Counterpoise Corrected Ion/Molecule Complexes Using Two or Three Fragments

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We report counterpoise (CP) corrected geometric optimizations for hydrated OH^-, H_3O^+, and NH_4^+ using various basis sets at the HF and MP2 levels. The CP corrections are calculated using two (CP2) and three (CP3) fragments. When three fragments are used, one is always H^+. Symmetrical structures for $H_5O_2^+$ and $H_3O_2^+$ cannot be obtained with only two (necessarily nonequivalent) fragments. There are no significant differences in the CP-optimized interaction energies for these systems. Nevertheless, unlike the more traditional two fragment procedure, the three fragment procedure allows convergence to symmetrical structures. This latter procedure is clearly preferable for systems such as OH^-/H_2O and H_3O^+/H_2O while introducing no significant error when used for unambiguously unsymmetrical systems, such as NH_4^+/H_2O.

Introduction

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 basis functions of the aggregate formed by association of the units are different from those employed for the isolated units before association. The larger basis set used for the aggregate causes its calculated energy to be relatively lower than the sum of the energies of the individual units calculated with their individual bases. Consequently, BSSE introduces a nonphysical attraction between the two units. Thus, the CP correction generally makes intermolecular complexes less stable with longer intermolecular distances than apparent from the normally optimized structure. Although 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 others (but without the nuclei or electrons), using so-called "ghost orbitals". Following the notation employed previously,[3] 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, respectively, and the asterisk (*) denotes monomers calculated with "ghost" orbitals for the other components of the supermolecule. The CP method has proven to be somewhat controversial.[4] Nevertheless, van Duijneveldt has shown that CP rigorously corrects for BSSE in certain cases.[4h] This equation is a modification of the original procedure which accounts for the changes in the geometries of the monomeric units upon forming the intermolecular complex.[5] As the original procedure was conceived for atoms, geometric optimization was not considered. One should note that other procedures for calculating CP in multifragment systems have been proposed.[6] Ordinarily, one adds CP correction as a single-point correction to a previously optimized geometry of the complex. Because the BSSE introduces a nonphysical attraction between the two units, the CP correction should make the complexes less stable (with consequently longer intermolecular distances) than is apparent from the normally optimized structure. Thus, one should use CP to correct the optimized geometry as well as the interaction 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.[7] Several recent reports of geometric optimizations on BSSE corrected PES's have appeared.[8]

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

Problems of definition arise when a charged species interacts with a neutral molecule. First, the charge on the unassociated species becomes partially delocalized into the domain of the neutral species upon association. This introduces an ambiguity into the definition of the calculations that involves one species with the ghost orbitals of the other. For example, should the ghost orbitals of the charged species carry the effect of the charge? If so, how can this best be accomplished? Let us consider two illustrative examples: NH_4^+/H_2O and OH^-/H_2O. Calculating H_2O with the ghosts of NH_4^+ is equivalent to calculating it with the ghosts of NH_4^- or NH_4 radical. Because NH_4^+ is positive, the energy of its molecular orbitals is lowered by the charge. Thus, one might expect the BSSE upon the water due to NH_4^+ to be greater than that due to neutral or negative NH_4 because the orbitals of the cation might attract the electrons of the water more than the neutral ghost orbitals. Conversely, one might expect the ghost orbitals of H_2O to affect the energy

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of a positive species, such as NH_4^+ less than a neutral or negative one, as the electrons in a negative species might be more stabilized by added basis functions. Second, the proper definition of the interacting species is unclear, particularly if the species may be symmetrical or nearly so. For example, OH^-/H_2O (which might be a symmetric species with H bonds of equal length) would be inherently asymmetric if optimized with CP correction using two species: OH^- and H_2O.

One possible solution to these apparent problems might be the use of more than two fragments for defining the CP and using the CP-optimization procedure. This technique has proven useful for the definition of certain transition states using the CP-opt procedure.[9]

In this paper, we compare the two (CP2) and thee (CP3) fragment definitions of CP for the hydrations of OH^-, H_3O^+, and NH_4^+. For CP3, we divide the complexes into three fragments, one of which is a proton, whereas the other two are neutral (in the cases of the positive complexes) or negative (in the case of the negative one). We used a proton as the third fragment (rather than a hydride anion), so that all fragments that contain electrons would be singlets. Of the two individual species (from which the complexes are formed), one is calculated using two fragments (the proton and one of the other two) in order to preserve the continuity of the reaction surface. This procedure is discussed in more detail elsewhere.[9] We shall first consider each complex and then provide a general discussion. For each, we present calculations using eight different basis sets of varying complexity at the HF and MP2(full)) levels. We have previously shown that the CP-optimized water dimer is within 0.15 kcal/mol of the "MP2 limit"[10,11] at the MP2(full)/d95++** level.[12] The frozen core calculation was 0.16 kcal/mol farther from this limit.

