{\text{corr}}^{\text{CP,acc}}$	$\Delta E_{\text{corr}}$	$\Delta E_{\text{corr}}^{\text{CP}}$	$\Delta E_{\text{corr}}^{\text{ave}}$
				(HF) <sub>2</sub>				
2	-0.461 501	-0.230 109	-0.230 109	-0.230 491	-0.230 622	-1.2841	-0.3883	-0.8362
3	-0.578 542	-0.288 480	-0.288 480	-0.288 741	-0.288 861	-1.5823	-0.9395	-1.2609
4	-0.619 085	-0.308 815	-0.308 815	-0.308 933	-0.308 991	-1.4551	-1.1613	-1.3082
5	-0.633 515	-0.316 049	-0.316 049	-0.316 138	-0.316 152	-1.4165	-1.2251	-1.3208
4–5	-0.648 654	-0.323 639	-0.323 639	-0.323 697	-0.323 665	-1.3760	-1.2920	-1.3340
3–4	-0.648 670	-0.323 654	-0.323 654	-0.323 667	-0.323 680	-1.3624	-1.3232	-1.3428
2–3	-0.627 822	-0.313 057	-0.313 057	-0.313 267	-0.313 383	-1.7078	-1.1716	-1.4397
				(HCl) <sub>2</sub>				
2	-0.361 749	-0.179 498	-0.179 498	-0.179 834	-0.180 156	-2.7526	-1.7601	-2.2563
3	-0.474 210	-0.235 630	-0.235 630	-0.235 816	-0.235 994	-2.9490	-2.3994	-2.6742
4	-0.508 380	-0.252 766	-0.252 766	-0.252 855	-0.252 926	-2.8472	-2.5993	-2.7232
5	-0.520 393	-0.258 787	-0.258 787	-0.258 847	-0.258 890	-2.8181	-2.6555	-2.7368
4–5	-0.532 996	-0.265 104	-0.265 104	-0.265 135	-0.265 147	-2.7875	-2.7146	-2.7510
3–4	-0.533 315	-0.265 271	-0.265 271	-0.265 288	-0.265 281	-2.7729	-2.7451	-2.7590
2–3	-0.521 562	-0.259 265	-0.259 265	-0.259 388	-0.259 505	-3.0317	-2.6685	-2.8501
				H <sub>2</sub> OHF				
2	-0.464 468	-0.230 109	-0.232 313	-0.230 676	-0.233 263	-2.0471	-0.5301	-1.2886
3	-0.572 416	-0.288 480	-0.281 676	-0.288 840	-0.282 122	-2.2600	-1.4542	-1.8571
4	-0.608 642	-0.308 815	-0.297 581	-0.309 014	-0.297 799	-2.2459	-1.8282	-2.0371
5	-0.621 187	-0.316 049	-0.302 973	-0.316 174	-0.303 077	-2.1653	-1.9362	-2.0508
4–5	-0.634 349	-0.323 639	-0.308 629	-0.323 686	-0.308 614	-2.0808	-2.0494	-2.0651
3–4	-0.635 077	-0.323 654	-0.309 187	-0.323 736	-0.309 240	-2.2356	-2.1011	-2.1683
2–3	-0.617 868	-0.313 057	-0.302 461	-0.313 331	-0.302 694	-2.3497	-1.8433	-2.0965
				H <sub>2</sub> CNH				
2	-0.548 702	-0.230 109	-0.315 840	-0.230 694	-0.316 572	-2.7540	-1.4365	-2.0953
3	-0.663 181	-0.288 480	-0.371 860	-0.288 865	-0.372 219	-2.8409	-2.0970	-2.4690
4	-0.700 429	-0.308 815	-0.388 776	-0.309 050	-0.389 019	-2.8374	-2.3594	-2.5984
5	-0.713 143	-0.316 049	-0.394 444	-0.316 183	-0.394 530	-2.6498	-2.4312	-2.5405
4–5	-0.726 483	-0.323 639	-0.400 391	-0.323 666	-0.400 311	-2.4529	-2.5066	-2.4798
3–4	-0.727 609	-0.323 654	-0.401 121	-0.323 780	-0.401 279	-2.8348	-2.5508	-2.6928
2–3	-0.711 383	-0.313 057	-0.395 448	-0.313 358	-0.395 649	-2.8775	-2.3751	-2.6263
				(H <sub>2</sub> O) <sub>2</sub>				
2 <sup>a</sup>	-0.466 934	-0.232 313	-0.232 313	-0.232 676	-0.233 031	-2.3083	-1.2262	-1.7672
3 <sup>a</sup>	-0.565 882	-0.281 676	-0.281 676	-0.281 949	-0.282 041	-2.5295	-1.8919	-2.2107
4 <sup>a</sup>	-0.597 550	-0.297 581	-0.297 581	-0.297 675	-0.297 754	-2.3881	-2.1213	-2.2547
3–4	-0.620 660	-0.309 187	-0.309 187	-0.309 150	-0.309 221	-2.2849	-2.2887	-2.2868
2–3	-0.607 544	-0.302 461	-0.302 461	-0.302 677	-0.302 695	-2.6226	-2.1722	-2.3974

