

# How does basis set superposition error change the potential surfaces for hydrogen-bonded dimers?

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(Received 28 June 1996; accepted 16 September 1996)

We describe a simple method to automate the geometric optimization of molecular orbital calculations of supermolecules on potential surfaces that are corrected for basis set superposition error using the counterpoise (CP) method. This method is applied to the H-bonding complexes HF/HCN, HF/H<sub>2</sub>O, and HCCH/H<sub>2</sub>O using the 6-31G(d,p) and D95++(d,p) basis sets at both the Hartree–Fock and second-order Møller–Plesset levels. We report the interaction energies, geometries, and vibrational frequencies of these complexes on the CP-optimized surfaces; and compare them with similar values calculated using traditional methods, including the (more traditional) single point CP correction. Upon optimization on the CP-corrected surface, the interaction energies become more negative (before vibrational corrections) and the H-bonding stretching vibrations decrease in all cases. The extent of the effects vary from extremely small to quite large depending on the complex and the calculational method. The relative magnitudes of the vibrational corrections cannot be predicted from the H-bond stretching frequencies alone. © 1996 American Institute of Physics. [S0021-9606(96)04047-0]

## I. INTRODUCTION

The importance of the basis set superposition error (BSSE) to the calculation of intermolecular interactions using *ab initio* calculations with basis sets below the Hartree–Fock limit has been appreciated for some time. The origin of this error lies in the possibility that the unused basis functions of the second unit in the associated complex may augment the basis set of the first unit, thereby lowering its energy compared to a calculation of this unit alone. The first unit will cause a similar error on the second. Although several other approaches to correcting this error have been discussed in the literature, the counterpoise (CP) correction proposed by Boys and Bernardi<sup>1</sup> has been the most popular means of correcting for BSSE. The CP method calculates each of the units with just the basis functions of the other (without the nuclei or electrons), using so-called “ghost orbitals.” This method has proven to be somewhat controversial.<sup>2</sup> A problem with the normal use of the CP correction in accurate calculations of intermolecular interactions arises from the fact that the CP correction is usually added to the previously optimized geometry of the complex. In principle, since the BSSE causes the intermolecular interactions to be artifactually too attractive, the CP correction should make the complexes less stable. Consequently, the intermolecular distance will be greater when the complex is optimized with the CP correction included in the energetic expression. Furthermore, the vibrational force constants are

generally reported on the uncorrected surface. This tends to make the intermolecular vibrations appear too strong, resulting in zero-point vibration energies (ZPVE), and vibrational corrections to enthalpy calculations that are incorrect. A striking result of this problem is the interaction energy of acetylene with ozone, which has a well-defined minimum but becomes repulsive after both CP and ZPVE corrections.<sup>3</sup> Several examples of molecular orbital (MO) calculations where CP has been included in the optimization have been performed.<sup>4</sup> However, the optimizations were done point by point as there are no options for this procedure in the common *ab initio* programs. Very recently, several authors have addressed the importance of relocating stationary points in the CP-corrected potential energy surface. Also, they have suggested the convenience of having an automated optimization procedure which uses the CP-corrected energy.<sup>2(h),5</sup>

In this paper, we outline a procedure that allows automatic calculation of the CP correction within a normal *ab initio* optimization calculation including analytic first and second derivatives. This allows us to optimize geometries, locate transition states, and perform vibrational analyses on the CP-corrected potential surface. We describe a program that automates GAUSSIAN 94 to perform this procedure, then provide several examples where the CP-optimized complexes differ significantly both energetically and structurally from the analogous structures calculated the traditional way,

$$E_{\text{super}}^{\text{CP}} = E_{\text{super}} + \text{CP}, \quad (1)$$

$$\text{CP} = \sum_{i=1}^n (E_{m_i} - E_{m_i^*}). \quad (2)$$

<sup>a)</sup>Fundación Banco Bilbao Vizcaya Visiting Professor at the Universitat Autònoma de Barcelona.

TABLE I. Selected energetic results for HF/HCN. Total energies are in hartrees, all others in kcal/mol.

