TABLE I. Ground-state energies E and expectation values of several symmetric three-particle systems.

System	He	He	$e^+e^-e^-$	$p\mu p$	$d\mu d$	H_2^+
$M_1=M_2$	1	1	1	1836.12	3671.42	1836.12
M_3	∞	7296.19	1	206.8	206.8	1
$e_1=e_2$	-1	-1	-1	1	1	1
e_3	2	2	1	-1	-1	-1
$\alpha_{13}=\alpha_{23}$	1.9	1.9	0.3737	0.738	0.855	0.798
α_{12}	0.22	0.22	0	0	0	0.228
n^{a}	60	50	50	32	32	32
$-E^{b}$	2.9037237	2.9033037	0.2619956	2778 ev	2981 ev	0.58305
$-E^{b}$ (from other sources)	2.903724376^{d}	2.90330464^{d}		2771 ev^{e}	2986 ev^{e}	0.59715^{f}
$\langle r_{13}\rangle^{c}$	0.929472	0.929604	5.506			
$\langle r_{13}^2\rangle^{c}$	1.193477	1.19380	48.75			
$\langle r_{12}\rangle^{c}$	1.422069	1.42224	8.580			
$\langle r_{12}^2\rangle^{c}$	2.516430	2.51700	93.94			

[a] Number of terms in the wave function.
[b] In atomic units (1 a.u. =27.21 ev), except for $p\mu p$ and $d\mu d$.
[c] In Bohr radii (1 a.u. =0.529 A).
[d] See reference 3.
[e] See reference 7.
[f] See reference 5.

small zero-point vibration the wave function as function of r_{12} has a sharp peak which can be well approximated by (2) only with a large number of terms. An alternative scheme, which can accommodate longer expansions with little increase in the rounding off errors, is being developed.

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Self-Consistent Field Theory for Open Shells of Electronic Systems*

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1. REVIEW OF THE CLOSED-SHELL THEORY

IT is well known that the Hartree-Fock equation for a closed-shell ground state of an electronic system can be derived from the variational principle.[1,2] The wave function is put forward as an antisymmetrized product of one-electron functions or orbitals φ_i, each orbital being doubly occupied:

$$\begin{aligned}\Phi&=(\varphi_1\alpha)(\varphi_1\beta)\cdots(\varphi_n\alpha)(\varphi_n\beta)\\&=[(2n)!]^{\frac{1}{2}}(\varphi_1\alpha)^{[1}(\varphi_1\beta)^{2}\cdots(\varphi_n\alpha)^{2n-1}(\varphi_n\beta)^{2n]}\\&=[(2n)!]^{-\frac{1}{2}}\begin{vmatrix}(\varphi_1\alpha)^1 & (\varphi_1\beta)^1 & \cdots & (\varphi_n\alpha)^1 & (\varphi_n\beta)^1\\(\varphi_1\alpha)^2 & (\varphi_1\beta)^2 & \cdots & (\varphi_n\alpha)^2 & (\varphi_n\beta)^2\\\cdots & \cdots & \cdots & \cdots & \cdots\\\cdots & \cdots & \cdots & \cdots & \cdots\\(\varphi_1\alpha)^{2n-1} & (\varphi_1\beta)^{2n-1} & \cdots & (\varphi_n\alpha)^{2n-1} & (\varphi_n\beta)^{2n-1}\\(\varphi_1\alpha)^{2n} & (\varphi_1\beta)^{2n} & \cdots & (\varphi_n\alpha)^{2n} & (\varphi_n\beta)^{2n}\end{vmatrix}.\end{aligned}\tag{1}$$

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[1] D. R. Hartree, Repts. Progr. Phys. **11**, 113 (1948); *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

[2] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951). The notation and terminology introduced in that paper are adhered to to in the present paper.

The orbitals are conveniently collected in a row vector, namely,

$$\boldsymbol{\varphi} = (\varphi_1\,\varphi_2 \cdots \varphi_n), \tag{2}$$

and may be assumed, without loss of generality, to form an orthonormal set

$$\langle \varphi_i | \varphi_j \rangle = \int \bar{\varphi}_i \varphi_j dV = \delta_{ij}. \tag{3}$$

Different orbital sets can yield essentially the same total wave function, namely, if a set $\boldsymbol{\varphi}'$ is obtained from $\boldsymbol{\varphi}$ by a unitary transformation

$$\boldsymbol{\varphi}' = \boldsymbol{\varphi}\mathbf{U}, \quad \mathbf{U}^*\mathbf{U} = \mathbf{E}, \tag{4}$$

the total wave function transforms according to

$$\Phi' = \Phi\,\mathrm{Det}^2(\mathbf{U}), \tag{5}$$

so that Φ' represents the same physical situation as Φ.

