

THE WATER DIMER - COMPARISON OF RESULTS OBTAINED BY BOTH AB INITIO SUPERMOLECULE AND SAPT METHODS. DERIVATION OF SIMPLIFIED FORMULAS

O. HESS¹, M. CAFFAREL¹, J. LANGLET¹, J. CAILLET¹, C. HUISZON²,
+ P. CLAVERIE¹,

¹Dynamique des Interactions Moléculaires, Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris (France)

²Chemical Physics Laboratory, Twente University of Technology, P. O. Box 217, 7500 AE Enschede, The Netherlands

+ Deceased, January 24, 1988.

SUMMARY.

Following explicit formulae for the calculation of second-order exchange contributions (induction as well as dispersion) within the framework of Symmetry-Adapted-Perturbation-Theories (SAPT), exchange contributions can be expressed as a combination of electrostatic interaction energies between suitably generalized charge distributions (overlap intermolecular distributions). Numerical calculations for the interaction of two water molecules are presented. The possibility of defining simple analytical functions representing each contribution of the interaction energy is discussed.

INTRODUCTION

In the field of theoretical evaluations of interaction energies, two types of approach are generally distinguished. The first approach is the so-called supermolecule method (ref. 1) in which the interaction energy is obtained as a difference between the total energy of the interacting molecules (the supermolecule) and the sum of the total energies of each monomer, all energies being calculated by using the same method. But the dispersion contribution cannot be obtained at the SCF level, in other words, an extensive CI calculation would be necessary to recover this important contribution. In the second approach, the intermolecular interaction energy is calculated from perturbation theory using the intermolecular potential as 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 wavefunctions are used. Due to the large separation between monomers no antisymmetrization of the factorized wave functions is necessary. For shorter distances, e.g. distances corresponding to the region around the equilibrium configuration, the usual Rayleigh-Schrödinger perturbation theory must be abandoned (ref. 2) and in order to take into account, at least to some extent, the exchange of electrons between the interacting molecules, some form of exchange per-

turbation theory (the so-called Symmetry Adapted Perturbation Theories (SAPT), (refs. 3-4) must be used. It is important to emphasize that this approach is particularly attractive with regard to the usual supermolecular approach since 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 in their pioneering work on the water dimer (ref. 5). Neglecting all intramonomer correlation effects, they evaluated the complete first-order interaction energy $E^{(1)} = E_{RS}^{(1)} + E_{exch}^{(1)}$ (explicitly, the sum of the Rayleigh-Schrödinger and first-order exchange energies) and only the Rayleigh-Schrödinger second-order interaction energy.

Very recently Hess *et al.* (ref. 6) have presented 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-Theory. Numerical results for the interaction of two water molecules have been presented, putting into evidence the nonnegligible role of the complete second-order exchange contributions. But it is well known that the quality of the results strongly depends on the size of the basis set used in the calculations, thus such a method cannot be applied to arbitrarily large systems. In fact the ability to determine with a high accuracy the values of each component of intermolecular interaction energy opens a way towards representing them through simple analytical functions fitted on values calculated in the framework of this perturbation treatment. In this present work we have been interested by the development of simplified formulae for the calculation of the dispersion and exchange-dispersion energies.

The organization of the present paper is as follows. In Sec. I and II we summarize the formal development of the second-order exchange contributions derived by Hess *et al.* (ref. 6) together with the most important results obtained by these authors for the water dimer. Sec. III is devoted to the investigation of basis set effects upon the different interaction energy components calculated with the method here-above cited. In section IV we will present and discuss some simplified formulae elaborated for dispersion and exchange dispersion contributions.

I. METHOD

We will just summarize the formal development of second-order exchange contributions presented by Hess *et al.* (ref. 6)

Following standard Symmetry-Adapted Perturbation Theories (refs. 3,4) the complete first- and second-order interaction energies are written as:

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

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

where R_0 denotes the reduced resolvent of H_0 given by

$$R_0 = \sum'_{ij} \frac{|\Psi_i^A \Psi_j^B\rangle \langle \Psi_i^A \Psi_j^B|}{(E_i^A + E_j^B) - (E_0^A + E_0^B)}, \quad (3)$$

(the prime in \sum' 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 is written in the form (ref. 7).

$$\mathbf{A} = 1 - \mathbf{A}' = 1 - P_{(1)} + P_{(2)} - \dots + (-1)^{N_{inf}} P_{(N_{inf})}, \quad (4)$$

where $P_{(1)} = \sum_i^A \sum_j^B P_{ij}$ 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 $P_{(2)}$, $P_{(3)}$, ... (N_{inf} denotes the smallest value of N_A and N_B , the numbers of electrons of molecule A and B respectively).

