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General SCF operator satisfying correct variational condition

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We have shown that the correct variational equations for the general SCF orbitals are $[F_i - \sum_j |\psi_j\rangle\langle\psi_j| G_{ji}]\,|\psi_i\rangle = 0$, where $G_{ji} = \lambda_{ji}F_j + (1-\lambda_{ji})F_i$; $\lambda_{ji} \neq 0$ and how these may be combined into simple eigenvalue problems. In the course of discussions, we re-examined whether the coupling operators suggested previously are based on the correct variational conditions.

I. INTRODUCTION

A variety of general SCF operator (coupling operator) methods in Hartree–Fock (HF)[1–4] and multiconfigurational (MC)[5–7] SCF theory have been developed. The nature of the coupling operator method was fully discussed by Huzinaga[8] and it was shown that there is an arbitrariness in the definition of the general SCF operators. However, Huzinaga's developments depend heavily on the equations which become valid only when the final self-consistent solutions are obtained. On the other hand, it was shown that some of the coupling operators are incomplete and have the nonunique solution in open-shell SCF computations.[6] The meaning of the nonunique solution originates from the fact, as explored by Levy,[9] that such a coupling operator fails to satisfy the necessary variational condition on the orbitals to be optimum. In this paper we will make a slight extension of the theory developed by Huzinaga and Levy. The emphasis will be on getting the general SCF operators which satisfy the correct variational condition. In Sec. II, the correct variational equations are first discussed in connection with the generalized Brillouin theorem. Then we derive the general form of the coupling operator which satisfies the correct variational condition. In addition, some simplifications are made which can be useful in practical applications. In Sec. III, we re-examine whether the coupling operators suggested previously are based on the correct variational condition.

II. CORRECT VARIATIONAL CONDITIONS

We will limit ourselves to restricted SCF treatment of many electron systems, i.e., to states whose wavefunction of an n-electron system is expressed as the sum of several configurations:

$$\Phi_0 = \sum_k a_k \Psi_k, \tag{1}$$

where Ψ_k's are antisymmetric many-electron functions, built up from n spin orbitals $\{\phi_m\}$, and each refers to a configuration of occupied orbitals. We assume that the spin orbitals are taken in the form

$$\phi_m = \psi_i\alpha \text{ or } \phi_m = \psi_i\beta. \tag{2}$$

Their corresponding spatial orbitals $\{\psi_i\}$ are chosen from the eigenfunctions of certain effective one-electron Hamiltonians. The wavefunction defined above is general enough for closed- and open-shell systems; it includes general HF theory[1–4] and many types of MC SCF[5–7] theory. In most cases the coefficients a_k and the orbitals $\{\psi_i\}$ are simultaneously determined by the variational method. Various methods differ only in the choice of the effective one-electron Hamiltonians.

In the SCF theory, we require that the total energy E be stationary under all variations of the orbitals consistent with the orthonormality conditions, namely

$$\langle\psi_i \mid \psi_j\rangle = \delta_{ij}. \tag{3}$$

These constraints are usually incorporated by introducing the Lagrangian multipliers $\{\theta_{ji}\}$, and requiring that

$$E' = E - 2\sum_i\sum_j \theta_{ji}\langle\psi_i \mid \psi_j\rangle \tag{4}$$

be stationary. The result is

$$\delta E' = 2\sum_i \{\langle\delta\psi_i \mid F_i \mid \psi_i\rangle + \langle\psi_i \mid F_i \mid \delta\psi_i\rangle\} - 2\sum_i\sum_j \theta_{ji}\{\langle\delta\psi_i \mid \psi_j\rangle + \langle\psi_i \mid \delta\psi_j\rangle\} = 0, \tag{5}$$

where F_i is an effective one-electron Hamiltonian. Equation (5) should hold for any infinitesimal variations $|\delta\psi_i\rangle$ and $\langle\delta\psi_i|$, with suitable values for the Lagrangian multipliers. Therefore, one can obtain

