Effect of Basis Set Superposition Error on the Water Dimer Surface Calculated at Hartree−Fock, Møller−Plesset, and Density Functional Theory Levels

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Received: October 27, 1998; In Final Form: December 21, 1998

Counterpoise (CP) corrected optimizations of water dimer using the D95++(d,p) basis set at various levels of MP and DFT are presented. The MP2(full) calculations predict an interaction energy of −4.75 kcal/mol, close to the "MP2 limit" and to reported MP2 calculations with much large basis sets. DFT (B3PLYP) CP-corrected optimization provided the best interaction energy (−5.22 kcal/mol). The optimized O···O separations are larger on the CP-optimized than on the uncorrected surface, as expected. These increases improve the separations predicted by DFT and worsen those predicted by the MP methods. However, the MP2 surface is so flat that the distortions of the O···O separations needed to make the calculations agree with the experimental value require less than 0.1 kcal/mol.

Correction for basis set superposition error (BSSE) is often applied to the calculation of intermolecular interactions using ab initio calculations with basis sets below the Hartree−Fock limit. This error occurs because the unused basis functions of the second unit in the associated complex can augment the basis set of the first, thereby lowering its energy compared to a calculation of the first unit, alone. The first can cause a similar error on the second. While other approaches to correcting this error have been discussed in the literature,[1] the counterpoise (CP) correction proposed by Boys and Bernardi[2] continues to be the most prominent means of correcting for BSSE. The CP method calculates each of the units with the basis functions of the other (but without the nuclei or electrons), using so-called "ghost orbitals". By use of the notation employed previously,[3] the CP-corrected interaction energy, $E^{\mathrm{CP}}{}_{\mathrm{interaction}}$, is stated 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. This method has proven to be somewhat controversial.[4] This equation is a modification of the original procedure that accounts for the changes in the geometries of the monomeric units upon forming the intermolecular complex. Since the original procedure was conceived for atoms, geometric optimization was not considered. Normally, one adds CP correction as a single-point correction to a previously optimized geometry of the complex. Since the BSSE introduces a nonphysical attraction between the two units, the CP correction should make the complexes less stable with consequent longer intermolecular distances than apparent from the normally optimized structure. Thus, one should use CP to correct the optimized geometry, as well as the interactions energy. We have recently developed a simple general method for optimizing geometries on CP-corrected potential energy surfaces.[3] Others have previously optimized some surfaces using point-by-point calculations, a tedious procedure.[5]

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

Many studies have shown that the CP correction for BSSE generally increases upon going from Hartree−Fock (HF) to second-order Møller−Plesset[6] (MP2) calculations of H-bonding dimers with the same basis set.[7] Many other studies show that the calculated stabilizations at the MP2 level are generally too attractive. Thus, the increased CP corrections appear to be reasonable in that it counters this overstabilization. In fact, a recent report shows that CP correction to MP2 calculations is essential for the prediction of the experimentally observed planar dimer of pyrimidine and *p*-benzoquinone to prevail over a stacked dimer, which has a larger BSSE.[8] On the other hand, the validity of CP correction for MP calculations has been questioned because of its apparent utilization of perturbative corrections related to excitations due to ghost orbitals that do not exist in the dimer.[4g] Consequently, some have claimed that CP results in overcorrection for MP2 calculations.[9] As a result of our ability to rapidly calculate CP-optimized geometries, we have found that CP-optimized geometries using MP2 calculations often have significantly larger separations between the monomeric units of the H-bonded dimer than in the normally optimized structure.[3]

Water dimer has been extensively studied. The reported experimental gas-phase interaction energy[10] is −5.4 ± 0.7 [11] or −5.4 ± 0.2 [12] kcal/mol. Several studies have shown that uncorrected and CP-corrected MP2 calculations appear to converge toward the same value from above and below as the basis sets are improved. By use of this rationale, an "MP2 limit" of −4.9 ± 0.1 [13] or 4.9 ± 0.02 [14] kcal/mol has been suggested. Water dimer has a very flat surface;[15] therefore, its geometry should be extremely sensitive to changes in the calculational method. In fact, the O···O distance is sensitive to the calculational method. The experimental O···O distance is 2.98 Å.[16,17] This value corresponds to an energy minimum on a potential

10.1021/jp9842188 CCC: $18.00

TABLE 1: Data from CP-Optimized Calculations on Water Dimer Using the D95++(d,p) Basis Set

