Theor Chem Account (2007) 118:733–738
DOI 10.1007/s00214-007-0345-z

REGULAR ARTICLE

On the application of the counterpoise correction for the basis set superposition error in geometry optimization calculations of molecular systems: some inconsistent results

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Received: 19 October 2006 / Accepted: 21 November 2006 / Published online: 12 June 2007

Abstract It is shown that the conjecture that the total energy for a given molecular or supermolecular system is affected by basis set superposition error (BSSE) leads to inconsistent results. While the calculations of interaction energies, dissociation energies, or energy barriers depend on the fragments (reactants, products) involved in their definitions and, consequently, are affected by BSSE, the total energies of molecular or supermolecular systems do not depend on any virtual fragment partition and are, therefore, BSSE free.

1 Introduction

Szalewicz and Jeziorski [1] have stressed the important point that the basis set superposition error (BSSE) is intimately related to the concept of intermolecular interaction energy. The interaction potential of two atoms A and B at a distance R apart can be computed exactly from the definition

$$\Delta_{AB}W(R) = W_{AB}(R) - W_A - W_B \tag{1}$$

where the total energy of the interacting system W_{AB} and the energies of the two separate atoms, W_{A} and W_{B}, are obtained from solutions of the appropriate Schrödinger equations (exact values). Roothaan's algebraic approach [2] allows us to estimate interaction energies as

$$\Delta_{\mathrm{AB}}E(R) = E[\mathrm{AB}|\alpha\cup\beta](R) - E[A|\alpha] - E[\mathrm{B}|\beta] \tag{2}$$

where $E[\mathrm{AB}|\alpha\cup\beta](R)$ represents the energy of the diatomic molecule AB as computed with the $\alpha\cup\beta$ basis set (α centred at atom A and β centred at atom B) and $E[\mathrm{A}|\alpha]$, $E[\mathrm{B}|\beta]$ are the atomic energies of A and B as computed with basis sets α and β, respectively. When unsaturated basis sets are employed, the representation of the atomic systems A and B is better in the molecular than in the atomic calculations ($\alpha\cup\beta$ is a more extended basis set than α or β). Boys and Bernardi [3] proposed the so-called function counterpoise procedure (CP) to estimate the interaction energy as

$$\begin{aligned}\Delta_{\mathrm{AB}}E(R)^{\mathrm{CP}} &= E[\mathrm{AB}|\alpha\cup\beta](R) - E[\mathrm{A}|\alpha\cup\beta](R)\\ &\quad - E[\mathrm{B}|\alpha\cup\beta](R)\end{aligned} \tag{3}$$

where $E[\mathrm{A}|\alpha\cup\beta](R)$ means the atomic energy of A as computed using a two-centre basis set: α centred at atom A and β centred at a point in space located at a distance R from atom A. Now the three terms on the right-hand side of Eq. 3 are computed at the same level of accuracy (same basis set) and it represents a consistent way of estimating interaction energies provided $\alpha\cup\beta$ is a well-balanced basis set for the diatomic molecule AB [4,5]. Of course, basis set incompleteness errors are still present in Eq. 3 as $\alpha\cup\beta$ is not a complete basis set.

The BSSE is defined as

$$\begin{aligned}\mathrm{BSSE}(R) &= \Delta_{\mathrm{AB}}E(R)^{\mathrm{CP}} - \Delta_{\mathrm{AB}}E(R)\\ &= E[\mathrm{A}|\alpha] - E[A|\alpha\cup\beta](R) + E[\mathrm{B}|\beta]\\ &\quad - E[\mathrm{B}|\alpha\cup\beta](R)\end{aligned} \tag{4}$$

Contribution to the Serafin Fraga Memorial Issue.