	6-31G(d,p)		D95++(d,p)		Expt.
	HF	MP2	HF	MP2	
Normal surface					
Minimum <sup>a</sup>	-192.899 010	-193.372 455	-192.955 471	-193.432 884	
CP minimum <sup>b</sup>	-192.898 978	-193.372 324	-192.955 379	-193.432 656	
HF	-100.011 691	-100.194 639	-100.050 932	-100.238 385	
HCN	-92.877 138	-93.166 729	-92.893 125	-93.180 492	
ZPVE					
Dimer	19.3	17.62	19.97	18.58	
HF	6.42	5.99	6.43	5.95	
HCN	11.22	10.04	11.12	9.87	
CP-optimized surface					
Minimum <sup>c</sup>	-192.898 132	-193.370 514	-192.953 796	-193.429 108	
Normal minimum <sup>d</sup>	-192.898 117	-193.370 361	-192.953 735	-193.428 925	
ZPVE	19.49	17.88	19.53	17.79	
Normal surface					
$E_{\text{interaction}}$	-6.39	-6.96	-7.16	-8.79	
CP corr	0.56	1.31	1.09	2.48	
ZPVE corr	1.66	1.59	2.42	2.76	
$E_{\text{interaction}}^{\text{CP}}$	-5.83	-5.64	-6.07	-6.30	
$E_{\text{interaction}}^{\text{CP}}(\text{corr})$	-4.17	-4.05	-3.65	-3.54	
CP optimized					
$E_{\text{interaction}}^{\text{CP}}$	-5.84	-5.74	-6.11	-6.42	
CP corr	0.53	1.14	0.99	2.23	
ZPVE corr	1.85	1.85	1.98	1.97	
$E_{\text{interaction}}^{\text{CP}}(\text{corr})$	-3.99	-3.89	-4.13	-4.45	-4.52±0.26 <sup>e</sup>

<sup>a</sup>Point *a* in Fig. 2.<sup>b</sup>Point *b* in Fig. 2.<sup>c</sup>Point *c* in Fig. 2.<sup>d</sup>Point *d* in Fig. 2.<sup>e</sup>Reference 11(b).

The basic problem can be stated as the need to optimize  $E_{\text{super}}^{\text{CP}}$  where  $E_{\text{super}}^{\text{CP}}$  is described in Eq. (1), and  $E_{\text{super}}$  represents the total energy of the supermolecular aggregate containing  $n$  monomeric units. Using the notation employed previously,<sup>3(d)</sup> the CP correction is stated in Eq. (2), 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 (\*) represents monomers calculated with "ghost" orbitals. Equation (1) can be rewritten as Eq. (3). The CP-corrected interaction energy *calculated at the CP-optimized geometry*,  $E_{\text{interaction}}^{\text{CP}}$ , is expressed by Eq. (4),

$$E_{\text{super}}^{\text{CP}} = E_{\text{super}} + \sum_{i=1,n} (E_{m_f^i} - E_{m_f^{i*}}), \quad (3)$$

$$E_{\text{interaction}}^{\text{CP}} = E_{\text{super}} - \sum_{i=1}^n E_{m_{\text{opt}}^i} + \sum_{i=1}^n (E_{m_f^i} - E_{m_f^{i*}}), \quad (4)$$

$$\frac{\partial E_{\text{interaction}}^{\text{CP}}}{\partial p_j} = \frac{\partial E_{\text{super}}^{\text{CP}}}{\partial p_j} = \frac{\partial E_{\text{super}}}{\partial p_j} + \sum_{i=1}^n \left( \frac{\partial E_{m_f^i}}{\partial p_j} - \frac{\partial E_{m_f^{i*}}}{\partial p_j} \right). \quad (5)$$

In order to find a stationary point with respect to geometrical variation of the supermolecule, we require that the derivatives of  $E_{\text{super}}^{\text{CP}}$  with respect to all internal coordinates of

TABLE II. Comparison of the geometric parameters of HF/HCN on the normal and CP-optimized surfaces. Distances in Å.

