

SOME FORMAL ASPECTS OF THE THEORY OF INTERMOLECULAR INTERACTIONS AND OF THE BSSE PROBLEM

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Dedicated with deepest respect to Professor Rudolf Zahradník on the occasion of his 80th birthday.

Some results of mathematical character concerning the theory of intermolecular interactions and the BSSE problem are presented. It is shown that the concept of complete basis set may be introduced for intermolecular potential surfaces only by considering explicitly the limiting process in which the basis sets of both monomers approach completeness simultaneously. That does not lead to any overcompleteness problem if we do not postulate the existence of two complete basis sets from the outset. The intimate connection between the BSSE and the differences of some biorthogonal integrals and their "original" counterparts is also discussed. The operator of BSSE is given in terms of such differences. It is shown that in a special case, when only the overlap of the occupied orbitals is considered, the "bi-expectation" value of the energy coincides with the conventional expectation value for the single determinant wave function built up of the unperturbed orbitals of the individual monomers. It is discussed, by using a model of the biorthogonal perturbation theory, why the conceptually fully different *a priori* (CHA) and *a posteriori* (CP) schemes of BSSE correction usually give very close numerical results. (The necessary biorthogonal perturbation formalism is developed in the Appendices.) The results give justification for the additivity assumptions inherent in the CP method.

Keywords: Quantum chemistry; Hamiltonian; Basis set superposition error; Wave function; Biorthogonal Hylleraas functional.

The present author has been involved for some decades in the theory of intermolecular interactions (one of the favorable fields of Prof. Zahradník). During that time a number of interesting results have been obtained which, however, remained unpublished as they did not fit well in the papers we had actually written. The aim of this note is to collect some of these minor results and present them in this special issue.

Our considerations will be, in that or another manner, related to the so called “basis set superposition error” (BSSE) problem. BSSE is not a physical phenomenon, but a mathematical effect of using finite – hence incomplete – basis sets. If one calculates the interaction energy between two weakly bonded molecules (“subsystems” or “monomers”) A and B in the seemingly most straightforward manner, i.e., as the difference between the energy of the supersystem (“dimer” or “supermolecule”) AB and the sum of the free monomer energies:

$$\Delta E_{AB}^{\text{uncorr}} = E_{AB}(\text{AB}) - E_A(\text{A}) - E_B(\text{B}) \quad (1)$$

then too deep minima are often obtained, especially if small basis sets are applied. Hereafter the subscripts denote the systems calculated and the basis set applied in a calculation is indicated in parentheses. (In the present paper all the basis functions are assumed to belong either to monomer A or monomer B, as is the case in most practical calculations.) As it can be seen, in this simplest “uncorrected” calculation every (sub)system is calculated by using its own basis set. BSSE appears as the consequence of the fact that the supermolecule is calculated by using a larger basis than that of the monomers, and the appearance of the partner monomer basis orbitals leads to an energetically somewhat better description of the internal electronic structure of the individual monomers, i.e., to some lowering of $E_{AB}(\text{AB})$ which is out of balance with respect of the free monomer energies $E_A(\text{A})$ and $E_B(\text{B})$ calculated by using only the monomer basis sets. The basic method of correcting BSSE is the classical (and ingenious) “counterpoise correction” (CP) scheme of Boys and Bernardi¹ (BB), applied even somewhat before by Ross and Jansen² in an actual application. In this scheme the interaction energy between two molecules A and B is determined by using the union of the basis sets (“dimer” or “supermolecule” basis) for calculating every quantity:

$$\Delta E_{AB}^{\text{CP}} = E_{AB}(\text{AB}) - E_A(\text{AB}) - E_B(\text{AB}) . \quad (2)$$

It may be noted that Boys and Bernardi¹ devised their scheme considering it explicitly as a method for “error cancellation”, which “does not so much solve the various difficulties (...) as much as arrange that they do not occur in explicit form”. Later some researchers assumed the BB scheme to be “exact”, which we cannot accept (see below), although we definitely do not wish to question the importance and usefulness of this method.

The BB scheme is an *a posteriori* correction scheme as it uses the supermolecule energy “spoiled” by BSSE and corrects it by adapting the monomer energies to the situation “to be occupied” in the complex. The present author has introduced the *a priori* method of excluding BSSE by using the “Chemical Hamiltonian Approach” (CHA), in which the free monomer energies $E_A(A)$, $E_B(B)$ are not manipulated, but the Hamiltonian of the interacting system is analyzed as to identify and exclude the terms causing BSSE. (As most important references we give refs³⁻⁷.) As BSSE is not a physical phenomenon, it does not correspond to any Hermitian operator, and the BSSE-free CHA Hamiltonian is non-Hermitian. This non-Hermitian Hamiltonian is used for calculating the BSSE-free wave functions, while the energy corresponding to that wave function is calculated as a conventional expectation value with the usual (Hermitian) Hamiltonian of the system (“CHA with conventional energy”, CHA/CE method).

An interesting and very rewarding observation is that the CP and CHA methods usually give very close numerical results at any level of theory. Moreover, it is the general observation that when the basis set improves, the difference between the results of these BSSE-corrected methods diminishes much faster than BSSE disappears from the uncorrected interaction energies. Thus the results obtained by using these two, conceptually quite different schemes corroborate each other to a very great extent. Despite some theoretical consideration already presented^{8,9}, this success still needs some more detailed explanations.

APPROACHING THE COMPLETE BASIS LIMIT

We cannot accept the most common argument used in favor of the assumption that the CP correction scheme is ideal or even “exact”, just because “everything is computed in the same basis”. In fact, this recipe can not be used to account for the changes of the monomer geometries (“monomer relaxation”) taking place during the intermolecular interactions. It has been found that the shape of the CP-corrected potential energy surfaces (gradients of the CP-corrected energy, differences of conformer energies, etc.) need to be computed by considering the monomer distortions in the free monomer (and not dimer) basis sets^{10,11}. One indeed must compute the monomer relaxation by using the monomer basis, because in the dimer basis the relaxation energy becomes mathematically meaningless: it becomes ill-defined and one obtains different results for the same configuration depending on what cross-section of the potential surface is studied¹¹. Therefore monomer relaxation may be computed in the free monomer

basis only. This means that the interaction energy in the most general case should be calculated as^{10,11}

$$\Delta E_{AB}^{CP} = E_{AB}^{CP}(AB) - E_A^R(AB) - E_B^R(AB) + E_A^R(A) - E_A^0(A) + E_B^R(B) - E_B^0(B) \quad (3)$$

where the superscripts R indicate the monomer geometry within the complex and subscript 0 that of the free monomer. The first 3 terms give the CP-corrected interaction energy between the monomers in their actual configurations within the complex, while the remaining ones account for the energy that is necessary to distort the monomers. Geometry optimization of complexes, based on this algorithm (as implemented by P. Salvador) is available in the Gaussian program system. By finding the minimum of the expression on the right-hand side of Eq. (3) one can determine the geometry of the complex corresponding to the deepest CP-corrected interaction energy.

One must also keep in mind that calculating the monomers in the dimer basis set may lead to quite non-physical distortions of the wave functions – e.g., free atoms acquire a non-zero dipole moment. Therefore, they are not really adequate as starting wave functions for calculating the actual interactions; instead, they should only be considered as auxiliary entities used to estimate the actual BSSE content of the supermolecule energy.

A more challenging, abstract argument used to support the assumption of the CP method being “exact” is the following. (Monomer relaxation is not considered in that case.) Let us assume that neither of monomers A and B have a complete basis, but the union of these basis sets (the basis “AB”) is complete. Then all the energies entering Eq. (2) are exact and the same holds for the energy difference calculated by its use. This is obviously true for a single point for the (fictitious) case considered. However, we are usually interested in full potential curves. Changing the intersystem distance, sooner or later the basis “AB” ceases to be complete as the basis orbitals will be shifted; it definitely cannot be complete in the limit of infinite separation, where one has two free monomers. At infinite distance one should get the sum of the monomer energies calculated in two independent monomer calculations – this is a must in any meaningful theory. But neither of monomers carries a complete basis, so the energies obtained in the limit of infinite separation cannot be exact. This means that – when computing whole potential curves – one can approach the limit of exact calculations only if the basis sets on both monomers become complete simultaneously.