$$F_i \mid \psi_i\rangle = \sum_j \mid \psi_j\rangle\,\theta_{ji}, \tag{6}$$

$$\langle\psi_i \mid F_i = \sum_j \langle\psi_j \mid \theta_{ij}. \tag{7}$$

As known well, subtracting the complex conjugate of Eq. (7) from Eq. (6) establishes that the Lagrangian multipliers are the elements of an Hermitian matrix

$$\theta_{ji} = \theta_{ij}^*. \tag{8}$$

However, this does not mean that Eq. (7) is equivalent to Eq. (6) but Eq. (6) together with the additional condition Eq. (8) are the correct variational conditions. The orthonormality conditions given by Eq. (3) permit us to rewrite Eqs. (6) and (8) as

$$F_i \mid \psi_i \rangle = \sum_j \mid \psi_j \rangle \langle \psi_j \mid F_i \mid \psi_i \rangle \tag{9a}$$

$$\langle \psi_j \mid F_i - F_j \mid \psi_i \rangle = 0 . \tag{9b}$$

Note here that Eq. (9b) is automatically satisfied in the closed-shell HF theory since F_i is independent of i.[10] So in this case Eq. (9a) alone corresponds to the correct variational condition. However, this is not true, in general, for the open-shell case. It must be stressed again that Eqs. (9b) as well as (9a) is the necessary variational condition for the orbitals to be optimum. That is, the Hermitian property of Lagrangian multipliers is one of the necessary variational conditions in the open-shell theory although it originates from the nature of the Lagrange multipliers method.[11] However, in past treatment for deriving the coupling operator, this supplementary condition Eq. (9b) has often been neglected. For instance, in Birss–Fraga formalism,[4] Eq. (6) is considered to be equivalent to Eq. (7) and only Eq. (9a) without (9b) is dealt with as the variational condition. Later in this paper, we will consider how to put the variational conditions Eqs. (9a) and (9b) into more general and useful form.

Before proceeding to the main subject, let us make clear the physical meaning of the above variational conditions in connection with the generalized Brillouin theorem. According to the generalized Brillouin theorem derived by Levy and Berthier,[12] the Hamiltonian matrix elements between the ground-state wavefunction and some well-defined linear combination of excited Slater determinants are equal to zero:

$$\langle \Phi_0 \mid H \mid \Phi_0(i \to j) \rangle = 0, \tag{10}$$

where Φ_0 is the normalized total wavefunction given by Eq. (1) and $\Phi_0(i \to j)$ are defined as

$$\Phi_0(i \to j) = \sum_k a_k [\Psi_k(i \to j) - \Psi_k(j \to i)] . \tag{11}$$

Here $\Psi_k(i \to j)$ are defined as follows: If spin orbital ϕ_m is singly occupied in Ψ_k, $\Psi_k(i \to j)$ is obtained simply by replacing $\psi_i \alpha$ (or $\psi_i \beta$) in Ψ_k with $\psi_j \alpha$ (or $\psi_j \beta$); if ϕ_m is doubly occupied in Ψ_k, the original Slater determinant is replaced by a sum of two determinants, one with $\psi_i \alpha$ replaced by $\psi_j \alpha$, and the other one with $\psi_i \beta$ replaced by $\psi_j \beta$. Here, of course, $\psi_j \alpha$ and $\psi_j \beta$ in $\Psi_k(i \to j)$ must not be the already occupied orbitals.

In terms of the effective one-electron Hamiltonian, these matrix elements given by Eq. (10) can be rewritten as

$$\langle \Phi_0 \mid H \mid \Phi_0(i \to a) \rangle = 2 \langle \psi_a \mid F_i \mid \psi_i \rangle = 0, \quad 1 \le i \le n < a \tag{12a}$$

$$\langle \Phi_0 \mid H \mid \Phi_0(i \to j) \rangle = 2 \langle \psi_j \mid F_i - F_j \mid \psi_i \rangle = 0, \quad 1 \le i, j \le n. \tag{12b}$$

Here, $\Phi_0(i \to a)$ corresponds to a single excitation from an occupied orbital ψ_i to a virtual orbital ψ_a which is not occupied in Φ_0 and $\Phi_0(i \to j)$ gives those which only involve the original n orbitals. On the other hand, by taking the inner product of any orbital ψ_a with $F_i \mid \psi_i \rangle$ given by Eq. (9a), we obtain

$$\langle \psi_a \mid F_i \mid \psi_i \rangle = 0, \quad 1 \le i \le n < a . \tag{13}$$

Thus, the variational conditions Eqs. (9a) and (9b) are equivalent to the generalized Brillouin condition Eqs. (12a) and (12b), respectively. Hence, if the optimum orbitals are obtained, the generalized Brillouin theorem given by Eq. (10) or (12) is satisfied.

