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The d^2 and d^8 Noncubic Ligand Field Spectrum

I. The Complete Theory of Quadrate, Trigonal, and Cylindrical Ligand Fields [1]

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The complete theory of Liehr and Ballhausen for d^2 and d^8 electronic configurations immersed in cubic fields has been extended to include noncubic ligand fields of quadrate, trigonal, and cylindrical symmetry. The complete set of symmetry adapted eigenvectors for the three symmetries have been derived in various coupling schemes in which the spin-orbit interaction, electron correlation, and ligand field in turn are varied from minor to dominant perturbations. The corresponding energy matrices as a function of the parameters of the ligand field, electron correlation, and spin-orbit constant have been constructed in all the representations. Unitary transformations connecting different formalisms were obtained. The energy matrices have been solved for representative sets of parametric values and energy diagrams have been plotted in all the symmetries as well as in the square planar limit of the quadrate crystalline field. The secular determinants, the eigenfunctions, the energy diagrams, and the unitary transformations presented here are extremely useful in the study of the various aspects of spectroscopic, magnetic, and other properties of appropriate systems. The theory is applicable to quadrately distorted or substituted, trigonally distorted or substituted, octahedral and tetrahedral complexes and to compounds of cylindrical symmetry of d^2 and d^8 electronic configurations.

I. Introduction

Although the ligand field theory of cubic fields for all d^n, $n = 1$ to 9, electronic configurations has been developed with the inclusion of spin-orbit perturbation [3], such has not been the case with the theory of noncubic ligand fields. The noncubic theory advanced so far with a very few exceptions [4] has been mainly either with complete or part neglect of spin-orbit perturbation or configuration interaction or both. Even such restricted calculations have been limited to a few of the d^n configurations. Spin-orbit interaction acts as a minor perturbation in the case of the first members of the $3d^n$ iron group elements but becomes dominant for the last members of the $3d^n$ and for all members of the $4d^n$ palladium and the $5d^n$ platinum group metal ions. Exact calculations including spin-orbit perturbation and full configuration interaction will be necessary for a thorough interpretive investigations of the spectral and magnetic properties of the appropriate complex compounds.

In this series of reports we will undertake to study the d^2 and d^8 electronic configurations immersed in various noncubic ligand fields. The present paper will cover the underlying theory for the fields of quadrate (tetragonal), trigonal and cylindrical (axial) symmetry. Applications of these calculations to actual experimental situations will be the concern of the future series, with interpreting the vast amount of available spectroscopic data on nickel(II) complexes [5] exemplifying the d^8 configuration as the beginning.

In order that the basic theory presented be applicable to all the transition-metal ions including lanthanides and actinides, we shall consider various coupling schemes in which the role of the ligand field, electron correlation, and spin-orbit interaction is varied each in turn from minor to dominant perturbation.

The appropriate compounds of d^2 and d^8 electronic configurations that can be studied by the theory expounded here are the following: 1) tetragonally distorted or substituted octahedral and tetrahedral complexes, including five coordinate square pyramidal and four coordinate square planar systems, 2) trigonally ditorted or substituted octahedral and tetrahedral complexes, and 3) cylindri-

cal ($D_{\infty h}$, $C_{\infty v}$) and n polygonal prismoidal ($n>4$, D_{nh}, D_{nd}, D_n, C_{nv}, C_{nh}, C_n) compounds which include gaseous dihalides and metallocenes.

II. Theory

A) The Perturbation

We are concerned with the total perturbation

$$\mathcal{H}' = V^{\text{L.F.}}(r, \theta, \varphi) + \sum_{i>j} e^2/r_{ij} + \sum_i \xi(r_i)\, \boldsymbol{l}_i \cdot \boldsymbol{s}_i \qquad (1)$$

where $V^{\text{L.F.}}$ represents the nonspherical potential field of the encompassing ligands, $\sum_{i>j} e^2/r_{ij}$ the electron correlation, and $\sum_i \xi(r_i)\, \boldsymbol{l}_i \cdot \boldsymbol{s}_i$ the spin-orbit interaction. The various coupling schemes refer to the diagonal nature of these individual perturbations. If the basis functions are so chosen that the ligand field potential is diagonalized, construction of symmetry eigenfunctions from this basis set to incorporate the remaining perturbations is known as the strong field formalism. We note in the case of quadrate and trigonal symmetry the ligand field can be expressed as the sum of cubic and axial fields so that the cubic ligand field potential alone can be made diagonal and the axial ligand field potential is added as minor perturbation or the complete ligand field potential can be made diagonal as is possible in the case of quadrate fields. The former scheme is applicable in te study of the substituted and slightly distorted cubic complexes and the latter scheme is applicable in the study of the substituted in the study of the highly distorted cubic complexes of which square planar systems will form a special case. If the basis set in which the electron correlation is digonal is used to include the ligand field and spin-orbit perturbations, such a procedure is called the weak-field or the free-ion formalism. Utilization of a basis set that diagonalizes the spin-orbit interaction to carry out the ligand field and electron correlation perturbations is called (j, j) coupling scheme. In addition to these, there is one other formalism which may be employed in the case of quadrate and trigonal fields to determine the final eigenfunctions and eigenvalues. This method is to use one electron spin-orbital functions, which are the symmetry eigenfunctions for the ligand field and spin-orbit perturbations, as the basis set to carry out electron correlation perturbation. The cubic ligand field is diagonal in this (γ, γ) scheme and although the axial ligand field and the spin-orbit interaction are not completely diagonal, they act as major perturbations compared to electron correlation [6].

For reasons which will become apparent in the following, we choose to call the strong field, weak-field, (j, j), and the (γ, γ) coupling schemes of the quadrate and trigonal fields the $\{X, S, t_{2g}, e_g, \Gamma_j\}$, $\{L, S, J, \Gamma_j\}$, $\{j, j, J, \Gamma_j\}$, and $\{\gamma_7(t_{2g}), \gamma_8(t_{2g}), \gamma_8(e_g), \Gamma_j\}$ representations, respectively. The strong field, weak-field ,and the (j, j) formalisms in the case of cylindrical fields are called $\{\Xi, \Sigma, \delta, \pi, \sigma, \Gamma_j\}$, $\{\Lambda, \Sigma, \Omega, \Gamma_j\}$, and $\{\omega, \omega, \Omega, \Gamma_j\}$ representations, respectively, to conform to the quantum mechanical notation of the diatomic molecules. The additional scheme of the quadrate fields for which the one electron quadrate functions form the basis set is named $\{X, S, e_g, b_{2g}, a_{1g}, b_{1g}, \Gamma_j\}$ representation.

B) Octahedral Orientation in Quadrate and Trigonal Fields [4a]

Except in the case of the four coordinate square planar and perhaps five-coordinate square pyramidal complexes, axial fields of the quadrate and of the trigonal compounds are usually of smaller magnitude compared to the cubic fields so that the quadrate and trigonal systems under consideration can be treated as slightly deviated from cubic symmetry. This means that the symmetry adapted wave functions in all representations except $\{X, S, e_g, b_{2g}, a_{1g}, b_{1g}, \Gamma_j\}$ are constructed in octahedral orientation and properly decomposed on going to quadrate and trigonal symmetry as shown in Table 1 [7].

Table 1. Decomposition of the Representations of Cubic Symmetry Relative to Quadrate and Trigonal Symmetries.

Cubic	Quadrate	Trigonal
Γ_1^{C}	Γ_1^{Q}	Γ_1^{T}
Γ_2^{C}	Γ_3^{Q}	Γ_2^{T}
$\Gamma_{3\text{a}}^{\text{C}}$	Γ_1^{Q}	$\Gamma_{3\text{a}}^{\text{T}}$
$\Gamma_{3\text{b}}^{\text{C}}$	Γ_3^{Q}	$\Gamma_{3\text{b}}^{\text{T}}$
$\Gamma_{4\text{a}}^{\text{C}}$	Γ_2^{Q}	Γ_2^{T}
$\Gamma_{4(\text{c})}^{\text{C}}$	$\Gamma_{5(\text{b})}^{\text{Q}}$	$\Gamma_{3(\text{b})}^{\text{T}}$
$\Gamma_{5\text{a}}^{\text{C}}$	Γ_4^{Q}	Γ_1^{T}
$\Gamma_{5(\text{c})}^{\text{C}}$	$\Gamma_{5(\text{b})}^{\text{Q}}$	$\Gamma_{3(\text{b})}^{\text{T}}$

C) Symmetry Adapted Wave Functions

1. $\{X, S, t_{2g}, e_g, \Gamma_j\}$ Representation of Quadrate and Trigonal Fields

The basis functions are the crystal field eigenfunctions of cubic symmeary, i. e., the t_{2g} and e_g

Table 2. Crystal Field Eigenfunctions of Cubic Symmetry in Tetragonal and Trigonal Orientations.

Cubic	Tetragonal	Trigonal
t_{2ga}	d_{xy}	$d_{\sigma'}=d_{z'^2}$
t_{2gb}	d_{zx}	$\sqrt{\frac{1}{3}}\, d_{\pi_+'} - \sqrt{\frac{2}{3}}\, d_{\delta_-'} = \sqrt{\frac{1}{3}}\,\frac{[d_{z'x'}+i\, d_{y'z'}]}{\sqrt{2}} - \sqrt{\frac{2}{3}}\,\frac{[d_{x'^2-y'^2}-i\, d_{x'y'}]}{\sqrt{2}}$
t_{2gc}	d_{yz}	$\sqrt{\frac{1}{3}}\, d_{\pi_-'} - \sqrt{\frac{2}{3}}\, d_{\delta_+'} = \sqrt{\frac{1}{3}}\,\frac{[d_{z'x'}-i\, d_{y'z'}]}{\sqrt{2}} - \sqrt{\frac{2}{3}}\,\frac{[d_{x'^2-y'^2}+i\, d_{x'y'}]}{\sqrt{2}}$
e_{ga}	d_{z^2}	$\sqrt{\frac{2}{3}}\, d_{\pi_+'} + \sqrt{\frac{1}{3}}\, d_{\delta_-'} = \sqrt{\frac{2}{3}}\,\frac{[d_{z'x'}+i\, d_{y'z'}]}{\sqrt{2}} + \sqrt{\frac{1}{3}}\,\frac{[d_{x'^2-y'^2}-i\, d_{x'y'}]}{\sqrt{2}}$
e_{gb}	$d_{x^2-y^2}$	$\sqrt{\frac{2}{3}}\, d_{\pi_-'} + \sqrt{\frac{1}{3}}\, d_{\delta_+'} = \sqrt{\frac{2}{3}}\,\frac{[d_{z'x'}-i\, d_{y'z'}]}{\sqrt{2}} + \sqrt{\frac{1}{3}}\,\frac{[d_{x'^2-y'^2}+i\, d_{x'y'}]}{\sqrt{2}}$

orbitals. These orbitals in tetragonal and trigonal quantization [3b] are given in Table 2.

In Table 2, $d_{\sigma'}$, $d_{\pi'\pm}$, and $d_{\delta'\pm}$ denote the $|l, m_l\rangle$ functions $|2, 0\rangle$, $\mp|2, \pm 1\rangle$, and $|2, \pm 2\rangle$, respectively, prime refering to trigonal quantization. The trigonal oriented orbitals in Cartesian coordinates are related to the tetragonal oriented orbitals by means of the orthonormal transformation

$$\begin{pmatrix} z' \\ y' \\ x' \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} \\ 0 & -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \end{pmatrix} \begin{pmatrix} z \\ y \\ x \end{pmatrix}. \qquad (2)$$

The two electron symmetry eigenstates are constructed from this set by using their symmetry transformation properties, which along with those

Table 3. Symmetry Transformation Properties of Cubic and Quadrate Functions in $\{X, S\}$ Representation.

Cubic	Quadrate	$C_4(z)$	$C_2(y)$	$C_3(z')$
$t_{1ua}=(z)$	a_2	t_{1ua}	$-t_{1ua}$	t_{1ub}
$t_{1ub}=(y)$	e_a	t_{1uc}	t_{1ub}	t_{1uc}
$t_{1uc}=(x)$	e_b	$-t_{1ub}$	$-t_{1uc}$	t_{1ua}
$t_{2ga}=(xy)$	b_2	$-t_{2ga}$	$-t_{2ga}$	t_{2gb}
$t_{2gb}=(zx)$	e_a	$-t_{2gc}$	t_{2gb}	t_{2gc}
$t_{2gc}=(yz)$	e_b	t_{2gb}	$-t_{2gc}$	t_{2ga}
$e_{ga}=(z^2)$	a_1	e_{ga}	e_{ga}	$-\frac{1}{2}\, e_{ga} - e_{ga}\sqrt{3}/2$
$e_{gb}=(x^2-y^2)$	b_1	$-e_{gb}$	e_{gb}	$-\frac{1}{2}\, e_{gb} + e_{gb}\sqrt{3}/2$
$a_1=(\alpha\beta-\beta\alpha)/\sqrt{2}$	a_1	a_1	a_1	a_1
$t_{1a}=(\alpha\beta+\beta\alpha)/\sqrt{2}$	a_2	t_{1a}	$-t_{1a}$	t_{1b}
$t_{1b}=i(\alpha\alpha+\beta\beta)/\sqrt{2}$	e_a	t_{1c}	t_{1b}	t_{1c}
$t_{1c}=-(\alpha\alpha-\beta\beta)/\sqrt{2}$	e_b	$-t_{1b}$	$-t_{1c}$	t_{1a}

Table 4. Symmetry Transformation Properties of Cubic and Trigonal Functions in $\{X, S\}$ Representation.

Cubic	Trigonal	$C_3(z')$	$C_2(y')$	$C_4(z)$
$t_{1ua}=(z')$	a_2	t_{1ua}	$-t_{1ua}$	$\frac{1}{3}\, t_{1ua}+\frac{2}{3}\,\omega^{-1/2}\, t_{1ub}+\frac{2}{3}\,\omega^{1/2}\, t_{1uc}$
$t_{1u(^b_c)}=(\pi'_\pm)$	$e_\pm$	$\omega^{\pm 1}\, t_{1u(^b_c)}$	$-t_{1u(^c_b)}$	$\frac{2}{3}\,\omega^{\mp 1/2}\, t_{1ua}+\frac{1}{3}\, t_{1u(^c_b)}+\frac{2}{3}\,\omega^{\pm 1/2}\, t_{1u(^b_c)}$
$t_{2ga}=(z'^2)$	a_1	t_{2ga}	t_{2ga}	$-\frac{1}{3}\, t_{2ga}+\frac{2}{3}\,\omega^{-1/2}\, t_{2gb}+\frac{2}{3}\,\omega^{1/2}\, t_{2gc}$
$t_{2g(^b_c)}=\sqrt{\frac{1}{3}}(\pi'_\pm)-\sqrt{\frac{2}{3}}(\delta'_\mp)$	$e_\pm$	$\omega^{\pm 1}\, t_{2g(^b_c)}$	$t_{2g(^c_b)}$	$\frac{2}{3}\,\omega^{\mp 1/2}\, t_{2ga}-\frac{1}{3}\, t_{2g(^c_b)}-\frac{2}{3}\,\omega^{\pm 1/2}\, t_{2g(^b_c)}$
$e_{g(^a_b)}=\sqrt{\frac{2}{3}}(\pi'_\pm)+\sqrt{\frac{1}{3}}(\delta'_\mp)$	$e_\pm$	$\omega^{\pm 1}\, e_{g(^a_b)}$	$e_{g(^b_a)}$	$e_{g(^b_a)}$
$a_1=(\alpha'\beta'-\beta'\alpha')/\sqrt{2}$	a_1	a_1	a_1	a_1
$t_{1a}=(\alpha'\beta'+\beta'\alpha')/\sqrt{2}$	a_2	t_{1a}	$-t_{1a}$	$\frac{2}{3}\,\omega^{-1/2}\, t_{1b}+\frac{1}{3}\, t_{1a}+\frac{2}{3}\,\omega^{+1/2}\, t_{1c}$
$t_{1b}=-(\alpha'\alpha')$	e_+	$\omega^{+1}\, t_{1b}$	$-t_{1c}$	$\frac{2}{3}\,\omega^{-1/2}\, t_{1a}+\frac{1}{3}\, t_{1c}+\frac{2}{3}\,\omega^{+1/2}\, t_{1b}$
$t_{1c}=\beta'\beta'$	e_-	$\omega^{-1}\, t_{1c}$	$-t_{1b}$	$\frac{2}{3}\,\omega^{+1/2}\, t_{1a}+\frac{1}{3}\, t_{1b}+\frac{2}{3}\,\omega^{-1/2}\, t_{1c}$

Table 5. Quadrate Wave Functions and Energy Matrices in $\{X, S, t_{2g}, e_g, \Gamma_j\}$ Representation.

(a) $|X, S, t_{2g}, e_g, \Gamma_j\rangle$ **Functions**

$[\Psi_0=(\alpha\beta+\beta\alpha)/\sqrt{2},\quad \Psi_1=i(\alpha\alpha+\beta\beta)/\sqrt{2},\ \Psi_{-1}=-(\alpha\alpha-\beta\beta)/\sqrt{2}]$

Γ_1Q Representation

$$|1\rangle=\Gamma_1{}^{\mathrm{C}}[{}^1A_{1g}(e_g{}^2)]=i\sqrt{\tfrac{1}{2}}[|(z^2)(z^2)|+|(x^2-y^2)\ (x^2-y^2)|](\alpha\beta-\beta\alpha)/\sqrt{2}$$

$$|2\rangle=\Gamma_1{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}\,e_g)]=\sqrt{\tfrac{1}{3}}\{|(xy)(x^2-y^2)|\Psi_0+[-\tfrac{1}{2}|(zx)(x^2-y^2)|+(\sqrt{3}/2)\ |(zx)(z^2)|]\Psi_1 +[-\tfrac{1}{2}|(yz)(x^2-y^2)|-(\sqrt{3}/2)\ |(yz)(z^2)|]\Psi_{-1}\}$$

$$|3\rangle=\Gamma_1{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}{}^2)]=\sqrt{\tfrac{1}{3}}\{|(zx)(yz)|\Psi_0+|(yz)(xy)|\Psi_1-|(zx)(xy)|\Psi_{-1}\}$$

$$|4\rangle=\Gamma_1{}^{\mathrm{C}}[{}^1A_{1g}(t_{2g}{}^2)]=i\sqrt{\tfrac{1}{3}}[|(zx)(zx)|+|(yz)(yz)|+|(xy)(xy)|](\alpha\beta-\beta\alpha)/\sqrt{2}$$

$$|5\rangle=\Gamma_{3a}{}^{\mathrm{C}}[{}^1E_g(e_g{}^2)]=\sqrt{\tfrac{1}{2}}[|(x^2-y^2)(x^2-y^2)|-|(z^2)(z^2)|](\alpha\beta-\beta\alpha)/\sqrt{2}$$

$$|6\rangle=\Gamma_{3a}{}^{\mathrm{C}}[{}^3T_{2g}(t_{2g}\,e_g)]=i\sqrt{\tfrac{1}{2}}\{[-\tfrac{1}{2}|(zx)(z^2)|-\sqrt{3}/2-[-\tfrac{1}{2}|(yz)(z^2)|+(\sqrt{3}/2)\ |(zx)(x^2-y^2)|]\Psi_1\,|(yz)(x^2-y^2)|]\Psi_{-1}\}$$

$$|7\rangle=\Gamma_{3a}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}\,e_g)]=i\sqrt{\tfrac{1}{6}}\{2|(xy)(x^2-y^2)|\Psi_0-[-\tfrac{1}{2}|(zx)(x^2-y^2)|+(\sqrt{3}/2)|(zx)(z^2)|]\Psi_1 -[-\tfrac{1}{2}|(yz)(x^2-y^2)|-(\sqrt{3}/2)|(yz)(z^2)|]\Psi_{-1}\}$$

$$|8\rangle=\Gamma_{3a}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}{}^2)]=-i\sqrt{\tfrac{1}{6}}\{-2|(yz)(zx)|\Psi_0-|(yz)(xy)|\Psi_1+|(zx)(xy)|\Psi_{-1}\}$$

$$|9\rangle=\Gamma_{3a}{}^{\mathrm{C}}[{}^1E_g(t_{2g}{}^2)]=\sqrt{\tfrac{1}{6}}[|(zx)(zx)|+|(yz)(yz)|-2|(xy)(xy)|](\alpha\beta-\beta\alpha)/\sqrt{2}.$$

Γ_2Q Representation

$$|1\rangle=\Gamma_{4a}{}^{\mathrm{C}}[{}^3T_{2g}(t_{2g}\,e_g)]=\sqrt{\tfrac{1}{2}}\{[-\tfrac{1}{2}|(zx)(z^2)|-(\sqrt{3}/2)|(zx)(x^2-y^2)|]\Psi_{-1}+[-\tfrac{1}{2}|(yz)(z^2)|+(\sqrt{3}/2)|(yz)(x^2-y^2)|]\Psi_1\}$$

$$|2\rangle=\Gamma_{4a}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}\,e_g)]=\sqrt{\tfrac{1}{2}}\{[-\tfrac{1}{2}|(zx)(x^2-y^2)|+(\sqrt{3}/2)|(zx)(z^2)|]\Psi_{-1}-[-\tfrac{1}{2}|(yz)(x^2-y^2)|-(\sqrt{3}/2)|(yz)(z^2)|]\Psi_1\}$$

$$|3\rangle=\Gamma_{4a}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}{}^2)]=\sqrt{\tfrac{1}{2}}[|(yz)(xy)|\Psi_{-1}+|(zx)(xy)|\Psi_1]$$

$$|4\rangle=\Gamma_{4a}{}^{\mathrm{C}}[{}^1T_{1g}(t_{2g}\,e_g)]=i\sqrt{\tfrac{1}{2}}[|(xy)(x^2-y^2)|+|(x^2-y^2)(xy)|](\alpha\beta-\beta\alpha)/\sqrt{2}.$$

Γ_3Q Representation

$$|1\rangle=\Gamma_2{}^{\mathrm{C}}[{}^3T_{2g}(t_{2g}\,e_g)]=i\sqrt{\tfrac{1}{3}}\{|(xy)(z^2)|\Psi_0+[-\tfrac{1}{2}|(zx)(z^2)|-(\sqrt{3}/2)|(zx)(x^2-y^2)|]\Psi_1 +[-\tfrac{1}{2}|(yz)(z^2)|+(\sqrt{3}/2)|(yz)\ (x^2-y^2)|]\Psi_{-1}\}$$

$$|2\rangle=\Gamma_{3b}{}^{\mathrm{C}}[{}^1E_g(e_g{}^2)]=\sqrt{\tfrac{1}{2}}[|(z^2)(x^2-y^2)|+|(x^2-y^2)(z^2)|](\alpha\beta-\beta\alpha)/\sqrt{2}$$

$$|3\rangle=\Gamma_{3b}{}^{\mathrm{C}}[{}^3T_{2g}(t_{2g}\,e_g)]=i\sqrt{\tfrac{1}{6}}\{2|(xy)(z^2)|\Psi_0-[-\tfrac{1}{2}|(zx)(z^2)|-(\sqrt{3}/2)\ |(zx)(x^2-y^2)|]\Psi_1 -[-\tfrac{1}{2}|(yz)(z^2)|+(\sqrt{3}/2)\ |(yz)(x^2-y^2)|]\Psi_{-1}\}$$

$$|4\rangle=\Gamma_{3b}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}\,e_g)]=i\sqrt{\tfrac{1}{2}}\{[\tfrac{1}{2}|(zx)(x^2-y^2)|-(\sqrt{3}/2)|(zx)(z^2)|]\Psi_1+[-\tfrac{1}{2}|(yz)(x^2-y^2)|-(\sqrt{3}/2)|(yz)(z^2)|]\Psi_{-1}\}$$

$$|5\rangle=\Gamma_{3b}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}{}^2)]=i\sqrt{\tfrac{1}{2}}[-|(yz)(xy)|\Psi_1-|(zx)(xy)|\Psi_{-1}]$$

$$|6\rangle=\Gamma_{3b}{}^{\mathrm{C}}[{}^1E_g(t_{2g}{}^2)]=\sqrt{\tfrac{1}{2}}[|(zx)(zx)|-|(yz)(yz)|](\alpha\beta-\beta\alpha)/\sqrt{2}$$

Γ_4Q Representation

$$|1\rangle=\Gamma_{5a}{}^{\mathrm{C}}[{}^3A_{2g}(e_g{}^2)]=-|(z^2)(x^2-y^2)|\Psi_0$$

$$|2\rangle=\Gamma_{5a}{}^{\mathrm{C}}[{}^3T_{2g}(t_{2g}\,e_g)]=\sqrt{\tfrac{1}{2}}\{[\tfrac{1}{2}|(zx)(z^2)|+(\sqrt{3}/2)\ |(zx)(x^2-y^2)|]\Psi_{-1}+[-\tfrac{1}{2}|(yz)(z^2)|+(\sqrt{3}/2)|(yz)\ (x^2-y^2)|]\Psi_1\}$$

$$|3\rangle=\Gamma_{5a}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}\,e_g)]=\sqrt{\tfrac{1}{2}}\{[-\tfrac{1}{2}|(zx)(x^2-y^2)|+(\sqrt{3}/2)|(zx)(z^2)|]\Psi_{-1}+[-\tfrac{1}{2}|(yz)(x^2-y^2)-(\sqrt{3}/2)|(yz)(z^2)|]\Psi_1\}$$

$$|4\rangle=\Gamma_{5a}{}^{\mathrm{C}}[{}^1T_{2g}(t_{2g}\,e_g)]=i\sqrt{\tfrac{1}{2}}[|(xy)(z^2)|+|(z^2)(xy)|](\alpha\beta-\beta\alpha)/\sqrt{2}$$

$$|5\rangle=\Gamma_{5a}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}{}^2)]=\sqrt{\tfrac{1}{2}}[-|(yz)(xy)|\Psi_{-1}+|(zx)(xy)|\Psi_1]$$

$$|6\rangle=\Gamma_{5a}{}^{\mathrm{C}}[{}^1T_{2g}(t_{2g}{}^2)]=i\sqrt{\tfrac{1}{2}}[|(zx)(yz)|+|(yz)(zx)|](\alpha\beta-\beta\alpha)/\sqrt{2}$$

Γ_{5a}Q Representation

$$|1\rangle=\Gamma_{4b}{}^{\mathrm{C}}[{}^3T_{2g}(t_{2g}\,e_g)]=\sqrt{\tfrac{1}{2}}\{|(xy)(z^2)|\Psi_{-1}+[-\tfrac{1}{2}|(yz)(z^2)|+(\sqrt{3}/2)\ |(yz)(x^2-y^2)|]\Psi_0\}$$

$$|2\rangle=\Gamma_{4b}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}\,e_g)]=\sqrt{\tfrac{1}{2}}\{-|(xy)(x^2-y^2)|\Psi_{-1}+[-\tfrac{1}{2}|(yz)(x^2-y^2)|-(\sqrt{3}/2)|(yz)(z)|]\Psi_0\}$$

$$|3\rangle=\Gamma_{4b}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}{}^2)]=\sqrt{\tfrac{1}{2}}[|(xy(zx)|\Psi_0+|(yz)(zx)\Psi_{-1}]$$

$$|4\rangle=\Gamma_{4b}{}^{\mathrm{C}}[{}^1T_{1g}(t_{2g}\,e_g)]=i[-\tfrac{1}{2}|(zx)(x^2-y^2)|+(\sqrt{3}/2)|(zx)(z^2)|](\alpha\beta-\beta\alpha)/\sqrt{2}$$

$$|5\rangle=\Gamma_{5b}{}^{\mathrm{C}}[{}^3A_{2g}(e_g{}^2)]=-|(z^2)(x^2-y^2)|\Psi_1$$

$$|6\rangle=\Gamma_{5b}{}^{\mathrm{C}}[{}^3T_{2g}(t_{2g}\,e_g)]=\sqrt{\tfrac{1}{2}}\{|(xy)(z^2)|\Psi_{-1}-[-\tfrac{1}{2}|(yz)(z^2)|+(\sqrt{3}/2)\ |(yz)(x^2-y^2)|]\Psi_0\}$$

$$|7\rangle=\Gamma_{5b}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}\,e_g)]=\sqrt{\tfrac{1}{2}}\{|(xy)(x^2-y^2)|\Psi_{-1}+[-\tfrac{1}{2}|(yz)(x^2-y^2)|-(\sqrt{3}/2)\ |(yz)(z^2)|]\Psi_0\}$$

$$|8\rangle=\Gamma_{5b}{}^{\mathrm{C}}[{}^1T_{2g}(t_{2g}\,e_g)]=i[-\tfrac{1}{2}|(zx)(z^2)|-(\sqrt{3}/2)|(zx)(x^2-y^2)|](\alpha\beta-\beta\alpha)/\sqrt{2}$$

$$|9\rangle=\Gamma_{5b}{}^{\mathrm{C}}[{}^3T_{1g}(t_{2g}{}^2)]=\sqrt{\tfrac{1}{2}}[-|(xy)(zx)|\Psi_0+|(yz)(zx)|\Psi_{-1}]$$

$$|10\rangle=\Gamma_{5b}{}^{\mathrm{C}}[{}^1T_{2g}(t_{2g}{}^2)]=i\sqrt{\tfrac{1}{2}}[|(yz)(xy)|+|(xy)(yz)|](\alpha\beta-\beta\alpha)/\sqrt{2}.$$

Tab. 5. (b) $\{X, S, t_{2g}, e_g, \Gamma_j\}$ Energy Matrices.

