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Molecular Orbital Calculations of Water Clusters on Counterpoise-Corrected Potential Energy Surfaces

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Water dimer and the cyclic trimer and tetramer are calculated using the Hartree−Fock (HF), second-order Møller−Plesset (MP2), and two density functional theory (DFT) methods, B3PW91 and B3LYP for a wide variety of different basis sets. The interaction energies and O···O distances as calculated on the normal and counterpoise (CP) corrected potential energy surfaces (PES) are compared as a function of basis set quality (as measured by the energies for optimized water monomer) for each of the four methods. The HF and DFT procedures lead to reasonably rapid conversion to the large basis set values for both interaction energies and O···O distances. Even moderate basis sets can be used to obtain results similar to the extrapolated values when optimizations are performed on the CP-corrected PES's. For MP2, these energies and distances converge to the extrapolated values much more slowly. Basis set superposition error (BSSE) remains significant even for the best basis sets used (aug-cc-pVQz and aug-cc-pVTZ). Nevertheless, the extrapolated MP2 interaction energies could also be reproduced with moderate sized basis sets on the CP-corrected PES, although the calculated O···O distances were less well reproduced with moderate sized basis sets. We calculated the CP using the procedure where each fragment is calculated in the basis if the entire aggregate. The results show this procedure to be well-behaved, as the normal and CP-optimized calculations converged systematically to the same values as the basis set improved for all four methods used. The advantages of this practice over a proposed hierarchical procedure for calculating the CP are discussed. A misconception about the supposed superiority of the latter procedure is remedied.

Clusters of water molecules have long interested both experimental and theoretical chemists for many different reasons.[1,2] Studies of the vibrational modes (which can be very anharmonic) of these clusters has been of particular interest.[3] As the literature on these subjects is extremely extensive, we have restricted our citations but include major reviews[1−3] and a very recent report that includes the most recent literature.[4] While very accurate calculations have been performed on the water dimer, the difficulty of performing calculations at similar levels on more complex clusters increases enormously with their size. Both the complexity of the individual energy evaluations and the quantity of these evaluations increase markedly as the clusters grow. We have recently shown that we could reproduce the results of very high level calculations on the water dimer with calculations using smaller basis sets where the geometry is optimized on a counterpoise-optimized (CP-opt) potential energy surface (PES).[5] In particular, the calculated energy at the MP2/d95++** level is within 0.15 kcal/mol of the "MP2 limit" of 4.90 kcal/mol.[6] The results of this work imply that calculations on larger water clusters ought to benefit from this procedure, as the calculational complexity would be greatly reduced. We used a program that drove Gaussian for the previous calculations. While this program was made readily available, the user needed to obtain and learn how to use it. Recently, the algorithm for these calculations has been incorporated into GAUSSIAN 98 (revisions A10 and later)[7] and GAUSSIAN 03,[8] making the procedure more readily accessible.

$$E^{\mathrm{CP}}_{\mathrm{interaction}} = E_{\mathrm{super}} - \sum_{i=1}^{n} E_{\mathrm{m}^{i}_{\mathrm{opt}}} + \sum_{i=1}^{n} (E_{\mathrm{m}^{i}_{\mathrm{f}}} - E_{\mathrm{m}^{i*}_{\mathrm{f}}}) \quad (1)$$

The procedure that we use for calculating the CP-opt geometries for clusters containing several fragments has been outlined by us previously.[9] Following the notation employed,[10] the CP-corrected interaction energy, $E^{\mathrm{CP}}_{\mathrm{interaction}}$, is defined in eq 1, where the E_{m}'s represent the energies of the individual monomers with the subscripts "opt", and "f" denoting the individually optimized and the monomers frozen in their supermolecular geometries; and the asterisk (*) denoting monomers calculated with "ghost" orbitals. The individual fragments are calculated in the basis of the entire cluster. The counterpoise (CP) correction for each fragment is the difference between the energy of that fragment in its own basis and that calculated in the basis of the entire cluster, at the geometry of the fragment in the cluster. This procedure for performing CP-opt on clusters containing more than two fragments has been used by others for neutral aggregates of water[11−13] and by us for preserving the symmetry in transitions states[14] and charged complexes.[15]

Valiron and Mayer[16] have both criticized this procedure and suggested that a hierarchical CP correction (originally proposed by White and Davidson[17]) be employed. The calculations presented here provide a test of the CP correction as we have defined it. We shall discuss why we question the validity of the arguments by Valiron and Mayer below.

In addition to the problem raised by Valiron and Mayer, Cook, Sordo and Sordo[18] have suggested that CP corrections of MP2

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calculations might be inappropriate due to the perturbation interactions to states that might only exist in the monomer with ghost orbitals, but not in the monomer, itself. The CP-correction is generally larger for MP2 than for HF or DFT calculations with equivalent basis sets.

Several reports have suggested that CP overestimates the BSSE for MP2 calculations. We have shown that CP does overestimate the BSSE for single point a posteriori calculations *because the geometry of the CP-corrected species is not optimized on the CP-corrected surface*. However, the CP-correction on the CP-optimized surface does not overestimate BSSE.[5] Since the CP corrections for MP2 calculations are generally larger than for HF or DFT, the single point a posteriori CP-corrections are generally made at a geometry farther from that on the CP-optimized surface. The apparently larger MP2 overcorrections are due to the larger energy difference between this and the CP-optimized geometry. We note this apparent overcorrection to be different from the problems described by Cook et al. above. As we shall see, these problems lead to a slower convergence to the limiting basis set values when MP2 is used, rather than an overcorrection.

In this paper, we evaluate the appropriateness of using the CP-correction procedure (as we define it) for complexes or clusters composed of more than two monomeric units. We also consider whether this CP procedure properly corrects for BSSE in MP2 calculations. To exemplify the problems that we have delineated, we explored the convergence of the energies and geometries of water dimer, trimer, and tetramer at various levels of ab initio MO theory. For simplicity, only the symmetric (where applicable) cyclic structures have been considered in ths work. While the calculations presented here may be useful to those studying water clusters, clarifying the questions raised about CP-corrections remains the primary goal of this paper.

Methods

The molecular orbital calculations were performed at the Hartree−Fock (HF), density functional theory (DFT), and second-order Møller−Plesset (MP2) levels using the Gaussian 98 program release A11.[7] The MP2 calculations used the frozen core (FC) protocol. The DFT calculations used the B3LYP and B3PW91 hybrid functionals. The complexes were completely optimized without any geometric restraints except those used to keep the symmetry of the tetramer. We used the same variety of basis sets for each of the MO methods. The basis sets used in this study are: 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-311++G(d,p), D95++(d,p), cc-pVDZ, cc-pVTZ, cc-pVQZ, aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ. The most complete basis set used was aug-cc-pVQZ for all methods except for the MP2(FC) calculations on the trimer and tetramer. The MP2(FC) calculations for these species required more scratch disk space than the 32-bit version of G98 could address. For this reason, the largest basis set used for the MP2(FC) calculations of these two species was aug-cc-pVTZ.

Results and Discussion

We shall discuss the results of the calculations on the individual species first, then continue to a more general discussion. To reduce the number of figures, we have plotted the data for all three species together for each method that we used. Linear fits to the data presented in the figures are provided to make the figures easier to follow and show general trends. We do not mean to imply that linear relationships are expected theoretically.

