

EXACT EXPRESSION FOR THE FOCK OPERATOR IN THE UNIFIED
COUPLING OPERATOR METHOD

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In the unified coupling operator method [1-5], which is the most general formulation of the restricted Hartree-Fock method for open-shell systems, the following expression is used for the energy functional [4, Eq. (20-II)]:

$$E_{RHF} = 2 \sum_i f_i H_{ii} + \sum_i \sum_j f_i f_j (2a_{ij} J_{ij} - b_{ij} K_{ij}), \quad (1)$$

where a_{ij} and b_{ij} are invariant coefficients characterizing the state (term) under consideration and the configuration, the so-called "vector coupling coefficients" [5]; the f_i are the fractional occupation numbers of the one-electron orbitals φ_i ; H_{ii} , J_{ij} , and K_{ij} are the core, Coulomb, and exchange integrals respectively.

Application of the variational principle to expression (1) with the additional orthonormality conditions $(\varphi_i | \varphi_j) = \delta_{ij}$ leads to the Euler equations [3, 4]

$$\hat{F}_i \varphi_i = \sum_j \varphi_j \theta_{ji}, \quad (2a)$$

$$\theta_{ji} = \theta_{ij}^*, \quad (2b)$$

where the θ_{ji} are undetermined Lagrange multipliers and \hat{F}_i is the Fock operator, for which the following expression is obtained in the literature:

$$\hat{F}_i = f_i \{ \hat{h} + \sum_j f_j (2a_{ij} \hat{J}_j - b_{ij} \hat{K}_j) \} \quad (3)$$

(see, for example, Eqs. (22-11) in [4] and (2.1) in [3]). The coefficients a_{ij} and b_{ij} entering into expressions (1) and (3) form (as was suggested in [4-6]) symmetric matrices: $\|a_{ij}\| = \|a_{ij}\|^T$ and $\|b_{ij}\| = \|b_{ij}\|^T$. (The superscript T indicates transposition.)

The hypothesis that the vector coupling coefficient matrix is symmetric is based [4] on formal symmetry considerations stemming from the form of the energy functional (1): Due to the symmetry of the Coulomb $J_{ij} = J_{ji}$ and exchange $K_{ij} = K_{ji}$ integrals, the coefficients a_{ij} and b_{ij} under the double summation sign in (1) can always be chosen to be symmetric.

On the other hand, in [7, 8] it is shown that in atoms and ions of transition metals with electronic configurations d^N and $p^M d^N$ ($1 \leq N \leq 9$; $1 \leq M \leq 5$), in certain (non-Roothaan) spectroscopic states the indicated matrices should be asymmetric: $\|a_{ij}\| \neq \|a_{ij}\|^T$ and/or $\|b_{ij}\| \neq \|b_{ij}\|^T$. This result follows from analysis of the set of conditions which the energy functional (1) and the Fock operators in form (3) should satisfy in the atomic problem under consideration [7, 8].

As will be shown below, the resulting discrepancy with respect to the (a)symmetry of the coefficients a_{ij} and b_{ij} is fundamental. Bearing this in mind, in this paper we have reconsidered the variational procedure (1)-(3). As the major result, we have obtained a new, more exact expression for the Fock operator, derived from the energy functional (1). We briefly discuss the major consequences of the result obtained, touching on the symmetry of the vector coupling coefficients.

In order to simplify subsequent formulas, let us use the following symbols [4]:

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$$\omega_i = 2f_i; \quad \alpha_{ij} = 2f_i f_j a_{ij}; \quad \beta_{ij} = f_i f_j b_{ij}. \quad (4)$$

Using these symbols, the energy functional (1) has the form

$$E = \sum_i \omega_i H_{ii} + \sum_i \sum_j (\alpha_{ij} J_{ij} - \beta_{ij} K_{ij}), \quad (5)$$

where the integrals J_{ij} and K_{ij} can be expressed in terms of the corresponding Coulomb \hat{J}_i and exchange \hat{K}_i operators [9]:

$$J_{ij} = \langle i | \hat{J}_j | i \rangle = \langle j | \hat{J}_i | j \rangle; \quad (6)$$

$$K_{ij} = \langle ij | ji \rangle = \langle i | \hat{K}_j | i \rangle = \langle j | \hat{K}_i | j \rangle; \quad (7)$$

$$\hat{J}_i(1) \varphi(1) = [\int \varphi_i^*(2) \varphi_i(2) (1/r_{12}) dV_2] \varphi(1); \quad (8)$$

$$\hat{K}_i(1) \varphi(1) = [\int \varphi_i^*(2) \varphi(2) (1/r_{12}) dV_2] \varphi_i(1). \quad (9)$$

