of including the BSSE. The interaction energies are given in Table III. For structure I we get in contradiction to Mezei and Dannenberg a repulsive interaction energy and an acceptable basis set superposition error (0.14 kcal/mol) using the ANO basis set. For the 6-311G** basis set one finds that the configuration is attractive (-0.87 kcal/mol). However, if one takes the BSSE of 2.86 kcal/mol into account, the interaction energy is 1.99 kcal/mol, which is close to the value calculated with the ANO basis set and is more in line with the analytical potentials. The relative importance of these trifurcated waters dimers is obviously artificially enhanced by the BSSE. One can argue that structure I is an extreme case, with short intermolecular distances, but if we look at structure II, which is, as Smith et al.[20] pointed out, a second-order saddle point important for breaking and forming hydrogen bonds, we come to the same conclusion. The 6-311G** basis set gives large basis set superposition errors which need to be corrected for to give reasonably accurate results. This would also include calculations on the MP2 and MP4 level. Thus, one have to be careful with choosing a basis set that gives a small BSSE, and as these results indicate one should correct for the BSSE with the counterpoise method if the basis set superposition error is large. The counterpoise method overestimates this error, but it is our opinion that it is better to correct for the BSSE than to do nothing at all. Finally, we conclude that most analytical potentials give a fairly good description of this region except for AM1 and CM[21] potentials, which both are much too attractive for both structures.

(18) Newton, M. D.; Kestner, N. R. *Chem. Phys. Lett.* **1983**, *94*, 198.
(19) Szalewicz, K.; Cole, S. J.; Kolos, W.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *89*, 3662.
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Reply to the Comment on the Application of Basis Set Superposition Error to ab Initio Calculation of Water Dimer

Sir: The authors of the accompanying Comment suggest that the ab initio calculations on water dimer that we have previously published[1] are flawed by neglect of the basis set superposition error (BSSE); consequently, our conclusions about the utility of empirical water calculations[2] are likewise flawed. By implication, our conclusion that the water dimer potential surface is flat in one or more directions is also called into question.

We should initially note that our conclusions were based upon calculations that accounted for various levels of correction for the electron correlation error (up to MP4SDQ), while the Comment only refers to Hartree-Fock calculations (which disfavor trifurcated structures). As such, our calculations were at a higher level, providing total energies for water approximately 0.22 hartree lower than the ANO RHF calculations described in Table I of the Comment. Also, the Comment is confined to BSSE, which appears to disfavor trifurcated structures, but ignores zero-point vibrational energy (ZPVE) corrections, which tend to favor trifurcated structures.

(1) Dannenberg, J. J. *J. Phys. Chem.* **1988**, *92*, 6869.
(2) Mezei, M.; Dannenberg, J. J. *J. Phys. Chem.* **1988**, *92*, 5860.

TABLE I: Counterpoise Corrections (kcal/mol)

method	I	II	VI[a]
6-311**G			
RHF	2.89	2.36	1.36
MP2	5.30	4.01	2.36
MP3	4.54	3.41	2.03
MP4DQ	4.62	3.48	2.07
MP4SDQ	4.88	3.67	2.18
6-311+G(2d,2p)			
RHF	0.36	0.26	0.43[b]
MP2	0.93	0.57	0.95[b]
MP3	0.83	0.49	0.88[b]
MP4DQ	0.84	0.50	
MP4SDQ	0.91	0.55	
MP4SDTQ	1.06	0.64	1.00[b]

[a] Structure 1 from ref 6 used for 6-31+G(2d,2p) calculations. [b] Values from ref 6.

The BSSE is essentially due to the use of incomplete basis sets for the comparison of individual and associated species. The origin of the error lies in the possibility that the unused basis functions of the second unit in the complex may sufficiently augment the basis set of the first unit so as to effectively lower its energy, thereby making the stabilization energy of association appear too large.