TABLE 1: Comparison of Counterpoise Correction (CP) in kcal/mol, CP-corrected Interaction Energy (ΔE_{int}) in kcal/mol, O···O Distance, and Change in O···O Distance (ΔO···O) in Å for the Two Best Basis Sets[a]

aug-vv-pVQZ

	total CP			CP/H-bond		
	dimer	trimer	tetramer	dimer	trimer	tetramer
HF	−0.02	−0.08	−0.12	−0.02	−0.03	−0.03
B3PW91	−0.04	−0.12	−0.18	−0.04	−0.04	−0.05
B3LYP	−0.03	−0.07	−0.10	−0.03	−0.02	−0.02
MP2(FC)	−0.23			−0.23	0.00	0.00

	CP-Corrected ΔE_{int}			CP-Corrected ΔE_{int}/H Bond		
	dimer	trimer	tetramer	dimer	trimer	tetramer
HF	−3.70	−11.01	−19.55	−3.70	−3.67	−4.89
B3PW91	−3.97	−12.81	−23.78	−3.97	−4.27	−5.95
B3LYP	−4.54	−14.21	−24.39	−4.54	−4.74	−6.10
MP2(FC)	−4.86			−4.86		

	O···O			ΔO···O		
	dimer	trimer	tetramer	dimer	trimer	tetramer
HF	3.036	2.927	2.883	0.009	0.000	0.000
B3PW91	2.915	2.788	2.725	0.001	0.002	0.002
B3LYP	2.920	2.809	2.756	0.001	0.002	0.001
MP2(FC)	2.925			0.022		

aug-vv-pVTZ

	total CP			CP/H-bond		
	dimer	trimer	tetramer	dimer	trimer	tetramer
HF	−0.06	−0.18	−0.29	−0.06	−0.06	−0.07
B3PW91	−0.07	−0.20	−0.37	−0.07	−0.07	−0.09
B3LYP	−0.05	−0.13	−0.27	−0.05	−0.04	−0.07
MP2(FC)	−0.47	−1.30	−2.29	−0.47	−0.43	−0.57

	CP-Corrected ΔE_{int}			CP-Corrected ΔE_{int}/H Bond		
	dimer	trimer	tetramer	dimer	trimer	tetramer
HF	−3.68	−10.96	−19.47	−3.68	−3.65	−4.87
B3PW91	−3.96	−12.80	−23.79	−3.96	−4.27	−5.95
B3LYP	−4.52	−14.21	−25.78	−4.52	−4.74	−6.44
MP2(FC)	−4.71	−14.98	−26.30	−4.86	−4.99	−6.58

	O···O			ΔO···O		
	dimer	trimer	tetramer	dimer	trimer	tetramer
HF	3.042	2.928	2.884	0.016	0.000	0.004
B3PW91	2.917	2.788	2.719	0.002	0.004	0.006
B3LYP	2.920	2.807	2.740	0.004	0.003	0.003
MP2(FC)	2.936	2.810	2.755	0.028	0.021	0.023

Experiment (from Ref 19)

ΔE_{int}	4.85	16.05	28.76
O···O	2.952	2.776	2.703

G3 (from ref 4, Including Supporting Information)

ΔE_{int}	5.140	15.760	28.220
O···O	2.914	2.789	2.748

[a] CP is taken as the difference in energy between normal and CP-optimized aggregates. This value is less than single point a posteriori CP.

Water Dimer. Water dimer had been extensively studied using theoretical techniques by many groups. We have previously published a study that shows that geometrical optimization on the CP-corrected surface provides reasonable energies and geometries for MP2 calculations using only a moderate basis set (D95++**).[5] The principal reason to extend this study lies in elucidating the convergence of MP2 energy and geometry calculations with increasingly large basis sets toward the limiting value. Since the BSSE will disappear at the limiting value, convergence of energy is equivalent to the asymptotic conver-

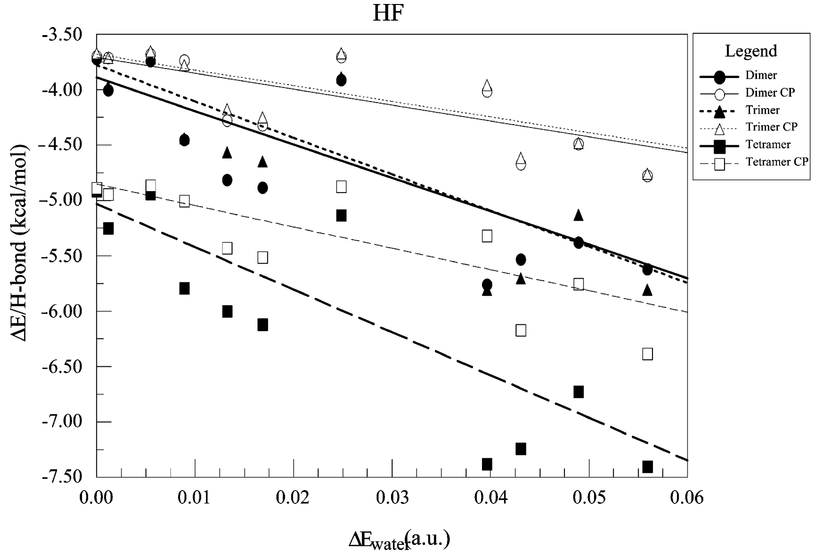

Figure 1. HF interaction energy per H-bond (ΔE_{int}) in kcal/mol plotted vs energy difference between water monomer in a given basis set and the lowest water energy for all basis sets (see text).

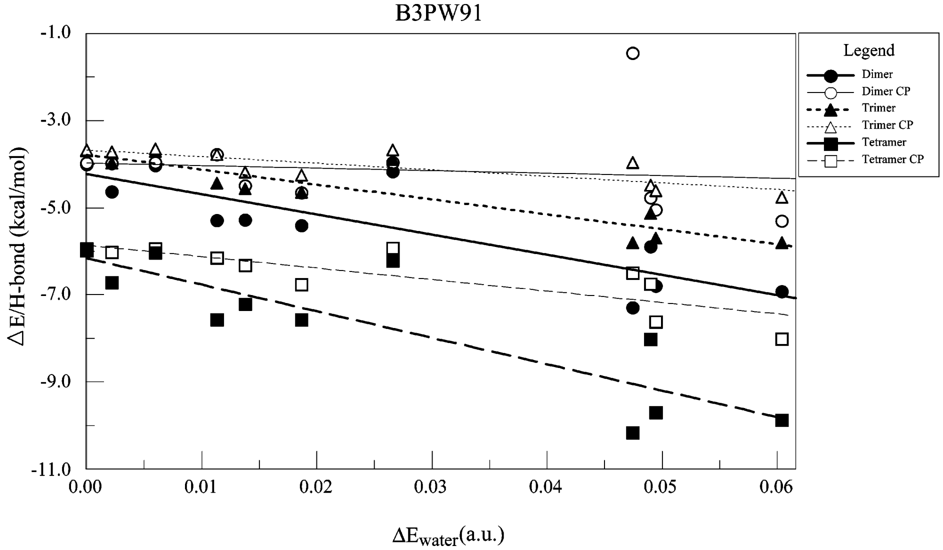

Figure 2. B3PW91 interaction energy per H-bond (ΔE_{int}) in kcal/mol plotted vs energy difference between water monomer in a given basis set and the lowest water energy for all basis sets (see text).

