

THE PROPER TREATMENT OF OFF-DIAGONAL LAGRANGE MULTIPLIERS
AND COUPLING OPERATORS IN SELF-CONSISTENT FIELD EQUATIONS †

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We show that past treatments of the off-diagonal Lagrange multipliers or coupling operators in the self-consistent field equations for open-shell systems and in the multi-configuration SCF equations are incomplete. In addition, we obtain the complete variational equations and show how these may be combined into one simple eigenvalue problem which is solved for all orbitals.

Consider a Slater determinant wave function

$$\Psi = a\Phi\chi, \quad (1)$$

where a is the N -electron antisymmetrizer, Φ is a product of orbitals, and χ is a suitable product of one-electron spin functions. In the Hartree-Fock method we require that the total energy be stationary under all variations of the orbitals consistent with the orthogonality conditions

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad i, j = 1, \dots, n. \quad (2)$$

(n is the number of different spatial orbitals, which may be less than the total number of electrons, N , since some orbitals are doubly occupied.) The constraints are usually incorporated by introducing the Lagrange multipliers $\{\epsilon_{ij}\}$, and requiring that [1-5]

$$I = E - \sum_{i,j} \epsilon_{ij} \langle \phi_i | \phi_j \rangle$$

be stationary. The result is ‡‡

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‡‡ If (2) is not used to eliminate the terms in the energy expression proportional to

$$\langle \phi_k | \phi_j \rangle, \quad \sum_{k,j} \langle \phi_k | \phi_j \rangle A_{kj},$$

we obtain additional terms in (3) such as

$$A_{kj} [\langle \delta \phi_k | \phi_j \rangle + \langle \phi_k | \delta \phi_j \rangle].$$

However, they can also be combined with the Lagrange multipliers ϵ_{kj} to obtain new effective multipliers $\epsilon'_{kj} = \epsilon_{kj} - A'_{kj}$. We assume this to be done and drop the primes.

$$\delta' I = \left\{ \sum_{l=1}^n [\langle \delta \phi_l | H^l | \phi_l \rangle + \langle \phi_l | H^l | \delta \phi_l \rangle] - \sum_{l,j=1}^n \epsilon_{lj} [\langle \delta \phi_l | \phi_j \rangle + \langle \phi_l | \delta \phi_j \rangle] \right\} = 0, \quad (3)$$

where H^l is the usual Hartree-Fock one-electron operator for orbital ϕ_l . Now we wish to select out the parts of (3) that involve the variations of orbital ϕ_k . In so doing we must recognize the effects of the orthogonality constraints in (2). In order that $\langle \phi_k | \phi_j \rangle = 0$ we must have to first order that

$$\langle \delta \phi_k | \phi_j \rangle + \langle \phi_k | \delta \phi_j \rangle = 0 \quad (4)$$

for all j , including k . Thus if $\delta \phi_k$ contains a component of ϕ_j ,

$$\delta \phi_k \sim c \phi_j = \langle \phi_j | \delta \phi_k \rangle \phi_j,$$

where c is small, then $\delta \phi_j$ must necessarily be nonzero and contain a component of ϕ_k consistent with (4),

$$\delta \phi_j \sim c' \phi_k = \langle \phi_k | \delta \phi_j \rangle \phi_k = -\langle \delta \phi_k | \phi_j \rangle \phi_k. \quad (5)$$

Thus allowing general changes in ϕ_k , but only the constraint-required changes in the other orbitals, (3) becomes

$$\langle \delta \phi_k | H^k | \phi_k \rangle + \langle \phi_k | H^k | \delta \phi_k \rangle - \sum_j [\langle \phi_j | \delta \phi_k \rangle \langle \phi_k | H^j | \phi_j \rangle + \langle \delta \phi_k | \phi_j \rangle \langle \phi_j | H^j | \phi_k \rangle] = 0. \quad (6)$$

Note that explicit use of (4) eliminates the multipliers, ϵ_{jk} . Since (6) now involves only changes in ϕ_k and must be true for all $\delta \phi_k$, we can use the usual process of replacing $\delta \phi_k$ by $i\delta \phi_k$

and subtracting from (6) to obtain

$$\langle \delta \phi_k | H^k | \phi_k \rangle - \sum_j \langle \delta \phi_k | \phi_j \rangle \langle \phi_j | H^j | \phi_k \rangle = 0. \quad (7)$$

