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Second-order energy components in basis-set-superposition-error-free intermolecular perturbation theory

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Abstract. Recently a basis-set-superposition-error-free second-order perturbation theory was introduced based on the "chemical Hamiltonian approach" providing the full antisymmetry of all wave functions by using second quantization. Subsequently, the "Heitler–London" interaction energy corresponding to the sum of the zero- and first-order perturbational energy terms was decomposed into different physically meaningful components, like electrostatics, exchange and overlap effects. The first-order wave function obtained in the framework of this perturbation theory also consists of terms having clear physical significance: intramolecular correlation, polarization, charge transfer, dispersion and combined polarization–charge transfer excitations. The second-order energy, however, does not represent a simple sum of the respective contributions, owing to the intermolecular overlap. Here we propose an approximate energy decomposition scheme by defining some "partial Hylleraas functionals" corresponding to the different physically meaningful terms of the first-order wave functions. The sample calculations show that at large and intermediate intermolecular distances the total second-order intermolecular interaction energy contribution is practically equal to the sum of these "physical" terms, while at shorter distances the overlap-caused interferences become of increasing importance.

Key words: Energy decomposition – Energy components – Intermolecular interactions – Intermolecular perturbation theory – Chemical Hamiltonian approach

1 Introduction

One may get a deeper insight in the physics of intermolecular interactions if the calculated interaction energy can be decomposed into physically meaningful terms. Such a decomposition scheme has been introduced at the self-consistent-field (SCF) level of theory by Kitaura and Morokuma [1] and Umeyama and Morokuma [2]. Analogously, it is customary to introduce polarization, dispersion, etc. energy components in the framework of "symmetry-adapted perturbation theory" (SAPT) [3, 4]. A detailed analysis of the second-order energy components has also been given in the determinant-based intermolecular PT for overlapping systems introduced by Hayes and Stone [5, 6].

In the recent work [7] we have considered the simplest "Heitler–London" approximation, in which one computes the energy of the single determinant wave function of the supermolecule, built up by using the unperturbed monomer SCF orbitals. This very simple scheme permits one to account qualitatively for the leading interactions present in a hydrogen-bonded system, giving an energy which roughly corresponds to the terms of "ESX" type in the nomenclature of Kitaura and Morokuma [1] and Umeyama and Morokuma [2] (see also Ref. [5]). By using Löwdin's pairing theorem, we have succeeded in giving the explicit analytical expression for this "Heitler–London" energy and we decomposed it into a sum of different physically relevant contributions such as electrostatics, exchange, overlap effects, etc. [7].

The "Heitler–London" energy, in turn, represents the sum of the zero- and first-order energies in the framework of the second-order basis-set-superposition-error-(BSSE)-free PT of intermolecular interactions which we have recently developed [8, 9] by using second quantization and applying the so-called "chemical Hamiltonian approach" (CHA) [10] to eliminate BSSE. In this theory the use of the second quantization formalism ensures that all the wave functions are automatically antisymmetric with respect to interchanges of all electrons – including those between the interacting monomers. Usually, there is a dilemma that the wave function is either correctly antisymmetric or represents an eigenfunction of the unperturbed Hamiltonian – which is hard to resolve without second quantization. Second quantization permits the perturbative calculation of intermolecular interactions to be realized in a fully

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rigorous manner, without using any nonphysical (i.e. not completely antisymmetrized) wave functions. In this sense, such a second-quantization-based PT can be considered as the conceptually best approach to the problem SAPT is devoted to solve – as stressed by Surján [11], the interaction operator used in the CHA formalism is the second quantized counterpart of the L^2 interaction operator used in SAPT.[1]

In the PT considered (it may be denoted CHA–PT2) the zero-order Hamiltonian is the sum of the free monomer Fockians, and the energy is computed in the framework of the "CHA with conventional energy" scheme [15], in which the BSSE-free CHA Hamiltonian is used to obtain the wave function excluding any BSSE effects on it, and then the conventional Hamiltonian is used to compute the energy. In this manner one obtains the total energy of the system up to second order as

$$E^{(2)} = \frac{\langle\Psi_0|\hat{H}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} + J_2 \ , \tag{1}$$

where the first ("Heitler–London") term represents the sum of zero- and first-order energy components, written as the expectation value of the total Hamiltonian over the unperturbed zero-order wave function [8]. J_2 is the second-order energy contribution, given by the Hylleraas-type functional for a non-Hermitian unperturbed Hamiltonian [16]. It represents a generalization of the usual Hylleraas functionals [17] and can be obtained by expanding in series the expectation value of the energy with the zero- and first-order wave functions and conserving terms up to second order. As our PT is based on the BSSE-free CHA theory, the interaction energy is obtained from Eq. (1) by subtracting the SCF energies of the two monomers, each calculated in the respective free monomer basis set.

As pointed out in Ref. [9], the first-order wave function of the CHA–PT2 consists of terms having clear physical significance: intramolecular correlation, polarization, dispersion, etc; however, the second-order energy J_2 represents a simple sum of these effects only in the asymptotic region of large intermolecular distances, where all the orbitals can be considered orthogonal. At intermediate distances, however, intermolecular overlap is not negligible anymore and owing to this overlap one cannot perform a quite strict decomposition of the second-order interaction energy into "physical" components. Nevertheless, as will be seen, an approximate decomposition is often possible. Accordingly, here we propose a scheme in which one computes some "partial Hylleraas functionals" corresponding to each physically distinguishable term of the first-order wave function and checks in which cases the sum of the latter approximates well the total second-order energy contribution. Obviously, if this is not the case and the overlap-caused interference terms between the different physical effects are too large, one cannot assign any simple interpretation to the second-order interaction energy values obtained.

The aim of the present work is to investigate in some detail the possibility of such an energy decomposition and to perform some sample calculations by using different basis sets for some typical hydrogen-bonded systems. We discuss that our perturbation method and decomposition scheme have some similarities with those of Hayes and Stone [5, 6], but they are not identical with them. In addition, our theory significantly differs from SAPT. The basic difference is in the fact that we use a properly antisymmetrized unperturbed wave function which is also the eigenfunction of the unperturbed Hamiltonian. (This is possible owing to our use of the second quantized formalism.) At the same time, SAPT usually applies the "weak symmetry forcing" approximation, i.e. introduces the intermolecular antisymmetrization only when the energy is calculated (but not the wave function), and several other simplifications should also be introduced from a practical point of view (the "single exchange" approximation and recurring to the supermolecule HF wave functions with counterpoise correction). Our formalism does not contain any approximations except cutting the wave function after the first order and energy after the second.

2 The CHA-PT2 energy formula and its decomposition

2.1 The energy formula

The first-order or "Heitler–London" energy term in Eq. (1) is the energy corresponding to the wave function obtained by antisymmetrizing the unperturbed wave functions of the monomers put at a given (finite) distance from each other. As the monomers are treated at the HF level, this antisymmetrized wave function is still a single determinant. Its energy can be computed very simply, by orthonormalizing the unperturbed monomer orbitals φ_i. Alternatively, one can use the analytical expressions we have derived for this energy

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[1] There is, in fact, also another dilemma which is usually not even formulated explicitly. The use of a finite basis set defines a model Hamiltonian, the exact solution of which can be obtained (at least in principle) by solving the relevant full configuration interaction (CI) problem or can be approximated by using the appropriate methods of quantum chemistry. If the system consists of two weakly interacting monomers, then it is a quite natural approach to find the approximate solutions by building up a PT which starts from the Hartree–Fock (HF) solutions of the free monomers and converges to the full CI energy value of the supermolecule. Such a PT has been proposed, for example, by Kvasnička et al. [12] by using orthogonalized orbitals - also see [13, 14]. The results of such a PT (similarly to the calculations performed directly at the supermolecule level) are "contaminated" by BSSE – one may, of course perform "ghost orbital" calculations for the monomers to obtain a posteriori counterpoise-corrected interaction energies. On the other hand, it is known that SAPT gives interaction energy values which are a priori free of BSSE. However, SAPT is conceptually unable to get the BSSE-uncorrected interaction energies, which is not only a drawback from the formal mathematical point of view, but also limits the generalization of SAPT for describing strong (intramolecular) interactions. Our formalism permits the development of both BSSE-free and BSSE-uncorrected versions of the intermolecular PT, depending on whether the CHA analysis of the Hamiltonian is invoked or not for eliminating the terms causing BSSE; here we concentrate on the BSSE-free CHA version, but the relevant second-order energy formulae were given in the Appendix of Ref. [8] for the case when BSSE is not separated out from the Hamiltonian.

and its different physical components [7]. We shall not discuss this term here in any detail.