Methods

The molecular orbital calculations were performed at the Hartree−Fock (HF) and second-order Møller−Plesset (MP2) levels using the Gaussian 98 program release A7 and a preliminary version of A10.[13] The MP2 calculations used the full (not the frozen core) protocol. The older version (A7) was driven by the CP-opt program that is freely available from the web site of one of us.[14] The complexes were completely optimized without any geometric restraints. Vibrational calculations using the harmonic approximation were performed on the CP-optimized surface. These provided the force constants and the vibrational constants necessary to calculate the enthalpies of association at 298 K. When we used three fragments for the CP optimization of the H-bonded supermolecule, we used the same three fragments for the non-H-bonded references states in order to provide a continuous potential energy surface (for example, NH_4^+, would be composed of two fragments, NH_3 and H^+). We used the same procedure for the calculation of transition states using CP3.[9] In certain optimizations for NH_4^+/H_2O, we found one imaginary vibration corresponding to the torsional rotation about the H bond. As this virtually free rotation contributes less than 10^{-4} kcal/mol to the total energy, further optimization was not attempted. However, Gaussian 98 corrects transition states by KT (0.59 kcal/mol at 298 K) when calculating enthalpies. The enthalpies that we report here remove this correction to be consistent with the true minima (see discussion below).

Hydration of OH^-. The gas-phase hydration of OH^- is reported to be 26.5 kcal/mol by Mautner[15] and 25.0 kcal/mol by Kebarle.[16] Recent MP sudies have been reported by Xantheas[17] and Grimm,[18] whereas DFT studies have been reported by Wei et al.[19] and by Pudzianowski.[20] Theoretical procedures that use basis sets that include diffuse functions and electron correlation were deemed necessary for reasonable agreement with experimental results. Earlier work involving calculations that were either at the Hartree−Fock (HF) level or did not include diffuse functions for the geometry optimizations have been reported by several groups.[21] The results of our calculations are presented in Table 1.

Let us first consider the HF calculations. The 6-31G series of basis sets (6-31G through 6-311++G(3df,2pd) show very large deviations from the value for the most extended basis set. At the largest basis set employed, the interaction enthalpy is −22.10 kcal/mol after CP optimization using either the two or three fragment procedure. Without CP optimization (using single point a posterieri CP), the interaction enthalpy is −22.77 kcal/mol, a difference of only 0.57 kcal/mol. All of the calculations that do not use diffuse (++) functions have analogous differences of over 7 kcal/mol. All calculations with diffuse function in this series give CP-optimized enthalpies within 1 kcal/mol of the value for the largest basis set, 6-311G** is within about 2 kcal/mol, whereas the other two, 6-31G and 6-31G** differ significantly from the best HF value before (by 12−16 kcal/mol). Using CP optimization, these last two basis sets provide deviations that are about 7 kcal/mol less. Curiously, the HF/6-31G** result is accidently in good agreement with the experimental value.

The D95 series of basis sets (here only D95 and D95**) behave similarly except that the small basis set, D95, gives much better results than 6-31G both with and without CP optimization. At the HF level, there seems to be little difference between the two- and three-fragment CP procedures.

The MP2 calculations behave somewhat differently. The most extended basis set calculation gives an interaction enthalpy of 26.66 kcal/mol, in excellent agreement with the reported experimental result. Once again, the basis sets lacking diffuse functions give results that greatly deviate form that of the large basis set. This effect is diminished with the use of CP optimization. However, for the MP2 calculations, the three fragment procedure gives consistently lower (i.e., greater in magnitude) stabilization enthalpies. The MP2/D95++** CP3 optimization gives an interaction enthalpy within 1 kcal/mol of the most extensive calculation.

Because CP correction removes an artificial attractive force between the fragments, the O···H distances increase upon CP optimization. The changes in these distances are greater for the poorer basis sets and greater for MP2 than HF, in accord with previous results. These changes can be quite large (up to 0.278 Å for MP2/6-311G**). They are greater than 0.08 Å even for the most extensive MP2 calculations when CP2 is used. The effect is larger for the CP2 than for CP3 calculations in all cases save two (both HF). Because the O···H distance is specifically defined between the two fragments with CP2, this method leads to greater deviations from symmetrical geometries.

