Symmetry-adapted perturbation theory for the calculation of Hartree–Fock interaction energies

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A symmetry-adapted perturbation theory is formulated for the calculation of Hartree–Fock interaction energies of closed-shell dimers. The proposed scheme leads to a basis-set-independent interpretation of the Hartree–Fock interaction energy in terms of basic concepts of the theory of intermolecular forces: electrostatics, exchange and induction. Numerical results for different geometries of He₂, Ne₂, He–C₂H₂, He–CO, Ar–HF, (HF)₂, and (H₂O)₂ complexes show that in the region of the van der Waals minimum the proposed perturbation theory reproduces accurately the Hartree–Fock interaction energy. This fast convergence and relatively small computational cost of the proposed perturbation scheme suggest that this method is a practical alternative for the standard supermolecular approach.

1. Introduction

Recent advances in the experimental investigations of the intermolecular interaction phenomenon have stimulated associated developments of various theoretical models. In many cases the experimental data can be successfully explained using, for example, the electrostatic model [1, 2]. However, the quantitative agreement with the experimental results necessitates the use of more sophisticated approaches to analyse the intermolecular interaction energies. Present theories have difficulties, especially in the region around the van der Waals minimum. This situation made Buckingham, Fowler and Hutson [3] refer to this part of the interaction potential as the theoretically intractable ‘intermediate region’.

Modern ab initio techniques used to calculate the interaction energy can be classified as supermolecular and perturbational. The interaction energy is defined as,

\[ E_{\text{int}} = E_{\text{AB}} - (E_A + E_B), \]

where \( E_A \), \( E_B \) and \( E_{\text{AB}} \) are the exact ground-state energies of the monomers A, B and of the complex AB, respectively. In a supermolecule approach, the exact energies in
equation (1) are replaced by approximations $\hat{E}_{AB}$, $\hat{E}_A$ and $\hat{E}_B$ computed using an available method of solving the clamped-nuclei Schrödinger equation. The main drawback of this approach is that it does not permit an analysis of the interaction energy in terms of distinct, physically meaningful components. It is not a priori obvious which contributions are neglected and which are included in a given supermolecular approach. By contrast, the symmetry-adapted perturbation theory (SAPT) [4–6] defines the interaction energy $E_{\text{int}}$ directly as the sum of the electrostatic, exchange, induction and dispersion contributions.

Among various supermolecular methods the Hartree–Fock (HF) model has gained the greatest popularity, and most of the supermolecular methods use the HF approximation as a starting point for further considerations. Numerous attempts have been made to interpret the interaction energy at the Hartree–Fock level in terms of some physically meaningful contributions [7–26]. The majority of these attempts are based on the Kitaura–Morokuma partitioning of the Fock matrix [7–13]. In this method, one removes from the Fock matrix the integrals (in the atomic basis) which are assumed to be unrelated to the considered type of interaction. Then, by calculating the energy with such a partial Fock matrix, one gets the contribution coming from this type of interaction. Unfortunately, the sum of such contributions does not reproduce the Hartree–Fock interaction energy, and therefore some non-physical, sometimes large, correcting terms have to be added. Moreover, the definitions of the contributions to the interaction energy are clearly basis-set-dependent. In particular, they depend on which atomic orbitals are considered as belonging to the molecule A and which to molecule B. Such an assignment is in general arbitrary, e.g., a basis function centred off the nuclei may cause troubles because it is difficult to decide a priori which molecule it belongs to. As a consequence some contributions to the interaction energy do not have well-defined limits when the basis set becomes complete. For example, the basis-set saturated values of the so-called polarization component require two complete basis sets centred A and B. In such a case, however, the charge-transfer term becomes (partly) redundant and the interaction energy cannot be viewed as containing independent polarization and charge-transfer components [22, 23].

An early symmetry-adapted perturbation theory study on the water dimer [27] suggested that the Hartree–Fock interaction energy can be accurately approximated by the sum of the Heitler–London term [28] and the induction energy, both calculated with the neglect of the intramonomer electron correlation effects. The calculations performed for the He [29], Ne [30] and Be [31] dimers failed to confirm this conjecture. Moreover, the introduction of the exchange-induction energy [32] only worsens the agreement between the sum of the perturbation corrections and the supermolecular result. Sadlej [33] suggested that the calculation of the induction and exchange-induction components using the coupled Hartree–Fock (CHF) scheme may resolve the existing discrepancy. However, subsequent calculations for the Be dimer [34] did not confirm this prediction. A possible explanation of this problem has been proposed by Gutowski et al. [35]. These authors have shown that in the case of the interaction of Li$^+$ and Na$^+$ with F$^-$, the exchange effects strongly affect the orbitals of the interacting ions. This means that the purely electrostatic deformation of the interacting molecules (assumed in [29–32]) does not describe properly the interaction at the Hartree–Fock level and it is necessary to introduce the exchange terms into the equations defining the perturbed wavefunctions, i.e., to use the strong symmetry forcing [4–6].
These results have led to the development of the so-called Pauli Blockade (PB) method [24–26]. In this approach, the Hartree–Fock interaction energy is computed by solving step-by-step the coupled set of equations describing the series of mutual polarizations of the interacting molecules, with the requirement that the occupied spaces of the orbitals of both monomers are orthogonal to one another. This procedure leads to a partitioning of the interaction energy into various components. These contributions cannot be easily related to any quantities defined by the symmetry-adapted perturbation theory and, consequently, do not have a well-defined asymptotic limit at large intermonomer distances. This is a consequence of the fact that even the first iteration of the PB method is an infinite-order treatment in the intermolecular interaction potential. Moreover, this method of solving the Hartree–Fock equations is rather costly, and can hardly be applied in practice to interactions of large systems. Each iteration requires an effort comparable to solving the SCF equations for the dimer, although this cost can be reduced, cf. [26]. One can expect that, at least for weakly interacting systems, the infinite-order PB treatment in the intermolecular interaction operator $V$ may not be necessary, and a calculation through a low, preferably second, order in $V$ will prove to be sufficiently accurate.

A symmetry-adapted perturbation theory approach for the calculation of the Hartree–Fock interaction energies has been proposed by Jeziorska et al. [36]. These authors introduced a basis-set-independent perturbation scheme developed specifically for the interaction of two identical two-electron systems. The numerical results for the helium dimer presented in their paper are very encouraging, and suggest that the Hartree–Fock interaction energy can be very accurately reproduced in low orders of the perturbation theory, at low computational cost. If this good convergence would hold for larger systems as well, this method could be a practical alternative for the standard supermolecular approach.

The purpose of the present paper is to present a symmetry-adapted perturbation theory for the calculation of the Hartree–Fock interaction energies for arbitrary many-electron systems, and to show that the Hartree–Fock interaction energy can be interpreted in a basis-set-independent way in terms of the first-order Heitler–London energy, and second-order induction, exchange-induction and exchange-deformation energies. The plan of the paper is as follows. In Section 2, we present the formulation of the perturbation theory employing the strong symmetry forcing, which can be viewed as a generalization of that used in the Hirschfelder–Silbey perturbation theory [37]. In this section we also derive the equations for the perturbed orbitals and propose low-order approximations to the Hartree–Fock interaction energy. In section 3, we describe the details of the numerical procedure. In section 4, we report numerical results for weak interactions in He$_2$, Ne$_2$, He–C$_2$H$_2$, He–CO and Ar–HF systems, as well as for stronger interactions in the HF and H$_2$O dimers. Finally, concluding remarks are given in section 5.

