A perturbational study of some hydrogen-bonded dimers

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We present a detailed study of several hydrogen-bonded dimers consisting of H₂O, NH₃, and HF molecules using the Symmetry Adapted Perturbation Theory (SAPT) at different levels of approximations. The relative importance of each individual perturbational components and the quality of the total interaction energies obtained are discussed. The dependence of the results on the relative orientation of the molecules of the dimers and on the intermolecular distance is also investigated. © 1995 American Institute of Physics.

I. INTRODUCTION

It is well-known that evaluating intermolecular interaction energies with the level of accuracy required by the physics and chemistry of complex molecular systems is very difficult. There are two basic reasons for that. First, the interaction energy (defined as the difference between the total energy of the complex and the sum of the total energies of the individual noninteracting species) is really a tiny fraction of the total energies involved. Typically, this fraction can vary from about 10⁻⁷ (weakly interacting van der Waals complexes) to about 10⁻⁴ (strong hydrogen-bonded systems). Second, there is no exact method to compute directly this very small difference. In absence of such a procedure, two different theoretical strategies are usually employed. A first natural strategy consists in computing the total energy of each species separately (the complex and the individual molecules) and then to subtract out these energies according to the very definition of the interaction energy (the so-called supermolecular method). To do that is difficult due to the very high level of control required on the different sources of approximation of the particular method used to compute the total energies. Without entering into the technical details (choice of the basis set functions, finite-basis-set error, basis set superposition error (BSSE), etc... it is fair to say that current state-of-the-art ab initio calculations are not able to reach the necessary level of accuracy, except of course for very small interacting species. A second quite natural approach is to consider that the interaction energy is the result of a very small physical perturbation of the isolated monomers and thus to employ some kind of perturbational method. This line of research has been intensively followed during the last decades and has led to the so-called Symmetry Adapted Perturbation Theory (SAPT) (see e.g., Refs. 1, 2, or 3), a variety of methods based on the usual Rayleigh–Schrödinger perturbation theory supplemented by some technique to force the change of antisymmetry property of the wave function between the monomers and the interacting complex (as known there is not a unique way to do that and, then, various schemes have been proposed, see references in Ref. 1). It is this constraint which is at the origin of the strong repulsion at short distances (exchange contributions).

In order to take account of the continuum contribution present in the infinite sums involved in the perturbational components (except, of course, for the first-order), a variation-perturbation scheme is usually employed (it can be shown that this can be reduced to a calculation in a suitable dimer basis set). In their pioneering work on the use of SAPT Jeziorski and van Hemert (JvH) have proposed to compute the interaction energy using the following minimal representation:

\[ \Delta E_{int} = E_{RS}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(2)} + E_{disp}^{(2)}, \]

where all quantities are computed using the wave functions issued from a SCF calculation of the monomers. \( E_{RS}^{(1)} \) is the standard Rayleigh–Schrödinger first-order component (physically, the classical electrostatic interaction of the unperturbed charge distributions in the monomers), \( E_{exch}^{(1)} \) is the first-order exchange part resulting from the change of the antisymmetry property of the wave function (physically, the dominant part of the repulsive interaction at short distances) and where \( E_{ind}^{(2)} \) and \( E_{disp}^{(2)} \) are the second-order Rayleigh–Schrödinger induction and dispersion energy, respectively (physically, the energy of interaction of one monomer within the electric field of the other, and the major attractive contribution to the interaction energy for neutral systems, respectively). It is important to emphasize that Eq. (1) describes the main physical facts of the intermolecular interaction (electrostatic interaction, repulsive force, induction and dispersive forces). However, a number of corrections are neglected when using Eq. (1). The numerical experience shows that their importance is very system-dependent. It is therefore very important to compute them if a reliable (although approximate) answer for any interacting system and not just for a specific class of systems is wanted. Three types of corrections may be distinguished:

(i) corrections to the exchange part due to effects beyond the first-order,
(ii) corrections due to higher-order perturbational Rayleigh–Schrödinger components (\( E_{RS}^{(n)} \) with \( n > 2 \)),
(iii) corrections due to the intramolecular correlation effects.

A great deal of activity has been devoted to the calculation of these corrections. First of all, it has been very soon realized that the first-order exchange contribution was not sufficient to give a proper description of the repulsive part at

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intermediate distances and different methods have been proposed to evaluate the second-order exchange contributions.\textsuperscript{5–12} Note that at much shorter distances no satisfactory approach seems to exist.\textsuperscript{13} Incorporating these important contributions we arrive at the following decomposition

\[
\Delta E_{\text{int}}^{\text{SAPT}} \sim E_{R}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{disp}}^{(2)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{2-exch}}^{(2)},
\]

which we shall refer to in the following as the SAPT decomposition. An alternative way of going beyond Eq. (1) is to combine both perturbational and supermolecular worlds as follows:

\[
\Delta E_{\text{int}}^{\text{hybrid}} \sim \Delta E_{\text{SCF}} + E_{\text{disp}}^{(2)} + E_{\text{exch-ind}}^{(2)},
\]

where \(\Delta E_{\text{SCF}}\) is the SCF binding energy computed with the supermolecular method (corrected for the BSSE). Such a procedure is attractive since the SCF interaction energy is supposed to contain most of the second-order exchange-induction energy, some induction part of third- and higher-order perturbational terms and even some intramolecular correlation contribution introduced when doing a SCF supermolecular calculation,\textsuperscript{14} contributions which are all neglected when using Eq. (1). In the following we shall refer to it as the hybrid method. However, when resorting to Eq. (3) it is important to realize that mixing both approaches renders difficult the control on the errors made. How much of the higher-order perturbational contributions, what part of the exchange-induction energy, etc... is gotten with a SCF supermolecular calculation is not easy to estimate. Note that it can be argued that a pure perturbational treatment where individual errors are in a better control may be preferable. In the same idea of incorporating nonperturbational effects it has been proposed to include the so-called apparent correlation or self-consistency effects into the second-order induction energy, \(E_{\text{ind}}^{(2)}\). In short, it consists in resorting to a coupled Hartree-Fock (CHF) which implicitly sum up to infinity certain diagrams appearing in the many-body expansion of the induction energy. This is expected to give a better approximation of the total induction energy. Note that this can also be done for the exchange-induction part.\textsuperscript{19} Concerning the explicit calculation of higher-order perturbational components very little is found in the literature (see, references in Refs. 1,20,21). Finally, let us note that very recently several hydrogen-bonded dimers (consisting of \(\text{H}_2\text{O}, \text{NH}_3, \text{and HF}\)). We discuss in detail the validity of the different representations for the interaction energy presented above and investigate the peculiar role of the second-order exchange-induction energy.

The organization of the present paper is as follows. In section II we give a rapid summary of the formalism used in this work. In particular we give the rather unfamiliar expressions for the exchange-induction and -dispersion energies derived within SAPT theories by Hess \textit{et al.}\textsuperscript{12} Section III contains the computational details. In section IV, we present our numerical results for the different contributions of the intermolecular interaction energy and a comparison between the interaction energies obtained with the different approaches. Finally, some conclusions are presented in section V.

II. METHOD

In this section we give a rapid overview of the formalism used in this work; for a very detailed and self-contained presentation the reader is referred to the original work of Hess \textit{et al.}\textsuperscript{12} In the perturbation theory of interactions the total Hamiltonian is decomposed as \(H = H_0 + V^{AB}\) where \(H_0\) denotes the sum of the non-interacting Hamiltonians of the two monomers \(A\) and \(B\) (we shall consider here only dimers, formulas can be trivially generalized to an arbitrary number of monomers) and \(V^{AB}\) is the intermolecular interaction potential. Following standard Symmetry Adapted Perturbation Theories (SAPT) (see, e.g., Refs. 1–3) and using standard notations, the complete first- and second-order interaction energies are written in the form:

\[
E_{(1)} = \frac{\left\langle \Psi_0^{0} | \Psi_0^{B} | V^{AB} | A | \Psi_0^{0} \Psi_0^{B} \right\rangle}{\left\langle \Psi_0^{0} | \Psi_0^{B} | \Psi_0^{0} \Psi_0^{B} \right\rangle},
\]

\[
E_{(2)} = -\frac{\left\langle \Psi_0^{4} | \Psi_0^{0} | A | V^{AB} - E_{(1)} | \Psi_0^{4} \Psi_0^{B} \right\rangle}{\left\langle \Psi_0^{4} | \Psi_0^{0} | \Psi_0^{4} \Psi_0^{B} \right\rangle},
\]

where \(R_0\) denotes the reduced resolvent of \(H_0\) given by

\[
R_0 = \sum_{ij} \left( \frac{|\Psi_0^{4} \Psi_0^{B} | \langle \Psi_0^{i} | \Psi_0^{B} \rangle | \Psi_0^{4} \Psi_0^{B} |}{(E_0^{i} + E_0^{j}) - (E_0^{0} + E_0^{0})} \right)
\]