In Eq. (1) the factor $[(2n)!]^{\frac{1}{2}}$ is chosen so that the orthonormality condition for the orbitals (3) implies that the total wave function Φ is normalized:

$$\langle \Phi | \Phi \rangle = \int \cdots \int \bar{\Phi}\Phi dV^1 \cdots dV^{2n} = 1. \tag{6}$$

The expectation value of the energy of the wave function (1) is

$$\langle \Phi | \mathcal{H} | \Phi \rangle = \int \cdots \int \bar{\Phi}\mathcal{H}\Phi dV^1 \cdots dV^{2n}, \tag{7}$$

where the total Hamiltonian $\mathcal{H}$ is given by

$$\mathcal{H} = \sum_{\mu} H^\mu + \tfrac{1}{2} \sum_{\mu \neq \nu} (1/r^{\mu\nu}); \tag{8}$$

H^μ 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. By using (8) in (7), the expectation value becomes a sum of integrals over the orbitals, namely,

$$\langle \Phi | \mathcal{H} | \Phi \rangle = 2\sum_i H_i + \sum_{ij} (2J_{ij} - K_{ij}), \tag{9}$$

where

$$\begin{aligned} H_i &= \langle \varphi_i | H | \varphi_i \rangle, \\ J_{ij} &= \langle \varphi_i | J_j | \varphi_i \rangle = \langle \varphi_j | J_i | \varphi_j \rangle, \\ K_{ij} &= \langle \varphi_i | K_j | \varphi_i \rangle = \langle \varphi_j | K_i | \varphi_j \rangle, \end{aligned} \tag{10}$$

and

$$\begin{aligned} J_i^\mu \varphi^\mu &= \left[\int \bar{\varphi}_i^\nu \varphi_i^\nu (1/r^{\mu\nu}) dV^\nu \right] \varphi^\mu, \\ K_i^\mu \varphi^\mu &= \left[\int \bar{\varphi}_i^\nu \varphi^\nu (1/r^{\mu\nu}) dV^\nu \right] \varphi_i^\mu. \end{aligned} \tag{11}$$

J_i and K_i are commonly called the Coulomb and exchange operators, respectively, associated with the orbital φ_i; they are defined in Eqs. (11) by how they operate on an *arbitrary* one-electron function φ.

The Hartree-Fock equation is obtained by requiring that the orbitals minimize the expectation value of the energy. Those orbitals satisfy

$$F\boldsymbol{\varphi} = \boldsymbol{\varphi}\boldsymbol{\varepsilon}, \tag{12}$$

where the *Hartree-Fock Hamiltonian* F is given by

$$F = H + \sum_i (2J_i - K_i), \tag{13}$$

and $\boldsymbol{\varepsilon}$ is a Hermitian matrix of Lagrangian multipliers, which are introduced by the orthonormality constraints (3). The operator F, which is defined in terms of the orbital set $\boldsymbol{\varphi}$, is easily shown to be invariant when $\boldsymbol{\varphi}$ is subjected to the transformation (4). Accordingly, the set $\boldsymbol{\varphi}'$ satisfies

$$F\boldsymbol{\varphi}' = \boldsymbol{\varphi}'\boldsymbol{\varepsilon}',$$

where

$$\boldsymbol{\varepsilon}' = \mathbf{U}^*\boldsymbol{\varepsilon}\mathbf{U}.$$

We may therefore single out that set of orbitals for which $\boldsymbol{\varepsilon}$ becomes diagonal, so that all the orbitals satisfy

$$F\varphi_i = \epsilon_i \varphi_i. \tag{14}$$

Equation (14) is a pseudo-eigenvalue problem, inasmuch as the operator F is defined in terms of the solutions of (14). Ordinarily, Eq. (14) is called the Hartree-Fock equation, although that term is sometimes used for Eq. (12).

The total energy can be expressed in terms of the *orbital energies* ϵ_i and the one-electron integrals H_i, namely,

$$E = \sum_i (H_i + \epsilon_i). \tag{15}$$

The orbital energies also have a direct physical interpretation, namely, $-\epsilon_i$ is approximately equal to the ionization potential for removal of an electron occupying φ_i.

2. OPEN-SHELL THEORY

We consider open-shell wave functions of the following specifications:

(1) The total wave function is, in general, a sum of several antisymmetrized products, each of which contains a (doubly occupied) closed-shell core $\boldsymbol{\varphi}_C$, and a partially occupied open shell chosen from a set $\boldsymbol{\varphi}_O$, the different antisymmetrized products containing different subsets of $\boldsymbol{\varphi}_O$. The combined set of orbitals $\boldsymbol{\varphi}$ is defined by

$$\boldsymbol{\varphi} = (\boldsymbol{\varphi}_C, \boldsymbol{\varphi}_O), \tag{16}$$

and is assumed to be orthonormal, so that the two sets $\boldsymbol{\varphi}_C$ and $\boldsymbol{\varphi}_O$ are orthonormal and 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 set.

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

$$E=2\sum_k H_k+\sum_{kl}(2J_{kl}-K_{kl})$$
$$+f[2\sum_m H_m+f\sum_{mn}(2aJ_{mn}-bK_{mn})$$
$$+2\sum_{km}(2J_{km}-K_{km})], \quad (17)$$

where a, b, and f are numerical constants depending on the specific case. The first two sums in Eq. (17) represent the closed-shell energy, the next two sums the open-shell energy, and the last sum the interaction energy of the closed and open shell. The number f is, in general, the fractional occupation of the open shell, that is, it is equal to the number of *occupied* open-shell spin orbitals divided by the number of *available* open-shell spin orbitals; obviously $0<f<1$. The numbers a and b differ for different states of the same configuration. In Sec. 5 we examine which states of atoms and molecules satisfy the restrictions just stated.

