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Counterpoise corrections to the evaluation of the bimolecular interaction energy components

On the decoupling of the E_{MIX} term

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Counterpoise corrections to the coupling terms of the bimolecular interaction energy decomposition are introduced and examined on a set of electron donor-acceptor dimers $X \cdot BH_3$ ($X = H_2O$, NH_3, PH_3, LiH, CO). The interaction energy decomposition of Kitaura and Morokuma, and the decoupling of E_{MIX} suggested by Nagase Fueno, Yamabe and Kitaura have been employed.

Counterpoise corrections have numerical influence on two terms only of the NFYK decoupling. This decoupling gives useful additional information on the nature of the chemical interaction when applied to STO-3G minimal basis set wavefunctions, but fails when applied the 4-31G wavefunctions.

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

1. Introduction

In a preceding paper [1] (hereafter called paper I) we have presented a method to correct the components of the intermolecular interaction energy $\Delta E_{AB}(R_{AB})$ with respect to the unphysical errors introduced by the use of incomplete basis sets for the monomers A and B. (Basis set superposition error: BSSE).

The method of [1] is related to the decomposition of ΔE_{AB} proposed in 1976 by Kitaura and Morokuma [2] for interaction energies evaluated with the supermolecule SCF scheme.

According to that decomposition, $\Delta E_{AB}(R_{AB})$ is divided into the following terms:

$$\Delta E_{AB}(R) = E_{AB}(R) - E_A^0 - E_B^0 = E_{ES} + E_{PL} + E_{EX} + E_{CT} + E_{MIX}. \tag{1}$$

While the first four contributions are evaluated independently and have a specific physical meaning, the last one, E_{MIX}, is given as difference. In paper I counterpoise (CP) corrections [3, 4] to the BSSE of the first four terms of the right side of Eq. (1) have been introduced on the basis of partial enlargements of the basis set for the calculation of the monomer energies, leaving again the correction to the E_{MIX} terms as a difference between the full CP correction, in which the monomer energies E_M^t ($M = A, B$) are computed with the total available functional space,

$$\chi_M^t = \chi_A \oplus \chi_B \tag{2}$$

and partial CP corrections.

An extension of the Morokuma decomposition scheme has been suggested by Nagase, Fueno, Yamabe and Kitaura (NFYK) [5] with the aim of extracting from E_{MIX} other contributions having physical meaning. In that paper a separate calculation of couplings between charge transfer and polarization terms is introduced. Accordingly, the interaction energy is decomposed in the following way:

$$\Delta E_{AB} = E_{ES} + E_{PL} + E_{CT} + E_{EX} + E_I + E_{II} + E_{III} + E_{IV} + E_{RES} \tag{3}$$

where

$$E_I + E_{II} + E_{III} + E_{IV} + E_{RES} = E_{MIX} \tag{4}$$

and

$$E_{RES} = E_{EXPL} + E_{RES'}. \tag{5}$$

The definition of the new energy components introduced in Eqs. (4) and (5) will be done in the following.

In the present paper we examine the extension of our method of CP corrections to the ΔE_{AB} components of the NFYK method. In addition, since this decomposition is rarely employed, attention will be paid to the merits of the decomposition itself.

2. Method

A short summary of the method of *KM* and of the further extension given by NFYK is in order.

The Fock matrix $\mathbb{F}$ for the system $A + B$, written in terms of MO's of the subsystems is partitioned into blocks referring to occupied and vacant orbitals of A and B respectively (A_0, A_v, B_0, B_v); by introducing the Fock matrix of infinite separation, $\mathbb{F}^0$, an interaction matrix $\mathbf{\Sigma}$ can be defined:

$$\mathbf{\Sigma} = (\mathbb{F} - \varepsilon \mathbb{S}) - (\mathbb{F}^0 - \varepsilon \mathbb{S}^0). \tag{6}$$

This matrix has the form in the following scheme:

	A_0	A_v	B_0	B_v
A_0	ESX	$PLX(A)$	$EX'(A_0-B_0)$	$CT(AB)$
A_v		ESX	$CT(BA)$	$EX'(A_vB_v)$
B_0			ESX	$PLX(B)$
B_v				ESX

The terms of Eqs. (1) and (3) are obtained by deleting some blocks of Σ and solving the corresponding pseudo H-F equations. From the E^X values (X upper index, stays for the blocks of Σ maintained in the calculation), the values of interaction energy components E_X (lower index) are obtained making suitable differences between E^X and E^Y terms, including the reference energy of the separate monomers: $E^0 = E^0_A + E^0_B$.

