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Counterpoise corrections to the interaction energy components in bimolecular complexes

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A new definition of counterpoise corrections (CP) to the components of ΔE evaluated with the Kitaura and Morokuma method is presented and tested on the $(H_2O)_2$ and $(NH_3 \cdot HF)$ molecular systems with two different basis sets. The CP corrections are further decomposed into subsystems contributions, facilitating their interpretation and the elaboration of computationally simplified procedures.

Key words: Interaction energy decomposition — Hydrogen bond — Basis set superposition error — Counterpoise corrections

1. Introduction

The decomposition of the intermolecular interaction energy ΔE has been largely employed in the past years to classify molecular interactions into a few classes, to put in evidence the basic factors of the interaction act, to obtain some help in the elaboration of simplified methods to evaluate stabilization energies, to improve the performances of numerical fitting procedures to get analytical representations of the interaction energy hypersurface [1, 2].

The largest part of this work has been done using ΔE values obtained with the SCF method, which is more practical than the perturbation theory to get ΔE values over a wide range of distances, especially for molecules of relatively large size.

The same practical reasons have suggested the use, in the majority of cases, of basis sets very far from completeness, although ΔE values obtained with basis sets of modest size are affected by a mathematical (unphysical) error, usually called basis set superposition error (BSSE). In fact ΔE is obtained as the difference of the separately computed energies of the supersystem (say AB) and of the isolated subsystems (A and B):

$$\Delta E(R_{AB}) = E_{AB}(R_{AB}) - (E^{\circ}_{A} + E^{\circ}_{B}). \tag{1}$$

$E_{AB}(R_{AB})$, however, is calculated with the union of the subsystems basis sets:

$$\chi = \chi_A \oplus \chi_B \tag{2}$$

and this fact introduces a relatively better description of AB with respect to the subsystems, with obvious consequences on the value of ΔE.

The occurrence of the BSSE error has long been recognized and it is universally accepted that the counterpoise method (CP) [3], or some variants, permits the correction of a substantial part of it. The CP corrections can be performed with ease, because they merely correspond to the introduction of a variable, R_{AB} dependent, reference energy obtained by evaluating the subsystems energies at each R_{AB} with the complete basis set (2):

$$\Delta E(R_{AB}) = E_{AB}(R_{AB}) - (E^{t}_{A}(R_{AB}) + E^{t}_{B}(R_{AB})) \tag{3}$$

with:

$$E^{t}_{M}(R_{AB}) = E^{\circ}_{M} + \Delta^{T}_{M}(R_{AB}) \qquad M = A, B. \tag{4}$$

The calculation of $E^{t}_{M}(R_{AB})$ values represents a modest increment of the computational time necessary to get $E_{AB}(R_{AB})$.

It has been also clearly demonstrated [4] that with appropriate care SCF minimal basis set calculations with CP corrections given interaction energies comparable with those obtained with more sophisticated methods.

In spite of these well recognized facts, until recent times little attention has been paid to the correction of BSSE's in the SCF ΔE decompositions. A definition of BSSE corrections to ΔE components has been proposed by Sokalski et al. [5] in 1983 and applied in subsequent papers [6, 7]. To the best of our knowledge the other contributions to this subject are an unpublished study of Groen and van Duijneveldt [8], the formalism of which has been summarized in [4], a parenthetical remark of Morokuma and Kitaura in a review on ΔE dcecomposition [9], a partial decomposition adopted by Urban and Hobza [10], an oral communication of Claverie et al. to a recent Congress [11] and a proposal by Tolosa and Olivares [12] based on Morokuma's older version of the ΔE decomposition [13].

Since ΔE decompositions as well as BSSE corrections are arbitrary in some sense - they are in fact not related to basic theorems of quantum mechanics, but rather suggested and supported by intuitive considerations - it is worth exploring different combinations of ΔE decompositions and BSSE corrections to the ΔE components, in order to find a method which better combines practical execution with the attainment of the goals for which ΔE decompositions are currently employed.

