one or two moments of the line, and not the detailed shape. It is difficult to include the effect of the transverse radiation field in this method. Our approach is in some respects more fundamental than either of these, as we attempt to directly construct stationary states of the whole system consisting of field and matter. There is no ambiguity in the definition of states, and radiative processes on the energy shell are taken into account in all orders. The main new physical effect is the frequency dependence of the damping term in the resonance denominator, which is easily overlooked in the above two methods.

Applicability of Roothaan's Self-Consistent Field Theory*

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Roothaan's open-shell self-consistent field theory is extended in such a way that it can cover a number of important classes of atomic and molecular states which are not included in the range of applicability originally claimed.

I. INTRODUCTION

IN a recent paper[1] Roothaan described a new self-consistent field (SCF) theory for electronic systems which can accommodate open shells as well as the closed shells. However, his paper made a rather modest claim on the range of applicability. The purpose of the present paper is to extend the applicability of the theory in such a way that it includes a number of open-shell cases of practical importance which are not accommodated in the original form of Roothaan's scheme.

The relevant points of Roothaan's open-shell SCF theory are as follows. It is stated that the scheme is of practical value if the total energy can be represented by the following equation:

$$E = 2\sum_k H_k + \sum_{kl}(2J_{kl}-K_{kl})$$
$$+ f[2\sum_m H_m + f\sum_{mn}(2aJ_{mn}-bK_{mn})$$
$$+ 2\sum_{km}(2J_{km}-K_{km})]. \quad (1)$$

This is the expectation value of the total Hamiltonian (in a.u.),

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

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. In Eq. (1), H_i, J_{ij}, and K_{ij} are defined as usual by using Dirac's notation:

$$H_i = \langle \varphi_i | H | \varphi_i \rangle,$$
$$J_{ij} = \langle \varphi_i | J_j | \varphi_i \rangle = \langle \varphi_j | J_i | \varphi_j \rangle, \quad (3)$$
$$K_{ij} = \langle \varphi_i | K_j | \varphi_i \rangle = \langle \varphi_j | K_i | \varphi_j \rangle,$$

where

$$J_i{}^\mu\varphi^\mu = \left[\int \bar\varphi_i{}^\nu\varphi_i{}^\nu(1/r^{\mu\nu})dV^\nu\right]\varphi^\mu,$$
$$K_i{}^\mu\varphi^\mu = \left[\int \bar\varphi_i{}^\nu\varphi^\nu(1/r^{\mu\nu})dV^\nu\right]\varphi_i{}^\mu. \quad (4)$$

J_i and K_i are commonly called the Coulomb and exchange operators, respectively, associated with the orbital φ_i. In referring to the individual orbitals, the indices k, l are used for the closed-shell orbitals and m, n for the open-shell orbitals in Eq. (1). a, b, and f are numerical constants depending on the specific case. The first two sums in Eq. (1) 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. The numbers a and b differ for different states of the same configuration.

Two alternative formulations of the SCF problem are given in Roothaan's paper.[1] The first is the following set of equations:

$$F_C\varphi_k = \eta_k\varphi_k,$$
$$F_O\varphi_m = \eta_m\varphi_m, \quad (5)$$

where

$$F_C = H + 2J_C - K_C + 2J_O - K_O + 2\alpha L_O - \beta M_O,$$
$$F_O = H + 2J_C - K_C + 2aJ_O - bK_O + 2\alpha L_C - \beta M_C, \quad (6)$$

$$\alpha = (1-a)/(1-f),$$
$$\beta = (1-b)/(1-f). \quad (7)$$

[1] C. C. J. Roothaan, Revs. Modern Phys. 32, 179 (1960).

TABLE I. Coefficients for the configurations sp^N of atoms $S(f=1/2, a=b=0, \alpha=\beta=2)$, $p^N(f',a',b',\alpha',\beta')$.

