

Hartree-Fock equations for open shell states

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Fock equations are derived for multideterminantal single configuration states with any number of open shells of any symmetry. New operators, "projection-transition" operators and "off-diagonal" Coulomb and exchange operators, are required for cases that do not fit a Roothaan-like mold.

I. INTRODUCTION

Roothaan's open shell Hartree-Fock method¹ does not seem to have been extended to certain states having two or more open shells of the same symmetry. Yarkony, Schaefer, and Bender² were able to treat the singlet states of the $1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 7a_1^2 1e^4 2e^3 3e$ configuration of the acetyl cation self-consistently only by inventing a new, completely general computational procedure, which they call "symmetry restricted annihilation of single excitations" (SRAS). The purpose of this paper is to derive Hartree-Fock equations applicable to any multideterminantal state of a single configuration that has any number of open shells of any symmetry.

One-electron Hartree-Fock Hamiltonians, or Fock operators, generally have the form

$$F = h_{\text{BN}} + V_{\text{SCF}} \quad (1)$$

Here h_{BN} denotes the Hamiltonian for a single electron in the field of the bare nuclei. In the closed shell case, the self-consistent field potential V_{SCF} is a sum of Coulomb and exchange operators. In Roothaan's open shell cases,¹ V_{SCF} also involves "coupling" operators that are anticommutators of projection operators with Coulomb and exchange operators.

The major limitation of Roothaan's treatment¹ and of the extensions to certain doubly open shell states by Huzinaga^{3,4} and by Hunt, Dunning, and Goddard,^{5,6} and others⁷⁻¹⁰ is the requirement that $1/r_{12}$ enter the energy expression only through Coulomb and exchange integrals. Relaxation of this requirement is what leads to the "off-diagonal" Coulomb and exchange operators, and to "projection-transition" operators in V_{SCF} .

(In fact, the rotation-matrix procedure of Hunt, Dunning, and Goddard,^{11a} used to solve the system of equations discussed by them earlier,^{5,6} need not start from such a limited energy expression. The generalization by Yaffe and Goddard^{11b} to any multiconfigurational state has recently been given.)

A second limitation is the requirement that the Coulomb and exchange integrals enter in a "symmetric" way, so that the resulting V_{SCF} are invariant under certain unitary transformations. The appropriate formula may not be the energy expectation value with any convenient wavefunction. The derivation given below starts with an energy expectation value—any convenient one will do. Even though the energy expression is not "symmetrized," one can completely determine V_{SCF} in matrix form.

It is then straightforward to convert the Fock matrix

into a more conventional integrodifferential operator, with the use of group theory. A symmetrized energy expression is obtained as a byproduct.

The results here are similar to Roothaan's at the stage that the open shell and closed shell orbitals have different Fock operators, but they are somewhat different at the single, combined Fock-operator stage. A direct comparison is made in Sec. VI. The results here are no more general than SRAS, but they do represent a more conventional treatment of the open shell restricted Hartree-Fock problem.

The Fock matrices are defined by Eqs. (8), (9), (21), (24), (25), (26), and (33). The integrodifferential forms of the Fock operators are given by Eq. (57)–(60), (38), and (39). Some of these equations are illustrated in Sec. VII for the excited states of the acetyl cation that led to SRAS.

II. THE ENERGY EXPRESSION

The energy expectation value for a single configuration multideterminantal wavefunction ψ has the form

$$E = \sum_{a \in \psi} f_a n_a \langle \phi_1^{(a)} | h_{\text{BN}} | \phi_1^{(a)} \rangle + \sum_{\substack{a \in \psi \\ b \in \psi}} \sum_{\substack{i=1 \\ j=1}}^{(1/2)n_a} \sum_{\substack{k=1 \\ l=1}}^{(1/2)n_b} f_a f_b [2q_{aj; bkl} \\ \times \langle \phi_i^{(a)}(1) \phi_k^{(b)}(2) | 1/r_{12} | \phi_j^{(a)}(1) \phi_l^{(b)}(2) \rangle - q'_{aj; bkl} \\ \times \langle \phi_i^{(a)}(1) \phi_k^{(b)}(2) | 1/r_{12} | \phi_i^{(b)}(1) \phi_j^{(a)}(2) \rangle] \quad (2)$$

Here a and b denote shells; we use " $a \in \psi$ " to mean, "Shell a which contributes to the wavefunction ψ "; the $\phi_i^{(a)}$ ($i = 1, 2, \dots, \frac{1}{2}n_a$) denote the spatial orbitals of Shell a ; n_a denotes the number of spin orbitals belonging to Shell a ; and $f_a n_a$ denotes the number of spin orbitals from Shell a to be found in each determinant in ψ . The f_a is the fractional occupation of Shell a . The q and q' are constants that lump together sums of products of the coefficients of the determinants closed shell case, one would find $f_a = f_b = 1$, and $q_{aj; bkl} = q'_{aj; bkl} = \delta_{ij} \delta_{kl}$.

If E is degenerate, then different ψ yield the same value of E , but possibly with different q and q' . By summing over the degenerate states, or by exploiting relations among the $1/r_{12}$ matrix elements, one can obtain a symmetrized set of q and q' . Such symmetrization is not necessary for the derivation below, but will fall out later automatically, when the integrodifferential form of the operators is derived.

In general the spatial orbitals transform irreducibly under the symmetry group of the Hamiltonian. This fact has been used to simplify the h_{BN} term in Eq. (2).

Two shells, a and b , of the same symmetry type will be called *equivalent* if ψ is invariant under all 2×2 unitary transformations of Shell a with Shell b .

$$\phi_i^{(c)} = U_{ac}\phi_i^{(a)} + U_{bc}\phi_i^{(b)} \quad (i = 1, 2, \dots, \frac{1}{2}n_a), \quad (3)$$

$$\phi_i^{(d)} = U_{ad}\phi_i^{(a)} + U_{bd}\phi_i^{(b)} \quad (i = 1, 2, \dots, \frac{1}{2}n_a). \quad (4)$$

Closed shells of the same symmetry type are necessarily equivalent.

It may be necessary to make a minor modification in the expression (2) for E , in a specific case. Since ψ is invariant, the *value* of E cannot change under a unitary transformation of equivalent shells. If $q_{a'ij;ckl}$ and $q_{bij;ckl}$ are identical when a and b are equivalent, and q' also, then E would clearly not change. But because the $1/r_{12}$ matrix elements in Eq. (2) are not all independent, it is possible for $q_{a'ij;ckl}$ and $q_{bij;ckl}$ not to be the same for equivalent a and b . In such a case, it is always possible to pick a set of $q_{a'ij;ckl}$ by which $q_{a'ij;ckl}$ can be replaced, so that even the *form* of E will be invariant. Similar remarks apply to q' , and to the second shell label in q , and in q' . Without loss in generality then, we assume this to have been done. That is, we require that the q and q' of the expectation value (2) be modified, if necessary, to satisfy

$$\left. \begin{aligned} q_{a'ij;b'lk} &= q_{a'ij;bkl} \\ q_{a'ij;b'lk} &= q'_{a'ij;bkl} \end{aligned} \right\} \begin{aligned} &(a' \text{ equivalent to } a, b' \text{ equivalent to } b, \\ &\text{for all } i, j, k, \text{ and } l). \end{aligned} \quad (5)$$

Moreover, because the $1/r_{12}$ matrix elements of Eq. (2) are unchanged in value by the interchange of Electrons 1 and 2, we may also require that

$$q_{bkl;a'ij} = q_{a'ij;bkl}, \quad q'_{bkl;a'ij} = q'_{a'ij;bkl}, \quad (6)$$

$$q_{a'ij;b'lk} = (q_{a'ij;bkl})^* \quad q'_{a'ij;b'lk} = (q'_{a'ij;bkl})^* \quad (7)$$

The formula (2) for E seems to be completely general, for a single configuration with any number of open shells. The "standardization" of the q and q' values [Eqs. (5)–(7)], without being a loss in generality, simplifies the derivation of pseudoeigenvalue equations in Sec. IV.

