Analytical Methods in Hartree-Fock Self-Consistent Field Theory*

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Two alternative schemes are proposed for the determination of electronic self-consistent field (SCF) orbitals in atoms and molecules. They are designed to be applied principally to electronic configurations consisting of two open shells. Both schemes are based upon the idea that the SCF orbitals are expanded in terms of adequate basis functions but they are different in the way of solving the SCF problem. An attempt is made to rate relative merits of both schemes, though they have not yet received any actual application.

I. INTRODUCTION

TWO alternative formulations of the analytical method are presented for solving the Hartree-Fock self-consistent field (SCF) problem in atoms and molecules. The first one is an explicit exposition of the treatment described in a previous paper[1] (hereafter referred to as I) and is a direct generalization of the Roothaan procedure.[2] The second one is closely connected with an idea indicated in the fourth section of I and here the idea is developed to the ultimate point. A rough statement of the applicability of these two methods is as follows. The first one covers various electron configurations with two open shells of *different* symmetry species, while the second one can be applied to two open shells of *same* as well as *different* symmetry species. A simple molecular example: the electron configurations $(1\pi_u)^M(1\pi_g)^N$ and $(1\pi)^M(2\pi)^N$ $(1 \leqslant M, N \leqslant 3)$ can be handled with the second method but only $(1\pi_u)^M(1\pi_g)^N$ with the first one. An obvious advantage of the first method over the second one is its more or less established practicability since the Roothaan procedure has already been used efficiently for atomic and molecular calculations. This does not, however, imply that the second method could be practically useless. It seems formidable for desk calculations but we may reasonably hope that it is well within the reach of modern automatic computers.

Among other works on the present subject a recent paper by Lefebvre[3] should be mentioned, in which he adopts a different approach to the subject. Apparently the methods described in the present paper seem to have a wider range of applicability than Lefebvre's one, but the comparison between them should be based upon actual experiences of applications to various electronic systems of practical importance.

2. SPECIFICATION OF PROBLEM

We consider electronic systems of the following specifications:

(1) The total Hamiltonian $\mathfrak{JC}$ is given by

$$\mathfrak{JC} = \sum_{\mu} H(\mu) + \tfrac{1}{2}\sum_{\mu \neq \nu} (1/r_{\mu\nu}), \tag{1}$$

$H(\mu)$ is the nuclear field plus kinetic energy operator for the μth electron, and $r_{\mu\nu}$ the distance between the μth and the νth electron.

(2) The total wave function Φ is, in general, a sum of several Slater determinants Ψ_κ:

$$\Phi = \sum_{\kappa} C_{\kappa} \Psi_{\kappa}, \tag{2}$$

where the C_κ's are fixed coefficients. Each Ψ_κ is an antisymmetrized product of one-electron functions or orbitals $\{\varphi_i\}$, some of them being doubly occupied and others singly occupied. Since we use the spin-free Schrödinger Hamiltonian, the C_κ's may be determined by requiring that the function Φ is the simplest of wave functions which belong to a certain spin-multiplicity. The orbitals $\{\varphi_i\}$ may be assumed, without loss of generality, to be mutually orthogonal. In referring to the individual orbitals, we use the indices k, l for the closed-shell orbitals, m, n for the open-shell orbitals, and i, j for orbitals of either group.

(3) The expectation value of the energy is given by

$$E = \langle \Phi | \mathfrak{JC} | \Phi \rangle / \langle \Phi | \Phi \rangle, \tag{3}$$

where

$$\langle \Phi | \Phi \rangle = \int \cdots \int \Phi^* \Phi \prod_{\mu} dV_{\mu}, \tag{4}$$

$$\langle \Phi | \mathfrak{JC} | \Phi \rangle = \int \cdots \int \Phi^* \mathfrak{JC} \Phi \prod_{\mu} dV_{\mu}. \tag{5}$$

It is usual to normalize functions in the following way:

$$\langle \varphi_i | \varphi_j \rangle = \int \varphi_i^* \varphi_j dV = \delta_{ij}, \tag{6}$$

$$\langle \Phi | \Phi \rangle = 1. \tag{7}$$

Now we specify the explicit formula of the expec-

[1] S. Huzinaga, Phys. Rev. **120**, 866 (1960).
[2] C. C. J. Roothaan, Revs. Modern Phys. **32**, 179 (1960).
[3] R. Lefebvre, Cahiers phys. **110**, 1 (1959).

tation value of the total energy:

$$E= 2\sum_k H_k + \sum_k \sum_l (2J_{kl} - K_{kl}) + f\left[2\sum_m H_m + f\sum_m \sum_n (2aJ_{mn} - bK_{mn}) + 2\sum_k \sum_m (2J_{km} - K_{km})\right]$$
$$+ f'\left[2\sum_{m'} H_{m'} + f'\sum_{m'}\sum_{n'} (2a'J_{m'n'} - b'K_{m'n'}) + 2\sum_k \sum_{m'} (2J_{km'} - K_{km'})\right] + 2ff'\sum_m \sum_{m'} I_{mm'}. \quad (8)$$

Two sets of subscripts, (m,n) and (m',n'), are used here in order to distinguish the two open shells which we are concerned about in the following formulations. a, b, f, and a', b', f' are numerical constants depending on the specific case. The first two sums in Eq. (8) represent the closed-shell energy, the next two sums the energy of the first open shell, and the fifth sum the interaction energy between the closed and the first open shell. The next three sums are related to the second open shell and have analogous meanings to those of the foregoing three sums. The last sum represents the interaction energy between the first and the second open-shell. H_i, J_{ij}, and K_{ij} are defined as usual:

$$H_i = \langle \varphi_i | H | \varphi_i \rangle, \quad (9)$$

$$J_{ij} = \langle \varphi_i | J_j | \varphi_i \rangle = \langle \varphi_j | J_i | \varphi_j \rangle, \quad (10)$$

$$K_{ij} = \langle \varphi_i | K_j | \varphi_i \rangle = \langle \varphi_j | K_i | \varphi_j \rangle, \quad (11)$$

and

$$J_i(\mu)\varphi(\mu) = \left[\int \varphi_i^*(\nu)\varphi_i(\nu)(1/r_{\mu\nu})dV_\nu\right]\varphi(\mu), \quad (12)$$

$$K_i(\mu)\varphi(\mu) = \left[\int \varphi_i^*(\nu)\varphi(\nu)(1/r_{\mu\nu})dV_\nu\right]\varphi_i(\mu). \quad (13)$$

The last term in Eq. (8), $2ff'\sum_{mm'} I_{mm'}$, cannot be given an explicit and general expression. It depends on the specific case. In some cases, it is expressed as a linear combination of J_{ij} and K_{ij} but this is not always true. (See I for more detailed discussions.)

Now our problem is to find the method by which we can get the "best" orbitals $\{\varphi_i\}$, that is to say, the orbitals which minimize the expectation value of the total energy. This is achieved by applying the variational principle to Eq. (8). In I, we derived a set of equations (the Hartree-Fock equations) to be satisfied by the orbitals $\{\varphi_i\}$ and those equations were essentially partial differential equations in three dimensions.