Config.	State	f'	a'	b'	α'	β'	$2ff' \Sigma_{mm'} I_{mm'}$ $J(s,p)$	$K(s,p)$
sp	$^3P^\circ$	1/6	0	0	6/5	6/5	1	-1
	$^1P^\circ$							1
sp^2	^4P	1/3	3/4	3/2	3/8	$-3/4$	2	-2
	^2D		9/20	$-3/10$	33/40	39/20		-1
	^2S		0	-3	3/2	6		-1
	^2P		3/4	3/2	3/8	$-3/4$		1
sp^3	$^5S^\circ$	1/2	1	2	0	-2	3	-3
	$^3D^\circ$		4/5	4/5	2/5	2/5		-2
	$^3P^\circ$		2/3	0	2/3	2		-2
	$^1D^\circ$		4/5	4/5	2/5	2/5		0
	$^3S^\circ$		1	2	0	-2		1
	$^1P^\circ$		2/3	0	2/3	2		0
sp^4	^4P	2/3	15/16	9/8	3/16	$-3/8$	4	-3
	^2D		69/80	27/40	33/80	39/40		-2
	^2S		3/4	0	3/4	3		-2
	^2P		15/16	9/8	3/16	$-3/8$		0
sp^5	$^3P^\circ$	5/6	24/25	24/25	6/25	6/25	5	-3
	$^1P^\circ$							-1

The second is a more elegant scheme in which the closed and open-shell orbitals are solutions of the *same* eigenvalue equation:

$$F\varphi_i = \epsilon_i \varphi_i, \qquad (8)$$

where

$$F = H + 2J_T - K_T + 2\alpha(L_T - J_O) - \beta(M_T - K_O). \qquad (9)$$

The definitions of various operators in (6) and (9) are listed below.

$$
\begin{aligned}
J_C &= \sum_k J_k, \\
J_O &= f \sum_m J_m, \\
J_T &= J_C + J_O, \\
K_C &= \sum_k K_k, \\
K_O &= f \sum_m K_m, \\
K_T &= K_C + K_O,
\end{aligned} \qquad (10)
$$

$$
\begin{aligned}
L_i\varphi &= \langle \varphi_i | J_O | \varphi \rangle \varphi_i + \langle \varphi_i | \varphi \rangle J_O \varphi_i, \\
M_i\varphi &= \langle \varphi_i | K_O | \varphi \rangle \varphi_i + \langle \varphi_i | \varphi \rangle K_O \varphi_i,
\end{aligned} \qquad (11)
$$

$$
\begin{aligned}
L_C &= \sum_k L_k, \\
L_O &= f \sum_m L_m, \\
L_T &= L_C + L_O, \\
M_C &= \sum_k M_k, \\
M_O &= f \sum_m M_m, \\
M_T &= M_C + M_O.
\end{aligned} \qquad (12)
$$

Roothaan's theory as it stands covers a number of important cases but unfortunately the electron configurations with two (or more) open shells drop out of the range of applicability, with one important exception. This exception is the case in which the open shell consists of singly occupied, complete degenerate sets of orbitals,

and all the spins are parallel. Examples of atomic states in this class are C $1s^2 2s 2p^3$, ^5S; Cr $1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^5$, ^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.

II. EXTENSION OF ROOTHAAN'S SCF THEORY

It is, however, not necessary to restrict ourselves within the form of the energy expression given by Eq. (1). Consider the following formula for the total energy which includes (1) as a special case:

$$
\begin{aligned}
E = {} & 2 \sum_k H_k + 2 \sum_{k'} H_{k'} + \sum_{kl}(2J_{kl} - K_{kl}) \\
& + \sum_{kl'}(2J_{kl'} - K_{kl'}) + \sum_{k'l}(2J_{k'l} - K_{k'l}) \\
& + \sum_{k'l'}(2J_{k'l'} - K_{k'l'}) + f[2 \sum_m H_m \\
& + f \sum_{mn}(2aJ_{mn} - bK_{mn}) + 2 \sum_{km}(2J_{km} - K_{km}) \\
& + 2 \sum_{k'm}(2J_{k'm} - K_{k'm})] + f'[2 \sum_{m'} H_{m'} \\
& + f' \sum_{m'n'}(2a'J_{m'n'} - b'K_{m'n'}) \\
& + 2 \sum_{km'}(2J_{km'} - K_{km'}) + 2 \sum_{k'm'}(2J_{k'm'} - K_{k'm'})] \\
& + 2ff' \sum_{mm'} I_{mm'}. \qquad (13)
\end{aligned}
$$

The indices k,l refer to the first group of closed shells with a corresponding set of orbitals $\{\varphi_k\}$, k', l' to the second group of closed shells with $\{\varphi_{k'}\}$, m, n to the first open shell with $\{\varphi_m\}$ and finally m', n' to the second open shell with $\{\varphi_{m'}\}$. *The most essential condition is that these two open shells should belong to different symmetries.* More precisely, the orbital $\{\varphi_m\}$ and $\{\varphi_{m'}\}$ should belong to different symmetry species. A possible way out of this restriction will be discussed in the fourth section of the present paper. The reason for dividing the whole closed shell family into two groups will soon become clear. In Eq. (13) all sums except the last one hardly need explanation, Eq. (13) being a straight-

TABLE II. Coefficients for the configurations $\sigma\pi^N$ of linear molecules, $\sigma(f=1/2,\ a=b=0,\ \alpha=\beta=2),\ \pi^N(f',a',b',\alpha',\beta')$.

