Second-order exchange effects in intermolecular interactions. The water dimer

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A new method of deriving explicit formulas for the calculation of second-order exchange contributions (induction as well as dispersion) within the framework of symmetry-adapted perturbation theories is presented. It is shown how exchange contributions can be expressed as a combination of electrostatic interaction energies between suitably generalized charge distributions (overlap intermolecular charge distributions). Each of these contributions are derived within the Hartree–Fock approximation (neglect of all electron correlation effects within the noninteracting molecules) and by considering only single-electron exchange between interacting molecules. Numerical calculations for the interaction of two water molecules are presented. In the region of the equilibrium geometry, it is found that the complete second-order exchange contribution accounts for about 20% of the total intermolecular interaction energy. This contribution is essentially dominated by the exchange induction component which is found to represent approximately 1 kcal/mol (using a basis set containing 94 orbitals). To our knowledge, this is the first example of calculation of exchange induction interaction energy for a molecular system. Concerning the less important, but non-negligible, exchange dispersion component, our result is found to agree with a very recent calculation for the water dimer.

I. INTRODUCTION

Calculating intermolecular interaction energies in the important region around the equilibrium configuration with a high level of accuracy (say with an error less than 10% of the experimental interaction energy) is known to be a difficult task. As an illustrative example, Szalewicz *et al.* pointed out in a recent paper[1] that for a relatively simple system as the water dimer, the calculated values of the interaction energy range from -4.1 to -6.1 kcal/mol, even after having rejected results obtained with too small basis sets or based on low-quality theoretical methods. In particular, the spread on the calculated values is larger than the commonly accepted experimental range of -5.4 ± 0.7 kcal/mol.[2] Obviously, the situation generally becomes worse when more complex systems are considered.

In the field of theoretical evaluations of interaction energies, two types of approach are generally distinguished. The first approach (certainly the most commonly employed) is the so-called supermolecule method[3] in which the interaction energy is obtained by subtracting from the total energy of the interacting molecules (the supermolecule) the sum of the total energies of each monomer, all energies being calculated by using the same method. A major difficulty inherent to this type of approach is that a particularly high level of accuracy on calculated energies is required. The basic reason is that interaction energies represent only an extremely small fraction of the total energy of the supermolecule (about 5×10^{-5} for the favorable case of the water dimer). In addition, it is, in general, difficult to know whether errors made in calculating total energies for interacting and noninteracting molecules are of comparable magnitude or not, which may lead to an important relative error for the interaction energy (basically one is dealing with the very general problem associated with the evaluation of a small quantity expressed as a difference of two large and approximately evaluated quantities). As an important example, let us mention calculations done at the self-consistent-field (SCF) level for which it is not at all clear *a priori* whether a favorable cancellation of the errors due to the lack of electron correlation contributions for monomers and dimer may occur or not. In fact, it is known that the intermolecular electron correlation effects (dispersion contributions) cannot be, in general, neglected. Accurate values for electron correlation contributions can be, in principle, obtained by application of some form of configuration interaction (CI), but in practice this may lead to prohibitively large computer time and memory requirements. Another well-known difficulty one has to cope with is the occurrence of the so-called basis-set superposition error (BSSE). A great amount of work dealing with this difficulty has been done (see, e.g., Refs. 4–6). However, it should be emphasized that the most commonly used solution to this problem, namely the so-called counterpoise method proposed by Boys and Bernardi,[7] is still in discussion. In the second approach, which will be followed in the present study, the intermolecular interaction energy is calculated from perturbation theory using the intermolecular potential as the perturbing operator. When the intermolecular distance R is large, one is dealing with the Rayleigh–Schrödinger perturbation theory in which only simple products of monomer wave functions are used. Due to the large separation between monomers no antisymmetrization of the

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factorized wave functions is necessary. Also, in this particular case, the multipole expansion[8] for the interaction operator can be applied to obtain the interaction energy as a series of inverse powers of R (such terms being, in general, orientationally dependent). For shorter distances, e.g., distances corresponding to the region around the equilibrium configuration, the usual Rayleigh–Schrödinger perturbation theory must be abandoned,[9] and in order to take into account, at least to some extent, the exchange of electrons between the interacting molecules, some form of exchange perturbation theory [the so-called symmetry-adapted perturbation theories (SAPT), see, e.g., Refs. 10 and 11] must be used. Before entering into the details of SAPT, it is important to emphasize two general features of perturbation theory which make this approach particularly attractive with regard to the usual supermolecular approach. First, the difficult problem just discussed above of evaluating the interaction energy as a difference of two large and approximate quantities is avoided since a direct evaluation of the interaction energy is done. Second, the interaction energy is decomposed into a sum of terms for each of which it is possible to give some physical interpretation (at least for terms up to and including second-order terms). This is a very appealing feature for a qualitative understanding of the interaction and can be very helpful for the development of simplified formulas for intermolecular interactions.

To our knowledge, the first example of an exchange–perturbation-theory calculation is due to Jeziorski and van Hemert (JvH) in their pioneering work on the water dimer.[12] Neglecting all intramonomer correlation effects, they evaluated the complete first-order interaction energy $E^{(1)} = E^{(1)}_{\mathrm{RS}} + E^{(1)}_{\mathrm{exch}}$ (explicitly, the sum of the Rayleigh–Schrödinger and first-order exchange energies) and the Rayleigh–Schrödinger second-order interaction energy which is known to decompose into the induction $E^{(2)}_{\mathrm{ind}}$ and dispersion $E^{(2)}_{\mathrm{disp}}$ components. In particular, no calculations of second-order exchange contributions were done. One of their major results was that the dispersion contribution was found to greatly stabilize the water dimer. More precisely, the dispersion energy turned out to amount to 50% of the SCF binding energy at the equilibrium geometry. This result is important since, as a part of the intermolecular correlation energy, the dispersion contribution cannot be obtained in a SCF calculation of the interaction energy. In other words, an extensive CI calculation would be necessary to recover this important contribution in a supermolecular approach. A second major result of JvH was that, for interoxygen distances greater than 5.0 a.u. (5.67 a.u. being the equilibrium distance) the SCF binding energy was found to be very well represented by the sum of the complete first-order energy and the second-order induction energy, thus leading to the approximate equality:

$$E^{\mathrm{SCF}}_{\mathrm{int}} \simeq E^{(1)} + E^{(2)}_{\mathrm{ind}}. \tag{1}$$

On the other hand, it is known that besides the first-order and the second-order induction energies, the SCF binding energy contains some part of the second-order exchange induction contribution, and of the third- and higher-order "induction" energies as well as some intramonomer electron correlation contributions due to the self-consistency at the dimer level.[13] Accordingly, the preceding equality (1) was interpreted by supposing that, at least for interoxygen distances greater than 5.0 a.u., the three effects just quoted did not contribute significantly to the interaction energy. In fact, further calculations done by Chalasinski and Jeziorski for atomic van der Waals dimers such as He_2, Be_2, and Ne_2 failed to confirm this assertion.[14–17] More precisely, in contrast to JvH, they observed that the SCF binding energy was poorly represented by Eq. (1). A number of reasons have been given to explain this result (see, e.g., the discussion in Ref. 18). Actually, one of these reasons (not the only one) is the non-negligible role of second-order exchange terms. In order to study quantitatively the importance of these contributions, Chalasinski and Jeziorski developed a method of evaluating second-order exchange energies (induction as well as dispersion) for the interaction of closed-shell atoms or molecules.[15] In practice, they performed calculations on atomic van der Waals systems such as He_2, Be_2, and Ne_2.[14–17] One of their main conclusions is that, as a general rule, the second-order exchange energy is repulsive and quenches a significant fraction of the interaction energy, at least for the van der Waals dimers studied. Concerning molecular interactions, no systematic calculations have been performed that would show the importance of second-order induction and dispersion exchange effects. To our knowledge, the first calculation for a molecular system is due to Chalasinski.[19] He showed that for the HF dimer at the equilibrium geometry, $E^{(2)}_{\mathrm{exch\text{-}disp}}$ represents about 10% of $E^{(2)}_{\mathrm{disp}}$. Very recently, Rybak[20,21] found a similar contribution for the water dimer. Finally, it seems that no calculations exist concerning the exchange induction energy for molecular systems.

The main purpose of this paper is to present a new method of deriving explicit formulas for the calculation of second-order exchange contributions. Following Claverie's point of view,[22] the strategy adopted in this work is essentially to express exchange contributions as a combination of formal electrostatic interaction energies between suitably generalized charge distributions (so-called overlap intermolecular charge distributions). To do that, two basic ingredients are used: (1) the so-called Longuet–Higgins representation of the intermolecular interaction operator in terms of molecular charge distributions,[23] and (2) the possibility of reducing the action of the intersystem antisymmetrizer (appearing in SAPT, see Sec. II) on factorized SCF wave functions to a sum of simple products of SCF determinants pertaining to each subsystem. These determinants are formally "charge-transfer" determinants corresponding to a certain number of opposite transfers (depending on the number of exchange of electrons between interacting molecules which are considered) between all possible pairs of spin orbitals of each monomer.

