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Perturbative calculation of intermolecular interactions in orthogonalized or biorthogonal basis sets

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Abstract. Two versions of a many-body perturbation theory for the computation of molecular interaction energies are investigated. The methods are based on the partitioning of the second-quantized form of the dimer Hamiltonian written either in the orthogonalized basis of the monomer MOs, or, alternatively, in the original non-orthogonal dimer basis set handling the overlap by the biorthogonal formalism. The zeroth-order Hamiltonian H^0 is the sum of effective monomer Fockians and the zeroth-order wave functions are exact eigenfunctions of H^0. Full antisymmetry is ensured by the second-quantized formalism. Basis set superposition error is accounted for by the counterpoise correction recipe. Results for He_2, $(H_2)_2$ and $(H_2O)_2$ indicate the reliability of the biorthogonal technique.

Key words: Intermolecular interactions – Perturbation theory – Second quantization – Biorthogonal basis

1 Introduction

Different versions of exchange-perturbation theories (X-PT) [1–4] meet the difficulty that the eigenfunctions of the sum of the isolated monomer Hamiltonians are not antisymmetric. As antisymmetry was proved to be very important to all orders [5–7], complicated formulae have been derived to fulfill this requirement. Using second quantization, however, it is possible to develop a transparent formalism to deal with this problem [8, 9]. The idea is to construct a zeroth-order effective Hamiltonian whose eigenvalues are the sums of isolated monomer energies, while antisymmetry is automatically ensured by the Fermion anticommutation rules.

Second-quantization-based perturbation theories as applied to intermolecular interactions may differ from each other in selecting the basis set in which the calculations are performed and in choosing the interaction Hamiltonian. Both questions are related to the partitioning of the dimer Hamiltonian [9, 10]. The

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second-quantization-based X-PT developed previously [8] dealt with a perturbation operator describing pure interaction terms excluding local correlation and basis set extension effects completely [11]. In spite of promising preliminary results [12], difficulties have been encountered in the short-range limit of inter-molecular potential curves [13, 14], which have been attributed to the improper partitioning of the dimer Hamiltonian [14].

The aim of this work is to investigate the peformance of second-quantization-based exchange perturbation theory for the case when all terms in the interaction Hamiltonian are kept. By the examples studied, it will be shown that this method does yield qualitatively correct results over the full range of the potential curves. This holds if one uses the biorthogonal technique to work in the non-orthogonal basis set of the monomer MOs as well as if one turns to an orthogonalized MO basis.

2 Theory

2.1 PT in orthogonalized basis set

The working formulae for the perturbation theory take the simplest form if they are written in an orthogonal basis. Such a set can, e.g. be constructed in the following way. First, the MOs of the monomers constituting the molecular complex are computed. These MOs are then put together to form dimer orbitals, and the occupied MOs are projected out from the virtual subspace. Subsequently, the occupied and the virtual sets are orthogonalized separately, by Löwdin's procedure. Accordingly, the projected virtuals are defined as

$$\bar{\psi}_{l^*} = \psi_{l^*} - \hat{P}\psi_{l^*}, \tag{1}$$

where the asterisk refers to virtual MOs and $\hat{P}$ is the projector to the occupied subspace, which is non-diagonal due to overlap of occupied MOs on different fragments:

$$\hat{P} = \sum_{ik}^{\text{occ}} |\psi_i\rangle (T^{-1})_{ik} \langle\psi_k| \tag{2}$$

with $\boldsymbol{T}$ being the occupied block of the MO overlap matrix. Equation (1) can also be specified in terms of the MO coefficients $c_{l^*\mu}$:

$$\bar{c}_{l^*\mu} = c_{l^*\mu} - \sum_{ik}^{\text{occ}} R_{l^*i}(T^{-1})_{ik} c_{k\mu}, \tag{3}$$

where the Greek labels indicate AO indices and $\boldsymbol{R}$ is the full MO overlap matrix. After this projection, the occupied MOs ψ_k (as well as the virtuals ψ_{l^*}) are still overlapping among themselves, and they are not normalized either. The working basis set was obtained by orthonormalizing them separately by Löwdin's procedure.

In this basis set the dimer Hamiltonian has the standard form

$$\hat{H} = \sum_{\mu\nu} h_{\mu\nu} a_\mu^+ a_\nu + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] a_\mu^+ a_\nu^+ a_\sigma a_\lambda \tag{4}$$

in terms of spin orbitals. The integrals $h_{\mu\nu}$ contain kinetic energy and nuclear attraction, while electron repulsion integrals $[\mu\nu|\lambda\sigma]$ are written in the [12|12] convention.