As shown above, Eq. (9a) corresponds to the variational condition between the virtual and occupied orbitals and Eq. (9b) does to the one among occupied orbitals.

III. THE PROPER GENERAL SCF OPERATOR

Now we consider how the complete variational conditions may be combined into simple eigenvalue problems which are solved for all orbitals. Equations (9a) and (9b) can be unified equivalently to the form

$$\left[F_i - \sum_j \mid \psi_j \rangle \langle \psi_j \mid G_{ji} \right] \mid \psi_i \rangle = 0, \tag{14}$$

where

$$G_{ji} = \lambda_{ji} F_j + (1 - \lambda_{ji}) F_i ; \quad \lambda_{ji} \neq 0. \tag{15}$$

Here, λ_{ji}'s are arbitrary nonzero real numbers. These G operators were first introduced by Huzinaga.[8,13] It is easily checked that Eq. (14) is equivalent to the correct variational conditions, Eqs. (13) and (9b) if one multiply Eq. (14) by $\psi_a (n < a)$ and by $\psi_j \, (j \neq i)$, respectively. We remark that if λ_{ji} equals zero, Eq. (14) becomes identical with Eq. (9a) and no longer equivalent to the correct variational equations. It must be noted that *Eq. (14) with $\lambda_{ji} \neq 0$ is the correct variational equation* and the condition which such an improper coupling operator as Birss–Fraga one failed to satisfy. With $\lambda_{ji} = 1$, we obtain

$$\left[F_i - \sum_j \mid \psi_j \rangle \langle \psi_j \mid F_j \right] \mid \psi_i \rangle = 0 \tag{16}$$

which is identical with the necessary variational condition derived by Goddard III *et al.*[14] and Dahl *et al.*[15] This seems to be simpler than Eq. (14)

but is not general and available form for the derivation of the coupling operator.

By adding to each side of Eq. (14) $|\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle$, we have

$$\Big[F_i - \sum_{j(\neq i)} |\psi_j\rangle\langle\psi_j|G_{ji}\rangle\Big]|\psi_i\rangle = |\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle. \quad (17)$$

Since the operator in the left-side of Eq. (17) is meaningful only when it acts on $|\psi_i\rangle$, we may rewrite it by using the projection operator as

$$r_i' = F_i|\psi_i\rangle\langle\psi_i| - \sum_{j(\neq i)} |\psi_j\rangle\langle\psi_j|G_{ji}|\psi_i\rangle\langle\psi_i|. \quad (18)$$

Here, the operator given by Eq. (18) are not Hermitian in general unless $\{\psi_i\}$ included in r_i' satisfy Eq. (14). If the operators are chosen as Hermitian, we will get the coupling operator in the general SCF theory.[16] By symmetrizing the operator r_i' to be Hermitian, we can define a general SCF operator

$$\begin{aligned} r_i = (F_i|\psi_i\rangle\langle\psi_i| + |\psi_i\rangle\langle\psi_i|F_i) - |\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle\langle\psi_i| \\ - \sum_{j(\neq i)} |\psi_j\rangle\langle\psi_j|G_{ji}|\psi_i\rangle\langle\psi_i| \\ - \sum_{j(\neq i)} |\psi_i\rangle\langle\psi_i|G_{ji}|\psi_j\rangle\langle\psi_j| \end{aligned} \quad (19)$$

and obtain the SCF equations

$$r_i|\psi_i\rangle = |\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle. \quad (20)$$

