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Exchange Polarization Effects in the Interaction of Closed-Shell Systems

The Beryllium-Beryllium Interaction

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Explicit formulae for the calculation of the exchange polarization energy in the interaction of closed-shell atoms or molecules have been derived by assuming neglect of the electron correlation within the noninteracting systems. The dispersion part of the exchange polarization energy has been represented as a sum of contributions arising from the interaction of two, three or four orbitals at a time. Each of these contributions is given by an integral involving the orbitals engaged in the interaction and the pair functions describing the dispersion interaction between these orbitals. The numerical calculations for the interaction of two ground-state beryllium atoms show that the exchange dispersion energy is positive and quenches about 5 to 10 per cent of the dispersion term. This results in a decrease of the interaction energy, computed as a sum of the SCF and dispersion components, by 6 to 30 per cent for interatomic distances ranging from 10 to 7 bohrs.

Simplified formulae for estimating the exchange dispersion energy in the interaction of larger systems are also proposed and their accuracy is discussed.

Key words: Exchange perturbation theory–Weak intermolecular interactions

1. Introduction

For many years there has been considerable interest in perturbation theory treatments of weak interatomic or intermolecular interactions. In the long-range region the interaction energy has been calculated by employing the Rayleigh–Schrödinger perturbation theory combined usually with an extensive use of multipole expansion [1], whereas the short-range repulsive part of the interaction potential has been obtained by using the first-order perturbation procedure devised by Heitler and London [2]. The symmetry-adapted perturbation theory developed in the late sixties [3] provided a theoretical justification for the above treatment and indicated a systematic way to obtain more accurate values of the interaction theory. However, it was recognized early that there is no unique method of forcing the symmetry within the framework of perturbation theory. In fact very many symmetry-adapted perturbation expansions have been proposed to date [3]. Among them the Murrell–Shaw [4] and Musher–Amos [5] (MSMA) expansion has won the greatest popularity [6–12], because of its simplicity and clear physical interpretation of the low-order energy contributions. The numerical calculations for model systems such as H_2^+ [13, 14] or H_2 [15] show that the MSMA expansion truncated after the second order duplicates the depth of the van der Waals well with an error of less than 1%. It should be stressed that this accuracy can be obtained only if the second-order exchange contribution to the interaction energy, $E^{(2)}_{\mathrm{exch}}$, is taken into account. The exchange polarization energy, $E_{\mathrm{exch\text{-}pol}}$, introduced in 1965 by Murrell, Randić and Williams [16] is the main, "single-exchange" part of $E^{(2)}_{\mathrm{exch}}$. In the region of the van der Waals minimum the multiple electron exchanges do not play an appreciable role and the $E_{\mathrm{exch\text{-}pol}}$ represents more than 99.9% of $E^{(2)}_{\mathrm{exch}}$ [13, 17]. It is worthwhile to remark that the exchange polarization energy is not related to the MSMA theory alone. It also represents an overwhelming part of the second-order energies arising in the Hirschfelder–Silbey and Hirschfelder–van der Avoird theories [13] and can be identified in many van Vleck type perturbation formalisms [3, 15] based on the Rayleigh–Ritz variational principle. It appears that among the many second- and higher-order exchange terms that have been generated by the symmetry-adapted perturbation theory, the exchange polarization energy alone needs to be calculated in order to obtain a quantitatively correct description of the interaction energy in the van der Waals minimum region [13–15].

Since the exchange polarization energy is much more difficult to calculate than the other first- and second-order contributions to the energy, it has been calculated up to this time only for the interaction of one- and two-electron systems [13–15, 17]. Perturbational studies of the interaction energy for larger systems such as rare gas atoms [18–20] or water molecules [21] have neglected this quantity, assuming that it is small as compared to other components of the interaction energy. The validity of such a treatment can be justified only by establishing the actual significance of the exchange polarization energy in building up the total interaction energy.

Another reason for being interested in the exchange polarization interaction is that it has been invoked to explain some physical phenomena. It has been argued, for example, that the exchange polarization interaction is responsible for the quenching of the polarization of ions within the alkali halide molecules [22, 23], or that the non-additive three-body part of $E_{\mathrm{exch\text{-}pol}}$ determines the structure of the rare gas crystals [24].

The aim of this paper is to present a method for the evaluation of the exchange polarization energy in the interaction of many-electron closed-shell atoms or molecules. The method neglects the electron correlation within the noninteracting systems, which means that only the first term in a suitable multiple perturbation theory expansion for $E_{\text{exch-pol}}$ is taken into account. This approximation is necessary because the accurate correlated wave functions for many-electron systems are either unknown or so complicated that they cannot be employed in practice. We present the explicit expressions for the calculation of both the induction and the dispersion components of the exchange polarization energy, the latter component being considered in more detail since the exchange dispersion energy, as an intermolecular correlation effect, is not taken into account by the standard Hartree–Fock calculations. These expressions have been derived without invoking any particular basis set and can be evaluated in practice by using arbitrary one-electron or explicitly correlated basis functions.

The practical applicability of our method is illustrated by numerical calculations of the interaction energy of two ground-state beryllium atoms. This system has recently been the subject of growing interest [25–28]. However, most studies that have been performed thus far have been based on the first-order [25], or the Hartree–Fock approach and, except in the case of very large interatomic distances [29–32], little has been known about those components of the interaction energy which are due to the electron correlation [27].

Our calculations are also aimed at explaining the role that particular electronic shells play in the exchange dispersion interaction and at testing approximate formulae that can be used to estimate the exchange dispersion energy in the interaction of larger systems.