Γ_1^Q Representation

$\langle 1|1\rangle = 12Dq+7Dt+8B+4C$
$\langle 1|2\rangle = -\sqrt{3}\zeta$
$\langle 1|3\rangle = 0$
$\langle 1|4\rangle = \sqrt{6}(2B+C)$
$\langle 1|5\rangle = i(4Ds+5Dt)$
$\langle 1|6\rangle = \langle 1|7\rangle = \langle 1|8\rangle = \langle 1|9\rangle = 0$

$\langle 2|2\rangle = (1/6)(12Dq+7Dt)+4B-(1/2)\zeta$
$\langle 2|3\rangle = -6B+\zeta$
$\langle 2|4\rangle = -\sqrt{2}\zeta$
$\langle 2|5\rangle = 0$
$\langle 2|6\rangle = (-i\sqrt{2}/4)(4Ds+5Dt)$
$\langle 2|7\rangle = (i\sqrt{2}/12)(-24Ds+5Dt)$
$\langle 2|8\rangle = \langle 2|9\rangle = 0$

$\langle 3|3\rangle = -(2/3)(12Dq+7Dt)-5B+\zeta$
$\langle 3|4\rangle = \sqrt{2}\zeta$
$\langle 3|5\rangle = \langle 3|6\rangle = \langle 3|7\rangle = 0$
$\langle 3|8\rangle = (i\sqrt{2}/3)(3Ds-5Dt)$
$\langle 3|9\rangle = 0$

$\langle 4|4\rangle = -(2/3)(12Dq+7Dt)+10B+5C$
$\langle 4|5\rangle = \langle 4|6\rangle = \langle 4|7\rangle = \langle 4|8\rangle = 0$
$\langle 4|9\rangle = -(i2\sqrt{2}/3)(3Ds-5Dt)$

$\langle 5|5\rangle = 12Dq+7Dt+2C$
$\langle 5|6\rangle = (\sqrt{6}/2)\zeta$
$\langle 5|7\rangle = (\sqrt{6}/2)\zeta$
$\langle 5|8\rangle = 0$
$\langle 5|9\rangle = 2\sqrt{3}B$

$\langle 6|6\rangle = (1/4)(8Dq-7Dt)-8B+(1/4)\zeta$
$\langle 6|7\rangle = (1/4)(4Ds+5Dt)-(3/4)\zeta$
$\langle 6|8\rangle = (-3/2)\zeta$
$\langle 6|9\rangle = 0$

$\langle 7|7\rangle = (1/12)(24Dq-24Ds+19Dt)+4B+(1/4)\zeta$
$\langle 7|8\rangle = -6B-(1/2)\zeta$
$\langle 7|9\rangle = -\sqrt{2}\zeta$

$\langle 8|8\rangle = (1/3)(-24Dq+3Ds-19Dt)-5B-(1/2)\zeta$
$\langle 8|9\rangle = (-\sqrt{2}/2)\zeta$

$\langle 9|9\rangle = (-2/3)(12Dq+3Ds+2Dt)+B+2C$

Γ_2^Q Representation

$\langle 1|1\rangle = (1/4)(8Dq-7Dt)-8B+(1/4)\zeta$
$\langle 1|2\rangle = (-\sqrt{3}/4)(4Ds+5Dt)+(\sqrt{3}/4)\zeta$
$\langle 1|3\rangle = (\sqrt{3}/2)\zeta$
$\langle 1|4\rangle = (\sqrt{6}/4)\zeta$

$\langle 2|2\rangle = (1/4)(8Dq+8Ds+3Dt)+4B-(1/4)\zeta$
$\langle 2|3\rangle = -6B+(1/2)\zeta$
$\langle 2|4\rangle = (\sqrt{2}/4)\zeta$

$\langle 3|3\rangle = -8Dq-Ds-3Dt-5B+(1/2)\zeta$
$\langle 3|4\rangle = (\sqrt{2}/2)\zeta$

$\langle 4|4\rangle = 2Dq-4Ds+2Dt+4B+2C$

Γ_3^Q Representation

$\langle 1|1\rangle = (1/6)(12Dq+7Dt)-8B-(1/2)\zeta$
$\langle 1|2\rangle = 0$
$\langle 1|3\rangle = (35\sqrt{2}/12)Dt$
$\langle 1|4\rangle = (\sqrt{2}/4)(4Ds+5Dt)$
$\langle 1|5\rangle = \langle 1|6\rangle = 0$

$\langle 2|2\rangle = 12Dq+7Dt+2C$
$\langle 2|3\rangle = (\sqrt{6}/2)\zeta$
$\langle 2|4\rangle = (\sqrt{6}/2)\zeta$
$\langle 2|5\rangle = 0$
$\langle 2|6\rangle = 2\sqrt{3}B$

$\langle 3|3\rangle = (1/12)(24Dq+49Dt)-8B+(1/4)\zeta$
$\langle 3|4\rangle = (-1/4)(4Ds+5Dt)-(3/4)\zeta$
$\langle 3|5\rangle = (-3/2)\zeta$
$\langle 3|6\rangle = 0$

$\langle 4|4\rangle = (1/4)(8Dq+8Ds+3Dt)+4B+(1/4)\zeta$
$\langle 4|5\rangle = -6B-(1/2)\zeta$
$\langle 4|6\rangle = -\sqrt{2}\zeta$

$\langle 5|5\rangle = -8Dq-Ds-3Dt-5B-(1/2)\zeta$
$\langle 5|6\rangle = (-\sqrt{2}/2)\zeta$

$\langle 6|6\rangle = -8Dq+2Ds-8Dt+B+2C$

Γ_4^Q Representation

$\langle 1|1\rangle = 12Dq+7Dt-8B$
$\langle 1|2\rangle = \sqrt{2}\zeta$
$\langle 1|3\rangle = 0$
$\langle 1|4\rangle = \zeta$
$\langle 1|5\rangle = \langle 1|6\rangle = 0$

$\langle 2|2\rangle = (1/4)(8Dq-7Dt)-8B-(1/4)\zeta$
$\langle 2|3\rangle = (\sqrt{3}/4)(4Ds+5Dt)+(\sqrt{3}/4)\zeta$
$\langle 2|4\rangle = (-\sqrt{2}/4)\zeta$
$\langle 2|5\rangle = (-\sqrt{3}/2)\zeta$
$\langle 2|6\rangle = (\sqrt{6}/2)\zeta$

$\langle 3|3\rangle = (1/4)(8Dq+8Ds+3Dt)+4B+(1/4)\zeta$
$\langle 3|4\rangle = (-\sqrt{6}/4)\zeta$
$\langle 3|5\rangle = 6B+(1/2)\zeta$
$\langle 3|6\rangle = (\sqrt{2}/2)\zeta$

$\langle 4|4\rangle = 2Dq+7Dt+2C$
$\langle 4|5\rangle = (-\sqrt{6}/2)\zeta$
$\langle 4|6\rangle = 2\sqrt{3}B$

$\langle 5|5\rangle = -8Dq-Ds-3Dt-5B-(1/2)\zeta$
$\langle 5|6\rangle = (\sqrt{2}/2)\zeta$

$\langle 6|6\rangle = -8Dq+2Ds-8Dt+B+2C$

Γ_5^Q Representation

$\langle 1|1\rangle = (1/8)(16Dq+21Dt)-8B+(1/4)\zeta$
$\langle 1|2\rangle = =(\sqrt{3}/8)(4Ds+5Dt)+(\sqrt{3}/4)\zeta$
$\langle 1|3\rangle = (\sqrt{3}/2)\zeta$
$\langle 1|4\rangle = (\sqrt{6}/4)\zeta$

Tabelle 5 b

$$\langle 1|5\rangle = 0$$
$$\langle 1|6\rangle = (35/8)\,D\,t$$
$$\langle 1|7\rangle = (\sqrt{3}/8)\,(4\,D\,s+5\,D\,t)$$
$$\langle 1|8\rangle = \langle 1|9\rangle = \langle 1|10\rangle = 0$$
$$\langle 2|2\rangle = (1/8)\,(16\,D\,q-8\,D\,s+11\,D\,t)+4\,B-(1/4)\,\zeta$$
$$\langle 2|3\rangle = -6\,B+(1/2)\,\zeta$$
$$\langle 2|4\rangle = (\sqrt{2}/4)\,\zeta$$
$$\langle 2|5\rangle = 0$$
$$\langle 2|6\rangle = (-\sqrt{3}/8)\,(4\,D\,s+5\,D\,t)$$
$$\langle 2|7\rangle = (1/8)\,(24\,D\,s-5\,D\,t)$$
$$\langle 2|8\rangle = \langle 2|9\rangle = \langle 2|10\rangle = 0$$
$$\langle 3|3\rangle = (1/2)\,(-16\,D\,q+D\,s-11\,D\,t)-5\,B+(1/2)\,\zeta$$
$$\langle 3|4\rangle = (\sqrt{2}/2)\,\zeta$$
$$\langle 3|5\rangle = \langle 3|6\rangle = \langle 3|7\rangle = \langle 3|8\rangle = 0$$
$$\langle 3|9\rangle = (1/2)\,(3\,D\,s-5\,D\,t)$$
$$\langle 3|10\rangle = 0$$
$$\langle 4|4\rangle = (1/4)\,(8\,D\,q+8\,D\,s+3\,D\,t)+4\,B+2\,C$$
$$\langle 4|5\rangle = \langle 4|6\rangle = \langle 4|7\rangle = 0$$
$$\langle 4|8\rangle = (-\sqrt{3}/4)\,(4\,D\,s+5\,D\,t)$$
$$\langle 4|9\rangle = \langle 4|10\rangle = 0$$
$$\langle 5|5\rangle = 12\,D\,q+7\,D\,t-8\,B$$
$$\langle 5|6\rangle = \sqrt{2}\,\zeta$$
$$\langle 5|7\rangle = 0$$
$$\langle 5|8\rangle = \zeta$$
$$\langle 5|9\rangle = \langle 5|10\rangle = 0$$
$$\langle 6|6\rangle = (1/8)\,(16\,D\,q+21\,D\,t)-8\,B-(1/4)\,\zeta$$
$$\langle 6|7\rangle = (-\sqrt{3}/8)\,(4\,D\,s+5\,D\,t)+(\sqrt{3}/4)\,\zeta$$
$$\langle 6|8\rangle = (-\sqrt{2}/4)\,\zeta$$
$$\langle 6|9\rangle = (-\sqrt{3}/2)\,\zeta$$
$$\langle 6|10\rangle = (\sqrt{6}/2)\,\zeta$$
$$\langle 7|7\rangle = (1/8)\,(16\,D\,q-8\,D\,s+11\,D\,t)+4\,B+(1/4)\,\zeta$$
$$\langle 7|8\rangle = (-\sqrt{6}/4)\,\zeta$$
$$\langle 7|9\rangle = 6\,B+(1/2)\,\zeta$$
$$\langle 7|10\rangle = (\sqrt{2}/2)\,\zeta$$
$$\langle 8|8\rangle = (1/4)\,(8\,D\,q-7\,D\,t)+2\,C$$
$$\langle 8|9\rangle = (-\sqrt{6}/2)\,\zeta$$
$$\langle 8|10\rangle = 2\sqrt{3}\,B$$
$$\langle 9|9\rangle = (1/2)\,(-16\,D\,q+D\,s-11\,D\,t)-5\,B-(1/2)\,\zeta$$
$$\langle 9|10\rangle = (\sqrt{2}/2)\,\zeta$$
$$\langle 10|10\rangle = -8\,D\,q-D\,s-3\,D\,t+B+2\,C$$

of the other states are given in Tables 3 and 4. The symmetry transformation properties of linear combinations of spin functions follow from those of the single spin functions $|1/2, 1/2\rangle$ and $|1/2, -1/2\rangle$ denoted by α and β. The transformation matrices of the spin functions can be obtained by the substitution of angular values into the spinor array of GOLDSTEIN [8], once the angles are fixed by identifying the transformation matrix of the symmetry operation with the Eulerian matrix of Goldstein. For instance, C_3 operation results in the following spinor matrix:

$$C_3(z')\begin{pmatrix}\alpha\\ \\ \beta\end{pmatrix}=\begin{pmatrix}\frac{e^{\pi i/4}}{\sqrt{2}} & \frac{i\,e^{\pi i/4}}{\sqrt{2}}\\ \frac{i\,e^{-\pi i/4}}{\sqrt{2}} & \frac{e^{-\pi i/4}}{\sqrt{2}}\end{pmatrix}\begin{pmatrix}\alpha\\ \\ \beta\end{pmatrix}. \tag{3}$$

It should be noted that the spin functions of Table 4 are also azimuthally quantized along the three-fold z'-axis rather than along the tetragonal z-axis. Thus, the transformation matrices of the symmetry operations on the trigonally quantized spin functions are as follows.

$$C_3(z')\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix}=\begin{pmatrix}\omega^{1/2} & 0\\ 0 & \omega^{-1/2}\end{pmatrix}\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix}, \tag{4 a}$$

$$C_2(y')\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix}=\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix}, \tag{4 b}$$

$$C_4(z)\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix}=\begin{pmatrix}\sqrt{\tfrac{2}{3}}\,e^{\pi i/6} & i\sqrt{\tfrac{1}{3}}\\ i\sqrt{\tfrac{1}{3}} & \sqrt{\tfrac{2}{3}}\,e^{-\pi i/6}\end{pmatrix}\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix} \tag{4 c}$$

where $\omega = e^{2\pi i/3}$. The triplet spin function transforms as t_1 representation and the linear combinations are so constructed with exactly the same behavior under symmetry operations as the t_1 orbital representation. Construction of two electron symmetry adapted wave functions in both spin and coordinate space is best illustrated by considering an example. For this purpose we choose the ${}^3T_{1g}{}^{C}$ of $t_{2g}{}^2$ configuration and discuss the quadrate and trigonal cases separately.

The ${}^3T_{1g}\,(t_{2g}{}^2)$ state under inclusion of spin-orbit interaction gives rise to the cubic spin-orbital states $\Gamma_1{}^{C}+\Gamma_3{}^{C}+\Gamma_4{}^{C}+\Gamma_5{}^{C}$ which on going to quadrate symmetry further decompose to $\Gamma_1{}^{Q}+(\Gamma_1{}^{Q}+\Gamma_3{}^{Q})+(\Gamma_2{}^{Q}+\Gamma_5{}^{Q})+(\Gamma_4{}^{Q}+\Gamma_5{}^{Q})$ quadrate states. The orbital components of the ${}^3T_{1g}$ state are, $a=|(z\,x)(y\,z)|$, $b=|(y\,z)\,(x\,y)|$, and $c=-|(z\,x)\,(x\,y)|$. The a, b, c components of t_1 representation to which the triplet spin function transforms are listed in Table 3. Those quadrate states which occur only once can be written down immediately by identifying with the transformation behavior of orbital-spin determinants. Thus, since $[|t_{1b}\,t_{1c}|-|t_{1c}\,t_{1b}|]$, $[|t_{1b}\,t_{1b}|-|t_{1c}\,t_{1c}|]$, and $[|t_{1b}\,t_{1c}|+|t_{1c}\,t_{1b}|]$ transform, respectively, as $\Gamma_2{}^{Q}$, $\Gamma_3{}^{Q}$, and $\Gamma_4{}^{Q}$, the corresponding wave functions, including normalization, are:

$$\Gamma_2^{Q}\{\Gamma_{4a}^{C}[^3T_{1g}(t_{2g}^2)]\} = \frac{1}{\sqrt{2}}\left\{|(yz)(xy)|\left[-\frac{(\alpha\alpha-\beta\beta)}{\sqrt{2}}\right]+|(zx)(xy)|\left[i\frac{(\alpha\alpha+\beta\beta)}{\sqrt{2}}\right]\right\},$$

$$\Gamma_3^{Q}\{\Gamma_{3b}^{C}[^3T_{1g}(t_{2g}^2)]\} = \frac{1}{\sqrt{2}}\left\{|(yz)(xy)|\left[i\frac{(\alpha\alpha+\beta\beta)}{\sqrt{2}}\right]+|(zx)(xy)|\left[-\frac{(\alpha\alpha-\beta\beta)}{\sqrt{2}}\right]\right\},$$

$$\Gamma_4^{Q}\{\Gamma_{5a}^{C}[^3T_{1g}(t_{2g}^2)]\} = \frac{1}{\sqrt{2}}\left\{|(yz)(xy)|\left[-\frac{(\alpha\alpha-\beta\beta)}{\sqrt{2}}\right]-|(zx)(xy)|\left[i\frac{(\alpha\alpha+\beta\beta)}{\sqrt{2}}\right]\right\}.$$

One of the Γ_1^{Q}, namely the $\Gamma_1^{Q}\{\Gamma_{3a}^{C}\}$ can be immediately obtained by carrying out $C_3(z')$ operation on $\Gamma_3^{Q}\{\Gamma_{3b}^{C}\}$ and equating the result with $-1/2\,\Gamma_{3b}+\sqrt{3}/2\,\Gamma_{3a}$. The other Γ_1^{Q}, i. e., $\Gamma_1^{Q}\{\Gamma_1^{C}[^3T_{1g}(t_{2g}^2)]\}$ should be orthogonal to $\Gamma_1^{Q}\{\Gamma_{3a}^{C}\}$. The correctness of this orthogonal function can be checked by its deportment under $C_4(z)$ and $C_3(z')$ operations by which it should be transformed into itself. The a component of the Γ_5^{Q} states of Γ_4^{C} and Γ_5^{C} can be derived by $C_3(z')$ operation on Γ_2^{Q} and Γ_4^{Q}, respectively. Further $C_3(z')$ operation on the a component will yield the other component of the Γ_5^{Q} state. The complete set of symmetry adapted octahedrally oriented quadrate d^2 wave functions thus obtained are given in Table 5 a [9].

The $\Gamma_1^{C}+\Gamma_3^{C}+\Gamma_4^{C}+\Gamma_5^{C}$ cubic spin-orbital states of $^3T_{1g}(t_{2g}^2)$ in trigonal symmetry give rise to $\Gamma_1^{T}+\Gamma_3^{T}+(\Gamma_2^{T}+\Gamma_3^{T})+(\Gamma_1^{T}+\Gamma_3^{T})$ states. By an examination of the transformation behavior of the determinantal products under symmetry operations, the orbital components of $^3T_{1g}(t_{2g}^2)$ are seen to be [4a, 10]

a: $|e_+(t_{2g})\,e_-(t_{2g})|$, b: $-|a_1(t_{2g})\,e_+(t_{2g})|$, and c: $|a_1(t_{2g})\,e_-(t_{2g})|$.

Now the triplet spin function transforms as t_1, the three components of which along with their symmetry properties are included in Table 4. Denoting the a, b, c components of t_1 (both spin and space) as $a_2(t_1)$, $e_+(t_1)$, and $e_-(t_1)$, we investigate the symmetry properties of the determinantal products $|a_2(t_1)\,a_2(t_1)|$, $|a_2(t_1)\,e_\pm(t_1)|$, and $|e_\pm(t_1)\,e_\pm(t_1)|$ arriving at the results collected in Table 6.

Table 6. Transformation Properties of Trigonal Orbital-Spin Determinants.

Function	$C_3(z')$	$C_2(y')$
$\lvert a_2(t_1)\ \ a_2(t_1)\rvert=\varphi_1$	φ_1	φ_1
$\lvert a_2(t_1)\ \ e_+(t_1)\rvert=\varphi_2$	$\omega^{+1}\varphi_2$	φ_3
$\lvert a_2(t_1)\ \ e_-(t_1)\rvert=\varphi_3$	$\omega^{-1}\varphi_3$	φ_2
$\lvert e_+(t_1)\ e_+(t_1)\rvert=\varphi_4$	$\omega^{-1}\varphi_4$	φ_5
$\lvert e_-(t_1)\ e_-(t_1)\rvert=\varphi_5$	$\omega^{+1}\varphi_5$	φ_4
$\lvert e_+(t_1)\ e_-(t_1)\rvert=\varphi_6$	φ_6	φ_7
$\lvert e_-(t_1)\ e_+(t_1)\rvert=\varphi_7$	φ_7	φ_6
$\varphi_6+\varphi_7=\psi_1$	ψ_1	ψ_1
$\varphi_6-\varphi_7=\psi_2$	ψ_2	$-\psi_2$

It is immediately obvious that ψ_2 is the desired function correctly transforming as the unique Γ_2^{T} state. Thus,

$$\Gamma_2^{T}=\Gamma_{4a}^{C}=1/\sqrt{2}\,[-|a_1(t_{2g})\,e_+(t_{2g})|\,(\beta'\beta') -|a_1(t_{2g})\,e_-(t_{2g})|\,(-\alpha'\alpha')].$$

The two components of Γ_3^{T} corresponding to $\Gamma_{4b,c}^{C}$ can be obtained by carrying out $C_4(z)$ operation on Γ_2^{T}. Thus, after some algebraic manipulation, it can be shown that

$$\begin{aligned}C_4(z)\,[\Gamma_2^{T}(\Gamma_{4a}^{C})] &= C_4(z)\{1/\sqrt{2}[-|a_1(t_{2g})\,e_+(t_{2g})|\,(\beta'\beta') -|a_1(t_{2g})\,e_-(t_{2g})|\,(-\alpha'\alpha')]\}\\ &= 1/\sqrt{2}\,\Big\{1/3[-|a_1(t_{2g})\,e_+(t_{2g})|\,(\beta'\beta') -|a_1(t_{2g})\,e_-(t_{2g})|\,(-\alpha'\alpha')]\\ &\quad +2/3\,\omega^{-1/2}\Big[|e_+(t_{2g})\,e_-(t_{2g})|\,(-\alpha'\alpha') +|a_1(t_{2g})\,e_+(t_{2g})|\,\frac{(\alpha'\beta'+\beta'\alpha')}{\sqrt{2}}\Big]\\ &\quad +2/3\,\omega^{+1/2}\Big[-|e_+(t_{2g})\,e_-(t_{2g})|\,(\beta'\beta') +|a_1(t_{2g})\,e_-(t_{2g})|\,\frac{(\alpha'\beta'+\beta'\alpha')}{\sqrt{2}}\Big]\Big\}\end{aligned}$$

which when compared with the transformation properties of Table 4 yields the result that

$$1/\sqrt{2}\left[|e_+(t_{2g})\,e_-(t_{2g})|\,(-\alpha'\alpha') +|a_1(t_{2g})\,e_+(t_{2g})|\frac{(\alpha'\beta'+\beta'\alpha')}{\sqrt{2}}\right]=\Gamma_{3a}^{T}(\Gamma_{4b}^{C})$$

and

$$1/\sqrt{2}\left[-|e_+(t_{2g})\,e_-(t_{2g})|\,(\beta'\beta') +|a_1(t_{2g})\,e_-(t_{2g})|\frac{(\alpha'\beta'+\beta'\alpha')}{\sqrt{2}}\right]=\Gamma_{3b}^{T}(\Gamma_{4c}^{C}).$$

It can also be noted from Table 6 that a generalized combination of functions for a $\Gamma_1{}^{\mathrm{T}}$ state is $c_1\varphi_1+c_2\psi_1$. The coefficients c_1 and c_2 in the $\Gamma_1{}^{\mathrm{T}}\{\Gamma_1{}^{\mathrm{C}}\}$ state are obtained by insuring that the $\mathrm{C}_4(z)$ operation carries it into itself. The $\Gamma_1{}^{\mathrm{T}}\{\Gamma_{5\mathrm{a}}{}^{\mathrm{C}}\}$ state is then formed as the orthogonal combination to $\Gamma_1{}^{\mathrm{T}}\{\Gamma_1{}^{\mathrm{C}}\}$. The $\mathrm{C}_4(z)$ operation on $\Gamma_1{}^{\mathrm{T}}\{\Gamma_{5\mathrm{a}}{}^{\mathrm{C}}\}$ state yields the two components of $\Gamma_3{}^{\mathrm{T}}$ corresponding to $\Gamma_{5\mathrm{b,c}}{}^{\mathrm{C}}$. Finally, the $\Gamma_3{}^{\mathrm{T}}$ state resulting from the $\Gamma_3{}^{\mathrm{C}}$ can be gotten by making it orthogonal to the other two $\Gamma_3{}^{\mathrm{T}}$ states. The complete set of symmetry adapted spin-orbital wave functions thus derived are listed in Table 7 a [9].

Table 7. Trigonal Wave Functions and Energy Matrices in $\{X, S, t_{2\mathrm{g}}, e_{\mathrm{g}}, \Gamma_j\}$ Representation.

(a) $|X, S, t_{2\mathrm{g}}, \mathrm{e_g}, \Gamma_j\rangle$ Functions

$\Gamma_1{}^{\mathrm{T}}$ Representation

$$|1\rangle=\Gamma_1{}^{\mathrm{C}}[{}^1A_{1\mathrm{g}}(e_{\mathrm{g}}{}^2)] = \sqrt{\tfrac{1}{2}}[|e_+(e_{\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_-(e_{\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(\alpha'\beta'-\beta'\alpha')/\sqrt{2}$$

$$\begin{aligned}|2\rangle=\Gamma_1{}^{\mathrm{C}}[{}^3T_{1\mathrm{g}}(t_{2\mathrm{g}}\,e_{\mathrm{g}})] = \sqrt{\tfrac{1}{6}}\{&[-|e_+(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_-(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(\alpha'\beta'+\beta'\alpha')/\sqrt{2}\\ &+[|a_1(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_+(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(-\alpha'\alpha')\\ &-[|a_1(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|+|e_-(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|]\,(\beta'\beta')\}\end{aligned}$$

$$\begin{aligned}|3\rangle=\Gamma_1{}^{\mathrm{C}}[{}^3T_{1\mathrm{g}}(t_{2\mathrm{g}}{}^2)] = \sqrt{\tfrac{1}{3}}[&-|e_+(t_{2\mathrm{g}})\,e_-(t_{2\mathrm{g}})|\,(\alpha'\beta'+\beta'\alpha')/\sqrt{2}\\ &-|a_1(t_{2\mathrm{g}})\,e_-(t_{2\mathrm{g}})|\,(-\alpha'\alpha')+|a_1(t_{2\mathrm{g}})\,e_+(t_{2\mathrm{g}})|\,(\beta'\beta')]\end{aligned}$$

$$|4\rangle=\Gamma_1{}^{\mathrm{C}}[{}^1A_{1\mathrm{g}}(t_{2\mathrm{g}}{}^2)] = \sqrt{\tfrac{1}{3}}[|a_1(t_{2\mathrm{g}})\,a_1(t_{2\mathrm{g}})|+|e_+(t_{2\mathrm{g}})\,e_-(t_{2\mathrm{g}})|+|e_-(t_{2\mathrm{g}})\,e_+(t_{2\mathrm{g}})|]\,(\alpha'\beta'-\beta'\alpha')/\sqrt{2}$$

$$|5\rangle=\Gamma_{5\mathrm{a}}{}^{\mathrm{C}}[{}^3A_{2\mathrm{g}}(e_{\mathrm{g}}{}^2)] = |e_+(e_{\mathrm{g}})\,e_-(e_{\mathrm{g}})|\,(\alpha'\beta'+\beta'\alpha')/\sqrt{2}$$

$$\begin{aligned}|6\rangle=\Gamma_{5\mathrm{a}}{}^{\mathrm{C}}[{}^3T_{2\mathrm{g}}(t_{2\mathrm{g}}\,e_{\mathrm{g}})] = \tfrac{1}{2}\{&[|a_1(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|-|e_+(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(-\alpha'\alpha')\\ &-[|a_1(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|-|e_-(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|]\,(\beta'\beta')\}\end{aligned}$$

$$\begin{aligned}|7\rangle=\Gamma_{5\mathrm{a}}{}^{\mathrm{C}}[{}^3T_{1\mathrm{g}}(t_{2\mathrm{g}}\,e_{\mathrm{g}})] = \frac{1}{2\sqrt{3}}\{&2[|e_+(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|-|e_-(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(\alpha'\beta'+\beta'\alpha')/\sqrt{2}\\ &+[|a_1(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_+(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(-\alpha'\alpha')-[|a_1(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|+|e_-(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|]\,(\beta'\beta')\}\end{aligned}$$

$$\begin{aligned}|8\rangle=\Gamma_{5\mathrm{a}}{}^{\mathrm{C}}[{}^1T_{2\mathrm{g}}(t_{2\mathrm{g}}\,e_{\mathrm{g}})] = \tfrac{1}{2}[&|e_+(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_-(e_{\mathrm{g}})\,e_+(t_{2\mathrm{g}})|\\ &+|e_-(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|+|e_+(e_{\mathrm{g}})\,e_-(t_{2\mathrm{g}})|]\,(\alpha'\beta'-\beta'\alpha')/\sqrt{2}\end{aligned}$$

$$\begin{aligned}|9\rangle=\Gamma_{5\mathrm{a}}{}^{\mathrm{C}}[{}^3T_{1\mathrm{g}}(t_{2\mathrm{g}}{}^2)] = \sqrt{\tfrac{1}{6}}[&-2|e_+(t_{2\mathrm{g}})\,e_-(t_{2\mathrm{g}})|\,(\alpha'\beta'+\beta'\alpha')/\sqrt{2}\\ &+|a_1(t_{2\mathrm{g}})\,e_-(t_{2\mathrm{g}})|\,(-\alpha'\alpha')-|a_1(t_{2\mathrm{g}})\,e_+(t_{2\mathrm{g}})|\,(\beta'\beta')]\end{aligned}$$

$$|10\rangle=\Gamma_{5\mathrm{a}}{}^{\mathrm{C}}[{}^1T_{2\mathrm{g}}(t_{2\mathrm{g}}{}^2)] = \sqrt{\tfrac{1}{6}}[-2|a_1(t_{2\mathrm{g}})\,a_1(t_{2\mathrm{g}})|+|e_+(t_{2\mathrm{g}})\,e_-(t_{2\mathrm{g}})|+|e_-(t_{2\mathrm{g}})\,e_+(t_{2\mathrm{g}})|]\,(\alpha'\beta'-\beta'\alpha')/\sqrt{2}$$

$\Gamma_2{}^{\mathrm{T}}$ Representation

$$\begin{aligned}|1\rangle=\Gamma_2{}^{\mathrm{C}}[{}^3T_{2\mathrm{g}}(t_{2\mathrm{g}}\,e_{\mathrm{g}})] = \sqrt{\tfrac{1}{6}}\{&[|e_+(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_-(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(\alpha'\beta'+\beta'\alpha')/\sqrt{2}\\ &-[|a_1(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|-|e_+(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(-\alpha'\alpha')\\ &-[|a_1(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|-|e_-(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|]\,(\beta'\beta')\}\end{aligned}$$

$$\begin{aligned}|2\rangle=\Gamma_{4\mathrm{a}}{}^{\mathrm{C}}[{}^3T_{2\mathrm{g}}(t_{2\mathrm{g}}\,e_{\mathrm{g}})] = \frac{1}{2\sqrt{3}}\{&2[|e_+(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_-(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(\alpha'\beta'+\beta'\alpha')/\sqrt{2}\\ &+[|a_1(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|-|e_+(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(-\alpha'\alpha')\\ &+[|a_1(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|-|e_-(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|]\,(\beta'\beta')\}\end{aligned}$$

$$\begin{aligned}|3\rangle=\Gamma_{4\mathrm{a}}{}^{\mathrm{C}}[{}^3T_{1\mathrm{g}}(t_{2\mathrm{g}}\,e_{\mathrm{g}})] = \tfrac{1}{2}\{&[|a_1(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_+(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(-\alpha'\alpha')\\ &+[|a_1(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|+|e_-(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|]\,(\beta'\beta')\}\end{aligned}$$

$$|4\rangle=\Gamma_{4\mathrm{a}}{}^{\mathrm{C}}[{}^3T_{1\mathrm{g}}(t_{2\mathrm{g}}{}^2)] = -\sqrt{\tfrac{1}{2}}[|a_1(t_{2\mathrm{g}})\,e_-(t_{2\mathrm{g}})|(-\alpha'\alpha')+|a_1(t_{2\mathrm{g}})\,e_+(t_{2\mathrm{g}})|\,(\beta'\beta')]$$

$$\begin{aligned}|5\rangle=\Gamma_{4\mathrm{a}}{}^{\mathrm{C}}[{}^1T_{1\mathrm{g}}(t_{2\mathrm{g}}\,e_{\mathrm{g}})] = \tfrac{1}{2}[&-|e_+(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|-|e_-(e_{\mathrm{g}})\,e_+(t_{2\mathrm{g}})|\\ &+|e_-(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|+|e_+(e_{\mathrm{g}})\,e_-(t_{2\mathrm{g}})|]\,(\alpha'\beta'-\beta'\alpha')/\sqrt{2}\end{aligned}$$