When CP corrections are introduced, the E^0_A and E^0_B terms will be replaced by the modified reference energies:

$$E^x_M = E^0_M - \Delta^X_M \qquad M = A, B. \tag{7}$$

The correction Δ^X_M refers to the same enlargement of the basis set induced by the inclusion of the appropriate Σ terms in the evaluation of E^X. The exposition of the method will result clearer when the separate terms E_X are considered.

1) E_{ES}. Only the ESX blocks of Σ are considered, with the additional deletion of intermolecular exchange terms. From the resulting energy E^{ES} (including also nuclear repulsion contributions) one has:

$$E_{ES} = E^{ES} - E^0. \tag{8}$$

There is no enlargement of basis set in the calculation of E^{ES} and of consequence no CP corrections are needed.

2) E_{PL}. ESX and PLX blocks of Σ are employed, with the additional deletion of intermolecular exchange contributions. From E^{ES+PL} one has:

$$E_{PL} = E^{ES+PL} - E^{ES} = (E^{ES+PL} - E^0) - E_{ES}. \tag{9}$$

There is now a mixing between occupied and vacant MO's of each monomer, but no enlargement of the monomers' basis sets. Of consequence no CP corrections are introduced.

When ESX and PLX blocks including intermolecular exchange are employed one obtains:

$$E_{PLX} = E^{ESX+PLX} - E^{ESX} \tag{10}$$

and then, by definition:

$$E_{EXPL} = E_{PLX} - E_{PL}. \tag{11}$$

E_{EXPL} will be employed in the following. No CP corrections are needed for this term too.

3) E_{EX}. ESX and EX' blocks of $\boldsymbol{\Sigma}$ are employed and the calculation is interrupted at the first cycle. From E^{ESX+EX} one has

$$E_{EX} = E^{ESX+EX} - E^{ES} = (E^{ESX+EX} - E^0) - E_{ES}. \tag{12}$$

There is now an extension of the basis set, because there is a mixing between occupied MO's of A and B. The reference energies are computed with the basis set

$$\chi_M^{ex} = \varphi_A^0 + \varphi_B^0 \qquad M = A, B \tag{13}$$

and the corresponding energies are called E_A^{ex}, E_B^{ex}.

The term $E^0 = E_A^0 + E_B^0$ in eq. (12) is replaced by:

$$E_{(ex)}^0 = E_A^{ex} + E_B^{ex} = (E_A^0 - \Delta_A^{EX}) + (E_B^0 - \Delta_B^{EX}) \tag{14}$$

$\Delta^{EX} = (\Delta_A^{EX} + \Delta_B^{EX})$ is the CP corrections to E_{EX}.

4) E_{CT}. This term may be divided into two components regarding the electron charge transfers $A \rightarrow B$ and $B \rightarrow A$. We consider here only one of these two terms: the extension to the second term and to the complete charge transfer contribution is immediate.

The blocks of $\boldsymbol{\Sigma}$ included in the calculation are ESX and $\mathrm{CT}(A \rightarrow B)$. One has:

$$\begin{aligned} E_{\mathrm{CT}(A\rightarrow B)} &= E^{ESX+\mathrm{CT}(A\rightarrow B)} - E^{ESX} \\ &= (E^{ESX+\mathrm{CT}(A\rightarrow B)} - E^0) - E_{ESX}. \end{aligned} \tag{15}$$

There is a mixing between occupied orbitals of A and vacant orbitals of B. The energy of A is calculated on the basis set

$$\chi_A^{ct} = \varphi_A^0 + \varphi_B^v \tag{16}$$

and the corresponding energy is called E_A^{ct}:

$$E_A^{ct} = E_A^0 - \Delta_A^{\mathrm{CT}}. \tag{17}$$

The CP corrected term is

$$E_{\mathrm{CT}(A\rightarrow B)}^{\mathrm{CP}} = E_{\mathrm{CT}(A\rightarrow B)} + \Delta_A^{\mathrm{CT}}. \tag{18}$$

The preceding terms, and the related CP corrections, have been discussed with reference to some actual cases in paper I. We pass to examine the further decomposition of E_{MIX} given in Eq. (4).