In the present paper we present a computational scheme strictly based on the Kitaura and Morokuma (KM) decomposition scheme [14], this being the most largely employed decomposition method. However, the algorithm could be applied to other decomposition schemes (for example we mention the extension of the KM method given by Nagase et al. [15] and the polarized MO decomposition [16]) and to BSSE corrections obtained as variant of the original CP method [17–21].

2. Method

First of all we shall summarize the KM method. The interaction energy is partitioned in the following contributions:

$$\Delta E = E_{ES} + E_{PL} + E_{EX} + E_{CT} + E_{MIX}. \tag{5}$$

The first four contributions are calculated independently, the last one is obtained by difference. The contributions are evaluated with the usual HF SCF method employing a Fock matrix $\mathbb{F}$ written in terms of the MO's of the subsystems, with a partition into blocks referring to occupied and vacant orbitals of the two subsystems (A_0, A_V, B_0, B_V). For the reader's convenience we report here the block form and the names of the submatrices (to speak more properly, of the interaction matrix related to $\mathbb{F}$, for details see source paper [14]).

$$\begin{array}{c|cccc|} & A_0 & A_B & B_0 & B_V \\ \hline A_0 & ESX & PLX & EX' & CT \\ A_V & & ESX & CT & EX' \\ B_0 & & & ESX & PLX \\ B_V & & & & ESX \\ \hline \end{array}$$

The components of ΔE are obtained via E^x values (upper index, x stands for the names of the blocks) calculated by solving the HF equation with only a portion of the blocks. The E_x values of Eq. (5) are obtained as a difference of E^x values with respect to the appropriate reference energy. Further details may be found in the source paper [14] or in one of the numerous reviews (see e.g. [2] and [9]). What is important to remark here is that the BSSE connection may be introduced by modifying this reference energy.

We shall now pass on to examine the single components paying attention to what type of orbital mixing is involved in each E^x calculation.

2.1. E_{ES}

The coulombic interaction between rigid charges is calculated with the aid of the energy obtained by using only diagonal blocks (ESX) with the further cancellation of the subsystem exchange operator. There is no mixing of the MO's of the isolated subsystems, and accordingly we do not introduce CP corrections to this term.

A different philosophy could however be adopted, and it will be discussed in the last section of the paper.

2.2. E_{PL}

The electronic polarization energy is referred to the E^x value obtained using *ESX* and *PLX* blocks, with the further cancellation of the contribution of subsystem exchange operators. There is now a mixing between occupied and vacant orbitals belonging to the same subset, but no mixing between MO's of different subsets. For this reason we shall not introduce CP corrections to this term.

2.3. E_{EX}

The exchange terms, which introduces the correct antisymmetry properties in the supersystem wavefunction, is calculated in the KM method on the rigid orbitals of the subsystems. The considered blocks are *ESX* and *EX'*. This allows a mixing between occupied MO's of the subsystems:

$$\varphi'_M = \sum_{k}^{occ} C_{Mk}\varphi_k^0 + \sum_{j}^{occ} C_{Mj}\varphi_j^0, \tag{6}$$

with M, $N = A$, B; $k \in M, j \in N$. The corresponding E^x energy is obtained at the first cycle of the iterative procedure, corresponding to a symmetric orthogonalization process only.

There is the need of a CP corrrection. This may be obtained by enlarging the basis set of M to the occupied MO's of N:

$$\chi_M^{EX} = \varphi_M^O \oplus \varphi_N^O. \tag{7}$$

The general computational scheme of KM may be retained. A further calculation on the above mentioned blocks with the Hamiltonian reduced to H_M gives a CP corrected subsystem energy:

$$E_M^{ex}(R_{AB}) = E_M^0 - \Delta_M^{EX}. \tag{8}$$

Introducing these energies in the KM definition of reference energy for E_{EX} one obtains:

$$E_{EX}^{CP} = E_{EX} + (\Delta_A^{EX} + \Delta_B^{EX}). \tag{9}$$

Another correction related to the mixing of A and B occupied MO's could be defined in terms of E_M values calculated with Schmidt or Löwdin orthogonalized subsystem wavefunctions. This correction has been applied in [10] to the sum $E_{EL} + E_{EX}$, with Schmidt orthogonalization. The symmetric orthogonalization performed in the KM scheme leads to relatively large changes, generally going in the wrong direction (the corrected contribution is more stabilizing than the uncorrected one). This is easily understandable because orthogonalization of the wavefunction to a functional space not considered in the HF process does not insure, per se, an improvement of the energy. We have enclosed in the program as optional the calculation of sub-system energies with orthogonalized MO's.

