Theor Chem Acc (1998) 99:68–70

Theoretical
Chemistry Accounts

Letter

On the validity of the counterpoise correction for the basis set superposition error including the fragment relaxation terms

V.M. Rayón, J.A. Sordo

Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Julián Clavería 8, E-33006 Oviedo, Principado de Asturias, Spain

Received: 23 September 1997 / Accepted: 31 October 1997

Abstract. It is demonstrated that relatively large geometrical changes make Emsley et al.'s assumption (J Am Chem Soc (1978) 100:3303) on the counterpoise correction for the basis set superposition error including the fragment relaxation terms unacceptable.

Key words: Basis set superposition error –
Boys-Bernardi counterpoise algorithm –
Fragment relaxation

1 Introduction

In 1970, Boys and Bernardi [1] proposed the so-called counterpoise procedure (CP) to correct for the basis set superposition error (BSSE) [2, 3]. Let us consider two interacting systems, A and B, forming a supermolecule, AB. The uncorrected interaction energy ($\Delta E^{NCP}(AB)$) can be written as

$$\Delta E^{NCP}(AB) = E_{AB}^{\alpha\cup\beta}(AB) - E_{A}^{\alpha}(A) - E_{B}^{\beta}(B) \ , \qquad (1)$$

where $E_X^{\sigma}(Y)$ is the energy of system Y at the geometry X computed with the basis set σ (α, β and $\alpha \cup \beta$ represent the basis sets used to compute the systems A, B and AB, respectively).

The CP corrected interaction energy ($\Delta E^{CP}(AB)$) is computed as [1]

$$\Delta E^{CP}(AB) = E_{AB}^{\alpha\cup\beta}(AB) - E_{A}^{\alpha\cup\beta}(A) - E_{B}^{\alpha\cup\beta}(B) \ . \qquad (2)$$

According to Boys and Bernardi [1], the difference $\Delta E^{CP}(AB) - \Delta E^{NCP}(AB)$ is an estimate of the BSSE

$$\begin{aligned}\Delta E^{CP}(AB) - \Delta E^{NCP}(AB) = {} & \left[E_{A}^{\alpha}(A) - E_{A}^{\alpha\cup\beta}(A)\right] \\ & + \left[E_{B}^{\beta}(B) - E_{B}^{\alpha\cup\beta}(B)\right] \ . \end{aligned} \qquad (3)$$

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 supermolecule AB, then all the four terms appearing on the right-hand side of Eq. (3) are readily computed. To compute $E_{A}^{\alpha\cup\beta}(A)$ or $E_{B}^{\alpha\cup\beta}(B)$ one performs a calculation on the supermolecule AB putting to zero the nuclear charges of all nuclei belonging to system B (or A) and subtracting the appropriate number of electrons from the calculation. However, when A and B are not atoms, there is always a change in the geometry of two systems when they interact with each other to form a supermolecule. Under such circumstances the question arises whether $E_{A}^{\alpha\cup\beta}(A)$ and $E_{B}^{\alpha\cup\beta}(B)$ are the most appropriate quantities to use to compute BSSE.

In this vein Emsley et al. [4] proposed the following expression as an alternative to Eq. (3):

$$\begin{aligned}\Delta E^{CP}(AB) - \Delta E^{NCP}(AB) = {} & \left[E_{AB}^{\alpha}(A) - E_{AB}^{\alpha\cup\beta}(A)\right] \\ & + \left[E_{AB}^{\beta}(B) - E_{AB}^{\alpha\cup\beta}(B)\right] \ . \end{aligned} \qquad (4)$$

which is valid (i.e. equivalent to Eq. 2) under the assumption that "*the ghost orbitals will stabilize the isolated molecule at its equilibrium geometry and at its geometry in the complex to the same extent*" [4]; that is to say

$$\begin{aligned} & E_{A}^{\alpha}(A) + E_{B}^{\beta}(B) - E_{A}^{\alpha\cup\beta}(A) - E_{B}^{\alpha\cup\beta}(B) \\ & \quad = E_{AB}^{\alpha}(A) + E_{AB}^{\beta}(B) - E_{AB}^{\alpha\cup\beta}(A) - E_{AB}^{\alpha\cup\beta}(B) \ . \end{aligned} \qquad (5)$$

All terms in Eq. (4) are well-defined and can be easily computed whether or not the change in geometry in A or B when forming the supermolecule AB is considered. It is important to mention that, as Xantheas has pointed out recently [5], according to what should be expected, Eq. (4) predicts a null BSSE ($\Delta E^{CP}(AB) - E^{NCP}(AB) = 0$) as the basis sets α and β tend towards the complete basis set limit. The remaining question is to assess the degree of validity of Emsley et al.'s [4] assumption (Eq. 5).