The second-order perturbation energy $E^{(2)}$ (Eq. (2)) may be decomposed into the usual second-order Rayleigh-Schrödinger (RS) perturbation energy $E_{RS}^{(2)}$ (obtained by putting $\mathbf{A} = 1$ in Eq. (1)) and into the so-called second-order exchange energy $E_{exch}^{(2)}$

$$E_{exch}^{(2)} \equiv E^{(2)} - E_{RS}^{(2)} = - \frac{\langle \Psi_0^A \Psi_0^B | (V^{AB} - E^{(1)}) (\mathbf{A}' - \langle \mathbf{A}' \rangle) | \Phi^{(1)} \rangle}{\langle \mathbf{A} \rangle}, \quad (5)$$

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 wavefunction $\Psi_0^A \Psi_0^B$ and $\Phi^{(1)}$ stands for the first-order correction to the wavefunction in the perturbation theory (ref. 4).

$$\Phi^{(1)} = -R_0 V^{AB} \Psi_0^A \Psi_0^B. \quad (6)$$

Now, since multiple exchanges are supposed to contribute weakly in the region around the equilibrium geometry (ref. 8-9) only the leading contribution to $E_{exch}^{(2)}$ corresponding to a single exchange of electrons between molecules A and B has been calculated. Thus, putting $\mathbf{A}' = P_{(1)}$ in Eq. (5) 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, $E_{exch}^{(2)}$ is obtained

$$E_{exch}^{(2)} = - \langle \Psi_0^A \Psi_0^B | (V^{AB} - \langle V^{AB} \rangle) (P_{(1)} - \langle P_{(1)} \rangle) | \Phi^{(1)} \rangle, \quad (7)$$

Rewriting $\Phi^{(1)}$ (Eq. (6)) as follows

$$\Phi^{(1)} = \Psi_0^A \Phi_{ind}^B + \Phi_{ind}^A \Psi_0^B + \Phi_{disp}^{AB} \quad , \quad (8)$$

and inserting the previous decomposition of $\Phi^{(1)}$ into Eq. (7), the second-order exchange energy decomposes into three terms

$$E_{exch}^{(2)} = E_{exch-ind}^{(2)}(A \rightarrow B) + E_{exch-ind}^{(2)}(B \rightarrow A) + E_{exch-disp}^{(2)} \quad . \quad (9)$$

The sum of the first two terms in Eq. (9) will be referred to in the following as the exchange induction energy, while $E_{exch-disp}^{(2)}$ will be referred to as the exchange dispersion energy.

In fact following Claverie (ref. 7) the method adopted by Hess *et al.* (ref. 6) 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 have been used, namely:

1) The possibility of reducing the action of intersystem antisymmetrizer (appearing in SAPT) on factorized SCF wave functions to a sum of simple products of SCF determinants pertaining to each subsystem, namely

$$P_{(1)}[\Psi^A \Psi^B] = \sum_{i \in A} \sum_{j \in B} \Psi^A \begin{pmatrix} b_j \\ a_i \end{pmatrix} \Psi^B \begin{pmatrix} a_i \\ b_j \end{pmatrix} \quad , \quad (10)$$

where the summation is over the spin-orbitals of determinants Ψ^A (here labeled by i) and Ψ^B (labeled by j). Using Eq. (10) all integrals involving functions of the type $P_{(1)}[\Psi^A \Psi^B]$ are reduced to sums of integrals involving simple products $\Psi^A \begin{pmatrix} b_j \\ a_i \end{pmatrix} \Psi^B \begin{pmatrix} a_i \\ b_j \end{pmatrix}$ of "opposite transfer" determinants.