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As discussed elsewhere [6], if there are no geometrical variations when passing from the isolated systems, A and B, to the corresponding subsystems A and B forming part of the diatomic molecule AB, then BSSE can be readily computed from Eq. 4. However, when A and B are not atoms, there is always a change in their geometry as they interact with each other to form a supermolecular system. Such changes make $E[A|\alpha \cup \beta](R)$ and $E[\mathrm{B}|\alpha \cup \beta](R)$ in Eq. 4 not well-defined magnitudes. Indeed, in the case of $E[\mathrm{A}|\alpha \cup \beta](R)$, for example, one should compute the energy of the isolated monomer A using the extended basis set $\alpha \cup \beta$. However, due to the changes in geometry of monomer B, the spatial allocation of the β basis set becomes ambiguous. Emsley et al. [7] circumvented this problem by proposing the following expression to estimate BSSE:

$$\begin{aligned}\mathrm{BSSE}(R) = {} & E[\mathrm{A(AB)}|\alpha] - E[\mathrm{A(AB)}|\alpha \cup \beta](R) \\ & + E[\mathrm{B(AB)}|\beta] - E[\mathrm{B(AB)}|\alpha \cup \beta](R) \qquad (5)\end{aligned}$$

where $E[\mathrm{A(AB)}|\alpha \cup \beta](R)$ represents the energy of the subsystem A with identical geometry as in the supermolecule AB, when computed with the $\alpha \cup \beta$ basis set (β centred on the positions of the atoms of subsystem B with identical geometry as in the supermolecule AB).

Now, all terms on the right-hand side can be unambiguously computed.

The possible overcorrection commonly associated with the CP algorithm when applied at the correlated level has deserved much debate in the literature and it is not our present aim to resume here the galaxy of articles analysing this aspect during the past 20 years. The proof that even today a definitive conclusion has not been reached yet can be found in the fact that in the latter issue of Chemical Reviews devoted to weakly-bound systems [8], contradictory conclusions are presented on the subject. While on p. 4231 Chalasinski and Szczesniak [9] emphasize that overcompensation does not take place, on p. 4150 Kim et al. [10] conclude that it is useful to employ a 50% BSSE correction when comparing the theoretically evaluated quantities such as interaction energies, enthalpies, and free energies with the experimentally determined ones. Theoretical arguments [11] as well as numerical results [12] from our laboratory do support the latter viewpoint. Indeed, it has been shown [11] that, when computing the BSSE using the CP algorithm, there is a larger number of charge-transfer excitations in the case of the monomer plus ghost calculations than in the dimer calculation. Therefore, the representation of each monomer at the correlated level will be different in both cases. The orbitals of the monomers are improved by the ghost basis (the so-called ghost virtual orbitals) but at the expense of a non-physical increase in the dimension of the virtual space, thus being excellent candidates to account for the reported overcorrection when applying the CP algorithm. Van Duijneveldt's conclusion that our concerns are "reminiscent of the (unfounded) arguments leading to the virtual-only recipe" [13] represents a coarse misinterpretation of our arguments [11]. Gutowski and Chalasinski [14] tried to make an analysis of the contribution of the ghost virtual orbitals for a particular case. However, their analysis was oversimplified and general validity cannot be claimed from it. As mentioned in [11], the problem is very complicated. Indeed, we failed so far in finding some practical procedure to quantify *all* the ghost virtual contributions in a general case.

On the other hand, in a series of numerical works from our laboratory on weakly bound systems we systematically found that the CP corrected interaction energies lie in between the (BSSE-free) symmetry adapted perturbation theory (SAPT) [15] estimates and the corresponding CP uncorrected values, thus strongly suggesting that overcorrection must exist to some extent [12].

As the difference between the application of the CP method with and without inclusion of the ghost virtual orbitals should become negligible as the basis set tends to be saturated, the best option seems to be that proposed 20 years before by Schwenke and Truhlar [16], namely, it is better to increase the basis set to the maximum size affordable for noncounterpoise corrected calculations.

