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A generalized restricted open-shell Fock operator*

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We reexamine the open shell restricted Hartree-Fock theory and develop Fock-like operators that are quite general and easy to implement on a computer. We present a table of 'vector coupling coefficients' that define this operator for most of the cases that commonly arise. We compare the form of this operator with that suggested by others, and discuss the orbitals obtained by this procedure with respect to the generalised Brillouin's theorem, and the orbital energies with respect to Koopmans' approximation.

Key words: Open-shell Hartree-Fock — Restricted Hartree-Fock — Open-shell molecular orbital theory — Generalized Hartree-Fock theory

1. Introduction

With the introduction of inexpensive computing it has become possible for nearly every chemist to do large scale molecular orbital calculations in their own lab. Consequently, these calculations are now being used extensively, both as an aid to interpreting experimental results and as a predictive tool. For closed-shell molecules these calculations have been of the Restricted Hartree-Fock Self Consistent Field (RHF-SCF) type [1, 2] where the theory is well developed and the procedures are standardized. Unfortunately, this method, in its simplest form, can only be applied to closed-shell systems. Since chemists are also interested in excited states, ions, radicals, and open-shell transition metal complexes, there is a renewed interest in molecular orbital methods applicable to these systems.

Open-shell calculations have generally been of the Unrestricted Hartree-Fock (UHF) type [3], where the procedures are reasonably standardized [4]. However, for a given number of open-shell orbitals, the UHF method is appropriate only

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

for the state of highest multiplicity, for only here can the UHF wavefunction approximate a proper spin eigenfunction. States of lower multiplicity are often badly contaminated by unwanted spin components. Although various schemes have been designed to project out proper spin states [5, 6], or to annihilate near lying spin components [7–9], these schemes are either disproportionately expensive in terms of computing time, or not accurate enough to be of general value. A powerful advantage of UHF schemes is their amenability to the inclusion of correlation through perturbative correction [10–12], though the improvements to UHF wavefunctions using configuration interaction (CI) methods is difficult.

Since Roothaan's paper on restricted open-shell Fock operators (ROHF) first appeared in 1960 [13], there have been a large number of methods proposed to address the problem of open-shell molecules at the SCF level. All ROHF methods have the advantage of easy interpretability within the independent particle approximation since they are restricted to be eigenfunctions of S^2. Although such wavefunctions are difficult to improve using perturbation theory, they are easily correlated through standard CI techniques [14].

ROHF methods can be considered specific cases of the more general Multi-Configuration Self Consistent Field (MCSCF) methods. In each case, the total wavefunction is constructed from a linear combination of Slater determinants. In ROHF calculations, the coefficients of the Slater determinants are chosen to represent a particular spin state and/or symmetry. In MCSCF calculations, these coefficients are allowed to freely vary, and only their relative phasing must be specified. Although of greater general utility, MCSCF methods consume a great deal of computer time through cycling, integral transformations, etc., merely to determine coefficients that are fixed by spin symmetry.

In this paper we reexamine the ROHF problem, and develop Fock-like operators that are quite general and easy to implement on a computer. The method handles degenerate situations in a fashion similar to that suggested by others [15–20], combined with a projection operator technique similar to that suggested by Davidson [21]. The method described below has been in use for some time within the INDO semi-empirical framework [9, 22–24] although it is certainly not limited to this type Hamiltonian. We have tried to make this development both as general and as complete as possible since we have found it difficult to extract this information from any one source. Veillard has given a clear description of a related ROHF method [25] but the technique described is not of the same general utility as that which we describe below. Interested readers are also encouraged to examine the work of Carbo and Riera [19c] and the references therein.

In the next section we develop the general theory in term of Fock-like operators and projectors. Section 3 describes a single operator construction, and compares this development with those of others; Sect. 4 presents the matrix formulation of these operators and, along with Sect. 5, describes the detailed construction of the operator for a specific case. Section 6 shows the connection between the ROHF operator and the the generalized Brillouin conditions [26], and Sect. 7

gives the relationship between the orbital eigenvalues and the frozen orbital approximation for ionization processes (Koopmans' approximation).

2. General theory

For a set of orthonormal spin orbitals $\{\phi_k\}$, the energy of any single determinant, ψ can be written as

$$
\begin{aligned}
E &= \langle\psi|H|\psi\rangle \\
&\sum_i \langle i|h|i\rangle n_i + \tfrac{1}{2}\sum_{i,j} \langle ij||ij\rangle n_i n_j,
\end{aligned}
\tag{1}
$$

where $\langle\psi|\psi\rangle = 1$ and the spin orbitals have occupancies of $n_i = 0$ or 1.

The two electron integrals have the following form.

$$\langle ij||ij\rangle = \langle ij|ij\rangle - \langle ij|ji\rangle \tag{2a}$$

$$
\begin{aligned}
\langle ij|kl\rangle &= (ik|jl) \\
&= \int d\tau(1)\, d\tau(2) \phi_i^*(1)\phi_j^*(2) r_{12}^{-1} \phi_k(1)\phi_l(2).
\end{aligned}
\tag{2b}
$$

In general for a linear combination of determinants constructed from this set of orbitals:

$$\Psi = \sum_A d_A \psi_A \tag{3}$$

$$E = \langle\Psi|H|\Psi\rangle = \sum_A E_A d_A^2 + \sum_{A\neq B} d_A d_B E_{AB}, \tag{4}$$

with E_A given in Eq. (1) and $E_{AB} = \langle\psi_A|H|\psi_B\rangle$.