Thus, it is an interesting mathematical problem whether one can consider the limiting case in which the basis sets of both monomers approach completeness without meeting the problem of overcompleteness. Obviously, if we postulate from the outset that both monomers carry an infinite and complete basis set, then we have overcompleteness. But one may avoid any overcompleteness problem by constructing properly the limiting process leading to complete basis sets on each monomer.

To illustrate the idea, let us consider a simple mathematical problem, in which we have two unit vectors in a plane, \mathbf{r}_1^0 and \mathbf{r}_2^0 , which approach each other. The normalized sum and difference of them determines the direction of two orthogonal vectors spanning the plane. These two vectors exist even in the limit $\mathbf{r}_1^0 \rightarrow \mathbf{r}_2^0$, so the two-dimensionality of the manifold (plane) is conserved even in this limit. Only if we start by assuming $\mathbf{r}_1^0 \equiv \mathbf{r}_2^0$, the plane will degenerate to a line and we will have overcompleteness. As another analogy, we recall the known fact that the limit of the normalized difference of two s orbitals with the same exponent, approaching each other, is a p orbital with the same exponent.

Thus, we think that a mathematically correct study of approaching the complete basis limit should not be based on the assumption that we do already have a complete basis distributed “half here – half there”, but rather on investigating the process in which the basis sets on both monomers increase and in the limit become complete. That is a meaningful task, as we may indeed study the monomers with larger and larger basis sets, while we will never have in practice a situation in which basis “AB” is already complete.

The problem may be dealt by making use of Löwdin’s “pairing theorem”¹²⁻¹⁴. Let us consider two sets of basis functions a_i and b_i put at some distance with respect to each other. With no loss of generality one may assume that they form two orthonormal sets, i.e.,

$$\langle a_i | a_j \rangle = \langle b_i | b_j \rangle = \delta_{ij} . \quad (4)$$

According to Löwdin’s pairing theorem, it is always possible to subject the sets $\{a_i\}$ and $\{b_i\}$ to separate unitary transformations to ensure that the intersets overlaps differ from zero only in pairs:

$$\langle a_i | b_j \rangle = \lambda_i \delta_{ij} . \quad (5)$$

As the number of functions in sets $\{a_i\}$ and $\{b_i\}$ increases, and they approach completeness, the λ_i values will tend to unity¹⁵, always remaining (at least

infinitesimally) smaller than unity. They still define a two-dimensional subspace even when the limiting process is performed, in which both sets tend to completeness, and the λ_i -s tend to 1. (All the λ_i values are strictly equal to 1, so all $a_i = b_i$, only when the basis sets are already strictly complete, but not when approaching completeness.) That means that increasing the basis sets on both monomers in a manner that they approach completeness simultaneously will not lead to any overcompleteness problem (in a strict mathematical sense, of course). Here we are, in fact, faced with a delicate problem of infinities, like that the cardinality of the even numbers is equal to that of all the natural ones. So we may conclude that overcompleteness appears only if we start our considerations by assuming that we already have two complete sets – one on each monomer – but one may consider the simultaneous convergence of the both molecular bases to the basis set limit without entering a mathematical trouble.

BIORTHOGONAL INTEGRALS AND THE BSSE PROBLEM

By using second quantization formalism, the Born–Oppenheimer Hamiltonian H of a molecule can be written in terms of the integrals over the orthonormalized (occupied and virtual) molecular spin-orbitals φ_i and the creation and annihilation operators $\hat{\varphi}_i^+$, $\hat{\varphi}_i^-$ corresponding to them (we use Longuet–Higgins's¹⁶ notations indicating explicitly to what orbital the creation/annihilation operators do refer) as

$$\hat{H} = \sum_{a < b} \frac{Z_a Z_b}{R_{ab}} + \sum_{i,j} \langle \varphi_i | \hat{h} | \varphi_j \rangle \hat{\varphi}_i^+ \hat{\varphi}_j^- + \frac{1}{2} \sum_{i,j,k,l} [\varphi_i \varphi_j | \varphi_k \varphi_l] \hat{\varphi}_i^+ \hat{\varphi}_j^+ \hat{\varphi}_l^- \hat{\varphi}_k^- \quad (6)$$

where the first term describes nuclear–nuclear repulsion, \hat{h} is the one-electron Hamiltonian and the convention [12|12] is used for the two-electron integrals. (All integrals include summations over the spins.)

If one considers two interacting molecules A and B and describes the supermolecule AB by using the union of the two molecular basis sets, then a number of complications arise because of the intermolecular overlap:

$$\langle \varphi_i | \varphi_j \rangle = S_{ij} \neq \delta_{ij} \quad (7)$$

if i and j refer to different subsystems. (Intrasubsystem orthogonality is conserved, of course.) In the paper³ the present author proposed to keep using in such situations the creation operators $\hat{\varphi}_i^+$ creating electrons on the (non-orthogonal) basis spin-orbitals and defined the respective “effective”

annihilation operators $\hat{\tilde{\varphi}}_i^-$. The terms “effective” means that the set of operators obeys the fermion anticommutation rules

$$\{\hat{\varphi}_i^+; \hat{\tilde{\varphi}}_j^-\} = \hat{\varphi}_i^+ \hat{\tilde{\varphi}}_j^- + \hat{\tilde{\varphi}}_j^- \hat{\varphi}_i^+ = \delta_{ij} \quad (8)$$

thus operator $\hat{\tilde{\varphi}}_i^-$ behaves as the annihilation operator for the MO φ_i , but it is not the adjoint of the creation operator $\hat{\varphi}_i^+$ creating an electron in that spin-orbital; in fact it can be defined as the adjoint of the creation operator for the biorthogonal counterpart to φ_i ; this fact is indicated by the tilde in its notation:

$$\tilde{\varphi}_i = \sum_j S_{ji}^{-1} \varphi_j \quad (9)$$

where S_{ji}^{-1} is a short-hand notation for an element of the inverse overlap matrix. Alternatively, one can consider operator $\hat{\tilde{\varphi}}_j^-$ as an abstract mathematical entity defined by the fermion anticommutation rule (8).

There is a number of ways of writing down the overall Hamiltonian in this formalism; a very compact one is¹⁷

$$\hat{H} = \sum_{a<b} \frac{Z_a Z_b}{R_{ab}} + \sum_{i,j} \langle \tilde{\varphi}_i | \hat{h} | \varphi_j \rangle \hat{\varphi}_i^+ \hat{\tilde{\varphi}}_j^- + \frac{1}{2} \sum_{i,j,k,l} [\tilde{\varphi}_i \tilde{\varphi}_j | \varphi_k \varphi_l] \hat{\varphi}_i^+ \hat{\varphi}_j^+ \hat{\tilde{\varphi}}_l^- \hat{\tilde{\varphi}}_k^- . \quad (10)$$

Of course, now all subscripts run over both subsystems A and B.

Besides using “effective” annihilation operators, this form of the Hamiltonian differs from Eq. (6), which is valid in the case of an orthonormal basis, by using the biorthogonal orbitals (9) in the “bra” parts of the one- and two-electron integrals. That difference of the integrals, however, is an important one, and is intimately related to the BSSE problem.

It may be noted for completeness, that the biorthogonal orbitals, however, do not appear in final expressions of the energy expectation values. In fact, one has³ the equality for the expectation values of the operator string occurring in the one-electron part of the Hamiltonian: $\langle \hat{\varphi}_i^+ \hat{\tilde{\varphi}}_j^- \rangle = (\mathbf{PS})_{ji}$, where \mathbf{P} is the usual finite basis “density matrix” (in terms of spin-orbitals). Then the overlap matrix \mathbf{S} in this expectation value and the inverse overlap matrix in the definition of the biorthogonal orbitals just cancel. Similarly, for the two-electron strings one has³ in the single-determinant case $\langle \hat{\varphi}_i^+ \hat{\varphi}_j^+ \hat{\tilde{\varphi}}_l^- \hat{\tilde{\varphi}}_k^- \rangle = (\mathbf{PS})_{ki} (\mathbf{PS})_{lj} - (\mathbf{PS})_{kj} (\mathbf{PS})_{li}$, again canceling the biorthogonality. (Of course, analogous expressions should also hold in the correlated case, but in the terms of the respective second-order density matrix.)