	E_{tot}[a]	E_{tot} (noCP)[a,c]	$R_{\mathrm{O\cdots O}}$ (CP) Å	E_{inter}[b]	CP correction[b]
D95++**					
HF	−152.106 542	−152.107 441	3.041	−4.31	0.56
B3PW91	−152.854 056	−152.855 234	2.912	−4.66	0.74
B3LYP	−152.913 760	−152.914 905	2.912	−5.22	0.72
MP2(FC)	−152.506 584	−152.509 395	2.998	−4.59	1.76
MP2 (Full)	−152.535 694	−152.538 234	3.010	−4.75	1.59
MP3 (FC)	−152.516 447	−152.518 930	3.011	−4.50	1.56
MP3 (Full)	−152.546 366	−152.548 654	3.022	−4.62	1.44
MP4SDQ (FC)	−152.523 070	−152.525 629	3.029	−4.39	1.61
MP4SDQ (full)	−152.552 988	−152.555 573	3.034	−4.49	1.62
expt			2.946[d], 2.952[f]	−5.4 ± 0.7,[e] −5.4 ± 0.2[g]	

[a] In hartrees. [b] In kcal/mol. [c] Uncorrected energy at geometry optimized with CP. [d] After anharmonicity correction (see ref 16). [e] Reference 10. [f] After anharmonicity correction (see ref 17). [g] Reference 11.

surface at 2.946 [17] or 2.952 [18]Å after correction for the anharmonicity of the dimer vibrations. HF calculations generally give O···O separations that are longer than the corrected experimental value, while MP2 calculations generally predict O···O distances that are slightly too short.[13] DFT calculations predict O···O interactions that are often shorter than MP2.[19] Thus, water dimer provides a sensitive test of the effect of CP correction on both the interaction energy and the O···O separation.

In this paper, we study the effect of geometrical optimization on the potential energy surface that includes the counterpoise correction for BSSE for water dimer at the Hartree−Fock (HF), Møller−Plesset second (MP2), third (MP3), and fourth with singles, doubles, and quartets (MP4SDQ), using both frozen-core and full perturbations; and two levels of hybrid density functional theory (DFT), B3W91 and B3LYP. We shall show that the "CP-overcorrection" of the MP2 interaction energies is largely due to the failure of most previous calculations to correctly optimize the dimers on the CP-corrected surface. We shall also show the moderately sized D95++(d,p) basis set to be adequate for estimating the interaction energy on the CP-optimized surface.

Methods

All molecular orbital (MO) calculations were performed using the GAUSSIAN 94 suite of computer programs.[20] We obtained the CP-optimized surfaces by minimizing the energy of the CP-corrected dimers by means of derivatives calculated using eq 2 as previously described in ref 3. All calculations used the D95++(d,p) basis set. We report both frozen core (FC) and complete (full) calculations at the MP2, MP3, and MP4(SDQ) levels. We also report density functional theory (DFT) calculations using the B3LYP and B3PW91 functionals. The B3PW91 method combines Becke's three-parameter functional[21] with the nonlocal correlation provided by the Perdew−Wang expression,[22] while the B3PLYP combines the same Becke functional with the correlation functional of Lee, Yang, and Parr.[23]

$$\frac{\partial E^{\mathrm{CP}}{}_{\mathrm{interaction}}}{\partial p_j} = \frac{\partial E^{\mathrm{CP}}{}_{\mathrm{super}}}{\partial p_j} = \frac{\partial E_{\mathrm{super}}}{\partial p_j} + \sum_{i=1}^{n}\left(\frac{\partial E_{\mathrm{m_f}}{}^{i}}{\partial p_j} - \frac{\partial E_{\mathrm{m_f}}{}^{i*}}{\partial p_j}\right) \tag{2}$$

Results and Discussion

The CP-optimized interaction energies are necessarily more negative than those calculated by applying a static CP correction to the "normal" optimized complex. This must clearly be true, since the interaction energy on the CP-corrected surface obtained from a static application of the CP correction to the "normal" minimum must be higher than that at the CP-corrected minimum (see Figure 1). All of the corrected interaction MP2 energies are less negative than the reported experimental value of 5.4 ± 0.7 kcal/mol except MP2(full), which is barely within the range of experimental error. However, they are quite similar to those reported by Jordan[18] and Xantheas[24] for CP-corrected MP2 interactions normally optimized with much larger basis sets. In fact the MP2(full)/D95++(d,p) CP-corrected interaction energy of −4.75 kcal/mol is more negative than any reported by Jordan (none of which are within the range of experimental error), only 0.13 kcal/mol less than the best (MP2/aug-cc-pV5Z) MP2 result of Xantheas[23] or Schütz et al.[13] and reasonably close to the estimated "MP2 limit" of 4.9 kcal/mol. On the other hand, all of the "normal", uncorrected MP2 calculations predict interaction energies that are too negative compared to the experimental result and outside the range of experimental error.

