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On the non-additivity of the basis set superposition error and how to prevent its appearance

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An analytical consideration is made for the simplest possible model in which the BSSE problem may appear. The results demonstrate that BSSE cannot be corrected in any consistent manner by readjusting the monomer energies to the enlarged basis, because the energy effects caused by BSSE and by the true interactions are *not additive.* The way out is to correct BSSE, or prevent its appearance by an appropriate analysis and special treatment *at the supermolecule level,* permitting to keep the supermolecule problem consistent with the monomer calculations, as provided by the "chemical Hamiltonian" approach recently introduced.

Key words: Basis set superposition error (BSSE) — BSSE, non-additivity of — BSSE, preventing appearance of — Intermolecular interactions — Supermolecule calculations

1. Introduction

It is well known that "supermolecule" calculations of intermolecular interactions usually exhibit a spurious energy lowering called "basis set superposition error" (BSSE). Its source is that the *intra*molecular energy of the individual constituent molecules ("monomers") becomes lower *within the supermolecule* than that for the free molecules, because the basis orbitals of the partner molecule also become (at least in part) available. Thus, BSSE represents an artefact arising from the incompleteness of the monomer basis sets.

Usual schemes for correcting the results of calculations for BSSE consist of *readjusting the monomer energies* to the enlarged basis. For this reason the monomers are recalculated at every supermolecule geometry either in the whole supermolecule basis [1-3], or in the monomer basis extended only with the virtual orbitals of the intervening partner molecule [4]. It is much debated until now (e.g. [5-10]) which scheme is more appropriate. However, we shall show here that neither of them is really satisfactory, because it is *conceptually wrong* to correct BSSE by manipulating the monomer energies; instead, BSSE must be eliminated by an appropriate analysis and special treatment of the supermolecule problem. Therefore, we shall consider analytically the simplest possible model for which the BSSE problem may appear.

2. The model

Let us consider two molecules and take into account explicitly only one orbital on each: the occupied orbital φ_1 on molecule A and the empty orbital φ_2 on molecule B. For the sake of simplicity we consider explicitly only the one-electron part $\hat{h}$ of the Hamiltonian and restrict ourselves to the cases in which all effects (both BSSE and true physical interactions) are weak enough to justify a perturbational treatment up to first order in wave function and second order in energy. We have to take into account the overlap $s_{12}=\langle\varphi_1|\varphi_2\rangle$ and perform the very simple calculations giving the orbital $\varphi_1'=\mathcal{N}(\varphi_1+\eta\varphi_2)$ and the energy $E=h_{11}+\varepsilon^{(2)}$. Here $\mathcal{N}$ is a normalization constant, η is the parameter describing the delocalization (charge transfer), $h_{ij}=\langle\varphi_i|\hat{h}|\varphi_j\rangle$, and $\varepsilon^{(2)}$ is the second order energy correction (h_{12}, s_{12} and η are considered first order quantities).

Now we shall compare the results obtained for $\varepsilon^{(2)}$ by specifying the Hamiltonian for two different cases. The first corresponds to the usual "counterpoise" methods of correcting BSSE: the nuclei of molecule A are considered only, whereas φ_2 is a "ghost orbital". Thus in this case the Hamiltonian is that of molecule A: $\hat{h}^{\mathrm{A}}=\frac{1}{2}\Delta+U_{\mathrm{A}}$ ($U_{\mathrm{A}}=-\sum_{\alpha\in\mathrm{A}}Z_\alpha/r_\alpha$ is the potential of molecule A). For this case we introduce the subscript "BSSE" because both η and $\varepsilon^{(2)}$ differ from zero due only to the incompleteness of basis set on A, being unrelated to any physical interaction between the two molecules[1]. We have

$$\eta_{\mathrm{BSSE}}=-\frac{h_{21}^{\mathrm{A}}-s_{21}h_{11}^{\mathrm{A}}}{h_{22}^{\mathrm{A}}-h_{11}^{\mathrm{A}}};\qquad \varepsilon_{\mathrm{BSSE}}^{(2)}=(h_{12}^{\mathrm{A}}-s_{12}h_{11}^{\mathrm{A}})\eta_{\mathrm{BSSE}}. \tag{1}$$