Config.	State	f'	a'	b'	α'	β'	$J(\sigma,\pi)$	$2ff'\ \Sigma_{mm'}\ I_{mm'}$ $K(\sigma,\pi)$
$\sigma\pi$	$^3\Pi$	1/4	0	0	4/3	4/3	1	-1
	$^1\Pi$						1	1
$\sigma\pi^2$	$^4\Sigma^-$	1/2	1	2	0	-2	2	-2
	$^2\Delta$		1/2	0	1	2	2	-1
	$^2\Sigma^+$		0	-2	2	6	2	-1
	$^2\Sigma^-$		1/2	1	1	0	2	1
$\sigma\pi^3$	$^3\Pi$	3/4	8/9	8/9	4/9	4/9	3	-2
	$^1\Pi$						3	0

forward generalization of Eq. (1). We have two open shells here and so we need two sets of parameters f, a, b, and f', a', b'. *The last term $2ff'\ \sum_{mm'}\ I_{mm'}$ represents the interaction between the two open shells.* In some cases it is expressed with familiar J_{ij} and K_{ij} integrals, but in some other cases it is not. See Tables I, II, and III.

It is necessary to divide the whole family of closed shells into two groups. The first group $\{\varphi_k\}$ contains all the closed shell orbitals which have the same symmetry property as that of the first open-shell orbitals $\{\varphi_m\}$; the second group $\{\varphi_{k'}\}$ contains all the closed-shell orbitals which have the same symmetry property as that of the second open-shell orbitals $\{\varphi_{m'}\}$. If there are remaining closed-shell orbitals of symmetry species different from both $\{\varphi_m\}$ and $\{\varphi_{m'}\}$, these closed shells can be grouped either within the first group or within the second one. For example, suppose we have to deal with the following electronic configuration. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s 4p^N$ $(1 \leqslant N \leqslant 5)$. It is possible to divide it in the following two alternative ways:

(I) $1s^2,\ 2s^2,\ 3s^2,\ 3d^{10},\ 4s;\ 2p^6,\ 3p^6,\ 4p^N$.

(II) $1s^2,\ 2s^2,\ 3s^2,\ 4s;\ 2p^6,\ 3p^6,\ 3d^{10},\ 4p^N$.

Keeping this kind of grouping in mind, we recast Eq. (13) into the following form:

$$E = 2\sum_k(H_k+h_{Ck}) + \sum_{kl}(2J_{kl}-K_{kl})$$
$$+f[2\sum_m(H_m+h_{0m}) + f\sum_{mn}(2aJ_{mn}-bK_{mn})$$
$$+2\sum_{km}(2J_{km}-K_{km})] + 2\sum_{k'}H_{k'}$$
$$+\sum_{k'l'}(2J_{k'l'}-K_{k'l'}) + f'[2\sum_{m'}H_{m'}$$
$$+f'\sum_{m'n'}(2a'J_{m'n'}-b'K_{m'n'})$$
$$+2\sum_{k'm'}(2J_{k'm'}-K_{k'm'})], \quad (14)$$

where

$$h_{Ck} = \sum_{l'}(2J_{kl'}-K_{kl'}) + f'\sum_{m'}(2J_{km'}-K_{km'}),$$
$$h_{0m} = \sum_{l'}(2J_{ml'}-K_{ml'}) + f'\sum_{m'}I_{mm'}. \quad (15)$$