2.4. E_{CT}

The change transfer contribution is obtained in the KM scheme via the energy obtained with retention of ESX and CT blocks. This allows a mixing of occupied MO's of *M* with vacant MO's of *N*.

The corresponding CP correction is obtained, in analogy with the preceding case, by using the same route to compute subsystem energies on the space:

$$\chi_M^{CT} = \varphi_M^O \oplus \varphi_N^V. \tag{10}$$

From the energies:

$$E_M^{CT} = E_M^0 - \Delta_M^{CT} \tag{11}$$

one obtains:

$$E_{CT}^{CP} = E_{CT} + (\Delta_A^{CT} + \Delta_B^{CT}). \tag{12}$$

2.5. E_{MIX}

The mixing term is a residuum, calculated as the difference

$$E_{MIX} = \Delta E - (E_{EL} + E_{PL} + E_{EX} + E_{CT}) \tag{13}$$

We introduce a correction based on the difference between the partial CP corrections introduced above and the total CP correction computed for each subsystem on the whole functional space

$$\chi_M^T = \chi_M \oplus \chi_N. \tag{14}$$

The subsystem energies being:

$$E_M^t = E^0 - \Delta_M^T \tag{15}$$

we shall have:

$$E_{MIX}^{CP} = E_{MIX} + \Delta^{MIX} = E_{MIX} + (\Delta^T - \Delta^{EX} - \Delta^{CT}). \tag{16}$$

We remark that all the CP corrections Δ^x and Δ_M^x are positive. The correction proposed in [12] considers Δ^T only, which is assigned to the E_{MIX} term (we recall that in the Morokuma's original decomposition [13] E_{CT} and E_{MIX} terms were not separated).

The E_{MIX} term could be subjected to a further decomposition (Nagase et al. [15]). We have not yet introduced this additional feature in the CP corrected ΔE decomposition, and this extension, which should be of interest for special classes of strong interactions, will be the subject of a future investigation.

The program has been coded for a GOULD sel minicomputer, as modification of the already existing KM program in Pisa, and appended to a modified version of the GAUSSIAN 70 package.

3. Numerical results

We report some results for two sets of intermolecular distances for the H_2O dimer, the first leading to the more favorable geometry of the complex, the second one repulsive on the whole distance range, and for a set of geometries of the $H_3N.HF$ supersystem. The internal geometry of the monomers are taken from literature (H_2O: $R_{OH} = 0.956$ Å, $\angle HOH = 105.2°$; NH_3: $R_{NH} = 1.002$ Å, $\angle HNH = 107.6°$; HF: $R_{HF} = 0.930$ Å) and kept fixed. The reciprocal orientation of the monomers in the linear $H_2O.HOH$ dimer is that found experimentally ($\theta = 60°$ [22]); the dimers $H_2O.OH_2$ and $H_3N.HF$ have respectively D_{2h} and C_{3v} symmetry. The calculations have been performed with standard STO-3G and 4-31G basis sets.

The main body of results is collected in Tables 1, 2 and 3. The present method making it possible to decompose each CP correction into subsystem's contributions, this additional information is reported in Tables 4, 5 and 6.

3.1. CP corrections to E_{EX}

The values of Δ_{EX} regularly decrease when R_{AB} increases. Corrections are larger for the minimal basis, and, in general, larger for the electron donor subunit (note, however, the 4-31G values for $H_3N.HF$).

Δ^{EX} should not be confused with the $BSSE^{(1)}$ correction of Sokalski et al. [5] to the E_{EX} contribution, because the two corrections refer to a different philosophy. $BSSE^{(1)}$ is in fact a correction obtained on the complete basis set, $\chi_A \oplus \chi_B$, and refers to the energy of a fully antisymmetrized wavefunction of the supersystem with MO's of the subsystems subjected only to symmetrical orthonormalization. This procedure does not present the inconveniencies remarked in Sect. 2 when the energies of the subsystems obtained with mutually orthogonalized MO's are employed, but the definition of $BSSE^{(1)}$ does not ensure that it is always positive. The result for the $H_2O.HOH$ system, obtained with the same basis set (4-31G) and the same geometries as those adopted here make the point evident (see Table 7).