There are three cases that must be considered in calculating E_{AB}. In the first case, ψ_A and ψ_B differ only in $|\phi_i\rangle$ and $|\phi_j\rangle$, and have the remaining $\{|\phi_k\rangle\}$ in common. The determinants ψ_A and ψ_B are thus related by a single excitation and

$$E_{AB} = \left[\langle i|h|j\rangle + \sum_k \langle ik||jk\rangle\right] \theta_i^j. \tag{4a}$$

In the second case, ψ_A and ψ_B differ only in spin orbitals $|\phi_i\rangle$, $|\phi_j\rangle$ and $|\phi_k\rangle$, $|\phi_l\rangle$ respectively; ψ_A and ψ_B are related by double excitations and

$$E_{AB} = \langle ij||kl\rangle \theta_{ij}^{kl}. \tag{4b}$$

In the third case, ψ_A and ψ_B differ by more than two spin orbitals and $E_{AB} = 0$. The factor θ is the phase of ψ_B after arranging the spin orbitals of ψ_B to have maximum coincidence with ψ_A.

It is possible to write E in compact form as

$$E = \operatorname{Tr} \rho H = \sum \gamma_{ij} \langle i|h|j\rangle + \tfrac{1}{2}\sum \Gamma_{ijkl} \langle ij||kl\rangle, \tag{5}$$

where γ_{ij} and Γ_{ijkl} are the density matrices over spin orbitals:

$$\gamma_{ii} = \sum_A d_A^2 \langle \psi_A | a_i^+ a_i | \psi_A \rangle \tag{6a}$$

$$\gamma_{ij} = \sum_A d_A^2 \langle \psi_A | a_i^+ a_j | \psi_A \rangle + \sum_{A<B} d_A d_B \langle \psi_B | a_i^+ a_j | \psi_A \rangle \theta_i^j \tag{6b}$$

and

$$\Gamma_{ijkl} = \sum_A d_A^2 \langle \psi_A | a_i^+ a_j^+ a_l a_k | \psi_A \rangle + \sum_{A<B} d_A d_B \langle \psi_B | a_i^+ a_j^+ a_1 a_k | \psi_A > \theta_{ij}^{kl}, \tag{6c}$$

where a_j and a_i^+ are the usual Fermion annihilation and creation operators (27). The operator $a_i^+ a_j$ moves an electron from the occupied orbital ϕ_j to the empty orbital ϕ_i. If orbital ϕ_j is empty or if orbital ϕ_i is doubly occupied, the operator gives zero. Note that in Eq. (6b), the second summation is in fact restricted to run over those determinants in which ψ_A and ψ_B differ only in orbitals $|\phi_i\rangle$ and $|\phi_j\rangle$ (single excitations). Similarly Eq. (6c) is restricted to those determinants in which ψ_A and ψ_B differ only in the sets $|\phi_i\rangle$, $|\phi_j\rangle$, and $|\phi_k\rangle$, $|\phi_l\rangle$ (double excitations).

Equation (5) is general, and is the basis for multiconfiguration methods such as MC-SCF in which the $\{d_A\}$ and $\{|\phi_i\rangle\}$ are varied simultaneously for an energy minimum, or for natural orbital methods in which γ_{ij} is made diagonal.

We are interested here in examining general Hartree Fock like methods in which the energy can be written as

$$E = \sum \gamma_{ii} \langle i|h|i \rangle + \tfrac{1}{2} \sum \Gamma_{ijij} \langle ij \| ij \rangle \tag{7}$$

that is, of the form of Eq. (1). This generalization of Eq. (1) will include all possible spin adapted states that can be generated from a given electronic configuration, and will include most of the spatially degenerate situations met in considerating the highly symmetric transition metal complexes. In situations without spatial degeneracies the method that we discuss is similar but not equivalent to that of Davidson [21]. The general approach we take is similar to that of Hirao [17]. Further generalizations of Eq. (7) with coefficients fixed by symmetry have been developed [28], but the resulting equations are considerably more difficult to solve than those we present below.

We wish to minimize the energy of Eq. (7) with respect to orbital changes and subject to the orthonormality constraint $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ under which the energy expression is valid. We vary the functional

$$E' = E - 2 \sum_{i,j} \lambda_{ij} \langle \phi_i | \phi_j \rangle \tag{8}$$

where λ_{ij} are the Lagrange constraints. This leads to

$$\delta E' = 2 \sum_i [\langle \delta\phi_i | F^i | \phi_i \rangle + \langle \phi_i | F^i | \delta\phi_i \rangle]$$

$$- 2 \sum_{i,j} \lambda_{ij} [\langle \delta\phi_i | \phi_j \rangle + \langle \phi_i | \delta\phi_j \rangle] = 0. \tag{9a}$$

The appropriate form of the operator F^i will be derived later. Since $|\delta\phi_i\rangle$ is arbitrary, one obtains from (9a) the Euler-Lagrange equations of the familiar form

$$F^i|\phi_i\rangle=\sum_j|\phi_j\rangle\lambda_{ji} \tag{9b}$$

$$\langle\phi_i|F^i=\sum_j\langle\phi_j|\lambda_{ij}. \tag{9c}$$

Equations (9b) and (9c) must be solved simultaneously to ensure a proper variational procedure, easily seen by setting $\langle\delta\phi_i|=\langle i\delta\phi_i|$ in Eq. (9a). These two equations will become identical if and only if:

$$\lambda_{ji}=\lambda_{ij}^{*}. \tag{10}$$

From (9b) and (9c)

$$\lambda_{ji}=\langle\phi_j|F^i|\phi_i\rangle=\langle\phi_j|F^j|\phi_i\rangle \tag{11}$$

and

$$\langle\phi_j|F^i-F^j|\phi_i\rangle=0. \tag{12}$$

Closed-shell Hartree Fock procedures usually only consider Eq. (9b). Since there is only one Fock operator, $F^i=F^j=F$, the condition expressed in Eq. (12) is automatically satisfied. If more than one Fock operator is required, Eq. (12) must be imposed as a constraint.