The second-order energy contribution in the CHA-PT2 framework is given by the generalized Hylleraas functional J_2,

$$J_2 = \frac{1}{\langle\Psi_0|\Psi_0\rangle}[2Re(\langle\hat{Q}\chi|\hat{V}|\Psi_0\rangle) + Re(\langle\chi|\hat{H}^0 - E_0|\chi\rangle)] \ , \qquad (2)$$

introduced in Ref. [16]. Here $\hat{H}$ is the total Hamiltonian of the supermolecule, $\hat{V} = \hat{H} - \hat{H}^0$ is the perturbation, $\hat{H}^0$ being the zero-order effective one-electron Hamiltonian combining the HF problems of both free monomers [8]. Furthermore, Ψ_0 is the unperturbed wave function, E_0 is the zero-order energy, $\hat{Q}$ is the projection operator on the orthogonal complement to Ψ_0 and χ is the first-order CHA wave function [8].

2.2 *Components of the first-order wave function*

In order to obtain the second-order energy contribution, one has to calculate the first-order CHA wave function $|\chi\rangle$, which is [8, 9]

$$\begin{aligned}|\chi\rangle =& \frac{1}{4}\sum_{i,j\in\mathrm{A}}^{\mathrm{occ}}\sum_{p,q\in\mathrm{A}}^{\mathrm{virt}}\frac{-[pq\|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j}|\Psi_{ij}^{pq}\rangle \\ &+ \sum_{i\in\mathrm{A}}^{\mathrm{occ}}\sum_{p}^{\mathrm{virt}}\frac{-\langle\tilde{p}|\hat{V}_{\mathrm{B}}^{\mathrm{aux}}|i\rangle}{\varepsilon_p - \varepsilon_i}|\Psi_i^p\rangle \\ &+ \frac{1}{4}\sum_{i\in\mathrm{A}}^{\mathrm{occ}}\sum_{j\in\mathrm{B}}^{\mathrm{occ}}\sum_{p,q}^{\mathrm{virt}}\frac{-[\tilde{p}\tilde{q}\|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j}|\Psi_{ij}^{pq}\rangle \\ &+ (\mathrm{A} \leftrightarrow \mathrm{B}) \ , \end{aligned} \qquad (3)$$

where $(\mathrm{A} \leftrightarrow \mathrm{B})$ indicates that all terms with monomers A and B interchanged should be added. $|\Psi_i^p\rangle$ and $|\Psi_{ij}^{pq}\rangle$ are singly and doubly excited determinants in terms of the original occupied and virtual monomer orbitals φ_i, φ_p etc., and $\hat{V}_{\mathrm{B}}^{\mathrm{aux}}$ is an auxiliary operator, defined through its matrix element as

$$\langle\tilde{p}|\hat{V}_{\mathrm{B}}^{\mathrm{aux}}|i\rangle = \langle\tilde{p}|\sum_{a\in\mathrm{B}}\frac{-Z_a}{r_a}|i\rangle + \sum_{j\in\mathrm{B}}^{\mathrm{occ}}[\tilde{p}\tilde{j}\|ij] \ . \qquad (4)$$

We use the notation $[ab\|cd]$ for the usual differences of the two-electron Coulomb and exchange integrals in the $[12|12]$ convention and the tilde denotes the biorthogonal counterparts of the respective monomer molecular orbitals.

One can see upon inspection that the first-order wave function (Eq. 3) is a sum of terms of different, well-defined physical meaning:

$$|\chi\rangle = |\chi\rangle_{\mathrm{intra-corr.}} + |\chi\rangle_{\mathrm{pol}} + |\chi\rangle_{\mathrm{CT}} + |\chi\rangle_{\mathrm{disp}} + |\chi\rangle_{\mathrm{pol-CT}} \ . \qquad (5)$$

Here, $|\chi\rangle_{\mathrm{intra-corr.}}$ describes the intramolecular correlation of the free monomers:

$$\begin{aligned}|\chi\rangle_{\mathrm{intra-corr.}} =& \frac{1}{4}\sum_{i,j\in\mathrm{A}}^{\mathrm{occ}}\sum_{p,q\in\mathrm{A}}^{\mathrm{virt}}\frac{-[pq\|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j}|\Psi_{ij}^{pq}\rangle \\ &+ (\mathrm{A} \leftrightarrow \mathrm{B}) \ . \end{aligned} \qquad (6)$$

Note that the unperturbed wave functions are built of the single HF determinants of the monomers, so the intramonomer correlation is also contained in the second-order energy we are calculating. However, when computing intermolecular interaction energies, we can extract the correlation energy of the free monomers and deal only with the change of the intramonomer correlation taking place during the complex formation. (Although all the coefficients in Eq. (6) are the same as those in the free monomers, the corresponding second-order correlation energy may change owing to the intermolecular overlap.)

Considering the second term in Eq. (3), one should distinguish the cases in which the virtual orbital φ_p is on the same monomer as the occupied orbital φ_i ($p \in \mathrm{A}$) or on another monomer ($p \in \mathrm{B}$). The former type obviously corresponds to excitations of polarization type, the latter one describes charge transfers (CT) between the monomers:

$$|\chi\rangle_{\mathrm{pol}} = \sum_{i\in\mathrm{A}}^{\mathrm{occ}}\sum_{p\in\mathrm{A}}^{\mathrm{virt}}\frac{-\langle\tilde{p}|\hat{V}_{\mathrm{B}}^{\mathrm{aux}}|i\rangle}{\varepsilon_p - \varepsilon_i}|\Psi_i^p\rangle + (\mathrm{A} \leftrightarrow \mathrm{B}) \qquad (7)$$

$$|\chi\rangle_{\mathrm{CT}} = \sum_{i\in\mathrm{A}}^{\mathrm{occ}}\sum_{p\in\mathrm{B}}^{\mathrm{virt}}\frac{-\langle\tilde{p}|\hat{V}_{\mathrm{B}}^{\mathrm{aux}}|i\rangle}{\varepsilon_p - \varepsilon_i}|\Psi_i^p\rangle + (\mathrm{A} \leftrightarrow \mathrm{B}) \ . \qquad (8)$$

The third term in Eq. (3) describes the conventional dispersion-type excitations if both excitations have local character, i.e. the two virtual orbitals belong to different monomers ($\varphi_p \in \mathrm{A}; \varphi_q \in \mathrm{B}$), similarly to the occupied orbitals from which they are excited:

$$\begin{aligned}|\chi\rangle_{\mathrm{disp}} =& \frac{1}{2}\sum_{i\in\mathrm{A}}^{\mathrm{occ}}\sum_{j\in\mathrm{B}}^{\mathrm{occ}}\sum_{p\in\mathrm{A}}^{\mathrm{virt}}\sum_{q\in\mathrm{B}}^{\mathrm{virt}}\frac{-[\tilde{p}\tilde{q}\|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j}|\Psi_{ij}^{pq}\rangle \\ &+ (\mathrm{A} \leftrightarrow \mathrm{B}) \ . \end{aligned} \qquad (9)$$

