ON THE MATRIX ELEMENTS OF THE HAMILTONIAN BETWEEN SLATER DETERMINANTS

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The rule of the matrix elements formation of the Hamiltonian between Slater determinants was generalized for n-electron molecules.

Introduction

It is well known, that in the configuration-interaction method the zero-order eigenfunction of a molecule with n electrons has to be constructed as the linear combination of the Slater determinants:

$$\varphi = \frac{1}{\sqrt{n!}} \begin{vmatrix} (a\alpha)_1 & \dots & (n\beta)_1 \\ \vdots & & \\ (a\alpha)_n & \dots & (n\beta)_n \end{vmatrix}, \tag{1}$$

where $a, b, c, \dots, n$ mean orbital eigenfunctions, α and β one-particle spin functions and $(a\alpha)_1 = a(1)\alpha(1)$, *etc.* The energy, to the first order, of the system given by the linear combination of all the possible different configurations can be obtained from the roots of the usual secular equation:

$$|H_{ij} - ES_{ij}| = 0, \tag{2}$$

where

$$H_{ij} = \int \varphi_i^* H \varphi_j \, d\tau \quad \text{and} \quad S_{ij} = \int \varphi_i^* \varphi_j \, d\tau . \tag{3}$$

In the work of EYRING, WALTER and KIMBALL [1] one can read about rules for the matrix elements formation of the Hamiltonian between Slater determinants in the case of four-electron molecules. In this work the results obtained by the above mentioned authors will generalized for n-electron molecules. The orbital eigenfunctions of the Slater determinants in terms of the configuration-interaction method agree with each other, the difference between two Slater determinants occurs only in the arrangement of the spin on the orbital functions. Therefore one must consider Slater determinants only containing the same orbital eigenfunctions.

Reduction of the matrix element

Let us assume that the one-electron functions $a, b, \ldots, n$ are mutually orthogonal and let us further consider two arbitrary Slater determinants:

$$\varphi_1 = \frac{1}{\sqrt{n!}} \sum_{\nu} (-1)^{\nu} P_{\nu}^{1} (a\alpha)_1 \ldots (i\alpha)_i \ldots (n\beta)_n, \tag{4}$$

$$\varphi_2 = \frac{1}{\sqrt{n!}} \sum_{\nu'} (-1)^{\nu'} P_{\nu'}^{2} (a\alpha)_1 \ldots (i\beta)_i \ldots (n\alpha)_n, \tag{5}$$

where P_{ν}^{1} and $P_{\nu'}^{2}$ mean permutation operators. The integral $\int \varphi_1^* H \varphi_2 d\tau$ is therefore

$$H_{12} = \frac{1}{n!} \int \Big[\sum_{\nu} (-1)^{\nu} P_{\nu}^{1} (a\alpha)_1 \ldots (i\alpha)_i \ldots (n\beta)_n\Big]^* \times \\ \times H\Big[\sum_{\nu'} (-1)^{\nu'} P_{\nu'}^{2} (a\alpha)_1 \ldots (i\beta)_i \ldots (n\alpha)_n\Big] d\tau. \tag{6}$$

The value of the integral remained unchanged by a new notation of its variables. The new notation of the variables can be accomplished by the inverse operator $(-1)^{\nu}(P_{\nu}^{1})^{-1}$. Let the inverse operator work on all the three factors of the integrand. Due to the symmetry of the Hamiltonian this new notation of the variables does not cause any change. Taking into consideration, that in the first summation the identical permutation operator takes place:

$$(-1)^{\nu}(P_{\nu}^{1})^{-1}(-1)^{\nu} P_{\nu}^{1} = E, \tag{7}$$

one obtains for the first summation

$$\sum (-1)^{\nu}(P_{\nu}^{1})^{-1} (-1)^{\nu} P_{\nu}^{1} (a\alpha)_1 \ldots (i\alpha)_i \ldots (n\beta)_n = \\ = n!(a\alpha_1) \ldots (i\alpha)_i \ldots (n\beta)_n, \tag{8}$$

since there are $n!$ identical terms. If the permutation operator $(-1)^{\nu'} P_{\nu'}^{2}$ in the second summation was running over all the variables in all possible way, the application of the permutation operator $(-1)^{\nu}(P_{\nu}^{1})^{-1}(-1)^{\nu'} P_{\nu'}^{2} = (-1)^{\nu''} P_{\nu''}$ has the same result — maybe — except of order. The matrix element is thus reduced to

$$H_{12} = \int [(a\alpha)_1 \ldots (i\alpha)_i \ldots (n\beta)_n]^* \times \\ \times H\Big[\sum_{\nu''} (-1)^{\nu''} P_{\nu''} (a\alpha)_1 \ldots (i\beta)_i \ldots (n\alpha)_n\Big] d\tau. \tag{9}$$