Although Eq. (9b) suggests that each operator is associated with only one spin orbital, this restriction can be relaxed. To express this we introduce the concept of a shell of orbitals, designated by a superscript, $\{|\phi_i^\mu\rangle\}$, all of which are associated with a single operator F^μ. Equation (9b) becomes

$$F^\mu|\phi_i^\mu\rangle=\sum_{j\in\mu}\lambda_{ji}|\phi_j^\mu\rangle+\sum_{\nu\neq\mu}\sum_{k\in\nu}\lambda_{ki}|\phi_k^\nu\rangle \tag{13}$$

$$\left\{F^\mu-\sum_{\nu\neq\mu}\sum_{k\in\nu}\lambda_{ki}|\phi_k^\nu\rangle\langle\phi_i^\mu|\right\}|\phi_i^\mu\rangle=\sum_{j\in\mu}\lambda_{ji}|\phi_j^\mu\rangle. \tag{14}$$

In the representation in which λ_{ji} has been diagonalized to ω_i for subshell μ, Eq. (14) takes on the appearance of an eigenvalue problem, however ω_i is not an orbital energy. In Sect. 5 we will show that F^μ in Eq. (14) has the structure $F^\mu=n^\mu(h+G-Q^\mu)$ where h is the usual one electron operator, G the usual two electron operator, and Q^μ a two electron operator characteristic of shell μ. The spatial orbitals in each shell μ all have the same occupancy, n^μ where $0\leq n^\mu\leq 2$. For this reason the usual orbital energies ε_i are given by

$$\varepsilon_i=\omega_i/n^\mu, \qquad i\in\mu. \tag{15}$$

In order to ensure the constraint expressed in Eq. (12), we can write Eq. (11) as:

$$\lambda_{ki}=\Lambda^{\mu\nu}\langle\phi_k^\nu|F^\nu|\phi_i^\mu\rangle+(1-\Lambda^{\mu\nu})\langle\phi_k^\nu|F^\mu|\phi_i^\mu\rangle, \tag{16}$$

where the arbitrary constants $\Lambda^{\mu\nu} \neq 0$. Incorporating Eq. (16), into Eq. (14) gives:

$$\left\{F^{\mu} - \sum_{\nu\neq\mu} \sum_{k\in\nu} |\phi_k^{\nu}\rangle\langle\phi_k^{\nu}|F^{\mu\nu}|\phi_i^{\mu}\rangle\langle\phi_i^{\mu}|\right\}|\phi_i^{\mu}\rangle = \omega_i|\phi_i^{\mu}\rangle, \tag{17a}$$

where $F^{\mu\nu} = \Lambda^{\mu\nu}F^{\nu} + (1-\Lambda^{\mu\nu})F^{\mu}$. (17b)

Note that the new Fock-like operator $F^{\mu\nu}$ is not symmetric in $\mu\nu$. Introducing the projection operators defined below into Eq. (17a) gives

$$P^{\nu} = \sum_{k\in\nu} |\phi_k^{\nu}\rangle\langle\phi_k^{\nu}|$$

$$\left\{F^{\mu} - \sum_{\nu\pm\mu} P^{\nu}F^{\mu\nu}P^{\mu}\right\}|\phi_i^{\mu}\rangle = \omega_i|\phi_i^{\mu}\rangle. \tag{17c}$$

We note that the operator in Eq. (17c) when operating on $|\phi_i^{\mu}\rangle$ has the same matrix elements as the simpler operator

$$\left\{F^{\mu} - \sum_{\nu\neq\mu} P^{\nu}F^{\mu\nu}\right\}|\phi_i^{\mu}\rangle = \omega_i|\phi_i^{\mu}\rangle, \tag{17d}$$

namely $\langle\phi_j^{\mu}|F^{\mu}|\phi_i^{\mu}\rangle = \omega_i\delta_{ij}$ and

$$\begin{aligned}&\langle\phi_k^{\nu}|F^{\mu}|\phi_i^{\mu}\rangle - \langle\phi_k^{\nu}|F^{\mu\nu}|\phi_i^{\mu}\rangle\\ &\quad= \langle\phi_k^{\nu}|F^{\mu}|\phi_i^{\mu}\rangle - \Lambda^{\mu\nu}\langle\phi_k^{\nu}|F^{\nu}|\phi_i^{\mu}\rangle - (1-\Lambda^{\mu\nu})\langle\phi_k^{\nu}|F^{\mu}|\phi_i^{\mu}\rangle = 0\end{aligned}$$

satisfying the condition of defining the set of one electron operators.

The operator of Eq. (17d) is not Hermitian, and so for convenience we define R^{μ} as

$$R^{\mu} \equiv F^{\mu} - \sum_{\nu\neq\mu} [P^{\nu}F^{\mu\nu} + F^{\mu\nu}P^{\nu}] \tag{17e}$$

$$R^{\mu}|\phi_i^{\mu}\rangle = \omega_i|\phi_i^{\mu}\rangle. \tag{17f}$$

The additional term $F^{\mu\nu}P^{\nu}$ when operating of $|\phi_i^{\mu}\rangle$ adds zero. The form of R^{μ} given in (17e) is particularly easy to calculate, but we note that dropping the projector P^{μ} of the Hermitian form of Eq. (17c)

$$\left\{F^{\mu} - \sum_{\nu\neq\mu} [P^{\nu}F^{\mu\nu}P^{\mu} + P^{\mu}F^{\mu\nu}P^{\nu}]\right\} \rightarrow \left\{F^{\mu} - \sum_{\nu\neq\mu} [P^{\nu}F^{\mu\nu} + F^{\mu\nu}P^{\nu}]\right\}$$

requires that one recall that R^{μ} operates only on $|\phi_i^{\mu}\rangle$.

In the above we have assumed that all $\langle\phi_i^{\mu}|\phi_j^{\nu}\rangle = \delta_{ij}$. By the construction of an Hermitian operator R^{μ}, orthonormality is guaranteed for each set $\{|\phi_i^{\mu}\rangle\}$. When $\mu \neq \nu$ there is no such a priori guarantee unless set μ and ν transform as different irreducible representations of the symmetry group. This is a restriction in many methods at present, but will not be satisfactory for work, for example, on transition metal complexes.