TABLE 2: Total Energies (hartrees) of Geometrically Optimized Water (Monomer) Using Different MO Methods

basis set	HF	B3PW91	B3LYP	MP2(FC)
6-31G(d)	−76.010750	−76.381610	−76.408950	−76.196850
6-31+G(d)	−76.017743	−76.393007	−76.422572	−76.209777
6-31G(d,p)	−76.023620	−76.392550	−76.419740	−76.219790
D95++(d,p)	−76.049830	−76.423320	−76.452720	−76.249640
6-311++G(d,p)	−76.053420	−76.428220	−76.458530	−76.274920
cc-pVDZ	−76.027054	−76.394575	−76.420627	−76.228667
cc-pVTZ	−76.057770	−76.430685	−76.459840	−76.318658
cc-pVQZ	−76.065519	−76.439823	−76.469646	−76.347640
aug-cc-pVDZ	−76.041844	−76.415398	−76.444643	−76.260910
aug-cc-pVTZ	−76.061203	−76.436027	−76.466197	−76.328992
aug-cc-pVQZ	−76.066676	−76.441990	−76.472240	−76.351919

gence of the BSSE (or CP) to zero. Similarly, the differences in geometries on the optimized surfaces with and without CP-correction should converge to zero at the complete basis set. We have calculated the HF, B3LYP, and B3PW91 energies and geometries with the same basis sets to provide a comparison. The energetic and structural results are presented in Table 1 and in Figures 1−8. Detailed numeric results that are presented only graphically are included in the Supporting Information. The graphical presentation presents a problem. While energy of interaction is a logical candidate for one axis, the appropriate coordinate for the other is less so. Often the energy is plotted vs some arbitrarily spaced points representing the different basis sets with the corrected and uncorrected energies seen to be converging. However, by changing the spacing between the arbitrary points chosen for the basis sets, the extrapolated corrected and uncorrected energies could be made to appear not to converge (if the points are too widely spaced), or to cross (if the points are too closely spaced). Another approach might be to plot the energies vs the number of basis functions used. However, the contribution of individual functions to the overall energy can be extremely variable. At or near the HF limit, additional functions would not change the energy at all. In such a plot, the number of functions could approach infinity while the energy remains constant. To avoid these problems, we have chosen to plot the interaction energies vs the energy of a water monomer calculated using the same procedure as that used for the dimer. Using the monomer energy effectively limits the value of the axis to the best value for this energy (rather than infinity as in the number of basis functions). The interaction and the

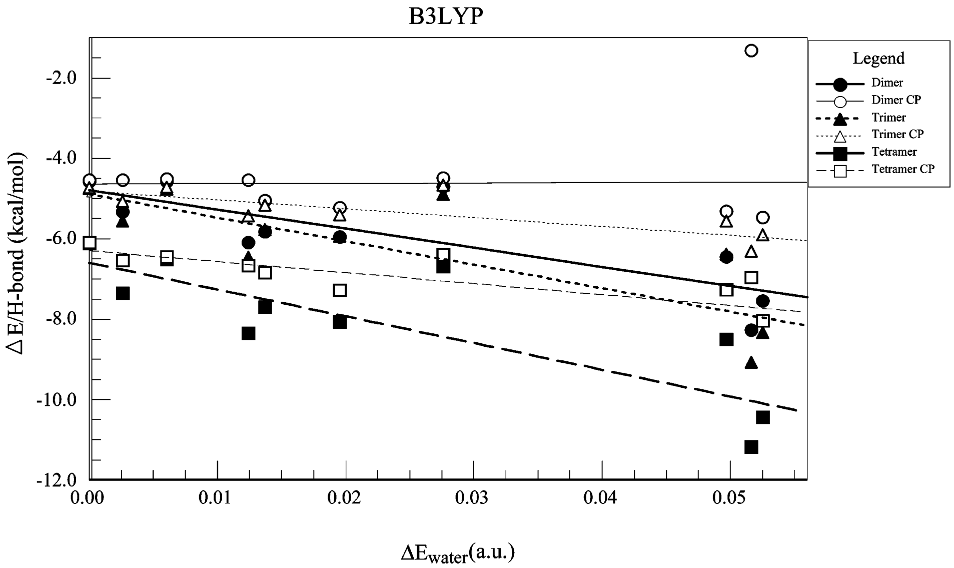

Figure 3. B3PLYP interaction energy per H-bond (ΔE_{int}) in kcal/mol plotted vs energy difference between water monomer in a given basis set and the lowest water energy for all basis sets (see text).

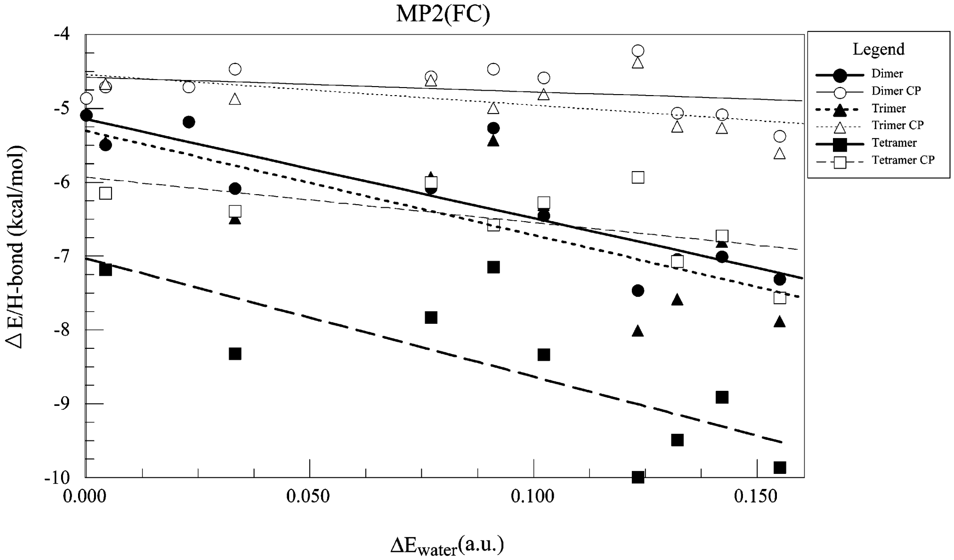

Figure 4. MP2(FC) interaction energy per H-bond (ΔE_{int}) in kcal/mol plotted vs energy difference between water monomer in a given basis set and the lowest water energy for all basis sets (see text).

monomer (isolated water) energies are expressed as the difference from that of the best calculation within a series in order to keep the energies for the differing calculations on the same scale. Table 2 presents the water monomer energies for the basis sets used in this study.

As can be seen from Figure 1, the CP-correction for the HF calculations converges almost to zero (0.02 kcal/mol) as the basis set improves. Convergence of the CP is almost as good for the two DFT methods used. The convergence for MP2 is good if one considers only the slopes of the lines. However, MP2(FC)/aug-cc-pVQZ has a residual CP of 0.23 kcal/mol, which is almost the same value as that for HF/cc-pVQZ, and an order of magnitude higher than that for HF/aug-cc-pVQZ. The O···O distances and, in particular, the differences in these distances before and after CP-optimization provide a measure of the geometric convergence as these distances are very sensitive to changes in the energies of interaction (i.e., the surface is quite flat with respect to variation of O···O distance with interaction energy).[5] Table 1 shows that the change in this distance upon CP-optimization for MP2/aug-cc-pVQZ (0.023 Å) is more than twice that for the HF calculation with the same basis set (0.009 Å). These calculations can be compared with the latest experimental interaction energy of 4.85 kcal/mol.[19]

Water dimer is a relatively small system compared with those that are currently of chemical importance. The fact that BSSE is still appreciable at the MP2/aug-cc-pVQZ level suggests that CP-optimization be necessary for MP2 calculations up to and including this quality basis set. Since using such large basis sets in MP2 calculations is rarely practical, use of CP-corrected optimizations seems appropriate for MP2 calculations of interaction energies.