2) The 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 ($M = A, B$) (ref. 10), namely:

$$V^{AB} = \iint \frac{\rho^A(\vec{r}^A) \rho^B(\vec{r}^B)}{|\vec{r}^A - \vec{r}^B|} d\vec{r}^A d\vec{r}^B \quad , \quad (11)$$

with

$$\begin{aligned} \rho^M(\vec{r}) &= \rho_{nuclear}^M(\vec{r}) + \rho_{electronic}^M(\vec{r}) \\ &= \sum_{\mu \in M} Z_{\mu} \delta(\vec{r} - \vec{r}_{\mu}) - \sum_{i \in M} \delta(\vec{r} - \vec{r}_i) \quad M = A, B \quad . \end{aligned} \quad (12)$$

The use of these two ingredients allows this development to have a systematic character. Within the SCF approximation, the different components of interaction

energy are now written as appropriate combinations of (mono- bielectronic and overlap) integrals involving spin-orbitals of closed-shell isolated systems (for more details see ref. 6).

Now, when performing the practical evaluation of the quantities necessary to the above calculation, one is faced to 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 (ref. 5), such summations are practically inexecutable integration. To overcome this difficulty, it has been used the variational-perturbation method proposed by these authors. This method which is essentially based on the minimization of a Hylleraas-type functional, has been already described in detail (see e.g. refs. 5,11)

II. NUMERICAL RESULTS AND DISCUSSION

All 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 Jeziorski and van Hemert in their original work on the water dimer (ref. 5). Calculations have been performed using a substantially larger basis set. The so-called isotropic part of the basis (functions describing orbitals occupied in the ground-states of the atoms, see ref. 12) has been taken from ref. 13 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 in order to minimize the dispersion as well as the complementary exchange energies (see ref. 7). Exponents $\alpha_d = 1$ and 0.3 , $\alpha_p = 0.6$ and 0.15 have been obtained. The complete contracted basis consists of 94 basis functions for the water dimer.

The energy of the water monomer calculated by using this basis set equals -76.06004 a.u.. The SCF binding energies obtained for the water dimer are -3.96 kcal/mol 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* (ref. 14) using a very large basis set containing 212 contracted orbitals. The values of the particular contributions to the interaction energy are listed in Table I.

The essential results to point out are the following ones:

- 1) the second order exchange-induction was found to be quite important. At equilibrium distance, it compensates approximatively for 50% the induction energy. The importance of this contribution has been already noticed for inert gas dimers (refs. 9,11,15,16).

2) the second order exchange-dispersion energy represents about 20% of the dispersion energy, thus confirming the non-negligible role of this contribution.

R_{oo}^b	$E_{RS}^{(1)}$	$E_{exch}^{(1)}$	$E_{ind}^{(2)}$	$E_{disp}^{(2)}$	$E_{exch-ind}^{(2)}$	$E_{exch-disp}^{(2)}$
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

Table I. Particular contributions to the interaction energy of the water dimer (in kcal/mol) calculated with a 94 AO basis set.^a

a. Basis set described in the text.

b. Atomic units.

It has seemed interesting to compare the SCF binding energy to the sum of the complete first-order and second-order induction energies; these values are displayed in table II (columns 3 and 2 respectively).

R_{oo}^a	$E_{ind}^{(1)} + E_{exch-ind}^{(2)}$	E_{int}^{SCF}	$E_{int}^{pert}^b$	$E_{int}^{SCF} + E_{disp}^{(2)}$	$E_{int}^{SCF} + E_{disp}^{(2)} + E_{exch-disp}^{(2)}$
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

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

a. Atomic units.

b. Pure perturbational interaction energy calculated as :

$$E_{int}^{pert} = E_{RS}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(2)} + E_{disp}^{(2)} + E_{exch-ind}^{(2)} + E_{exch-disp}^{(2)}$$

Except at large distances, Table II clearly demonstrates the non-coincidence of these two quantities. In fact 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

(ref. 8)) contribute in a non negligible way, even in the neighborhood of the equilibrium geometry. It may be noticed that these additional contributions become more and more important as the intermolecular distance is decreased. One might expect that the difference between E_{int}^{SCF} and $E^{(1)} + E_{ind}^{(2)}$ would be partly cancelled if in the perturbational approach the induction part of third and higher-order contributions would be considered. Thus presently, as a possibility, one may calculate the interaction energy by adding to the SCF binding energy the dispersion term calculated within a perturbation method, but in that case one has to be cautious to also take into account the exchange-dispersion terms. Thus one has to use the following decomposition:

$$E_{int} \approx E_{int}^{SCF} + E_{disp}^{(2)} + E_{exch-disp}^{(2)} \quad (13)$$

Table II shows that the location of the energy minimum is different following that the second order exchange- dispersion term is (or is not) taken into account. The values we have obtained are $R_{o-o} = 5.67$ a.u. and 5.20 a.u. respectively.