Before applying the variational principle to Eq. (17) to derive the equations for the orbitals, we define the Coulomb operators J_C and J_O associated with the closed and open shells, respectively, the total Coulomb operator J_T, and similar exchange operators K_C, K_O, K_T by

$$\begin{aligned}&J_C=\sum_k J_k, \quad J_O=f\sum_m J_m, \quad J_T=J_C+J_O,\\&K_C=\sum_k K_k, \quad K_O=f\sum_m K_m, \quad K_T=K_C+K_O.\end{aligned} \quad (18)$$

We also introduce the following (Hermitian) *Coulomb* and *exchange coupling operators* associated with the orbital φ_i:

$$\begin{aligned}L_i\varphi&=\langle\varphi_i|J_O|\varphi\rangle\varphi_i+\langle\varphi_i|\varphi\rangle J_O\varphi_i,\\M_i\varphi&=\langle\varphi_i|K_O|\varphi\rangle\varphi_i+\langle\varphi_i|\varphi\rangle K_O\varphi_i,\end{aligned} \quad (19)$$

and corresponding closed-shell, open-shell, and total Coulomb and exchange coupling operators by

$$\begin{aligned}&L_C=\sum_k L_k, \quad L_O=f\sum_m L_m, \quad L_T=L_C+L_O,\\&M_C=\sum_k M_k, \quad M_O=f\sum_m M_m, \quad M_T=M_C+M_O.\end{aligned} \quad (20)$$

All the operators (18) and (20) are invariant under the transformation

$$\boldsymbol{\varphi}_C'=\boldsymbol{\varphi}_C\mathbf{U}_C, \quad \boldsymbol{\varphi}_O'=\boldsymbol{\varphi}_O\mathbf{U}_O, \quad (21)$$

where $\mathbf{U}_C$ and $\mathbf{U}_O$ are unitary matrices of the appropriate dimensions. The closed-shell transformation of (21) does not alter the total wave function(s), except for a possible phase factor; the open-shell transformation of (21), in general, transforms degenerate total wave functions among each other.

The effect of the closed- and open-shell coupling operators, when they operate on the occupied orbitals, is of particular interest. These results are easily obtained from Eqs. (19) by specifying $\varphi=\varphi_k$ or $\varphi=\varphi_m$, and summing the index on L or M over the closed or open shells; this yields

$$\begin{aligned}(L_C-J_O)\varphi_k&=\sum_l \varphi_l\langle\varphi_l|J_O|\varphi_k\rangle,\\(M_C-K_O)\varphi_k&=\sum_l \varphi_l\langle\varphi_l|K_O|\varphi_k\rangle,\\L_C\varphi_m&=\sum_l \varphi_l\langle\varphi_l|J_O|\varphi_m\rangle,\\M_C\varphi_m&=\sum_l \varphi_l\langle\varphi_l|K_O|\varphi_m\rangle,\\L_O\varphi_k&=f\sum_n \varphi_n\langle\varphi_n|J_O|\varphi_k\rangle,\\M_O\varphi_k&=f\sum_n \varphi_n\langle\varphi_n|K_O|\varphi_k\rangle,\\(L_O-fJ_O)\varphi_m&=f\sum_n \varphi_n\langle\varphi_n|J_O|\varphi_m\rangle,\\(M_O-fK_O)\varphi_m&=f\sum_n \varphi_n\langle\varphi_n|K_O|\varphi_m\rangle.\end{aligned} \quad (22)$$

We turn now to the variational problem. We have to minimize the energy (17) with respect to the orbitals, subject to the constraints (3). We put the variation of the energy equal to zero, and add to it the variations of the constraints (3), each one multiplied with a Lagrangian multiplier. If we designate the Lagrangian multiplier for the ijth constraint (3) with $-2\theta_{ji}$, the resulting equation becomes, after some manipulation,

$$2\sum_k\langle\delta\varphi_k|(H+2J_C-K_C+2J_O-K_O)\varphi_k-\sum_j\varphi_j\theta_{jk}\rangle$$
$$+2\sum_k\langle\delta\bar{\varphi}_k|(H+2J_C-K_C+2J_O-K_O)\bar{\varphi}_k-\sum_j\bar{\varphi}_j\theta_{kj}\rangle$$
$$+2\sum_m\langle\delta\varphi_m|f(H+2J_C-K_C$$
$$+2aJ_O-bK_O)\varphi_m-\sum_j\varphi_j\theta_{jm}\rangle$$
$$+2\sum_m\langle\delta\bar{\varphi}_m|f(H+2J_C-K_C$$
$$+2aJ_O-bK_O)\varphi_m-\sum_j\bar{\varphi}_j\theta_{mj}\rangle=0. \quad (23)$$