We consider a manifold of operators, where the closed-shell operator is specified first, R^c, and for convenience open-shell operators R^1, R^2, etc., are arranged according to decreasing number of electrons in each shell. Then

$$R^c|\phi_i^c\rangle = \omega_i|\phi_i^c\rangle, \qquad \langle\phi_i^c|\phi_j^c\rangle = \delta_{ij} \tag{18}$$

$$P^c = \sum_{k\in c} |\phi_k^c\rangle\langle\phi_k^c|.$$

Similarly we want

$$R^1|\phi_j^1\rangle = \omega_j|\phi_j^1\rangle, \qquad \langle\phi_i^1|\phi_j^1\rangle = \delta_{ij} \tag{19a}$$

and

$$\langle\phi_j^1|\phi_i^c\rangle = 0. \tag{19b}$$

Equation (19b) is guaranteed if

$$(1-P^c)|\phi_j^1\rangle = |\phi_j^1\rangle. \tag{19c}$$

Since $(1-P^c)$ is a projector onto the orthogonal complement of $\{|\phi_i^c\rangle\}$,

$$(1-P^c)(1-P^c) = (1-P^c),$$

and

$$\begin{aligned}(1-P^c)R^1(1-P^c)|\phi_j^1\rangle &= (1-P^c)R^1|\phi_j^1\rangle = (1-P^1)\omega_j|\phi_j^1\rangle \\ &= \omega_j|\phi_j^1\rangle = R^1|\phi_j^1\rangle.\end{aligned} \tag{20a}$$

Note that this guarantees that $(1-P^c)R^1(1-P^c)|\phi_i^c\rangle = 0.$ (20b)

Similarly, we constrain the remaining shells so that

$$(1-P^1)(1-P^c)|\phi_k^2\rangle = (1-P^1-P^c)|\phi_k^2\rangle = |\phi_k^2\rangle \tag{20c}$$

$$(1-P^1-P^c)R^2(1-P^1-P^c)|\phi_k^2\rangle = \omega_k|\phi_k^2\rangle \tag{20d}$$

etc. This procedure defines the eigenvectors of each successive operator in the orthogonal complement of all those proceeding.

Another way suggested would be to create the operators

$$\hat{R}^c = P^cR^cP^c$$

$$\hat{R}^1 = P^1R^1P^1$$

etc, with $\{P^i\}$ obtained from the previous SCF cycle. We note the similarity of this structure and

$$R^\mu = P^\mu F^\mu P^\mu$$

obtained by setting all $\Lambda^{\mu\nu}$ in Eq. (16) equal to zero. Such a procedure does not guarantee a minimum energy principle.

3. Single operator formalism

The most general structure is that of Eq. (20) with R_i defined as in Eq. (17e). Although we will use this formulation for the calculations which follow, for completeness and for comparison with others, we briefly pursue a single operator formalism. We derive from Eq. (17e)

$$\left\{F^{\mu} - \sum_{\nu} [P^{\nu}F^{\mu\nu}P^{\mu} + P^{\mu}F^{\mu\nu}P^{\nu}] + P^{\mu}F^{\mu\mu}P^{\mu} + P^{\mu}F^{\mu\mu}P^{\mu}\right\}|\phi_i^{\mu}\rangle = \omega_i|\phi_i^{\mu}\rangle. \tag{21}$$

Subtracting $(1 - P^{\mu})F^{\mu\mu}(1 - P^{\mu})$ from the operator on the left side, which yields zero when acting on $|\phi_i^{\mu}\rangle$, and recalling that $F^{\mu\mu} = F^{\mu}$, we derive

$$\begin{aligned} r^{\mu}|\phi_i^{\mu}\rangle &\equiv \frac{1}{n^{\mu}}\left\{F^{\mu}P^{\mu} + P^{\mu}F^{\mu} + P^{\mu}F^{\mu}P^{\mu} - \sum_{\nu}[P^{\nu}F^{\mu\nu}P^{\mu} + P^{\mu}F^{\mu\nu}P^{\nu}]\right\}|\phi_i^{\mu}\rangle \\ &= \frac{1}{n^{\mu}}\,\omega_i|\phi_i^{\mu}\rangle = \varepsilon_i|\phi_i^{\mu}\rangle. \end{aligned} \tag{22}$$

The operator of Eq. (22) yields ε_i when operating on any $|\phi_i^{\mu}\rangle$, and zero when operating on any $|\phi_j^{\alpha}\rangle$, $\alpha \neq \mu$.

Then

$$\begin{aligned} \tilde{R} &\equiv \sum r^{\mu} \\ &= \sum_{\mu}\frac{1}{n^{\mu}}[F^{\mu}P^{\mu} + P^{\mu}F^{\mu} + P^{\mu}F^{\mu}P^{\mu}] - \sum_{\mu}\frac{1}{n^{\mu}}\sum_{\nu}[P^{\nu}F^{\mu\nu}P^{\mu} + P^{\mu}F^{\mu\nu}P^{\nu}]. \end{aligned} \tag{23a}$$

