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Influence of the counterpoise correction on the optimized relative degrees of freedom in the H-bonded complex water-formamide

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Summary. The correction of the basis set superposition error by the counterpoise method has been investigated at the SCF level for the weak H-bonded water-formamide complex and the results have been compared with the uncorrected results at the SCF, post SCF and semi-empirical AM1 and MNDO levels. Our particular concern has been the determination of the three optimized relative degrees of freedom and the relative stability of three C_s geometrical conformations. The conclusions are that the counterpoise correction weakly conditions the variation in the degrees of freedom and the relative stabilities of the three conformers. The correction is obviously inadequate to describe intramolecular deformation.

Key words: BSSE – Counterpoise correction – Weak H-bonded complex

1. Introduction

The determination of the interaction energies between two or more partners is an exceedingly difficult problem. The generalized statistical method of Santamaria et al. [1] based on a density functional approach is not sufficiently reliable in the equilibrium region and, in the opinion of the authors themselves, it needs refinements.

The most common way to derive interaction energies is to work in the supermolecule framework using a variational procedure. However, this approach is subject to the basis set superposition error (BSSE) [2–5] resulting from the basis set size differences for the partners and the complex, respectively. Jansen and Ros [6] have proposed to correct the protonation energies of CO by taking into account the effect of the basis set extension of CO with that of H in the COH^+ and HCO^+ ions but the resulting corrections, 1.25 kcal/mol for HCO^+ and 6.9 kcal/mol for COH^+, are very different for the two configurations. Similarly, Clementi [7] and Morokuma et al. [8] have suggested that the calculated interaction energy of the hydrogen-bonded NH_3–HCl and $(H_2O)_2$ complexes is too large because of the extension of the basis of the separated partners in the complex.

The bigger the investigated systems are, the smaller the basis set has to be. Unfortunately, small basis sets provide important BSSE and the results thus obtained must be corrected. The counterpoise (CP) correction, as proposed by

Boys and Bernardi [9] implies that BSSE is additive. But according to Mayer [10], BSSE is essentially non-additive since it is related to delocalization parameters upon which the intermolecular interaction energy also depends. This coupling between the BSSE and the interaction energy led Mayer to propose another type of approach that is based on a "chemical hamiltonian" [11].

In addition, within the CP scheme, the corrections depend on how the complex is constructed from its constituents [12]. It remains that for a system composed of only two monomers, BSSE is clearly defined in the CP framework since the interacting partners are univocal.

Whether a full (FCP) [13] or only a virtual (VCP) [14–16] counterpoise correction is to be employed is a matter of controversy. An inherent difficulty is the use of the virtual M.O. in the VCP treatment. In addition, it seems to us that the VCP version is not adequate because it neglects the first order correction noted $BSSE^{(1)}$ by Sokalski et al. [13]. This term is related to the evaluation of the exchange repulsion term, and thus to the basis set extension of any partner as a result of the inclusion of the occupied orbitals of the other. Consequently and according to the work of Alagona et al. [3] on noncovalent interactions of medium strength, we have adopted the full counterpoise correction in order to study its influence on the equilibrium geometrical parameters and the interaction energy of a small H-bonded water-formamide complex.

The work is aimed at defining the effect that the counterpoise correction exerts on the relative stability of several conformers and on the optimized internal coordinates. This study was performed on three stable structures with C_s symmetry in four split basis sets: 3-21G, 4-31G, 6-31G and 6-311G. The complementary energy decomposition analysis will show the importance of the different components in this particular complex, as well as in others, and highlights general features of H-bonded complexes [17]. Finally, in order to assess the adequacy of the semi-empirical AM1 [18] and MNDO [19] hamiltonians, the results were compared with those derived from *ab-initio* calculations, the final goal being to apply these semi-empirical methods to systems involving several hundreds of atoms, as for example, an enzyme active site [20].