2. Theory

2.1. Hartree–Fock equations in localized representation

We consider the interaction of a closed-shell $N_A$-electron monomer A with a closed-shell $N_B$-electron monomer B. Our goal is to define a perturbation theory solution of the Hartree–Fock equations for the $(N_A + N_B)$-electron dimer AB using the free monomer solutions as the zeroth-order approximation. For this purpose we have to introduce a localization scheme, i.e., to replace the delocalized canonical occupied
orbitals $\psi_c$, $c = 1, \ldots, (N_A + N_B)/2$, defined as eigenfunctions of the dimer Fock operator $f$,

$$\hat{f}\psi_c = \varepsilon_c \psi_c,$$  

(2)

to two sets of (non-canonical) orbitals $\phi_a$ and $\phi_b$ localized on monomers A and B, respectively,

$$\phi_a = \sum_c C_{ca} \psi_c,$$  

(3)

$$\phi_b = \sum_c C_{cb} \psi_c.$$  

(4)

Equations (3) and (4) represent a general linear transformation and we do not impose any orthogonality restrictions on the coefficients $C_{ca}$ and $C_{cb}$. Throughout this paper we shall use the convention that the indices $a$ and $b$, ranging over $N_A/2$ and $N_B/2$ values, respectively, enumerate occupied orbitals associated with monomers A and B, respectively. At large intermonomer distances the localized orbitals $\phi_a$ and $\phi_b$ should approach the unperturbed monomer orbitals $\phi_a^{(0)}$ and $\phi_b^{(0)}$ satisfying the zeroth-order equations,

$$\hat{f}_A^{(0)} \phi_a^{(0)} = \varepsilon_a^{(0)} \phi_a^{(0)}$$  

(5)

$$\hat{f}_B^{(0)} \phi_b^{(0)} = \varepsilon_b^{(0)} \phi_b^{(0)},$$  

(6)

where the Fock operator of the monomer X, X = A or B, is given by

$$\hat{f}_x^{(0)} = -\frac{1}{2} \nabla^2 + U_x + \hat{g}[\rho_x^{(0)}].$$  

(7)

The operator $\hat{g}[\rho_x^{(0)}]$ is defined as

$$\hat{g}[\rho_x^{(0)}] = 2\hat{f}[\rho_x^{(0)}] - \hat{k}[\rho_x^{(0)}],$$  

(8)

where $\rho_x^{(0)}$ is the one-particle density matrix defined for the monomer A by the equation

$$\rho_x^{(0)}(1' | 1) = \sum_a \phi_a^{(0)*}(1') \phi_a^{(0)}(1).$$  

(9)

A similar definition holds for monomer B. The Coulomb and exchange operators are defined in terms of an arbitrary density matrix $\rho(1' | 1)$ as

$$(\hat{f}[\rho] \psi)(1) = \int \frac{\rho(2|1) \psi(1)}{r_{12}} d^2 \quad (\hat{k}[\rho] \psi)(1) = \int \frac{\rho(2|1) \psi(2)}{r_{12}} d^2.$$  

(10)

(11)

Finally, the operator $U_x = -\sum_{i \in X} Z_i / r_i$ is the electrostatic potential of the nuclei of the monomer X. The index $i$ enumerates here the nuclei in the monomer X, $Z_i$ denotes the charge of the $i$th nucleus and $r_i$ is the distance between this nucleus and the electron.

Several localization procedures have been proposed in the literature thus far (see [36] and references therein). For our purposes, however, it will be convenient to adopt the following localization criterion for $\phi_a$ and $\phi_b$ (valid for all pairs of indices $a$ and $b$)

$$\langle \phi_b^{(0)} | (\hat{f}_A^{(0)} - \varepsilon_a^{(0)}) \phi_a^{(0)} \rangle = 0, \quad \langle \phi_a^{(0)} | (\hat{f}_B^{(0)} - \varepsilon_b^{(0)}) \phi_b^{(0)} \rangle = 0.$$  

(12)

In the Appendix we show that, when the considered system has sufficiently rich symmetry, this localization criterion uniquely defines the primitive function of the
symmetry-adapted perturbation theory of Hirschfelder and Silbey [37]. Thus, the localization procedure defined by equation (12) can be viewed as a generalization of that used in the Hirschfelder–Silbey theory. The localization equations (12) were adopted here because they are linear in the localized orbitals, which leads to a particularly simple formalism. The so-called Kato or Bloch localizations of [36] give localized orbitals which are the closest in a certain sense to the orbitals of the unperturbed monomers. These localizations, as well as the highly nonlinear localization procedure proposed by Adams [38], would lead to a considerably more complex perturbation formalism. One can show, however, that the localized orbitals obtained using the Kato, Bloch and our criterion differ only by terms vanishing exponentially at large intermonomer distances, and are very close to each other at the distance of the van der Waals minimum. To completely specify the localized orbitals we will also assume that they satisfy the intermediate normalization conditions

\[ \langle \phi_a^{(0)} | \phi_a' \rangle = \delta_{aa'}, \quad \langle \phi_b^{(0)} | \phi_b' \rangle = \delta_{bb'}. \]  

To develop a perturbation expansion for \( \phi_a \) and \( \phi_b \) we combine equations (2), (3) and (4) and write

\[ (f^0 - E_a^{(0)}) \phi_a = \sum_{a'} Q_{a'a} \phi_{a'} + \sum_b K_{ba} \phi_b \]

\[ (f^0 - E_b^{(0)}) \phi_b = \sum_{b'} Q_{b'b} \phi_{b'} + \sum_a K_{ab} \phi_a, \]

where the sets of constants \( Q_{a'a}, \ K_{ba} (Q_{b'b}, \ K_{ab}) \) can be expressed through the coefficients \( C_{aa}, \ C_{cb} \) and energies \( \varepsilon_c \). Using the localization conditions (12) and (13), one can derive explicit expressions for these constants

\[ Q_{a'a} = \sum_b S_{a'a}^{A} \langle \phi_c^{(0)} | \sum_b \sigma_{ab} \phi_b^{(0)} | \phi_a' \rangle \]

\[ K_{ba} = \sum_{b'} S_{ba}^{B} \langle \phi_b^{(0)} | \sum_a \sigma_{ba'} \phi_a^{(0)} | \phi_a' \rangle, \]

where \( \sigma_{ab} = \langle \phi_a^{(0)} | \phi_b \rangle \). The matrices \( S_{a'a}^{A} \) and \( S_{ba}^{B} \) are inverses of the matrices \( Z_{a'a}^{A} \) and \( Z_{ba}^{B} \), where

\[ Z_{a'a}^{A} = \delta_{aa'} - \sum_b \sigma_{ab} \sigma_{ba'}, \]

\[ Z_{bb'}^{B} = \delta_{bb'} - \sum_a \sigma_{ba} \sigma_{ab}. \]

Equations (16) and (17) represent a generalization of equations (19a) and (19b) of [36] to an arbitrary \( N \)-electron system. Finally, the operator \( \delta_B \) is defined as \( f^0 - f_{A}^{(0)} \), and is given explicitly by

\[ \delta_B = U_B + \eta[\delta_B], \]

where

\[ \delta_B(1'|1) = \rho(1'|1) - \rho_T^{(0)}(1'|1) \]

and \( \rho(1'|1) \) is the one-particle density matrix corresponding to the normalized \( (N_A + N_B) \)-electron Slater determinant built from the localized orbitals \( \phi_a \) and \( \phi_b \). Similar equations for the constants \( K_{ab} \) and \( Q_{ba} \) can be found by interchanging in equations (16)–(21) the indices \( a \) and \( b \), and \( A \) and \( B \).
The expression for the Hartree–Fock interaction energy can be formally written as

\[ E_{\text{int}}^{\text{HF}} = \frac{\langle \Phi_A \Phi_B | \mathcal{H} \mathcal{A} \Phi_A \Phi_B \rangle}{\langle \Phi_A \Phi_B | \mathcal{A} \Phi_A \Phi_B \rangle} - E_A^{(0)} - E_B^{(0)}, \]

where \( E_A^{(0)} \) and \( E_B^{(0)} \) are the Hartree–Fock energies of the isolated monomers A and B, respectively, \( \Phi_A \) (\( \Phi_B \)) is the normalized Slater determinant built from the localized orbitals \( \phi_a \) (\( \phi_b \)), \( \mathcal{H} \) is the total Hamiltonian for the dimer AB, and \( \mathcal{A} \) is the \((N_A + N_B)\)-electron antisymmetrizer.