	6-31G(d,p)		D95++(d,p)		
	HF	MP2	HF	MP2	
H-F					
Normal	0.906	0.928	0.912	0.939	
CP opt	0.906	0.928	0.911	0.936	0.938 <sup>c</sup>
Diff	0.000	0.000	-0.001	-0.003	
H...N					
Normal	2.011	1.929	1.914	1.809	
CP opt	2.054	2.012	1.975	1.901	1.827 <sup>c</sup>
Diff	0.043	0.083	0.061	0.092	
N-C					
Normal	1.131	1.174	1.131	1.177	
CP opt	1.131	1.175	1.133	1.180	1.167 <sup>c</sup>
Diff	0.000	0.001	0.002	0.003	
C-H					
Normal	1.060	1.066	1.061	1.069	
CP opt	1.060	1.065	1.062	1.069	1.07 <sup>c</sup>
Diff	0.000	-0.001	0.001	0.000	
F-N					
Normal	2.917	2.857	2.826	2.748	2.795±0.003 <sup>a</sup>
CP opt	2.96	2.94	2.886	2.837	2.796 <sup>b</sup>
Diff	0.043	0.083	0.060	0.089	2.765 <sup>c</sup>

<sup>a</sup>Reference 11(a).<sup>b</sup>Reference 11(b).<sup>c</sup>Reference 4(c) (calculated).

TABLE III. Comparison of the calculated vibrational frequencies ( $\text{cm}^{-1}$ ) on the normal and CP-corrected surfaces for HF/HCN.

	6-31G(d,p)		D95++(d,p)	
	HF	MP2	HF	MP2
Normal	73	70	116	127
CP opt	75	71	86	78
Diff	2	1	-30	-49
Normal	156	166	179	200 168 <sup>a</sup>
CP opt	147	151	154	164
Diff	-9	-15	-25	-36
Normal	475	466	712	729
CP opt	484	481	737	765
Diff	9	15	25	36
Normal	893	726	891	826
CP opt	894	734	881	714
Diff	1	8	-10	-112
Normal	2451	2069	2437	2051
CP opt	2450	2066	2427	2032
Diff	-1	-3	-10	-19
Normal	3647	3528	3636	3504
CP opt	3647	3531	3636	3502
Diff	0	3	0	-2
Normal	4367	4040	4289	3875
CP opt	4367	4054	4314	3935
Diff	0	14	25	60

<sup>a</sup>Reference 9.

the supermolecule be zero [Eq. (5)]. The energies of the optimized monomers are not a function of the supermolecular calculation, so their derivatives with respect to the geometrical parameters of the supermolecule are always zero. Equation (5) illustrates that the first derivative of either  $E_{\text{interaction}}^{\text{CP}}$ , or  $E_{\text{super}}^{\text{CP}}$  with respect to any internal coordinate,  $p_j$ , can be expressed as a simple sum of the first derivatives of  $E_{\text{super}}$  and the energies of each monomer frozen in its supermolecular geometry with and without ghost orbitals. Thus  $2n+1$  derivatives must be evaluated for each internal parameter. Since each  $p_j$  will be the same for the supermolecule and the monomers, the derivatives at each geometric point are readily available from GAUSSIAN 94 or any other program that provides these derivatives.

Force constants and vibrational frequencies can be derived from the matrix of second derivatives. Each element of the Hessian matrix can be calculated in a manner similar to the first derivatives as indicated by

$$\frac{\partial^2 E_{\text{interaction}}^{\text{CP}}}{\partial p_j \partial p_k} = \frac{\partial^2 E_{\text{super}}}{\partial p_j \partial p_k} + \sum_{i=1}^n \left( \frac{\partial^2 E_{m_f^i}}{\partial p_j \partial p_k} - \frac{\partial^2 E_{m_f^{i*}}}{\partial p_j \partial p_k} \right). \quad (6)$$

In principle, not only the geometric variables,  $p_j$ , will differ from those normally obtained from optimizations that