In the present paper we adopt a different line of approach to the actual procedure of variation, an approach most extensively developed by Roothaan.[2] The idea is to expand each orbital φ_i in terms of a given set of suitable *basis functions* X_p:

$$\varphi_i = \sum_p X_p C_{pi}. \quad (14)$$

This expansion leads to a variational problem for the coefficients $\{C_i\}$ and this time we deal with a set of algebraic equations instead of partial differential equations. The possible merits of this procedure are discussed by Roothaan in his recent paper.[2]

3. FIRST METHOD

We start by imposing a further restriction on Eq. (8), in that the two open shells should belong to different symmetries. It is also necessary to divide the whole family of closed shells into two groups. The first group $\{\varphi_k\}$ contains all the closed-shell orbitals which have the same symmetry property as that of the first open-shell orbitals $\{\varphi_m\}$; the second group $\{\varphi_{k'}\}$ contains all the closed-shell orbitals which have the same symmetry property as that of the second open-shell orbitals $\{\varphi_{m'}\}$. If there are remaining closed-shell orbitals of symmetry species different from both $\{\varphi_m\}$ and $\{\varphi_{m'}\}$, those closed shells can be grouped either within the first group or within the second one.

Following Roothaan,[2] we introduce the notation $\varphi_{\lambda\alpha i}$ in lieu of φ_i. In general, λ or μ refers to the irreducible representation, or *symmetry species*; α or β refers to the *subspecies*, that is, it labels the individual members of the degenerate set that transforms according to the representation λ; and i (or j, $\cdots$) is a numbering index which labels orbitals which cannot be distinguished by symmetry any more. Correspondingly, we introduce symmetry basis functions $X_{\lambda\alpha p}$. Each occupied orbital of a given species and subspecies is a linear combination of the basis orbitals of the same species and subspecies, and the expansion coefficients are independent of the subspecies, in order to guarantee that a degenerate set of occupied orbitals has the correct transformation properties. Hence

$$\varphi_{\lambda\alpha i} = \sum_p X_{\lambda\alpha p} C_{\lambda p i}. \quad (15)$$

Here and in the following, the $\{C_{\lambda p i}\}$ are considered to be real. If we normalize $\varphi_{\lambda\alpha i}$ to unity, then

$$\langle \varphi_{\lambda\alpha i} | \varphi_{\lambda\alpha j}\rangle = \sum_{pq} C_{\lambda p i}\langle X_{\lambda\alpha p} | X_{\lambda\alpha q}\rangle C_{\lambda q j} = \delta_{ij}.$$

This can be written as

$$\sum_{pq} C_{\lambda p i} S_{\lambda p q} C_{\lambda q j} = \delta_{ij}, \quad (16)$$

where

$$S_{\lambda p q} = d_\lambda^{-1}\sum_\alpha \langle X_{\lambda\alpha p} | X_{\lambda\alpha q}\rangle. \quad (17)$$

Here d_λ is the dimension of the representation λ. Following Roothaan,[2] we modify the normalization conditions for $\{C_{\lambda p}\}$ in the following way:

$$\sum_{pq} C_{\lambda p k} S_{\lambda p q} C_{\lambda q l} = d_\lambda \delta_{kl},$$
$$\sum_{pq} C_{\lambda p m} S_{\lambda p q} C_{\lambda q n} = f d_\lambda \delta_{mn},$$
$$\sum_{pq} C_{\lambda' p m'} S_{\lambda' p q} C_{\lambda' q n'} = f' d_{\lambda'} \delta_{m'n'}, \quad (18)$$
$$\sum_{pq} C_{\lambda p k} S_{\lambda p q} C_{\lambda q m} = 0,$$
$$\sum_{pq} C_{\lambda' p k} S_{\lambda' p q} C_{\lambda' q m'} = 0.$$

These conditions constitute the constraints for the variation process of the energy formula. It should be

noted that it is not necessary to include the conditions between $\{C_{\lambda pm}\}$ and $\{C_{\lambda' pm'}\}$ as constraints because these two open shells belong to different symmetry species.

Our next task is to get the expression of the total energy E in terms of $\{C_{\lambda pi}\}$ specified as above. This is done straightforwardly with due attention to the normalization conditions (18) which are a bit unusual:

$$E = 2\sum_\lambda \sum_{pq} \sum_k C_{\lambda pk}(H_{\lambda pq}+h_{C,\lambda pq})C_{\lambda qk}+\sum_\lambda \sum_{pq} \sum_k \sum_\mu \sum_{rs} \sum_l C_{\lambda pk}C_{\mu rl}(2\mathcal{G}_{\lambda pq,\mu rs}-\mathcal{K}_{\lambda pq,\mu rs})C_{\mu sl}C_{\lambda qk}$$

$$+2\sum_\lambda \sum_{pq} \sum_m C_{\lambda pm}(H_{\lambda pq}+h_{O,\lambda pq})C_{\lambda qm}+\sum_\lambda \sum_{pq} \sum_m \sum_\mu \sum_{rs} \sum_n C_{\lambda pm}C_{\mu rn}(2a\mathcal{G}_{\lambda pq,\mu rs}-b\mathcal{K}_{\lambda pq,\mu rs})C_{\mu sn}C_{\lambda qm}$$

$$+2\sum_\lambda \sum_{pq} \sum_k \sum_\mu \sum_{rs} \sum_n C_{\lambda pk}C_{\mu rn}(2\mathcal{G}_{\lambda pq,\mu rs}-\mathcal{K}_{\lambda pq,\mu rs})C_{\mu sn}C_{\lambda qk}+2\sum_{\lambda'} \sum_{pq} \sum_{k'} C_{\lambda' pk'}H_{\lambda' pq}C_{\lambda' qk'}$$

$$+\sum_{\lambda'} \sum_{pq} \sum_{k'} \sum_{\mu'} \sum_{rs} \sum_{l'} C_{\lambda' pk'}C_{\mu' rl'}(2\mathcal{G}_{\lambda' pq,\mu' rs}-\mathcal{K}_{\lambda' pq,\mu' rs})C_{\mu' sl'}C_{\lambda' qk'}+2\sum_{\lambda'} \sum_{pq} \sum_{m'} C_{\lambda' pm'}H_{\lambda' pq}C_{\lambda' qm'}$$

$$+\sum_{\lambda'} \sum_{pq} \sum_{m'} \sum_{\mu'} \sum_{rs} \sum_{n'} C_{\lambda' pm'}C_{\mu' rn'}(2a'\mathcal{G}_{\lambda' pq,\mu' rs}-b'\mathcal{K}_{\lambda' pq,\mu' rs})C_{\mu' sn'}C_{\lambda' qm'}$$

$$+2\sum_{\lambda'} \sum_{pq} \sum_{k'} \sum_{\mu'} \sum_{rs} \sum_{n'} C_{\lambda' pk'}C_{\mu' rn'}(2\mathcal{G}_{\lambda' pq,\mu' rs}-\mathcal{K}_{\lambda' pq,\mu' rs})C_{\mu' sn'}C_{\lambda' qk'}, \quad (19)$$

where

$$h_{C,\lambda pq}=\sum_{\mu'} \sum_{rs} \sum_{i'} C_{\mu' ri'}(2\mathcal{G}_{\lambda pq,\mu' rs}-\mathcal{K}_{\lambda pq,\mu' rs})C_{\mu' si'}, \quad (20)$$