Equation (23) now should hold for *any* variations $\delta\varphi_i$ with suitable values for the Lagrangian multipliers; hence,

$$(H+2J_C-K_C+2J_O-K_O)\varphi_k=\sum_j\varphi_j\theta_{jk}=\sum_j\varphi_j\bar{\theta}_{kj},$$
$$f(H+2J_C-K_C+2aJ_O-bK_O)\varphi_m \quad (24)$$
$$=\sum_j\varphi_j\theta_{jm}=\sum_j\varphi_j\bar{\theta}_{mj}.$$

We conclude that the Lagrangian multipliers form a Hermitian matrix, $\theta_{ij}=\bar{\theta}_{ji}$, and rewrite Eqs. (24) in the form

$$(H+2J_C-K_C+2J_O-K_O)\varphi_k$$
$$=\sum_l\varphi_l\theta_{lk}+\sum_n\varphi_n\theta_{nk}, \quad (25a$$

$$f(H+2J_C-K_C+2aJ_O-bK_O)\varphi_m \\ =\sum_l \varphi_l\theta_{lm}+\sum_n \varphi_n\theta_{nm}. \qquad (25b)$$

In the closed-shell case, the orbitals can always be subjected to a unitary transformation (4), which brings the matrix of Lagrangian multipliers into diagonal form; when this has been done, the orbitals all satisfy the pseudo-eigenvalue equation (14). In the open-shell case, however, we have available only the transformation (21) which transforms the open and closed shells within themselves. Such a transformation can eliminate only the off-diagonal multipliers θ_{lk} and θ_{nm}, but not the multipliers θ_{nk} and θ_{lm} which couple the closed and open shells. There is one exception to this, namely, when the closed- and open-shell orbitals have no common symmetry. In that case, θ_{nk} and θ_{lm} vanish automatically, and Eqs. (25) become equivalent to two pseudo-eigenvalue problems of the type (14), one for the closed and one for the open shell; the two Hartree-Fock Hamiltonians are different, and each one is defined in terms of both the inner- and outer-shell orbitals. For this case, our SCF formalism yields the same equations which Hartree obtains by minimizing the total energy expression for *one component* of the degenerate state, and subsequently averaging the field over all directions.[1] A recent molecular example of this case is the LCAO-SCF calculations on B_2 by Padgett and Griffing.[3]

At first sight it seems that the general open-shell case cannot be reduced to pseudo-eigenvalue problems, due to the off-diagonal multipliers θ_{nk} and θ_{lm}. Hartree,[1] and later Nesbet,[4] made further approximations in the SCF equations so that they *did* obtain pseudo-eigenvalue problems. Recently, Lefebvre[5] formulated a method by which the LCAO form of Eqs. (25) can be solved directly, without attempting to obtain pseudo-eigenvalue problems. An application of the method was given by Brion et al.[6] in a calculation on the NO molecule.

We present here an alternative to Lefebvre's method which *does* reduce to pseudo-eigenvalue problems. This is achieved by re-expressing the closed-open shell coupling terms in Eqs. (25), with the aid of the coupling operators (20), in such a way that those terms can be absorbed into the left-hand sides of Eqs. (25).

We multiply Eqs. (25a, b) by $\bar{\varphi}_m$ and $\bar{\varphi}_k$, respectively, and integrate; the results are

$$\langle\varphi_m|H+2J_C-K_C+2J_O-K_O|\varphi_k\rangle=\theta_{mk}, \qquad (26a)$$

$$f\langle\varphi_k|H+2J_C-K_C+2aJ_O-bK_O|\varphi_m\rangle=\theta_{km}. \qquad (26b)$$

By multiplying Eq. (26a) by $-f/(1-f)$, the complex conjugate of (26b) by $1/(1-f)$, and adding, we obtain, since $\theta_{mk}=\bar{\theta}_{km}$,

$$\theta_{mk}=-f\langle\varphi_m|2\alpha J_O-\beta K_O|\varphi_k\rangle, \qquad (27)$$

where

$$\alpha=(1-a)/(1-f), \quad \beta=(1-b)/(1-f). \qquad (28)$$

By using the third through the sixth Eqs. (22) and Eq. (27), one easily establishes

$$\begin{aligned}(2\alpha L_O-\beta M_O)\varphi_k&=-\sum_n \varphi_n\theta_{nk},\\ f(2\alpha L_C-\beta M_C)\varphi_m&=-\sum_l \varphi_l\theta_{lm}.\end{aligned} \qquad (29)$$

Equations (29) now allow us to re-express the coupling terms between the closed and open shells in Eqs. (25) in the desired manner; the orbitals satisfy

$$F_C\boldsymbol{\varphi}_C=\boldsymbol{\varphi}_C\boldsymbol{\eta}_C, \qquad (30a)$$

$$F_O\boldsymbol{\varphi}_O=\boldsymbol{\varphi}_O\boldsymbol{\eta}_O, \qquad (30b)$$

where

$$\begin{aligned}F_C&=H+2J_C-K_C+2J_O-K_O+2\alpha L_O-\beta M_O,\\ F_O&=H+2J_C-K_C+2aJ_O-bK_O+2\alpha L_C-\beta M_C,\end{aligned} \qquad (31)$$

and $\boldsymbol{\eta}_C$, $\boldsymbol{\eta}_O$ are Hermitian matrices with elements θ_{lk} and θ_{nm}/f, respectively. We still have available arbitrary unitary transformations for the closed and open shells separately; these can be chosen so that the matrices $\boldsymbol{\eta}_C$ and $\boldsymbol{\eta}_O$ become diagonal. Hence, there is (at least) one set of orbitals which satisfies

$$F_C\varphi_k=\eta_k\varphi_k, \quad F_O\varphi_m=\eta_m\varphi_m. \qquad (32)$$