Incorporating the occupation numbers n^{μ} into a new Fock operator $\hat{F}^{\mu} = F^{\mu}/n^{\mu}$ gives

$$\begin{aligned} \tilde{R} &= \sum_{\mu}[\hat{F}^{\mu}P^{\mu} + P^{\mu}\hat{F}^{\mu} + P^{\mu}\hat{F}^{\mu}P^{\mu}] - \sum_{\mu}\sum_{\nu}P^{\nu}[\hat{F}^{\mu} + \hat{F}^{\nu}]P^{\mu} \\ &\quad - \sum_{\nu}\sum_{\mu}P^{\mu}\{\hat{F}^{\nu}[(n^{\nu}/n^{\mu})\Lambda^{\mu\nu} - \Lambda^{\nu\mu}] - \hat{F}^{\mu}[\Lambda^{\mu\nu} - (n^{\mu}/n^{\nu})\Lambda^{\nu\mu}]\}P^{\mu} \end{aligned} \tag{24}$$

$$\begin{aligned} \tilde{R} &= \sum_{\mu}\frac{1}{n^{\mu}}[(1 - P)\hat{F}^{\mu}P^{\mu} + P^{\mu}\hat{F}^{\mu}(1 - P) + P^{\mu}\hat{F}^{\mu}P^{\mu}] \\ &\quad - \sum_{\nu}\sum_{\mu}P^{\nu}\{\hat{F}^{\nu}[(n^{\nu}/n^{\mu})\Lambda^{\mu\nu} - \Lambda^{\nu\mu}] - \hat{F}^{\mu}[\Lambda^{\mu\nu} - (n^{\mu}/n^{\nu})\Lambda^{\nu\mu}]\}P^{\mu}, \end{aligned}$$

where $P \equiv \sum P^{\mu}$. This equation has the same general form as obtained by Huzinaga [16] or Hirao [17]. Since r^{μ} only gives non-zero values when operating on an orbital of the μ-th manifold, we have

$$\tilde{R}|\phi_i^{\mu}\rangle = \varepsilon_i|\phi_i^{\mu}\rangle. \tag{25c}$$

As discussed by Hirao, the obvious choice of $(n^{\nu}/n^{\mu})\Lambda^{\mu\nu} = \Lambda^{\nu\mu}$ is not satisfactory, as the constraint of Eq. (12) is again dropped [17]. The function of $F^{\mu\nu}$ is to act as a shift of the off-block-diagonals of a one Hamiltonian method.

4. Matrix formulation and the form of the Fock operator

We expand Eq. (7) in terms of real spatial orbitals as

$$\begin{aligned} E = {} & 2\sum_{i\in c} h_i + \sum_{i\in c}\sum_{j\in c}(2J_{ij}-K_{ij}) && i \text{ closed; } j \text{ closed} \\ & + \sum_{\mu\neq c}\sum_{k\in\mu} n^{\mu}h_k + \frac{1}{4}\sum_{\mu\neq c}\sum_{\nu\neq c}\sum_{k\in\mu}\sum_{l\in\nu} n^{\mu}n^{\nu}(2a^{\mu\nu}J_{kl} \\ & - b^{\mu\nu}K_{kl}) && k \text{ open; } l \text{ open} \\ & + \sum_{\mu\neq c}\sum_{i\in c}\sum_{k\in\mu} n^{\mu}(2J_{ik}-K_{ik}) && i \text{ closed; } k \text{ open,} \end{aligned} \tag{26}$$

with $J_{ik} = \langle ik|ik\rangle$, $K_{ik} = \langle ik|ki\rangle$, $h_i = \langle i|h|i\rangle$.

For the connection with conventional trace formulas:

$$E = \sum_{p,q} D^{T}_{pq}h_{pq} + \tfrac{1}{2}\sum_{p,q} D^{T}_{pq}G_{pq} - \tfrac{1}{2}\sum_{\mu}\sum_{p,q} D^{\mu}_{pq}Q^{\mu}_{pq}, \tag{27}$$

with the density of shell μ given by

$$D^{\mu}_{pq} = \sum_{i} C^{\mu}_{ip}C^{\mu}_{iq}n^{\mu}. \tag{28a}$$

The total density D^{T}_{pq} is:

$$D^{T}_{pq} = \sum_{\mu} D^{\mu}_{pq} \tag{28b}$$

each orbital $|\phi^{\mu}_{i}\rangle$ expanded as a linear combination of atomic orbitals

$$|\phi^{\mu}_{i}\rangle = \sum_{p} C^{\mu}_{ip}|\chi_p\rangle \tag{29}$$

and the matrix elements G_{pq} and Q^{μ}_{pq} defined through

$$G_{pq} = \sum_{r,s}[(pq|rs) - \tfrac{1}{2}(ps|qr)]D^{T}_{rs} \tag{30a}$$

$$Q^{\mu}_{pq} = \sum_{r,s}[A^{\mu}_{rs}(pq|rs) - \tfrac{1}{2}B^{\mu}_{rs}(ps|qr)] \tag{30b}$$

$$A^{\mu}_{rs} \equiv \sum_{\nu\neq c}(1-a^{\mu\nu})D^{\nu}_{rs} \quad \text{and} \quad B^{\mu}_{rs} \equiv \sum_{\nu\neq c}(1-b^{\mu\nu})D^{\nu}_{rs}. \tag{30c}$$

The A and B matrices are special weighted density matrices.

Expanding Eq. (27) term by term in the atomic orbital basis, Eq. (29) gives

$$\sum_{p,q} D^{T}_{pq}h_{pq} = \sum_{p,q}\sum_{\mu}\sum_{i\in\mu} n^{\mu}C^{\mu}_{ip}C^{\nu}_{iq}h_{pq} = 2\sum_{i\in c}h_i + \sum_{\mu\neq c}\sum_{k\in\mu}n^{\mu}h_k \tag{31a}$$

$$\tfrac{1}{2}\sum_{p,q} D^{T}_{pq}G_{pq} = \tfrac{1}{2}\sum_{\substack{p,q\\ r,s}}\sum_{\mu,\nu}\sum_{i\in\mu}\sum_{j\in\nu} n^{\mu}n^{\nu}C^{\mu}_{ip}C^{\mu}_{iq}C^{\nu}_{jr}C^{\nu}_{js}[(pq|rs) - \tfrac{1}{2}(ps|qr)] \tag{31b}$$

$$\begin{aligned} -\tfrac{1}{2}\sum_{p,q}\sum_{\mu} D^{\mu}_{pq}Q^{\mu}_{pq} = {} & -\tfrac{1}{2}\sum_{\substack{p,q\\ r,s}}\sum_{\mu}\sum_{\nu\neq c}\sum_{i\in\mu}\sum_{j\in\nu} n^{\mu}n^{\nu}C^{\mu}_{ip}C^{\mu}_{iq}C^{\nu}_{jr}C^{\nu}_{js} \\ & \times[(1-a^{\mu\nu})(pq|rs) - \tfrac{1}{2}(1-b^{\mu\nu})(ps|qr)]. \end{aligned} \tag{31c}$$