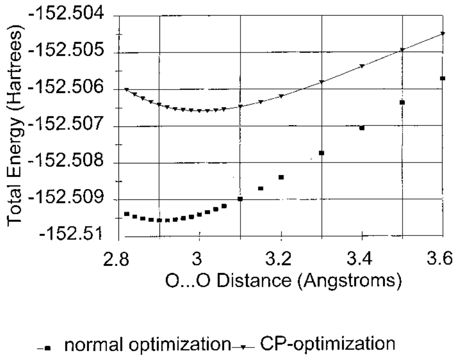

Figure 1. Total energy vs O···O distance in water dimer as calculated at the MP2(FC)/D95** level optimized with and without counterpoise correction.

The results of the CP-optimized calculations are collected in Table 1. One immediately sees that the MP calculations predict much longer (about 0.1 Å) O···O distances at the CP-optimized geometries than at their "normal" optimized structures. Thus, what previously seemed to be reasonable agreement with the experimental geometry now appears to be seriously in error. Going from MP2 to higher order (MP3 and MP4SDQ) causes similar increases in both the CP-optimized and "normal" optimized O···O distances. The DFT O···O distance also increases substantially, changing from values that are significantly too small to somewhat too large.

Thus, the uncorrected MP2 calculations (optimized on the uncorrected surface) predict a water dimer that is too stable with an O···O distance that is somewhat too short, while the CP-corrected MP2 calculations predict one that is not quite stable enough with an O···O distance that is clearly too long. Single-

TABLE 2: Comparison with Data from Normal Optimizations

	E_{tot}[a]	$R_{O\cdots O}$[b]	ΔE_{tot}[c]	$\Delta R_{O\cdots O}$[b]
D95++(d.p)				
HF	−152.107 471	2.998	−0.019	0.043
B3PW91	−152.855 258	2.878	−0.015	0.034
B3LYP	−152.914 935	2.880	−0.019	0.032
MP2 (FC)	−152.509 558	2.907	−0.102	0.091
MP2 (full)	−152.538 443	2.906	−0.131	0.104
MP3 (FC)	−152.519 069	2.927	−0.087	0.084
MP3 (full)	−152.548 828	2.925	−0.109	0.097
MP4SDQ (FC)	−152.525 805	2.935	−0.110	0.094
MP4SDQ (full)	−152.555 595	2.931	−0.014	0.103

[a] Normal optimization; energy in hartrees. [b] In angstroms. [c] In kcal/mol.

point CP correction of the minimum on the normal surface (an obvious overcorrection) leads to an inadequately stabilized dimer. Where is the problem? Figure 1 shows the total energies for water dimer at the MP2(FC)/D95++(d,p) level optimized both with and without CP correction as a function of O···O separation. Notice flatness of the function near the minimum of each curve. The results of recent MP2 calculations using the Dunning aug-cc-pVxZ (where x = D, T, Q, 5) suggest that optimizing the geometries with BSSE leads to more accurate O···O separations without significantly changing the energy with the larger basis sets. For example, the MP2/aug-cc-pVTZ calculations predicted an O···O separation of 2.933 Å.[23] Curiously, using larger basis sets (x = Q, 5) did not improve the agreement of the O···O separation with the corrected experimental value.

Figure 1 illustrates the predominant cause of the CP overcorrection. The energy difference between the lower (normal optimization) curve and the upper (CP optimization) curve represents a lower limit[25] to the CP correction. In the region of O···O separations between the two mminima, the variation of energy with O···O varies in opposite directions for the two curves. The energy minimum on the normally optimized surface comes at a much shorter O···O distance than on the CP-corrected surface. This leads to a larger apparent CP for the single-point correction on the normal surface than for that at the minimum on the CP-corrected surface. This difference is approximately 0.3 kcal/mol. On the other hand, the energy varies by less than 0.1 kcal/mol (less than the difference between the MP2(full) and the MP2 limit) over the range 2.9−3.1 Å for the CP-corrected curve. Thus, the energetic and geometric results are consistent. The surface is simply too flat to allow confidence in the predicted geometry of any but the most sophisticated calculation. However, the interaction energy is predicted almost as well by optimization on the CP-corrected MP2/D95++(d,p) surface as on the MP2/aug-cc-pV5Z surface with considerably less computational effort.