More recently, Simon et al. [17] conjectured that not only interaction energies but also total energies of any molecule or supermolecular aggregate (molecular associations or transition structures), $E(\mathrm{AB})$, should be affected by BSSE. According to these authors, the CP-corrected (super) molecular energy should be written as

$$E_{\mathrm{AB}}(R)^{\mathrm{CP}} = E[\mathrm{AB}|\alpha \cup \beta](R) + \mathrm{BSSE}(R) \qquad (6)$$

It should be stressed at this point that Eq. 6 cannot be derived from Eq. 4. Equation 6 represents just a *conjecture*. As mentioned above, it has been emphasized that BSSE is intimately related to the concept of intermolecular interactions [1]. Therefore, Eq. 6 should be considered with extreme caution. Furthermore, it is possible to show that Eq. 6 is mathematically inconsistent. As the proof is more mathematical than practical, we decided to incorporate it in the Appendix, in order to avoid deflecting reader's attention from the practical impact of the conclusions reached in our study (see below).

A direct consequence of Eq. 6 is the fact that the geometry of any system (molecules, molecular associations, and transition structures) is affected by BSSE. This result contradicts the fact that the total energy of a given system, $E(\mathrm{AB})$, is variationally computed on the potential energy surface (PES) by taking as the zero-energy reference that corresponding to particles at rest infinitely far apart [18]. Such a zero energy is common for all basis sets (basis set independent) and consequently no BSSE operates [19,20]. It should be stressed at this point that in sharp contrast with the situation for total energies, the interaction energies are computed by taking as a reference, the energies of the interacting monomers (see Eq. 2) which do depend on the basis set chosen, thus giving rise to the BSSE originally analysed by Boys and Bernardi [3].

In the next section, we will analyse different situations where the CP-corrected geometry optimizations (i.e., application of Eq. 6) give rise to inconsistent results. We try to promote a reasonable debate to provide a balanced view on the subject that deals with the evident drawbacks of the CP algorithm. This might serve as a warning for researchers who use as a black-box the codes that implemented this algorithm. Our aim is not to write a review article on the results reported by researchers that used Eq. 6 but to present in a short paper some disappointing conclusions about the unsuitability of that equation. In this context, other alternative methods to deal with BSSE like the chemical Hamiltonian approach (CHA) introduced by Mayer [21] are not considered in the present article.

2 Practical cases

In this section, we will illustrate the kind of problems arising from the application of Eq. 6 by focusing on two paradigmatic cases, representing rather common situations in computational chemistry. The reader can extrapolate the present results to a great variety of chemical processes.

We will compute and analyse the geometries of the two chemically meaningful structures on a given PES: minima and transition structures. The selected structures are involved in two well-known chemical processes.

2.1 $H^- + CH_3F \rightarrow CH_4 + F^-$ S_N2 reaction

This reaction proceeds through the formation of two intermediate complexes and one transition structure according to [22],

$$H^- + CH_3F \rightarrow H^- \cdots CH_3 \cdots F \rightarrow [(H \cdots CH_3 \cdots F)^-]^{\ddagger}$$
$$\rightarrow H \cdots CH_3 \cdots F^- \rightarrow CH_4 + F^-$$

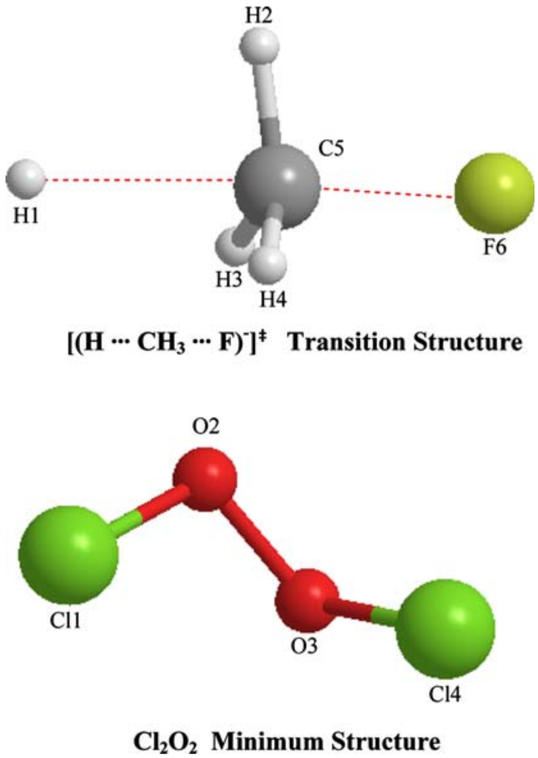
Table 1 MP2/6-311+G(d,p) [MP2/aug-cc-pV5Z values in parentheses] geometrical parameters (distances in Angstroms and angles in degrees; see Fig. 1), BSSE (kcal mol^{-1}), and imaginary frequency (cm^{-1}) for the $[(H \cdots CH_3 \cdots F)^-]^{\ddagger}$ transition structure of the S_N2 reaction between H^- and CH_3F

