

DOUBLE-EXCHANGE CONTRIBUTIONS TO THE FIRST-ORDER INTERACTION ENERGY BETWEEN CLOSED-SHELL MOLECULES

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Explicit formulas are presented for the double-exchange first-order interaction energy of two closed-shell molecules. Calculations on He_2 show that the double-exchange terms contribute significantly for $R < 3.5$ au.

For a system consisting of two closed-shell molecules R and T with N^R and N^T electrons, respectively, the total hamiltonian may be written as

$$H = H^0 + U = H^R + H^T + U,$$

where U collects the coulombic interactions between the electrons and nuclei of R on the one hand and those of T on the other hand. A good trial function for the interacting system in its ground state is the anti-symmetrized product $A\phi^0 = A\psi^R\psi^T$ where ψ^R and ψ^T are the ground-state eigenfunctions of H^R and H^T , respectively. In symmetry-adapted perturbation theory the corresponding first-order interaction energy is given by [1]

$$\tilde{U} = \langle A\phi^0 | U | \phi^0 \rangle / \langle \phi^0 | \phi^0 \rangle. \quad (1)$$

In the usual case where only approximations ϕ^R , ϕ^T to the exact eigenfunctions ψ^R , ψ^T are available one may still use this expression to estimate a first-order energy.

Following Murrell et al. [2] \tilde{U} may be decomposed into the classical electrostatic energy, $E_C = \langle \phi^0 | U | \phi^0 \rangle$, and a remainder called the exchange energy by expanding the antisymmetrizer A . One may write

$$A = N(P_0 - P_1 + P_2 \dots), \quad (2)$$

where N is a numerical constant, P_0 is the identity operator and P_1 , P_2 , etc. are sums of operators exchanging one, two, etc. pairs of electrons between the interacting molecules. The P_0 term gives rise to E_C ,

and most of the short-range repulsion energy comes from the P_1 terms.

In refs. [2, 3] it was argued that the P_1 terms in (1) are of the order S^2 , the P_2 terms of the order S^4 , etc. (where S is a typical overlap integral between occupied orbitals on R and T) and hence if the intermolecular overlap is small then terms beyond those arising from P_1 may be neglected. Consequently, explicit formulas for \tilde{U} have so far only been given up to terms of the order S^2 [4, 5]. However, in practice the P_0 and P_1 terms can be of the same magnitude (the latter in fact dominate \tilde{U} at short distances) and while the P_2 terms are an order of S^2 smaller than the P_1 terms it is not clear under what circumstances they are truly negligible. The purpose of this letter is to provide explicit formulas for the P_2 terms in terms of single-determinant MO wavefunctions for the separate molecules. We also present some preliminary results for the He_2 interaction*.

Carrying through the expansion of A in (1) we find

* First-order energies for He_2 have recently also been studied by Block et al. [6] and by Beltrán-López et al. [7]. The partitioning of interaction energies into orders of S^2 has recently been studied by Dacre and McWeeny [8] and by Matsen and Klein [9]. In the spin-free formulation of the latter authors the partitioning is achieved by performing a double coset decomposition of the symmetric group $S^{N^R+N^T}$ with respect to the subgroup $S^{N^R} \otimes S^{N^T}$. There is a one-to-one correspondence between these double cosets and the various terms (P_0 or P_1 or $P_2 \dots$) in our eq. (2).

$$\begin{aligned}\tilde{U} &= \frac{\langle (1-P_1+P_2\dots)\phi^0 | U | \phi^0 \rangle}{\langle (1-P_1+P_2\dots)\phi^0 | \phi^0 \rangle} \\ &= \frac{E_C - \langle P_1 \phi^0 | U | \phi^0 \rangle + \langle P_2 \phi^0 | U | \phi^0 \rangle - \dots}{1 - \langle P_1 \phi^0 | \phi^0 \rangle + \langle P_2 \phi^0 | \phi^0 \rangle - \dots} \\ &= E_C + \frac{-\langle P_1 \phi^0 | U - E_C | \phi^0 \rangle + \langle P_2 \phi^0 | U - E_C | \phi^0 \rangle - \dots}{1 - \langle P_1 \phi^0 | \phi^0 \rangle + \langle P_2 \phi^0 | \phi^0 \rangle - \dots} \\ &\equiv E_C + \frac{X_1 + X_2 + \dots}{1 + S_1 + S_2 + \dots}.\end{aligned}\quad (3)$$

In the next step we use the explicit form of P_1 and P_2 , viz.,

$$P_1 = \sum_i \sum_k P_{ik} \quad \text{and} \quad P_2 = \sum_{i<j} \sum_{k<l} P_{ik} P_{jl},$$

where i and j are electrons on R and k and l are electrons on T. Inserting $\phi^0 = \phi^R \phi^T$, with $\phi^R = |\bar{r}\bar{r}'\bar{r}''\bar{r}'''\dots\rangle$ and $\phi^T = |\bar{t}\bar{t}'\bar{t}''\bar{t}'''\dots\rangle$ one finds after some tedious algebra (a detailed derivation of S_1 and X_1 may be found in [10]; the derivation of S_2 and X_2 is similar but more involved):

$$S_1 = -\langle P_1 \phi^0 | \phi^0 \rangle = -2 \sum_t \sum_r S_{rt}^2, \quad (4)$$

$$\begin{aligned}S_2 &= \langle P_2 \phi^0 | \phi^0 \rangle \\ &= \sum_{t'} \sum_{r'} \sum_t \sum_r S_{r't'} S_{rt} \{2S_{r't'} S_{rt} - S_{r't'} S_{r't'}\},\end{aligned}\quad (5)$$

