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Perturbation calculation of the interaction energy using orthogonalized orbitals

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Abstract. The diagrammatic Rayleigh-Schrödinger perturbation theory for the interaction of two closed-shell systems is developed up to the third order of perturbation using orthogonalized orbitals. The interaction energy is expressed by the Rayleigh-Schrödinger perturbation expansion. A simple approach for the estimation of basis set superposition error is introduced. The preliminary calculations of the intermolecular interactions for the He dimer within the augmented cc-pVTZ basis set are compared with the supermolecular approach, perturbation calculation in biorthogonal basis sets and symmetry adapted perturbation theory results.

Key words: Perturbation theory – Weak molecular interaction – Basis set superposition error – He dimer interaction

1 Introduction

Different branches of science benefit from the knowledge of intermolecular interaction, and many methods have been proposed for their study. The progress made during the last two decades has been reviewed in a number of articles and monographs [1–13]. It is especially worthwhile reading the recent work of Jeziorski et al. [14] in which the results achieved in this field are critically reviewed. Methods for ab initio calculations of the intermolecular interactions fall into two categories:

1. A supermolecular approach in which the interaction energy between atomic or molecular systems is calculated as the difference $E_{AB} - E_A - E_B$, where $E_{A(B)}$ and E_{AB} are approximations to the energies of the isolated systems and "supersystem" AB, respectively. An attractive aspect of the supermolecular approach is the fact that all techniques developed within the single-molecule calculation can be used without any changes.

As a rule the interaction energy is several orders of magnitude smaller than the total energy, and so very precise calculations are mandatory. The methods used must be size consistent [15], they must sufficiently account for electron correlation, and monomer energies, E_A and E_B, must be calculated using the full orbital basis of the AB system in order to avoid the basis set superposition error (BSSE) [16]. In the supermolecular approach, the interaction energy is obtained as a single number, its decomposition into contributions with a clear physical interpretation is not straightforward, and for a deeper physical understanding of the interaction additional calculations are necessary [17].

2. In the perturbation theory (PT) approach, the interaction energy is calculated directly as a sum of contributions with direct physical interpretations. The Hamiltonian for system AB is written as

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_B + \hat{V} , \tag{1}$$

where $\hat{H}_{A(B)}$ is the Born-Oppenheimer Hamiltonian and $\hat{V}$ is the perturbation operator, which represents the interaction [3].

When the exact wave functions for the interacting systems are known and distances between them are large, the standard Rayleigh-Schrödinger expansion is applicable. At distances with non-negligible overlap the following main problems can be formulated:

1. The wave function of the "supersystem" should be antisymmetric according to all electrons.
2. The antisymmetric products of the wave functions of isolated systems are not eigenfunctions of $\hat{H}_0$, where $\hat{H}_0$ is formed as the sum of Hamiltonians $\hat{H}_A$ and $\hat{H}_B$ of isolated systems.
3. The exact eigenfunctions of $\hat{H}_0$ are usually not available and $\hat{H}_0$ is then formed from Hamiltonians of the Hartree-Fock (HF) type; the perturbation operator has to include also the correlation operators for isolated systems.

Many different theories have been proposed for solving these problems. The "symmetry-adapted" perturbation theories (SAPTs) are, in principle, of two types [14].

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1. Theories based on the zero-order wave function in the form of simple products of the zero-order wave functions of isolated systems. These theories have to force the proper symmetry in consecutive order of perturbation expansion – SAPT. The most elaborate of them is the many-body formulations of SAPT [18–21].

2. Theories based on a zero-order wave function that has the correct symmetry with respect to all electrons [22–37]. Such unperturbed wave functions are not eigenfunctions of the naturally formulated unperturbed Hamiltonian

$$\hat{H}_0 = \hat{H}_A + \hat{H}_B \ , \tag{2}$$

and an alternative zero-order operator must be constructed. The concept of the so-called "chemical Hamiltonian" of Mayer [38, 39] was used for the BSSE-free PT for intermolecular interaction proposed by Surján et al. [40–43]. A generally accepted and successful zero-order Hamiltonian of these types was not formulated until now [3, 14, 44]. Within the supermolecular approach, the second-order BSSE-free theory based upon the "chemical Hamiltonian approach" was developed by Noga and Vibók [45].

The presented perturbation procedure starts from the zero-order approximation with correct symmetry properties as suggested by Basilevsky and Berenfeld [22] and generalized by Kvasnička et al. [46]. Here the non-orthogonality problem was transformed into a Hamiltonian, and antisymmetry was ensured by the second quantization formalism.

The purpose of our work is to extend the diagrammatic Rayleigh-Schrödinger perturbation theory (RSPT) for the interaction of two closed-shell systems suggested by Kvasnička et al. [46] up to the third order and to compare the interaction energy values for He_2 obtained by the presented method with the supermolecular approach, perturbation calculation in biorthogonal basis sets and SAPT results. Laurinc et al. [47] and Surján and del Valle [48] presented the first results in this approach up to the second order for $(He)_2$, $(H_2)_2$ and $(H_2O)_2$ systems.

