PHYSICAL REVIEW B VOLUME 4, NUMBER 6 15 SEPTEMBER 1971

# Open-Shell Self-Consistent-Field Molecular-Orbital Theory for Transition-Metal Clusters*

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(Received 2 February 1971)

Detailed formulations are developed for the theoretical calculation of molecular-orbital (MO) wave functions and electronic excitation energies for transition-metal clusters. The procedures are based upon the spin- and symmetry-restricted Hartree-Fock-Roothaan self-consistent-field (SCF) equations for open-shell systems. All diagonal electrostatic matrix elements have been derived to permit determining MO's for all states of all electronic configurations arising from the $d^n$ states of the free metal ion. In addition, configuration-interaction matrix elements among all states occurring in the $d^2$ and $d^3$ ($d^8$ and $d^7$) systems are also presented. The frozen-core approximations and some aspects of achieving converged SCF MO's are briefly discussed.

## I. INTRODUCTION

Interest in optical, magnetic, thermodynamic, kinetic, and structural properties of transition-metal clusters (or complexes) arising from the occurrence of unfilled shells associated with the metal ion has led to a wide variety of attempts at theoretical explanation.[1] Due to the complexity of these systems, however, most theoretical efforts have been semiempirical in character and, while explaining some properties, are unreliable for any consistent explanation of the entire range of behavior. Originating in the basic crystal-field theory, on the other hand, has been a sequence of successively refined *ab initio* calculations, mainly treating the $Cr(H_2O)_6{}^{+3}$ and $NiF_6{}^{-4}$ systems. In the earlier works, *ad hoc* theoretical models were devised and only recently has there been explicitly employed the general full-scale computational procedures developed in connection with the theory of simpler molecular systems.[2–11] Even in the latter case, the theoretical formalism has essentially been limited to those cases in which the wave function for the cluster can adequately be represented by a single antisymmetrized product (Slater determinant) of molecular orbitals (MO's).

In order to present the basic formalism for a more general treatment of these systems according to the self-consistent-field (SCF) MO procedure, we present here an outline of the total energy and SCF equations specific to these systems. In particular, the detailed formulations are presented for calculating MO wave functions and energies for any state of any electronic configuration arising from transition-metal ions in cubic clusters.

Preliminary results indicate that good agreement with, and understanding of, experimental spectral and magnetic data can be obtained from these theoretical procedures for a variety of systems of this type.[10] While the basic methodology is well known in application to simpler systems,[12] the specific forms given here are valuable in further presentation of our results and in guiding the refinement of semiempirical procedures for octahedral clusters.

## II. WAVE FUNCTIONS AND TOTAL ENERGY

The system $ML_6$ is referred to the usual Cartesian coordinate system as indicated in Fig. 1. The metal ($M$) center is located at the origin and each ligand ($L$) center is located at equal distances along the axes. $L$ may be an ion like $F^-$ or $CN^-$, or even a molecule like $H_2O$ if the reduction in symmetry is taken care of.

### Molecular-Orbital Basis

Molecular orbitals (MO's-$\phi$'s) will be constructed as linear combinations of symmetry-adapted orbitals ($\lambda$'s), which are combinations of

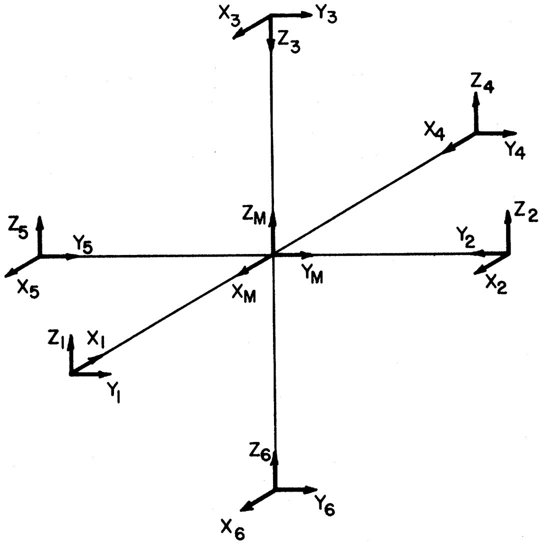

FIG. 1. Definition of coordinate system.

TABLE I. Symmetry-adapted orbitals.

| $\Gamma$ | $\gamma$ | Metal-centered | Ligand-centered[a, b] |
|---|---|---|---|
| $a_{1g}$ | | $ns$ | $6^{-1/2}N(\sigma a_{1g})\ [\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6]$ |
| $t_{1u}$ | $x$ | $np_x$ | $2^{-1/2}N(\sigma t_{1u})\ [\sigma_1-\sigma_4]$<br>$\frac{1}{2}N(\pi t_{1u})\ [x_2+x_3+x_5+x_6]$ |
| | $y$ | $np_y$ | $2^{-1/2}N(\sigma t_{1u})\ [\sigma_2-\sigma_5]$<br>$\frac{1}{2}N(\pi t_{1u})\ [y_1+y_3+y_4+y_6]$ |
| | $z$ | $np_z$ | $2^{-1/2}N(\sigma t_{1u})\ [\sigma_3-\sigma_6]$<br>$\frac{1}{2}N(\pi t_{1u})\ [z_1+z_2+z_4+z_5]$ |
| $e_g$ | $\theta$ | $nd_{z^2}$ | $12^{-1/2}N(\sigma e_g)\ [-\sigma_1-\sigma_2+2\sigma_3-\sigma_4-\sigma_5+2\sigma_6]$ |
| | $\epsilon$ | $nd_{x^2-y^2}$ | $\frac{1}{2}N(\sigma e_g)\ [\sigma_1-\sigma_2+\sigma_4-\sigma_5]$ |
| $t_{2g}$ | $\xi$ | $nd_{yz}$ | $\frac{1}{2}N(\pi t_{2g})\ [z_2+y_3-z_5-y_6]$ |
| | $\eta$ | $nd_{xz}$ | $\frac{1}{2}N(\pi t_{2g})\ [z_1+x_3-z_4-x_6]$ |
| | $\zeta$ | $nd_{xy}$ | $\frac{1}{2}N(\pi t_{2g})\ [y_1+x_2-y_4-x_5]$ |
| $t_{1g}$ | $x$ | $yz(y^2-z^2)$ | $\frac{1}{2}N(\pi t_{1g})\ [z_2-y_3-z_5+y_6]$ |
| | $y$ | $zx(z^2-x^2)$ | $\frac{1}{2}N(\pi t_{1g})\ [-z_1+x_3+z_4-x_6]$ |
| | $z$ | $xy(x^2-y^2)$ | $\frac{1}{2}N(\pi t_{1g})\ [y_1-x_2-y_4+x_5]$ |
| $t_{2u}$ | $\xi$ | $x(y^2-z^2)$ | $\frac{1}{2}N(\pi t_{2u})\ [x_2-x_3+x_5-x_6]$ |
| | $\eta$ | $y(z^2-x^2)$ | $\frac{1}{2}N(\pi t_{2u})\ [-y_1+y_3-y_4+y_6]$ |
| | $\zeta$ | $z(x^2-y^2)$ | $\frac{1}{2}N(\pi t_{2u})\ [z_1-z_2+z_4-z_5]$ |

[a] $\sigma_i$ is any AO which is rotationally symmetric about the $M-L_i$ bond axis; $x_i$, $y_i$, $z_i$ refer to the Cartesian components of degenerate $\pi$-type AO's referred to the $M-L_i$ bond axis; see Fig. 1.

[b] $N(\sigma a_{1g})=(1+4\langle\sigma_1\mid\sigma_2\rangle+\langle\sigma_1\mid\sigma_4\rangle)^{-1/2}$, $N(\sigma t_{1u})=(1-\langle\sigma_1\mid\sigma_4\rangle)^{1/2}$, $N(\sigma e_g)=(1-2\langle\sigma_1\mid\sigma_2\rangle+\langle\sigma_1\mid\sigma_4\rangle)^{-1/2}$, $N(\pi t_{1u})=(1+2\langle z_1\mid z_2\rangle+\langle z_1\mid z_4\rangle)^{-1/2}$, $N(\pi t_{2g})=(1+2\langle y_1\mid x_2\rangle-\langle y_1\mid y_4\rangle)^{-1/2}$, $N(\pi t_{1g})=(1-2\langle y_1\mid x_2\rangle-\langle y_1\mid y_4\rangle)^{-1/2}$, $N(\pi t_{2u})=(1-2\langle z_1\mid z_2\rangle+\langle z_1\mid z_4\rangle)^{-1/2}$.

atomic (like) orbitals (AO's-$\psi$'s). These in turn may be linear combinations of real Slater-type orbitals (STO's-$\chi$'s) or Gaussian orbitals (GO's). The AO's may have parameters appropriate to free $M$ or $L$, or those parameters may be chosen by other criteria.