One can separate the terms in the Hamiltonian (10), all subscripts of which belong to monomer A, and get an operator \hat{H}'_A which in some sense describes monomer A in the overlapping basis of the supersystem

$$\hat{H}'_A = \sum_{\substack{a < b \\ (a, b \in A)}} \frac{Z_a Z_b}{R_{ab}} + \sum_{\substack{i, j \\ (i, j \in A)}} \langle \tilde{\varphi}_i | \hat{h}_A | \varphi_j \rangle \hat{\varphi}_i^+ \hat{\varphi}_j^- + \frac{1}{2} \sum_{\substack{i, j, k, l \\ (i, j, k, l \in A)}} [\tilde{\varphi}_i \tilde{\varphi}_j | \varphi_k \varphi_l] \hat{\varphi}_i^+ \hat{\varphi}_j^+ \hat{\varphi}_l^- \hat{\varphi}_k^- \quad (11)$$

where \hat{h}_A is the one-electron Hamiltonian corresponding to monomer A:

$$\hat{h}_A = \frac{1}{2} \Delta - \sum_{a \in A} \frac{Z_a}{r_A} \quad (12)$$

Obviously, if one considers the full CI wave function of monomer A, which is exact in the finite basis of the free monomer, it will not be an eigenfunction of the operator \hat{H}'_A , written down in terms of the extended AB basis, because \hat{H}'_A contains the biorthogonal integrals. That reflects the fact that the extension of the basis set changes the “free” monomer problem – owing to the variation principle, it will lower the monomer ground state energy even within the complex. This is the cause of BSSE. (The use of the “effective” annihilation operators does not explicitly manifest itself, because they have been constructed to ensure that they behave in the supermolecule basis exactly in the manner as the original annihilation operators do in the original monomer basis.)

When introducing the CHA³, we have performed a special analysis of the “ket functions” entering the one- and two-electron integrals, to exclude the effects giving rise to BSSE. (For a first-quantized discussion, we refer to ref.¹⁸) For that reason, it was requested that the expansion of every function of intramonomer character should be restricted to the respective intramonomer basis, i.e., one should replace them by their projection on the “own” basis

$$\begin{aligned} \hat{h}_A \varphi_i &\Rightarrow \hat{P}_A \hat{h}_A \varphi_i & (i \in A) \\ \frac{1}{r_{12}} \varphi_i(1) \varphi_j(2) &\Rightarrow \hat{P}_A(1) \hat{P}_A(2) \frac{1}{r_{12}} \varphi_i(1) \varphi_j(2) & (i, j \in A) \end{aligned} \quad (13)$$

where the projection operator \hat{P}_A can be written in the “bra-ket” notations simply as:

$$\hat{P}_A = \sum_{i \in A} |\varphi_i\rangle \langle \varphi_i| \quad (14)$$

Applying these substitutions, we arrived after lengthy manipulations to some “effective” monomer Hamiltonians (In the original paper all the expressions were much more complicated because non-orthogonality of the basis orbitals was admitted also within the individual monomers, and the inverse overlap matrices were not “compressed” into the biorthogonal “ket” vectors.)

$$\hat{H}_A^{\text{eff}} = \sum_{\substack{a < b \\ (a, b \in A)}} \frac{Z_a Z_b}{R_{ab}} + \sum_{\substack{i, j \\ (i, j \in A)}} \langle \varphi_i | \hat{h}_A | \varphi_j \rangle \hat{\varphi}_i^+ \hat{\varphi}_j^- + \frac{1}{2} \sum_{\substack{i, j, k, l \\ (i, j, k, l \in A)}} [\varphi_i \varphi_j | \varphi_k \varphi_l] \hat{\varphi}_i^+ \hat{\varphi}_j^+ \hat{\varphi}_l^- \hat{\varphi}_k^- \quad (15)$$

Operators \hat{H}_A^{eff} have the special property, that they act on a monomer wave function in the full supermolecule basis exactly in the same way as the original monomer Hamiltonian does in the monomer basis. As a consequence, if one considers a supermolecule wave function which is built up as an appropriately antisymmetrized product of the exact eigenfunctions (in the finite basis, i.e. full CI, sense) of the individual monomers, then this wave function is an eigenfunction of the sum $\hat{H}_A^{\text{eff}} + \hat{H}_B^{\text{eff}}$, and the sum of eigenvalues is the sum of the free monomer energies³. We use the term “effective” monomer Hamiltonians because, owing to the intermolecular overlap, these properties are achieved at the expense that operators \hat{H}_A^{eff} are non-Hermitian: they contain the “effective” annihilation operators $\hat{\varphi}_i^-$.

As it is easy to see, operator \hat{H}_A^{eff} differs from \hat{H}'_A by replacing all the biorthogonal functions in the one- and two-electron integrals with the respective “original” ones. (As operator \hat{H}'_A “as such” has not actually been defined previously, this juxtaposition has not yet been explicitly made.) We note that the biorthogonal integrals remain in terms of the Hamiltonian describing true intermolecular interactions. The differences between the functions on the two sides of Eqs (13) need not be neglected – they are collected in a special term of the Hamiltonian, responsible for BSSE.

Thus the BSSE effects have an intimate relation with the differences of the biorthogonal and “original” values of those (both intramonomer and intermonomer) one- and two-electron integrals, in which the function in “ket” can be assigned an intramonomer character. It may be worthwhile to look on this point more in detail. Let us consider, for instance, the difference of integrals $\langle \tilde{\varphi}_i | \hat{h}_A | \varphi_j \rangle - \langle \varphi_i | \hat{h}_A | \varphi_j \rangle$, for which $j \in A$, and introduce a resolution of identity as $1 = \hat{P}_A + (1 - \hat{P}_A)$, in accord with the fact that the function $\hat{h}_A | \varphi_j$ has an intramonomer character of monomer A. Then we may write

$$\begin{aligned}
\langle \tilde{\varphi}_i | \hat{h}_A | \varphi_j \rangle - \langle \varphi_i | \hat{h}_A | \varphi_j \rangle &= \langle \tilde{\varphi}_i | (\hat{P}_A + 1 - \hat{P}_A) \hat{h}_A | \varphi_j \rangle - \langle \varphi_i | \hat{h}_A | \varphi_j \rangle \\
&= \langle \tilde{\varphi}_i | \hat{P}_A \hat{h}_A | \varphi_j \rangle - \langle \varphi_i | \hat{h}_A | \varphi_j \rangle + \langle \tilde{\varphi}_i | (1 - \hat{P}_A) \hat{h}_A | \varphi_j \rangle \\
&= \langle \tilde{\varphi}_i | \sum_{k \in A} |\varphi_k\rangle \langle \varphi_k | \hat{h}_A | \varphi_j \rangle - \langle \varphi_i | \hat{h}_A | \varphi_j \rangle + \langle \tilde{\varphi}_i | (1 - \hat{P}_A) \hat{h}_A | \varphi_j \rangle \\
&= \sum_{k \in A} \delta_{ik} \langle \varphi_k | \hat{h}_A | \varphi_j \rangle - \langle \varphi_i | \hat{h}_A | \varphi_j \rangle + \langle \tilde{\varphi}_i | (1 - \hat{P}_A) \hat{h}_A | \varphi_j \rangle \\
&= \langle \tilde{\varphi}_i | (1 - \hat{P}_A) \hat{h}_A | \varphi_j \rangle \tag{16}
\end{aligned}$$

which would vanish if the function $\hat{h}_A | \varphi_j \rangle$ could exactly be expanded with the aid of the basis orbitals assigned to monomer A – thus it is associated with the BSSE effects. Analogous considerations apply to the difference of those two-electron integrals $[\tilde{\varphi}_i \tilde{\varphi}_j | \varphi_k \varphi_l] - [\varphi_i \varphi_j | \varphi_k \varphi_l]$, too, for which the spin-orbitals φ_k and φ_l are centered on the same monomer. (It is to be stressed that the difference between the biorthogonal and “ordinary” integrals does not correspond to a BSSE effect in the cases when the “ket” does not have a well-defined intramonomer character – i.e., for integrals like $\langle \varphi_i | \frac{Z_a}{r_a} | \varphi_j \rangle$ when $a \in A$; $j \in B$ or $[\varphi_i \varphi_j | \varphi_k \varphi_l]$ when $k \in A$; $l \in B$.)