2 Construction of the Hamiltonian in an orthogonalized basis set

Let us consider two interacting closed-shell systems A and B (atoms or molecules) characterized by two sets of spin orbitals (localized on systems A and B). We assume that these spin orbitals are the HF molecular orbitals (MOs) for isolated systems A and B

$$\Phi_0^A = \left\{ |\varphi_I\rangle, I \in A \right\} \ , \tag{3a}$$

$$\Phi_0^B = \left\{ |\varphi_J\rangle, J \in B \right\} \ . \tag{3b}$$

The supersystem MO vector $|\Phi_0^{AB}\rangle$ is formed from the above vectors Eqs. (3a, b). The block scheme of the MO coefficients for supersystem AB has the following form.

$$\begin{bmatrix} C_0^A & 0 \\ 0 & C_0^B \end{bmatrix} \ . \tag{4}$$

Let us assume that a transformation of the MO vector $|\Phi_0^{AB}\rangle$ from Eq. (4) into the new orthonormal vector $|\Psi_0^{AB}\rangle$ exists satisfying the following condition

$$\lim_{R \to \infty} |\Psi_0^{AB}\rangle = |\Phi_0^{AB}\rangle \ . \tag{5}$$

The Hamiltonian of the dimer AB in the second quantization formalism may be expressed as

$$\hat{H}_{AB} = \langle \Psi_0^{AB} | \hat{H}^{AB} | \Psi_0^{AB} \rangle + \hat{H}_0^{AB} + \hat{H}_1^{AB} \ . \tag{6}$$

After subtracting the HF energies of the isolated systems $\langle \Psi_0^{AB} | \hat{H}^{AB} | \Psi_0^{AB} \rangle$ we obtain the zero-order interaction energy e_0:

$$e_0 = \langle \Psi_0^{AB} | \hat{H}^{AB} | \Psi_0^{AB} \rangle - \langle \Phi_0^A | \hat{H}^A | \Phi_0^A \rangle - \langle \Phi_0^B | \hat{H}^B | \Phi_0^B \rangle \ . \tag{7}$$

The e_0 can be separated into the electrostatic and exchange-penetration parts [46]

$$e_0 = e_{\text{elst}} + e_{\text{ex-pn}} \ . \tag{8}$$

This energy is equal to the ΔE^1 interaction energy in the Morokuma decomposition of the SCF interaction energy [17]. The e_{elst} represents the electrostatic interaction between the nuclear and electronic charge distributions given by wave functions Φ_0^A and Φ_0^B [49]. The first-order exchange-penetration energy $e_{\text{ex-pn}}$ results from the antisymmetry of the zero-order wave functions of the dimer system and from the orthogonalization of the MOs [4]. The decomposition of the e_0 into the electrostatic and exchange contributions was discussed by Jeziorski et al. [50], where the explicit formula for the first-order interaction energy of many closed-shell molecules was derived.

A zero-order Hamiltonian $\hat{H}_0^{AB}$ is defined as the sum of Fock operators constructed from isolated orbital energies of monomers A and B:

$$\hat{H}_0^{AB} = \sum_{I \in A} \varepsilon_I N\left[\hat{X}_I^+ \hat{X}_I\right] + \sum_{J \in B} \varepsilon_J N\left[\hat{X}_J^+ \hat{X}_J\right] \ . \tag{9}$$

The perturbation operator $\hat{H}_1^{AB}$ is

$$\hat{H}_1^{AB} = \sum_{I,J \in AB} \langle I|u|J\rangle N\left[\hat{X}_I^+ \hat{X}_J\right]$$
$$+ \frac{1}{2} \sum_{I,J,K,L \in AB} \langle IJ|KL\rangle N\left[\hat{X}_I^+ \hat{X}_J^+ \hat{X}_L \hat{X}_K\right] \ , \tag{10}$$

where the one-particle elements $\langle I|u|J\rangle$ are the matrix elements of the HF operator in an orthogonalized basis set without isolated monomer orbital energies [46] and capital letters are used for spin orbitals.

2.1 Second-order contributions to the interaction energy

The interaction energy up to the second order of the PT is given in [46] and has the following orbital form

$$E^{\text{PT2}} = e_0 + \sum_{p \in AB}^{\text{un}} \sum_{i \in AB}^{\text{occ}} 2(u)_i^p (u)_p^i \Big/ \varepsilon_p^i$$
$$+ \sum_{p,q \in AB}^{\text{un}} \sum_{i,j \in AB}^{\text{occ}} v_{ij}^{pq} \tilde{v}_{ij}^{pq} \Big/ \varepsilon_{pq}^{ij} - E_A^{\text{MP2}} - E_B^{\text{MP2}} \ , \tag{11}$$