The $n$th AO (which is associated with a particular center in the system) is written in the form

$$\psi_n=\sum_m \chi_m d_{mn}\ , \tag{1}$$

with the STO or GO set $\chi_m$ and coefficient set $d_{mn}$ completely specified from the outset. The set $\psi_n$ is normal but not necessarily completely orthogonal. To take advantage of symmetry, the $\psi_n$ set is transformed into the corresponding set of normalized symmetry-adapted orbitals $\lambda_{k\Gamma\gamma}$ belonging to the subspecies $\gamma$ of the irreducible representation $\Gamma$:

$$\lambda_{k\Gamma\gamma}=N_{k\Gamma\gamma}\sum_n \psi_n\, p_{nk\Gamma\gamma}\ , \tag{2}$$

with the constants $p_{nk\Gamma\gamma}$ such that

$$\mathcal{O}(\Gamma\gamma)\lambda_{k\Gamma\gamma}=\lambda_{k\Gamma\gamma}\ , \tag{3}$$

where $\mathcal{O}(\Gamma\gamma)$ is the projection operator belonging to $\Gamma\gamma$ and $N_{\Gamma\gamma k}$ is the normalization factor required to make

$$\int(\lambda_{k\Gamma\gamma})^2\,dv=1\ . \tag{4}$$

The familiar functional form of pertinent $\lambda$'s is given in Table I.

Each MO is approximated by a linear combination of symmetry-adapted orbitals and thus transforms according to the irreducible representations of $\mathcal{O}_h$:

$$\phi_{i\Gamma\gamma}=\sum_k \lambda_{k\Gamma\gamma}C_{ki\Gamma}\ . \tag{5}$$

In most, but not all, succeeding applications, "perfect pairing" is assumed; namely, two electrons, formally occupying the same MO, are assigned to two molecular-spin orbitals differing *only* in spin factors. A collection of all MO's having identical $i\Gamma$ values is called a shell.[13] If all MO's of a shell are formally doubly occupied, the shell is termed closed; a partially occupied shell is termed open.

The variational coefficients $C_{ki\Gamma}$ are thus defined to be independent of $\gamma$. Each MO will occur multiplied by a spin function ($\alpha$ or $\beta$) to form a molecular-spin orbital.

### Electronic Configurations and States

For the cluster $M^{+z}L_6$, with $A$ being the atomic number of $M$ belonging to the first transition series and $L$ being a first-row ion, there are $A-z+6\times 10$ electrons to be accommodated in MO's. One may assume that the 11 lowest-energy MO's will be essentially undisturbed free-ion inner-shell AO's of $M$ and $L$. The valence MO's, which may be (though not necessarily) approximated by linear combinations only of the $3d$, $4s$, $4p$, and ligand-centered orbitals of Table I, will be given appropriate group-theoretic symbols and assigned a principal quantum number. Thus the $(60+A-z)$-electron configurations of principal interest are

$$\{(1s_M)^2(2s_M)^2(2p_M)^6(1s_{L1})^2(1s_{L2})^2(1s_{L3})^2$$

$$(1s_{L4})^2(1s_{L5})^2(1s_{L6})^2(3s_M)^2(3p_M)^6\}$$

$$\{(1a_{1g})^2(1e_g)^4(1t_{1u})^6\}\{(2a_{1g})^2(2t_{1u})^6(2e_g)^4\}$$

$$\{(3t_{1u})^6(1t_{2g})^6\}\{(1t_{1g})^6(1t_{2u})^6\}\{(2t_{2g})^x(3e_g)^y\}\ .$$

Braces have been introduced to indicate groups of MO's having similar bonding character: The first group contains localized inner-shell, or core, AO's; the second contains MO's largely $2s_L$ in character; the third group is largely $2p\sigma_L$ in character; the fourth is $M$-$L$ $\pi$ bonding; the fifth is nonbonding ligand $2p\pi$; and the sixth contains $x+y=A-z$ electrons in antibonding MO's which are largely $3d$ in character and which give rise to most of the chemical and physical properties of interest.

For a given state of a given configuration let $\Phi$ be the total electronic wave function in the MO approximation. $\Phi$ will be an antisymmetrized product (Slater determinant) of all the occupied molecular-spin orbitals, or a linear combination of such determinants.

For each assignment of the $x+y$ electrons to the $2t_{2g}$ and $3e_g$ MO's there will generally be several states, as documented by Griffith,[14] for example. Each (many-electron) state is further classified according to its total spin- and space-symmetry properties. Thus it may, in most cases, be identified by giving values for $x$ and $y$ for the total spin ($S$) and its projection ($M_S$) and indicating the irreducible representation ($\Gamma$) and subspecies ($\gamma$) according to which it transforms. In a few cases ambiguities remain, and for those it is necessary to specify also $S$, $M_S$, $\Gamma$, and $M_\Gamma$ for the $(2t_{2g})^x$ and $(3e_g)^y$ portions of the configuration.

For the above-described configurations, the precise functional form of $\Phi$ can be obtained simply by appending the product of all the closed-shell molecular-spin orbitals to the $(2t_{2g})^x(3e_g)^y$ wave functions given in, or derivable from, the tables in Ref. 14, for example, and completing the antisymmetrization.

### Total Energy

We shall employ a nonrelativistic Hamiltonian operator and assume fixed internuclear distances. Thus, in atomic units,

$$\mathcal{H}=\sum_{\mu}\left(-\tfrac{1}{2}\nabla_{\mu}^{2}+\sum_{a}\frac{Z_a}{r_{a\mu}}+V_{\mathrm{ext}}(\mu)\right)+\sum_{\mu>\nu}\frac{1}{r_{\mu\nu}}+\sum_{a>b}\frac{Z_aZ_b}{R_{ab}}\ . \tag{6}$$

$V_{\mathrm{ext}}(\mu)$ is a one-particle approximation to contributions to the electronic energy which arise from the environment of the complex and here presumably has at least full cubic symmetry. Here $\mu, \nu$ index the electrons and $a, b$ the nuclei; $Z_a$ is the charge of nucleus $a$. Using the Hamiltonian of Eq. (6), the total energy of the state described by $\Phi$ is independent of $M_S$ and

$$E=\langle\Phi|\mathcal{H}|\Phi\rangle\ . \tag{7}$$

By standard methods, Eq. (7) reduces to

$$E-V_{\mathrm{nuc}}=2\sum_{i\Gamma\gamma}^{c}H(i\Gamma\gamma)+\tfrac{1}{2}\sum_{i\Gamma\gamma}^{c}\sum_{i'\Gamma'\gamma'}^{c}[2J(i\Gamma\gamma,i'\Gamma'\gamma')-K(i\Gamma\gamma,i'\Gamma'\gamma')]$$
$$+\sum_{i\Gamma\gamma}^{c}[2xJ(i\Gamma\gamma,2t_{2g})-xK(i\Gamma\gamma,2t_{2g})+2yJ(i\Gamma\gamma,3e_g)-yK(i\Gamma\gamma,3e_g)]+G(x,y;S\Gamma)\ . \tag{8}$$

The superscript $c$ limits the summation over $i\Gamma$ to orbitals associated with closed shells. The various terms in Eq. (8) are defined as follows:

$$V_{\mathrm{nuc}}=\sum_{a>b}\frac{Z_aZ_b}{R_{ab}}\ . \tag{9}$$

The "one-electron" energy

$$H(i\Gamma\gamma)=\langle\phi_{i\Gamma\gamma}(\mu)|-\tfrac{1}{2}\nabla_{\mu}^{2}+\sum_{a}\frac{Z_a}{r_{a\mu}}+V_{\mathrm{ext}}(\mu)|\phi_{i\Gamma\gamma}(\mu)\rangle \tag{10}$$

is independent of $\gamma$. The Coulombic interaction (or "direct") integral is

$$J(i\Gamma\gamma,i'\Gamma'\gamma')=(\phi_{i\Gamma\gamma}{}^{2}|\phi_{i'\Gamma'\gamma'}{}^{2})$$
$$=\int\int\phi_{i\Gamma\gamma}{}^{2}(1)\,(1/r_{12})\,\phi_{i\Gamma\gamma}{}^{2}(2)\,dv_1\,dv_2\ . \tag{11}$$

The exchange integral is

$$K(i\Gamma\gamma,i'\Gamma'\gamma')=(\phi_{i\Gamma\gamma}\phi_{i'\Gamma'\gamma'}|\phi_{i\Gamma\gamma}\phi_{i'\Gamma'\gamma'})$$

$$=\iint \phi_{i\Gamma\gamma}(1)\,\phi_{i'\Gamma'\gamma'}(1)\,(1/r_{12})\,\phi_{i\Gamma\gamma}(2)\times\phi_{i'\Gamma'\gamma'}(2)\,dv_1 dv_2\,. \qquad (12)$$

The last term, $G(x,y;S\Gamma)$, includes all electrostatic interactions among open-shell electrons and will be considered later.