$$h_{O,\lambda pq}=\sum_{\mu'} \sum_{rs} \sum_{k'} C_{\mu' rk'}(2\mathcal{G}_{\lambda pq,\mu' rs}-\mathcal{K}_{\lambda pq,\mu' rs})C_{\mu' sk'}+\sum_{\mu'} \sum_{rs} \sum_{m'} C_{\mu' rm'}T_{\lambda pq,\mu' rs}C_{\mu' sm'}, \quad (21)$$

and

$$H_{\lambda pq}=d_\lambda^{-1}\sum_\alpha \langle \chi_{\lambda\alpha p}|H|\chi_{\lambda\alpha q}\rangle, \quad (22)$$

$$\mathcal{G}_{\lambda pq,\mu rs}=(d_\lambda d_\mu)^{-1}\sum_{\alpha\beta} \chi_{\lambda\alpha p}{}^*(1)\chi_{\mu\beta r}{}^*(2)(1/r_{12})\chi_{\lambda\alpha q}(1)\chi_{\mu\beta s}(2)dV_1dV_2, \quad (23)$$

$$\mathcal{K}_{\lambda pq,\mu rs}=(d_\lambda d_\mu)^{-1}\sum_{\alpha\beta} \chi_{\lambda\alpha p}{}^*(1)\chi_{\mu\beta r}{}^*(2)(1/r_{12})\chi_{\mu\beta s}(1)\chi_{\lambda\alpha q}(2)dV_1dV_2. \quad (24)$$

It is not possible to give here a general expression for $T_{\lambda pq,\mu rs}$ and a proper expression must be sought in each case. This is not a difficult task in most cases. In many cases of practical interest it is expressed as a linear combination of $\mathcal{G}_{\lambda pq,\mu rs}$ and $\mathcal{K}_{\lambda pq,\mu rs}$:

$$T_{\lambda pq,\mu rs}=A\mathcal{G}_{\lambda pq,\mu rs}+B\mathcal{K}_{\lambda pq,\mu rs}, \quad (25)$$

though this does not exhaust all the important cases. It is easily seen that $\mathcal{G}_{\lambda pq,\mu rs}$ and $\mathcal{K}_{\lambda pq,\mu rs}$ are symmetrical for the exchange of indices $\lambda pq \leftrightarrow \mu rs$, and Hermitian for the *simultaneous* exchange $p \leftrightarrow q$, $r \leftrightarrow s$. Since these properties are required for the successful derivation of the necessary equations, $T_{\lambda pq,\mu rs}$ should also have the same properties. This is all we need for the formal development of the present treatment. From the practical point of view, however, we put forward further requirements on their mathematical properties, which turn out to be of great help to reduce the size of the whole numerical procedure. First, we require that $\mathcal{G}_{\lambda pq,\mu rs}$, $\mathcal{K}_{\lambda pq,\mu rs}$, and $T_{\lambda pq,\mu rs}$ should all be *real*. The second requirement is that they should be *symmetrical* for the *independent* exchanges $p \leftrightarrow q$ and $r \leftrightarrow s$. This is usually achieved through a proper symmetrization procedure, for example:

$$\mathcal{K}_{\lambda pq,\mu rs} \rightarrow \tfrac{1}{2}(\mathcal{K}_{\lambda pq,\mu rs}+\mathcal{K}_{\lambda pq,\mu sr}), \quad (26)$$

as discussed in a paper by Roothaan, Sachs, and Weiss.[4] These two additional requirements do not constitute any serious restrictions for the actual applications planned for the future.

It seems convenient to list a number of equations which we need later in the course of the derivation of

[4] C. C. J. Roothaan, Lester M. Sachs, and A. W. Weiss, Revs. Modern Phys. **32**, 186 (1960).

the Hartree-Fock equations for the linear coefficients $\{C_{\lambda pi}\}$. First we define the following various quantities:

$$D_{C,\lambda pq}=\sum_k C_{\lambda pk}C_{\lambda qk},$$

$$D_{O,\lambda pq}=\sum_m C_{\lambda pm}C_{\lambda qm}, \quad (27)$$

$$D_{T,\lambda pq}=D_{C,\lambda pq}+D_{O,\lambda pq}.$$

$$J_{C,\lambda pq}=\sum_\mu \sum_{rs} \mathcal{G}_{\lambda pq,\mu rs}D_{C,\mu rs},$$

$$J_{O,\lambda pq}=\sum_\mu \sum_{rs} \mathcal{G}_{\lambda pq,\mu rs}D_{O,\mu rs},$$

$$K_{C,\lambda pq}=\sum_\mu \sum_{rs} \mathcal{K}_{\lambda pq,\mu rs}D_{C,\mu rs}, \quad (28)$$

$$K_{O,\lambda pq}=\sum_\mu \sum_{rs} \mathcal{K}_{\lambda pq,\mu rs}D_{O,\mu rs}.$$

$$h_{\lambda pq}=h_{C,\lambda pq}-h_{O,\lambda pq}. \quad (29)$$

$$\Delta_{\lambda pqi}=d_\lambda^{-1}\sum_{uw} S_{\lambda pu}C_{\lambda ui}C_{\lambda wi}h_{\lambda wq}$$
$$+d_\lambda^{-1}\sum_{uw} h_{\lambda pu}C_{\lambda ui}C_{\lambda wi}S_{\lambda wq},$$

$$L_{\lambda pqi}=d_\lambda^{-1}\sum_{uw} S_{\lambda pu}C_{\lambda ui}C_{\lambda wi}J_{O,\lambda wq}$$
$$+d_\lambda^{-1}\sum_{uw} J_{O,\lambda pu}C_{\lambda ui}C_{\lambda wi}S_{\lambda wq}, \quad (30)$$

$$M_{\lambda pqi}=d_\lambda^{-1}\sum_{uw} S_{\lambda pu}C_{\lambda ui}C_{\lambda wi}K_{O,\lambda wq}$$
$$+d_\lambda^{-1}\sum_{uw} K_{O,\lambda pu}C_{\lambda ui}C_{\lambda wi}S_{\lambda wq}.$$

$$\Delta_{C,\lambda pq}=\sum_l \Delta_{\lambda pql},$$

$$\Delta_{O,\lambda pq}=\sum_n \Delta_{\lambda pqn}, \quad (31)$$

$$\Delta_{T,\lambda pq}=\Delta_{C,\lambda pq}+\Delta_{O,\lambda pq}.$$

$$L_{C,\lambda pq}=\sum_l L_{\lambda pql},$$

$$L_{O,\lambda pq}=\sum_n L_{\lambda pqn}, \quad (32)$$

$$L_{T,\lambda pq}=L_{C,\lambda pq}+L_{O,\lambda pq}.$$

$$M_{C,\lambda pq}=\sum_l M_{\lambda pql},$$

$$M_{O,\lambda pq}=\sum_n M_{\lambda pqn}, \quad (33)$$

$$M_{T,\lambda pq}=M_{C,\lambda pq}+M_{O,\lambda pq}.$$

From the above equations, together with Eq. (18), we derive easily the following results:

