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Improved SCF Interaction Energy Decomposition Scheme Corrected for Basis Set Superposition Effect

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Abstract

A modified scheme for SCF interaction energy decomposition has been proposed where the nonphysical basis set superposition error (BSSE) has been corrected by means of the counterpoise method. A new procedure to separate the exchange and induction energy terms free of nonphysical BSSE has been tested in the case of the H_2O dimer. The first order BSSE appears to be non-negligible for strong hydrogen bonded complexes. In addition the scheme allows separation of the long-controversial charge-transfer contribution within the induction term, which has been considerably overestimated in previous studies.

1. Introduction

Most nonempirical studies on intermolecular interactions are performed at present with the variational SCF LCAO-MO supermolecular approach. Exchange perturbation theory [1] provides a more detailed insight into the nature of interactions. In 1976 Jeziorski and van Hemert [2] demonstrated that the SCF interaction energy ΔE_{SCF} corrected for basis set superposition effect [3-6] (BSSE) is approximately equivalent to the sum of first order electrostatic $E_{EL}^{(1)}$ and exchange $E_{EX}^{(1)}$ and second order induction $E_{IND}^{(2)}$ terms derived from exchange perturbation theory [1,2,7]:

$$\Delta E_{SCF} = E_{AB} - E_{A(B)} - E_{B(A)}$$
$$= E_{AB} - E_A - E_B - \text{BSSE} \approx E_{EL}^{(1)} + E_{EX}^{(1)} + E_{IND}^{(2)}, \quad (1)$$

where $E_{A(B)}$, $E_{B(A)}$ correspond to the energy of isolated components A and B evaluated in the AB basis set. However, all previously proposed SCF interaction energy decomposition schemes [8-11] include BSSE [4-6,12]. The present contribution proposes a modified decomposition scheme corrected for BSSE.

2. Method

Neglecting intramolecular correlation effects [1] one may expand the interaction energy ΔE in exchange perturbation theory as

$$\Delta E = \sum_{n=1}^{\infty} E^{(n)} = E_{EL}^{(1)} + E_{EX}^{(1)} + E_{IND}^{(2)} + E_{DISP}^{(2)} + E_{EX-IND}^{(2)} + E_{EX-DISP}^{(2)} + \cdots, \quad (2)$$

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where $E^{(1)}$ is the first order and $E^{(2)}$ the second order interaction energy. $E_{EL}^{(1)}$ denotes first order electrostatic, $E_{EX}^{(1)}$ exchange terms, $E_{IND}^{(2)}$ second order induction, $E_{DISP}^{(2)}$ dispersion, $E_{EX-IND}^{(2)}$ exchange induction, and $E_{EX-DISP}^{(2)}$ exchange dispersion contributions. In bimolecular interactions of closed shell molecules, the total interaction energy is quite well approximated [2] by the first four terms in Eq. (2). On the other hand the interaction energy, with the exception of the dispersion contribution, may be quite easily estimated by standard *ab initio* SCF LCAO-MO procedures in the supermolecular approach

$$\Delta E_{SCF} = E_{AB} - E_{A(B)} - E_{B(A)}, \tag{3}$$

where E_{AB}, $E_{A(B)}$, and $E_{B(A)}$ correspond to the SCF energy of the AB supermolecule, and the A and B subsystems, respectively, evaluated in the AB basis set. The use of monomer basis sets alone to evaluate subsystem energies E_A and E_B in Eq. (3) leads to a basis set superposition error (BSSE) [4–6,12,13]