The total energy also can be expressed, in this case, in terms of the orbital energies η_i and the one-electron integrals H_i, namely,

$$E=\sum_k (H_k+\eta_k)+f\sum_m (H_m+\eta_m), \qquad (33)$$

which can easily be verified by using Eqs. (10), (17), (22), (31), and (32).

The analogy with the closed-shell case would be complete if $-\eta_k$ and $-\eta_m$ were approximately equal to the ionization potentials for removal of an (the) electron from φ_k or φ_m, respectively. This is not true in general, however; we take up this matter in a subsequent paper.

When solving the SCF equations (32), care has to be exercised in picking the correct solutions. Let us assume that we have a set of trial closed- and open-shell orbitals which are reasonably close to the SCF solution. We construct the operators F_C and F_O and determine their eigenfunctions. The eigenfunctions of F_C are usually those belonging to the *lowest* eigenvalues, say, p in number. Since F_C and F_O are physically little different, the eigenfunctions of F_O belonging to *its* p lowest eigenvalues are expected to resemble closely the closed-shell orbitals and obviously must be rejected as open-shell orbitals; instead, we must take for the latter

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those eigenfunctions belonging to the $p+1$ eigenvalue and up.

Clearly, a formulation of the SCF problem in which the closed- and open-shell orbitals are solutions of the *same* eigenvalue equation would be desirable. This is indeed possible. From the first two and the last two Eqs. (22) we find

$$[2\alpha(L_C-J_O)-\beta(M_C-K_O)]\varphi_C=\varphi_C\zeta_C, \quad (34a)$$

$$[2\alpha(L_O-fJ_O)-\beta(M_O-fK_O)]\varphi_O=\varphi_O\zeta_O, \quad (34b)$$

where

$$\zeta_{kl}=\langle\varphi_k|2\alpha J_O-\beta K_O|\varphi_l\rangle, \quad (35a)$$

$$\zeta_{mn}=f\langle\varphi_m|2\alpha J_O-\beta K_O|\varphi_n\rangle. \quad (35b)$$

By adding Eqs. (34a) and (34b) to Eqs. (30a) and (30b), respectively, we obtain two equations of the same form as (30), with new operators on the left-hand sides and new matrices on the right-hand sides. The two operators are identical and equal to

$$F=H+2J_T-K_T+2\alpha(L_T-J_O)-\beta(M_T-K_O), \quad (36)$$

which follows easily from Eqs. (18), (20), and (28). Hence, the orbitals satisfy

$$F\boldsymbol{\varphi}_C=\boldsymbol{\varphi}_C\boldsymbol{\varepsilon}_C, \quad F\boldsymbol{\varphi}_O=\boldsymbol{\varphi}_O\boldsymbol{\varepsilon}_O, \quad (37)$$

where $\boldsymbol{\varepsilon}_C$ and $\boldsymbol{\varepsilon}_O$ are the new matrices $\boldsymbol{\eta}_C+\boldsymbol{\zeta}_C$ and $\boldsymbol{\eta}_O+\boldsymbol{\zeta}_O$, respectively. Now Eqs. (37) can be diagonalized by a transformation of the type (21), so that the orbitals can be chosen to satisfy

$$F\varphi_i=\epsilon_i\varphi_i. \quad (38)$$

The set φ_i which satisfies Eq. (38) is equivalent to, but not identical with, the set φ_k, φ_m satisfying Eqs. (32): the two sets are connected by a transformation of the type (21). Also, the eigenvalues of Eq. (38) are not identical with the eigenvalues of Eqs. (32); as a matter of fact, the two sets are not even approximately the same. If, we attempt to express the total energy in terms of ϵ_i and H_i, analogous to Eq. (33), we find that we need some additional terms:

$$E=\sum_k(H_k+\epsilon_k)+f\sum_m(H_m+\epsilon_m)$$
$$-f\sum_{km}(2\alpha J_{km}-\beta K_{km})-f^3\sum_{mn}(2\alpha J_{mn}-\beta K_{mn}). \quad (39)$$

3. SYMMETRY CONSIDERATIONS

The open-shell treatment developed in the preceding section is constructed so that the SCF equations permit *symmetry orbitals* as solutions, that is, the orbitals can be grouped in sets, each set transforming under symmetry operations according to an irreducible representation of the symmetry group. This state of affairs is assured by the expression for the total energy, Eq. (17). We assume that the orbitals do belong in sets to irreducible representations, and include in the summations in Eq. (17) only *complete* degenerate sets. This is obvious for the closed-shell contribution; for the open-shell contribution the partial occupation of a degenerate set is taken into account by summing over all the members of that set and introducing the fractional occupation number f. This is tantamount to writing down the total energy as the *average* expectation value for all the degenerate total wave functions of the state under consideration. Obviously, our variational procedure for determining the orbitals asks for the best orbitals to represent a *set* of degenerate total wave functions, in contrast to the customary procedure which asks for the best orbitals to represent a *single component* of a set of degenerate total wave functions.