$\Gamma_{3\mathrm{a}}{}^{\mathrm{T}}$ Representation

$$|1\rangle=\Gamma_{3\mathrm{a}}{}^{\mathrm{C}}[{}^1E_{\mathrm{g}}(e_{\mathrm{g}}{}^2)] = |e_-(e_{\mathrm{g}})\,e_-(e_{\mathrm{g}})|\,(\alpha'\beta'-\beta'\alpha')/\sqrt{2}$$

$$\begin{aligned}|2\rangle=\Gamma_{3\mathrm{a}}{}^{\mathrm{C}}[{}^3T_{2\mathrm{g}}(t_{2\mathrm{g}}\,e_{\mathrm{g}})] = \sqrt{\tfrac{1}{6}}\{&[|a_1(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|-|e_-(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|]\,(\alpha'\beta'+\beta'\alpha')/\sqrt{2}\\ &-[|e_+(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_-(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(-\alpha'\alpha')\\ &-[-|a_1(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_+(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(\beta'\beta')\}\end{aligned}$$

$$\begin{aligned}|3\rangle=\Gamma_{3\mathrm{a}}{}^{\mathrm{C}}[{}^3T_{1\mathrm{g}}(t_{2\mathrm{g}}\,e_{\mathrm{g}})] = \sqrt{\tfrac{1}{6}}\{&-[|a_1(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|+|e_-(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|]\,(\alpha'\beta'+\beta'\alpha')/\sqrt{2}\\ &-[|e_+(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|-|e_-(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(-\alpha'\alpha')\\ &+[|a_1(t_{2\mathrm{g}})\,e_-(e_{\mathrm{g}})|+|e_+(t_{2\mathrm{g}})\,e_+(e_{\mathrm{g}})|]\,(\beta'\beta')\}\end{aligned}$$

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$$|4\rangle = \Gamma_{3a}{}^{C}[{}^3T_{1g}(t_{2g}{}^2)] = \sqrt{\tfrac{1}{3}}[|a_1(t_{2g})\ e_+(t_{2g})|\ (\alpha'\beta'+\beta'\alpha')/\sqrt{2} - |e_+(t_{2g})\ e_-(t_{2g})|\ (-\alpha'\alpha') - |a_1(t_{2g})\ e_-(t_{2g})|\ (\beta'\beta')]$$

$$|5\rangle = \Gamma_{3a}{}^{C}[{}^1E_g(t_{2g}{}^2)] = \sqrt{\tfrac{1}{3}}[-|a_1(t_{2g})\ e_+(t_{2g})| - |e_+(t_{2g})\ a_1(t_{2g})| + |e_-(t_{2g})\ e_-(t_{2g})|]\ (\alpha'\beta'-\beta'\alpha')/\sqrt{2}$$

$$|6\rangle = \Gamma_{4b}{}^{C}[{}^3T_{2g}(t_{2g}\ e_g)] = \frac{1}{2\sqrt{3}}\{[|a_1(t_{2g})\ e_+(e_g)| - |e_-(t_{2g})\ e_-(e_g)|]\ (\alpha'\beta'+\beta'\alpha')/\sqrt{2}$$
$$-[|e_+(t_{2g})\ e_-(e_g)| + |e_-(t_{2g})\ e_+(e_g)|]\ (-\alpha'\alpha')$$
$$+2[-|a_1(t_{2g})\ e_-(e_g)| + |e_+(t_{2g})\ e_+(e_g)|]\ (\beta'\beta')\}$$

$$|7\rangle = \Gamma_{4b}{}^{C}[{}^3T_{1g}(t_{2g}\ e_g)] = \tfrac{1}{2}\{-[|a_1(t_{2g})\ e_+(e_g)| + |e_-(t_{2g})\ e_-(e_g)|]\ (\alpha'\beta'+\beta'\alpha')/\sqrt{2}$$
$$+[|e_+(t_{2g})\ e_-(e_g)| - |e_-(t_{2g})\ e_+(e_g)|]\ (-\alpha'\alpha')\}$$

$$|8\rangle = \Gamma_{4b}{}^{C}[{}^3T_{1g}(t_{2g}{}^2)] = \sqrt{\tfrac{1}{2}}[|a_1(t_{2g})\ e_+(t_{2g})|\ (\alpha'\beta'+\beta'\alpha')/\sqrt{2} + |e_+(t_{2g})\ e_-(t_{2g})|\ (-\alpha'\alpha')]$$

$$|9\rangle = \Gamma_{4b}{}^{C}[{}^1T_{1g}(t_{2g}\ e_g)] = -\tfrac{1}{2}[|a_1(t_{2g})\ e_+(e_g)| + |e_+(e_g)\ a_1(t_{2g})| + |e_-(t_{2g})\ e_-(e_g)| + |e_-(e_g)\ e_-(t_{2g})|]\ (\alpha'\beta'-\beta'\alpha')/\sqrt{2}$$

$$|10\rangle = \Gamma_{5b}{}^{C}[{}^3A_{2g}(e_g{}^2)] = -|e_+(e_g)\ e_-(e_g)|\ (-\alpha'\alpha')$$

$$|11\rangle = \Gamma_{5b}{}^{C}[{}^3T_{2g}(t_{2g}\ e_g)] = \tfrac{1}{2}\{[-|a_1(t_{2g})\ e_+(e_g)| + |e_-(t_{2g})\ e_-(e_g)|]\ (\alpha'\beta'+\beta'\alpha')/\sqrt{2}$$
$$-[|e_+(t_{2g})\ e_-(e_g)| + |e_-(t_{2g})\ e_+(e_g)|]\ (-\alpha'\alpha')\}$$

$$|12\rangle = \Gamma_{5b}{}^{C}[{}^3T_{1g}(t_{2g}\ e_g)] = \frac{1}{2\sqrt{3}} = \tfrac{1}{2}\{[|a_1(t_{2g})\ e_+(e_g)| + |e_-(t_{2g})\ e_-(e_g)|]\ (\alpha'\beta'+\beta'\alpha')/\sqrt{2}$$
$$+[|e_+(t_{2g})\ e_-(e_g)| - |e_-(t_{2g})\ e_+(e_g)|]\ (-\alpha'\alpha')$$
$$+2[|a_1(t_{2g})\ e_-(e_g)| + |e_+(t_{2g})\ e_+(e_g)|]\ (\beta'\beta')\}$$

$$|13\rangle = \Gamma_{5b}{}^{C}[{}^1T_{2g}(t_{2g}\ e_g)] = \tfrac{1}{2}[|a_1(t_{2g})\ e_+(e_g)| + |e_+(e_g)\ a_1(t_{2g})| - |e_-(t_{2g})\ e_-(e_g)| - |e_-(e_g)\ e_-(t_{2g})|]\ (\alpha'\beta'-\beta'\alpha')/\sqrt{2}$$

$$|14\rangle = \Gamma_{5b}{}^{C}[{}^3T_{1g}(t_{2g}{}^2)] = \sqrt{\tfrac{1}{8}}[|a_1(t_{2g})\ e_+(t_{2g})|\ (\alpha'\beta'+\beta'\alpha')/\sqrt{2}$$
$$-|e_+(t_{2g})\ e_-(t_{2g})|\ (-\alpha'\alpha') + 2|a_1(t_{2g})\ e_-(t_{2g})|\ (\beta'\beta')]$$

$$|15\rangle = \Gamma_{5b}{}^{C}[{}^1T_{2g}(t_{2g}{}^2)] = \sqrt{\tfrac{1}{6}}[|a_1(t_{2g})\ e_+(t_{2g})| + |e_+(t_{2g})\ a_1(t_{2g})| + 2|e_-(t_{2g})\ e_-(t_{2g})|]\ (\alpha'\beta'-\beta'\alpha')/\sqrt{2}$$

Table 7. (**b**) $\{X, S, t_{2g}, e_g, \Gamma_j\}$ Energy Matrices.

$\Gamma_1{}^T$ **Representation**

$\langle 1|1\rangle = (2/3)(18Dq-7D\tau)+8B+4C$
$\langle 1|2\rangle = -\sqrt{3}\,\zeta$
$\langle 1|3\rangle = 0$
$\langle 1|4\rangle = (\sqrt{6})(2B+C)$
$\langle 1|5\rangle = \langle 1|6\rangle = \langle 1|7\rangle = 0$
$\langle 1|8\rangle = (2/3)(3D\sigma-5D\tau)$
$\langle 1|9\rangle = \langle 1|10\rangle = 0$

$\langle 2|2\rangle = (1/9)(18Dq-7D\tau)+4B-(1/2)\zeta$
$\langle 2|3\rangle = -6B+\zeta$
$\langle 2|4\rangle = -\sqrt{2}\,\zeta$
$\langle 2|5\rangle = (-2\sqrt{3}/9)(3D\sigma-5D\tau)$
$\langle 2|6\rangle = (\sqrt{6}/18)(9D\sigma+20D\tau)$
$\langle 2|7\rangle = (\sqrt{2}/18)(9D\sigma+20D\tau)$
$\langle 2|8\rangle = 0$
$\langle 2|9\rangle = (\sqrt{2}/3)(3D\sigma-5D\tau)$
$\langle 2|10\rangle = 0$

$\langle 3|3\rangle = (-4/9)(18Dq-7D\tau)-5B+\zeta$
$\langle 3|4\rangle = \sqrt{2}\,\zeta$
$\langle 3|5\rangle = 0$
$\langle 3|6\rangle = (-\sqrt{6}/9)(3D\sigma-5D\tau)$
$\langle 3|7\rangle = (-\sqrt{2}/3)(3D\sigma-5D\tau)$
$\langle 3|8\rangle = 0$
$\langle 3|9\rangle = (-\sqrt{2}/9)(9D\sigma+20D\tau)$
$\langle 3|10\rangle = 0$

$\langle 4|4\rangle = (-4/9)(18Dq-7D\tau)+10B+5C$
$\langle 4|5\rangle = \langle 4|6\rangle = \langle 4|7\rangle = 0$
$\langle 4|8\rangle = (2\sqrt{6}/9)(3D\sigma-5D\tau)$
$\langle 4|9\rangle = 0$
$\langle 4|10\rangle = (-2\sqrt{2}/9)(9D\sigma+20D\tau)$

$\langle 5|5\rangle = (2/3)(18Dq-7D\tau)-8B$
$\langle 5|6\rangle = \sqrt{2}\,\zeta$
$\langle 5|7\rangle = (2\sqrt{6}/9)(3D\sigma-5D\tau)$
$\langle 5|8\rangle = \zeta$
$\langle 5|9\rangle = \langle 5|10\rangle = 0$

$\langle 6|6\rangle = (1/6)(12Dq+3D\sigma+2D\tau)-8B-(1/4)\zeta$
$\langle 6|7\rangle = (\sqrt{3}/18)(9D\sigma+20D\tau)+(\sqrt{3}/4)\zeta$
$\langle 6|8\rangle = (-\sqrt{2}/4)\zeta$
$\langle 6|9\rangle = (\sqrt{3}/9)(3D\sigma-5D\tau)-(\sqrt{3}/2)\zeta$
$\langle 6|10\rangle = (\sqrt{6}/2)\zeta$

$\langle 7|7\rangle = (1/18)(36Dq-9D\sigma-34D\tau)+4B+(1/4)\zeta$
$\langle 7|8\rangle = (-\sqrt{6}/4)\zeta$
$\langle 7|9\rangle = (-1/3)(3D\sigma-5D\tau)+6B+(1/2)\zeta$
$\langle 7|10\rangle = (\sqrt{2}/2)\zeta$

$\langle 8|8\rangle = 2Dq-D\sigma-3D\tau+2C$
$\langle 8|9\rangle = (-\sqrt{6}/2)\zeta$
$\langle 8|10\rangle = (2\sqrt{3}/9)(3D\sigma-5D\tau)+2\sqrt{3}B$

$\langle 9|9\rangle = (1/9)(-72Dq-9D\sigma+8D\tau)-5B-(1/2)\zeta$
$\langle 9|10\rangle = (\sqrt{2}/2)\zeta$

$\langle 10|10\rangle = (2/9)(-36Dq+9D\sigma+34D\tau)+B+2C$

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Γ_2T **Representation**

$\langle 1|1\rangle = (1/9)(18\,Dq-7\,D\tau)-8\,B-(1/2)\,\zeta$
$\langle 1|2\rangle = (-\sqrt{2}/18)(9\,D\sigma+20\,D\tau)$
$\langle 1|3\rangle = (-\sqrt{6}/18)(9\,D\sigma+20\,D\tau)$
$\langle 1|4\rangle = (\sqrt{6}/9)(3\,D\sigma-5\,D\tau)$
$\langle 1|5\rangle = 0$

$\langle 2|2\rangle = (1/18)(36\,Dq-9\,D\sigma-34\,D\tau)-8\,B+(1/4)\,\zeta$
$\langle 2|3\rangle = (\sqrt{3}/18)(9\,D\sigma+20\,D\tau)+(\sqrt{3}/4)\,\zeta$
$\langle 2|4\rangle = (-\sqrt{3}/9)(3\,D\sigma-5\,D\tau)+(\sqrt{3}/2)\,\zeta$
$\langle 2|5\rangle = (\sqrt{6}/4)\,\zeta$

$\langle 3|3\rangle = (1/6)(12\,Dq+3\,D\sigma+2\,D\tau)+4\,B-(1/4)\,\zeta$
$\langle 3|4\rangle = (-1/3)(3\,D\sigma-5\,D\tau)-6\,B+(1/2)\,\zeta$
$\langle 3|5\rangle = (\sqrt{2}/4)\,\zeta$

$\langle 4|4\rangle = (1/3)(-24\,Dq+3\,D\sigma+16\,D\tau)-5\,B+(1/2)\,\zeta$
$\langle 4|5\rangle = (\sqrt{2}/2)\,\zeta$

$\langle 5|5\rangle = 2\,Dq-D\sigma-3\,D\tau+4\,B+2\,C$

Γ_3T **Representation**

$\langle 1|1\rangle = (2/3)(18\,Dq-7\,D\tau)+2\,C$
$\langle 1|2\rangle = (\sqrt{6}/2)\,\zeta$
$\langle 1|3\rangle = (\sqrt{6}/2)\,\zeta$
$\langle 1|4\rangle = 0$
$\langle 1|5\rangle = 2\sqrt{3}\,B$
$\langle 1|6\rangle = \langle 1|7\rangle=\langle 1|8\rangle=0$
$\langle 1|9\rangle = (-\sqrt{2}/3)(3\,D\sigma-5\,D\tau)$
$\langle 1|10\rangle = \langle 1|11\rangle=\langle 1|12\rangle=0$
$\langle 1|13\rangle = (-\sqrt{2}/3)(3\,D\sigma-5\,D\tau)$
$\langle 1|14\rangle = \langle 1|15\rangle=0$
$\langle 2|2\rangle = (1/9)(18\,Dq-7\,D\tau)-8\,B+(1/4)\,\zeta$
$\langle 2|3\rangle = (-3/4)\,\zeta$
$\langle 2|4\rangle = (-3/2)\,\zeta$
$\langle 2|5\rangle = 0$
$\langle 2|6\rangle = (-\sqrt{2}/36)(9\,D\sigma+20\,D\tau)$
$\langle 2|7\rangle = (-\sqrt{6}/36)(9\,D\sigma+20\,D\tau)$
$\langle 2|8\rangle = (\sqrt{6}/18)(3\,D\sigma-5\,D\tau)$
$\langle 2|9\rangle = \langle 2|10\rangle=0$
$\langle 2|11\rangle = (-\sqrt{6}/36)(9\,D\sigma+20\,D\tau)$
$\langle 2|12\rangle = (\sqrt{2}/12)(9\,D\sigma+20\,D\tau)$
$\langle 2|13\rangle = 0$
$\langle 2|14\rangle = (\sqrt{2}/6)(3\,D\sigma-5\,D\tau)$
$\langle 2|15\rangle = 0$

$\langle 3|3\rangle = (1/9)(18\,Dq-7\,D\tau)+4\,B+(1/4)\,\zeta$
$\langle 3|4\rangle = -6\,B-(1/2)\,\zeta$
$\langle 3|5\rangle = -\sqrt{2}\,\zeta$
$\langle 3|6\rangle = (-\sqrt{2}/12)(9\,D\sigma+20\,D\tau)$
$\langle 3|7\rangle = (\sqrt{6}/36)(9\,D\sigma+20\,D\tau)$
$\langle 3|8\rangle = (-\sqrt{6}/6)(3\,D\sigma-5\,D\tau)$
$\langle 3|9\rangle = 0$
$\langle 3|10\rangle = (2\sqrt{3}/9)(3\,D\sigma-5\,D\tau)$
$\langle 3|11\rangle = (\sqrt{6}/36)(9\,D\sigma+20\,D\tau)$
$\langle 3|12\rangle = (\sqrt{2}/36)(9\,D\sigma+20\,D\tau)$
$\langle 3|13\rangle = 0$
$\langle 3|14\rangle = (\sqrt{2}/6)(3\,D\sigma-5\,D\tau)$
$\langle 3|15\rangle = 0$

$\langle 4|4\rangle = (-4/9)(18\,Dq-7\,D\tau)-5\,B-(1/2)\,\zeta$
$\langle 4|5\rangle = (-\sqrt{2}/2)\,\zeta$
$\langle 4|6\rangle = (\sqrt{2}/6)(3\,D\sigma-5\,D\tau)$
$\langle 4|7\rangle = (-\sqrt{6}/6)(3\,D\sigma-5\,D\tau)$
$\langle 4|8\rangle = (\sqrt{6}/18)(9\,D\sigma+20\,D\tau)$
$\langle 4|9\rangle = \langle 4|10\rangle=0$
$\langle 4|11\rangle = (-\sqrt{6}/18)(3\,D\sigma-5\,D\tau)$
$\langle 4|12\rangle = (-\sqrt{2}/6)(3\,D\sigma-5\,D\tau)$
$\langle 4|13\rangle = 0$
$\langle 4|14\rangle = (-\sqrt{2}/18)(9\,D\sigma+20\,D\tau)$
$\langle 4|15\rangle = 0$

$\langle 5|5\rangle = (-4/9)(18\,Dq-7\,D\tau)+B+2\,C$
$\langle 5|6\rangle = \langle 5|7\rangle=\langle 5|8\rangle=\langle 5|9\rangle=\langle 5|10\rangle=\langle 5|11\rangle$
$=\langle 5|12\rangle=0$
$\langle 5|13\rangle = (-2\sqrt{6}/9)(3\,D\sigma-5\,D\tau)$
$\langle 5|14\rangle = 0$
$\langle 5|15\rangle = (-\sqrt{2}/9)(9\,D\sigma+20\,D\tau)$

$\langle 6|6\rangle = (1/36)(72\,Dq+9\,D\sigma-8\,D\tau)-8\,B+(1/4)\,\zeta$
$\langle 6|7\rangle = (-\sqrt{3}/36)(9\,D\sigma+29\,D\tau)+(\sqrt{3}/4)\,\zeta$
$\langle 6|8\rangle = (\sqrt{3}/18)(3\,D\sigma-5\,D\tau)+(\sqrt{3}/2)\,\zeta$
$\langle 6|9\rangle = (\sqrt{6}/4)\,\zeta$
$\langle 6|10\rangle = 0$
$\langle 6|11\rangle = (-\sqrt{3}/36)(9\,D\sigma+20\,D\tau)$
$\langle 6|12\rangle = (-1/12)(9\,D\sigma+20\,D\tau)$
$\langle 6|13\rangle = 0$
$\langle 6|14\rangle = (-1/6)(3\,D\sigma-5\,D\tau)$
$\langle 6|15\rangle = 0$

$\langle 7|7\rangle = (1/12)(24\,Dq-3\,D\sigma-16\,D\tau)+4\,B-(1/4)\,\zeta$
$\langle 7|8\rangle = (1/6)(3\,D\sigma-5\,D\tau)-6\,B+(1/2)\,\zeta$
$\langle 7|9\rangle = (\sqrt{2}/4)\,\zeta$
$\langle 7|10\rangle = (-\sqrt{2}/3)(3\,D\sigma-5\,D\tau)$
$\langle 7|11\rangle = (1/12)(9\,D\sigma+20\,D\tau)$
$\langle 7|12\rangle = (-\sqrt{3}/36)(9\,D\sigma+20\,D\tau)$
$\langle 7|13\rangle = 0$
$\langle 7|14\rangle = (-\sqrt{3}/6)(3\,D\sigma-5\,D\tau)$
$\langle 7|15\rangle = 0$

$\langle 8|8\rangle = (1/2)(-16\,Dq-\mathrm{D}\,\sigma+4\,D\tau)-5\,B+(1/2)\,\zeta$
$\langle 8|9\rangle = (\sqrt{2}/2)\,\zeta$
$\langle 8|10\rangle = 0$
$\langle 8|11\rangle = (-1/6)(3\,D\sigma-5\,D\tau)$
$\langle 8|12\rangle = (\sqrt{3}/6)(3\,D\sigma-5\,D\tau)$
$\langle 8|13\rangle = 0$
$\langle 8|14\rangle = (\sqrt{3}/18)(9\,D\sigma+20\,D\tau)$
$\langle 8|15\rangle = 0$

$\langle 9|9\rangle = (1/6)(12\,Dq+3\,D\sigma+2\,D\tau)+4\,B+2\,C$
$\langle 9|10\rangle = \langle 9|11\rangle=\langle 9|12\rangle=0$
$\langle 9|13\rangle = (-1/6)(9\,D\sigma+20\,D\tau)$
$\langle 9|14\rangle = 0$
$\langle 9|15\rangle = (-\sqrt{3}/3)(3\,D\sigma-5\,D\tau)$

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$\langle 10 \mid 10 \rangle = (2/3)(18\,Dq - 7\,D\tau) - 8\,B$
$\langle 10 \mid 11 \rangle = \sqrt{2}\,\zeta$
$\langle 10 \mid 12 \rangle = (-\sqrt{6}/9)(3\,D\sigma - 5\,D\tau)$
$\langle 10 \mid 13 \rangle = \zeta$
$\langle 10 \mid 14 \rangle = \langle 10 \mid 15 \rangle = 0$

$\langle 11 \mid 11 \rangle = (1/12)(24Dq - 3\,D\sigma - 16\,D\tau) - 8\,B - (1/4)\,\zeta$
$\langle 11 \mid 12 \rangle = (-\sqrt{3}/36)(9\,D\sigma + 20\,D\tau) + (\sqrt{3}/4)\,\zeta$
$\langle 11 \mid 13 \rangle = (-\sqrt{2}/4)\,\zeta$
$\langle 11 \mid 14 \rangle = (-\sqrt{3}/18)(3\,D\sigma - 5\,D\tau) - (\sqrt{3}/2)\,\zeta$
$\langle 11 \mid 15 \rangle = (\sqrt{6}/2)\,\zeta$

$\langle 12 \mid 12 \rangle = (1/36)(72\,Dq + 9\,D\sigma - 8\,D\tau) + 4\,B + (1/4)\,\zeta$
$\langle 12 \mid 13 \rangle = (-\sqrt{6}/4)\,\zeta$
$\langle 12 \mid 14 \rangle = (1/6)(3\,D\sigma - 5\,D\tau) + 6\,B + (1/2)\,\zeta$
$\langle 12 \mid 15 \rangle = (\sqrt{2}/2)\,\zeta$

$\langle 13 \mid 13 \rangle = (1/6)(12\,Dq + 3\,D\sigma + 2\,D\tau) + 2\,C$
$\langle 13 \mid 14 \rangle = (-\sqrt{6}/2)\,\zeta$
$\langle 13 \mid 15 \rangle = (-\sqrt{3}/9)(3\,D\sigma - 5\,D\tau) + 2\sqrt{3}\,B$

$\langle 14 \mid 14 \rangle = (1/18)(-144\,Dq + 9\,D\sigma + 76\,D\tau) - 5\,B - (1/2)\,\zeta$
$\langle 14 \mid 15 \rangle = (\sqrt{2}/2)\,\zeta$

$\langle 15 \mid 15 \rangle = (1/9)(-72\,Dq - 9\,D\sigma + 8\,D\tau) + B + 2\,C$

2. $\{X, S, e_g, b_{2g}, a_{1g}, b_{1g}, \Gamma_j\}$ Representation of Quadrate and $\{\Xi, \Sigma, \delta, \pi, \sigma, \Gamma_j\}$ Representation of Cylindrical Fields

The quadrate one electron basis functions which diagonalize the total ligand field are $b_{1g}(d_{x^2-y^2})$, $a_{1g}(d_{z^2})$, $b_{2g}(d_{xy})$, and $e_g(d_{yz}, d_{zx})$. Since octahedral orientation is not maintained in this representation, suffice it to use the transformation properties of the orbital and spin functions under $C_4(z)$ and $C_2(y)$ symmetry operations (Table 3) in manufacturing the two electron symmetry adapted wave functions. The same spin functions of the quadrate $\{X, S, t_{2g}, e_g, \Gamma_j\}$ representation can be used here also. The procedure of fabricating the wave functions in this representation had been described already elsewhere[11], hence will not be repeated here. The complete set of symmetry adapted wave functions derived by us[12] are listed in Appendix A.1 (a)[13].

The orbital and spin functions of the cylindrical case along with their transformation properties[14] under σ_v symmetry operation are given in Table 8. The complete set of two electron symmetry adapted wave functions arise from the configurations (δ^2), (π^2), (σ^2), $(\delta\pi)$, $(\delta\sigma)$, and $(\pi\sigma)$. As an example, the (δ^2) configuration gives rise to the orbital states Σ^- (spin triplet), Σ^+ (spin singlet), and Γ (spin singlet), which when combined with their corresponding spin functions yield the spin-orbital states $\Gamma_0^+ + \Gamma_1$, Γ_0^+, and Γ_4, respectively. The two components of $\Gamma_{\pm 4}[{}^1\Gamma(\delta^2)]$ are obviously[15]

$$[(\delta_\pm)(\delta_\pm)] \cdot (\alpha\beta - \beta\alpha)/\sqrt{2}\,.$$

Since the orbital combinations

$$[(\delta_+)(\delta_-) + (\delta_-)(\delta_+)]$$

and

$$[(\delta_+)(\delta_-) - (\delta_-)(\delta_+)]\,,$$

respectively, transform as Σ^+ and Σ^-, the remaining spin-orbital states are obtained as follows:

$$\Gamma_0^+[{}^1\Sigma^+(\delta^2)] = 1/\sqrt{2}[(\delta_+)(\delta_-) + (\delta_-)(\delta_+)](\alpha\beta - \beta\alpha)/\sqrt{2}\,,$$

$$\Gamma_0^+[{}^3\Sigma^-(\delta^2)] = 1/\sqrt{2}[(\delta_+)(\delta_-) - (\delta_-)(\delta_+)](\alpha\beta + \beta\alpha)/\sqrt{2}\,,$$

$$\Gamma_{\pm 1}[{}^3\Sigma^-(\delta^2)] = \pm 1/\sqrt{2}[(\delta_+)(\delta_-) - (\delta_-)(\delta_+)]\begin{pmatrix}\alpha\alpha\\ \beta\beta\end{pmatrix}.$$

The wave functions thus derived are given in Table 9 a.

Table 8. Transformation Properties of Orbital and Spin Functions in Cylindrical Symmetry.

Function	σ_v
$\delta_\pm = \mid 2, \pm 2\rangle$	$\delta_\mp$
$\pi_\pm = \mp \mid 2, \pm 1\rangle$	$\pi_\pm$
$\sigma^+ = \mid 2, 0\rangle$	σ^+
$\sigma^+ = (1/\sqrt{2})(\alpha\beta - \beta\alpha)$	σ^+
$\sigma^- = (1/\sqrt{2})(\alpha\beta + \beta\alpha)$	$-\sigma^-$
$\pi_+ = (\alpha\alpha)$	π_-
$\pi_- = (\beta\beta)$	π_+

3. $\{L, S, J, \Gamma_j\}$ Representation of Quadrate and Trigonal Fields and $\{\Lambda, \Sigma, \Omega, \Gamma_j\}$ Representation of Cylindrical Fields

In this representation, the $\mid J, M_J\rangle$ wave functions of the free-ion serve as the basis functions. The atomic M_J is a good quantum number in cylindrical symmetry. Thus Γ_4 comes from $M_J = 4$ of ${}^3F_4$ and ${}^1G_4$, Γ_3 from $M_J = 3$ of ${}^3F_{4,3}$, and ${}^1G_4$, Γ_2 from $M_J = 2$ of ${}^3F_{4,3,2}$, ${}^1G_4$, ${}^3P_2$, and ${}^1D_2$, Γ_1 from $M_J = 1$ of ${}^3F_{4,3,2}$, ${}^1G_4$, ${}^3P_{2,1}$ and ${}^1D_2$, Γ_0^+ from

Table 9. Cylindrical Wave Functions and Energy Matrices in $\{\Xi, \Sigma, \delta, \pi, \sigma, \Gamma_j\}$ Representation.