5) E_{MIX}. The basic energies, obtained by solving the pseudo H-F equations with the appropriate blocks of $\boldsymbol{\Sigma}$ are:

$$\begin{aligned} E^{I} &= E^{ESX+\mathrm{CT}(A\rightarrow B)+PLX(A)+EX(A_v-B_v)} \\ E^{II} &= E^{ESX+\mathrm{CT}(A\rightarrow B)+PLX(B)+EX(A_0-B_0)} \\ E^{III} &= E^{ESX+\mathrm{CT}(B\rightarrow A)+PLX(A)+EX(A_0-B_0)} \\ E^{IV} &= E^{ESX+\mathrm{CT}(B\rightarrow A)+PLX(B)+EX(A_v-B_v)}. \end{aligned} \tag{19}$$

The terms of Eq. (3) are given by:

$$\begin{aligned} E_I &= (E^{I} - E^{ESX}) - (E_{\mathrm{CT}(A\to B)} + E_{PLX(A)}) \\ E_{II} &= (E^{II} - E^{ESX+EX'}) - (E_{\mathrm{CT}(A\to B)} + E_{PLX(B)}) \\ E_{III} &= (E^{III} - E^{ESX+EX'}) - (E_{\mathrm{CT}(B\to A)} + E_{PLX(A)}) \\ E_{IV} &= (E^{IV} - E^{ESX}) - (E_{\mathrm{CT}(B\to A)} + E_{PLX(B)}). \end{aligned} \tag{20}$$

E_I and E_{IV} give an estimate of the coupling of the polarization of M and of the charge transfer $(M\to N)$; E_{II} and E_{III} an estimate of the coupling of the polarization of M with the charge transfer $(N\to M)$.

We have already introduced CP corrections to the $E_{CT(M\to N)}$ terms (Eq. 18). Other enlargement of the MO basis set and of consequence in our scheme other CP corrections, are present in the E^{I}, E^{II}, E^{III}, E^{IV}, $E^{ESX+EX'}$ calculations. We define a new set of CP corrected monomer energies:

$$\begin{aligned} E_M^1 &= E_M^0 - \Delta_M^1 \\ E_M^2 &= E_M^0 - \Delta_M^2 \\ E_M^3 &= E_M^0 - \Delta_M^3 \end{aligned} \tag{21}$$

related to the following basis sets:

$$\begin{aligned} \chi_M^1 &= \chi_M + \varphi_N^v \\ \chi_M^2 &= \varphi_M^0 + \chi_N \\ \chi_M^3 &= \chi_M + \varphi_N^0. \end{aligned} \tag{22}$$

The CP corrected expressions for the terms of Eq. (3) are:

$$\begin{aligned} E_I^{\mathrm{CP}} &= E_I + (\Delta_A^1 - \Delta_A^{\mathrm{CT}}) \\ E_{II}^{\mathrm{CP}} &= E_{II} + \Delta_A^2 - (\Delta_A^{EX} + \Delta_A^{\mathrm{CT}}) + (\Delta_B^3 - \Delta_B^{EX}) \\ E_{III}^{\mathrm{CP}} &= E_{III} + \Delta_B^2 - (\Delta_B^{EX} + \Delta_B^{\mathrm{CT}}) + (\Delta_A^3 - \Delta_A^{EX}) \\ E_{IV}^{\mathrm{CP}} &= E_{IV} + (\Delta_B^1 - \Delta_B^{\mathrm{CT}}) \\ E_{RES}^{\mathrm{CP}} &= E_{RES} + \Delta^T - (\Delta^1 + \Delta^2 + \Delta^3) + (\Delta^{\mathrm{CT}} + \Delta^{EX}). \end{aligned} \tag{23}$$

These expressions will be numerically tested in the following section.

It may be remarked that some extensions of the basis set considered in definitions (22) are active through indirect coupling. It is presumable that the following approximate expressions numerically hold:

$$\begin{aligned} \Delta_M^1 &\simeq \Delta_M^{\mathrm{CT}} \\ \Delta_M^3 &\simeq \Delta_M^{EX}. \end{aligned} \tag{24}$$

If this is the case, approximate expressions for the CP corrected energy components (ACP) could be written

$$\begin{aligned} E_I^{ACP} &= E_I \\ E_{II}^{ACP} &= E_{II} + \Delta_A^{MIX} \\ E_{III}^{ACP} &= E_{III} + \Delta_B^{MIX} \\ E_{IV}^{ACP} &= E_{IV} \\ E_{RES}^{ACP} &= E_{RES}. \end{aligned} \tag{25}$$

This last formulation does not require additional monomers' energy calculation with respect to those already employed in the *KM* BSSE correction scheme given in paper I.