(the prime in \(\Sigma\) means as usual that the term corresponding to \(i = 0\) and \(j = 0\) is excluded from the summation) and \(A\) is the intersystem antisymmetrizer.
\[
\mathbf{A} = 1 - \mathbf{A}' = 1 - P_{(1)} + P_{(2)} - \ldots + (-1)^{N_{\text{inf}}} P_{(N_{\text{inf}})}.
\]

where \( P_{(i)} = \sum_{i}^{} A_{ij} P_{ij} \) 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 \( P_{(2)}, P_{(3)}, \ldots \) \( N_{\text{inf}} \) denotes the smallest of \( N_{A} \) and \( N_{B} \), the numbers of electrons of molecule \( A \) and \( B \), respectively. The role played by the antisymmetrizer \( \mathbf{A} \) is essential: it forces the correct antisymmetry of the dimer wave function with respect to the exchange of electrons between both monomers. In formulas (4)–(6) \( \Psi_{i}^{M} (M = A, B) \) are supposed to be the exact eigenfunctions of the Hamiltonian \( H^{M} (M = A, B) \). In what follows we shall restrict ourselves to the use of approximate wave functions and energies calculated at the SCF level. The role of the intramonomer correlation effects will not be considered here.

As usual the first-order interaction energy (Eq. (4)) is written as a sum of two contributions:

\[
E_{\text{exch}}^{(1)} = E_{RS}^{(1)} + E_{\text{exch}}^{(1)},
\]

where \( E_{RS}^{(1)} \) (the subscript RS stands for Rayleigh-Schrödinger) can be interpreted as the energy of the electrostatic interaction of the unperturbed charge distributions of the isolated monomers (this quantity is often referred to as the electrostatic part or also as the first-order polarization energy) and \( E_{\text{exch}}^{(1)} \) is the first-order exchange energy resulting from the presence of the antisymmetrizer. Note that in the present work all multiple exchange of electrons (quantum-mechanical tunneling) between molecules \( A \) and \( B \) have been considered when calculating \( E_{\text{exch}}^{(1)} \).

In the same way the second-order perturbation energy \( E_{\text{exch}}^{(2)} \) (Eq. (5)) is decomposed into two terms: the usual second-order Rayleigh-Schrödinger (RS) perturbation energy \( E_{RS}^{(2)} \) (obtained by setting \( A = 1 \) in Eq. (5)) and the second-order exchange energy \( E_{\text{exch}}^{(2)} \) given by

\[
E_{\text{exch}}^{(2)} = E_{RS}^{(2)} - E_{RS}^{(1)}
= - \left[ \langle \mathbf{A}' \mathbf{A} \mathbf{B} \mathbf{B} \rangle \left( V_{AB} - E_{\text{exch}}^{(1)} - \langle \mathbf{A}' \mathbf{A} \mathbf{B} \mathbf{B} \rangle \right) \right] \frac{\Phi_{(1)}}{\langle \mathbf{A} \rangle},
\]

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 \( \Psi_{0}^{A} \Phi_{0}^{B} \) and \( \Phi_{(1)} \) stands for the first-order correction to the wave function in the perturbation theory

\[
\Phi_{(1)} = - R_{0} V_{AB} \Psi_{0}^{A} \Psi_{0}^{B}.
\]

Now, we shall suppose that multiple exchanges contribute weakly in the region around the equilibrium geometry, so that only the leading contribution to \( E_{\text{exch}}^{(2)} \) corresponding to a single exchange of electrons between molecules \( A \) and \( B \) is considered. Thus, the approximate expression for \( E_{\text{exch}}^{(2)} \) used here is obtained by setting \( \mathbf{A}' = P_{(1)} \) in Eq. (9). Neglecting terms which correspond to contributions of order higher than \( S^{2} \) (where \( S \) stands for overlap integrals between orbitals of monomers \( A \) and \( B \)), we get

\[
E_{\text{exch}}^{(2)} = - \left[ \langle \mathbf{A}' \mathbf{A} \mathbf{B} \mathbf{B} \rangle \left( V_{AB} - \langle V_{AB} \rangle \right) \langle P_{(1)} \rangle \right] \frac{\Phi_{(1)}}{\langle \mathbf{A} \rangle}.
\]

By rewriting \( \Phi_{(1)} \) (Eq. (10)) in the form:

\[
\Phi_{(1)} = - \Psi_{0}^{A} \Phi_{\text{ind}}^{B} + \Psi_{\text{ind}}^{A} \Phi_{0}^{B} + \Phi_{\text{disp}}^{A} \Phi_{0}^{B}.
\]

it is clear that the second-order exchange energy may be decomposed into three terms

\[
E_{\text{exch}}^{(2)} = E_{\text{exch} - \text{ind}}^{(2)} (A \rightarrow B) + E_{\text{exch} - \text{ind}}^{(2)} (B \rightarrow A) + E_{\text{exch} - \text{disp}}^{(2)}.
\]

The sum of the first two terms in Eq. (13) are referred to as the exchange-induction energy and \( E_{\text{exch} - \text{disp}}^{(2)} \) as the exchange-dispersion energy. These two terms take their origin in the coupling between the induction or dispersion forces and the electron exchange.

In order to compute these various perturbational quantities we have used the formalism presented in Ref. 12. In a few words, the main idea is to express exchange contributions as a combination of formal electrostatic interaction energies between suitably generalized charge distributions, a form particularly suitable for calculations. To do that, the main ingredients used are:

(i) The possibility of reducing the action of the inter-system antisymmetrizer (appearing in SAPT) on factorized SCF wave functions to a sum of simple products of SCF determinants corresponding to each subsystem, namely:

\[
P_{(1)} \left[ \Psi_{A}^{A} \Psi_{B}^{B} \right] = \sum_{i \in A} \sum_{j \in B} \Psi_{A}^{i j} \left( a_{i} \right) \Psi_{B}^{j i} \left( b_{j} \right),
\]

where \( \Psi_{A}^{i j} \) denotes the Slater determinant of molecule \( A \) in which the occupied spin-orbital \( a_{i} \) has been replaced by the spin-orbital \( b_{j} \) of molecule \( B \), the summation is over the spin-orbitals of determinants \( \Psi_{A}^{A} \) (here labeled by \( i \) and \( \Psi_{B}^{B} \) (labeled by \( j \)). Using Eq. (14) all integrals involving functions of the type \( P_{(1)} \left[ \Psi_{A}^{A} \Psi_{B}^{B} \right] \) are reduced to sums of integrals involving simple products \( \Psi_{A}^{i j} \) \( \Psi_{B}^{j i} \) of “opposite transfer” determinants.

(ii) The use of the so-called Longuet–Higgins representation of the interaction operator \( V_{AB} \) in terms of the molecular charge distributions \( \rho_{M} (M = A, B) \), namely:

\[
V_{AB} = \int \int \frac{\rho_{A} (\mathbf{r}) \rho_{B} (\mathbf{r})}{| \mathbf{r} - \mathbf{r}^{' } |} d\mathbf{r} d\mathbf{r}^{'} ,
\]

with

\[
\rho_{M} (\mathbf{r}) = \rho_{nuclear}^{M} (\mathbf{r}) + \rho_{\text{electronic}}^{M} (\mathbf{r})
= \sum_{\mu \in M} Z_{\mu} \delta (\mathbf{r} - \mathbf{r}_{\mu}) - \sum_{i \in M} \delta (\mathbf{r} - \mathbf{r}_{i}), \quad M = A, B.
\]

(iii) The possibility of using a variational-perturbation method to compute efficiently the infinite sums involved in the second-order expressions. In practice, this can be easily implemented by making a variational calculation in a dimer basis set.12

Let us now describe briefly the main steps followed to derive the rather unfamiliar formulas used in this work to compute the exchange-induction and dispersion energies.
A. Exchange–induction energy