2. Methods and tools

The BSSE is a purely mathematical artefact due to the size inconsistency of the basis set and related to the more general problem of its incompleteness. The CP correction is a method dedicated to remove this former problem by using the same basis set for the complex and for the isolated interacting species. Thus, the determination of one value of the interaction energy requires three energy calculations:

$$\Delta E_{\text{int}} = E_{\text{AB}} - E_{\text{A}}(\text{B}) - E_{\text{B}}(\text{A}) \tag{1}$$

where $E_{\text{A}}(\text{B})$ is the total energy of A calculated with the basis set of the complex, i.e. including the basis set of B, and vice versa, and E_{AB} is the total energy of the complex.

The geometries of the water and formamide molecules are the optimized ones and the minimum of ΔE_{int} is searched for the C_s symmetric conformations corresponding to three structures of Jasien and Stevens [21], hereafter noted st. I, st. II, st. III. Thus, only the three relative internal coordinates d, α and γ are varied (Fig. 1).

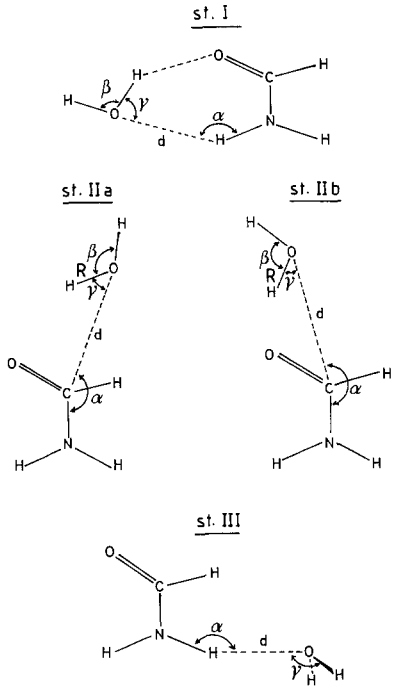

Fig. 1. The three structures I, II and II (see text)

An exhaustive analysis of the complex energy has been carried out according to four types of calculation:

*1. Geometry scan-*CP *correction*
To derive the CP corrected values, the interaction energy minimum can be located only by a scan of the three energy values involved in Eq. (1). These very time-consuming scans were performed with stepsizes of 0.01 Å for d and 1° for the two angles α and γ (st. I and III) or $(\gamma + \beta)$ (st. II);

2. Geometry scan-uncorrected results
For the CP uncorrected values, the same scanning procedure and the same stepsizes were used in order to localize the minimum;

3. Partial optimization
The stepsize incidence was calibrated by the gradient minimization of the three internal d, α, γ coordinates.

4. Full optimization
The comparison was subsequently extended to the equilibrium values obtained from an optimization of all the inter- and intramolecular degrees of freedom.

All the calculations were performed at the SCF level with the four basis sets and, in the uncorrected CP framework, at the full MP2 level with the 6-31G** basis set. Note that the minimal STO-3G basis set was not included in the study given that the critical point corresponding to the st. I arrangement was found to be a transition state and not a minimum. Finally, semi-empirical MNDO and AM1 hamiltonians were also used for comparison purposes, in view of current studies dealing with large-size H-bonded complexes.

Informatic environment

The geometry optimizations were performed using the GAUSSIAN86-88 [22] and MONSTERGAUSS [23] programs. The geometry scans were run with the GAUSSIAN link 108 package. Most of the calculations were made on a FPS264 attached processor (38 Mflops) linked to a VAX 11/780. As an example, a scan of 125 points in MP2(FULL)/6-31G** level (85 a.o.) takes more than two days. At this level, the geometry optimizations were performed on an IBM 3090/180E with one VF running under VM/CMS. In spite of the fact that the GAUSSIAN86-88 MP2 derivative does no longer require the very large D2E file of the GAUSSIAN82 version, the calculations remain extremely heavy in both computer time and scratch space disk resources.

3. Results and discussion

The results are summarized in Tables 1–3.

Uncorrected CP *results*

First and foremost (Table 2), two minima were found for st. II with 3-21G whereas only one minimum (hereafter noted st. IIa) (Fig. 1) was found with the other basis sets. A transition state was then searched between these two minima. Though the curvature of the surface is very low (since the negative eigenvalue of the analytical hessian was equal to -0.00043 a.u.), the associated eigenvector well combines the relative degrees of freedom involved in the motion from one minimum to the other. It thus seems that 3-21G is not well suited to describe a complex for which the region of the minimum interaction energy is so shallow. Also note that the Jasien and Stevens [21] st. II optimized geometry corresponds to our optimized st. IIb.