In the cases when both virtual orbitals are on the same monomer ($\varphi_p, \varphi_q \in \mathrm{A}$), the third term in Eq. (3) describes configurations in which there is a simultaneous polarization of one monomer and a CT to it from the other one. This corresponds to the combined "polarization–CT" component of $|\chi\rangle$:

$$\begin{aligned}|\chi\rangle_{\mathrm{pol-CT}} =& \frac{1}{2}\sum_{i\in\mathrm{A}}^{\mathrm{occ}}\sum_{j\in\mathrm{B}}^{\mathrm{occ}}\sum_{p,q\in\mathrm{A}}^{\mathrm{virt}}\frac{-[\tilde{p}\tilde{q}\|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j}|\Psi_{ij}^{pq}\rangle \\ &+ (\mathrm{A} \leftrightarrow \mathrm{B}) \ . \end{aligned} \qquad (10)$$

Although both CT and polarization are one-electron effects, this term originates from two-electron excitations, so it is not included in the SCF-type energy analyses [1, 2]. At the same time, the presence of a CT effect causes this term to be absent also in the asymptotic dispersion-type expansions. Nevertheless, it seems that one cannot attribute this term to some "interference" of polarization and CT effects, as there is a respective independent component $|\chi\rangle_{\mathrm{pol-CT}}$ in the first-order wave function $|\chi\rangle$. Experience (vide infra) shows that in some cases this term can be of comparable importance with $|\chi\rangle_{\mathrm{CT}}$.

In the work of Hayes and Stone [5, 6] all these excitations are listed as well as two others which do not appear here because of the genuinely BSSE-free character of our formalism. Hayes and Stone [5, 6] also considered these terms as approximately compensated in the assumed “ghost orbital” calculations and therefore they also eventually omitted them. As Hayes and Stone [5, 6] did not use the BSSE-free CHA Hamiltonian, the BSSE on the CT terms is handled by performing actual “ghost orbital” calculations. They also omitted the terms describing intramonomer correlation, which do not contribute (at least to a first approximation) to the intermolecular interaction energy. Despite some similarities, their theory is significantly different from ours: it is based on a Hermitian unperturbed Hamiltonian which is diagonal for the determinants composed of the different monomer orbitals, without having them as eigenfunctions. Our theory is based on a non-Hermitian Hamiltonian for which these determinants are (right) eigenfunctions, but it is not diagonal in their subspace.

2.3 Components of the second-order energy

In the case of an ordinary second-order PT, different terms of the first-order wave function give additive contributions to the resulting second-order energy. This is not our case, however, because the intramolecular overlap causes interferences between the different excitations. Moreover, an excited state which is orthogonal to the ground state in a free molecule may become nonorthogonal to the latter if the system is extended by an interacting partner molecule, the ground state of which has nonzero overlap with both the ground state and excited states of the first molecule. (Analogously, molecular states which were noninteracting may acquire nonzero interaction matrix elements.) This fact causes different quantities of intramonomer character (including intramonomer correlation energy) to depend on the position of the second interacting molecule.

According to the previous discussion, the second-order energy, calculated with our first-order wave function (Eq. 3), does not represent a simple sum of different physical terms which can be attributed to the components of the first-order wave function, listed earlier, however, one can substitute Eqs. (6), (7), (8), (9) and (10) one by one into Eq. (2) of the generalized Hylleraas functional and obtain in this manner some “partial Hylleraas functionals”, which have well-defined physical meaning: polarization, CT, intramonomer correlation, dispersion and the combined polarization–CT term as introduced earlier. These terms may or may not be of real physical significance depending on whether or not their sum approximates well the resulting J_2 value of the Hylleraas functional (Eq. 2), calculated by using the total first-order wave function $|\chi\rangle$ defined in Eq. (3).

Owing to the nonorthogonality of the monomer orbitals, the direct substitution of the first-order wave function (Eq. 3) or its individual components (Eqs. 6, 7, 8, 9, 10) into the generalized Hylleraas functional (Eq. 2) is not feasible. Instead, in Refs. [8, 9] we introduced an auxiliary orthogonalized set ϑ_i of spin orbitals which spans the same space as the original functions. This permitted the explicit calculation of all the necessary matrix elements occurring in the PT. The same transformations can be done for the different individual components of the first-order wave function introduced earlier; their explicit expressions in terms of ϑ_i and some auxiliary coefficients are given in the Appendix. The explicit formulae obtained for the respective “partial Hylleraas functionals” J_2^{pol}, J_2^{CT}, J_2^{disp} and $J_2^{\mathrm{pol-CT}}$ are also given in the Appendix.

We assume that the “physical” value of the intramonomer correlation is the second-order correlation energy $E_{\mathrm{A}}^{(2)} + E_{\mathrm{B}}^{(2)}$, as calculated for the free monomers: the changes of the intramonomer correlation, which are due to the intermolecular overlap, are typical interference effects. (Accordingly, we do not compute any “partial Hylleraas functionals” corresponding to $|\chi\rangle_{\mathrm{intra-corr.}}$). We also introduce the remainder term (denoted “cross-term”) describing all overlap-caused interferences as the difference of the total J_2 and of the “physical” terms:

$$J_2^{\mathrm{cross-term}} = J_2 - \left(J_2^{\mathrm{pol}} + J_2^{\mathrm{CT}} + J_2^{\mathrm{disp}} + J_2^{\mathrm{pol-CT}} + E_{\mathrm{A}}^{(2)} + E_{\mathrm{B}}^{(2)} \right) . \tag{11}$$

Our energy components differ in many respects from those introduced in different versions of SAPT. In particular, in contrast to SAPT our dispersion energy is calculated by using the correctly antisymmetrized wave function component (Eq. 9). It can be seen, however, that the asymptotic behaviour of dispersion is the same in the two theories.

3 Results and discussions

The computations were carried out using an SGI Power challenge workstation. We utilized the HONDO-8 ab initio package [18] for generating the integrals and for the SCF calculations of the monomers. The energy decomposition was performed using a modified version of the CHA-PT2 code used in Refs. [8, 9].

We performed sample calculations for some of the hydrogen-bonded complexes considered in Ref. [9]. The basis sets (ranging from 6-31G to TZV**++) and simplified geometries were also the same as in Ref. [9]. To illustrate the energy decomposition scheme proposed in the present paper, we selected four hydrogen-bonded systems, $H_2O\ldots H_2O$, $H_2O\ldots HF$, $H_2O\ldots H_2S$ and $NH_3\ldots NH_3$, and three basis sets, 6-31G, DZV and TZV**++, and we discuss the results obtained in their case in some detail. The systems selected range from weak to strong hydrogen bonds. [For the water dimer some calculations using the TZV(2d,2p) basis as described in Ref. [19] were also performed.]