2. Method

Let us consider the interaction of two ground-state closed-shell atoms or molecules, denoted below by A and B. The total spin-free Born–Oppenheimer Hamiltonian H of the interacting systems can be divided most naturally in the following way

$$H = H_0 + V, \tag{1}$$

where $H_0 = H_A + H_B$ is the sum of the Hamiltonians of the free systems and V is the interaction operator collecting the Coulombic interactions between the electrons and the nuclei of system A on the one hand, and those of system B on the other. For our purposes it is convenient to express V through a generalized two-electron potential $v(ij)$

$$V = \sum_{i \in A} \sum_{j \in B} v(ij). \tag{2}$$

The explicit form of $v(ij)$ depends on the nuclear framework of the total system. For the interaction of two neutral atoms we have

$$v(ij) = R^{-1} - r_{Aj}^{-1} - r_{Bi}^{-1} + r_{ij}^{-1}, \tag{3}$$

where R is the internuclear separation and r_{Aj}, r_{Bi} and r_{ij} are distances between the nuclei and electrons specified by the subscripts A, B, j and i. The ground-state eigenfunction of H_0 is

$$\Phi_0 = \Phi_A \cdot \Phi_B, \tag{4}$$

where Φ_A and Φ_B are the ground-state eigenfunctions of H_A and H_B corresponding to the energies E_A and E_B respectively.

The expression defining the exchange polarization energy can now be written in the form [16, 33]

$$E_{\text{exch-pol}} = \langle \Phi_A \Phi_B | (V - \langle V \rangle)(\mathscr{P} - \langle \mathscr{P} \rangle) | \Phi_{\text{pol}}^{(1)} \rangle \tag{5}$$

where

$$\mathscr{P} = -\sum_{i \in A} \sum_{j \in B} P_{ij}$$

is the sum of the permutation operators P_{ij} interchanging the coordinates of the ith and jth electrons, $\langle V \rangle$ and $\langle \mathscr{P} \rangle$ are the expectation values of V and $\mathscr{P}$ calculated with the function Φ_0, and $\Phi_{\text{pol}}^{(1)}$ is the first-order polarization function [34] defined as the only solution to the equation

$$(H_A + H_B - E_A - E_B)\Phi_{\text{pol}}^{(1)} = -(V - \langle \Phi_0 | V | \Phi_0 \rangle)\Phi_0 \tag{6}$$

satisfying the symmetry requirements and the orthogonality condition

$$\langle \Phi_0 | \Phi_{\text{pol}}^{(1)} \rangle = 0.$$

For a simple derivation of formula (5) the reader is referred to Ref. [33].

For the interaction of many-electron systems the solution of Eq. (6) as well as the evaluation of expression (5) by using the accurate correlated wave-functions Φ_A and Φ_B is impossible for the present because these functions are either unknown or too complicated to be handled in practice. Therefore, we are forced to neglect the intra-atomic or intra-molecular correlation. This can be accomplished by employing the multiple perturbation theory formalism [21] based on the Møller–Plesset decomposition [35, 36] of the Hamiltonians H_A and H_B:

$$H_X = H_X^{(0)} + W_X, \quad X = A \text{ or } B, \tag{7}$$

where $H_X^{(0)}$ is the sum of the Fock operators for the system X

$$H_X^{(0)} = \sum_{i \in X} h^X(i), \quad X = A \text{ or } B \tag{8}$$

and W_X is the difference between H_X and $H_X^{(0)}$. Using the decomposition (7) and applying the usual Rayleigh–Schrödinger perturbation theory one can express the functions Φ_A, Φ_B and $\Phi_{\text{pol}}^{(1)}$ as sums of an infinite number of perturbation corrections due to the perturbations W_A and W_B.

$$\Phi_X = \sum_{n=0}^{\infty} \Phi_X^{(n)} \quad \text{for } X = A \text{ or } B \tag{9}$$

and

$$\Phi_{\text{pol}}^{(1)} = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \Phi_{\text{pol}}^{(1nm)} \tag{10}$$

where, e.g. the correction $\Phi_{\text{pol}}^{(1nm)}$ is of the first order with regard to the perturbation V, and of the nth and mth order with regard to the perturbations W_A and W_B, respectively. The zeroth-order term, $\Phi_X^{(0)}$, in the expansion (9) is the normalized closed-shell determinant constructed from the Hartree–Fock orbitals:

$$\Phi_{\mathrm{X}}^{(0)}=(N_{\mathrm{X}}!)^{1/2}\mathscr{A}_{\mathrm{X}}\prod_{k\in\mathrm{X}}\varphi_k(k), \tag{11}$$

where N_{X} is the number of electrons in the system X, $\mathscr{A}_{\mathrm{X}}$ is the idempotent antisymmetrizer for the electrons belonging to this system and φ_k, $k=1, 2,\ldots, N_{\mathrm{A}}+N_{\mathrm{B}}$ is the set of all occupied Hartree–Fock spin orbitals for the noninteracting systems. We assume that the electrons and spin orbitals of the system A are numbered by $1, 2,\ldots, N_{\mathrm{A}}$ and those of the system B by $N_{\mathrm{A}}+1$, $N_{\mathrm{A}}+2,\ldots, N_{\mathrm{A}}+N_{\mathrm{B}}$. Then, "$k\in\mathrm{A}$" means that $k=1,2,\ldots,N_{\mathrm{A}}$ and "$k\in\mathrm{B}$" means that $k=N_{\mathrm{A}}+1, N_{\mathrm{A}}+2,\ldots, N_{\mathrm{A}}+N_{\mathrm{B}}$. The leading term in the expansion (10) is the "Hartree–Fock polarization function", $\Phi_{\mathrm{pol}}^{(100)}$, defined by the equation

$$(H_{\mathrm{A}}^{(0)}+H_{\mathrm{B}}^{(0)}-E_{\mathrm{A}}^{(0)}-E_{\mathrm{B}}^{(0)})\Phi_{\mathrm{pol}}^{(100)}=-(V-\langle\Phi_0^{(0)}|V|\Phi_0^{(0)}\rangle)\Phi_0^{(0)}, \tag{12}$$

where $E_{\mathrm{A}}^{(0)}$ and $E_{\mathrm{B}}^{(0)}$ are the sums of orbital energies for the systems A and B respectively, and $\Phi_0^{(0)}=\Phi_{\mathrm{A}}^{(0)}\Phi_{\mathrm{B}}^{(0)}$. To make a solution of Eq. (12) unique, the orthogonality condition $\langle\Phi_0^{(0)}|\Phi_{\mathrm{pol}}^{(100)}\rangle=0$ must also be imposed.