Some economies result from defining two-electron integrals averaged over the subspecies of the $d_\Gamma$-fold degenerate shells according to

$$\bar{I}(i\Gamma,i'\Gamma')=(1/d_\Gamma)\textstyle\sum_\gamma I(i\Gamma\gamma,i'\Gamma'\gamma')\quad\text{for } I=J,K\,. \qquad (13)$$

Also let

$$P=J-\tfrac{1}{2}K\,,\quad \bar{P}=\bar{J}-\tfrac{1}{2}\bar{K}. \qquad (14)$$

Now Eq. (8) may be written

$$E-V_{\text{nuc}}=2\sum_{i\Gamma}^{c}d_\Gamma H(i\Gamma)+\frac{1}{2}\sum_{i\Gamma}^{c}\sum_{i'\Gamma'}^{c}d_\Gamma d_{\Gamma'}\bar{P}(i\Gamma,i'\Gamma')+xH(2t_{2g})+yH(3e_g)+2\sum_{i\Gamma}^{c}[xd_\Gamma\bar{P}(i\Gamma,2t_{2g})+yd_\Gamma\bar{P}(i\Gamma,3e_g)]+G(x,y;S\Gamma)\,. \qquad (15)$$

Note that here the sums include *only one* member of a degenerate closed-shell set of orbitals.

$G(x,y;S\Gamma)$ includes the Coulombic and exchange interactions among the electrons of $2t_{2g}$ and $3e_g$ as determined by the particular state of the indicated configuration. For all cases in which these two MO's are radially identical *d atomic* orbitals, expressions for $G$ have been tabulated by many authors in terms of the Slater-Condon integrals $F_0$, $F_2$, and $F_4$ or Racah parameters $A$, $B$, and $C$. For more general orbitals it has been shown by Griffith that nine independent integrals are required.[14] (A tenth occurs only in configuration-interaction calculations.)

We have chosen to use a different independent set of integrals, namely, $\bar{J}(tt)$, $\bar{K}(tt)$, $\bar{J}(et)$, $\bar{K}(et)$, $\bar{J}(ee)$, $\bar{K}(ee)$, $K(t\xi,t\zeta)$, $J(t\zeta,e\epsilon)$, and $K(t\zeta,e\epsilon)$. Here, and wherever else it is clear from context, the symbols $t$ and $e$ will indicate the $2t_{2g}$ and $3e_g$ MO's, respectively. In Table II, the relationship of our $(e-t)$ integrals to Griffith's and Racah's parameters is given. Now define

$$G(x,y;S\Gamma)=\alpha_1\bar{J}(tt)+\beta_1\bar{K}(tt)+\gamma_1K(tt)+\alpha_2\bar{J}(et)+\beta_2\bar{K}(et)+\gamma_2J(et)+\delta_2K(et)+\alpha_3\bar{J}(ee)+\beta_3\bar{K}(ee)\,. \qquad (16a)$$

We have derived appropriate coefficients for all states of the $t_{2g}^x\,e_g^y$ configurations. They are given in Table III. Note that when $x+y\geq 5$

$$G(x,y;S\Gamma)=G(6-x,4-y;S\Gamma)+6(x-3)\bar{P}(tt)+(4x+6y-24)\bar{P}(et)+4(y-2)\bar{P}(ee)\,. \qquad (16b)$$

All the integrals in Eq. (15) depend upon the MO variational coefficients $C_{ki\Gamma}$ and integrals over the preselected basis functions $\lambda_{k\Gamma\gamma}$. If the expression for each $\lambda_{k\Gamma\gamma}$ is inserted into Eq. (15), then that equation may be restated in the following matrix form, which is useful in formulating actual computational procedures:

$$E-V_{\text{nuc}}=\underline{\text{HD}}_t^\dagger-\tfrac{1}{2}\underline{\text{D}}_t\,\mathcal{P}\underline{\text{D}}_t^\dagger-\tfrac{1}{2}\underline{\text{D}}_o\,\mathcal{Q}\underline{\text{D}}_o^\dagger\,. \qquad (17)$$

TABLE II. Independent integrals in $t_{2g}$-$e_g$ interactions.

| Present work[a] | Griffith | Racah |
|---|---|---|
| $\bar{J}(tt)\equiv\frac{1}{3}[\langle\xi\xi\mid\xi\xi\rangle+\langle\xi\xi\mid\eta\eta\rangle+\langle\xi\xi\mid\zeta\zeta\rangle]$ | $\frac{1}{3}(a+2b)$ | $A+\dfrac{5C}{3}$ |
| $\bar{K}(tt)\equiv\frac{1}{3}[\langle\xi\xi\mid\xi\xi\rangle+\langle\xi\eta\mid\eta\xi\rangle+\langle\xi\zeta\mid\zeta\xi\rangle]$ | $\frac{1}{3}(a+2j)$ | $\frac{1}{3}A+\dfrac{10B}{3}+\dfrac{5C}{3}$ |
| $K(t\zeta,t\zeta)\equiv\langle\xi\eta\mid\eta\xi\rangle$ | $j$ | $3B+C$ |
| $\bar{J}(et)\equiv\frac{1}{2}[\langle\xi\xi\mid\epsilon\epsilon\rangle+\langle\xi\xi\mid\theta\theta\rangle]$ | $d+c/\sqrt{3}$ | $A+C$ |
| $\bar{K}(et)\equiv\frac{1}{2}[\langle\xi\epsilon\mid\epsilon\xi\rangle+\langle\xi\theta\mid\theta\xi\rangle]$ | $g+h/\sqrt{3}$ | $2B+C$ |
| $J(e\theta,t\zeta)\equiv\langle\theta\theta\mid\zeta\zeta\rangle$ | $d-c/\sqrt{3}$ | $A-4B+C$ |
| $K(e\theta,t\zeta)\equiv\langle\theta\zeta\mid\zeta\theta\rangle$ | $g+\sqrt{3}\,h$ | $4B+C$ |
| $\bar{J}(ee)\equiv\frac{1}{2}[\langle\theta\theta\mid\theta\theta\rangle+\langle\theta\theta\mid\epsilon\epsilon\rangle]$ | $e-f$ | $A+2C$ |
| $\bar{K}(ee)\equiv\frac{1}{2}[\langle\theta\theta\mid\theta\theta\rangle+\langle\theta\epsilon\mid\epsilon\theta\rangle]$ | $\frac{1}{2}(e+f)/2$ | $\frac{1}{2}A+4B+2C$ |
| $i\equiv\langle\theta\xi\mid\eta\zeta\rangle$ | $i$ | $B\sqrt{3}$ |

[a] $\langle uv\mid wz\rangle\equiv\iint u(1)\,v(1)\,(1/r_{12})\,w(2)\,z(2)\,dv_1\,dv_2$.

TABLE III. Cubic-field electrostatic matrix elements $G(x,y;\ S\Gamma)$,[a,b] $G(x,y;S\Gamma)=\alpha_1\bar{J}(tt)+\beta_1\bar{K}(tt)+\gamma_1 K(t\zeta,t\zeta)+\alpha_2\bar{J}(et)+\beta_2\bar{K}(et)+\gamma_2 J(e\theta,t\zeta)+\delta_2 K(e\theta,t\zeta)+\alpha_3\bar{J}(ee)+\beta_3\bar{K}(ee)$.

| Configuration | Term | $\alpha_1$ | $\beta_1$ | $\gamma_1$ | $\alpha_2$ | $\beta_2$ | $\gamma_2$ | $\delta_2$ | $\alpha_3$ | $\beta_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $t$ | ${}^2T_2$ | 0 | 0 | | | | | | | |
| $e$ | ${}^2E$ | | | | | | | | 0 | 0 |
| $t^2$ | ${}^3T_1$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | | | | | | |
| | ${}^1T_2$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 2 | | | | | | |
| | ${}^1E$ | 0 | 3 | $-3$ | | | | | | |
| | ${}^1A_1$ | 0 | 3 | 0 | | | | | | |
| $te$ | ${}^3T_1$ | | | | 2 | $-2$ | $-1$ | 1 | | |
| | ${}^3T_2$ | | | | 0 | 0 | 1 | $-1$ | | |
| | ${}^1T_1$ | | | | 2 | 2 | $-1$ | $-1$ | | |
| | ${}^1T_2$ | | | | 0 | 0 | 1 | 1 | | |
| $e^2$ | ${}^3A_2$ | | | | | | | | 2 | $-2$ |
| | ${}^1A_1$ | | | | | | | | 0 | 2 |
| | ${}^1E$ | | | | | | | | 1 | 0 |
| $t^3$ | ${}^4A_2$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 0 | | | | | | |
| | ${}^2E$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | | | | | | |
| | ${}^2T_1$ | 3 | 0 | $-2$ | | | | | | |
| | ${}^2T_2$ | 3 | 0 | 0 | | | | | | |
| $t^2e$ | $({}^3T_1\times{}^2E)\ {}^4T_1$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | 3 | $-3$ | $-1$ | $+1$ | | |
| | ${}^4T_2$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | 1 | $-1$ | 1 | $-1$ | | |
| | ${}^2T_2$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | 1 | $\frac{1}{2}$ | 1 | $\frac{1}{2}$ | | |
| | ${}^2T_1$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | 3 | $\frac{3}{2}$ | $-1$ | $-\frac{1}{2}$ | | |
| | $({}^1T_2\times{}^2E)\ {}^2T_2$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 2 | 3 | $-\frac{3}{2}$ | $-1$ | $\frac{1}{2}$ | | |
| | ${}^2T_1$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 2 | 1 | $-\frac{1}{2}$ | 1 | $-\frac{1}{2}$ | | |
| | $({}^1E\times{}^2E)\ {}^2A_2$ | 0 | 3 | $-3$ | 4 | $-2$ | $-2$ | 1 | | |
| | ${}^2A_1$ | 0 | 3 | $-3$ | 0 | 0 | 2 | $-1$ | | |
| $t^2e$ | $({}^1A_1\times{}^2E)\ {}^2E$ | 0 | 3 | 0 | 2 | $-1$ | 0 | 0 | | |
| | $({}^1E\times{}^2E)\ {}^2E$ | 0 | 3 | $-3$ | 2 | $-1$ | 0 | 0 | | |
| $te^2$ | $({}^2T_2\times{}^3A_2){}^4T_1$ | | | | 2 | $-2$ | 0 | 0 | 2 | $-2$ |
| | $({}^2T_2\times{}^1E)\ {}^2T_1$ | | | | 2 | $-1$ | 0 | 0 | 1 | 0 |
| | ${}^2T_2$ | | | | 2 | $-1$ | 0 | 0 | 1 | 0 |
| | $({}^2T_2\times{}^1A_1){}^2T_2$ | | | | 2 | $-1$ | 0 | 0 | 0 | 2 |
| | $({}^2T_2\times{}^3A_2){}^2T_1$ | | | | 2 | 1 | 0 | 0 | 2 | $-2$ |
| $e^3$ | ${}^2E$ | | | | | | | | 4 | $-2$ |
| $t^4$ | ${}^3T_1$ | $\frac{15}{2}$ | $-\frac{9}{2}$ | 0 | | | | | | |
| | ${}^1A_1$ | 6 | 0 | 0 | | | | | | |
| | ${}^1T_2$ | $\frac{15}{2}$ | $-\frac{9}{2}$ | 2 | | | | | | |
| | ${}^1E$ | 6 | 0 | $-3$ | | | | | | |