An overview of the results of the calculations is given in Figs. 1, 2, 3 and 4: the total second-order energies are compared with the “Heitler–London” ones representing the sum of the zero- and first-order PT contributions, the resulting second-order interaction energy contribution J_2 (actually J_2 of Eq. 2 with the intramolecular correlation energies of the free monomers extracted) and its de-

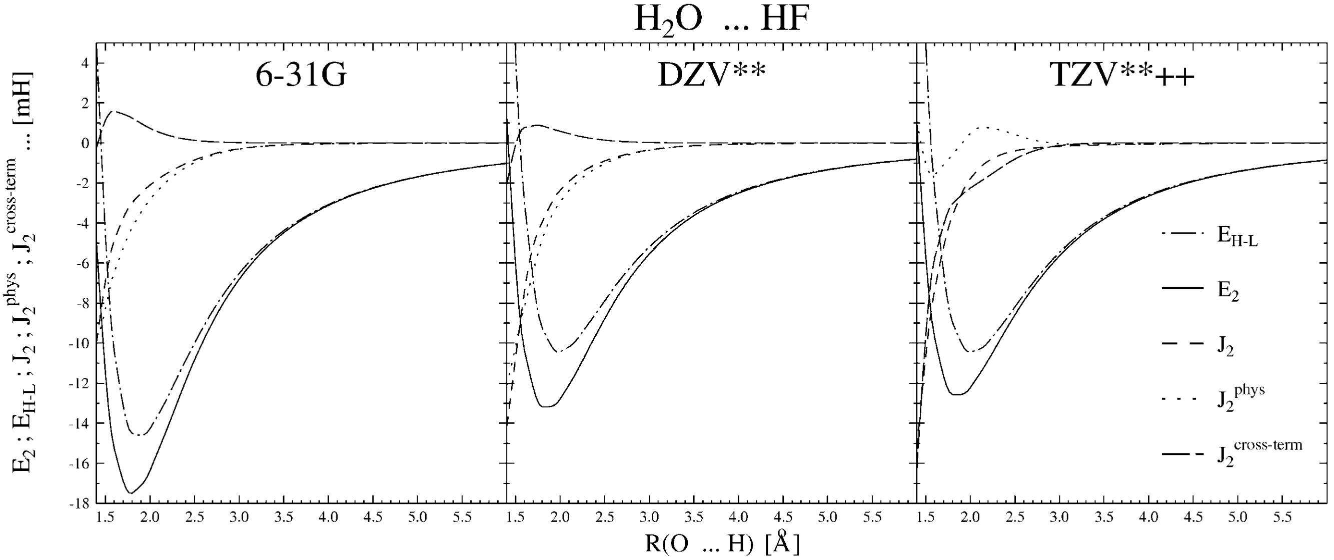

Fig. 1. Potential curves of the H_2O...HF system calculated in three different basis sets (6-31G, DZV, TZV**++) as a function of the hydrogen-bond length. The *curves* display the "Heitler–London" energy (E_{H-L}), the total second-order energy (E_2), the second-order energy correction (J_2), the second-order "physical" term (J_2^{phys}) and the "cross-term"($J_2^{cross-term}$)

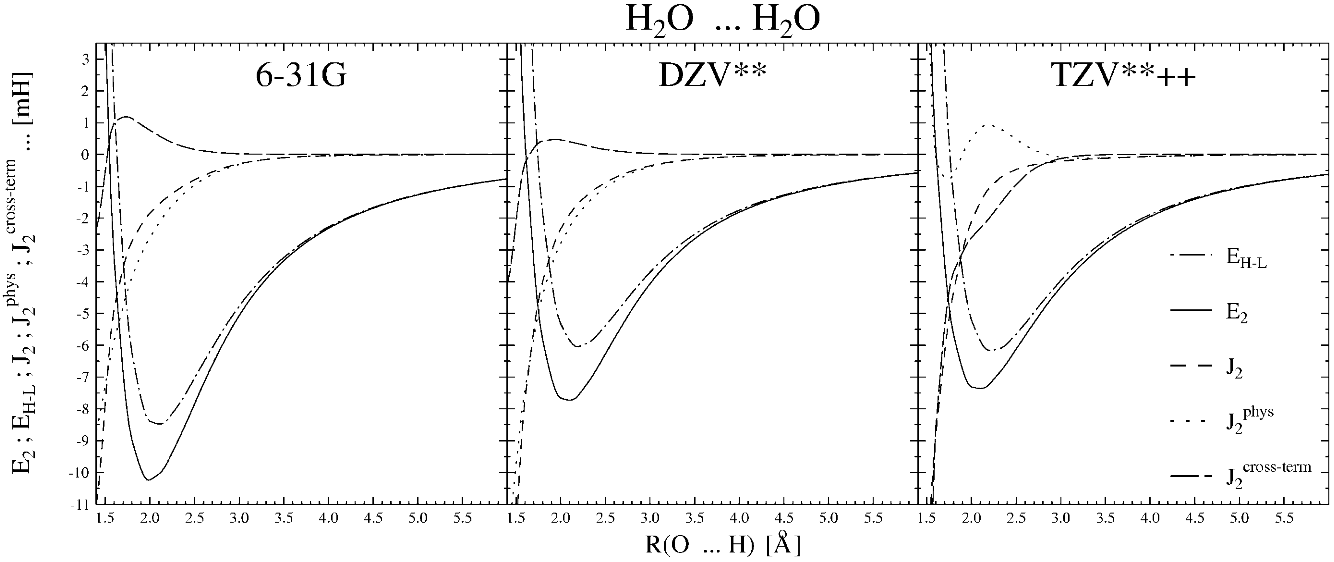

Fig. 2. Potential curves of the H_2O...H_2O system calculated in three different basis sets as a function of the hydrogen-bond length. The notation of the curves is the same as for Fig. 1

composition into "physical" and interference ("cross") components.

All the curves indicate that the simplest first-order ("Heitler–London") level of theory gives a qualitatively correct description of the hydrogen bond; however, the bonding energies are strongly underestimated and the equilibrium bond lengths are significantly shifted to larger intermolecular distances. The difference between the first- and second-order results is strongly basis- and system-dependent, which is of course obvious because, for instance, dispersion can be described appropriately only by using significantly larger basis sets than those which are needed to get good results at the SCF level.

At very large intermolecular separations, the overlap tends to zero and the matrix **K** of Eq. (A1) approaches the unit matrix. If matrix **K** equalled the unit matrix, the different second-order energy contributions would be strictly additive and the "cross-terms" would vanish. We can see that at large distances this limit is well approached for all basis sets considered; however, different basis sets and hydrogen-bonded systems differ in that respect whether this behaviour can be observed at the large distances only or also around the equilibrium one.

For all basis sets, the total second-order interaction energy is well approximated by the sum of the "physical" terms at distances which are larger than some (system- and basis-dependent) value. The total second-order contribution (J_2) behaves smoothly at all distances, while the sum of the "physical" contributions (and thus the "cross-term" too) may exhibit quite

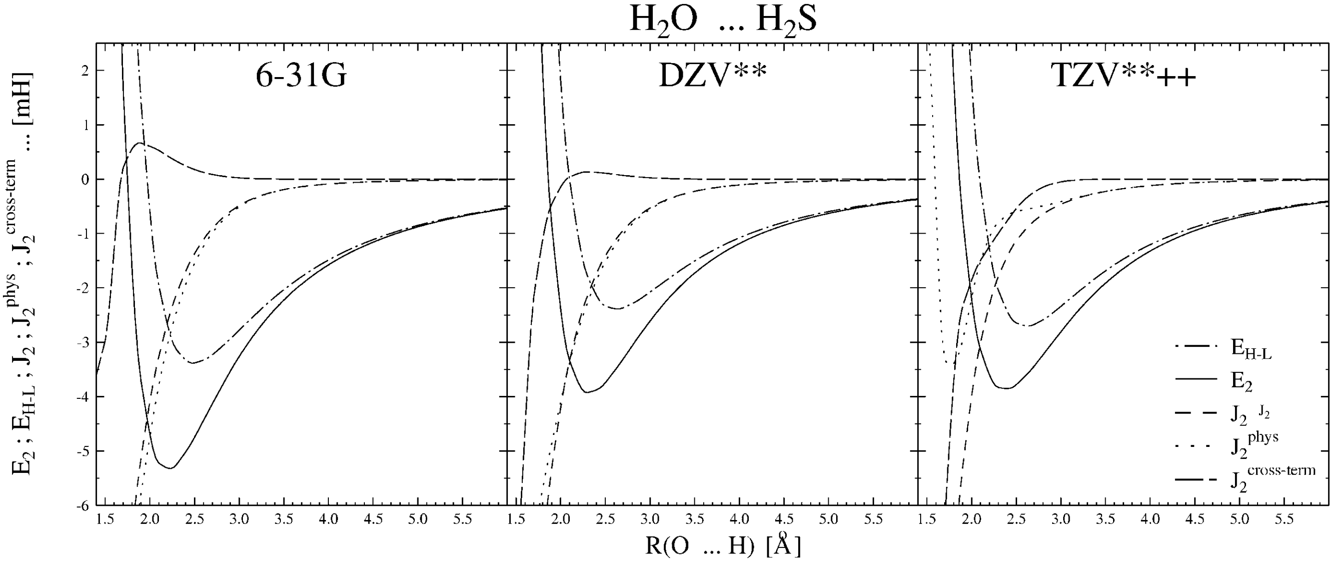

Fig. 3. Potential curves of the H_2O...H_2S system calculated in three different basis sets as a function of the hydrogen-bond length. The notation of the curves is the same as for Fig. 1