Differences between the optimized internal coordinates of the partners, whether they are isolated or interacting, are, at the most, ≈ 0.015 Å for the bond lengths and $\approx 2°$ for the angles. A large difference of 4° is found with 3-21G for the angle of H_2O in st. I. Thus, the formation of these complexes induce only small modifications in the geometry of the constituents. This is not surprising in consideration with the low interaction energies (≈ 10 kcal/mol).

A comparison of the relative internal coordinates derived from the aforementioned types of calculations was then made. Again, the scan and the partial optimization performed for st. IIb (Fig. 1) with the 3-21G basis set provided somewhat different results. The difference is essentially on d which differs by 0.0135 Å and is related to the surface flatness. For the other structures and basis sets, the differences between the two procedures are meaningless.

Performing either a full optimization, a partial optimization or a scan, has a very small effect on the intermolecular parameters, except on γ that differs by 10° in st. III with 3-21G. For instance, the largest difference on d found in st. I with 3-21G is 0.05 Å. Thus, as observed with the internal coordinates of the fragments isolated or in the fully optimized complex, the modification of the geometries of the monomers does not much influence their final relative positions.

Finally, all the energies, except the 3-21G values which are too large, and all the internal coordinates optimized at the SCF level are in good agreement with

Table 1. Equilibrium values of d(Å), α, γ (°) and ΔE_{int} (kcal/mol) for the structure st. I

	Without CP correction							
	In the fully optimized complex				From a scan on the 3 relative internal coordinates			
Basis set or semi-empirical method	d	α	γ	ΔE_{int}	d	α	γ	ΔE_{int}
3-21G	1.8702	139.50	86.66	−17.246	1.92	138.0	86.0	−16.453
4-31G	2.0018	138.13	85.82	−13.152	2.02	138.0	86.0	−12.725
6-31G	2.0159	138.22	86.44	−12.489	2.05	138.0	86.0	−12.098
6-311G	2.0188	138.49	87.54	−12.157	2.06	138.0	87.0	−11.779
6-31G**MP2	1.9936	138.20	83.71	−11.924	2.02	139.0	83.0	−11.515
AM1	2.1971	139.13	85.89	−5.860	2.20	139.0	86.0	−5.800
MNDO	3.6478	141.67	61.25	−0.952	3.81	141.0	56.0	+0.354

	With CP			
	From a scan on the 3 relative internal coordinates			
Basis set	d	α	γ	ΔE_{int}
3-21G	2.02	139.0	85.0	−8.968
4-31G	2.05	138.0	86.0	−10.233
6-31G	2.05	138.0	87.0	−10.324
6-311G	2.07	139.0	87.0	−10.094

Table 2. Equilibrium values of d (Å), α, γ (°) and ΔE_{int} (kcal/mol) for the structure st. II. Upperscript (s): obtained by a scan; upperscript (po): obtained by a partial optimization of the 3 internal coordinates. (a): st. IIa; (b): st. IIb; (T): transition state

	Without CP correction							
	In the fully optimized complex				From a scan on the 3 relative internal coordinates			
Basis set or semi-empirical method	d	α	γ	ΔE_{int}	d	α	γ	ΔE_{int}
3-21G (a)	2.8881	165.63	49.57	−10.744	2.91	165.0	49.32	−10.421
3-21G (T)	3.4610	186.05	25.30	−10.128	/	/	/	/
3-21G (b)	3.5361	189.23	22.07	−10.129	$3.57^{(s)}$	$190.0^{(s)}$	$20.32^{(s)}$	$-9.981^{(s)}$
					$3.5835^{(po)}$	$190.62^{(po)}$	$20.00^{(po)}$	$-9.981^{(po)}$
4-31G	3.0367	169.98	46.36	−8.9568	3.04	169.0	46.75	−8.761
6-31G	3.0567	170.59	46.53	−8.5911	3.07	170.0	46.45	−8.408
6-311G	3.0585	170.90	46.98	−8.4727	3.06	170.0	47.17	−8.300
6-31G**MP2	3.0432	167.55	42.95	−8.0301	3.06	167.0	42.13	−7.8559
AM1	2.9572	163.58	58.69	−4.3371	2.96	163.0	58.48	−4.300
MNDO	4.1345	162.87	61.15	−0.7433	4.33	163.0	59.22	−0.757