III. IMPORTANCE OF THE BASIS SET QUALITY

Now, we will pay some attention to the important problem of the quality of the basis set used. The results listed in table III clearly show that the different components of perturbation development are quite sensible to the choice of the basis set.

Base	STO-3G	4-31G	6-31G**	JvH ^a	O.H ^b
$E_{RS}^{(1)}$	-4.12	-8.88	-7.13	-7.11	-6.89
$E_{exch}^{(1)}$	1.72	2.10	2.60	4.89	4.85
$E_{ind}^{(2)}$	-0.64	-0.94	-1.04	-1.63	-1.82
$E_{disp}^{(2)}$	-0.20	-0.42	-0.93	-1.54	-1.79
$E_{ind-exch}^{(2)}$	0.45	0.25	0.33	0.80	0.99
$E_{disp-exch}^{(2)}$	0.04	0.05	0.13	0.27	0.32
E^{pert}	-2.75	-7.84	-6.04	-4.32	-4.34
Dipole moment	1.72	2.60	2.18	2.06	1.98

Table III. Different components of intermolecular interaction energies calculated within different basis sets. All energy values are given in kcal/mol. The dipole moments are given in Debyes. (a) JvH stands for a gaussian basis (11,7,2/6,1) contracted into (4,3,2/2,1), this means 70 functions for the dimer (ref. 5). (b) This basis set containing 94 AO for the dimer has been discussed in section III. Results obtained using the geometry of ref. 5 with $R_{o-o} = 5.67$ a.u.

1) The electrostatic component is well reproduced only if the wave function of the unperturbed system correctly describes the charge distribution of isolated molecules (monomers). The calculation of multipolar moments gives a good criterion for the quality of the basis set. In this work we have calculated the dipole moment of the water molecule within the different basis sets studied, results presented in Table 3 (last line) have to be compared to the experimental value of 1.85 Debyes (ref. 17). When using the very large basis set (47 AO for water monomer), we have obtained a value which is in a very good agreement with the Hartree-Fock limit value (1.98 Debyes) estimated by Szalewicz et al. (ref.14). In fact, it is well known that at the SCF level, dipole moments are calculated with an error of about 10% because of the lack of electronic correlation at this level (ref. 12,14).

2) The exchange energy increases with the size of the basis set used; even 6-31G** basis set underestimates this contribution. This result proceeds from the imperfect behaviour of the wave function at long range leading to an underestimation of overlap effects between electronic clouds of different sub-systems. It has been noticed that nearly same values have been obtained when using basis sets including 70 and 94 AO for a water dimer.

It has appeared interesting to compare the first order energy we have calculated with the so-called Heitler-London first order energy defined as:

$$E_{HL}^{(1)} = \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \quad (14)$$

where Ψ_0 is the antisymmetrized wave function calculated with the exact wave function of the two monomers,

$$\Psi_0 = \mathbf{A} \Phi_0 = \mathbf{A} \Psi_0^A \Psi_0^B \quad (15)$$

and H the total Hamiltonian of the system in interaction. In (in and only) that case the Heitler London energy may be written as:

$$E_{HL}^{(1)} = E_0 + \frac{\langle \Phi_0 | V^{AB} | \mathbf{A} \Phi_0 \rangle}{\langle \Phi_0 | \mathbf{A} | \Phi_0 \rangle} \quad (16)$$

where E_0 is the eigenvalue of H_0 , and the second term of this equation is nothing else than the total first order perturbation component. In practice we do not use exact wave functions for calculating isolated molecules, so Eq.16 is written as:

$$E_{HL}^{(1)} = \bar{E}_0 + \frac{\langle \Phi_0 | (\bar{E}_0 - H_0) \mathbf{A}' | \Phi_0 \rangle}{\langle \Phi_0 | \mathbf{A} \Phi_0 \rangle} + \frac{\langle \Phi_0 | V^{AB} \mathbf{A} | \Phi_0 \rangle}{\langle \Phi_0 | \mathbf{A} | \Phi_0 \rangle} \quad (17)$$

where \bar{E}_0 represents the mean energy associated to approximate wave functions of the monomers. The last term of the second member of Eq.17 is the first order perturbation contribution including both Rayleigh-Schrodinger and exchange terms, the second term