### 2.2. Perturbation expansion of the localized orbitals

Using the decomposition \( \hat{f} = \hat{f}_A^{(0)} + \hat{f}_B \), equations (14) and (15) can be rewritten as

\[
(f_A^{(0)} - E_A^{(0)}) \phi_a = -\hat{v}_B \phi_a + \sum_{a'} Q_{a'a} \phi_{a'} + \sum_{b} K_{ba} \phi_b
\]  

(23)

\[
(f_B^{(0)} - E_B^{(0)}) \phi_b = -\hat{v}_A \phi_b + \sum_{b'} Q_{b'b} \phi_{b'} + \sum_{a} K_{ba} \phi_a.
\]  

(24)

To derive the perturbation expansion based on equations (16), (17), (23) and (24), one has to parametrize the operators \( \hat{v}_A \) and \( \hat{v}_B \) with a (generally complex) parameter \( \zeta \). The orbitals \( \phi_a \) and \( \phi_b \) become then functions of \( \zeta \) and can be expanded as a power series

\[ \phi_a(\zeta) = \sum_{k=0} \zeta^k \phi_a^{(k)} \]  

(25)

\[ \phi_b(\zeta) = \sum_{k=0} \zeta^k \phi_b^{(k)} \]  

(26)

\[ Q_{aa}(\zeta) = \sum_{k=0} \zeta^k Q_{aa}^{(k)} \]  

(27)

\[ K_{ba}(\zeta) = \sum_{k=0} \zeta^k K_{ba}^{(k)}. \]  

(28)

The functions \( \phi_a^{(k)} \) and \( \phi_b^{(k)} \) can be calculated recursively from the perturbation equations obtained by inserting equations (25)–(28) into equations (16), (17) and (23), (24) and collecting terms of the same order in \( \zeta \). One can show that the simplest parametrization,

\[ \hat{v}_A \rightarrow \zeta \hat{v}_A, \quad \hat{v}_B \rightarrow \zeta \hat{v}_B, \]  

(29)

leads to a perturbation expansion which, for large intermonomer distances \( R \), gives the uncoupled Hartree–Fock (UCHF) expansion of the induction energy [33, 34]. The parametrization (29) was also tacitly assumed in [36], although the resulting equations were solved iteratively rather than by a conventional order-by-order perturbation procedure. The main drawback of the UCHF scheme is that the leading term in the large \( R \) asymptotic expansion of \( \phi_a \) is not recovered in the first order in \( \zeta \). This difficulty is circumvented in the so-called coupled Hartree–Fock (CHF) perturbation treatment [33, 34]. This type of perturbation expansion is obtained if the interelectronic interaction operator \( r_{12}^{-1} \) [entering the definitions of \( \hat{v}_A \) and \( \hat{v}_B \) via equations (8)–(11), (20) and (21)] corresponding to the intramonomer interaction (i.e., the interaction
between electrons belonging to the same monomer) is not treated as a perturbation
and is not multiplied by $\zeta$. The resulting parametrization of $\hat{v}_A$ and $\hat{v}_B$ is

$$\hat{v}_A(\zeta) = \zeta U_A + \hat{g}[\rho_B - \rho_B^{(0)}] + \zeta \hat{g}[\rho - \rho_B],$$

(30)

$$\hat{v}_B(\zeta) = \zeta U_B + \hat{g}[\rho_A - \rho_A^{(0)}] + \zeta \hat{g}[\rho - \rho_A],$$

(31)

where $\rho_A$ and $\rho_B$ are the one-particle density matrices corresponding to the
(normalized) Slater determinants $\Phi_A$ and $\Phi_B$. One can easily see that, for $\zeta = 0$,
equations (23) and (24) are satisfied by the monomer Hartree–Fock orbitals $\phi^{(0)}_A$ and $\phi^{(0)}_B$. Equations (30) and (31) account already in the first order for the perturbation-
induced modification of the monomer Hartree–Fock potentials $\hat{g}[\rho_A]$ and $\hat{g}[\rho_B]$, i.e.,
for the so-called response or self-consistency effects. The specific form of the resulting
nth-order perturbation equations is as follows

$$\langle \hat{f}^{(n)}_A - \varepsilon^{(n)}_a \rangle \phi^{(n)}_a = - \sum_{i=1}^{n} \hat{w}^{(i)}_B \phi^{(n-i)}_a - \sum_{i=1}^{n} \hat{g}[\rho^{(i)}_A] \phi^{(n-i)}_a + \sum_{i=1}^{n} \sum_{a} Q^{(i)}_{Aa} \phi^{(n-i)}_a + \sum_{i=1}^{n} \sum_{b} K^{(i)}_{ba} \phi^{(n-i)}_b,$$

(32)

where

$$\hat{w}^{(i)}_B = U_B \delta_{i1} + \hat{g}[\rho^{(i-1)} - \rho_A^{(i-1)}],$$

(33)

and $\rho^{(i)}$ is the $ith$-order term of the perturbation expansion of the one-particle density
matrix corresponding to the normalized Slater determinant $\Phi_A$. The quantities $Q^{(i)}_{Aa}$
and $K^{(i)}_{ba}$ can be calculated by substituting equations (25)–(28), (30) and (31) into
equations (16) and (17) and comparing coefficients of $\zeta^i$. The density matrices $\rho^{(i)}$ and $\rho^{(0)}$ can be obtained by the $\zeta$-expansion of the well known formula for the density
matrix corresponding to a Slater determinant built from non-orthogonal orbitals [39].
In particular, the first-order equations are given by

$$\langle \hat{f}^{(0)}_A - \varepsilon^{(0)}_a \rangle \phi^{(1)}_A = - \hat{w}^{(0)}_B \phi^{(1)}_a - \hat{g}[\rho^{(1)}_A] \phi^{(0)}_a + \sum_{b} Q^{(1)}_{Aa} \phi^{(0)}_b + \sum_{b} K^{(1)}_{ba} \phi^{(0)}_b,$$

(34)

where

$$\rho^{(1)}(1|1) = \sum_{a} [\phi^{(1)*}_a(1)| \phi^{(0)}_a(1) + \phi^{(0)*}_a(1)| \phi^{(1)}_a(1)],$$

(35)

and the expressions for $Q^{(1)}_{Aa}$, $K^{(1)}_{ba}$ and $\hat{w}^{(1)}_B$ can be simply found by replacing in
equations (16), (17) and (33) the exact localized orbitals of the dimer by the
unperturbed orbitals. A similar equation for $\phi^{(1)}_b$ can be found by interchanging the
indices $a$ and $b$, and $A$ and $B$.