In the second case both BSSE and the actual intermolecular interactions are present; the Hamiltonian is that of the "supermolecule": $\hat{h}^{\mathrm{AB}}=-\frac{1}{2}\Delta+U_{\mathrm{A}}+U_{\mathrm{B}}=\hat{h}_{\mathrm{A}}+U_{\mathrm{B}}$ ($U_{\mathrm{B}}=-\sum_{\alpha\in\mathrm{B}}Z_\alpha/r_\alpha$). In this case the delocalization correction is

$$\eta_{\mathrm{AB}}=-\frac{h_{21}^{\mathrm{AB}}-s_{21}h_{11}^{\mathrm{AB}}}{h_{22}^{\mathrm{AB}}-h_{11}^{\mathrm{AB}}}=K\eta_{\mathrm{BSSE}}+\eta_{U_{\mathrm{B}}}. \tag{2}$$

Here $K=(h_{22}^{\mathrm{A}}-h_{11}^{\mathrm{A}})/(h_{22}^{\mathrm{A}}-h_{11}^{\mathrm{A}}+U_{22}^{\mathrm{B}}-U_{11}^{\mathrm{B}})$, which may differ considerably from unity. The delocalization component due to the true interaction (potential U_{B})

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[1] $\eta\equiv 0$ and $E\equiv h_{11}^{\mathrm{A}}$ if φ_1 is a true eigenfunction of $\hat{h}^{\mathrm{A}}$

is $\eta_{U_\mathrm{B}} = -(U^\mathrm{B}_{21} - s_{21} U^\mathrm{B}_{11})/(h^\mathrm{AB}_{21} - h^\mathrm{AB}_{11})$. The second order energy correction becomes

$$\begin{aligned}\varepsilon^{(2)}_\mathrm{AB} &= (h^\mathrm{AB}_{12} - h^\mathrm{AB}_{11} s_{12})\eta_\mathrm{AB} \\ &= K\varepsilon^{(2)}_\mathrm{BSSE} + K(U^\mathrm{B}_{12} - U^\mathrm{B}_{11} s_{12})\eta_\mathrm{BSSE} + (h^\mathrm{AB}_{12} - h^\mathrm{AA}_{11} s_{12})\eta_{U_\mathrm{B}}.\end{aligned} \tag{3}$$

Equation (3) shows that the energy effects connected with the delocalization (charge transfer) caused by BSSE and by true intermolecular interactions, respectively, *are not additive*, while all the usual schemes of BSSE correction tacitly assume such an additivity. (Note that usual second order PT also exhibits a similar non-additivity, even for weak interactions, if they involve the same excited states; this is, in fact, the case in our model, too. For another example of non-additive delocalization effects see [11].) The non-additive terms of the present simple model also enter all realistic calculations. We must conclude, therefore, that BSSE *cannot be corrected consistently by readjusting the monomer energies.* Consequently, one has to correct BSSE *at the level of supermolecule calculations.* The necessary theoretical tools are provided by the recent "chemical Hamiltonian" approach [12, 13], offering the possibility to prevent the appearance of BSSE at the very beginning. Therefore all terms like η_BSSE must be annihilated by readjusting the supermolecule treatment (the intermolecular one- and two-electron integrals). Excluding all the non-physical BSSE components, the interferences (cross-terms) between BSSE and true interactions will also be avoided.