Symmetric H bonding is associated with strong, short H bonds. Because HF calculations use one electron wave functions, they overestimate repulsions leading to an error often attributed to electron correlation (rather than the deficiency of the one-electron effective Hamiltonian). Because MP2 corrects for much of this, the O···O repulsion is reduced leading to shorter O···O separations and stronger H bonds that are closer to the symmetric structure. Without CP optimization, four of the MP2 calculations give symmetric species. CP optimization leads to longer O···O distances which weaken the H-bonding interactions. The three-fragment procedure (CP3) breaks the symmetry of two of those

TABLE 1: Interaction Energetics (−kcal/mol) and Selected Geometric Parameters (Å) for $H_3O_2^-$

	normal		CP2				CP3			
method	ΔE_{int}	ΔH_{int}	ΔE_{int}	ΔH_{int}	$\Delta\Delta E_{int}$	$\Delta\Delta H_{int}$	ΔE_{int}	ΔH_{int}	$\Delta\Delta E_{int}$	$\Delta\Delta H_{int}$
HF										
6-31G	38.95	38.41	32.31	31.39	−6.64	−7.02	31.83	31.05	−6.07	−7.36
6-31G**	35.18	34.52	27.99	27.21	−7.19	−7.31	27.22	26.44	−7.96	−8.08
6-31++G**	24.85	23.78	23.95	22.89	−0.91	−0.89	24.04	22.98	−0.82	−0.80
6-311G**	34.68	33.74	25.51	24.42	−9.17	−9.32	24.84	23.93	−9.84	−9.81
6-311++G**	24.34	23.23	23.53	22.43	−0.81	−0.80	23.54	22.46	−0.80	−0.77
D95**	31.84	31.21	28.49	27.66	−3.35	−3.55	27.64	26.91	−4.21	−4.30
D95++**	24.84	23.78	24.00	22.95	−0.84	−0.83	24.10	23.04	−0.75	−0.74
6-311++G(3df,2pd)	23.73	22.77	23.05	22.10	−0.68	−0.67	23.05	22.10	−0.68	−0.67
MP2										
6-31G	44.29	45.15	33.14	32.79	−11.15	−12.36	32.88	33.24	−11.42	−11.91
6-31G**	43.57	44.52	30.87	30.96	−12.70	−13.56	30.70	31.92	−12.87	−12.60
6-31++G**	28.56	28.67	25.00	24.64	−3.56	−4.03	25.49	25.46	−3.06	−3.21
6-311G**	44.36	45.17	27.00	26.39	−17.35	−18.78	26.55	26.56	−17.81	−18.61
6-311++G**	28.35	28.60	24.28	23.69	−4.06	−4.91	24.48	24.31	−3.86	−4.29
D95**	39.52	40.30	32.00	31.94	−7.52	−8.36	32.25	33.15	−7.27	−7.15
D95++**	28.71	28.83	25.09	24.69	−3.62	−4.14	25.78	25.88	−2.93	−2.95
6-311++G(3df,2pd)	28.62	29.23	25.83	25.76	−2.79	−3.47	26.01	26.66	−2.60	−2.57
aug-cc-pVDZ[a]	26.8	27.0								
aug-cc-pVTZ[a]	27.6	27.8								
exp[b]		26.5								

	O···O	O···H	O···O	O···H	O···O	O···H	O···O	O···H	O···O	O···H	O−H
HF											
6-31G	2.473	1.400	2.505	1.457	0.032	0.057	2.501	1.445	0.028	0.045	−0.017
6-31G**	2.499	1.459	2.525	1.494	0.026	0.035	2.532	1.501	0.032	0.042	−0.011
6-31++G**	2.571	1.569	2.580	1.578	0.009	0.009	2.578	1.577	0.008	0.008	−0.001
6-311G**	2.521	1.501	2.566	1.566	0.046	0.065	2.570	1.567	0.050	0.066	−0.017
6-311++G**	2.577	1.581	2.585	1.588	0.008	0.007	2.584	1.586	0.006	0.005	−0.000
D95**	2.494	1.452	2.519	1.489	0.026	0.037	2.521	1.487	0.028	0.035	−0.008
D95++**	2.570	1.567	2.575	1.571	0.005	0.004	2.574	1.570	0.004	0.003	−0.000
6-311++G(3df,2pd)	2.561	1.555	2.570	1.566	0.008	0.011	2.568	1.562	0.007	0.007	−0.001
MP2											
6-31G	2.486	1.244	2.545	1.435	0.059	0.191	2.521	1.362	0.035	0.118	−0.083
6-31G**	2.443	1.223	2.497	1.388	0.053	0.165	2.471	1.256	0.027	0.033	−0.008
6-31++G**	2.489	1.396	2.548	1.487	0.058	0.091	2.511	1.412	0.022	0.016	0.005
6-311G**	2.423	1.216	2.539	1.494	0.117	0.278	2.508	1.418	0.085	0.202	−0.122
6-311++G**	2.473	1.380	2.559	1.515	0.087	0.135	2.538	1.458	0.065	0.078	−0.022
D95**	2.433	1.217	2.490	1.382	0.057	0.165	2.469	1.235	0.036	0.018	0.017
D95++**	2.493	1.405	2.548	1.489	0.055	0.084	2.524	1.430	0.031	0.025	0.007
6-311++G(3df,2pd)	2.455	1.332	2.512	1.439	0.056	0.107	2.491	1.384	0.035	0.052	−0.017
aug-cc-pVDZ[a]		1.089 0.969[c]									
aug-cc-pVTZ[a]		1.107 0.961[c]									