MP2 calculations use second-order perturbation theory to adjust a wave function that is (usually) calculated using an HF procedure. The interactions are calculated using terms such as those indicated in eq 3, where the summations are over all possible excitations from occupied to unoccupied orbitals.

$$\sum_{i=1}^{n}\left|\frac{\langle\Delta_i F\Delta_k\rangle^2}{\langle\Delta_i F\Delta_i\rangle - \langle\Delta_k F\Delta_k\rangle}\right| \tag{3}$$

All interactions are the result of perturbations involving double excitations from the reference state. Since the numerator is a square of an interaction term, it is always positive. The denominator always involves energy differences between filled and unfilled orbitals. Thus, these cannot change sign either. As a result, every possible MP2 term is a stabilization. One expects the denominator to increase with augmentation of the basis set, since the HF ground state follows the variational principle. This will reduce (but not eliminate) the effect of each perturbative interaction. Each term representing a specific excitation interacts only with the reference state, not with other excited states. As a result, adding basis functions (which makes new excitations possible) will always stabilize the reference function as long as the overlap with the reference state is not zero. At the HF limit, the BSSE will disappear for HF calculations. However, it will not necessarily disappear at the HF limit for MP2 calculations. In fact, BSSE will exist for MP2 calculations (which do not follow a variational principle) at all levels of calculation, even when the exact wave function is used. Of course, complete MP of infinite order will have no effect upon the exact wave function. Better basis sets lead to better MP2 calculations as well as better HF calculations. Augmenting the basis set will improve the reference HF function to which the MP2 perturbations are applied. Thus, adding a new basis function will have two competing effects: (1) providing additional excited states that can interact with the ground state, thus increasing the MP2 stabilization of that state; (2) improving the HF ground state, thus making it less sensitive to stabilization from the MP2 perturbations. For example, Jordan's uncorrected MP2 calculations are all within experimental error of the reported interaction energy.[18]

Should an "MP2 limit" for the water dimer interaction energy exist? The evidence in favor relies on the apparent convergence of the corrected and uncorrected MP2 interaction energies with increasing basis sets. The data are usually plotted with the basis sets arbitrarily evenly spaced, since there is no appropriate numerical value associated with them.[26] Plots of this kind appear to be asymptotically converging toward a common value. However, spacing the basis sets along the ordinate in a different manner could make them appear to cross upon extrapolation. Since MP2 calculations are not variational and all augmentations of basis sets will be stabilizing, such a crossing seems possible. In such a case, "MP2 limit" would lose meaning. Similarly, the suggestion that CP overcorrects MP2 interactions due to excitations to physically artifactual excited states involving ghost orbitals,[4g] which we have shown not to be the predominant cause of the apparent overcorrection for moderately sized basis sets, could eventually contribute to a crossing as described above.

Higher order MP generally makes the interaction energies less negative and the interaction distances longer (as long as the basis set used is reasonably good[27]). Both trends are evident in the present results. For higher order MP, the perturbations are not all necessarily stabilizing. In particular, the numerators of the terms are not always even exponentials of the interactions terms. We see from Table 1 that the CP corrections are generally smaller than those for MP2. This is likely the result of the longer O···O separations at the corresponding CP-corrected minima. Figure 1 illustrates the decease in CP with increasing O···O separation. At infinite separation, the CP must disappear.

The CP-optimized DFT/B3LYP results are the most satisfactory. The −5.22 kcal/mol interaction energy and 2.912 Å O···O separation are both closest to the experimental values of all the present calculations. The uncorrected O···O separation is somewhat too short (2.880 Å). These observations expand upon those of Jordan, who reported the favorable energetic results obtained with DFT methods. The CP-optimized O···O distances reported here bring the geometries closer to experimental values.

The CP corrections to the DFT calculations are significantly lower than those using MP2.

Conclusions

Calculations on water dimer show that optimization on the CP-corrected MP2(full)/D95++(d,p) potential surface provides interaction energies comparable to those of MP2 calculations using much larger basis sets at significantly less computational expense. The corresponding O···O separations are less predictable, owing to the flatness of the potential surface. DFT (B3LYP) calculations provided the best energetic and geometric results on the CP-corrected potential surfaces.

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