where $(u)_i^p$ are the matrix elements of the $\langle p|u|i\rangle$, v_{ij}^{pq} are the two particle molecular integrals $\langle pq|ij\rangle$,
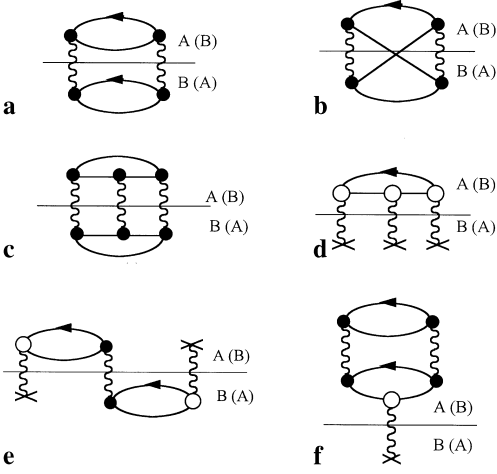
Fig. 1a–f. The Goldstone diagrams for **a** dispersion ($\varepsilon_{\text{disp}}^{(2)}$), **b** exchange-dispersion ($\varepsilon_{\text{ex-disp}}^{(2)}$) effects of the second-order perturbation theory (PT) and **c** dispersion ($\varepsilon_{\text{bi}}^{(3)}$). This diagram has four possible orientations: **d** polarization, **e** polarization-dispersion, **f** polarization-correlation effects of the third-order PT. A two-particle operator in an orthogonalized basis set is denoted by –●–, and a one-particle operator u by –○–

$\tilde{v}_{ij}^{pq} = 2v_{ji}^{pq} - v_{ij}^{pq}$ and the $\varepsilon_p^i = \varepsilon_i - \varepsilon_p$ and $\varepsilon_{pq}^{ij} = \varepsilon_i + \varepsilon_j - \varepsilon_p - \varepsilon_q$. In all cases the occupied (virtual) orbitals are labelled by i, j, k, l (p, q, r, s) indices. $E_A^{\text{MP2}}(E_B^{\text{MP2}})$ denotes the second-order Møller-Plesset correlation energy for $A(B)$.

The second term in Eq. (11) represents the second-order mono-excited contributions to the interaction energy ($\varepsilon_{\text{mono}}^{(2)}$); it can be expressed as the sum of polarization energy $\varepsilon_{\text{pol}}^{(2)}$ ($p, i \in A(B)$) and delocalization energy $\varepsilon_{\text{del}}^{(2)}$ ($p \in B(A)$, $i \in A(B)$). The sum of the last three terms in Eq. (11) (later denoted as $\varepsilon_{\text{bi}}^{(2)}$) corresponds to ΔE_{disp}^2 in a notation of Surján and del Valle [48] and represents bi-excited contributions to the interaction energy up to the second-order of the PT. In the $\varepsilon_{\text{bi}}^{(2)}$ the second-order dispersion ($\varepsilon_{\text{disp}}^{(2)}$) and second-order exchange-dispersion ($\varepsilon_{\text{ex-disp}}^{(2)}$) energy in orthogonalized basis set might be distinguished (see Fig. 1).

2.2 Third-order contributions to the interaction energy

The interaction energy contributions up to the third order of the PT may be formulated in a similar way. However, the number of individual diagrammatic terms grows significantly. The standard form of the third-order diagrams with two- and one-particle vertices may be found for example in [51]. When the orbitals are real functions, the algebraic interpretations of the diagrams lead to the following expression for the interaction energy up to the third order

$$E^{\text{PT3}} = E^{\text{PT2}} + \sum_{p,q \in AB}^{\text{un}} \sum_{i,j,k,l \in AB}^{\text{occ}} v_{ij}^{pq} v_{kl}^{ij} \tilde{v}_{kl}^{pq} \Big/ \varepsilon_{pq}^{ij} \varepsilon_{pq}^{kl}$$

$$+ \sum_{p,q,r,s \in AB}^{\text{un}} \sum_{i,j \in AB}^{\text{occ}} v_{ij}^{pq} v_{rs}^{pq} \tilde{v}_{ij}^{rs} \Big/ \varepsilon_{pq}^{ij} \varepsilon_{rs}^{ij}$$

$$+ \sum_{p,q,r \in AB}^{\text{un}} \sum_{i,j,k \in AB}^{\text{occ}} \left[\tilde{v}_{ij}^{pq} \left(2v_{jk}^{qr} - v_{kr}^{jq} \right) \tilde{v}_{ik}^{pr} - 3v_{ij}^{qp} v_{kr}^{jq} v_{ik}^{rp} \right] \Big/ \varepsilon_{pq}^{ij} \varepsilon_{pr}^{ik}$$

$$- E_A^{\text{MP3}} - E_B^{\text{MP3}} + \sum_{p,q \in AB}^{\text{un}} \sum_{i \in AB}^{\text{occ}} 2(u)_i^p (u)_q^p (u)_i^q \Big/ \varepsilon_p^i \varepsilon_q^i$$

$$- \sum_{p \in AB}^{\text{un}} \sum_{i,j, \in AB}^{\text{occ}} 2(u)_p^i (u)_j^i (u)_p^j \Big/ \varepsilon_p^i \varepsilon_p^j$$