[a] Reference 15. [b] Reference 13. [c] O−H distance.

four symmetric structures, leaving the 6-31G** and the D95** as the only basis sets predicting symmetric interactions (CP2 cannot give a symmetric solution). The largest MP2 calculation, while unsymmetrical, is much closer to the symmetric structure than any of the other unsymmetrical examples. Thus, although this result is in accord with an unsymmetrical structure, we cannot be confident that a higher level calculation would not lead to a symmetrical structure.

Hydration of H_3O^+. The protonated water dimer has been extensively studied theoretically and experimentally. Mautner has reported the ΔH of hydration of the hydronium ion to be 31.8 kcal/mol in the gas phase.[8] Other reports vary from 31.6 to 44 kcal/mol.[22] Theoretical calculations differed with respect to the structure of the $H_5O_2^+$ aggregate. RHF calculations predicted a structure with the H-bonding proton closer to one of the oxygens (C_s), whereas more recent higher level calculations that include corrections for the electron-correlation error tend to predict a more symmetrical structure with the H-bonding proton equidistant from the oxygens (C_2).[23] The most recent and presumably most accurate calculations for this species predict the C_2 structure with H-bonding distances of 1.1947 Å [TZ2P(f,d) B−CCD(T)] and 1.1938 Å.[24] Unfortunately, neither of the most recent reports gives the interaction energy for $H_2O + H_3O^+$. For this, we refer to an earlier report by Schaefer of 33.4[25] and 32.9 kcal/mol (137.7 kj/mol) reported by Berning and Sauer.[26] We note that these values are interaction *energies* not *enthalpies*, which require vibrational and thermal correction.

We have performed normal (uncorrected for CP) geometry optimizations at both the RHF (which give C_s structures) and the MP2 (which give C_2 structures) levels. The only exceptions are the 6-31G calculations which predict D_{2d} structures at both HF and MP2 levels. The results can be found in Table 2. As seen from this table, the interaction energies are generally stronger for the CP3 procedure. The only exceptions are HF/6-31G++** and HF/D95++** (where the CP2 and CP3 interaction energies are virtually identical). The CP corrections are also generally lower for the CP3 calculations (with the same two exceptions noted above).

Because the CP2 procedure is inherently unsymmetrical, it cannot lead to a C_2 solution. Therefore, we found it particularly interesting to compare the MP2 (C_2) optimizations for the CP2 and CP3 procedures. The interaction energies are about 1 kcal/

TABLE 2: Interaction Energetics (−kcal/mol) and Selected Geometric Parameters (Å) for $H_5O_2^+$

