

## LETTER TO THE EDITOR

### CALCULATION OF THE ENERGY EXPRESSION IN CASE OF A WAVE FUNCTION BUILT UP FROM TWO ELECTRON ORBITS

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The wave function of a system is built up by the HLSP and LCAO methods from one electron orbitals. In principle, however, also many electron orbitals may be used as building units. The use of two-electron orbitals has been primarily suggested by FOX [1]. In the case examined by him, two electron orbitals are symmetric in the space coordinates. Then the whole wave function can be written as the linear combination of determinants. The energy expression for a wave function of this type has been derived by HURLEY LENNARD-JONES and POPLE [2].

By us the wave function of the system is built up from antisymmetric two electron orbitals  $\psi(1|2)$  i. e.

$$\psi(1|2) = -\psi(2|1).$$

Here also the spin coordinates are included in the arguments. Let us assume that :

1. the number  $N$  of the electrons of the system is even ;
2. The wave function of the system can be approximated as the product of  $\frac{N}{2}$  two electron functions :

$$\psi_1(1|2) \psi_2(3|4) \psi_3(5|6) \dots \psi_{\frac{N}{2}}(N-1|N).$$

By the Pauli principle it is required to antisymmetrize this product :

$$\Phi = C \sum_P (-1)^P P \psi_1(1|2) \dots \psi_i(\kappa|\lambda) \dots \psi_j(\mu|\nu) \dots \psi_{\frac{N}{2}}(N-1|N). \quad (1)$$

Here  $C$  is the normalization factor, whereas  $P$  signifies those permutations by which electrons are interchanged between the individual two electron orbitals. We have to sum over these. (Permutations by which electrons are interchanged within the individual two electron orbitals should not be con-

sidered, since two electron orbitals are already antisymmetrical in themselves.)

In our case  $\frac{N!}{2^2}$  different permutations exist.

For the sake of further simplification of computations let us assume that the two electron orbitals are orthonormalized, i. e.

$$\begin{aligned} \int \psi_i^*(1|2) \psi_i(1|2) d\tau_1 d\tau_2 &= 1, \\ \int \psi_i^*(1|\kappa) \psi_i(1|\lambda) d\tau_1 &= 0, \quad \text{if } i \neq j. \end{aligned} \quad (2)$$

Considering these, we obtain from the condition  $\int \Phi^* \Phi d\tau = 1$ , that

$$C = \frac{2^{\frac{N}{2}}}{\sqrt{N!}}. \quad (3)$$

If mean values of physical quantities (energy, dipolmomentum, diamagnetic susceptibility etc.) should be determined, then it is advisable to produce the density matrices  $\Gamma^\nu$  of  $\Phi$ :

$$\begin{aligned} \Gamma^\nu(1' 2' \dots \nu' | 12 \dots \nu) &= \binom{N}{\nu} \int \Phi^*(1' 2' \dots \nu' \nu + 1 \dots N) \Phi(12 \dots \nu \dots \\ &\dots N) d\tau_{\nu+1} \dots d\tau_N. \end{aligned} \quad (4)$$

By using these, the physical quantities can be easily computed. If our aim set is the calculation of the energy, then it is sufficient to compute the first and second order density matrices (if we confine ourselves to two-body forces).

Considering formulae (1), (2), (3) and (4) as well as the fact, that operator  $H$  is symmetric in the electron coordinates, the first order density matrix will be the following:

$$\Gamma(1'|1) = 2 \sum_{i=1}^{\frac{N}{2}} \int \psi_i^*(1'|2) \psi_i(1|2) d\tau_2,$$

whereas the second order density matrix:

$$\begin{aligned} \Gamma^2(1' 2' | 12) &= \sum_{i=1}^{\frac{N}{2}} \psi_i^*(1'|2') \psi_i(1|2) + 4 \sum_{1=i < j}^{\frac{N}{2}} \int \{ \psi_i^*(1'|3) \psi_j^*(2'|4) \psi_i(1|3) \psi_j(2|4) - \\ &- \psi_i^*(1'|3) \psi_j^*(2'|4) \psi_i(2|3) \psi_j(1|4) \} d\tau_3 d\tau_4, \end{aligned}$$

and the energy can be written :

$$E = H(0) + \int H(1) \Gamma(1'|1) d\tau_1 + \int H(12) \Gamma^2(1' 2'|12) d\tau_1 d\tau_2.$$

Here  $H(0)$  signifies the part of the Hamilton operator not depending on electron coordinates,  $H(1)$  that one depending only on the coordinates of one electron, whereas  $H(12)$  the part which depends on the coordinates of two electrons.

Let us introduce the following denotations :

$$E_i = 2 \int \psi_i^*(1|2) \left[ H(1) + \frac{1}{2} H(12) \right] \psi_i(1|2) d\tau_1 d\tau_2,$$

$$C_i = \sum_j' \int \psi_i^*(1|3) \psi_j^*(2|4) H(12) \psi_i(1|3) \psi_j(2|4) d\tau_1 d\tau_2 d\tau_3 d\tau_4,$$

$$A_i = \sum_j' \int \psi_i^*(1|3) \psi_j^*(2|4) H(12) \psi_i(2|3) \psi_j(1|4) d\tau_1 d\tau_2 d\tau_3 d\tau_4.$$

( $\sum_j'$  means that the term  $j = i$  should be omitted from the summation).  
As a final result we obtain the following simple formula

$$E = H(0) + \sum_i (E_i + 2C_i - 2A_i).$$

The descriptive meaning of the individual terms is the following :  $E_i$  is the energy of an electron pair being on the  $i$ -th orbit,  $C_i$  is the Coulomb-like interaction energy of one of the electrons on the  $i$ -th orbit with electrons being on other orbits. Whereas  $A_i$  is the exchange energy of one of the electrons on the  $i$ -th orbit with electrons on other orbits.

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#### LITERATURE

1. F. A. FOK, Dokl. Akad. Nauk U.R. S. S., **73**, 735, 1950.
2. A. C. HURLEY, J. LENNARD-JONES and J. A. POPLE, Proc. Roy Soc., **A**, **320**, 446, 1953.