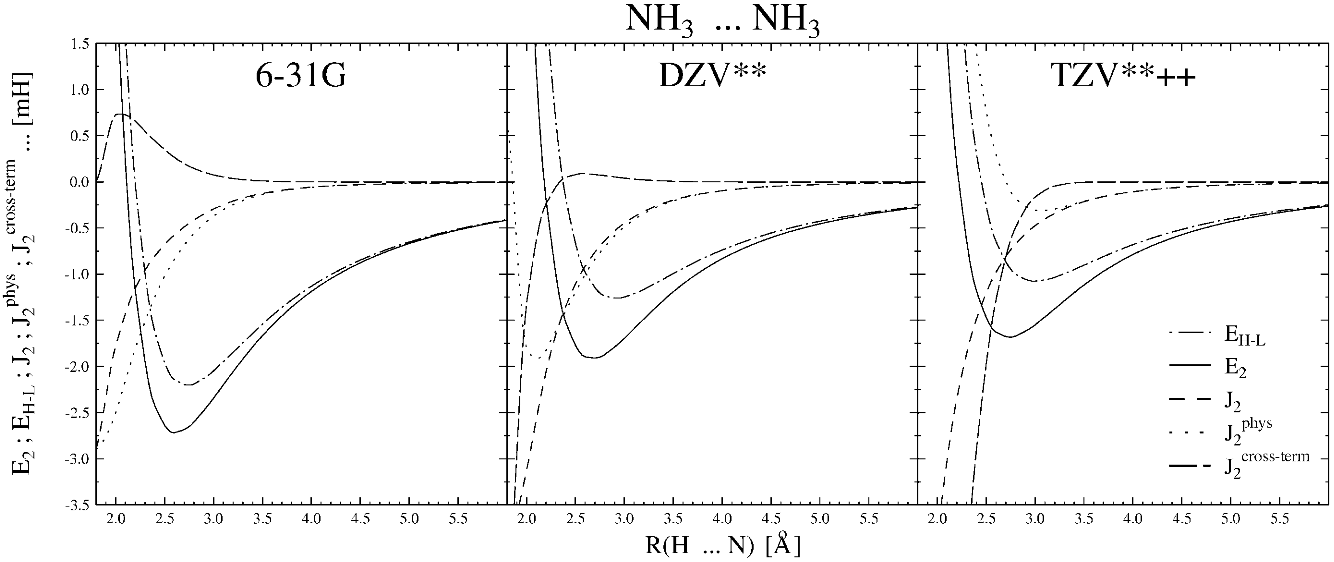

Fig. 4. Potential curves of the NH_3...NH_3 system calculated in three different basis sets as a function of the hydrogen-bond length. The notation of the curves is the same as for Fig. 1

strange behaviour at shorter distances where the deviation from J_2 is significant. This is especially the case for basis sets containing diffuse functions: as the diffuse functions spread over very large parts of the space, at smaller intermolecular separations it becomes unphysical that they are formally assigned to either of the interacting subsystems, and this leads to artifacts on the curves describing the "physical" terms.

There seems to be no monotonous behaviour with the improving basis sets: for instance, in the case of the water dimer the use of the double-polarized basis set TZV(2d,2p) exhibits a curve (Fig. 5) in which the total J_2 is well approximated by the sum of the "physical" component even at distances comparable with the equilibrium one.

The individual energy components discussed previously for the asymptotic region are displayed in Figs. 6, 7, 8 and 9 at large intermolecular separations. At distances larger than 5 or 6 Å, the sum of the "physical" energy components is not distinguishable from the true second-order energy contribution, in accord with expectations. For basis sets not containing diffuse functions the "cross-term" remains small even at shorter distances. Again we observe qualitatively different behaviour for the basis sets containing diffuse functions for which intermolecular overlap becomes considerable at relatively larger distances, leading to more complex behaviour of the different energy components.

As expected, for the smaller basis sets dispersion and polarization represent the most important second-order energetic effects at larger distances. The relative importance of them, however, strongly depends on the system and basis set applied. At a much shorter distance a CT component suddenly appears and this then exhibits a very steep increase in absolute value with decreasing intermolecular distance.

The "polarization–CT" energy contribution introduced earlier represents a minor term only, and appears only at even shorter distances. This explains why terms of this type have not usually been considered in the qualitative discussions of the intermolecular interactions: these integrals defining the coefficients in the respective terms of the first-order wave functions contain an intermolecular "differential overlap", which is negligible where the interaction is dominated by the true two-electron dispersion effects and becomes significant only at distances usually characterized in terms of typical one-electron effects such as polarization and CT.

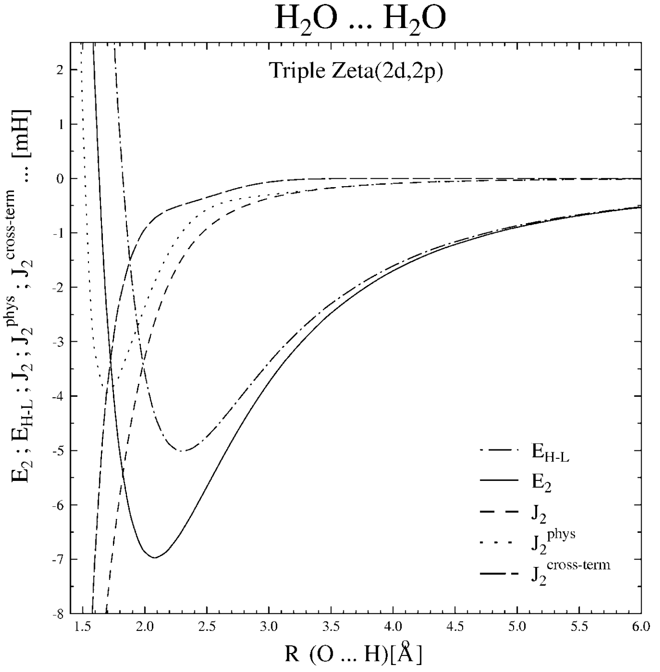

Fig. 5. Potential curves of the H_2O...H_2O system calculated in the TZV(2p, 2d) basis set as a function of the hydrogen-bond length. The notation of the curves is the same as for Fig. 1

For the calculations performed using the TZV**++ basis sets the asymptotic regime ends at larger distances. The second-order energy contribution in this region is again dominated by the dispersion and/or polarization terms; however, no significant attractive CT components are observed, but the combined polarization–CT terms are relatively significant and the deviation from additivity is more pronounced at smaller distances.

Finally, we should note that the concept of CT terms formally loses its meaning as the basis sets on the individual molecules are increased and gradually become applicable to describe the orbitals of the partner molecule. However, it is known that there are a number of more-or-less stable intermolecular systems which, following Mulliken [20], can physically best be characterized as "CT complexes". We think it may be of importance to distinguish between such terms of the wave function in which the electron transfer takes place to some valence-like orbital and those in which there is an electron transfer to an accidental atomic orbital, maybe of diffuse type without any well-defined molecular character. Such a distinction, however, would require some systematic analysis of the first-order wave function from this specifically "chemical" point of view.