When the electron exchange, i.e., the tunnelling of electrons between monomers, is
neglected, the overlap integrals $\sigma_{ab}$ and $\sigma_{ba}$ as well as the corresponding intermonomer
overlap densities $\phi^{(0)}_a(r) \phi^*_b(r)$ and $\phi^{(0)}_b(r) \phi^*_a(r)$, can be set equal to zero. Equation (32)
reduces then to

$$\langle \hat{f}^{(0)}_A - \varepsilon^{(0)}_a \rangle \phi^{(0)}_{a,\text{ind}} = - \sum_{i=1}^{n} \hat{w}^{(i)}_{b,\text{ind}} \phi^{(n-i)}_{a,\text{ind}} - \sum_{i=1}^{n} \hat{g}[\rho^{(i)}_A] \phi^{(n-i)}_{a,\text{ind}} + \sum_{i=1}^{n} \sum_{a} Q^{(i)}_{a' a} \phi^{(n-i)}_{a',\text{ind}} + \sum_{i=1}^{n} \sum_{b} K^{(i)}_{b' b} \phi^{(n-i)}_{b',\text{ind}},$$

(36)

where $\phi^{(0)}_{a,\text{ind}} \equiv \phi^{(0)}_a$,

$$\hat{w}^{(i)}_{b,\text{ind}} = U_B \delta_{i1} + 2 \hat{g}[\rho^{(i-1)}_B],$$

(37)

and

$$Q^{(i)}_{a' a} = \sum_{k=0}^{l-1} \langle \phi^{(0)}_{a'} | \phi^{(i-k)}_{a,\text{ind}} \rangle + \sum_{k=0}^{l-1} \langle \phi^{(0)}_{a} | \delta[\rho^{(i-k)}_A] \phi^{(k)}_{a,\text{ind}} \rangle.$$

(38)
Note that \( \rho = \rho_A + \rho_n \) when the intermonomer overlap integrals are neglected, so we can replace \( \rho^{(0)} - \rho^{(0)}_A \) by \( \rho^{(0)}_B \). Equations (36) and (38) are identical with the equations of the so-called Hartree–Hartree–Fock (HHF) theory of Sadlej [33]. Since this theory gives a complete description of the induction (polarization) effects at the HF level, the localized orbitals in equations (36)–(38) are denoted by the subscript ind. The HHF theory of Sadlej [33] can be derived variationally starting with a Hartree product of determinants corresponding to monomers A and B. Thus this theory completely neglects the exchange effects, and the perturbation expansion given by equation (38) can be viewed as the polarization expansion of the HF equations. Consequently, our equation (32) can be regarded as a generalization of Sadlej's theory allowing for the electron exchange.

It is worth noting that the nth-order correction to the localized orbital \( \phi_a \) can be written as the sum of induction and exchange functions,

\[
\phi_a^{(n)} = \phi_{a, \text{ind}}^{(n)} + \phi_{a, \text{exch}}^{(n)},
\]

where \( \phi_{a, \text{ind}}^{(n)} \) is given by equation (36), and the \( \phi_{a, \text{exch}}^{(n)} \) is defined as the difference, i.e.,

\[
\phi_{a, \text{exch}}^{(n)} = \phi_{a}^{(n)} - \phi_{a, \text{ind}}^{(n)}.
\]

In particular, the first-order exchange function \( \phi_{a, \text{exch}}^{(1)} \) fulfills the following equation

\[
(\tilde{F}_A - \tilde{F}_B) \phi_{a, \text{exch}}^{(1)} = - \psi_{a, \text{exch}}^{(0)} - \left[ \rho_{A, \text{exch}}^{(1)} \right] \phi_a^{(0)} + \sum_{a'} Q_{a, a', \text{exch}} (\phi_{a'}^{(n)} + \sum_{b} K_{ab}^{(n)} \phi_b^{(0)}),
\]

where \( \psi_{a, \text{exch}}^{(1)} = \psi_{a}^{(1)} - \tilde{\omega}_{a, \text{ind}}^{(1)} \phi_{a, \text{exch}}^{(1)} \) is given by equation (35) with \( \phi_{a, \text{exch}}^{(1)} \) replaced by \( \phi_{a, \text{exch}}^{(1)} \) and \( Q_{a, a', \text{exch}}^{(1)} = Q_{a, a', \text{exch}}^{(1)} - Q_{a, a', \text{ind}}^{(1)} \). It can be shown that the exchange function \( \phi_{a, \text{exch}}^{(1)} \) is localized mainly on the monomer B, and vanishes exponentially for large intermonomer distances. This suggests that the exchange effects deform the orbitals of the monomer A mainly in the vicinity of the monomer B. Thus, the deformation effects are due to the small component of \( \phi_a \) localized on the monomer B. This result is very similar to that obtained by Certain and Hirschfelder [40]. Using the \( \text{H}_2^+ \) ion as an example, these authors have found that the exchange component of the perturbed wavefunction is mainly responsible for the appearance of the ionic terms in the total wavefunction of the dimer.

### 2.3. Energy expressions

In principle, the perturbation expansion of the Hartree–Fock interaction energy could be obtained by parametrizing equation (22) with the parameter \( \zeta \), and expanding the function \( E_{\text{HF}}(\zeta) \) as a power series in \( \zeta \). In the present paper we did not follow this route. Instead, we consider a series of approximations to \( E_{\text{HF}}^{(n)} \) defined by the equation:

\[
E_{\text{HF}}^{(2n+1)} = \frac{\langle \Phi_A(n) | \mathcal{H} | \Phi_B(n) \rangle}{\langle \Phi_A(n) | \mathcal{H} | \Phi_B(n) \rangle} - E_{\text{HF}}^{(0)},
\]

where \( \Phi_A(n) \) is the Slater determinant built from the orbitals of the form,

\[
\phi_a^{(n)} = \sum_{l=0}^n \phi_a^{(l)},
\]

and a similar definition holds for \( \Phi_B(n) \). Since the wavefunctions \( \Phi_A(n) \) and \( \Phi_B(n) \) are accurate through the nth-order of perturbation theory, the approximation to \( E_{\text{HF}}^{(n)} \) of equation (41) should be accurate through the order \( 2n+1 \), in accordance with the Wigner’s \( (2n+1) \)-rule.
One may note that for \( n = 0 \), equation (41) reduces to the well-known expression for the Heitler–London energy,

\[
E^{\text{HF}}_{\text{int}}(1) \equiv E^{(1)}_{\text{HL}} = \frac{\langle \Phi_A^{(0)} \Phi_B^{(0)} | \mathcal{H} | \Phi_A^{(0)} \Phi_B^{(0)} \rangle}{\langle \Phi_A^{(0)} | \mathcal{S} | \Phi_A^{(0)} \rangle} - E_{A}^{(0)} - E_{B}^{(0)},
\]

where \( \Phi_X^{(0)} \equiv \Phi_X(0), X = A \) or B. The Heitler–London energy can be decomposed as follows [28]:

\[
E^{(1)}_{\text{HL}} = E^{(10)}_{\text{pol}} + E^{(10)}_{\text{exch}} + \Delta,
\]

where \( E^{(10)}_{\text{pol}} \) and \( E^{(10)}_{\text{exch}} \) are the electrostatic and the first-order exchange energies, respectively, neglecting the intramonomer electron correlation effects (the second superscript 0 indicates here the zeroth order with respect to the intramonomer correlation potential). The quantity \( \Delta \) denotes the small zeroth-order exchange term which vanishes as the fourth power of the overlap integral, provided that the dimer-centred basis set is used in the calculations.

A similar decomposition of the third-order approximation to the Hartree–Fock interaction energy, \( E^{\text{HF}}_{\text{int}}(3) \), is rather difficult to derive. In this paper we also consider a simpler second-order approximation, \( E^{\text{HF}}_{\text{int}}(2) \), defined as,

\[
E^{\text{HF}}_{\text{int}}(2) = E^{(1)}_{\text{HL}} + E^{(20)},
\]

where \( E^{(20)} = \langle \Phi_A^{(0)} \Phi_B^{(0)} | (V - E^{(10)}_{\text{pol}})(1 + \mathcal{P} - \langle \mathcal{P} \rangle) | \Phi_A^{(0)} \Phi_B^{(0)} \rangle \)\).