These equations can be recognized as the terms in Eq. (26). Adding the orthonormality constraint with the Lagrangian multipliers λ_{ij} and taking the derivatives of this equation with respect to the expansion coefficients C^{μ}_{ip} leads to

$$\sum_{q} n^{\mu}[h_{pq} + G_{pq} - Q^{\mu}_{pq}]C^{\mu}_{iq} = \sum_{q}\sum_{\nu}\sum_{j\in\nu} C^{\nu}_{jq}\lambda_{ij}\Delta_{pq} \tag{32a}$$

$$Q^{c}_{pq} \equiv 0. \tag{32b}$$

Equations (32) are the matrix form of Eq. (9b) or (13) and Δ_{pq} is the overlap between χ_p and χ_q. For convenience we redefine the operator F^{μ} so that its eigenvalues are conventional orbital energies. In matrix representation, F^{μ} is:

$$F^{\mu}_{pq} = h_{pq} + G_{pq} - Q^{\mu}_{pq}. \tag{33}$$

The presence of n^{μ}_{i} in (32a) is the origin of Eq. (15). Again, restricting all $n^{\mu}_{i} = n^{\mu}$ Eq. (17e) now becomes

$$\begin{aligned}\frac{1}{n^{\mu}}\sum_{p} C^{\mu}_{ip}R^{\mu}_{pq} &\equiv \sum_{p} C^{\mu}_{ip}\left(F^{\mu}_{pq} - \sum_{r}\sum_{\nu\neq\mu}\frac{1}{n^{\nu}}[D^{\nu}_{pr}F^{\mu\nu}_{rq} + F^{\mu\nu}_{pr}D^{\nu}_{rq}]\right)\\ &= \varepsilon_i C^{\mu}_{iq},\end{aligned} \tag{34a}$$

where the matrix element F^{μ}_{iq} is defined according to Eq. (17b) as:

$$F^{\mu\nu}_{pq} = (n^{\nu}/n^{\mu})\Lambda^{\mu\nu}F^{\nu}_{pq} + (1 - \Lambda^{\mu\nu})F^{\mu}_{pq} \tag{34b}$$

and from Eq. (27), after some algebra

$$\begin{aligned}E &= \tfrac{1}{2}\sum_{p,q} D^{T}h_{qp} + \tfrac{1}{2}\sum_{\mu}\sum_{p,q} D^{\mu}_{pq}\Bigg(h_{pq} + G_{qp} - Q^{\mu}_{qp}\\ &\quad - \sum_{r}\sum_{\nu\neq\mu}\frac{1}{n^{\nu}}[D^{\nu}_{pr}F^{\mu\nu}_{rq} + F^{\mu\nu}_{pr}D^{\nu}_{rq}]\Bigg)\\ &= \tfrac{1}{2}\sum_{\mu}\sum_{i\in\mu} n^{\mu}(h_i + \varepsilon_i).\end{aligned} \tag{35a}$$

This follows since

$$\sum_{p,q} D^{\mu}_{pq}\sum_{r}\sum_{\nu\neq\mu}\frac{1}{n^{\nu}}[D^{\nu}_{pr}F^{\mu\nu}_{rq} + F^{\mu\nu}_{pr}D^{\nu}_{rq}] = 0. \tag{35b}$$

5. Detailed construction of the Fock operator

A linear combination of determinants is constructed to represent a given spin and space symmetry. The function is normalized and the energy expectation evaluated. The energy must be of the form of Eq. (7); i.e. must not contain two electron terms other than $\langle ij|ij\rangle$ or $\langle ij|ji\rangle$ [28]. A comparison is then made with the derived form and Eq. (26) to derive the values of $a^{\mu\nu}$ and $b^{\mu\nu}$. There is often some arbitrariness in the selection of $a^{\mu\nu}$ and $b^{\mu\nu}$ values, as in certain cases one equation arises for two unknowns [25]. In such cases it is advantageous to choose