<sup>a</sup>From Ref. 17.

correction, the  $X^{-3}$  form describes the basis set convergence of the interaction energy very well.

Comparing the extrapolated results with the averages of  $\Delta E_{\text{corr}}$  and  $\Delta E_{\text{corr}}^{\text{CP}}$ , we see that at the aug-cc-pVTZ level, the simple average performs better than the 2–3 extrapolated  $\Delta E_{\text{corr}}^{\text{CP}}$  results, which is not that surprising since the extrapolation is known to degrade in performance when double-zeta results are included.<sup>45,47</sup> Otherwise, the simple average at the aug-cc-pVQZ level and the 3–4 extrapolated  $\Delta E_{\text{corr}}^{\text{CP}}$  results are very similar, and also the simple average at the aug-cc-pV5Z level and the 4–5 extrapolated  $\Delta E_{\text{corr}}^{\text{CP}}$  results are very close to each other.

#### D. Convergence and extrapolations of the CCSD(T) correlation contribution

The results for the CCSD(T) correlation contributions are given in Table V and illustrated in Figs. 11–15. The situation for the CCSD(T) correlation contributions is prac-

tically the same as the one for the MP2 correlation contributions, which is not unexpected as the CCSD(T) and MP2 correlation energies usually display similar basis set convergence.<sup>45</sup> Again, the convergence of  $\Delta E_{\text{corr}}^{\text{CP}}$  is always monotonic, smooth, slow, and from above, with large errors at the aug-cc-pVDZ basis set, and the convergence of  $\Delta E_{\text{corr}}$  is always nonmonotonic, decreasing from aug-cc-pVDZ to aug-cc-pVTZ and increasing from aug-cc-pVTZ to aug-cc-pV5Z. The performance of the extrapolations is therefore also virtually the same as at the MP2 level, and the 4–5 extrapolated  $\Delta E_{\text{corr}}^{\text{CP}}$  results are therefore used in Figs. 11–14 as representatives of the basis set limit (the horizontal dashed lines), which, according to the findings above, should be accurate to at least 0.05 kcal/mol. Due to the unsystematic convergence of  $\Delta E_{\text{corr}}$ , the two-point  $X^{-3}$  extrapolation based on  $\Delta E_{\text{corr}}$  results does not perform very well, whereas the extrapolation based on  $\Delta E_{\text{corr}}^{\text{CP}}$  results and the simple average of  $\Delta E_{\text{corr}}$  and  $\Delta E_{\text{corr}}^{\text{CP}}$  both perform very well. Only in a