Having assumed that the orbitals belong in sets to irreducible representations, it is easily seen that the Coulomb and exchange operators (18), the Coulomb and exchange coupling operators (20), and consequently the Hartree-Fock Hamiltonian operators (31) and (36), are totally symmetrical. As a result, the orbitals which are the solutions of the eigenvalue problems (32) and (38) are symmetry orbitals. We therefore see that our assumption about the symmetry properties of the orbitals is a consistent one, and we can say with confidence that the SCF equations have symmetry orbitals as *a* solution; that such a solution corresponds to an *absolute minimum*, not just a *stationary value*, of the total energy is a plausible assumption, although this is difficult to prove in general. We proceed from this assumption.

The requirement that the SCF orbitals are symmetry orbitals has usually been felt as necessary.[1,4] However, in the past, this was not rigorously possible with the customary method where the best orbitals were determined for just *one* component of the open-shell total wave functions; in order to satisfy this requirement, additional approximations had to be made once the SCF equations had been obtained. In the present treatment, no such additional approximations are called for.

To make the best possible use of the symmetry properties of the orbitals, we introduce the notation $\varphi_{i\lambda\alpha}$ in lieu of φ_i. In general, λ (or μ, $\nu\cdots$) refers to the irreducible representation, or *symmetry species*; α (or β, $\gamma\cdots$) 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, k, l, m, n) is a numbering index which labels orbitals which cannot be distinguished by symmetry any more. As before, we use k, l for closed-shell orbitals, m, n for open-shell orbitals, and i, j for orbitals of either closed or open shell. The notation $i\lambda\alpha$ is analogous to the familiar *nlm* in atomic spectra.

4. LCAO FORM OF THE OPEN-SHELL THEORY

The solution of the Hartree-Fock equations for relatively simple problems, like small molecules, presents formidable mathematical difficulties. The reason is that they are partial differential equations in three dimensions, a very small class of which permits solution in terms of standard functions, usually by separation of variables. Actually, only for atoms, where this separation is possible and leads to ordinary differential equations for the radial functions, have they been solved. For molecules (molecular orbitals) and solids (Bloch functions), it appears more profitable to put forward an expansion of each orbital φ_i in terms of a given set of suitable *basis functions* χ_p:

$$\varphi_i=\sum_p \chi_p C_{pi}=\boldsymbol{\chi}\mathbf{c}_i; \tag{40}$$

obsiously, $\boldsymbol{\chi}$ is the row vector which collects all the basis functions, and $\mathbf{c}_i$ is the column vector with components C_{pi}. Since the occupied orbitals must form an orthonormal set, the vectors $\mathbf{c}_i$ must satisfy the constraints

$$\mathbf{c}_i^*\mathbf{S}\mathbf{c}_j=\delta_{ij}, \tag{41}$$

where the *overlap matrix* $\mathbf{S}$ is given by

$$S_{pq}=\langle\chi_p|\chi_q\rangle. \tag{42}$$

The expansion in terms of basis functions leads to a variational problem for the vectors $\mathbf{c}_i$, namely, the determination of the best set $\boldsymbol{\varphi}$ that can be constructed from a given basis set $\boldsymbol{\chi}$ by minimizing the total energy. This process was originally conceived for molecules to construct somewhat crude molecular orbitals from the atomic orbitals contributed by the individual atoms, and accordingly called the LCAO (linear combination of atomic orbitals) SCF method. It is, however, not necessary to restrict the process to such relatively crude applications; rather, we wish to use it as a practical method to obtain the fully optimized Hartree-Fock orbitals by making the basis set $\boldsymbol{\chi}$ sufficiently large and flexible. That this is possible without having to take an impractically large basis set has been shown in a number of recent calculations on atoms[7] and the H_2 molecule.[8] In fact, even for atoms this process is very desirable inasmuch as it yields the Hartree-Fock orbitals with considerably less labor than by numerical integration of the differential equations.

To take full advantage of the symmetry properties, we first reformulate Eqs. (40)–(42) by introducing *symmetry basis functions* $\chi_{p\lambda\alpha}$, analogous to the $\varphi_{i\lambda\alpha}$ of the previous section. Each occupied orbital of a given species and subspecies is a linear combination of the basis orbitals of the same species and subspecies only, 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

$$\varphi_{i\lambda\alpha}=\sum_p \chi_{p\lambda\alpha}C_{\lambda pi}=\boldsymbol{\chi}_{\lambda\alpha}\mathbf{c}_{\lambda i}; \tag{43}$$

clearly, $\boldsymbol{\chi}_{\lambda\alpha}$ is the row vector collecting all the basis functions of species λ and subspecies α, and $\mathbf{c}_{\lambda i}$ is the column vector with components $C_{\lambda pi}$.