In our model we can rewrite η_BSSE as

$$\eta_\mathrm{BSSE} = -\frac{1}{h^\mathrm{A}_{22} - h^\mathrm{A}_{11}} \langle\varphi_2|(1 - |\varphi_1\rangle\langle\varphi_1|)\hbar^\mathrm{A}|\varphi_1\rangle \tag{4}$$

indicating explicitly that BSSE originates from the non-zero projection of the function $\hbar^\mathrm{A}|\varphi_1\rangle$ on the orthogonal complement of $|\varphi_1\rangle$. In the general case we must take into account all the basis orbitals $|\chi_\mu\rangle$ of molecule A and introduce the operator of projection onto their subspace, $\mathscr{P}_\mathrm{A} = \sum_{\mu,\nu\in\mathrm{A}} |\chi_\mu\rangle(\boldsymbol{S}^{-1}_\mathrm{A})_{\mu\nu}\langle\chi_\nu|$ ($\boldsymbol{S}^{-1}_\mathrm{A}$ is the inverse overlap matrix of the monomer). Using this operator, every function $\hbar^\mathrm{A}|\chi_\mu\rangle$ ($\mu \in \mathrm{A}$) can be decomposed (cf. also [13, 14]) into "physical" and "non-physical" (basis incompleteness, BSSE) components: $\hbar^\mathrm{A}|\chi_\mu\rangle \equiv \mathscr{P}_\mathrm{A}\hbar^\mathrm{A}|\chi_\mu\rangle + (1 - \mathscr{P}_\mathrm{A})\hbar^\mathrm{A}|\chi_\mu\rangle$. The first term is the component within the molecular basis; it is the only term present in the monomer calculation. The second term gives rise to BSSE, as it represents the projection of $\hbar^\mathrm{A}|\chi_\mu\rangle$ onto the orthogonal complement of the molecular basis. This term is absent (neglected) in the monomer calculation, and must be excluded from the supermolecule calculation as well, to keep the latter consistent with the description of the monomers. Accordingly, in order to eliminate BSSE we have to readjust the intermolecular integrals in the supermolecule by conserving their physical (BSSE-free) components only. Thus in the supermolecule calculation one has to replace $\langle\chi_\nu|\hbar_\mathrm{A}|\chi_\mu\rangle$ ($\mu \in \mathrm{A}$; $\nu \notin \mathrm{A}$) with $\langle\chi_\nu|\mathscr{P}_\mathrm{A}\hbar^\mathrm{A}\chi_\mu\rangle = \sum_{\rho,\tau\in\mathrm{A}} S_{\nu\rho}(\boldsymbol{S}^{-1}_\mathrm{A})_{\rho\tau}\langle\chi_\tau|\hbar^\mathrm{A}|\chi_\mu\rangle$ and drop the BSSE component $\langle\chi_\nu|(1 - \mathscr{P}_\mathrm{A})\hbar^\mathrm{A}\chi_\mu\rangle$. Similarly, using Eq. (35b) of Ref. [12] we get the BSSE-free component of the two-electron integral $[\chi_\lambda(1)\chi_\sigma(2)|\chi_\mu(1)\chi_\nu(2)]$ (μ, $\nu \in \mathrm{A}$; $\lambda \notin B$ and/or $\sigma \notin \mathrm{B}$) as $\sum_{\rho,\tau,\eta,\gamma\in\mathrm{A}} S_{\lambda\rho}S_{\sigma\tau}(\boldsymbol{S}^{-1}_\mathrm{A})_{\rho\eta}(\boldsymbol{S}^{-1}_\mathrm{A})_{\tau\gamma}[\chi_\eta\chi_\gamma|\chi_\mu\chi_\nu]$. In this manner BSSE can be completely eliminated at the supermolecule level: by performing a monomer calculation in the whole supermolecule basis with the readjusted integral values one recovers the energy of the free monomer molecule.

Combining these modifications of integrals with a specific second quantized formalism, the total many-electron Hamiltonian can be decomposed [12] into effective intramolecular Hamiltonians, the operator of intermolecular interactions and that of BSSE. The expectation value of the latter gives the actual BSSE content of a usual supermolecule energy [12], whereas by dropping it from the Hamiltonian one can develop perturbation [14-16], SCF [17] etc. theories of intermolecular interactions intrinsically free of BSSE.

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