In full accord with these considerations, the explicit expression Eq. (70) in ref.³, giving the term of the Hamiltonian that is responsible for BSSE, can be transformed in the present notations to the very compact form

$$\begin{aligned}
\hat{B} &= \sum_{j \in A} \sum_i \left(\langle \tilde{\varphi}_i | \hat{h}_A | \varphi_j \rangle - \langle \varphi_i | \hat{h}_A | \varphi_j \rangle \right) \hat{\varphi}_i^+ \hat{\varphi}_j^- + \\
&+ \sum_{j \in B} \sum_i \left(\langle \tilde{\varphi}_i | \hat{h}_B | \varphi_j \rangle - \langle \varphi_i | \hat{h}_B | \varphi_j \rangle \right) \hat{\varphi}_i^+ \hat{\varphi}_j^- + \\
&+ \sum_{k, l \in A} \sum_{ij} \left([\tilde{\varphi}_i \tilde{\varphi}_j | \varphi_k \varphi_l] - [\varphi_i \varphi_j | \varphi_k \varphi_l] \right) \hat{\varphi}_i^+ \hat{\varphi}_j^+ \hat{\varphi}_i^- \hat{\varphi}_k^- + \\
&+ \sum_{k, l \in B} \sum_{ij} \left([\tilde{\varphi}_i \tilde{\varphi}_j | \varphi_k \varphi_l] - [\varphi_i \varphi_j | \varphi_k \varphi_l] \right) \hat{\varphi}_i^+ \hat{\varphi}_j^+ \hat{\varphi}_i^- \hat{\varphi}_k^- . \tag{17}
\end{aligned}$$

(Among other steps, the intramonomer overlap matrix considered in ref.³ was substituted a unit matrix and a number of restrictions on the summations were omitted, as they correspond to exclusion of terms which would vanish anyway.)

WHEN THE EXPECTATION AND "BI-EXPECTATION" VALUES COINCIDE

Let us consider a determinant wave function built up of non-orthogonal spin-orbitals φ_i like the "Heitler-London type" zeroth-order wave function which one obtains by using the unperturbed orbitals of two interacting monomers:

$$|\Phi\rangle = \hat{\varphi}_1^+ \hat{\varphi}_2^+ \dots \hat{\varphi}_{N_A}^+ \hat{\varphi}_{N_A+1}^+ \dots \hat{\varphi}_{N_A+N_B}^+ |0\rangle. \quad (18)$$

The energy E corresponding to this wave function is defined by the expectation value

$$E = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}. \quad (19)$$

Direct calculation of the integrals $\langle \Phi | \hat{H} | \Phi \rangle$, $\langle \Phi | \Phi \rangle$ occurring in this expression is troublesome due to the overlap of the orbitals; instead one introduces any set of orthonormalized orbitals spanning the same subspace as the occupied non-orthogonal orbitals φ_i , e.g. the Löwdin-orthogonalized ones

$$\psi_j = \sum_i S_{ij}^{-1/2} \varphi_i \quad (20)$$

where $S_{ij}^{-1/2}$ is a shorthand for the elements of the matrix $\mathbf{S}^{-1/2}$, and calculates the same energy E which is defined in Eq. (19) by using these orthonormalized orbitals and Slater rules:

$$E = \sum_{a < b} \frac{Z_a Z_b}{R_{ab}} + \sum_i \langle \psi_i | \hat{h} | \psi_i \rangle + \frac{1}{2} \sum_{i,j} [\psi_i \psi_j | | \psi_i \psi_j] \quad (21)$$

where the "double bars", as usual, indicate the difference

$$[\psi_i \psi_j | | \psi_i \psi_j] = [\psi_i \psi_j | \psi_i \psi_j] - [\psi_i \psi_j | \psi_j \psi_i]. \quad (22)$$

We recall that Eq. (21) is written down in terms of spin-orbitals.

Now, pairs of $S_{ij}^{-1/2}$ matrix elements can be combined to give one matrix element of matrix \mathbf{S}^{-1} , which leads to the appearance of the biorthogonal orbitals; we write down explicitly the one-electron term:

$$\begin{aligned} \sum_i \langle \psi_i | \hat{h} | \psi_i \rangle &= \sum_i \langle \sum_j S_{ji}^{-1/2} \varphi_j | \hat{h} | \sum_k S_{ki}^{-1/2} \varphi_k \rangle = \sum_{i,j,k} S_{ki}^{-1/2} S_{ij}^{-1/2} \langle \varphi_j | \hat{h} | \varphi_k \rangle \\ &= \sum_{j,k} S_{kj}^{-1} \langle \varphi_j | \hat{h} | \varphi_k \rangle = \sum_k \langle \tilde{\varphi}_k | \hat{h} | \varphi_k \rangle. \end{aligned} \quad (23)$$

Proceeding analogously also with the two-electron part, we arrive at

$$E = \sum_{a < b} \frac{Z_a Z_b}{R_{ab}} + \sum_i \langle \tilde{\varphi}_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_{i,j} [\tilde{\varphi}_i \tilde{\varphi}_j | | \varphi_i \varphi_j]. \quad (24)$$

If we define the determinant wave function $|\tilde{\Phi}\rangle$ built up of the biorthogonal orbitals $\tilde{\varphi}_i$, then we have the equality (as $\langle \tilde{\Phi} | \Phi \rangle = 1$)

$$E = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\langle \tilde{\Phi} | \hat{H} | \Phi \rangle}{\langle \tilde{\Phi} | \Phi \rangle}. \quad (25)$$

It is to be stressed that this equality between expectation and “bi-expectation” values holds only due to the fact that no virtual orbitals were considered when forming the matrix $S^{-1/2}$. In the general case, Eq. (25) represents only an approximation, which deteriorates with the increase of the overlap of the occupied orbitals of one monomer with the virtual orbitals of another one.

INTERRELATION BETWEEN THE *a priori* CHA AND *a posteriori* CP SCHEMES OF BSSE CORRECTION: A BIORTHOGONAL ANALYSIS

As noted in Introduction, the *a priori* CHA and *a posteriori* CP schemes of BSSE correction usually give surprisingly close numerical results, and their agreement improves as the basis sets improve. A qualitative discussion of this phenomenon has been given by using a very simple model in which different perturbations of an unperturbed Hermitian operator were analyzed⁹. However, Hermiticity means orthogonality of the unperturbed basis functions, while the natural basis for studying intermolecular interactions consists of the antisymmetrized pairs of wave functions describing different states of the free monomers (including electron transfer states); owing to intermolecular overlap, these functions form a non-orthogonal many-electron basis. For that reason we are going to extend the analysis given in⁹ to the case when the problem is treated in the framework of biorthogonal generalizations of the Rayleigh–Schrödinger perturbation theory (PT) and of the Hylleraas functional. (The necessary formalism is developed in Appendices.)

The Additivity Assumption of the CP Scheme

The problem of the relations between the CHA and CP schemes is directly related to the implicit additivity assumption inherent in the CP scheme. That additivity assumption can be best seen if one does not restrict the consideration to a single geometric arrangement of the interacting molecules, but constructs their potential energy surface (PES). The sum of the free monomer energies $E_A + E_B$ fixes the value of the PES at the infinite distance, so the CP-corrected interaction energy (Eq. (2) defines in a natural manner also the CP-corrected total energy⁶:

$$E_{AB}^{CP} = \Delta E_{AB}^{CP} + E_A(A) + E_B(B). \quad (26)$$

Substituting here Eq. (2) and regrouping the terms, we get

$$E_{AB}^{CP} = E_{AB}(AB) + [E_A(A) - E_A(AB)] + [E_B(B) - E_B(AB)]. \quad (27)$$

Here the total energy is subjected to a correction by using the results of the “ghost orbitals” calculations. Although the difference between using Eq. (2) and Eq. (27) may appear immaterial when a single point is considered, there are different theoretical arguments in favor of using Eq. (27) as the basic entity^{6,9}.