TABLE III. *(Continued)*

| Configuration | Term | $\alpha_1$ | $\beta_1$ | $\gamma_1$ | $\alpha_2$ | $\beta_2$ | $\gamma_2$ | $\delta_2$ | $\alpha_3$ | $\beta_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $t^3e$ | $(^4A_1\times{}^2E)^5E$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 0 | 3 | −3 | 0 | 0 | | |
| | $(^2E\times{}^2E)\ {}^3A_1$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 3 | −1 | 0 | −1 | | |
| | $^3A_2$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 3 | −3 | 0 | 1 | | |
| | $^3E$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 3 | −2 | 0 | 0 | | |
| | $(^4A_1\times{}^2E)\ {}^3E$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 0 | 3 | 1 | 0 | 0 | | |
| | $(^2T_1\times{}^2E)\ {}^3T_1$ | 3 | 0 | −2 | 3 | $-\frac{3}{2}$ | 0 | $-\frac{1}{2}$ | | |
| | $^3T_2$ | 3 | 0 | −2 | 3 | $-\frac{5}{2}$ | 0 | $\frac{1}{2}$ | | |
| | $^1T_1$ | 3 | 0 | −2 | 3 | $-\frac{3}{2}$ | 0 | $\frac{3}{2}$ | | |
| | $^1T_2$ | 3 | 0 | −2 | 3 | $\frac{3}{2}$ | 0 | $-\frac{3}{2}$ | | |
| | $(^2T_2\times{}^2E)\ {}^3T_2$ | 3 | 0 | 0 | 3 | $-\frac{3}{2}$ | 0 | $-\frac{1}{2}$ | | |
| | $^3T_1$ | 3 | 0 | 0 | 3 | $-\frac{5}{2}$ | 0 | $\frac{1}{2}$ | | |
| | $^1T_2$ | 3 | 0 | 0 | 3 | $-\frac{3}{2}$ | 0 | $\frac{3}{2}$ | | |
| | $^1T_1$ | 3 | 0 | 0 | 3 | $\frac{3}{2}$ | 0 | $-\frac{3}{2}$ | | |
| | $(^2E\times{}^2E)\ {}^1A_1$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 3 | −3 | 0 | 3 | | |
| | $^1A_2$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 3 | 3 | 0 | −3 | | |
| | $^1E$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 3 | 0 | 0 | 0 | | |
| $t^2e^2$ | $(^3T_1\times{}^3A_2)^5T_2$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | 4 | −4 | 0 | 0 | 2 | −2 |
| | $(^1A_1\times{}^3A_2)^3A_2$ | 0 | 3 | 0 | 4 | −2 | 0 | 0 | 2 | −2 |
| | $(^1E\times A_2)^3E$ | 0 | 3 | −3 | 4 | −2 | 0 | 0 | 2 | −2 |
| | $(^3T_1\times{}^1E)^3T_1$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | 4 | −2 | 0 | 0 | 1 | 0 |
| | $^3T_2$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | 4 | −2 | 0 | 0 | 1 | 0 |
| | $(^3T_1\times{}^1A_1)^3T_1$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | 4 | −2 | 0 | 0 | 0 | 2 |
| | $(^1T_2\times{}^3A_2)^3T_1$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 2 | 4 | −2 | 0 | 0 | 2 | −2 |
| | $(^3T_2\times{}^3A_2)^3T_2$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | 4 | 0 | 0 | 0 | 2 | −2 |
| | $(^1A_1\times{}^1A_1)^1A_1$ | 0 | 3 | 0 | 4 | −2 | 0 | 0 | 0 | 2 |
| | $(^1E\times{}^1E)^1A_1$ | 0 | 3 | −3 | 4 | −2 | 0 | 0 | 1 | 0 |
| | $(^1T_2\times{}^1E)^1T_1$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 2 | 4 | −2 | 0 | 0 | 1 | 0 |
| | $(^3T_1\times{}^3A_2)^1T_2$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 0 | 4 | 2 | 0 | 0 | 2 | −2 |
| | $(^1T_2\times{}^1E)^1T_2$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 2 | 4 | −2 | 0 | 0 | 1 | 0 |
| | $(^1T_2\times{}^1A_1)^1T_2$ | $\frac{3}{2}$ | $-\frac{3}{2}$ | 2 | 4 | −2 | 0 | 0 | 0 | 2 |
| | $(^1E\times{}^1E)^1E$ | 0 | 3 | −3 | 4 | −2 | 0 | 0 | 1 | 0 |
| | $^1A_2$ | 0 | 3 | −3 | 4 | −2 | 0 | 0 | 1 | 0 |
| | $(^1E\times{}^1A_1)^1E$ | 0 | 3 | −3 | 4 | −2 | 0 | 0 | 0 | 2 |
| | $(^1A_1\times{}^1E)^1E$ | 0 | 3 | 0 | 4 | −2 | 0 | 0 | 1 | 0 |
| $te^3$ | $(^2T_2\times{}^2E)^3T_2$ | | | | 4 | −2 | −1 | 0 | 4 | −2 |
| | $^3T_1$ | | | | 2 | −2 | 1 | 0 | 4 | −2 |
| | $^1T_2$ | | | | 4 | −2 | −1 | 2 | 4 | −2 |
| | $^1T_1$ | | | | 2 | 2 | 1 | −2 | 4 | −2 |
| $e^4$ | $^1A_1$ | | | | | | | | 8 | −4 |
| $t^5$ | $^2T_2$ | 12 | −6 | | | | | | | |

TABLE III. (*Continued*)