$$\sum_q \Delta_{C,\lambda pq} C_{\lambda qm} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{C,\lambda uw} h_{\lambda wq} C_{\lambda qm},$$

$$\sum_q \Delta_{O,\lambda pq} C_{\lambda qk} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{O,\lambda uw} h_{\lambda wq} C_{\lambda qk},$$

$$\sum_q (\Delta_{C,\lambda pq} - h_{\lambda pq}) C_{\lambda qk} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{C,\lambda uw} h_{\lambda wq} C_{\lambda qk},$$ (34)

$$\sum_q (\Delta_{O,\lambda pq} - f h_{\lambda pq}) C_{\lambda qm} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{O,\lambda uw} h_{\lambda wq} C_{\lambda qm}.$$

$$\sum_q L_{C,\lambda pq} C_{\lambda qm} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{C,\lambda uw} J_{O,\lambda wq} C_{\lambda qm},$$

$$\sum_q L_{O,\lambda pq} C_{\lambda qk} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{O,\lambda uw} J_{O,\lambda wq} C_{\lambda qk},$$

$$\sum_q (L_{C,\lambda pq} - J_{O,\lambda pq}) C_{\lambda qk} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{C,\lambda uw} J_{O,\lambda wq} C_{\lambda qk},$$ (35)

$$\sum_q (L_{O,\lambda pq} - f J_{O,\lambda pq}) C_{\lambda qm} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{O,\lambda uw} J_{O,\lambda wq} C_{\lambda qm}.$$

$$\sum_q M_{C,\lambda pq} C_{\lambda qm} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{C,\lambda uw} K_{O,\lambda wq} C_{\lambda qm},$$

$$\sum_q M_{O,\lambda pq} C_{\lambda qk} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{O,\lambda uw} K_{O,\lambda wq} C_{\lambda qk},$$

$$\sum_q (M_{C,\lambda pq} - K_{O,\lambda pq}) C_{\lambda qk} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{C,\lambda uw} K_{O,\lambda wq} C_{\lambda qk},$$ (36)

$$\sum_q (M_{O,\lambda pq} - f K_{O,\lambda pq}) C_{\lambda qm} = d_\lambda^{-1} \sum_q \sum_{uw} S_{\lambda pu} D_{O,\lambda uw} K_{O,\lambda wq} C_{\lambda qm}.$$

In addition to the above thirty-two equations [from (27) to (36)] pertinent to the first group of the electron shells, we need the corresponding thirty-two equations for the second group. Since they can be obtained simply by changing λ, k, m, f to λ', k', m', f' in Eqs. (27)–(36), they are omitted here. The above list of equations may still seem formidable at first glance, but it will be realized that the real content is rather simple and straightforward.

We now apply the variational principle to the total energy in order to obtain the SCF equations for the determination of the best set of coefficients $\{C_{\lambda pi}\}$ and $\{C_{\lambda' pi'}\}$. Let us first look into Eq. (19) a little bit more closely. The expression is not symmetrical with respect to $\{C_{\lambda pi}\}$ and $\{C_{\lambda' pi'}\}$. This has been done intentionally. Strictly speaking, we have to prepare another expression in which the roles of the first and the second group are reversed. Now suppose that we have a reasonable starting approximation for the second group coefficients $\{C_{\lambda' pi'}\}$. Instead of varying all the coefficients (i.e., orbitals) simultaneously, we first give variations only to the first group coefficients $\{C_{\lambda pi}\}$ with the second group coefficients held fixed. This is permissible because the orthogonality conditions are always secured between $\{C_{\lambda pi}\}$ and $\{C_{\lambda' pi'}\}$ from symmetry considerations and it is not necessary to include the orthogonality relations as constraints for the variational process. The coefficients $\{C_{\lambda' pi'}\}$ being fixed, the last five sums in Eq. (19) drop out of the expression for δE. This means that the expression for δE assumes essentially the same form as that treated in Roothaan's paper,[2] which covers mainly one-open-shell cases. The only difference is the appearance of the additional terms $h_{C,\lambda pq}$ and $h_{O,\lambda pq}$ as indicated in (19), (20), and (21).

The derivation of the SCF equations for the coefficients $\{C_{\lambda pi}\}$ closely parallels the derivation of the SCF equations in the second section of Roothaan's paper.[2] In the course of the derivation, we make use of Eqs. (34), (35), and (36). The whole algebra is fairly straightforward if one proceeds in the fashion of Roothaan,[2] and we restrict ourselves here to writing down the results. The SCF equations for $\{C_{\lambda pi}\}$, which correspond to Eqs. (32) in Roothaan's paper,[2] are:

$$\sum_q F_{C,\lambda pq} C_{\lambda qk} = \eta_{\lambda k} \sum_q S_{\lambda pq} C_{\lambda qk},$$
$$\sum_q F_{O,\lambda pq} C_{\lambda qm} = \eta_{\lambda m} \sum_q S_{\lambda pq} C_{\lambda qm},$$ (37)

where

$$F_{C,\lambda pq} = H_{\lambda pq} + 2 J_{C,\lambda pq} - K_{C,\lambda pq} + 2 J_{O,\lambda pq}$$
$$- K_{O,\lambda pq} + 2\alpha L_{O,\lambda pq} - \beta M_{O,\lambda pq}$$
$$+ h_{C,\lambda pq} + \gamma \Delta_{O,\lambda pq},$$

$$F_{O,\lambda pq} = H_{\lambda pq} + 2 J_{C,\lambda pq} - K_{C,\lambda pq} + 2a J_{O,\lambda pq}$$
$$- b K_{O,\lambda pq} + 2\alpha L_{C,\lambda pq} - \beta M_{C,\lambda pq}$$
$$+ h_{O,\lambda pq} + \gamma \Delta_{C,\lambda pq}.$$ (38)

Next we write down a unified scheme of equations which corresponds to Eq. (22) of I, or to Eq. (53) of Roothaan's paper[2]:

$$\sum_q \bar{F}_{\lambda pq} C_{\lambda qi} = \epsilon_{\lambda i} \sum_q S_{\lambda pq} C_{\lambda qi}.$$ (39)