Or alternatively,

$$E = 2\sum_{k'}(H_{k'}+h_{Ck'}') + \sum_{k'l'}(2J_{k'l'}-K_{k'l'})$$
$$+f'[2\sum_{m'}(H_{m'}+h_{0m'}')$$
$$+f'\sum_{m'n'}(2a'J_{m'n'}-b'K_{m'n'})$$
$$+2\sum_{k'm'}(2J_{k'm'}-K_{k'm'})]$$
$$+2\sum_k H_k + \sum_{kl}(2J_{kl}-K_{kl})$$
$$+f[2\sum_m H_m + f\sum_{mn}(2aJ_{mn}-bK_{mn})$$
$$+2\sum_{km}(2J_{km}-K_{km})], \quad (16)$$

where

$$h_{Ck'}' = \sum_l(2J_{k'l}-K_{k'l}) + f\sum_m(2J_{k'm}-K_{k'm}),$$
$$h_{0m'}' = \sum_l(2J_{m'l}-K_{m'l}) + f\sum_m I_{m'm}. \quad (17)$$

Application of the variational principle to Eq. (14) [or to Eq. (16)] will yield the SCF equations for the orbitals. Instead of varying all the orbitals simultaneously, we proceed in the following way. Assume that we have a reasonable starting approximation for the orbitals $\{\varphi_{k'}\}$ and $\{\varphi_{m'}\}$. Now apply the variational principle to Eq. (14) by varying the orbitals $\{\varphi_k\}$ and $\{\varphi_m\}$ (the first group) only with $\{\varphi_{k'}\}$ and $\{\varphi_{m'}\}$ held fixed. This is permissible because the orthogonality conditions between $\{\varphi_k,\varphi_m\}$ and $\{\varphi_{k'},\varphi_{m'}\}$ are always secured.

TABLE III. Coefficients for the configurations $\pi_u{}^3\pi_g{}^N$ of linear molecules $\pi_u{}^3(f=3/4,\ a=b=8/9,\ \alpha=\beta=4/9),\ \pi_g{}^N(f',a',b',\alpha',\beta')$.

Config.	State	f'	a'	b'	α'	β'	$J(\pi_u{}^+,\pi_g{}^+)$	$K(\pi_u{}^+,\pi_g{}^-)$	$2ff'\ \Sigma_{mm'}\ I_{mm'}$ $K(\pi_u{}^+,\pi_g{}^+)$	$(\pi_u{}^+\pi_u{}^+|\pi_g{}^-\pi_g{}^-)$
$\pi_u{}^3\pi_g$	$^3\Sigma_u{}^+$	1/4	0	0	4/3	4/3	3	-1	-1	-1
	$^3\Sigma_u{}^-$						3	-1	-1	1
	$^1\Sigma_u{}^+$						3	-1	3	-1
	$^1\Sigma_u{}^-$						3	-1	-1	1
	$^3\Delta$						3	-1	-1	0
	$^1\Delta$						3	1	-1	0
$\pi_u{}^3\pi_g{}^2$	$^4\Pi_u$	1/2	1	2	0	-2	6	-2	-2	0
	$^2\Pi_u$		0	-2	2	6	6	-1	-1	0
	$^2\Phi_u$		1/2	0	1	2	6	-1	-2	0
$\pi_u{}^3\pi_g{}^3$	$^3\Sigma_u{}^+$	3/4	8/9	8/9	4/9	4/9	9	-3	-3	1
	$^3\Sigma_u{}^-$						9	-3	-1	-1
	$^1\Sigma_u{}^+$						9	-1	-1	1
	$^1\Sigma_u{}^-$						9	-1	-3	-1
	$^3\Delta_u$						9	-2	-3	0
	$^1\Delta_u$						9	-2	-1	0

The orbitals $\{\varphi_{k'}\}$ and $\{\varphi_{m'}\}$ being fixed, the last five sums in Eq. (14) drop out from the expression for δE. This means that the expression for δE assumes essentially the same form as that derived from Eq. (1) as far as the present variation is concerned, with some modification only in the one-electron part of the energy as indicated in (15).

Before applying the variational principle to Eq. (14) [or to (16)] in the way just described, we define the operators, h_C, h_O, h, Δ_i, Δ_C, Δ_O, Δ_T and the corresponding ones with prime by

$$h_{Ck} = \langle \varphi_k | h_C | \varphi_k \rangle,$$
$$h_{Om} = \langle \varphi_m | h_O | \varphi_m \rangle, \tag{18}$$
$$h = h_C - h_O,$$

$$h_{Ck}' = \langle \varphi_{k'} | h_C' | \varphi_{k'} \rangle,$$
$$h_{Om}' = \langle \varphi_{m'} | h_O' | \varphi_{m'} \rangle, \tag{18'}$$
$$h' = h_C' - h_O',$$