	normal			CP2			differences		CP3			differences	
method	ΔE_{int}	ΔH_{int}	symm.	ΔE_{int}	ΔH_{int}	symm	$\Delta\Delta E_{int}$	$\Delta\Delta H_{int}$	ΔE_{int}	ΔH_{int}	symm.	$\Delta\Delta E_{int}$	$\Delta\Delta H_{int}$
HF													
6-31G	42.64	42.64	D_{2d}	41.28	41.24	C_s	−1.36	−1.40	41.83	41.77	D_{2d}	−0.81	−0.87
6-31G**	33.89	34.05	C_s	32.65	32.62	C_s	−1.24	−1.43	32.92	32.95	C_s	−0.97	−1.10
6-31++G**	31.41	31.21	C_s	30.13	29.88	C_s	−1.29	−1.33	30.00	29.74	C_s	−1.41	−1.47
6-311G**	33.38	33.14	C_s	30.43	29.99	C_s	−2.95	−3.15	31.45	31.15	C_s	−1.93	−1.99
6-311++G**	31.05	30.63	C_s	29.63	29.23	C_s	−1.42	−1.40	29.88	29.48	C_s	−1.16	−1.15
D95**	32.51	32.46	C_s	31.92	31.82	C_s	−0.58	−0.64	32.09	32.13	C_s	−0.41	−0.33
D95++**	31.22	30.98	C_s	30.20	29.93	C_s	−1.02	−1.05	30.19	29.95	C_s	−1.03	−1.03
6-311++G(3df,2pd)	29.92	29.54	C_s	29.36	28.94	C_s	−0.56	−0.60	29.55	29.23	C_s	−0.37	−0.31
MP2													
6-31G	45.40	44.79	D_{2d}	42.67	41.98	C_1	−2.73	−2.81	43.87	43.30	D_{2d}	−1.53	−1.49
6-31G**	39.46	39.71	C_2	36.27	36.24	C_1	−3.19	−3.47	37.35	37.58	C_2	−2.11	−2.13
6-31++G**	36.01	36.35	C_2	32.52	32.70	C_1	−3.49	−3.65	33.07	33.61	C_2	−2.94	−2.74
6-311G**	39.07	39.28	C_2	33.91	33.51	C_1	−5.16	−5.77	34.81	35.37	C_2	−4.26	−3.91
6-311++G**	35.61	35.92	C_2	31.95	31.71	C_1	−3.66	−4.21	32.41	33.07	C_2	−3.20	−2.85
D95**	37.51	37.96	C_2	35.23	35.17	C_1	−2.28	−2.79	36.40	36.80	C_2	−1.11	−1.16
D95++**	35.69	36.11	C_2	32.38	32.31	C_1	−3.31	−3.80	33.27	33.82	C_2	−2.42	−2.29
6-311++G(3df,2pd)	34.87	35.28	C_2	32.81	33.14	C_1	−2.06	−2.14	33.66	34.15	C_2	−1.21	−1.13
		33.4[a]											
		32.9[b]											
experiment		31.8[c]											

	O···O	O···H	O−H	O···O	O···H	O−H	O···O	O···H	O−H	O···O	O···H	O−H	O···O	O···H	O−H
HF															
6-31G	2.366	1.183	1.183	2.372	1.216	1.156	0.006	0.033	−0.027	2.371	1.186	1.186	0.004	0.003	
6-31G**	2.392	1.314	1.081	2.402	1.329	1.074	0.010	0.015	−0.007	2.398	1.325	1.076	0.006	0.010	−0.004
6-31++G**	2.409	1.348	1.064	2.422	1.365	1.058	0.013	0.017	−0.006	2.424	1.372	1.055	0.015	0.024	−0.009
6-311G**	2.403	1.342	1.064	2.431	1.384	1.047	0.028	0.042	−0.017	2.419	1.366	1.056	0.015	0.024	−0.008
6-311++G**	2.415	1.363	1.056	2.432	1.386	1.048	0.017	0.023	−0.008	2.428	1.381	1.050	0.012	0.018	−0.006
D95**	2.406	1.341	1.068	2.411	1.347	1.065	0.005	0.006	−0.002	2.404	1.337	1.070	−0.002	−0.004	0.002
D95++**	2.417	1.361	1.060	2.425	1.370	1.057	0.008	0.009	−0.003	2.425	1.372	1.056	0.008	0.011	−0.003
6-311++G(3df,2pd)	2.424	1.374	1.052	2.431	1.383	1.048	0.006	0.009	−0.004	2.427	1.377	1.052	0.003	0.002	−0.000
MP2															
6-31G	2.398	1.199	1.199	2.402	1.251	1.162	0.004	0.052	−0.037	2.413	1.208		0.015	0.009	
6-31G**	2.383	1.193	1.193	2.410	1.276	1.128	0.027	0.083	−0.065	2.396	1.200		0.013	0.007	
6-31++G**	2.385	1.194	1.194	2.423	1.288	1.124	0.038	0.094	−0.070	2.403	1.203		0.018	0.009	
6-311G**	2.376	1.190	1.190	2.422	1.337	1.087	0.046	0.147	−0.103	2.392	1.200		0.016	0.010	
6-311++G**	2.380	1.191	1.191	2.410	1.332	1.092	0.030	0.141	−0.099	2.397	1.199		0.017	0.008	
D95**	2.381	1.192	1.192	2.422	1.307	1.105	0.041	0.115	−0.087	2.396	1.200		0.015	0.008	
D95++**	2.385	1.194	1.194	2.397	1.320	1.104	0.012	0.126	−0.090	2.407	1.206		0.022	0.012	
6-311++G(3df,2pd)	2.379	1.191	1.191	2.413	1.266	1.135	0.034	0.075	−0.056	2.393	1.199		0.014	0.008	
TZ2P(f,d) B−CCD(T)[d]		1.1947													