In order to demonstrate the applicability of the present approach, some numerical results on the interaction between two water molecules are presented.

The organization of the present paper is as follows. In Sec. II, we present the formal development of second-order exchange contributions. In order to make as far as possible

the present paper self-contained, the theory is presented in a systematic and comprehensive way. Section III is devoted to the presentation of numerical calculations for the two water molecules. Results for the different components of the interaction energy as a function of the interoxygen distance are presented and the importance of second-order exchange contributions are discussed. The role of the basis set used is also investigated. Finally, some concluding remarks are given in Sec. IV.

II. THEORY

Let us consider two interacting systems A and B. The total Hamiltonian H of the complex is written as

$$H = H_0 + V^{AB}, \tag{2}$$

with

$$H_0 = H^A + H^B, \tag{3}$$

where H^M ($M = A,B$) denotes the Hamiltonian of the noninteracting systems and V^{AB} is the intermolecular interaction potential

$$V^{AB} = \sum_{\alpha\in A}\sum_{\beta\in B}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} - \sum_{\alpha\in A}\sum_{j\in B}\frac{Z_\alpha}{r_{\alpha j}} - \sum_{\beta\in B}\sum_{i\in A}\frac{Z_\beta}{r_{\beta i}} + \sum_{i\in A}\sum_{j\in B}\frac{1}{r_{ij}}, \tag{4}$$

where $r_{ab} = |\mathbf{r}_a - \mathbf{r}_b|$. Italic indices label electronic coordinates and Greek indices label nuclear coordinates. Z_μ is the charge number of nucleus μ belonging to molecule M ($M = A,B$). The eigenfunctions of the Hamiltonian H^M of molecule M ($M = A,B$) are denoted Ψ_i^M with the corresponding energies E_i^M. Then, the eigenfunctions of $H_0 = H^A + H^B$ are merely the products $\Psi_i^A\Psi_j^B$ with the corresponding energies $E_i^A + E_j^B$.

Following standard symmetry-adapted perturbation theories,[10,11] the complete first- and second-order interaction energies are written in the form[24,25]

$$E^{(1)} = \frac{\langle\Psi_0^A\Psi_0^B|V^{AB}\mathbf{A}|\Psi_0^A\Psi_0^B\rangle}{\langle\Psi_0^A\Psi_0^B|\mathbf{A}|\Psi_0^A\Psi_0^B\rangle}, \tag{5}$$

$$E^{(2)} = -\frac{\langle\Psi_0^A\Psi_0^B|V^{AB}R_0\mathbf{A}(V^{AB} - E^{(1)})|\Psi_0^A\Psi_0^B\rangle}{\langle\Psi_0^A\Psi_0^B|\mathbf{A}|\Psi_0^A\Psi_0^B\rangle}, \tag{6}$$

where R_0 denotes the reduced resolvent of H_0 given by

$$R_0 = \sum_{ij}{}' \frac{|\Psi_i^A\Psi_j^B\rangle\langle\Psi_i^A\Psi_j^B|}{(E_i^A + E_j^B) - (E_0^A + E_0^B)} \tag{7}$$

(the prime in Σ' means as usual that the term corresponding to $i = 0$ and $j = 0$ is excluded from the summation) and $\mathbf{A}$ is the intersystem antisymmetrizer which we shall write in the form[22]

$$\mathbf{A} = 1 - \mathbf{A}' = 1 - P_{(1)} + P_{(2)} - \cdots + (-1)^{N_{\inf}}P_{(N_{\inf})}, \tag{8}$$

where $P_{(1)} = \Sigma_i^A\Sigma_j^B P_{ij}$ denotes the sum of all permutations exchanging (space and spin) coordinates of electron i of molecule A with coordinates of electron j of molecule B, and similar definitions hold for $P_{(2)}, P_{(3)},\ldots$ ($N_{\inf}$ denotes the smallest value of N_A and N_B, the numbers of electrons of molecule A and B, respectively).

Remark that a number of definitions of $\mathbf{A}$ differing from one another by the normalization factor have been given elsewhere (see Appendix A in Ref. 22). However, this is of no importance since $\mathbf{A}$ appears in both numerator and denominator of Eqs. (5) and (6) and therefore the normalization of $\mathbf{A}$ is immaterial.

Now, by using the decomposition $\mathbf{A} = 1 - \mathbf{A}'$, where $\mathbf{A}' = P_{(1)} - P_{(2)} + \cdots$, the second-order perturbation energy $E^{(2)}$ [Eq. (6)] may be decomposed into the usual second-order Rayleigh–Schrödinger (RS) perturbation energy $E_{\rm RS}^{(2)}$ [obtained by setting $\mathbf{A} = 1$ in Eq. (6)] and into the so-called second-order exchange energy $E_{\rm exch}^{(2)}$ in which we are interested here.

After elementary algebra, the complete second-order exchange term is found to be

$$E_{\rm exch}^{(2)} \equiv E^{(2)} - E_{\rm RS}^{(2)} = -\frac{\langle\Psi_0^A\Psi_0^B|(V^{AB} - E^{(1)})(\mathbf{A}' - \langle\mathbf{A}'\rangle)|\Phi^{(1)}\rangle}{\langle\mathbf{A}\rangle}, \tag{9}$$

where $\langle\mathbf{A}'\rangle$ and $\langle\mathbf{A}\rangle$ are the expectation values of $\mathbf{A}'$ and $\mathbf{A}$ calculated with the ground-state wave function $\Psi_0^A\Psi_0^B$ and $\Phi^{(1)}$ stands for the first-order correction to the wave function in the perturbation theory[11]

$$\Phi^{(1)} = -R_0V^{AB}\Psi_0^A\Psi_0^B. \tag{10}$$

Now, since multiple exchanges are supposed to contribute weakly in the region around the equilibrium geometry,[13,14] here we shall limit ourselves to the calculation of the leading contribution to $E_{\rm exch}^{(2)}$ corresponding to a single exchange of electrons between molecules A and B. Thus, setting $\mathbf{A}' = P_{(1)}$ in Eq. (9) and neglecting terms which will correspond to contributions of order higher than S^2 (where S stands for overlap integrals between orbitals of monomers A and B) within the Hartree–Fock formalism used below, the following expression of $E_{\rm exch}^{(2)}$ is obtained:

$$E_{\rm exch}^{(2)} = -\langle\Psi_0^A\Psi_0^B|(V^{AB} - \langle V^{AB}\rangle)\times(P_{(1)} - \langle P_{(1)}\rangle)|\Phi^{(1)}\rangle, \tag{11}$$

where $\langle V^{AB}\rangle$ is the first-order Rayleigh–Schrödinger interaction energy obtained by setting $\mathbf{A} = 1$ in Eq. (5).

Note that our formula (11) seems to differ from those given in other works (see, e.g., Refs. 14–17) by a minus sign. In fact, this is not true because the convention of sign we have adopted for the decomposition of the antisymmetrizer $\mathbf{A}$ is different [compare, e.g., Eq. (5) in Ref. 15 with our definition (8)].

For our purposes it is convenient to rewrite $\Phi^{(1)}$ [Eq. (10)] as follows:

$$\Phi^{(1)} = \Psi_0^A\Phi_{\rm ind}^B + \Phi_{\rm ind}^A\Psi_0^B + \Phi_{\rm disp}^{AB}, \tag{12a}$$

with

$$\Phi_{\rm ind}^B = \sum_{i\neq 0}\Psi_i^B\frac{\langle\Psi_0^A\Psi_0^B|V^{AB}|\Psi_0^A\Psi_i^B\rangle}{E_0^B - E_i^B}, \tag{12b}$$

$$\Phi_{\rm ind}^A = \sum_{i\neq 0}\Psi_i^A\frac{\langle\Psi_0^A\Psi_0^B|V^{AB}|\Psi_i^A\Psi_0^B\rangle}{E_0^A - E_i^A}, \tag{12c}$$

$$\Phi^{AB}_{\text{disp}} = \sum_{\substack{i\neq 0\\ j\neq 0}} \Psi^A_i \Psi^B_j \frac{\langle \Psi^A_0 \Psi^B_0 | V^{AB} | \Psi^A_i \Psi^B_j \rangle}{(E^A_0 - E^A_i) + (E^B_0 - E^B_j)}. \quad (12d)$$

When inserting the previous decomposition of $\Phi^{(1)}$ into Eq. (11), the second-order exchange energy decomposes into three terms

$$E^{(2)}_{\text{exch}} = E^{(2)}_{\text{exch-ind}}(A\rightarrow B) + E^{(2)}_{\text{exch-ind}}(B\rightarrow A) + E^{(2)}_{\text{exch-disp}}. \quad (13)$$

The sum of the first two terms in Eq. (13) will be referred to in the following as the exchange induction energy, while $E^{(2)}_{\text{exch-disp}}$ will be referred to as the exchange dispersion energy.