$$\Delta_i \varphi = \langle \varphi_i | h | \varphi \rangle \varphi_i + \langle \varphi_i | \varphi \rangle h \varphi_i, \tag{19}$$

$$\Delta_i' \varphi = \langle \varphi_i | h' | \varphi \rangle \varphi_i + \langle \varphi_i | \varphi \rangle h' \varphi_i, \tag{19'}$$

$$\Delta_C = \sum_k \Delta_k,$$
$$\Delta_O = f \sum_m \Delta_m, \tag{20}$$
$$\Delta_T = \Delta_C + \Delta_O,$$

$$\Delta_C' = \sum_{k'} \Delta_{k'},$$
$$\Delta_O' = f' \sum_{m'} \Delta_{m'}, \tag{20'}$$
$$\Delta_T' = \Delta_C' + \Delta_O'.$$

A close relationship between (19), (19'), (20), (20'), and (11), (12) is evident and the derivation of the SCF equations closely parallels the derivation of the SCF equations (5) and (8), which are described in detail in Sec. 2 of Roothaan's paper.[1] We restrict ourselves here to writing down the results and only for the scheme employing the combined Hartree-Fock Hamiltonian:

$$F \varphi_i = \epsilon_i \varphi_i \quad (i = k, m), \tag{21}$$

where

$$F = \bar{H} + \bar{G},$$
$$\bar{H} = H + \gamma(h_O - f h_C + \Delta_T), \tag{22}$$
$$\bar{G} = 2J_T - K_T + 2\alpha(L_T - J_O) - \beta(M_T - K_O),$$

$$\alpha = (1-a)/(1-f),$$
$$\beta = (1-b)/(1-f), \tag{23}$$
$$\gamma = 1/(1-f).$$

This is the equation for $\{\varphi_k, \varphi_m\}$ and a generalization of Eq. (8) with (9). The corresponding equation for $\{\varphi_{k'}, \varphi_{m'}\}$ is

$$F' \varphi_{i'} = \epsilon_{i'} \varphi_{i'} \quad (i' = k', m'), \tag{24}$$

where

$$F' = \bar{H}' + \bar{G}',$$
$$\bar{H}' = H + \gamma'(h_O' - f' h_C' + \Delta_T'), \tag{25}$$
$$\bar{G}' = 2J_T' - K_T' + 2\alpha'(L_T' - J_O') - \beta'(M_T' - K_O'),$$

$$\alpha' = (1-a')/(1-f'),$$
$$\beta' = (1-b')/(1-f'), \tag{26}$$
$$\gamma' = 1/(1-f').$$

The operators J_O', K_O', J_T', K_T', L_T', M_T' are obtained by replacing $\{\varphi_k, \varphi_m\}$ with $\{\varphi_{k'}, \varphi_{m'}\}$ in the definitions of the corresponding operators without prime. The additional terms $\gamma(h_O - f h_C + \Delta_T)$ or $\gamma'(h_O' - f' h_C' + \Delta_T')$ may be regarded as a kind of force field for the electrons in nonfixed orbitals due to the electrons in fixed orbitals.

The following is a summary of the self-consistent field procedure:

(I) Fix $\{\varphi_{k'}, \varphi_{m'}\}$. Determine $\{\varphi_k, \varphi_m\}$ from Eq. (21).

(II) Fix $\{\varphi_k, \varphi_m\}$ as obtained above. Determine a new set of $\{\varphi_{k'}, \varphi_{m'}\}$ from Eq. (24).

(III) Fix $\{\varphi_{k'}, \varphi_{m'}\}$ as obtained above. Determine a new set of $\{\varphi_k, \varphi_m\}$ from Eq. (21).

(IV) Continue the above procedure until the cycle produces no appreciable changes in all the orbitals $\{\varphi_k, \varphi_m\}$ and $\{\varphi_{k'}, \varphi_{m'}\}$.

(V) With thus determined orbitals $\{\varphi_k, \varphi_m\}$ and $\{\varphi_{k'}, \varphi_{m'}\}$ calculate the total energy from the full expression (13) or (14) or (15).

III. APPLICABILITY

The iterative procedure described in the previous section is directly applicable to electron configurations which have two open shells of different symmetries. Three tables presented in this paper constitute useful supplements of Tables I and II of Roothaan's paper.[1] It is to be noted that these tables cover only a part of the applicable range of the procedure proposed here.