III. RESTRICTED VARIATION OF ψ AND E

In the restricted Hartree-Fock method, E is required to be stationary with respect to arbitrary variations $\delta\phi_i^{(a)}$ of the $\phi_i^{(a)}$, subject to two restrictions of symmetry and orthogonality. The symmetry restriction is that an entire shell must be varied at once: the $\delta\phi_i^{(a)}$, $i = 1, 2, \dots, \frac{1}{2}n_a$, must change simultaneously and consistently, i. e., the $\delta\phi_i^{(a)}$ must transform according to the same irreducible representation as the $\phi_i^{(a)}$. The orthogonality restriction is that the $\phi_i^{(a)} + \delta\phi_i^{(a)}$ must remain mutually orthogonal and normalized. The aim of this section is to derive formulas for δE and a "first stage" Fock matrix. The equations satisfied by the $\phi_i^{(a)}$ are the subject of the next section.

First let us define a Fock matrix $F^{(a)}$. After characterizing $F^{(a)}$, we will obtain the formula for δE that

motivated its definition. Let $\xi_i^{[a]}$ and $\eta_j^{[a]}$ be arbitrary functions with the same symmetry properties as $\phi_i^{(a)}$. Define $F^{(a)}$ by

$$\langle \xi_i^{[a]} | F^{(a)} | \eta_j^{[a]} \rangle = \delta_{ij} \langle \xi_i^{[a]} | F^{(a)} | \eta_i^{[a]} \rangle, \quad (8)$$

$$\begin{aligned} \langle \xi_i^{[a]} | F^{(a)} | \eta_j^{[a]} \rangle &\equiv \langle \xi_i^{[a]} | h_{BN} | \eta_j^{[a]} \rangle \\ &+ n_a^{-1} \sum_{b \in \psi} \sum_{j=1}^{(1/2)n_a} \sum_{k=1}^{(1/2)n_b} f_b [4q_{a'ij;bkl} \langle \xi_i^{[a]} \phi_k^{(b)} | 1/r_{12} | \eta_j^{[a]} \phi_i^{(b)} \rangle \\ &- 2q'_{a'ij;bkl} \langle \xi_i^{[a]} \phi_k^{(b)} | 1/r_{12} | \phi_i^{(b)} \eta_j^{[a]} \rangle]. \end{aligned} \quad (9)$$

There are four things the reader should note about $F^{(a)}$.

- (1) All $\frac{1}{2}n_a$ of the $\xi_i^{[a]}$ and all $\frac{1}{2}n_a$ of the $\eta_j^{[a]}$ are involved in the definition of the $\xi_i^{[a]}\eta_j^{[a]}$ matrix element.
- (2) $F^{(a)}$ by definition is diagonal in the index "i," and the matrix elements are independent of the value of i.
- (3) As a consequence of Eq. (7), $F^{(a)}$ is Hermitian.
- (4) As a consequence of the standardization of q and q' , Eq. (5), $F^{(a')}$ and $F^{(a)}$ are identical if Shells a' and a are equivalent.

Notation. The symbol " $\{a\}$ " will be used to mean, "Shell a , and all shells contributing to ψ that are equivalent (in the sense of Sec. II) to Shell a ." The symbol " $[a]$ " will be used to mean, "the symmetry class, i. e., irreducible representation, corresponding to Shell a ." Thus, $F^{(a)}$ is defined with respect to the equivalence class $\{a\}$ on the space of functions of symmetry class $[a]$.

Now consider the change in E resulting from the variation of Shell a . If the $\delta\phi_i^{(a)}$ are orthogonal to all the $\phi_i^{(b)}$ of all shells contributing to ψ , then δE can be found from Eqs. (2) and (5)–(9) to be

$$\delta E_I = f_a n_a [\langle \delta\phi_1^{(a)} | F^{(a)} | \phi_1^{(a)} \rangle + \langle \phi_1^{(a)} | F^{(a)} | \delta\phi_1^{(a)} \rangle]. \quad (10)$$

The choice of the subscript "1" is purely arbitrary: by Eq. (8), any of the values $1, 2, \dots, \frac{1}{2}n_a$ would do.

If $\delta\phi_i^{(a)}$ is not orthogonal to all the $\phi_i^{(b)}$, namely,

$$\delta\phi_i^{(a)} = \epsilon\phi_i^{(b)}, \quad (11)$$

then to maintain orthogonality, $\phi_i^{(b)}$ must undergo a reciprocal change,

$$\delta\phi_i^{(b)} = -\epsilon^*\phi_i^{(a)}. \quad (12)$$

For δE one then obtains^{6,10}

$$\begin{aligned} \delta E_{II} &= \epsilon^* n_a \langle \phi_1^{(b)} | f_a F^{(a)} - f_b F^{(b)} | \phi_1^{(a)} \rangle \\ &+ \epsilon n_a \langle \phi_1^{(a)} | f_a F^{(a)} - f_b F^{(b)} | \phi_1^{(b)} \rangle. \end{aligned} \quad (13)$$

Again, the choice of subscript "1" is purely arbitrary: any value would do. Note that for Eqs. (11)–(13), one has $[a] = [b]$ and $n_a = n_b$. Note also that if Shells a and b are equivalent, δE_{II} vanishes identically.

IV. FOCK EQUATIONS. MATRIX FORM

Four steps are required to obtain the "Fock equations" in a canonical form. First, δE is set equal to zero, which gives a system of equations for the orbitals. Second, the equations for orbitals of each equivalence

class are put into pseudo-eigenvalue form by an appropriate unitary transformation and the introduction of "coupling" operators. Third, the Fock operators for each equivalence class of a given symmetry are combined to give a single Fock operator for that symmetry class. Fourth, the symmetry-class Fock operators are combined to give a single F for all the orbitals.