$$BSSE + \Delta E_{SCF} = E_{AB} - E_A - E_B. \tag{4}$$

The attempts to use scaled BSSE correction, BSSE*k $(0 < k < 1)$ [14,15], instead of the full counterpoise correction (CC) $(k = 1)$ suggested by Boys [3] does not seem to be justified by recent calculations [4–6,12,16]. The reasoning behind the use of scaled BSSE correction $(0 < k < 1)$ is [14,15] that only the virtual MO of molecule B may be available for improving MO of molecule A (and vice versa). This implies that BSSE should be attributed to higher order interaction energy only. However, as we will later demonstrate, the first order basis set superposition error BSSE$^{(1)}$, entirely due to interactions between occupied MO's only, is non-negligible in some cases also. A similar idea was recently discussed by Karlström [16]. Another justification for applying full BSSE correction $(k = 1)$ comes from our systematic extended studies on hydrogen bonded dimers [17] and the independent study of Groen and van Duijneveldt [12]. These show that the basis set dependence of uncorrected SCF interaction energy ΔE_{SCF} + BSSE is considerably reduced for second order interaction energy term when applying $k = 1$. The remaining basis set dependence of the interaction energy, even after correcting ΔE_{SCF} for BSSE, resides almost entirely in the first order electrostatic term $E_{EL}^{(1)}$. The basis set dependence of $E_{EL}^{(1)}$ may be related to intramolecular basis set balance which cannot be corrected in the counterpoise method [3].

The SCF approach does not include dispersion $E_{DISP}^{(2)}$. ΔE_{SCF} can be partitioned into various energy contributions which are generated from different initial wave functions Ψ. In Table I all previously proposed forms of the initial wave function Ψ have been related to particular components of interaction energy and basis set superposition error components. A_0 and B_0 denote the ground state single determinant wave functions of the isolated A and B subsystems. The superscripts A or B refer to the basis set used to evaluate monomer wave functions. The first order contributions correspond to the AB supermolecule energy change in the first SCF iteration before the charge distribution of both interacting molecules becomes mutually polarized. $\hat{A}$ denotes antisymmetrization operator. Interaction energy contributions evaluated within polarization approximation [18] ($E_{EL}^{(1)}$ and $E_{IND,LE}^{(2)}$)

$$\Psi_1 = A_0^A B_0^B \tag{5}$$

TABLE I. Components of SCF interaction energy ΔE_{SCF} in different decomposition schemes. (The names above brackets correspond to contributions defined in Refs. [8-12].)