$$\begin{aligned}X_1 &= -\langle P_1 \phi^0 | U - E_C | \phi^0 \rangle \\ &= -2 \sum_t \sum_r \{ (S_{rt} V^T | \rho_{rt}^R) + (\rho_{rt}^T | S_{rt} V^R) + (\rho_{rt}^T | \rho_{rt}^R) \},\end{aligned}\quad (6)$$

$$\begin{aligned}X_2 &= \langle P_2 \phi^0 | U - E_C | \phi^0 \rangle = 2 \sum_{t'} \sum_{r'} \sum_t \sum_r \{ S_{r't'} S_{rt} \\ &\times [\langle V^T | 2\rho_{r't'}^R S_{rt} - \rho_{r't'}^R S_{rt} \rangle + \langle V^R | 2\rho_{r't'}^T S_{rt} - \rho_{r't'}^T S_{rt} \rangle] \\ &+ \langle S_{r't'} \rho_{r't'}^R + S_{r't'} \rho_{r't'}^R | 2S_{rt} \rho_{r't'}^T - \rho_{r't'}^T S_{rt} \rangle \}.\end{aligned}\quad (7)$$

In these expressions the summations over r and r' run over all occupied space orbitals of R. Similarly, the summations over t and t' are over the occupied space orbitals of T. The quantities V^T and V^R represent the potential energy of an electron in the field of T and R, respectively:

$$V^T(1) = 2 \sum_t \int [t(k)]^2 r_{1k}^{-1} d\tau_k - \sum_\nu Z_\nu r_{1\nu}^{-1}, \quad (8)$$

$$V^R(1) = 2 \sum_r \int [r(i)]^2 r_{i1}^{-1} d\tau_i - \sum_\mu Z_\mu r_{1\mu}^{-1},$$

where the summations over μ and ν run over the nuclei of R and T. (The respective nuclear charges are Z_μ and Z_ν .) The quantities ρ_{rt}^R and ρ_{rt}^T have been called [2] overlap transition densities. They are defined by

$$\rho_{rt}^R(1) = t(1)r(1) - \sum_{r'} S_{r't'} r'(1)r(1), \quad (9)$$

$$\rho_{rt}^T(1) = r(1)t(1) - \sum_{r'} S_{r'r'} t'(1)t(1).$$

A simple example to which we have applied these formulas is that of two interacting He atoms where A does not contain higher exchanges than the double exchange $P_2 = P_{13} P_{24}$. Using Slater determinants $|1s^R(1)1s^R(2)|$ and $|1s^T(3)1s^T(4)|$ to describe the unperturbed atoms and using an expansion of the 1s Hartree-Fock AO as a sum of ten 1s gaussians [11] we obtained the results shown in table 1*.

As noted above, X_1 dominates \tilde{U} at short distances, and in fact since E_C for He₂ merely arises from penetration, X_1 here remains the largest contribution even at long distances. Thus X_1 cannot be treated as being an order of S^2 smaller than E_C . By contrast, X_2 is an order of S^2 smaller than X_1 at all distances ($X_2 \approx 0.7 S_1 X_1$) and its contribution to \tilde{U} is less than 1% from $R = 3.5$ onwards. Likewise, the S_1 contribution to the denominator of (3) is negligible from $R = 3.5$ au onwards, while the S_2 contribution is already small at $R = 2.0$ au. Thus for $R > 3.5$ au one has $\tilde{U} \approx E_C + X_1$, which is the expression employed

* The calculations were performed on an IBM 360/65 (IBM Computing Centre, Rijswijk) using a special version of Clementi and Veillard's IBMOL-4 program.

Table 1.
Break-down of the first-order interaction energy \tilde{U} for He₂ a)

	R (au)		
	2.0	4.0	6.0
S_1	-1.95931 (-1)	-3.632(-3)	-3.9(-5)
S_2	9.597 (-3)	3 (-6)	≈(-10)
EC	-3180.57	-28.333	-0.169
X_1	16204.72	175.506	1.120
X_2	-1996.17	-0.455	-0.000
\tilde{U}	14281.81	147.356	0.951
ΔE b)	15050.41	147.466	1.108

a) In this case $S_1 = 2S^2$, $S_2 = S^4$ where $S = \int 1s^R 1s^T d\tau$.
Energies in units 10^{-5} au.

b) ΔE is a first-order interaction energy comparable to \tilde{U} (see text).

by Murrell and Shaw [12] in the region $R \geq 4.0$ au. Contrary to what one might expect this expression underestimates \tilde{U} at shorter distances.

The last column of table 1 contains values (for the same 1Cs basis set) of the alternative first-order energy ΔE , defined as $\langle H \rangle_{\phi_0} - \langle H^R \rangle_{\phi_R} - \langle H^T \rangle_{\phi_T}$. This quantity can be obtained routinely in SCF calculations on interacting systems, but it has been emphasized that ΔE and \tilde{U} are very different for approximate ϕ^R , ϕ^T [1, 13]. By contrast, we find ΔE to be nearly equal to \tilde{U} at all distances. As we will show elsewhere, this arises because the difference between ΔE and \tilde{U} is approximately equal to $\langle P_1 \phi^0 | H^0 - \langle \phi^0 | H^0 | \phi^0 \rangle | \phi^0 \rangle$ and this integral is rigorously zero if Hartree-Fock

wavefunctions are used for R and T. Further calculations on He₂ and Ne₂ are in progress and will be published elsewhere.

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