The present scheme refers to a full CP correction, related to the basis set defined in (2): a limitation of the CP correction to the virtual space of the partner as advocated e.g. by Morokuma and Kitaura [6] would produce further simplifications which can be immediately derived from the preceding formulas.

The program for the NFYK decomposition has been written on the basis of the *KM* original program, kindly provided by the authors several years ago, and implemented for the GAUSSIAN series of programs on a GOULD SEL CONCEPT 32/87 computer.

When the A–B interaction is strong, diagonalization of the pseudo Hartree–Fock equations with $X = I$–IV, may produce a considerable mixing of orbitals, especially with non-minimal basis sets. It has been considered necessary to add to the decomposition programs a series of orbital-following tests, based on projections on the different orbital subspaces, to ensure that the pseudoeigenvectors employed in the following calculations actually were those requested.

3. Some numerical examples

The NFYK decomposition has not been widely employed. It is thus of some interest to examine the performance of this method, also without CP corrections. We have selected a small set of bimolecular interactions involving BH_3 as electron acceptor. Interacting monomers are kept at a fixed internal geometry, and the potential surface scan has been limited to the R_{AB} distance with fixed orientation of the partners. For BH_3 we have assumed a pyramidal C_{3v} geometry deduced from previous calculations on the dimers [7–10]. The direction of attack is along the C_3 axis of BH_3; in $H_3N \cdot BH_3$ and $H_3P \cdot BH_3$ a staggered conformation has been chosen; the $H_2O \cdot BH_3$ has a C_5 symmetry; $LiH \cdot BH_3$ and $OC \cdot BH_3$ have C_{3v} symmetry.

In Table 1 we report the values of the equilibrium distance and of ΔE obtained without and with CP corrections; calculations refer to the STO-3G and 4-31G basis sets.

Table 1. ΔE and R_{eq} values obtained without and with CP corrections. STO-3G and 4-31G values[a]

	STO-3G				4-31G			
	no CP		CP		no CP		CP	
	ΔE[b]	R_{eq}[c]	ΔE	R_{eq}	ΔE	R_{eq}	ΔE	R_{eq}
$H_2O \cdot BH_3$	−57.0	1.57	−36.4	1.64	−27.9	1.70	−25.5	1.72
$H_3N \cdot BH_3$	−66.0	1.65	−49.0	1.70	−44.1	1.70	−40.8	1.74
$H_3P \cdot BH_3$	−48.0	2.02	−30.4	2.10	−24.0	2.16	−20.1	2.20
$LiH \cdot BH_3$	−28.9	1.35	−25.5	1.36	−42.3	1.29	−40.7	1.30
$OC \cdot BH_3$	−41.4	1.60	−33.7	1.62	−28.0	1.58	−23.7	1.60

[a] Internal geometries. BH_3: $R(BH) = 1.19$ Å; $\angle HBX = 106.3°$ (in PH_3BH_3: $R(BH) = 1.212$ Å, $\angle HBX = 103.6°$). H_2O: $R(OH) = 0.951$ Å, $\angle HOH = 105.2°$. NH_3: $R(NH) = 1.01$ Å; $\angle HNX = 109.46°$. PH_3: $R(PH) = 1.399$ Å; $\angle HPX = 116.9°$. LiH: $R(LiH) = 1.515$ Å. CO: $R(CO) = 1.13$ Å. × is a point on the symmetry axis

[b] ΔE and ΔE^{CP}: values in Kcal/mol

[c] R_{eq} values in Å

Total CP corrections (including occupied and vacant MO's of the partners) have a trend similar to that found in other cases (see e.g. paper I and references quoted therein). There is a remarkable lowering of the absolute value of ΔE in both basis sets: the effect on ΔE is larger in STO-3G calculations which gives, after CP corrections, $\Delta E(R_{eq})$ values more negative than the uncorrected 4-31G estimates (the exception being $LiH \cdot BH_3$). The increase of R_{eq} produced by CP corrections is in general less than 0.1 Å. With both basis sets there are non negligible changes in the relative value of the interaction energy produced by CP corrections: in one case there is an inversion of relative stability ($H_3P \cdot BH_3$ and $OC \cdot BH_3$). Also remark the noticeable increase of the relative stability of $LiH \cdot BH_3$ in passing from STO-3G to 4-31G calculations.