Initial Wave Function		Components of AB Supermolecule Energy	
Ref.		First Iteration	Converged
[8]	$\Psi_2 = \hat{\mathscr{A}}\, A_o^A\, B_o^B$	$\overbrace{E_{EL}^{(1)} + E_{EX}^{(1)} + BSSE^{(1)}}^{ELECT} + E_A + E_B$	$\overbrace{E_{EL}^{(1)} + E_{EX}^{(1)} + BSSE^{(1)}}^{ELECT} + \overbrace{E_{IND,LE}^{(2)} + E_{IND,CT}^{(2)} + BSSE^{(2)}}^{DELOC} + E_A + E_B$
[9]	$\Psi_1 = A_o^A\, B_o^B$	$E_{EL}^{(1)} \qquad\qquad + E_A + E_B$	$E_{EL}^{(1)} + E_{IND,LE}^{(2)} \qquad\qquad + E_A + E_B$
	$\Psi_2 = \hat{\mathscr{A}}\, A_o^A\, B_o^B$	$\overbrace{E_{EL}^{(1)}}^{C} + \overbrace{E_{EX}^{(1)} + BSSE^{(1)}}^{E} + E_A + E_B$	$\overbrace{E_{EL}^{(1)}}^{C} + \overbrace{E_{EX}^{(1)} + BSSE^{(1)}}^{E} + \overbrace{E_{IND,LE}^{(2)} + E_{IND,CT}^{(2)} + BSSE^{(2)}}^{P+CT} + E_A + E_B$
[10]	$\Psi_1 = A_o^A\, B_o^B$	$\overbrace{E_{EL}^{(1)}}^{ES} + E_A + E_B$	$\overbrace{E_{EL}^{(1)}}^{ES} + \overbrace{E_{IND,LE}^{(2)}}^{PD} + E_A + E_B$
	$\Psi_2 = \hat{\mathscr{A}}\, A_o^A\, B_o^B$	$\overbrace{E_{EL}^{(1)}}^{ES} + \overbrace{E_{EX}^{(1)} + BSSE^{(1)}}^{EX} + E_A + E_B$	$\overbrace{E_{EL}^{(1)}}^{ES} + \overbrace{E_{IND,LE}^{(2)}}^{PD} + \overbrace{E_{EX}^{(1)} + BSSE^{(1)}}^{EX} + \overbrace{E_{IND,CT}^{(2)} + BSSE^{(2)}}^{CT} + E_A + E_B$
[11]	$\Psi_1 = A_o^A\, B_o^B$	$\overbrace{E_{EL}^{(1)}}^{ES} \qquad\qquad + E_A + E_B$	$\overbrace{E_{EL}^{(1)}}^{ES} + \overbrace{E_{IND,LE}^{(2)}}^{PL} + E_A + E_B$
	$\Psi_2 = \hat{\mathscr{A}}\, A_o^A\, B_o^B$	$\overbrace{E_{EL}^{(1)}}^{ES} + \overbrace{E_{EX}^{(1)} + BSSE^{(1)}}^{EX} + E_A + E_B$	$\overbrace{E_{EL}^{(1)}}^{ES} + \overbrace{E_{IND,LE}^{(2)}}^{PL} + \overbrace{E_{EX}^{(1)} + BSSE^{(1)}}^{EX} + \overbrace{E_{IND,CT}^{(2)} + BSSE^{(2)}}^{CT+MIX+EXPL} + E_A + E_B$
[12]	$\Psi_1 = A_o^A\, B_o^B$	$E_{EL}^{(1)} \qquad\qquad + E_A + E_B$	$E_{EL}^{(1)} + E_{IND,LE}^{(2)} \qquad\qquad + E_A + E_B$
	$\Psi_2 = \hat{\mathscr{A}}\, A_o^A\, B_o^B$	$\overbrace{E_{EL}^{(1)}}^{E_{coul}^{ab}} + \overbrace{E_{EX}^{(1)} + BSSE^{(1)}}^{E_{ex}^{ab}} + E_A + E_B$	$\overbrace{E_{EL}^{(1)}}^{E_{coul}^{ab}} + \overbrace{E_{IND,LE}^{(2)}}^{E_{ind}^{ab}}$
	$\Psi_3 = \hat{\mathscr{A}}\, A_o^{A(B)}\, B_o^{B(A)}$	$\overbrace{E_{EL}^{(1)} + E_{EX}^{(1)} + BSSE^{(1)}}^{} + E_{A(B)} + E_{B(A)}$	$E_{EL}^{(1)} + E_{IND,LE}^{(2)} + \overbrace{E_{EX}^{(1)} + BSSE^{(1)}}^{E_{ex}^{ab}} + \overbrace{E_{IND,CT}^{(2)} - BSSE^{(1)}}^{E_{ctx}^{ab}} + E_{A(B)} + E_{B(A)}$
This work	$\Psi_1 = A_o^A\, B_o^B$	$E_{EL}^{(1)} \qquad\qquad + E_A + E_B$	$E_{EL}^{(1)} + E_{IND,LE}^{(2)} \qquad\qquad + E_A + E_B$
	$\Psi_2 = \hat{\mathscr{A}}\, A_o^A\, B_o^B$	$E_{EL}^{(1)} + E_{EX}^{(1)} + BSSE^{(1)} + E_A + E_B$	$E_{EL}^{(1)} + E_{EX}^{(1)} + BSSE^{(1)} + E_{IND,LE}^{(2)} + E_{IND,CT}^{(2)} + BSSE^{(2)} + E_A + E_B$
	$\Psi_3 = \hat{\mathscr{A}}\, A_o^{A(B)}\, B_o^{B(A)}$	$E_{EL}^{(1)} + E_{EX}^{(1)} \qquad + E_{A(B)} + E_{B(A)}$	$E_{EL}^{(1)} + E_{EX}^{(1)} + E_{IND,LE}^{(2)} + E_{IND,CT}^{(2)} + E_{A(B)} + E_{B(A)}$