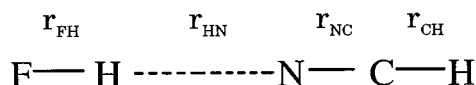
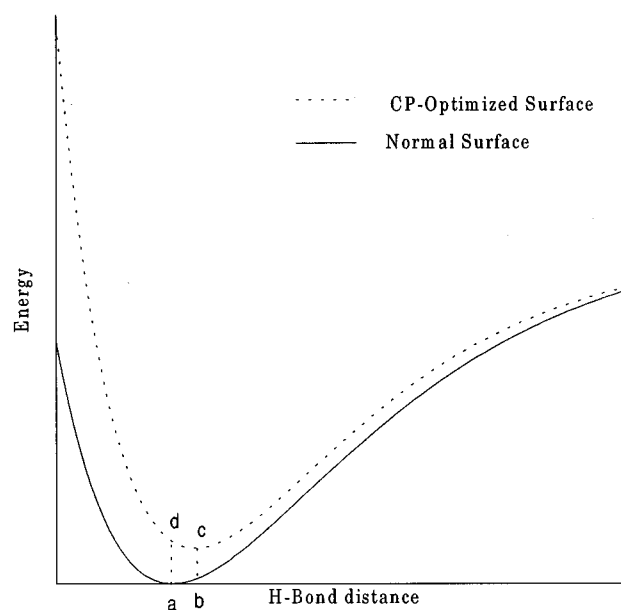


FIG. 1. Geometrical parameters for HF/HCN.

FIG. 2. Comparison of normal and CP-optimized surfaces. Points *a* and *c* represent the optimized structures on the normal and CP-optimized surfaces, respectively, while points *b* and *d* represent each optimized system on the other surface.

do not contain CP corrections, but other molecular properties such as one-electron density, electric field values at nuclei, electrostatic potentials, dipole moments, polarizabilities, IR frequencies and intensities, etc., will differ as well. In general, any property that can be defined as a derivative of the energy can be calculated by using a variant of Eq. (5).

The purpose of this paper is twofold: first, to devise a procedure to build CP-corrected potential energy surfaces; and second, to apply this procedure to systems of chemical interest. Thus, in this paper we utilize the procedure described below to examine the CP-corrected surfaces of three complexes: (a) HF/HCN; (b) HF/H<sub>2</sub>O; and (c) HCCH/H<sub>2</sub>O. One should note that the effects of CP correction on potential energy surfaces can be considered to be similar to those due to basis set changes, the inclusion of electron correlation, the application of electric fields, etc. All of these will change the energies, equilibrium geometry, and curvatures at stationary points, i.e., harmonic frequencies. These three aspects will be analyzed in this paper. We report the CP-corrected surfaces of three complexes: (a) HF/HCN; (b) HF/H<sub>2</sub>O; and (c) HCCH/H<sub>2</sub>O. The first of these systems was previously studied by Bouteiller.<sup>4(a),4(c)</sup> We shall compare our results with his. The second and third systems have been studied using more common procedures. HF/H<sub>2</sub>O has been found to be a nonplanar complex,<sup>4(c),12</sup> while HCCH/H<sub>2</sub>O has been reported to be either planar<sup>3</sup> or nonplanar<sup>6</sup> depending upon the calculational methods used. In some cases, CP, applied in the traditional way (as a single point correction) lowers the energy of the planar below that of the nonplanar system.<sup>3</sup>



TABLE V. Comparison of the geometric parameters of HF/H<sub>2</sub>O on the normal and CP-optimized surfaces. Distances in Å and angles in degrees.

Geometry	6-31G(dp)		D95++(d,p)		
	HF	MP2	HF	MP2	
H-F					
Normal	0.910	0.935	0.915	0.943	
CP opt	0.910	0.933	0.914	0.940	
Diff	0.000	-0.003	-0.001	-0.003	
H...O					
Normal	1.811	1.749	1.792	1.709	
CP opt	1.851	1.823	1.818	1.768	
Diff	0.040	0.074	0.026	0.059	
O...F					2.662 <sup>a</sup>
Normal	2.718	2.675	2.706	2.652	
CP opt	2.760	2.755	2.732	2.708	
Diff	0.042	0.080	0.026	0.056	
O-H					
Normal	0.944	0.963	0.945	0.966	
CP opt	0.944	0.962	0.945	0.965	
Diff	0.000	-0.001	0.000	-0.001	
<i>a</i> 1					
Normal	96.2	99.8	92.2	92.5	
CP opt	92.3	93.6	91.9	92.8	
Diff	-3.9	-6.2	-0.3	0.3	
<i>a</i> 2					
Normal	116.3	108.3	121.5	116.3	
CP opt	122.2	117.7	123.3	117.4	
Diff	5.9	9.4	1.7	1.0	
<i>d</i> 1					
Normal	116.4	123.4	108.7	117.4	
CP opt	108.2	116.4	104.9	116.1	
Diff	-8.2	-7.0	-3.8	-1.3	