To save space we do not report extensive tabulations of ΔE components in function of R_{AB} selecting only one distance, near R_{eq}, for each dimer.

STO-3G values are reported in Tables 2 and 3. Let us now consider the first three complexes of the series. They are homogeneous in the sense that a lone pair of a heteroatom acts in all cases as electron donor. This homogeneity turns out evident by inspecting the data of Table 2. Without CP corrections the classical terms $(E_{ES} + E_{PL})$ give an estimate of ΔE by defect, in line with what has been found in general for STO-3G dimers of different type: with CP corrections, which leave unaltered the classical term, the classical approximation gives a better guess, in one case by excess ($NH_3 \cdot BH_3$).

The CP corrections affect both E_{EX} and E_{CT}: from Table 2 is easy to verify that $\Delta^{MIX} = \Delta^T - (\Delta^{EX} + \Delta^{CT})$ is a small amount of the rotal CP correction Δ^T. In minimal basis sets calculations the relative importance of E_{CT} is exaggerated: CP corrections bring the value of E_{CT} more in line with that obtained with a larger basis set.

The NFYK addition to the original decomposition scheme works well, at this level of accuracy. The unresolved E_{RES} term is smaller, in absolute value, than

Table 2. Comparison of ΔE components without and with CP corrections. STO-3G results (in kcal/mol)

	$H_2O \cdot BH_3$		$H_3N \cdot BH_3$		$H_3P \cdot BH_3$		$LiH \cdot BH_3$		$OC \cdot BH_3$	
	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP
ΔE	−53.75	−35.60	−65.21	−49.04	−46.95	−30.44	−28.93	−25.38	−41.37	−33.53
E_{ES}	−33.33	−33.33	−58.29	−58.29	−30.85	−30.85	−28.36	−28.36	−65.70	−65.70
E_{PL}	−2.26	−2.26	−1.95	−1.95	−0.89	−0.89	−10.37	−10.37	−7.32	−7.32
E_{EX}	37.42	46.09	59.04	68.61	48.92	59.48	63.77	64.48	96.96	102.37
E_{CT}	−44.58	−38.44	−39.38	−35.97	−43.29	−39.92	−27.95	−26.89	−32.81	−31.95
E_{MIX}	−10.99	−7.65	−24.62	−21.43	−20.85	−18.27	−26.03	−25.24	−32.22	−30.92
E_I	−2.15	−2.12	−4.56	−4.54	−0.73	−0.72	1.02	1.02	1.56	1.57
E_{II}	−1.28	1.76	−4.72	−2.04	−10.62	−8.19	−16.73	−16.04	19.32	20.46
E_{III}	1.44	1.45	0.58	0.80	1.30	1.39	7.36	7.45	9.61	9.69
E_{IV}	0.16	0.16	0.11	0.11	0.24	0.24	0.34	0.34	4.62	4.62
E_{RES}	−9.16	−8.99	−16.03	−15.76	−11.04	−10.99	−18.03	−18.02	−67.33	−67.26
R_{AB}	1.700	1.700	1.705	1.705	2.10	2.10	1.35	1.35	1.60	1.60

E_{MIX} and the sign and values of E_I, E_{II}, E_{III} and E_{IV} can be interpreted and justified.

E_I is the coupling between polarization of the electron donor (*ED*) and charge transfer to the electron acceptor (*EA*). The molecular field of *EA* induces a polarization of *ED* which makes more efficient the $ED \rightarrow EA$ charge transfer. The coupling gives in fact a stabilizing (i.e. negative) contribution to ΔE. The opposite happens for the E_{IV} term (coupling between polarization of *EA* and $EA \rightarrow ED$ charge transfer). The absolute value E_{IV} is of course decidedly smaller than that of E_I. For both terms the CP corrections are modest.