A. Primitive equations for the orbitals

From $\delta E_{\perp} = 0$, we conclude from Eqs. (8)–(10) that

$$f_a F^{(a)} \phi_i^{(a)} = \sum_{\substack{b \in \emptyset \\ b \in [a]}} \theta_b^a \phi_i^{(b)} \quad (a \in \psi; i = 1, 2, \dots, \frac{1}{2}n_a). \quad (14)$$

The constants θ_b^a , which are independent of i by the definition of $F^{(a)}$ [Eq. (8)], are given by

$$\theta_b^a = \langle \phi_i^{(b)} | f_a F^{(a)} | \phi_i^{(a)} \rangle. \quad (15)$$

From $\delta E_{\parallel} = 0$ and Eqs. (13) and (15), we conclude that for the restricted Hartree-Fock orbitals,

$$\theta_b^a = \theta_a^{b*}, \quad (16)$$

i. e., the quantities θ_b^a , calculated with restricted Hartree-Fock orbitals, form a Hermitian matrix. Equations (14) and (16) are a set of coupled equations that determine the $\phi_i^{(a)}$.

We have deliberately used the notation θ_b^a rather than θ_{ba} to emphasize that θ_b^a and θ_a^b are matrix elements of different operators, $f_a F^{(a)}$ and $f_b F^{(b)}$. Equation (16) is one of the necessary and sufficient conditions for the $\phi_i^{(a)}$ to be the Hartree-Fock orbitals. In the manipulations below, one must be cautious not to regard Eq. (16) as an identity and inadvertently eliminate it from the working equations used to determine the Hartree-Fock orbitals.^{12a}

B. Pseudo-eigenvalue equations for each symmetry class

To put Eqs. (14) and (16) into pseudo-eigenvalue form, we first note that $F^{(a)}$ is invariant to unitary transformations among equivalent shells, like Eqs. (3) and (4), that do not scramble the i indices of the $\phi_i^{(b)}$. This fact follows from Eqs. (5) and (9), and is the motivation for the standardization of the q and q' . Consequently the $\phi_i^{(b)}$, for $b \in [a]$, can be chosen to make diagonal over $[a]$, the matrix of the θ associated with $f_a F^{(a)}$, and we may take instead of Eq. (14),

$$f_a F^{(a)} \phi_i^{(a)} = f_a \epsilon_a \phi_i^{(a)} + \sum_{\substack{b \in \emptyset \\ b \in [a] \\ b \in [a]}} \theta_b^a \phi_i^{(b)} \quad (a \in \psi, i = 1, 2, \dots, \frac{1}{2}n_a). \quad (17)$$

In the light of the caution just voiced, we note that the implication of Eq. (17) is that $\theta_a^{a'}$ vanish for $a' \neq a$, both $\in [a]$. For these a', a'' , Eq. (16) is automatically satisfied.

Next we introduce Eq. (16) into Eq. (17) by means of "coupling" operators, so that the remaining θ_b^a are cancelled when Eq. (16) is satisfied. Let $\Lambda_{[b]}^{[a]}$ be Hermitian and satisfy^{12b}

$$f_a \langle \phi_i^{(b)} | \Lambda_{[b]}^{[a]} | \phi_i^{(a)} \rangle = -\delta_{ij} [\theta_a^{b*} + k_b^a (\theta_b^a - \theta_a^{b*})] \quad (b \notin [a], b \in [a]), \quad (18)$$

where $k_b^a \neq 1$ is an arbitrary constant to be specified later. Define the projection operator $P^{(b)}$ by

$$P^{(b)} \equiv \sum_{c \in [b]} \sum_{i=1}^{(1/2)n_b} | \phi_i^{(c)} \rangle \langle \phi_i^{(c)} |, \quad (19)$$

and let $\{\Lambda_{[b]}^{[a]}, P^{(b)}\}$ denote the anticommutator,

$$\{\Lambda_{[b]}^{[a]}, P^{(b)}\} \equiv \Lambda_{[b]}^{[a]} P^{(b)} + P^{(b)} \Lambda_{[b]}^{[a]}. \quad (20)$$

Define the "second-stage" Fock operator $\hat{F}^{(a)}$ by

$$\hat{F}^{(a)} \equiv F^{(a)} + \sum_{\substack{(b) \in \emptyset \\ (b) \neq [a]}} \{\Lambda_{[b]}^{[a]}, P^{(b)}\}. \quad (21)$$

The restricted Hartree-Fock orbitals $\phi_i^{(a)}$ are eigenfunctions of $\hat{F}^{(a)}$:

$$\hat{F}^{(a)} \phi_i^{(a)} = \epsilon_a \phi_i^{(a)} + f_a^{-1} \sum_{\substack{b \in \emptyset \\ b \in [a] \\ b \in [a]}} \phi_i^{(b)} (\theta_b^a - \theta_a^{b*}) (1 - k_b^a) \quad (22)$$

$$= \epsilon_a \phi_i^{(a)}. \quad (23)$$

Note how Eq. (16) is implied by Eq. (23).

One choice for $\Lambda_{[b]}^{[a]}$ that fixes the anticommutator of Eq. (20) as the appropriate "coupling" operator, in the spirit of Goddard, Dunning, and Hunt,⁶ is

$$\Lambda_{[b]}^{[a]} \equiv - (f_a)^{-1} f_b F^{(b)}. \quad (24)$$

For this choice, $k_b^a = 0$ in Eq. (18).

If $f_a \neq f_b$, then another choice is possible that is more in the spirit of Roothaan¹ in that it involves only $1/r_{12}$ and not h_{BN} . This choice has $k_b^a = f_b / (f_b - f_a)$:

$$\Lambda_{[b]}^{[a]} = (f_a - f_b)^{-1} f_b (F^{(a)} - F^{(b)}). \quad (25)$$

C. The Fock matrix for a symmetry class

It is not difficult to combine the $\hat{F}^{(a)}$ into a single $F^{[a]}$ for each symmetry class.¹³ The basic idea is to start with a given equivalence class $[a]$, then add to $\hat{F}^{(a)}$ terms like $\{P^{(b)}, \hat{F}^{(b)} - \hat{F}^{(a)}\}$ that "switch" from $\hat{F}^{(a)}$ to $\hat{F}^{(b)}$ when operating on $\phi_i^{(b)}$. At this step some unwanted terms are introduced that must be cancelled by a third set of terms, $-\frac{1}{2} P^{(b)} (\hat{F}^{(b)} + \hat{F}^{(c)} - 2\hat{F}^{(a)}) P^{(c)}$. When $f_b = f_c$, however, Eq. (16) becomes "cancelled out," and it is necessary to reintroduce it with a fourth set of terms involving $\Lambda_{[c]}^{[b]} - \Lambda_{[b]}^{[c]}$.

A feature of $F^{[a]}$ as described above is that all the "correction terms" involve differences of \hat{F} 's, so that if Eq. (25) is always applicable for the $\Lambda_{[b]}^{[a]}$, then $F^{[a]}$ will differ from $F^{(a)}$ (and $\hat{F}^{(a)}$) only by terms involving $1/r_{12}$, not h_{BN} .

The recipe for $F^{[a]}$ is not unique. It depends on which $\hat{F}^{(a)}$ one starts with. Also the fourth set of (correction) terms, involving $\Lambda_{[c]}^{[b]} - \Lambda_{[b]}^{[c]}$, can be put in with an arbitrary factor. Further, in order to put in the last set of terms, it is necessary to order the equivalent sets of a given symmetry, $\{a\}, \{b\}, \{c\}, \dots$. We reserve $\{a\}$ for the first, and $\{b\}$ and $\{c\}$ for others, and write $\{b\} < \{c\}$ or $\{c\} > \{b\}$ to mean that $\{b\}$ precedes $\{c\}$ in the list. $F^{[a]}$ also depends on the ordering.