Eq. (7) can be written

$$\int d\tau_1 \delta \phi_k^*(1) [H^k(1) \phi_k(1) - \sum_j \langle \phi_j | H^j | \phi_k \rangle \phi_j(1)] = 0 \quad (8)$$

which must be true for *all* $\delta \phi_k^*$. Thus the bracketed term in (8) must be zero and we find that

$$H^k \phi_k - \sum_{j \neq k} \langle \phi_j | H^j | \phi_k \rangle \phi_j = \eta_{kk} \phi_k, \quad (9)$$

where we have set $\eta_{kk} = \langle \phi_k | H^k | \phi_k \rangle$. Eq. (9) is the necessary variational condition for the orbitals to be optimum and can be referred to as the Hartree-Fock equation for orbital ϕ_k . If we have found the optimum orbital so that (9) is satisfied, then taking the inner product of ϕ_l ($l \neq k$) with (9) we obtain

$$\langle \phi_l | H^k - H^l | \phi_k \rangle = 0 \quad (10)$$

which must be satisfied for the converged solutions. However, in general (10) need *not* be satisfied until convergence is obtained.

However, if ϕ_k and ϕ_l are both doubly occupied in Φ or if ϕ_k and ϕ_l are each singly occupied and both correspond to the same spin of χ , then an additional simplification can be made. In this case

$$H^k + \mathcal{J}_k - \mathcal{K}_k = H^l + \mathcal{J}_l - \mathcal{K}_l \equiv H^{kl}$$

where

$$\begin{aligned} H^{kl} \phi_k &= H^k \phi_k \\ H^{kl} \phi_l &= H^l \phi_l \end{aligned}$$

and thus

$$\langle \phi_l | H^k - H^l | \phi_k \rangle = \langle \phi_l | H^{kl} - H^{kl} | \phi_k \rangle = 0 \quad (11)$$

for *all* choices of ϕ_l and ϕ_k . Thus (11) can be used to simplify the HF equations. (In these cases the orthogonality restriction (2) is not really a restriction since the antisymmetrizer leaves in only the orthogonal parts.)

In the usual way of deriving HF equations [1-6], one allows only variations in one orbital, say, ϕ_k (variations are allowed in all orbitals but the variations are assumed to be independent, which is equivalent to varying one orbital at a time). Then by (4) we have

$$\langle \delta \phi_k | \phi_j \rangle = 0 \quad (12a)$$

for all occupied orbitals ϕ_j , and for all variations in ϕ_k we require

$$\langle \delta \phi_k | H^k | \phi_k \rangle = 0. \quad (12b)$$

The solution of (12) is that [6]

$$H^k \phi_k = \sum_j \eta_{kj} \phi_j \quad (13)$$

where the sum is over the occupied orbitals and the η_{kj} are undetermined multipliers. Now if eq. (13) has converged, we can take the inner product of ϕ_j with (13) we obtain [1-5]

$$\eta_{kj} = \langle \phi_j | H^k | \phi_k \rangle, \quad (14)$$

which is the coupling operator usually used in the HF equations. As we saw in (9) and (10), (13) and (14) do correspond to the correct variational equations *if* the solutions have already converged. However, from (9) the correct form of the coupling operator to use *before* complete convergence is

$$\eta_{kj} = \langle \phi_j | H^j | \phi_k \rangle. \quad (15)$$

The reason that the usual derivations do not determine the correct form, (15), for η_{kj} is that because of (12a) they do *not* account for the optimal mixing of the occupied orbitals among themselves. In order for ϕ_k to mix into ϕ_j we must simultaneously allow ϕ_j to mix into ϕ_k . Although (13) and (14) are satisfied at convergence, they are *not* the proper variational equations to use while iterating the equations (before convergence).

As an example we will consider the ground state of the Li atom, $2s[(1s)^2(2s)]$. From (9) we obtain

$$\begin{aligned} 2(h + 2\mathcal{J}_1 - \mathcal{K}_1 + \mathcal{J}_2 - \frac{1}{2}\mathcal{K}_2)\phi_1 \\ - \langle \phi_2 | h + \mathcal{J}_1 | \phi_1 \rangle \phi_2 = \eta_{11} \phi_1 \\ (h + 2\mathcal{J}_1 - \mathcal{K}_1)\phi_2 - \langle \phi_1 | 2h + 2\mathcal{J}_1 + \mathcal{J}_2 | \phi_2 \rangle \phi_1 = \eta_{22} \phi_2, \end{aligned}$$

which are the correct variational equations at all steps of the iteration; whereas the usual approach [2-4] assumes (10), which is equivalent to assuming that

$$\langle \phi_1 | h + \mathcal{J}_1 + \mathcal{J}_2 | \phi_2 \rangle = 0, \quad (16)$$

and thus obtains [2]