A zeroth-order Hamiltonian can be conveniently defined as the sum of the Fockians constructed by the isolated orbital energies of the constituting monomers A and B (cf. Møller–Plesset partitioning):

$$\hat{H}^0 = \hat{F}_A + \hat{F}_B = \sum_i^{(A)} \varepsilon_i^A a_i^+ a_i + \sum_i^{(B)} \varepsilon_i^B a_i^+ a_i. \tag{5}$$

This operator is formally written in the orthogonalized dimer basis set, but its eigenvalues are the sums of the orbital energies of the isolated fragments:

$$\hat{H}^0 \Psi^0 = (E_A^0 + E_B^0)\Psi^0, \tag{6}$$

where

$$E_A^0 = \sum_i^{(A)} n_i \varepsilon_i^A \tag{7}$$

and similarly for B. The zeroth-order wave function Ψ^0 is an eigenfunction of $\hat{H}^0$ and it is the *antisymmetrized* product of the eigenfunctions of $\hat{F}_A$ and $\hat{F}_B$:

$$|\Psi^0\rangle = a_{A,N_A}^+ \cdots a_{A,2}^+ a_{A,1}^+ a_{B,N_B}^+ \cdots a_{B,2}^+ a_{B,1}^+ |\text{vac}\rangle. \tag{8}$$

Zeroth-order excited states are easily obtained by changing the occupation of the MOs.

The physical meaning of the zeroth-order effective Hamiltonian in Eq. (5) is given by Eqs. (6) and (7). It is the operator which acts in the basis of orthogonalized monomer orbitals exactly in the same manner as the pure monomer Fockians act in the original monomer basis sets. Consequently, it has the same eigenvalues.

One may ask the question whether or not the effective Fockians $\hat{F}_A$ and $\hat{F}_B$ depend on the basis orbitals or on the intermolecular overlap. The answer is no, because the orbital dependence of a second quantized operator originates only from the integral list, while the creation/annihilation operators are abstract quantities which, e.g. need not be varied when evaluating energy derivatives [9, 15–18]. As the "integral list" in $\hat{F}_A$ and $\hat{F}_B$ consists merely of the orbital energies of the isolated fragments, these operators do not depend on the orbitals and on the intermolecular overlap. Any matrix elements of $\hat{H}^0$ in the configuration space constructed by orthonormalized MOs will contain only ε_i^A and ε_i^B yielding the standard Møller–Plesset denominators.

The above consideration justifies to define the perturbation operator $\hat{W}$ as the difference between the total and the zeroth-order Hamiltonians:

$$\hat{H} = \hat{H}^0 + \hat{W}. \tag{9}$$

With this definition, the working formulae of the perturbation theory can be derived in a straightforward manner. The results up to the second order are listed below in terms of spin orbitals. The total electronic energy of the dimer is developed as

$$E = E^0 + E^1 + E^2,$$

where

$$E^0 + E^1 = \langle \Psi^0 | \hat{H}^0 + \hat{W} | \Psi^0 \rangle$$

$$= \sum_i^{\text{occ}} h_{ii} + \sum_{i,k}^{\text{occ}} ([ik|ik] - [ik|ki]), \tag{10}$$

$$E^2 = E^2_{\text{pol-del}} + E^2_{\text{disp-corr}} \tag{11}$$

in which the polarization–delocalization term $E^2_{\text{pol-del}}$ emerges from single excitations and shifts the energy towards the dimer SCF value:

$$E^2_{\text{pol-del}} = -\sum_{i}^{\text{occ}} \sum_{j^*}^{\text{virt}} \frac{(h_{ij^*} + \sum_k^{\text{occ}}([ik|j^*k] - [ik|kj^*]))^2}{\varepsilon_{j^*} - \varepsilon_i}. \tag{12}$$

The term $E^2_{\text{disp-corr}}$ is due to double excitations:

$$E^2_{\text{disp-corr}} = -\frac{1}{4} \sum_{i,k}^{\text{occ}} \sum_{j^*,l^*}^{\text{virt}} \frac{([ik|j^*l^*] - [ik|l^*j^*])^2}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k}. \tag{13}$$

In the above equations the ε_i are the orbital energies of the monomers.