$$+ \sum_{p,q, \in AB}^{\text{un}} \sum_{i,j, \in AB}^{\text{occ}} 4(u)_q^i (u)_p^j \tilde{v}_{ji}^{pq} \Big/ \varepsilon_{pq}^{ij} \varepsilon_q^i$$

$$+ \sum_{p,q \in AB}^{\text{un}} \sum_{i,j \in AB}^{\text{occ}} 2(u)_i^p (u)_q^j \left(2v_{ij}^{pq} - v_{pi}^{qj} \right) \Big/ \varepsilon_p^i \varepsilon_q^j$$

$$- \sum_{p,q \in AB}^{\text{un}} \sum_{i,j,k \in AB}^{\text{occ}} 2v_{ik}^{pq} (u)_j^i \tilde{v}_{jk}^{pq} \Big/ \varepsilon_{pq}^{ik} \varepsilon_{pq}^{jk}$$

$$+ \sum_{p,q,r \in AB}^{\text{un}} \sum_{i,j \in AB}^{\text{occ}} 2v_{ij}^{pr} (u)_q^p \tilde{v}_{ij}^{qr} \Big/ \varepsilon_{pr}^{ij} \varepsilon_{rq}^{ij}$$

$$+ \sum_{p,q,r \in AB}^{\text{un}} \sum_{i,j \in AB}^{\text{occ}} 4(u)_j^r v_{ij}^{pq} \tilde{v}_{ir}^{pq} \Big/ \varepsilon_{pq}^{ij} \varepsilon_r^j$$

$$- \sum_{p,q \in AB}^{\text{un}} \sum_{i,j,k \in AB}^{\text{occ}} 4(u)_k^q v_{ij}^{pq} \tilde{v}_{ij}^{pk} \Big/ \varepsilon_{pq}^{ij} \varepsilon_q^k. \tag{12}$$

The physical interpretation of the higher than second-order diagrams is not straightforward. Introducing the border line for the orbital separation from system $A(B)$ it is possible to distinguish the pure dispersion, pure polarization as well as the so-called mixed terms (i.e. polarization-correlation, polarization-dispersion) (Fig. 1). The sum of the second to fifth terms in Eq. (12) was denoted as $\varepsilon_{\text{bi}}^{(3)}$. They represent the third-order biexcited contributions to the interaction energy.

2.3 The problem of BSSE

If the monomer HF wave functions are calculated in the framework of a subset of finite basis functions localized on system $A(B)$, the interaction energies will suffer from the BSSE. To correct for this artefact in calculation of intermolecular energies in orthogonalized basis sets the counterpoise correction recipe has been used by Surján and del Valle [48]. In this section we suggest another treatment for correction of this error.

In the case of infinite distance between system A and the dummy functions on the centres [B], the following limit relations are valid for system A (and similarly for B with dummy functions on the centres [A]):

$$\lim_{R \to \infty} E_{A[B]}^{\text{SCF}} = E_A^{\text{SCF}} , \tag{13a}$$

$$\lim_{R \to \infty} E_{A[B]}^{\text{MP2}} = E_A^{\text{MP2}} , \tag{13b}$$

$$\lim_{R \to \infty} E_{A[B]}^{\text{MP3}} = E_A^{\text{MP3}} . \tag{13c}$$

Let us assume that the solution for this system is known and the matrix-block scheme for system A (in dimer-centred basis set, $R_{A[B]} = \infty$) has the following form

$$\begin{bmatrix} C_0^A & 0 \\ 0 & C_0^{[B]} \end{bmatrix} \quad . \tag{14}$$

For $R_{A[B]} \neq \infty$ we must find a new orthonormal vector $|\Psi_0^{A[B]}\rangle$ via the same orthogonalization procedure as for the supersystem. The Hamiltonian for subsystem $A[B]$ in the second quantization formalism may be expressed as

$$\hat{H}_{A[B]} = \left\langle \Psi_0^{A[B]} \middle| \hat{H}^{A[B]} \middle| \Psi_0^{A[B]} \right\rangle + \hat{H}_0^{A[B]} + \hat{H}_1^{A[B]} \quad . \tag{15}$$

After subtracting the scalar parts of the isolated systems in the dimer-centered basis set from $\langle \Psi_0^{AB} | \hat{H}^{AB} | \Psi_0^{AB} \rangle$ we obtain the BSSE-corrected zero-order interaction energy e_0^{CP}:

$$e_0^{\mathrm{CP}} = \left\langle \Psi_0^{AB} \middle| \hat{H}^{AB} \middle| \Psi_0^{AB} \right\rangle - \left\langle \Psi_0^{A[B]} \middle| \hat{H}^{A[B]} \middle| \Psi_0^{A[B]} \right\rangle \\ - \left\langle \Psi_0^{[A]B} \middle| \hat{H}^{[A]B} \middle| \Psi_0^{[A]B} \right\rangle \quad . \tag{16}$$