Inserting (9) and (10) into (5) one obtains the triple perturbation theory expansion for $E_{\text{exch-pol}}$, the leading term of which is

$$E_{\text{exch-pol}}^{(200)}=\langle\Phi_{\mathrm{A}}^{(0)}\Phi_{\mathrm{B}}^{(0)}|(V-\langle V\rangle)(\mathscr{P}-\langle\mathscr{P}\rangle)|\Phi_{\mathrm{pol}}^{(100)}\rangle, \tag{13}$$

where the expectation values $\langle V\rangle$ and $\langle\mathscr{P}\rangle$ are now calculated with the function $\Phi_0^{(0)}$. The role of the terms proportional to $\langle V\rangle$ and $\langle\mathscr{P}\rangle$ is to cancel unlinked clusters appearing when the matrix element $\langle\Phi_{\mathrm{A}}^{(0)}\Phi_{\mathrm{B}}^{(0)}|V\mathscr{P}|\Phi_{\mathrm{pol}}^{(100)}\rangle$ is expanded in terms of eigenfunctions of the operators h^{A} and h^{B}.

Making use of the spectral expansion of the operator $H_{\mathrm{A}}^{(0)}+H_{\mathrm{B}}^{(0)}$ it is not difficult to show that the solution to Eq. (12) can be written in the following form

$$\Phi_{\mathrm{pol}}^{(100)}=\Phi_{\mathrm{A}}^{(0)}\cdot\Phi_{\mathrm{B}}^{\mathrm{ind}}+\Phi_{\mathrm{A}}^{\mathrm{ind}}\cdot\Phi_{\mathrm{B}}^{(0)}+\Phi_{\mathrm{AB}}^{\mathrm{disp}}, \tag{14}$$

where

$$\Phi_{\mathrm{X}}^{\mathrm{ind}}=(N_{\mathrm{X}}!)^{1/2}\sum_{k\in\mathrm{X}}\mathscr{A}_{\mathrm{X}}f_k^{\mathrm{X}}(k)\prod_{\substack{p\in\mathrm{X}\\p\neq k}}\varphi_p(p),\quad \mathrm{X}=\mathrm{A}\text{ or }\mathrm{B} \tag{15}$$

$$\Phi_{\mathrm{AB}}^{\mathrm{disp}}=(N_{\mathrm{A}}!N_{\mathrm{B}}!)^{1/2}\sum_{k\in\mathrm{A}}\sum_{l\in\mathrm{B}}\mathscr{A}_{\mathrm{A}}\mathscr{A}_{\mathrm{B}}\bar{u}_{kl}(kl)\prod_{p\neq k,l}\varphi_p(p). \tag{16}$$

The one- and two-electron functions f_k^{X} and $\bar{u}_{kl}$, referred to below as induction and disperson pair functions respectively are uniquely defined by Eqs (14)–(16), provided that the following orthogonality constraints are imposed

$$\int\varphi_k^*(1)f_l^{\mathrm{X}}(1)\,d\tau_1=0, \tag{17}$$

$$\int\varphi_k^*(1)\bar{u}_{lm}(12)\,d\tau_1=\int\varphi_l^*(2)\bar{u}_{mk}(12)\,d\tau_2=0, \tag{18}$$

for k and l belonging to the same system. By substituting Eqs. (14), (15) and (16) into Eq. (12), multiplying both sides of the resulting equation by the product of all spinorbitals except for φ_k and integrating over the coordinates of $N_{\mathrm{A}}+N_{\mathrm{B}}-1$

electrons one can easily find that the functions $\bar{f}_k^{\mathrm{X}}$ satisfy the equation

$$[h^{\mathrm{X}}(i)-e_k^{\mathrm{X}}]\,\bar{f}_k^{\mathrm{X}}(i)=-P_{\mathrm{X}}(i)\omega^{\mathrm{Y}}(i)\varphi_k(i), \tag{19}$$

where $\mathrm{X}=\mathrm{A}$, $\mathrm{Y}=\mathrm{B}$ or $\mathrm{Y}=\mathrm{A}$, $\mathrm{X}=\mathrm{B}$, e_k^{X} is the orbital energy corresponding to the kth spinorbital, P_{X} is a projection operator that projects out of the occupied space

$$P_{\mathrm{X}}=1-\sum_{k\in\mathrm{X}}|\varphi_k\rangle\langle\varphi_k|, \quad \mathrm{X}=\mathrm{A} \text{ or } \mathrm{B} \tag{20}$$

and $\omega^{\mathrm{X}}(i)$ is the electrostatic potential of the system X:

$$\omega^{\mathrm{X}}(i)=\sum_{k\in\mathrm{X}}\int v(ij)\varphi_k^*(j)\varphi_k(j)\,d\tau_j, \quad \mathrm{X}=\mathrm{A} \text{ or } \mathrm{B}. \tag{21}$$

Similarly, the dispersion pair function $\bar{u}_{kl}$ satisfies the equation

$$[h^{\mathrm{A}}(1)+h^{\mathrm{B}}(2)-e_k^{\mathrm{A}}-e_l^{\mathrm{B}}]\bar{u}_{kl}(12)=-P_{\mathrm{A}}(1)P_{\mathrm{B}}(2)v(12)\varphi_k(1)\varphi_l(2) \tag{22}$$