By using Eqs. (11) and (12), \( E_{\text{exch-ind}}^{(2)}(A \rightarrow B) \) is written as

\[
E_{\text{exch-ind}}^{(2)}(A \rightarrow B) = - \langle \Psi_A^0 | \Psi_B^0 | \{ V^{AB} - \langle V^{AB} \rangle \} \rangle \times (P_{(1)} - \langle P_{(1)} \rangle) | \Psi_A^0 \rangle | \Phi_{\text{ind}}^B \rangle,
\]

with a similar formula for \( E_{\text{exch-ind}}^{(2)}(B \rightarrow A) \). A first point is that it is possible to rewrite \( \Phi_{\text{ind}}^B \) in the form:

\[
\Phi_{\text{ind}}^B = \sum_{k \in B} \Psi_B^B \left( \frac{f_k}{b_k} \right),
\]

where the summation runs over all occupied spin orbitals \( b_k \) of monomer \( B \) and where the so-called “induction functions” \( f_k^B \)'s are some well-defined linear combinations of the virtual spin orbitals of \( B \) (one associated with each occupied orbital). Using Eq. (18) it is not difficult to show that the exchange induction energy may be now written

\[
E_{\text{exch-ind}}^{(2)}(A \rightarrow B) = - \sum_{k \in B} (\{ V^{AB} P_{(1)} \}_k - \langle V^{AB} \rangle [P_{(1)}]_k)
- \langle P_{(1)} \rangle [V^{AB}]_k),
\]

with the notation

\[
[O]_k = \left\langle \Psi_A^0 | \Psi_B^0 \right| O \left| \Psi_A^0 \right| \left| \Psi_B^0 \right| \left( \frac{f_k}{b_k} \right).
\]

where \( O \) stands for an arbitrary operator. Now, by using the fact that the action of the permutation operator \( P_{(1)} \) on a product of two determinants \( \Psi_A \) and \( \Psi_B \) may be expressed as a linear combination of simple products of determinants corresponding to subsystems \( A \) and \( B \) and by using the Longuet-Higgins representation of the interaction operator \( V^{AB} \) (Eqs. (15), (16)) it is possible to show that the three basic contributions in (19) may be written as some specific combinations of electrostatic interactions between some generalized intermolecular charge densities. For example, we obtain for the major contribution:

\[
[V^{AB} P_{(1)}]_k = \sum_{i \in A} \sum_{j \neq k} \int \frac{f^A_{\alpha i}(a_i) f^B_{\beta j}(b_j)}{|r^A - r^B|} dr^A dr^B
+ \sum_{i \in A} \int \frac{f^A_{\alpha i}(a_i) f^B_{\beta j}(b_j)}{|r^A - r^B|} dr^A dr^B,
\]

where

\[
f^A_{\alpha i}(a_i) = \left\langle \Psi_A^0 | \rho^A(r^A) | \Psi_B^0 \right| \left. \frac{\partial}{\partial a_i} \right| \left. \frac{\partial}{\partial \rho^A} \right|_{\rho^A = 0},
\]

with similar definitions for the other generalized charge distributions involved in Eq. (21). Finally, explicit expressions for the generalized charge distributions in terms of mono- and bi-electronic integrals involving spin orbitals \( a_i, b_j \), and \( f^B_k \) may be easily obtained.

B. Exchange-dispersion energy

A similar route to that followed for the exchange-induction energy can be used for the exchange-dispersion component. Writing \( \Phi_{\text{disp}}^{AB} \) (see, Eq. (12)) as:

\[
\Phi_{\text{disp}}^{AB} = \sum_{k \in A} \sum_{l \in B} \sum_{c kl} c_{kl}^{rs} | \Psi_{0}^{A} \rangle \langle a_r | \langle a_k | \Psi_{0}^{B} \rangle \langle b_s | \langle b_l |,
\]

where indices \( k \) and \( l \) are associated with summations over the corresponding set of occupied spin orbitals while \( c_{kl}^{rs} \) refer to summations over the corresponding set of virtual spin orbitals and where \( c_{kl}^{rs} \) are some coefficients analogous to the linear coefficients of the “induction functions” introduced above, we can express \( E_{\text{exch-disp}}^{(2)} \) in a form very similar to Eq. (19):

\[
E_{\text{exch-disp}}^{(2)} = - \sum_{k \in A} \sum_{l \in B} \sum_{c kl} c_{kl}^{rs} \langle \{ V^{AB} P_{(1)} \}_k | \langle V^{AB} \rangle [P_{(1)}]_l \rangle,
\]

with the notation

\[
[O]_k = \left\langle \Psi_A^0 | \Psi_B^0 \right| O \left| \Psi_A^0 \right| \left| \Psi_B^0 \right| \left( \frac{f_k}{b_k} \right). \]

Exactly in the same way as before it is possible to write the elementary contributions of \( E_{\text{exch-disp}}^{(2)} \) as a combination of some electrostatic interactions between generalized charge distributions which are ultimately written in terms of mono- and bi-electronic integrals. As an example, the major contribution to \( E_{\text{exch-disp}}^{(2)} \) writes:

\[
[V^{AB} P_{(1)}]_{kl} = \sum_{i \in A} \sum_{j \neq k} \int \frac{f^A_{\alpha i}(a_i) f^B_{\beta j}(b_j)}{|r^A - r^B|} dr^A dr^B
+ \sum_{i \in A} \int \frac{f^A_{\alpha i}(a_i) f^B_{\beta j}(b_j)}{|r^A - r^B|} dr^A dr^B,
\]

and similar formulas for the other contributions.

III. COMPUTATIONAL DETAILS

A. Dimers

We have studied five different hydrogen-bonded dimers made of the molecules H₂O, NH₃, and HF. The intramolecular geometry of the monomers has been taken to be the experimental geometry for isolated monomers (water molecule: \( R_{OH} = 1.8088 \) bohr, \( \theta_{HOH} = 104.87^\circ \); ammonia molecule: \( R_{NH} = 1.9219 \) bohr, \( \theta_{HNH} = 107.81^\circ \); HF molecule:...
described by the quantities the proton donor molecule. The dimer geometries will be
that NH3 acts as a proton acceptor when it is involved in a
no experimental evidence of its existence. It is well-known
far no known example of systems in the gas phase where the

FIG. 1. The five hydrogen-bonded dimers studied. For a definition of the
angles $\theta_A$, and $\theta_B$, see text.

B. Basis set

Our calculations for the different dimers have been performed with a very large basis set ($13s 8p 3d)/(7s 2p)$ contracted into ($8s 5p 3d)/(4s 2p)$ (the first set of basis functions corresponds to the heavy atom N, O, or F, the second to the hydrogen atoms). The basis set used has been taken from Voisin44 and has been built as follows. First, based on atomic calculations the sets of primitives optimized by van Duijneveldt (12s 7p)/(6s),45 have been contracted into some reduced set (7s 4p)/(3s). Then, a set of diffuse functions $s$ and $p$ has been added. Their exponents have been obtained according to the averaging procedure presented in Ref. 46. Finally, to better describe the heavy atoms (N, O, and F), three polarization functions $d$ have been added according to the rules proposed by Werner and Meyer.47 The two orbitals $p$ of hydrogen are those given by Christiansen and McCullough.48

In order to evaluate the quality of our basis set we have performed a number of checks.

1. Basis-set quality: Some monomer properties

The SCF energy and dipole moment have been compared to the some recently estimated Hartree–Fock limits for the three molecules (Table I). Our values for the SCF energies appear to be quite close to the nearly-infinite-basis-set results. The values of the dipole moments are also quite good. It is important to emphasize that reproducing correctly
the permanent dipole moments is crucial since the interaction energy of hydrogen-bonded systems is dominated by the electrostatic interaction.

2. Basis-set quality: Some dimer properties

a. Complementary exchange energy. A very useful quantity to evaluate the quality of a given finite basis set for computing intermolecular interactions is the so-called “complementary exchange energy.” A very detailed presentation of this quantity can be found in references 1,50 However, since the use of this quantity is not very common, let us first give a short presentation of it. The complementary exchange energy, \( \epsilon_{\text{compl-exch}} \), is defined via the following formula

\[
E_0 = \frac{\langle \Psi^A \Psi^B | H | \Psi^A \Psi^B \rangle}{\langle \Psi^A \Psi^B | \Psi^A \Psi^B \rangle} = \tilde{E}_0 + \epsilon_{\text{compl-exch}}
\]

\[
+ \frac{\langle \Psi^A \Psi^B | V_{AB} | \Psi^A \Psi^B \rangle}{\langle \Psi^A \Psi^B | \Psi^A \Psi^B \rangle}
\]

(26)

where

\[
\epsilon_{\text{compl-exch}} = \frac{\langle \Psi^A \Psi^B | (\tilde{E}_0 - H_0) A' | \Psi^A \Psi^B \rangle}{\langle \Psi^A \Psi^B | \Psi^A \Psi^B \rangle}.
\]

(27)