The corresponding interaction terms are obtained as

$$\Delta E^1 = E^0 + E^1 - E^{\text{SCF}}_A - E^{\text{SCF}}_B. \tag{14}$$

The term $E^2_{\text{pol-del}}$ is an interaction energy by itself, while $E^2_{\text{disp-corr}}$ will also contain the local correlation energy up to the second order:

$$\Delta E^2_{\text{disp}} = E^2_{\text{disp-corr}} - E^{\text{MP2}}_A - E^{\text{MP2}}_B. \tag{15}$$

If the local Hartree–Fock and second-order Møller–Plesset correlation energies, E^{SCF}_A and E^{MP2}_A, are computed in the subset of basis functions on monomer A (and similarly for B), then the above interaction energies will suffer from basis set superposition error. To correct for this artifact we computed them in the dimer basis set according to the counterpoise correction recipe [19]. Another possibility to eliminate superposition error would be the application of the BSSE-free interaction operator [9, 8, 11]. In the present work we decided to use the conventional Boys–Bernardi method which is commonly used for supermolecule calculations and permits us to investigate the performance of the many-body X-PT without mixing other kinds of problems which might appear if BSSE is corrected by other means.

As the occupied orbitals are projected out from the virtuals ones prior to orthogonalizing the entire dimer basis set, the energy up to the first order is the correct expectation value of the dimer Hamiltonian calculated by the antisymmetrized monomer wave functions. This feature is very important to get reliable interaction energies.

A closely related theory was published several years ago by Kvasnička et al. [20]. They have also developed a second-quantized intermolecular PT using an orthogonalized basis sets and the Møller–Plesset-type partitioning scheme. They separated the interaction terms from local ones by forming the differences between the integral lists in the original and orthogonalized basis sets. The basic difference between the present formulation and that in Ref. [20] is that Kvasnička et al. used a different basis set as they allowed the occupied and virtual MOs to mix in course of orthogonalization. To our knowledge, no numerical results have yet been published for their theory, though some calculations are in progress [21]. For the comparison of the present approach with other versions of intermolecular PT, see also the discussion in Sect. 4.

2.2 *Biorthogonal formalism*

Slightly different formulae emerge if the above PT is developed in the non-orthogonal basis set constructed by the monomer MOs. The biorthogonal formulation is convenient to handle the problem [8, 9, 22–24]. In this case, the dimer Hamiltonian takes the form

$$\hat{H} = \sum_{\mu\nu} h_{\tilde{\mu}\nu} a_\mu^+ \tilde{a}_\nu + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\tilde{\mu}\tilde{\nu}|\lambda\sigma] a_\mu^+ a_\nu^+ \tilde{a}_\sigma \tilde{a}_\lambda, \tag{16}$$

where the tildes refer to the reciprocal space: $h_{\tilde{\mu}\nu} = \sum_\lambda (S^{-1})_{\lambda\mu} h_{\mu\nu}$, $\tilde{a}_\mu = \sum_\omega (S^{-1})_{\omega\mu} a_\omega$, etc., where $\boldsymbol{S}$ is the MO overlap matrix. Test calculations and preliminary studies [14] indicated that it is essential to keep the occupied and virtual subspaces orthogonal to each other. Therefore, prior to constructing the biorthogonal orbitals, we applied the same projections as defined in Eqs. (1)–(3). Accordingly, the MO overlap matrix $\boldsymbol{S}$ is block-diagonal.

As the direct-space creation operators a_μ^+ and the reciprocal-space annihilation operators $\tilde{a}_\nu$ obey the standard anticommutation rules [9], the similarity between the biorthogonal and the orthogonal formalism is obvious. The details of this formalism have already been published [8, 9, 14], so we report here merely the working formulae. The zeroth-order effective Hamiltonian is defined as

$$\hat{H}^0 = \hat{F}_A + \hat{F}_B = \sum_i^{(A)} \varepsilon_i^A a_i^+ \tilde{a}_i + \sum_i^{(B)} \varepsilon_i^B a_i^+ \tilde{a}_i. \tag{17}$$

The Hamiltonian $\hat{H}^0$ has the same physical significance as in the orthogonal case, its eigenvalues being the orbital energies of the isolated monomers. Again, it is independent of the orbitals and orbital overlaps. Up to the first order, we get

$$E^0 + E^1 = \langle \hat{H}^0 + \hat{W} \rangle = \sum_i^{\text{occ}} h_{\tilde{i}i} + \sum_{i,k}^{\text{occ}} ([\tilde{i}\tilde{k}|ik] - [\tilde{i}\tilde{k}|ki]). \tag{18}$$