The unperturbed part of the Hamiltonian Eq. (15) is defined as the sum of the Fock operators constructed from the orbital energies of the constituting monomer A and centres [B]. It may be written in the diagonal form

$$\hat{H}_0^{A[B]} = \sum_{I \in A} \varepsilon_I N[\hat{X}_I^+ \hat{X}_I] + \sum_{J \in [B]} \varepsilon_J N[\hat{X}_J^+ \hat{X}_J] \quad , \tag{17}$$

and the perturbation operator $\hat{H}_1^{A[B]}$ has the form

$$\hat{H}_1^{A[B]} = \sum_{I,J \in A[B]} \langle I|u|J \rangle^{A[B]} N[\hat{X}_I^+ \hat{X}_J] \\ + \frac{1}{2} \sum_{I,J,K,L \in A[B]} \langle IJ|KL \rangle^{A[B]} N[\hat{X}_I^+ \hat{X}_J^+ \hat{X}_L \hat{X}_K] \quad . \tag{18}$$

Applying the many-body diagrammatic formalism, the second-order contribution to the subsystem energy $A[B]$ in the orthogonalized basis set may be expressed as

$$E_{A[B]}^{\mathrm{PT2}} = \sum_{p \in A[B]}^{\mathrm{un}} \sum_{i \in A[B]}^{\mathrm{occ}} 2 \left(u^{A[B]}\right)_i^p \left(u^{A[B]}\right)_p^i \Big/ \left(\varepsilon^{A[B]}\right)_p^i \\ + \sum_{p,q \in A[B]}^{\mathrm{un}} \sum_{i,j \in A[B]}^{\mathrm{occ}} \left(v^{A[B]}\right)_{ij}^{pq} \left(\tilde{v}^{A[B]}\right)_{ij}^{pq} \Big/ \left(\varepsilon^{A[B]}\right)_{pq}^{ij} \quad . \tag{19}$$

The first term in Eq. (19) represents the BSSE correction of the polarization and delocalization energies of the subsystem $A[B]$. The second term is the second-order monomer correlation energy calculated in the dimer-centred orthogonalized basis set. After substituting $E_{A[B]}^{\mathrm{PT2}}$ and $E_{[A]B}^{\mathrm{PT2}}$ for E_A^{MP2} and E_B^{MP2} in Eq. (11) we obtain the BSSE corrected interaction energy $E_{\mathrm{CP}}^{\mathrm{PT2}}$. The same ideas were used in the calculation of the $E_{\mathrm{CP}}^{\mathrm{PT3}}$.

3 Basis set orthogonalization

Löwdin's symmetric $S^{-1/2}$ transformation [52] may be applied as a straightforward method for the orthogo-

nalization of the MOs of the interacting systems. This treatment minimizes the "distance" between the non-orthogonal and orthogonal sets [53]. In the global $S^{-1/2}$ transformation, the occupied orbitals on fragment A are mixed with the virtual orbitals on fragment B. However, this leads to repulsion and delocalization energies being too large [54], and to a slow convergence of the perturbation expansion. In order to avoid the occupied-virtual mixing in an orthogonalization over the whole basis set we used the method suggested in [55]. MOs occupied in the ground state determinants of the subsystems were orthogonalized by means of the $S^{-1/2}$ procedure in the first step. Afterwards, the virtual orbitals were projected onto the subspace orthogonal to the space of the orthogonalized occupied orbitals and then mutually reorthonormalized by the $S^{-1/2}$ procedure.

4 Results and discussion

In order to check the applicability of the proposed perturbation treatment, we present a study of the interaction energy of the He...He system. To compare our results with those of Woon [56] and Surján and del Valle [48], we used the same augmented correlation-consistent basis set of Woon and Dunning (aug-cc-pVTZ [$6s2p1d/3s2p1d + 1s1p1d$]) [57]. All calculations in the presented PT and supermolecular approach were done within our program code interfaced with the MOLCAS-3 package [58]. The atomic one- and two-electron integrals, the SCF orbital energies and eigenvectors generated with the GAUSSIAN 92 package [59] were used for the calculations of the SAPT interaction energy contributions [60].

In Fig. 2 we summarize our BSSE non-corrected results obtained by the presented perturbation method. The second-order interaction energy curve E^{PT2} is comparable with the supermolecular approach, but the third-order results display an opposite behaviour. The non-corrected third-order contribution ($E^{\mathrm{PT3}} - E^{\mathrm{PT2}}$) is repulsive and leads to larger equilibrium distance and larger differences between E^{PT3} and E^{MP3} potential curves.
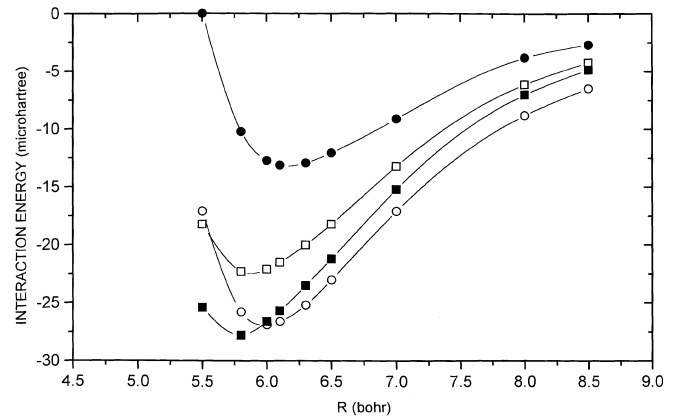