E_{II} is the coupling between polarization of *EA* and $ED \rightarrow EA$ charge transfer. The molecular field of *EA* facilitates the flow of electrons from *ED* to *EA*. CP corrections are in this case relatively important and are positive; in other words the BSSE apparently makes this coupling easier. The same considerations explain

Table 3. CP corrections to the BSSE divided into electron donor (*ED*) and electron acceptor (*EA*) contributions. STO-3G results (in kcal/mol)[a]

	$H_2O \cdot BH_3$		$H_3N \cdot BH_3$		$H_3P \cdot BH_3$		$LiH \cdot BH_3$		$OC \cdot BH_3$	
	ED	*EA*	*ED*	*EA*	*ED*	*EA*	*ED*	*EA*	*ED*	*EA*
Δ^T	17.80	0.35	15.62	0.55	15.92	0.59	2.50	1.06	7.18	0.66
Δ^{EX}	8.40	0.26	9.14	0.42	10.10	0.47	1.31	0.39	5.29	0.39
Δ^{CT}	6.12	0.02	3.40	0.02	3.34	0.03	0.57	0.49	0.79	0.06
Δ^1	6.16	0.02	3.42	0.02	3.34	0.03	0.57	0.49	0.81	0.06
Δ^2	17.54	0.32	15.15	0.48	15.80	0.53	2.49	0.96	7.06	0.49
Δ^3	8.48	0.29	9.32	0.49	10.15	0.52	1.33	0.47	5.32	0.54

[a] $\Delta_M^{MIX} = \Delta_M^T - (\Delta_M^{EX} + \Delta_M^{CT})$
$\Delta_M^{RES} = \Delta_M^T + (\Delta_M^{EX} + \Delta_M^{CT}) - (\Delta_M^1 + \Delta_M^2 + \Delta_M^3)$

the opposite sign of E_{III} (coupling between polarization of *ED* and $EA \rightarrow ED$ charge transfer).

The other two molecular complexes belong to different classes of interaction, and as a consequence the interpretation should be supported by the examination of other cases of the same type.

The geometry of $LiH \cdot BH_3$ actually is a saddle point on the energy surface: the most stable structure roughly corresponds to a tetrahedral BH_4 surrounded by a relatively mobile Li, with noticeable charge separation [9, 11, 12]. Limiting ourselves at the deformed geometry considered in Tables 2 and 3 it may be remarked that classical terms give an estimate of ΔE by excess. CP corrections to E_{EX} and E_{CT} are smaller than in the preceding cases: the distance between the charge center of *A* and *B* is larger than in the lone-pair bound complexes. CP corrections to E_{CT} are of the same magnitude for *EA* and for *ED*, in contrast with the preceding cases.

The NFYK decomposition of E_{MIX} gives a residuum lower than the original term ($|E_{RES}| < |E_{MIX}|$). The prominent terms are in this case E_{II} and E_{III}, slightly affected by CP corrections. The interpretation of the sign of these two contributions is similar to that already done for complexes of BH_3 with a lone-pair *ED*.

The interaction between OC and BH_3 belongs to a third different category. An interpretation of it, in terms of the *KM* decomposition, has been done some years ago by Umeyama and Morokuma [7]. CP corrections do not modify this interpretation[1]. The NFYK decomposition fails here ($|E_{RES}| > |E_{MIX}|$). An interpretation of E_I-E_{IV} terms is less easy than in the preceding cases. The trend of the term is different from that found in the other complexes. A separation into σ and π subinteractions, examined at larger values of *R*, could aid the interpretation, but it remains that at R_{eq} the residue is larger than the term under examination.

On the whole set of compounds, the approximations introduced in Eq. (24) are almost satisfied: Tables 2 and 3 give the data one needs to compute interaction energy components according to Eq. (25).

4-31G values are reported in Tables 4 and 5. The results of the *KM* decomposition correspond to what experience on other cases suggests. A comparison of the ΔE terms with those of Table 2 evidences a remarkable increase of E_{ES} (the 4-31G basis emphasizes electrostatic interactions), a noticeable increase of E_{PL} (split-valence shell or *DZ* basis sets reproduce this term better than minimal basis sets), a remarkable reduction of E_{CT} when the complex regard lone pair *ED*'s. CP corrections are lower than in the preceding case: it is worth remarking that CP corrections to the *EA* are however of comparable magnitude and in some cases larger than with the STO-3G basis. Passing now to the results of the NYFK

