On the Importance of CP-corrected Gradient Optimization in the Study of Hydrogen Bonded Systems

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Geometries, harmonic vibrational frequencies and interaction energies of the water-hydrogen sulfide dimer, hydrogen fluoride dimer and glycine zwitterion-water dimer were determined by the counterpoise-corrected (CP-corrected) gradient optimization that explicitly corrects for the basis set superposition error (BSSE) and CP-uncorrected (normal) gradient optimization respectively at the B3LYP and MP2 levels of theory, employing the popular Pople's standard 6-31G(d), 6-31G(d,p) and 6-311++G(d,p) basis sets in order to assess the importance of CP-corrected gradient optimization in the study of hydrogen bonded systems. The normal optimization of these three H-bonded systems obtained using these popular basis sets all yielded erratic results, whereas use of CP-corrected gradient optimization led to consistent results with those from larger basis sets. So this CP receipt becomes useful and necessary to correctly describe large systems, where the use of small basis sets may be necessary.

Keywords *ab initio* calculation, density functional theory, BSSE, CP-corrected gradient optimization

Introduction

It is well known that the theoretical study of hydrogen-bonded systems under the supermolecular approach with the use of truncated monoelectronic basis sets originates the so-called basis set superposition error (BSSE). The most widely used method to handle BSSE has been the function counterpoise (CP) procedure, introduced by Boys and Bernardi in 1970.[1] It consists of calculations of the dimer energy and the monomer energies with the full basis set of the dimer. Although the legitimacy of this procedure has frequently been questioned[2-5] on the basis that in the dimer calculations, owning to the Pauli repulsion principle, the occupied orbitals of one monomer are not available to the electrons of the other monomer and vice versa, and there is enough theoretical and numerical evidence that the counterpoise method is a rigorously correct procedure.[6]

But the things are not all. Routinely, the structure of a complex is optimized by a gradient technique on the basis set superposition error (BSSE)-uncorrected potential-energy surface and the final stabilization energy determined for the calculated structure by a *posteriori* BSSE correction, *e. g.* the CP scheme. Some authors claimed that this normal recipe of counterpoise correction of carrying out a single-point correction without further optimization could not find the correctly optimized structures and vibration frequencies. They advocated that geometrical parameters, vibrational frequencies and energies should be determined using explicit BSSE corrections.[7-9] So an automated optimization procedure which uses the CP-corrected energy is necessary. Fortunately, a program recently developed by Salvador *et al.*[10] for the calculation of CP-corrected geometry optimizations and vibrational frequencies offered a straightforward and elegant solution. The method has now been implemented in Gaussian 98 Rev A10 (and further) package. Several authors have applied the CP-corrected gradient optimization on some small H-bonded complexes and demonstrated that various properties obtained from CP-corrected geometry optimizations and standard geometry optimizations differed significantly.[11-26]

Compared with the standard geometry optimizations, it is generally agreed now that the CP-corrected gradient optimizations increase the H-bond distance, certainly decrease the intermolecular stretching frequency and decrease the red-shift of the donor H—X frequency. Sometimes, the normal optimization of the H-bond structure with a small or medium basis set without consideration of BSSE can lead to a completely different structure. In this paper, three such H-bonded systems are reported where the normal geometry gradient optimizations give the complete erroneous results. It must be mentioned that by employing the larger basis sets the correct structures can be obtained by the standard gradient optimizations. However, we know, for rather large hydrogen-bonded systems, the

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large basis sets that would reduce the BSSE are often too computationally demanded or even impossible. So we chose here three popular small basis sets used frequently in the study of large hydrogen-bonded systems, 6-31G(d), 6-31G(d,p) and 6-311++G(d,p) respectively to illustrate the importance of CP-corrected geometry gradient optimizations. Note that the main aim of this paper is not to accurately calculate the geometries and energies of the three selected hydrogen-bonded systems but rather to discuss the effect of CP-corrected geometry gradient optimizations with medium basis sets in the study of H-bonded systems and to try to give some useful information on the study of large H-bonded complexes.