(a) $|\Xi, \Sigma, \delta, \pi, \sigma, \Gamma_j\rangle$ Functions

$[\Psi_0=(\alpha\beta+\beta\alpha)/\sqrt{2}, \quad \Psi_{+1}=\alpha\alpha, \quad \Psi_{-1}=\beta\beta]$

$\Gamma_0{}^+$ Representation

$$
\begin{aligned}
|1\rangle &= {}^3\Pi(\delta\pi) = \sqrt{\tfrac{1}{2}}[|(\delta_+)(\pi_-)|\Psi_{-1}+|(\delta_-)(\pi_+)|\Psi_{+1}] \\
|2\rangle &= {}^3\Pi(\pi\sigma) = \sqrt{\tfrac{1}{2}}[|(\pi_+)(\sigma)|\Psi_{-1}+|(\pi_-)(\sigma)|\Psi_{+1}] \\
|3\rangle &= {}^3\Sigma^-(\delta^2) = |(\delta_+)(\delta_-)|\Psi_0 \\
|4\rangle &= {}^3\Sigma^-(\pi^2) = |(\pi_+)(\pi_-)|\Psi_0 \\
|5\rangle &= {}^1\Sigma^+(\delta^2) = |(\delta_+)(\delta_-)|(\alpha\beta-\beta\alpha)/\sqrt{2} \\
|6\rangle &= {}^1\Sigma^+(\pi^2) = |(\pi_+)(\pi_-)|(\alpha\beta-\beta\alpha)/\sqrt{2} \\
|7\rangle &= {}^1\Sigma^+(\sigma^2) = |(\sigma)(\sigma)|(\alpha\beta-\beta\alpha)\sqrt{2}
\end{aligned}
$$

$\Gamma_0{}^-$ Representation

$$
\begin{aligned}
|1\rangle &= {}^3\Pi(\delta\pi) = \sqrt{\tfrac{1}{2}}[|(\delta_+)(\pi_-)|\Psi_{-1}-|(\delta_-)(\pi_+)|\Psi_{+1}] \\
|2\rangle &= {}^3\Pi(\pi\sigma) = \sqrt{\tfrac{1}{2}}[|(\pi_+)(\sigma)|\Psi_{-1}-|(\pi_-)(\sigma)|\Psi_{+1}]
\end{aligned}
$$

$\Gamma_{\pm 1}$ Representation

$$
\begin{aligned}
|1\rangle &= {}^3\Sigma^-(\delta^2) = |(\delta_\pm)(\delta_\mp)|\Psi_{\pm 1} \\
|2\rangle &= {}^3\Pi(\delta\pi) = \pm|(\delta_\pm)(\pi_\mp)|\Psi_0 \\
|3\rangle &= {}^3\Delta(\delta\sigma) = |(\delta_\pm)(\sigma)|\Psi_{\mp 1} \\
|4\rangle &= {}^3\Sigma^-(\pi^2) = |(\pi_\pm)(\pi_\mp)|\Psi_{\pm 1} \\
|5\rangle &= {}^3\Pi(\pi\sigma) = \pm|(\pi_\pm)(\sigma)|\Psi_0 \\
|6\rangle &= {}^1\Pi(\delta\pi) = |(\delta_\pm)(\pi_\mp)|(\alpha\beta-\beta\alpha)/\sqrt{2} \\
|7\rangle &= {}^1\Pi(\pi\sigma) = |(\pi_\pm)(\sigma)|(\alpha\beta-\beta\alpha)/\sqrt{2}
\end{aligned}
$$

$\Gamma_{\pm 2}$ Representation

$$
\begin{aligned}
|1\rangle &= {}^3\Phi(\delta\pi) = |(\delta_\pm)(\pi_\pm)|\Psi_{\mp 1} \\
|2\rangle &= {}^3\Pi(\delta\pi) = |(\delta_\pm)(\pi_\mp)|\Psi_{\mp 1} \\
|3\rangle &= {}^3\Delta(\delta\sigma) = \pm|(\delta_\pm)(\sigma)|\Psi_0 \\
|4\rangle &= {}^3\Pi(\pi\sigma) = |(\pi_\pm)(\sigma)|\Psi_{\pm 1} \\
|5\rangle &= {}^1\Delta(\delta\sigma) = |(\delta_\pm)(\sigma)|(\alpha\beta-\beta\alpha)/\sqrt{2} \\
|6\rangle &= {}^1\Delta(\pi^2) = |(\pi_\pm)(\pi_\pm)|(\alpha\beta-\beta\alpha)/\sqrt{2}
\end{aligned}
$$

$\Gamma_{\pm 3}$ Representation

$$
\begin{aligned}
|1\rangle &= {}^3\Phi(\delta\pi) = \pm|(\delta_\pm)(\pi_\pm)|\Psi_0 \\
|2\rangle &= {}^3\Delta(\delta\sigma) = |(\delta_\pm)(\sigma)|\Psi_{\pm 1} \\
|3\rangle &= {}^1\Phi(\delta\pi) = |(\delta_\pm)(\pi_\pm)|(\alpha\beta-\beta\alpha)/\sqrt{2}
\end{aligned}
$$

$\Gamma_{\pm 4}$ Representation

$$
\begin{aligned}
|1\rangle &= {}^3\Phi(\delta\pi) = |(\delta_\pm)(\pi_\pm)|\Psi_{\pm 1} \\
|2\rangle &= {}^1\Gamma(\delta^2) = |(\delta_\pm)(\delta_\pm)|(\alpha\beta-\beta\alpha)/\sqrt{2}
\end{aligned}
$$

Table 9. (b) $\{\Xi, \Sigma, \delta, \pi, \sigma, \Gamma_j\}$ Energy Matrices.

$\Gamma_0{}^+$ Representation

$$
\begin{aligned}
\langle 1|1\rangle &= -D\mathfrak{s}-3D\mathfrak{t}-2B-(1/2)\zeta \\
\langle 1|2\rangle &= 3\sqrt{6}B \\
\langle 1|3\rangle &= \zeta \\
\langle 1|4\rangle &= \langle 1|5\rangle=\langle 1|6\rangle=-\zeta \\
\langle 1|7\rangle &= 0
\end{aligned}
$$

$$
\begin{aligned}
\langle 2|2\rangle &= 3D\mathfrak{s}+2D\mathfrak{t}+B-(1/2)\zeta \\
\langle 2|3\rangle &= 0 \\
\langle 2|4\rangle &= (\sqrt{6}/2)\zeta \\
\langle 2|5\rangle &= 0 \\
\langle 2|6\rangle &= (-\sqrt{6}/2)\zeta \\
\langle 2|7\rangle &= -\sqrt{3}\zeta
\end{aligned}
$$

$$
\begin{aligned}
\langle 3|3\rangle &= -4D\mathfrak{s}+2D\mathfrak{t}+4B \\
\langle 3|4\rangle &= 6B \\
\langle 3|5\rangle &= 2\zeta \\
\langle 3|6\rangle &= \langle 3|7\rangle=0
\end{aligned}
$$

$$
\begin{aligned}
\langle 4|4\rangle &= 2D\mathfrak{s}-8D\mathfrak{t}-5B \\
\langle 4|5\rangle &= 0 \\
\langle 4|6\rangle &= \zeta \\
\langle 4|7\rangle &= 0
\end{aligned}
$$

$$
\begin{aligned}
\langle 5|5\rangle &= -4D\mathfrak{s}+2D\mathfrak{t}+4(B+C) \\
\langle 5|6\rangle &= 2(3B+C) \\
\langle 5|7\rangle &= \sqrt{2}(4B+C)
\end{aligned}
$$

$$
\begin{aligned}
\langle 6|6\rangle &= 2D\mathfrak{s}-8D\mathfrak{t}+7B+4C \\
\langle 6|7\rangle &= \sqrt{2}(B+C)
\end{aligned}
$$

$$
\langle 7|7\rangle = 4D\mathfrak{s}+12D\mathfrak{t}+4B+3C
$$

$\Gamma_0{}^-$ Representation

$$
\begin{aligned}
\langle 1|1\rangle &= -D\mathfrak{s}-3D\mathfrak{t}-2B-(1/2)\zeta \\
\langle 1|2\rangle &= 3\sqrt{6}B
\end{aligned}
$$

$$
\langle 2|2\rangle = 3D\mathfrak{s}+2D\mathfrak{t}+B-(1/2)\zeta
$$

Γ_1 Representation

$$
\begin{aligned}
\langle 1|1\rangle &= -4D\mathfrak{s}+2D\mathfrak{t}+4B \\
\langle 1|2\rangle &= (\sqrt{2}/2)\zeta \\
\langle 1|3\rangle &= 0 \\
\langle 1|4\rangle &= 6B \\
\langle 1|5\rangle &= 0 \\
\langle 1|6\rangle &= (\sqrt{2}/2)\zeta \\
\langle 1|7\rangle &= 0
\end{aligned}
$$

$$
\begin{aligned}
\langle 2|2\rangle &= -D\mathfrak{s}-3D\mathfrak{t}-2B \\
\langle 2|3\rangle &= (\sqrt{3}/2)\zeta \\
\langle 2|4\rangle &= (-\sqrt{2}/2)\zeta \\
\langle 2|5\rangle &= 3\sqrt{6}B \\
\langle 2|6\rangle &= (3/2)\zeta \\
\langle 2|7\rangle &= 0
\end{aligned}
$$

$$
\begin{aligned}
\langle 3|3\rangle &= 7D\mathfrak{t}-8B-\zeta \\
\langle 3|4\rangle &= 0 \\
\langle 3|5\rangle &= (-\sqrt{2}/2)\zeta \\
\langle 3|6\rangle &= (-\sqrt{3}/2)\zeta \\
\langle 3|7\rangle &= (-\sqrt{2}/2)\zeta
\end{aligned}
$$

$$
\begin{aligned}
\langle 4|4\rangle &= 2D\mathfrak{s}-8D\mathfrak{t}-5B \\
\langle 4|5\rangle &= (\sqrt{3}/2)\zeta \\
\langle 4|6\rangle &= (\sqrt{2}/2)\zeta \\
\langle 4|7\rangle &= (\sqrt{3}/2)\zeta
\end{aligned}
$$

$$
\begin{aligned}
\langle 5|5\rangle &= 3D\mathfrak{s}+2D\mathfrak{t}+B \\
\langle 5|6\rangle &= 0 \\
\langle 5|7\rangle &= (1/2)\zeta
\end{aligned}
$$

$$
\begin{aligned}
\langle 6|6\rangle &= -D\mathfrak{s}-3D\mathfrak{t}-2B+2C \\
\langle 6|7\rangle &= -\sqrt{6}B
\end{aligned}
$$

$$
\langle 7|7\rangle = 3D\mathfrak{s}+2D\mathfrak{t}+3B+2C
$$

Γ_2 **Representation**

$$\langle 1|1\rangle = -D\mathfrak{s}-3D\mathfrak{t}-8B-(3/2)\zeta$$
$$\langle 1|2\rangle = 0$$
$$\langle 1|3\rangle = (-\sqrt{3}/2)\zeta$$
$$\langle 1|4\rangle = 0$$
$$\langle 1|5\rangle = (\sqrt{3}/2)\zeta$$
$$\langle 1|6\rangle = \zeta$$

$$\langle 2|2\rangle = -D\mathfrak{s}-3D\mathfrak{t}-2B+(1/2)\zeta$$
$$\langle 2|3\rangle = (\sqrt{3}/2)\zeta$$
$$\langle 2|4\rangle = 3\sqrt{6}B$$
$$\langle 2|5\rangle = (\sqrt{3}/2)\zeta$$
$$\langle 2|6\rangle = 0$$

$$\langle 3|3\rangle = 7D\mathfrak{t}-8B$$
$$\langle 3|4\rangle = (-\sqrt{2}/2)\zeta$$
$$\langle 3|5\rangle = \zeta$$
$$\langle 3|6\rangle = 0$$

$$\langle 4|4\rangle = 3D\mathfrak{s}+2D\mathfrak{t}+B+(1/2)\zeta$$
$$\langle 4|5\rangle = (\sqrt{2}/2)\zeta$$
$$\langle 4|6\rangle = (\sqrt{6}/2)\zeta$$

$$\langle 5|5\rangle = 7D\mathfrak{t}+2C$$
$$\langle 5|6\rangle = -2\sqrt{3}B$$

$$\langle 6|6\rangle = 2D\mathfrak{s}-8D\mathfrak{t}+B+2C$$

Γ_3 **Representation**

$$\langle 1|1\rangle = -D\mathfrak{s}-3D\mathfrak{t}-8B$$
$$\langle 1|2\rangle = (-\sqrt{3}/2)\zeta$$
$$\langle 1|3\rangle = (1/2)\zeta$$

$$\langle 2|2\rangle = 7D\mathfrak{t}-8B+\zeta$$
$$\langle 2|3\rangle = (-\sqrt{3}/2)\zeta$$

$$\langle 3|3\rangle = -D\mathfrak{s}-3D\mathfrak{t}+4B+2C$$

Γ_4 **Representation**

$$\langle 1|1\rangle = -D\mathfrak{s}-3D\mathfrak{t}-8B+(3/2)\zeta$$
$$\langle 1|2\rangle = -\zeta$$

$$\langle 2|2\rangle = -4D\mathfrak{s}+2D\mathfrak{t}+4B+2C$$

$M_J=0$ of $^3F_{4,2}$, $^1G_4$, $^3P_{2,0}$, $^1D_2$ and $^1S_0$, and Γ_0^- from $M_J=0$ of $^3F_3$ and $^3P_1$. The formation of these $|J, M_J\rangle$ functions as linear combinations of $|L, S\rangle$ and the construction of $|L, S\rangle$ functions from the one electron $|l, m_l\rangle\,|s, m_s\rangle$ functions have been described elsewhere [16].

For the quadrate and trigonal representations, the $|J, M_J\rangle$ wave functions are linearly combined to form the symmetry wave functions of the cubic $\{\Gamma_j\}$ representation by the use of tetragonal [17, 18] and trigonal oriented cubic harmonics [19], respectively, and then properly decomposed. The various transformations involved in this scheme are given in Appendix [13], A.1.(b), A.2.(a), and A.3.(a).

4. $\{j, j, J, \Gamma_j\}$ Representation of Quadrate and Trigonal Fields and $\{\omega, \omega, \Omega, \Gamma_j\}$ Representation of Cylindrical Fields

The procedure here is similar to the above scheme except the $|J, M_J\rangle$ functions are obtained from coupling of the $|j, m_j\rangle$ of one electron functions. The process of finding the allowed levels in (j, j) coupling [16] also follows that in the (L, S) coupling. Considering the configuration nd^2, the j and j' may take on values 5/2 and 3/2. In Table 10 are given all possible values of (m, m') for different (j, j') combinations. The resulting J values are given at the foot of each column of the Table. These J values check, as they should, with those obtained in (L, S) coupling, namely, $^1G_4$, $^3F_{4,3,2}$, $^1D_2$, $^3P_{2,1,0}$, and $^1S_0$.

The symmetry eigenfunctions are constructed from the one electron $|j, m_j\rangle$ basis functions which are related to the $|l, m_l\rangle\,|s, m_s\rangle$ basis by the Clebsch-Gordon or Wigner coefficients [16]. In the $|l, m_l\rangle\,|s, m_s\rangle$ functions listed in the Appendix, the l and s being common to all, are suppressed and denoted by (m_l) for the orbital part with + or − sign over m_l to indicate $|1/2, 1/2\rangle$ or $|1/2, -1/2\rangle$ spin coordinates. The two electron $|j_1, j_2, J, M_J\rangle$ functions are related to the $|j_1, j_2, m_{j1}, m_{j2}\rangle$ functions also by the Wigner coefficients. For $j_2=3/2$ and $j_1=5/2$ and 3/2 Table 3 [3] of CONDON and SHORTLEY [16] can be used for this purpose. For $j_2=5/2$ and $j_1=5/2$, these transformations have been derived by others [20].

Once the $|J, M_J\rangle$ functions are available, the linear combination of these to satisfy the symmetry requirements of quadrate and trigonal fields is achieved again by the use of tetragonal and trigonal oriented cubic harmonics, respectively, in exactly similar manner to the procedure used in $\{L, S, J, \Gamma_j\}$ coupling. Appendix [13], A.1.(c), A.2.(b), and A.3.(b) contain the necessary transformations in this representation.

5. $\{\gamma_7(t_{2g}), \gamma_8(t_{2g}), \gamma_8(e_g), \Gamma_j\}$ Representation of Quadrate and Trigonal Fields

The single electron spin-orbital functions used in this scheme [3b] are given in Table 11. The transformation properties of these functions under $C_4(z)$, $C_2(y)$, and $C_3(z')$ symmetry operations for quadrate case and under $C_3(z')$, $C_2(y')$, and $C_4(z)$ for trigonal case are listed in Tables 12 and 13.

Table 10. J Values of $n\,d^2$ Configuration in (j, j) Coupling.

$n\,d^2$		(j, j') $(\frac{5}{2}, \frac{5}{2})$	$(\frac{5}{2}, \frac{3}{2})$	$(\frac{3}{2}, \frac{3}{2})$
	4	$(\frac{5}{2}, \frac{3}{2})$	$(\frac{5}{2}, \frac{3}{2})$	
	3	$(\frac{5}{2}, \frac{1}{2})$	$(\frac{5}{2}, \frac{1}{2})\,(\frac{3}{2}, \frac{3}{2})$	
	2	$(\frac{5}{2}, -\frac{1}{2})\,(\frac{3}{2}, \frac{1}{2})$	$(\frac{5}{2}, -\frac{1}{2})\,(\frac{3}{2}, \frac{1}{2})\,(\frac{1}{2}, \frac{3}{2})$	$(\frac{3}{2}, \frac{1}{2})$
	1	$(\frac{5}{2}, -\frac{3}{2})\,(\frac{3}{2}, -\frac{1}{2})$	$(\frac{5}{2}, -\frac{3}{2})\,(\frac{3}{2}, -\frac{1}{2})\,(\frac{1}{2}, \frac{1}{2})\,(-\frac{1}{2}, \frac{3}{2})$	$(\frac{3}{2}, -\frac{1}{2})$
M_j	0	$(\frac{5}{2}, -\frac{5}{2})\,(\frac{3}{2}, -\frac{3}{2})\,(\frac{1}{2}, -\frac{1}{2})$	$(\frac{3}{2}, -\frac{3}{2})\,(\frac{1}{2}, -\frac{1}{2})\,(-\frac{1}{2}, \frac{1}{2})\,(-\frac{3}{2}, \frac{3}{2})$	$(\frac{3}{2}, -\frac{3}{2})\,(\frac{1}{2}, -\frac{1}{2})$
	-1	$(-\frac{5}{2}, \frac{3}{2})\,(-\frac{3}{2}, \frac{1}{2})$	$(-\frac{5}{2}, \frac{3}{2})\,(-\frac{3}{2}, \frac{1}{2})\,(-\frac{1}{2}, -\frac{1}{2})\,(\frac{1}{2}, -\frac{3}{2})$	$(-\frac{3}{2}, \frac{1}{2})$
	-2	$(-\frac{5}{2}, \frac{1}{2})\,(-\frac{3}{2}, -\frac{1}{2})$	$(-\frac{5}{2}, \frac{1}{2})\,(-\frac{3}{2}, -\frac{1}{2})\,(-\frac{1}{2}, -\frac{3}{2})$	$(-\frac{3}{2}, -\frac{1}{2})$
	-3	$(-\frac{5}{2}, -\frac{1}{2})$	$(-\frac{5}{2}, -\frac{1}{2})\,(-\frac{3}{2}, -\frac{3}{2})$	
	-4	$(-\frac{5}{2}, -\frac{3}{2})$	$(-\frac{5}{2}, -\frac{3}{2})$	
J Values		4, 2, 0	4, 3, 2, 1	2, 0

Table 11. Cubic Single Electron Spin-Orbital Functions in Quadrate and Trigonal Orientations.

Cubic Representation	Quadrate	Trigonal [a]
$\gamma_{7a}(t_{2g})$	$-i/\sqrt{3}[(xy)(\beta)+i\sqrt{2}\,\pi_+(\alpha)]$	$-\sqrt{\frac{1}{3}}\,a_1(\beta')-\sqrt{\frac{2}{3}}\,e_-(\alpha')$
$\gamma_{7b}(t_{2g})$	$-i/\sqrt{3}[(xy)(\alpha)+i\sqrt{2}\,\pi_-(\beta)]$	$\sqrt{\frac{1}{3}}\,a_1(\alpha')-\sqrt{\frac{2}{3}}\,e_+(\beta')$
$\gamma_{8a}(t_{2g})$	$-i/\sqrt{3}[\sqrt{2}(xy)(\beta)-i\,\pi_+(\alpha)]$	$\sqrt{\frac{2}{3}}\,a_1(\beta')-\sqrt{\frac{1}{3}}\,e_-(\alpha')$
$\gamma_{8b}(t_{2g})$	$-i/\sqrt{3}[\sqrt{2}(xy)(\alpha)-i\,\pi_-(\beta)]$	$-\sqrt{\frac{2}{3}}\,a_1(\alpha')-\sqrt{\frac{1}{3}}\,e_+(\beta')$
$\gamma_{8c}(t_{2g})$	$\pi_-(\alpha)$	$e^{-i\beta/4}/\sqrt{2}[e_+(\alpha')+i\,e_-(\beta')]$
$\gamma_{8d}(t_{2g})$	$\pi_+(\beta)$	$e^{i\beta/4}/\sqrt{2}[e_+(\alpha')-i\,e_-(\beta')]$
$\gamma_{8a}(e_g)$	$(x^2-y^2)(\beta)$	$e_-(\alpha')$
$\gamma_{8b}(e_g)$	$-(x^2-y^2)(\alpha)$	$e_+(\beta')$
$\gamma_{8c}(e_g)$	$(z^2)(\beta)$	$e^{i\beta/4}/\sqrt{2}[e_+(\alpha')+i\,e_-(\beta')]$
$\gamma_{8d}(e_g)$	$-(z^2)(\alpha)$	$e^{-i\beta/4}/\sqrt{2}[e_+(\alpha')-i\,e_-(\beta')]$

[a] The exponential terms in $\gamma_{8c,d}$, containing the tetrahedral angle β, are introduced as phase factors.

Table 12. Symmetry Transformation Properties of Cubic and Quadrate Functions in $\{\gamma, \gamma\}$ Representation.

Cubic	Quadrate	$C_4(z)$	$C_2(y)$	$C_3(z')$
γ_{7a}	$\gamma_{7a}^{(1)}$	$-e^{-\pi i/4}\gamma_{7a}$	γ_{7b}	$\sqrt{\frac{1}{2}}[e^{-\pi i/4}\gamma_{7a}-e^{+\pi i/4}\gamma_{7b}]$
γ_{7b}	$\gamma_{7b}^{(1)}$	$-e^{+\pi i/4}\gamma_{7b}$	$-\gamma_{7a}$	$\sqrt{\frac{1}{2}}[e^{-\pi i/4}\gamma_{7a}+e^{+\pi i/4}\gamma_{7b}]$
γ_{8a}	$\gamma_{7a}^{(2)}$	$-e^{-\pi i/4}\gamma_{8a}$	γ_{8b}	$-\sqrt{\frac{1}{8}}[e^{-\pi i/4}\gamma_{8a}-e^{+\pi i/4}\gamma_{8b}]$ $+\sqrt{\frac{3}{8}}[e^{-\pi i/4}\gamma_{8c}-e^{+\pi i/4}\gamma_{8d}]$
γ_{8b}	$\gamma_{7b}^{(2)}$	$-e^{+\pi i/4}\gamma_{8b}$	$-\gamma_{8a}$	$-\sqrt{\frac{1}{8}}[e^{-\pi i/4}\gamma_{8a}+e^{+\pi i/4}\gamma_{8b}]$ $+\sqrt{\frac{3}{8}}[e^{-\pi i/4}\gamma_{8c}+e^{+\pi i/4}\gamma_{8d}]$
γ_{8c}	γ_{6a}	$e^{-\pi i/4}\gamma_{8c}$	γ_{8d}	$-\sqrt{\frac{3}{8}}[e^{-\pi i/4}\gamma_{8a}-e^{+\pi i/4}\gamma_{8b}]$ $-\sqrt{\frac{1}{8}}[e^{-\pi i/4}\gamma_{8c}-e^{+\pi i/4}\gamma_{8d}]$
γ_{8d}	γ_{6b}	$e^{+\pi i/4}\gamma_{8d}$	$-\gamma_{8c}$	$-\sqrt{\frac{3}{8}}[e^{-\pi i/4}\gamma_{8a}+e^{+\pi i/4}\gamma_{8b}]$ $-\sqrt{\frac{1}{8}}[e^{-\pi i/4}\gamma_{8c}+e^{+\pi i/4}\gamma_{8d}]$

Examination of the transformation behavior of the two electron determinantal products will then aid in the formation of the symmetry eigenfunctions. We will discuss the quadrate and trigonal cases independently by considering examples.

The $\gamma_8(t_{2g})^2$ configuration yields the cubic states Γ_1^C, Γ_3^C, and Γ_5^C which in quadrate symmetry decompose to Γ_1^Q, $\Gamma_1^Q+\Gamma_3^Q$, and $\Gamma_4^Q+\Gamma_5^Q$ states. The $\Gamma_3^Q(\Gamma_{3b}^C)$ and $\Gamma_4^Q(\Gamma_{5a}^C)$ states are found to be:

$$\Gamma_3^Q\{\Gamma_{3b}^C[\gamma_8(t_{2g})^2]\} = 1/\sqrt{2}[|\gamma_{8a}(t_{2g})\,\gamma_{8d}(t_{2g})| - |\gamma_{8b}(t_{2g})\,\gamma_{8c}(t_{2g})|]\,,$$

$$\Gamma_4^Q\{\Gamma_{5a}^C[\gamma_8(t_{2g})^2]\} = 1/\sqrt{2}[|\gamma_{8a}(t_{2g})\,\gamma_{8d}(t_{2g})| + |\gamma_{8b}(t_{2g})\,\gamma_{8c}(t_{2g})|]\,.$$

Table 13. Symmetry Transformation Properties of Cubic and Trigonal Functions in $\{\gamma, \gamma\}$ Representation.

Cubic	Trigonal	$C_3(z')$	$C_2(y')$	$C_4(z)$
γ_{7a}	$\gamma_{6a}^{(1)}$	$e^{-\pi i/3}\gamma_{7a}$	γ_{7b}	$-\sqrt{\frac{2}{3}}\,\omega^{-1/4}\gamma_{7a}-\sqrt{\frac{1}{3}}\,\omega^{3/4}\gamma_{7b}$
γ_{7b}	$\gamma_{6b}^{(1)}$	$e^{+\pi i/3}\gamma_{7b}$	$-\gamma_{7a}$	$-\sqrt{\frac{1}{3}}\,\omega^{3/4}\gamma_{7a}-\sqrt{\frac{2}{3}}\,\omega^{1/4}\gamma_{7b}$
γ_{8a}	$\gamma_{6a}^{(2)}$	$e^{-\pi i/3}\gamma_{8a}$	γ_{8b}	$\sqrt{\frac{1}{3}}\,\omega^{1/4}[\omega^{1/2}\gamma_{8b}+e^{-i\beta/4}\gamma_{8c}+e^{i\beta/4}\gamma_{8d}]$
γ_{8b}	$\gamma_{6b}^{(2)}$	$e^{+\pi i/3}\gamma_{8b}$	$-\gamma_{8a}$	$\sqrt{\frac{1}{3}}\,\omega^{1/2}[\omega^{1/4}\gamma_{8a}-e^{-i\beta/4}\gamma_{8c}+e^{i\beta/4}\gamma_{8d}]$
γ_{8c}	γ_5	$-\gamma_{8c}$	$-i\,\gamma_{8c}$	$\sqrt{\frac{1}{3}}\,\omega^{1/4}\,e^{i\beta/4}[\gamma_{8a}+\omega^{1/4}\gamma_{8b}-\omega^{-1/4}\,e^{i\beta/4}\gamma_{8d}]$
γ_{8d}	γ_4	$-\gamma_{8d}$	$+i\,\gamma_{8d}$	$\sqrt{\frac{1}{3}}\,\omega^{1/4}\,e^{-i\beta/4}[\gamma_{8a}-\omega^{1/4}\gamma_{8b}+\omega^{-1/4}\,e^{-i\beta/4}\gamma_{8c}]$

The corresponding quadrate components $\Gamma_1^{Q}(\Gamma_{3a}^{C})$ and $\Gamma_{5a,b}^{Q}(\Gamma_{5b,c}^{C})$ are obtainend immediately by $C_3(z')$ operation. The other Γ_1^{Q}, i. e., $\Gamma_1^{Q}(\Gamma_1^{C})$ can then be formed by orthogonalization to $\Gamma_1^{Q}(\Gamma_{3a}^{C})$. A check on this $\Gamma_1^{Q}(\Gamma_1^{C})$ is provided by $C_4(z)$ symmetry operation which carries it into itself.

For the trigonal case let us consider the configuration $\gamma_8(t_{2g})\,\gamma_8(e_g)$ which gives rise to the cubic states Γ_1^{C}, Γ_2^{C}, Γ_3^{C}, $2\,\Gamma_4^{C}$, and $2\,\Gamma_5^{C}$. These cubic states on going to trigonal symmetry yield Γ_1^{T}, Γ_2^{T}, Γ_3^{T}, $2(\Gamma_2^{T}+\Gamma_3^{T})$, and $2(\Gamma_1^{T}+\Gamma_3^{T})$ states. Since the determinantal products $|a\,b|$, $|b\,a|$, $|c\,d|$, and $|d\,c|$, where a, b, c, d are the four components of γ_8, correctly transform as Γ_1^{C}, a linear combination of all of these can be chosen in such a way that the combination is invariant under $C_4(z)$ operation. Once this combination is found, the other two Γ_1^{T} coming from Γ_{5a}^{C} can be obtained as orthogonal functions to $\Gamma_1^{T}(\Gamma_1^{C})$ and to each other. A check is provided on these orthogonal functions as they should transform properly as Γ_1^{T}, i. e.,

$$\chi[C_3(z')]=1 \quad \text{and} \quad \chi[C_2(y')]=1\,.$$

The $C_4(z)$ symmetry operation on the Γ_{5a}^{C} components and comparison with the symmetry properties of Table 13 produces the remaining components of these states, i. e., $\Gamma_{3a,b}^{T}(\Gamma_{5b,c}^{C})$. Similarly once the linear combination of two electron determinantal products that transform as Γ_2^{C} is found (note that $\chi[C_3(z')]=1$, $\chi[C_2(y')]=-1$, and $\chi[C_4(z)]=-1$) the other two Γ_2^{T} states of Γ_4^{C} can be formed as orthogonal functions to it. The $\Gamma_{3a,b}^{T}$ $(\Gamma_{4b,c}^{C})$ components can then be generated by $C_4(z)$ operation as above. The Γ_{3a}^{T} state coming from Γ_{3a}^{C} can be found immediately as the orthogonal function to the two Γ_{3a}^{T} states. The correctness of this Γ_{3a}^{T} state can be checked by carrying out the $C_2(y')$ and the $C_4(z)$ symmetry operation both resulting in the formation of its second component Γ_{3b}^{T} (cf. Table 4).

The complete set of symmetry adapted quadrate and trigonal wave functions obtained by the above procedure are listed in the Appendix [13], A.1.(d) and A.2.(c), respectively.