Here \( V \) is the intermolecular interaction operator, \( \mathcal{P} \) is the single-exchange operator [32] and \( \langle \mathcal{P} \rangle = \langle \Phi_A^{(0)} \Phi_B^{(0)} | \mathcal{P} | \Phi_A^{(0)} \Phi_B^{(0)} \rangle \). The function \( \Phi_A^{(1)} \) is defined by

\[
\Phi_A^{(1)} = \sum_{\alpha} \Phi_A(\phi_{\alpha}^{(0)} \rightarrow \phi_{\alpha}^{(1)}),
\]

where \( \Phi_A(\phi_{\alpha}^{(0)} \rightarrow \phi_{\alpha}^{(1)}) \) denotes the Slater determinant for the monomer A in which the orbital \( \phi_{\alpha}^{(0)} \) is replaced by \( \phi_{\alpha}^{(1)} \), and a similar definition holds for \( \Phi_B^{(1)} \). Equation (46) is formally identical with the sum of the (CHF) induction and the exchange-induction energies \( E^{\text{ind,resp}} \) and \( E^{\text{exch-ind,resp}} \) appearing in the symmetrized Rayleigh–Schrödinger (SRS) perturbation theory. The difference between these expressions is that equation (46) is calculated with the orbitals fully deformed by the exchange effects, whereas the corresponding SRS expression contains the ‘exchangeless’ orbitals \( \phi_{\alpha}^{(1)} \) defined by equation (36). A more rigorous analysis shows that equation (46) is not exact through the second order of perturbation theory. Nevertheless, we consider it in this paper because it is closely related to the second-order approximation, as defined by the SRS perturbation theory [41], and it accurately reproduces the Hartree–Fock interaction energy, at least for weakly bound van der Waals complexes (cf. Section 4).

For comparison, in Section 4 we also report approximations to the HF interaction energies computed using the second-order SRS theory:

\[
E^{\text{HF}}_{\text{SRS}}(2) = E^{(10)}_{\text{pol}} + E^{(10)}_{\text{exch}} + E^{(20)}_{\text{ind,resp}} + E^{(20)}_{\text{exch-ind,resp}},
\]

where \( E^{(20)}_{\text{ind,resp}} \) and \( E^{(20)}_{\text{exch-ind,resp}} \) are the induction and exchange-induction energies [34] mentioned above. One could also consider the third-order SRS approximation defined by equations (41) and (42), with \( \phi_{\alpha}(n) \) replaced by \( \phi_{\alpha,\text{ind}}(n) \). Numerical results reported in [24, 36, 42] show that this approximation represents a minor improvement over equation (48). It will not be applied in the present paper.
3. Computational aspects

In numerical calculations the first-order orbital \( \phi_{\alpha}^{(1)} \) is represented as

\[
\phi_{\alpha}^{(1)} = \sum_r C_r^{\alpha} \phi_r^{(0)},
\]

(49)

where \( \phi_r^{(0)} \) are the virtual orbitals of the unperturbed monomer A. Note, that this representation of the first-order function automatically fulfills the intermediate normalization condition (13). Substituting the expansion (49) into equation (34) and projecting on \( \phi_r^{(0)} \) leads to the following system of linear equations:

\[
(\varepsilon_r^{(0)} - \varepsilon_i^{(0)}) C_r^{\alpha} + g_{rr}^{\alpha\beta} C_r^{\beta} + g_{sr}^{\alpha\beta} C_s^{\beta} + (i\psi_B^{(1)} r)^\alpha - K_s^{\alpha} S_r^{\beta} = 0.
\]

(50)

Summation over repeated lower and upper indices is implied in equation (50). For simplicity, we have introduced the following short-hand notations:

\[
K_s^{\alpha} = K_{ba}^{\alpha}, \quad S_r^{\beta} = \langle \phi_r^{(0)} | \phi_\beta^{(0)} \rangle,
\]

\[
g_{kk}^{\alpha\beta} = \langle \phi_k^{(0)} | \phi_k^{(0)} \rangle \left[ 2 - \frac{r_{12}}{\varepsilon} \right] \langle \phi_k^{(0)} | \phi_i^{(0)} \phi_i^{(0)} \rangle, \quad (i\psi_B^{(1)} r)^\alpha = \langle \phi_r^{(0)} | \psi_B^{(1)} r \phi_r^{(0)} \rangle.
\]

It is interesting to note that the equations for the first-order orbitals \( \phi_{\alpha}^{(1)} \) localized in the monomer A are fully decoupled from those for the first-order orbitals localized on monomer B. This property significantly simplifies the numerical calculations of these orbitals. The system of linear equations (50) is identical to the coupled perturbed-Hartree-Fock (CPHF) equations [43] with the matrix element of the perturbation operator given by \( (i\psi_B^{(1)} r)^\alpha - K_s^{\alpha} S_r^{\beta} \).

Calculation of \( \phi_{\alpha}^{(1)} \) by solving equation (50) requires explicit calculation of all virtual orbitals and subsequent four-index transformation of two-electron integrals. This procedure may be more time-consuming than the straightforward solution of the SCF equations for the dimer. This four-index transformation can be eliminated, however, when the first-order orbitals are expanded directly in terms of atomic orbitals.

The linear coefficients \( C_{\alpha}^{(1)} \) and the non-linear parameters in \( \chi_t \) can be obtained variationally by minimizing the functional [44],

\[
\mathcal{J}[\tilde{\phi}_1^{(1)}, \ldots, \tilde{\phi}_{N_{\lambda}}^{(1)}, 2] = \sum_a \left\langle \tilde{\phi}_a^{(1)} | \tilde{f}_\lambda^{(0)} - \varepsilon_a^{(0)} + \xi_a^{(0)} + \tilde{\rho}_0^{(0)} | \tilde{\phi}_a^{(1)} \right\rangle + \text{Re} \sum_a \left\langle \tilde{\phi}_0^{(0)} | \tilde{\phi}_a^{(1)} \right\rangle \mathcal{J}[\tilde{\phi}_a^{(1)}, \tilde{\phi}_a^{(1)}] \phi_a^{(0)}
\]

\[
+ 2 \text{Re} \sum_a \left( \langle \tilde{\phi}_0^{(0)} | \psi_B^{(1)} r \phi_a^{(0)} \rangle - \sum_b K_{ba}^{(1)} \langle \tilde{\phi}_a^{(1)} | \tilde{\phi}_0^{(0)} \right\rangle,
\]

(52)

where \( \tilde{\rho}_0 = \sum_a | \phi_a^{(0)} \rangle \langle \phi_a^{(0)} |, \tilde{\rho}_0 = 1 - \tilde{\rho}_0 \) and \( \xi_a = \varepsilon_a^{(0)} - \varepsilon_a^{(0)} + \eta \), with \( \eta \) being an arbitrary positive number. Finally, \( \tilde{\rho}_a^{(1)} \) is essentially defined by equation (35) with projected trial orbitals,

\[
\tilde{\rho}_a^{(1)} (1' | 1) = \sum_a [\phi_a^{(0)} (1) \tilde{\phi}_a^{(1)^*} (1') + \phi_a^{(0)^*} (1') \tilde{\phi}_a^{(1)} (1)].
\]

(53)

If the non-linear parameters are not optimized, the minimization of the functional (52) requires solving a system of \( MN_{\lambda}/2 \) linear equations once. When large basis sets are
used in the calculations, the solution of a system of $MN_A/2$ linear equations may become demanding of computer time. A way around this problem is to solve $N_A/2$ systems of $M$ linear equations for $C_{i_a}^{(1)}$ with fixed $a$ iteratively, starting, for example, from $C_{i_a}^{(1)} = 0$ for $a' \neq a$. Then, in each iteration the solution of one system of linear equations for $C_{i_a}^{(1)}$ with fixed $a$ is equivalent to the minimization of the following functional,

$$J[a]^{(1)} = \langle \hat{\phi}_a^{(1)} | f^H_a^{(0)} - \sigma_a^{(0)} + \xi_a \hat{p}_0 | \hat{\phi}_a^{(1)} \rangle + 2\text{Re}\langle \hat{q}_0 \hat{\phi}_a^{(1)} | \hat{w}_b^{(1)} + \hat{g} \rho_a^{(1)} | \hat{\phi}_a^{(0)} \rangle$$

$$- \sum_b K_{ia}^{(1)} \langle \hat{\phi}_a^{(1)} | \hat{q}_0 \hat{\phi}_b^{(0)} \rangle$$

(54)

where it is assumed that $\rho_a^{(1)}$ is constructed using the orbitals from the previous iteration, except for $\rho_a^{(1)}$. Since the computational effort needed to solve iteratively $N_A/2$ systems of $M$ linear equations scales with the number of basis functions $M$ as $N_A M^2/2$, our approach represents an alternative to the standard supermolecule method.