The same logic can be applied to Eq. (3) with no difficulties. Instead of the BSSE-corrected interaction energy pertinent to the monomer geometries in the complex, we may collect the “ghost-orbitals” energy lowerings corresponding to the same geometries; the terms with the unrelaxed monomer energies $E_A^0(A)$, $E_B^0(B)$ cancel with the energy in the infinity. Thus we get for the CP-corrected total energy with relaxed monomers the formula with exactly the same structure as that of Eq. (27):

$$E_{AB}^{CP} = E_{AB}(AB) + [E_A^R(A) - E_A^R(AB)] + [E_B^R(B) - E_B^R(AB)] \quad (28)$$

which is in full agreement with the notion that BSSE is related to the monomers within the complex.

Equations (27) and (28) mean that we transform the energy lowerings obtained in the “ghost orbitals” calculations to the exactly the same energy increase in the complex total energy. That is the equivalent of stating that the BSSE which is present in the uncorrected energy of the complex is just equal to the sum of energy lowerings obtained in the “ghost orbitals” calculations. This means that BSSE and the true interactions are considered additive. This very strong additivity assumption requires some justification.

The existence of such an additivity is by far not trivial. The energy corrections of the CP scheme (energy lowerings in the ghosts orbitals calculations) are governed by the matrix elements of the BSSE operator only. At the same time, in the supermolecule the excitation from the ground state to each excited state is caused, in general, by the sum of the matrix elements of BSSE and of the true physical interaction. It is easy to see that such a sum leads to additive first-order wave functions in a perturbational approach, but to non-additive energy corrections; there will be interferences (cross-terms between these matrix elements) spoiling additivity¹⁹.

Therefore, the evident success of the CP scheme requires some refined discussion, superseding that in¹⁹. It is easy to see that the CP scheme can be considered a conceptually correct approach if (and only if) one can show that there is a “true” (or “best”) BSSE-free energy which differs from the uncorrected one by terms expressed in the matrix elements of the BSSE operator only; that difference is determined (or, at least, approximated) by the “ghost orbitals” calculations. Such an improved energy value is indeed available – it is provided by the CHA/CE scheme.

Thus, in order to give support to the CP method, one has to show that the deviation of the uncorrected energy from the “best” (CHA/CE) energy value can be expressed by the matrix elements of the BSSE-operator only.

The CHA/CE Scheme Justifying the Additivity Assumption of CP

The key point is that for systems exhibiting BSSE, the correct energy must not be calculated by considering the net effect of the pure interactions only. That has been known since the early days of symmetry adapted perturbation theory, when calculating the first-order energy in the standard manner as the expectation value of the “true” intermolecular perturbation (i.e., electrostatic interactions of the electrons and nuclei of one molecule with those of the other one) over the unperturbed wave functions led to completely wrong results. That behaviour was directly associated with the fact that the wave functions used for the monomers were not the exact solutions of the individual monomer problems. (If the monomer wave functions were exact, no BSSE problem existed, of course, either.) Then the situation was corrected by introducing the so called Murrell corrections²⁰, which means that one has to calculate explicitly the expectation value of the total intermolecular Hamiltonian if approximate monomer functions are used, and not only the expectation value of the pure perturbation. In terms of operators introduced in³ this means that one has to calculate the expectation value of the sum of the “pure” intermolecular interactions and

of BSSE – that is inevitable to account properly for the “overlap repulsion of closed shells”. The same holds if one approaches the non-orthogonality by using biorthogonal theory: the results in²¹ are very instructive both in the sense that for a moderate basis biorthogonal PT may be quite accurate if used with the total Hamiltonian, and that the use of the pure perturbation alone in estimating energy leads to complete failure. (It can be easily verified that the difference between Eq. (5) in²¹ used in the successful Method II and Eq. (4) there, defining the failing Method I, can be expressed as the “bi-expectation” value of operator \hat{B} discussed below.) In full accord with these considerations, in the CHA/CE method of *a priori* BSSE correction, only the wave function is determined by using the non-Hermitian BSSE-free CHA Hamiltonian, but the energy corresponding to that wave function is calculated as an expectation or “bi-expectation” value with the conventional Hermitian Hamiltonian of the system^{6,22}.

Thus we are going to compare the results of two biorthogonal perturbation treatments. In one of them, giving BSSE-uncorrected results, all the quantities are calculated by using the total perturbation

$$\hat{V} = \hat{W} + \hat{B} \quad (29)$$

where \hat{W} describes the true interactions and \hat{B} the BSSE effects. In another one (CHA/CE) the wave function corrections are calculated by using only the interaction operator \hat{W} , but the energy is calculated as the “bi-expectation” value of the total Hamiltonian $\hat{W} + \hat{B}$. The first-order energy corrections coincide in the two cases, because they in both cases require calculating the “bi-expectation” value of the total Hamiltonian over the unperturbed wave function.

Turning to the second order, for the uncorrected result we have, according to Eqs (60) of Appendix I:

$$\begin{aligned} E_{\text{uncorr}}^2 &= -\langle \tilde{\Psi}_0 | \hat{V} \hat{R}^0 \hat{V} | \Psi_0 \rangle = -\langle \tilde{\Psi}_0 | (\hat{W} + \hat{B}) \hat{R}^0 (\hat{W} + \hat{B}) | \Psi_0 \rangle \\ &= -\langle \tilde{\Psi}_0 | \hat{W} \hat{R}^0 \hat{W} | \Psi_0 \rangle - \langle \tilde{\Psi}_0 | \hat{W} \hat{R}^0 \hat{B} | \Psi_0 \rangle - \langle \tilde{\Psi}_0 | \hat{B} \hat{R}^0 \hat{W} | \Psi_0 \rangle - \langle \tilde{\Psi}_0 | \hat{B} \hat{R}^0 \hat{B} | \Psi_0 \rangle \end{aligned} \quad (30)$$

where operator \hat{R}^0 is the biorthogonal reduced resolvent.

To get the second-order energy correction in the CHA/CE case, we have to substitute the Hamiltonian (29) into the biorthogonal Hylleraas functional (76) of Appendix II:

$$\begin{aligned}
 E_{\text{CHA/CE}}^2 &= -\langle \tilde{\Psi}_0 | (\hat{W} + \hat{B}) \hat{R}^0 \hat{W} | \Psi_0 \rangle - \langle \tilde{\Psi}_0 | \hat{W} \tilde{R}^0 (\hat{W} + \hat{B}) | \Psi_0 \rangle + \langle \tilde{\Psi}_0 | \hat{W} \tilde{R}^0 \hat{W} | \Psi_0 \rangle \\
 &= -\langle \tilde{\Psi}_0 | \hat{W} \hat{R}^0 \hat{W} | \Psi_0 \rangle - \langle \tilde{\Psi}_0 | \hat{B} \hat{R}^0 \hat{W} | \Psi_0 \rangle - \langle \tilde{\Psi}_0 | \hat{W} \tilde{R}^0 \hat{B} | \Psi_0 \rangle.
 \end{aligned}
 \tag{31}$$

For the difference we get simply

$$E_{\text{uncorr}}^2 - E_{\text{CHA/CE}}^2 = -\langle \tilde{\Psi}_0 | \hat{B} \hat{R}^0 \hat{B} | \Psi_0 \rangle
 \tag{32}$$

which, indeed, depends on the BSSE operator \hat{B} only, but not on the operator \hat{W} of true interactions, thus justifying the additivity assumption inherent in the CP scheme. This is because the cross-terms between operators \hat{W} and \hat{B} discussed above (and actually contained in the uncorrected energy E_{uncorr}^2) are also present in the “best” CHA/CE energy because of using the total Hamiltonian for energy calculations in the latter.