D) Parameters

If the quadrate and trigonal ligand field potentials, V_Q and V_T, are taken to be the resultant of a cubic and an axial potential, V_C and V_∞, i. e.,

$$V_{Q,T}=V_C+V_\infty^{Q,T} \tag{5}$$

the cubic potential has the alternant forms [21]

$$V_C=\sum_i\{Y_4^0(\theta_i,\varphi_i)+\sqrt{\tfrac{5}{14}}\,[Y_4^4(\theta_i,\varphi_i)+Y_4^{-4}(\theta_i,\varphi_i)]\}\,R_4(r_i) \tag{6}$$

or

$$V_C=-2/3\sum_i\{Y_4^0(\theta_i',\varphi_i')+\sqrt{\tfrac{10}{7}}\,[Y_4^3(\theta_i',\varphi_i')-Y_4^{-3}(\theta_i',\varphi_i')]\}\,R_4(r_i) \tag{7}$$

in quadrate and trigonal orientations, respectively, and

$$V_\infty=\sum_i[R_2(r_i)\,Y_2^0(\bar\theta_i,\bar\varphi_i)+R_4'(r_i)\,Y_4^0(\bar\theta_i,\bar\varphi_i)] \tag{8}$$

where $(\bar\theta_i\,\bar\varphi_i)\equiv(\theta_i,\varphi_i)$ for quadrate and $(\bar\theta_i,\bar\varphi_i)\equiv(\theta_i',\varphi_i')$ for trigonal. The ligand field parameters have been defined as the matrix elements [4a]:

$$\langle 2,\pm 2\,|\,V_C\,|\,\pm 2,2\rangle=(1/14\sqrt{\pi})\,\langle R_4(r_i)\rangle=D\,q\,, \tag{9 a}$$

$$\langle 2,\pm 2\,|\,V_\infty(Y_4^0)\,|\,\pm 2,2\rangle=(1/14\sqrt{\pi})\,\langle R_4'(r_i)\rangle=D\,\nu\,, \tag{9 b}$$

and

$$\langle 2,\pm 1\,|\,V_\infty(Y_2^0)\,|\,\pm 1,2\rangle=(\sqrt{5}/14\sqrt{\pi})\,\langle R_2'(r_i)\rangle=D\,\mu \tag{9 c}$$

where $\mu \equiv s$, σ, and $\mathfrak{s}$, and $\nu \equiv t$, τ, and $\mathfrak{t}$, respectively for quadrate, trigonal, and cylindrical symmetries. With these definitions, the nonvanishing one electron matrix elements become:

quadrate:

$$\begin{aligned}
\langle 2, \pm 2 \,|\, V_Q \,|\, \pm 2, 2 \rangle &= D\,q - 2\,D\,s + D\,t\,, \\
\langle 2, \pm 1 \,|\, V_Q \,|\, \pm 1, 2 \rangle &= -4\,D\,q + D\,s - 4\,D\,t\,, \\
\langle 2, 0 \,|\, V_Q \,|\, 0, 2 \rangle &= 6\,D\,q + 2\,D\,s + 6\,D\,t\,, \\
\langle 2, \pm 2 \,|\, V_Q \,|\, \mp 2, 2 \rangle &= 5\,D\,q\,, \qquad (10\,\mathrm{a}) \\
\langle (x^2 - y^2) \,|\, V_Q \,|\, (x^2 - y^2) \rangle &= 6\,D\,q - 2\,D\,s + D\,t\,, \\
\langle (z^2) \,|\, V_Q \,|\, (z^2) \rangle &= 6\,D\,q + 2\,D\,s + 6\,D\,t\,, \\
\langle (x\,y) \,|\, V_Q \,|\, (x\,y) \rangle &= -4\,D\,q - 2\,D\,s + D\,t\,, \\
\langle (z\,x) \,|\, V_Q \,|\, (z\,x) \rangle &= \langle (y\,z) \,|\, V_Q \,|\, (y\,z) \rangle \qquad (10\,\mathrm{b}) \\
&= -4\,D\,q + D\,s - 4\,D\,t\,.
\end{aligned}$$

trigonal [22]**:**

$$\begin{aligned}
\langle 2, \pm 2 \,|\, V_T \,|\, \pm 2, 2 \rangle &= -\tfrac{2}{3}\,D\,q - 2\,D\,\sigma + D\,\tau\,, \\
\langle 2, \pm 1 \,|\, V_T \,|\, \pm 1, 2 \rangle &= \tfrac{8}{3}\,D\,q + D\,\sigma - 4\,D\,\tau\,, \\
\langle 2, 0 \,|\, V_T \,|\, 0, 2 \rangle &= -4\,D\,q + 2\,D\,\sigma + 6\,D\,\tau\,, \\
\langle 2, \pm 2 \,|\, V_T \,|\, \mp 1, 2 \rangle &= \langle 2, \mp 1 \,|\, V_T \,|\, \pm 2, 2 \rangle \\
&= \pm\, \frac{10\sqrt{2}}{3}\,D\,q\,, \qquad (11\,\mathrm{a})
\end{aligned}$$

$$\begin{aligned}
\langle a_1(t_{2g}) \,|\, V_T \,|\, a_1(t_{2g}) \rangle &= -4\,D\,q + 2\,D\,\sigma + 6\,D\,\tau\,, \\
\langle e_\pm(t_{2g}) \,|\, V_T \,|\, e_\pm(t_{2g}) \rangle &= -4\,D\,q - D\,\sigma - \tfrac{2}{3}D\,\tau\,, \\
\langle e_\pm(e_g) \,|\, V_T \,|\, e_\pm(e_g) \rangle &= 6\,D\,q - \tfrac{7}{3}D\,\tau\,, \qquad (11\,\mathrm{b}) \\
\langle e_\pm(e_g) \,|\, V_T \,|\, e_\pm(t_{2g}) \rangle &= (\sqrt{2}/3)\,(3\,D\,\sigma - 5\,D\,\tau)\,.
\end{aligned}$$

cylindrical [23]**:**

$$\begin{aligned}
\langle 2, \pm 2 \,|\, V_\infty \,|\, \pm 2, 2 \rangle &= \langle \delta_\pm \,|\, V_\infty \,|\, \delta_\pm \rangle \\
&= -2\,D\,\mathfrak{s} + D\,\mathfrak{t}\,, \\
\langle 2, \pm 1 \,|\, V_\infty \,|\, \pm 1, 2 \rangle &= \langle \pi_\pm \,|\, V_\infty \,|\, \pi_\pm \rangle \\
&= D\,\mathfrak{s} - 4\,D\,\mathfrak{t}\,, \qquad (12) \\
\langle 2, 0 \,|\, V_\infty \,|\, 0, 2 \rangle &= \langle \sigma \,|\, V_\infty \,|\, \sigma \rangle \\
&= 2\,D\,\mathfrak{s} + 6\,D\,\mathfrak{t}\,.
\end{aligned}$$

The radial portion of the spin-orbit and electron correlation integrals of the matrix elements in the atomic case are parametrically substituted as ζ, the spin-orbit coupling constant [24], and A, B, C, the Racah electron correlation parameters [25]. Purely symmetry arguments require more generalized 5 such spin-orbit interaction parameters and 23 electron correlation parameters in the theory of quadrate fields, 6 spin-orbit and 27 electron correlation parameters in trigonal fields, and 4 spin-orbit and 14 electron correlation parameters in cylindrical fields [4a]. Assuming that the relative differences among these various sets of parameters are small, we shall still use only one spin-orbit interaction parameter and three electron correlation parameters as in the free-ion case [26] but as adjustable parameters as in the cubic case.

E) Energy Matrices

The appropriate secular determinants can be easily derived with the necessary matrix elements of the ligand field, electron correlation, and spin-orbit perturbations expressed in terms of the corresponding parameters, using the symmetry wave functions derived above.

The ligand field matrix elements in all representations of the cylindrical and in all except the $\{\gamma, \gamma\}$ representation of the quadrate and trigonal symmetries are calculated by using Eqs. (10), (11), and (12). The one electron matrix elements of Eqs. (13 a) and (13 b) simplify the calculation of ligand field matrix elements in the $\{\gamma, \gamma\}$ coupling scheme of the quadrate and trigonal symmetries.

$$\left.\begin{aligned}
\langle \gamma_{7a}(t_{2g}) \,|\, V_Q \,|\, \gamma_{7a}(t_{2g}) \rangle &= \langle \gamma_{7b}(t_{2g}) \,|\, V_Q \,|\, \gamma_{7b}(t_{2g}) \rangle = -4\,D\,q - \tfrac{7}{3}\,D\,t\,, \\
\langle \gamma_{8a}(t_{2g}) \,|\, V_Q \,|\, \gamma_{8a}(t_{2g}) \rangle &= \langle \gamma_{8b}(t_{2g}) \,|\, V_Q \,|\, \gamma_{8b}(t_{2g}) \rangle = -4\,D\,q - D\,s - \tfrac{2}{3}\,D\,t\,, \\
\langle \gamma_{8c}(t_{2g}) \,|\, V_Q \,|\, \gamma_{8c}(t_{2g}) \rangle &= \langle \gamma_{8d}(t_{2g}) \,|\, V_Q \,|\, \gamma_{8d}(t_{2g}) \rangle = -4\,D\,q + D\,s - 4\,D\,t\,, \\
\langle \gamma_{7a}(t_{2g}) \,|\, V_Q \,|\, \gamma_{8a}(t_{2g}) \rangle &= \langle \gamma_{7b}(t_{2g}) \,|\, V_Q \,|\, \gamma_{8b}(t_{2g}) \rangle = -\frac{\sqrt{2}}{3}\,(3\,D\,s - 5\,D\,t)\,, \\
\langle \gamma_{8a}(e_g) \,|\, V_Q \,|\, \gamma_{8a}(e_g) \rangle &= \langle \gamma_{8b}(e_g) \,|\, V_Q \,|\, \gamma_{8b}(e_g) \rangle = 6\,D\,q - 2\,D\,s + D\,t\,, \\
\langle \gamma_{8c}(e_g) \,|\, V_Q \,|\, \gamma_{8c}(e_g) \rangle &= \langle \gamma_{8d}(e_g) \,|\, V_Q \,|\, \gamma_{8d}(e_g) \rangle = 6\,D\,q + 2\,D\,s + 6D\,t\,;
\end{aligned}\right\} \qquad (13\,\mathrm{a})$$

$$\left.\begin{aligned}
\langle \gamma_{7a}(t_{2g}) \,|\, V_T \,|\, \gamma_{7a}(t_{2g}) \rangle &= \langle \gamma_{7b}(t_{2g}) \,|\, V_T \,|\, \gamma_{7b}(t_{2g}) \rangle = -4\,D\,q + \tfrac{14}{9}\,D\,\tau\,, \\
\langle \gamma_{8a}(t_{2g}) \,|\, V_T \,|\, \gamma_{8a}(t_{2g}) \rangle &= \langle \gamma_{8b}(t_{2g}) \,|\, V_T \,|\, \gamma_{8b}(t_{2g}) \rangle = -4\,D\,q + D\,\sigma + \tfrac{34}{9}\,D\,\tau\,, \\
\langle \gamma_{8c}(t_{2g}) \,|\, V_T \,|\, \gamma_{8c}(t_{2g}) \rangle &= \langle \gamma_{8d}(t_{2g}) \,|\, V_T \,|\, \gamma_{8d}(t_{2g}) \rangle = -4\,D\,q - D\,\sigma - \tfrac{2}{3}\,D\,\tau \\
\langle \gamma_{8a}(e_g) \,|\, V_T \,|\, \gamma_{8a}(e_g) \rangle &= \langle \gamma_{8b}(e_g) \,|\, V_T \,|\, \gamma_{8b}(e_g) \rangle = \\
\langle \gamma_{8c}(e_g) \,|\, V_T \,|\, \gamma_{8c}(e_g) \rangle &= \langle \gamma_{8d}(e_g) \,|\, V_T \,|\, \gamma_{8d}(e_g) \rangle = 6\,D\,q - \tfrac{7}{3}\,D\,\tau\,,
\end{aligned}\right\} \qquad (13\,\mathrm{b})$$

$$\left.\begin{aligned}
\langle \gamma_{7a}(t_{2g}) | V_T | \gamma_{8a}(t_{2g}) \rangle &= \langle \gamma_{7b}(t_{2g}) | V_T | \gamma_{8b}(t_{2g}) \rangle = -\frac{\sqrt{2}}{9}(9\,D\,\sigma + 20\,D\,\tau),\\
\langle \gamma_{7a}(t_{2g}) | V_T | \gamma_{8a}(e_g) \rangle &= \langle \gamma_{7b}(t_{2g}) | V_T | \gamma_{8b}(e_g) \rangle = -\frac{2\sqrt{3}}{9}(3\,D\,\sigma - 5\,D\,\tau),\\
\langle \gamma_{8a}(t_{2g}) | V_T | \gamma_{8a}(e_g) \rangle &= \langle \gamma_{8b}(t_{2g}) | V_T | \gamma_{8b}(e_g) \rangle = -\frac{\sqrt{6}}{9}(3\,D\,\sigma - 5\,D\,\tau),\\
\langle \gamma_{8c}(t_{2g}) | V_T | \gamma_{8c}(e_g) \rangle &= e^{i\beta/2}\cdot\frac{\sqrt{2}}{3}(3\,D\,\sigma - 5\,D\,\tau),\\
\langle \gamma_{8d}(t_{2g}) | V_T | \gamma_{8d}(e_g) \rangle &= e^{-i\beta/2}\cdot\frac{\sqrt{2}}{3}(3\,D\,\sigma - 5\,D\,\tau).
\end{aligned}\right\} \tag{13b}$$

The matrix elements due to electron correlation can be obtained by the use of the coulomb (J) and exchange (K) integrals of $|l, m_l\rangle\,|s, m_s\rangle$ functions in both $\{L, S\}$ [27] and $\{j, j\}$ representations of quadrate and trigonal fields and in the corresponding $\{\Lambda, \Sigma\}$ [27] and $\{\omega, \omega\}$ representations and also in the $\{\Xi, \Sigma\}$ representation of cylindrical fields. The J and K integrals of tetragonal oriented t_{2g} and e_g orbitals [28] aid in the calculation of the electron correlation matrix elements of the quadrate fields in both the $\{X, S\}$ representations as well as in the $\{\gamma, \gamma\}$ representation. In the latter case, the $|\gamma, \gamma\rangle$ wave functions have to be expanded in terms of the t_{2g}, e_g orbitals by the relations given in Table 11. Calculation of the electron correlation matrix elements in the case of the trigonal fields in the $\{X, S\}$ representation (and also in the $\{\gamma, \gamma\}$ scheme, once the $|\gamma, \gamma\rangle$ functions are expanded in terms of the trigonal oriented t_{2g}, e_g orbitals by the relations of Table 11) is facilitated by the use of the nonvanishing coulomb and exchange integrals of the trigonally quantized d-orbitals [29] listed in Table 14.

Table 14. The Nonvanishing Electron Correlation Integrals of Trigonally Quantized d Orbitals.

$J(t_{2ga}, t_{2ga})$	$= A+4\,B+3\,C$
$J(t_{2gb}, t_{2gb})$	$= J(t_{2gc}, t_{2gc}) = J(t_{2gb}, t_{2gc}) = A+B+2\,C$
$J(t_{2ga}, t_{2gb})$	$= J(t_{2ga}, t_{2gc}) = A-2\,B+C$
$J(e_{ga}, e_{ga})$	$= J(e_{gb}, e_{gb}) = J(e_{ga}, e_{gb}) = A+2\,C$
$J(t_{2ga}, e_{ga})$	$= J(t_{2ga}, e_{gb}) = J(t_{2gb}, e_{ga}) =$
$J(t_{2gb}, e_{gb})$	$= J(t_{2gc}, e_{ga}) = J(t_{2gc}, e_{gb}) = A+C$
$K(t_{2ga}, t_{2gb})$	$= K(t_{2ga}, t_{2gc}) = 3\,B+C$
$K(t_{2gb}, t_{2gc})$	$= 6\,B+2\,C$
$K(t_{2ga}, e_{ga})$	$= K(t_{2ga}, e_{gb}) = K(t_{2gb}, e_{ga}) =$
$K(t_{2gb}, e_{gb})$	$= K(t_{2gc}, e_{ga}) = K(t_{2gc}, e_{gb}) = 2\,B+C$
$K(e_{ga}, e_{gb})$	$= 8\,B+2\,C$

a	b	c	d	$\langle a\,b \mid e^2/r_{12} \mid c\,d\rangle$
(t_{2ga})	(t_{2gb})	(t_{2ga})	(e_{ga})	$2\sqrt{2}\,B$
(t_{2ga})	(t_{2gc})	(t_{2ga})	(e_{gb})	$2\sqrt{2}\,B$
(t_{2gb})	(t_{2gc})	(t_{2gc})	(e_{ga})	$2\sqrt{2}\,B$
(t_{2gc})	(t_{2gb})	(t_{2gb})	(e_{gb})	$2\sqrt{2}\,B$
(t_{2ga})	(t_{2gb})	(e_{ga})	(t_{2ga})	$-\sqrt{2}\,B$
(t_{2ga})	(t_{2gc})	(e_{gb})	(t_{2ga})	$-\sqrt{2}\,B$
(t_{2gb})	(t_{2gc})	(e_{ga})	(t_{2gc})	$-\sqrt{2}\,B$
(t_{2gc})	(t_{2gb})	(e_{gb})	(t_{2gb})	$-\sqrt{2}\,B$
(t_{2ga})	(t_{2ga})	(t_{2gb})	(e_{gb})	$-\sqrt{2}\,B$
(t_{2ga})	(t_{2ga})	(t_{2gc})	(e_{ga})	$-\sqrt{2}\,B$
(t_{2gb})	(t_{2gb})	(t_{2gb})	(e_{ga})	$-\sqrt{2}\,B$
(t_{2gc})	(t_{2gc})	(t_{2gc})	(e_{gb})	$-\sqrt{2}\,B$
(t_{2ga})	(t_{2gb})	(t_{2gc})	(e_{gb})	$\sqrt{2}\,B$
(t_{2ga})	(t_{2gc})	(t_{2gb})	(e_{ga})	$\sqrt{2}\,B$
(t_{2gb})	(t_{2gb})	(t_{2ga})	(e_{gb})	$\sqrt{2}\,B$
(t_{2gc})	(t_{2gc})	(t_{2ga})	(e_{ga})	$\sqrt{2}\,B$
(t_{2ga})	(t_{2gb})	(e_{gb})	(t_{2gc})	$-2\sqrt{2}\,B$
(t_{2ga})	(t_{2gc})	(e_{ga})	(t_{2gb})	$-2\sqrt{2}\,B$
(t_{2ga})	(e_{ga})	(t_{2gc})	(e_{gb})	$4\,B$
(t_{2ga})	(e_{gb})	(t_{2gb})	(e_{ga})	$4\,B$
(t_{2ga})	(e_{ga})	(e_{gb})	(t_{2gc})	$-2\,B$
(t_{2ga})	(e_{gb})	(e_{ga})	(t_{2gb})	$-2\,B$
(e_{ga})	(e_{ga})	(t_{2ga})	(t_{2gc})	$-2\,B$
(e_{gb})	(e_{gb})	(t_{2ga})	(t_{2gb})	$-2\,B$
(t_{2gb})	(t_{2gc})	(e_{ga})	(e_{gb})	$2\,B+C$
(t_{2gb})	(t_{2gc})	(e_{gb})	(e_{ga})	$2\,B+C$
(t_{2ga})	(t_{2ga})	(e_{ga})	(e_{gb})	$2\,B+C$
(t_{2gb})	(e_{gb})	(t_{2gc})	(e_{ga})	$-4\,B$
(t_{2gb})	(e_{gb})	(e_{ga})	(t_{2gc})	$2\,B$
(t_{2gb})	(t_{2gb})	(e_{ga})	(e_{ga})	$2\,B$
(t_{2gc})	(t_{2gc})	(e_{gb})	(e_{gb})	$2\,B$
(t_{2ga})	(t_{2ga})	(t_{2gb})	(t_{2gc})	$3\,B+C$

The spin-orbit matrix elements in the $\{X, S\}$ and $\{L, S\}$ representations of the quadrate and trigonal fields and the corresponding $\{\Xi, \Sigma\}$ and $\{\Lambda, \Sigma\}$ representations of the cylindrical fields have been calculated from the expanded functions in the $|l, m_l\rangle\,|s, m_s\rangle$ form. Spin-orbit is diagonal in the (j, j) coupling scheme of all the three symmetries and the diagonal element is given by [16a]

$$\sum_i \zeta_{n_i l_i}\{j_i(j_i+1) - l_i(l_i+1) - s_i(s_i+1)\}/2$$

which depends only on the values of n_i, l_i, and j_i. Thus, the spin-orbit energies for the states (j, j')

are: $(5/2, 5/2) = 2\,\zeta_{nd}$, $(5/2, 3/2) = -1/2\,\zeta_{nd}$, and $(3/2, 3/2) = -3\,\zeta_{nd}$. Calculation of the spin-orbit matrix elements in the (γ, γ) scheme of the quadrate and trigonal fields is easily carried out by the use of the nonvanishing single electron matrix elements of Eq. (14)

$$\begin{aligned}
&\langle \gamma_{7a}(t_{2g}) | \boldsymbol{l}\cdot\boldsymbol{s} | \gamma_{7a}(t_{2g}) \rangle \\
&\qquad = \langle \gamma_{7b}(t_{2g}) | \boldsymbol{l}\cdot\boldsymbol{s} | \gamma_{7b}(t_{2g}) \rangle = \zeta\,, \\
&\langle \gamma_{8a}(t_{2g}) | \boldsymbol{l}\cdot\boldsymbol{s} | \gamma_{8a}(t_{2g}) \rangle = \langle \gamma_{8b}(t_{2g}) | \boldsymbol{l}\cdot\boldsymbol{s} | \gamma_{8b}(t_{2g}) \rangle = \\
&\langle \gamma_{8c}(t_{2g}) | \boldsymbol{l}\cdot\boldsymbol{s} | \gamma_{8c}(t_{2g}) \rangle \\
&\qquad = \langle \gamma_{8d}(t_{2g}) | \boldsymbol{l}\cdot\boldsymbol{s} | \gamma_{8d}(t_{2g}) \rangle = -\zeta/2\,, \\
&\langle \gamma_{8a}(t_{2g}) | \boldsymbol{l}\cdot\boldsymbol{s} | \gamma_{8a}(e_g) \rangle = \langle \gamma_{8b}(t_{2g}) | \boldsymbol{l}\cdot\boldsymbol{s} | \gamma_{8b}(e_g) \rangle = \\
&\langle \gamma_{8c}(t_{2g}) | \boldsymbol{l}\cdot\boldsymbol{s} | \gamma_{8c}(e_g) \rangle \\
&\qquad = \langle \gamma_{8d}(t_{2g}) | \boldsymbol{l}\cdot\boldsymbol{s} | \gamma_{8d}(e_g) \rangle = \frac{\sqrt{6}}{2}\,\zeta\,.
\end{aligned} \tag{14}$$

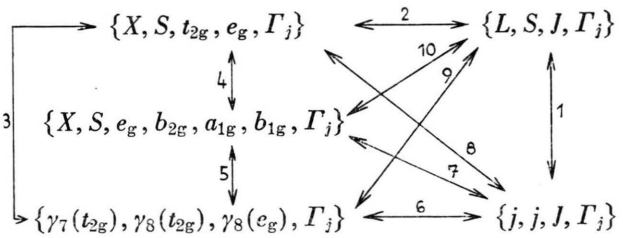
In the case of the cylindrical fields, the strong-field scheme diagonalizes the ligand field parameters, the weak-field scheme diagonalizes the electron correlation parameters, and the (ω, ω) coupling diagonalizes the spin-orbit parameter. The energy matrices [30] of the strong field formalism are given in Table 9 b and those of the weak field and (ω, ω) representation are included in Appendix [13] A.3 (a) and (b).

In the representations of the quadrate and trigonal fields in which octahedral orientation is maintained, cubic ligand field, electron correlation, and spin-orbit will be diagonal in cubic quantum number $\{\Gamma_j^{C}\}$ but not the axial part of the ligand field. The members in each pair of the cubic states, Γ_1^{C} and Γ_{3a}^{C}, Γ_2^{C} and Γ_{3b}^{C}, and $\Gamma_{4b,c}^{C}$ and $\Gamma_{5b,c}^{C}$ transforming as the quadrate Γ_1^{Q}, Γ_3^{Q}, and Γ_5^{Q} representations, respectively, will be connected by nonzero offdiagonal axial field parameters $D\,s$ and $D\,t$. Similarly, the members in each set of the cubic states, Γ_1^{C} and Γ_{5a}^{C}, Γ_2^{C} and Γ_{4a}^{C}, and $\Gamma_{3a,b}^{C}$, $\Gamma_{4b,c}^{C}$, and $\Gamma_{5b,c}^{C}$ transforming as the trigonal Γ_1^{T}, Γ_2^{T} and Γ_3^{T} representations, respectively, will be connected by nonzero offdiagonal axial field parameters $d\,\sigma$ and $d\,\tau$. Complete ligand field, including axial, will be diagonal in the quadrate $\{X, S, e_g, b_{2g}, a_{1g}, b_{1g}, \Gamma_j\}$ coupling scheme. The energy matrices in the form of matrix elements [30] in the $\{X, S, t_{2g}, e_g, \Gamma_j\}$ representation for both quadrate and trigonal symmetries are given in Tables 5 b and 7 b and in all other representations are listed in Appendix [13], A.1 and A.2. It should be noted that in the limit of the cubic crystalline field, i. e., zero axial ligand field parameters, btoh quadrate and trigonal energy matrices in the $\{X, S, t_{2g}, e_g, \Gamma_j\}$ and $\{L, S, J, \Gamma_j\}$ representations reduce to the corresponding cubic energy matrices of LIEHR and BALLHAUSEN [3a]. If, in addition, the spin-orbit coupling constant also vanishes, the energy matrices in the $\{X, S, t_{2g}, e_g, \Gamma_j\}$ representation will be identical to those of the TANABE and SUGANO [31].

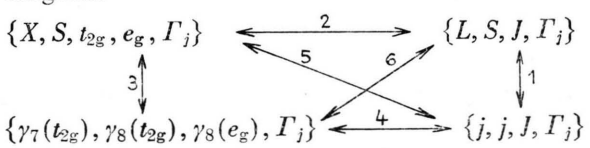
F) Unitary Transformations

The various transformations connecting different coupling schemes in the three cases of symmetry are as follows:

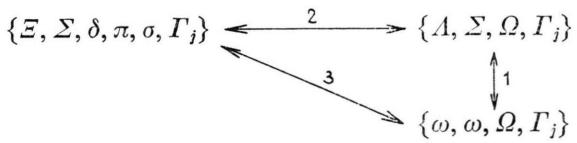
Quadrate



Trigonal



Cylindrical



The above unitary transformations can be promptly derived when the separate basis vectors are expanded, one in terms of the other. Appendix B [13] includes transformation matrices 1, 2, 3, and 4 of quadrate, 1, 2, and 3 of trigonal, and 1 and 2 of cylindrical symmetry. It is a straightforward matter to obtain the remaining connections in each case from these transformations.

The relationship $\mathcal{H}_a = \widetilde{T}(\Gamma_j)\mathcal{H}_b\,T(\Gamma_j)^*$ conjoining the transformations a and b by the transformation matrices $T(\Gamma_j)$ enables one to derive the complete set of energy matrices of scheme a from the known energy matrices of scheme b, and vice versa (l. c. [3b, 4a]). Such a computation has been carried

out by the author for all the transformations discussed, thus, providing an independent check on the calculation of perturbation matrices of all representations. Other checks available on the derived energy equations are described below.

In each symmetry, the energy matrices of different representations will give exactly the same eigenvalues for the same set of parametric values. In addition, for a given set of B, C, Dq, and ζ with $Ds = D\sigma = 0$ and $Dt = D\tau = 0$, identical (cubic) eigenvalues will be obtained from both quadrate and trigonal energy matrices (in any representation), providing a check on all except the axial ligand field parameters. Finally, if we set $Dq = 0$, with $Ds = D\sigma = D\mathfrak{s}$ and $Dt = D\tau = D\mathfrak{t}$ and same set of B, C, and ζ parameters, the same set of (cylindrical) eigenvalues will result from cylindrical, quadrate, and trigonal energy matrices (in any representation), thus, providing a check on the axial ligand field parameters also.

G) Wave Functions and Energy Matrices of d^8 Configuration

The symmetry adapted wave functions of d^8 electronic configuration in any representation can be easily written down, if needed, from the two electron functions given here by recourse to electron-hole conjugation. The appropriate energy matrices can be obtained by simply reversing the sign of all parameters of one electron operators, namely, ζ, Dq, $D\mu$, and $D\nu$. There will be a constant energy difference, $27A - 42B + 21C$, only in the diagonal elements with respect to electron correlation terms. It need not concern us, however, since our interest is in energy differences and not in absolute eigenvalues.

H) Energy Diagrams

From the secular determinants we see that the characteristic functions and values of Schroedinger's equation are parametrically dependent upon six quantities ζ, B, C, Dq, $D\mu$, and $D\nu$ in the case of quadrate and trigonal symmetries and five quantities ζ, B, C, $D\mu$, and $D\nu$ in the case of cylindrical symmetry. It is well-known that the spin-orbit coupling constant ζ and the electron correlation parameters B and C are, in general, reduced in magnitude in complexes relative to the free-ion. We have thus fixed the ζ values to be 130 cm^{-1} and 550 cm^{-1} for d^2 and d^8 configurations, respectively, appropriate to trivalent vanadium and divalent nickel [32]. The corresponding B values were chosen to be 600 cm^{-1} and 800 cm^{-1} considering again the vanadium(III) and nickel(II) compounds as exemplary systems [32]. We have also assumed the relation $C = 4B$ which is fairly well fulfilled within the elementary theory of atomic term values [32].

The parametric set of secular equations in the quadrate and trigonal $\{X, S, t_{2g}, e_g, \Gamma_j\}$ and quadrate $\{X, S, e_g, b_{2g}, a_{1g}, b_{1g}, \Gamma_j\}$ representations have been programmed [33] to obtain the energy levels as a function of Dq which is varied from 0 cm^{-1} to $\pm 4{,}000$ cm^{-1}. Positive Dq values correspond to quadrate and trigonal fields of octahedral d^2 and tetrahedral d^8 and the negative Dq to those of the tetrahedral d^2 and octahedral d^8 configurations. The $D\nu$ and $\varkappa$, which is the ratio of $D\mu$ to $D\nu$, are fixed in the $\{X, S, t_{2g}, e_g, \Gamma_j\}$ representation of the quadrate and trigonal fields whereas the relation $Dt = -4/9\,Dq$, appropriate to square planar geometry [34], has been used in the quadrate $\{X, S, e_g, b_{2g}, a_{1g}, b_{1g}, \Gamma_j\}$ representation with a fixed value of $\varkappa$. The selected values of Dt (quadrate) and $D\tau$ (trigonal) in cm^{-1} for various distortions and substitutions [35] in the $\{X, S, t_{2g}, e_g, \Gamma_j\}$ representation of quadrate and trigonal fields are listed below:

	d^2		d^8	
	Octahedral	Tetrahedral	Octahedral	Tetrahedral
Quadrate	± 250	± 125	± 125	± 60
Trigonal	± 75	± 35	± 35	± 15

Such diagrams have been constructed for $\varkappa$ values [36] of ± 2 and ± 5. The energy plots [37] with one set of $D\nu$ values, and a $\varkappa$ value of 2 are shown in Figures 1 to 8 and 49 to 56. The d^8 square planar energy diagram is displayed in Figure 41. All other plots, Figures 9 to 40, 42 to 48, 57 to 80 are included in Appendix [13] C. 1 and 2.

The energy diagrams of cylindrical fields in the $\{\Xi, \Sigma\}$ representation are obtained by varying $D\mathfrak{t}$ for a fixed value of $\varkappa$. The value of $D\mathfrak{t}$ is varied from -2000 cm^{-1} to $+2000$ cm^{-1} and once again $\varkappa$ values of ± 2 and ± 5 have been used for both d^2 and d^8. The plots with $\varkappa = 2$ for d^2 and d^8 are shown in Figs. 81 and 85 and the others in Figs. 82 to 84 and 86 to 88, Appendix [13] C.3.