Calculations have been performed for the He$_2$, Ne$_2$, He–C$_2$H$_2$, He–CO, Ar–HF, (HF)$_2$ and (H$_2$O)$_2$ complexes. See table 1 for the specification of geometries and basis sets. For all complexes with the exception of He$_2$ and Ne$_2$ we used spherical Gaussian basis functions (5 d functions, 7 f functions and 9 g functions). In order to fully account for the charge overlap effects all calculations were made with the full dimer basis sets. This means that, e.g., the occupied and virtual orbitals of the monomer A (obtained by diagonalizing the Fock operator $f^H$) are expanded in the full dimer basis set. With the supermolecular calculations, this prescription amounts to applying the Boys–Bernardi counterpoise correction for the basis set superposition error [52–54]. Atomic units are used throughout this paper (distances in bohrs and energies in hartrees).

4. Numerical results and discussion

To illustrate the theory presented above we have performed calculations for several representative van der Waals complexes:

1. rare gas dimers: He$_2$ and Ne$_2$, for different internuclear distances $R$;
2. a rare gas atom and a non-polar molecule: He–C$_2$H$_2$;
3. a rare gas atom and a heteronuclear diatom: He–CO and Ar–HF;
4. two polar molecules: (HF)$_2$ and (H$_2$O)$_2$.

These systems can be considered as representative of van der Waals molecules bound by dispersion, induction and dispersion, and electrostatic forces. The strength of the interaction in these complexes varies: the binding energy ranges from $\approx 7.6$ cm$^{-1}$ for He$_2$ to $\approx 1889$ cm$^{-1}$ for the water dimer. Finally, the physical interpretation of the Hartree–Fock deformation energy,

$$E_{\text{def}}^{HF} = E_{\text{HF}}^{\text{int}} - E_{\text{HF}}^{\text{LL}}$$

(55)

also varies. For the He and Ne dimers $E_{\text{def}}^{HF}$ is not interpretable classically, while for other systems considered in this paper it is dominated, at least in the long range, by the second-order induction energy. Our discussion will be mainly focused on the following points:

(a) How accurate are the approximations to the Hartree–Fock interaction energy proposed in Section 3?
Table 1. Geometries and basis sets of complexes studied in this paper. All coordinates are in bohr.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Basis set</th>
<th>Ref.</th>
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<td>He₂</td>
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<td></td>
<td></td>
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<td></td>
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<td>Ne: 5s 3p 2d</td>
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<tr>
<td>He–C₂H₄⁺</td>
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<td>0.0</td>
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<td>[46]</td>
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<td>(HF)₂</td>
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<td>0.16500</td>
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<td>0.0</td>
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<td>(H₂O)₂</td>
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<td>0.0</td>
<td>0.0</td>
<td>O: 4s 3p 2d 1f</td>
<td>[49]</td>
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<td>H</td>
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<td>0.0</td>
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<td>6.62796</td>
<td>-0.55355</td>
<td>-1.43047</td>
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a Geometry corresponding to the global minimum of the potential energy surface of [46].

b Geometry corresponding to the global minimum of the potential energy surface of [47].

c Geometry corresponding to the secondary minimum of the potential energy surface of [48]. In the region of the global minimum the Hartree–Fock interaction energy goes through zero, and the comparison of perturbative and supermolecular results is not meaningful in this case.

d Geometry corresponding to the global minimum [50].

e Geometry corresponding to the global minimum [51].

Table 2. Comparison of low-order approximations to the Hartree–Fock interaction energies of the He and Ne dimers. The expression (- N) denotes the factor 10^-N.

<table>
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<tr>
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<th>He₂</th>
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<tr>
<td>E_{HF}</td>
<td>-0.2831(-3)</td>
<td>-0.4933(-5)</td>
<td>-0.135(-2)</td>
<td>0.3283(-2)</td>
<td>-0.208(-4)</td>
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<td>E_{HF}</td>
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<td>0.3563(-4)</td>
<td>0.1075(-5)</td>
<td>0.1213(-1)</td>
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<td>0.5762(-6)</td>
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<td>E_{HF}</td>
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<td>-0.7964(-6)</td>
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<td>E_{HF}</td>
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<tr>
<td>E_{HF}</td>
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<tr>
<td>E_{HF}</td>
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<tr>
<td>E_{HF}</td>
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<td>-0.1250(-5)</td>
<td>-0.2772(-7)</td>
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<td>-0.190(-5)</td>
<td>-0.2184(-7)</td>
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<tr>
<td>E_{HF}</td>
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<tr>
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Table 3. Comparison of low-order approximations to the Hartree–Fock interaction energies of the He–C$_2$H$_4$, He–CO and Ar–HF complexes. The expression \((-N)\) denotes the factor $10^{-N}$.

<table>
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<tr>
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<th>He–CO</th>
<th>Ar–HF</th>
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<td>$E^{(10)}$</td>
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<td>-0.1999(-4)</td>
<td>-0.1921(-3)</td>
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<td>$E^{(1)}$</td>
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<td>0.9907(-4)</td>
<td>0.6362(-3)</td>
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<td>$E^{(20)}$</td>
<td>-0.1915(-4)</td>
<td>-0.5908(-5)</td>
<td>-0.2272(-3)</td>
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<td>$E^{(20)}_{\text{exch}}$</td>
<td>0.3508(-5)</td>
<td>0.5691(-5)</td>
<td>0.1570(-3)</td>
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<tr>
<td>$E^{(20)}_{\text{ind, resp}}$</td>
<td>0.6294(-4)</td>
<td>0.7887(-4)</td>
<td>0.3738(-3)</td>
</tr>
<tr>
<td>$E^{(2)}_{\text{HF}}$</td>
<td>0.7859(-4)</td>
<td>0.7911(-4)</td>
<td>0.4447(-3)</td>
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<tr>
<td>$E^{(2)}_{\text{HF, ett}}$</td>
<td>-0.2022(-4)</td>
<td>-0.4123(-5)</td>
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<tr>
<td>$E^{(3)}_{\text{HF}}$</td>
<td>0.5837(-4)</td>
<td>0.7498(-4)</td>
<td>0.3427(-3)</td>
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<td>$E^{(3)}_{\text{HF, ett}}$</td>
<td>0.5713(-4)</td>
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<td>0.3384(-3)</td>
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<td>$E^{(3)}_{\text{HF, ett}}$</td>
<td>0.5652(-4)</td>
<td>0.7417(-4)</td>
<td>0.3326(-3)</td>
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</table>

Table 4. Comparison of low-order approximations to the Hartree–Fock interaction energies of the HF and H$_2$O dimers. The expression \((-N)\) denotes the factor $10^{-N}$.