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[1] The origin of bond formation and charge transfer in this adduct has been the object of an accurate study by Kato et al. [13]. Supplementary information on this interesting case can be drawn from the relatively large existing literature [14–20]

Table 4. Comparison of ΔE components without and with CP corrections. 4-31G results (in kcal/mol)

	$H_2O \cdot BH_3$		$H_3N \cdot BH_3$		$H_3P \cdot BH_3$		$LiH \cdot BH_3$		$OC \cdot BH_3$	
	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP
ΔE	−27.95	−25.37	−44.14	−40.40	−23.72	−19.69	−41.75	−40.29	−27.88	−23.73
E_{ES}	−58.19	−58.19	−93.49	−93.49	−54.01	−54.01	−53.57	−53.57	−65.02	−65.02
E_{PL}	−11.58	−11.58	−17.27	−17.27	−8.97	−8.97	−42.36	−42.36	−71.74	−71.74
E_{EX}	55.73	56.43	88.57	89.29	68.88	70.15	74.12	74.25	108.34	109.45
E_{CT}	−16.96	−15.92	−27.08	−25.44	−31.04	−29.21	−52.48	−51.70	−78.73	−77.86
E_{MIX}	3.05	3.89	5.14	6.53	1.42	2.41	32.55	33.10	79.27	80.44
E_I	−7.59	−7.49	−90.09	−89.77	−26.13	−25.81	−373.06	−372.87	−256.55	−286.38
E_{II}	86.34	86.79	140.66	141.59	100.14	100.85	37.32	37.60	242.01	249.39
E_{III}	16.93	17.06	34.16	34.26	19.53	19.61	134.09	134.06	195.12	195.45
E_{IV}	−237.78	−237.78	−229.44	−229.44	−49.55	−49.55	−27.94	−27.91	−208.91	−208.83
E_{RES}	145.15	145.31	149.85	149.88	−42.55	−42.69	262.14	262.19	130.60	131.39
R_{AB}	1.700	1.700	1.705	1.705	2.10	2.10	1.35	1.35	1.60	1.60

decomposition, given in the second half of Table 4, it turns out evident that this decomposition fails here. It is sufficient to compare the absolute values of E_{MIX} and of E_{RES}. Moreover, the relative values and signs of the coupling components E_I–E_{IV} do not correspond to intuition.

For the sake of documentation we report in Table 4 also the CP corrections to these coupling terms, but clearly it makes little sense to correct for the BSSE such values.

5. Conclusions and comments

We have examined a set of electron donor-acceptor couples (or Lewis acid-base couples) having all BH_3 as electron acceptor (or Lewis acid), to test the NFYK decomposition of coupling terms and the corrections given by the introduction of a counterpoise procedure. The NFYK decomposition scheme gives, when applied to STO-3G calculations at R_{eq}, reasonable values, which improve our understanding of the interaction act. The examination of these terms makes more

Table 5. CP corrections to the BSSE divided into electron donor (*ED*) and electron acceptor (*EA*) contributions. STO-3G results (in kcal/mol)

	$H_2O \cdot BH_3$		$H_3N \cdot BH_3$		$H_3P \cdot BH_3$		$LiH \cdot BH_3$		$OC \cdot BH_3$	
	ED	*EA*	*ED*	*EA*	*ED*	*EA*	*ED*	*EA*	*ED*	*EA*
Δ^T	2.14	0.44	3.24	0.51	3.38	0.36	0.93	0.54	3.58	0.56
Δ^{EX}	0.60	0.10	0.60	0.12	1.13	0.14	0.07	0.06	0.99	0.11
Δ^{CT}	0.98	0.07	1.56	0.08	1.81	0.02	0.48	0.30	0.77	0.11
Δ^1	1.08	0.07	1.88	0.08	2.13	0.02	0.67	0.33	0.93	0.13
Δ^2	2.00	0.25	3.04	0.26	3.55	0.19	0.46	0.34	1.98	0.22
Δ^3	0.63	0.12	0.64	0.17	1.18	0.24	0.09	0.13	1.33	0.20

evident, inter alia, the different nature of interaction involving a lone pair, with respect to others involving a more complex *EA*–*ED* interaction or a hydride group. CP corrections are numerically important only for the coupling involving polarization of the *EA* and the $EA \rightarrow ED$ back electron transfer. This correction may induce some revision in models of *ED*–*EA* interactions.