Fig. 2. Potential curves for the He...He interaction; ○ presented PT (E^{PT2}); ● presented PT (E^{PT3}); □ supermolecular calculation (E^{MP2}); ■ supermolecular calculation (E^{MP3})

The BSSE-corrected results are presented in Fig. 3. The curves of the total interaction energy E_{CP}^{PT2} and E_{CP}^{MP2} are almost identical. Presented E^{PT2} data corrected on the BSSE using the method described in Sect. 2.3 are in better agreement with E_{CP}^{MP2} than E^{PT2} data published by Surján and del Valle [48]. Their formulation of the PT in orthogonal basis set was practically identical with our treatment except the correction of E_A^{MP2} and E_B^{MP2} Eq. (11).

The total interaction energy E_{CP}^{PT3} is very close to the value obtained by the SAPT approach. The partitioning of the interaction energy contributions at the experimental minimum is given in Table 1. The sum of the
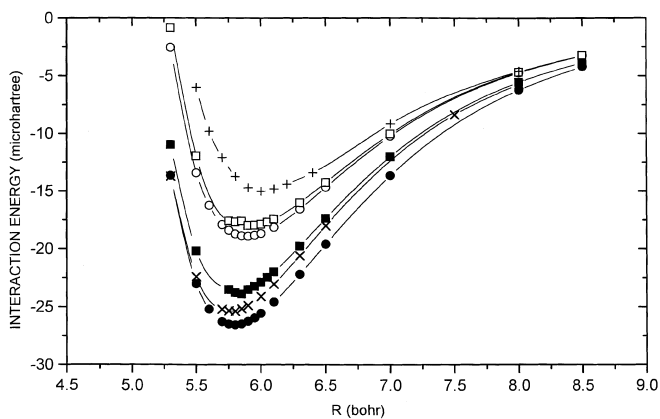
polarization energy $\varepsilon_{pol}^{(2)}$ and the delocalization energy $\varepsilon_{del}^{(2)}$ represents the second-order mono-excited $\varepsilon_{mono}^{(2)}$ contribution. In order to compare these terms with the supermolecular approach, we used the Morokuma decomposition of the SCF interaction energy. The decomposition of ΔE^{SCF} into the ΔE^1 (sum of the electrostatic and first-order exchange-penetration energies) and ΔE^2 (sum of the delocalization and polarization energies) is performed in two steps [61]. ΔE^1 is obtained easily from the supersystem SCF energy in the first iteration, if the orthogonalized occupied orbitals of isolated subsystems are used as starting vectors (Eq. 4) and the monomer energies are subtracted ($\Delta E^1 = E_{AB}^{SCF-1} - E_A^{SCF} - E_B^{SCF}$). In the second step the SCF calculation is allowed to reach self-consistency and from the converged supersystem energy we obtain $\Delta E^2 (\Delta E^2 = E_{AB}^{SCF} - E_{AB}^{SCF-1})$. Using the similar scheme in BSSE-corrected calculation of the monomer energies in dimer-centred basis set, we may define the terms ΔE_{CP}^1 and ΔE_{CP}^2:

$$\Delta E_{CP}^1 = \Delta E^1 - \left(E_{A[B]}^{SCF-1} + E_{[A]B}^{SCF-1} - E_A^{SCF} - E_B^{SCF} \right) , \tag{20}$$

$$\Delta E_{CP}^2 = \Delta E^2 - \left(E_{A[B]}^{SCF} + E_{[A]B}^{SCF} - E_{A[B]}^{SCF-1} - E_{[A]B}^{SCF-1} \right) . \tag{21}$$

In the above equations, $E_{A[B]}^{SCF-1}$ represents the first iteration SCF energy for the system A in the dimer-centred basis set, if orthogonalized occupied orbitals of eigenvectors matrix (Eq. 14) are used. $E_{A[B]}^{SCF}$ is the converged SCF energy of system A with dummy functions on $[B]$. A similar notation is used also for the system B with dummy functions on the centres $[A]$.

Fig. 3. Potential curves for the He...He interaction with basis set superposition error (BSSE) correction; ○ presented PT (E^{PT2}); ● presented PT (E^{PT3}); □ supermolecular calculation (E^{MP2}); ■ supermolecular calculation (E^{MP3}); + biorthogonal formalism up to the second order of PT (data are taken from [48]); × SAPT formalism (E_{int}^{SAPT})

Table 1. Individual contributions to the interaction energy (in microhartree) at the experimental minimum ($R = 5.6$ bohr). Values in parentheses are corrected for basis set superposition error (BSSE). PT, Perturbation theory; SAPT, symmetry adapted perturbation theory