	TS	**TS′**	**TS″**
$r_{C5–H1}$	1.927 (1.893)	1.929	1.979
$r_{C5–F6}$	1.668 (1.672)	1.702	1.669
α(H1–C5–H2)	80.5 (81.2)	82.0	79.8
β(F6–C5–H2)	99.5 (98.8)	98.1	100.2
δ(H1–C5-H2–F6)	180.0 (180.0)	180.0	180.0
BSSE	13.8[a]	13.7	
	5.2[b]		5.2
Frequency	874.1	918.3	807.4

TS, TS′ y **TS″** stands for the $[(H \cdots CH_3 \cdots F)^-]^{\ddagger}$ single-point CP calculation, CP-optimized PES results with respect to reactants ($H^- + CH_3F$), and CP-optimized PES results with respect to products ($F^- + CH_4$), respectively

[a] With respect to reactants ($H^- + CH_3F$)

[b] With respect to products ($CH_4 + F^-$)



$[(H \cdots CH_3 \cdots F)^-]^{\ddagger}$ **Transition Structure**

Cl_2O_2 **Minimum Structure**

Fig. 1 Geometries for the $[(H \cdots CH_3 \cdots F)^-]^{\ddagger}$ transition structure and the Cl_2O_2 minimum structure considered in this work. Atoms numbering is the one used in Tables 1 and 2

Let us focus on the transition structure $[(H \cdots CH_3 \cdots F)^-]^{\ddagger}$. The geometry optimization on the CP-corrected PES leads to two different geometries depending on the fragment considered (either $H^- + CH_3F$ or $CH_4 + F^-$) to compute BSSE according to Eq. 6 (see Table 1 and Fig. 1). This is clearly an unphysical result. Indeed, the solution of the Schrödinger equation, within Roothaan's approach, at a given level of theory (Hartree–Fock, Moller–Plesset, configuration interaction, coupled cluster or density functional theory), and for a given system ($[(H \cdots CH_3 \cdots F)^-]^{\ddagger}$ in the present case), depends on the basis set chosen but not on any virtual definition of monomer fragments in which the system could be artificially partitioned.

The energy of the transition structure is variationally computed with respect to the geometrical coordinates, taking as a reference a given state with electrons at rest at an infinite distance from the nuclei [18]. Energy equals zero for this reference state no matter the basis set chosen. Consequently, no BSSE operates, and therefore the conjecture represented by Eq. 6 is not acceptable as it leads to unphysical results.

Incidentally, from the analysis of the data in Table 1 one concludes that the MP2 standard optimization (**TS**) leads, in general, to better geometrical predictions than the MP2 CP-corrected optimizations (**TS**′ and **TS**″), taking as a reference the MP2/aug-cc-pV5Z values which are expected to be close to the BSSE-free MP2 limit [23–26].

Application of Eq. 6 to locate transition structures on the PES led Kobko and Dannenberg [27] to conclude that the BSSE will depend on the choice of fragments, just as it will depend on the choice of a basis set. However, it should be emphasized that while the basis set dependence is a hindrance forced by the approximations required to solve the Schrödinger equation for the $[(H\cdots CH_3\cdots F)^-]^\ddagger$ transition structure, the dependence on fragments choice is an artefact arising from the adoption of the conjecture associated with Eq. 6.