III. Summary

Complete theory of d^2 and d^8 electronic configurations immersed in quadrate, trigonal, and cylindrical fields including spin-orbit perturbation and full configuration interaction has been detailed. Such a treatment has been carried out in five different representations for quadrate fields, four representa-

tions for trigonal fields and three representations for cylindrical fields. The symmetry adapted spin-orbital wave functions in all the representations, the corresponding energy matrices, and the unitary transformations connecting the various representations have been derived. The energy levels in the strong field scheme have been obtained for appropriate sets of parametric values in all three symmetries. The symmetry adapted wave functions, the secular determinants, the unitary transformations, and the energy level diagrams will be useful in a precise study of optical and magnetic properties of quadrately or trigonally distorted or substituted octahedral or tetrahedral complexes and of compounds of cylindrical symmetry of d^2 and d^8 electronic configurations.

IV. Acknowledgments

The author is deeply indebted to Dr. A. D. LIEHR for suggesting the problem and for many stimulating discussions. The author gratefully acknowledges the constant encouragement received from Dr. H. P. KLUG and Dr. P. C. CROSS during this investigation. Thanks are due to Mr. R. L. ANDERSON and Mr. J. BEASLEY for computer programming and Mr. J. F. BENES and Mr. E. L. HELGERMAN for expert tracing of the complicated energy diagrams obtained from the computer. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Florida Atlantic University Division of Sponsored Research, for financial support in the preparation of the manuscript.

Appendix A [13]

Wave Functions and Energy Matrices [30]

1. **Quadrate**
   (a) $\{X, S, e_g, b_{2g}, a_{1g}, b_{1g}, \Gamma_j\}$ Representation
   (b) $\{L, S, J, \Gamma_j\}$ Representation
   (c) $\{j, j, J, \Gamma_j\}$ Representation
   (d) $\{\gamma_7(t_{2g}), \gamma_8(t_{2g}), \gamma_8(e_g), \Gamma_j\}$ Representation
2. **Trigonal**
   (a) $\{L, S, J, \Gamma_j\}$ Representation
   (b) $\{j, j, J, \Gamma_j\}$ Representation
   (c) $\{\gamma_7(t_{2g}), \gamma_8(t_{2g}), \gamma_8(e_g), \Gamma_j\}$ Representation
3. **Cylindrical**
   (a) $\{\Lambda, \Sigma, \Omega, \Gamma_j\}$ Representation
   (b) $\{\omega, \omega, \Omega, \Gamma_j\}$ Representation

Appendix B [13]

Unitary Transformation Matrices

1. **Quadrate**
   (a) $(L, S, J, \Gamma_j \mid X, S, t_{2g}, e_g, \Gamma_j)$
   (b) $(j, j, J, \Gamma_j \mid L, S, J, \Gamma_j)$
   (c) $(\gamma_7(t_{2g}), \gamma_8(t_{2g}), \gamma_8(e_g), \Gamma_j \mid X, S, t_{2g}, e_g, \Gamma_j)$
   (d) $(X, S, t_{2g}, e_g, \Gamma_j \mid X, S, e_g, b_{2g}, b_{1g}, a_{1g}, \Gamma_j)$
2. **Trigonal**
3. **Cylindrical**
   (a) $(\Lambda, \Sigma, \Omega, \Gamma_j \mid \Xi, \Sigma, \delta, \pi, \sigma, \Gamma_j)$
   (b) $(\omega, \omega, \Omega, \Gamma_j \mid \Lambda, \Sigma, \Omega, \Gamma_j)$

Appendix C [13]

Energy Level Diagrams [37]

[d^2: $B=600\ \mathrm{cm}^{-1}$, $C/B=4$, and $\zeta=130\ \mathrm{cm}^{-1}$;
d^8: $B=800\ \mathrm{cm}^{-1}$, $C/B=4$, and $\zeta=-550\ \mathrm{cm}^{-1}$].

1. **Quadrate**

Figures 9–11	d^2 Octahedral-Quadrate;
$Dt = 250\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 12–14	d^2 Octahedral-Quadrate;
$Dt = -250\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 15–17	d^2 Tetrahedral-Quadrate;
$Dt = 125\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 18–20	d^2 Tetrahedral-Quadrate;
$Dt = -125\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 21–23	d^8 Octahedral-Quadrate;
$Dt = 125\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 24–26	d^8 Octahedral-Quadrate;
$Dt = -125\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 27–29	d^8 Tetrahedral-Quadrate;
$Dt = 60\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 30–32	d^8 Tetrahedral-Quadrate;
$Dt = -60\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 33–36	Octahedral d^2-Square Planar; $\varkappa = 2, -2, 5, -5$.
Figures 37–40	Tetrahedral d^2-Square Planar; $\varkappa = -2, 5, -5$.
Figures 42–44	Octahedral d^8-Square Planar; $\varkappa = 2, -2, 5, -5$.
Figures 45–48	Tetrahedral d^8-Square Planar; $\varkappa = 2, -2, 5, -5$.

2. **Trigonal**

Figures 57–59	d^2 Octahedral-Trigonal;
$D\tau = 75\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 60–62	d^2 Octahedral-Trigonal;
$D\tau = -75\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 63–65	d^2 Tetrahedral-Trigonal;
$D\tau = 35\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 66–68	d^2 Tetrahedral-Trigonal;
$D\tau = -35\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 69–71	d^8 Octahedral-Trigonal;
$D\tau = 35\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 72–74	d^8 Octahedral-Trigonal;
$D\tau = -35\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 75–77	d^8 Tetrahedral-Trigonal;
$D\tau = 15\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.
Figures 78–80	d^8 Tetrahedral-Trigonal;
$D\tau = -15\ \mathrm{cm}^{-1}$,	$\varkappa = -2, 5, -5$.

3. **Cylindrical**

Figures 82–84	d^2 Cylindrical; $\varkappa = -2, 5, -5$.
Figures 86–88	d^8 Cylindrical; $\varkappa = -2, 5, -5$.

[1] Presented in part at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 14–19, 1965, and at the 150th National Meeting of the American Chemical Society, Atlantic City, New Jersey, September 1965.

[2] Reprint requests to the present address: Department of Chemistry, Florida Atlantic University, *Boca Raton*, Florida 33432.

[3] (a) A. D. LIEHR and C. J. BALLHAUSEN, Ann. Phys. New York **6**, 134 [1959]; (b) A. D. LIEHR, J. Phys. Chem. **64**, 43 [1960]; (c) Ibid. **67**, 1314 [1963]; (d) J. C. EISENSTEIN, J. Chem. Phys. **34**, 1628 [1961]; [Errata, ibid. **35**, 2246 [1961]]; (e) W. A. RUNCIMAN and K. A. SCHROEDER, Proc. Roy. Soc. London **A 265**, 489 [1962]; (f) K. A. SCHROEDER, J. Chem. Phys. **37**, 2553 [1962]; (g) T. M. DUNN and W.-K. LI, ibid. **47**, 3783 [1967]; (h) K. A. SCHROEDER, ibid. **37**, 1587 [1962]; (i) A. D. LIEHR, unpublished; (j) H. A. WEAKLIEM, J. Chem. Phys. **36**, 2117 [1962]; (k) J. FERGUSON, Austr. J. Chem. **23**, 635 [1970].

[4] See for these and for the restricted calculations, references cited in (a) J. R. PERUMAREDDI, J. Phys. Chem. **71**, 3144 [1967]. Recent complete and restricted calculations include (b) C. W. DEKOCK and D. M. GRUEN, J. Chem. Phys. **44**, 4387 [1966]; (c) Ibid. **46**, 1096 [1967]; (d) D. R. SCOTT and F. A. MATSEN, J. Phys. Chem. **72**, 16 [1968]; (e) C. A. L. BECKER, D. W. MEEK, and T. M. DUNN, ibid. **72**, 3588 [1968]; (f) Ibid. **74**, 1568 [1970]; (g) T. W. COUCH and G. P. SMITH, J. Chem. Phys. **53**, 1337 [1970].

[5] N. S. HUSH and R. J. M. HOBBS, in "Progress in Inorganic Chemistry," vol. 10, Ed. F. A. COTTON, Interscience Publishers, New York 1968.

[6] Read 3(b) and references cited therein for the importance and applicability of this coupling scheme.

[7] (a) Either of the $\{X, S\}$ representations of the quadrate fields can be employed in the case of the square pyramidal systems; (b) we shall always use Bethe's Γ notation for spin-orbital states and reserve Mulliken's A, B, E, and T notation for orbital representations alone. In either case, the many electron states are denoted by capital letters and the one electron functions by lower case letters.

[8] H. GOLDSTEIN, "Classical Mechanics", Addison-Wesley, Cambridge 1951.

[9] These functions have been adjusted with phase factors so that in the limit of cubic ligand field, our energy matrices will become identical to those of LIEHR and BALLHAUSEN [3a].

[10] A. D. LIEHR, J. Phys. Chem. **68**, 665 [1964].

[11] (a) R. F. FENSKE, D. S. MARTIN, Jr., and K. RUEDENBERG, Inorg. Chem. **1**, 441 [1962]; (b) R. F. FENSKE and D. S. MARTIN, A. E. C. Report IS-342, Ames Laboratory, Iowa State University, Ames, Iowa, 1961. Available from the office of Technical Services, Department of Commerce, Washington 25, D. C.

[12] Our functions differing only in phase factors from those of reference 11(b) are included in the appendix because of the reason that our corresponding energy matrices contain ligand field parameters somewhat differently defined. A comparison and interrelationship of the variously defined ligand field parameters can be found in 11(b).

[13] The entire Appendix has been deposited with the National Auxiliary Publications Service. For orders, order NAPS Document 01984, from MICROFICHE PUBLICATIONS, Division of Microfiche Systems Corporation, 305 East 46 Street, New York, N. Y., 10017; remitting $1.50 for each microfiche or $26.45 for each photocopy.

[14] (a) The single electron σ orbital function in this representation is actually σ^+, but for convenience the + superscript is being omitted in this report; (b) It should be noted that as a matter of definition, we have taken our spin functions to be even under inversion in the origin. Hence, we have that the reflection $\sigma(x-z)$ is mathematically equivalent to a rotation by $\pi(C_2)$ about the y-axis.

[15] We may consider that the σ_v symmetry operation transforms any doubly degenerate representation $\xi_\pm$ to $\xi_\mp$. Thus, $\sigma_v(\varphi_\pm) = \varphi_\mp$, $\sigma_v(\gamma_\pm) = \gamma_\mp$ and so on.

[16] (a) E. U. CONDON and G. H. SHORTLEY, "The Theory of Atomic Spectra", Cambridge University Press, New York 1957. See also (b) J. C. SLATER, "Quantum Theory of Atomic Structure", Vol. II, McGraw-Hill Book Co., Inc., New York 1960.

[17] H. A. BETHE, Ann. Physik **3**, 133 [1929]. A complete English translation of this article is available from Consultants Bureau, New York *.

* Footnotes 18–37 on page 1860.

Figs. 1 and 2. Energy level diagrams for a d^2 electronic system immersed in an octahedral field with a quadrate component; $B=600\ cm^{-1}$, $C/B=4$, $\zeta=130\ cm^{-1}$, $\varkappa=2$, $Dt=+250$ and $-250\ cm^{-1}$.

Figs. 3 and 4. Energy level diagrams for a d^2 electronic system immersed in a tetrahedral field with a quadrate component; $B=600\ cm^{-1}$, $C/B=4$, $\zeta=130\ cm^{-1}$, $\varkappa=2$, $Dt=+125$ and $-125\ cm^{-1}$.

Figs. 5 and 6. Energy level diagrams for a d^8 electronic system immersed in an octahedral field with a quadrate component; $B=800\ cm^{-1}$, $C/B=4$, $\zeta=-550\ cm^{-1}$, $\varkappa=2$, $Dt=+125$ and $-125\ cm^{-1}$.

Figs. 7 and 8. Energy level diagrams for a d^8 electronic system immersed in a tetrahedral field with a quadrate component; $B=800\ cm^{-1}$, $C/B=4$, $\zeta=-550\ cm^{-1}$, $\varkappa=2$, $Dt=+60$ and $-60\ cm^{-1}$.

Fig. 41. Energy level diagram for a d^8 electronic system immersed in quadrate fields in the electrostatic limit of square planar physics, i. e., $Dt=-4/7\,Dq$. Other parameters are: $\varkappa=2$, $B=800\ cm^{-1}$, $C/B=4$, and $\zeta=-550\ cm^{-1}$.

Figs. 49 and 50. Energy level diagrams for a d^2 electronic system immersed in an octahedral field with a trigonal component; $B=600\ cm^{-1}$, $C/B=4$, $\zeta=130\ cm^{-1}$, $\varkappa=2$, $D\tau=+75$ and $-75\ cm^{-1}$.

Figs. 51 and 52. Energy level diagrams for a d^2 electronic system immersed in a tetrahedral field with a trigonal component; $B=600\ cm^{-1}$, $C/B=4$, $\zeta=130\ cm^{-1}$, $\varkappa=2$, $D\tau=+35$ and $-35\ cm^{-1}$.

Figs. 53 and 54. Energy level diagrams for a d^8 electronic system immersed in an octahedral field with a trigonal component; $B=800\ cm^{-1}$, $C/B=4$, $\zeta=-550\ cm^{-1}$, $\varkappa=2$, $D\tau=+35$ and $-35\ cm^{-1}$.

Fig. 55. Energy level diagrams for a d^8 electronic system immersed in a tetrahedral field with a trigonal component; $B=800\ cm^{-1}$, $C/B=4$, $\zeta=-550\ cm^{-1}$, $\varkappa=2$, $D\tau=+15$ and $-15\ cm^{-1}$.

Figures 1–8, 41, 49–56, 81 and 85 (see the following pages 1841–1856) have already been reduced from a large size. The other Figures are only mentioned in Appendix C.

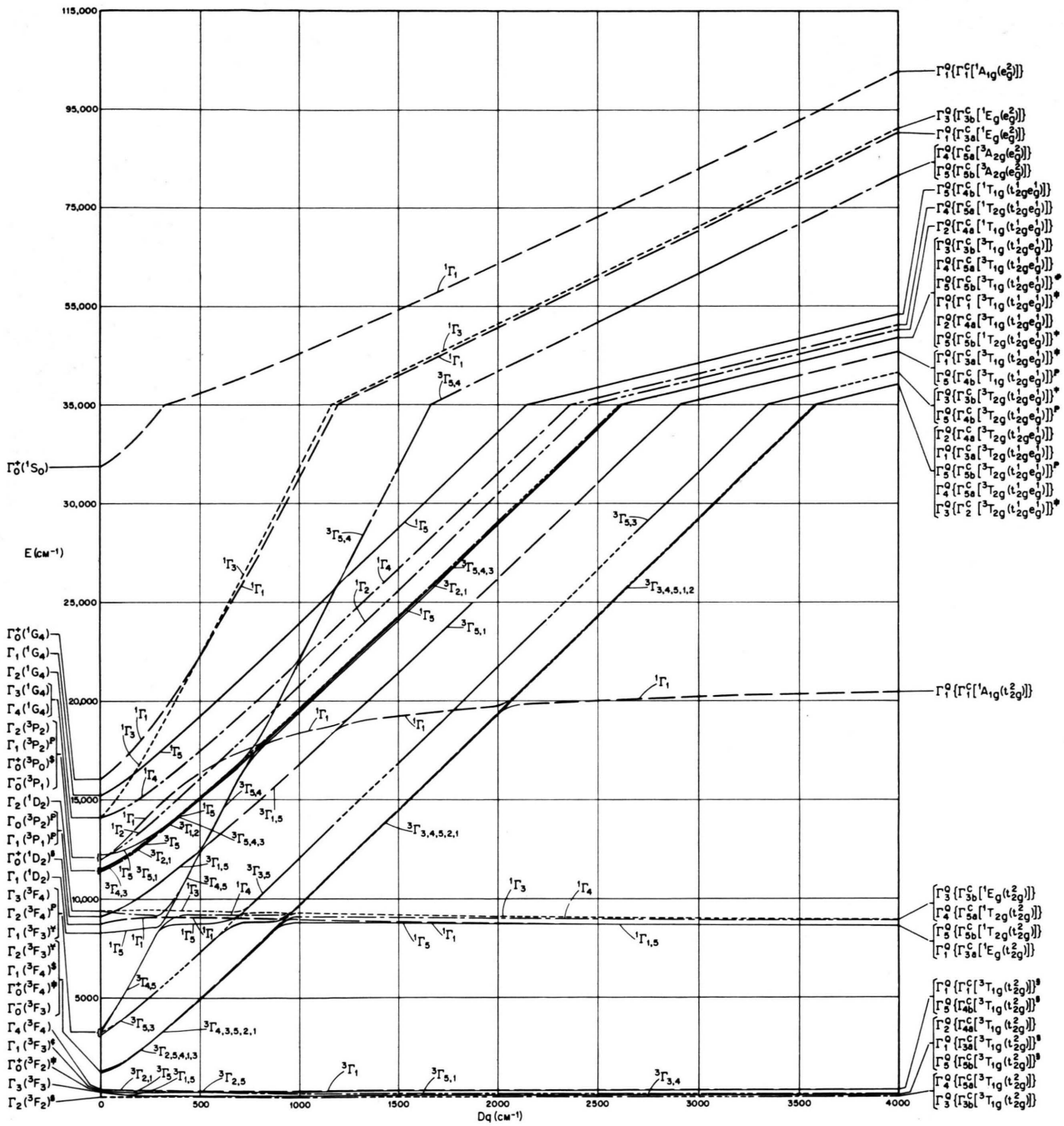


Figure 1

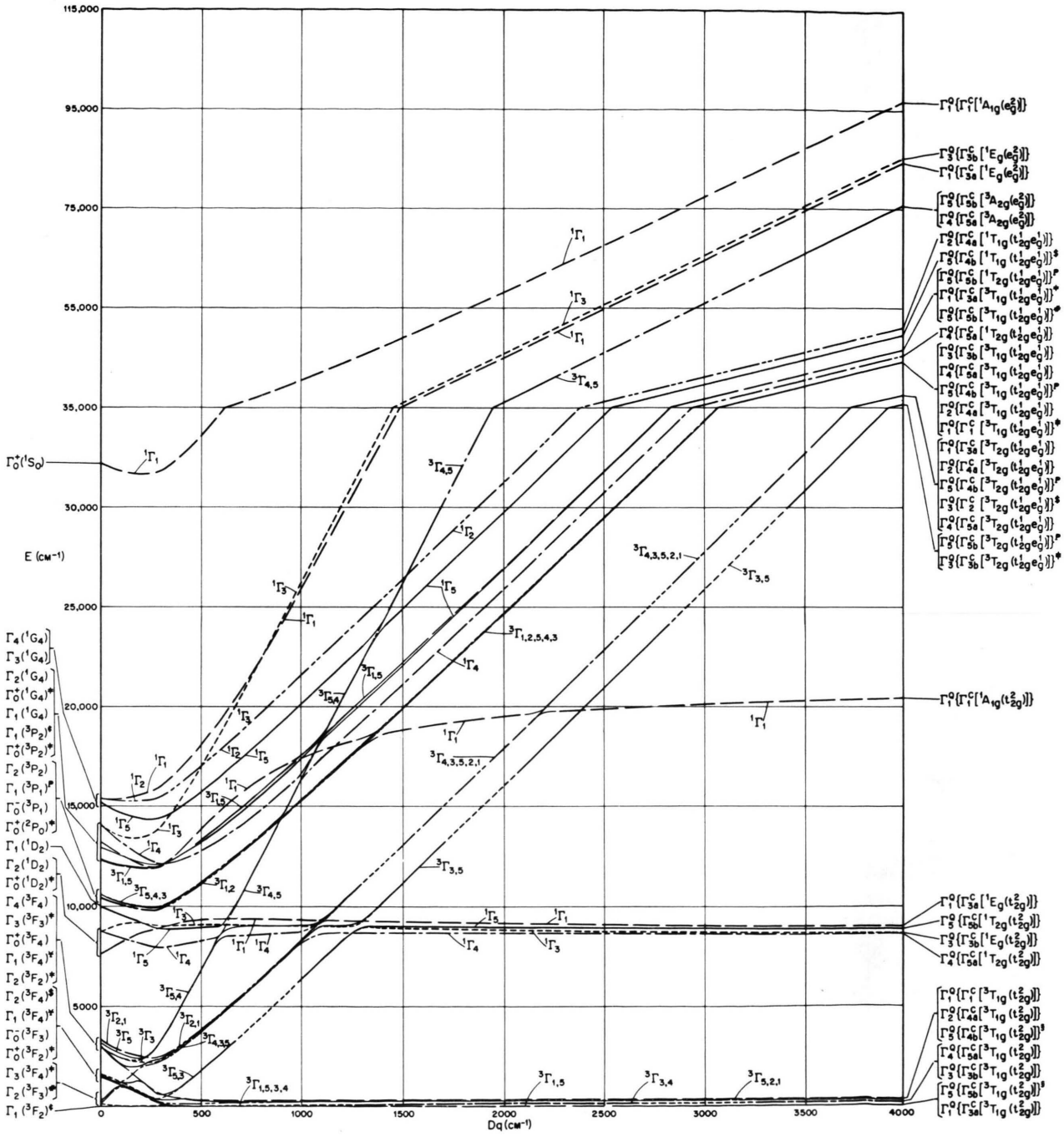
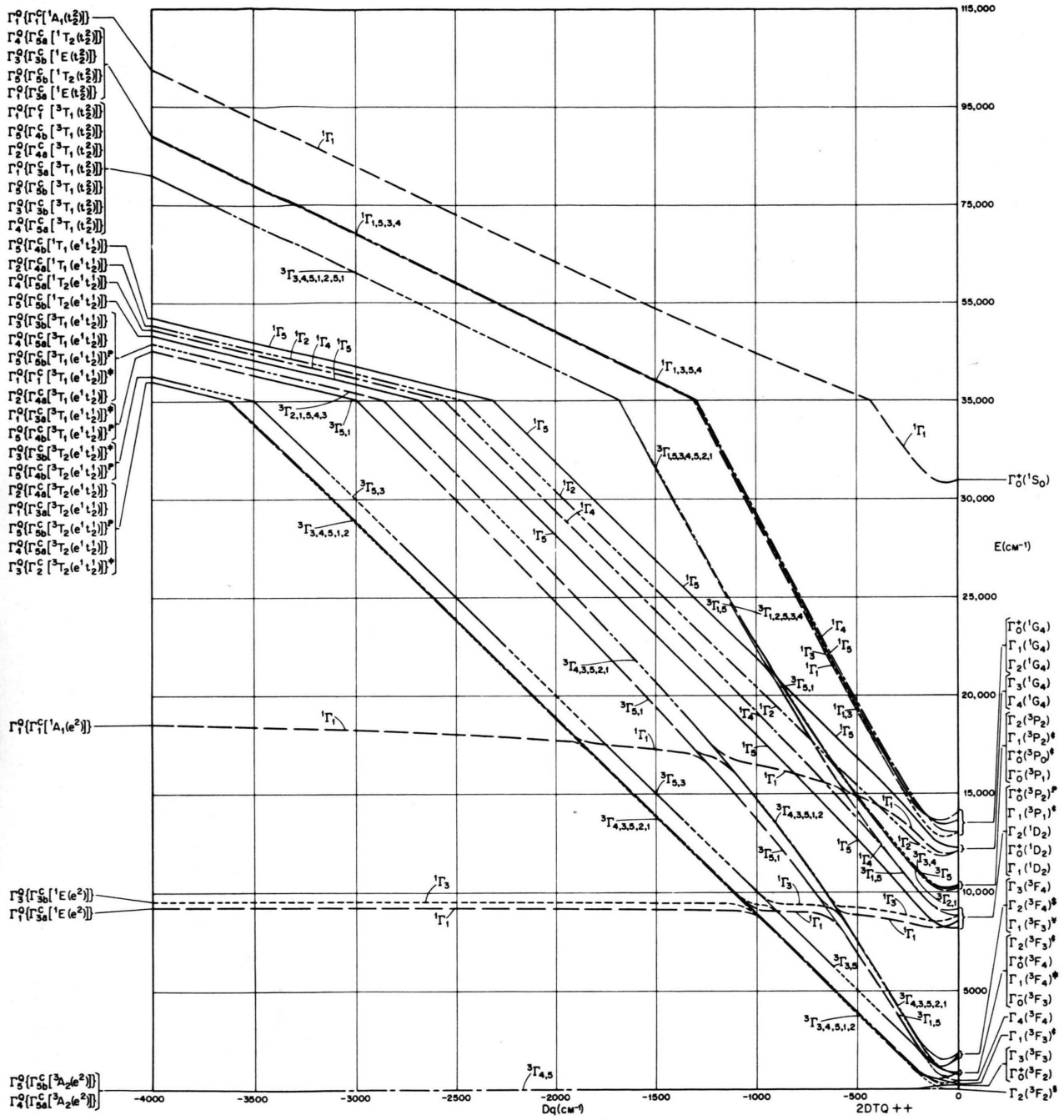


Figure 2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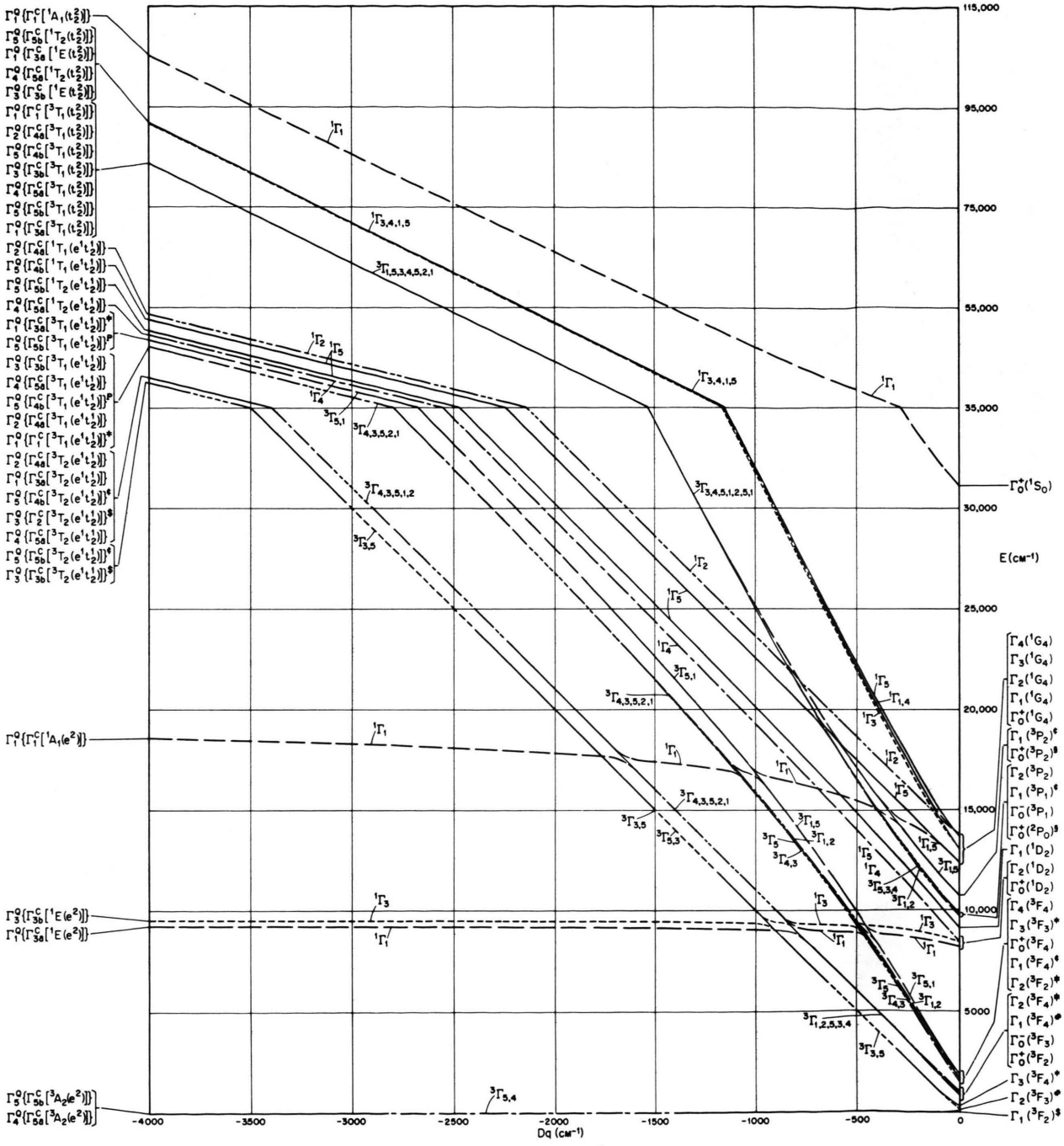
75,000
55,000
35,000
30,000
25,000
20,000
15,000
10,000
5000
-4000
-3500
-3000
-2500
-2000
-1500
-1000
-500
0
Dq(cm⁻¹)
2DTQ++
Tet.-Quad. d²
ζ = 130, B = 600, Dt = 125cm⁻¹, κ = 2, C/B = 4