Table I $(sp^N, 1 \leqslant N \leqslant 5)$. This table is a supplement to Table II of Roothaan's paper.[1] With these two tables one can now cover all atomic states arising from distributing the electrons in all possible ways over the s and p atomic orbitals. Here and in the following,

$$J(\varphi_i, \varphi_j) = \int \bar{\varphi}_i(1) \bar{\varphi}_j(2) (1/r^{12}) \varphi_i(1) \varphi_j(2) dV^1 dV^2$$
$$= \int \bar{\varphi}_i(1) \varphi_i(1) (1/r^{12}) \bar{\varphi}_j(2) \varphi_j(2) dV^1 dV^2, \tag{27}$$

$$K(\varphi_i, \varphi_j) = \int \bar{\varphi}_i(1) \bar{\varphi}_j(2) (1/r^{12}) \varphi_j(1) \varphi_i(2) dV^1 dV^2$$
$$= \int \bar{\varphi}_i(1) \varphi_j(1) (1/r^{12}) \bar{\varphi}_j(2) \varphi_i(2) dV^1 dV^2. \tag{28}$$

If we denote the three components of the p orbital by p_1, p_2 and p_3,

$$J(s,p) = J(s,p_1) = J(s,p_2) = J(s,p_3),$$
$$K(s,p) = K(s,p_1) = K(s,p_2) = K(s,p_3).$$

For example, in the case of the sp^2 ^2P state we see that

$$2ff' \sum_{mm'} I_{mm'} = 2J(s,p) + K(s,p)$$
$$= 2(1/2)(1/3)[\{2J(s,p_1) + K(s,p_1)\}$$
$$+ \{2J(s,p_2) + K(s,p_2)\}$$
$$+ \{2J(s,p_3) + K(s,p_3)\}].$$

Table II ($\sigma\pi^N$, $1 \leqslant N \leqslant 3$). This table, together with the next table, is a supplement to Table I of Roothaan's paper.[1] The π molecular orbital has two degenerate components. (See comments to Table III). With this table one can treat several important electronic states of molecules, for example, N_2 $3\sigma_g 1\pi_g$, $^3\Pi_g$ and $^1\Pi_g$.

Table III ($\pi_u{}^3\pi_g{}^N$, $1 \leqslant N \leqslant 3$). In this table π^+ and π^- are the molecular orbitals with the component of angular momentum $+1$ and -1, respectively, along the molecular axis. There are several identity relations among integrals over π molecular orbitals:

$$J(\pi^+,\pi^+) = J(\pi^-,\pi^-) = J(\pi^+,\pi^-) = J(\pi^-,\pi^+),$$
$$K(\pi^+,\pi^+) = K(\pi^-,\pi^-),$$
$$K(\pi^+,\pi^-) = K(\pi^-,\pi^+).$$
(29)

As is seen in Table III, 8Σ states contain the integral $(\pi_u{}^+\pi_u{}^+|\pi_g{}^-\pi_g{}^-)$ which is not expressible with the J and K integrals:

$$(\varphi_i\varphi_i|\varphi_j\varphi_j)$$

$$= \int \varphi_i(1)\varphi_j(2)(1/r^{12})\varphi_i(1)\varphi_j(2)dV^1 dV^2$$
(30)

$$= \int \varphi_i(1)\varphi_i(1)(1/r^{12})\varphi_j(2)\varphi_j(2)dV^1 dV^2.$$

Note that

$$(\pi_u{}^+\pi_u{}^+|\pi_g{}^-\pi_g{}^-) = (\pi_u{}^-\pi_u{}^-|\pi_g{}^+\pi_g{}^+),$$
$$(\pi_u{}^+\pi_u{}^+|\pi_g{}^+\pi_g{}^+) = (\pi_u{}^-\pi_u{}^-|\pi_g{}^-\pi_g{}^-) = 0.$$
(31)

It seems sensible to examine a little more closely the structure of the interaction between two open shells $2ff' \sum_{mm'} I_{mm'}$ by taking an example from Table III. The table gives the following expression for $2ff' \sum_{mm'} I_{mm'}$ of the $\pi_u{}^3\pi_g{}^3$ $^3\Sigma_u{}^+$ state:

$$9J(\pi_u{}^+,\pi_g{}^+) - 3K(\pi_u{}^+,\pi_g{}^-)$$
$$- 3K(\pi_u{}^+,\pi_g{}^+) + (\pi_u{}^+\pi_u{}^+|\pi_g{}^-\pi_g{}^-).$$