In calculating the variation δE , we need expressions for the variations of the integrals, δJ_{ij} and δK_{ij} :

$$\delta \langle ij | jj \rangle = \langle \delta i | i | jj \rangle + \langle i | \delta i | jj \rangle + \langle ij | \delta j | j \rangle + \langle ij | j | \delta j \rangle = \quad (10)$$

$$= \langle \delta i | \hat{J}_j | i \rangle + \langle i | \hat{J}_j | \delta i \rangle + \langle \delta j | \hat{J}_i | j \rangle + \langle j | \hat{J}_i | \delta j \rangle;$$

$$\delta \langle ij | ji \rangle = \langle \delta i | j | ji \rangle + \langle i | \delta j | ji \rangle + \langle ij | \delta i | i \rangle + \langle ij | i | \delta i \rangle = \quad (11)$$

$$= \langle \delta i | \hat{K}_j | i \rangle + \langle j | \hat{K}_i | \delta j \rangle + \langle \delta j | \hat{K}_i | j \rangle + \langle i | \hat{K}_j | \delta i \rangle,$$

where the symbol $\langle ij | kl \rangle$ for the four-index integrals corresponds to the definition

$$\langle ij | kl \rangle = \int \varphi_i^*(1) \varphi_k^*(2) (1/r_{12}) \varphi_j(1) \varphi_l(2) dV_1 dV_2. \quad (12)$$

The expression for the first variation of the energy functional (5)

$$\delta E = \sum_i \omega_i \delta \langle i | \hat{h} | i \rangle + \sum_i \sum_j [\alpha_{ij} \delta \langle ij | jj \rangle - \beta_{ij} \delta \langle ij | ji \rangle] \quad (13)$$

taking into account the formulas in (10) and (11) has the form

$$\begin{aligned} \delta E = & \sum_i \omega_i [\langle \delta i | \hat{h} | i \rangle + \langle i | \hat{h} | \delta i \rangle] + \sum_i \sum_j [\alpha_{ij} \{ \langle \delta i | \hat{J}_j | i \rangle + \langle i | \hat{J}_j | \delta i \rangle \} - \\ & - \beta_{ij} \{ \langle \delta i | \hat{K}_j | i \rangle + \langle i | \hat{K}_j | \delta i \rangle \}] + \sum_i \sum_j [\alpha_{ij} \{ \langle \delta j | \hat{J}_i | j \rangle + \langle j | \hat{J}_i | \delta j \rangle \} - \\ & - \beta_{ij} \{ \langle \delta j | \hat{K}_i | j \rangle + \langle j | \hat{K}_i | \delta j \rangle \}]. \end{aligned} \quad (14)$$

In the last sum, let us interchange the indices i and j ;

$$\begin{aligned} \delta E = & \sum_i \omega_i [\langle \delta i | \hat{h} | i \rangle + \langle i | \hat{h} | \delta i \rangle] + \sum_i \sum_j [\alpha_{ij} \{ \langle \delta i | \hat{J}_j | i \rangle + \langle i | \hat{J}_j | \delta i \rangle \} - \\ & - \beta_{ij} \{ \langle \delta i | \hat{K}_j | i \rangle + \langle i | \hat{K}_j | \delta i \rangle \}] + \sum_i \sum_j [\alpha_{ji} \{ \langle \delta j | \hat{J}_i | j \rangle + \langle j | \hat{J}_i | \delta j \rangle \} - \\ & - \beta_{ji} \{ \langle \delta j | \hat{K}_i | j \rangle + \langle j | \hat{K}_i | \delta j \rangle \}]. \end{aligned} \quad (15)$$

Rearranging the terms in (15), we obtain the following expression for the variation of the energy functional:

$$\begin{aligned} \delta E = & \sum_i [\langle \delta i | \omega_i \hat{h} + \sum_j \{ (\alpha_{ij} + \alpha_{ji}) \hat{J}_j - (\beta_{ij} + \beta_{ji}) \hat{K}_j \} | i \rangle] + \\ & + \sum_i [\langle i | \omega_i \hat{h} + \sum_j \{ (\alpha_{ij} + \alpha_{ji}) \hat{J}_j - (\beta_{ij} + \beta_{ji}) \hat{K}_j \} | \delta i \rangle] = 2 \sum_i [\langle \delta i | \hat{F}_i | i \rangle + \langle i | \hat{F}_i | \delta i \rangle], \end{aligned} \quad (16)$$

where \hat{F}_i is the Fock operator

$$\hat{F}_i = (\omega_i/2) \hat{h} + \sum_j [(\alpha_{ij} + \alpha_{ji}) \hat{J}_j - (\beta_{ij} + \beta_{ji}) \hat{K}_j] / 2, \quad (17)$$

which is Hermitian (since the operators \hat{h} , \hat{j} , and \hat{K}_j are Hermitian).