We did not take the BSSE into account in our ab initio calculations as we observed the surface of the water dimer to be both flat and very dependent upon the level of calculation employed. On such a flat surface, the positions of the minima and other extrema vary with the calculational method used. Therefore, they are not very well defined geometrically. We did not take the ZPVE into account for similar reasons. To be completely accurate, the geometry should be optimized at the highest level of theory used (including all corrections for electron correlation, BSSE, and ZPVE). Unfortunately, both the BSSE and the ZPVE are difficult to correctly evaluate. In view of the comments we shall consider both corrections here.

The most common method of correcting for the BSSE is the counterpoise (CP) method. In this procedure, each of the individual units is calculated with the basis functions (but not the atoms, themselves) of the other unit defined in space as in the associated complex. This method must overestimate the error, as it allows all of the basis functions (not just the unoccupied orbitals) of the second unit to be used by the first. There is some disagreement concerning the usefulness of CP, both in general and with respect to specific basis sets, as exemplified in the following discussion.

The use of CP has been systematically studied by Schwenke and Truhlar,[3] who studied the effect on hydrogen fluoride dimers using 34 different basis sets. They state in their abstract, "...we show that using a large enough basis set so that the counterpoise correction is small does not guarantee accurate results. Furthermore even for smaller basis sets the inclusion of counterpoise corrections does not systematically improve the accuracy of the calculations." In their study, they bracketed the likely ranges for the interaction energies of two different dimer geometries. They included the 6-311**G basis in their study. It is one of three bases that contain 25 contracted basis functions. From Figures 3 and 4 of their paper, one can see that the bases containing 25 contracted basis functions had relatively large CP's but that the corrections often significantly worsened the accuracy of the calculated interaction energies. They state, as part of their conclusion, "We have found that the counterpoise-corrected interaction energy is not more reliably accurate than the uncorrected interaction energy."

In a subsequent paper on hydrogen-bonded complexes (including water dimer), Frisch, Del Bene, Binkley, and Schaefer reached

(3) Schwenke, D. W.; Truhlar, D. G. *J. Chem. Phys.* **1984**, *82*, 2418.
(4) Frisch, M. J.; Del Bene, J. E.; Binkley, J. S.; Schaefer, H. F. III *J. Chem. Phys.* **1986**, *84*, 2279.

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TABLE II: Binding Energies (kcal/mol)

	I			II			VI	
method		Z[a]	Z/C[b]		Z[a]	Z/C[b]		C[c]
6-311**G								
RHF	-0.83	-1.51	1.38	-3.76	-4.44	-2.08	-5.56	-4.20
MP2	-3.60	-4.28	-1.39	-5.96	-6.64	-4.28	-6.77	-4.41
MP3	-2.91	-3.59	-0.70	-5.44	-6.12	-3.76	-6.35	-4.32
MP4DQ	-2.82	-3.50	-0.61	-5.47	-6.15	-3.79	-6.28	-4.21
MP4SDQ	-3.08	-3.76	-0.87	-5.68	-6.36	-4.00	-6.40	-4.22
6-31+G(2d,2p)								
RHF	2.03	1.35	1.71					
MP2	0.12	-0.56	0.37					
MP3	0.19	-0.49	0.34					
MP4DQ	0.42	-0.26	0.58					
MP4SDQ	0.28	-0.40	0.51					
MP4SDTQ	-0.08	-0.76	0.30	-3.52[d]	-4.20[d]	-3.56[d]	-5.36[e]	-4.36[e]

[a] Corrected for differential ZPVE relative to linear structure. [b] Corrected for both ZPVE and BSSE (counterpoise). [c] Corrected for BSSE; relative ZPVE does not apply. [d] Using data for structure 7 from ref 6. [e] Using data for structure 1 from ref 6.