For the scheme that follows, it is convenient to normalize the vectors $\mathbf{c}_{\lambda i}$ not to unity, but to *half the number of electrons* they represent, namely,

$$\begin{gathered}\mathbf{c}_{\lambda k}^*\mathbf{S}_\lambda\mathbf{c}_{\lambda l}=d_\lambda\delta_{kl},\quad \mathbf{c}_{\lambda k}^*\mathbf{S}_\lambda\mathbf{c}_{\lambda m}=0,\\ \mathbf{c}_{\lambda m}^*\mathbf{S}_\lambda\mathbf{c}_{\lambda n}=fd_\lambda\delta_{mn},\end{gathered} \tag{44}$$

where d_λ is the dimension of the representation λ, and the matrix $\mathbf{S}_\lambda$ is defined by[9]

$$S_{\lambda pq}=d_\lambda^{-1}\sum_\alpha\langle\chi_{\lambda p\alpha}|\chi_{\lambda q\alpha}\rangle. \tag{45}$$

In addition to the matrices $\mathbf{S}_\lambda$ we need the matrices $\mathbf{H}_\lambda$ of the bare nuclear field Hamiltonian, the elements of which are, analogous to Eq. (45), given by[9]

$$H_{\lambda pq}=d_\lambda^{-1}\sum_\alpha\langle\chi_{p\lambda\alpha}|H|\chi_{q\lambda\alpha}\rangle. \tag{46}$$

Each matrix which enters the Hartree-Fock Hamiltonian has the same structure, splitting up in smaller matrices, one for each species. In some instances we need to consider such matrices as vectors, called *supervectors*; we construct the supervector corresponding to a matrix by writing down all the components, say $H_{\lambda pq}$, in dictionary order on λpq, and denote this supervector by the symbol $\mathbf{H}$. Such a supervector can be operated on by *supermatrices*, the rows and columns of which are denoted by the components of $\mathbf{H}$. In particular, we need the *Coulomb* and *exchange supermatrices* $\mathfrak{J}$ and $\mathfrak{K}$ defined by

$$\begin{aligned}\mathcal{J}_{\lambda pq,\mu rs}&=(d_\lambda d_\mu)^{-1}\sum_{\alpha\beta}\iint\bar{\chi}_{p\lambda\alpha}{}^1\bar{\chi}_{r\mu\beta}{}^2(1/r_{12})\\&\qquad\times\chi_{q\lambda\alpha}{}^1\chi_{s\mu\beta}{}^2dV^1dV^2,\\ \mathcal{K}_{\lambda pq,\mu rs}&=(d_\lambda d_\mu)^{-1}\sum_{\alpha\beta}\iint\bar{\chi}_{p\lambda\alpha}{}^1\bar{\chi}_{r\mu\beta}{}^2(1/r_{12})\\&\qquad\times\chi_{s\mu\beta}{}^1\chi_{q\lambda\alpha}{}^2dV^1dV^2;\end{aligned} \tag{47}$$

they are symmetrical for the exchange of indices $\lambda pq\leftrightarrow\mu rs$, and Hermitian for the simultaneous exchange $p\leftrightarrow q$, $r\leftrightarrow s$.

We now apply the variational principle to the total energy in order to obtain the SCF equations for the vectors $\mathbf{c}_{\lambda i}$. This derivation closely parallels the derivation of the SCF equations in Sec. 2. We restrict ourselves here to writing down the results, and only for the scheme which is formally the simplest, namely, the

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[7] C. C. J. Roothaan, L. M. Sachs, A. W. Weiss, Revs. Modern Phys. **32**, 186 (1960), this issue; R. E. Watson, Tech. Rept. No. 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (1959).

[8] W. Kolos and C. C. J. Roothaan, Revs. Modern Phys. **32**, 219 (1960), this issue.

[9] Actually, all the terms under the summation signs in Eqs. (45) and (46) are equal.

scheme employing the combined Hartree-Fock Hamiltonian.

From the supermatrices $\mathfrak{J}$ and $\mathfrak{K}$ we compute two other supermatrices, namely,

$$\mathfrak{P}=2\mathfrak{J}-\mathfrak{K},\quad \mathfrak{Q}=2\alpha\mathfrak{J}-\beta\mathfrak{K}. \tag{48}$$

Next, from a set of trial vectors $\mathbf{c}_{\lambda i}$ which satisfy the constraints (44), we compute the closed-shell, open-shell, and total *density matrices*

$$\mathbf{D}_{C\lambda}=\sum_k \mathbf{c}_{\lambda k}\mathbf{c}_{\lambda k}{}^*,\quad \mathbf{D}_{O\lambda}=\sum_m \mathbf{c}_{\lambda m}\mathbf{c}_{\lambda m}{}^*,$$
$$\mathbf{D}_{T\lambda}=\mathbf{D}_{C\lambda}+\mathbf{D}_{O\lambda}. \tag{49}$$

These density matrices give rise to supervectors, as explained previously; with the supermatrices (48), they permit the evaluation of two contributions to the Hartree-Fock Hamiltonian, namely,

$$\mathbf{P}=\mathfrak{P}\mathbf{D}_T,\quad \mathbf{Q}=\mathfrak{Q}\mathbf{D}_O. \tag{50}$$