Here

$$\bar{F}_{\lambda pq} = F_{\lambda pq} + \gamma (h_{O,\lambda pq} - f h_{C,\lambda pq} + \Delta_{T,\lambda pq}),$$
$$\gamma = (1-f)^{-1},$$ (40)

where

$$F_{\lambda pq} = H_{\lambda pq} + P_{\lambda pq} - Q_{\lambda pq} + R_{\lambda pq},$$ (41)

$$P_{\lambda pq} = \sum_\mu \sum_{rs} \mathcal{P}_{\lambda pq,\mu rs} D_{T,\mu rs},$$ (42)

$$Q_{\lambda pq} = \sum_\mu \sum_{rs} \mathcal{Q}_{\lambda pq,\mu rs} D_{O,\mu rs},$$ (43)

$$\mathcal{P}_{\lambda pq,\mu rs} = 2 \mathcal{J}_{\lambda pq,\mu rs} - \mathcal{K}_{\lambda pq,\mu rs},$$ (44)

$$\mathcal{Q}_{\lambda pq,\mu rs} = 2\alpha \mathcal{J}_{\lambda pq,\mu rs} - \beta \mathcal{K}_{\lambda pq,\mu rs},$$ (45)

$$R_{\lambda pq} = d_\lambda^{-1} \sum_{uw} S_{\lambda pu} D_{T,\lambda uw} Q_{\lambda wq}$$
$$+ d_\lambda^{-1} \sum_{uw} Q_{\lambda pu} D_{T,\lambda uw} S_{\lambda wq},$$ (46)

$$h_{\lambda pq}=h_{C,\lambda pq}-h_{O,\lambda pq}, \tag{47}$$

$$h_{C,\lambda pq}=\sum_{\mu'}\sum_{rs}\mathcal{P}_{\lambda pq,\mu'rs}D_{T,\mu'rs}, \tag{48}$$

$$h_{O,\lambda pq}=\sum_{\mu'}\sum_{rs}\mathcal{P}_{\lambda pq,\mu'rs}D_{C,\mu'rs}$$
$$+\sum_{\mu'}\sum_{rs}\mathcal{T}_{\lambda pq,\mu'rs}D_{O,\mu'rs}, \tag{49}$$

$$\Delta_{T,\lambda pq}=d_\lambda^{-1}\sum_{uw}S_{\lambda pu}D_{T,\lambda uw}h_{\lambda wq}$$
$$+d_\lambda^{-1}\sum_{uw}h_{\lambda pu}D_{T,\lambda uw}S_{\lambda wq}. \tag{50}$$

The SCF equations (39) determine the coefficients $\{C_{\lambda pi}\}$ for the first group of orbitals under the condition that all the coefficients $\{C_{\lambda'pi'}\}$ of the second group of orbitals are held fixed. Now we turn to the determination of $\{C_{\lambda'pi'}\}$ with $\{C_{\lambda pi}\}$ held fixed as determined above. For this purpose we need the SCF equations for $\{C_{\lambda'pi'}\}$ which correspond to Eqs. (39):

$$\sum_q\bar{F}_{\lambda'pq}C_{\lambda'qi'}=\epsilon_{\lambda'i}\sum_qS_{\lambda'pq}C_{\lambda'qi'}, \tag{51}$$

where

$$\bar{F}_{\lambda'pq}=F_{\lambda'pq}+\gamma'(h_{O,\lambda'pq}-f'h_{C,\lambda'pq}+\Delta_{T,\lambda'pq}), \tag{52}$$

$$F_{\lambda'pq}=H_{\lambda'pq}+R_{\lambda'pq}-Q_{\lambda'pq}+R_{\lambda'pq}. \tag{53}$$

Expressions for the various quantities which appear in (52) and (53) are obtained by replacing $\lambda\rightarrow\lambda'$, $\mu\rightarrow\mu'$, $\mu'\rightarrow\mu$, $\alpha\rightarrow\alpha'$, and $\beta\rightarrow\beta'$ in (42)–(50). After getting $\{C_{\lambda'pi'}\}$ from Eqs. (51), we go back to Eqs. (39) and this back and forth process must be continued until over-all self-consistency is attained.

Finally we need a convenient expression from which we may calculate the total energy. Noting that

$$2a\mathcal{J}_{\lambda pq,\mu rs}-b\mathcal{K}_{\lambda pq,\mu rs}=\mathcal{P}_{\lambda pq,\mu rs}-(1-f)\mathcal{Q}_{\lambda pq,\mu rs},$$

we immediately obtain the following expression from (19):

$$E=2\sum_\lambda\sum_{pq}(H_{\lambda pq}+h_{C,\lambda pq})D_{C,\lambda pq}+\sum_\lambda\sum_{pq}\sum_\mu\sum_{rs}D_{C,\lambda pq}\mathcal{P}_{\lambda pq,\mu rs}D_{C,\mu rs}+2\sum_\lambda\sum_{pq}(H_{\lambda pq}+h_{O,pq})D_{O,\lambda pq}$$
$$+\sum_\lambda\sum_{pq}\sum_\mu\sum_{rs}D_{O,\lambda pq}[\mathcal{P}_{\lambda pq,\mu rs}-(1-f)\mathcal{Q}_{\lambda pq,\mu rs}]D_{O,\mu rs}+2\sum_\lambda\sum_{pq}\sum_\mu\sum_{rs}D_{C,\lambda pq}\mathcal{P}_{\lambda pq,\mu rs}D_{O,\mu rs}$$
$$+2\sum_{\lambda'}\sum_{pq}H_{\lambda'pq}D_{C,\lambda'pq}+\sum_{\lambda'}\sum_{pq}\sum_{\mu'}\sum_{rs}D_{C,\lambda'pq}\mathcal{P}_{\lambda'pq,\mu'rs}D_{C,\mu'rs}$$
$$+2\sum_{\lambda'}\sum_{pq}H_{\lambda'pq}D_{O,\lambda'pq}+2\sum_{\lambda'}\sum_{pq}\sum_{\mu'}\sum_{rs}D_{O,\lambda'pq}[\mathcal{P}_{\lambda'pq,\mu'rs}-(1-'f)\mathcal{Q}_{\lambda'pq,\mu'rs}]D_{O,\mu'rs}$$
$$+\sum_{\lambda'}\sum_{pq}\sum_{\mu'}\sum_{rs}D_{C,\lambda'pq}\mathcal{P}_{\lambda'pq,\mu'rs}D_{O,\mu'rs}. \tag{54}$$

However, the above formula lacks desirable compactness, and we must seek another expression which corresponds to Eq. (54) of Roothaan's paper.[2] First we note that

$$\sum_{pu}D_{T,\lambda pq}S_{\lambda pu}D_{T,\lambda uw}=d_\lambda D_{C,\lambda qw}+fd_\lambda D_{O,\lambda qw},$$

$$\sum_{qw}D_{T,\lambda uw}S_{\lambda wq}D_{T,\lambda pq}=d_\lambda D_{C,\lambda pu}+fd_\lambda D_{O,\lambda pu}. \tag{55}$$

By using (55) we find that

$$E=\sum_\lambda\sum_{pq}(H_{\lambda pq}+\bar{F}_{\lambda pq})D_{T,\lambda pq}$$
$$-\sum_\lambda\sum_{pq}(Q_{\lambda pq}+\gamma h_{\lambda pq})(D_{C,\lambda pq}+fD_{O,\lambda pq})$$
$$+\sum_{\lambda'}\sum_{pq}(H_{\lambda'pq}+\bar{F}_{\lambda'pq})D_{T,\lambda'pq}$$
$$-\sum_{\lambda'}\sum_{pq}Q_{\lambda'pq}(D_{C,\lambda'pq}+f'D_{O,\lambda'pq}). \tag{56}$$

The applicability of the method described above is discussed in the third section of the previous paper I. It is hoped that this method will in the near future receive some actual applications, especially to several excited states of simple diatomic molecules.

4. SECOND METHOD

In the application of the SCF method to the general open-shell case, the most serious trouble comes from the fact that we need so-called off-diagonal Lagrangian multipliers when we add orthogonality conditions between orbitals to the variational problem as constraints.