As constructed, $F^{[a]}$ is Hermitian.

We now write the definition of $F^{[a]}$ and verify that each $\phi_i^{(a)}$ is an eigenfunction with eigenvalue ϵ_a . We use Eq. (22) for $\hat{F}^{(a)}\phi_i^{(a)}$ to follow the contribution of Eq. (16):

$$F^{[a]} \equiv \hat{F}^{(a)} + \sum_{\substack{\{b\} > \{a\} \\ \{b\} \in \{a\}}} \{P^{(b)}, \hat{F}^{(b)} - \hat{F}^{(a)}\} - \frac{1}{2} \sum_{\substack{\{b\} > \{a\} \\ \{c\} > \{a\} \\ \{b\} \in \{a\} \\ \{c\} \in \{a\}}} P^{(b)} (\hat{F}^{(b)} + \hat{F}^{(c)} - 2\hat{F}^{(a)}) P^{(c)} + \frac{1}{2} \sum_{\substack{\{c\} > \{b\} > \{a\} \\ \{b\} \in \{a\} \\ \{c\} \in \{a\}}} \delta_{f_b f_c} [P^{(b)} (\Lambda_{[c]}^{(b)} - \Lambda_{[b]}^{(c)}) P^{(c)} + P^{(c)} (\Lambda_{[c]}^{(b)} - \Lambda_{[b]}^{(c)}) P^{(b)}] . \tag{26}$$

For $d \in \{a\}$, we have

$$F^{[a]} \phi_i^{(d)} = \hat{F}^{(a)} \phi_i^{(d)} + \sum_{\{b\} > \{a\}} P^{(b)} (\hat{F}^{(b)} - \hat{F}^{(a)}) \phi_i^{(d)} \tag{27}$$

$$= \epsilon_a \phi_i^{(d)} + \sum_{\{b\} > \{a\}} \sum_{e \in \{b\}} \phi_i^{(e)} (\theta_e^a - \theta_e^a) (1 - k_e^a) / f_e \tag{28}$$

$$= \epsilon_a \phi_i^{(d)} \quad (d \in \{a\}) . \tag{29}$$

For $d \notin \{a\}$, we have

$$F^{[a]} \phi_i^{(d)} = \hat{F}^{(a)} \phi_i^{(d)} + \frac{1}{2} \sum_{\{b\} > \{a\}} P^{(b)} (\hat{F}^{(b)} - \hat{F}^{(a)}) \phi_i^{(d)} + \frac{1}{2} \left(\sum_{\{c\} > \{a\}} - \sum_{\substack{\{c\} < \{d\} \\ \{c\} > \{a\}}} \right) \delta_{f_c f_d} P^{(c)} (\Lambda_{[c]}^{(d)} - \Lambda_{[d]}^{(c)}) \phi_i^{(d)} \tag{30}$$

$$= \epsilon_a \phi_i^{(d)} + \sum_{e \in \{a\}} \phi_i^{(e)} (\theta_e^d - \theta_e^{a*}) (1 - k_e^d) / f_e + \frac{1}{2} \sum_{\{b\} > \{a\}} \sum_{e \in \{b\}} \phi_i^{(e)} (\theta_e^d - \theta_e^{a*}) [(1 - k_e^d) / f_e - (1 - k_e^a) / f_a + \delta_{f_d f_e} / f_d] + \frac{1}{2} \sum_{\substack{\{b\} < \{d\} \\ \{b\} > \{a\}}} \sum_{e \in \{b\}} \phi_i^{(e)} (\theta_e^d - \theta_e^{a*}) [(1 - k_e^d) / f_e - (1 - k_e^a) / f_a - \delta_{f_d f_e} / f_d] \tag{31}$$

$$= \epsilon_a \phi_i^{(d)} \quad (d \notin \{a\}) . \tag{32}$$

D. Final unified Fock matrix

One can easily define a single Fock matrix F from the $F^{[a]}$ via

$$\langle \xi_i^{[a]} | F | \eta_j^{[b]} \rangle = \delta_{[a][b]} \delta_{ij} \langle \xi_i^{[a]} | F^{[a]} | \eta_j^{[a]} \rangle , \tag{33}$$

$$F \phi_i^{(a)} = \epsilon_a \phi_i^{(a)} \quad (a \in \psi) . \tag{34}$$

The comments on the nonuniqueness of $F^{[a]}$ pertain also to F . To avoid confusion, it is particularly important to keep in mind the dependence on the ordering, $\{a\}$, $\{b\}$, $\{c\}, \dots$, of the equivalence sets of symmetry $[a]$.

F is defined by the sequence of Eqs. (33), (26), (21), (8), (9), and (24) and/or (25). Primarily because of the form of Eq. (9), the various Fock operators are defined as matrices. For computations based on matrix algebra, such a definition is to be preferred. But in other circumstances, an integrodifferential form is preferable. This form is taken up in the next section.

V. FOCK OPERATORS. INTEGRODIFFERENTIAL FORM

In the *closed shell* case, one has $q_{a1j; bki} = q_{a1j; bki}^i = \delta_{ij} \delta_{ki}$. The formula for $F^{[a]}$, Eq. (9), can be rewritten using Coulomb and exchange operators,

$$\langle \xi_1^{[a]} | F^{[a]} | \eta_1^{[a]} \rangle = \langle \xi_1^{[a]} | h_{BN} | \eta_1^{[a]} \rangle + \sum_{b \in \psi} \sum_{i=1}^{(1/2)n_a} \sum_{k=1}^{(1/2)n_b} n_a^{-1}$$

$$\times \langle \xi_i^{[a]} | 4J_{(b)k} - 2K_{(b)k} | \eta_i^{[a]} \rangle \tag{35}$$

$$= \langle \xi_1^{[a]} | h_{BN} + \sum_{b \in \psi} \sum_{k=1}^{(1/2)n_b} (2J_{(b)k} - K_{(b)k}) | \eta_1^{[a]} \rangle \tag{36}$$

(closed shell case) .

By $J_{(b)k}$ and $K_{(b)k}$, we mean the Coulomb and exchange operators associated with orbital $\phi_k^{(b)}$. All $F^{[a]}$ and F correspond to the same integrodifferential operator,

$$F = h_{BN} + \sum_{b \in \psi} \sum_{k=1}^{(1/2)n_b} (2J_{(b)k} - K_{(b)k}) \tag{37}$$

(closed shell case).

Of paramount importance is that the operator in Eq. (36) is invariant under the symmetry group of h_{BN} . Thus it is diagonal with respect to the symmetry indices $[a]$, i its matrix elements are independent of i , and we may extract it from the matrix element of Eq. (36) as the integrodifferential operator for $F^{[a]}$ and F .