Table 1. Coupling coefficients for common cases

N	M	Op.	Mult.	Diagram	$a^{\mu\nu}$	$b^{\mu\nu}$	n^{μ}
1	M	1	2	$\underline{\uparrow}\ \underline{\ }\ \underline{\ }\cdots$	0	0	$1/M$
N	N	1	$M+1=N+1$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\cdots$	1	2	1
N	M	1	$N+1$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\cdots\ \underline{\ }\ \underline{\ }\cdots$	$\dfrac{M(N-1)}{N(M-1)}$	$\dfrac{(2M(N-1)}{N(M-1)}$	$\dfrac{N}{M}$
$M+1$	M	1	$M=N-1$	$\underline{\updownarrow}\ \underline{\uparrow}\ \underline{\uparrow}\cdots$	$\dfrac{M(M+2)}{(M+1)^2}$	$\dfrac{2M^2}{(M+1)^2}$	$\dfrac{M+1}{M}$
M	N	1	$2M-N+1$	$\underline{\updownarrow}\ \underline{\updownarrow}\cdots\underline{\uparrow}\ \underline{\uparrow}\cdots$	$\dfrac{M(2M+N^2-3N)}{N^2(M-1)}$	$\dfrac{2M(2M^2N^2-N-2NM)}{N^2(M-1)}$	$\dfrac{N}{M}$
2	2	2	1	$\underline{\uparrow}\ \underline{\downarrow}$	(1, 1, 1)	(2, −2, 2)	(1, 1)
2	3	2	1	$\underline{\uparrow}\ \underline{\downarrow}\ \underline{\ }$	3/4(1, 1, 1)	3/2(1, −1, 1)	(2/3, 2/3)
3	3	3	2^a	$\underline{\uparrow}\ \underline{\downarrow}\ \underline{\uparrow}$	(1, 1, 1, 1, 1, 1)	(2, 1, 2, 1, −2, 2)	(1, 1, 1)
4	3	3	1	$\underline{\updownarrow}\ \underline{\uparrow}\ \underline{\downarrow}$	15/16(1, 1, 1, 1, 1, 1)	9/16(2/3, 1, 2/3, 1, 1, 2/3)	4/3(1, 1, 1)
1 1	2 3	2	3^b	$\begin{bmatrix}\underline{\uparrow} & \underline{\ } & \\ \underline{\uparrow} & \underline{\ } & \underline{\ }\end{bmatrix}$	(0, 1, 0)	(0, 2, 0)	(1/3, 1/2)
1 1	2 3	2	1^b	$\begin{bmatrix}\underline{\uparrow} & \underline{\ } & \\ \underline{\downarrow} & \underline{\ } & \underline{\ }\end{bmatrix}$	(0, 1, 0)	(0, −2, 0)	(1/3, 1/2)
1 2	2 3	2	4^b	$\begin{bmatrix}\underline{\uparrow} & \underline{\ } & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\ }\end{bmatrix}$	(3/4, 3/4, 0)	(3/2, 3/2, 0)	(2/3, 1/2)
2 1	2 3	2	4	$\begin{bmatrix}\underline{\uparrow} & \underline{\uparrow} & \\ \underline{\uparrow} & \underline{\ } & \underline{\ }\end{bmatrix}$	(0, 1, 1)	(0, 2, 2)	(1/3, 1)
1 3	2 3	2	5	$\begin{bmatrix}\underline{\uparrow} & \underline{\ } & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow}\end{bmatrix}$	(1, 1, 0)	(2, 2, 0)	(1, 1/2)
2 2	2 3	2	5	$\begin{bmatrix}\underline{\uparrow} & \underline{\uparrow} & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\ }\end{bmatrix}$	(3/4, 1, 1)	(3/2, 2, 2)	(2/3, 1)
2 3	2 3	1	6	$\begin{bmatrix}\underline{\uparrow} & \underline{\uparrow} & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow}\end{bmatrix}$	1	2	1
2 5	2 3	2	4	$\begin{bmatrix}\underline{\uparrow} & \underline{\uparrow} & \\ \underline{\updownarrow} & \underline{\updownarrow} & \underline{\ }\end{bmatrix}$	(0.96, 1, 1)	(0.96, 1.2, 2)	(5/3, 1)

See [30] for footnotes

as many $a^{\mu\nu}$ equal and as many corresponding $b^{\mu\nu}$ equal. By reordering the operators, the matrices $\boldsymbol{a}$ and $\boldsymbol{b}$ can be placed in block form; i.e.

$$\boldsymbol{a} = \left[\begin{array}{cc|c} 1 & 1 & 2 \\ 1 & 1 & 2 \\ \hline 2 & 2 & 2 \end{array}\right] \qquad \boldsymbol{b} = \left[\begin{array}{cc|c} -1 & -1 & 3 \\ -1 & -1 & 3 \\ \hline 3 & 3 & 2 \end{array}\right].$$

If $n^1 = n^2$, this system can be reduced from three to two operators with coupling coefficients $\boldsymbol{a} = (1, 2, 2)$ and $\boldsymbol{b} = (-1, 3, 2)$ as evident from the form of Eq. (33) and Eq. (30).

For example, consider the two electron triplet

$$^3\Psi = |\text{closed } \phi_1\phi_2|$$

$$E = \langle {}^3\psi|H|{}^3\psi\rangle = h_1 + h_2 + J_{12} - K_{12} + E \text{ (closed)}.$$

Comparison with Eq. (26) yields (since $J_{ii} = K_{ii}$)

$$(\tfrac{1}{2}a^{11} - \tfrac{1}{4}b^{11})J_{11} = 0 \qquad 2a^{11} = b^{11}$$

$$(\tfrac{1}{2}a^{22} - \tfrac{1}{4}b^{22})J_{22} = 0 \qquad 2a^{22} = b^{22}$$

$$a^{12}J_{12} = J_{12} \qquad a^{12} = 1$$

$$-\tfrac{1}{2}b^{12}K_{12} = -K_{12} \qquad b^{12} = 2.$$

Then if a^{11} and $a^{22} = 1$, $b^{12} = 2$ one open-shell operator is obtained. The corresponding singlet requires two one-electron open-shell operators. Several common cases are tabulated in Table 1. The coefficients $a^{\mu\nu}$ and $b^{\mu\nu}$ are a generalization of the "vector coupling coefficients" of Roothaan [13].

6. Brillouin's theorem

Following the generalized Brillouin's theorem of Levy and Berthier [26], we minimize the energy of a wavefunction constructed as

$$\Psi_0 = \sum d_A\psi_A, \tag{36a}$$

with

$$\sum d_A^2 = 1. \tag{36b}$$

We then create "singly excited functions" using particle/hole operators as:

$$|\Psi_i^b\rangle = [(a_b^+a_i)_\alpha + (a_b^+a_i)_\beta]|\Psi_0\rangle. \tag{37}$$

The particle/hole operators operate on each component determinant of Ψ_0 in turn, removing an electron from an occupied orbital ϕ_i and creating an electron in the empty orbital ϕ_b. Note that if orbital ϕ_i is empty or orbital ϕ_b is doubly occupied, these operators give zero.