Roothaan[2] succeeded in surmounting the difficulty in the case of the single open shell by an ingenious mathematical device. A direct generalization of

Roothaan's treatment to the two-open-shell case was proposed in I and the explicit exposition has been given in the previous section of the present paper. However, it should be noted that the treatment in the previous section can be applied only to the two-open-shell case in which the two open-shell orbitals have *no common symmetry*. The point is that the orthogonality between them is always guaranteed by symmetry and it is not necessary to add the orthogonality condition as a constraint to the variational problem. Thus we should say that so far we have done nothing to overcome the difficulty arising of the off-diagonal multipliers in the general open-shell case. Roothaan's original scheme[2] and its extension discussed above cover a fairly wide range of application, but unfortunately some simple but important cases slip out of the range; the simplest of them is the $1s2s\,^1S$ state of the helium atom.

Now we propose a new scheme to tackle the general two-open-shell case in which the total energy is expressed by Eq. (8). The central idea is that we preserve the orthogonality conditions between orbitals in some way other than adding them to the energy variation as constraints. If this is achieved, we have no trouble with the off-diagonal Lagrangian mutlipliers simply because we do not need them.

We state the problem as follows: Suppose we have the (i)th approximation for the orbitals, $\{\varphi_{\lambda\alpha p}^{(i)}\}$, which form a finite orthonormal set of functions. Let us find a next approximation for the orbitals, $\{\varphi_{\lambda\alpha p}^{(i+1)}\}$, avoiding the inclusion of any troublesome off-diagonal multipliers in the course of deriving the SCF equations.

We take the (i)th approximate orbitals $\{\varphi_{\lambda\alpha p}^{(i)}\}$ as the *basis functions* (just like $\{X_{\lambda\alpha p}\}$ in the previous section) and expand each of the $(i+1)$th approximate orbitals $\{\varphi_{\lambda\alpha j}^{(i+1)}\}$ in terms of the *temporal basis functions* $\{\varphi_{\lambda\alpha p}^{(i)}\}$:

$$\varphi_{\lambda\alpha j}^{(i+1)} = \sum_p \varphi_{\lambda\alpha p}^{(i)} C_{\lambda p j}^{(i+1)}, \qquad (57)$$

where the $\{C_{\lambda p j}^{(i+1)}\}$ are assumed to be real for simplicity. We require that the orbitals $\{\varphi_{\lambda\alpha j}\}$ must form an orthonormal set at all stages of approximation:

$$\langle \varphi_{\lambda\alpha j}^{(i+1)} \mid \varphi_{\lambda\alpha k}^{(i+1)} \rangle$$
$$= \sum_{pq} C_{\lambda p j}^{(i+1)} \langle \varphi_{\lambda\alpha p}^{(i)} \mid \varphi_{\lambda\alpha q}^{(i)} \rangle C_{\lambda q k}^{(i+1)}$$
$$= \sum_p C_{\lambda p j}^{(i+1)} C_{\lambda p k}^{(i+1)} = \delta_{jk}. \qquad (58)$$

This is the conditions which the coefficients $\{C_{\lambda p j}^{(i+1)}\}$ must satisfy. This implies that we go back to the usual normalization convention, (16), instead of the modified one, (18), adopted in the previous section. Thus we write

$$\sum_{pq} C_{\lambda p j}^{(i+1)} S_{\lambda p q}^{(i)} C_{\lambda q k}^{(i+1)} = \delta_{jk}, \qquad (59)$$

where

$$S_{\lambda p q}^{(i)} = d_\lambda^{-1} \sum_\alpha \langle \varphi_{\lambda\alpha p}^{(i)} \mid \varphi_{\lambda\alpha q}^{(i)} \rangle = \delta_{pq}, \qquad (60)$$

$H_{\lambda p q}^{(i)}$ is defined as follows:

$$H_{\lambda p q}^{(i)} = \sum_\alpha \langle \varphi_{\lambda\alpha p}^{(i)} \mid H \mid \varphi_{\lambda\alpha q}^{(i)} \rangle. \qquad (61)$$

Notice the difference between (22) and (61). Similarly,

$$\mathcal{J}_{\lambda pq, \mu rs}^{(i)} = \sum_{\alpha\beta} \int\int \varphi_{\lambda\alpha p}^{(i)*}(1) \varphi_{\mu\beta r}^{(i)*}(2) (1/r_{12}) \varphi_{\lambda\alpha q}^{(i)}(1) \varphi_{\mu\beta s}^{(i)}(2) dV_1 dV_2, \qquad (62)$$

$$\mathcal{K}_{\lambda pq, \mu rs}^{(i)} = \sum_{\alpha\beta} \int\int \varphi_{\lambda\alpha p}^{(i)*}(1) \varphi_{\mu\beta r}^{(i)*}(2) (1/r_{12}) \varphi_{\mu\beta s}^{(i)}(1) \varphi_{\lambda\alpha q}^{(i)}(2) dV_1 dV_2. \qquad (63)$$

It is, however, rather annoying to put superscripts (i) or $(i+1)$ on each of $\{\varphi_{\lambda\alpha p}\}$ and $\{C_{\lambda p j}\}$, and so hereafter we suppress them, bearing in mind that we are passing from the (i)th to the $(i+1)$th approximation for the orbitals, $\{\varphi_{\lambda\alpha p}^{(i+1)}\}$, by using the (i)th approximate orbitals $\{\varphi_{\lambda\alpha p}^{(i)}\}$ as temporal basis functions.

The expectation value of the total energy is now given by

$$E = 2 \sum_\lambda \sum_{pq} \sum_k C_{\lambda pk} H_{\lambda pq} C_{\lambda qk} + \sum_\lambda \sum_{pq} \sum_k \sum_\mu \sum_{rs} \sum_l C_{\lambda pk} C_{\mu rl} (2\mathcal{J}_{\lambda pq,\mu rs} - \mathcal{K}_{\lambda pq,\mu rs}) C_{\mu sl} C_{\lambda qk}$$

$$+ 2f \sum_\lambda \sum_{pq} \sum_m C_{\lambda pm} H_{\lambda pq} C_{\lambda qm} + f^2 \sum_\lambda \sum_{pq} \sum_m \sum_\mu \sum_{rs} \sum_n C_{\lambda pm} C_{\mu rn} (2a\mathcal{J}_{\lambda pq,\mu rs} - b\mathcal{K}_{\lambda pq,\mu rs}) C_{\mu sn} C_{\lambda qm}$$

$$+ 2f \sum_\lambda \sum_{pq} \sum_k \sum_\mu \sum_{rs} \sum_m C_{\lambda pk} C_{\mu rm} (2\mathcal{J}_{\lambda pq,\mu rs} - \mathcal{K}_{\lambda pq,\mu rs}) C_{\mu sm} C_{\lambda qk} + 2f' \sum_\lambda \sum_{pq} \sum_{m'} C_{\lambda pm'} H_{\lambda pq} C_{\lambda qm'}$$

$$+ f'^2 \sum_\lambda \sum_{pq} \sum_{m'} \sum_\mu \sum_{rs} \sum_{n'} C_{\lambda pm'} C_{\mu rn'} (2a'\mathcal{J}_{\lambda pq,\mu rs} - b'\mathcal{K}_{\lambda pq,\mu rs}) C_{\mu sn'} C_{\lambda qm'}$$

$$+ 2f' \sum_\lambda \sum_{pq} \sum_k \sum_\mu \sum_{rs} \sum_{m'} C_{\lambda pk} C_{\mu rm'} (2\mathcal{J}_{\lambda pq,\mu rs} - \mathcal{K}_{\lambda pq,\mu rs}) C_{\mu sm'} C_{\lambda qk}$$

$$+ 2ff' \sum_\lambda \sum_{pq} \sum_m \sum_\mu \sum_{rs} \sum_{m'} C_{\lambda pm} C_{\mu rm'} T_{\lambda pq,\mu rs} C_{\mu sm'} C_{\lambda qm}. \qquad (64)$$