In Eq. (26) \( \tilde{E}_0 \) denotes the total Heitler–London energy and \( E_0 \) the total energy corresponding to the approximate wave function \( | \Psi^A \Psi^B \rangle \) for the unperturbed Hamiltonian \( H_0 \). When \( \Psi^M \) \((M = A, B)\) are chosen to be the exact (ground-state) wave functions of the monomers the complementary exchange energy vanishes and the Heitler–London interaction energy (defined as \( E_0 - \tilde{E}_0 \)) coincides with the complete first-order interaction energy. Note that, due to the presence of the operator \( A' \) at the numerator, \( \epsilon_{\text{compl-exch}} \) decreases exponentially as a function of the distance. This is the reason why this quantity, which may be viewed as a correction to the ordinary exchange energy, is called “complementary exchange energy.” Now, the important property we shall use is that within the one-exchange approximation the complementary exchange energy vanishes if and only if the approximate functions used for the unperturbed monomers are the exact Hartree–Fock solutions. Since for not too small intermolecular distances the exact and one-exchange complementary exchange energies are almost identical \( \epsilon_{\text{compl-exch}} \) is a good indicator of how far an approximate SCF wave function built from some given basis set is from the Hartree–Fock limit. Of course, for very small values of \( \epsilon_{\text{compl-exch}} \) it would be necessary to consider the true one-exchange complementary energy instead of \( \epsilon_{\text{compl-exch}} \). In Table II we present for the different dimers treated the values obtained for \( \epsilon_{\text{compl-exch}} \) at a few representative distances \( R_{AB} \). To compare with, we also report the values of the Heitler–London exchange energy defined as

\[
E_{\text{exch-HL}}^{(1)} = E_{\text{exch}}^{(1)} + \epsilon_{\text{compl-exch}}.
\]

(28)

The values obtained for \( \epsilon_{\text{compl-exch}} \) are found to be rather small when compared with typical values (see, e.g., Refs. 1 or 51). This illustrates the good quality of the basis sets used in this work.

b. Counterpoise correction at the SCF level. In a supermolecular calculation of a complex the better the basis set used for describing each monomer is, the smaller the basis-set-supposition error (BSSE) is. We have computed this error by using the standard counterpoise method of Boys and Bernardi.52 Some of our results are displayed in Table III. As a general rule, we get a very small counterpoise correction.

c. Second-order dispersion energy. Szalewicz et al.53 pointed out that the use of \( f \) functions improved considerably the dispersion energy. Their estimate of the exact value was \(-2.0\) kcal/mol for the water dimer near the equilibrium distance \((R_{O...O}=3. Å)\). In a recent work, Rybak et al.20 have obtained a value of \(-1.90\) kcal/mol by using a very large basis set. Here, although no \( f \) functions are present in our calculations, our 122 atomic-orbital dimer basis set leads, for the water dimer, to a value of \(-1.89\) kcal/mol which is almost identical to the value obtained by Rybak et al. and quite close to the exact one estimated by Szalewicz et al.

<table>
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<tr>
<th>Molecule</th>
<th>( E_{\text{SCF}} )</th>
<th>( E_{\text{exch-HF}} ) limit</th>
<th>( \mu_{\text{SCF}} )</th>
<th>( \mu_{\text{exch-HF}} ) limit</th>
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<td>H(_2)O</td>
<td>-76.0606</td>
<td>-76.0673(^a)</td>
<td>1.98</td>
<td>1.98(^a)</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>-56.2179</td>
<td>-56.2246(^a)</td>
<td>1.56</td>
<td>1.62(^a)</td>
</tr>
<tr>
<td>HF</td>
<td>-100.064</td>
<td>-100.0706(^a)</td>
<td>1.93</td>
<td>1.92(^a)</td>
</tr>
</tbody>
</table>

\(^a\)Reference 49. 

\(^b\)Reference 53.

---

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IV. PERTURBATIONAL RESULTS

A. Total interaction energies at equilibrium geometries

In Table IV we present the total interaction energies obtained for the different dimers studied. We also present the optimized geometries, $R_{AB}$, $\theta_A$, and $\theta_B$. We have used three different approaches:

(i) The pure perturbational approach, SAPT, including all perturbational components up to the second-order

$$\Delta E^{\text{SAPT}}_{\text{int}} = E_{RS}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{disp}}^{(2)}$$

(ii) A truncated approach we shall refer to in the following as $\text{SAPT}_{\text{trunc}}$ in which the exchange part of the induction is neglected (this method will play an important role in the discussion to follow)

$$\Delta E^{\text{SAPT}_{\text{trunc}}} = E_{RS}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{exch-disp}}^{(2)} + E_{\text{disp}}^{(2)}$$

(iii) The hybrid approach mixing the SCF interaction energy (counterpoise-corrected) and the complete dispersion contribution calculated with SAPT:

$$\Delta E^{\text{hybrid}}_{\text{int}} = \Delta E^{\text{SCF}}_{\text{int}} + E_{\text{exch-disp}}^{(2)}$$

For the three different approaches the geometries have been optimized by varying the angles $\theta_A (I= A$ and B) and the distance $R_{AB}$ around the estimated equilibrium geometry ($\theta_A$ within $-30^\circ$ and $+30^\circ$ around $\theta_A^{\text{exp}}$ using $\pm 5^\circ$ steps, $R_{AB}$ within $-0.40$ Å and 0.4 Å around $R_{AB}^{\text{exp}}$ with 0.03 Å steps).

From a qualitative point of view, both SAPT, $\text{SAPT}_{\text{trunc}}$, and the hybrid methods lead essentially to the same results. The force of the hydrogen bond (importance of the total interaction energy) for the dimers we have studied may be classified as follows: H$_2$O...HNH$_2$ < H$_3$N...HNH$_2$ < H$_2$O...HOH ~ HF...HF < H$_3$N...HOH, where the notation $X < Y$ means that the dimer $X$ is less bounded than the dimer $Y$. We verify the well-known result that NH$_3$ acts preferentially as a proton acceptor rather than a proton donor since here H$_3$N...HOH is much more stable than H$_2$O...HNH$_2$. Note also that NH$_3$ acts as a better acceptor than H$_2$O since

<table>
<thead>
<tr>
<th>$R_{AB}$</th>
<th>H$_2$O...HNH$_2$</th>
<th>H$_3$N...HNH$_2$</th>
<th>H$_2$O...HOH</th>
<th>HF...HF</th>
<th>H$_3$N...HOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.75</td>
<td>$\Delta E_{\text{SAPT}}^{\text{SCF}}$</td>
<td>$\epsilon_{\text{cp}}$</td>
<td>-2.46</td>
<td>-3.64</td>
<td>-2.78</td>
</tr>
<tr>
<td>3.00</td>
<td>$\Delta E_{\text{SAPT}}^{\text{SCF}}$</td>
<td>$\epsilon_{\text{cp}}$</td>
<td>-0.01</td>
<td>-3.65</td>
<td>-3.48</td>
</tr>
<tr>
<td>3.70</td>
<td>$\Delta E_{\text{SAPT}}^{\text{SCF}}$</td>
<td>$\epsilon_{\text{cp}}$</td>
<td>-1.38</td>
<td>-2.50</td>
<td>-1.90</td>
</tr>
</tbody>
</table>

TABLE IV. Intermolecular interaction energy, $\Delta E_{\text{int}}$, obtained from different methods (see text) at the corresponding equilibrium geometry. The values of $\theta_A$, $\theta_B$, and $R_{AB}$ are given together with the known experimental values. Energies in kcal/mol, distances in bohr.

<table>
<thead>
<tr>
<th></th>
<th>H$_2$O...HNH$_2$</th>
<th>H$_3$N...HNH$_2$</th>
<th>H$_2$O...HOH</th>
<th>HF...HF</th>
<th>H$_3$N...HOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{\text{SAPT}}$</td>
<td>-2.09</td>
<td>-2.50</td>
<td>-4.22</td>
<td>-3.75</td>
<td>-5.19</td>
</tr>
<tr>
<td>$\Delta E_{\text{SAPT}_{\text{trunc}}}$</td>
<td>-2.50</td>
<td>-3.15</td>
<td>-5.45</td>
<td>-5.82</td>
<td>-7.55</td>
</tr>
<tr>
<td>$\Delta E_{\text{SAPT}}$</td>
<td>-2.49</td>
<td>-3.13</td>
<td>-5.31</td>
<td>-4.89</td>
<td>-6.76</td>
</tr>
<tr>
<td>$\Delta E^{\text{hybrid}}_{\text{int}}$</td>
<td><em>a</em></td>
<td><em>b</em></td>
<td>-5.4±0.7</td>
<td>-4.9±0.1</td>
<td>-6</td>
</tr>
<tr>
<td>$R_{\text{eq}}^{\text{SAPT}}$</td>
<td>3.40</td>
<td>3.50</td>
<td>3.15</td>
<td>2.83</td>
<td>3.15</td>
</tr>
<tr>
<td>$R_{\text{eq}}^{\text{SAPT}_{\text{trunc}}}$</td>
<td>3.20</td>
<td>3.20</td>
<td>2.68</td>
<td>2.48</td>
<td>2.70</td>
</tr>
<tr>
<td>$R_{\text{eq}}^{\text{SAPT}}$</td>
<td>3.25</td>
<td>3.30</td>
<td>2.91</td>
<td>2.68</td>
<td>2.93</td>
</tr>
<tr>
<td>$\theta_A$</td>
<td>50°</td>
<td>0°</td>
<td>60°</td>
<td>68°</td>
<td>20°</td>
</tr>
<tr>
<td>$\theta_B$</td>
<td><em>a</em></td>
<td><em>b</em></td>
<td>60°</td>
<td>62°</td>
<td>11° &lt; $\theta_B$ &lt; 23°</td>
</tr>
</tbody>
</table>

*a* Unphysical molecule, see text.