(second member) called *complementary exchange* energy represents a correction which is zero when Ψ_0 is the exact eigen function of H_0 . Now, the Heitler-London energy is now decomposed into:

$$E_{HL}^{(1)} = \bar{E}_0 + E_{RS}^{(1)} + E_{exch}^{(1)} + E_{exch-compl}^{(1)} \quad (18)$$

We may denote:

$$E_{exch-HL}^{(1)} = E_{exch}^{(1)} + E_{exch-compl}^{(1)} \quad (19)$$

The value of the complementary exchange energy is a good mean to check the quality of the basis set. (For more details see ref. 7, 17). Table IV displays the calculated values of $E_{exch}^{(1)}$ and $E_{exch-compl}^{(1)}$. It appears that only very large basis sets (at least 70 AO for a water dimer) lead to quite correct values of first order exchange contributions.

Basis	STO-3G	4-31G	6-31G**	JvH ^a	O.H ^b
$E_{exch}^{(1)}$	1.72	2.10	2.60	4.89	4.85
$E_{exch-compl}^{(1)}$	1.74	1.48	1.12	-0.32	-0.17
$E_{exch-HL}^{(1)}$	3.46	3.58	3.72	4.57	4.68

Table IV. Dependence of the contributions $E_{exch}^{(1)}$, $E_{exch-compl}^{(1)}$, $E_{exch-HL}^{(1)}$ with the basis set. For (a) and (b) see comments in Table III. All values (in kcal/mol) have been calculated for the geometry of ref. 5 and for $R_{O-O} = 5.67$ a.u.

3) The total induction and dispersion terms are correctly taken into account only if very large basis sets are used. We may notice that the basis consisting in 94 AO which includes neither f-orbitals on oxygen nor d-orbitals on hydrogen leads to a value of the dispersion term which is very close to the limit value estimated by Szalewicz et al. (-2.kcal/mol) (ref. 14)

IV. DERIVATION OF SEMI-EMPIRICAL FORMULAE FOR SECOND ORDER DISPERSION CONTRIBUTION

These two contributions have been calculated as a sum of atom-atom interactions :

$$E_X^{(2)} = \sum_{i \in A} \sum_{j \in B} E_X(i,j) \quad (20)$$

where i (and j) are atoms belonging to molecule A (and B); the subscript X stands for dispersion or exchange-dispersion.

1) Second-order dispersion energy

This contribution is represented by:

$$E_{disp}^{(2)}(i,j) = - \left(\frac{C_6}{z^6} + \frac{C_8}{z^8} + \frac{C_{10}}{z^{10}} \right) k_i k_j \quad (21)$$

with $z = R_{ij}/R_{ij}^0$ and $R_{ij}^0 = [(2R_i^w)(2R_j^w)]^{1/2}$ where R_i^w and R_j^w are the van der Waals radii of atom i and j . R is the distance between atoms i and j . Factors k_i, k_j allow the energy minimum of $E = E_{disp} + E_{exch}$, to have different values according to the atomic species involved (ref. 21).

Coefficients $C_6, C_8,$ and C_{10} have been calculated by identifying Eq. (21) with the one given by Stogryn *et al.* (ref. 19) for He...He interaction:

$$E_{disp}^{(2)} = - \left[\frac{1.471}{R^6} + \frac{14.1}{R^8} + \frac{182.0}{R^{10}} \right] \quad (22)$$

Namely: $C_6 = 0.143$ kcal A^6 /mol, $C_8 = 0.0381$ kcal A^8 /mol, $C_{10} = 0.0137$ kcal A^{10} /mol.

The terms besides C_6/R^6 are not negligible in the equilibrium distance. For He...He, for instance, these two terms amount to 1/3 of the main term $-C_6/R^6$.