3.2. CP correction to E_{CT}

In general, the minimal basis sets give an overestimation of charge transfer corrections. This artifact is partly corrected by Δ^{CT}. Moreover there is a clear indication that with the STO-3*G* basis the electron donor (*ED*) contribution to Δ^{CT} is decidedly larger than the electron acceptor (*EA*) contribution, and the latter could be neglected without substantial changes.

The corrected E_{CT}^{CP} values obtained with the STO-3G basis are presumably still too large. It would be interesting to examine E_{CT}^{CP} values obtained with the *MINI*

Table 1. CP Corrections to ΔE components: comparison of ΔE components corrected and uncorrected[a] (in parenthesis) for BSSE. STO-3G and 4-31G results for the linear $H_2O.HOH$ complex

Basis set	STO-3G					4-31G				
R_{AB}(Å)	2.38	2.68	2.98	3.28	3.58	2.38	2.68	2.98	3.28	3.58
ES	−21.30	−8.59	−4.20	−2.53	−1.73	−31.34	−15.72	−8.90	−5.73	−4.03
PL	−0.21	−0.18	−0.10	−0.06	−0.03	−3.27	−0.93	−0.46	−0.25	−0.14
EX	48.66 (44.36)	15.60 (13.62)	4.77 (4.00)	1.37 (1.11)	0.38 (0.29)	45.30 (44.84)	14.22 (13.89)	4.40 (4.18)	1.33 (1.22)	0.38 (0.33)
CT	−16.28 (−19.61)	−9.06 (−10.97)	−3.80 (−4.80)	−1.37 (−1.81)	−0.44 (−0.60)	−9.12 (−9.99)	−2.95 (−3.42)	−1.75 (−2.14)	−1.1 (−1.62)	−0.64 (−1.22)
MIX	1.03 (−4.62)	3.12 (−0.37)	1.74 (0.10)	0.67 (0.05)	0.22 (0.01)	3.16 (1.79)	0.40 (−0.68)	0.50 (−0.34)	0.45 (−0.11)	0.29 (−0.03)
ΔE	11.90 (−0.38)	0.87 (−6.39)	−1.68 (−5.10)	−1.91 (−3.25)	−1.60 (−2.06)	4.74 (2.03)	−4.98 (−6.86)	−6.21 (−7.66)	−5.31 (−6.49)	−4.15 (−5.09)

[a] Values in Kcal/mol.

Table 2. CP Corrections to ΔE components: comparison of ΔE components corrected and uncorrected (in parenthesis) for BSSE. STO-3G and 4-31G results for the linear $H_2O.OH_2$ complex

Basis set	STO-3G					4-31G				
R_{AB}(Å)	2.38	2.68	2.98	3.28	3.58	2.38	2.68	2.98	3.28	3.58
ES	4.74	3.54	2.65	2.03	1.59	9.26	8.06	6.27	4.84	3.78
PL	−0.16	−0.09	−0.05	−0.03	−0.02	−0.59	−0.39	−0.23	−0.14	−0.08
EX	4.21 (2.89)	0.77 (0.46)	0.11 (0.06)	0.01 (0.01)	0.00 (0.00)	9.27 (8.86)	2.74 (2.46)	0.80 (0.66)	0.21 (0.16)	0.05 (0.03)
CT	−0.49 (−0.61)	−0.13 (−0.18)	−0.03 (−0.04)	−0.01 (−0.01)	−0.00 (−0.00)	−0.82 (−0.93)	−0.13 (−0.26)	−0.11 (−0.28)	−0.09 (−0.21)	−0.04 (−0.10)
MIX	0.04 (0.00)	0.01 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.29 (−0.08)	0.43 (−0.06)	0.40 (−0.01)	0.21 (0.00)	0.07 (0.00)
ΔE	8.33 (6.86)	4.10 (3.74)	2.69 (2.62)	2.01 (2.00)	1.57 (1.57)	17.41 (16.52)	10.71 (9.81)	7.12 (6.41)	5.03 (4.65)	3.77 (3.63)