Evaluating such quantities requires expressions of Ψ^A_i and Ψ^B_j, the exact eigenfunctions of monomers A and B. Unfortunately, it is well known that exact or even accurate correlated eigenfunctions for atomic or molecular systems are, in general, not available, except for very simple systems. As a consequence, approximate wave functions are generally used. However, it should be remarked that such an approximation is not inherent to the perturbation theory but is rather related to the way adopted in *ab initio* frameworks for evaluating perturbation quantities which consists in performing explicitly the infinite summation involved in the reduced resolvent of H_0. As an example, it is possible by using a Monte Carlo path integral formalism to calculate *exactly* perturbation quantities without doing such a summation. The problem of finding good approximations of *all* exact eigenfunctions of H_0 [needed for evaluating R_0; see Eq. (7)] is then avoided.[26,27]

Here, we shall limit ourselves to the use of approximate eigenfunctions obtained from a SCF calculation, thus neglecting the internal electron correlation of monomers. By denoting $a_i = a_i(\mathbf{r})\sigma^A_i$ and $b_i = b_i(\mathbf{r})\sigma^B_i$ as the SCF orthonormalized spin orbitals of monomers A and B (occupied as well as virtual), the approximate (normalized) eigenfunctions of H^A and H^B constructed from these spin orbitals will be the following determinants:

$$\Psi^A = \frac{1}{\sqrt{N_A!}} \mathbf{A}^A [a_1(1)\cdots a_{N_A}(N_A)], \quad (14a)$$

$$\Psi^B = \frac{1}{\sqrt{N_B!}} \mathbf{A}^B [b_1(1)\cdots b_{N_B}(N_B)], \quad (14b)$$

where $\mathbf{A}^M$ $(M = A,B)$ is the intrasystem antisymmetrizer for the electrons belonging to the monomer M [*intra*system antisymmetrizer in contrast with the *inter*system antisymmetrizer defined above in Eq. (8)].

In order to avoid any risk of confusion, we shall systematically use different types of indices for labeling occupied and virtual spin orbitals. More precisely, occupied and virtual spin orbitals will be indiced by using subscripts i, j, k, l and p, q, r, s, respectively.

A. Second-order exchange induction energy

By using Eqs. (11), (12a), and (13), $E^{(2)}_{\text{exch-ind}}(A\rightarrow B)$ may be written as

$$E^{(2)}_{\text{exch-ind}}(A\rightarrow B) = -\langle \Psi^A_0 \Psi^B_0 | (V^{AB} - \langle V^{AB}\rangle) \times (P_{(1)} - \langle P_{(1)}\rangle) | \Psi^A_0 \Phi^B_{\text{ind}} \rangle, \quad (15)$$

with a similar formula for $E^{(2)}_{\text{exch-ind}}(B\rightarrow A)$. Because of symmetry, only the expression for $E^{(2)}_{\text{exch-ind}}(A\rightarrow B)$ will be considered in the following.

For our purposes let us introduce the quantity $\Psi^B_0\binom{b_r}{b_k}$ defined as the Slater determinant obtained by replacing in Ψ^B_0 the occupied spin orbital b_k by the virtual spin orbital b_r. A similar definition holds for monomer A.

Let us define c^r_k as

$$c^r_k = \frac{\langle \Psi^A_0 \Psi^B_0 | V^{AB} | \Psi^A_0 \Psi^B_0\binom{b_r}{b_k} \rangle}{E^B_0 - E^B_0(k\rightarrow r)}, \quad (16)$$

where $E^B_0(k\rightarrow r)$ are eigenvalues of the Fock operator associated with monoexcited wave functions $\Psi^B_0\binom{b_r}{b_k}$.

Using this notation and Eq. (12b), Φ^B_{ind} may be rewritten in the form

$$\Phi^B_{\text{ind}} = \sum_{k\in B}\sum_{r\in B} c^r_k \Psi^B_0 \binom{b_r}{b_k}, \quad (17)$$

where summations run over all occupied and virtual spin orbitals b_k and b_r, respectively. Note that Eq. (17) involves only single excitations since the interaction operator V^{AB} is a mono-electronic operator with respect to each of the interacting subsystems.

Now, defining the so-called "induction functions" f^B_k (see Ref. 15) associated with the occupied spin orbital b_k,

$$f^B_k = \sum_{r\in B} c^r_k b_r, \quad (18)$$

and using standard properties of determinants, Eq. (17) takes the following form:

$$\Phi^B_{\text{ind}} = \sum_{k\in B} \Psi^B_0 \binom{f^B_k}{b_k}, \quad (19)$$

where $\Psi^B_0\binom{f^B_k}{b_k}$ is an obvious generalization of the previous notation indicating the replacement of the occupied spin orbital b_k by the associated induction function f^B_k. By inserting Eq. (19) into Eq. (15), the exchange induction energy is written

$$E^{(2)}_{\text{exch-ind}}(A\rightarrow B) = -\sum_{k\in B} \left\langle \Psi^A_0 \Psi^B_0 \middle| (V^{AB} - \langle V^{AB}\rangle) \times \middle| (P_{(1)} - \langle P_{(1)}\rangle) \Psi^A_0 \Psi^B_0 \binom{f^B_k}{b_k} \right\rangle. \quad (20)$$

In order to make our notation more compact, the following convention is introduced

$$[O]_k \equiv \left\langle \Psi^A_0 \Psi^B_0 \middle| O \middle| \Psi^A_0 \Psi^B_0 \binom{f^B_k}{b_k} \right\rangle, \quad (21)$$

where O stands for an arbitrary operator. Thus, $E^{(2)}_{\text{exch-ind}}(A\rightarrow B)$ may be written in the expanded form

$$E^{(2)}_{\text{exch-ind}}(A\to B) = -\sum_{k\in B}\Big([V^{AB}P_{(1)}]_k - \langle V^{AB}\rangle[P_{(1)}]_k - \langle P_{(1)}\rangle[V^{AB}]_k\Big). \quad (22)$$

Note that the contribution associated with $\langle V^{AB}\rangle\langle P_{(1)}\rangle$ vanishes because of orthogonality between spin orbitals.

Before expliciting further the three basic contributions $[V^{AB}P_{(1)}]_k$, $[P_{(1)}]_k$, and $[V^{AB}]_k$, involved in Eq. (22), let us present the very important formula expressing the action of the permutation operator $P_{(1)}$ on a product of two determinants Ψ^A and Ψ^B in terms of a linear combination of simple products of determinants pertaining to subsystems A and B (see Sec. III B in Ref. 22):

$$P_{(1)}[\Psi^A\Psi^B] = \sum_{i\in A}\sum_{j\in B}\Psi^A\begin{pmatrix} b_j \\ a_i\end{pmatrix}\Psi^B\begin{pmatrix} a_i \\ b_j\end{pmatrix}, \quad (23)$$

where the summation is over the spin orbitals of determinants Ψ^A (here labeled by i) and Ψ^B (labeled by j). Let us emphasize that no subscript 0 has been used for denoting Ψ^A and Ψ^B since they must be viewed as rather arbitrary determinants and, in particular, are not necessarily constructed from a set of occupied spin orbitals. Using Eq. (23), all integrals involving functions of the type $P_{(1)}[\Psi^A\Psi^B]$ are reduced to sums of integrals involving simple products $\Psi^A\binom{b_j}{a_i}\Psi^B\binom{a_i}{b_j}$ of "opposite transfer" determinants.

1. Expression of $[V^{AB}P_{(1)}]_k$

By applying the property just presented $[V^{AB}P_{(1)}]_k$ is written as

$$[V^{AB}P_{(1)}]_k = \sum_{i\in A}\sum_{\substack{j\in B\\ j\neq k}}\left\langle\Psi^A_0\Psi^B_0\middle|V^{AB}\middle|\Psi^A_0\begin{pmatrix} b_j \\ a_i\end{pmatrix}\Psi^B_0\begin{pmatrix} f^B_k\ a_i \\ b_k\ b_j\end{pmatrix}\right\rangle + \sum_{i\in A}\left\langle\Psi^A_0\Psi^B_0\middle|V_{AB}\middle|\Psi^A_0\begin{pmatrix} f^B_k \\ a_i\end{pmatrix}\Psi^B_0\begin{pmatrix} a_i \\ b_k\end{pmatrix}\right\rangle, \quad (24)$$

where $\Psi^B_0\binom{f^B_k\ a_i}{b_k\ b_j}$ denotes the Slater determinant of molecule B in which the occupied spin orbital b_k has been replaced by f^B_k (sum of virtual spin orbitals of B) and the occupied spin orbital b_j ($b_j\neq b_k$) has been replaced by the occupied spin orbital a_i of molecule A. Indices i and j in summations of Eq. (24) run over occupied spin orbitals of A and B, respectively.