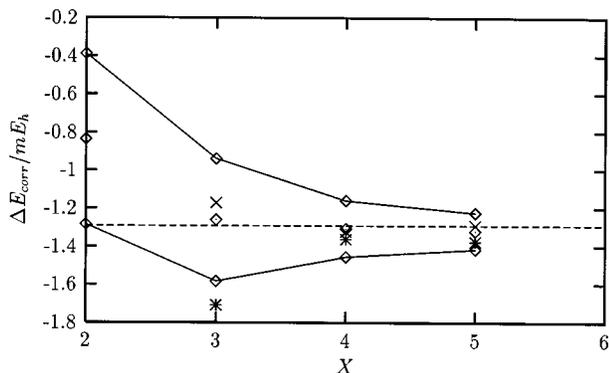


FIG. 11.  $\Delta E_{\text{corr}}^{\text{CP}}$  (upper curve) and  $\Delta E_{\text{corr}}$  (lower curve) for  $(\text{HF})_2$  at the CCSD(T) level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E_{\text{corr}}^{\text{CP}}$  and  $\Delta E_{\text{corr}}$  results, the unconnected crosses ( $\times$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, the asterisks (\*) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}$  results, and the horizontal dashed line is the 4–5  $\Delta E_{\text{corr}}^{\text{CP}}$   $X^{-3}$  extrapolated result.

few cases (at the aug-cc-pVTZ level) the simple average performs noteworthy better than the extrapolation based on  $\Delta E_{\text{corr}}^{\text{CP}}$  results; otherwise, these two schemes give results that are very close to each other. Finally, at the aug-cc-pV5Z level, the simple average is always slightly lower than the 4–5  $\Delta E_{\text{corr}}^{\text{CP}}$  extrapolated result, which is also in accordance with our findings at the MP2 level.

For the correlation contribution to the interaction energy, the basis set errors are much larger than for the SCF part. The reduction of the basis set errors for the correlation contribution is thus very important. For the aug-cc-pVDZ basis set, the basis set errors of the  $\Delta E_{\text{corr}}$  results are significantly smaller than those of the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, and the  $\Delta E_{\text{corr}}$  results are also better than the simple average of  $\Delta E_{\text{corr}}$  and  $\Delta E_{\text{corr}}^{\text{CP}}$ . The good performance of  $\Delta E_{\text{corr}}$  at the aug-cc-pVDZ level, however, is due to a fortuitous cancellation of errors between BSSE and the other (ordinary) basis set errors, and the aug-cc-pVDZ basis set is in general not sufficiently reliable for high-accuracy studies (see the results for HCNHF in Table

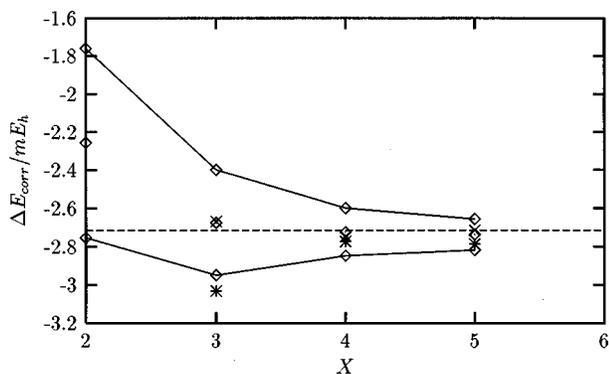


FIG. 12.  $\Delta E_{\text{corr}}^{\text{CP}}$  (upper curve) and  $\Delta E_{\text{corr}}$  (lower curve) for  $(\text{HCl})_2$  at the CCSD(T) level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E_{\text{corr}}^{\text{CP}}$  and  $\Delta E_{\text{corr}}$  results, the unconnected crosses ( $\times$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, the asterisks (\*) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}$  results, and the horizontal dashed line is the 4–5  $\Delta E_{\text{corr}}^{\text{CP}}$   $X^{-3}$  extrapolated result.