TABLE III: Relative Energies to the Linear Dimer[c] in kcal/mol[f]

	I				II				best
method		Z[a]	Z/C[b]	E_{inter}		Z[a]	Z/C[b]	E_{inter}	dimer E_{inter}
6-311**G									
RHF	4.73	4.05	5.57	0.01	0.98	0.30	1.29	-4.27	-5.56
MP2	3.17	2.49	5.44	-1.33	0.33	-0.35	1.30	-5.47	-6.77
MP3	3.44	2.76	5.27	-1.08	0.48	-0.20	1.18	-5.17	-6.35
MP4DQ	3.47	2.79	5.33	-0.95	0.45	-0.23	1.17	-5.11	-6.28
MP4SDQ	3.32	2.64	5.34	-1.06	0.38	-0.30	1.19	-5.21	-6.40
6-31+G(2d,2p)									
RHF	7.39	6.71	6.64						
MP2	5.48	4.80	4.78						
MP3	5.55	4.87	4.83						
MP4DQ	5.78	5.10							
MP4SDQ	5.64	4.96							
MP4SDTQ	5.28	4.60	4.66	-0.70	1.84[d]	1.16[d]	0.80[d]	-4.56	-5.36

[a] Corrected for the difference in ZPVE's. [b] Corrected for ZPVE's and BSSE (counterpoise correction). [c] Either VI of ref 1 or 1 of ref 6. [d] Calculated using the data for 7 in ref 6. [e] From refs 1 and 6. [f] Interaction energies (E_{inter}) for I and II are Z/C corrected energies + E_{inter} for the best dimer.

a similar conclusion: "Counterpoise estimates of basis set superposition error do not provide quantitative information about basis set deficiencies in studies of hydrogen bonded complexes...".[4] Another point of view is presented by Szalewicz, Cole, Kolos, and Bartlett.[5]

ZPVE errors cannot be easily calculated for nonstationary points on a potential surface. When single-point calculations are performed on geometries optimized at a lower level of approximation, the ZPVE's calculated at the lower level are usually taken as an approximation for the higher level calculation (which is not necessarily a stationary point as it has not been geometrically optimized). In a recent paper, Smith, Swanton, Pople, Shaefer, and Radom came to the conclusions (essentially similar to our own) that, "Our findings highlight the overall flatness of the water dimer potential energy surface" and that the surface for the water dimer was "...particularly sensitive to both level of theory and basis set."[6] At the highest level of theory that they applied to the trifurcated structure (MP4SDTQ/6-31+G(2d,2p), they calculated a trifurcated structure (structure 7 in ref 6) to be 1.84 kcal/mol higher than the best structure, which has a binding energy of 5.36 kcal/mol at this level of theory.[7] (This value, when appropriately corrected, would give an enthalpy of association of 3.44, compared to the experimentally measured[8] value of 3.59 kcal/mol at 373 K.) If one applies the ZPVE correction (using the ZPVE's from the same paper), the energy difference is lowered by 0.68 to 1.16 kcal/mol.

Nevertheless, for completeness, we have calculated the BSSE's for our structures I, II, and the linear dimer, VI (following the numbering of ref 1), using both the 6-311**G (used previously by us) and the 6-31+G(2d,2p) (used by Smith et al.) basis sets at each MP level employed. The results are collected in Tables I–III. Table I presents the CP calculated at each level of theory (using the IBM RS/6000 version of GAUSSIAN 88). Table II presents the binding energies with corrections for relative ZPVE and BSSE (counterpoise). Table III presents the relative energies of I and II as compared to the best (linear) dimer structure. Thus, Table III contains the information relevant to the potential surface. For the 6-311**G calculations, the best dimer is the AM1-optimized structure with the H bond constrained to be linear (structure VI of ref 1), while for the 6-31+G(2d,2p) calculations the best structure was that optimized at the MP2/6-31+G(d,p) level (structure 1 of ref 6). The bonding energy for the best dimer is 6.40 kcal/mol for MP4SDQ/6-311**G[1] or 5.36 kcal/mol for MP4SDTQ/6-31+G(2d,2p).[6]

As can be seen from Table I, we reproduce[9] the value of 2.89 kcal/mol for the CP presented in the Comment above for the HF/6-311**G calculation of I. We also obtain a CP for the linear structure, VI, of 1.36 kcal/mol. If one assumes that the differential ZPVE energy calculated in ref 6 can be applied to structures I and II, one obtains the binding energies of Table II. Structure I is predicted to be repulsive at the HF level but bound at all MP levels.