In the open shell case, the q and q' may not be diagonal in i, j and in k, l , so that one may need "off-diagonal" Coulomb and exchange operators, $J_{(b)ki}$ and $K_{(b)ki}$, defined by

$$\langle \xi_i^{[a]} | J_{(b)ki} | \eta_j^{[a]} \rangle = \langle \xi_i^{[a]} \phi_k^{(b)} | 1/r_{12} | \eta_j^{[a]} \phi_i^{(b)} \rangle , \tag{38}$$

$$\langle \xi_i^{[a]} | K_{(b)ki} | \eta_j^{[a]} \rangle = \langle \xi_i^{[a]} \phi_k^{(b)} | 1/r_{12} | \eta_i^{(b)} \phi_j^{[a]} \rangle . \tag{39}$$

The off-diagonal Coulomb and exchange operators are not Hermitian. We can make (38) and (39) look like ma-

trix elements diagonal in i by introducing projection-transition operators $P_{ji}^{[a]}$, defined by

$$P_{ji}^{[a]} \eta_k^{[a]} = \delta_{ik} \eta_j^{[a]} \quad (\text{for all } \eta_k^{[a]} \in [a]) . \quad (40)$$

Then, analogous to Eqs. (35) and (36), Eq. (9) for $F^{[a]}$ can be rewritten,

$$\langle \xi_1^{[a]} | F^{[a]} | \eta_1^{[a]} \rangle = \langle \xi_1^{[a]} | h_{\text{BN}} | \eta_1^{[a]} \rangle + n_a^{-1} \sum_{b \in \psi} \sum_{i=1}^{(1/2)n_a} \sum_{k=1}^{(1/2)n_b} f_b \langle \xi_i^{[a]} | 4q_{aij; bki} J_{(b)ki} - 2q'_{aij; bki} K_{(b)ki} | \eta_j^{[a]} \rangle \quad (41)$$

$$= \langle \xi_1^{[a]} | h_{\text{BN}} + n_a^{-1} \sum_{b \in \psi} \sum_{i=1}^{(1/2)n_a} \sum_{k=1}^{(1/2)n_b} f_b P_{ii}^{[a]\dagger} (4q_{aij; bki} J_{(b)ki} - 2q'_{aij; bki} K_{(b)ki}) P_{ji}^{[a]} | \eta_1^{[a]} \rangle . \quad (42)$$

Because of the projection-transition operators $P_{ji}^{[a]}$ and $P_{ii}^{[a]\dagger} (= P_{ii}^{[a]})$, the operator is "diagonal" with respect to the subscript index and independent of its value. We can therefore identify for $F^{[a]}$,

$$F^{[a]} = h_{\text{BN}} + n_a^{-1} \sum_{b \in \psi} \sum_{i=1}^{(1/2)n_a} \sum_{k=1}^{(1/2)n_b} f_b P_{ii}^{[a]} (4q_{aij; bki} J_{(b)ki} - 2q'_{aij; bki} K_{(b)ki}) P_{ji}^{[a]} . \quad (43)$$

Equation (43) can be considerably simplified by group theory.

A. Group theory

To proceed further, we require the theory of group representations.¹⁴ Denote by G the group of coordinate transformations g that leave h_{BN} invariant. Denote by $\mathbf{D}^{[a]}(g)$ the matrices of the unitary irreducible representations $\Gamma^{[a]}$ of G . The dimension of $\Gamma^{[a]}$ is $\frac{1}{2}n_a$. We assume the order N of the group to be finite. For atoms, N is actually infinite, so that the details of the derivation would need modification. The orbitals $\phi_i^{[a]}$ transform under the transformation g according to $\Gamma^{[a]}$:

$$g \phi_i^{[a]} = \sum_{j=1}^{(1/2)n_a} D_{ji}^{[a]}(g) \phi_j^{[a]} . \quad (44)$$

A group-theoretical formula for $P_{ji}^{[a]}$ of Eq. (40) is¹⁵

$$P_{ji}^{[a]} = \frac{1}{N} \sum_{g \in G} D_{ji}^{[a]}(g) * g . \quad (45)$$

B. Intermediate formula for $F^{[a]}$. Symmetrized q and q'

$F^{[a]}$ can be put in the simpler form

$$F^{[a]} = h_{\text{BN}} + \sum_{b \in \psi} \sum_{j=1}^{(1/2)n_a} \sum_{k=1}^{(1/2)n_b} f_b (2Q_{ai'j'; bki'J_{(b)ki'}} - Q'_{ai'j'; bki'K_{(b)ki'}}) P_{j'i'}^{[a]} . \quad (46)$$

The Q and Q' are symmetrized q and q'

$$Q_{ai'j'; bki'J_{(b)ki'}} = N^{-1} \sum_{g \in G} \sum_{j=1}^{(1/2)n_a} \sum_{k=1}^{(1/2)n_b} D_{i'i}^{[a]}(g) * D_{j'j}^{[a]}(g) * D_{k'k}^{[b]}(g) * D_{i'i}^{[b]}(g) q_{aij; bki} , \quad (47)$$

$$Q'_{ai'j'; bki'K_{(b)ki'}} = N^{-1} \sum_{g \in G} \sum_{j=1}^{(1/2)n_a} \sum_{k=1}^{(1/2)n_b} D_{i'i}^{[a]}(g) * D_{j'j}^{[a]}(g) * D_{k'k}^{[b]}(g) * D_{i'i}^{[b]}(g) q'_{aij; bki} . \quad (48)$$

These results are derived by using Eqs. (45) and (44) in Eq. (43):

$$F^{[a]} = h_{\text{BN}} + \sum_b \sum_{i, i', j, j', k, k'} f_b \frac{1}{2} n_a N^{-2} \sum_{g, g'} D_{i'i}^{[a]}(g) * D_{j'j}^{[a]}(g') * g (2q_{aij; bki} J_{(b)ki} - q'_{aij; bki} K_{(b)ki}) g^{-1} (gg') \quad (49)$$

$$= h_{\text{BN}} + \sum_b \sum_{i, i', j, j', k, k'} f_b \frac{1}{2} n_a N^{-2} \sum_{g, g'} D_{i'i}^{[a]}(g) * D_{j'j}^{[a]}(g) * D_{k'k}^{[b]}(g) * D_{i'i}^{[b]}(g) D_{j'i'}^{[a]}(gg') * (2q_{aij; bki} J_{(b)ki} - q'_{aij; bki} K_{(b)ki}) gg' , \quad (50)$$

from which Eqs. (46)–(48) follow.

The Q and Q' are symmetrized in the sense that

(1) They are also the result of applying g to each of the orbitals in Eq. (2) for E , collecting the coefficients of the $1/r_{12}$ integrals, and then averaging over all g in G .

(2) Both Q and Q' satisfy

$$\sum_{i=1}^{(1/2)n_a} \sum_{j=1}^{(1/2)n_b} D_{i'i}^{[a]}(g) * D_{j'j}^{[a]}(g) D_{k'k}^{[b]}(g) * D_{i'i}^{[b]}(g) Q_{atj;bk} = Q_{at'j';bk'i'} \quad (51)$$

Equation (46) is a suitable interodifferential representation of $F^{[a]}$. However, it too can be further simplified by explicitly accounting for the closed shells.