Our next step consists of the use of the so-called Longuet–Higgins representation of the interaction operator V^{AB} in terms of the molecular charge distributions ρ^M ($M=A,B$), namely,[23]

$$V^{AB} = \int\int\frac{\rho^A(\mathbf{r}^A)\rho^B(\mathbf{r}^B)}{|\mathbf{r}^A-\mathbf{r}^B|}\,d\mathbf{r}^A d\mathbf{r}^B, \quad (25)$$

with

$$\rho^M(\mathbf{r}) = \rho^M_{\text{nuclear}}(\mathbf{r}) + \rho^M_{\text{electronic}}(\mathbf{r}) = \sum_{\mu\in M}Z_\mu\delta(\mathbf{r}-\mathbf{r}_\mu) - \sum_{i\in M}\delta(\mathbf{r}-\mathbf{r}_i), \quad M=A,B. \quad (26)$$

By using this representation, $[V^{AB}P_{(1)}]_k$ is written as

$$[V^{AB}P_{(1)}]_k = \sum_{i\in A}\sum_{\substack{j\in B\\ j\neq k}}\int\int\frac{f^A_{00}\binom{b_j}{a_i}f^B_{00}\binom{f^B_k\ a_i}{b_k\ b_j}}{|\mathbf{r}^A-\mathbf{r}^B|}\,d\mathbf{r}^A\,d\mathbf{r}^B + \sum_{i\in A}\int\int\frac{f^A_{00}\binom{f^B_k}{a_i}f^B_{00}\binom{a_i}{b_k}}{|\mathbf{r}^A-\mathbf{r}^B|}\,d\mathbf{r}^A\,d\mathbf{r}^B, \quad (27)$$

with the definitions

$$f^A_{00}\begin{pmatrix} b_j \\ a_i\end{pmatrix} = \left\langle\Psi^A_0\middle|\rho^A(\mathbf{r}^A)\middle|\Psi^A_0\begin{pmatrix} b_j \\ a_i\end{pmatrix}\right\rangle, \quad (28a)$$

$$f^B_{00}\begin{pmatrix} f^B_k\ a_i \\ b_k\ b_j\end{pmatrix} = \left\langle\Psi^B_0\middle|\rho^B(\mathbf{r}^B)\middle|\Psi^B_0\begin{pmatrix} f^B_k\ a_i \\ b_k\ b_j\end{pmatrix}\right\rangle\ (j\neq k), \quad (28b)$$

$$f^A_{00}\begin{pmatrix} f^B_k \\ a_i\end{pmatrix} = \left\langle\Psi^A_0\middle|\rho^A(\mathbf{r}^A)\middle|\Psi^A_0\begin{pmatrix} f^B_k \\ a_i\end{pmatrix}\right\rangle, \quad (28c)$$

$$f^B_{00}\begin{pmatrix} a_i \\ b_k\end{pmatrix} = \left\langle\Psi^B_0\middle|\rho^B(\mathbf{r}^B)\middle|\Psi^B_0\begin{pmatrix} a_i \\ b_k\end{pmatrix}\right\rangle. \quad (28d)$$

Note that the quantities of Eqs. (28a)–(28d) can be viewed as generalizations of the usual intramolecular charge density associated with the ground-state wave function of molecule M ($M=A,B$)

$$f^M_{00}(\mathbf{r}^M) = \langle\Psi^M_0|\rho^M(\mathbf{r}^M)|\Psi^M_0\rangle = \sum_{\mu\in M}Z_\mu\delta(\mathbf{r}^M-\mathbf{r}_\mu) - \sum_{i\in M}|c_i(\mathbf{r}^M)|^2, \quad (28e)$$

where $c\equiv a$ for $M=A$ and $c\equiv b$ for $M=B$, and thus may be referred to as "overlap intermolecular charge densities." Using this terminology, $[V^{AB}P_{(1)}]_k$, as given by Eq. (27), may be interpreted as a combination of electrostatic interactions between these various overlap intermolecular charge densities.

In order to write down simple formulas for these formal charge densities it is convenient to rewrite the determinental wave functions in terms of orthogonal spin orbitals. Let Ψ be a determinant constructed from a set of N orthonormal spin orbitals $\{u_k\}_{k=1,N}$ and let v_j be an arbitrary spin orbital (that is with no particular orthogonality relations with respect to $\{u_k\}$), then the following property holds:

$$\Psi\begin{pmatrix} v_j \\ u_i\end{pmatrix} = \Psi\begin{pmatrix} v'_j \\ u_i\end{pmatrix} + \langle u_i|v_j\rangle\Psi, \quad (29)$$

where v'_j is constructed to be orthogonal on the set $\{u_k\}_{k=1,N}$, namely,

$$v'_j = v_j - \sum_{k=1}^{N}\langle u_k|v_j\rangle u_k. \quad (30)$$

Applying this property and denoting S^{AB}_{ij} and $S^{AB}_{if^B_k}$ as the spin-orbital overlaps

$$S^{AB}_{ij} = \langle a_i|b_j\rangle = \int d\mathbf{r}\,a_i(\mathbf{r})b_j(\mathbf{r})\langle\sigma^A_i|\sigma^B_j\rangle, \quad (31a)$$

and

$$S^{AB}_{if^B_k} = \langle a_i|f^B_k\rangle = \int d\mathbf{r}\,a_i(\mathbf{r})f^B_k(\mathbf{r})\langle\sigma^A_i|\sigma^B_{f^B_k}\rangle, \quad (31b)$$

we obtain the following relations:

$$\Psi_0^A\begin{pmatrix} b_j \\ a_i \end{pmatrix} = \Psi_0^A\begin{pmatrix} b'_j \\ a_i \end{pmatrix} + S_{ij}^{AB}\Psi_0^A$$

with $b'_j = b_j - \Sigma_{l\in A} S_{ij}^{AB} a_l$,

$$\Psi_0^A\begin{pmatrix} f_k^B \\ a_i \end{pmatrix} = \Psi_0^A\begin{pmatrix} f_{k'}^{B'} \\ a_i \end{pmatrix} + S_{if_k^B}^{AB}\Psi_0^A$$

with $f_{k'}^{B'} = f_k^B - \Sigma_{l\in A} S_{lf_k^B}^{AB} a_l$,

and

$$\Psi_0^B\begin{pmatrix} a_i \\ b_k \end{pmatrix} = \Psi_0^B\begin{pmatrix} a'_i \\ b_k \end{pmatrix} + S_{ik}^{AB}\Psi_0^B$$

with $a'_i = a_i - \Sigma_{l\in B} S_{il}^{AB} b_l$.

For convenience, the expression of $\Psi_0^B\left(\begin{smallmatrix} f_k^B & a_i \\ b_k & b_j \end{smallmatrix}\right)$ will be written down by using a slightly generalized version of property (29). Direct application of (29) would require constructing a spin orbital a'_i orthogonal with the set $\{b_j\}_{j\neq k}$ and f_k^B. In particular, a'_i would have no particular orthogonality relation with respect to the spin orbital b_k. However, as will become evident below, it is very convenient to impose also the orthogonality between these two spin orbitals. We thus define the new primed orbital a'_i as

$$a'_i = a_i - \sum_{l\in B} S_{il}^{AB} b_l - S_{if_k^B}^{AB} f_k^B,$$

which leads to the following expression:

$$\Psi_0^B\begin{pmatrix} f_k^B & a_i \\ b_k & b_j \end{pmatrix} = \Psi_0^B\begin{pmatrix} f_k^B & a'_i \\ b_k & b_j \end{pmatrix} + S_{ij}^{AB}\Psi_0^B\begin{pmatrix} f_k^B \\ b_k \end{pmatrix} - S_{ik}^{AB}\Psi_0^B\begin{pmatrix} f_k^B \\ b_j \end{pmatrix} \quad (j\neq k),$$

which contains an extra term resulting from our new additional constraint.

Now, to evaluate matrix elements of Eqs. (28a)–(28d) we take advantage of the previous expressions and of the monoelectronic character of operators $\rho^A(\mathbf{r}^A)$ and $\rho^B(\mathbf{r}^B)$ (nonzero matrix elements only when evaluated between two determinants differing by at most one spin orbital). Note that this property holds here merely because we have introduced new spin orbitals (labeled with a prime) constructed to be orthogonal with original spin orbitals.