(5) Szalewicz, K.; Cole, S. J.; Kolos, W.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *89*, 3662.

(6) Smith, B. J.; Swanton, D. J.; Pople, J. A.; Shaefer, H. F. III; Radom, L. *J. Chem. Phys.* **1990**, *92*, 1240.

(7) At the highest level of theory used for structure 1 of ref 5, MP4SDTQ6-311++G(d,p), the binding energy is 5.40, or 3.48 kcal/mol after correction.

(8) Curtiss, L. A.; Frurip, D. J.; Blander, H. *J. Chem. Phys.* **1979**, *71*, 2703.

(9) The small differences in energies between our calculations and the analogous calculations in the preceding Comment are probably due to the rounding errors accumulated by using the published geometries.

For the 6-31G+(2d,2p) calculations, applying the CP's has a smaller effect. At the MP4SDTQ/6-31+G(2d,2p) level it is slightly repulsive by 0.30 kcal/mol.

We call attention to the fact that Smith et al. obtained excellent agreement with experiment for the enthalpy of association of water dimer without applying the CP. Table II shows that had they applied the correction (1.00 kcal/mol) the experimental agreement would have been much worse.[6] A similar result would have obtained had we applied the CP to our optimal structure. Perhaps it is better to treat the counterpoint correction relative to the linear structure (which agrees with experiment without correction).

If one takes into account the correction for the linear (optimal) dimer, the *relative* CP for the 6-311**G basis decreases to 1.53 kcal/mol at the HF level. Moeller–Plesset correction causes an increase in the CP for all three structures. For structure I, the greater CP more or less cancels the increased stabilization as more correlation correction is applied. Structure I is predicted to be very weakly bound. At the MP4SDQ/6-311**G level, it is bound by 1.06 kcal/mol (using the binding energy of 6.40 for VI). At the MP4SDTQ/6-31+G(2d,2p) level, it is predicted to be bound by 0.70 kcal/mol (taking the binding energy of the linear dimer as 5.36).

It is interesting that applying the CP and correcting for ZPVE lowers the relative energy of the trifurcated structure (II or 7) for MP4SDTQ/6-31+G(2d,2p) but raises it for MP4SDQ/6-311**G.

The goal of studies of water dimer is to better understand the correct potential surface for water dimer by means of molecular orbital calculations. In order to achieve this goal, all meaningful corrections should be included in the calculations. If (a) the surface is shown to be flat and (b) the corrections are difficult to apply properly, it is not clear that making such corrections is meaningful. Nevertheless, if such corrections are made, one should consider all corrections (in this case electron correlation and ZPVE in addition to BSSE). Furthermore, one must not apply these corrections selectively, but to all relevant points on the surface. This is particularly true of CP, which has been shown to behave erratically with some basis sets.

The additional calculations presented here reinforce our original conclusions that the water dimer surface is flat and that pairwise additive models for water "...should be used with caution when individual water molecules are important..."[2] as the empirical models studied predict (repulsive) interactions of 0.4–6.9 kcal/mol for I and (attractive) interactions of only −2.85 to −3.45 kcal/mol for II[2] compared to corrected ab initio interactions of −1.33 to 0.70 kcal/mol for I and −5.47 to −4.56 kcal/mol for II (E_{inter} from Table III for MP2 and higher calculations). Smith et al. have put it another way: "Empirical potential functions for the water dimer could also usefully be adjusted to describe more accurately the potential energy surface...".[6]

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