The matrix elements H_{ii}

We will first focus our attention on the integrals of the type $\int \varphi_i^* H \varphi_i d\tau$. Then Eq. (9) has the following form:

$$H_{11} = \int [(a\alpha)_1 \ldots (i\alpha)_i \ldots (n\beta)_n]^* \times \\ \times H\Big[\sum_{\nu''} (-1)^{\nu''} P_{\nu''} (a\alpha)_1 \ldots (i\alpha)_i \ldots (n\beta)_n\Big] d\tau. \tag{10}$$

It is well known that

$$H = K + L, \tag{11}$$

where

$$K = \sum K_i \quad \text{and} \quad L = \sum L_{ik} \tag{12}$$

$$K_i = -\frac{1}{2}\nabla_i^2 + \sum_{\alpha} \frac{1}{r_{\alpha i}} \quad \text{and} \quad L_{ik} = \frac{1}{r_{ik}}. \tag{13}$$

Owing to Eq. (11), (10) must be studied separately for K and L.

Let us first consider the integral $\int \varphi_1^* K \varphi_1 d\tau$. Its i-th term has the form as follows:

$$\int [(a\alpha)_1 \dots (i\alpha)_i \dots (n\beta)_n]^* \times K_i [\sum_{\nu''} (-1)^{\nu''} P_{\nu''}(a\alpha)_1 \dots (i\alpha)_i \dots (n\beta)_n] d\tau. \tag{14}$$

The identical permutation leaves all the indices unchanged and results the following contribution to the matrix element H_{11}:

$$\begin{aligned} \int (a\alpha)_1^* (a\alpha)_1 d\tau_1 \dots \int (i\alpha)_i^* K_i (i\alpha)_i d\tau_i \times \dots \int (n\beta)_n^* (n\beta)_n d\tau_n = \\ = \int (i\alpha)_i^* K_i (i\alpha)_i d\tau. \end{aligned} \tag{15}$$

All the other permutations change indices and so all the other terms in Eq. (14) will vanish containing mutually orthogonal one-electron functions.

The situation is the same in all other terms of the integral $\int \varphi_1^* K \varphi_1 d\tau$.

Let us next consider the integral $\int \varphi_1^* L \varphi_1 d\tau$. Its term containing the indices i and k has the form as follows:

$$\begin{aligned} \int [(a\alpha)_1 \dots (i\alpha)_i \dots (k\alpha)_k \dots (n\beta)_n]^* \times \\ \times L_{ik} [\sum_{\nu''} (-1)^{\nu''} P_{\nu''}(a\alpha)_1 \dots (i\alpha)_i \dots (k\alpha)_k \dots (n\beta)_n] d\tau. \end{aligned} \tag{16}$$

In Eq. (16) two permutations result effective contribution to the matrix element H_{11}:

1. the identical permutation, with a contribution of

$$\int (i\alpha)_i^* (k\alpha)_k^* L_{ik} (i\alpha)_i (k\alpha)_k d\tau_i d\tau_k; \tag{17}$$

2. the permutation of i, k, with a contribution of

$$-\int (i\alpha)_i^* (k\alpha)_k^* L_{ik} (k\alpha)_i (i\alpha)_k d\tau_i d\tau_k. \tag{18}$$

All the other permutation change indices and so all the other terms in Eq. (16) vanish containing mutually orthogonal one-electron functions.

The situation is the same in all the other terms of the integral $\varphi_1^* L \varphi_1 d\tau$.

The integration in every term means an integration over the orbital variables and a summation regarding the spin variables. Because of the orthogonality of the spin function all terms in Eqs. (15), (17) and (18) vanish except those for which the spins match identically.