This particle/hole operator is a single electron operator. Thus, in terms of the Fock operators of the previous section

$$\langle\Psi_0|H|\Psi_i^b\rangle = 2\langle\phi_i^c|F^c|\phi_b^e\rangle = 0 \tag{38a}$$

which follows from Eq. (17f), where $|\phi_i^c\rangle$ is doubly occupied in Ψ_0, $|\phi_b^e\rangle$ is not occupied in Ψ_0 and if $\langle\phi_i^c|\phi_b^e\rangle = 0$. Similarly

$$\langle\Psi_0|H|\Psi_i^k\rangle = \langle\phi_i^c|F^c|\phi_k^\mu\rangle = 0 \tag{38b}$$

$$\langle\Psi_0|H|\Psi_k^1\rangle = \langle\phi_k^\mu|F^\mu - F^\nu|\phi_1^\nu\rangle = 0 \tag{38c}$$

which follows from Eq. (12), when $|\phi_k^\mu\rangle$ and $|\phi_1^\nu\rangle$ are both open shell orbitals.

Lastly, we examine

$$\langle\Psi_0|H|\Psi_k^b\rangle = \langle\phi_k^\mu|F^\mu|\phi_b^e\rangle = 0 \tag{38d}$$

which follows from Eqs. (9b) and (12), if $\langle\phi_k^\mu|\phi_b^e\rangle = 0$.

Equations (38a) and (38b) hold only if $|\phi_b\rangle$, virtual orbitals that are considered in the variational space, are orthogonal to those that are obtained as eigenfunctions of the set of operators $\{F^\mu\}$. This is a condition fulfilled by Eq. (17c) and the procedure suggested by Eqs. (20). In the matrix representation of these equations discussed above, $|\phi_b\rangle$ was chosen as the unoccupied orbitals that are obtained from the last open-shell operator diagonalized. They are orthogonal to all other orbitals through the projection operators of Eq. (20) and with other orbitals of the same operator through the diagonalization procedure itself.

Equations (38) are the generalized "Brillouin conditions". These conditions refer to "single excitations" with the structure of Eq. (37), and not necessarily to proper spin adapted single excitations from the reference Ψ_0.

7. Koopmans' approximation

Koopmans' approximation states that the negative of the orbital energies in a closed-shell SCF calculation are the ionization potentials of the system in the absence of orbital relaxation (29). That is, removing an electron from orbital $|\phi_i\rangle$ in Φ_0 and recalculating the energy using the remaining orbitals of Φ_0 yields $E_i^+ - E_0 = -\varepsilon_i$.

Koopmans' approximation gives a good "feel" for a wave function and its components, and is a useful feature in examining the ground and excited states of atoms and molecules. Koopmans' approximation is not generally valid for open shell systems, where it would be particularly useful in determining the occupancy of orbitals in different shells. Indeed the construction of the projection operators in Eq. (20) requires the assignment of orbitals to shells and the usual aufbau principle is determined with the tacit assumption (sometimes incorrectly) of Koopmans' approximations.

Using Eq. (35b), it is easy to show from Eq. (34a) that

$$\begin{aligned}\varepsilon_i^\mu &= h_i + G_{ii} - Q_{ii}^\mu \\ &= h_i + \sum_\nu \sum_{j\in\nu} n^\nu[J_{ij} - \tfrac{1}{2}K_{ij}] \\ &\quad - \sum_{\nu\neq c} \sum_{j\in\nu} n^\nu[(1 - a^{\mu\nu})J_{ij} - \tfrac{1}{2}(1 - b^{\mu\nu})K_{ij}].\end{aligned} \tag{39}$$

For a closed-shell molecular orbital, $\mu = c$ and by our construction ε_i^c obeys Koopmans' approximation with an "average" exchange energy for each open-shell orbital since from Eq. (26)

$$E_i^+(c) - E_0 = -h_i - \sum_{j\in c} (2J_{ij} - K_{ij}) - \sum_{\mu\neq c} \sum_{k\in\mu} n^\mu (2J_{ik} - K_{ik})$$

$$= -(h_i + G_{ii}) = -\varepsilon_i^c. \tag{40a}$$

For a open-shell molecular orbital, again from Eq. (26)

$$E_i^+(\mu) - E_0 = -h_i - \sum_{j\in c} (2J_{ij} - K_{ij}) - \tfrac{1}{4} \sum_{\nu\neq c} \sum_{k\in\nu} n^\nu [2a^{\mu\nu} J_{ik} - b^{\mu\nu} K_{ik}]$$

$$= -\varepsilon_i^\mu + \tfrac{1}{4} \sum_{\nu} \sum_{j\in\nu} n^\nu [a^{\mu\nu} J_{ij} - \tfrac{1}{2} b^{\mu\nu} K_{ij}]$$

$$= -\varepsilon_i^\mu - \Delta\varepsilon_i^\mu. \tag{40b}$$

The term $\Delta\varepsilon_i^\mu$ is a correction to the orbital energy required to approximate an ionization process. In general, $\Delta\varepsilon$ is not equal to zero. However, for some specific cases, $a^{\mu\nu}$ nd $b^{\mu\nu}$ are zero and the correction term vanishes, and Koopmans' theorem is obeyed for all orbitals.

8. Summary

In this paper we have developed a general open-shell restricted Hartree–Fock formulation that is capable of dealing with the most general case in which the energy can be written in terms of only one electron terms and Coulomb and exchange integrals $\langle ij|ij\rangle$ and $\langle ij|ji\rangle$. The solutions of the closed-shell and each previous open-shell are projected from each-shell in turn, allowing for an easy separation of the orbitals into shells, and rapid convergence of the procedure.

This paper has been written in response to many inquiries concerning open-shell "vector coupling coefficients". To calculate these coefficients, a and b, it is not necessary to go through the derivations of this paper or of others, but only to follow the procedure of Sect. 5, and only this if the case of interest is not found in the Table.

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30. [a] Not unique. Such situations should be followed by configuration interaction treatment within the active orbital manifold
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