Table 3. CP Corrections to ΔE components: comparison of ΔE components corrected and uncorrected (in parenthesis) for BSSE. STO-3G and 4-31G results for the linear $H_3N.HF$ complex

Basis set			STO-3G						4-31G			
R_{AB}(Å)	2.16	2.46	2.76	3.06	3.36	3.66	2.16	2.46	2.76	3.06	3.36	3.66
ES	−58.69	−24.90	−11.63	−6.33	−3.97	−2.76	−68.14	−38.74	−22.76	−14.22	−9.52	−6.76
PL	−0.49	−0.54	−0.43	−0.25	−0.14	−0.08	−8.72	−3.32	−1.69	−0.89	−0.47	−0.26
EX	119.18 (115.39)	42.50 (40.12)	14.46 (13.23)	4.68 (4.13)	1.45 (1.23)	0.43 (0.35)	105.75 (105.04)	37.26 (36.79)	12.57 (12.26)	4.09 (3.90)	1.27 (1.17)	0.37 (0.33)
CT	−11.67 (−12.61)	−13.16 (−14.38)	−8.19 (−9.17)	−3.84 (−4.45)	−1.51 (−1.82)	−0.53 (−0.66)	−42.24 (−43.69)	−8.77 (−9.62)	−3.20 (−3.58)	−2.16 (−2.36)	−1.53 (−1.80)	−0.95 (−1.35)
MIX	−15.21 (−19.62)	−0.27 (−4.31)	2.33 (−0.42)	1.58 (0.09)	0.73 (0.06)	0.27 (0.02)	20.72 (19.09)	1.31 (0.31)	0.07 (−0.69)	0.32 (−0.31)	0.37 (−0.11)	0.32 (−0.04)
ΔE	33.01 (23.88)	3.64 (−4.00)	−3.46 (−8.42)	−4.16 (−6.81)	−3.45 (−4.64)	−2.66 (−3.12)	7.37 (3.48)	−12.27 (−14.58)	−15.02 (−16.46)	−12.86 (−13.86)	−9.88 (−10.73)	−7.32 (−8.08)

Table 4. CP Corrections to ΔE components: total (*TOT*) electron acceptor (*EA*) and electron donor (*ED*) contributions. Comparison of STO-3G and 4-31G results for the linear $H_2O.HOH$ complex

Basis set		STO-3G					4-31G				
	R_{AB}(Å)	2.38	2.68	2.98	3.28	3.58	2.38	2.68	2.98	3.28	3.58
TOT	Δ^{EX}	4.30	1.98	0.77	0.27	0.08	0.47	0.33	0.21	0.11	0.05
	Δ^{CT}	2.33	1.81	1.01	0.44	0.16	0.88	0.47	0.40	0.51	0.58
	Δ^{MIX}	5.65	3.47	1.64	0.63	0.21	1.36	1.08	0.84	0.56	0.32
	Δ^{T}	12.28	7.26	3.42	1.34	0.45	2.71	1.88	1.45	1.17	0.95
EA	Δ^{EX}	0.36	0.16	0.06	0.02	0.01	0.20	0.13	0.07	0.03	0.01
	Δ^{CT}	0.01	0.01	0.01	0.00	0.00	0.20	0.10	0.09	0.07	0.03
	Δ^{MIX}	0.05	0.02	0.01	0.01	0.00	0.51	0.36	0.23	0.10	0.03
	Δ^{T}	0.42	0.19	0.08	0.03	0.01	0.91	0.59	0.38	0.20	0.08
ED	Δ^{EX}	3.94	1.82	0.71	0.24	0.07	0.26	0.20	0.15	0.08	0.03
	Δ^{CT}	2.32	1.80	1.01	0.44	0.16	0.68	0.37	0.31	0.44	0.55
	Δ^{MIX}	5.60	3.45	1.63	0.63	0.21	0.85	0.72	0.61	0.46	0.28
	Δ^{T}	11.86	7.07	3.34	1.31	0.44	1.79	1.29	1.07	0.98	0.86