Since for closed-shell systems P_{X} is in essence a spin-free operator the spin part of $\bar{u}_{kl}$ is the same as the spin part of the product $\varphi_k\cdot\varphi_l$ and the space part of $\bar{u}_{kl}$, denoted by u_{kl}, satisfies an equation identical to Eq. (22) except that the spinorbitals are replaced by their orbital parts. A similar result holds for the space part of $\bar{f}_k^{\mathrm{X}}$ denoted by f_k^{X}. The function u_{kl} can be interpreted as a result of the dispersion interaction of an electron occupying the kth orbital with that occupying the lth orbital. The overall effect of the dispersion interaction is given by the function $\Phi_{\mathrm{AB}}^{\mathrm{disp}}$ of Eq. (14). The sum of the remaining two terms in Eq. (14), denoted by $\Phi_{\mathrm{AB}}^{\mathrm{ind}}$ corresponds to the induction interaction and is interpreted as an effect of the mutual polarization of the interacting systems by their static electric fields. This interaction is very important when the interacting systems have large permanent multipole moments. However, at smaller distances, even for the interaction of spherically symmetric atoms the induction interaction may account for a considerable portion of the interaction energy [37].

When inserted into (13), formula (14) leads to the following decomposition of the exchange polarization energy

$$E_{\text{exch-pol}}^{(200)}=E_{\text{exch-ind}}^{(200)}(\mathrm{A}\rightarrow\mathrm{B})+E_{\text{exch-ind}}^{(200)}(\mathrm{A}\leftarrow\mathrm{B})+E_{\text{exch-disp}}^{(200)} \tag{23}$$

where the first term in (23) corresponds to the first term in (14) etc. The sum of the first two terms in (23), hereafter denoted by $E_{\text{exch-ind}}^{(200)}$ is the exchange induction energy and is interpreted as a result of the antisymmetrization of the wave function deformed previously by the induction interaction [38]. The third term $E_{\text{exch-disp}}^{(200)}$, is the exchange dispersion energy resulting from the antisymmetrization of the corrections to the wave function due to the dispersion interaction [33]. The explicit expressions for $E_{\text{exch-ind}}^{(200)}$ and $E_{\text{exch-disp}}^{(200)}$ can be obtained by substituting Eqs. (14), (15) and (16) into Eq. (13) and performing all possible integrations. The result, which is a rather complicated one, can be written in a transparent form by using the following cluster expansion

$$E=\sum_i\sum_j \varepsilon_{ij}^{\mathrm{AB}}+\sum_{i<k}\sum_j \varepsilon_{ikj}^{\mathrm{AAB}}+\sum_i\sum_{j<l}\varepsilon_{ijl}^{\mathrm{ABB}}+\sum_{i<k}\sum_{j<l}\varepsilon_{ikjl}^{\mathrm{AABB}} \tag{24}$$

where, for instance, the symbol $\varepsilon_{ikj}^{\mathrm{AAB}}$, indicates that the corresponding three-orbital contribution depends only on the *i*th and *k*th orbitals of system A, *j*th orbital of system B and on the pair functions describing the dispersion interaction between these orbitals. The contributions $\varepsilon_{ikj}^{\mathrm{AAB}}$, $\varepsilon_{ijl}^{\mathrm{ABB}}$ and $\varepsilon_{ikjl}^{\mathrm{AABB}}$ are defined to be symmetric with regard to the interchange of indices i and k or j and l and can be obtained by symmetrization of the corresponding primitive quantities, denoted by $\tilde{\varepsilon}$. For instance:

$$\varepsilon_{ikj}^{\mathrm{AAB}}=\tilde{\varepsilon}_{ikj}^{\mathrm{AAB}}+\tilde{\varepsilon}_{kij}^{\mathrm{AAB}}$$

or

$$\varepsilon_{ikjl}^{\mathrm{AABB}}=\tilde{\varepsilon}_{ikjl}^{\mathrm{AABB}}+\tilde{\varepsilon}_{kijl}^{\mathrm{AABB}}+\tilde{\varepsilon}_{iklj}^{\mathrm{AABB}}+\tilde{\varepsilon}_{kilj}^{\mathrm{AABB}}$$

The explicit expressions for the many-orbital contributions to $E_{\text{exch-disp}}^{(200)}$, denoted by e_{ij}^{AB}, $e_{ikj}^{\mathrm{AAB}}, \ldots$, etc. ($\varepsilon \equiv \mathrm{e}$), are as follows

$$\begin{aligned} e_{ij}^{\mathrm{AB}}= & -2\langle u_{ij}|v_{12}|b_j a_i\rangle \\ & -2\langle u_{ij}b_j|v_{23}(1+P_{23})|b_j b_j a_i\rangle-2\langle u_{ij}a_i|v_{13}(1+P_{13})|a_i a_i b_j\rangle \\ & -2\langle u_{ij}a_i|v_{32}|b_j b_j a_i\rangle S_{ij}-2\langle u_{ij}b_j|v_{13}|a_i a_i b_j\rangle S_{ij} \\ & +6\langle u_{ij}|v_{12}|a_i b_j\rangle S_{ij}^2+6\langle u_{ij}|b_j a_i\rangle\langle a_i b_j|v_{12}|a_i b_j\rangle \end{aligned} \tag{25}$$

$$\begin{aligned} \tilde{e}_{ikj}^{\mathrm{AAB}}= & 2\langle u_{ij}a_k|v_{13}(2-P_{13})|a_i a_k b_j\rangle-2\langle u_{ij}a_k|v_{13}(2-P_{12})|a_i a_k b_j\rangle \\ & +2\langle u_{ij}a_k b_j|v_{34}(2+P_{23})|b_j a_i a_k b_j\rangle \\ & +2\langle u_{ij}a_k b_j|v_{12}(2+P_{14})|a_i b_j b_j a_k\rangle \\ & +2\langle u_{ij}a_k b_j|v_{14}(2-P_{12})|a_i a_k b_j b_j\rangle \\ & +2\langle u_{ij}a_k b_j|v_{32}(2-P_{34})|b_j b_j a_k a_i\rangle \end{aligned} \tag{26}$$