Considering the supervector $\mathbf{Q}$ now as a collection of matrices $\mathbf{Q}_\lambda$, we compute the last contribution to the Hartree-Fock Hamiltonian from

$$\mathbf{R}_\lambda=d_\lambda{}^{-1}(\mathbf{S}_\lambda\mathbf{D}_{T\lambda}\mathbf{Q}_\lambda+\mathbf{Q}_\lambda\mathbf{D}_{T\lambda}\mathbf{S}_\lambda). \tag{51}$$

The Hartree-Fock Hamiltonian is then given by

$$\mathbf{F}_\lambda=\mathbf{H}_\lambda+\mathbf{P}_\lambda-\mathbf{Q}_\lambda+\mathbf{R}_\lambda, \tag{52}$$

and the corresponding eigenvalue problem is

$$\mathbf{F}_\lambda\mathbf{c}_{\lambda i}=\epsilon_{\lambda i}\mathbf{S}_\lambda\mathbf{c}_{\lambda i}. \tag{53}$$

Equation (53) is then solved, yielding a new set of trial vectors; the process is then repeated until the assumed and calculated vectors agree to a prescribed limit of accuracy.

Finally, the total energy may be calculated from scalar products between supervectors, namely,

$$E=(\mathbf{H}+\mathbf{F})^\dagger\mathbf{D}_T-\mathbf{Q}^\dagger(\mathbf{D}_C+f\mathbf{D}_O), \tag{54}$$

which is analogous to Eq. (39).

TABLE I. Coefficients for the configurations π^N, δ^N of linear molecules.

N	1	2			3
f	$\frac{1}{4}$		$\frac{1}{2}$		$\frac{3}{4}$
π^N	$^2\Pi$	$^3\Sigma^-$	$^1\Delta$	$^1\Sigma^+$	$^2\Pi$
δ^N	$^2\Delta$	$^3\Sigma^-$	$^1\Gamma$	$^1\Sigma^+$	$^2\Delta$
a	0	1	$\frac{1}{2}$	0	8/9
b	0	2	0	-2	8/9
α	$\frac{4}{3}$	0	1	2	4/9
β	$\frac{4}{3}$	-2	2	6	4/9

TABLE II. Coefficients for the configurations p^N of atoms.

N	1	2			3			4			5
f	$\frac{1}{6}$		$\frac{1}{3}$			$\frac{1}{2}$			$\frac{2}{3}$		$\frac{5}{6}$
p^N	^2P	^3P	^1D	^1S	^4S	^2D	^2P	^3P	^1D	^1S	^2P
a	0	$\frac{3}{4}$	9/20	0	1	$\frac{4}{5}$	$\frac{2}{3}$	$\frac{15}{16}$	69/80	$\frac{3}{4}$	24/25
b	0	$\frac{3}{2}$	$-\frac{3}{10}$	-3	2	$\frac{4}{5}$	0	9/8	27/40	0	24/25
α	6/5	$\frac{3}{8}$	33/40	$\frac{3}{2}$	0	$\frac{2}{5}$	$\frac{2}{3}$	$\frac{3}{16}$	33/80	$\frac{3}{4}$	6/25
β	6/5	$-\frac{3}{4}$	39/20	6	-2	$\frac{2}{5}$	2	$-\frac{3}{8}$	39/40	3	6/25

5. APPLICABILITY OF THE PRESENT THEORY

Clearly, the open-shell scheme developed in the previous sections is of practical value if and only if the total energy can be represented by Eq. (17), with certain values for a, b, and f. There are three important classes of states which satisfy this limitation:

(1) The half-closed shell: the open shell consists of singly occupied, complete degenerate sets of orbitals, and all the spins are parallel.[10] This is the ground state of this configuration; the wave function is (at least for the two components with all spin functions equal) a single determinant, and $f=\frac{1}{2}$, $a=1$, $b=2$, so that $\alpha=0$, $\beta=-2$, from Eqs. (28). Examples of atomic states in this class are C $1s^22s2p^3$, ^5S; Cr $1s^22s^22p^63s^23p^64s3d^5$, ^7S. A general molecular example is the lowest excited triplet of a molecule with a closed-shell ground state, the excitation being *from* a nondegenerate *to* a nondegenerate orbital.

(2) *All* the states arising from the configurations π^N, $\delta^N,\cdots,1\leqslant N\leqslant 3$, of a linear molecule: Table I summarizes the constants applicable to each such state.

(3) *All* the states arising from the configurations p^N, $1\leqslant N\leqslant 5$, of an atom: Table II summarizes the constants applicable to each state.

It is a relatively simple matter to extend the open-shell theory just presented in such a way that other important classes of atomic states can be accommodated, as for instance, the d^N configurations for the transition elements. We postpone such generalizations for the present, and include whatever new treatments may be necessary with the actual applications planned for the future.

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[10] This case has often been handled by allowing the orbitals for opposite spins to be spatially different. See J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954); G. W. Pratt, Jr., Phys. Rev. **102**, 1303 (1956). This method leads to a wave function which is a mixture of different multiplets.