Thus, after some algebra we obtain

$$f_{00}^A\begin{pmatrix} b_j \\ a_i \end{pmatrix} = -a_i(\mathbf{r}^A)\left[b_j(\mathbf{r}^A)\langle\sigma_i^A|\sigma_j^B\rangle - \sum_{l\in A} S_{lj}^{AB} a_l(\mathbf{r}^A)\langle\sigma_i^A|\sigma_l^A\rangle\right] + S_{ij}^{AB} f_{00}^A(\mathbf{r}^A), \tag{32a}$$

$$f_{00}^B\begin{pmatrix} f_k^B & a_i \\ b_k & b_j \end{pmatrix} = -b_k(\mathbf{r}^B) f_k^B(\mathbf{r}^B)\langle\sigma_k^B|\sigma_{f_k^B}^B\rangle S_{ij}^{AB} + b_j(\mathbf{r}^B) f_k^B(\mathbf{r}^B)\langle\sigma_j^B|\sigma_{f_k^B}^B\rangle S_{ik}^{AB} \quad (j\neq k), \tag{32b}$$

$$f_{00}^A\begin{pmatrix} f_k^B \\ a_i \end{pmatrix} = -a_i(\mathbf{r}^A)\left[f_k^B(\mathbf{r}^A)\langle\sigma_i^A|\sigma_{f_k^B}^B\rangle - \sum_{l\in A} S_{lf_k^B}^{AB} a_l(\mathbf{r}^A)\langle\sigma_i^A|\sigma_l^A\rangle\right] + S_{if_k^B}^{AB} f_{00}^A(\mathbf{r}^A), \tag{32c}$$

$$f_{00}^B\begin{pmatrix} a_i \\ b_k \end{pmatrix} = -b_k(\mathbf{r}^B)\left[a_i(\mathbf{r}^B)\langle\sigma_i^A|\sigma_k^B\rangle - \sum_{l\in B} S_{il}^{AB} b_l(\mathbf{r}^B)\langle\sigma_i^B|\sigma_l^B\rangle\right] + S_{ik}^{AB} f_{00}^B(\mathbf{r}^B), \tag{32d}$$

where $f_{00}^M(\mathbf{r})$ $(M = A,B)$ stands for the usual molecular charge density at $\mathbf{r}$, Eq. (28e). Finally, $[V^{AB}P_{(1)}]_k$ given by expression (27) can be written as a sum of mono- and bielectronic integrals involving spin orbitals a_i, b_j, and f_k^B.

2. Expression of $\langle V^{AB}\rangle[P_{(1)}]_k$

The quantity $\langle V^{AB}\rangle$ is nothing but the electrostatic energy of interaction between the systems A and B which may be expressed as usual in terms of mono- and bielectronic integrals involving occupied spin orbitals $\{a_i\}$ and $\{b_j\}$ of the two monomers.[22]

Now, to evaluate $[P_{(1)}]_k$, we simply set $V^{AB} = 1$ in Eq. (24),

$$[P_{(1)}]_k = \sum_{i\in A}\sum_{\substack{j\in B \\ j\neq k}} \left\langle \Psi_0^A\Psi_0^B \middle| \Psi_0^A\begin{pmatrix} b_j \\ a_i \end{pmatrix}\Psi_0^B\begin{pmatrix} f_k^B & a_i \\ b_k & b_j \end{pmatrix}\right\rangle + \sum_{i\in A}\left\langle \Psi_0^A\Psi_0^B \middle| \Psi_0^A\begin{pmatrix} f_k^B \\ a_i \end{pmatrix}\Psi_0^B\begin{pmatrix} a_i \\ b_k \end{pmatrix}\right\rangle. \tag{33}$$

Due to the orthogonality of the spin orbitals f_k^B with the occupied spin orbitals of B, only the second contribution in Eq. (33) does not vanish, and we obtain

$$[P_{(1)}]_k = \sum_{i\in A}\left\langle \Psi_0^A \middle| \Psi_0^A\begin{pmatrix} f_k^B \\ a_i \end{pmatrix}\right\rangle\left\langle \Psi_0^B \middle| \Psi_0^B\begin{pmatrix} a_i \\ b_k \end{pmatrix}\right\rangle, \tag{34}$$

which may be expressed in terms of overlaps between spin orbitals as follows:

$$[P_{(1)}]_k = \sum_{i\in A} S_{if_k^B}^{AB} S_{ik}^{AB}. \tag{35}$$

3. Expression of $\langle P_{(1)}\rangle[V^{AB}]_k$

Using Eq. (23), $\langle P_{(1)}\rangle$ is written as

$$\langle P_{(1)}\rangle = \sum_{i\in A}\sum_{j\in B}\left\langle \Psi_0^A\Psi_0^B \middle| \Psi_0^A\begin{pmatrix} b_j \\ a_i \end{pmatrix}\Psi_0^B\begin{pmatrix} a_i \\ b_j \end{pmatrix}\right\rangle, \tag{36}$$

which leads to

$$\langle P_{(1)}\rangle = \sum_{i\in A}\sum_{j\in B}|S_{ij}^{AB}|^2. \tag{37}$$

On the other hand, $[V^{AB}]_k$ is written

$$[V^{AB}]_k = \left\langle \Psi_0^A\Psi_0^B \middle| V^{AB} \middle| \Psi_0^A\Psi_0^B\begin{pmatrix} f_k^B \\ b_k \end{pmatrix}\right\rangle.$$

We shall not make explicit this latter expression further since, when the summation over k is performed, it corre-

sponds to the usual second-order Rayleigh–Schrödinger induction energy of A on B.[12]

B. Second-order exchange dispersion energy

The derivation of the second-order exchange dispersion energy is actually very similar to the derivation just presented for the induction term. Introducing the following coefficients

$$c_{kl}^{rs} = \frac{\langle \Psi_0^A \Psi_0^B | V^{AB} | \Psi_0^A(^{a_r}_{a_k}) \Psi_0^B(^{b_s}_{b_l}) \rangle}{(E_0^A + E_0^B) - [E_0^A(k \to r) + E_0^B(l \to s)]} \tag{38}$$

and defining the so-called "dispersion pair functions" (which play a role here similar to the "induction functions" f_k^B introduced for the induction term) as follows:[15]

$$u_{kl}^{AB}(1,2) = \sum_{r \in A} \sum_{s \in B} c_{kl}^{rs} a_r(1) b_s(2), \tag{39}$$

the expression of Φ_{disp}^{AB} may be rewritten as [using Eqs. (12d) and (14)]

$$\Phi_{\text{disp}}^{AB} = \sum_{k \in A} \sum_{l \in B} \mathbf{A}^A \mathbf{A}^B \left[u_{kl}^{AB}(k,l) \prod_{i \neq k} a_i(i) \prod_{j \neq l} b_j(j) \right]. \tag{40}$$

Now, by inserting Φ_{disp}^{AB} into formula (11) [Φ_{disp}^{AB} is the dispersion part of $\Phi^{(1)}$ according to Eq. (12a)] it is possible to express $E_{\text{exch-disp}}^{(2)}$ in terms of the previous dispersion pair functions.[15] However, we shall not follow this method. In the present work we shall prefer to show how the exchange dispersion energy may also be formally written as a sum of contributions which may interpreted as the electrostatic interaction between suitable "overlap intermolecular charge distributions" localized on monomers A and B, respectively, thus pursuing what has been done for the exchange induction term. It should be remarked that such a point of view is no longer possible when introducing the dispersion pair functions since such functions connect explicitly variables of monomers A and B [Eq. (39)]. The two ways of writing down expressions for the exchange dispersion energy are of course equivalent but the latter approach will be particularly simple to handle.

By using Eqs. (11), (12a), (12d), (13), and (38) the following form for $E_{\text{exch-disp}}^{(2)}$ is obtained:

$$E_{\text{exch-disp}}^{(2)} = -\sum_{k \in A} \sum_{l \in B} \sum_{r \in A} \sum_{s \in B} c_{kl}^{rs} \left\langle \Psi_0^A \Psi_0^B \right| (V^{AB} - \langle V^{AB} \rangle) \times (P_{(1)} - \langle P_{(1)} \rangle) \left| \Psi_0^A \begin{pmatrix} a_r \\ a_k \end{pmatrix} \Psi_0^B \begin{pmatrix} b_s \\ b_l \end{pmatrix} \right\rangle, \tag{41}$$

where the two first summations are performed over the set of occupied spin orbitals of A and B, while the two last ones run over the virtual spin orbitals of A and B. Here also, $E_{\text{exch-disp}}^{(2)}$ is expressed as a sum of three nonzero contributions resulting from the expansion of the bracketed product. For future use, the following compact notation is defined:

$$[O]_{kl}^{rs} \equiv \left\langle \Psi_0^A \Psi_0^B \right| O \left| \Psi_0^A \begin{pmatrix} a_r \\ a_k \end{pmatrix} \Psi_0^B \begin{pmatrix} b_s \\ b_l \end{pmatrix} \right\rangle, \tag{42}$$

where O stands for an arbitrary operator.