and

$$\begin{aligned} \tilde{e}_{ikjl}^{\mathrm{AABB}}= & -2\langle u_{ij}a_k b_l|v_{12}(1-2P_{12}-2P_{34}+4P_{12}P_{34})|b_j b_l a_i a_k\rangle \\ & -2\langle u_{ij}a_k b_l|v_{14}(1-2P_{12}-2P_{34}+4P_{12}P_{34})|a_k a_i b_l b_j\rangle \\ & -2\langle u_{ij}a_k b_l|v_{34}(1-2P_{14}-2P_{23})|b_l a_k a_i b_j\rangle \\ & -2\langle u_{ij}a_k b_l|v_{12}(1-2P_{14}-2P_{23})|a_k b_l b_j a_i\rangle \end{aligned} \tag{27}$$

where the occupied orbitals of systems A and B are denoted by a_i, a_k and b_j, b_l respectively and $S_{ij}=\langle a_i|b_j\rangle$. While writing down the formulae (25), (26) and (27) we assumed that all the orbitals and pair functions are real. The corresponding expression for $\tilde{e}_{ijl}^{\mathrm{ABB}}$ can be obtained from (26) by substituting b_l for a_k, $u_{ij}(21)$ for $u_{ij}(12)$ and interchanging a_i and b_j. For the sake of brevity in Eqs. (25), (26) and (27) we used the notation $v_{ij}=v(ij)$. We also omit the arguments of the pair functions and the orbitals assuming that they always occur in the natural order, for example: $u_{ij}a_k b_j=u_{ij}(12)a_k(3)\mathrm{b}_j(4)$ or $a_i b_j b_j a_k=a_i(1)b_j(2)b_j(3)a_k(4)$.

The many-orbital contributions to $E_{\text{exch-ind}}^{(200)}$ (A→B), denoted by p_{ij}^{AB}, $p_{ikj}^{\mathrm{AAB}}, \ldots$, etc. ($\varepsilon \equiv p$), are

$$\begin{aligned} p_{ij}^{\mathrm{AB}} = &-2\langle a_i b_j | v_{12} | f_j^{\mathrm{B}} a_i \rangle - 2\langle a_i b_j | v_{12} | a_i a_i \rangle \langle a_i | f_j^{\mathrm{B}} \rangle \\ &-2\langle a_i b_j | v_{12}(1+P_{12}) | f_j^{\mathrm{B}} b_j \rangle S_{ij} + 6\langle a_i b_j | v_{12} | a_i f_j^{\mathrm{B}} \rangle S_{ij} \\ &+6\langle a_i b_j | v_{12} | a_i b_j \rangle \langle a_i | f_j^{\mathrm{B}} \rangle S_{ij} \end{aligned} \tag{28}$$

$$\begin{aligned} \tilde{p}_{ikj}^{\mathrm{AAB}} = &\,2\langle a_i b_j | v_{12}(1-2P_{12}) | a_k a_i \rangle \langle a_k | f_j^{\mathrm{B}} \rangle \\ &+4\langle a_i b_j | v_{12} | a_i f_j^{\mathrm{B}} \rangle S_{kj}^2 + 2\langle a_i b_j | v_{12} | a_k f_j^{\mathrm{B}} \rangle S_{kj} S_{ij} \\ &+2\langle a_i b_j | v_{12} | a_k b_j \rangle \langle a_k | f_j^{\mathrm{B}} \rangle S_{kj} + 4\langle a_k b_j | v_{12} | a_k b_j \rangle \langle a_i | f_j^{\mathrm{B}} \rangle S_{ij} \end{aligned} \tag{29}$$

$$\begin{aligned} \tilde{p}_{ijl}^{\mathrm{ABB}} = &\,2\langle a_i b_j | v_{12}(1-2P_{12}) | f_j^{\mathrm{B}} b_l \rangle S_{il} \\ &+2\langle a_i b_l | v_{12}(1-2P_{12}) | b_l f_j^{\mathrm{B}} \rangle S_{ij} \\ &+4\langle a_i b_j | v_{12} | a_i f_j^{\mathrm{B}} \rangle S_{ij}^2 + 2\langle a_i b_l | v_{12} | a_i f_j^{\mathrm{B}} \rangle S_{il} S_{ij} \\ &+4\langle a_i b_l | v_{12} | a_i b_l \rangle \langle a_i | f_j^{\mathrm{B}} \rangle S_{ij} + 2\langle a_i b_j | v_{12} | a_i b_l \rangle \langle a_i | f_j^{\mathrm{B}} \rangle S_{il} \end{aligned} \tag{30}$$

and

$$\begin{aligned} \tilde{p}_{ikjl}^{\mathrm{AABB}} = &\,4\langle a_i b_j | v_{12} | a_k f_j^{\mathrm{B}} \rangle S_{kl} S_{il} + 4\langle a_i b_j | v_{12} | a_i b_l \rangle \langle a_k | f_j^{\mathrm{B}} \rangle S_{kl} \\ &-2\langle a_i b_j | v_{12} | a_k b_l \rangle \langle a_k | f_j^{\mathrm{B}} \rangle S_{il} + 4\langle a_i b_l | v_{12} | a_k b_l \rangle \langle a_k | f_j^{\mathrm{B}} \rangle S_{ij} \\ &-2\langle a_i b_l | v_{12} | a_k f_j^{\mathrm{B}} \rangle S_{kl} S_{ij} + 4\langle a_i b_l | v_{12} | a_i f_j^{\mathrm{B}} \rangle S_{kl} S_{kj}. \end{aligned} \tag{31}$$

The expressions for the components of $E_{\text{exch-ind}}^{(200)}$ (A ← B) can easily be obtained from Eqs. (28)–(31) by substituting f_i^{A} for f_j^{B}, v_{21} for v_{12}, and interchanging a_i and b_j as well as a_k and b_l.