Table 5. CP Corrections to ΔE components: total (*TOT*) contributions[a]. Comparison of STO-3G and 4-31G results for the linear $H_2O.OH_2$ complex

Basis set		STO-3G					4-31G				
	R_{AB}(Å)	2.38	2.68	2.98	3.28	3.58	2.38	2.68	2.98	3.28	3.58
TOT	Δ^{EX}	1.31	0.30	0.05	0.01	0.00	0.41	0.28	0.14	0.05	0.01
	Δ^{CT}	0.12	0.05	0.01	0.00	0.00	0.11	0.13	0.17	0.12	0.06
	Δ^{MIX}	0.04	0.01	0.00	0.00	0.00	0.37	0.49	0.41	0.21	0.07
	Δ^{T}	1.47	0.36	0.07	0.01	0.00	0.89	0.90	0.71	0.38	0.14

[a] Because of symmetry only *TOT* contributions are displayed

basis set introduced by Tatewaki and Huzinaga [23] and successfully tested in CP-corrected calculations of ΔE by Hobza and Sauer [24]. The Δ^{CT} results obtained with the 4-31G basis set indicate that there is not a monotonic decreasing of the correction when R_{AB} increases. A simple explanation of this fact can be done in terms of changes, with R_{AB}, of the capability of mixing of occupied orbitals of M with virtual orbitals of N, a capability which can be numerically appreciated in terms of second order perturbation theory. Intuitively the vacant MO's are more spread out than the occupied ones, and when R_{AB} increases, the overlap and the interaction matrix elements may reach a maximum. According to intuition this effect is more evident in the Δ^{CT} correction to the electron donor subsystem. A similar explanation has been put forward by Wells and Wilson [25] for the total CP correction in the case of two subsystems held at a fixed geometry while the basis set increases. Our dissection of Δ^{T} into separate components allows a more precise identification of specific basis set superposition error.

Table 6. CP Corrections to ΔE components: total (*TOT*), electron acceptor (*EA*) and electron donor (*ED*) contributions. Comparison of STO-3G and 4-31G results for the linear $H_3N.HF$ complex

Basis set		STO-3G						4-31G					
	R_{AB}(Å)	2.16	2.46	2.76	3.06	3.36	3.66	2.16	2.46	2.76	3.06	3.36	3.66
TOT	Δ^{EX}	3.79	2.38	1.23	0.55	0.22	0.08	0.71	0.46	0.31	0.19	0.10	0.04
	Δ^{CT}	0.94	1.21	0.99	0.61	0.31	0.13	1.55	0.83	0.37	0.19	0.27	0.39
	Δ^{MIX}	4.41	4.04	2.75	1.49	0.67	0.25	1.63	1.02	0.74	0.62	0.48	0.33
	Δ^{T}	9.13	7.64	4.96	2.65	1.19	0.46	3.89	2.31	1.43	1.00	0.85	0.76
EA	Δ^{EX}	0.84	0.45	0.21	0.09	0.04	0.01	0.44	0.31	0.19	0.10	0.04	0.02
	Δ^{CT}	0.03	0.01	0.01	0.00	0.00	0.00	0.65	0.32	0.16	0.11	0.07	0.04
	Δ^{MIX}	0.13	0.02	0.01	0.00	0.00	0.00	1.29	0.76	0.47	0.24	0.09	0.03
	Δ^{T}	1.00	0.49	0.23	0.10	0.04	0.01	2.37	1.40	0.82	0.45	0.21	0.08
ED	Δ^{EX}	2.94	1.93	1.01	0.45	0.18	0.06	0.27	0.15	0.12	0.09	0.06	0.03
	Δ^{CT}	0.91	1.21	0.98	0.61	0.31	0.13	0.90	0.51	0.21	0.08	0.20	0.36
	Δ^{MIX}	4.28	4.02	2.74	1.48	0.67	0.25	0.35	0.25	0.29	0.39	0.39	0.30
	Δ^{T}	8.13	7.15	4.74	2.55	1.15	0.45	1.51	0.91	0.62	0.56	0.64	0.68

Table 7. BSSE and $BSSE^{(x)}$ components data, for the linear complex $H_2O.HOH$ and 4-31G basis set, from [7]

R_{AB}(Å)	2.68	2.98	3.28
$BSSE^{(1)}$	1.277	0.197	−0.105
$BSSE^{(2)}$	0.602	1.244	1.275
BSSE	1.875	1.442	1.170

In spite of this non monotonic behaviour, also with the 4-31G basis the *ED* contributions to Δ^{CT} are larger than the *EA* contributions (the exception is $H_3N.HF$ at $R = 3.06$ Å).