But it is well known that the multipolar part ($-1/R^n$) of the dispersion energy overestimates it at short distances owing to the neglect of the penetration part of the intermolecular integrals which appear in the numerators of the perturbation expansion (for more details see ref. 20 and references therein). In order to take into account the reduction of different multipolar terms, we have applied the process defined by Caillet *et al.* (ref. 21) when dealing with the sixth order power term of dispersion. Namely, we choose two distances, $R_M = R_i^w + R_j^w$ and $R_m = \frac{1}{2.42} R_M$. Then for $R > R_M$ we use the normal parameters C_n ($n=6, 8, 10$), for $R < R_m$ we use modified reduced parameters C'_n and for $R_m < R < R_M$ we use interpolated values of these parameters according to:

$$C_n(x) = \frac{(C_n + C'_n)}{2} + (0.375x^5 - 1.25x^3 + 1.875x) \frac{(C_n - C'_n)}{2} \quad (23)$$

where:

$$x = \left[R - \frac{(R_M + R_m)}{2} \right] / \left[\frac{(R_M - R_m)}{2} \right]$$

The polynomial $P(x)$ has been chosen in order that: a) $P(1) = 1$ and $P(-1) = -1$;

b) the first and second derivatives of $P(x)$ are continuous.

$$C'_6 = C_6/6.25 ; C'_8 = C_8/7.38 \text{ and } C'_{10} = C_{10}/10.44.$$

Using the geometrical arrangement studied by Jeziorski *et al.* (ref. 5) and varying only R_{O-O} , $E_{disp}^{(2)}$ has been fitted with regards to values calculated by SAPT method.

2) Second-order exchange energy

It has been found that this component which is purely short-range varies exponentially with the distance R. The best fit has been given by the following analytical function

$$E_{exch-disp}^{(2)} = k_i k_j \left(1 - \frac{Q_i}{N_i^{val}}\right) \left(1 - \frac{Q_j}{N_j^{val}}\right) C e^{-\alpha z} \quad (24)$$

where Q_x ($x=i$ or j) is the net charge of atom x and N_x^{val} the number of valence electrons of atom x .

In the same way, as recommended by Caillet *et al.* (ref. 21), we have used the factor $(-Q_i)/N_i^{val}$ corresponding to the influence of the real electronic population of each atom on short range terms.

$C = 484.98$ kcal/mol and $\alpha = 9.18$.

3) Results.

Roo	$E_{disp-M}^{(2)}$	$E_{disp}^{(2)}$	$E_{disp-exch}^{(2)}$
4.50	-20.87	-7.65 (-7.80)	2.57 (2.92)
4.80	-13.88	-5.04 (-5.27)	1.52 (1.51)
5.00	-8.73	-3.98 (-4.10)	1.07 (1.07)
5.20	-5.77	-3.20 (-3.18)	0.75 (0.75)
5.67	-2.34	-1.91 (-1.80)	0.33 (0.32)
6.00	-1.47	-1.33 (-1.22)	0.19 (0.18)
7.00	-0.42	-0.42 (-0.47)	0.03 (0.03)

Table V. Values (in kcal/mol) calculated with simplified formulas, and by ab initio SAPT method (in parenthesis). For notations see the text.

In Table V, we have listed the values of the multipolar part of the second order dispersion denoted $E_{disp-M}^{(2)}$ (Eq. 21), the values obtained for $E_{disp}^{(2)}$ when the penetration part is taken into account and the value of second order exchange-dispersion terms $E_{exch}^{(2)}$, the values between brackets are the ones calculated, within SAPT method (6). It may be noticed that even in the equilibrium region the taking in account of only the multipolar part of dispersion overestimates this contribution. The agreement between values calculated using simplified formulae or SAPT method is quite good in the case of second order exchange-dispersion energy and good enough as concerns the second order dispersion term.

IV. CONCLUSION

At this point, it is important to emphasize that the goal of this work was not to obtain a very accurate value of the interaction energy between two water molecules, since it is clear that for such a simple system, the supermolecule approach based on very large CI (refs. 10,11) are preferable. Actually, one of the basic motivation of our work was to demonstrate the nonnegligible role of the complete second-order exchange contribution (exchange induction as well as exchange-dispersion components). Furthermore the ability to determine quantitatively the importance of each component of the total interaction energy has opened the way towards representing them through simple analytical functions fitted on calculated values. It has appeared that such a fitting has to be done departing from results obtained within a very large basis set. But as it has been discussed in this paper the induction part of third (and perhaps higher orders) contributions should be considered. In fact, these contributions may be obtained from SCF results. As a first step simplified formulas for the calculation of the second-order dispersion (including exchange-dispersion) terms have been given. Work is under progress in order to verify other contributions (mainly first order exchange energy) of interaction energy. Such a possibility is essential with respect to the problem of elaborating *high quality simplified* functions for the calculation of the interaction energy between *arbitrarily large* molecules.

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