The second-order formulae become

$$E^2_{\text{pol-del}} =$$

$$-\sum_i^{\text{occ}} \sum_{j^*}^{\text{virt}} \frac{(h_{\tilde{i}j^*} + \sum_k^{\text{occ}}([\tilde{i}\tilde{k}|j^*k] - [\tilde{i}\tilde{k}|kj^*]))(h_{\tilde{j}^*i} + \sum_k^{\text{occ}}([\tilde{j}^*\tilde{k}|ik] - [\tilde{j}^*\tilde{k}|ki]))}{\varepsilon_{j^*} - \varepsilon_i} \tag{19}$$

and

$$E^2_{\text{disp-corr}} = -\frac{1}{4} \sum_{i,k}^{\text{occ}} \sum_{j^*,l^*}^{\text{virt}} \frac{([\tilde{i}\tilde{k}|j^*l^*] - [\tilde{i}\tilde{k}|l^*j^*])([\tilde{j}^*\tilde{l}^*|ik] - [\tilde{j}^*\tilde{l}^*|ki])}{\varepsilon_{j^*} + \varepsilon_{l^*} - \varepsilon_i - \varepsilon_k}. \tag{20}$$

In deriving the above terms we have again used the full dimer Hamiltonian to define the perturbation operator $\hat{W} = \hat{H} - \hat{H}^0$ [14]. Different results are obtained for the energy corrections if one used merely the "physical" Coulombic interaction operator [8, 10, 11, 22, 23].

As mentioned above, it was found essential to project the occupied MOs out from the virtual subspace before forming the biorthogonal orbitals. This is in agreement with previous findings [13, 25]. Due to this orthogonality the first-order results as counted by Eqs. (10) and (18) are identical. The interaction energy terms as the second and higher orders, however, are different in the orthogonal and biorthogonal formulations, though naturally they converge to the same limit if both perturbation series are convergent.

3 Numerical results

To illustrate the performance of the above formalism, sample calculations are reported below for the cases of He–He, H_2–H_2 and H_2O–H_2O interactions. The basis sets chosen are medium-sized or somewhat larger; they have been used formerly by other authors to compute interaction energies for these systems [26–28].

Our aim was not to reproduce experimental potential curves, but to compare the accuracies of the two versions of the X-PT discussed above. Accordingly, we have also computed the MP2 potential curves in each case, which serve as references since they represent the supermolecule results [29] containing correlation energies to the same order. The MP2 curves, of course, were also corrected for basis set superposition error by the counterpoise method.

The He–He interaction was studied in two different basis sets (Figs. 1 and 2). We can observe that the potential curves are qualitatively correct for both cases, i.e. they are similar to the MP2 reference. In both basis sets the results of the biorthogonal X-PT are closer to that of MP2. The X-PT curve in orthogonal basis is somewhat displaced; it predicts less interaction in the [4*s*,3*p*,2*d*,1*f*] basis while it is too deep in [4*s*,3*p*,2*d*] one. (Note that this latter basis, though composed of lesser number of contracted functions, is much better for the He–He interaction.) At the long range all the three curves coincide. The short-range behavior of the X-PT curves is also correct, even in the range $R < 5$ a.u. not displayed in Figs. 1 and 2.