This can be rewritten in the following way by using

(29) and (31);

$$(9/4)J(\pi_u{}^+,\pi_g{}^+) - (3/2)K(\pi_u{}^+,\pi_g{}^+)$$
$$+ (1/2)(\pi_u{}^+\pi_u{}^+|\pi_g{}^+\pi_g{}^+)$$
$$+ (9/4)J(\pi_u{}^+,\pi_g{}^-) - (3/2)K(\pi_u{}^+,\pi_g{}^-)$$
$$+ (1/2)(\pi_u{}^+\pi_u{}^+|\pi_g{}^-\pi_g{}^-)$$
$$+ (9/4)J(\pi_u{}^-,\pi_g{}^+) - (3/2)K(\pi_u{}^-,\pi_g{}^+)$$
$$+ (1/2)(\pi_u{}^-\pi_u{}^-|\pi_g{}^+\pi_g{}^+)$$
$$+ (9/4)J(\pi_u{}^-,\pi_g{}^-) - (3/2)K(\pi_u{}^-,\pi_g{}^-)$$
$$+ (1/2)(\pi_u{}^-\pi_u{}^-|\pi_g{}^-\pi_g{}^-).$$

This means that

$$I_{mm'} = 2J(m,m') - (4/3)K(m,m') + (4/9)(mm|m'm').$$

Generally speaking, however, it is not necessary that all $I_{mm'}$'s have the same functional form as it is in the above example. They may all be different from one another.

It is hoped that the SCF wave functions will be worked out for the lower lying electronic energy levels of N_2, $O_2{}^+$ and O_2 molecules arising from the configurations listed in Table III.

IV. POSSIBLE EXTENSIONS OF THE APPLICABILITY

With additional elaborations described in the preceding sections Roothaan's open-shell SCF theory now covers electron configurations which have two open shells of *different* symmetry. Generally speaking, however, if we have two open shells of the *same* symmetry, the scheme is not directly applicable. Here we describe briefly a possible scheme to include such cases, taking the $1s^2 2s^2 2p 3p$ configuration of an atom as an illustrative example. This electronic configuration yields ^1P, ^3D, ^3S, ^3P, ^1D, and ^1S states. On the other hand, the lower lying configuration $1s^2 2s^2 2p^2$ yields the lowest ^3P, ^1D, and ^1S states and so the straightforward variational treatment is applicable only to the first three states, ^1P, ^3D, and ^3S. We choose the ^1P state. Now we start with the application of the LCAO form of Roothaan's theory to the $1s^2 2s^2 2p^2$ ^3P state which is described in Sec. IV of Roothaan's paper.[1] In general, we expect that the SCF orbitals can be expressed with sufficient accuracy in terms of a given set of suitable basis functions $\chi_{p\lambda\alpha}$:

$$\varphi_{i\lambda\alpha} = \sum_p \chi_{p\lambda\alpha} C_{\lambda pi}.$$

Here λ refers to the irreducible representation, or symmetry species; α refers to the subspecies, that is, it labels the individual members of the degenerate set that transform according to the representation λ; and i is a numbering index which labels orbitals which cannot be distinguished by symmetry any more. The notation $i\lambda\alpha$ is analogous to the familiar nlm in atomic spectra. Now focus our attention on the p orbitals. First, we may drop the subscript λ. Second, we may group together three degenerate functions (α; $m = +1, 0, -1$) and simply write $\chi_{p(\alpha)}$ or $\varphi_{i(\alpha)}$, which actually represents three

functions. For the $2p^2$ configuration we need only one $\varphi_{(\alpha)}$ for the $2p$ orbital. But if the subscript p of the basis functions $\chi_{p(\alpha)}$ runs, say, from 1 to n, we are supplied with a set of orbitals $\varphi_{i(\alpha)}$ where i also runs from 1 to n and the usual procedure is that we pick up one orbital $\varphi_{i(\alpha)}$ which corresponds to the lowest "orbital energy." It is important to note that the set of orbitals $\{\varphi_{i(\alpha)}\}$ spans the same functional space as the one spanned by the original set $\{\chi_{p(\alpha)}\}$ and each member of the new set $\varphi_{i(\alpha)}$ is orthogonal to one another. Taking advantage of this property we can treat the $1s^2 2s^2 2p3p\ {}^1P$ state in the following way.

