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The effect of the basis set superposition error on the geometry optimization of the p-DFB–N$_2$ complex

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Abstract

In this Letter, a case is reported where a small basis set superposition error (BSSE) dependence on the geometry leads to a large change in the optimized structure. The rotational potential energy curves of the p-difluorobenzene–N$_2$ (p-DFB–N$_2$) complex were calculated with MP2, MP3, MP4(SDQ) and basis sets at different levels. For all calculations with the BSSE correction, similar rotational potential curves and the same minimum point were obtained. On the other hand, the uncorrected potential curves were quite different from the above ones and from each other. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently many experimental and theoretical investigations on van der Waals (vdW) complexes have been reported. Among them, the complexes of benzene and its derivatives with rare gases or small molecules are typical examples [1–17]. There are extensive experimental studies on p-difluorobenzene–N$_2$ [13–15] (p-DFB–N$_2$). The geometry of p-DFB–N$_2$ is similar to the geometries of p-DFB–Ar [9–12], and benzene–N$_2$ [4,7,8]. N$_2$ rotates almost freely around the symmetry axis of the benzene ring. It was estimated to be about 3.5 Å above the ring plane with the N–N bond parallel to the ring plane [13]. Another similar value 3.3 Å was reported based on the Lennard-Jones empirical

potential [15]. The upper limit of the binding energy was experimentally determined to be 240 cm^{-1} by Parmenter et al. [13]. In the same paper the rotational spectrum of p-DFB–N$_2$ was also presented. Besides the experimental study, a simulation of the rotational spectrum was carried out by Yang et al. [14,15] using a model potential.

Theoretical calculation of the rotational potential curve of p-DFB–N$_2$ with molecular orbital methods should be undertaken with care. Since p-DFB–N$_2$ is composed of two weakly bonded closed shell systems, any method used to calculate the interaction between them should take electron correlation into account. Another important consideration is the effect of basis set superposition error (BSSE) [18–22]. In the early calculations on the potential curves for diatomic molecules, Mulliken [18] recognized the need for a balanced basis set since the relative quality of the basis set could vary with the bond length. This is also true for the

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rotational potential curve in the present case. There are many ways to deal with BSSE (e.g. [21]).

In the calculation reported in this Letter, the rotational potential curves of p-DFB–N_2 were calculated with different basis sets. The variation of the BSSE effect with rotation was as large as the barrier height. This resulted in quite different potential curves in comparison with the ones without the BSSE correction.

2. Computation details and results

The basis sets used are 6-311++G(2d,2f) [23–25], 6-311++G(3df,2pd) [23,25–27] and Dunning's correlation consistent valence triple zeta basis set augmented with diffuse functions [28,29], aug-cc-pVTZ. Perturbation theory is an efficient tool to account for the dispersion interaction in the vdW complex system, p-DFB + N_2. All calculations were carried out with MP2, MP3 and MP4(SDQ) in GAUSSIAN 98 [30]. The binding energy for the dimer was corrected with the basis set superposition error following the terminology used in the previous Letter by Davidson and Chakravorty [21]

$$E = E(a^*b^*/AB)$$
$$- \{E(a/A) + [E(a^*/AB) - E(a^*/A)]\}$$
$$- \{E(b/B) + [E(b^*/AB) - E(b^*/B)]\}, \quad (1)$$

where the symbol star $*$ indicates a monomer geometry in the dimer, A is the basis set of monomer a and AB is the union of the two basis sets used for dimer a^*b^*. $E(a/A)$ is the energy of the monomer a with its own geometry and basis set while $E(a^*/A)$ means the energy of monomer with its own basis set but the geometry in the dimer, and so on. Eq. (1) can be interpreted as saying that the dimer energy is correct in the limit that the combined AB basis sets are complete, but the monomer energies need to be corrected. The corrections are those terms in the square bracket. If the geometry of each monomer is the same as it is in the dimer Eq. (1) can be written in a simple form

$$E = E(ab/AB) - E(a/AB) - E(b/AB). \quad (2)$$

In the rest of this section, Eqs. (1) and (2) are used to calculate the MP2 binding energies of the p-DFB–N_2 complex with different basis sets.