Water Trimer. The cyclic trimer of water contains three H-bonds. The optimized structure for this species has two of the non-H-bonding hydrogens above and one below the plane defined by the three oxygen atoms. Thus, the three H-bond are not equivalent. The O···O distances reported in Table 1 and those of the Supporting Information represent the average of the three distances. Experimental reports indicate that all six H atoms interchange positions via a very low-lying normal vibrational mode of the aggregate.

All of the MO methods used predict the average O···O distance (therefore H-bond) to be shorter than in the dimer. The

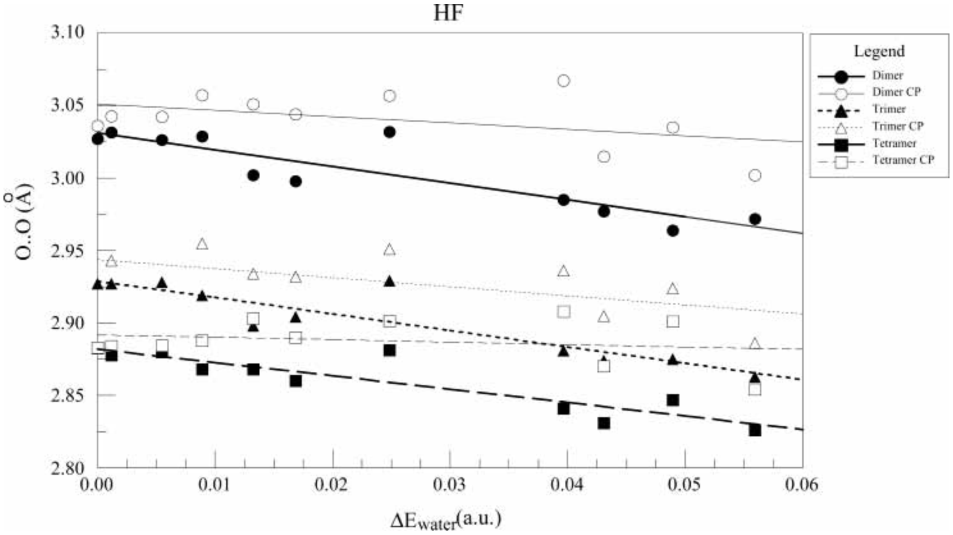

Figure 5. O···O distance (Å) plotted vs energy difference between water monomer in a given basis set and the lowest water energy for all basis sets (see text) for HF calculations.

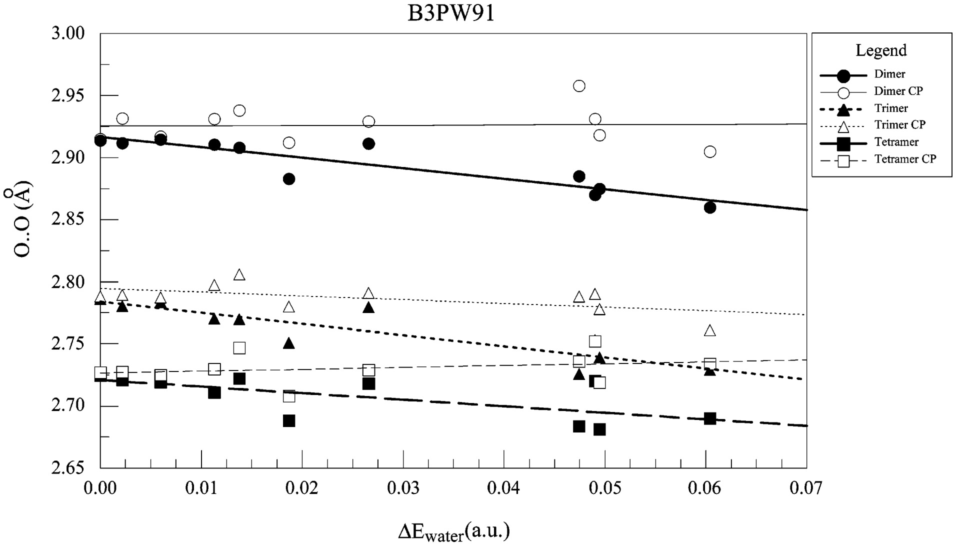

Figure 6. O···O distance (Å) plotted vs energy difference between water monomer in a given basis set and the lowest water energy for all basis sets (see text) for B3PW91 calculations.

two DFT and MP2 methods predict stronger H-bonds in the trimer than in the dimer, in accord with the shorter H-bond lengths, while the HF calculations do not. (see Table 1). The rather acute O−O−O angles of this structure will increase the electron correlation error per water monomer in the HF calculations compared to the dimer and tetramer. This error would lead to a lower average H-bond energy for the HF calculations.

The latest reported experimental interaction energy is −16.05 kcal/mol, which is slightly larger in magnitude, while the O···O separation at the minimum of 2.776 Å is a bit shorter than the best calculated values.[19]

Water Tetramer. The geometry for the cyclic water tetramer was constrained to be centrosymmetric. All methods predict a stronger H-bonding interaction per H-bond and a shorter O···O distances than in either the dimer or trimer. The correlation error per water monomer in the HF calculations will be less than in the trimer, as the larger O−O−O angles keep the average O···O distances (including those between non-H-bonding waters) longer. Thus, the energetic cooperativity becomes evident for the HF calculations, as well as the others. Here the latest reported experimental interaction energy is −28.76 kcal/mol, which is slightly larger in magnitude, while the O···O separation at the minimum of 2.703 Å is a bit shorter than the best calculated values, as in the timer.[19]

Effects of Optimization with CP. The data of Figures 1−4 clearly indicate that the CP-corrections to the energies decrease as the basis sets improve for each type of calculation performed and for each of the three water clusters. The difference in energy between the fitted lines for the open symbols (the CP-optimized structures) and the filled symbols (normally optimized structures) clearly decreases as the basis set improves. However, the extent of the CP corrections are much larger for the MP2 than for the HF and DFT calculations. Using the best (aug-cc-pVQZ for HF and DFT, aug-cc-pVTZ for MP2)) basis set, the CP corrections for HF an DFT vary from 0.02 to 0.05 kcal/mol per H-bond for all calculated species. Furthermore, the CP per H-bond remains relatively constant upon increasing aggregate size form dimer to tetramer. We have previously observed similar constant CP correction per H-bond in chains of formamides.[20,21] On the other hand, the CP corrections per H-bond for the MP2 calculations are significantly larger (from 0.47 to 0.57 kcal/mol). The analogous correction for DFT and HF using the same (aug-cc-pVTZ) basis are 0.05 to 0.09 kcal/mol. Since