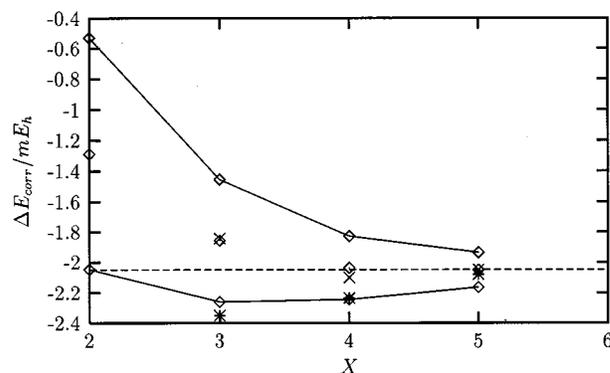


FIG. 13.  $\Delta E_{\text{corr}}^{\text{CP}}$  (upper curve) and  $\Delta E_{\text{corr}}$  (lower curve) for  $\text{H}_2\text{O}/\text{HF}$  at the CCSD(T) level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E_{\text{corr}}^{\text{CP}}$  and  $\Delta E_{\text{corr}}$  results, the unconnected crosses ( $\times$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, the asterisks (\*) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}$  results, and the horizontal dashed line is the 4–5  $\Delta E_{\text{corr}}^{\text{CP}}$   $X^{-3}$  extrapolated result.

III, and Figs. 9 and 14, where the basis set error of the aug-cc-pVDZ  $\Delta E_{\text{corr}}$  result is about  $0.2 mE_h$ ). For larger systems whose size prohibits the use of basis sets larger than the aug-cc-pVDZ set, the  $\Delta E_{\text{corr}}$  results obtained in the aug-cc-pVDZ basis set are expected to be the ones with the smallest basis set error. However, for systems where the larger basis sets can be employed, both the simple average of  $\Delta E_{\text{corr}}$  and  $\Delta E_{\text{corr}}^{\text{CP}}$  and the two-point  $X^{-3}$  extrapolated  $\Delta E_{\text{corr}}^{\text{CP}}$  results have significantly smaller basis set errors than the original  $\Delta E_{\text{corr}}$  and  $\Delta E_{\text{corr}}^{\text{CP}}$  results. At the aug-cc-pVTZ level, both schemes give results that are within  $0.2 \text{ kcal/mol}$  of the basis set limit, and for the larger aug-cc-pVXZ basis sets, the results are within  $0.05 \text{ kcal/mol}$  of the basis set limit. Both schemes are thus very effective and useful in reducing the basis set error for the correlation contribution to the interaction energy.

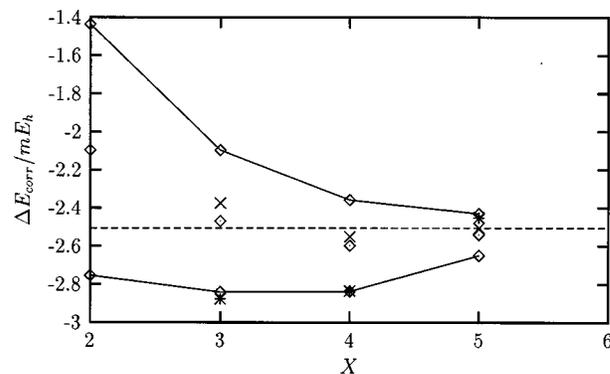


FIG. 14.  $\Delta E_{\text{corr}}^{\text{CP}}$  (upper curve) and  $\Delta E_{\text{corr}}$  (lower curve) for HCNHF at the CCSD(T) level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E_{\text{corr}}^{\text{CP}}$  and  $\Delta E_{\text{corr}}$  results, the unconnected crosses ( $\times$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, the asterisks (\*) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}$  results, and the horizontal dashed line is the 4–5  $\Delta E_{\text{corr}}^{\text{CP}}$   $X^{-3}$  extrapolated result.