	With CP			
	From a scan on the 3 relative internal coordinates			
Basis set	d	α	γ	ΔE_{int}
3-21G (a)	—	—	—	—
3-21G (b)	3.81	199.0	13.32	−6.263
4-31G	3.27	176.0	37.75	−7.020
6-31G	3.18	173.0	42.45	−7.119
6-311G	3.16	172.0	44.17	−6.994

Table 3. Equilibrium values of d (Å), α, γ (°) and ΔE_{int} (kcal/mol) for the structure st. III

	Without CP correction							
	In the fully optimized complex				From a scan on the 3 relative internal coordinates			
Basis set or semi-empirical method	d	α	γ	ΔE_{int}	d	α	γ	ΔE_{int}
3-21G	1.8567	175.92	178.25	−11.019	1.88	177.0	168.0	−10.781
4-31G	1.9366	173.83	178.24	−8.2304	1.95	174.0	178.0	−8.088
6-31G	1.9483	173.49	178.27	−7.9303	1.96	174.0	178.0	−7.793
6-311G	1.9326	173.53	178.42	−8.1500	1.95	173.0	179.0	−8.020
6-31G**MP2	1.9827	175.59	145.79	−6.8796	2.00	176.0	145.0	−6.772
AM1	2.1286	173.15	177.82	−3.5401	2.13	173.0	178.0	−3.517
MNDO	3.3941	142.82	172.93	−0.9389	3.40	143.0	173.0	−0.9365

	With CP			
	From a scan on the 3 relative internal coordinates			
Basis set	d	α	γ	ΔE_{int}
3-21G	1.94	178.0	178.0	−6.959
4-31G	1.97	176.0	177.0	−7.126
6-31G	1.98	176.0	177.0	−7.148
6-311G	2.02	174.0	178.0	−6.988

those obtained at the 6-31G**/MP2 level. The greatest coordinate difference observed affected the angle of the water by about 8°. The other differences are much lower, emphasizing the reliability of the SCF method for the study of this type of H-bonded complex.

Corrected CP *results*

Difficulties to localize the minima of st. II with the 3-21G basis set also arise. Moreover, the largest differences between CP corrected and uncorrected results are also found for the st. II ($\Delta d = 0.23$, 0.11 and 0.10 Å in 4-31G, 6-31G and 6-311G, respectively, to be compared with 0.02 Å for the two other structures). For both st. I and st. III, the changes in the CP corrected internal coordinates are minor, except for the γ angle in st. III with the 3-21G basis set (Table 3).

The most important variations in the CP corrected results concern the interaction energies. The spread of the energy values versus the basis set expansion is less important for the CP corrected ones, the greatest correction to be applied concerning the 3-21G results. As also found by Jasien and Stevens, st. I is always the most stable arrangement with or without CP correction. The energy difference between st. I and st. II ranges from 3.4 to 6.0 kcal/mol for the uncorrected CP values and from 2.7 to 3.2 kcal/mol for the corrected ones. These variations may be compared with the 2.0 to 3.4 kcal/mol range variations obtained with the DZ or TZ type basis sets using a core effective potential (CEP) for the inner electrons [21] for which BSSE is small and nearly constant over the whole energy hypersurface. Concerning st. II and st. III, Jasien and Stevens also found an energy difference from 0.2 to 0.7 kcal/mol, st. II being always the most stable conformation. In the present study and as far as the uncorrected CP values are concerned, st. II is more stable than st. III except with the 3-21G basis set and the energy difference ranges from 0.3 to 0.7 kcal/mol. With the CP corrected values, this range becomes 0.006 to 0.7 kcal/mol but, except with 6-311G, the most stable conformation has shifted to st. III. However, this feature is meaningless since the energy differences between st. II and st. III are very small irrespective of the basis set and correction level used.