<table>
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<tr>
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</thead>
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<tr>
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<tr>
<td>$E^{(2)}_{\text{HF}}$</td>
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<td>$E^{(2)}_{\text{HF, ett}}$</td>
<td>-0.3799(-2)</td>
<td>-0.3053(-2)</td>
</tr>
<tr>
<td>$E^{(2)}_{\text{HF, ett}}$</td>
<td>0.1752(-2)</td>
<td>0.1444(-2)</td>
</tr>
<tr>
<td>$E^{(2)}_{\text{HF, ett}}$</td>
<td>-0.4846(-2)</td>
<td>-0.5478(-2)</td>
</tr>
<tr>
<td>$E^{(1)}_{\text{HF, ett}}$</td>
<td>-0.2759(-2)</td>
<td>-0.3826(-2)</td>
</tr>
<tr>
<td>$E^{(2)}_{\text{HF, ett}}$</td>
<td>-0.2186(-2)</td>
<td>-0.1812(-2)</td>
</tr>
<tr>
<td>$E^{(3)}_{\text{HF, ett}}$</td>
<td>-0.4945(-2)</td>
<td>-0.5638(-2)</td>
</tr>
<tr>
<td>$E^{(3)}_{\text{HF, ett}}$</td>
<td>-0.5411(-2)</td>
<td>-0.6054(-2)</td>
</tr>
<tr>
<td>$E^{(3)}_{\text{HF, ett}}$</td>
<td>-0.5812(-2)</td>
<td>-0.6378(-2)</td>
</tr>
</tbody>
</table>

(b) What is the role of various physical contributions to $E^{\text{HF}}_{\text{HF}}$ and $E^{\text{HF}}_{\text{HF, ett}}$?

(c) How important are the exchange-deformation effects neglected by the SRS theory?

The results of our calculations are summarized in table 2–4. Also reported in these tables are the interaction energies as computed from the second-order SRS approximation, $E^{\text{HF, ett}}_{\text{HF, ett}}$. An inspection of tables 2–4 shows that the second-order SRS theory reproduces the Hartree–Fock interaction energy with an error of 3% to 8% for dimers of rare gas atoms, 6% to 17% for other systems. These inaccuracies in $E^{\text{HF}}_{\text{HF}}$ would translate into a 4% to 10% error in the total interaction energies for these complexes. Since modern experimental techniques very accurately probe the region of the van der Waals minimum, this shows that $E^{\text{HF, ett}}_{\text{HF, ett}}$ may not be a sufficiently good approximation to $E^{\text{HF}}_{\text{HF}}$. By contrast, the second-order approximation of equation (45), $E^{\text{HF}}_{\text{HF}}$, works well. For dimers of rare gas atoms it reproduces the Hartree–Fock interaction energy within 1.6% or better, while for the rare gas atom–molecule interactions it overestimates $E^{\text{HF}}_{\text{HF}}$ by 3% at worst. The third-order approximation, $E^{\text{HF}}_{\text{HF}}$, works even better, and a typical approximation error for these systems is 1%. It is remarkable that this accuracy is achieved by solving linear CPHF equations, i.e., by considering only a linear response of each monomer to the presence of the...
Table 5. Decomposition of the Hartree–Fock deformation energy for the Ne$_2$, Ar–HF and (H$_2$O)$_2$ complexes. The expression ($-N$) denotes the factor $10^{-N}$.

<table>
<thead>
<tr>
<th></th>
<th>Ne$_2$, $R = 6$</th>
<th>Ar–HF</th>
<th>(H$_2$O)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{ind}, \text{resp}}^{(20)}$</td>
<td>$-0.1648(-4)$</td>
<td>$-0.2272(-3)$</td>
<td>$-0.3053(-2)$</td>
</tr>
<tr>
<td>$E_{\text{exch-ind}, \text{resp}}^{(20)}$</td>
<td>$0.1674(-4)$</td>
<td>$0.1570(-3)$</td>
<td>$0.1444(-2)$</td>
</tr>
<tr>
<td>$E_{\text{exch-def}, \text{resp}}^{(20)}$</td>
<td>$-0.1450(-5)$</td>
<td>$-0.3182(-4)$</td>
<td>$-0.2033(-3)$</td>
</tr>
<tr>
<td>$E_{\text{exch-def}}^{(20)}$</td>
<td>$-0.1190(-5)$</td>
<td>$-0.1020(-3)$</td>
<td>$-0.1812(-2)$</td>
</tr>
<tr>
<td>$E_{\text{exch-ind}, \text{resp}}^{(3)}$</td>
<td>$-0.1682(-6)$</td>
<td>$-0.4301(-5)$</td>
<td>$-0.4164(-3)$</td>
</tr>
<tr>
<td>$E_{\text{exch-def}, \text{resp}}^{(3)}$</td>
<td>$-0.1358(-5)$</td>
<td>$-0.1063(-3)$</td>
<td>$-0.2228(-2)$</td>
</tr>
<tr>
<td>$E_{\text{HF}}^{\text{def}}$</td>
<td>$-0.1402(-5)$</td>
<td>$-0.1121(-3)$</td>
<td>$-0.2552(-2)$</td>
</tr>
</tbody>
</table>

Thus, for weakly interacting systems, our perturbation expansion of the Hartree–Fock interaction energy appears to be quickly convergent. For strong interactions in the hydrogen-bonded complexes, this fast convergence deteriorates and the second-order approximation recovers only $\approx 85\%$ of $E_{\text{HF}}^{\text{int}}$. This is not surprising, since the convergence rate of any perturbation expansion depends on the strength of the perturbation. Even for these systems, however, the third-order formula reproduces the Hartree–Fock interaction energy within $\sim 5\%$, and one may expect that the knowledge of the second-order orbitals $\phi_a^{(2)}$ and $\phi_b^{(3)}$ would be sufficient to reproduce $E_{\text{HF}}^{\text{int}}$ within $1\%$ or $2\%$. This suggests that with a proper inclusion of the exchange effects, the low-order perturbation theory approach may provide accurate results for a much wider class of complexes than one would normally expect.

Since the second-order approximation of equation (45) works so well for weakly interacting systems, it is interesting to find which contribution to $E_{\text{HF}}^{\text{int}}(2)$ is so important. It is not difficult to show that the expression for the second-order contribution to the Hartree–Fock interaction energy, equation (46), can be rewritten as follows,

$$E^{(20)} = E_{\text{ind}, \text{resp}}^{(20)} + E_{\text{exch-ind}, \text{resp}}^{(20)} + E_{\text{exch-def}, \text{resp}}^{(20)},$$  

(56)

where the exchange-deformation energy $E_{\text{exch-def}, \text{resp}}^{(20)}$ is given by

$$E_{\text{exch-def}, \text{resp}}^{(20)} = \langle \phi_A^{(0)} \phi_B^{(0)} | (V - E_{\text{pol}}^{(10)}) (1 + \mathcal{P} - \langle \mathcal{P} \rangle) (\phi_A^{(1)}_{\text{exch}} + \phi_B^{(1)}_{\text{exch}}) \phi_A^{(0)} + \phi_B^{(0)} \phi_B^{(1)}_{\text{exch}}) \rangle,$$

(57)

and the function $\phi_{A, \text{exch}}^{(1)}$ is constructed in the same way as the function $\phi_A^{(1)}$ of equation (47),

$$\phi_{A, \text{exch}}^{(1)} = \sum a \phi_A^{(0)} \phi_a^{(1)}.$$

(58)

A similar definition holds for $\phi_{B, \text{exch}}^{(1)}$. In view of equations (45), (48) and (56), the difference $E_{\text{SRSS}}^{\text{HF}}(2) - E_{\text{HF}}^{\text{int}}(2)$ is given by the exchange-deformation energy. This additional contribution can be viewed as that part of the exchange energy which cannot be recovered by the SRS perturbation theory (i.e., perturbation theory employing weak symmetry-forcing). For systems with long-range induction interactions, this contribution vanishes faster at large intermonomer distances than the exchange-induction energy itself [40, 55].