Figure 3



Tet. – Quad. d^2

$\zeta = 130$, $B = 600$, $Dt = -125\,cm^{-1}$, $\kappa = 2$, $C/B = 4$

Figure 4

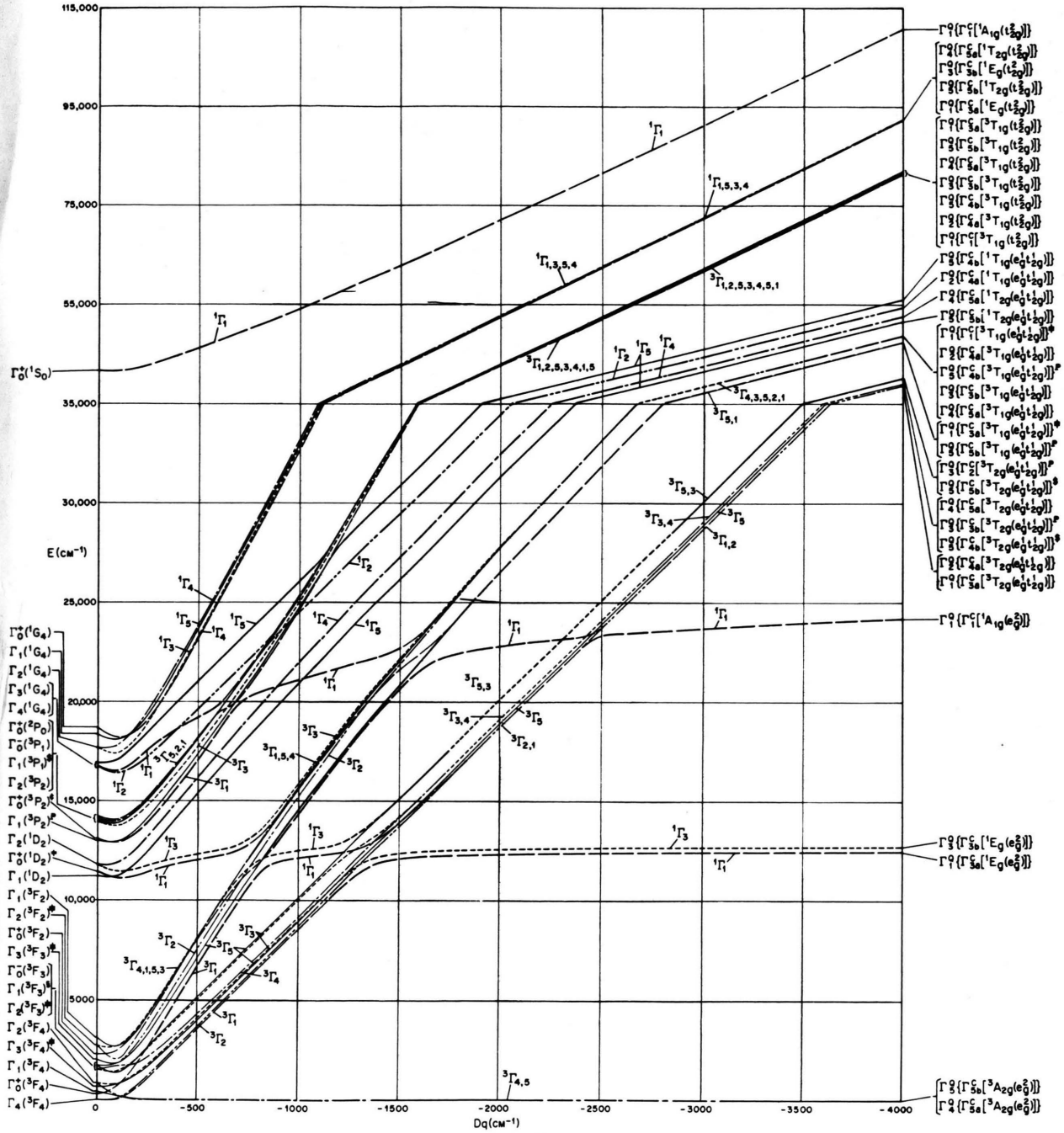


Figure 5

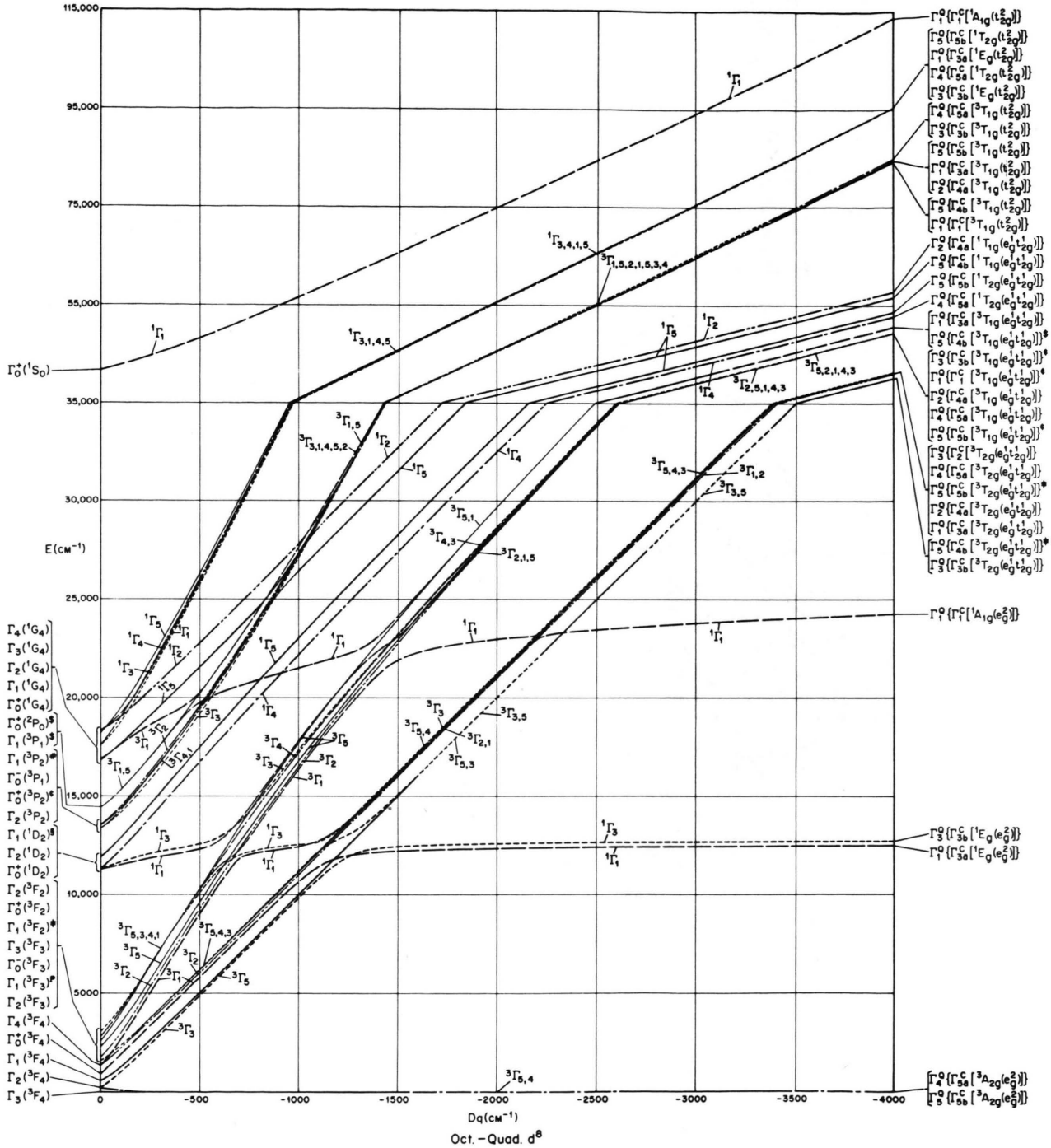


Figure 6

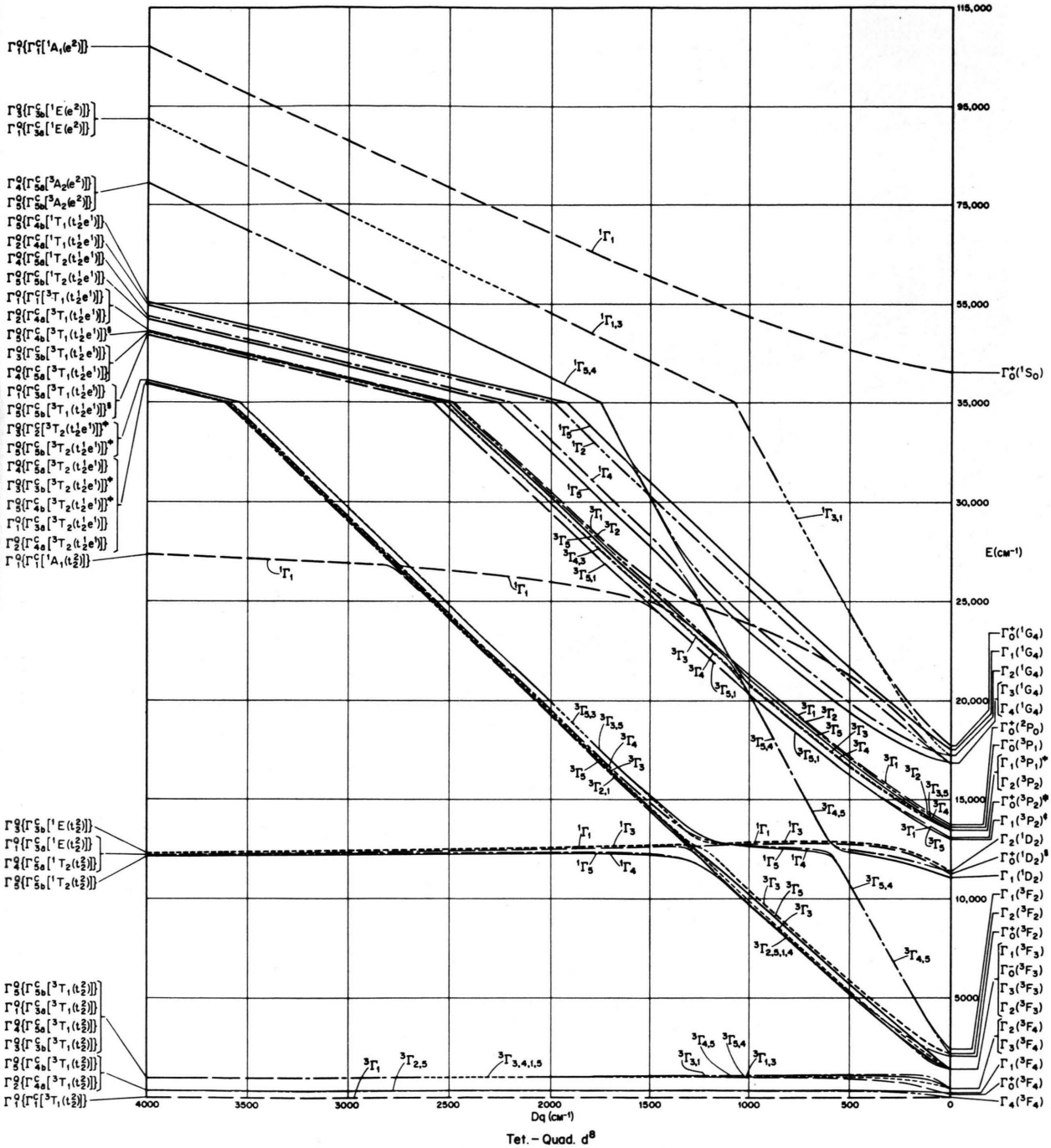
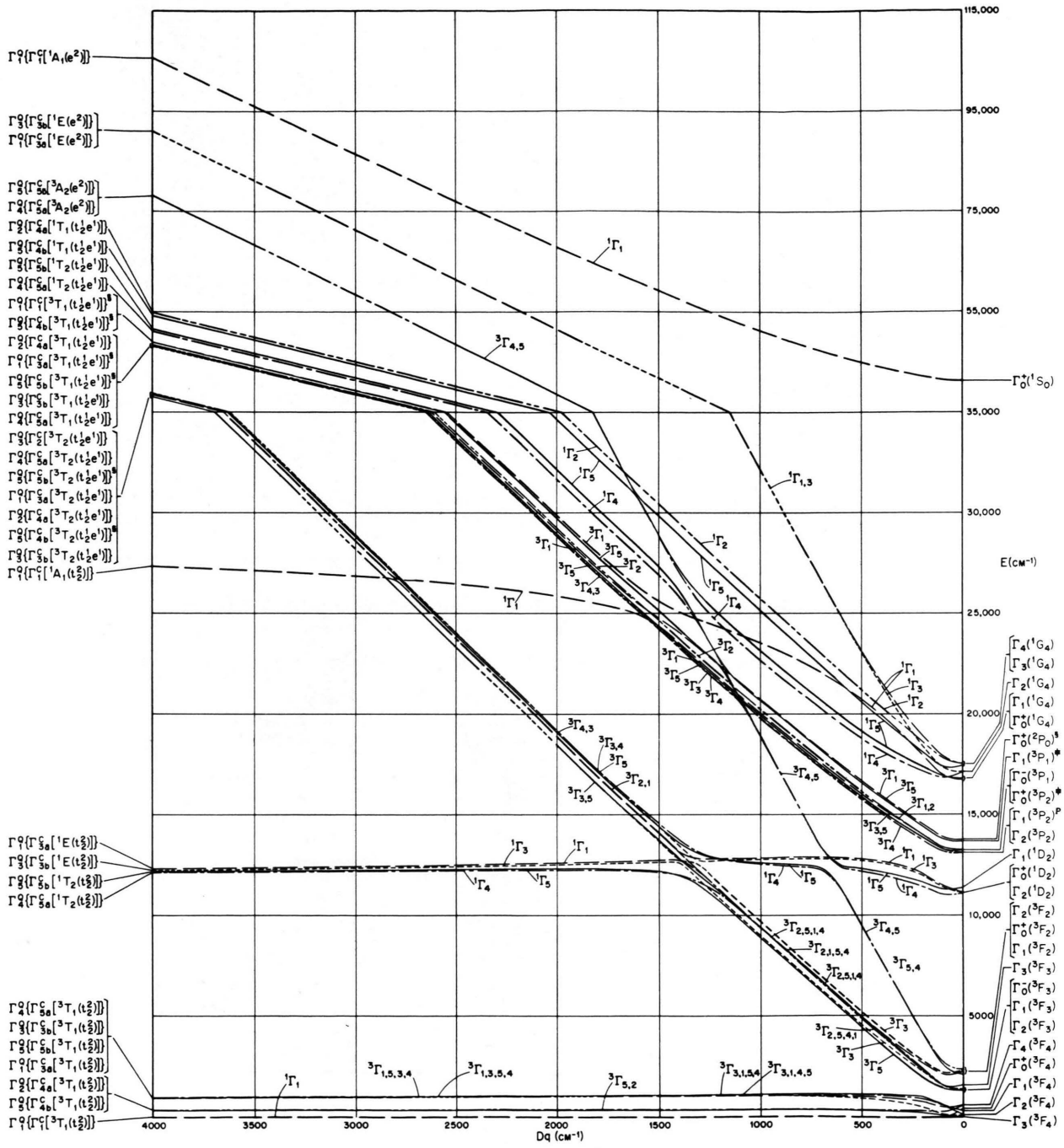


Figure 7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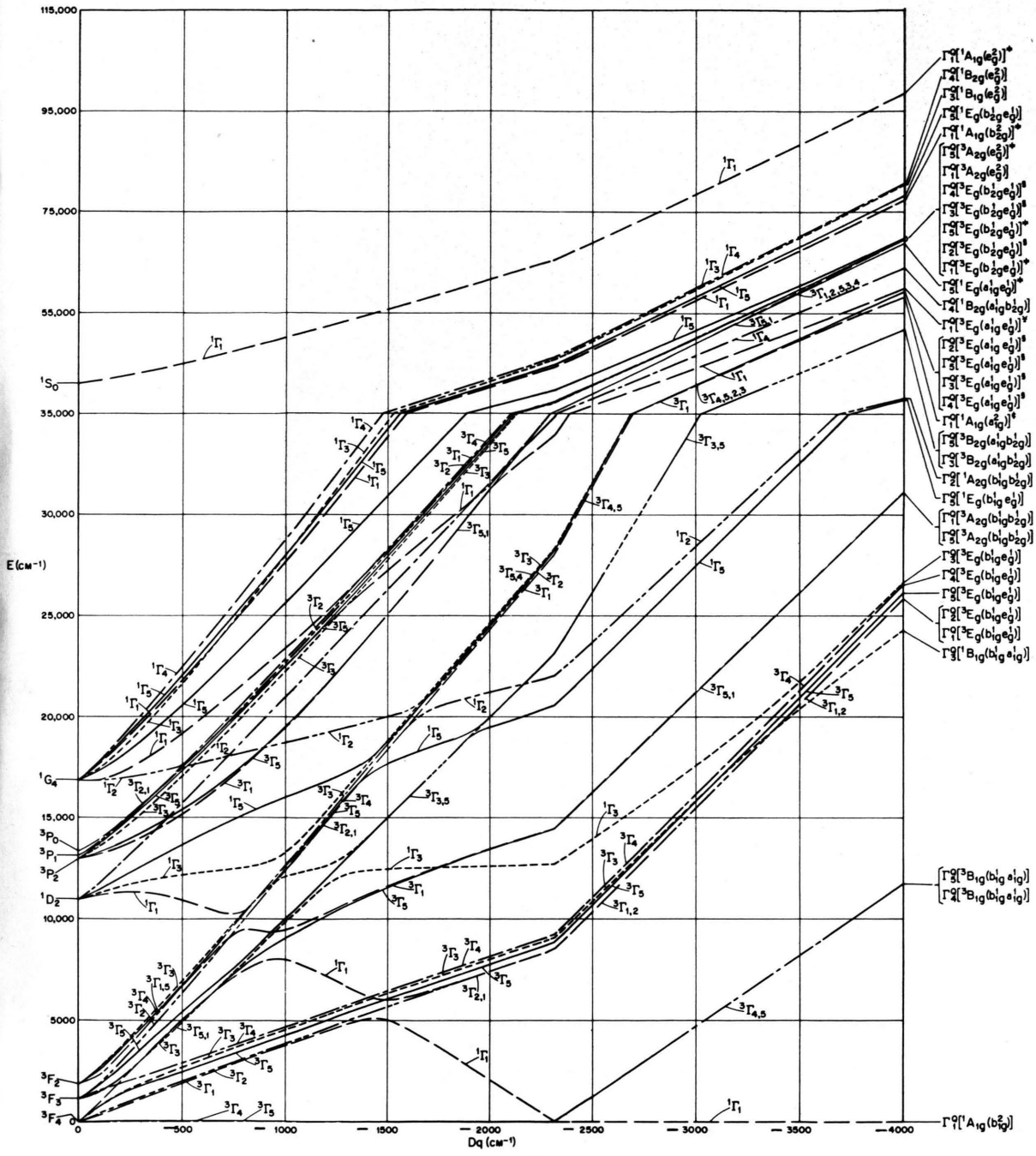
55,000
35,000
30,000
25,000
20,000
15,000
10,000
5000
0
500
1000
1500
2000
2500
3000
3500
4000
Dq (cm⁻¹)
Tet.-Quad. d⁸
ζ=-550, B=800, Dt=-60cm⁻¹, κ=2, C/B=4

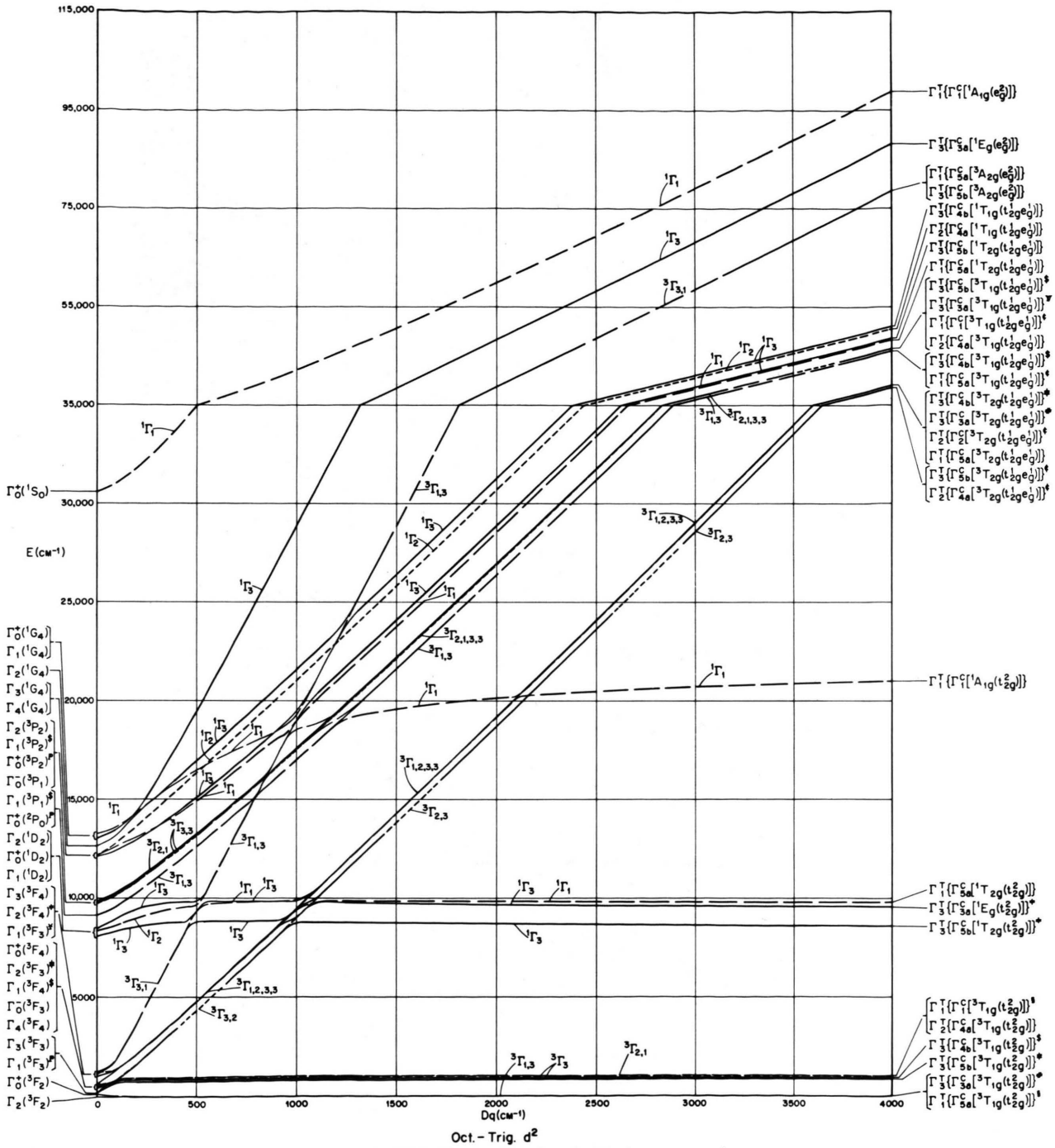
Figure 8



Oct.- Sq. Pl. d^8

ζ=-550, B=800, Dt=-4/7Dq, κ=2, C/B=4

Figure 41



Oct.- Trig. d^2

$\zeta = 130$, $B = 600$, $D\tau = 75\,cm^{-1}$, $\kappa = 2$, $C/B = 4$

Figure 49

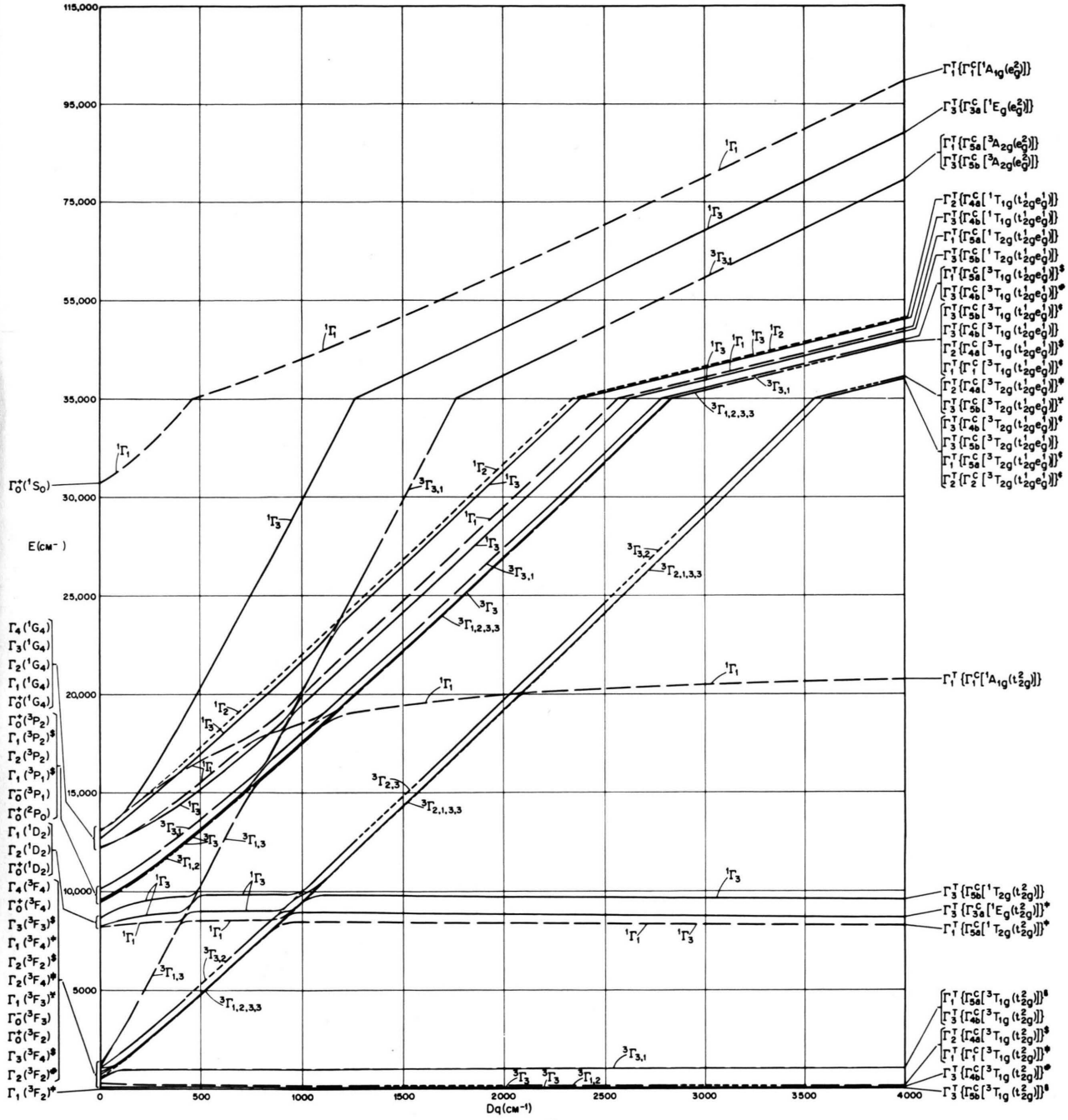

115,000
95,000
75,000
55,000
35,000
30,000
25,000
20,000
15,000
10,000
5000
E(cm⁻¹)
0
500
1000
1500
2000
2500
3000
3500
4000
Dq(cm⁻¹)
Γ₀⁺(¹S₀)
Γ₄(¹G₄)
Γ₃(¹G₄)
Γ₂(¹G₄)
Γ₁(¹G₄)
Γ₀⁺(¹G₄)
Γ₀⁺(³P₂)
Γ₁(³P₂)$
Γ₂(³P₂)
Γ₁(³P₁)$
Γ₀⁻(³P₁)
Γ₀⁺(²P₀)
Γ₁(¹D₂)
Γ₂(¹D₂)
Γ₀⁺(¹D₂)
Γ₄(³F₄)
Γ₀⁺(³F₄)
Γ₃(³F₃)$
Γ₁(³F₄)*
Γ₂(³F₂)$
Γ₂(³F₄)*
Γ₁(³F₃)*
Γ₀⁻(³F₃)
Γ₀⁺(³F₂)
Γ₃(³F₄)$
Γ₂(³F₂)*
Γ₁(³F₂)*
Γ₁ᵀ{Γ₁ᶜ[¹A₁g(e_g²)]}
Γ₃ᵀ{Γ₃ₐᶜ[¹Eg(e_g²)]}
Γ₁ᵀ{Γ₅ₐᶜ[³A₂g(e_g²)]}
Γ₃ᵀ{Γ₅ᵇᶜ[³A₂g(e_g²)]}
Γ₂ᵀ{Γ₄ₐᶜ[¹T₁g(t₂g¹e_g¹)]}
Γ₃ᵀ{Γ₄ᵇᶜ[¹T₁g(t₂g¹e_g¹)]}
Γ₁ᵀ{Γ₅ₐᶜ[¹T₂g(t₂g¹e_g¹)]}
Γ₃ᵀ{Γ₅ᵇᶜ[¹T₂g(t₂g¹e_g¹)]}
Γ₁ᵀ{Γ₅ₐᶜ[³T₁g(t₂g¹e_g¹)]}$
Γ₃ᵀ{Γ₄ᵃᶜ[³T₁g(t₂g¹e_g¹)]}*
Γ₃ᵀ{Γ₅ᵇᶜ[³T₁g(t₂g¹e_g¹)]}*
Γ₃ᵀ{Γ₄ᵇᶜ[³T₁g(t₂g¹e_g¹)]}
Γ₂ᵀ{Γ₄ₐᶜ[³T₁g(t₂g¹e_g¹)]}$
Γ₁ᵀ{Γ₁ᶜ[³T₁g(t₂g¹e_g¹)]}*
Γ₂ᵀ{Γ₄ₐᶜ[³T₂g(t₂g¹e_g¹)]}*
Γ₃ᵀ{Γ₅ᵇᶜ[³T₂g(t₂g¹e_g¹)]}*
Γ₃ᵀ{Γ₄ᵇᶜ[³T₂g(t₂g¹e_g¹)]}*
Γ₃ᵀ{Γ₅ᵇᶜ[³T₂g(t₂g¹e_g¹)]}
Γ₁ᵀ{Γ₅ₐᶜ[³T₂g(t₂g¹e_g¹)]}*
Γ₂ᵀ{Γ₂ᶜ[³T₂g(t₂g¹e_g¹)]}*
Γ₁ᵀ{Γ₁ᶜ[¹A₁g(t₂g²)]}
Γ₃ᵀ{Γ₅ᵇᶜ[¹T₂g(t₂g²)]}
Γ₃ᵀ{Γ₃ₐᶜ[¹Eg(t₂g²)]}*
Γ₁ᵀ{Γ₅ₐᶜ[¹T₂g(t₂g²)]}*
Γ₁ᵀ{Γ₅ₐᶜ[³T₁g(t₂g²)]}*
Γ₃ᵀ{Γ₄ᵇᶜ[³T₁g(t₂g²)]}
Γ₂ᵀ{Γ₄ₐᶜ[³T₁g(t₂g²)]}$
Γ₁ᵀ{Γ₁ᶜ[³T₁g(t₂g²)]}*
Γ₃ᵀ{Γ₄ᵇᶜ[³T₁g(t₂g²)]}*
Γ₃ᵀ{Γ₅ᵇᶜ[³T₁g(t₂g²)]}*
Oct.–Trig. d²
ζ=130, B=600, Dτ=−75cm⁻¹, κ=2, C/B=4