are not subject to BSSE as there is no intermolecular electron exchange allowed either in first or higher order polarization contributions. However, BSSE is present when the monomer eigenfunctions $A_0 B_0$ are antisymmetrized to allow intermolecular electron exchange. Using Ψ_3, where the wave functions of monomers A and B have been calculated in the dimer basis set AB, avoids including BSSE in the interaction energy decomposition. In particular the use of Ψ_2 and Ψ_3 allowed separation of the first order basis set superposition error $BSSE^{(1)}$ and the higher order BSSE $^{(R)}$, which is dominated by second order term $BSSE^{(2)}$. Although $BSSE^{(1)}$ is quite small for weak complexes [such as $(H_2O)_2$], it becomes non-negligible for stronger dimers (such as $H_3N\cdots HF$) [17]. Within the scaled BSSE approach [14,15] $(0 < k < 1)$, $BSSE^{(1)}$ will not appear since there are no vacant orbitals involved. The higher order SCF interaction energy contributions are dominated by the induction term

$$E_{IND}^{(2)} \approx \Delta E_{SCF} - E^{(1)}.$$

In exchange perturbation theory [7,19] the induction term may be obtained when the supersystem wave function is expanded in terms of locally excited configurations (LE)

$$\Psi_3 = \hat{A} A_0 B_0 + \sum_{m=1}^{\infty} a_m \psi_m, \tag{6}$$

$$\psi_m^{LE} = A_m(i \to k)B_0 = 2^{-1/2}(|\cdots i\bar{k}\cdots| + |\cdots k\bar{i}\cdots|)|\cdots j\bar{j}\cdots|, \tag{7}$$

or

$$\psi_m^{LE} = A_0 B(j \to l) = 2^{-1/2}|\cdots i\bar{i}\cdots|(|\cdots j\bar{l}\cdots| + |\cdots l\bar{j}\cdots|). \tag{8}$$

However, there is an alternative expansion of $E_{\text{IND}}^{(2)}$ in terms of ionic charge transfer configurations

$$\psi_m^{\text{CT}} = A^+B^-(i \rightarrow l) = 2^{-1/2}(|\cdots i\bar{l}\cdots| + |\cdots l\bar{i}\cdots|)|\cdots j\bar{j}\cdots| \tag{9}$$

or
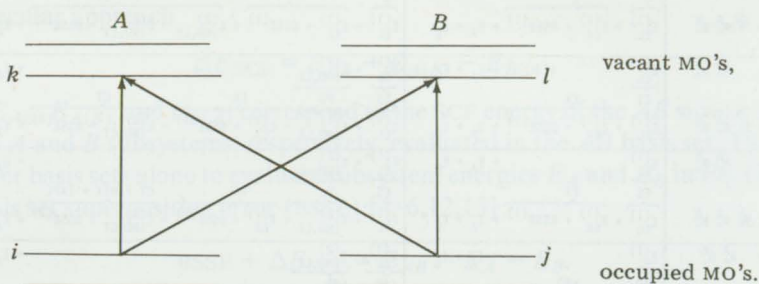
$$\psi_m^{\text{CT}} = A^-B^+(j \rightarrow k) = 2^{-1/2}|\cdots i\bar{i}\cdots|(|\cdots j\bar{k}\cdots| + |\cdots k\bar{j}\cdots|), \tag{10}$$

If a sufficiently large number of excited configurations is taken into account, both expansions converge to the same induction energy. However, for limited expansions [7] in terms of locally excited configurations ψ_m^{LE}, the short range induction interactions are seriously underestimated. On the other hand, the use of the charge transfer configurations by themselves leads to a poor representation of long range induction. Unfortunately it is not possible to use both kinds of configurations at the same time as they overlap to some extent, i.e.,

$$<\psi^{\text{LE}}|\psi^{\text{CT}}> \neq 0, \tag{11}$$

and the terms evaluated in such an overcomplete set of configurations will not be additive.

Fortunately, such a dilemma does not arise within the SCF approach. In addition one may separate from $E_{\text{IND}}^{(2)}$ the additive classical long range contribution referred to locally excited configurations only $E_{\text{IND,LE}}^{(2)}$.

The remaining part of the SCF induction energy $E_{\text{IND}}^{(2)}$ consists mainly of the short range charge transfer term $E_{\text{IND,CT}}^{(2)}$. Again, due to possible electron delocalization over the whole AB supersystem a BSSE correction has to be applied.