On the other hand, there are two energy barriers associated with $[(H\cdots CH_3\cdots F)^-]^\ddagger$ transition structure, namely, the one leading to reactants ($H^- + CH_3F$) and the one leading to products ($CH_4 + F^-$). As the quality of the representation of the corresponding fragments for a given basis set is not the same whether isolated or when forming part of the transition structure, the BSSE should be considered via Eq. 5. As expected, reactants and products energy barriers will not be affected to the same extent by BSSE (see Table 1). This situation has been analysed in detail by Lendvay and Mayer [28] and by us [29]. Lendvay and Mayer recommended that when one needs the energy of the reactants, transition structures, and products, it is better not to do any correction for the BSSE. We concluded that the use of well-balanced basis sets, without application of the CP method, leads to consistent estimates of barrier heights whose accuracy directly depends upon the quality (degree of completeness) of the basis set employed.

The above arguments, of course, also apply to the calculation of rotation barriers [19,20]. The energies of the conformers and that of the transition structure associated with the rotation must be computed without unnecessary artificial consideration of virtual fragments. The unphysical application of the CP procedure, as recommended by van Duijneveldt et al. [30], will necessarily lead to incorrect results.

Another interesting point refers to the computed vibrational frequencies. From studies on hydrogen bonded complexes, Hobza and Havlas [31] concluded that the use of CP-corrected geometries leads to more appropriate estimates of the blue-shift experimentally observed in this type of systems than when the standard optimizations are carried out. Table 1 shows that the imaginary frequency for the $[(H\cdots CH_3\cdots F)^-]^\ddagger$ transition structure increases when computing the CP-corrected geometry with respect to reactants ($H^- + CH_3F$) and decreases when using as a reference the products ($CH_4 + F^-$). That means that for this particular case, the red or blue shifts arising from the CP-corrected geometries are physically meaningless as they depend on the fragments choice.

2.2 Thermal and photolytic decomposition of Cl_2O_2

Thermal (Δ) and photolytic ($h\nu$) decomposition of Cl_2O_2,

$$Cl + ClOO \xleftarrow{h\nu} Cl_2O_2 \xrightarrow{\Delta} ClO + ClO$$

are important processes forming part of the mechanisms, controlling the stratospheric ozone layer [32].

As expected, the variational solution of the Schrödinger equation ($\partial E_{Cl_2O_2}/\partial p_i = 0$, with p_i being the geometrical coordinates) leads to a unique geometry for Cl_2O_2 for a given basis set, no matter the pathway (thermal or photolytic) considered. The values for the most representative geometrical parameters (see Fig. 1) are collected in Table 2.

Application of Eq. 6 implies the choice of fragments in order to compute BSSE according to Eq. 5. Bearing in mind the two possible pathways, the natural (although not unique) choices are (a) Cl and ClOO (photolytic products) and (b) ClO + ClO (thermal products). The corresponding geometry optimizations on the CP-corrected PESs give rise, as in the preceding case, to two different geometries for Cl_2O_2 (see Table 2). This is an unacceptable result from the physical viewpoint, arising from the conjecture that the total energy of a molecular system depends on BSSE (Eq. 6). Indeed, no definition of fragments is needed to solve the Schrödinger equation for a given molecular structure. As mentioned in

Table 2 MP2/6-311+G(d,p) [MP2/aug-cc-pV5Z values in parentheses] geometrical parameters (distances in Angstroms and angles in degrees; see Fig. 1) and BSSE (kcal mol^{-1}) for the Cl_2O_2 minimum structure (M) involved in the $Cl + ClOO \leftarrow Cl_2O_2 \rightarrow ClO + ClO$ reactions

	M	**M**′	**M**″
$r_{Cl1–O2}$	1.755 (1.696)	1.750	1.789
$r_{Cl4–O3}$	1.755 (1.696)	1.750	1.758
$r_{O2–O3}$	1.381 (1.415)	1.415	1.372
α(Cl1–O2–O3)	110.4 (108.8)	109.8	110.7
β(Cl4–O3–O2)	110.4 (108.8)	109.8	110.8
δ(Cl1–O2–O3–Cl4)	−84.4 (-81.1)	−86.1	−85.5
BSSE	9.2^a	8.8	
	6.5^b		6.2