2 Discussion and illustration

It has been stressed recently [6] that the calculation of energy barriers of processes implying the previous formation of an intermediate (see Fig. 1) does not involve BSSE. In particular, the barrier to internal

---

Correspondence to: J.A. Sordo

rotation, h, for a van der Waals complex should be computed as [6]

$$h = E_{TS}^{\alpha\cup\beta}(AB) - E_{I}^{\alpha\cup\beta}(AB) \ . \tag{6}$$

If Eq. (5) were exact, an alternative way of computing h would be

$$h = \Delta E^{CP}(TS) - \Delta E^{CP}(I) \ . \tag{7}$$

where $\Delta E^{CP}(X)$ $(X = TS, I)$ is computed by means of Eq. (4) giving

$$\begin{aligned} h = {} & E_{TS}^{\alpha\cup\beta}(AB) - E_{I}^{\alpha\cup\beta}(AB) \\ & + [E_{TS}^{\alpha}(A) + E_{TS}^{\beta}(B) - E_{TS}^{\alpha\cup\beta}(A) - E_{TS}^{\alpha\cup\beta}(B)] \\ & - [E_{I}^{\alpha}(A) + E_{I}^{\beta}(B) - E_{I}^{\alpha\cup\beta}(A) - E_{I}^{\alpha\cup\beta}(B)] \ . \end{aligned} \tag{8}$$

Indeed, if Emsley et al.'s assumption [4] (Eq. 5) were correct, the second and third terms (in brackets) on the right-hand side of Eq. (8) will cancel each other and one obtains for h an expression equivalent to Eq. (6). This demonstrates that the formulation including the fragment relaxation terms [4, 5] is fully consistent. In conclusion, differences between the energy barriers computed using Eq. (6) (*rigorous*) and Eq. (8) (*approximate*) would provide a quantitative assessment of the degree of validity of Emsley et al.'s assumption [4].

To illustrate this point we present in Table 1 the barriers to internal rotation as computed with Eqs. (6) and (8) for two van der Waals complexes, namely, $C_2H_4\cdots SO_2$ and $BF_3\cdots NH_3$. Figure 2 depicts the optimized structures of these two complexes (**I1, I2**) and the corresponding transition structures involved in the internal rotation (**TS1, TS2**) obtained at the second-order Møller-Plesset correlated level [7] using Dunning-Huzinaga's double-ζ polarization ([4*s*, 2*p*, 1*d*]) basis set [8] (i.e. MP2/D95(*d,p*)). Examination of data in Table 1 clearly shows that while Emsley et al.'s [4] assumption is acceptable in the case of $BF_3\cdots NH_3$ (the error involved is about 10%), it is much less reliable for $C_2H_4\cdots SO_2$ (the error involved is about 74%). Figure 2 helps us to rationalize these results. Indeed, a greater difference in the stabilizations of the isolated systems C_2H_4 and SO_2 produced by the ghost orbitals at the geometries **I1** and **TS1** (123 cm^{-1}) should be expected [9] as compared with that for BF_3 and NH_3 at the geometries **I2** and **TS2** (45 cm^{-1}) since the geometrical variation **I1** → **TS1** is considerably more drastic than **I2** → **TS2**.