The solid curve in Fig. 1 is the MP2 6-311++G(2d,2p) rotation potential curve of the p-DFB–N_2 complex with N_2 rotating above the benzene ring. The geometry of the complex was fully optimized at each dihedral angle from 0° to 90° and the curve is shown in the lower part of the figure. The minimum ground state energy was at the angle zero (i.e. aligned with the F–F axis). This is also consistent with results of the full optimization of the complex. However, when the BSSE effect was taken into account by Eq. (1) the rotational potential curve was quite different as shown in the upper part of the figure. The minimum point at angle zero in the former becomes the maximum point in the latter while the maximum point at angle 90° in the former becomes the minimum point in the latter. The binding energy at the minimum with the BSSE correction is 555 cm^{-1}
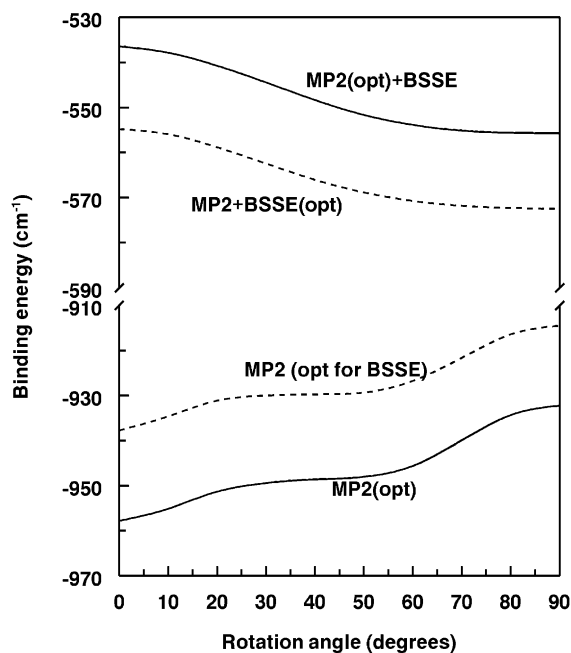

Fig. 1. The rotation potential curves of p-DFB–N_2 complex with basis set 6-311++G(2d,2p) at the MP2 level. The solid lower curve was fully optimized at each angle. The upper solid one was calculated with the BSSE correction using the same geometry as the lower one.

without the zero point energy included. It is still far from the experiment magnitude (less than 240 cm^{-1}) [2] but is only half of the binding energy at angle zero without the BSSE correction. The zero point binding energy correction -116.5 cm^{-1} for MP2 is mostly due to the N_2–p-DFB stretching vibration. Zero point corrections are not available for BSSE energies.

In order to study the BSSE in the present case and also to simplify the calculation, the geometries of p-DFB and N_2 were optimized separately and were kept fixed in the complex in all further calculations reported here. The only free parameter considered was the distance R between N_2 and p-DFB. This parameter was then optimized with the BSSE correction included at each angle. The rotational potential curve thus obtained is shown as a dashed one in the upper part of Fig. 1, while the lower curve is the corresponding one without BSSE correction. This optimization lowered the energy of the BSSE curve by about 20 cm^{-1} while raising the MP2 curve by 20 cm^{-1}. The curves are parallel to the MP2 curves. The minimum state with the BSSE correction was at angle 90° and is consistent with the MP2 optimized results. The similarity between these calculations indicates that the simplified calculations are reasonable and the main effect to the rotational potential curve comes from the BSSE. Therefore, these MP2 6-311++G(2d,2p) optimized geometries with the BSSE correction were used for all later calculations with a larger basis set and for those cases with ghost atoms. As shown in Fig. 2, after increasing the basis set to 6-311++G(3df,3pd) or aug-cc-pVTZ the rotational potential curves with the BSSE correction are still similar to those in Fig. 1. However, the corresponding curves without the BSSE correction changed significantly with the minimum state shifting from 0° to around 30°.