It should be stressed that the expressions for e_{ij}^{AB} and p_{ij}^{AB} are identical with the expressions for the exchange dispersion and exchange induction energies in the interaction of two helium-like systems [17]. Therefore the contributions e_{ij}^{AB} and p_{ij}^{AB} can be interpreted as the result of the exchange polarization interaction between the orbital a_i of system A and the orbital b_j of system B. The last three terms in Eq. (24) are responsible for the pair-wise orbital nonadditivity of $E_{\text{exch-pol}}^{(200)}$. The contribution e_{ikj}^{AAB}, for instance, can be defined as a three-orbital pair-wise nonadditive part of the exchange dispersion energy in the interaction between a beryllium-like system, having orbitals a_i and a_k, and a helium-like system described by an orbital b_j. Similarly, e_{ikjl}^{AABB} is defined as a four-orbital contribution to the exchange dispersion interaction of two beryllium-like systems with orbitals a_i, a_k and b_j, b_l.

We think that the many-orbital cluster expansion (24) provides the most convenient way of representing the exchange contributions to the interaction energy. While neglecting two-, three- or four-orbital contributions involving very weakly overlapping orbitals we can obtain well defined and well controlled approximations to the total exchange dispersion or exchange induction effect. Conversely, the accuracy of formula (24) can be systematically improved by allowing for multiple exchanges of electrons occupying strongly overlapping orbitals. This can be done, for example, replacing e_{ij}^{AB} by the quantities which one obtains evaluating accurately the formula (10) of Ref. [17].

It is worthwhile to remark that it is also possible to expand the exchange polarization energy in terms of shells or other subgroups of orbitals. The two-shell contributions are defined directly from Eq. (24) by limiting the running indices to particular shells. The three- and four-shell contributions are defined as follows

$$E^{\mathrm{AAB}}_{KLM} = \sum_{i\in K}\sum_{k\in L}\sum_{j\in M}\varepsilon^{\mathrm{AAB}}_{ikj} + \sum_{i\in K}\sum_{k\in L}\sum_{j,l\in M}\varepsilon^{\mathrm{AABB}}_{ikjl} \tag{32}$$

and

$$E^{\mathrm{AABB}}_{KIMN} = \sum_{i\in K}\sum_{k\in L}\sum_{j\in M}\sum_{l\in N}\varepsilon^{\mathrm{AABB}}_{ikjl} \tag{33}$$

The multi-shell expansion is useful to study how the inner shells influence the exchange polarization interaction.

A minor remark concerning the exchange induction energy is necessary. While deriving Eqs. (28)–(31) we assumed that the induction function formula f_j^{B} was a result of an action of the overall electric field of system A. However, this field can also be considered as a sum of contributions from individual orbitals of system A. This would lead to splitting of f_j^{B} into orbital contributions and consequently to much more complicated many-orbital expansion involving five-orbital terms. We did not pursue this idea because in practical calculations of f_j^{B} it is more convenient to treat the potential ω^{A} as an entity, without expanding it into orbital contributions.

It is interesting to compare our formulae with the expression for the second-order exchange energy derived by van Duijneveldt [6]. It can be shown that van Duijneveldt's results can be obtained from ours provided that:

1. Our induction functions f_i^{A} and f_j^{B} are expanded in terms of the virtual orbitals of systems A and B respectively.
2. Our dispersion pair functions $u_{ij}(12)$ are expanded in terms of the "polarization structures" [33] of the type $a_r(1)b_s(2)$ only.
3. Unlinked cluster terms present in van Duijneveldt's expression are omitted. They appeared because van Duijneveldt neglected in Eq. (5) the normalization term proportional to $\langle\mathscr{P}\rangle$.
4. The charge transfer term of van Duijneveldt's expression is omitted. The charge transfer term of Murrell, Randić and Williams [16] cannot be defined in a basis independent way and should not be considered in a nonempirical theory. The exchange polarization energy by itself allows for the charge transfer interaction because the induction and dispersion functions do contain ionic contributions [21, 33, 37].
5. Two-electron integrals in the denominators of van Duijneveldt's expression are disregarded. This is a consequence of a different procedure of neglecting the intra-atomic correlation used by van Duijneveldt.

It should be stressed that our procedure of calculating the exchange polarization effects gives also, without any additional effort, the induction ($E^{(200)}_{\mathrm{ind}}$), dispersion ($E^{(200)}_{\mathrm{disp}}$) and the first-order exchange ($E^{(100)}_{\mathrm{exch}}$) contributions to the interaction energy. The corresponding expression for $E^{(200)}_{\mathrm{ind}}$ is

$$E^{(200)}_{\text{ind}} = 2\sum_i \langle a_i|\omega^{\text{B}}|f_i^{\text{A}}\rangle + 2\sum_j \langle b_j|\omega^{\text{A}}|f_j^{\text{B}}\rangle \tag{34}$$

while $E^{(200)}_{\text{disp}}$ and $E^{(100)}_{\text{exch}}$ can be conveniently expressed by using formula (24). The three- and four-orbital contributions to $E^{(200)}_{\text{disp}}$ vanish and the two-orbital ones, denoted by d_{ij}^{AB}, are

$$d_{ij}^{\text{AB}} = 4\langle u_{ij}|v_{12}|a_i b_j\rangle \tag{35}$$

The many-orbital components of $E^{(100)}_{\text{exch}}$ can easily be written down using the formulae given in Ref. [39].