The variational procedures to be adopted here are specified as follows: First we choose a set of closed- or open-shell orbitals (or a single orbital if it is not degenerate) specified by particular λ and j. Let us choose arbitrarily a closed shell first and specify it by Λ and K. Small variations are given only to $\{C_{\Lambda pK}\}$ with all other coefficients $\{C_{\lambda pj}\}$ held fixed. This is, in general, *not* permissible unless we have a certain mathematical device or trick to preserve the orthogonality conditions between the nonfixed and fixed orbitals. We are going to propose such a device which is expected to work, but just for convenience we defer a detailed explanation of the device for a while and perform the variational process as stated above.

The total energy E suffers only a partial variation with respect to the orbitals (Λ, K). We denote the variation by $\delta E_{\Lambda K}$:

$$\delta E_{\Lambda K} = \delta \left[2 \sum_{pq} C_{\Lambda pK} \bar{H}_{\Lambda pq} C_{\Lambda qK} + \sum_{pq} \sum_{rs} C_{\Lambda pK} C_{\Lambda rK} (2\mathcal{J}_{\Lambda pq,\Lambda rs} - \mathcal{K}_{\Lambda pq,\Lambda rs}) C_{\Lambda sK} C_{\Lambda qK} \right] + \cdots = 0, \qquad (65)$$

where

$$\bar{H}_{\Lambda pq} = H_{\Lambda pq} + \sum_{rs} \sum_{l \neq K} C_{\Lambda rl} (2\mathcal{J}_{\Lambda pq,\Lambda rs} - \mathcal{K}_{\Lambda pq,\Lambda rs}) C_{\Lambda sl} + \sum_{\mu \neq \Lambda} \sum_{rs} \sum_l C_{\mu rl} (2\mathcal{J}_{\Lambda pq,\mu rs} - \mathcal{K}_{\Lambda pq,\mu rs}) C_{\mu sl}$$

$$+ f \sum_\mu \sum_{rs} \sum_m C_{\mu rm} (2\mathcal{J}_{\Lambda pq,\mu rs} - \mathcal{K}_{\Lambda pq,\mu rs}) C_{\mu sm} + f' \sum_\mu \sum_{rs} \sum_m C_{\mu rm'} (2\mathcal{J}_{\Lambda pq,\mu rs} - \mathcal{K}_{\Lambda pq,\mu rs}) C_{\mu sm'}. \qquad (66)$$

The bracket $\delta[\cdots]$ includes all the terms containing $\{C_{\Lambda pK}\}$ in (64) and this is all we have to take care of, since all the other terms vanish under the present partial variation. Thanks to the device just mentioned, the only constraint to be added is

$$\delta\left(\sum_{pq} C_{\Lambda pK} S_{\Lambda pq} C_{\Lambda qK}\right) = 0. \qquad (67)$$

If we designate the Lagrangian multiplier by $-2\epsilon_{\Lambda K}$, the resulting equations become

$$\sum_q F_{\Lambda pq} C_{\Lambda qK} = \epsilon_{\Lambda K} \sum_q S_{\Lambda pq} C_{\Lambda qK}, \qquad (68)$$

where

$$F_{\Lambda pq} = \bar{H}_{\Lambda pq} + G_{\Lambda pq}, \qquad (69)$$

$$G_{\Lambda pq} = \sum_{rs} C_{\Lambda rK} (2\mathcal{J}_{\Lambda pq,\Lambda rs} - \mathcal{K}_{\Lambda pq,\Lambda rs}) C_{\Lambda sK}. \qquad (70)$$

We turn to the explanation of the device which makes it possible to perform the partial variation procedure shown above. It is based upon a special choice of the expansion coefficients $\{C_{\lambda pj}\}$ in the formula,

$$\varphi_{\lambda\alpha j}{}^{(i+1)} = \sum_p \varphi_{\lambda\alpha p}{}^{(i)} C_{\lambda pj}, \tag{71}$$

where the $\{\varphi_{\lambda\alpha p}\}$ are labeled in such a way that $p=1$ gives the lowest orbital, $p=2$ the second, $p=3$ the third and so forth. We choose the coefficients $\{C_{\lambda pj}\}$ as follows:

$$
\left.
\begin{aligned}
&C_{\Lambda KK} \neq 0, \\
&C_{\Lambda pK} \neq 0, \quad \text{if} \quad M_\Lambda < p \leqslant N_\Lambda,
\end{aligned}
\right\} \text{subject to variation}
$$

$$C_{\Lambda pK} = 0, \quad \text{if} \quad 1 \leqslant p \leqslant M_\Lambda \quad \text{and} \quad p \neq K,$$

$$C_{\Lambda pk} = \delta_{pk}, \quad \text{if} \quad k \neq K, \tag{72}$$

$$C_{\lambda pk} = \delta_{pk}, \quad \text{if} \quad \lambda \neq \Lambda,$$

$$C_{\lambda pm} = \delta_{pm},$$

$$C_{\lambda pm'} = \delta_{pm'}.$$

Here M_Λ is the highest occupied orbital number and N_Λ is the total number of the basis functions of symmetry species Λ. The first two lines give the variational coefficients and the third line guarantees the orthogonalities among the nonfixed and fixed orbitals which belong to the same symmetrical species. The implication of the remaining four lines is that we are trying to improve just one orbital (set) at a time. To be more explicit,

$$
\begin{aligned}
\varphi_{\Lambda\alpha k}{}^{(i+1)} &= \varphi_{\Lambda\alpha k}{}^{(i)}, \quad (k \neq K), \\
\varphi_{\lambda\alpha k}{}^{(i+1)} &= \varphi_{\lambda\alpha k}{}^{(i)}, \quad (\lambda \neq \Lambda), \\
\varphi_{\lambda\alpha m}{}^{(i+1)} &= \varphi_{\lambda\alpha m}{}^{(i)}, \\
\varphi_{\lambda\alpha m'}{}^{(i+1)} &= \varphi_{\lambda\alpha m'}{}^{(i)}.
\end{aligned}
\tag{73}
$$