[a] Reference 23. [b] Reference 24. [c] Reference 8. [d] Reference 22.

mol greater, whereas the CP corrections are about 1 kcal/mol less for the CP3 calculations. The CP correction remains quite significant even for the largest basis set. The geometries are fairly consistent at the CP3 level, even for the small basis sets. However, the CP2 calculations generally yield quite unsymmetrical structures, especially with the moderately large basis sets. For example, 6-311G** predicts a difference in the two O···H distances of 0.25 Å. Even the largest basis set predicts a difference of 0.13 Å. Clearly, CP2 would lead to qualitatively incorrect results for this geometry, even with large basis sets.

For the HF calculations, the differences between the results obtained for CP2 and CP3 are not very different. The CP corrections are smaller, as might be expected.

Hydration of NH_4^+. Unlike the hydrated OH^- and H_3O^+ species, the hydrated NH_4^+ cation cannot attain a symmetrical structure with two equivalent H bonds. Because of the higher basicity of NH_3, the proton is expected to be unambiguously covalently bonded to this species and H-bonded to the water. Thus, the hydrated species could be defined using the CP2 procedure without influencing the symmetry of the H-bonding complex. However, if a double-well potential exits, with the proton transferred to the water, the PES and TS for this process would require the CP3 procedure for continuity. The experimental hydration enthalpy for NH_4^+ in the gas phase has been variously reported as 17.2[20c] and 19.9[20d] kcal/mol. The best CP3 calculation (19.53 kcal/mol) is in excellent agreement with the latter (probably more accurate) of these two values. Several theoretical studies of this system have also been reported.[27] The most elaborate of these, QCISD/6-311++G** optimized at the MP2/6-311++G** level, predicts an interaction energy of −17.82 kcal/mol after correction for CP and ZPVE.[25a]

The calculated enthalpies of interaction and H-bonding distances are collected in Table 3. Bueker and Uggerud have reported the MP2/6-31G(d,p) interaction *energy* to be −22.8 kcal/mol (reported as −95.1 kj/mol),[25b] somewhat less binding than our value of 24.33 kcal/mol (uncorrected). The reason for this discrepancy is unclear. The previously reported H-bonding distance of 1.616 Å agrees with our result for the same calculation.

As seen from Table 3, both CP2 and CP3 improve the energetic and geometric results for the smaller basis sets although the overall effect of BSSE is less dramatic than for the previous examples. Both methods converge to the same large basis set value. There appears to be no disadvantage to using the CP3 method despite the expected significant differences in the O···O and H···O distances.

TABLE 3: Interaction Energetics (−kcal/mol) and Selected Geometric Parameters (Å) for NH_4^+/H_2O

	normal		CP2		differences		CP3		differences	
method	ΔE_{int}	ΔH_{int}	ΔE_{int}	ΔH_{int}	$\Delta\Delta E_{int}$	$\Delta\Delta H_{int}$	ΔE_{int}	ΔH_{int}	$\Delta\Delta E_{int}$	$\Delta\Delta H_{int}$
HF										
6-31G	27.01	25.32	26.29	24.56	−0.72	−0.76	26.13	24.43	−0.88	−0.89
6-31G**	21.53	20.14	20.80	19.37	−0.73	−0.77	20.62	19.11	−0.91	−1.03
6-31++G**	19.72	18.26	18.90	17.49	−0.82	−0.77	18.82	17.42	−0.90	−0.84
6-311G**	21.43	19.97	20.10	18.61	−1.33	−1.36	20.14	18.63	−1.29	−1.34
6-311++G**	19.56	18.06	18.88	17.42	−0.69	−0.64	18.86	17.40	−0.71	−0.66
D95**	20.53	19.12	20.17	18.75	−0.36	0.37	19.89	18.53	−0.65	−0.59
D95++**	19.63	18.18	18.95	17.52	−0.67	−0.66	18.95	17.32	−0.68	−0.86
6-311++G(3df,2pd)	18.32	16.93	18.13	16.73	−0.19	0.39	18.15	16.74	−0.17	−0.19
MP2										
6-31G	28.51	26.87	26.89	25.20	−1.62	−1.67	26.82	25.21	−1.69	−1.66
6-31G**	24.33	23.17	22.52	21.27	−1.81	−1.90	22.47	21.26	−1.85	−1.91
6-31++G**	21.85	20.55	19.79	18.52	−2.06	−2.03	19.71	18.43	−2.14	−2.12
6-311G**	24.46	23.27	21.61	20.27	−2.84	−3.00	21.75	20.45	−2.71	−3.82
6-311++G**	21.70	20.44	19.81	18.47	−1.89	−1.97	19.77	18.45	−1.93	−1.99
D95**	23.08	21.91	21.83	20.58	−1.25	−1.33	21.42	20.31	−1.66	−1.60
D95++**	21.85	20.58	19.91	18.61	−1.94	−1.97	19.91	18.64	−1.95	−1.94
6-311++G(3df,2pd)	20.88	19.96	19.93	18.99	−0.95	−0.97	20.11	18.94	−0.77	−1.02
QCISD/6-311++G**[a]	20.62	17.82								
CCD/6-311++G** [a]	19.31	17.51								
experiment		19.9[20d] 17.2[20c]								