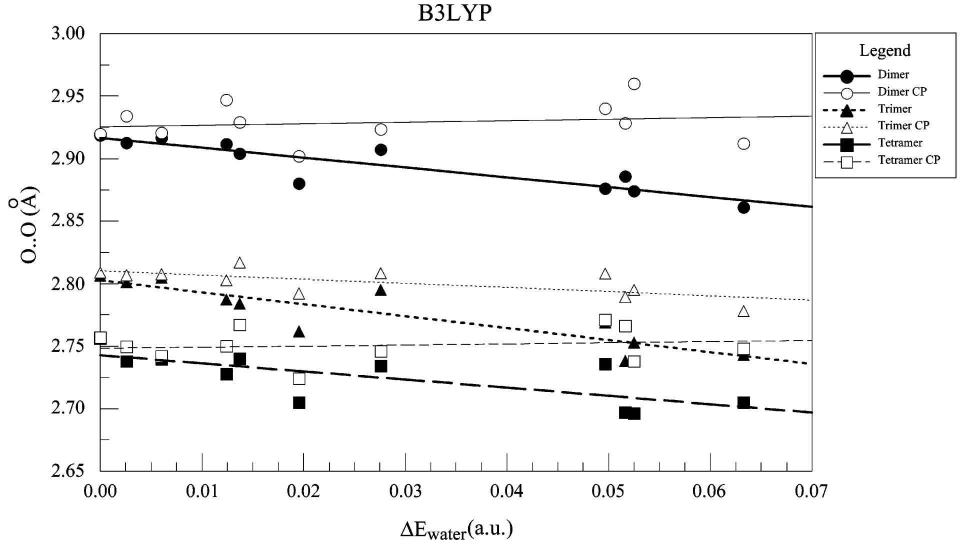

Figure 7. O···O distance (Å) plotted vs energy difference between water monomer in a given basis set and the lowest water energy for all basis sets (see text) for B3LYP calculations.

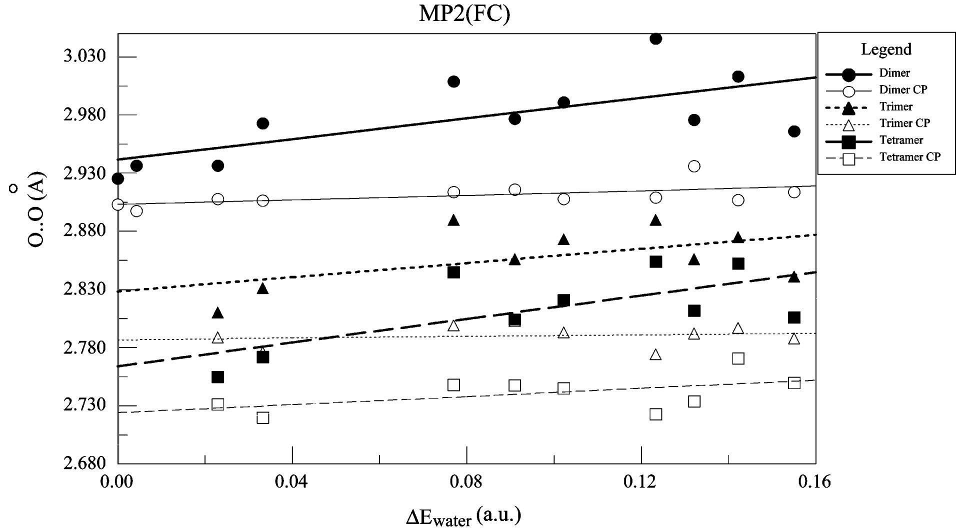

Figure 8. O···O distance (Å) plotted vs energy difference between water monomer in a given basis set and the lowest water energy for all basis sets (see text) for MP2(FC) calculations.

the ground state energies obtained from MP2 calculations, which are applications of second order perturbation theory (PT2), can only be lowered by interactions of doubly excited states, increasing the number of virtual orbitals present in a system can only lower the calculated ground state energy of that system. Both extending the basis set used and increasing the size of the system will increase the number of virtual orbitals in the system. As a result, the number of PT2 interactions (all of which can only stabilize) will increase. Let us consider the effects of increasing the basis set and the aggregate size separately.

Increasing the basis set of MP2 calculations in H-bonding (or other) aggregates has the normal effect of reducing the BSSE, as in HF and DFT calculations. However, the consequent increases in PT2 interactions include excitations from electron pairs on one monomer to virtual orbitals on another. This effect increases the BSSE. The fact that MP2 calculations generally converge to the limiting basis set value (as they do in the cases presented here), confirms the utility of CP corrections for MP2 calculations. Nevertheless, the increases in the number of PT2 interactions as the basis set increases tempers this convergence (without reversing it), which results in slower approaches to the limiting energy values, at least for the examples presented here.

Increasing the size of the aggregate (from two to four waters in this study) with a given basis set will increase the number of PT2 interactions from an electron pair on one monomer to virtual orbitals on the others simply because there will be more other monomers, thus more virtual orbitals on them collectively.

The O···O distances generally *increase* as one improves the basis set for HF and DFT calculations (Figures 5−7). Optimization with CP corrects the O···O distances even for small basis sets to values similar to those obtained with aug-cc-pVQZ for both DFT methods. Both B3LYP and B3PW91 (Figures 6 and 7) predict the O···O distance for water dimer to be about 2.93 Å, close to the experimental values for the PES minimum (corrected for the anharmonic zero-point vibrations) of 2.946[22] or 2.952 Å.[6,19] For HF, the CP-corrected O···O distance increases slightly as the basis set is improved, but less rapidly as the normally optimized geometries (see Figure 5). However, the trend is reversed with MP2 calculations (Figure 8). Here, the normally optimized O···O distances change only slightly

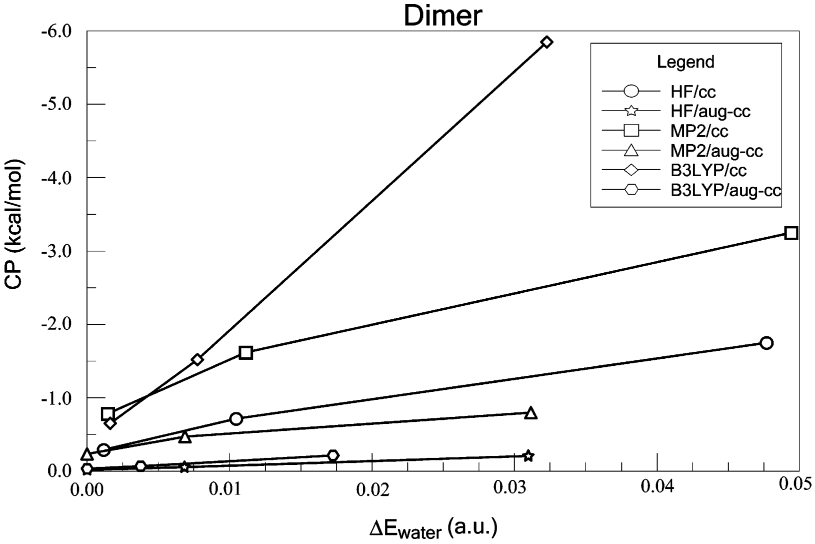

Figure 9. CP correction for water dimer in kcal/mol plotted vs energy difference between water monomer in a given basis set and the lowest water energy for the cc-pVXZ and aug-cc-pVXZ series of basis sets using HF, B3PW91, B3LYP, and M2(FC) methods.

as the basis set improves while the corresponding CP-optimized distances *decrease*. For the MP2/cc-aug-pVQZ, the Cp-corrected O••O distance is close to the experimental and DFT values but is still 0.02 Å longer than the normally optimized distance. The O•••O distances predicted by HF and MP2 are longer and shorter, receptively, than the experimental values for water dimer. The CP-corrected O•••O distances are larger than the normally optimized ones as CP correction removes an artifactual attraction. This is especially evident for the smaller basis sets. That the magnitudes these geometric corrections remain approximately constant for each basis set rather than increasing as the aggregate expands from two to four waters despite the increase in BSSE per H-bond associated with this expansion results from the offsetting effects of the larger CP correction and the deeper energy wells associated with the stronger and shorter H-bonds. One should note that while the extrapolated O•••O distances for the two DFT methods for the dimer are similar, those calculated by B3LYP extrapolate to slightly longer O•••O distances than B3PW91 for the trimer and tetramer.