| Configuration | Term | $\alpha_1$ | $\beta_1$ | $\gamma_1$ | $\alpha_2$ | $\beta_2$ | $\gamma_2$ | $\delta_2$ | $\alpha_3$ | $\beta_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $t^4e$ | $(^3T_1\times{}^2E)^4T_1$ | $\frac{15}{2}$ | $-\frac{9}{2}$ | 0 | 3 | $-3$ | 1 | 0 | | |
| | $^4T_2$ | $\frac{15}{2}$ | $-\frac{9}{2}$ | 0 | 5 | $-3$ | $-1$ | 0 | | |
| | $^2T_1$ | $\frac{15}{2}$ | $-\frac{9}{2}$ | 0 | 3 | $\frac{3}{2}$ | 1 | $-\frac{3}{2}$ | | |
| | $^2T_2$ | $\frac{15}{2}$ | $-\frac{9}{2}$ | 0 | 5 | $-\frac{3}{2}$ | $-1$ | $\frac{3}{2}$ | | |
| | $(^1T_1\times{}^2E)^2T_1$ | $\frac{15}{2}$ | $-\frac{9}{2}$ | 2 | 5 | $-\frac{5}{2}$ | $-1$ | $\frac{1}{2}$ | | |
| | $^2T_2$ | $\frac{15}{2}$ | $-\frac{9}{2}$ | 2 | 3 | $-\frac{3}{2}$ | 1 | $-\frac{1}{2}$ | | |
| | $(^1E\times{}^2E)^2A_1$ | 6 | 0 | $-3$ | 6 | $-3$ | $-2$ | 1 | | |
| | $^2A_2$ | 6 | 0 | $-3$ | 2 | $-1$ | 2 | $-1$ | | |
| | $^2E$ | 6 | 0 | $-3$ | 4 | $-2$ | 0 | 0 | | |
| | $(^1A_1\times{}^2E)^2E$ | 6 | 0 | 0 | 4 | $-2$ | 0 | 0 | | |
| $t^3e^2$ | $(^4A_2\times{}^3A_2)^6A_1$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 0 | 6 | $-6$ | 0 | 0 | 2 | $-2$ |
| | $(^2T_2\times{}^3A_2)^4T_1$ | 3 | 0 | 0 | 6 | $-4$ | 0 | 0 | 2 | $-2$ |
| | $(^2T_1\times{}^3A_2)^4T_2$ | 3 | 0 | $-2$ | 6 | $-4$ | 0 | 0 | 2 | $-2$ |
| | $(^2E\times{}^3A_2)^4E$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 6 | $-4$ | 0 | 0 | 2 | $-2$ |
| | $(^4A_2\times{}^1E)^4E$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 0 | 6 | $-3$ | 0 | 0 | 1 | 0 |
| | $(^4A_2\times{}^1A_1)^4A_2$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 0 | 6 | $-3$ | 0 | 0 | 0 | 2 |
| | $(^4A_2\times{}^3A_2)^4A_1$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 0 | 6 | $-1$ | 0 | 0 | 2 | $-2$ |
| | $(^4A_2\times{}^3A_2)^2A_1$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 0 | 6 | 2 | 0 | 0 | 2 | $-2$ |
| | $(^2E\times{}^1E)^2A_1$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 6 | $-3$ | 0 | 0 | 1 | 0 |
| | $^2A_2$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 6 | $-3$ | 0 | 0 | 1 | 0 |
| | $^2E$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 6 | $-3$ | 0 | 0 | 1 | 0 |
| | $(^2E\times{}^1A_1)^2E$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 6 | $-3$ | 0 | 0 | 0 | 2 |
| | $(^2E\times{}^1E)^2E$ | $\frac{9}{2}$ | $-\frac{9}{2}$ | 3 | 6 | $-1$ | 0 | $-2$ | 1 | 0 |
| | $(^2T_1\times{}^1A_1)^2T_1$ | 3 | 0 | $-2$ | 6 | $-3$ | 0 | 0 | 0 | 2 |
| | $(^2T_1\times{}^1E)^2T_1$ | 3 | 0 | $-2$ | 6 | $-3$ | 0 | 0 | 1 | 0 |
| | $^2T_2$ | 3 | 0 | $-2$ | 6 | $-3$ | 0 | 0 | 1 | 0 |
| | $(^2T_1\times{}^3A_2)^2T_2$ | 3 | 0 | $-2$ | 6 | $-1$ | 0 | 0 | 2 | $-2$ |
| | $(^2T_2\times{}^1A_1)^2T_2$ | 3 | 0 | 0 | 6 | $-3$ | 0 | 0 | 0 | 2 |
| | $(^2T_1\times{}^1E)^2T_2$ | 3 | 0 | 0 | 6 | $-3$ | 0 | 0 | 1 | 0 |
| | $^2T_1$ | 3 | 0 | 0 | 6 | $-3$ | 0 | 0 | 1 | 0 |
| | $(^2T_2\times{}^3A_2)^2T_1$ | 3 | 0 | 0 | 6 | $-1$ | 0 | 0 | 2 | $-2$ |

[a] For $x+y\geq 5$, $G[x,\ y;\ S,\ \Gamma]=G[6-x,\ 4-y;\ S,\ \Gamma]+6(x-3)\bar{P}(tt)+(4x+6y-24)\bar{P}(et)+4(y-2)\bar{P}(ee)$.

[b] All missing entries are zero.

The matrices in Eq. (16) are defined in the following equations.[12] (a) Density matrices: First let

$$D(i\Gamma;k,l)=C_{ki\Gamma}C_{li\Gamma}(2-\delta_{kl})\ . \tag{18}$$

Then we have

$$D_c(\Gamma;k,l)=2\textstyle\sum_i^c d_\Gamma D(i\Gamma;k,l)\ , \tag{19a}$$

$$D_o(\Gamma;k,l)=n(i\Gamma)\,D(i\Gamma;kl)\ , \tag{19b}$$

where $n(i\Gamma)$ is the number of electrons in the open shell $i\Gamma$. The row matrices (vectors) for $\underline{D}=\underline{D}_c$ or $\underline{D}_o$ $(k\geq l)$

$$\underline{D}(\Gamma)=\|D(\Gamma;11),\ D(\Gamma;21),\ D(\Gamma;22)\cdots D(\Gamma;kl)\cdots\| \tag{20}$$

are inserted into the complete density vectors

$$\underline{D}_c = \| \underline{D}_c(a_{1g}),\ \underline{D}_c(t_{1u}),\ \underline{D}_c(e_g),\ \underline{D}_c(t_{2g}),\ \underline{D}_c(t_{1g}),\ \underline{D}_c(t_{2u}) \| , \tag{21a}$$

$$\underline{D}_o = \| \underline{0}\ ,\ \underline{0}\ ,\ \underline{D}_o(e_g),\ \underline{D}_o(t_{2g}),\ \underline{0}\ ,\ \underline{0}\ \| , \tag{21b}$$

wherein the ordering over $\Gamma$ (arbitrarily) follows that in Table I. Then we have

$$\underline{D}_t = \underline{D}_c + \underline{D}_o \ .$$

For the cases specifically considered, $n(2t_{2g}) = x$ and $n(3e_g) = y$; for other open-shell configurations there will be different $n(i\Gamma)$ and different contributions to $\underline{D}_o$. (b) The one-electron matrix $\underline{H}$ is set up in form identical to $\underline{D}_c$, merely by replacing the elements $D(i\Gamma; k, l)$ by

$$H(\Gamma; k, l) = \langle \lambda_{k\Gamma\gamma}(\mu) | -\tfrac{1}{2}\nabla_\mu^2 + \textstyle\sum_a Z_a/r_{a\mu} + V_{\text{ext}}(\mu) | \lambda_{l\Gamma\gamma}(\mu) \rangle \ . \tag{22}$$

(c) Two-electron matrices: With the elements of $\underline{D}_t$ and $\underline{D}_o$ indexed by the triplet $(\Gamma; k, l)$, $\mathcal{P}$ and $\mathcal{Q}$ must be symmetric square (super-) matrices[12] correspondingly indexed. A typical element of $\mathcal{P}$ is

$$\begin{aligned}\mathcal{P}(\Gamma; k, l \,|\, \Gamma'; k', l') = {} & (\lambda_{k\Gamma\gamma}\lambda_{l\Gamma\gamma} \,|\, \lambda_{k'\Gamma'\gamma'}\lambda_{l'\Gamma'\gamma'})_{\text{av}} \\ & - \tfrac{1}{4}(\lambda_{k\Gamma\gamma}\lambda_{k'\Gamma'\gamma'} \,|\, \lambda_{l\Gamma\gamma}\lambda_{l'\Gamma'\gamma'})_{\text{av}} \\ & - \tfrac{1}{4}(\lambda_{k\Gamma\gamma}\lambda_{l'\Gamma'\gamma'} \,|\, \lambda_{k'\Gamma'\gamma'}\lambda_{l\Gamma\gamma})_{\text{av}} \ ,\end{aligned} \tag{23}$$

where the subscript av indicates averaging over $\gamma$ or $\gamma'$ as in Eq. (13). The elements of $\mathcal{Q}$ are defined so that, for the specific cases at hand,

$$\tfrac{1}{2}\underline{D}_o \mathcal{Q} \underline{D}_o^\dagger = \tfrac{1}{2}\underline{D}_o \mathcal{P} \underline{D}_o^\dagger - G(x, y; S\Gamma) \ . \tag{24}$$

Suppressing the $k, l$ indices for clarity and letting $\mathcal{G}(t|t)$, $\mathcal{G}(e|t)$, and $\mathcal{G}(e|e)$ be supermatrix elements such that

$$\begin{aligned}\underline{D}_o(t)\,\mathcal{G}(e|t)\underline{D}_o(t)^\dagger + 2\underline{D}_o|(t)\,\mathcal{G}(e|t)\underline{D}_o(e)^\dagger & \\ + \underline{D}_o(e)\,\mathcal{G}(e|e)\underline{D}_o(e)^\dagger & = G(x, y; S\Gamma) \ ,\end{aligned}$$

then the nonzero elements of $\mathcal{Q}$ are of the form

$$\begin{aligned}\mathcal{Q}(t|t) &= \mathcal{P}(t|t) - (2/x^2)\,\mathcal{G}(t|t) \ , \\ \mathcal{Q}(e|t) &= \mathcal{P}(e|t) - (2/xy)\,\mathcal{G}(e|t) \ , \\ \mathcal{Q}(e|e) &= \mathcal{P}(e|e) - (2/y^2)\,\mathcal{G}(e|e) \ .\end{aligned} \tag{25}$$

Thus $\mathcal{Q}$ depends upon the particular state considered, as $G(x, y; S\Gamma)$ is drawn from data in Table III. $\mathcal{Q}$ is zero, except for elements arising from symmetry species ($\Gamma$'s) in which open shells occur.

## III. SCF EQUATIONS

Configurations containing only completely filled shells may be treated by the regular Hartree-Fock-Roothaan SCF procedure. Open-shell configurations, on the other hand, give rise to problems basically centering around the matter of maintaining orthogonality among all (completely or partially) occupied MO's upon solution of the SCF equations.