	N···O	O···H	N−H	N···O	O···H	N−H	N···O	O···H	N−H	N···O	O···H	N−H	N···O	O···H	N−H
HF															
6-31G	2.675	1.629	1.046	2.686	1.641	1.050	0.011	0.012	0.004	2.686	1.636	1.045	0.011	0.007	−0.001
6-31G**	2.754	1.719	1.035	2.764	1.730	1.034	0.010	0.011	−0.000	2.764	1.729	1.034	0.011	0.010	−0.001
6-31++G**	2.789	1.759	1.031	2.811	1.779	1.030	0.022	0.020	−0.000	2.809	1.781	1.030	0.019	0.022	−0.001
6-311G**	2.756	1.723	1.034	2.781	1.751	1.032	0.025	0.028	−0.002	2.782	1.749	1.032	0.026	0.026	−0.002
6-311++G**	2.782	1.751	1.031	2.797	1.767	1.030	0.015	0.016	−0.001	2.797	1.767	1.030	0.015	0.016	−0.001
D95**	2.762	1.729	1.034	2.772	1.738	1.033	0.010	0.009	−0.000	2.771	1.739	1.033	0.008	0.010	−0.001
D95++**	2.780	1.748	1.032	2.793	1.761	1.032	0.013	0.013	−0.001	2.792	1.762	1.031	0.012	0.014	−0.001
6-311++G(3df,2pd)	2.777	1.748	1.030	2.782	1.754	1.029	0.005	0.006	−0.000	2.782	1.752	1.029	0.005	0.004	−0.001
MP2															
6-31G	2.675	1.603	1.073	2.698	1.629	1.070	0.023	0.026	−0.003	2.698	1.616	1.082	0.023	0.013	0.010
6-31G**	2.674	1.616	1.058	2.702	1.648	1.055	0.028	0.032	−0.004	2.700	1.636	1.064	0.026	0.020	0.006
6-31++G**	2.722	1.672	1.050	2.764	1.718	1.047	0.042	0.046	−0.003	2.769	1.714	1.055	0.047	0.042	0.005
6-311G**	2.668	1.607	1.060	2.728	1.675	1.053	0.060	0.068	−0.007	2.725	1.666	1.059	0.057	0.059	−0.001
6-311++G**	2.701	1.647	1.054	2.748	1.698	1.050	0.047	0.051	−0.004	2.750	1.695	1.056	0.049	0.048	0.001
D95**	2.690	1.632	1.058	2.714	1.660	1.055	0.025	0.028	−0.003	2.717	1.652	1.065	0.027	0.020	0.007
D95++**	2.716	1.664	1.053	2.749	1.700	1.050	0.033	0.036	−0.003	2.752	1.693	1.058	0.035	0.029	0.006
6-311++G(3df,2pd)	2.688	1.635	1.053	2.712	1.662	1.051	0.024	0.027	−0.003	2.711	1.656	1.055	0.023	0.021	0.001
B3LYP/6-31+G*	2.728[a]														
MP2/6-31+G*	2.766[a]														

[a] Reference 25a.

Discussion

The BSSEs for the ion/molecule complexes studied here are rather larger than for molecule/molecule interactions, as might be expected. Reasonably large BSSEs (1.1−3.5 kcal/mol) persist even for the largest basis set used, 6-311++G(3df,2pd), for hydrated OH^- and H_3O^+ as indicated by the differences in energy and enthalpy between the normally optimized and CP-optimized structures for these species.