C. Final formula for $F^{[a]}$

Further simplification results from evaluating the Q and Q' that involve closed shells. If either a or b refers to a closed shell, the other being open or closed, then (with the choice, $q_{atj;bk} = q'_{atj;bk} = 1$, for Shell a closed)

$$Q_{atj;bk} = \delta_{ij} \delta_{kl} \quad (\text{either Shell } a \text{ or } b \text{ closed}), \quad (52)$$

$$Q'_{atj;bk} = \delta_{ij} \delta_{kl} \quad (\text{either Shell } a \text{ or } b \text{ closed}). \quad (53)$$

Certain open shells may satisfy similar equations: we call Shell a , *Roothaan open* if, for every open shell b ,

$$Q_{atj;bk} = \gamma_{ab} \delta_{ij} \delta_{kl} \quad (a, \text{ Roothaan open}), \quad (54)$$

$$Q'_{atj;bk} = \gamma'_{ab} \delta_{ij} \delta_{kl} \quad (a, \text{ Roothaan open}). \quad (55)$$

When Eqs. (52)–(55) for Q and Q' are substituted into Eq. (46) for $F^{[a]}$, the sum over i' and j' decouples, yielding a symmetry projection operator $P^{[a]}$,

$$\sum_{i'j'} \delta_{i'j'} P_{i'i'}^{[a]} = \sum_{i'} P_{i'i'}^{[a]} = P^{[a]}. \quad (56)$$

In fact, we will drop $P^{[a]}$ from $F^{[a]}$, since $F^{[a]}$ only is meant to operate on functions transforming according to $\Gamma^{[a]}$. (Strictly speaking, this omission of $P^{[a]}$ is a minor redefinition of the integrodifferential form of $F^{[a]}$.) The results of substituting these explicit values of Q and Q' in $F^{[a]}$ are

$$F^{[a]} = h_{BN} + \sum_{b \in \delta} \sum_{k=1}^{(1/2)n_b} f_b (2J_{(b)k} - K_{(b)k}) = F_{cs} \quad (\text{Shell } a, \text{ closed}), \quad (57)$$

$$F^{[a]} = h_{BN} + \sum_{b, \text{ closed}} \sum_{k=1}^{(1/2)n_b} (2J_{(b)k} - K_{(b)k}) + \sum_{b, \text{ open}} \sum_{k=1}^{(1/2)n_b} f_b (\gamma_{ab} 2J_{(b)k} - \gamma'_{ab} K_{(b)k}) \quad (\text{Shell } a, \text{ Roothaan open}), \quad (58)$$

$$F^{[a]} = h_{BN} + \sum_{b, \text{ closed}} \sum_{k=1}^{(1/2)n_b} (2J_{(b)k} - K_{(b)k}) + \sum_{b, \text{ Roothaan open}} \sum_{k=1}^{(1/2)n_b} f_b (\gamma_{ab} 2J_{(b)k} - \gamma'_{ab} K_{(b)k}) + \sum_{b, \text{ non-Roothaan open}} \sum_{i=1}^{(1/2)n_a} \sum_{j=1}^{(1/2)n_b} f_b (2Q_{atj;bk} J_{(b)ki} - Q'_{atj;bk} K_{(b)ki}) P_{ji}^{[a]} \quad (\text{Shell } a, \text{ non-Roothaan open}), \quad (59)$$

D. Integrodifferential formulas for $\hat{F}^{[a]}$, $F^{[a]}$, and F

As regards $\hat{F}^{[a]}$ and $F^{[a]}$, both are ultimately defined in terms of the $F^{[a]}$, and so both come out automatically in integrodifferential form if $F^{[a]}$ is. As regards F , we let F_{cs} denote the closed shell $F^{[a]}$ of Eq. (57). Then we can write

$$F = F_{cs} + \sum_{[a]} (F^{[a]} - F_{cs}) P^{[a]}, \quad (60)$$

where $P^{[a]}$ is given by Eq. (56). We remark in passing, that when Eq. (25) can be used for all the $\Lambda_{[a]}^{[a]}$, then F differs from F_{cs} only by *open shell* (ordinary and off-diagonal) Coulomb and exchange operators times projection and projection-transition operators.

VI. ROOTHAAN'S CASES

We show in this section that Roothaan's¹⁶ F_C and F_O are almost identical with appropriate $\hat{F}^{[a]}$, and we obtain the difference between Roothaan's F and ours.

The cases treated by Roothaan have a single open shell, which in this section will always correspond to the index "b." Equations (52)–(55) give Q and Q' . The parameters $\gamma = \gamma_{bb}$ and $\gamma' = \gamma'_{bb}$, here, are denoted by a and b , respectively, by Roothaan. To make the equa-

tions easier to read, we define total Coulomb and exchange operators for the open shell by

$$J_{(b)} = \sum_{k=1}^{(1/2)n_b} J_{(b)k}, \quad K_{(b)} = \sum_{k=1}^{(1/2)n_b} K_{(b)k}. \quad (61)$$

(Roothaan's J_O is $f_b J_{(b)}$.)

The Fock operators $\hat{F}^{[a]}$ are special cases of Eqs. (57) and (58):

$$\hat{F}^{[c]} = F_{cs} \quad (c, \text{ closed}; c \notin [b]), \quad (62)$$

$$\hat{F}^{[a]} = F_{cs} + (1 - f_b)^{-1} f_b^2 \{ P^{[b]}, (1 - \gamma) 2J_{(b)} - (1 - \gamma') K_{(b)} \} \quad (a, \text{ closed}; a \in [b]), \quad (63)$$

$$\hat{F}^{[b]} = F_{cs} + f_b (\gamma - 1) 2J_{(b)} - f_b (\gamma' - 1) K_{(b)} + (1 - f_b)^{-1} f_b \left\{ \sum_{\substack{[a], \text{ closed} \\ [a] \in [b]}} P^{[a]}, (1 - \gamma) 2J_{(b)} - (1 - \gamma') K_{(b)} \right\} \quad (b, \text{ the open shell}). \quad (64)$$

Apart from notational differences, one finds that Roothaan's F_C is identical with $\hat{F}^{[a]}$ of Eq. (63). Roothaan's F_C also applies to the $\phi_i^{[c]}$ of Eq. (62). Although $\hat{F}^{[c]}$ and $\hat{F}^{[a]}$ [Eqs. (62) and (63)] are not identical, both give the same result on functions not of $[b]$ symmetry:

TABLE I. Values^a of q , q' , Q , and Q' for $1a_1^2 \cdots 7a_1^2 1e^4 2e^3 3e$ CH_3CO^+ .