In the variational problem, let us consider additional orthonormality conditions on the one-electron orbitals

$$I = E - \sum_i \sum_j 2\theta_{ij} (\langle i | j \rangle - \delta_{ij}), \quad (18)$$

where the θ_{ij} are Lagrange multipliers. The variation δI is equal to

$$\delta I = \delta E - \sum_i \sum_j 2\theta_{ij} (\langle \delta i | j \rangle + \langle i | \delta j \rangle) = \delta E - \sum_i \sum_j 2\theta_{ij} \langle \delta i | j \rangle - \sum_i \sum_j 2\theta_{ij} \langle j | \delta i \rangle = 0. \quad (19)$$

Substituting the expression for δE from (16) into (19) and taking into account the Hermitian property of the Fock operators, we obtain

$$\sum_i \left[\left\{ \langle \delta i | \hat{F}_i | i \rangle - \sum_j \theta_{ij} \langle \delta i | j \rangle \right\} + \left\{ \langle \delta i | \hat{F}_i | i \rangle - \sum_j \theta_{ij}^* \langle \delta i | j \rangle \right\} \right] = 0. \quad (20)$$

As a result, we arrive at the Euler Eqs. (2) with the Fock operators defined in Eq. (17).

Going back to the original symbols in (1) and (3), Eq. (17) can be rewritten in the form

$$\hat{F}_i = f_i \left[\hat{h} + \sum_j f_j (2A_{ij}\hat{j} - B_{ij}\hat{K}_j) \right], \quad (21)$$

where the coefficients are

$$A_{ij} = (a_{ij} + a_{ji})/2; \quad B_{ij} = (b_{ij} + b_{ji})/2. \quad (22)$$

Thus the expression obtained for the Fock operator (21) differs from the previously proposed one in (3) in the coefficients for the Coulomb and exchange operators. This difference is important for discussion of the problem of the symmetry of the vector coupling coefficients [4, 7] mentioned in the introduction. From the definition of the coefficients A_{ij} and B_{ij} in (22) it follows that they are symmetric ($A_{ij} = A_{ji}$, $B_{ij} = B_{ji}$), and this result follows directly from the variational principle.

Comparing the systems of Eqs. (1)-(3) and (1), (2), (21), (22) describing the variational procedure, it is not difficult to convince ourselves that they become equivalent if the first one is supplemented by the equation

$$a_{ij} = a_{ji}; \quad b_{ij} = b_{ji}. \quad (23)$$

In other words, the variational procedure (1)-(3) is rigorous only when we have the additional conditions (23).

On the other hand, in [7] when calculating the vector coupling coefficients a_{ij} and b_{ij} for atoms using the variational procedure (1)-(3), the additional conditions (23) were considered as possible but not necessary. The corresponding system of equations obtained in [7] for determination of the vector coupling coefficients in atoms with configurations d^N (see Eqs. (9) and (16) in [7]) uses only expressions for the energy functional (1) and the Fock operator in form (3). From the system of equations in [7] it follows that Roothaan-type terms in the d^N configuration can be described both by symmetric and asymmetric vector coupling coefficient matrices (the system of equations in [7] allows for a multiplicity of solutions). At the same time, the non-Roothaan terms in the d^N configuration are described (according to [7]) only by asymmetric vector coupling coefficient matrices: $\|a_{ij}\| \neq \|a_{ij}\|^T$ and/or $\|b_{ij}\| \neq \|b_{ij}\|^T$.

Including the additional conditions (23) in the system of Eqs. in [7] retains only the symmetric solutions for the Roothaan terms, while for the non-Roothaan terms the supplemented system of equations is inconsistent [7]. In other words, no set of symmetric vector coupling coefficients a_{ij} and b_{ij} exists which satisfies the necessary physical restrictions [7]. Considering that the additional conditions (23) are in fact necessary conditions, we might conclude that within the rigorous approach (1)-(3), (23), such terms are impossible to calculate in principle, in accordance with the previous hypothesis in [6]. Nevertheless, as shown by the analysis in [10], the results obtained in [7] are correct for the non-Roothaan terms. Here let us note the following two points.

1. Using the key property of the non-Roothaan terms (the dependence of the vector coupling coefficients a_{ij} and b_{ij} on the choice of basis for the degenerate orbitals [11]), we can rigorously show [10] that in a basis of complex d-orbitals (in contrast to the real d orbitals used in [7]) the corresponding system of Eqs. in [7] allows for a symmetric solution (23). Thus we have proven the possibility in principle of calculating the non-Roothaan terms within the Hartree-Fock approach (1)-(3), (23). Further considering that all the basis sets of degenerate orbitals connected by a unitary transformation and the corresponding sets of vector coupling coefficients are physically equivalent [11] (i.e., lead to the same SCF solution), the latter result essentially removes the major theoretical argument against asymmetric vector coupling coefficient matrices as (formally) not satisfying the variational principle.*

2. The asymmetric vector coupling coefficient matrices appear only in systems with degenerate open shells [7]. Therefore, for a more detailed analysis of the resulting contradiction we need to also consider the variational procedure with the energy functional (1) with additional conditions involving the degeneracy of the one-electron orbitals. We plan to publish the results of the corresponding analysis.

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*The results of the Hartree-Fock calculations (by the unified coupling operator method [1-3] for Roothaan-type terms are identical [7] when using different sets of symmetric and asymmetric vector coupling coefficients and agree with the results of calculations [8, 12] done within Roothaan-Hartree-Fock atomic theory [13]. The results of calculation by two Hartree-Fock methods are similarly identical for the non-Roothaan terms [7, 8].