*b* Linear H-bonded structure, no experimental values, see text.

Reference 55.

Reference 20.

To our knowledge no experimental value available. The value quoted is an ab initio estimate given by Latajka and Scheiner (Ref. 56).

Reference 57.

Reference 58.

Reference 59.
H$_3$N...HOH is more stable than H$_2$O...HOH. Concerning the geometrical parameters it appears that the value of the angle $\theta_A$ defining the angle between the axes $A...B$ (A and B being the heavy atoms of the complex) and the principal axis of the proton acceptor depends strongly on the chemical nature of the acceptor. A value of about 60° has been obtained when the proton acceptor is H$_2$O or HF. A smaller value is obtained when the proton acceptor is NH$_3$. The value of the angle $\theta_B$ characterizing the position of the bond A-H (A being N, O, or F) of the proton acceptor is always very close to 0°.

The smallest distance $R_{A...B}$ between the two heavy atoms at the equilibrium geometry has been obtained for the HF dimer. We get the following series: $R_{F...F}(HF)_2 < R_{O...O}(H_2O)_2 < R_{N...N}(NH_3)_2$. The equilibrium distance $R_{A...B}$ calculated for the heterodimer involving NH$_3$ and H$_2$O increases from the most stable dimer (H$_3$N...HOH) to the less stable one (H$_2$O...HNH$_2$).

From a more quantitative point of view, the first important point to note is that values of the interaction energy, $\Delta E_{\text{int}}$, depend appreciably on the method used and/or the dimer considered. First, it is clear that $\Delta E_{\text{int}}^{\text{SAPT trunc}}$ is always smaller in magnitude than $\Delta E_{\text{int}}^{\text{hybrid}}$ or $\Delta E_{\text{int}}^{\text{SAPT trunc}}$. The systematic difference is about 20%. The comparison between $\Delta E_{\text{int}}^{\text{SAPT trunc}}$ and $\Delta E_{\text{int}}^{\text{hybrid}}$ depends on the dimer. We can distinguish three different cases:

(i) the weak H-bonded dimers case (including H$_2$O...HNH$_2$ and (NH$_3$)$_2$) for which $\Delta E_{\text{int}}^{\text{SAPT trunc}}$ and $\Delta E_{\text{int}}^{\text{hybrid}}$ almost coincide.

(ii) the intermediate case of medium H-bonded dimers ((H$_2$O)$_2$ and (HF)$_2$) for which we obtain two different results. For the (H$_2$O)$_2$ dimer the total interaction energy calculated with SAPT$_{\text{trunc}}$ and the hybrid methods are almost identical (the difference is less than 3%). This is a result which has already been obtained by Refs. 4, 12, and 20. However, this is no longer true for the (HF)$_2$ dimer for which $\Delta E_{\text{int}}^{\text{SAPT trunc}}$ and $\Delta E_{\text{int}}^{\text{hybrid}}$ are off by about 20%, therefore, the equality of these two quantities cannot be considered as a general rule. We shall return to this important point later after having presented the individual components of the interaction energy (sec. C below).

(iii) the rather strong H-bonded dimer, H$_3$N...HOH, for which an important difference between the truncated and hybrid results is observed.

Regarding the equilibrium distance $R_{eq}$ we find that the SAPT results are systematically larger than those obtained with the two other methods. Once again, the situation is not so clear when we compare the values obtained with SAPT$_{\text{trunc}}$ and the hybrid methods. Almost identical results have been obtained for the case of weakly bonded dimers while shorter distances have been calculated with the SAPT$_{\text{trunc}}$ approach for the other dimers. If we compare with the known experimental values it is clear that the hybrid method is the method which gives the most plausible results. Now, regarding the calculated angular parameters ($\theta_A$ and $\theta_B$) defining the relative position of the two molecules within the H-bonded dimer we have systematically obtained almost the same values with the three different procedures. We have also found that not only the equilibrium angles are very similar but also the general shape of the interaction energy curves with respect to the relative angles for all dimers presented here. To illustrate this point we present in Figure 2 the energy curve obtained for the water dimer as calculated by SAPT, SAPT$_{\text{trunc}}$, and the hybrid methods.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Interaction energy curves, $\Delta E_{\text{int}}$, as a function of $\theta_A$ for the water dimer as calculated by SAPT, SAPT$_{\text{trunc}}$, and the hybrid methods.}
\end{figure}

B. Radial dependence of the perturbational contributions

Keeping the angular parameters $\theta_A$ and $\theta_B$ of each dimer fixed at their optimized values, we have investigated the radial dependence of the intermolecular interaction energy perturbational components.

Our main purpose is to study which contributions to the interaction energy are actually dominant in stabilizing the five studied complexes. We are also interested to trace back to its origin the poor stability of the dimer (NH$_3$)$_2$ and also the very short F...F distance in the (HF)$_2$ dimer.

In the next few tables we present the radial dependence of the following contributions:

(i) $E^{(1)}_{RS}$, $E^{(1)}_{\text{exch}}$, and the complete first-order, $E^{(1)\text{SAPT}}$ (Table V);

(ii) the second-order induction energy $E^{(2)}_{\text{ind}}$, its exchange part $E^{(2)\text{exch-ind}}$, and the complete induction energy $E^{(2)\text{SAPT}}$ (Table VI);

(iii) the second-order dispersion energy $E^{(2)}_{\text{disp}}$, its exchange part $E^{(2)\text{exch-disp}}$, and the complete dispersion energy $E^{(2)\text{SAPT}}$ (Table VII).

We make the following comments on the results presented in Tables V–VII:

(i) All contributions of the Rayleigh–Schrödinger (RS) treatment (no exchange terms), namely $E^{(1)}_{RS}$, $E^{(1)}_{\text{ind}}$, and
$E_{\text{disp}}$ have a stabilizing effect. Of course, the major contribution is the electrostatic interaction energy which represents between 55 and 70% of the total RS contribution. When we compare the relative force of the RS interaction energy for the different H-bonded dimers we get the following order: (NH$_3$)$_2$ ≈ H$_3$N...OH<H$_2$O...HNNH$_2$ ≈ (H$_2$O)$_2$ ≈ (HF)$_2$.

For an average distance of $R_{AB}$ = 3 Å, it appears that for the dimers (H$_2$O)$_2$ and (HF)$_2$, the electrostatic energy represents 75% and 50% of the value obtained for (NH$_3$)$_2$; for the dimers (H$_2$O)$_2$ and (HF)$_2$, $E_{\text{ind}}^{(2)}$ represents 75% and 40% of the value obtained for (NH$_3$)$_2$, respectively; and for (H$_2$O)$_2$ and (HF)$_2$, $E_{\text{disp}}$ represents, 50% and 20% of $E_{\text{disp}}^{(2)}$ of (NH$_3$)$_2$, respectively.

(ii) The total first- and total second-order exchange contributions (including both induction and dispersion contributions) reduce the stabilizing effect of the Rayleigh–Schrödinger terms just discussed. As expected, the major exchange contribution results from the first-order exchange term which represents 80% of the total exchange contribution at intermediate distances, while the second-order induction and dispersion exchange contributions have been obtained to represent 14% and 6% of the total exchange, respectively. Regarding the total exchange contribution we obtain the following order: (NH$_3$)$_2$ > (H$_2$O...HNNH$_2$) ≈ (H$_3$N...OH)<(H$_2$O)$_2$ > (HF)$_2$. We have investigated the behavior of each individual exchange component as a function of the distance $R_{AB}$. We have found that for distances greater than 3 Å the exchange contribution may be very well represented via a single exponential function, $C e^{-\alpha(R-R_0)}$.