State	$ijkl$	$q_{2eij;3ekl}$	$q'_{2eij;3ekl}$	$Q_{2eij;3ekl}$	$Q'_{2eij;3ekl}$	$Q_{2eij;3ekl}$	$Q'_{2eij;3ekl}$
1A_1	$xxxx$	2/3	-4/3	2/3	-4/3		
	$xyxy$	4/3	4/3	4/3	4/3		
	$xyxy$	-2/3	0	-2/3	0		
	$xyyx$	0	-8/3	0	-8/3		
	$yxyx$	0	-8/3	0	-8/3		
	$yxyx$	-2/3	0	-2/3	0		
	$yyxx$	4/3	4/3	4/3	4/3		
	$yyyy$	2/3	-4/3	2/3	-4/3		
	1A_2	$xxxx$	4/3	4/3	4/3	4/3	
$xyxy$		2/3	-4/3	2/3	-4/3		
$xyxy$		2/3	8/3	2/3	8/3		
$xyyx$		0	0	0	0		
$yxyx$		0	0	0	0		
$yxyx$		2/3	8/3	2/3	8/3		
$yyxx$		2/3	-4/3	2/3	-4/3		
$yyyy$		4/3	4/3	4/3	4/3		
1E_x		$xxxx$	2/3	-4/3	1	0	1
	$xyxy$	4/3	4/3	1	0	1	
	$xyxy$	2/3	0	-1/3	-4/3	0	
	$xyyx$	0	8/3	1/3	4/3	0	
	$yxyx$	0	8/3	1/3	4/3	0	
	$yxyx$	2/3	0	-1/3	-4/3	0	
	$yyxx$	4/3	4/3	1	0	1	
	$yyyy$	2/3	-4/3	1	0	1	
	1E_y	$xxxx$	4/3	4/3	1	0	1
$xyxy$		2/3	-4/3	1	0	1	
$xyxy$		-2/3	-8/3	-1/3	-4/3	0	
$xyyx$		0	0	1/3	4/3	0	
$yxyx$		0	0	1/3	4/3	0	
$yxyx$		-2/3	-8/3	-1/3	-4/3	0	
$yyxx$		2/3	-4/3	1	0	1	
$yyyy$		4/3	4/3	1	0	1	

^aThe q and q' values are obtained by comparing the energy, given by Eq. (15) and Tables XI, XIII, and XIV of Ref. 2(b), with Eqs. (2), (6), and (7) of the text. The Q and Q' values follow from Eqs. (47) and (48). Note that the q , q' , Q and Q' are symmetric in the two sets of indices, Eq. (6), that the $(2e3e)$ q , q' , Q and Q' for values of $ijkl$ not listed, are zero, and that for either a or b equal to $1a_1, \dots, 7a_1$, or $1e$, the $Q_{aij;3ekl} = Q'_{aij;3ekl} = \delta_{ij} \delta_{kl}$ [Eqs. (52) and (53)].

^bFor the 1E level, a simpler set of Q follows from the equality of $\langle \phi_x^{(2e)} \phi_x^{(3e)} | 1/r_{12} | \phi_y^{(2e)} \phi_y^{(3e)} \rangle$ and $\langle \phi_x^{(2e)} \phi_y^{(3e)} | 1/r_{12} | \phi_y^{(2e)} \phi_x^{(3e)} \rangle$, corresponding to $ijkl = xyxy$ and $xyyx$.

$$\hat{F}^{[a]} \xi_i^{[c]} = \hat{F}^{[c]} \xi_i^{[c]} \quad [c] \neq [b], \quad (65)$$

so that $\hat{F}^{[c]}$ could be replaced by $\hat{F}^{[a]}$. Roothaan's F_O corresponds to $\hat{F}^{[b]}$ [Eq. (64)], except that the restriction in the sum over $\{a\}$, viz., that $\{a\}$ have the same symmetry as $[b]$, is not a restriction in the definition of F_O . But the difference is again more apparent than real, because the omitted terms lead to zero when operating as functions of $[b]$ symmetry.

The equations for $F^{[a]}$ and F are more concise with

$$\Delta \equiv f_b [(1-\gamma)2J_{(b)} - (1-\gamma')K_{(b)}]. \quad (66)$$

Then for $F^{[c]}$ and $F^{[a]}$ we obtain

$$F^{[c]} = F_{cs} \quad (c \text{ closed}; c \in [b]), \quad (67)$$

$$F^{[a]} = F^{[b]} \quad (\text{if there are no closed shells of symmetry } [b]), \quad (68)$$

$$\begin{aligned} F^{[a]} &= F_{cs} + \{P^{[b]}, \hat{F}^{[b]} - \hat{F}^{[a]}\} - P^{[b]}(F^{[b]} - F^{[a]})P^{[b]} \quad (69a) \\ &= F_{cs} + P^{[b]} \Delta P^{[b]} - \{P^{[b]}, \Delta\} + (1-f_b)^{-1} \\ &\quad \times (P^{[b]} \Delta P^{[a]} + P^{[a]} \Delta P^{[b]}) \quad (a \text{ closed}; a \in [b]). \end{aligned} \quad (69b)$$

For F , we find (ignoring symmetries not represented in ψ) that

$$F = F_{cs} - \Delta \times P^{[b]} \quad (\text{if there are no closed shells of symmetry } [b]), \quad (70a)$$

$$= F^{[a]} \quad (a \text{ closed}; a \in [b]). \quad (70b)$$

In the present notation, Roothaan's F is

$$\begin{aligned} F_{\text{Roothaan}} &= F_{cs} + (1-f_b)^{-1} \left[-\Delta + \{\Delta, P^{[a]}\} \right. \\ &\quad \left. + \sum_{\substack{[c] \text{ closed}; \\ c \in [b]}} P^{[c]} + f_b P^{[b]} \right], \end{aligned} \quad (71)$$

which is certainly different from F here. The difference, when $F^{[a]}$ is given by Eqs. (70b) and (69b), is

$$\begin{aligned} F - F_{\text{Roothaan}} &= (1-f_b)^{-1} \left[\left(1 - \sum_{[d] \in \emptyset} P^{[d]}\right) \Delta \left(1 - \sum_{[d] \in \emptyset} P^{[d]}\right) \right. \\ &\quad \left. - \sum_{[d] \in \emptyset} P^{[d]} \Delta P^{[d]} \right] + P^{[b]} \Delta P^{[b]}, \end{aligned} \quad (72)$$

and only slightly more different in the case of Eq. (68). As might be expected, the difference is block diagonal with respect to equivalence classes. The difference is what keeps the eigenvalues of F here the same as of the $F^{[a]}$, vs those of F_{Roothaan} , which are different from those of F_C and F_O .

VII. YARKONY, SCHAEFER, AND BENDER'S CASES

As it was the $1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 7a_1^2 1e^4 2e^3 3e$ configuration of CH_3CO^+ that led Yarkony, Schaefer, and Bender to devise SRAS, it is of particular interest to examine the Fock operators for this case. There are two open shells, nonequivalent and non-Roothaan open, with $f_{2e} = \frac{3}{4}$, $f_{3e} = \frac{1}{4}$.

The first step is to evaluate the q and q' or the Q and Q' . From the preceding section, whenever one of the subscripts refers to a closed shell, the Q and Q' have the very simple $\delta_{ij} \delta_{kl}$ form given by Eqs. (52) and (53). We need only consider the interaction of the $2e$ shell with itself and with the $3e$ shell.