The data in Figures 1−4 clearly indicate that the CP-optimized interactions energies for small and moderate basis sets are all much closer than those from the normal optimizations to the values expected for extended or complete basis sets for all kinds of calculations (HF, DFT, and MP2(FC) on all three aggregates considered. The linearly fitted lines for the uncorrected calculations have slopes with the same sign in all cases indicating that the interaction energies become generally less negative as the basis set is improved. The corresponding lines for the CP-corrected calculations also have slopes of the same sign, but they are all less steep than those for the corresponding normal calculations. In particular, the MP2(FC) behave qualitatively similarly to the HF and DFT calculations. Several reports have suggested that CP overcorrects the BSSE for MP2 calculations similar to those reported here. For example, one group regularly uses half the CP to correct for BSSE in MP2 calculations of water hexamers.[23] While we have previously shown this to be a misconception due to the a posteriori nature of the single point CP corrections which lead to a CP-corrected structure that is not geometrically optimized, the idea persists. The observation that the interaction energies for all four methods and all three species considered tend to become less negative reinforces the conclusion that CP-optimized structures do not overcorrect the MP2 interaction energies. Had that been the case, the CP-corrected MP2 interaction energies should have become more negative as the basis sets improved, while the uncorrected ones became less negative. One should also note that small basis set HF calculations can have a posteriori CP corrections that exceed the stabilization energy of the H-bonding complex. An example of this phenomenon is the HF/STO-3G optimized water dimer., where the a posteriori CP is 6.6, while the interaction energy is only −5.9 kcal/mol. Thus, after a posteriori CP correction, the water dimer is repulsive by 0.7 kcal/mol at this level of calculation. However, optimization on the CP-corrected PES leads to an interaction energy of −2.1 kcal/mol.

While Figures 1−8 illustrate the general trends in the interaction energies and O•••O distances with improvement of basis set for the clusters studied, they show moderate scatter in the data. This scatter can be considerably reduced if one compares only those basis sets that form well-behaved series, such as cc-pVXZ and aug-cc-pVXZ. Figures 9−11 illustrate the dependence of the CP correction and Figures 12−14 the change in O•••O for X = D, T, or Q in these two series.

As noted above, we have calculated the CP-correction for aggregates containing more than two fragments by calculating each monomeric unit in the entire basis of the aggregate. When, this procedure is used, all fragments and the aggregate use exactly the same basis set. This procedure can easily be reconciled with the description of CP used by van Duijneveldt who emphasizes that the BSSE is not due to the augmentation of the basis set of the individual fragments. Rather, it is due to the inconsistency of the basis sets used for the fragments and the aggregate. One should also note that he has demonstrated that CP properly corrects for BSSE for specific cases.[24] While the proof is not general, one can expect it to be extendable to other systems, unless proven otherwise.

Nevertheless, there has been some controversy about the correct manner of performing CP on a system with more than two fragments. Valiron and Mayer[16] have proposed a hierarchical CP scheme, first used by Davidson, as a more correct approach than the more traditional method for CP correction that we use here and have used in previous work. Using this method requires calculating each subunit of the aggregate with its own CP-correction, then using these to build the next with its CP, etc. This method involves an intractably large number of CP calculations for aggregates containing several fragments. For example, calculating an aggregate containing four water

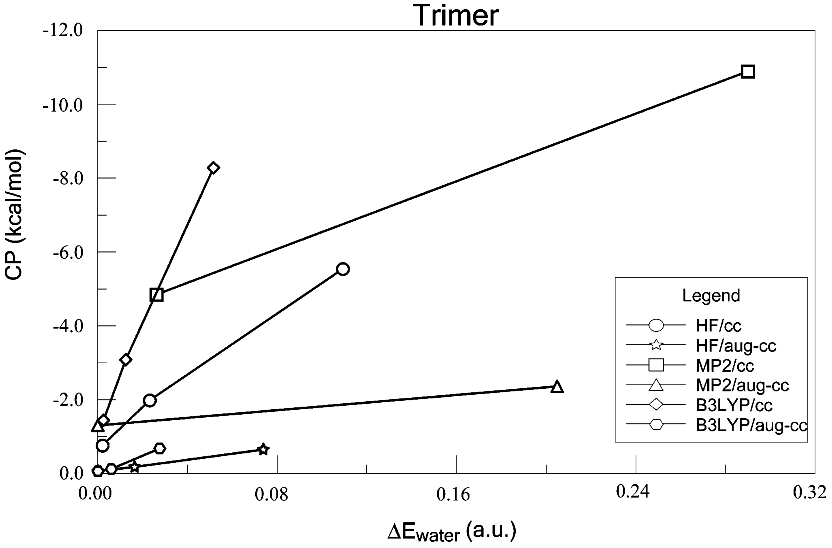

Figure 10. CP correction for water trimer in kcal/mol plotted vs energy difference between water monomer in a given basis set and the lowest water energy for the cc-pVXZ and aug-cc-pVXZ series of basis sets using HF, B3PW91, B3LYP, and M2(FC) methods.

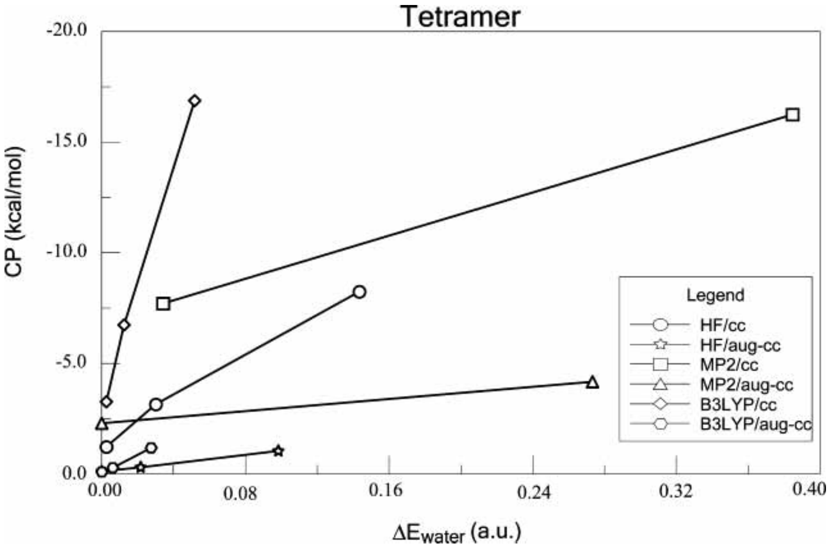

Figure 11. CP correction for water tetramer in kcal/mol plotted vs energy difference between water monomer in a given basis set and the lowest water energy for the cc-pVXZ and aug-cc-pVXZ series of basis sets using HF, B3PW91, B3LYP, and M2(FC) methods.