The set of parameters obtained for the different dimers and for the different components of the exchange part using the results for $R_{AB}$ = 3.00, 3.17, 3.70, and 4.00 Å are given in Table VIII (note that $R_0$ has been chosen to be fixed at 3 Å). The values of the parameters depend essentially on the nature of the exchange contribution (first-order, exchange-induction or exchange-dispersion) and on the chemical nature of the molecules involved in the complex.

### Table V. First-order Rayleigh–Schrödinger energy, $E_{\text{RS}}^{(1)}$, first-order exchange energy, $E_{\text{exch}}^{(1)}$, and complete first-order, $E_{\text{SAPT}}^{(1)} = E_{\text{RS}}^{(1)} + E_{\text{exch}}^{(1)}$, for different values of $R_{AB}$. Energies in kcal/mol and distances in Å.

<table>
<thead>
<tr>
<th>$R_{AB}$</th>
<th>H$_2$O...HNNH$_2$</th>
<th>H$_3$N...HNNH$_2$</th>
<th>H$_2$O...HNNH$_2$</th>
<th>HF...HF</th>
<th>H$_3$N...HOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.75</td>
<td>$E_{\text{RS}}^{(1)}$</td>
<td>$E_{\text{exch}}^{(1)}$</td>
<td>$E_{\text{SAPT}}^{(1)}$</td>
<td>$E_{\text{RS}}^{(1)}$</td>
<td>$E_{\text{exch}}^{(1)}$</td>
</tr>
<tr>
<td>2.90</td>
<td>$-11.28$</td>
<td>$-17.00$</td>
<td>$-11.51$</td>
<td>$-6.63$</td>
<td>$-16.36$</td>
</tr>
<tr>
<td>3.00</td>
<td>$19.75$</td>
<td>$30.07$</td>
<td>$13.10$</td>
<td>$5.21$</td>
<td>$19.87$</td>
</tr>
<tr>
<td>3.17</td>
<td>$8.48$</td>
<td>$13.08$</td>
<td>$1.59$</td>
<td>$-1.42$</td>
<td>$3.44$</td>
</tr>
<tr>
<td>4.00</td>
<td>$-7.62$</td>
<td>$-12.00$</td>
<td>$-8.40$</td>
<td>$-5.16$</td>
<td>$-12.30$</td>
</tr>
</tbody>
</table>

### Table VI. Second-order induction energy, $E_{\text{ind}}^{(2)}$, second-order exchange-induction energy, $E_{\text{exch}}^{(2)}$, and complete second-order induction, $E_{\text{exch}}^{(2)}$, for different values of $R_{AB}$. Energies in kcal/mol and distances in Å.

<table>
<thead>
<tr>
<th>$R_{AB}$</th>
<th>H$_2$O...HNNH$_2$</th>
<th>H$_3$N...HNNH$_2$</th>
<th>H$_2$O...HNNH$_2$</th>
<th>HF...HF</th>
<th>H$_3$N...HOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.75</td>
<td>$E_{\text{ind}}^{(2)}$</td>
<td>$E_{\text{exch}}^{(2)}$</td>
<td>$E_{\text{SAPT}}^{(2)}$</td>
<td>$E_{\text{ind}}^{(2)}$</td>
<td>$E_{\text{exch}}^{(2)}$</td>
</tr>
<tr>
<td>2.90</td>
<td>$-6.20$</td>
<td>$-9.60$</td>
<td>$-7.15$</td>
<td>$-4.42$</td>
<td>$-10.27$</td>
</tr>
<tr>
<td>3.00</td>
<td>$3.78$</td>
<td>$6.90$</td>
<td>$-1.00$</td>
<td>$-2.18$</td>
<td>$-0.07$</td>
</tr>
<tr>
<td>3.17</td>
<td>$8.32$</td>
<td>$13.80$</td>
<td>$5.33$</td>
<td>$2.04$</td>
<td>$8.83$</td>
</tr>
<tr>
<td>4.00</td>
<td>$-1.24$</td>
<td>$-1.76$</td>
<td>$-1.94$</td>
<td>$-1.39$</td>
<td>$-2.61$</td>
</tr>
</tbody>
</table>
Table VII. Second-order dispersion energy, $E_{\text{disp}}^{(2)}$, second-order exchange dispersion energy, $E_{\text{exch}}^{(2)}$, and complete second-order dispersion energy, $E_{\text{disp}}^{(2)\,\text{SAPT, SAPT}^\text{trunc}}$, and $E_{\text{disp}}^{(2)}$ for different values of $R_{AA}$. Energies in kcal/mol and distances in Å.

<table>
<thead>
<tr>
<th>$R_{AA}$</th>
<th>H$_2$O...HNH$_2$</th>
<th>H$_2$N...HNH$_2$</th>
<th>H$_2$O...HOH</th>
<th>HF...HF</th>
<th>H$_3$...HOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.75</td>
<td>$E_{\text{disp}}^{(2)}$</td>
<td>1.28</td>
<td>2.28</td>
<td>0.82</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{disp}}^{(2),\text{SAPT}}$</td>
<td>-3.35</td>
<td>4.50</td>
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<td>-1.22</td>
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<tr>
<td></td>
<td>$E_{\text{disp}}^{(2),\text{SAPT, SAPT}^\text{trunc}}$</td>
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<td>4.88</td>
<td>-2.32</td>
<td>-1.00</td>
</tr>
<tr>
<td>2.90</td>
<td>$E_{\text{disp}}^{(2),\text{SAPT, SAPT}^\text{trunc}}$</td>
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<td>1.45</td>
<td>0.48</td>
<td>0.14</td>
</tr>
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<td></td>
<td>$E_{\text{disp}}^{(2)}$</td>
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<td>3.43</td>
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<td>$E_{\text{disp}}^{(2),\text{SAPT}}$</td>
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<td>3.93</td>
<td>-1.89</td>
<td>-0.79</td>
</tr>
<tr>
<td>3.00</td>
<td>$E_{\text{disp}}^{(2),\text{SAPT, SAPT}^\text{trunc}}$</td>
<td>0.57</td>
<td>1.07</td>
<td>0.34</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{disp}}^{(2)}$</td>
<td>-2.02</td>
<td>-2.86</td>
<td>-1.55</td>
<td>-0.70</td>
</tr>
<tr>
<td>3.17</td>
<td>$E_{\text{disp}}^{(2),\text{SAPT, SAPT}^\text{trunc}}$</td>
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<td>-2.74</td>
<td>-1.31</td>
<td>-0.53</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{disp}}^{(2)}$</td>
<td>0.33</td>
<td>0.64</td>
<td>0.19</td>
<td>0.05</td>
</tr>
<tr>
<td>4.00</td>
<td>$E_{\text{disp}}^{(2),\text{SAPT, SAPT}^\text{trunc}}$</td>
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<td>-2.10</td>
<td>-1.13</td>
<td>-0.48</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{disp}}^{(2)}$</td>
<td>-0.34</td>
<td>-0.54</td>
<td>-0.24</td>
<td>-0.10</td>
</tr>
</tbody>
</table>

C. Radial dependence of the total interaction energy: A comparison between the different approaches

In Table IX we present the total interaction energy as calculated within SAPT, SAPT$_{\text{trunc}}$, and the hybrid methods (Eqs. (29), (30), and (31)) as a function of $R_{AA}$. We also present in Figures 3 and 4 the complete interaction energy curves for two representative examples: the NH$_3$ and HF dimers. A number of remarks are in order. First, it is clear that at very large distances the three approaches give the same results for the total interaction energy and thus, the same dissociative behavior. The results obtained by the different methods at small and intermediate distances may be quite different depending on the force of the hydrogen bond. For the two weak H-bonded cases (H$_2$O...HNH$_2$ and (NH$_3$)$_2$) the agreement between the truncated and hybrid

(iii) Clearly, at very short distances the repulsive exchange part of the first-order dominates the attractive RS contribution. However, at sufficiently large distances the exchange part vanishes and only the electrostatic term survives (it behaves as $1/R_{AA}^2$). Accordingly, the total first-order energy displays a minimum. The location of the minimum depends very much on the system studied. Looking at results of Table V we see that the weak H-bonded dimer (NH$_3$)$_2$ has a shallow minimum at a relatively large distance ($\sim 1.30$ kcal/mol with $R_{eq} \approx 3.8$ Å). In contrast, the stronger-bonded dimers (H$_2$O$_2$ and (HF)$_2$) have a larger total first-order interaction energy (about $-2.50$ kcal/mol). The minimum region of (HF)$_2$ is found to be quite broad within a range of values between 2.9 Å and 3.3 Å.