Now we seek for the unified SCF operator independent of the suffix i by summing r_i over all occupied orbitals:

$$\begin{aligned} R &= \sum_i r_i \\ &= \sum_i \{(F_i|\psi_i\rangle\langle\psi_i| + |\psi_i\rangle\langle\psi_i|F_i) \\ &\quad - |\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle\langle\psi_i|\} \\ &\quad - \sum\sum_{i\neq j} |\psi_i\rangle\langle\psi_i|G_{ij}+G_{ji}|\psi_j\rangle\langle\psi_j|. \end{aligned} \quad (21)$$

Then

$$\begin{aligned} R|\psi_i\rangle = &\Big\{F_i|\psi_i\rangle - \sum_j |\psi_j\rangle\langle\psi_j|F_i|\psi_i\rangle\Big\} \\ &+ \sum_{j(\neq i)} (\lambda_{ji}-\lambda_{ij})|\psi_j\rangle\langle\psi_j|F_i - F_j|\psi_i\rangle \\ &+ |\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle. \end{aligned} \quad (22)$$

From the variational condition that ψ_i satisfies both Eqs. (9a) and (9b), we obtain the simple unified SCF equation,

$$R|\psi_i\rangle = |\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle. \quad (23)$$

This SCF operator R has already been suggested by Huzinaga.[8] However, a further remark is necessary for the parameters $\{\lambda_{ji}\}$ introduced in Eq. (15). It is easily checked from Eq. (22) that if the parameters are symmetrical in their two indices, Eq. (9b) is not necessarily satisfied by the solutions of Eq. (23). Hence we conclude that when we use the unified operator R, λ_{ji} must not be chosen to equal to λ_{ij}. *The R with $\lambda_{ji} \neq \lambda_{ij}$ is a general form of the coupling operator which satisfies the correct variational condition.*

It must be noted that the matrix element of the total Hamiltonian H given by Eq. (12) are identical with the following matrix elements of R in Eq. (21);

$$\begin{aligned} \langle\Phi_0|H|\Phi_0(i\to a)\rangle &= 2\langle\psi_a|F_i|\psi_i\rangle \\ &= 2\langle\psi_a|R|\psi_i\rangle, \quad 1\le i\le n<a \end{aligned} \quad (24a)$$

$$\begin{aligned} \langle\Phi_0|H|\Phi_0(i\to j)\rangle &= 2\langle\psi_j|F_i - F_j|\psi_i\rangle \\ &= \{2/(\lambda_{ji}-\lambda_{ij})\}\langle\psi_j|R|\psi_i\rangle, \\ &\quad 1\le i, j\le n \end{aligned} \quad (24b)$$

which are easily derived from Eq. (22). Of course, these off-diagonal elements of R are equal to zero for the SCF solutions. Namely, the generalized Brillouin theorem holds for the solution of Eq. (23).

Now we consider the simplifications of the general SCF operator R by an appropriate choice of the parameters $\{\lambda_{ji}\}$. This choice of parameters is a sensible one in practical applications. The only limitation on the parameters is that λ_{ji} is not symmetrical in the two indices i and j. The term $G_{ij}+G_{ji}$ in R is rewritten as

$$G_{ij}+G_{ji} = (1-\lambda_{ji}+\lambda_{ij})F_i + (1+\lambda_{ji}-\lambda_{ij})F_j \quad (25)$$

which suggests the following simplification. By setting $\lambda_{ji}-\lambda_{ij}=1$ with $i>j$ for all pairs, we have

$$G_{ij}+G_{ji} = 2F_j, \quad i>j. \quad (26)$$

Then the R is reduced to

$$\begin{aligned} R = &\sum_i \{(F_i|\psi_i\rangle\langle\psi_i| + |\psi_i\rangle\langle\psi_i|F_i) \\ &- |\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle\langle\psi_i|\} \\ &- \sum\sum_{i>j} 2\{|\psi_i\rangle\langle\psi_i|F_j|\psi_j\rangle\langle\psi_j| \\ &+ |\psi_j\rangle\langle\psi_j|F_j|\psi_i\rangle\langle\psi_i|\}. \end{aligned} \quad (27)$$

In practice, this particular choice, $\lambda_{ji}-\lambda_{ij}=1$, is recommended since it preserves the balance, as we see from Eq. (22), between the variational conditions given by Eqs. (9a) and (9b) and is expected to give better convergence characteristics.