Computational details

All the *ab initio* calculations were performed using the GAUSSIAN 98 package of computer codes.[27] A range of different basis sets was employed, varying from the smaller 6-31G(d), 6-31G(d,p) and 6-311++G(d,p) to larger and flexible sets like 6-311++G(3df,3pd), which include multiple sets of polarization functions. Also considered was Dunning's aug-cc-pVDZ basis set. We mainly focused on the results obtained using smaller 6-31G(d), 6-31G(d,p) and 6-311++G(d,p) basis sets because they were very popular in the study of rather large systems where more sophisticated calculations are not feasible. It is well known that the reliably accurate description of hydrogen-bonded systems generally requires a treatment of electron correlation. So for all systems, computations are carried out only at two different levels of theory: the most economical post Hartree-Fock method MP2 and the Becke's three parameter (B3) exchange functional along with the Lee-Yang-Parr (LYP) nonlocal correlation functional (B3LYP).[28-30]

Results and discussion

Water-hydrogen sulfide dimer

There are several different stationary points on the potential energy surface of water-hydrogen sulfide dimer.[31] Here, we only chose structure **A** in which water is the proton donor as our model complex (Fig. 1). It is clearly seen from Table 1 that structure **A** is surprisingly a transition state (just one imaginary frequency) on the CP-uncorrected potential energy surface (PES) of the water-hydrogen sulfide dimer in the case of the 6-311++G(d,p) basis set. We did not impose point group symmetry at the beginning of the optimization for this complex. In order to avoid a premature identification of a minimum, we tightened the default cutoffs on forces and step size that are used to determine convergence. Furthermore, all electrons are included in the correlation calculation. Both of them can not change the fact, that is, the structure **A** is a saddle point on the PES when performing normal geometry gradient optimization with the 6-311++G(d,p) basis set. We know that the structure **A** is in fact a minimum (no imaginary frequency) on the PES of water-hydrogen sulfide dimer.[31] BSSE contamination distorted the curvature of the PES by transforming the optimized geometry into a saddle point. Performing CP-corrected geometry gradient optimization with the same basis set (6-311++G(d,p)) can give the correct result. As expected, we noticed that employing the larger basis sets, the correct result could also be obtained by the standard gradient optimizations and the CP-corrected geometry gradient optimization yielded longer intermolecular oxygen-sulfur distance. It should be pointed out that although the CP-optimized interaction energies are necessarily more negative than those calculated by applying a static CP crrection to the normal optimized

Table 1 Distance between O and S (in nm, see Fig. 1), interaction energies (kJ/mol) and the number of imaginary frequency (N_{Img}) from CP-corrected gradient optimization and CP-uncorrected gradient optimization at different levels for structure **A**[a]

Level	Optimization option	r_{OS}	ΔE	N_{Img}
MP2/6-311++G(d,p)	FC	0.3536	−8.01	1
MP2/6-311++G(d,p)	FC; Tight	0.3537	−8.02	1
MP2/6-311++G(d,p)	FC; CP-corrected	0.3620	−9.32	0
MP2/6-311++G(d,p)	Full; Tight	0.3534	−8.00	1
MP2/6-311++G(d,p)	Full; CP-corrected	0.3620	−9.32	0
MP2/6-311++G(d,p)	Full; Tight; CP-corrected	0.3620	−9.32	0
MP2/6-311++G(3d,3p)	Full; Tight	0.3455	−10.74	0
MP2/6-311++G(3d,3p)	Full; Tight; CP-corrected	0.3539	−10.99	0
MP2/aug-cc-pVDZ	Full; Tight; CP-corrected	0.3573	−10.88	0
MP2/6-311++G(3df,3pd)	Full; Tight	0.3458	−10.96	0
MP2/6-311++G(3df,3pd)	Full; Tight; CP-corrected	0.3521	−11.09	0

[a] Interaction energies from normal gradient optimization were corrected for BSSE by a posteriori counterpoise scheme.