1. Expression of $[V^{AB}P_{(1)}]_{kl}^{rs}$

In order to write down the expression of $[V^{AB}P_{(1)}]_{kl}^{rs}$, the permutation operator $P_{(1)}$ must be applied to the product of determinants $\Psi_0^A(^{a_r}_{a_k})\Psi_0^B(^{b_s}_{b_l})$. To do this, our basic formula (23) is used. When performing the double summation involved in (23), four different cases must be distinguished, depending on whether the spin orbitals a_r and/or b_s are considered in the summations or not. Next, the Longuet-Higgins representation of the interaction operator is used and then the quantity $[V^{AB}P_{(1)}]_{kl}^{rs}$ takes the form

$$\begin{aligned}[V^{AB}P_{(1)}]_{kl}^{rs} = &\sum_{\substack{i \in A \\ i \neq k}} \sum_{\substack{j \in B \\ j \neq l}} \int\int \frac{f_{00}^A(^{a_r\, b_j}_{a_k\, a_i}) f_{00}^B(^{b_s a_i}_{b_l b_j})}{|\mathbf{r}^A - \mathbf{r}^B|} d\mathbf{r}^A\, d\mathbf{r}^B \\ &+ \sum_{\substack{i \in A \\ i \neq k}} \int\int \frac{f_{00}^A(^{a_r\, b_s}_{a_k\, a_i}) f_{00}^B(^{a_i}_{b_l})}{|\mathbf{r}^A - \mathbf{r}^B|} d\mathbf{r}^A\, d\mathbf{r}^B \\ &+ \sum_{\substack{j \in B \\ j \neq l}} \int\int \frac{f_{00}^A(^{b_j}_{a_k}) f_{00}^B(^{b_s\, a_r}_{b_l\, b_j})}{|\mathbf{r}^A - \mathbf{r}^B|} d\mathbf{r}^A\, d\mathbf{r}^B \\ &+ \int\int \frac{f_{00}^A(^{b_s}_{a_k}) f_{00}^B(^{a_r}_{b_l})}{|\mathbf{r}^A - \mathbf{r}^B|} d\mathbf{r}^A\, d\mathbf{r}^B. \end{aligned} \tag{43}$$

Now, to calculate the "overlap intermolecular charge distributions" the same method as that used in the derivation of the exchange induction is employed. In fact, it is not difficult to convince oneself that calculations are identical with those accomplished for obtaining Eqs. (32). Let us just give the results in the following compact form:

$$\begin{aligned} f_{00}^M \begin{pmatrix} c_p\, d_k \\ c_i\, c_j \end{pmatrix} = &- c_i(\mathbf{r}^M) c_p(\mathbf{r}^M) \langle \sigma_i^M | \sigma_p^M \rangle S_{jk}^{AB} \\ &+ c_j(\mathbf{r}^M) c_p(\mathbf{r}^M) \langle \sigma_j^M | \sigma_p^M \rangle S_{ik}^{AB}, \end{aligned} \tag{44}$$

with $c \equiv a$, $d \equiv b$ for $M = A$ and $c \equiv b$, $d \equiv a$ for $M = B$.

Note that c_i, c_j, and d_k are occupied spin orbitals and $c_i \neq c_j$. With the same notations, we have

$$\begin{aligned} f_{00}^M \begin{pmatrix} d_\beta \\ c_i \end{pmatrix} = &- c_i(\mathbf{r}^M) \Big[d_\beta(\mathbf{r}^M) \langle \sigma_i | \sigma_\beta \rangle \\ &- \sum_{j \in M} S_{j\beta}^{AB} c_j(\mathbf{r}^M) \langle \sigma_i | \sigma_j \rangle \Big] + S_{i\beta}^{AB} f_{00}^M(\mathbf{r}^M). \end{aligned} \tag{45}$$

Note that c_i denotes an occupied spin orbital of one of the two monomers, while d_β may represent either an occupied or a virtual spin orbital of the other monomer.

2. Expression of $\langle V^{AB} \rangle [P_{(1)}]_{kl}^{rs}$

As already noticed, the quantity $\langle V_{AB} \rangle$ is nothing but the usual electrostatic interaction energy between monomers A and B. Expression of $[P_{(1)}]_{kl}^{rs}$ in terms of spin orbital overlaps is as usual obtained by making use of our basic property (23). One obtains

$$\begin{aligned}[P_{(1)}]_{kl}^{rs} &= \left\langle \Psi_0^A \Psi_0^B \right| P_{(1)} \left| \Psi_0^A \begin{pmatrix} a_r \\ a_k \end{pmatrix} \Psi_0^B \begin{pmatrix} b_s \\ b_l \end{pmatrix} \right\rangle \\ &= S_{ks}^{AB} S_{rl}^{AB}. \end{aligned} \tag{46}$$

3. Expression of $\langle P_{(1)} \rangle [V^{AB}]^{rs}_{kl}$

We shall not make explicit the expression of $[V^{AB}]^{rs}_{kl}$ further since, when summations over the indices are performed, it corresponds to the usual second-order Rayleigh–Schrödinger dispersion energy.[12] On the other hand, $\langle P_{(1)} \rangle$ has already been given in Eqs. (36) and (37).

C. Hylleraas variational procedure

Now, when performing the practical evaluation of the quantities written above, we are faced with the well-known problem of summing expressions defined over the infinite set of unoccupied orbitals of the Fock operator belonging to the continuous spectrum. As pointed out by Jeziorski and van Hemert,[12] such summations are practically inexecutable integration. To overcome this difficulty, here we will use the variational-perturbation method proposed by JvH. This method, which is essentially based on the minimization of a Hylleraas-type functional, has been already described in detail (see, e.g., Refs. 12 and 16) and therefore only its main features are summarized here. When applying the variational procedure, it is possible to show[12,16] that expressions of induction and dispersion may be rewritten in a form identical with that obtained by the direct procedure, except that expressions are expressed in a new basis set donated by JvH as a *molecular* (or dimer) basis set. This new basis set consists of the occupied spin orbitals of monomers A and B ($\{a_i\}$ and $\{b_j\}$ with the corresponding orbital energies ϵ_i^A and ϵ_j^B) and of a new set of virtual spin orbitals obtained by diagonalizing the one-electron Fock operator of A (respectively, B) within the space spanned by the basis set of the whole dimer AB (denoted as $\{\tilde{a}_r\}$ and $\{\tilde{b}_s\}$ with the corresponding orbital energies $\tilde{\epsilon}_r^A$ and $\tilde{\epsilon}_s^B$). Note that the symbols a and b do not indicate at which center the orbital is located (basis set delocalized on the whole dimer). It should be emphasized that $\{\tilde{a}_r\}$ and $\{\tilde{b}_s\}$ are sets of square-integrable functions whereas $\{a_r\}$ and $\{b_s\}$ form continuous sets of unnormalizable functions. When using the molecular basis set, the induction and dispersion pair functions f_k^B and u_{kl}^{AB} [defined by Eqs. (18) and (39), respectively] must be replaced by the following new functions:

$$\tilde{f}_k^B = \sum_{r \in B} \tilde{c}_k^r \tilde{b}_r, \tag{47a}$$

$$\tilde{u}_{kl}^{AB}(1,2) = \sum_{r \in A} \sum_{s \in B} \tilde{c}_{kl}^{rs} \tilde{a}_r(1) \tilde{b}_s(2), \tag{47b}$$

where

$$\tilde{c}_k^r = \langle b_k | \omega^A | \tilde{b}_r \rangle / (\epsilon_k^B - \tilde{\epsilon}_r^B), \tag{48a}$$

with

$$\omega^A(\mathbf{r}) = \int \frac{f_{00}^A(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

and

$$\tilde{c}_{kl}^{rs} = \left\langle a_k b_l \left| \frac{1}{r_{12}} \right| \tilde{a}_r \tilde{b}_s \right\rangle \quad (\epsilon_k^A + \epsilon_l^B - \tilde{\epsilon}_r^A - \tilde{\epsilon}_s^B). \tag{48b}$$

The practical evaluation of expressions of second-order exchange contributions derived in the preceding sections (II A) and (II B) are performed by using the dimer basis set $\{\tilde{a},\tilde{b}\}$ instead of the monomer basisset $\{a,b\}$ and by employing formulas (47a) and (48a) for the induction functions $\tilde{f}_k^B$ and formula (48b) for the coefficient $\tilde{c}_{kl}^{rs}$. Note that, in contrast with other works,[12,14–17] the new dispersion pair functions $\tilde{u}_{kl}^{AB}$ are not directly used (see discussion above, Sec. II B).

III. NUMERICAL RESULTS AND DISCUSSION

The implementation of the preceding expressions has been performed by modifying and extending an original program written by JvH. Since the main purpose of this work is to study the importance of the second-order exchange effects rather than to make a detailed investigation of the complete potential-energy surface, all numerical calculations have been done for a fixed relative orientation of the two interacting water molecules and by varying only the distance, R_{OO}, between the two oxygen atoms. In order to facilitate comparisons, the fixed orientation has been chosen to be identical with that used by JvH in their original work on the water dimer.[12] The nuclear coordinates of the water dimer are listed in Table I.

Second-order exchange induction and dispersion energies have been calculated by using the same basis set as JvH, namely a Gaussian basis (11,7,2/6,1) contracted into (4,3,2/2,1). This means 35 contracted basis functions for the monomer and 70 functions for the dimer. By employing this basis set, the total energy of the monomer and the binding energy of the water dimer are found to be -76.0576 a.u. and -3.87 kcal/mol, respectively.