The CP3 procedure usually produces a larger CP correction than CP2. Thus, the total energies of the CP3 calculations are generally higher than those for the corresponding CP2 calculations. The two-fragment CP calculation that one must perform on the separated fragment that contains the H^+ (e.g., NH_4^+ for hydrated ammonium) compensates for this when one compares interaction energies. We find no general trend to indicate that either the CP3 or CP2 gives larger interaction energies.

Within the 6-31G family of basis sets, both CP2 and CP3 give decreasing CP corrections as the basis set becomes more extensive. Thus, both seem to converge toward the limiting basis set value. We found a similar trend for the only two basis sets in the D95 family that we considered. Both procedures lead to significant improvements in calculated interactions energies as judged by comparison to our largest basis set and reported experimental results. Because both methods provide similar levels of correction, we can conclude that choosing a CP3 procedure when optimizing a structure that can potentially achieve a symmetric structure should not introduce any significant error. Therefore, we recommend the CP3 approach for such calculations.

The calculation of the zero-point vibrations and enthalpies for relatively flat surfaces using the harmonic approximation for the low frequency modes can introduce errors in these calculated values. These errors generally cancel when comparing similar structures. However, when low barriers occur on these surfaces, comparison of the enthalpies of the minima and transition states can be particularly problematic. We have discussed this problem before in two different contexts.[28] When in a shallow well, the harmonic approximation will give a vibration that is too strong for the mode that traverses the low barrier. On the other hand, at the transition state (TS) for this barrier, this mode is imaginary as if it is not bound. In the case of a 6-fold torsional rotational barrier such as in NH_4^+/H_2O, treating the vibration at the TS as not bound is a reasonable approximation as the torsional rotation is free. However, in other cases, such as the bending mode in HCCH/H_2O, this mode is not free. In such cases, treating the frequency as imaginary leads to an underestimation of the zero-point energy for this mode.

Comparing the enthalpies of minima and TSs requires summations involving KT in addition to the problem mentioned above for the zero-point vibrations. Thus, an additional difference of KT must be taken into account when comparing a TS structure for a freely rotating torsional mode. For NH_4^+/H_2O, where the rotational barrier is about 10^{-4} kcal/mol and the low frequencies are about ± 10 cm^{-1} (depending upon whether the optimized structure is a minimum or a TS), the calculated enthalpies will differ by approximately KT (0.59 kcal/mol at 298 K).[29] We have corrected those calculations that converged to a TS by this amount so that they can be compared with those that converged to a minimum. Only the enthalpies (not the energies) of interaction require this correction. We applied this procedure only to the calculations on NH_4^+/H_2O, where the surfaces are too flat to reliably converge to minima. For the other systems, the rotational barrier and torsional vibrations, while small, are significantly higher than for NH_4^+/H_2O.

One should note that there are four equivalent minima on the potential energy surface corresponding to the water H bonded to each of the equivalent H's of NH_4^+. Six equivalent transition states exist for conversion between them. Thus, the potential surface might resemble that for a 6-fold rotational barrier, in that the activation energies must necessarily be small. In such a situation the system might sample all of these minima even at the zero-point vibration in addition to essentially free rotation about the 3-fold rotational barrier about the H···O H-bond discussed in the methods section above. Perrin has shown that NH_4^+ rotates in aqueous solution with rapid exchange of the H-bonding donors and acceptors.[30]

Because the purpose of this paper is to compare the CP2 and CP3 approaches to CP correction rather than provide state-of-the-art calculations on the species studied, we have not corrected the enthalpies for the effects of low frequency torsional vibrations other than those mentioned above. In principle, these modes should be eliminated for the calculation of enthalpies as they are virtually free of constraint at 298 K. Other low-frequency modes, such as those that exchange the H-bonding and other H's in NH_4^+/H_2O, might also be properly eliminated from the enthalpy calculations.

Conclusions

We have shown that using a three-fragment counterpoise correction (CP3) for ion/molecule complexes can provide a viable approach to calculating potentially symmetric complexes without the bias toward unsymmetrical structures inherent in a two fragment (CP2) correction. On the other hand, the CP3 approach does not necessarily improve the calculated interaction energies over CP2. In fact, we observed no significant differences in the calculated interaction energies. Thus, the potential problem related to how the charges are distributed among the fragments that we mentioned in the Introduction seems to be of minor significance.

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