<sup>a</sup>Reference 13.

compare the normal and CP-corrected potential surfaces at the minimum geometries for each. Note that the corrected interaction energies on the normal surface include corrections for both CP ( $E_d - E_a$  in Fig. 2) and zero-point vibration energy (ZPVE), while the corrected interaction energy on the CP-corrected surface only includes the ZPVE correction. A CP correction is recorded in Table I only to indicate the energy difference between the two surfaces at the CP-corrected minimum ( $E_c - E_b$  in Fig. 2).

As expected, the H...N H-bonding distance is always longer on the CP-corrected surface. The largest change (0.092 Å) occurs for the MP2/D95++(d,p) calculations. As further expected, the interactions become more attractive (by from 0.1 to 0.9 kcal/mol). The MP2/D95++(d,p) calculation shows the largest effect. Here again, the MP2 calculations show the largest differences between the normal and CP-corrected surfaces. The ZPVE correction is not always lower on the CP-corrected surface, as might be anticipated from the changes in the *intermolecular* stretching frequencies. While the H-bond stretch was shifted to lower frequencies in all four cases; as expected, increases in other frequencies more than overcame these shifts in both HF calculations.

The H-bonding stretching frequency calculated on the CP-corrected surface agrees remarkably well with the experimental<sup>10</sup> value of 168 cm<sup>-1</sup>, but not with the reported harmonic CP-corrected value previously reported.<sup>11</sup> The

TABLE VI. Comparison of the calculated vibrational frequencies on the normal and CP-corrected surfaces for HF/H<sub>2</sub>O.

	6-31G(d,p)		D95++(d,p)	
	HF	MP2	HF	MP2
Normal	192	211	167	233
CP opt	151	199	119	187
Diff	-41	-12	-48	-46
Normal	209	215	218	272
CP opt	208	230	200	226
Diff	-1	15	-18	-46
Normal	236	272	237	290
CP opt	225	235	211	229
Diff	-11	-37	-26	-61
Normal	632	705	661	745
CP opt	631	660	631	670
Diff	-1	-45	-30	-75
Normal	766	824	806	894
CP opt	755	775	756	798
Diff	-11	-49	-50	-96
Normal	1764	1675	1748	1644
CP opt	1772	1685	1739	1637
Diff	8	10	-9	-7
Normal	4143	3867	4149	3784
CP opt	4147	3892	4152	3838
Diff	4	25	3	54
Normal	4259	3905	4221	3871
CP opt	4264	3957	4239	3879
Diff	5	52	18	8
Normal	4261	4010	4266	4006
CP opt	4284	4027	4270	4013
Diff	23	17	4	7

MP2/D95++(d,p) value for the F...N distance is in good agreement with the reported experimental values.<sup>12</sup>

## B. HF/H<sub>2</sub>O

The results for HF/H<sub>2</sub>O<sup>13</sup> are presented in Tables IV–VI and Fig. 3. Unlike the previous example, here the HF surfaces are more affected by CP correction than the MP2 surfaces. This can be seen from the differences in the normal and CP-corrected interaction energies. The CP correction is significantly diminished on the CP-corrected surfaces for the HF calculations, but relatively unchanged for the MP2's. The changes in the H...O H-bonding distances are most significant for the D95++(d,p) basis set in both HF and MP2 optimizations. The complex is predicted to be nonplanar in

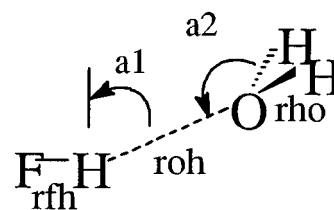
FIG. 3. Geometrical parameters for HF/H<sub>2</sub>O.

TABLE VII. Selected energetic results for HCCH/H<sub>2</sub>O. Total energies are in hartrees, all others in kcal/mol.