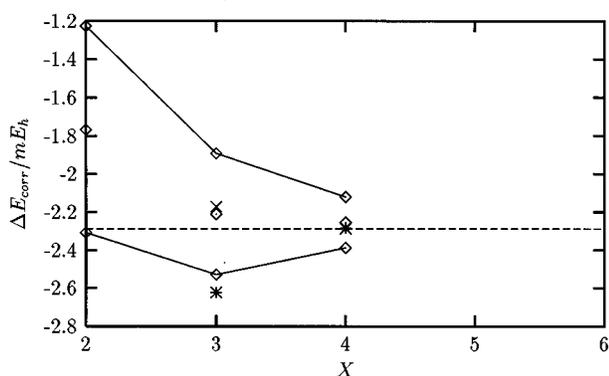


FIG. 15.  $\Delta E_{\text{corr}}^{\text{CP}}$  (upper curve) and  $\Delta E_{\text{corr}}$  (lower curve) for  $(\text{H}_2\text{O})_2$  at the CCSD(T) level as a function of the cardinal number  $X$ . The unconnected diamonds ( $\diamond$ ) are the simple average of the  $\Delta E_{\text{corr}}^{\text{CP}}$  and  $\Delta E_{\text{corr}}$  results, the unconnected crosses ( $\times$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}^{\text{CP}}$  results, the asterisks ( $*$ ) are the two-point  $X^{-3}$  extrapolated results based on the  $\Delta E_{\text{corr}}$  results, and the horizontal dashed line is the 3–4  $\Delta E_{\text{corr}}^{\text{CP}}$   $X^{-3}$  extrapolated result.

#### IV. CONCLUSION

The basis set convergence of the SCF and correlation contributions to the interaction energy of the five hydrogen-bonded complexes  $(\text{HF})_2$ ,  $(\text{HCl})_2$ ,  $\text{H}_2\text{OHF}$ ,  $\text{HCNHF}$ , and  $(\text{H}_2\text{O})_2$  has been investigated via conventional SCF, MP2, and CCSD(T) calculations for the aug-cc-pVXZ series of basis sets and explicitly correlated MP2-R12/A calculations. At the SCF level, the CP and uncorrected interaction energies both converge very unsystematically. The basis set errors in the SCF part, however, are significantly smaller than those in the correlation contribution, and the latter errors are therefore the most important. For the correlation contribution, the CP and uncorrected results converge toward the basis set limit from each side (the former from above), and their simple average is therefore remarkably close to the basis set limit.

The basis set convergence of the CP correlation contribution is very different from that of the uncorrected correlation contribution. While the latter is always nonmonotonic and very unsystematic, the former is always monotonic, smooth, slow, and systematic. The unsystematic convergence of the uncorrected results is a consequence of the combination of two different basis set errors; BSSE and the errors associated with the incomplete description of the electronic Coulomb cusp. However, once BSSE has been effectively removed by the counterpoise correction, the cusp dominates and the convergence becomes systematic and completely like that of the correlation energy. Consequently, the basis set convergence of the CP correlation contribution follows an  $X^{-3}$  form similar to the one for the correlation energy, and two-point extrapolations based on this form yield results that are closer to the basis set limit than the original CP and uncorrected correlation contributions are. In particular, when double-zeta results are not included in the extrapolations, results within 0.05 kcal/mol of the basis set limit are obtained.

Although the convergence of the uncorrected correlation contribution is very unsystematic, those results are never

more than 0.3 kcal/mol from the basis set limit, while the CP results within the aug-cc-pVDZ basis set have errors larger than 0.5 kcal/mol. For the smaller basis sets, the uncorrected results are closer to the basis set limit than are the CP results, but this is due to a fortuitous cancellation of errors. Following the discussion above, the basis set convergence of the CP correlation contribution is dominated by the incomplete description of the electronic Coulomb cusp, and the error associated with the cusp makes the correlation contribution to the interaction energy too high—see, e.g., Figs. 6–15. On the other hand, BSSE makes the interaction energy too low (compare the CP and uncorrected correlation contributions). The cancellation of these two oppositely directed errors leads to a fortuitously good performance of the uncorrected interaction energies—as well as the very unsystematic convergence of these—and the uncorrected results in the small basis sets should therefore be judged and employed with caution.

Finally, our most accurate results for the equilibrium interaction energies of the five complexes are obtained from combination of the SCF  $\Delta E^{\text{ave}}(5)$  results and the 4–5  $\Delta E_{\text{corr}}^{\text{CP}}$  extrapolated results at the valence only CCSD(T) level (3–4 extrapolated results for  $(\text{H}_2\text{O})_2$ ). These results are:  $-4.53$  for  $(\text{HF})_2$ ,  $-1.95$  for  $(\text{HCl})_2$ ,  $-8.51$  for  $\text{H}_2\text{OHF}$ ,  $-7.31$  for  $\text{HCNHF}$ , and  $-4.96$  kcal/mol for  $(\text{H}_2\text{O})_2$ .

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