3. Nature of the Basis Set Superposition Effect

Some interaction energy components defined in exchange perturbation theories [1,2,7] have been shown [2,11] to be equivalent [Eq. (2)] to the contributions obtained in variational SCF LCAO-MO approach. This equivalence has been demonstrated [11] in molecular orbital (MO) notation without specifying the nature of the atomic orbital (AO) expansion. However, the choice of the AO basis set is essential [2–6,12] for the removal of the nonphysical basis set superposition error (BSSE) from the intermolecular interaction energy [Eqs. (3) and (4)]. We now discuss the nature of the BSSE in terms of interaction energy components. This may be done by relating the various molecular

integrals involved to the different interaction energy contributions [7] listed below:

(a) terms defined in the polarization approximation [18]

$$E_{EL}^{(1)}: \quad V_{b,ii}, \langle ii|jj \rangle,$$

$$E_{IND,LE}^{(2)}: \quad V_{b,ii}, \langle ik|jj \rangle;$$

(b) terms involving intermolecular electron exchange and delocalization

$$E_{EX}^{(1)}: \quad V_{b,ii}, \langle ii|jj \rangle, \langle i|j \rangle, V_{b,ij}, \langle ij|ij \rangle, \langle ii|ij \rangle,$$

$$E_{IND,CT}^{(2)}: \quad V_{b,ii}, \langle ii|jj \rangle, \langle i|l \rangle, V_{b,ii}, \langle il|jj \rangle.$$

The following notation is used throughout:

overlap $\quad\quad \langle i|j \rangle \equiv \langle \phi_i(1)|\phi_j(1) \rangle,$ (12)

Coulomb $\quad\quad \langle ij|kl \langle \equiv \langle \phi_i(1)\phi_j(1)|r_{12}^{-1}|\phi_k(2)\phi_l(2) \rangle,$ (13)

nuclear attraction $\quad V_{a,ij} \equiv \langle \phi_i(1)|-Z_a/r_{a1}|\phi_j(1) \rangle,$ (14)

where $\phi_i \in A, \phi_j \in B$ denote occupied and $\phi_k \in A, \phi_l \in B$ vacant molecular orbitals; Z_a, Z_b denote nuclear (or core) charges of the A or B subsystem.

The monomer molecular orbitals may be generally written

$$\phi_i^{A(B)} = \sum_{r \in A}^{AO} c_{ir}\chi_r^A + \sum_{s \in B}^{AO} d_{is}\chi_s^B \quad\quad (15)$$

or

$$\phi_j^{B(A)} = \sum_{r \in A}^{AO} d_{jr}\chi_r^A + \sum_{s \in B}^{AO} c_{js}\chi_s^B. \quad\quad (16)$$

For atomic integrals we use the same notation as for molecular integrals (12)–(14), where r, r' corresponds to AO's in molecule A and s, s' to B subsystem AO's. When employing a monomer basis set ($d_{is} \equiv 0$ and $d_{ir} \equiv 0$) the BSSE is an unavoidable contribution to the interaction energy (4). On the other hand the use of dimer basis set for monomers ($d_{is} \neq 0$ and $d_{jr} \neq 0$) permits the correction of a substantial part of the BSSE by means of the counterpoise method of Boys and Bernardi (3). The d coefficients and the intermolecular atomic overlap integral $\langle r|s \rangle$ vary with the intermolecular distance R as $\sim\exp(-\alpha'R)$, whereas the Coulomb and nuclear attraction integral vary as $\sim R^{-1}$. To estimate the importance of "ghost" orbitals, expand each molecular integral in terms of AO's [Eqs. (15) and (16)], e.g.,

$$V_{b,ii} = \sum_{r \in A} \sum_{r' \in A} c_{ir}c_{ir'}V_{b,rr'} + \sum_{r \in A} \sum_{s \in B} c_{ir}d_{is}V_{b,rs}$$

$$+ \sum_{s \in B} \sum_{r \in A} d_{is}c_{ir}V_{b,rs} + \sum_{s \in B} \sum_{s' \in B} d_{is}d_{is'}V_{b,ss'}. \quad (17)$$

The last three terms, responsible for basis set extension effects, will be small as they involve the product of two small terms, a small d coefficient with a small intermolecular

integral $V_{b,rs}$. Since $V_{b,ii}$ and $\langle ii|jj \rangle$ typify all of the integrals in $E_{EL}^{(1)}$ and $E_{IND,LE}^{(2)}$, basis set extension effects will be negligible in these two contributions.