$$\begin{aligned} 2(h + 2\mathcal{J}_1 - \mathcal{K}_1 + \mathcal{J}_2 - \frac{1}{2}\mathcal{K}_2)\phi_1 + \langle \phi_2 | \mathcal{J}_2 | \phi_1 \rangle \phi_2 = \epsilon_{11} \phi_1 \\ (h + 2\mathcal{J}_1 - \mathcal{K}_1)\phi_2 + \langle \phi_1 | \mathcal{J}_2 | \phi_2 \rangle \phi_1 = \epsilon_{22} \phi_2, \end{aligned}$$

which is equivalent to the correct variational equations only when (15) is true. Eq. (16) is satisfied for the correct variational solutions but not necessarily during the iterative process. Note that transforming ϕ_1 and ϕ_2 among themselves so as to satisfy (16) at each step of the iteration [7] need not converge to the correct variational solutions because (16) need not be satisfied for the iterated orbitals.

The above analysis holds for other types of variational methods of solving for electronic wave functions. For example, in the multiconfiguration self-consistent field (MC SCF) [7-11] the wave function is taken as

$$\Psi = \sum_i c_i [a \Phi_i \chi]$$

involving several product functions, Φ_i . In this case the linear coefficients c_i and the orbitals in the Φ_i are required to be simultaneously optimized under the constraint (2). For nearly all cases treated so far [7-10, 12-14] (for which the various Φ_i differ by two in occupation numbers) the resulting variational equations have the form in (3) (of course, the resulting operator H^k is different than for HF). Thus the analysis is exactly the same as above and we obtain (9), whereas the usual derivations [7-10, 14] lead to (14). In the HF case most workers have just assumed [1-5] that (10) is true for all steps in the iterative procedure and have not bothered to calculate the quantities and check (10); however, for MC SCF the first general calculations (Das and Wahl, ref. [8] *did* check (10) and found that it was *not* satisfied at the various stages of convergence nor for the final converged solutions. Later Das [7, 13] suggested rotating all pairs of orbitals at each stage of the iterative procedure in order to satisfy (10) but noted that some cases are inherently divergent [7]. On the other hand, Hinze and Roothaan [9] and Huzinaga [11] replace ϵ_{kl} by $\frac{1}{2} \langle \phi_l | H^k + H^l | \phi_k \rangle$ presuming that this will lead to the correct converged solutions. We should point out here that given the correct solutions, any of these approaches would find the solution to be converged. However, in order to reliably solve iteratively for the optimum orbitals, we must work with the complete variational equations. It seems likely that the difficulties reported by various workers [7, 8, 12-14] in solving MC SCF equations stems from the use of the incomplete variational equations (14) rather than (9).

In addition the use of (14) in open shell HF calculations [15] may have led to unoptimum solutions in some cases and may be responsible for some difficulties in convergence [16].

We previously showed [17] that by transforming the basis set so that the first n basic functions are the occupied orbitals at one iteration and the others are orthogonal, eq. (12b) could be solved directly without ever using the off-diagonal multipliers. This same approach may be simply extended to solve (9).

We can write (9) as

$$\bar{H}^k |k\rangle = \eta_{kk} |k\rangle \quad k = 1, \dots, n \quad (17)$$

where

$$\bar{H}^k = H^k - \sum_{j \neq k} |j\rangle \langle j | H^j. \quad (18)$$

All n equations in (17) can be then combined into

$$\mathcal{H} |k\rangle = \eta_{kk} |k\rangle, \quad (19)$$

where \mathcal{H} is the operator

$$\mathcal{H} = \sum_l \{ H^l - \sum_{j \neq l} |j\rangle \langle j | H^j \} \{ 1 - \sum_{k \neq l} |k\rangle \langle k | \}. \quad (20)$$

Here \mathcal{H} is non-Hermitian unless (10) is satisfied; that is, unless the self-consistent field equations have converged. In order to solve for the solutions of \mathcal{H} , we form the Hermitian operator

$$B = \mathcal{H}^\dagger \mathcal{H} \quad (21)$$

and solve the eigenvalue problem

$$B \phi_k = b_k \phi_k \quad (22)$$

for the new orbitals ϕ_k . Upon convergence the solutions of (22) are then the solutions of (19) and hence of (17). In the case that a basis set expansion $\{\chi_\mu; \mu = 1, \dots, M\}$ is used, then it is necessary to solve only the one $M \times M$ matrix B to obtain all of the occupied orbitals for the next iteration.

In summary we have shown that the usual SCF equations for HF and for MC SCF wavefunctions are incomplete in that they do not account for optimal mixing of the occupied orbitals. In addition we have shown what the complete variational equations are and how to solve them.

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