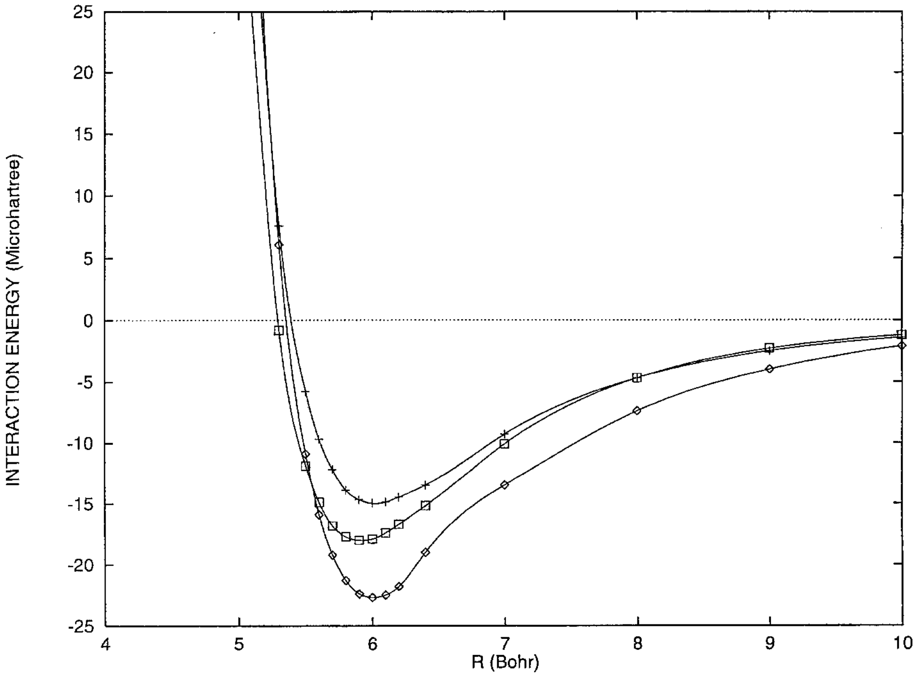

Fig. 1. Potential curves for the He–He interaction in a [4*s*,3*p*,2*d*] basis set ("aug-cc-pVTZ" in Ref. [26]). □: supermolecule calculation, MP2; + : exchange-perturbation theory, biorthogonal formalism; ◇: exchange-PT, orthogonal basis

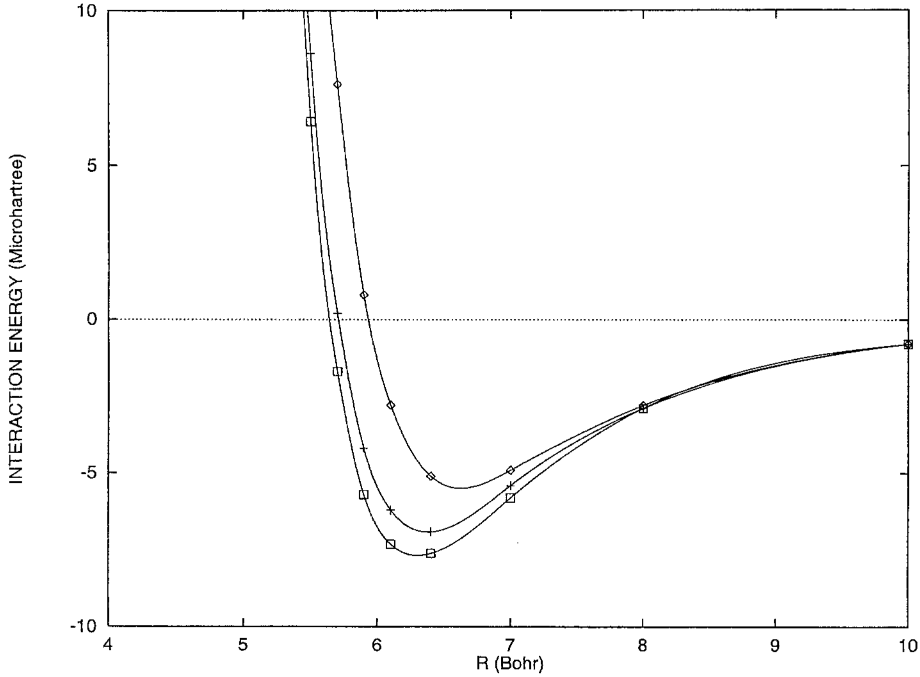

Fig. 2. Potential curves for the He–He interaction in a [4*s*,3*p*,2*d*,1*f*] basis set ("cc-pVQZ" in Ref. [26]). □: supermolecule calculation, MP2; + : exchange-PT, biorthogonal formalism; ◇: exchange-PT, orthogonal basis

Table 1. Individual contributions to the interaction energy (a.u.) at the experimental minima

		H_2–H_2 ($R = 6.5$ Bohr)		H_2O–H_2O ($R = 5.67$ Bohr)	
Order	Term	Biorthogonal	Orthogonal	Biorthogonal	Orthogonal
1	Electrostatic	+ 0.000092	+ 0.000092	– 0.00374	– 0.00374
2	Pol–Del	– 0.000019	– 0.000019	– 0.00182	– 0.00185
1 + 2	Subtotal	+ 0.000073	+ 0.000073	– 0.00556	– 0.00560
∞	SCF	+ 0.000070		– 0.00617	
2	Dispersion	– 0.000117	– 0.000099	– 0.00172	– 0.00081
1 + 2	Total	– 0.000044	– 0.000026	– 0.00729	– 0.00641
∞	MP2	– 0.000056		– 0.00724	