The correction for E_{CT} proposed by Sokalski et al. [5] actually applies to the sum $E_{CT} + E_{MIX}$. It is obtained as the difference between the total CP correction ($BSSE = \Delta^{T}$) and $BSSE^{(1)}$. The values for $H_2O.HOH$ reported in Table 7 show that the correction increases when R_{AB} increases. This trend is due in part to the differential mixing ability of occupied and virtual orbitals discussed above and in part to the definition of $BSSE^{(1)}$.

3.3. *CP correction to E_{MIX}*

The E_{MIX} term is obtained in the KM scheme as a difference and contains terms of different origin [9]. Its behavior with respect to R_{AB} in different compounds and with different basis sets is not easily amenable to simple rules. As a very rough rule it may be said that it is larger, in absolute value, for stronger interactions, but often it has a different sign (compare, for example, among the cases considered here, the values at small R for $H_3N.HF$ in the two basis sets, Table 3). Δ^{MIX}, always positive by definition, brings a correction which in some cases reduces, and in other cases increases $|E_{MIX}|$.

4. Conclusions

We would like to stress that the main motivation for introducing CP corrections to the BSSE error in ΔE calculations and in the decomposition of ΔE is of practical origin. In particular CP corrections to the interaction energy components should preserve the direct intuitive meaning of the original definitions and the possibility of practical applications mentioned in the introduction.

The present method leaves the classical components of ΔE unaltered, namely E_{ES} and E_{PL} which have been systematically employed in our elaboration of semiclassical models for chemical interactions [26]. We have selected the present version for this very reason, being aware, however, that other researchers, prompted by the same basic motivation, should prefer CP corrections to ΔE components which change the subsystems charge distributions and polarizabilities (see, e.g. [27–29]). It may be remarked that in the first use of a CP correction (prior to Ref. [3]) made by Jansen and Ros [30] this idea has been tacitly assumed. We shall examine other methods in the prosecution of the present study, but it is clear that a statement on the merits of a method for BSSE corrections to ΔE components must be based on empirical evidence, i.e. on the results it gives for an adequately large number of cases. In spite of the large number of CP corrections available in the literature, a systematic study of $\Delta^T(R_{AB})$ (not to speak of its components) in function of the chemical nature of the system and of the basis set has never been performed. The numerical data given in the present paper are not sufficient for this study, nor are those provided by Sokalski et al. [5, 6]. For the moment the question remains unanswered, and according to the pragmatic point of view considered here, both available methods show a potential validity.

It is worth remarking that the present method gives a detailed decomposition of Δ^T, facilitating its analysis and the selection of simplified procedures. We have already remarked that with minimal basis sets the Δ^{CT} corrections could be limited to the electron donor subsystem, and probably for specific but wide classes of molecular interactions the whole CP correction could be limited to the *ED* component alone (see, e.g. [29, 31]). An analysis of the Δ^T components could represent the empirical basis to support other versions of the BSSE correction, like that of limiting the CP calculations to the vacant space only [9, 18], or that of introducing a penalty function $k<1$ to Δ^T [17, 19, 20, 21] or to some components of it.

Several among these alternative versions lead to a reduction of the computational time. The computational time of the present version, which gives a detailed description perhaps unnecessary in routine applications, can be appreciated in the following way. A standard CP correction to ΔE requires the introduction of two additional SCF processes; the ΔE decomposition (without CP correction) requires the introduction of two new but different SCF processes; the CP correction to the ΔE components, in the present version, requires the combination of the already mentioned processes with two new SCF calculations. All the additional processes involve the knowledge of one- and two-electron integrals computed for the original supersystem calculation only. The increases of computational time will depend on the dimension of occupied and vacant spaces; for the cases examined here there is an increment of the order of 65-80% with respect to the original calculations.