In the case in which the fractional occupation numbers f_i in F_i and f_j in F_j are different, the following simplification is made. With the choice of λ_{ji} and λ_{ij} so as to satisfy

$$\lambda_{ji}-\lambda_{ij} = (f_i+f_j)/(f_i-f_j)$$

we have

$$G_{ij}+G_{ji}=\{2/(f_j-f_i)\}(f_jF_i-f_iF_j). \quad (28)$$

Thus, a kinetic energy term plus an electron-nuclear attraction term can be eliminated since such a one-electron part of Hamiltonian included in F_i is linearly dependent of f_i. For instance, assumed for simplicity the case in which F_i's have the form

$$F_i=f_i\left[h+\sum_j(2a_{ij}J_j-b_{ij}K_j)\right], \quad (29)$$

where J and K are usual Coulomb and exchange operators, Eq. (28) becomes

$$G_{ij}+G_{ji}=\{2f_if_j/(f_j-f_i)\}\sum_k\{2(a_{ik}-a_{jk})J_k - (b_{ik}-b_{jk})K_k\}. \quad (30)$$

The similar idea was employed in forming the Roothaan coupling operator.[17]

Next, by adding to R in Eq. (21) the operator of the form

$$V=\left(1-\sum_j|\psi_j\rangle\langle\psi_j|\right)\sum_i F_i\left(1-\sum_k|\psi_k\rangle\langle\psi_k|\right), \quad (31)$$

we obtain the following coupling operator

$$R'=R+V$$
$$=\sum_i\left(1-\sum_{j(\neq i)}|\psi_j\rangle\langle\psi_j|\right)F_i\left(1-\sum_{k(\neq i)}|\psi_k\rangle\langle\psi_k|\right) + \sum\sum_{i\neq j}(\lambda_{ji}-\lambda_{ij})|\psi_j\rangle\langle\psi_j|F_i-F_j|\psi_i\rangle\langle\psi_i|. \quad (32)$$

The addition of V is arbitrary but useful since it fixes the virtual orbitals and yields the virtual orbital energies.[18]

IV. PAST TREATMENT OF THE GENERAL SCF OPERATOR

In this section we shall re-examine whether the coupling operators suggested previously are based on the correct variational conditions. The one essential restriction on the parameters used to form the total coupling operator R in Eq. (21) or R' in Eq. (32) is that they cannot be symmetrical in their two indices, $\lambda_{ji}\neq\lambda_{ij}$, which originates from the variational condition among the occupied orbitals.

First, with $\lambda_{ji}=\lambda_{ij}$ for all choice of λ_{ij} and λ_{ji}, the R in Eq. (21) becomes as

$$R=\sum_i\{(F_i|\psi_i\rangle\langle\psi_i|+|\psi_i\rangle\langle\psi_i|F_i)\} - \sum_i\sum_j|\psi_i\rangle\langle\psi_i|F_i+F_j|\psi_j\rangle\langle\psi_j| + \sum_i|\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle\langle\psi_i|. \quad (33)$$

The R is the general coupling operator given by Birss and Fraga.[4] Therefore, the Birss-Fraga coupling operator method does not account for the optimal mixing of the occupied orbitals among themselves since Eq. (9b) is dropped. This is the essential source of trouble when used in practice.

With the same choice of parameters λ_{ji}'s, the R' in Eq. (32) becomes

$$R'=\sum_i\left(1-\sum_{j(\neq i)}'|\psi_j\rangle\langle\psi_j|\right)F_i\left(1-\sum_{k(\neq i)}|\psi_k\rangle\langle\psi_k|\right).$$

Then, by adding to the above R' the operator

$$-\sum\sum_{i\neq j}|\psi_j\rangle\langle\psi_j|F_i|\psi_j\rangle\langle\psi_j|$$

which merely shifts the occupied orbital energies, we obtain the following coupling operator

$$R'=\sum_i F_i-\sum\sum_{i\neq j}\{(F_i|\psi_j\rangle\langle\psi_j|+|\psi_j\rangle\langle\psi_j|F_i)\} + \sum\sum\sum_{\substack{i\neq j\neq k\\(i\neq k)}}|\psi_j\rangle\langle\psi_j|F_i|\psi_k\rangle\langle\psi_k|. \quad (34)$$

This R' is the one proposed by Huzinaga.[8] For the same reason as above, this coupling operator also fails to satisfy the correct variational condition given by Eq. (14) and may lead to unoptimum solutions.