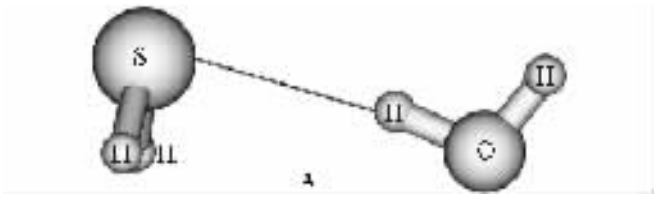

Fig. 1 Structure of the water-hydrogen sulfide dimer.

complex, the difference between them becomes smaller and smaller when increasing the basis sets.

Hydrogen fluoride dimer

The $(HF)_2$ dimer is often mentioned as an example of the failure of the standard gradient optimization technique.[9] It is well known that two stationary points exist on the PES of the HF dimer, structure **B** and structure **C** (Fig. 2). The former is an energy minimum and the later is a transtion structure. The "quasi-linear" structure **B** of $(HF)_2$ dimer (global minimum) does not exist at the MP2/6-31G(d,p) level with standard gradient optimization and it is found that only when performing the CP-corrected optimization at the same theoretical level. In this paper, we carried out a detailed study on this complex. From Table 2, it can be seen that the conclusions are almost the same as those obtained from water-hydrogen sulfide dimer. There was a little effect on the results from conventional (BSSE-contaminated) optimizations with the 6-31G(d,p) basis set when we tightened the four convergence criterions or considered the core-electron correlation. It is indeed the BSSE-contaminated optimization that leads to the erroneous results whereas the subsequent CP-corrected optimizations yield the expected linear geometry obtained with larger basis sets.

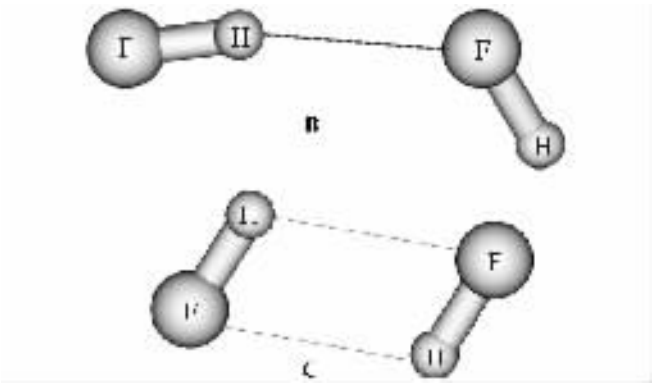

Fig. 2 Structures of the hydrogen fluoride dimer.

Glycine zwitterion-water dimer

Glycine is the simplest amino acid, and always being a prototype for larger systems, its zwitterionic form interaction with a water molecule is of particular interest.[32-38] Ding and Krogh-Jespersen[38] found that the zwitterionic form of the 1∶1 glycine-water complex (the structure **D**) (Fig. 3) corresponded to a local energy minimum already at the HF/4-31g level and that the charge-separated form remained stable in calculations with larger basis sets including the HF/6-31G * level. Table 3 shows that the structure **D** transforms into the neutral form **E** at the B3LYP/6-31G(d,p), MP2(full)/6-31G(d,p) or larger levels. That is to say, one water molecule does not stabilize the zwitterionic structure of glycine or the 1∶1 glycine zwitterion-water complex does not exist in the gas phase. With the 6-31G(d) basis set, the result from CP-uncorrected optimization and the corresponding one from CP-corrected optimization are contrary. Obviously, it is CP-corrected optimization that gives the correct result. This exemplifies

Table 2 Distances between F atoms (in nm, see Fig. 2), interaction energies (kJ/mol) and the number of imaginary frequency (N_{Img}) from CP-corrected gradient optimization and CP-uncrrected gradient optimization at different levels for structre **B**[a]