Calculations with R_{OO} ranging from 4.40 to 9.00 a.u. have been performed. Numerical results for each individual component of the interaction energy are listed in Table II. No particular comments on results obtained for the commonly calculated contributions $E_{RS}^{(1)}$, $E_{exch}^{(1)}$, $E_{ind}^{(2)}$, and $E_{disp}^{(2)}$ will be made here: for a discussion concerning these terms the interested reader is referred to the work of JvH.[12]

Before discussing our results, let us briefly present the few calculations performed so far for second-order exchange contributions. Most of calculations have been done for atomic van der Waals dimers (He_2, Be_2, Ne_2).[14–17] For distances around the equilibrium separation, two general features seem to emerge when treating inert gas dimers.

(1) There exists a large and systematic cancellation of $E_{ind}^{(2)}$ by the exchange induction contribution, $E_{exch\text{-}ind}^{(2)}$.

(2) The exchange dispersion energy cannot be considered as negligible and typically may represent a few percent

TABLE I. Nuclear coordinates for the water dimer (atomic units are used).

Atom	X	Y	Z
O	0.0	0.0	0.0
H	1.8088	0.0	0.0
H	−0.4641	1.7483	0.0
O	R_{OO}	0.0	0.0
H	$0.9551 + R_{OO}$	−0.5514	1.4338
H	$0.9551 + R_{OO}$	−0.5514	−1.4338

TABLE II. Particular contributions to the interaction energy of water dimer (in kcal/mol).

R_{OO} [a]	$E^{(1)}_{RS}$	$E^{(1)}_{exch}$	$E^{(2)}_{ind}$	$E^{(2)}_{disp}$	$E^{(2)}_{exch\text{-}ind}$	$E^{(2)}_{exch\text{-}disp}$
4.40	−27.10	51.59	−21.22	−8.42	14.31	3.11
4.80	−17.06	25.11	−9.30	−4.89	6.05	1.44
5.20	−11.10	12.03	−4.12	−2.86	2.45	0.67
5.67	−7.11	4.89	−1.63	−1.54	0.80	0.27
7.00	−2.79	0.30	−0.18	−0.31	0.03	0.02
9.00	−1.12	0.00	−0.02	−0.05	0.00	0.00

[a] Atomic units.

of the dispersion energy $E^{(2)}_{disp}$ [up to 10% for Be_2 (Ref. 15)].

With regard to molecular interactions, no systematic calculations have been performed that would show the importance of second-order induction and dispersion exchange effects. Indeed, it has been recommended[14–17] to calculate the interaction energy by using the following decomposition:

$$E_{int} \simeq E^{SCF}_{int} + E^{(2)}_{disp} + E^{(2)}_{exch\text{-}disp}, \tag{49}$$

and therefore attention has been focused on the evaluation of the intermolecular correlation effects represented by $E^{(2)}_{disp} + E^{(2)}_{exch\text{-}disp}$ and not on the evaluation of the exchange induction contribution which is supposed to be correctly taken into account in the SCF binding energy. To our knowledge the first calculation for a molecular system is due to Chalasinski.[19] He showed that for the HF dimer at the equilibrium geometry, $E^{(2)}_{exch\text{-}disp}$ represents about 10% of $E^{(2)}_{disp}$ which corresponds to a slightly more important contribution than for inert-gas dimers. His observation has been very recently confirmed by Rybak and co-workers,[20,21] who found a similar contribution for the water dimer. To our knowledge no calculations exist concerning the exchange induction energy for molecular systems.

Our results for second-order exchange contributions are presented in the two last columns of Table II. It should be noted that, in order to study basis-set size effects, we have performed an additional calculation with a substantially larger basis set than that employed by JvH.[12] The results presented in Tables IV and V will be discussed in detail below. However, anticipating our conclusions it is important to note that results are, in fact, not qualitatively changed. Therefore, the following discussion and conclusions based on results obtained by employing the JvH basis set will remain valid. A first remark would concern the magnitude of the second-order exchange dispersion energy which is found to represent about 20% of the dispersion energy, thus confirming the non-negligible role of this contribution.[14–17,20,21] Note that our result for $E^{(2)}_{exch\text{-}disp}$ is 0.27 kcal/mol while Rybak's result is 0.19 kcal/mol.[20,21] This difference may be interpreted as resulting from a basis-set size effect. Indeed, we observed a systematic lowering of our result when we repeated our calculation with basis sets of various smaller sizes (results not presented here). A particularly interesting result concerns the second-order exchange induction energy which is found to be quite important. At the equilibrium geometry, it compensates for approximately 50% of the induction energy. The importance of this contribution, which has been already noticed for inert-gas dimers,[14–17] is therefore confirmed for the water dimer. When combining both second-order exchange components a contribution of about 1 kcal/mol is obtained at the equilibrium geometry. Comparing this contribution to the estimated interaction energy of about 5.4 kcal/mol,[12] the importance of second-order exchange effects is clearly illustrated. It is therefore quite obvious that such an exchange contribution cannot be neglected when doing high-quality evaluations of intermolecular interactions (exactly or by means of high-quality simplified representations).

Having calculated the exchange induction energy, it is interesting to compare the SCF binding energy to the sum of the complete first-order and second-order induction energies (displayed in columns 2 and 1 of Table III, respectively). Except at large distances, results displayed in Table III clearly demonstrate the noncoincidence of these two quantities. As a consequence, it is concluded that the additional terms present in the SCF binding energy (induction part of third- and higher-order Rayleigh–Schrödinger terms, some intramolecular correlation contribution introduced when doing a SCF supermolecule calculation[13]) contribute in a non-negligible way, even in the neighborhood of the equilibrium geometry. It is seen that these additional contributions become more important as the intermolecular distance is decreased. It may be expected that the difference between

TABLE III. Comparison of the SCF and perturbation-theory interaction energies for the water dimer (in kcal/mol).

R_{OO} [a]	$E^{(1)}+E^{(2)}_{ind}+E^{(2)}_{exch\text{-}ind}$	E^{SCF}_{int}	E^{pert}_{int} [b]	$E^{SCF}_{int}+E^{(2)}_{disp}$	$E^{SCF}_{int}+E^{(2)}_{disp}+E^{(2)}_{exch\text{-}disp}$
4.40	17.57	10.72	12.27	2.30	5.41
4.80	4.79	0.92	1.35	−3.97	−2.53
5.20	−0.75	−2.77	−2.93	−5.62	−4.95
5.67	−3.05	−3.87	−4.32	−5.41	−5.14
7.00	−2.65	−2.69	−2.93	−3.00	−2.98
9.00	−1.14	−1.14	−1.19	−1.19	−1.19

[a] Atomic units.

[b] Pure perturbational interaction energy calculated as $E^{pert}_{int} = E^{(1)}_{RS} + E^{(1)}_{exch} + E^{(2)}_{ind} + E^{(2)}_{disp} + E^{(2)}_{exch\text{-}ind} + E^{(2)}_{exch\text{-}disp}$.

$E_{\text{int}}^{\text{SCF}}$ and $E^{(1)} + E_{\text{ind}}^{(2)}$ would be partly cancelled if in the perturbational approach the induction part of third- and higher-order contributions would be considered. At this point, let us recall that JvH (Ref. 12) obtained at $R_{\text{OO}} = 5.67$ a.u. a good agreement between the SCF binding energy $E_{\text{int}}^{\text{SCF}}$ (-3.87 kcal/mol) and $E^{(1)} + E_{\text{ind}}^{(2)}$ (-3.85 kcal/mol). Accordingly, their approximate equality

$$E_{\text{int}}^{\text{SCF}} \simeq E^{(1)} + E_{\text{ind}}^{(2)} \tag{50}$$

results essentially from a cancellation between $E_{\text{exch-ind}}^{(2)}$ and high-order contributions. Such a cancellation must be considered as fortuitous and cannot be generalized without further theoretical investigations. In conclusion, it does not seem justifiable to approximate the SCF binding energy by a sum of perturbation terms limited to second-order contributions, even at intermediate distances (including the equilibrium geometry).

Now, in order to compare calculations with experimentallly predicted values of the total interaction energy, it is necessary to take into account intermolecular correlation effects, that is, dispersion contributions. We present in Table III values of the total interaction energy as calculated by our pure perturbational approach (third column) and by the most commonly used approach consisting of supplementing the SCF binding energy with the dispersion contributions (fifth column). Both potential-energy curves reveal a minimum which is approximately located at the same intermolecular separation, namely, $R_{\text{OO}} = 5.67$ a.u. As is known, the experimental evaluation of the total interaction energy at the equilibrium geometry is not easy to perform,[1] in what follows we shall use the most commonly accepted value of -5.4 kcal/mol with an estimated error of ± 0.7 kcal/mol.[2] It is very interesting to note that supplementing the sum $E_{\text{int}}^{\text{SCF}} + E_{\text{disp}}^{(2)}$ with the exchange dispersion contribution noticeably deteriorates the very good value of -5.41 kcal/mol obtained at the equilibrium geometry (without inclusion of the exchange dispersion term). Once again, such a result must be interpreted as a consequence of a fortuitous cancellation of terms which are not evaluated. To be more precise, it is expected that the sum $E_{\text{int}}^{\text{SCF}} + E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$ cannot fit the exact interaction energy. Indeed, it is well known that the difference between the SCF and correlated dipole moments of the water molecule are non-negligible (relative error of 10%; see Ref. 28), thus indicating a large electron correlation contribution to the electrostatic interaction energy. Concerning the pure perturbational approach, it is clear that, besides intracorrelation contributions, high-order contributions must also be incorporated if a high accuracy is needed.