The second category of interactions, involving intermolecular electron exchange and delocalization, i.e., $E_{EX}^{(1)}$ and $E_{IND,CT}^{(CT)}$ contains $\langle i|j \rangle$, $V_{a,ij}$, $\langle ij|ij \rangle$, and $\langle ii|ij \rangle$ besides the above mentioned integrals. Expanding the intermolecular overlap integral one obtains

$$\langle i|j \rangle = \sum_{r \in A} \sum_{s \in B} c_{ir} c_{js} \langle r|s \rangle + \sum_{r \in A} \sum_{r' \in A} c_{ir} d_{ir'} \langle r|r' \rangle$$

$$+ \sum_{s \in B} \sum_{s' \in B} d_{is} c_{js'} \langle s|s' \rangle + \sum_{s \in B} \sum_{r \in A} d_{is} d_{jr} \langle r|s \rangle. \quad (18)$$

All four terms have about the same magnitude since each of them has a factor $\sim \exp(-\alpha' R)$. The situation is similar for $V_{a,ij}$, $\langle ij|ij \rangle$, and $\langle ii|ij \rangle$. It thus seems clear $E_{EX}^{(1)}$ and $E_{IND,CT}^{(2)}$ remain the main source of BSSE.

4. Test Results and Discussion

The new decomposition scheme has been implemented [20] in MOLASYS [21] as well as the GAUSSIAN 70 [22] program package. For test calculations we selected the hydrogen bonded water dimer at its experimentally determined gas phase structure [23] [Fig. 1(c)] ($R_{00} = 2.98$ Å, $\alpha = 0°$, $\theta = 60°$). In addition, we performed calculations for $R_{00} = 2.68$ and 3.28 Å, and $\alpha = 90°$, $180°$, $\theta = 0°$, $15°$, $45°$, and $75°$ (Table II). Calculations were carried out using the 4-31G basis set [24] and test calculations
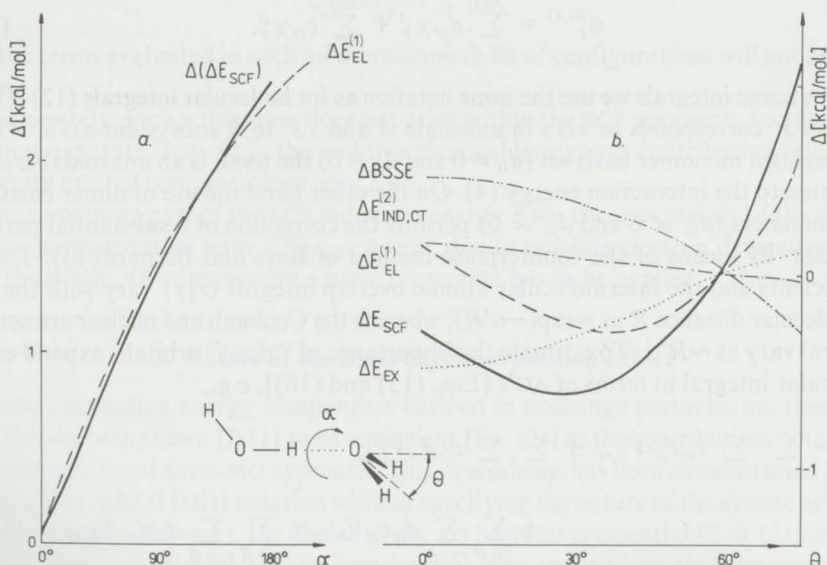

Figure 1. Difference of SCF interaction energy components for linear water dimer at $R_{00} = 2.98$ Å; (a) $\theta = 60°$; (b) $\alpha = 0°$.

TABLE II. SCF interaction energy components for $(H_2O)_2$ in kcal/mol.