molecules would require evaluation of 22 individual CP corrections: 6 dimers; 12 trimers (each of the dimers with each of the other two fragments), and 4 tetramers (each trimer with the remaining fragment). The method that we employ requires only four CP calculations (one for each fragment in the basis of the tetramer). While we see no reason this approach should give a clearly erroneous CP-correction for most systems, we see no advantage to using it. Both methods should converge to the same result as the basis sets increase in quality. Valiron and Mayer provide the example of three H atoms combining to form H_3 as an example of the correctness of their procedure. They note that, if one uses Slater orbitals for each H atom (which are the exact solutions for the Schrödinger equation for the H atom), the formation of H_3 form the three atoms is free of BSSE. Thus, there is no CP-correction, as adding basis function to the exact solution cannot lower the energy of the H atom. They note, however, that if one considers the addition of an H atom to H_2, there will be a CP correction for this process. Thus, while the direct combination of three H atoms to for H_3 is free of BSSE, the process of using two H atoms to form H_2 followed by addition of the third atom is not. They conclude that the former process is not correct as it ignores the BSSE present in the second step of the latter. This argument has been cited elsewhere in the literature.[12] Their conclusion is incorrect for several reasons:

(a) The purpose of using CP is to reduce the BSSE. If one can define a process that is free of BSSE, there is no advantage to finding an alternative path that introduces this error simply for the purpose of trying to eliminate it.

(b) The example they give is one case where the hierarchical method is demonstratably inferior to the method that we employ (which would have no CP correction). Consider the reaction of three H atoms to form H_3 using a variational MO method such as Hartree−Fock. If the energies of atoms are taken from the exact solution, they cannot be lowered by extending the basis. The H_3 species is not calculated with the exact wave function. Thus, its calculated energy is an upper limit to the correct energy. Therefore, the energy for the process 3H atoms → H_3 will be too high (not negative enough). Using the method suggested by Valiron and Mayer, the CP correction that appears will increase the energy of H_3 relative to the three H atoms, therefore also of this process (which which will become less

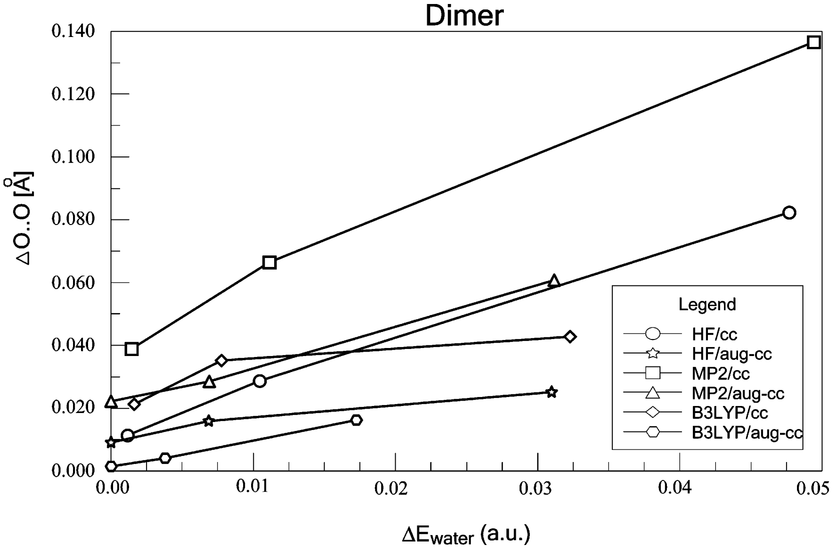

Figure 12. O···O difference between normal and CP-corrected optimizations for water dimer in Å plotted vs energy difference between water monomer in a given basis set and the lowest water energy for the cc-pVXZ and aug-cc-pVXZ series of basis sets using HF, B3PW91, B3LYP, and M2(FC) methods.

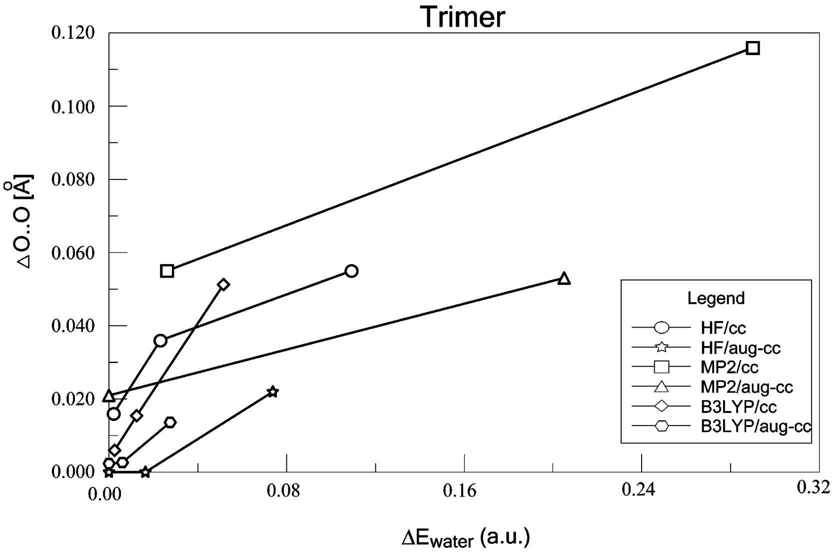

Figure 13. O···O difference between normal and CP-corrected optimizations for water trimer in Å plotted vs energy difference between water monomer in a given basis set and the lowest water energy for the cc-pVXZ and aug-cc-pVXZ series of basis sets using HF, B3PW91, B3LYP, and M2(FC) methods.

negative), which, in turn, will increase the error for the interaction energy of the three H atoms. Thus, the example chosen to illustrate the benefit of the hierarchical method is clearly poorly chosen, at best. One can show graphically that correcting for BSSE will only improve an interaction energy when the basis sets of the components are poorer than that of the complex (see Figure 15). The example chosen by Valiron and Mayer does not meet that criterion.

(c) The energy of a chemical process (i.e., four waters combining to form the tetramer) is independent of the reaction path. Thus, the counterpoise correction calculated for any path ought to be valid so long as no errors are introduced and the method converges to zero correction at the large basis set limit. While one can, in principle, compare the rates of conversion to the limiting value for the two different CP procedures as the basis set is improved, there is no clear definition of incremental improvement in general. For example, one method might converge to a limiting value more rapidly for water tetramer, while the other might do the same more efficiently for formamide tetramer. If one uses the hierarchical method, one needs to calculate the CP for each smaller cluster contained in the one under study (for the tetramer, one must consider the CP's of all possible dimers and trimers). Adding certain functions may improve the basis sets for some of these clusters more than others. Consequently, adding the same function(s) to the same basis set may have different effects on the CP for the different processes inherent in the hierarchical procedure.

Oddly, the application of the hierarchical method to the formation of H_3 provided by Valiron and Mayer provides a rare example where one can demonstrate that the method we use here converges to the correct result better and faster. The energy of the hierarchical calculation will always be higher than that of the three-fragment method by precisely the CP correction to H_2 upon adding the basis of the third H atom. As the basis set for H_2 improves, this difference will tend to zero as both methods converge to the correct interaction energies at the HF limit. Thus, we see no demonstrable advantage to using the hierarchical method, while the added complexity is a clear disadvantage.