For all complexes considered in this paper the Heitler–London energy is the dominant contribution to the Hartree–Fock interaction energy. It is interesting, however, to investigate the physical interpretation of the Hartree–Fock deformation effects. In table 5 we present a detailed analysis of the Hartree–Fock deformation...
Symmetry-adapted perturbation theory

energies for Ne\(_2\), Ar–HF and (H\(_2\)O)\(_2\) complexes in terms of the induction, exchange-induction and exchange-deformation energies. The results for other systems considered in this paper do not bring essentially new features, and are not presented. Also reported in table 5 is the third-order contribution to \(E_{\text{def}}^{\text{HF}}(3)\) \(\equiv E_{\text{def}}^{\text{HF}}(3) - E_{\text{def}}^{\text{HF}}(2)\), and the third-order approximation to the Hartree-Fock deformation energy, \(E_{\text{def}}^{\text{HF}}(3) \equiv E_{\text{int}}^{\text{HF}}(3) - E_{\text{int}}^{\text{HF}}(2)\). The results presented in table 5 show that \(E_{\text{def}}^{\text{HF}}(3)\) reproduc
tes quite accurately \(E_{\text{def}}^{\text{HF}}\). For weakly interacting systems like Ne\(_2\) and Ar–HF, the second-order treatment already provides very reasonable results. For the interaction of non-polar systems, the deformation effects are found to be more important than the induction and exchange-induction energies. For instance, for the Ne dimer at the equilibrium geometry, the exchange-deformation energy and the Hartree-Fock deformation energy are of the same order of magnitude. For interactions involving polar molecules, such effects are relatively less important than the classical electrostatic or induction interactions, and the exchange-deformation energy \(E_{\text{exch-def,resp}}^{(\text{HF})}\) is one order of magnitude smaller than the sum of the induction and exchange-induction energies. In all cases, however, the exchange-deformation energy is not negligible, and represents at least 8% of \(E_{\text{def}}^{\text{HF}}\). This shows that the Hartree-Fock deformation effects in weakly bound van der Waals molecules can be interpreted in terms of the induction, exchange-induction and exchange-deformation energies. Only for stronger interactions, e.g., in the water dimer, do fourth and higher-order induction and exchange effects contribute more than 10% of the Hartree-Fock deformation energy.

5. Summary and conclusions

We have formulated a symmetry-adapted perturbation theory for the calculation of the Hartree-Fock interaction energy. The proposed scheme leads to a basis-set-independent interpretation of the Hartree-Fock interaction energy in terms of the first-order Heitler-London energy and second-order induction, exchange-induction and exchange-deformation energies. It was shown that this perturbation theory is rapidly convergent even for strongly interaction systems. The necessary condition for achieving rapid convergence is the proper treatment of the exchange terms in the perturbation equations. Our results confirm the suggestions of [35, 36] concerning the importance of the exchange-deformation in the interaction of the closed-shell systems. The fast convergence and relatively small computational cost of the proposed perturbation scheme suggests that this method is a practical alternative to the standard supermolecular approach, at least for weakly interacting systems. For instance, this approach could be applied to compute the Hartree-Fock interaction energy for complexes of large organic molecules with rare gas atoms or for dimers of organic molecules. These systems have been widely investigated both experimentally and theoretically (see, for example [56–58]). It is also worth noting that the theory presented in this paper can be generalized to non-additive three-body interactions. Work in this direction is in progress.

We would like to thank Ad van der Avoird and Paul Wormer for reading and commenting on the manuscript. This work was supported by the Netherlands Foundation of Chemical Research (SON), the Netherlands Organization for Scientific Research (NWO) and by KBN funds through the Department of Chemistry, University of Warsaw, within the grant BW-1301/38/95.
In this Appendix we will prove that for systems possessing sufficiently rich symmetry, the localization conditions of equation (12) are equivalent to the criterion defining the primitive wavefunction of the Hirschfelder–Silbey perturbation theory [37]. This means that the method proposed by us can be viewed as a generalization of the Hirschfelder–Silbey method to systems with less symmetry. To save space and to simplify the notation, we shall explicitly consider only the case of the hydrogen atom interacting with a proton (H$_2^+$ ion). The general proof valid for larger systems does not involve new elements as long as the symmetry group of the system is sufficiently large, so that the exact, delocalized wavefunctions can be obtained from a primitive one (localized) by applying suitable projection operators.

The parametrized Hamiltonian for the H$_2^+$ ion can be written as,

$$\mathcal{H} = \mathcal{H}_0 + \zeta V,$$

where $\mathcal{H}_0$ is the Hamiltonian for the hydrogen atom with ground-state eigenvalue and eigenfunction denoted by $E_0$ and $\phi_a^{(0)}$, respectively, and $V$ is the interatomic interaction operator. The primitive function of the Hirschfelder–Silbey theory, $\phi_a(\zeta)$, is defined by the conditions [37]:

\begin{align*}
(\mathcal{H}_0 - E_0) \phi_a(\zeta) &= -\zeta V \phi_a(\zeta) + E_a(\zeta) A_x \phi_a(\zeta) + E_a(\zeta) A_u \phi_a(\zeta) \\
\langle \phi_a^{(0)} | (\zeta V - E_a(\zeta)) A_x \phi_a(\zeta) \rangle &= 0 \\
\langle \phi_a^{(0)} | (\zeta V - E_a(\zeta)) A_u \phi_a(\zeta) \rangle &= 0,
\end{align*}

(60)-(62)

where $A_x = (1 + I)/2$, $A_u = (1 - I)/2$ and $I$ is the inversion operator (we assume that the centre of the system is located at the origin of a Cartesian coordinate system). The projection of equation (60) on $\phi_a^{(0)}$ gives

$$\langle \phi_a^{(0)} | (\mathcal{H}_0 - E_0) \phi_a(\zeta) \rangle = \zeta \langle \phi_a^{(0)} | [V, I] \phi_a(\zeta) \rangle,$$

(63)

where we used the fact that $I^2 = I$, and that the primitive function $\phi_a(\zeta)$ satisfies (by definition) the following identities:

\begin{align*}
E_a(\zeta) \langle \phi_a^{(0)} | A_x \phi_a(\zeta) \rangle &= \langle \phi_a^{(0)} | \zeta V A_x \phi_a(\zeta) \rangle \\
E_a(\zeta) \langle \phi_a^{(0)} | A_u \phi_a(\zeta) \rangle &= \langle \phi_a^{(0)} | \zeta V A_u \phi_a(\zeta) \rangle,
\end{align*}

(64)-(65)

which follows directly from equations (61) and (62). Using the commutation relation,

$$[V, I] = [I, \mathcal{H}_0 - E_0],$$

(66)

one easily finds that equation (63) can be rewritten as

$$\langle \phi_a^{(0)} | (\mathcal{H}_0 - E_0) \phi_a(\zeta) \rangle = \zeta \langle \phi_a^{(0)} | (\mathcal{H}_0 - E_0) \phi_a(\zeta) \rangle,$$

(67)

or equivalently,

$$(1 - \zeta) \langle \phi_a^{(0)} | (\mathcal{H}_0 - E_0) \phi_a(\zeta) \rangle = 0.$$ 

(68)

Therefore, for $\zeta \neq 1$, equations (60)-(62) imply that

$$\langle \phi_a^{(0)} | (\mathcal{H}_0 - E_0) \phi_a(\zeta) \rangle = 0.$$ 

(69)

Since the primitive function $\phi_a(\zeta)$ is assumed to be analytic at $\zeta = 1$, equation (69) also holds for $\zeta = 1$. Because of symmetry $I \phi_a^{(0)} = \phi_b^{(0)}$, where $\phi_b^{(0)}$ is the hydrogenic 1s orbital located at the position of the nucleus B, and equation (69) becomes identical with equation (12). Conversely, one can prove along the same lines that equations (69) and
(60) imply the Hirschfelder–Silbey energy expressions of equations (61) and (62). One may note, that the localization criterion (69) is slightly more general than equations (60)–(62) since it uniquely defines the functions $E_q(\zeta)$ and $E_p(\zeta)$ also for $\zeta = 1$. Moreover, the condition (69), which is equivalent to our equation (12), can be used to generalize the conventional Hirschfelder–Silbey perturbation theory to systems without symmetry.

References