Uncorrected	6-31G(d,p)		D95++(d,p)	
	HF	MP2	HF	MP2
Normal surface				
Minimum <sup>a</sup>	-152.850 715	-153.308 568	-152.888 715	-153.345 998
CP minimum <sup>b</sup>	-152.850 583	-153.307 925	-152.888 710	-153.345 888
HCCH	-76.821 837	-77.081 668	-76.834 069	-77.090 090
H <sub>2</sub> O	-76.023 615	-76.219 786	-76.049 834	-76.249 638
ZPVE				
Dimer	34.08	31.54	33.72	31.18
HCCH	18.41	16.4	18.21	16.39
H <sub>2</sub> O	14.56	13.73	14.52	13.61
CP-optimized surface				
Minimum <sup>c</sup>	-152.849 766	-153.306 105	-152.888 123	-153.343 968
Normal minimum <sup>d</sup>	-152.849 487	-153.305 313	-152.888 092	-153.343 810
ZPVE	33.90	31.18	33.62	30.87
Normal surface				
$E_{\text{interaction}}$	-3.30	-4.46	-3.02	-3.93
CP corr	0.77	2.04	0.39	1.37
ZPVE corr	1.11	1.41	0.99	1.18
$E_{\text{interaction}}^{\text{CP}}$	-2.53	-2.42	-2.63	-2.56
$E_{\text{interaction}}^{\text{CP}}$ (corr)	-1.42	-1.01	-1.64	-1.38
CP-optimized surface				
$E_{\text{interaction}}^{\text{CP}}$	-2.70	-2.92	-2.65	-2.66
CP corr	0.52	1.14	0.37	1.20
ZPVE corr	0.96	1.05	0.89	0.87
$E_{\text{interaction}}^{\text{CP}}$ (corr)	-1.74	-1.87	-1.76	-1.79

<sup>a</sup>Point *a* in Fig. 2.<sup>b</sup>Point *b* in Fig. 2.<sup>c</sup>Point *c* in Fig. 2.<sup>d</sup>Point *d* in Fig. 2.

all calculations. However, each of the geometries becomes closer to planar upon CP correction. This can be seen by the decrease in the angles  $a_1$  and  $d_1$ , both of which should be 90° for a planar complex.

Bevan *et al.* have determined structural parameters of HF/H<sub>2</sub>O from analysis of the microwave spectra of various isotopically labeled species.<sup>14</sup> They have concluded that the complex contains a single H...O hydrogen bond with a F...O separation of 2.662 Å. While they emphasize the difficulty in distinguishing between  $C_{2v}$  (planar) and rapidly interconverting  $C_s$  (pyramidal) geometries, they prefer a  $C_s$  geometry based upon an analysis of the intensities of the vibrational satellites due to the thermal population of the lowest vibrational modes of the complex. The experimental<sup>15</sup> enthalpy of interaction of 6.2 kcal/mol is slightly greater than our best value of 5.4.

### C. HCCH/H<sub>2</sub>O

The results of HCCH/H<sub>2</sub>O are presented in Tables VII–IX and Fig. 4. The energies and geometries obtained on the normal surface confirm the results previously published<sup>3</sup> for the HF calculations. The slight differences between the present MP2 results with those previously published result<sup>3</sup> from the use of the frozen core approximation in the current calculations. Other calculations on this system have been reported by Miller *et al.*<sup>5</sup> As in the other examples, the O...H-bonding distances increase, and the H-bond stretching fre-

quencies decrease upon optimization with CP. In our previous report,<sup>3</sup> we noted that application of CP to an optimized nonplanar geometrical minimum and a planar saddle point had the effect of lowering the saddle point below the minimum. The present calculations show the optimized CP-corrected surfaces to be planar (or almost planar) in all cases, while the normal optimized geometries are nonplanar in the cases of both HF and MP2/6-31G (d,p), as previously reported. The difference in energy between the normal and CP-corrected surfaces is always less at the CP-corrected minimum. However, this difference is particularly large in the MP2/6-31 (d,p) case (going from 2.04 to 1.18 kcal/mol). All of the calculations are in reasonable agreement with the experimental<sup>16</sup> O...H distance.