The conclusions for the H_2–H_2 system are similar. We have used a [7*s*3*p*] basis set [27]. The supermolecule MP2 and the biorthogonal X-PT curves in this basis are quite similar, while the orthogonal X-PT predicts smaller interaction at around equilibrium. The short- and the long-range asymtotics are correct for both cases. Individual contributions to the interaction energies at $R = 6.5$ a.u. are given in Table 1. Adding the first-order correction to the second-order polarization–delocalization correction originating from single excitations, the supermolecule SCF results are recovered within an error of ~3 μH. This holds both for the biorthogonal and orthogonal formulations. As to the correlation contribution to the interaction energy, it amounts to $-56 - 70 = -126$ μH according to the supermolecule calculation, while it is -117 and -99 μH for the biorthogonal and orthogonal PTs, respectively.

The similarity of the supermolecule and X-PT results can also be demonstrated for the water–water interaction (Fig. 4). In the [4*s*,3*p*,2*d*/2*s*1*p*] basis set used, the long-range and the short-range parts of the potential curves obtained by the supermolecular MP2 and both X-PT calculations are almost identical. At around equilibrium, the biorthogonal formulation gives results closer to MP2. The differences in the predicted well depths and equilibrium distances are negligible.

The partitioning of the interaction energy contributions for the water–water case is also shown in Table 1. The relative errors of the estimation of the SCF energy are 9–10% for both versions. The dispersion energy is ca. 1.7 mH by biorthogonal X-PT, 0.8 mH in the orthogonal formulation, while the supermolecule result is 1.1 mH in this basis set.

We have not made a systematic numerical comparison of our results to those obtained by other formalisms as our aim was merely to test the applicability of biorthogonal and orthogonal versions of this PT. Some selected data for comparison, however, are listed below.

In the "aug-cc-pVTZ" basis set, MP2, MP3, MP4, CCSD, CCSD(T) and full-CI calculations were reported for the He dimer by Woon and Dunning [26]. The full-CI result gives 28 μH for the counterpoise-corrected interaction energy at the

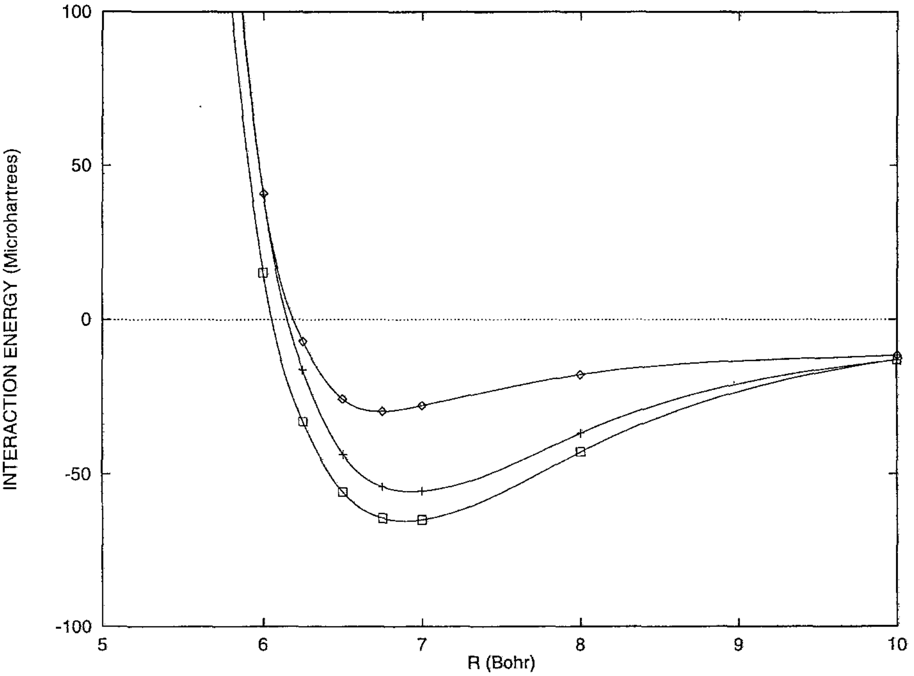

Fig. 3. Potential curves for the H_2–H_2 interaction. The two molecules are coplanar and are in a T-shape arrangement. *R* is the distance between the centers of masses of the two molecules. Basis set [7*s*,3*p*] of Ref. [27]. □: supermolecule calculation, MP2; + : exchange-PT, biorthogonal formalism; ◇: exchange-PT, orthogonal basis