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References

1. Politzer, P., Truhlar, D. G. (eds.): Chemical applications of atomic and molecular electrostatic potentials. New York: Plenum Press 1981
2. Morokuma, K., Kitaura, K.: In: Molecular interactions, Vol. 1, p. 20. Ratajczak, H., Orville-Thomas, W. J. (eds.) London: Wiley 1980
3. Boys, S. F., Bernardi, F.: Mol. Phys. **19**, 553 (1970)
4. Kolos, W.: Theoret Chim. Acta (Berl.) **51**, 219 (1979)
5. Sokalski, W. A., Roszak, S., Hariharan, P. C., Kaufman, J. J.: Int. J. Quant. Chem. **23**, 847 (1983)
6. Sokalski, W. A., Hariharan, P. C., Kaufman, J. J.: J. Phys. Chem. **87**, 2803 (1983)
7. Sokalski, W. A., Hariharan, P. C., Kaufman, J. J.: J. Comp. Chem. **4**, 506 (1983)
8. Groen, F. P., van Dujineveldt, F. B.: quoted in [4] and [6]
9. Morokuma, K., Kitaura, K.: In: Chemical Applications of atomic and molecular potentials, p. 215. Politzer, P., Truhlar, D. G. (eds.) New York: Plenum Press 1981
10. Urban, M., Hobza, P.: Theoret. Chim. Acta (Berl.) **36**, 215 (1975)
11. Langlet, J., Claverie, P., Pullman, A., XVII QTEL, Viana do Castelo, Sept. 1984
12. Tolosa, S., Olivares del Valle, F. J.: An. Quim. **80**, 211 (1984)
13. Morokuma, K.: J. Chem. Phys. **55**, 1236 (1971)
14. Kitaura, K., Morokuma, K.: Int. J. Quant. Chem. **10**, 325 (1976)
15. Nagase, S., Fueno, T., Yamabe, S., Kitaura, K.: Theoret. Chim. Acta (Berl.) **49**, 309 (1978)
16. Bonaccorsi, R., Cimiraglia, R., Palla, P., Tomasi, J.: Int. J. Quant. Chem. **24**, 207 (1983)
17. Johansson, A., Kollman, P., Rothenberg, S.: Theoret. Chim. Acta (Berl.) **29**, 167 (1973)
18. Daudey, J. P., Malrieu, J. P., Rojas, O.: Int. J. Quant. Chem. **8**, 17 (1973)
19. Jönsson, B., Nelander, B.: Chem. Phys. **25**, 263 (1977)
20. Emsley, J., Hoyte, O. P. A., Overill, R. E.: J. Am. Chem. Soc. **100**, 3303 (1978)
21. Maggiora, G. M., Williams, I. H.: J. Mol. Struct. (Theochem) **88**, 23 (1982)
22. Dyke, T. R., Muenter, J. S.: J. Chem. Phys., **60**, 2929 (1974)
23. Tatewaki, H., Huzinaga, S.: J. Comp. Chem. **1**, 205 (1980)
24. Hobza, P., Sauer, J.: Theoret. Chim. Acta (Berl.) **65**, 279, 29 (1984)
25. Wells, B. H., Wilson, S.: Mol. Phys. **50**, 1295 (1983)
26. Bonaccorsi, R., Ghio, C., Tomasi, J.: Int. J. Quant. Chem. **26**, 637 (1984)
27. Sokalski, W. A., Hariharan, P. C., Kaufman, J. J., Petrongolo, C.: Int. J. Quant. Chem. **18**, 165 (1980)
28. Sokalski, W. A.: J. Chem. Phys. **77**, 4529 (1982)
29. Karlström, G., Sadlej, A. J.: Theoret. Chim. Acta (Berl.) **61**, 1 (1982)
30. Jansen, H. B., Ros, P.: Chem. Phys. Letters **3**, 140 (1969)
31. Ghio, C., Tomasi, J., Weill, J., Sillion, B.: to be published