### III. DISCUSSION

The optimization of CP-corrected potential surfaces provides several interesting insights. Clearly, the CP-optimized geometry must be of lower energy than the normally optimized geometry plus the (single-point) CP correction. However, the difference in energy between these species can vary greatly. Since the CP correction must go to zero as the basis set approaches the Hartree–Fock limit, the two surfaces must converge at this point. However, it does not follow that any *particular* augmentation to the basis set will reduce either the energetic or geometric CP correction. For HF calculations, the variational principle dictates that the CP-corrected sur-

TABLE VIII. Comparison of the geometric parameters of HCCH/H<sub>2</sub>O on the normal and CP-optimized surfaces. Distances in Å and angles in degrees.

	6-31G(d,p)		D95++(d,p)		
	HF	MP2	HF	MP2	
C-H1					
Normal	1.057	1.062	1.060	1.068	
CP opt	1.057	1.062	1.060	1.068	
Diff	0.000	0.000	0.000	0.000	
C-H2					
Normal	1.062	1.068	1.065	1.073	
CP opt	1.062	1.068	1.064	1.073	
Diff	0.000	0.000	-0.001	0.000	
C-C					
Normal	1.187	1.220	1.192	1.228	
CP opt	1.187	1.220	1.192	1.228	
Diff	0.000	0.000	0.000	0.000	
O...H					2.229 <sup>a</sup>
Normal	2.273	2.204	2.296	2.196	
CP opt	2.276	2.232	2.320	2.285	
Diff	0.003	0.028	0.024	0.089	
O-H					
Normal	0.943	0.963	0.945	0.965	
CP opt	0.943	0.962	0.945	0.965	
Diff	0.000	-0.001	0.000	0.000	
<i>a</i> 1					
Normal	99.2	99.9	90.0	91.4	
CP opt	90.0	90.0	90.0	90.0	
Diff	-9.2	-9.9	0.0	-1.4	
<i>a</i> 2					
Normal	113.8	101.6	126.5	122.5	
CP opt	126.8	125.1	126.5	127.2	
Diff	13.0	23.5	0.0	4.7	
<i>d</i> 1					
Normal	119.0	126.4	89.9	109.9	
CP opt	92.4	105.4	89.9	94.5	
Diff	-27.4	-21.0	0.0	-15.4	

<sup>a</sup>Reference 15.

face must lie above the normal surface at all points. Thus, the CP correction will always decrease the interaction stabilization for calculations that satisfy the variational principle. As MP2 calculations are not variational, this may not be true for MP2 calculations. In these cases, the CP-corrected and normal surfaces may cross. Nevertheless, the corrected and uncorrected surfaces must converge at large intermolecular separations.

As previously noted, the BSSE provides a nonphysical attractive interaction. One might expect a correction for this interaction should cause the interacting molecules to separate and the frequency of the stretching vibration that separates the entities to decrease. We have observed these trends in all the cases studied here. Since vibrations involve the normal modes of molecules, these simple expectations may become incorrect in very complex systems. The simple conclusion that the ZPVE should decrease upon going from the normal to the CP-corrected surface<sup>3</sup> has proven incorrect in several instances (as noted above). The increase in the others more than counteracts the decrease in the H-bond stretching frequency. Moreover, the vibration that most represents the

TABLE IX. Comparison of the calculated vibrational frequencies on the normal and CP-corrected surfaces for HCCH/H<sub>2</sub>O.

	6-31G(d,p)		D95++(d,p)		
	HF	MP2	HF	MP2	
Normal	77	91	73	79	
CP opt	57	68	58	67	
Diff	-20	-23	-15	-27	
Normal	82	99	73	86	
CP opt	71	70	70	65	
Diff	-11	-29	-3	-21	
Normal	115	131	109	124	
CP opt	113	115	105	106	
Diff	-2	-16	-4	-18	
Normal	180	215	128	147	
CP opt	124	119	131	109	
Diff	-56	-96	3	-38	
Normal	231	242	218	235	
CP opt	210	194	201	184	
Diff	-21	-48	-17	-51	
Normal	815	493	790	553	
CP opt	812	492	786	546	
Diff	-3	-1	-4	-7	
Normal	819	516	792	569	
CP opt	815	505	788	552	
Diff	-4	-11	-4	-17	
Normal	937	835	913	791	
CP opt	926	802	899	767	
Diff	-11	-33	-14	-24	
Normal	960	873	927	824	
CP opt	946	824	910	780	
Diff	-14	-49	-17	-44	
Normal	1766	1677	1744	1639	
CP opt	1772	1684	1736	1629	
Diff	6	7	-8	-10	
Normal	2232	1990	2197	1945	
CP opt	2233	1990	2197	1946	
Diff	1	0	0	1	
Normal	3545	3441	3535	3406	3254.68 <sup>a</sup>
CP opt	3549	3454	3544	3428	
Diff	4	13	9	22	
Normal	3676	3564	3664	3524	
CP opt	3678	3567	3667	3534	
Diff	2	3	3	10	
Normal	4146	3880	4154	3872	3655.84 <sup>a</sup>
CP opt	4149	3894	4155	3878	
Diff	3	14	1		
Normal	4262	4016	4272	4014	3765.77 <sup>a</sup>
CP opt	4265	4030	4273	4021	
Diff	3	14	1	7	