Level	Optimization option	r_{FF}	ΔE	N_{Img}
P2/6-31G(d,p)	FC	0.2539[b]	10.33[b]	0
MP2/6-31G(d,p)	FC ; Tight	0.2539[b]	10.33[b]	0
MP2/6-31G(d,p)	FC ; CP-corrected	0.2794	19.84	0
MP2/6-31G(d,p)	FC ; CP-corrected ; Tight	0.2800	19.84	0
MP2/6-31G(d,p)	Full	0.2538[b]	10.28[b]	0
MP2/6-31G(d,p)	Full ; Tight	0.2538[b]	10.28[b]	0
MP2/6-31G(d,p)	Full ; CP-corrected	0.2794	19.84	0
MP2/6-31G(d,p)	Full ; Tight ; CP-corrected	0.2800	19.84	0
MP2/6-311 + + G(d,p)	Full	0.2782	15.90	0
MP2/6-311 + + G(d,p)	Full ; CP-corrected	0.2878	16.26	0
MP2/6-311 + + G(3d,3p)	Full	0.2749	17.06	0
MP2/6-311 + + G(3d,3p)	Full ; CP-corrected	0.2799	17.23	0
MP2/6-311 + + G(3df,3pd)	Full	0.2731	17.09	0
MP2/6-311 + + G(3df,3pd)	Full ; CP-corrected	0.2787	17.28	0

[a] Interaction energies from normal gradient optimization were corrected for BSSE by a posteriori counterpoise scheme. [b] Structure **C** was obtained for the normal optimization of the structure **B**.

Table 3 Structural transformation, the distances between N and H (in nm, see Fig. 3) and the number of imaginary frequency (N_{Img}) from CP-corrected gradient optimization and CP-uncorrected gradient optimization at different theoretical levels with different basis sets for structure **D**

Theory level	Transformation or not		Distance between N and H′		N_{Img}	
	Normal	CP^{opt}	Normal	CP^{opt}	Normal	CP^{opt}
B3LYP/6-31G(d)	NO	YES	0.1064	0.1866	0	0
B3LYP/6-31G(d,p)	YES	YES	0.1873	0.1861	0	0
3LYP/6-31 + G(d,p)	YES	YES	0.1893	0.1892	0	0
B3LYP/6-311 + + G(d,p)	YES	YES	0.1906	0.1906	0	0
MP2(full)/6-31G(d)	NO	YES	0.1069	0.1870	0	0
MP2(full)/6-31G(d,p)	YES	YES	0.1885	0.1866	0	0
MP2(full)/6-31 + G(d,p)	YES	YES	0.1895	0.1893	0	0
MP2(full)/6-311 + + G(d,p)	YES	YES	0.1876	0.1872	0	0

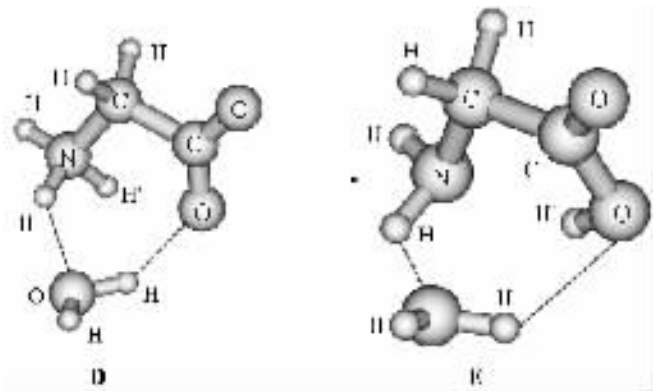

Fig. 3 Global minimum (**D**) on the HF glycine zwitterion-water potential energy surface and its corresponding structure (**E**) obtained by further optimizations at higher theoretical levels.

again the importance of CP-corrected optimization because the 6-31G(d) basis set is often used in the study of complex biological systems.

Conclusion

Three model complexes were investigated employing B3LYP and MP2 theory methods with three popular basis sets, 6-31G(d), 6-31G(d,p) and 6-311 + + G(d,p) in order to illustrate the importance of CP-corrected geometry gradient optimization in the study of hydrogen bonded systems. The normal BSSE-contaminated optimizations of the three systems all lead to completely wrong conclusions whereas the CP-corrected geometry gradient optimizations yield the correct ones. They are the clear evidence of using necessarily CP-corrected geometry gradient optimizations in the study of hydrogen-bonded systems.

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