The CP calculations permit to account for the main BSSE effects, but in practice the corrections they give do not exactly reproduce the difference between the uncorrected and CHA/CE results. This is explained partly by the fact that our considerations have been pertinent to an approximate theory only – even if BSSE can be assumed to be a basically second-order effect. It is probably more important that the CP calculations are not done under exactly the same conditions as the uncorrected and the CHA/CE ones: the BSSE is estimated in “ghost orbitals” calculations which are done separately for the individual monomers, and not as a procedure of estimating BSSE within the supermolecule. (We do not wish to enter here into the old polemics whether inclusion of the “ghost orbitals” occupied in the partner molecule causes an overcorrection; we think “yes”, but that may appear just useful for compensating some basis set deficiencies – cf. also ref.⁸ where this problem was analyzed on a detailed analytical model.) Nonetheless, we think that the present considerations help to understand the nearly quantitative agreement between the CP and CHA methods usually observed.

CONCLUSIONS

Some results of mathematical character concerning the theory of intermolecular interactions and the BSSE problem have been presented:

- It is shown that the concept of complete basis set may be introduced for intermolecular potential surfaces only by considering explicitly the limiting process in which the basis sets of both monomers approach completeness

simultaneously. That does not lead to any overcompleteness problem if we do not postulate the existence of two complete basis sets from the outset.

– The intimate connection between the BSSE and the differences of some biorthogonal integrals and their “original” counterparts is also discussed. The operator of BSSE is given in terms of such differences.

– It is shown that in a special case when only the overlap of the occupied orbitals is considered, the “bi-expectation” value of the energy coincides with the conventional expectation value for the single determinant wave function built up of the unperturbed orbitals of the individual monomers.

– It is discussed, by using a model of a biorthogonal perturbation theory, why the conceptually fully different *a priori* (CHA) and *a posteriori* (CP) schemes of BSSE correction usually give very close numerical results. (The necessary biorthogonal perturbation formalism is developed in Appendices.) The results give justification for the additivity assumptions inherent in the CP method.

APPENDIX I.

BIORTHOGONAL PERTURBATION THEORY USING REDUCED RESOLVENT

If the unperturbed Hamiltonian is non-Hermitian, one has to replace the standard Rayleigh–Schrödinger PT with its biorthogonal counterpart. Although low-order biorthogonal theory has been used in several papers (e.g., refs^{4,5,23}) and some general formulae were also given in the Appendix of ref.²¹, it may be worthwhile to develop here a complete biorthogonal generalization of the reduced resolvent formalism applied to the Rayleigh–Schrödinger PT.

Thus, let us consider the perturbed problem

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (33)$$

where

$$\hat{H} = \hat{H}^0 + \lambda \hat{V} \quad (34)$$

and neither the unperturbed Hamiltonian \hat{H}^0 nor the perturbation \hat{V} are assumed Hermitian. λ is the usual perturbation parameter, the powers of which are used to systematize the terms of the different expansions. It is assumed that we have a full set of left and right eigenvectors of \hat{H}^0 :

$$\hat{H}^0|\Psi_i^0\rangle = E_i^0|\Psi_i^0\rangle; \quad \langle\tilde{\Psi}_j^0|\hat{H}^0 = E_j^{0*}\langle\tilde{\Psi}_j^0|. \quad (35)$$

It is known that the left and right eigenvectors of an operator form biorthogonal sets; one can choose their normalization as to provide them to be biorthonormal:

$$\langle \tilde{\Psi}_j^0 | \Psi_i^0 \rangle = \delta_{ij} . \quad (36)$$

If one introduces the overlap matrix \mathbf{S} with the elements $S_{ki} = \langle \Psi_k^0 | \Psi_i^0 \rangle$, and its inverse \mathbf{S}^{-1} having the elements (in a short-hand notation) $S_{ki}^{-1} = S_{ik}^{-1*}$, then Eq. (36) is obviously equivalent to the explicit definitions

$$\langle \tilde{\Psi}_j^0 | = \sum_k S_{jk}^{-1} \langle \Psi_k^0 | ; \quad | \tilde{\Psi}_j^0 \rangle = \sum_k S_{kj}^{-1} | \Psi_k^0 \rangle . \quad (37)$$

Owing to the biorthonormal property (36) of the left and right eigenvectors, one can construct a resolution of identity by their use:

$$\sum_i | \Psi_i^0 \rangle \langle \tilde{\Psi}_i^0 | = 1 . \quad (38)$$

This is closely connected with the fact that if we have any linear combination

$$| \Psi \rangle = \sum_i C_i | \Psi_i^0 \rangle \quad (39)$$

then, by virtue of (36), an actual coefficient C_j can be obtained by multiplying with $\langle \tilde{\Psi}_j^0 |$:

$$\langle \tilde{\Psi}_j^0 | \Psi \rangle = \sum_i C_i \langle \tilde{\Psi}_j^0 | \Psi_i^0 \rangle = \sum_i C_i \delta_{ij} = C_j . \quad (40)$$

The Reduced Resolvent of Biorthogonal Formalism

Let us be interested in the perturbation of the non-degenerate state $i = 0$ with a real unperturbed energy E_0^0 . Then using (36) we may introduce the "cut-off" operators \hat{P} and \hat{Q} , such as

$$\hat{P} + \hat{Q} = 1 \quad (41)$$

where

$$\hat{P} = |\Psi_0^0\rangle\langle\tilde{\Psi}_0^0|; \quad \hat{Q} = 1 - \hat{P} = \sum_{i=1} |\Psi_i^0\rangle\langle\tilde{\Psi}_i^0|. \quad (42)$$

Using Eq. (36) one can write the biorthogonal “spectral resolution” of the operator $\hat{H}^0 - E_0^0$ (more rigorously, of the operator $\hat{H}^0 - E_i^0 \hat{1}$) as

$$\hat{H}^0 - E_0^0 = \sum_i (E_i^0 - E_0^0) |\Psi_i^0\rangle\langle\tilde{\Psi}_i^0|. \quad (43)$$

We can also define operator \hat{R}^0 via its spectral resolution:

$$\hat{R}^0 = \sum_{k=1} \frac{1}{E_k^0 - E_0^0} |\Psi_k^0\rangle\langle\tilde{\Psi}_k^0|. \quad (44)$$

As the summation runs from 1, and not 0, it is guaranteed that the denominator does not become zero. (E_0^0 has been assumed to be non-degenerate.) It is easy to see that this operator is a direct biorthogonal generalization of the standard reduced resolvent¹⁴, and has the property

$$(\hat{H}^0 - E_0^0)\hat{R}^0 = \hat{Q} \quad (45)$$

analogous to that for the “ordinary” reduced resolvent.

Corrections of the Wave Function

If one substitutes the perturbational expansions of the wave function and of the energy, the Schrödinger equation becomes

$$(\hat{H}^0 + \lambda \hat{V}) \left[|\Psi_0^0\rangle + \sum_{j=1}^{\infty} \lambda^j |\Psi^{(j)}\rangle \right] = \left[E_0^0 + \sum_{k=1}^{\infty} \lambda^k E^{(k)} \right] \left[|\Psi_0^0\rangle + \sum_{l=1}^{\infty} \lambda^l |\Psi^{(l)}\rangle \right]. \quad (46)$$

For sake of simplicity we do not indicate explicitly that the wave function corrections $|\Psi^{(j)}\rangle$ and the energy corrections $E^{(k)}$ are pertinent to the state with number 0 we are considering.

We introduce the biorthogonal version of the intermediate normalization

$$\langle\tilde{\Psi}_0^0|\Psi_0^0\rangle = 1; \quad \langle\tilde{\Psi}_0^0|\Psi^{(j)}\rangle = 0 \quad (j \geq 1) \quad (47)$$

for the fulfilment of which it is sufficient to require that the expansions of the wave function corrections $|\Psi^{(j)}\rangle$ do not contain the unperturbed wave function $|\Psi_0^0\rangle$.