3. Numerical Example: Interaction of Two Beryllium Atoms

The solutions of Eqs. (19) and (22) can be approximated in a most effective way by using the variation-perturbation method described in detail in Refs. [21] and [17]. In this method the trial function f_j^{B} is expanded in terms of basis functions localized at both atomic centers. Similarly, u_{ij} is expanded by using not only "polarization structures" $a_r(1)b_s(2)$ but also "ionic-type", $a_r(1)a_s(2)$, $b_r(1)b_s(2)$ and exchange-type", $b_s(1)a_r(2)$, functions [34]. Such a treatment has been shown [33] to be necessary to obtain reliable values of the exchange polarization energy. When the approximate, variationally determined functions f_i^{A}, f_j^{B} and u_{ij} are inserted into the formulae of the preceding section we obtain the numerical approximations to the induction, dispersion, exchange induction and exchange dispersion energies, denoted by $\bar{E}^{(200)}_{\text{ind}}$, $\bar{E}^{(200)}_{\text{disp}}$, $\bar{E}^{(200)}_{\text{exch-ind}}$, $\bar{E}^{(200)}_{\text{exch-disp}}$. Analogously, our value of the first-order energy is denoted by $\bar{E}^{(100)}$. Note that $|\bar{E}^{(200)}_{\text{ind}}|$ and $|\bar{E}^{(200)}_{\text{disp}}|$ are lower bounds to $|E^{(200)}_{\text{ind}}|$ and $|E^{(200)}_{\text{disp}}|$ and that this does not have necessarily to be the case for the exchange induction and exchange dispersion energies.

The basis set used in our calculations consisted of 28 contracted Gaussian functions shown in Table 1. The exponents and the contraction coefficients of two s functions were optimized to obtain the least square fit [40] to the accurate 1s and 2s SCF orbitals [41]. This ensures a faithful representation of the Hartree–Fock orbitals at large distances from the nucleus, which has been shown to be very important to obtain accurate values of the exchange energies [39, 42]. The exponents of p and d polarization functions were optimized to obtain the lowest value of the dispersion energy at $R=8$. It is interesting that these exponents differ markedly from those which one obtains by optimizing the van der Waals constants $C_6^{(200)}$ and $C_8^{(200)}$, i.e. by optimizing $E^{(200)}_{\text{disp}}$ at a very large interatomic distance R.

The numerical results of the individual components of the interaction energy calculated at $R=7$, 8, 9 and 10 a.u. are listed in Table 2. These results have been obtained by using the basis set specified in Table 1 with the exception of the SCF interaction energy, $E^{\text{SCF}}_{\text{int}}$, which has been computed employing the counterpoise method [43] and the basis set of Kołos *et al.* [28].

Our results clearly show that the exchange polarization effects are repulsive and suppress considerable fraction of the interaction energy. However, the attractive induction and dispersion forces are sufficiently strong to make the total interaction energy negative and to stabilize the Be$_2$ system. In fact, we have found that for

Table 1. Gaussian basis set used to represent f_j^A, f_j^B, u_{ij} and the ground-state Hartree–Fock orbitals for beryllium atom. Each function was centred both at nucleus A and at nucleus B. The exponents are given in the reciprocal bohrs

Type of function	Exponents	Contraction coefficients
s	0.229565	−0.345412
	0.232431	0.359649
	0.779701	0.386688
	1.778005	1.293875
	4.610553	1.426972
	18.124920	3.335985
	20.795090	−3.080523
	44.983110	0.833628
s	0.023114	−0.097077
	0.048643	−1.170286
	0.128737	−2.518049
	2.571581	1.516448
	2.935176	−0.853980
	8.637152	0.293200
	29.091680	−0.339087
	35.087120	0.418410
$p_x p_y p_z$	0.09	1.0
$p_x p_y p_z$	0.45	1.0
$d_{xx}\ d_{yy}\ d_{zz}\ d_{xy}\ d_{xz}\ d_{yz}$	0.07	1.0

$R<7$ the interaction energy, computed as a sum of the SCF, dispersion and exchange dispersion components, reveals a broad minimum. We have not examined this minimum in detail because our treatment cannot be expected to be sufficiently accurate in the region [25] where the multiple electron exchanges must be taken into account.

It is interesting to note that the exchange dispersion energy, being an interatomic correlation effect, is for Be_2 much more important than for H_2 [15] or He_2 [17]. This suggests that any reliable treatment of the electron correlation in the interaction of beryllium atoms must take into consideration the exchange dispersion effect.

It should be stressed that the values of the second-order energy contributions given in Table 2 may not be very accurate approximations to $E_{\text{ind}}^{(200)}$, $E_{\text{exch-ind}}^{(200)}$, $E_{\text{disp}}^{(200)}$ and $E_{\text{exch-disp}}^{(200)}$. This results from the incompleteness of our basis set which is lacking for example f functions. Our experience in the interaction of helium atoms suggests, however, that the extension of the basis set should not change the qualitative conclusions of our calculations.

Table 2. Individual components of the interaction energy obtained with neglect of the intra-atomic correlation effects. The energies are expressed in atomic units