Basis Set	4-31G[24]									MODPOT[25]	All electron[25] (as in MODPOT)
R_{oo}[Å]	2.68	2.98*	3.28	2.98	2.98	2.98	2.98	2.98	2.98	2.98*	2.98*
α	0	0	0	90	180	0	0	0	0	0	0
θ	60	60	60	60	60	0	15	45	75	60	60
$E_{EL}^{(1)}$	-15.720	-8.900	-5.726	-7.553	-6.540	-8.730	-8.976	-9.159	-8.252	-6.775	-6.877
$E_{EX}^{(1)}$	15.158	4.379	1.110	4.393	4.403	3.903	3.945	4.228	4.497	3.630	3.697
$BSSE^{(1)}$	-1.273	-0.197	0.105	-0.210	-0.222	-0.204	-0.203	-0.203	-0.180	0.343	0.242
$E^{(1)}$	-0.562	-4.520	-4.615	-3.159	-2.138	-4.826	-5.030	-4.931	-3.754	-3.145	-3.179
$E_{IND,LE}^{(2)}$	-0.926	-0.457	-0.253	-0.444	-0.437	-0.629	-0.623	-0.534	-0.369	-0.208	-0.200
$E_{IND,CT}^{(2)}$	-3.498	-1.241	-0.448	-1.242	-1.243	-1.062	-1.079	-1.188	-1.261	-1.077	-1.064
$BSSE^{(2)}$	-0.602	-1.244	-1.275	-1.250	-1.282	-0.714	-0.742	-1.002	-1.552	-1.773	-1.761
$E^{(2)}$	-4.424	-1.698	-0.701	-1.686	-1.679	-1.691	-1.702	-1.723	-1.630	-1.285	-1.263
BSSE	-1.875	-1.442	-1.170	-1.461	-1.504	-1.919	-0.945	-0.206	-1.732	-1.430	-1.519
ΔE_{SCF}	-4.986	-6.219	-5.316	-4.845	-3.817	-6.518	-6.733	-6.654	-5.385	-4.431	-4.443
ΔE_{SCF}^{*} BSSE	-6.862	-7.661	-6.487	-6.306	-5.321	-7.437	-7.678	-7.861	-7.118	-5.861	-5.962

* Experimental structure of $(H_2O)_2$ [23].

were carried out using our standard MODPOT basis set [25] along with the respective all electron basis set and compared with some 6-31G* and 6-31G** results. The results presented in Table II indicate the significant role of BSSE corrections in determining the short range exchange repulsion term $E_{EX}^{(1)}$ and charge transfer contribution to induction term $E_{IND,CT}^{(2)}$. At shorter intermolecular distances the first order BSSE[(1)] contribution dominates the total BSSE value. For longer distances the higher order $BSSE^{(R)}$ = BSSE − BSSE[(1)] prevails leading to a substantial error in the uncorrected CT term [10,11]. This finding has also been confirmed in our forthcoming systematic studies for 12 hydrogen bonded dimers [17]. To study the angular dependence we performed calculations for different angles α and θ at the equilibrium distance R_{oo} = 2.98 Å [Fig. 1(c)]. In the first case [Fig. 1(a)] and in $\Delta\Delta E_{SCF}$ energy changes are almost entirely due to electrostatic term changes $\Delta E_{EL}^{(1)}$. Also, the θ dependence is essentially determined by electrostatic contribution and to some extent by exchange term [Fig. 1(b)]. BSSE seems to be important in this case [Fig. 1(b)].

Finally, we compare the 4-31G results with the values obtained in our previously optimized minimal MODPOT basis set [25] with and without the use of the effective core model potential. The use of the model potential does not seem to introduce significant error and the corrected ΔE_{SCF} energies for the minimal MODPOT basis set (with and without the use of the model potential) are close to corrected 6-31G* and 6-31G** values (−4.698 and −4.572 kcal/mol) [17]. The corrected induction energies $E_{IND,LE}^{(2)} + E_{IND,CT}^{(2)}$ at equilibrium geometry [23] (−1.698 kcal/mol: 4-31G, −1.285 kcal/mol: MODPOT basis) seem to be close to the most accurate value (−1.63 kcal/mol) derived within exchange perturbation theory [2] in extended $(11,7,2/6,1) \rightarrow [4,3,2/2,1]$ basis set.

The recent work of Karlström [16] favors the full ($k = 1$) counterpoise correction, Higher order BSSE corrections have been also extensively discussed recently by Karlström and Sadlej [26].

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