This problem has been discussed in general by Roothaan[15] and others[16] and in this application by Watson and Freeman,[3] Sugano and Tanabe,[5] and by Šimánek and Šroubek.[4] Physically, one might say that an electron in an open shell is subjected to a Hartree-Fock potential different from that which acts upon an electron in a closed shell. These different potentials produce different effective one-electron operators. The open-shell MO obtained from the latter operator is therefore not automatically orthogonal to the closed-shell MO's of the same symmetry species obtained from the former. This orthogonality constraint may be imposed through the addition of certain "coupling operators." Although more general formulations have been given,[17] the original one of Roothaan is sufficient here.

When the total energy given by Eqs. (15) or (17) is a minimum with respect to the variational coefficients $C_{ki\Gamma}$ such that all MO's remain mutually orthogonal, it is found that the optimum coefficients satisfy certain pseudoeigenvalue equations, namely, the open-shell Hartree-Fock-Roothaan equations. The coefficients of any closed-shell MO belonging to $\Gamma$ are contained in the matrix equation

$$[\underline{F}_c(\Gamma) + \underline{R}_o(\Gamma)]\underline{C}_c(\Gamma) = \underline{\epsilon}_c \underline{S}(\Gamma)\,\underline{C}_c(\Gamma) \ , \tag{26a}$$

and if an open-shell MO also belongs to $\Gamma$ its coefficients are contained in

$$[\underline{F}_o(\Gamma) + \underline{R}_c(\Gamma)]\underline{C}_o(\Gamma) = \underline{\epsilon}_o \underline{S}(\Gamma)\,\underline{C}_o(\Gamma) \ . \tag{26b}$$

In the present formulation, these equations are independent of the subspecies $\gamma$ of the given species $\Gamma$. There is one Eq. (26a) for each $\Gamma$ occurring in the molecular system and one Eq. (26b) for each $\Gamma$ associated with an open shell. Each factor in these equations is an $N_\Gamma \times N_\Gamma$ matrix, where $N_\Gamma$ is the number of variational functions chosen to approximate $\phi_{i\Gamma\gamma}$, according to Eq. (5). The factors are as follows:

(a) $\underline{C}_c(\Gamma)$ and $\underline{C}_o(\Gamma)$ are matrices of MO coefficients whose rows are indexed according to the basis functions $\lambda_{k\Gamma\gamma}$ and whose columns are indexed according to the MO's $\phi_{i\Gamma\gamma}$, arranged so that the coefficients for occupied MO's occur first (on the left). The remaining columns describe the "virtual" MO's. Only one of the columns of $\underline{C}_o(\Gamma)$ corresponds to the open shell; its identification will be discussed later.

(b) $\underline{S}(\Gamma)$ is the (symmetric) overlap matrix whose elements are

$$S_{kl}(\Gamma) = S_{lk}(\Gamma) = \langle \lambda_{k\Gamma\gamma} | \lambda_{l\Gamma\gamma} \rangle \ , \qquad (27)$$

independent of $\gamma$.

(c) $\underline{\epsilon}_c$ and $\underline{\epsilon}_o$ are diagonal matrices, an element of which, $\epsilon_c(i\Gamma)$ or $\epsilon_o(i\Gamma)$, is the orbital energy of the $d_\Gamma$-fold degenerate MO $\phi_{i\Gamma\gamma}$ described by the $i$th column of $\underline{C}_c(\Gamma)$ or $\underline{C}_o(\Gamma)$, respectively.

(d) $\underline{F}_c(\Gamma)$ and $\underline{F}_o(\Gamma)$ are the effective one-electron operator matrices for the closed- and open-shell MO's, respectively, defined according to

$$\underline{F}_c(\Gamma) = \underline{H}(\Gamma) + \underline{P}(\Gamma) \ , \qquad (28a)$$

$$\underline{F}_o(\Gamma) = \underline{H}(\Gamma) + \underline{P}(\Gamma) - \underline{Q}(\Gamma) \ . \qquad (28b)$$

*Here,* $\underline{H}(\Gamma)$ is a symmetric matrix with elements defined in Eq. (22). $\underline{P}(\Gamma)$ and $\underline{Q}(\Gamma)$ are conveniently developed first as supervectors, namely, the segments belonging to $\Gamma$ of the respective row matrices

$$\underline{P} = \underline{D}_t \mathcal{P} \ , \qquad \underline{Q} = \underline{D}_o \mathcal{Q} \ . \qquad (29)$$

The elements of these segments are used to form the square matrix contributions to Eqs. (28a) and (28b).

(e) $\underline{R}_c(\Gamma)$ and $\underline{R}_o(\Gamma)$ are the previously mentioned "coupling operators" which maintain orthogonality among all MO's belonging to the same $\Gamma$. They are defined by

$$\underline{R}_o(\Gamma) = \frac{n_\Gamma}{2d_\Gamma - n_\Gamma} \sum_i^o [\underline{T}_i(\Gamma) + \underline{T}_i^\dagger(\Gamma)] \ , \qquad (30a)$$

$$\underline{R}_c(\Gamma) = \frac{2d_\Gamma}{2d_\Gamma - n_\Gamma} \sum_i^c [\underline{T}_i(\Gamma) + \underline{T}_i^\dagger(\Gamma)] \ , \qquad (30b)$$

where $n_\Gamma$ is the number of electrons in the open shell belonging to $\Gamma$ and

$$\underline{T}_i(\Gamma) = \underline{S}(\Gamma) \underline{C}_i(\Gamma) \underline{C}_i^\dagger(\Gamma) \underline{Q}^\dagger(\Gamma) \ ,$$

with $\underline{C}_i(\Gamma)$ being the $i$th column of $\underline{C}_o(\Gamma)$ or $\underline{C}_c(\Gamma)$ depending upon whether $\underline{T}_i(\Gamma)$ is used in Eqs. (30a) or (30b), respectively. Note that only one term occurs in the sum in Eq. (30a).

The eigenvalues and eigenvectors explicitly occurring in Eqs. (26a) and (26b) are obtained from the secular equations

$$\det|\underline{F}_c + \underline{R}_o - \epsilon_c \underline{S}| = 0 \ , \quad \det|\underline{F}_o + \underline{R}_c - \epsilon_o \underline{S}| = 0 \ .$$

Since the $\underline{F}$ and $\underline{R}$ matrices are implicit functions of the coefficients $C_{ki\Gamma}$, the usual iterative procedure must be used.

Trial vectors (input to the first iteration) may be chosen to approximate the ionic character of the complex.

For input vectors to the $(n+1)$th iteration our experience with transition-metal clusters indicates that, while one can usually pick the $m$ occupied closed shells as the $m$ vectors associated with the $m$ lowest eigenvalues of the $n$th iteration closed-shell Fock matrix, it is preferable to pick those $n$th iteration vectors which maximally overlap the $m$ vectors of the $(n-1)$th iteration. The choice of the open-shell eigenvector from the solutions of $\underline{F}_o$ is generally made also by choosing the vector which has the maximum overlap with the open-shell vector of the $(n-1)$th iteration. On convergence, the open-shell vector is orthogonal to the occupied closed-shell vectors.

At convergence we have

$$\underline{\epsilon}_o = \underline{C}_o^\dagger(\Gamma) \underline{F}_o(\Gamma) \underline{C}_o(\Gamma) \ ,$$

$$\underline{\epsilon}_c = \underline{C}_c^\dagger(\Gamma) \underline{F}_c(\Gamma) \underline{C}_c(\Gamma) \ ,$$

since

$$\underline{C}_o^\dagger(\Gamma) \underline{R}_c(\Gamma) \underline{C}_o(\Sigma) = \underline{C}_c^\dagger(\Gamma) \underline{R}_o(\Gamma) \underline{C}_c(\Gamma) = 0 \ .$$

The converged eigenvalues have been defined such that the total energy of the state considered is given by

$$E = V_{\text{nuc}} + \sum_{i\Gamma}^c d_\Gamma [H(i\Gamma) + \epsilon_c(i\Gamma)] + \sum_{i\Gamma}^o f(i\Gamma) d_\Gamma [H(i\Gamma) + \epsilon_o(i\Gamma)] \ , \qquad (31)$$

where $f(i\Gamma)$ is the fractional occupancy of the $i\Gamma$ shell; e.g., $f(2t_{2g}) = \frac{1}{6}x$ and $f(3eg) = \frac{1}{4}y$.

The eigenvalue for an occupied MO belonging to a closed shell or a virtual MO having a $\Gamma$ different from that of any occupied open shell is given by

$$\epsilon_c(i\Gamma) = H(i\Gamma) + 2 \sum_{i'\Gamma'}^c d_\Gamma \, \overline{P}(i'\Gamma', i\Gamma) + 2 \sum_{i'\Gamma'}^o f(i'\Gamma') d_\Gamma \overline{P}(i'\Gamma', i\Gamma) \ ; \qquad (32)$$

note that the sums include only *occupied* MO's.