(iv) The positive (repulsive) exchange contributions, $E_{\text{exch\,\,ind}}$ and $E_{\text{exch\,\,disp}}^{(2)}$ terms never dominate their Rayleigh–Schrödinger counterparts, $E_{\text{exch}}^{(2)}$ and $E_{\text{disp}}^{(2)}$. In fact, the second-order RS terms tend to decrease the intermolecular interaction energy and to push the equilibrium distance $R_{eq}$ towards shorter distances, this effect is slightly reduced by the second-order exchange terms whose main effect is to bring back $R_{eq}$ to more reasonable values. The effect of the second-order exchange contributions is more important for (NH$_3$)$_2$ than for the (HF)$_2$ dimer (see Tables IV, VI, and VII). In conclusion, the relative stability between the different H-bonded dimers results from a subtle balance between Rayleigh–Schrödinger and total exchange contributions.

Table VIII. Parameters of the representation $C e^{-\alpha(R-R_0)}$ ($R_0=3$ Å) for: (a) the first-order exchange energy, (b) the second-order exchange induction energy, (c) the second-order exchange dispersion energy. Parameters $C$ in kcal/mol and $\alpha$ in Å$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>H$_2$O...HNH$_2$</th>
<th>H$_2$N...HNH$_2$</th>
<th>H$_2$O...HOH</th>
<th>HF...HF</th>
<th>H$_3$...HOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{exch}}^{(1)}$</td>
<td></td>
<td>3.685</td>
<td>3.280</td>
<td>3.777</td>
<td>4.205</td>
</tr>
<tr>
<td>$C$</td>
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<td>13.910</td>
<td>5.397</td>
<td>2.121</td>
<td>8.860</td>
</tr>
<tr>
<td>$E_{\text{exch,,ind}}^{(2)}$</td>
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<td>3.585</td>
<td>3.906</td>
<td>5.489</td>
</tr>
<tr>
<td>$C$</td>
<td>1.473</td>
<td>2.444</td>
<td>0.893</td>
<td>0.474</td>
<td>1.893</td>
</tr>
<tr>
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<td>0.344</td>
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results is very good except at small distances (see Figure 3). For the rather strong dimers \((\text{HF})_2\) and \(\text{H}_2\text{O}...\text{HOH}\) the truncated and hybrid curves appear to differ quite substantially by about 20%. The water dimer appears as an intermediate species for which both methods are in reasonable agreement, by about 20%. The water dimer is systematically smaller than with the hybrid method. Regarding the SAPT results it is clear that \(\Delta E_{\text{SAPT}}\) is always smaller in magnitude than \(\Delta E_{\text{SAPT trunc}}\) or \(\Delta E_{\text{int}}\). The systematic difference for all dimers is about 20%. Note also that the equilibrium distance obtained by the pure perturbational method is also systematically greater than with the two other methods. In order to discuss further these results it is important to point out that the equality of the results obtained with the truncated and hybrid methods should result from the following equality:

\[
\Delta E_{\text{int}}^{\text{SAPT}} - E_{\text{in}}^{(1)} + E_{\text{ind}}^{(2)},
\]

(32)

where \(E_{\text{in}}^{(1)}\) is the complete first-order (electrostatic and exchange terms) and \(E_{\text{ind}}^{(2)}\) is the Rayleigh–Schrödinger part of the induction energy. It has been argued that this equality should result from a fortunate cancellation between the exchange part of the induction energy and some part of the higher-order perturbational contributions which are implicitly included in a SCF supermolecular calculation of the interaction energy. Despite the fact that it is roughly true for the water dimer, our results clearly demonstrate that it is wrong for the \((\text{HF})_2\) and \(\text{H}_3\text{N}...\text{HOH}\) dimers. To illustrate

![Figure 3](image1.png)

**FIG. 3.** Interaction energy curves, \(\Delta E_{\text{int}}\), as a function of \(R_{AB}\) for the \((\text{NH}_3)_2\) dimer as calculated by SAPT (curve with open squares), \(\text{SAPT}_\text{trunc}\) (solid squares), and the hybrid methods (crosses).

![Figure 4](image2.png)

**FIG. 4.** Interaction energy curves, \(\Delta E_{\text{int}}\), as a function of \(R_{AB}\) for the \((\text{HF})_2\) dimer as calculated by SAPT (curve with open squares), \(\text{SAPT}_\text{trunc}\) (solid squares), and the hybrid methods (crosses).

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**TABLE IX.** Total interaction energy calculated with SAPT, \(\text{SAPT}_\text{trunc}\), and the hybrid methods, see text. Energies in kcal/mol and distances in Å.

<table>
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<tr>
<th>(R_{AB})</th>
<th>(\text{H}_2\text{O}...\text{HNH}_2)</th>
<th>(\text{H}_3\text{N}...\text{HNH}_2)</th>
<th>(\text{H}_2\text{O}...\text{HOH})</th>
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this point we present in Figures 5 and 6 a comparison between the SCF interaction energy curve and the curve representing the perturbational sum $E^{(1)} + E^{(2)}_{\text{ind}}$ (dashed line with open squares) for the (NH$_3$)$_2$ dimer. Although the difference of minimum energies is small, the minimum. Although the difference of minimum energies is small (about 0.2 kcal/mol) this difference at the new corresponding minima is magnified when the total dispersion energy is added to lead to the complete interaction energy. Following the Morokuma decomposition (see e.g., Ref. 54) the SCF interaction energy may be written as:

$$\Delta E_{\text{int}}^{\text{SCF}} = E_{\text{elec}} + E_{\text{exch-\text{HL}}} + E_{\text{ind}}^{\text{SCF}},$$

where $E_{\text{elec}}$ is the electrostatic energy (identical to $E_{\text{RS}}^{(1)}$) as calculated here with SAPT, $E_{\text{exch-\text{HL}}}$ is the Heitler–London exchange energy which reduces almost to $E_{\text{exch}}^{(1)}$ when a very large basis set is used (see discussion on the complementary exchange in Sec. III.B) and $E_{\text{ind}}^{\text{SCF}}$ is by definition the induction part of the SCF interaction energy. In order to discuss the status of the SAPT induction energy (including not the exchange contribution) with respect to the SCF induction energy, we have presented in Table X the SCF induction energy, the difference between the SCF induction energy and the total SAPT induction energy (including exchange effects) and the same difference without the exchange terms, all quantities being given as a function of the distance $R_{AB}$. It immediately appears that at short and intermediate distances, the three calculated values of the induction energy are different. The nice agreement obtained for the water dimer at $R_{O...O}=3$ Å between $E_{\text{ind}}^{\text{SCF}}$ and $E_{\text{ind}}^{(2)}$ is actually fortuitous. In fact, $E_{\text{ind}}^{\text{SCF}}$ should not be compared to $E_{\text{ind}}^{(2)}$ because the so-called apparent correlation or self-consistency effects are included in the supermolecular Hartree–Fock interaction energy but not in our computation of $E_{\text{ind}}^{(2)}$. As emphasized by Sadlej$^{15}$ the second-order RS induction energy calculated within SAPT methodology by using the first-order perturbed wave function is equivalent to that computed within a UnCoupled Hartree–Fock (UCHF)

![Image](https://example.com/image.png)

**FIG. 5.** Comparison between the SCF interaction energy curve (solid line with crosses) and the curve representing the perturbational sum $E^{(1)} + E^{(2)}_{\text{ind}}$ (dashed line with open squares) for the (NH$_3$)$_2$ dimer.

![Image](https://example.com/image.png)

**FIG. 6.** Comparison between the SCF interaction energy (solid line with crosses) and the curve representing the perturbational sum $E^{(1)} + E^{(2)}_{\text{ind}}$ (dashed line with open squares) for the (HF)$_2$ dimer.

### Table X. Comparison between the SCF induction energy and the perturbational induction energy. Energies in kcal/mol and distances in Å.