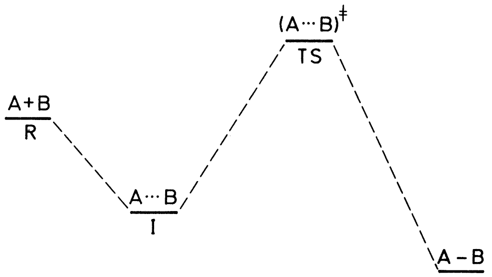

Fig. 1. Energy profile of a process involving an intermediate: **R** = reactives, **I** = intermediate, **TS** = transition structure and **P** = product

Table 1. MP2/D95(*d, p*) energies (cm^{-1}) for the internal rotation in the van der Waals complexes $C_2H_4\cdots SO_2$ and $BF_3\cdots NH_3$ as computed with Eqs. (6) and (8). The values of the different contributions in Eq. (8) are also given

Energy contributions and barriers	$C_2H_4\cdots SO_2$	$BF_3\cdots NH_3$
$E_{TS}^{\alpha\cup\beta}(AB) - E_{I}^{\alpha\cup\beta}(AB)$	166	457
$[E_{TS}^{\alpha}(A) + E_{TS}^{\beta}(B) - E_{TS}^{\alpha\cup\beta}(A) - E_{TS}^{\alpha\cup\beta}(B)]$	1088	2791
$[E_{I}^{\alpha}(A) + E_{I}^{\beta}(B) - E_{I}^{\alpha\cup\beta}(A) - E_{I}^{\alpha\cup\beta}(B)]$	1211	2836
h (Eq. 8) (*approximate*)	43	412
h (Eq. 6) (*rigorous*)	166	457

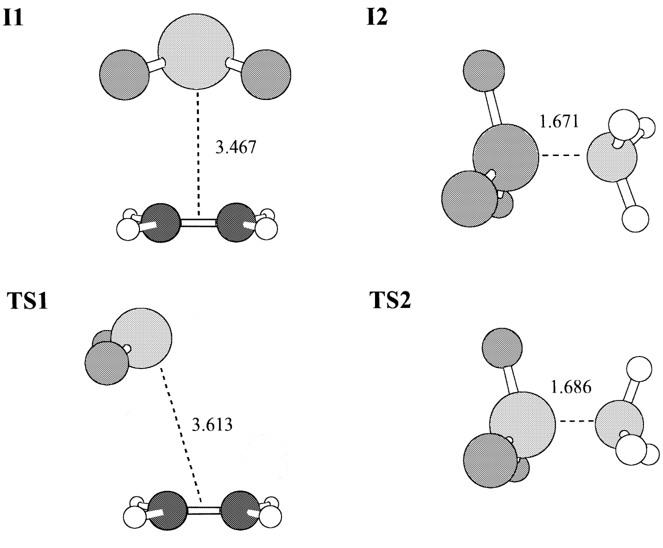

Fig. 2. MP2/D95(*d,p*) optimized structures of the van der Waals complexes $C_2H_4\cdots SO_2$ (**I1**) and $BF_3\cdots NH_3$ (**I2**) and the corresponding transition structures involved in the internal rotation (**TS1**, **TS2**). Distances are given in angstroms

Conclusion

In summary, it is demonstrated that extreme care must be exercised when using the counterpoise correction including the fragment relaxation energies (Eq. 4) to correct for BSSE. Relatively large geometrical changes make Emsley et al.'s assumption (Eq. 5), on which Eq. (4) is based, unacceptable.

References

1. Boys SF, Bernardi F (1970) Mol Phys 19: 553
2. Liu B, McLean AD (1973) J Chem Phys 59: 4557
3. For recent reviews, see: (a) Chalasinski G, Szczesniak MM (1994) Chem Rev 94: 1723; (b) van Duijneveldt FB, van Duijneveldt-van de Rijdt JGCM, van Lenthe JH (1994) Chem Rev 94: 1873
4. Emsley J, Hoyte OPA, Overill RE (1978) J Am Chem Soc 100: 3303
5. Xantheas SS (1996) J Chem Phys 104: 8821

6. (a) Sordo JA (1997) J Chem Phys 106: 6204; (b) Rayón VM, Sordo JA (1997) J Phys Chem 101: 7414
7. Szabo A, Ostlund NS (1982) Modern quantum chemistry: Introduction to advanced electronic structure theory. Macmillan, New York, Chap. 6
8. (a) Dunning TH Jr (1970) J Chem Phys 53: 2823; (b) Huzinaga S (1965) J Chem Phys 42: 1293
9. (a) Sordo JA, Chin S, Sordo TL (1988) Theor Chim Acta 74: 101; (b) Sordo JA, Sordo TL, Fernández GM, Gomperts R, Chin S, Clementi E (1989) J Chem Phys 90: 6361