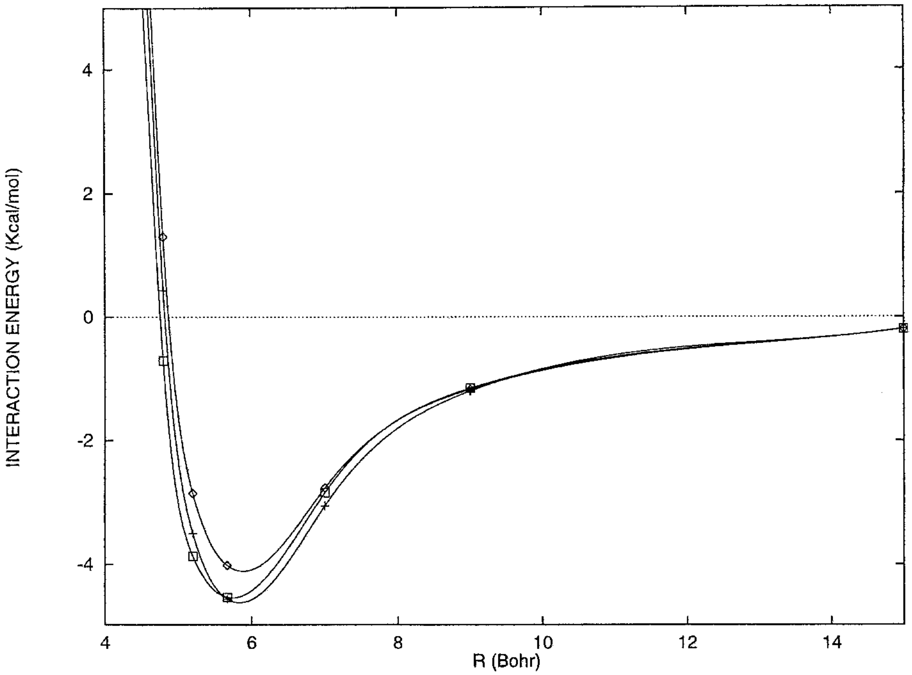

Fig. 4. Potential curves for the water–water interaction. The dimer is in a linear configuration, where each water molecule is frozen and R is the distance between the two oxygen atoms. The geometry and the $[4s,3p,2d/2s,1p]$ basis set are the same as in Ref. [28]. □: supermolecule calculation, MP2; + : exchange-PT, biorthogonal formalism; ◇: exchange-PT, orthogonal basis

$R = 5.73$ a.u. potential minimum. This compares to 17.9 μH at $R = 5.9$ a.u. (MP2, other supermolecule results are in between), and 15 (23) μH at 6 a.u. obtained by the present biorthogonal (orthogonal) version of PT (Fig. 1). This interaction energy is 84% (129%) of the MP2 result. In a larger basis set, Tachikawa et al. [34] got a second-order estimate 31.7 μH at 5.6 a.u., which is 91% of the quoted experimental result (they did not report the MP2 value). Using a more sophisticated (and more complicated) theory and an explicitly correlated Gaussian geminal basis, Rybak et al. [39] got 33.7 μH at the same distance. Earlier, Chałasiński and Szczęśniak [43] extracted second-order contributions obtained in different basis sets which gave 97% of the MP2 energy, 45 μH in their basis set. Recently, Ćwiok et al. [41] by symmetry adapted perturbation theory obtained 34.6 μH close to the van der Waals minimum in perfect agreement with experiments.

For the water–water interaction, we cite the work by Rybak et al. [40]. The potential energy curves obtained by their symmetry adapted PT calculation differ more significantly from the supermolecule results as the curves reported in Fig. 4. In particular, they got ca. 5.6 kcal (instead of 4.3) for the interaction energy, while we got 4.2 (4.7) instead of the 4.6 MP2 result in the biorthogonal (orthogonal) formulations, respectively (cf. Fig. 4). This constitutes a clear success of the present approach, especially in light of the fact that we treat also SCF interactions by means of X-PT, not merely the correlation effect.