In fact, due to Eqs. (15), (17) and (18) the matrix element H_{ii} is the coulombic integral Q minus the sum of all axchange integrals between orbitals having the same spin.

The matrix element H_{ij}

In that case, when the Slater determinant φ_1 differs from φ_2 only in the spin of one orbital function, Eq. (9) has the following form:

$$H_{12} = \int [(a\alpha)_1 \dots \underline{(i\alpha)_i} \dots (n\beta)_n]^* \times H\Big[\sum_{\nu''} (-1)^{\nu''} P_{\nu''}(a\alpha)_1 \dots \underline{(i\beta)_i} \dots (n\beta)_n\Big] d\tau. \quad (19)$$

According to Eq. (15) the result of the identical permutation is now

$$\int (i\alpha)_i^* K_i (i\beta)_i \, d\tau \quad (20)$$

and vanishes because of the orthogonality of the spin functions. In all other terms of the integral $\int \varphi_1^* K \varphi_2 d\tau$ there are terms containing mutually orthogonal one-electron eigenfunctions and as a matter of fact vanish, too.

By the permutation of the indices i and k Eqs. (17) and (18) has the form:

$$\int (i\alpha)_i^* (k\alpha)_k^* L_{ik} (i\beta)_i (k\alpha)_k \, d\tau_i \, d\tau_k, \quad (21)$$

$$-\int (i\alpha)_i^* (k\alpha)_k^* L_{ik} (i\beta)_k (k\alpha)_i \, d\tau_i \, d\tau_k. \quad (22)$$

They will, however, also vanish because of the orthogonality of the spin-functions. All the other terms of the integral $\int \varphi_1^* L \varphi_2 d\tau$ vanish due to the factors containing mutually orthogonal one-electron eigenfunctions.

Finally, let us consider the case, when the Slater determinant φ_1 differs from φ_2 in the spin of two orbital functions. Now, Eq. (9) has the following form:

$$\begin{aligned} &\int [(a\alpha)_1 \dots \underline{(i\alpha)_i} \dots \underline{(k\beta)_k} \dots (n\alpha)_n]^* \times \\ &\times H\Big[\sum_{\nu''} (-1)^{\nu''} P_{\nu''}(a\alpha)_1 \dots \underline{(i\beta)_i} \dots \underline{(k\alpha)_k} \dots (n\alpha)_n\Big] d\tau. \end{aligned} \quad (23)$$

The integral $\int \varphi_1^* K \varphi_2 d\tau$ vanishes again, since the circumstances are the same as in the previous case.

But, now the integral $\int \varphi_1^* L \varphi_2 d\tau$ does not vanish, namely, owing to Eq. (21) it has the following form:

$$-\int (i\alpha)_i^* (k\beta)_k^* L_{ik} (i\beta)_k (k\alpha)_i \, d\tau_i \, d\tau_k, \quad (24)$$

giving a contribution to H_{12}, which is the negative of the exchange integral between two orbitals having the same spin.

If the Slater determinant φ_1 differs from φ_2 in the spin of more then two orbitals, the integral $\int \varphi_1^* H \varphi_2 d\tau$ vanishes on account of the results of the previous cases.

In fact, the rule can be formulated as follows: *The matrix elements H_{ij} between two different Slater determinants are zero unless the Slater determinants differ*

only in the spin of two orbitals and are the negative of the corresponding exchange integrals.

If the one-electron functions $a, b, \ldots, n$ are not orthogonal, many terms in the formulas for the matrix elements of the Hamiltonian do not vanish, and the number of such terms increases almost astronomically as the number of electrons increases. Therefore, it seems to be advantageous to try to set up such orthonormal orbitals, which can be used for molecular calculation. This method was developed by LÖWDIN [2], SLATER [3] and WANNIER [4].

References

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К ПРАВИЛАМ ОБРАЗОВАНИЯ МАТРИЧНЫХ ЭЛЕМЕНТОВ ГАМИЛЬТОНОВА ОПЕРАТОРА МЕЖДУ ОПРЕДЕЛИТЕЛЯМИ СЛЕТЕРА

Ф. Берецц

Обобщается правило образования гамильтонова оператора между определителями *Слетера* для случая молекул с n электронами.