(I) Apply Roothaan's SCF scheme to the $1s^2 2s^2 2p^2\ {}^3P$ state. It gives a set of orthogonal functions for the p orbitals;

$$\varphi_{1(\alpha)},\ \varphi_{2(\alpha)},\ \cdots,\ \varphi_{n(\alpha)},$$

where

$$\varphi_{i(\alpha)} = \sum_{p=1}^{n} \chi_{p(\alpha)} C_{pi}.$$

Suppose that the above sequence is in the order of ascending "orbital energy." Thus $\varphi_{1(\alpha)}$ is taken for the $2p$ orbital.

(II) Now we consider the $1s^2 2s^2 2p3p\ {}^1P$ state. Represent the $2p$ orbital by $\varphi_{1(\alpha)}$ and keep it fixed. Apply the SCF procedures described in the present paper to $1s^2 2s^2 3p$ by using $\varphi_{2(\alpha)},\ \varphi_{3(\alpha)},\ \cdots,\ \varphi_{n(\alpha)}$ as a new set of basis functions for the $3p$ orbital. Thus we get

$$\varphi_{2(\alpha)}',\ \varphi_{3(\alpha)}',\ \cdots,\ \varphi_{n(\alpha)}',$$

where

$$\varphi_{i(\alpha)}' = \sum_{p=2}^{n} \varphi_{p(\alpha)} C_{pi}'.$$

Here $\varphi_{2(\alpha)}'$ is the first approximation for the $3p$ orbital.

Notice that these functions are all guaranteed to be orthogonal to the fixed $2p$ orbital $\varphi_{1(\alpha)}$.

(III) Represent the $3p$ orbital by $\varphi_{2(\alpha)}'$ and keep it fixed. Use $\varphi_{1(\alpha)},\ \varphi_{3(\alpha)}',\ \varphi_{4(\alpha)}',\ \cdots,\ \varphi_{n(\alpha)}'$ as a new set of basis functions for the $2p$ orbital. Thus we get

$$\varphi_{1(\alpha)}',\ \varphi_{3(\alpha)}'',\ \varphi_{4(\alpha)}'',\ \cdots,\ \varphi_{n(\alpha)}'',$$

where $\varphi_{1(\alpha)}'$ is the second approximation for the $2p$ orbital.

(IV) Represent the $2p$ orbital by $\varphi_{1(\alpha)}'$ and keep it fixed. Use $\varphi_{2(\alpha)}',\ \varphi_{3(\alpha)}'',\ \cdots,\ \varphi_{n(\alpha)}''$ as a new set of basis functions for the $3p$ orbital.

(V) Continue the above procedures until self-consistency is attained.

It should be admitted that the procedure described above is not at all simple and the convergence property of the whole process is not very clear mathematically. In some favorable cases, however, it could be of practical value because the number of necessary basis functions n is expected to be rather small in most cases.

V. CONCLUSION

It has been shown that with some additional elaborations Roothaan's SCF theory covers almost all the electronic configurations of atoms and molecules which are of immediate importance. It is easy to extend *formally* the SCF procedure described in the present paper in such a way that some classes of three, four or more open shells can be accommodated but it hardly seems worthwhile to make such a formal extension.

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K-Electron Capture Branch of Sr^{87m}†

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The existence of a $(0.65\pm0.25)\%$ K-electron capture branch in the decay of 2.8-hr Sr^{87m} has been established by means of an "internal source" technique. The low $\log ft = 4.25$ and small energy release of 115 kev make this K branch especially interesting because it establishes Rb^{87} as a possible low-threshold detector for the inverse neutrino capture reaction, Rb$^{87} + \nu \rightarrow$ Sr$^{87m} + e^-$, which could be identified by observing the characteristic decay of the Sr^{87m} isomer.

THE 2.8-hr Sr^{87m} isomer decays by an $M4$ transition of 388 kev to the Sr^{87} ground state. We find that it also decays by a previously undetected K-electron capture branch to Rb^{87}. From the measured ft value

we can calculate the rate of the inverse reaction and thus judge the potential usefulness of Rb^{87} as a low-energy neutrino detector.

In Sr^{87m}, the 49th neutron is in a $p_{\frac{1}{2}}$ state, while in the ground state it is in a $g_{9/2}$ state. Long-lived Rb^{87} ($t_{\frac{1}{2}} \approx 6 \times 10^{10}$ yr) decays to Sr^{87} by β^- emission, with a