The NFYK scheme fails, on the contrary, where applied to 4-31G calculations. The reason is due, in our opinion, to the use of pseudo-Hartree–Fock equations for computing the coupling terms. While the original decomposition blends classical concepts with quantum mechanical schemes (see e.g. the use of a modified operator of classical origin in the *KM* calculation of E_{ES} and E_{PL}) for the evaluation of couplings this blend is no more employed. As a consequence, the interactions are stronger and not balanced as in the full quantum mechanical calculation.

When the basis set is of limited size, there is a small probability that this unbalancement makes evident its influence; the 4-31G basis is sufficiently large to produce a blow up of the unwanted effects. In conclusion, the NKYF scheme cannot be recommended for general use in the present version. The STO-3G results show that an analysis of the E_{MIX} term may be of heuristic interest, and it could be worth to examine if in interactions of other type the NFYK scheme, applied to STO-3G wavefunction, gives interesting results[2].

For general applications it would be convenient, however, to modify the computational scheme, or to use an alternative approach. In our opinion this is possible.

As a final remark we note that the *KM* decomposition gives good results even when applied to 4-31G function. This fact was already known, and this ΔE decomposition is routinely employed in studies of molecular interaction performed at the 4-31G or better level. Interaction energy decomposition are however conceptually acceptable for calculations performed with basis sets far for completeness. In the realm of chemical application this condition is amply satisfied, but it must always be kept in mind.

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References

1. Cammi, R., Bonaccorsi, R., Tomasi, J.: Theor. Chim. Acta submitted for publication
2. Kitaura, K., Morokuma, K.: Int. J. Quant. Chem. **10**, 325 (1976)
3. Jansen, H. B., Ros, P.: Chem. Phys. Letters **3**, 140 (1969)
4. Boys, S. F., Bernardi, F.: Mol. Phys. **19**, 553 (1970)

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[2] The results obtained at the STO-3G level for the interaction between a couple of oppositely charged organic ions [21] actually improve our understanding of the interaction mechanism

5. Nagase, S., Fueno, T., Yamabe, S., Kitaura, K.: Theor. Chim. Acta **49**, 309 (1978)
6. Morokuma, K., Kitaura, K.: In: Politzer, P., Truhlar, D. G. (eds.) Chemical applications of atomic and molecular electrostatic potentials, p. 215. New York: Plenum Press, 1981
7. Umeyama, H., Morokuma, K.: J. Am. Chem. Soc. **98**, 7208 (1976)
8. Bonaccorsi, R., Palla, P., Cimiraglia, R., Tomasi, J.: Int. J. Quant. Chem. **24**, 307 (1983)
9. Bonaccorsi, R., Scrocco, E., Tomasi, J.: Theor. Chim. Acta **52**, 113 (1979)
10. Umeyama, K., Kudo, T., Nakagawa, S.: Chem. Pharm. Bull. **29**, 287 (1981)
11. Boldyrev, A. I., Charkin, O. P., Rambidi, N. G., Avdeev, V. I.: Chem. Phys. Lett. **44**, 20 (1976)
12. Charkin, O. P., Boldyrev, A. I.: Potential energy surfaces and structural non-rigidity of inorganic molecules, Adv. Sci. and Tech. Inorg. Chem. Ser. Vol. 8, Moscow 1980
13. Kato, S., Fujimoto, H., Yamabe, S., Fukui, K.: J. Am. Chem. Soc. **96**, 2024 (1974)
14. Ha, T. K.: J. Mol. Struct. **30**, 103 (1976)
15. Armstrong, O. R., Perkins, P. G.: J. Chem. Soc. A, 1044 (1969)
16. Ermler, L. T., Glasser, F. D., Kern, C. W.: J. Am. Chem. Soc. **98**, 3799 (1976)
17. Redmon, L. T., Purvis III, G. D., Bartlett, R. J.: J. Am. Chem. Soc. **101**, 2856 (1980)
18. Clark, D. T., Cromarty, B. J., Sgamellotti, A.: Chem. Phys. **46**, 43 (1980)
19. Breulet, J., Lievin, J.: Theor. Chim. Acta **61**, 59 (1982)
20. Garcia-Leigh, A., Murrell, J. N.: Croat. Chim. Acta **57**, 879 (1984)
21. Nakagawa, S., Umeyama, H.: J. Am. Chem. Soc. **100**, 7717 (1978)