In general, the eigenvalues for occupied $2t_{2g}$ and $3e_g$ MO's are given by

$$\epsilon(2t_{2g}) = H'(2t_{2g}) + \eta(2t_{2g}) \ , \qquad (33a)$$

$$\epsilon(3e_g) + H'(3e_g) + \eta(3e_g) \ , \qquad (33b)$$

where

$$H'(2t_{2g}) = H(2t_{2g}) + 2 \sum_{i\Gamma}^c \overline{P}(i\Gamma, 2t_{2g}) \ , \qquad (34a)$$

$$H'(3e_g) = H(3e_g) + 2\sum_{i\Gamma}^{c} \bar{P}(i\Gamma, 3e_g) , \qquad (34b)$$

and where

$$\eta(2t_{2g}) = (1/x)\,[2\alpha_1 \bar{J}(tt) + 2\beta_1 \bar{K}(tt) + 2\gamma_1 K(t\zeta, t\zeta) + \alpha_2 \bar{J}(et) + \beta_2 \bar{K}(et) + \gamma_2 J(e\theta, t\zeta) + \delta_2 K(e\theta, t\zeta)] , \qquad (35a)$$

$$\eta(3e_g) = (1/y)\,[\alpha_2 \bar{J}(et) + \beta_2 \bar{K}(et) + \gamma_2 J(e\theta, t\zeta) + \delta_2 K(e\theta, t\zeta) + 2\alpha_3 \bar{J}(ee) + 2\beta_2 \bar{K}(ee)] , \qquad (35b)$$

with the $\alpha_1, \ldots \delta_2$ coefficients drawn from Eqs. (16) and Table III.

## IV. CORE APPROXIMATION

No calculation implied by the preceding formulation is impossible to carry out at the present state of computer programming, especially if Gaussian functions are employed.[8-10] Considerations of time, cost, and the analysis of physically significant models prompt the investigation of certain approximations.[18] Here we shall merely present the "frozen-core" approximation and later report conclusions regarding certain other numerical approximations in connection with specific transition-metal clusters.

As was suggested above, the inner-shell (or core) AO's are often presumed not to be greatly disturbed in character upon molecular formation although significant changes in inner-shell orbital energies may be detected.[19] Theoretically, an improper treatment of inner shells has many serious implications. For instance, complete orthogonality among all occupied orbitals ought to be maintained. Once this is instituted, there is no practical benefit (except as certain classes of integrals become vanishingly small) to giving inner shells any special treatment.

We shall, however, consider the following approximation: MO's designated as inner shell AO's are maintained orthogonal to valence shell AO's on the same center, but their nonorthogonality to AO's on all *other* centers is neglected. These inner shell AO's will exactly retain their previously fixed free-ion character during the variational treatment.

This approximation amounts first to limiting the sum over $k$ in Eq. (5) to inner-shell *or* valence-shell symmetry orbitals, as $\phi_{i\Gamma\gamma}$ is an inner-shell or valence-shell MO, respectively, and second to restricting the variational calculation to valence-shell MO's only. For inner shells $\phi_{i\Gamma\gamma} = \lambda_{i\Gamma\gamma}$. There are no formal alterations in the total wave functions $\Phi$. Let us make the following definitions:

$$E_0 = V_{\text{nuc}} + 2 \sum_{i\Gamma \subset \text{core}} d_\Gamma H(i\Gamma) + \tfrac{1}{2} \sum_{i\Gamma} \sum_{i'\Gamma' \subset \text{core}} \bar{P}(i\Gamma, i'\Gamma') , \qquad (36)$$

$$W = E - E_0 , \qquad (37)$$

and

$$H^{\text{core}}(i\Gamma) = H(i\Gamma) + 2 \sum_{i'\Gamma' \subseteq \text{core}} d_{\Gamma'} \bar{P}(i\Gamma, i'\Gamma') . \qquad (38)$$

For a given basis and metal-ligand distance $E_0$ becomes a constant. Then $W$, the total electronic energy of the valence orbitals of a cluster, is

$$W = 2\sum_{i\Gamma}^{c} d_\Gamma H^{\text{core}}(i\Gamma) + \tfrac{1}{2}\sum_{i\Gamma}^{c} \sum_{i'\Gamma'}^{c} d_\Gamma d_{\Gamma'} \bar{P}(i\Gamma, i'\Gamma') + xH^{\text{core}}(2t_{2g}) + yH^{\text{core}}(3e_g) + 2\sum_{i\Gamma}^{c} [x d_\Gamma \bar{P}(i\Gamma, 2t_{2g}) + y d_\Gamma P(i\Gamma, 3e_g)] + G(x, y; S\Gamma) . \qquad (39)$$

Here, now, the indicated sums are over *valence orbitals* only.

Similarly, variation of $W$ with respect to the remaining valence MO coefficients yields Hartree-Fock-Roothaan equations identical in form to Eqs. (28) but containing the same restrictions as Eq. (39). Equations (18)–(35) are preserved in form, except with $W$ replacing $E - V_{\text{nuc}}$, with

$$H^{\text{core}}(\Gamma; k, l) = H(\Gamma; k, l) + 2 \sum_{i\Gamma' \subset \text{core}} d_{\Gamma'} \mathcal{P}(\Gamma'; i, i \mid \Gamma; k, l) \qquad (40)$$

replacing $H(\Gamma; k, l)$ in Eq. (22), with

$$H^{\text{core}}(i\Gamma) = \underline{C}_i^\dagger(\Gamma)\, \underline{H}^{\text{core}}(\Gamma)\, \underline{C}_i(\Gamma) \qquad (41)$$

replacing $H(i\Gamma)$ in Eqs. (31)–(34b), with the explicit sums over MO's ranging only over the occupied *valence* MO's, and with the indices $k, l, k'$, $l'$ no longer including the basis functions $\lambda_{k\Gamma\gamma}$ describing the inner-shell AO's.

## V. EXCITATION ENERGIES

Three classes of electronic transitions are often discussed: (a) the "*d-d*" transitions among the $2t_{2g}$ and $3e_g$ MO's, (b) the so-called "charge-transfer" transitions connecting those MO's largely centered on the ligand, and (c) excitation of core electrons to the valence-shell or virtual orbitals. In this section we shall discuss them only to first order. Configuration-interaction ("second-order") effects will be discussed in Sec. VI.

The energy expression for any state of any configuration can be set up and optimized with respect to the appropriate variational coefficients. In general, however, there is the serious problem of maintaining orthogonality among all the states having the same spin and space symmetry.[20] Wave functions for higher excited states may be constructed from occupied and virtual MO's obtained from the solution of Eqs. (26) for the ground state provided the solutions used are orthogonal. It is clear that the unoccupied MO's obtained from $\underline{F}_c(\Gamma)$ will not necessarily be orthogonal to the open-shell MO's defined by $\underline{F}_o(\Gamma)$. It may be possible in this case to obtain suitable MO's by construction. By this procedure, the orthogonality problem is circumvented, but the transition energy so computed will be more positive than that obtained by subtraction of independent ground- and excited-state SCF total energies by an amount called the "reorganization energy" by Mulliken.[21]

### *d-d* Transition Energies

Strong-field crystal and ligand-field theories have long been used to predict and interpret spectra arising from the *d-d* transitions among the states of the $(2t_{2g})^x(3e_g)^y$, $(2t_{2g})^{x-1}(3e_g)^{y+1}$, etc., configurations. By these theories, some particular transition energy $\Delta E$ is described, to first order, by

$$\Delta E = n\,(10Dq) + \Delta G\ , \tag{42}$$

where $n$ is the number of electrons passing from $2t_{2g}$ to $3e_g$, $10Dq$ is the crystal- or ligand-field splitting parameter, and $\Delta G$ is the change in the Coulombic and exchange interactions among the electrons of the $2t_{2g}$ and $3e_g$ shells during the transition.

Assume that the excited state $|x-n, y+n;\,^{S'}\Gamma'\rangle$ and the ground state $|x, y;\,^{S}\Gamma\rangle$ involved in the transition are both described by the same set of MO's. Take $E(S\Gamma)$ as given by Eq. (15) and $E(S'\Gamma')$ by

$$E(S'\Gamma') - V_{\text{nuc}} = 2\sum_{i\Gamma}^{c} d_\Gamma H(i\Gamma) + \frac{1}{2}\sum_{i\Gamma}^{c}\sum_{i'\Gamma'}^{c} d_\Gamma d_{\Gamma'} \overline{P}(i\Gamma, i'\Gamma') + (x-n)\,H(2t_{2g})$$
$$+ (y+n)\,H(3e_g) + 2\sum_{i\Gamma}^{c}[(x-n)\,\overline{P}(i\Gamma, 2t_{2g}) + (y+n)\,\overline{P}(i\Gamma, 3e_g)] + G(x-n, y+n; S'\Gamma')\ . \tag{43}$$

Direct subtraction, and cancellation of equal terms, gives

$$\Delta E = E(S', \Gamma') - E(S, \Gamma)$$
$$= n\{[\epsilon(3e_g) - \eta(3e_g)] - [\epsilon(2t_{2g}) - \eta(2t_{2g})]\}$$
$$+ \{G(x-n, y+n; S'\Gamma') - G(x, y; S\Gamma)\},$$
$$\Delta E = n\Delta H' + \Delta G\ , \tag{44}$$

where use has been made of Eqs. (32)–(35b).