4 Conclusions

In Refs. [8, 9] a BSSE-free second-order PT was introduced based on the CHA. Owing to the intermolecular

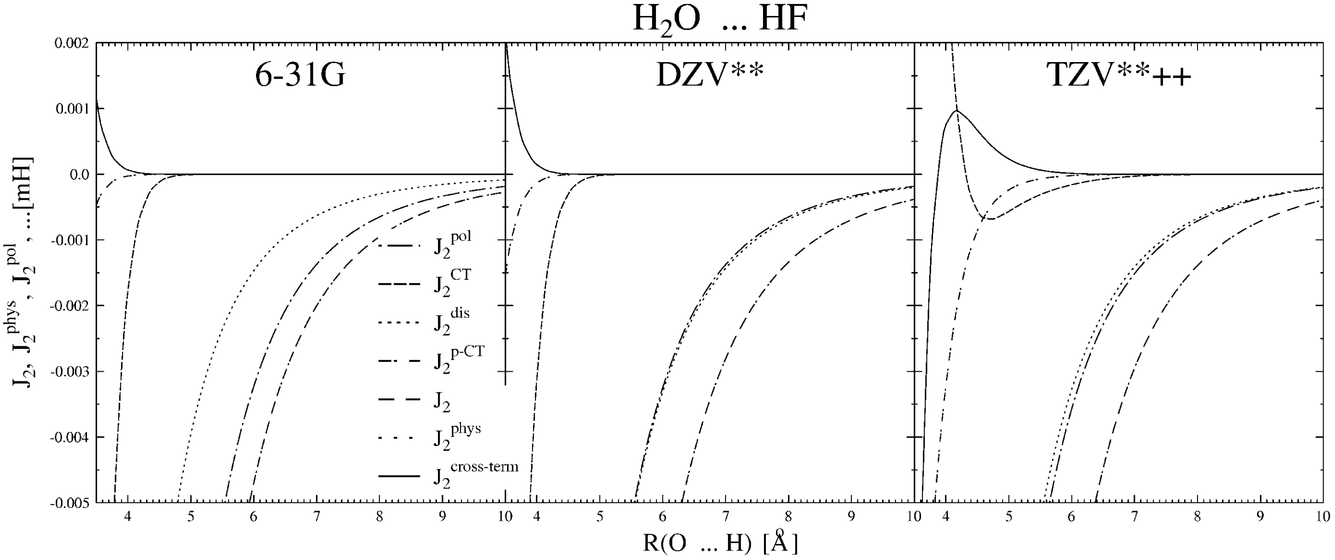

Fig. 6. Energy components for the H_2O...HF system calculated in three different basis sets (6-31G, DZV, TZV**++) as functions of the hydrogen-bond length. The curves display J_2, the sum of the physical terms (J_2^{phys}), $J_2^{\mathrm{cross-term}}$ and the different physical terms polarization (J_2^{pol}), charge transfer (J_2^{CT}), dispersion (J_2^{dis}) and the combined polarization-charge transfer ($J_2^{\mathrm{p-CT}}$)

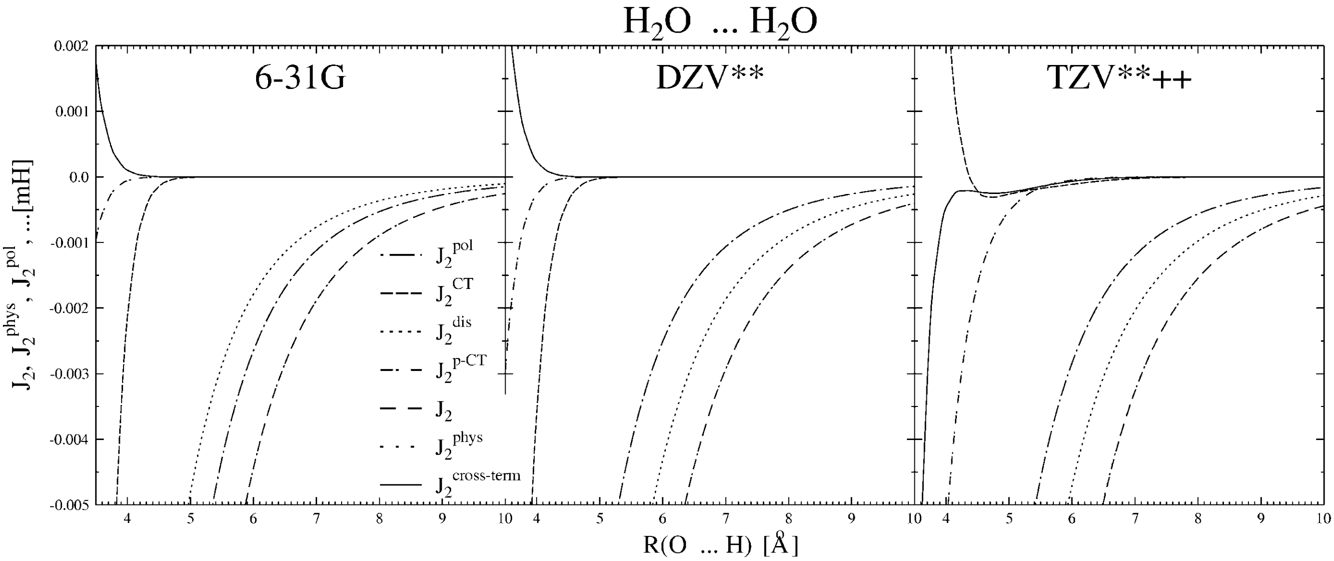

Fig. 7. Energy components for the H$_2$O...H$_2$O system calculated in three different basis sets as functions of the hydrogen-bond length. The notation of the curves is the same as for Fig. 6

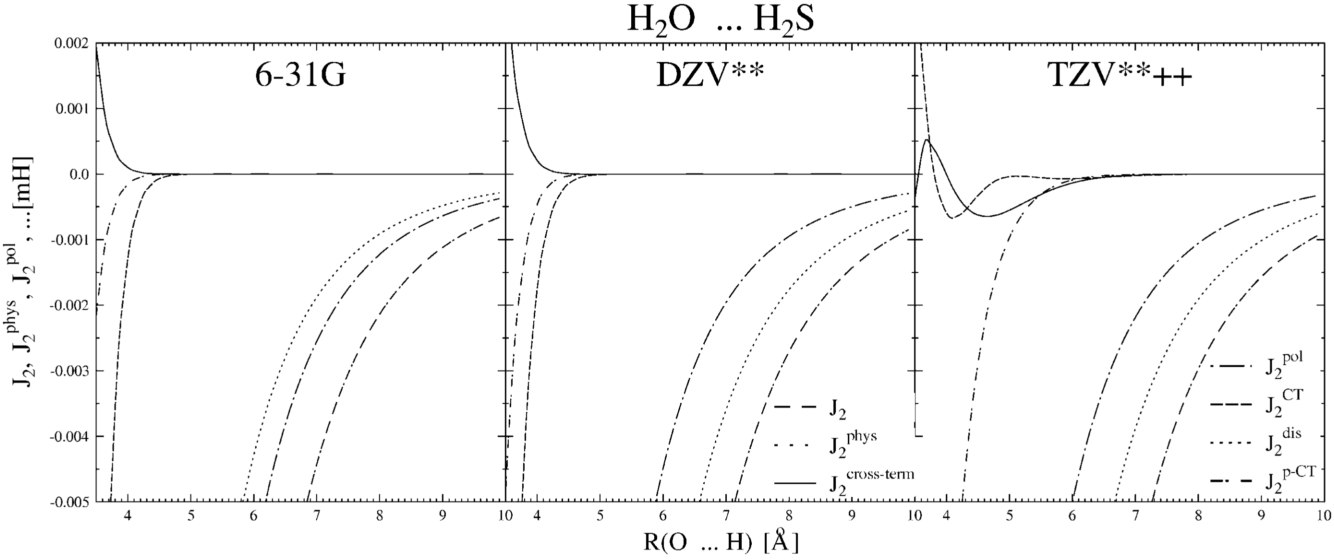

Fig. 8. Energy components for the H$_2$O...H$_2$S system calculated in three different basis sets as functions of the hydrogen-bond length. The notation of the curves is the same as for Fig. 6