In MC SCF theory, the SCF operators proposed by Das and Wahl[5] and by Veillard and Clementi[7] are also improper since the variational condition Eq. (9b) is not taken into account. If one use these improper coupling operators, one must ensure the Hermitian property of the Lagrangian multipliers through the iterative process.[6]

Hunt *et al.*[19] and Peters[20] proposed a simple device for use with the open-shell calculations. These methods, named as the orthogonality constrained basis set expansion method, eliminated the off-diagonal Lagrangian multipliers only in Eq. (6) and the variation condition among occupied orbitals, Eq. (9b), is left out of consideration. Therefore these may lead to unoptimum solutions.

While, starting with Eq. (17), we can define the coupling operator

$$r_i=-\sum_{j(\neq i)}[\,|\psi_j\rangle\langle\psi_j|G_{ji})+(G_{ji}|\psi_j\rangle\langle\psi_j|\,] \quad (35)$$

and we have

$$(F_i+r_i|\psi_i\rangle=|\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle. \quad (36)$$

The r_i is the general form of Roothaan coupling operator[1] as explained by Huzinaga.[8] The equivalent form of F_i+r_i in Eq. (36) is also derived by adding to the r_i in Eq. (19) the operator[16]

$$(1-|\psi_i\rangle\langle\psi_i|)F_i(1-|\psi_i\rangle\langle\psi_i|).$$

Hence, F_i+r_i satisfies the correct variational condition and the solutions are the optimum ones. In this case, there is no limitation on λ_{ji} but that $\lambda_{ji}\neq 0$. It would be, of course, convenient to unite those equations into a simple pseudoeigenvalue equation which is solved for all orbitals. The unified operator derived by Roothaan can be formed only in the case in which there are two distinct F

operators. For the purpose, one must take such necessary steps in general as done in Eqs. (18)–(21).

In the case in which there are only two distinct F operators, we can derive the following coupling operator from the R' given in Eq. (32) by setting $\lambda_{ji} - \lambda_{ij} = 1$ with $j > i$,

$$R' = (1 - |\psi_2\rangle\langle\psi_2|)F_1(1 - |\psi_2\rangle\langle\psi_2|) + (1 - |\psi_1\rangle\langle\psi_1|)F_2(1 - |\psi_1\rangle\langle\psi_1|) + (|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2|)(F_1 - F_2) \times (|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2|) \quad (37)$$

which is equivalent to the effective Hamiltonian suggested by McWeeny.[21] This one has the proper form.

Starting with Eq. (16), Goddard III *et al.*[13] proposed the following SCF operator[22]

$$R = \sum_i r_i^\dagger r_i, \quad (38)$$

where

$$r_i = \left[F_i - \sum_{j(\neq i)} |\psi_j\rangle\langle\psi_j|F_j\rangle\right]\left(1 - \sum_{k(\neq i)} |\psi_k\rangle\langle\psi_k|\right). \quad (39)$$

Then

$$R|\psi_i\rangle = |\psi_i\rangle\{|\langle\psi_i|F_i|\psi_i\rangle|^2 + \sum_j |\langle\psi_i|F_i - F_j|\psi_j\rangle|^2 + \sum_a |\langle\psi_i|F_i|\psi_a\rangle|^2\} + \sum_a |\psi_a\rangle\{\langle\psi_a|F_i|\psi_i\rangle\langle\psi_i|F_i|\psi_i\rangle + \sum_j \langle\psi_a|F_i - F_j|\psi_j\rangle\langle\psi_j|F_i - F_j|\psi_i\rangle + \sum_b \langle\psi_a|F_i|\psi_b\rangle\langle\psi_b|F_i|\psi_i\rangle\}, \quad (40)$$

where a, b summations run over all virtual orbitals. Hence if solutions have correctly converged, one has

$$R|\psi_i\rangle = |\psi_i\rangle\, |\langle\psi_i|F_i|\psi_i\rangle|^2. \quad (41)$$