On the other hand, the BSSE effect could be investigated in another way. The BSSE is due to the basis set interaction between the monomers if the basis set is not complete. The interaction is thus varied with the rotation angle in the present study and is largest when the N basis set is closest to the F atoms. Therefore, if ghost atoms are added to the rotation plane of N_2 and are distributed together with two nitrogen atoms in a square
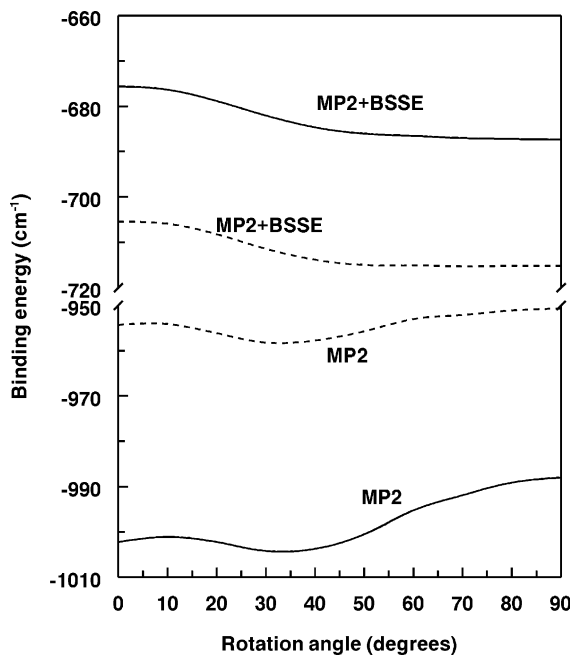

Fig. 2. The rotation potential curves of p-DFB–N_2 complex calculated with basis set 6-311++G(3df,3pd) (solid) and aug-cc-pVTZ (dashed) at the MP2 level. The upper and lower ones were calculated with and without the BSSE correction respectively. The geometries are those optimized with the BSSE correction with basis set 311++G(2d,2p) at the MP2 level.

around the center of the nitrogen bond, the BSSE influence will be decreased to some extent. The rotational potential curves with and without the BSSE correction are demonstrated in Fig. 4. The BSSE corrected one is similar to those before. However, there is maximum bump around the angle 50° for the uncorrected one. Though the minimum is now located at the angle 90°, it is just 0.7 cm^{-1} lower than the another local minimum at angle 0°. Similar rotational potential curves have been obtained with a larger basis set 6-311++G(3df,3pd). We considered adding another two ghost atoms to the rotation plane to form a hexagon of N basis sets, but they were so close together that the basis set was nearly linearly dependent. Another idea is to put the four ghost atoms on the other side of the benzene ring. The whole structure of the complex is like a sandwich with the benzene ring between them. The ghost atoms also rotate with the nitrogen atoms and

their projection in the ring forms a hexagon. The basis set interaction between the ghost atoms and benzene ring is nearly the same as if the ghost atoms were located in the nitrogen rotation plane though the interaction between the former and the nitrogen atoms are different. Consequently the BSSE correction to *p*-DFB should vary much less with angle. The BSSE corrected curve shown as the dashed line in Fig. 3 remains as before. The uncorrected one looks like those uncorrected ones in Fig. 2 with the basis set 6-311++G(3df,3pd) and aug-cc-pVTZ. The minimum point is changed from angle 0° to angle 40°. Clearly the complete basis limit is still not yet reached since the BSSE corrected and uncorrected energies do not agree.