<table>
<thead>
<tr>
<th>$R_{AB}$</th>
<th>H$_2$O...HNH$_2$</th>
<th>H$_3$N...HNH$_2$</th>
<th>H$_2$O...HOH</th>
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</tr>
<tr>
<td>3.17</td>
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</tbody>
</table>
perturbation scheme. In particular, the perturbation-induced modification of the Hartree–Fock (HF) potential is not taken into account. In a UCHF scheme, the results obtained for \(E^{(2)}_\text{ind}\) are underestimated. Sadlej emphasizes that if both unperturbed and perturbed many-electron systems are described in the HF approximation, then the appropriate perturbation theory is the Coupled Hartree–Fock (CHF) scheme. The induction computed at the CHF level is usually denoted as \(E^{(2)}_{\text{ind},\text{resp}}\), it sums up to infinity certain linear diagrams without rings and then fully accounts for the self-consistency effects. The CHF scheme corrects the HF potential of the unperturbed systems but no correlation corrections are introduced. The total exchange-induction contributions are also present in the SCF induction energy. However, at the SCF level, once again because of the self-consistency effects we get \(E^{(2)}_{\text{exch-ind},\text{resp}}\) instead of \(E^{(2)}_{\text{exch-ind}}\). Finally, the SCF induction contribution is written as:

\[
\Delta E^{\text{SCF}} = E^{(2)}_{\text{ind},\text{resp}} + E^{(2)}_{\text{exch-ind},\text{resp}} + \delta E_{\text{mixt}},
\]

where \(\delta E_{\text{mixt}}\) gathers all higher perturbational terms. A number of calculations of \(E^{(2)}_{\text{ind},\text{resp}}\) and \(E^{(2)}_{\text{exch-ind},\text{resp}}\) have been presented (see references in Ref. 28).

Although results obtained with the hybrid approach are good it is important to realize that escaping from a pure perturbational treatment has some drawbacks. How much of the higher-order perturbational contributions, what part of the exchange-induction energy, etc... is recovered from a SCF supermolecular calculation is not easy to estimate. It may be argued that the good results obtained with the hybrid approach could result from a subtle balance between neglected contributions very different in nature. It is not clear whether that balance will still hold when higher-order contributions will be evaluated. Of course, a similar problem is present in a pure perturbational scheme but it is important to emphasize that the neglected quantities not taken into account are much more clearly identified. Accordingly, in our opinion it is still important to study the pure perturbational treatments. From Tables IV and IX in particular the comparisons with experimental values it appears that the complete pure perturbational treatment (SAPT) is the approach which gives the less plausible results. Results from the truncated approach demonstrate that the main part of the disagreement between \(\Delta E^{\text{SAPT}}\) on one hand, and \(\Delta E^{\text{SAPT}}_{\text{true}}\) and \(\Delta E^{\text{hybrid}}\) on the other hand, comes from the second-order exchange-induction energy which destroys the overall quality of the results. To illustrate this point Figures 7 and 8 display a comparison between the \(\Delta E^{\text{SCF}}\) curve and the curve representing the perturbational sum \(E^{(1)} + E^{(2)}_{\text{ind}} + E^{(2)}_{\text{exch-ind}}\) for the dimers \(\text{H}_3\text{N}...\text{HNH}_2\) and (HF)\(_2\) (same curves as in Figures 5 and 6, except that the exchange-induction energy has been added). In Figure 7 it is seen that the very good agreement found in Figure 5 is destroyed. This result shows that the calculated values for \(E^{(2)}_{\text{exch-ind}}\) are overestimated since for a weak dimer such as \(\text{H}_3\text{N}...\text{HNH}_2\) the perturbational contributions beyond the second-order should be small and a perturbational description should be adequate. For stronger dimers like (HF)\(_2\) the clear disagreement between the two curves does not necessarily mean that we are in trouble (higher-order terms certainly play a role) but there is no reason not to believe that, in that case also, the exchange-induction term has been overestimated. Let us have a closer look to our estimate of the exchange-induction energy. Within the one-exchange approximation used in this work \(E^{(2)}_{\text{exch-ind}}\) is calculated as a sum of three terms (see Sec. II, Eq. (19)). The analysis of our results has shown that the first term is positive and represents the major part of \(E^{(2)}_{\text{exch-ind}}\) while the sum of the second and third terms is negative and essentially reduces \(E^{(2)}_{\text{exch-ind}}\) by a quantity which depends on \(R_{AB}\). For instance, for the \(\text{H}_3\text{N}...\text{HOH}\) dimer this quantity has been calculated to be 24%, 15% and 11% for \(R_{AB} = 2.54\) Å, 2.75 Å, and 2.93 Å, respectively. Quite similar results have been obtained with the other dimers. The sum of the two last terms entering into \(E^{(2)}_{\text{exch-ind}}\) (see Eq. (19)) may be rewritten as

\[
\begin{align*}
E^{(1)}_{\text{RS}} & = \sum_{i \neq j} \sum_{k \neq l} S_{ij}^A S_{ik}^B S_{jl}^A S_{lk}^B + \sum_{i \neq j} \sum_{k \neq l} S_{ij}^A S_{ik}^B S_{jk}^A S_{lk}^B + E^{(2)}_{\text{ind}} \sum_{i \neq j} \sum_{k \neq l} |S_{ij}^A|^2 |S_{kl}^B|^2. 
\end{align*}
\]

From Eq. (35) we see that an underestimation of the last term related to the induction part leads to an overestimation of the
exchange-induction energy. If, as emphasized by Sadlej,\textsuperscript{15} the induction part is underestimated within the SAPT treatment, then, it is plausible that there exists some reducing effect for the exchange-induction energy related to the induction part. In other words, higher-order terms (related to the apparent correlation effects) would contribute significantly to the total exchange-induction energy. Besides this effect, we can also argue that the one-exchange approximation is only valid for intermediate and large intermolecular distances and some bias could be introduced by neglecting multiple exchanges. The neat effect of the neglect of multiple exchange terms is not easy to estimate.

Finally, we would like to end with some remarks about the intramonomer correlation effects on the results presented here. Quite recently a number of studies have addressed the problem of evaluating the intramonomer correlations contributions to the interaction energy.\textsuperscript{11,13,20,22–28} Although a complete knowledge of all contributions is not at our disposal, the calculations made so far show clearly the importance of such effects. Of course, this is expected for the electrostatic energy of hydrogen-bonded systems which depends essentially on the magnitude of the permanent dipoles of the molecules known to be overestimated at the SCF level. However, it is more surprising to get even stronger corrections for the exchange contribution to the first-order.\textsuperscript{13} Some important effects (about 0.5 kcal/mol) have also been obtained for the dispersion and induction part (−0.42 kcal/mol for $E_{\text{disp}}^{(22)}$ and −0.60 kcal/mol for $E_{\text{ind}}^{(22)}$ in the case of the water dimer,\textsuperscript{20} the second superscript indicating the perturbational order in the Møller-Plesset expansion). These results are of particular importance for the discussion just presented on the exchange-induction. As mentioned above, an underestimation of the induction energy leads to an overestimation of the exchange-induction. Accordingly, the neat effect of the intramonomer correlation could be a reduction of the exchange-induction energy. However, it should be noted that there is an opposite trend for the electrostatic energy, although this effect is probably less pronounced. This discussion illustrates the fact that there is still much room left to fully understand the intricate balance between the different contributions to the interaction energy.

V. CONCLUSIONS

In this work we have presented a detailed perturbational study of several hydrogen-bonded dimers consisting of H$_2$O, NH$_3$, and HF molecules. Three different approaches have been used to compute the interaction energy: a pure perturbational approach, $\Delta E_{\text{int}}^{\text{SAPT}}$, including all perturbational components up to the second-order calculated at the SCF level, a so-called truncated approach, $\Delta E_{\text{int}}^{\text{SAPT trunc}}$, in which the exchange part of the induction is not considered, and the hybrid approach, $\Delta E_{\text{int}}^{\text{hybrid}}$, in which the supermolecular SCF interaction energy (counterpoise-corrected) is supplemented by the complete dispersion contribution calculated with SAPT (both Rayleigh-Schrödinger and exchange contributions). The quality of the large basis sets used has been checked by computing a number of properties for both the monomers and the corresponding dimers (SCF monomer energies, dipole moments, complementary exchange energies, etc...). From a qualitative point of view, the physical results obtained with the three approaches are essentially similar. The relative force of the different hydrogen bonds are in agreement with experimental results and, in particular, the acceptor or donor properties are correctly reproduced. From a quantitative point of view, a number of differences emerge when using the different approaches. These quantitative differences are particularly important for the radial properties, much less for the angular ones. A general result already emphasized by some authors is that, at the level of approximation employed here (SCF level, perturbational components up to the second-order only, etc.), the hybrid approach seems to be the most reliable approach (see Table IV). The pure perturbational approach including the main contributions up to the second-order (calculated at the SCF level) gives the less plausible results. Clearly, some of the neglected contributions must be introduced to get better results. In particular, the second-order exchange-induction energy is certainly overestimated. We have argued that this quantity is very probably reduced by some intramonomer correlation contribution. However, it is important to emphasize that the error on the known experimental quantities is in general of the same order of magnitude as the dispersion of the results obtained using the different approaches. Accordingly, there is still no clearcut conclusion on which method is the best at the present time. To analyze further the importance of each perturbational components is therefore essential if we want to reach in a controlled way the asymptotic regime of the perturbational expansion of the intermolecular interaction energy.

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