However, it is easily checked from Eq. (40) that only diagonalization of the operator R does not always lead to the correct solutions. In order to solve iteratively for the optimum orbitals one must ensure the equality

$$\langle\psi_i|R|\psi_i\rangle = |\langle\psi_i|F_i|\psi_i\rangle|^2$$

at each step of the iterative process in addition to diagonalization of R. On the contrary, in the case that the R in Eq. (21) or R' in Eq. (32) is used, only diagonalization of the operator leads to the correct converged solutions. This is expected to be preferable from a computational point of view. Generally speaking, the SCF operator formed through the symmetry product of the operator given by Eq. (18) has poorer convergence characteristics than that formed through the symmetry sum.[23] Preliminary calculations with INDO–MO's indicate that the coupling operator R' given by Eq. (32) with $\lambda_{ji} - \lambda_{ij} = 1 (j > i)$ leads satisfactorily to the correct converged solutions,[24] even for the case in which convergence difficulty is found in the usual Roothaan open-shell treatment.

IV. SUMMARY

We have shown how to put the variational conditions on the orbitals of the general SCF theory, Eqs. (9a) and (9b), into a more general and useful form, Eq. (14). The emphasis in this article has been on deriving the general SCF operators which satisfy the correct variational equation. In the course of the discussion, we re-examine whether the coupling operators suggested previously are based on the correct variational conditions.

In the present paper discussions have been limited within the case in which the variational condition is given by Eqs. (9) or (14). However, it is easy to extend the present development to the more general class of problems.[25]

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[22] In Ref. 14, the SCF operator R was defined as $R = \sum_i \sum_j r_i^\dagger r_j$ using the r_i given by Eq. (39). This R does not lead to an eigenvalue problem such as Eq. (41) since even if the solutions have already converged, one has $R|\psi_i\rangle = |\psi_i\rangle |\langle\psi_i|F_i|\psi_i\rangle|^2 + \sum_{j(\neq i)} \sum_a |\psi_a\rangle\langle\psi_a|F_j|\psi_i\rangle$. The SCF operator R should be defined as in Eq. (38).

[23] If the coupling operator formed through the symmetry product such as R in Eq. (38) is used, only mixing of occupied and virtual orbitals is required before complete convergence. While, in the other case, both mixing of occupied and virtual orbitals and mixing among occupied orbtials are required.

[24] It is useful to remark about the parameters λ_{ji}'s. These parameters are valid for arbitrary values except $\lambda_{ji} \neq \lambda_{ij}$, but the values have been found to play crucial roles when used in practice. We have found that the range of values, $1 \leq \lambda_{ji} - \lambda_{ij} \leq 2$, is satisfactory.

[25] In the case in which Euler equations have the form $\sum_k A_{ik}|\psi_k\rangle = \sum_j |\psi_j\rangle\theta_{ji}$, $\theta_{ji} = \theta_{ij}^*$, where A_{ik}'s are Hermitian operators [see S. Huzinaga, Progr. Theoret. Phys. 41, 307 (1969)], the SCF operator can be defined as $R = \sum_i [\sum_k (A_{ik}|\psi_k\rangle\langle\psi_i| + \sum_k |\psi_i\rangle\langle\psi_k|A_{ik}) - \sum_k |\psi_i\rangle \times \langle\psi_i|A_{ik}|\psi_k\rangle\langle\psi_i|] - \sum_{i\neq j} \sum |\psi_j\rangle\langle\psi_i| \{(1+\lambda_{ji}-\lambda_{ij}) \sum_k \times \langle\psi_i|A_{jk}|\psi_k\rangle + (1-\lambda_{ji}+\lambda_{ij}) \sum_k \langle\psi_j|A_{ik}|\psi_k\rangle\}$, where λ_{ji}'s are arbitrary parameters with $\lambda_{ji} \neq \lambda_{ij}$. Then one has $R|\psi_i\rangle = |\psi_i\rangle \sum_k \langle\psi_i|A_{ik}|\psi_k\rangle$. This R reduces to R in Eq. (21) in the case in which $A_{ik} = \delta_{ik}F_i$.