M, M′ and **M**″ stand for Cl_2O_2 single-point CP calculation, CP-optimized PES results with respect to thermal products (ClO + ClO), and CP-optimized PES results with respect to the photolytic products (Cl + ClOO), respectively

[a] With respect to the thermal products (ClO + ClO)

[b] With respect to the photolytic products (Cl + ClOO)

the preceding section, only the theoretical method employed as well as the basis set choice are required. The analysis of the quality (taking again as a reference the MP2/aug-cc-pV5Z values) of the geometrical parameters obtained by the different optimization methods (see Table 2) suggests that the CP-optimized geometry $\mathbf{M}'$, with respect to the thermal products (ClO + ClO) represents, in general, a notable improvement on the standard optimized geometry (**M**). However, the CP-optimized geometry ($\mathbf{M}''$) with respect to the protolytic products (Cl + ClOO) systematically leads to worse predictions. Therefore, no general conclusion can be reached about the comparative performances of the standard and CP-corrected PES optimizations in the present case.

Regarding dissociation energies of Cl_2O_2, we need to establish the dissociation process to be considered. Thus, we can compute the dissociation energies of Cl_2O_2 for the thermal (ClO + ClO) or photolytic (Cl + O) decompositions. By definition, dissociation energies depend on the energies of the dissociation fragments, BSSE operates, and Eq. 5 should be used to estimate them. As expected, Table 2 shows that the two possible dissociation energies are differently affected by BSSE.

3 Conclusion

The results presented in this work strongly suggest that the standard single-point CP algorithm works, in general [11,19,20], properly, rendering consistent estimates of the stabilization energies $\varDelta_{\mathrm{AB}}E(R)^{\mathrm{CP}}$, and it is more appropriate than that based on the constructions of the so-called CP-corrected PESs, unless we were ready to accept the suitability of an algorithm, based on a *conjecture* (Eq. 6), that predicts two different geometries for a given structure on the same PES.

As originally proposed by Boys and Bernardi [3], and later emphasized by Szalewicz and Jeziorski [1], the CP algorithm should be used to correct interaction energies. It can be safely extended to the computation of dissociation energies or energy barriers, as all of these calculations involve the simultaneous estimate of the energy for molecular or supermolecular systems and its constitutive fragments (reactant or products).

The variational optimizations of the geometry of molecular or supermolecular systems involve the calculation of the total energy which does not depend on any particular fragment partition, as its value is referred to a state defined by electrons at rest at an infinite distance from the nuclei. By definition, the energy of such a state is zero no matter the basis set employed in the calculations. Therefore, BSSE does not operate, and the conjecture represented by Eq. 6 is incorrect. It must be stressed that the consideration of different strategies based on the choice of "appropriate" fragments [33] cannot solve the kind of problems reported in this work.

The unnecessary and consequently artificial incorporation of the BSSE through Eq. 6, which involves the artificial definition of fragments, violates the ancient rule of economy that plurality should not be assumed without necessity ("non sunt multiplicanda entia praeter necessitatem" (Ockham's razor)), thus bringing about unwanted consequences.

Acknowledgements Through this article one of the authors (JAS) pays homage to his postdoctoral supervisor at the University of Alberta (Canada), Professor Serafín Fraga. He has been lucky of enjoying Serafín both as a friend and as a teacher.

Appendix

In this Appendix, we will proof a theorem showing the artificial extension of the BSSE concept through Eq. 6 could give rise to inconsistent results. The proof proceeds *by reductio ad absurdum*.