Obvious changes result from invoking the frozen-core approximation. Equation (38) exactly parallels Eq. (36). It represents a possible partitioning of the transition energy, one which corresponds to that used in crystal-field theory. Note, however, that "$10Dq$" by the open-shell SCF theory is found to be given not by the difference of the open-shell eigenvalues; rather, from each eigenvalue first must be subtracted the interelectronic contributions to it from the $2t_{2g}$ and $3e_g$ shells.

This specification is in close accord with the basic postulates of crystal-field theory, in which $10Dq$ contains the effects of all charge distributions *other* than the $3d$ electrons of the metal. This present identification of $10Dq$ differs from an alternate partitioning made by other workers, who define $10Dq$ as equal to $\Delta E$ of the lowest *d-d* excitation for which, *by crystal-field theory*, $\Delta G$ is zero.[22,11]

While formally the quantity $\Delta H' = H'(3e_g) - H'(2t_{2g})$ is here identified with $10Dq$, we anticipate the results of subsequent numerical calculations which often yield a great quantitative disparity.[11,23] The reason is that, within the SCF theory, the partitioning of $\Delta E$ by Eq. (38) is arbitrary. "Fluctuations" in $\Delta H'$ are accompanied by compensating fluctuations in $\Delta G$.

One should recall that only if $2t_{2g}$ and $3e_g$ were radially identical $3d$ orbitals would the large Racah $A$ parameter disappear from $\Delta G$. This is rarely the case; $2t_{2g}$ and $3e_g$ may both deviate, significantly and differently, from their free-ion character and the total Coulomb interaction may change appreciably in the excited state.

### Other Electronic Transition Energies

By the same reasoning as used for *d-d* transitions one may work out total energy and transition-energy expressions corresponding to Eqs. (15), (37), and (38), for the charge-transfer and core-excitation transitions.

Alternatively, an independent SCF calculation may be done for the excited state. Because of the significant relocation of charge density accompanying these transitions, an appreciable reorganization energy may be anticipated.

TABLE IV. Off-diagonal electrostatic interaction matrices for $t^{2-y}e^y$ and $t^{3-y}e^y$ configurations. $K'(et) = K(e\theta, t\zeta) - \bar{K}(et)$ and $P'(et) = \bar{P}(et) - P(e\theta, t\zeta)$. Elements for the complementary configurations $t^{4+y}e^{4-y}$ and $t^{3+y}e^{4-y}$ are the same apart from phase changes in the complementary wave functions, which are irrelevant for energy calculations.

(a) $t^{2-y}e^y$

| State | Configuration pair | Off-diagonal element |
|---|---|---|
| ${}^3T_{1g}$ | $(t^2)-(te)$ | $-2\sqrt{3}i$ |
| ${}^1A_{1g}$ | $(t^2)-(e^2)$ | $\sqrt{6}\bar{K}(et)$ |
| ${}^1E_g$ | $(t^2)-(e^2)$ | $\sqrt{3}K'(et)$ |
| ${}^1T_{2g}$ | $(t^2)-(te)$ | $-2i$ |

(b) $t^{3-y}e^y$

| ${}^4T_{1g}$ | $t^2({}^3T_{1g})e$ | $te^2({}^3A_{2g})$ |
|---|---|---|
| $t^2({}^3T_{1g})e$ | $\cdots$ | $2\sqrt{3}i$ |
| $te^2({}^3A_{2g})$ | $2\sqrt{3}i$ | $\cdots$ |

| ${}^2T_{1g}$ | $t^3$ | $t^2({}^3T_{1g})e$ | $t^2({}^1T_{1g})e$ | $te^2({}^3A_{2g})$ | $te^2({}^1E_g)$ |
|---|---|---|---|---|---|
| $t^3$ | $\cdots$ | $\sqrt{3}i$ | $-\sqrt{3}i$ | 0 | $-\sqrt{3}K'(et)$ |
| $t^2({}^3T_{1g})e$ | $\sqrt{3}i$ | $\cdots$ | $-\frac{3}{2}K'(et)$ | $-\sqrt{3}i$ | $-3i$ |
| $t^2({}^1T_{2g})e$ | $-\sqrt{3}i$ | $-\frac{3}{2}K'(et)$ | $\cdots$ | $\sqrt{3}i$ | $i$ |
| $te^2({}^3A_{2g})$ | 0 | $-\sqrt{3}i$ | $\sqrt{3}i$ | $\cdots$ | $\sqrt{3}K'(et)$ |
| $te^2({}^1E_g)$ | $-\sqrt{3}K'(et)$ | $-3i$ | $i$ | $\sqrt{3}K'(et)$ | $\cdots$ |

| ${}^2T_{2g}$ | $t^3$ | $t^2({}^3T_{1g})e$ | $t^2({}^1T_{2g})e$ | $te^2({}^1A_{1g})$ | $te^2({}^1E_g)$ |
|---|---|---|---|---|---|
| $t^3$ | $\cdots$ | $-3i$ | $5i$ | $2\bar{K}(et)$ | $K'(et)$ |
| $t^2({}^3T_{1g})e$ | $-3i$ | $\cdots$ | $-\frac{3}{2}K'(et)$ | $-3i$ | $-3i$ |
| $t^2({}^1T_{2g})e$ | $5i$ | $-\frac{3}{2}K'(et)$ | $\cdots$ | $i$ | $-i$ |
| $te^2({}^1A_{1g})$ | $2\bar{K}(et)$ | $-3i$ | $i$ | $\cdots$ | $2P'(et)$ |
| $te^2({}^1E_g)$ | $K'(et)$ | $-3i$ | $-i$ | $2P'(et)$ | $\cdots$ |

| ${}^2E_g$ | $t^3$ | $t^2({}^1A_{1g})e$ | $t^2({}^1E_g)e$ | $e^3$ |
|---|---|---|---|---|
| $t^3$ | $\cdots$ | $-2\sqrt{6}i$ | $\sqrt{6}i$ | 0 |
| $t^2({}^1A_{1g})e$ | $-2\sqrt{6}i$ | $\cdots$ | $-2P'(et)$ | $\sqrt{3}\bar{K}(et)$ |
| $t^2({}^1E_g)e$ | $\sqrt{6}i$ | $-2P'(et)$ | $\cdots$ | $-\sqrt{3}K'(et)$ |
| $e^3$ | 0 | $\sqrt{3}\bar{K}(et)$ | $-\sqrt{3}K'(et)$ | $\cdots$ |

## VI. CONFIGURATION INTERACTION

There generally are several first-order states of a particular spin and space symmetry (say $S\Gamma$) arising from different distributions of $x+y$ electrons among the $2t_{2g}$ and $3e_g$ MO's. A better (and often much better) representation of the true wave functions and energies for the system may be obtained by writing

$$\Psi(S\Gamma) = \sum_n a_n \Phi_n(S\Gamma) , \qquad (45)$$

where the $\Phi_n(S\Gamma)$ are the first-order SCF MO wave functions each defined for a definite configuration and constructed from the same orthonormal set of MO's, as described in the previous sections, such that $\langle \Phi_n | \Phi_m \rangle = \delta_{nm}$. The $a_n$ are new variational coefficients such that $\sum_n a_n^2 = 1$. Optimization of $\langle \Psi(S\Gamma) | \mathcal{H} | \Psi(S\Gamma) \rangle$ leads to the secular equation

$$\det | H_{nm} - \delta_{nm} W | = 0 . \qquad (46)$$

The $H_{nn} = \langle \Phi_n | \mathcal{H} | \Phi_n \rangle$ are the first-order energies, obtained as discussed in Sec. V. $H_{nm} = \langle \Phi_n | \mathcal{H} | \Phi_m \rangle$ have been derived by Tanabe and Sugano in terms of Racah $B$ and $C$ parameters for all possible cases where $2t_{2g}$ and $3e_g$ are $d$ orbitals with the same radial dependence.[24] Griffith has also given some results for the more general orbitals and has indicated how to derive the remainder.[14]

While it goes beyond the scope of the present investigation to develop all these elements for general $t_{2g}$ and $e_g$ orbitals, we do present in Table IV the elements for states arising from the $d^2$ and $d^3$ atomic configurations. Elements arising from complementary $d^8$ and $d^7$ configurations are the same except for sign changes due to phase relationships between complementary wave functions. Elements for other configurations can be worked out in a straightforward manner using the wave functions tabulated, for example, by Watanabe.[25]

In addition to the first-order states just considered is a great host of others arising from the same sorts of configurations as are involved in charge-transfer spectra. Although their diagonal energies, on the average, are at least several eV higher, they may be expected to influence significantly the positions of some of the higher *d*-*d* electronic states which have been observed.

## VII. GENERALIZATIONS

This present discussion has assumed a perfectly octahedral complex ion made from a first transition-series metal ion and first-row ions as ligands. This formulation is easily generalized to other systems with other symmetries, merely by the proper changes in basis, projection operators, Hamiltonian, limits on sums, and resulting modifications of specific energy expressions.

Furthermore, one may assume that any pertinent relativistic effects and consequences of nuclear motion, as well as transition probabilities, can be handled by methods already developed in the context of general ligand-field theory.

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*Supported by Contract No. SD-102 with the Advanced Research Projects Agency.

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