overlap, the second-order energy contribution does not represent a simple sum of terms having clear physical significance; however, the first-order wave function consists of different physically distinguishable terms: intramolecular correlation, polarization, CT, dispersion and combined polarization–CT excitations. We performed the energy decomposition by computing some "partial Hylleraas functionals". The sample calculations show that at large and intermediate intermolecular distances the total second-order intermolecular interaction energy contribution is practically equal to the sum of these physically meaningful terms, while at shorter distances the overlap-caused interferences become of increasing significance.

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Appendix

We consider the orthogonalization transformation with the matrix **K**, as specified in Refs. [8, 9].

$$\varphi_p = \sum_l K_{lp}\vartheta_l \qquad \text{(A1)}$$

In terms of the new orbitals ϑ_i the first-order wave function (Eq. 3) can be written as [8, 9]

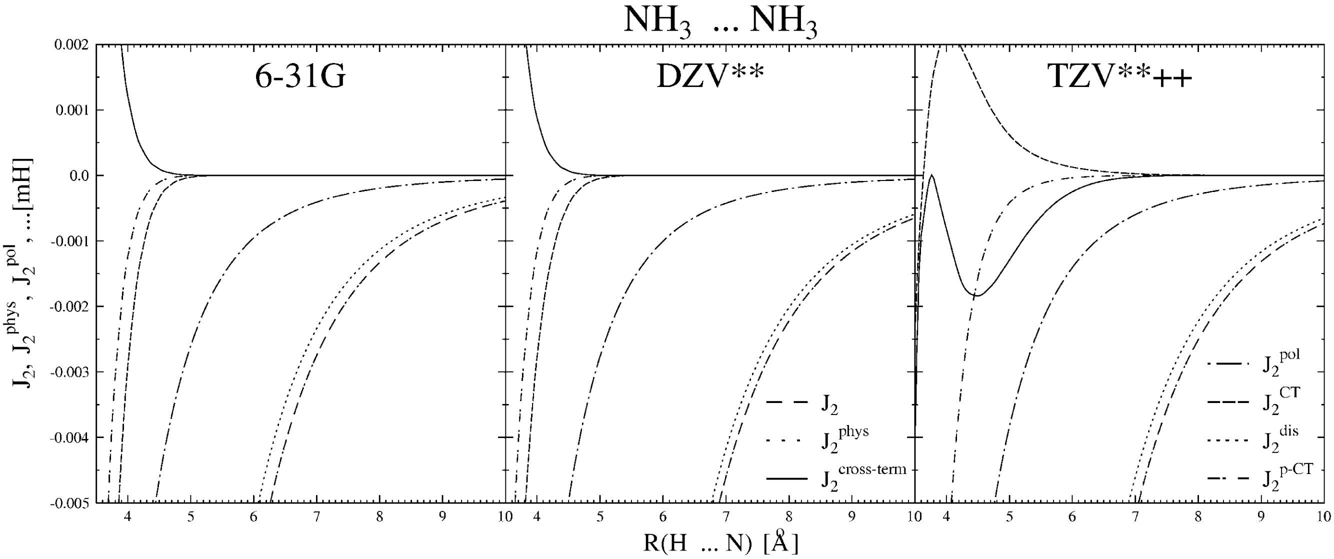

Fig. 9. Energy components for the $NH_3...NH_3$ system calculated in three different basis sets as functions of the hydrogen-bond length. The notation of the curves is the same as for Fig. 6

$$
\begin{aligned}
|\chi\rangle = e^{-i\sigma}\langle\Psi_0|\Psi_0\rangle^{1/2}\Bigg\{ & \left[\sum_{k}^{\text{occ}}\mathscr{A}(k|k) + \frac{1}{2}\sum_{k,l}^{\text{occ}}(\mathscr{B}(kl\|kl) + \mathscr{C}(kl\|kl))\right] \\
& \times|\Phi_0\rangle + \sum_{k}^{\text{occ}}\sum_{t}^{\text{virt}}\left[\mathscr{A}(t|k) + \sum_{l}^{\text{occ}}(\mathscr{B}(tl\|kl) + \mathscr{C}(tl\|kl))\right]|\Phi_k^t\rangle \\
& + \frac{1}{4}\sum_{k,l}^{\text{occ}}\sum_{r,t}^{\text{virt}}(\mathscr{B}(tr\|kl) + \mathscr{C}(tr\|kl))|\Phi_{kl}^{tr}\rangle\Bigg\} + (\mathrm{A}\leftrightarrow\mathrm{B})\ . \qquad \text{(A2)}
\end{aligned}
$$

$|\Phi_0\rangle$ is the unperturbed wave function and $|\Phi_k^t\rangle$ and $|\Phi_{kl}^{tr}\rangle$ represent the singly and doubly excited configurations, respectively, in terms of the auxiliary set of spin orbitals $\{\vartheta_i\}$. (σ is an unimportant phase factor which disappears from any final expression.) The auxiliary quantities $\mathscr{A}(t|k)$, $\mathscr{B}(tr\|kl)$ and $\mathscr{C}(tr\|kl)$, computed from the integrals over the unperturbed monomer spin orbitals were defined in Ref. [8]. For our present purposes, we had to modify some of these definitions in order to obtain separate terms corresponding to the different physical components of the first-order wave function $|\chi\rangle$. Essentially, we had to split the expressions of $\mathscr{A}(t|k)$ and $\mathscr{C}(tr\|kl)$ into terms in which the virtual orbitals are summed over different monomers:

$$
\mathscr{A}(t|k)_{\text{pol}} = \sum_{i\in\mathrm{A}}^{\text{occ}}\sum_{p\in\mathrm{A}}^{\text{virt}} K_{tp}\frac{-\langle\tilde{p}|\hat{V}_{\mathrm{B}}^{\text{aux}}|i\rangle}{\varepsilon_p - \varepsilon_i}K_{ik}^{-1}\ , \qquad \text{(A3)}
$$

$$
\mathscr{A}(t|k)_{\text{CT}} = \sum_{i\in\mathrm{A}}^{\text{occ}}\sum_{p\in\mathrm{B}}^{\text{virt}} K_{tp}\frac{-\langle\tilde{p}|\hat{V}_{\mathrm{B}}^{\text{aux}}|i\rangle}{\varepsilon_p - \varepsilon_i}K_{ik}^{-1}\ , \qquad \text{(A4)}
$$

$$
\begin{aligned}
& \mathscr{C}(tr\|kl)_{\text{disp}} \\
& \quad = \sum_{i\in\mathrm{A}}^{\text{occ}}\sum_{j\in\mathrm{B}}^{\text{occ}}\left(\sum_{p\in\mathrm{A},q\in\mathrm{B}}^{\text{virt}} K_{tp}K_{rq}\frac{-[\tilde{p}\tilde{q}\|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j}K_{jl}^{-1}K_{ik}^{-1}\right. \\
& \qquad \left. + \sum_{p\in\mathrm{B},q\in\mathrm{A}}^{\text{virt}} K_{tp}K_{rq}\frac{-[\tilde{p}\tilde{q}\|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j}K_{jl}^{-1}K_{ik}^{-1}\right)\ , \qquad \text{(A5)}
\end{aligned}
$$

$$
\begin{aligned}
& \mathscr{C}(tr\|kl)_{\text{pol}-\text{CT}} \\
& \quad = \sum_{i\in\mathrm{A}}^{\text{occ}}\sum_{j\in\mathrm{B}}^{\text{occ}}\left(\sum_{p\in\mathrm{A},q\in\mathrm{A}}^{\text{virt}} K_{tp}K_{rq}\frac{-[\tilde{p}\tilde{q}\|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j}K_{jl}^{-1}K_{ik}^{-1}\right. \\
& \qquad \left. + \sum_{p\in\mathrm{B},q\in\mathrm{B}}^{\text{virt}} K_{tp}K_{rq}\frac{-[\tilde{p}\tilde{q}\|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j}K_{jl}^{-1}K_{ik}^{-1}\right)\ . \qquad \text{(A6)}
\end{aligned}
$$