Using the CP-opt procedure as we have defined it, allows the facile calculation of any property that can be defined as a

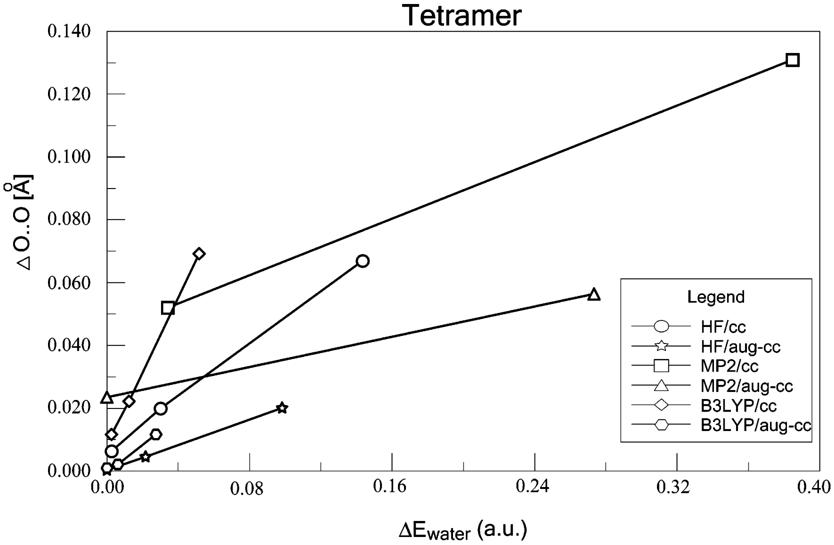

Figure 14. O···O difference between normal and CP-corrected optimizations for water tetramer in Å plotted vs energy difference between water monomer in a given basis set and the lowest water energy for the cc-pVXZ and aug-cc-pVXZ series of basis sets using HF, B3PW91, B3LYP, and M2(FC) methods.

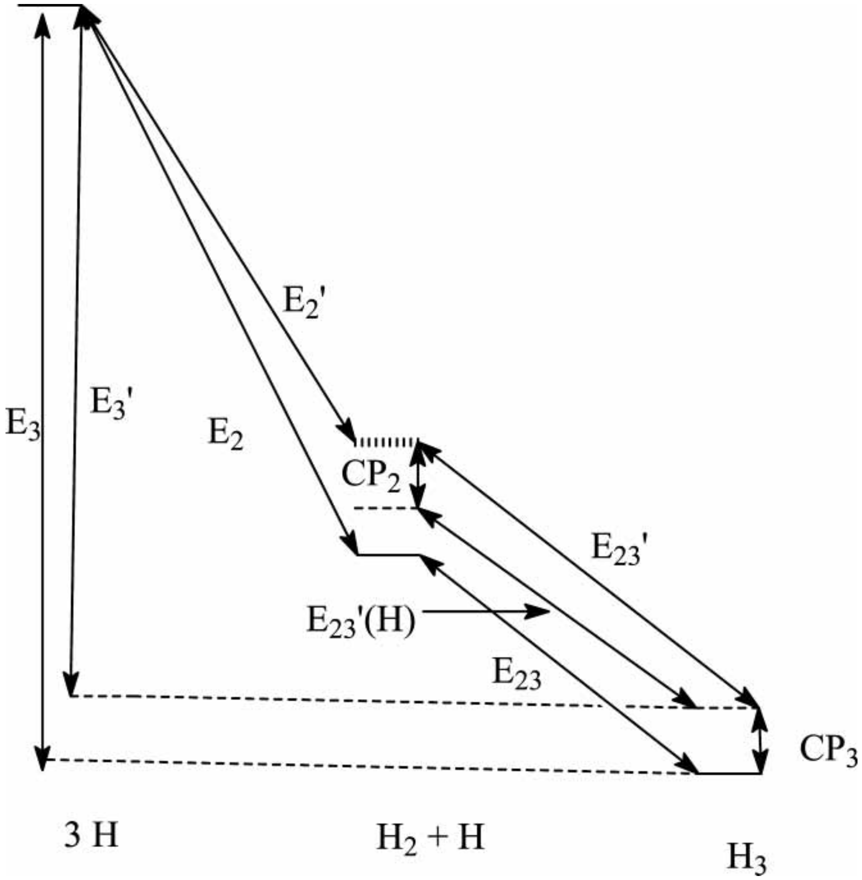

Figure 15. A graphic representation of the formation of H_3 from three H's using the preferred and the hierarchical CP method. The exact energies are represented by the solid lines. The energies in the basis for H_3 are represented by the normal dashed lines and the energies in the H_2 basis is represented by the stylized dashed line. The H atoms are calculated exactly using slater orbitals, so the is no CP correction for them. The calculated energy of interaction using the three fragment CP-method (E_3') is less negative than the exact energy (E_3) and the energy of interaction for H_2 using the basis for H_2 (E_2') is less than the exact energy (E_2). If one does no CP, then $E_3' = E_2' + E_{23}'$. However, if one uses the hierarchical method, one finds that $E_2' + E_{23}'$(H) adds an additional error equivalent to CP_2. As the basis set for is improved for the molecular species, CP_2 will tend to zero and the two methods will converge.

derivative of the CP corrected energy. Thus, vibrational force constants (and frequencies), polarizabilities, dipole, etc., are all readily available for CP-optimized structures. These quantities would be extremely tedious to calculate using the hierarchical methodology. The highly anharmonic vibrations that are important to the analyses of water clusters provide a useful example of the utility of a CP-corrected PES. While these cannot be directly calculated from the second derivatives of the energy with respect to distortions along the normal coordinates (which would give the harmonic vibrational frequencies), a CP-corrected PES would likely lead to improved calculated anharmonic vibrations. Since the BSSE generally increases as an inverse function of the distance between fragments (water molecules), the vibrations that involve changes in the distances between the oxygen atoms would become more anharmonic on a CP-corrected than on an uncorrected PES. Calculating a CP-corrected PES using the hierarchical method would rapidly become prohibitively difficult as one considers clusters of increasing size.

Conclusions

For a given level of calculation, the CP-optimized dimers, trimers, and tetramers of water afford more accurate interaction energies than the same aggregates optimized using normal procedures. This observation is true for MP2 as well as for HF and DFT calculations. CP-optimized MP2 calculations do not overestimate the CP correction. Nevertheless, CP is generally larger and conversion to the large basis limit slower for MP2 than for HF or DFT calculations using the same bases. Accurate MP2 calculations rapidly become computationally unmanageable as the size of the aggregate grows, as illustrated by the large residual BSSE's present using even the largest basis sets possible using the GAUSSIAN programs on 32-bit computers. However, CP-optimization using less extensive basis sets provides interaction energies that reasonably agree with the energies extrapolated from Figures 1−4, even for MP2 calculations.

Using the full bases of the aggregates for the individual fragments leads to well-behaved convergence of the CP-optimized to similar values for the interaction energies as the normally optimized structures; however, the convergence is more rapid with basis set extension. In each case, the CP-opt procedure provided more accurate interaction energies than the normal procedure.

The calculation of the vibrational modes of the water clusters (which is beyond the scope of this paper) could be improved if CP-corrected PES's be used with moderate basis sets. The computational cost of such calculations should be advantageous compared with the more extensive calculations necessary to achieve similar accuracy using normal optimizations.

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Supporting Information Available: Tables of energies and distances for dimer, trimers, and tetramers using various basis sets. This material is available free of charge via the Internet at http://pubs.acs.org.

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