$|\Psi_0^0\rangle$ is a solution of the unperturbed problem with a real eigenvalue, i.e., $\hat{H}^0|\Psi_0^0\rangle = E_0^0|\Psi_0^0\rangle$; $\langle\tilde{\Psi}_0^0|\hat{H}^0 = E_0^0\langle\tilde{\Psi}_0^0|$. The intermediate normalization (47) leads, therefore, to the equalities

$$\langle\tilde{\Psi}_0^0|\hat{H}^0|\Psi_0^0\rangle = E_0^0; \quad \langle\tilde{\Psi}_0^0|\hat{H}^0|\Psi^{(j)}\rangle = 0 \quad (j \geq 1). \quad (48)$$

We regroup the terms of Eq. (46) as

$$(\hat{H}^0 - E_0^0) \left[|\Psi_0^0\rangle + \sum_{j=1}^{\infty} \lambda^j |\Psi^{(j)}\rangle \right] = \left[-\lambda \hat{V} + \sum_{k=1}^{\infty} \lambda^k E^{(k)} \right] \left[|\Psi_0^0\rangle + \sum_{l=1}^{\infty} \lambda^l |\Psi^{(l)}\rangle \right]. \quad (49)$$

Now we apply operator \hat{R}^0 to both sides of (49), utilizing the relationship (45) as well as the facts that $(\hat{H}^0 - E_0^0)|\Psi_0^0\rangle = 0$, $\hat{R}^0|\Psi_0^0\rangle = 0$ and $\hat{Q}|\Psi^{(j)}\rangle = |\Psi^{(j)}\rangle$ for any $j \geq 1$, which follow from (45), and the intermediate normalization applied. We obtain, changing some summation indices:

$$\sum_{j=1}^{\infty} \lambda^j |\Psi^{(j)}\rangle = -\lambda \hat{R}^0 \hat{V} |\Psi_0^0\rangle - \sum_{j=2}^{\infty} \lambda^j \hat{R}^0 \hat{V} |\Psi^{(j-1)}\rangle + \sum_{j=2}^{\infty} \sum_{k=1}^{j-1} \lambda^j E^{(k)} \hat{R}^0 |\Psi^{(j-k)}\rangle. \quad (50)$$

We should request the coefficients at the different powers of λ to be equal on both the sides. Thus we get

$$|\Psi^{(1)}\rangle = -\hat{R}^0 \hat{V} |\Psi_0^0\rangle \quad (51)$$

and

$$|\Psi^{(j)}\rangle = -\hat{R}^0 \hat{V} |\Psi^{(j-1)}\rangle + \sum_{k=1}^{j-1} E^{(k)} \hat{R}^0 |\Psi^{(j-k)}\rangle \quad (52)$$

for the first power of λ and for λ^j ($j \geq 2$), respectively.

Substituting here the definition (44) of the biorthogonal reduced resolvent, we obtain the explicit expressions for the coefficients $c_p^{(j)}$ in the expansions of the different wave function corrections $|\Psi^{(j)}\rangle$ in terms of the unperturbed functions, $|\Psi^{(j)}\rangle = \sum_{p=1} c_p^{(j)} |\Psi_p^0\rangle$:

$$|\Psi^{(1)}\rangle = -\hat{R}^0 \hat{V} |\Psi_0^0\rangle = -\sum_{j=1} \frac{|\Psi_j^0\rangle \langle\tilde{\Psi}_j^0|\hat{V}|\Psi_0^0\rangle}{E_j^0 - E_0^0} = \sum_{j=1} \frac{-\hat{V}_{j0}}{E_j^0 - E_0^0} |\Psi_j^0\rangle \quad (53)$$

and

$$|\Psi^{(j)}\rangle = \sum_{p=1} |\Psi_p^0\rangle \frac{1}{E_j^0 - E_0^0} \left[-\sum_{l=1} \tilde{V}_{pl} c_l^{(j-1)} + \sum_{k=1}^{j-1} E^{(k)} c_p^{(j-k)} \right] \quad (54)$$

where the “mixed” matrix element \tilde{V}_{jk} of the perturbation operator \hat{V} has been introduced:

$$\tilde{V}_{jk} = \langle \tilde{\Psi}_j^0 | \hat{V} | \Psi_k^0 \rangle \equiv \sum_i S_{ji}^{-1} V_{ik} . \quad (55)$$

The Energy Corrections

We multiply (46) by $\langle \tilde{\Psi}_0^0 |$, taking into account the intermediate normalization, change the summation index and get

$$\lambda \langle \tilde{\Psi}_0^0 | \hat{V} | \Psi_0^0 \rangle + \sum_{k=2}^{\infty} \lambda^k \langle \tilde{\Psi}_0^0 | \hat{V} | \Psi^{(k-1)} \rangle = \sum_{k=1}^{\infty} \lambda^k E^k . \quad (56)$$

Requesting the equal coefficients at the different powers of λ on the two sides, we get for λ^1

$$E^{(1)} = \langle \tilde{\Psi}_0^0 | \hat{V} | \Psi_0^0 \rangle = \tilde{V}_{00} \quad (57)$$

and for λ^k ($k \geq 2$)

$$E^{(k)} = \langle \tilde{\Psi}_0^0 | \hat{V} | \Psi^{(k-1)} \rangle . \quad (58)$$

By substituting here the expansion of $|\Psi^{(k-1)}\rangle$ in terms of the zero-order functions, this can be expressed as

$$E^{(k)} = \langle \tilde{\Psi}_0^0 | \hat{V} | \sum_{p=1}^{\infty} c_p^{(k-1)} \Psi_p^0 \rangle = \sum_{p=1}^{\infty} c_p^{(k-1)} \tilde{V}_{0p} . \quad (59)$$

It may be worthwhile to write down explicitly also the second-order energy correction

$$E^{(2)} = -\langle \tilde{\Psi}_0^0 | \hat{V} \hat{R}^0 \hat{V} | \Psi_0^0 \rangle = -\sum_{i=1} \frac{\tilde{V}_{0i} \tilde{V}_{i0}}{E_i^0 - E_0^0} . \quad (60)$$

As $\tilde{V}_{0i}^* \neq \tilde{V}_{i0}$, this quantity is not necessarily real in the most general case.

APPENDIX II.

BIORTHOGONAL HYLLERAAS FUNCTIONAL

Let us consider a perturbation problem with the non-Hermitian Hamiltonian $\hat{H} = \hat{H}^0 + \lambda \hat{V}$ and $|\Psi_0\rangle$ as the eigenfunction of the unperturbed prob-

lem $\hat{H}^0|\Psi_0\rangle = E^0|\Psi_0\rangle$, and assume that we have some wave function $|\Psi\rangle = |\Psi_0\rangle + \lambda|\chi\rangle$, where $|\chi\rangle$ may or may not be equal to the first-order wave function derived above. We assume that this function satisfies the biorthogonal intermediate normalization, i.e.,

$$\langle\tilde{\Psi}_0|\Psi_0\rangle = 1; \quad \langle\tilde{\Psi}_0|\chi\rangle = 0. \quad (61)$$

We form the “bi-expectation” value

$$\tilde{E} = \frac{\langle\tilde{\Psi}_0 + \lambda\tilde{\chi}|\hat{H}^0 + \lambda\hat{V}|\Psi_0 + \lambda\chi\rangle}{\langle\tilde{\Psi}_0 + \lambda\tilde{\chi}|\Psi_0 + \lambda\chi\rangle} \quad (62)$$

and expand it up to the terms of second order (inclusively) in λ . The definition of the biorthogonal counterpart $|\tilde{\chi}\rangle$ of the wave function $|\chi\rangle$ will be discussed later, here we only request that it also should correspond to the intermediate normalization in the sense

$$\langle\tilde{\chi}|\Psi_0\rangle = 0. \quad (63)$$

The expansion of (62) can be done exactly as in the case of the conventional Hylleraas functional (e.g., ref.¹⁴); one obtains

$$\tilde{E} = E_0 + \lambda\tilde{E}^{(1)} + \lambda^2\tilde{J}_2 + O(\lambda^3) \quad (64)$$

where

$$\tilde{E}^{(1)} = \langle\tilde{\Psi}_0|\hat{V}|\Psi_0\rangle \quad (65)$$

is the biorthogonal first-order energy correction (see above) and the bi-orthogonal Hylleraas functional \tilde{J}_2 differs from the conventional one only by the appearance of the biorthogonal “bra-vectors” and biorthogonal first-order energy:

$$\tilde{J}_2 = \langle\tilde{\Psi}_0|\hat{V} - \tilde{E}^{(1)}|\chi\rangle + \langle\tilde{\chi}|\hat{V} - \tilde{E}^{(1)}|\Psi_0\rangle + \langle\tilde{\chi}|\hat{H}^0 - E^0|\chi\rangle. \quad (66)$$