Equations (6), (7), (8), (9) and (10) of the first-order wave function $|\chi\rangle$ can be obtained, if in Eq. (A2) one uses only one set of the auxiliary quantities $\mathscr{A}_{\text{pol}}$, $\mathscr{A}_{\text{CT}}$, $\mathscr{C}_{\text{disp}}$ or $\mathscr{C}_{\text{pol}-\text{CT}}$ and sets all the others to zero, together with the coefficients $\mathscr{B}$ contributing to $|\chi\rangle_{\text{intra}-\text{corr.}}$. Then one obtains the term of $|\chi\rangle$ which corresponds to the subscript in question.

The "partial Hylleraas functionals" J_2^{pol}, J_2^{CT}, J_2^{disp} and $J_2^{\text{pol}-\text{CT}}$ are defined as follows

$$
\begin{aligned}
J_2^{\text{pol}} = & \sum_{k}^{\text{occ}}\left[\mathscr{A}(k|k)_{\text{pol}} + \bar{\mathscr{A}}(k|k)_{\text{pol}}\right] \\
& \times\left[\mathscr{D}(k|k)_{\text{pol}} + \bar{\mathscr{D}}(k|k)_{\text{pol}}\right] \\
& + \sum_{k}^{\text{occ}}\sum_{t}^{\text{virt}}\left[\mathscr{A}(t|k)_{\text{pol}} + \bar{\mathscr{A}}(t|k)_{\text{pol}}\right] \\
& \times\left[2F_{tk} + \left(\mathscr{D}(t|k)_{\text{pol}} + \bar{\mathscr{D}}(t|k)_{\text{pol}}\right)\right]\ , \qquad \text{(A7)}
\end{aligned}
$$

$$
\begin{aligned}
J_2^{\text{CT}} = & \sum_{k}^{\text{occ}}\left[\mathscr{A}(k|k)_{\text{CT}} + \bar{\mathscr{A}}(k|k)_{\text{CT}}\right] \\
& \times\left[\mathscr{D}(k|k)_{\text{CT}} + \bar{\mathscr{D}}(k|k)_{\text{CT}}\right] \\
& + \sum_{k}^{\text{occ}}\sum_{t}^{\text{virt}}\left[\mathscr{A}(t|k)_{\text{CT}} + \bar{\mathscr{A}}(t|k)_{\text{CT}}\right] \\
& \times\left[2F_{tk} + \left(\mathscr{D}(t|k)_{\text{CT}} + \bar{\mathscr{D}}(t|k)_{\text{CT}}\right)\right]\ , \qquad \text{(A8)}
\end{aligned}
$$

$$J_2^{\mathrm{disp}} = \sum_{k<l}\left[\mathscr{C}(kl\|kl)_{\mathrm{disp}} + \bar{\mathscr{C}}(kl\|kl)_{\mathrm{disp}}\right] \times \sum_{i<j}\left[\mathscr{F}(ij\|ij)_{\mathrm{disp}} + \bar{\mathscr{F}}(kl\|kl)_{\mathrm{disp}}\right] + \sum_{k,l}^{\mathrm{occ}}\sum_{t}^{\mathrm{virt}}\left[\mathscr{C}(tl\|kl)_{\mathrm{disp}} + \bar{\mathscr{C}}(tl\|kl)_{\mathrm{disp}}\right] \times \left[2F_{tk} + \sum_{j}^{\mathrm{occ}}\left(\mathscr{F}(tj\|kj)_{\mathrm{disp}} + \bar{\mathscr{F}}(tj\|kj)_{\mathrm{disp}}\right)\right] + \sum_{k<l}^{\mathrm{occ}}\sum_{t<r}^{\mathrm{virt}}\left[\mathscr{C}(tr\|kl)_{\mathrm{disp}} + \bar{\mathscr{C}}(tr\|kl)_{\mathrm{disp}}\right] \times \left[2[\vartheta_t\vartheta_r\|\vartheta_k\vartheta_l] + \left(\mathscr{F}(tr\|kl)_{\mathrm{disp}} + \bar{\mathscr{F}}(tr\|kl)_{\mathrm{disp}}\right)\right], \tag{A9}$$

$$J_2^{\mathrm{pol-CT}} = \sum_{k<l}\left[\mathscr{C}(kl\|kl)_{\mathrm{pol-CT}} + \bar{\mathscr{C}}(kl\|kl)_{\mathrm{pol-CT}}\right] \times \sum_{i<j}\left[\mathscr{F}(ij\|ij)_{\mathrm{pol-CT}} + \bar{\mathscr{F}}(kl\|kl)_{\mathrm{pol-CT}}\right] + \sum_{k,l}^{\mathrm{occ}}\sum_{t}^{\mathrm{virt}}\left[\mathscr{C}(tl\|kl)_{\mathrm{pol-CT}} + \bar{\mathscr{C}}(tl\|kl)_{\mathrm{pol-CT}}\right] \times \left[2F_{tk} + \sum_{j}^{\mathrm{occ}}\left(\mathscr{F}(tj\|kj)_{\mathrm{pol-CT}} + \bar{\mathscr{F}}(tj\|kj)_{\mathrm{pol-CT}}\right)\right] + \sum_{k<l}^{\mathrm{occ}}\sum_{t<r}^{\mathrm{virt}}\left[\mathscr{C}(tr\|kl)_{\mathrm{pol-CT}} + \bar{\mathscr{C}}(tr\|kl)_{\mathrm{pol-CT}}\right] \times [2[\vartheta_t\vartheta_r\|\vartheta_k\vartheta_l] + (\mathscr{F}(tr\|kl)_{\mathrm{pol-CT}} + \bar{\mathscr{F}}(tr\|kl)_{\mathrm{pol-CT}})], \tag{A10}$$

where

$$F_{tk} = \langle\vartheta_t|\hat{F}|\vartheta_k\rangle \tag{A11}$$

and $\hat{F}$ is the usual Fock operator calculated by orthogonalizing the unperturbed monomer orbitals. The quantities with horizontal bars are obtained from the respective definitions by interchanging A and B everywhere. $\mathscr{D}(t|k)_{\mathrm{pol}}$, $\mathscr{D}(t|k)_{\mathrm{CT}}$, $\mathscr{F}(tr\|kl)_{\mathrm{disp}}$ and $\mathscr{F}(tr\|kl)_{\mathrm{pol-CT}}$ are defined in the same way as the quantities $\mathscr{A}(t|k)_{\mathrm{pol}}$, $\mathscr{A}(t|k)_{\mathrm{CT}}$, $\mathscr{C}(tr\|kl)_{\mathrm{disp}}$ and $\mathscr{C}(tr\|kl)_{\mathrm{pol-CT}}$, respectively, but without the energy denominators.

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