Presented PT		Supermolecular approach		SAPT[a]	
e_{elst}	−4.9	e_{elst}	−4.9	E_{elst}	−5.1
e_{ex-pn}	34.6	e_{ex-pn}	34.6	$E_{exch}^{(10)}$	35.6
e_0	29.7 (29.7)	ΔE^1	29.7 (29.7)		
$\varepsilon_{pol}^{(2)}$	−0.0				
$\varepsilon_{del}^{(2)}$	−1.9				
$\varepsilon_{mono}^{(2)}$	−1.9 (−0.7)	$\varepsilon_{pol+del}^{SCF}$	−2.1 (−0.7)	$E_{ind}^{(20)}$	−0.7
E_1^{PT}	27.8 (29.0)	ΔE^{SCF}	27.6 (29.0)	$E_{SAPT}^{SCF\,d}$	30.4
$\varepsilon_{disp}^{(2)}$	−41.1	$\varepsilon_{disp}^{HF(2)\,b}$	−44.2	$E_{disp}^{(20)}$	−47.4
$\varepsilon_{ex-disp}^{(2)}$	0.0			$E_{ex-disp}^{(20)}$	1.1
$\varepsilon_{disp}^{(3)}$	0.1	$\varepsilon_{disp}^{HF(3)\,c}$	0.2	$E_{disp}^{(30)}$	0.3
$\varepsilon_{bi}^{(2)}$	−49.2 (−45.3)	ΔE^{MP2}	−48.1 (−43.9)	$E_{disp}^{\{2\}}$	−57.3
$\varepsilon_{bi}^{(3)}$	−5.1 (−8.1)	ΔE^{MP3}	−6.5 (−7.5)	$E_{SAPT}^{corr\,e}$	−54.7
E^{PT2}	−21.4 (−16.3)	E^{MP2}	−20.5 (−14.9)	$E_{int}^{SAPT\,f}$	−24.3
E^{PT3}	−4.3 (−25.2)	E^{MP3}	−27.0 (−22.4)		

[a] For notation and explanation see [60]
[b] See Ref. [62]
[c] See Ref. [12]
[d] $E_{SAPT}^{SCF} = E_{elst} + E_{exch}^{(10)} + E_{ind}^{(20)} + E_{ex-ind}^{(20)}$
[e] $E_{SAPT}^{corr} = E_{disp}^{\{2\}} + E_{ex-disp}^{(20)} + E_{pol}^{\{1\}} + E_{exch}^{\{1\}}$
[f] $E_{int}^{SAPT} = E_{SAPT}^{SCF} + E_{SAPT}^{corr}$

In the SAPT formalism the leading exchange corrections of $E_{\mathrm{SAPT}}^{\mathrm{SCF}}$ are $E_{\mathrm{exch}}^{(10)}$ and $E_{\mathrm{exch-ind}}^{(10)}$ [60]. The sum of these terms is more repulsive (20%) than our $e_{\mathrm{ex-pn}}$. The attractive part of the HF interaction energy is formed by the electrostatic, delocalization, and polarization contributions.

Our results indicate that the dispersion energy contributions ($\varepsilon_{\mathrm{disp}}^{(2)} > \varepsilon_{\mathrm{disp}}^{\mathrm{HF(2)}} > E_{\mathrm{disp}}^{(20)}$) form the main attractive parts of the interaction energy for He_2. The exchange-dispersion energies $\varepsilon_{\mathrm{ex-disp}}^2$ and $E_{\mathrm{ex-disp}}^{(20)}$ and dispersion energies up to the third order ($\varepsilon_{\mathrm{disp}}^{(3)} < \varepsilon_{\mathrm{disp}}^{\mathrm{HF(3)}} < E_{\mathrm{disp}}^{(30)}$) (see Table 1) are relatively small positive values. The contribution $\varepsilon_{\mathrm{ex-disp}}^{(2)} = 1.5 \times 10^{-2}\ \mu\mathrm{H}$ is very small in relation to $E_{\mathrm{ex-disp}}^{(20)}$ from SAPT. So far the best estimates of the second- and third-order supermolecular interaction energies for $(\mathrm{He})_2$ were recently published by Bukowski et al. [63]. Our $\Delta E_{\mathrm{CP}}^{\mathrm{MP2}} = -43.9\ \mu\mathrm{H}$ represents 86.7% of $E_{\mathrm{int}}^{(2)}$, and $\Delta E_{\mathrm{CP}}^{\mathrm{MP3}}$ within our basis set forms 94.3% of their benchmark value $E_{\mathrm{int}}^{(3)} = 7.95\ \mu\mathrm{H}$ at $R = 5.6$ bohr. Our $E_{\mathrm{disp}}^{(2)}$ represents 75% of the saturated $E_{\mathrm{disp}}^{(20)}$ value.