	$R=7$	$R=8$	$R=9$	$R=10$
$\bar{E}^{(100)}$	0.3223(−2)	0.1066(−2)	0.3338(−3)	0.9862(−4)
$\bar{E}^{(200)}_{\text{ind}}$	−0.1352(−2)	−0.3279(−3)	−0.7755(−4)	−0.1757(−4)
$\bar{E}^{(200)}_{\text{disp}}$	−0.2955(−2)	−0.1476(−2)	−0.7411(−3)	−0.3802(−3)
$C_6^{(200)}/R^6+C_8^{(200)}/R^8$ $+\bar{C}_{qq}^{(200)}/R^{10}$[a]	−0.4821(−2)	−0.1819(−2)	−0.7925(−3)	−0.3844(−3)
$\bar{E}^{(200)}_{\text{exch-ind}}$	0.8847(−3)	0.2098(−3)	0.4687(−4)	0.9808(−5)
$\bar{E}^{(200)}_{\text{exch-disp}}$	0.3691(−3)	0.1550(−3)	0.5760(−4)	0.1990(−4)
$\bar{E}^{\text{SCF}}_{\text{int}}$	0.1808(−2)	0.5950(−3)	0.1850(−3)	0.5529(−4)
$\bar{E}^{(100)}+\bar{E}^{(200)}_{\text{ind}}$	0.1871(−2)	0.7381(−3)	0.2563(−3)	0.8105(−4)
$\bar{E}^{(100)}+\bar{E}^{(200)}_{\text{ind}}+\bar{E}^{(200)}_{\text{exch-ind}}$	0.2756(−2)	0.9479(−3)	0.3031(−3)	0.9086(−4)
$\bar{E}^{\text{SCF}}_{\text{int}}+\bar{E}^{(200)}_{\text{disp}}+\bar{E}^{(200)}_{\text{exch-disp}}$	−0.7779(−3)	−0.7400(−3)	−0.4985(−3)	−0.3092(−3)
$\bar{E}^{\text{SCF}}_{\text{int}}+\bar{E}^{(200)}_{\text{disp}}$	−0.1147(−2)	−0.8950(−3)	−0.5561(−3)	−0.3291(−3)

[a] $C_6^{(200)}=2.566(+2)$, $C_8^{(200)}=1.044(+4)$ [29], $\bar{C}_{qq}^{(200)}=2.344(+5)$ (this work).

It is somewhat disturbing to notice that the SCF interaction energy, $\bar{E}^{\text{SCF}}_{\text{int}}$, is poorly represented by the sum of the first-order and induction energies. Moreover, the situation gets only worse after adding the repulsive exchange induction contribution. At present it is impossible to resolve whether the large difference between $\bar{E}^{\text{SCF}}_{\text{int}}$ and $\bar{E}^{(100)}+\bar{E}^{(200)}_{\text{ind}}+\bar{E}^{(200)}_{\text{exch-ind}}$ is due to the intra-atomic correlation effects or to the higher-order induction and exchange induction interactions. It is possible that the well-known [44] $2s$–$2p$ quasidegeneracy of Be atom can result in appreciable intra-atomic correlation effects. The comparison of the "Hartree–Fock" van der Waals constants that can be obtained using our procedure, $C_6^{(200)}=256.6$ a.u. and $C_8^{(200)}=10440$ [29] with the accurate ones, $C_6=213.5$, $C_8=9088$ [31], suggests that the intra-atomic correlation correction to $E^{(200)}_{\text{disp}}$ is positive and represents about 20% of this quantity. Further work aimed at explaining the role of intra-atomic correlation effect is clearly necessary

From the practical as well as the interpretational point of view, it is interesting to establish the role which various many-orbital contributions play in the dispersion and the exchange dispersion interactions. The corresponding multi-shell partitioning of $\bar{E}^{(200)}_{\text{disp}}$ and $\bar{E}^{(200)}_{\text{exch-disp}}$ is reported in Table 3. It should be noted that for beryllium atom the electronic shells are identical with the orbitals, consequently the multi-shell contributions can be obtained directly from Eqs. (25), (26), (27) and (35). Since the contributions from d^{AB}_{KK}, e^{AB}_{KK}, e^{AAB}_{KLK}, e^{ABB}_{KKL} and e^{AABB}_{KLKL} are much smaller than 0.01% they are omitted in Table 3. Our results show that both the dispersion and the exchange dispersion energies can be very well approximated by the interaction of outer shells only. Similar conclusions concerning the multi-shell partitioning of the first-order electrostatic and exchange energies for Be_2 have been reported by Bulski [25]. Thus in an approximate treatment we can neglect the inner-shell electrons. Moreover, even if we want to go beyond the outer-shell approximation, we may restrict ourselves to appropriately chosen two- and three-

Table 3. The role of particular multi-shell contributions in the dispersion and exchange dispersion interaction of beryllium atoms. The interatomic distance R is expressed in atomic units

	$R=7$	$R=8$	$R=9$	$R=10$
$100\ d_{LL}^{\mathrm{AB}}/\bar{E}_{\mathrm{disp}}^{(200)}$	99.58	99.66	99.70	99.71
$100\ (d_{KL}^{\mathrm{AB}}+d_{LK}^{\mathrm{AB}})/\bar{E}_{\mathrm{disp}}^{(200)}$	0.42	0.34	0.30	0.29
$100\ e_{LL}^{\mathrm{AB}}/\bar{E}_{\mathrm{exch\text{-}disp}}^{(200)}$	94.91	96.97	98.04	98.70
$100\ (e_{KLL}^{\mathrm{AAB}}+e_{LKL}^{\mathrm{ABB}})/\bar{E}_{\mathrm{exch\text{-}disp}}^{(200)}$	4.73	2.83	1.84	1.22
$100\ (e_{KL}^{\mathrm{AB}}+e_{LK}^{\mathrm{AB}})/\bar{E}_{\mathrm{exch\text{-}disp}}^{(200)}$	0.36	0.20	0.12	0.08
$100\ \bar{e}_{LL}^{\mathrm{AB}}/\bar{E}_{\mathrm{exch\text{-}disp}}^{(200)}$ [a]	109.64	96.90	91.34	88.79

[a] $\bar{e}_{LL}^{\mathrm{AB}}$ is the approximation to e_{LL}^{AB} obtained by calculating only the first term in the right hand side of Eq. (25).

orbital contributions, neglecting entirely the four-orbital ones which are the most difficult and time consuming to evaluate.

It is interesting to observe that a reasonable approximation to e_{ij}^{AB} can be obtained by calculating only the first integral in Eq. (25). This fact, noted previously in Ref. [17] and confirmed by the results of Table 3, shows that the exchange dispersion energy can be estimated qualitatively by using the formula which is as simple as that for the dispersion energy.

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