The energy formulas for the three singlet levels, 1A_1 , 1A_2 , and 1E , are given by Eq. (15) and Tables XI, XIII, and XIV of Ref. 2(b). One finds, after unravelling the appropriate formulas, that within the $2e$ shell,

$$Q_{2e ij; 2e kl} = Q'_{2e ij; 2e kl} \quad (73)$$

$$= (8/9) \delta_{ij} \delta_{kl}. \quad (74)$$

One can also infer values for $q_{2e ij; 3e kl}$ and $q'_{2e ij; 3e kl}$, which we have listed in Table I. Note that the 1E_x and 1E_y states lead to different q and q' . CH_3CO^+ is invariant under the group C_3 (actually C_{3v} , but C_3 is all that is needed here). It takes only a few minutes to write a computer program to generate the Q and Q' ac-

cording to Eqs. (47) and (48), and these values are also listed in Table I. Note that 1E_x and 1E_y lead to the same Q and Q' , and that there is another, simpler set, which appears in Table I.

It remains to discuss the $F^{(a)}$. For the closed shells, $F^{(a)}$ has the traditional simple form given by Eq. (57). For $F^{(2e)}$ and $F^{(3e)}$, we write

$$F^{(2e)} = F_{cs} + \frac{2}{3}(2J_{(2e)} - K_{(2e)}) + \frac{1}{4}V_{(3e)}^{(2e)}, \quad (75)$$

$$F^{(3e)} = F_{cs} + \frac{3}{4}V_{(2e)}^{(3e)}. \quad (76)$$

By F_{cs} , we mean h_{BN} plus the term $\sum_{b, \text{closed}}$ in Eq. (59). The potential $V_{(ne)}^{(me)}$ depends on the state. From Eq. (59) and Table I, we find

$$V_{(ne)}^{(me)}({}^1A_1) = (4/3)[J_{(ne)x}(P_{xx}^{[e]} + 2P_{yy}^{[e]}) + J_{(ne)y}(2P_{xx}^{[e]} + P_{yy}^{[e]}) - J_{(ne)xy}P_{yx}^{[e]} - J_{(ne)yx}P_{xy}^{[e]}] + (K_{(ne)x} - K_{(ne)y})(P_{xx}^{[e]} - P_{yy}^{[e]}) + 2K_{(ne)yx}P_{yx}^{[e]} + 2K_{(ne)xy}P_{xy}^{[e]}, \quad (77)$$

$$V_{(ne)}^{(me)}({}^1A_2) = (4/3)[J_{(ne)x}(2P_{xx}^{[e]} + P_{yy}^{[e]}) + J_{(ne)y}(P_{xx}^{[e]} + 2P_{yy}^{[e]}) + J_{(ne)xy}P_{yx}^{[e]} + J_{(ne)yx}P_{xy}^{[e]}] - (K_{(ne)x} - K_{(ne)y})(P_{xx}^{[e]} - P_{yy}^{[e]}) - 2K_{(ne)xy}P_{yx}^{[e]} - 2K_{(ne)yx}P_{xy}^{[e]}, \quad (78)$$

$$V_{(ne)}^{(me)}({}^1E) = 2(J_{(ne)x} + J_{(ne)y}) + (4/3)(K_{(ne)xy} - K_{(ne)yx})(P_{yx}^{[e]} - P_{xy}^{[e]}). \quad (79)$$

VIII. ORBITAL ENERGIES AND TOTAL ENERGY

As in Roothaan's case, the orbital energies and the total energy are related by

$$E = \sum_{a \in \psi} f_a n_a (\epsilon_a + \langle \phi_1^{(a)} | h_{BN} | \phi_1^{(a)} \rangle). \quad (80)$$

IX. DISCUSSION AND SUMMARY

Four stages of Fock operators have been defined: $F^{(a)}$, $\hat{F}^{(a)}$, $F^{[a]}$, and F . A matrix element of $F^{(a)}$ between an occupied and an excited orbital gives the matrix element of the total Hamiltonian between the initial state and the corresponding symmetry-restricted singly excited state. $\hat{F}^{(a)}$ has the same property, but in addition, its matrix element between occupied orbitals is related to the total Hamiltonian matrix element between the initial state and a symmetry-restricted singly excited state involving only occupied orbitals. The Hartree-Fock orbitals are eigenfunctions of the appropriate $\hat{F}^{(a)}$. Each equivalence class of shells has its own $\hat{F}^{(a)}$, which are directly analogous to Roothaan's F_C and F_O . The $F^{[a]}$ is a combined Fock Hamiltonian that applies to all orbitals of a given symmetry. It is loosely analogous to Roothaan's F operator, but it is constructed somewhat differently. In particular, the orbital energies are the same as for the $\hat{F}^{(a)}$. The F operator here is a simple combination of the $F^{[a]}$ for the different symmetries.

The treatment applies to any single configuration multideterminant state having any number of open shells. One does not need at the start a symmetric expression for the energy. The symmetric energy would be required only to obtain an invariant integrodifferential representation of the operators $\hat{F}^{(a)}$, and the appropriate symmetrization can be carried out at the end rather than the beginning. In addition to the usual Coulomb, exchange, and coupling operators, $\hat{F}^{(a)}$ also involves projection-transition operators and off-diagonal Coulomb and exchange operators.

For practical calculations, the matrix form of the

operators is paramount, and several paths are possible. To insure orthogonality of the approximate orbitals during iterations, one may construct $F^{[a]}$ (for practical calculations, F is superfluous) from orbitals of iteration n , and diagonalize it to obtain the orbitals of iteration $n+1$. The $\hat{F}^{(a)}$ are simpler in structure than the $F^{[a]}$, but to insure convergence, if they are to be used directly to find the orbitals, it may be necessary to resort to *ad hoc* procedures for maintaining orthogonality of the not-yet-converged approximate orbitals of the same symmetry but different equivalence class. Various procedures exist.^{5,17}

The steps for carrying out a calculation are as follows:

- (1) Determine the formula for the energy [Eq. (2)].
- (2) Alter the energy formula, if necessary, to satisfy Eqs. (5)–(7). It should be noted that because of Eqs. (52) and (53), it is only necessary in Step 1 to examine $1/r_{12}$ matrix elements between pairs of open shells.
- (3) Construct the first stage Fock matrices $F^{[a]}$ [Eqs. (8) and (9); also cf. Eqs. (57)–(59)] and the second stage Fock matrices $\hat{F}^{(a)}$ [Eqs. (21), (24), and (25)]. One may solve self-consistently for the eigenfunctions of the $\hat{F}^{(a)}$, maintaining orthogonality by *ad hoc* procedures, if necessary, of the unconverged approximate orbitals of the same symmetry but different equivalence class.
- (4) Construct the third stage Fock matrices $F^{[a]}$ [Eq. (26)], and solve self-consistently for the orbitals. The unconverged approximate orbitals are automatically orthogonal.

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- ¹²(a) A careful discussion of the role of Eq. (16) is given by Hirao and Nakatsuji⁹; (b) cf. Ref. 9.
- ¹³The $F^{(a)}$ given here plays a role similar to R in Refs. 7-9, but it is different in some essential aspects.
- ¹⁴M. Hamermesh, *Group Theory* (Addison-Wesley, Reading, MA, 1962).
- ¹⁵Reference 14, Eq. (3-184).
- ¹⁶Reference 1, Eqs. (31) and (36).
- ¹⁷See also, M. T. Marron, N. C. Handy, R. G. Parr, and H. J. Silverstone, *Int. J. Quantum Chem.* **4**, 245 (1970).