Higher levels of correlation methods like MP3 and MP4(SDQ) have been also used in the present investigations with the basis set 6-311++G(2d,2p). The results are shown in Fig. 4. The potential
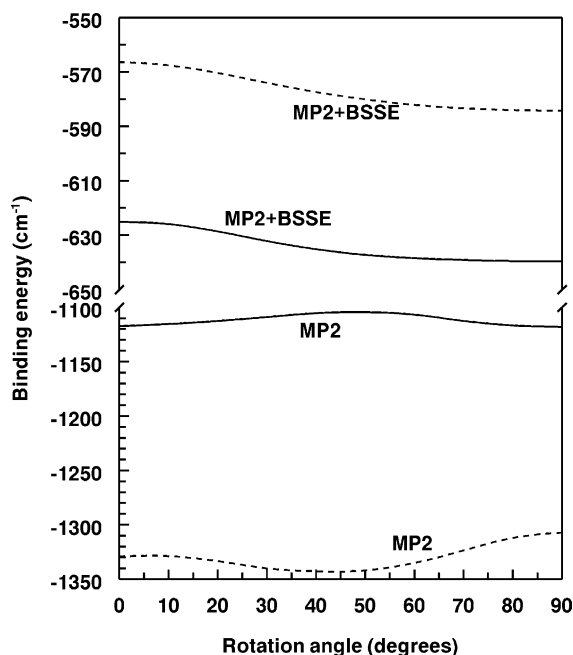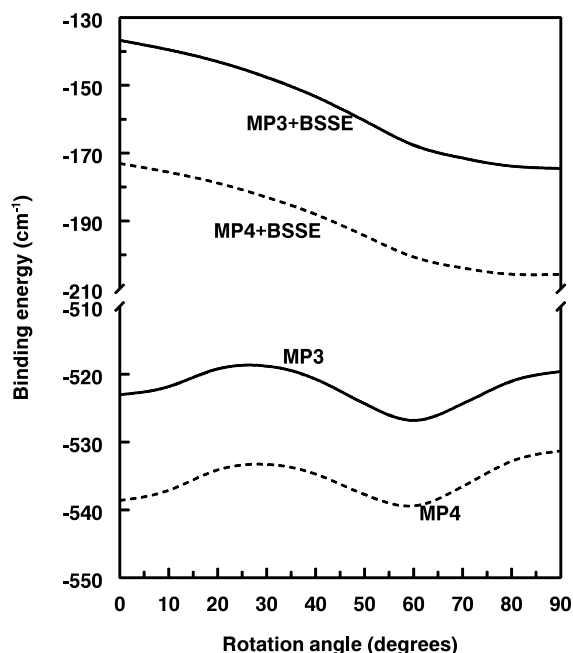

Fig. 4. The rotation potential curves of *p*-DFB–N_2 complex calculated with basis set 6-311++G(2d,2p) at the MP3 (solid) and MP4(SDQ) (dashed) level. The upper and lower ones were calculated with and without the BSSE correction respectively. The geometries are those optimized with the BSSE correction with the basis set 311++G(2d,2p) at the MP2 level.

curves without BSSE have two minimum points, one at angle zero and another one at angle 60°. The potential curves with the BSSE correction are similar as before. However, the BSSE corrected binding energies at the MP3 and MP4(SDQ) levels have been improved and are now less than the experimental value.

3. Conclusion

In this Letter, we have presented an example where a small variation in the BSSE correction causes a large change in the predicted equilibrium geometry. This happens because this is nearly a free-rotor situation with only a few cm^{-1} barrier. Hence the results are hypersensitive to small effects. The absolute binding energy of the N_2 to the ring was overestimated by MP2 with all basis sets. The BSSE correction improved this, but still left

Fig. 3. The rotation potential curves of *p*-DFB–N_2 complex plus two (solid) or four (dashed) ghost atoms calculated with basis set 6-311++G(2d,2p) at the MP2 level. The upper and lower ones were calculated with and without the BSSE correction respectively. The geometries are those optimized with the BSSE correction with basis set 311++G(2d,2p) at the MP2 level.

the N_2 overbound by a factor of 2. Higher order perturbation theory reduced the binding and MP4 with BSSE is in the right range.

In all of the above calculations, the rotation potential curves with the BSSE correction remain similar and the minimum point was at the angle 90°. As for the curves without the BSSE correction, in spite of all efforts, the complete basis set limit is still not reached and no agreement with the BSSE corrected curve was obtained. Private communication with David Pratt indicates that the correct result is for a minimum at the angle zero.

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