Let ω be an unsaturated basis set centred at A and $\mathcal{C}$, a uniformly complete basis set for the diatomic molecule AB constructed, according to Kutzelnigg's recipe [34], from complete basis sets $\mathcal{A}$ (centred at A) and $\mathcal{B}$ (centred at B) for atoms A and B, respectively. Let us represent A by $\mathcal{C}$ and B by ω. By definition, $\omega \cup \mathcal{C}$ must provide the exact values for (a) the total energy of the diatomic molecule, i.e., $E[\mathrm{AB}|\omega \cup \mathcal{C}] = W_{\mathrm{AB}}$, as well as its exact (opt) geometry, i.e., $R = R_{\mathrm{opt}}$, and (b) the total energies of atoms A, B, i.e., $E[\mathrm{A}|\omega \cup \mathcal{C}] = W_{\mathrm{A}}$; $E[\mathrm{B}|\omega \cup \mathcal{C}] = W_{\mathrm{B}}$. However, the stabilization energy [1] estimated by means of Eq. 2 (using $\mathcal{C}$ for A and ω for B), $\varDelta_{\mathrm{AB}}E(R_{\mathrm{opt}})$, will differ from the exact value, $\varDelta_{\mathrm{AB}}W(R_{\mathrm{opt}})$, because ω is not a complete basis set for B ($E[\mathrm{B}|\omega] \neq W_{\mathrm{B}}$). According to Boys and Bernardi [3], if we want to improve such an estimate we should use the CP correction (Eq. 3)

$$\begin{aligned}\varDelta_{\mathrm{AB}}E(R_{\mathrm{opt}})^{\mathrm{CP}} &= E[\mathrm{AB}|\omega \cup \mathcal{C}](R_{\mathrm{opt}}) - E[\mathrm{A}|\omega \cup \mathcal{C}](R_{\mathrm{opt}}) \\ &\quad - E[\mathrm{B}|\omega \cup \mathcal{C}](R_{\mathrm{opt}}) \\ &= \varDelta_{\mathrm{AB}}W(R_{\mathrm{opt}})(\text{exact value}) \qquad \text{(A1)}\end{aligned}$$

On the other hand, if Eq. 6 were correct

$$E_{\mathrm{AB}}(R_{\mathrm{opt}})^{\mathrm{CP}} = E[\mathrm{AB}|\omega \cup \mathcal{C}](R_{\mathrm{opt}}) + \mathrm{BSSE}(R_{\mathrm{opt}}) \qquad \text{(A2)}$$

and $\mathrm{BSSE}(R_{\mathrm{opt}})$ should vanish since $E[\mathrm{AB}|\omega \cup \mathcal{C}](R_{\mathrm{opt}}) = W_{\mathrm{AB}}(R_{\mathrm{opt}})$ (exact value). However, Eq. 4 applied to the present case

$$\begin{aligned}\mathrm{BSSE}(R_{\mathrm{opt}}) &= E[\mathrm{A}|\mathcal{C}](R_{\mathrm{opt}}) - E[\mathrm{A}|\omega \cup \mathcal{C}](R_{\mathrm{opt}}) \\ &\quad + E[\mathrm{B}|\omega](R_{\mathrm{opt}}) - E[\mathrm{B}|\omega \cup \mathcal{C}](R_{\mathrm{opt}}) \qquad \text{(A3)}\end{aligned}$$

shows that $\mathrm{BSSE}(R_{\mathrm{opt}}) \neq 0$. Indeed, $E[\mathrm{B}|\omega](R_{\mathrm{opt}}) - E[\mathrm{B}|\omega \cup \mathcal{C}](R_{\mathrm{opt}})$ is different from zero and positive as a consequence of the fact that ω is an unsaturated basis set while $\omega \cup \mathcal{C}$ is a complete basis set for B. On the other hand, BSSE(R) $\neq$ constant because as R varies $E[\mathrm{B}|\omega](R)$ will gradually change (ω is centred at A). Consequently, on the BSSE-CP corrected potential energy surface constructed using Eq. 6 [17], we will obtain a new distance, R_{CP}, different from the exact value (R_{opt}) which is in clear contradiction with the fact that the basis set used in the calculations, $\omega \cup \mathcal{C}$, is by definition a uniformly complete basis set for AB. Therefore, Eq. 6 has no general validity.

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