The main purpose of our work was not to reproduce experimental potential curves, but to compare the results of the presented PT with other approaches. In the last two rows of Table 1 we compare the total interaction energies for He_2 obtained by means of various methods. The potential energy parameters ε, R_{e} of Woon [56], Surján and del Valle [48] and our calculations are compared in Table 2. Our second- and third-order BSSE-corrected interaction energies are about 10% more attractive than supermolecular $E_{\mathrm{CP}}^{\mathrm{MP2}}$ and $E_{\mathrm{CP}}^{\mathrm{MP3}}$ and are very close to the SAPT interaction energy at the level coded in [60]. However, when the global $S^{-1/2}$ transformation of a monomer MO was used, we obtained non-physically large delocalization energy, and E_1^{PT} was significantly different from ΔE^{SCF} and the interaction energy from supermolecular approach. The occupied orbitals must be projected out from the virtual ones prior to orthogonalizing the dimer basis set to obtain reliable interaction energies. This conclusion was confirmed also in [48]. Computational artefacts due to the orthogonalization of the basis set still exist in this approach. We suppose that the BSSE correction described in Sect. 2.3 compensates for these artefacts and allows for better agreement between PT and the supermolecular approach than in [48].

Very good interaction energy values for the helium dimer interaction were calculated recently by Klopper and Noga [64] using a $11s8p6d5f4g$ basis set. They estimated the energy minimum of $-33.8\ \mu\mathrm{H}$ (at 5.6 a.u.) at the CCSDT-1a-R12 level and of $-34.8\ \mu\mathrm{H}$ for full CI. Similarly, Rybak et al. [65] obtained $-33.7\ \mu\mathrm{H}$ at the same distance using an explicitly correlated Gaussian geminal basis set. Another ab initio calculation has been published recently by yan Mourik and van Lenthe [66], Hayes et al. [67] and Cwiok et al. [68]. Our third-order energy minimum represents about 72% of these values, very close to the experimental minimum. From inspection of Table 2 we see that our energy minimum forms 94.6% of the CI value in the same basis and R_{e} is 0.02 bohr larger than the FCI value. The potential energy curve from the PT formulated in the biorthogonal basis is more repulsive with larger R_{e}.

5 Conclusion

We have extended the previously suggested [46] diagrammatic RSPT for the interaction of two closed-shell systems through the third order of perturbation. The preliminary calculation of the interaction energy of the He_2 system has confirmed the objections to the global $S^{-1/2}$ orthogonalization of the MOs of the interacting systems formulated earlier [54].

The second-order approximation to the SCF interaction energy obtained by the stepwise orthogonalization of occupied and virtual orbitals is in very good agreement with the SCF interaction energy values from the supermolecular approach. The presented PT offers an alternative to the separation of the SCF interaction energy with physical interpretation [69].

As discussed above, the problem of antisymmetry plays an important role in the intermolecular PT. Every PT type has its own peculiarity. The SAPT formalism is formulated in a basis set independent way and by definition is free from BSSE. A basis set convergence exists in the SAPT method for each physical component of interaction energy and contributions with slow convergence can be calculated in a larger basis set. However, assurance of the proper symmetry in SAPT is more complicated than in the "symmetric PT". In "symmetric PT" (orthogonal or biorthogonal formalism) the antisymmetry of the wave functions is automatically ensured and the resulting equations are more simple. The disadvantage of the "symmetric" formalism is that it is usually connected to a given basis set [48] and the presented PT cannot be formulated in a basis set independent way. The limiting factor for this approach as well as for the approaches based on the biorthogonal orbitals [31, 41] is the complete set of basis set functions. If basis sets Φ_0^A and Φ_0^B are complete, then set Φ_0^{AB} (Eq. 2) is overcomplete, the overlap matrix is singular and $S^{-1/2}$ does not exist.

The second- and third-order corrections appear as differences in large numbers, cf. Eq. (11) and Eq. (12). The direct formulation of these contributions [46] leads

Table 2. Well depth (ε) and equilibrium distance (R_{e}) for He_2. Values in parentheses are corrected for BSSE. Energies are in microhartree

Method/property	$-\varepsilon$	R_{e} (bohr)
E^{PT2}	26.9 (18.9)	6.05 (5.85)
E^{PT3}	13.2 (26.5)	6.15 (5.75)
E^{MP2} [a]	22.57 (17.9)	5.864 (5.921)
E^{MP3} [a]	27.97 (23.7)	5.764 (5.799)
CCSD[a]	28.05 (23.7)	5.775 (5.807)
CCSD(T)[a]	31.51 (27.0)	5.709 (5.744)
Full CI[a]	32.27 (28.0)	5.683 (5.729)
Biort.[b]	(15.0)	(6.0)
$E_{\mathrm{int}}^{\mathrm{SAPT}}$	(25.4)	(5.80)

[a] Woon [56]
[b] Surján and del Valle [48]

to a complicated computation algorithm and is significantly more expensive than the supermolecular approach.

We conclude that the presented version of the third-order MBPT produces qualitatively correct potential curves having a correct asymptotic behaviour, an acceptable estimation of the equilibrium distance, as well as the energy minimum. The interaction contributions are comparable with those obtained by other treatments (see Table 1). The inclusion of the suggested BSSE correction leads to a considerable improvement of the PT interaction energy curves (compare Figs. 2 and 3).

The dependence of the presented PT on the basis set and the inevitability of the BSSE correction reduce the applicability of this "symmetric" approach as compared to SAPT.

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