4 Discussion

As well known, a central problem in intermolecular PT is that of antisymmetry. It is manifested in the dilemma whether to use $\Psi^0 = \mathscr{A}\Phi^0$ or just $\Phi^0 = \Phi_A^0\Phi_B^0$ as the zeroth-order wave function the latter being an eigenfunction of the sum of the isolated monomer Hamiltonians written in the L_2 space while the former being asymptotically correct. A clear and logical classification of all possible types of methods capable of handling the problem is contained in a recent review by Jeziorski et al. [36]. They distinguish "symmetric theories" from "symmetry-adapted" perturbation theories (SAPT). The latter start from an asymmetric H^0 whose eigenfunction is $\Phi_A^0\Phi_B^0$, and it is the task of PT to enforce the wave function to be properly antisymmetric. In "symmetric" theories antisymmetry is always ensured at the expense of changing the partitioning the Hamiltonian so that $\Psi^0 = \mathscr{A}\Phi_A^0\Phi_B^0$ will be eigenfunction of H^0. In this terminology, the formalism used in this paper belongs to the "symmetric" theories while the recent development by Jeziorski and coworkers [33, 36, 40, 41] are made within the "symmetry-adapted" framework.

Both formalisms have their own significance. The SAPT has the advantage that it can be formulated in a basis-set-independent way, but it suffers from the drawback that symmetry adaptation can be quite complicated and in fact for many-electron systems it is possible to apply only when the antisymmetrizer does not enter the perturbation equations but merely in the energy corrections ("weak symmetry forcing"). In "symmetric" PTs all wave functions are automatically antisymmetric to any orders, which can be most conveniently done within the second-quantized formalism. This is a nice feature as, apart from the simplicity of the resulting equations, second quantization is a natural language for all many-body methods (MBPT, coupled cluster, etc.) so they can be discussed with intermolecular interactions on an equal footing. The disadvantage of the "symmetric" formalism is that it is usually connected to a given basis set. It does not necessarily mean, however, that second-quantization-based perturbation theories would yield more basis-set-dependent results as those obtained from other formulations, as in actual calculation one has to turn to a basis set anyway.

A different, though related, question to be discussed in connection with the present formalism is the possibility of direct evaluation of energy differences. As mentioned above, though Eqs. (12) and (19) are direct interaction terms, the first-order corrections and the second-order dispersion–correlation terms appear as differences of large numbers, cf. Eqs. (14, 15). This is quite normal in a supermolecule calculation but not very elegant in a perturbation approach[1]. The reason of this is that the perturbation operator as defined in Eq. (9) contains both monomer fluctuation and interaction potential. Accordingly, the present approach can be viewed from two entirely different standpoints.

– First, one can say that it is not an alternative of exchange-perturbation theories, rather a supermolecular approach. It differs from standard MP2 calculation in selecting the basis set, which does not consist of the dimer-optimized orthogonal MOs, but of the overlapping MOs of isolated fragments. In this view, the present perturbation theory is related to the formalism of Chałasiński and Szczęśniak [42].

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[1] We note that, following the idea suggested in Ref. [20], one can evaluate these energy terms directly by forming the differences between the integral lists of the interacting and non-interacting systems

– In the second view, one emphasizes that the present approach starts from the anti-symmetrized wave functions and the sum of the energies of the isolated subsystems at the zeroth order, and, assuming the PT series to converge, ends at the dimer wave function and energy. If one worked merely at the Hartree–Fock level or if one had a single electron in the system, this approach would indeed be an X-PT. At the correlated level, the formulae presented in Sect. 2 are plagued with mixing local correlation effects with interaction terms. From the pure theoretical point of view, this could be eliminated by starting from locally correlated functions instead of the HF ones. This would modify the working formulae and is feasible only for small, e.g. two-electron fragments for which similar procedures do exists within the framework of interacting geminals [37, 38].

We can conclude that both versions of the second-order MBPT investigated in this paper give qualitatively correct potential curves. The $R \to \infty$ and the $R \to 0$ asymptotic behaviors are quite exact, and acceptable estimates are obtained for equilibrium distances and well depths. The reliability of the results is that we can expect from a second-order theory [30–34]. The performance of the biorthogonal version is slightly better in the cases studied, and there is no sign of any "instability" of the biorthogonal formulation discussed previously [13, 14]. The two essential features which have led to this positive result are

(1) the use of the full dimer Hamiltonian in the interaction operator $\hat{W} = \hat{H} - \hat{H}^0$, and
(2) the orthogonalization of the virtual and occupied subspaces before constructing the dimer basis set.

Further improvement of the results presented in this paper is possible by evaluating third-order contributions. Preliminary calculations in this direction are encouraging [35].

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