Semi-empirical results

When compared with *ab-initio* results, AM1 optimization procedure provides very satisfactory geometrical results for the angles α and the distance d varies at the most by about 0.2 Å.

The interaction energies, however, are two-fold lower but this does not modify the relative stability. The energy difference between st. I and st. II is somewhat too low (Tables 1, 2) while it is somewhat too large between st. II and st. III (Tables 2, 3). Nevertheless, the results suggest that AM1 is well suited to determine the stable conformations of this type of H-bonded complexes. It also has the obvious advantage of being much faster than an *ab-initio* calculation.

MNDO, on the contrary, leads to completely uncorrect relative energies and to uncorrect values for the distance d. Yet the intrafragment internal coordinates are in good agreement with the *ab-initio* ones.

From the foregoing, it follows that, though both AM1 and MNDO are well calibrated for the two separate molecules, only AM1 provides stable conformations for the complex that are in agreement with the SCF ones.

CP *correction for the variation of an intramolecular internal coordinate*

When a complete geometry optimization is performed, the internal coordinates of the monomers, hereabove called intramolecular coordinates, change by an amount depending on the interaction strength. A partial optimization based on the minimization of the CP corrected interaction energy cannot be considered when the intramolecular coordinate changes are large since the identity of the monomers may be no longer obvious. For the studied complex, the interaction energies as well as the interaction induced deformations are small. The question is to know if the CP correction method is able to account for small distortions into the monomers geometries. The answer comes from the study of the variation of the water bond length R (see Fig. 1) directed towards the formamide for the st. IIa, within the 3-21G basis set. Concomitantly, variation of the angle α allowed the reorientation of the water molecule. The other internal coordinates were those of the fully optimized structure st. IIa. Going from $R = 0.93$ Å to 1.49 Å (stepsize of 0.02 Å) and from $\alpha = 155°$ to 169° (stepsize of 2°), the CP corrected interaction energy varies from −4.271 kcal/mol to −15.341 kcal/mol. The nearest point (0.97 Å, 165°) to the optimized geometry (0.9719 Å, 165.33°) corresponds to a CP corrected energy of −5.478 kcal/mol. Thus, the stretching of one bond length of the water until a value of 1.49 Å seemingly leads to a conformation that would be more stable by 9.863 kcal/mol than the nearly optimized one. The same variations of the CP corrected energy also occur with the 6-31G basis set. This result is due to the fact that the interaction energy rapidly becomes increasingly negative when the energies of the fragments $E_A(B)$ and/or $E_B(A)$ [see Eq. (1)] grow much faster than the energy of the complex.

4. Conclusion

Sadlej and Roos [24] have observed that with the CO_2–HF and N_2O–HF complexes, the inclusion of the electronic correlation decreases the equilibrium intersystem distance whereas the CP correction increases it. The same observation was made by Frisch et al. [25] in the case of $(H_2O)_2$ and other H-bonded complexes. This correlation related decrease of d is also found in the present study for the water-formamide complex as well as the CP increase, but the two effects are very small, particularly for st. I and st. III.

In agreement with Jasien and Stevens [21], the present results emphasize the fact that the CP correction varies along the energy hypersurfaces generated by the three structures. The question as to know why the correction for size inconsistency should be the same everywhere is not trivial. In fact, this problem, though related to the problem of the basis set completeness, is only a part of it and to correct the size inconsistency is not to solve the problem of the incompleteness of the basis set.

In the case of the H-bonded water-formamide complex, CP correction hardly changes both the optimized relative orientation of the two partners and the relative stabilities of the different conformations if one accepts that an energy

difference of about 1 kcal/mol is meaningless. However, the CP correction obviously produces artefacts if variations of intramolecular internal coordinates are taken into account.

Schwenke and Truhlar [26] and Frisch et al. [25] had pointed out that the improvement of the basis set was preferable to a CP correction on a small basis set. The present study also leads to the conclusion that this type of expensive treatment is not a requirement for obtaining satisfactory geometries and relative stabilities of H-bonded complexes of the type water-formamide.

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Remark. The optimized geometries of the water, the formamide and the complex within the four basis sets and semi-empirical hamiltonians are available on request on a masthead page.

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