Now, we will pay some attention to the important problem of the quality of the basis set used. There exists a large amount of calculations performed with various basis sets at the supermolecular SCF level. All these studies indicate that basis sets involving a very large number of basis functions are needed to accurately reproduce the total interaction energy. However, except in a very recent extensive study of Szalewicz *et al.*[1] in which the problem of the basis-set dependency of the dispersion energy for the water dimer is addressed, to date no systematic study has been performed that shows the dependence of each particular perturbational contribution on the quality of the basis set employed. Here, we shall not do such an extensive work. In order to test the sensitivity of our results to the basis set we shall limit ourselves to the use of one substantially larger basis set. The so-called isotropic part of our basis (functions describing orbitals occupied in the ground states of the atoms; see Ref. 28) has been taken from Ref. 29 and consists of a set of $(13s8p)$ and (6s) functions on the oxygens and hydrogens, respectively. This basis set has been extended with a set of $(2d)$ and $(2p)$ polarization functions on oxygen and hydrogen, respectively. The exponents were chosen to minimize the dispersion as well as the complementary exchange energies (see Ref. 22). Exponents $\alpha_d = 1$ and 0.3, $\alpha_p = 0.6$ and 0.15 have been obtained. The complete contracted basis represents 94 basis functions for the water dimer.

The energy of the water monomer calculated by using this basis set equals $-76.060\,04$ a.u. The SCF binding energies obtained for the water dimer are -3.96 and -3.73 kcal/mol without and with the counterpoise correction (CP), respectively. The latter value agrees very well with the SCF limit of -3.73 ± 0.05 kcal/mol (including CP correction) recently estimated by Szalewicz *et al.*[1] using a very large basis set containing 212 contracted orbitals. The values of the particular contributions to the interaction energy are listed in Tables IV and V. The essential result to point out is that the total interaction energy calculated as $E^{(1)} + E_{\text{RS}}^{(2)} + E_{\text{exch}}^{(2)}$ or as $E_{\text{int}}^{\text{SCF}} + E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$ with both basis sets (see Tables III and V) is not very different at the

TABLE IV. Particular contributions to the interaction energy of the water dimer (in kcal/mol) calculated with a 94 AO basis set.[a]

R_{OO} [b]	$E_{\text{RS}}^{(1)}$	$E_{\text{exch}}^{(1)}$	$E_{\text{ind}}^{(2)}$	$E_{\text{disp}}^{(2)}$	$E_{\text{exch-ind}}^{(2)}$	$E_{\text{exch-disp}}^{(2)}$
4.40	-23.66	50.31	-21.25	-8.90	14.28	3.32
4.80	-16.68	24.19	-9.42	-5.27	6.19	1.51
5.20	-10.81	11.61	-4.37	-3.18	2.70	0.75
5.67	-6.89	4.85	-1.82	-1.79	0.99	0.32
7.00	-2.67	0.39	-0.22	-0.46	0.06	0.03
9.00	-1.05	0.01	-0.03	-0.09	0.00	0.00

[a] Basis set described in the text.
[b] Atomic units.

TABLE V. Comparison of the SCF and perturbation-theory interaction energies for the water dimer (in kcal/mol) calculated with the 94 AO basis set.

R_{OO} [a]	$E^{(1)}+E^{(2)}_{ind}+E^{(2)}_{exch\text{-}ind}$	E^{SCF}_{int}	$E^{pert\ b}_{int}$	$E^{SCF}_{int}+E^{(2)}_{disp}$	$E^{SCF}_{int}+E^{(2)}_{disp}+E^{(2)}_{exch\text{-}disp}$
4.40	16.68	10.97	11.10	2.07	5.39
4.80	4.28	1.08	0.52	−4.19	−2.68
5.20	−0.87	−2.62	−3.30	−5.80	−5.05
5.67	−2.87	−3.73	−4.34	−5.52	−5.20
7.00	−2.44	−2.55	−2.87	−3.01	−2.98
9.00	−1.07	−1.08	−1.15	−1.16	−1.16

[a] Atomic units.

[b] Pure perturbational interaction energy calculated as $E^{pert}_{int}=E^{(1)}_{RS}+E^{(1)}_{exch}+E^{(2)}_{ind}+E^{(2)}_{disp}+E^{(2)}_{exch\text{-}ind}+E^{(2)}_{exch\text{-}disp}$.

equilibrium geometry and for large intermolecular separations. In addition, it should be noted that for these intermediate and large distances individual components appear to be more sensitive to the basis-set extension than the total sum. The two contributions to the total first-order interaction energy, namely, the electrostatic and first-order exchange terms, are not seriously affected when the size of the basis set is increased. However, the dipole moment of the water monomer calculated with the 94 atomic-orbital (AO) basis set (1.98 D) is in a better agreement with the experimental value[30] (1.85 D) than the value obtained with the JvH basis set (2.06 D).

With regard to the total second-order energy, it is interesting to note that the appreciable change of the RS contribution (− 3.61 kcal/mol vs − 3.17 kcal/mol with the JvH basis set) is partly compensated by a quite important increase of the exchange contribution (1.31 kcal/mol vs 1.07 kcal/mol with the JvH basis set). The total interaction energies calculated with the 70 and 94 AO basis set as the sum $E_{int}=E^{SCF}_{int}+E^{(2)}_{disp}+E^{(2)}_{exch\text{-}disp}$ equal − 5.14 and − 5.20 kcal/mol, respectively, and are consistent with the experimental value -5.4 ± 0.7 kcal/mol.[2] However, as already noticed above, non-negligible contributions to the interaction energy must be expected from intramolecular correlation effects which are known to decrease the dipole moment of the monomers and therefore are expected to modify noticeably the electrostatic contribution.

Szalewicz *et al.* pointed out that the use of *f* functions improved considerably their dispersion energy.[1] This observation is consistent with the results of Chalasinski for the neon dimer.[16] However, although no *f* functions are present in our calculations, our 94 AO basis set leads to a value for the dispersion energy of − 1.79 kcal/mol, close enough to the exact value of − 2 kcal/mol estimated by Szalewicz *et al.*[1] In addition, as just noticed, our SCF binding energy of the water dimer coincides with the SCF limit estimated by these authors. Accordingly, we do not think that inclusion of *f* orbitals should change the qualitative nature of our conclusions.

IV. CONCLUSIONS

In the present paper new expressions for the exchange induction and dispersion energies have been derived within the framework of symmetry-adapted perturbation theories. These expressions are valid for atomic and molecular systems having an arbitrary number of electrons. They have been derived by neglecting all electron correlation effects within the noninteracting molecules and by considering only single-electron exchange between interacting molecules. Within these approximations, numerical evaluation of second-order exchange contributions for the water dimer have been performed. Our major conclusion is that for such a polar system, second-order exchange effects are essentially dominated by the exchange induction energy and account for 20% of the total intermolecular interaction energy. As a conclusion, such contributions must be considered in any accurate calculation of the interaction energy. On the other hand, if a high accuracy on calculated interaction energies is needed, it is clear that going beyond the SCF approximation for the noninteracting systems is essential. In the case of the water molecule, it is known that the Hartree–Fock ground-state wave function overestimates the molecular dipole moment by about 10%, thus leading to an error of about 20% in the electrostatic contribution due to the lack of intramonomer electron correlation effects (let us recall that the electrostatic contribution is the leading component of the interaction energy at the equilibrium geometry). In addition, as already pointed out in our discussion of results, third-order (and higher-order) Rayleigh–Schrödinger contributions should be evaluated since they are expected not to be negligible in the region of the equilibrium geometry (see calculations of Jeziorski *et al.* in Ref. 21).

At this point, it is important to emphasize that the goal of the present work was not to obtain a very accurate value of the interaction energy between two water molecules. Indeed, it is clear that for a relatively simple system such as the water dimer, standard supermolecule approaches based on a very large CI calculation (or some form of it) are preferable (see, e.g., calculations of Diercksen, Kraemer, and Roos[31] and of Matsuoka, Clementi, and Yoshimine).[32] Actually, one of the basic motivations of our work was to put into evidence the non-negligible role of the complete second-order exchange contribution (exchange induction as well as exchange dispersion components). To be able to determine *quantitatively* the importance of each of these components opens the way towards representing second-order exchange contributions through simple analytical functions fitted on

calculated values. Knowledge of these functions will be required to derive high-quality parametrized formulas which describe quantitatively the interaction between molecules of arbitrary size.

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