To obtain this form, it is sufficient to assume the fulfilment of $\langle\tilde{\Psi}_0|\Psi_0\rangle = 1$; if the biorthogonality assumptions $\langle\tilde{\Psi}_0|\chi\rangle = 0$ and $\langle\tilde{\chi}|\Psi_0\rangle = 0$ of the intermediate normalization is also utilized, one gets

$$\tilde{J}_2 = \langle\tilde{\Psi}_0|\hat{V}|\chi\rangle + \langle\tilde{\chi}|\hat{V}|\Psi_0\rangle + \langle\tilde{\chi}|\hat{H}^0 - E^0|\chi\rangle. \quad (67)$$

Now, let us assume that the wave function $|\chi\rangle$ has been obtained as the first-order wave function, corresponding to the same \hat{H}^0 as considered above, but for the perturbation \hat{W} which may be different from \hat{V} . Then we have, in accord with (53) applied to operator \hat{W} (instead of \hat{V}):

$$|\chi\rangle = -\hat{R}^0 \hat{W} |\Psi_0\rangle. \quad (68)$$

Substituting this into Eq. (67), we get

$$\tilde{J}_2 = -\langle \tilde{\Psi}_0 | \hat{V} \hat{R}^0 \hat{W} |\Psi_0\rangle + \langle \tilde{\chi} | \hat{V} |\Psi_0\rangle - \langle \tilde{\chi} | (\hat{H}^0 - E^0) \hat{R}^0 \hat{W} |\Psi_0\rangle. \quad (69)$$

The last term of this equality can be transformed by using the property of Eq. (45) of the reduced resolvent and the equalities $\tilde{Q} = 1 - |\Psi_0\rangle\langle\tilde{\Psi}_0|$ and $\langle\tilde{\chi}|\Psi_0\rangle = 0$ as

$$\langle \tilde{\chi} | (\hat{H}^0 - E^0) \hat{R}^0 \hat{W} |\Psi_0\rangle = \langle \tilde{\chi} | (1 - |\Psi_0\rangle\langle\tilde{\Psi}_0|) \hat{W} |\Psi_0\rangle = \langle \tilde{\chi} | \hat{W} |\Psi_0\rangle. \quad (70)$$

Substituting this result, we get

$$\tilde{J}_2 = -\langle \tilde{\Psi}_0 | \hat{V} \hat{R}^0 \hat{W} |\Psi_0\rangle + \langle \tilde{\chi} | \hat{V} - \hat{W} |\Psi_0\rangle. \quad (71)$$

If $\hat{W} = \hat{V}$, then the second term on the right-hand side of Eq. (71) vanishes, and one recovers the second-order biorthogonal energy correction, Eq. (60), as expected – without even specifying the actual form of the biorthogonal function $\langle\tilde{\chi}|$.

In the general case, when $\hat{W} \neq \hat{V}$, equality (68) gives the first-order wave function correction obtained for the Schrödinger equation $(\hat{H}^0 + \lambda\hat{W})\Psi = E\Psi$. That Schrödinger equation for the right eigenvectors has a counterpart for the left eigenvectors:

$$\langle\Psi|(\hat{H}^0 + \lambda\hat{W}) = E\langle\Psi| \quad (72)$$

(E has been assumed real.) Using $\langle\tilde{\Psi}_0|$ (left eigenvector of \hat{H}^0) as the zeroth-order wave function, and turning to the right-hand side eigenvector problem for the adjoint operators, we get the biorthogonal counterpart of the Schrödinger equation as:

$$(\hat{H}^{0\dagger} + \lambda\hat{W}^\dagger)(|\tilde{\Psi}_0\rangle + \lambda|\tilde{\chi}\rangle\dots) = (E_0 + \lambda\tilde{E}_1\dots)(|\tilde{\Psi}_0\rangle + \lambda|\tilde{\chi}\rangle\dots). \quad (73)$$

Considerations quite similar to those discussed in detail above give for the first-order wave function correction $|\tilde{\chi}\rangle$ the expression

$$|\tilde{\chi}\rangle = -\hat{\mathbf{R}}^{0\dagger} \hat{\mathbf{W}}^\dagger |\tilde{\Psi}_0\rangle. \quad (74)$$

Thus we have to substitute into Eq. (71) the biorthogonal function $\langle\tilde{\chi}|$ as

$$\langle\tilde{\chi}| = -\langle\tilde{\Psi}_0|\hat{\mathbf{W}}\hat{\mathbf{R}}^0. \quad (75)$$

Thus finally we get

$$\tilde{J}_2 = -\langle\tilde{\Psi}_0|\hat{\mathbf{V}}\hat{\mathbf{R}}^0\hat{\mathbf{W}}|\Psi_0\rangle - \langle\tilde{\Psi}_0|\hat{\mathbf{W}}\hat{\mathbf{R}}^0\hat{\mathbf{V}}|\Psi_0\rangle + \langle\tilde{\Psi}_0|\hat{\mathbf{W}}\hat{\mathbf{R}}^0\hat{\mathbf{W}}|\Psi_0\rangle. \quad (76)$$

Again, we recover the second-order energy Eq. (60) if $\hat{\mathbf{W}} = \hat{\mathbf{V}}$.

REFERENCES

- Boys S. B., Bernardi F.: *Mol. Phys.* **1970**, *19*, 553.
- Jansen H. B., Ross P.: *Chem. Phys. Lett.* **1969**, *3*, 140.
- Mayer I.: *Int. J. Quantum Chem.* **1983**, *23*, 341.
- Mayer I., Vibók Á.: *Mol. Phys.* **1997**, *92*, 503.
- Mayer I., Valiron P.: *J. Chem. Phys.* **1998**, *109*, 3360.
- Mayer I.: *Int. J. Quantum Chem.* **1998**, *70*, 41.
- Salvador P., Mayer I.: *J. Chem. Phys.* **2004**, *120*, 5882.
- Mayer I., Túri L.: *J. Mol. Struct. (THEOCHEM)* **1991**, *227*, 43.
- Mayer I.: *Int. J. Quantum Chem.* **2004**, *100*, 559.
- White J. C., Davidson E. R.: *J. Chem. Phys.* **1990**, *93*, 8029.
- Mayer I., Surján P. R.: *Chem. Phys. Lett.* **1992**, *191*, 497.
- Löwdin P.-O.: *J. Appl. Phys.* **1962**, *33*, 251.
- Amos A. T., Hall G. G.: *Proc. R. Soc. London, Ser. A* **1961**, *263*, 483.
- Mayer I.: *Simple Theorems, Proofs, and Derivations in Quantum Chemistry*. Kluwer Academic/Plenum Publishers, New York 2003.
- Biczó G.: Personal communication (Budapest, middle 1970s).
- Longuet-Higgins H. C. in: *Quantum Theory of Atoms, Molecules and the Solid State* (P.-O. Löwdin, Ed.), p. 105. Academic Press, New York 1966.
- Surján P. R.: *Second Quantized Approach to Quantum Chemistry*. Springer, Berlin 1989.
- Mayer I.: *J. Mol. Struct. (THEOCHEM)* **1988**, *165*, 255.
- Mayer I.: *Theor. Chim. Acta* **1987**, *72*, 207.
- a) Conway A., Murrell J. N.: *Mol. Phys.* **1972**, *23*, 1143; b) Conway A., Murrell J. N.: *Mol. Phys.* **1974**, *27*, 873; c) Murrell J. N., Varandas A. J. C.: *Mol. Phys.* **1975**, *30*, 223.
- Surján P. R., Mayer I.: *J. Mol. Struct. (THEOCHEM)* **1991**, *226*, 47.
- Mayer I., Surján P. R.: *Int. J. Quantum Chem.* **1989**, *36*, 225.
- Vibók Á., Halász G., Mayer I.: *Mol. Phys.* **1998**, *93*, 873.