Under the specifications of $\{C_{\lambda pk}\}$ in (72), the SCF equations (68) become

$$F_{\Lambda pK}C_{\Lambda KK} + \sum_{q>M_\Lambda} F_{\Lambda pq}C_{\Lambda qK} = \epsilon_{\Lambda K}C_{\Lambda pK}, \quad (p=K, M_\Lambda+1, M_\Lambda+2, \cdots, N_\Lambda), \tag{74}$$

where

$$F_{\Lambda pq} = \bar{H}_{\Lambda pq} + G_{\Lambda pq}, \tag{75}$$

$$\bar{H}_{\Lambda pq} = H_{\Lambda pq} + \sum_{l \neq K}(2\mathcal{J}_{\Lambda pq,\Lambda ll} - \mathcal{K}_{\Lambda pq,\Lambda ll}) + \sum_{\mu \neq \Lambda}\sum_l(2\mathcal{J}_{\Lambda pq,\mu ll} - \mathcal{K}_{\Lambda pq,\mu ll}) + f\sum_\mu\sum_m(2\mathcal{J}_{\Lambda pq,\mu mm} - \mathcal{K}_{\Lambda pq,\mu mm})$$

$$+ f'\sum_\mu\sum_{m'}(2\mathcal{J}_{\Lambda pq,\mu m'm'} - \mathcal{K}_{\Lambda pq,\mu m'm'}), \tag{76}$$

$$G_{\Lambda pq} = \sum_{rs} C_{\Lambda rK}(2\mathcal{J}_{\Lambda pq,\Lambda rs} - \mathcal{K}_{\Lambda pq,\Lambda rs})C_{\Lambda sK}, \quad (p, q, r, s = K, M_\Lambda+1, M_\Lambda+2, \cdots, N_\Lambda). \tag{77}$$

These are the equations for the self-consistent determination of the coefficients $\{C_{\Lambda pK}\}$. Since the derivation of the corresponding equations for $\{C_{\Lambda pM}\}$ and $\{C_{\Lambda pM'}\}$ are quite similar to the preceding one, we simply write down the results:

$$F_{\Lambda pM}C_{\Lambda MM} + \sum_{q>M_\Lambda} F_{\Lambda pq}C_{\Lambda qM} = \epsilon_{\Lambda M}C_{\Lambda pM}, \quad (p=M, M_\Lambda+1, M_\Lambda+2, \cdots, N_\Lambda), \tag{78}$$

where

$$F_{\Lambda pM} = \bar{H}_{\Lambda pq} + G_{\Lambda pq}, \tag{79}$$

$$\bar{H}_{\Lambda pq} = H_{\Lambda pq} + f\sum_{n \neq M}(2a\mathcal{J}_{\Lambda pq,\Lambda nn} - b\mathcal{K}_{\Lambda pq,\Lambda nn}) + f\sum_{\mu \neq \Lambda}\sum_n(2a\mathcal{J}_{\Lambda pq,\mu nn} - b\mathcal{K}_{\Lambda pq,\mu nn})$$

$$+ \sum_\mu\sum_l(2\mathcal{J}_{\Lambda pq,\mu ll} - \mathcal{K}_{\Lambda pq,\mu ll}) + f'\sum_\mu\sum_{m'}\mathcal{T}_{\Lambda pq,\mu m'm'}, \tag{80}$$

$$G_{\Lambda pq} = f\sum_{rs} C_{\Lambda rM}(2a\mathcal{J}_{\Lambda pq,\Lambda rs} - b\mathcal{K}_{\Lambda pq,\Lambda rs})C_{\Lambda sM}, \quad (p, q, r, s = M, M_\Lambda+1, M_\Lambda+2, \cdots, N_\Lambda). \tag{81}$$

Similarly, the equations for $\{C_{\Lambda pM'}\}$ may be obtained by the replacements $M \to M'$, $n \to n'$, $m' \to m$, $f \to f'$, $f' \to f$, $a \to a'$, and $b \to b'$.

It seems practical to take a simple example for the illustration of the entire SCF procedure. Let us consider the $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^\alpha(2\pi)^\beta$ configuration of a molecule. Here we have two symmetry species, σ and π, and we may denote them by $\lambda=0$ and $\lambda=1$, respectively. In the $\sigma(\lambda=0)$ shells, k runs from 1 to 3

but there are no m and m' since there is no open shell of σ symmetry. On the other hand, in the $\pi(\lambda=1)$ shells, we have two open shells and no closed shell if $1 \leqslant \alpha$, $\beta \leqslant 3$. To begin with, we must have a starting set of orthonormal functions $\{\varphi_{\lambda\alpha p}{}^{(0)}\}$. This is obtained by a proper use of Schmidt orthogonalization procedure or by solving the SCF problem for an approximate configuration simpler than the one under consideration. For example, if $\alpha+\beta=4$ an obvious choice

should be a closed-shell configuration

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4.$$

Now, by using $\{\varphi_{\lambda\alpha p}{}^{(0)}\}$ as the basis functions, we apply the SCF equations for closed shells (74) to (1σ) with all the other orbitals (coefficients) held fixed. This process yields a better approximate orbital for (1σ) and at the same time a new orthonormal set of "basis" function $\{\varphi_{\lambda\alpha p}{}^{(1)}\}$ for the use in the next step. A natural (but not necessary) choice of the next step is the application of (74) to (2σ). Thus we apply consecutively appropriate SCF equations to (3σ), (1π) and (2π). After that, we restart again the whole process [from (1σ) to (2π)] until over-all self-consistency is attained.

The total energy may be calculated from (8) and we are ready to start the configuration interaction calculations to improve the SCF approximation.

5. DISCUSSION

Since we have proposed two SCF schemes for treating the electronic systems, we should make some comparison between them.

If we limit ourselves to the region where both methods can be equally applied, the first method seems more compact and elegant from the mathematical point of view and may actually be more convenient to use. In fact, Roothaan's scheme has already established its practicability in various cases and the same may be expected for the first method of the present paper, which is a straightforward generalization of Roothaan's method.

However, there are indications that we might get into trouble when we apply Roothaan's method to the system in which the number of electrons is large and/or some of the electrons are not firmly bound, because of the tendency of the oscillatory behavior of the solution. The trouble may be attributed to the topological com-

plexity of the energy surface which depends upon so many parameters in a very complicated way.

The apparent disadvantage of the second method is the necessity of wearisome repetition of many small SCF procedures. Furthermore we have to change the "basis" functions every time we pass to the next SCF procedure as it is seen in the above description of the procedure. This orthonormal transformation of the basis functions at every step would be a formidable task for desk calculations. However, it seems reasonably straightforward to program such a transformation for an automatic computer. In addition, each of partial SCF procedures contained in the entire SCF procedure in the second method is much simpler than the SCF procedures of the first method and the implication is that we are dealing with fairly simple energy surfaces. We may hope that the second method could be a relief to overcome the so-called convergence difficulty.

Finally it must be mentioned that the second method commands a wider range of applicability than the first method.

The underlying idea common to both methods is the partial fixation of orbitals during the variational procedure of the total energy. From this point of view, both methods are to be regarded as just two of many possible variations of the theme. The scheme proposed in the fourth section of I is one of the possible combinations of the two methods. The works of Pople and Nesbet,[5] Lykos and Parr,[6] and McWeeny[7] contain similar ideas.

[5] J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954).
[6] P. G. Lykos and R. G. Parr, J. Chem. Phys. **24**, 1164 (1956).
[7] R. McWeeny, Revs. Modern Phys. **32**, 335 (1960).