<sup>a</sup>Reference 5.

H-bond stretch is really a delocalized normal mode. The fact that some other higher frequencies increase is due to mixing of the intermolecular modes with the stiffer vibrations normally associated with the intramolecular modes. If the systems become sufficiently complex, the unique identification of a primary H-bond stretch may become obscure.

Equations (5) and (6) demonstrate that the derivatives of the energy with respect to any parameter of the system can be calculated as a simple sum of individual derivatives. Thus, any molecular property that can be written as a derivative of the energy with respect to some parameter can be calculated at any point upon the CP-corrected surface. For

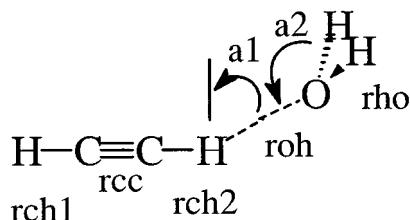


FIG. 4. Geometrical parameters for HCCH/H<sub>2</sub>O.

example, polarizabilities and hyperpolarizabilities can be calculated this way. We shall present some examples of this type of calculation in a forthcoming paper.

The question of whether the CP correction is the best method for correcting for BSSE has been extensively discussed in the literature.<sup>2(f)</sup> The objection that it overcorrects for BSSE has often been disputed. The ambiguity of how it is performed has been noted. For example, adding HF molecules to a growing chain of HF's gives different CP corrections depending upon how one defines the interacting species to which ghosts orbitals are assigned.<sup>2(d)</sup> We now can recognize that this is due to the normal practice of applying CP as a single-point correction. On a CP-optimized surface, all three CP methods used in the study of HF aggregates would necessarily converge to the same energy.

Other methods of correcting for BSSE have been proposed in the literature.<sup>17</sup> However, none of these have been programmed to obtain analytical derivatives of the BSSE-free surface (except at the Hartree–Fock limit which is by definition, BSSE-free). The methodology that we have outlined here provides a simple procedure to calculate CP-corrected potential energy surfaces. We have implemented the procedure to run the GAUSSIAN 94 program. Analogous procedures to run with other MO packages can easily be developed.

#### IV. CONCLUSIONS

Since the CP-corrected energy at any point on the potential surface can be expressed as a sum of energies at the same point on the surface, the first and second derivatives of this energy can be expressed as a sum of derivatives of the individual energies with respect to each parameter. If the individual derivatives in the summation can be expressed analytically, it follows that the corresponding derivatives of the CP-corrected energy can also be expressed analytically. Calculating the derivatives of the CP-correct energy with respect to geometric parameters easily leads to the optimization of the geometry of aggregates on the corresponding surface.

Determining other derivatives, such as with respect to electric fields, can lead to the determination of other properties of aggregates on the CP-corrected surface.

Since CP correction always leads to reduction of the apparent attraction between molecules (by correcting for the nonphysical attraction due to BSSE), the intermolecular separation of H-bonding dimers increases upon optimization with CP. For HF calculations that are far from the Hartree–Fock limit, the magnitude of these effects are not yet predictable. Similarly, while the H-bonding stretching frequencies generally decrease with CP-corrected optimization, the ZPVEs do not always do so, as other vibrational frequencies can increase sufficiently to counteract this effect.

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