Figure 50

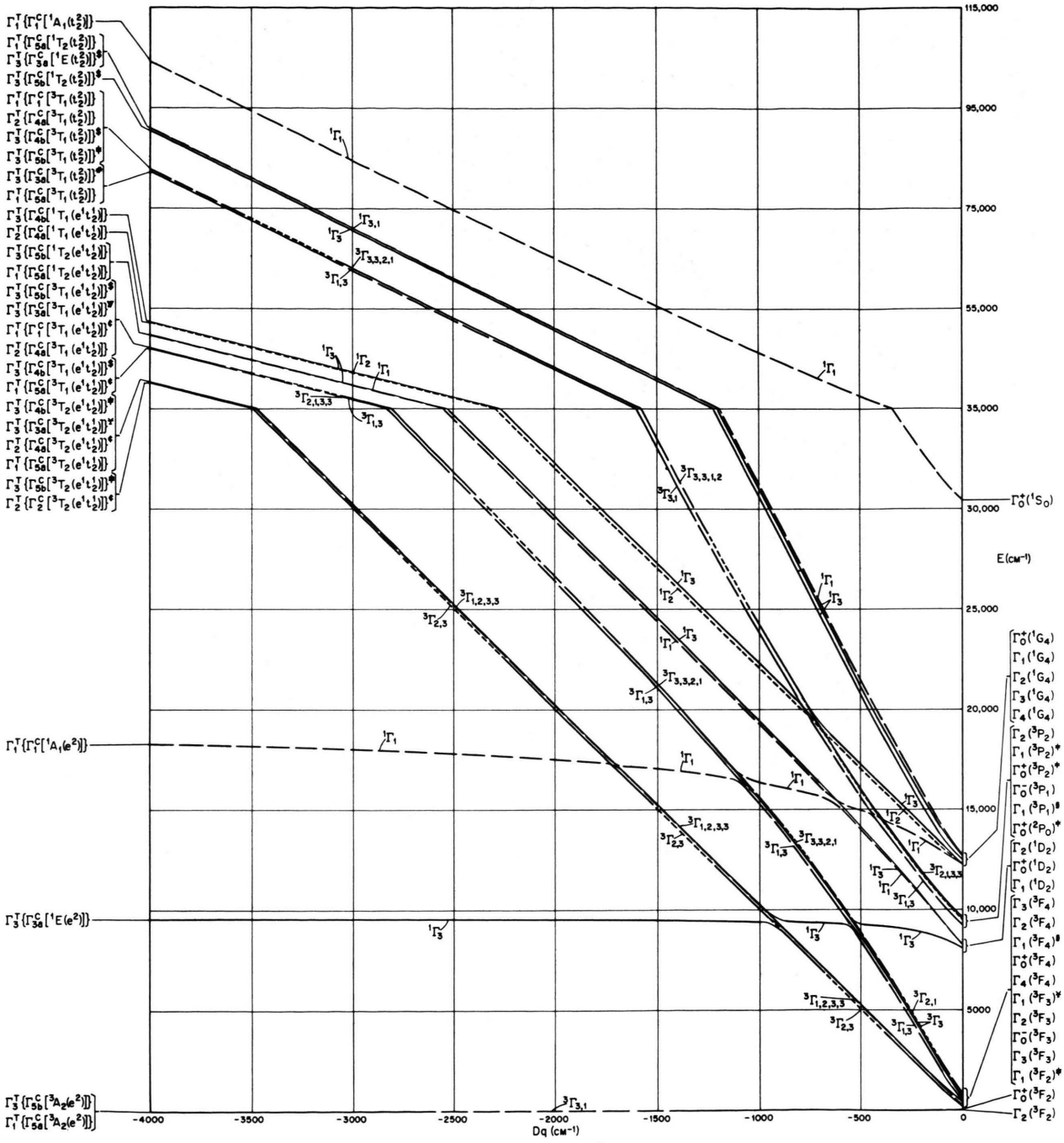
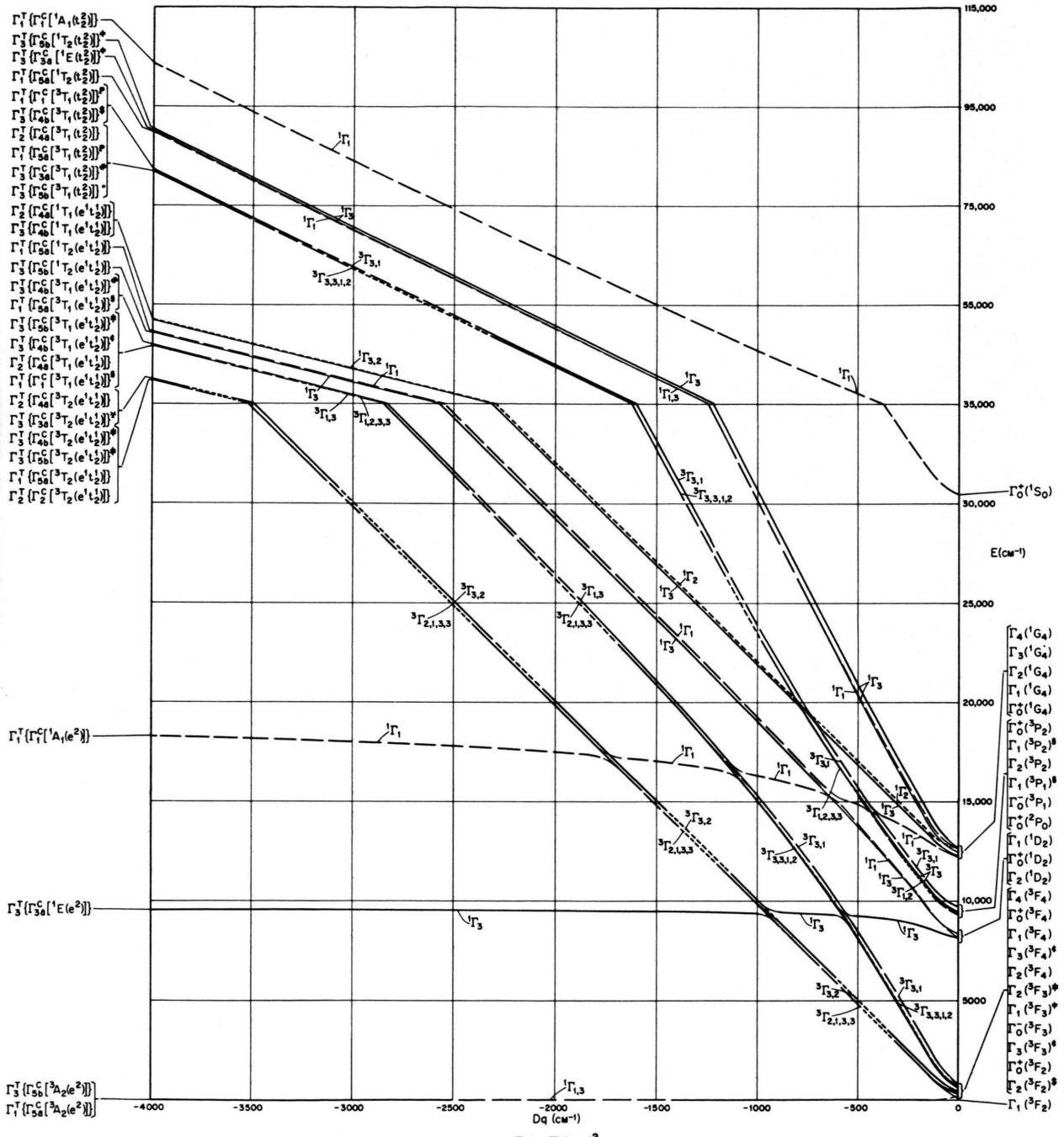

E (cm⁻¹)
115,000
95,000
75,000
55,000
35,000
30,000
25,000
20,000
15,000
10,000
5000
-4000
-3500
-3000
-2500
-2000
-1500
-1000
-500
0
Dq (cm⁻¹)
Tet.- Trig. d²
ζ = 130, B = 600, Dτ = 35cm⁻¹, κ = 2, C/B = 4

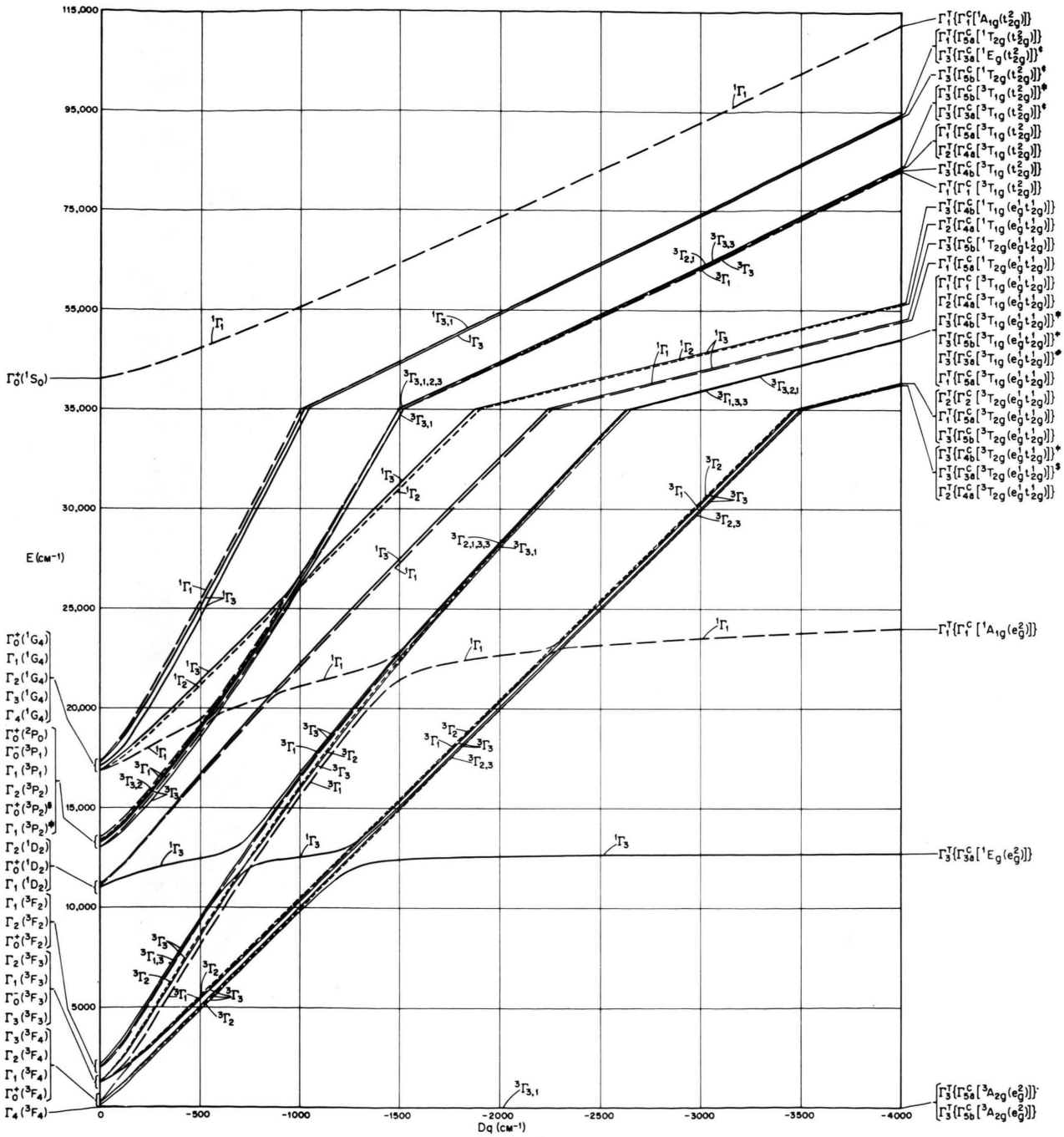
Figure 51



Tet.-Trig. d^2

$\zeta = 130$, $B = 600$, $D\tau = -35\,cm^{-1}$, $\kappa = 2$, $C/B = 4$

Figure 52



Oct.– Trig. d^8

$\zeta = -550$, $B = 800$, $D\tau = 35\,cm^{-1}$, $\kappa = 2$, $C/B = 4$

Figure 53

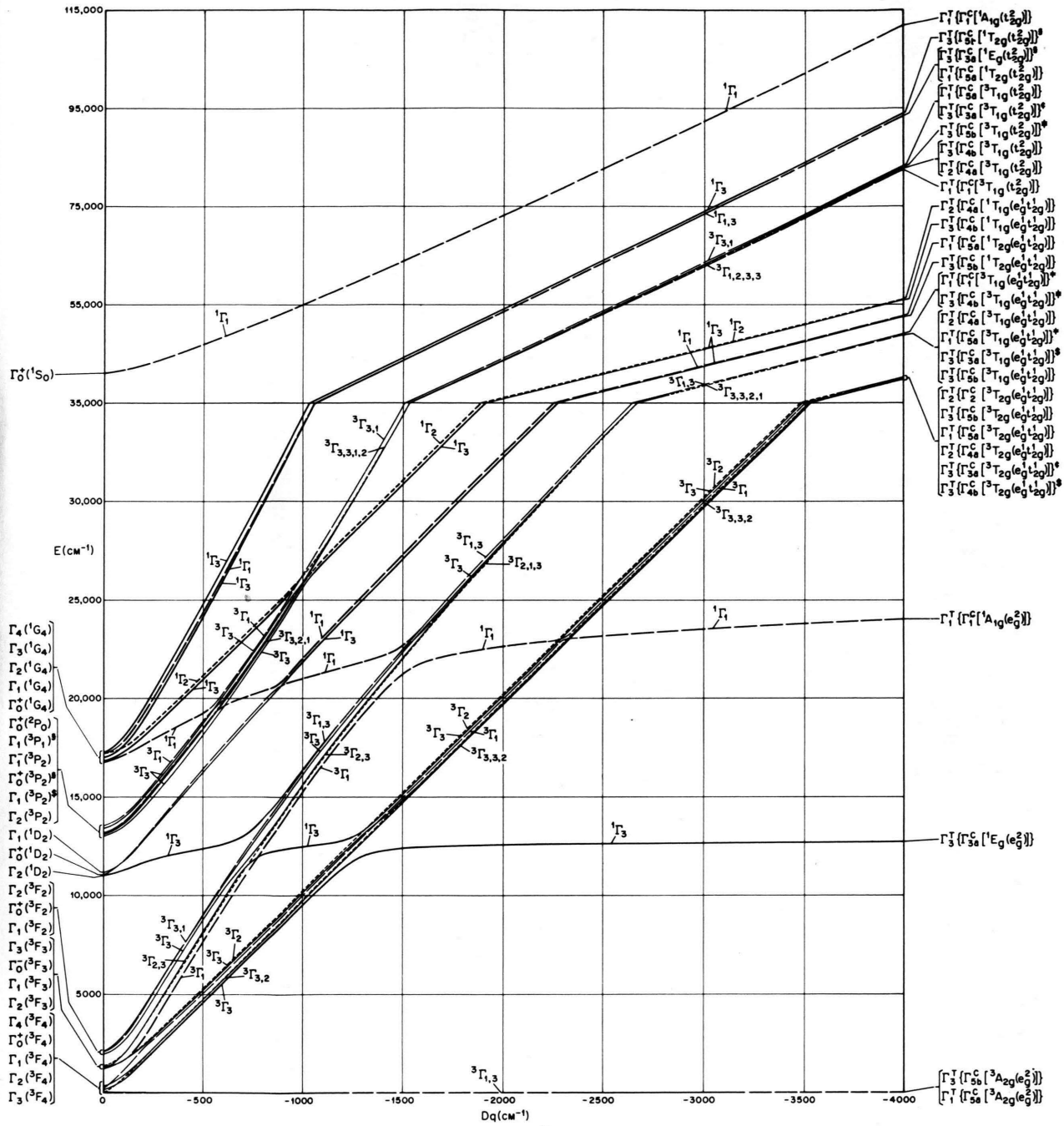
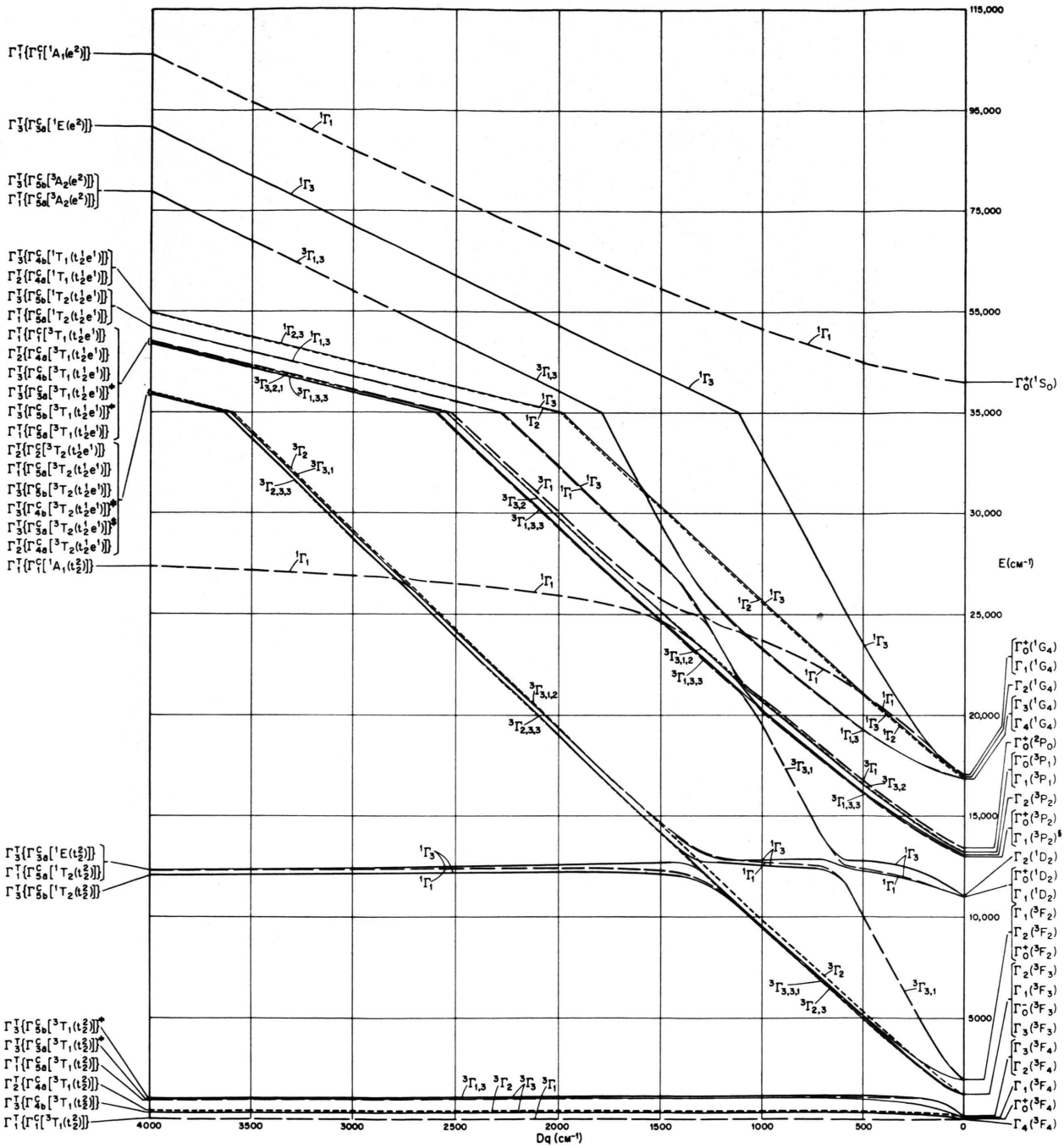


Figure 54



Tet.–Trig. d^8

$\zeta = -550$, $B = 800$, $D\tau = 15\,cm^{-1}$, $\kappa = 2$, $C/B = 4$

Figure 55

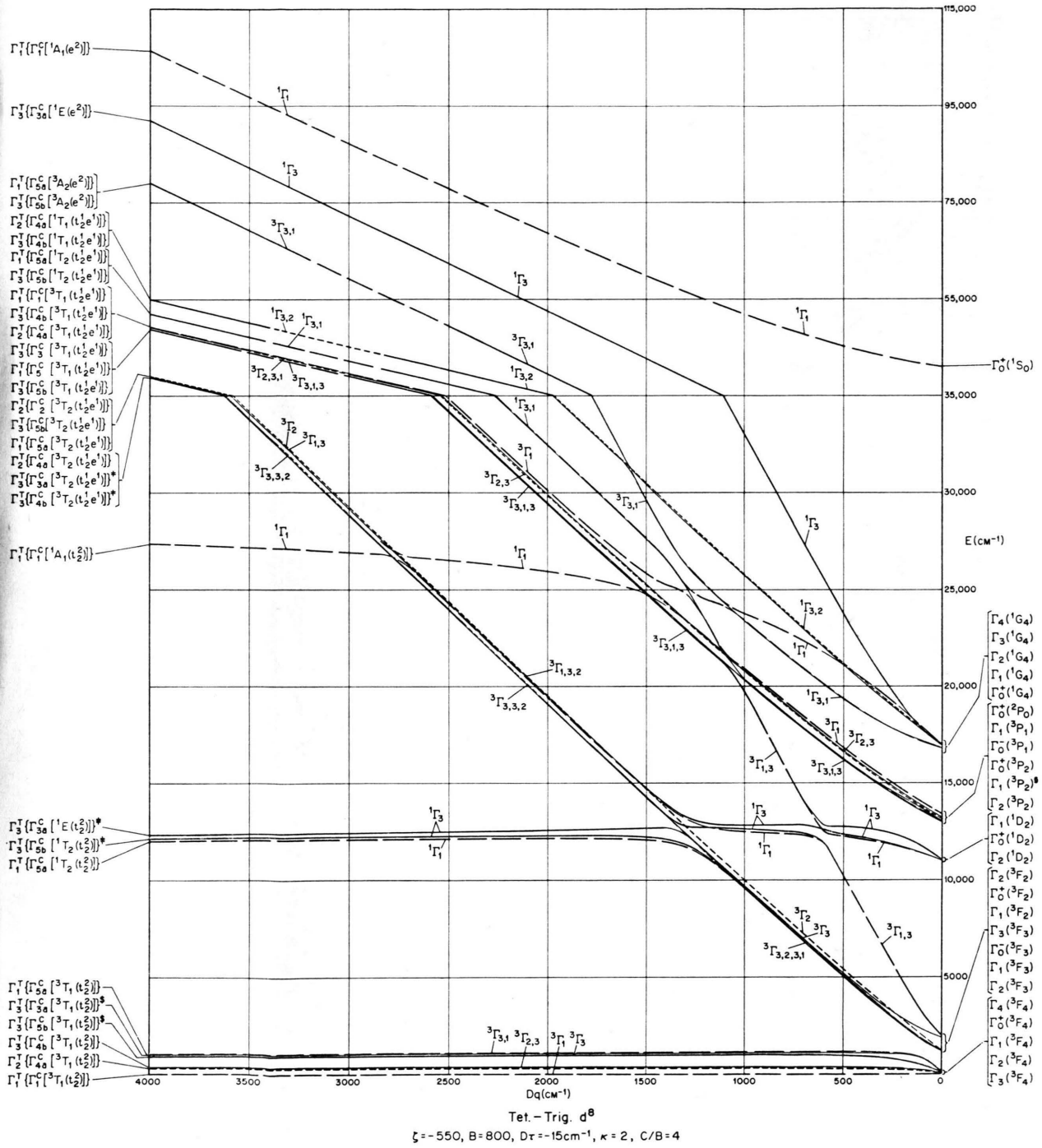


Fig. 56. Energy level diagrams for a d^8 electronic system immersed in a tetrahedral field with a trigonal component; $B=800\ \text{cm}^{-1}$, $C/B=4$, $\zeta=-550\ \text{cm}^{-1}$, $\varkappa=2$, $D\tau=-15\ \text{cm}^{-1}$.

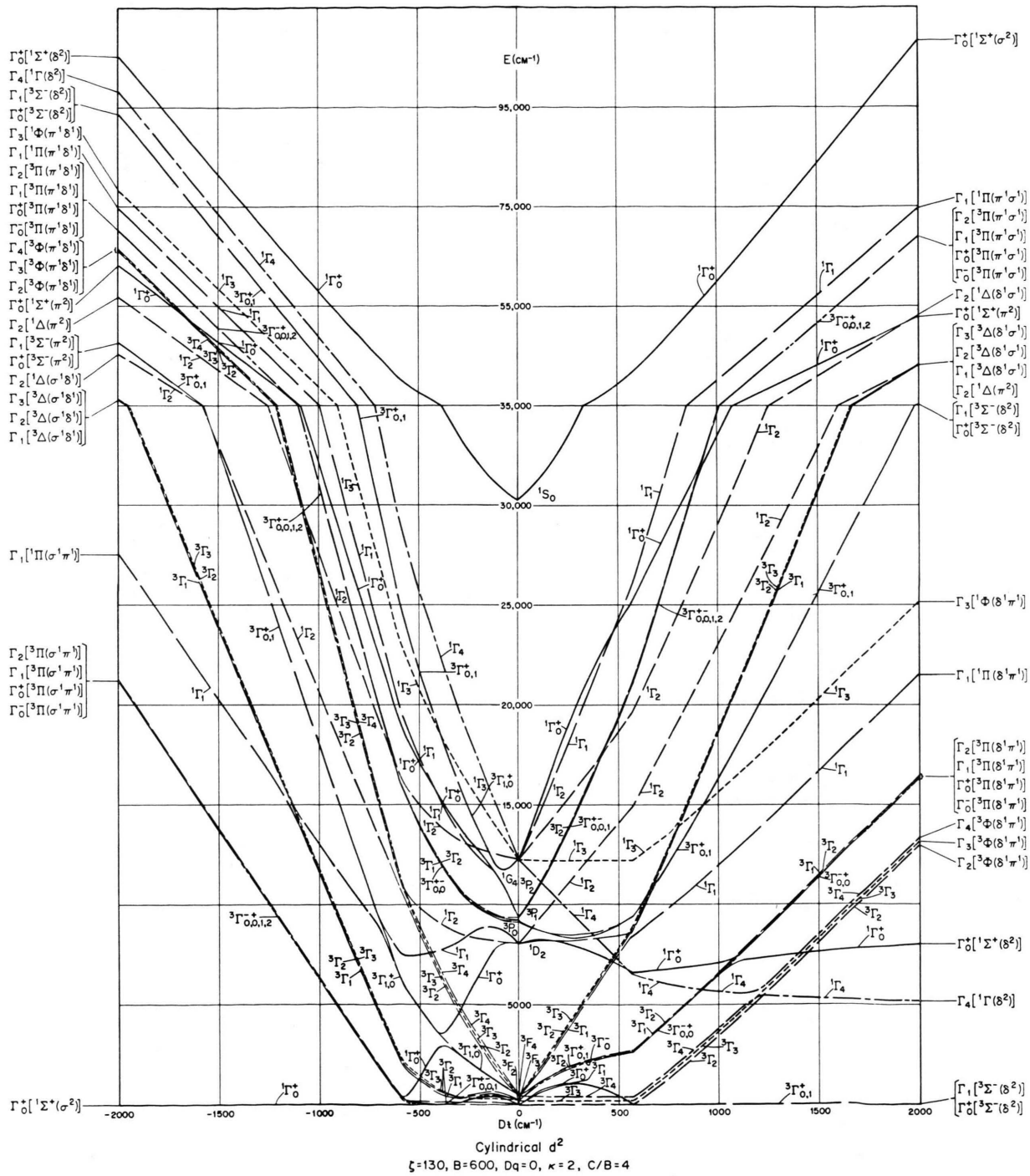


Fig. 81. Energy level diagram for a d^2 electronic system immersed in cylindrical fields; $\varkappa=2$, $B=600$ cm^{-1}, $C/B=4$, and $\zeta=130$ cm^{-1}.

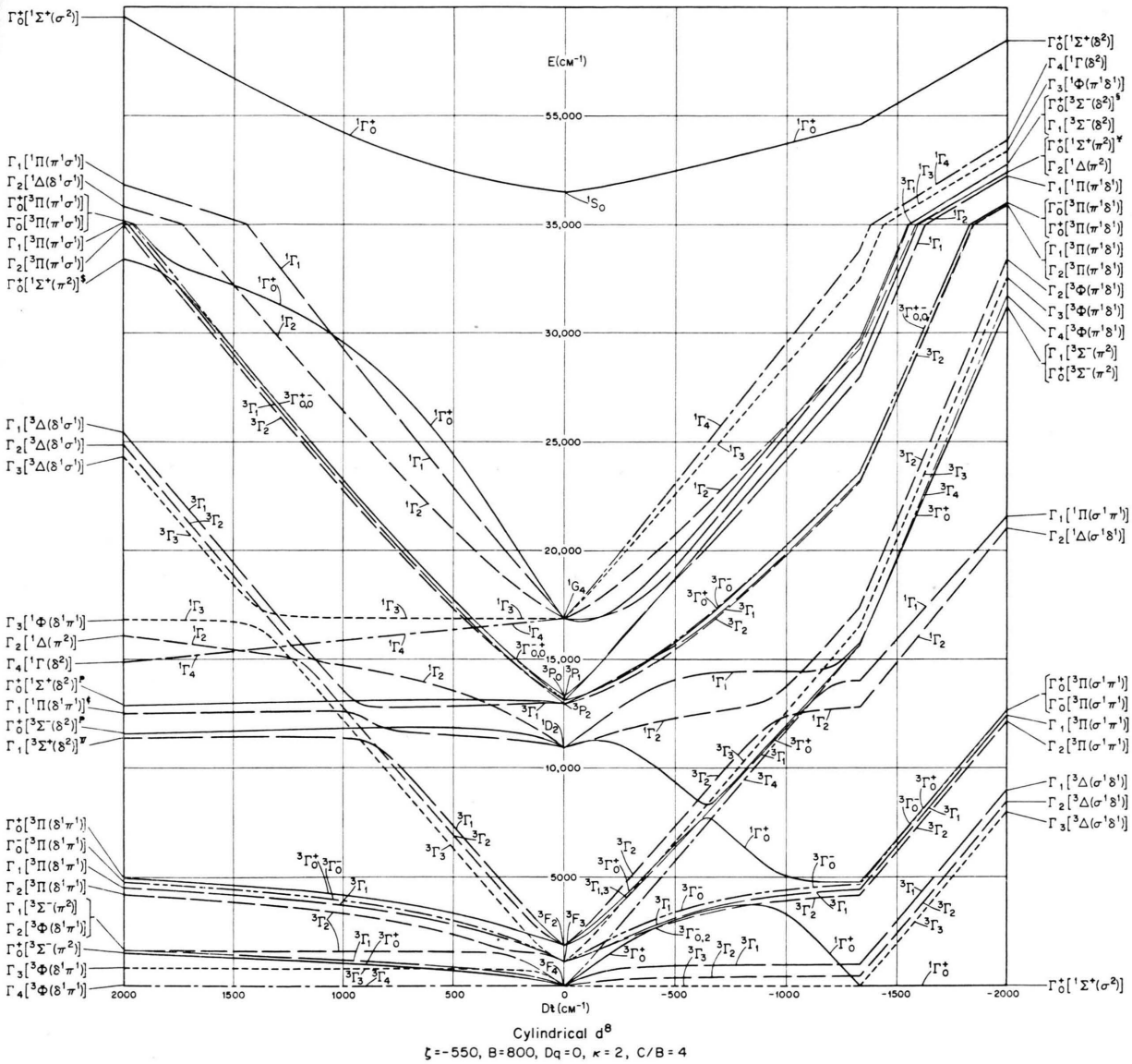


Fig. 85. Energy level diagram for a d^8 electronic system immersed in cylindrical fields; $\varkappa=2$, $B=800$ cm^{-1}, $C/B=4$, and $\zeta=-550$ cm^{-1}.

[18] R. FINKELSTEIN and J. H. VANVLECK, J. Chem. Phys. **8**, 790 [1940].

[19] S. R. POLO, Studies in Crystal Field Theory, Vol. I and II, to be published.

[20] (a) M. A. MELVIN and N. V. V. J. SWAMY, Phys. Rev. **107**, 186 [1957]; (b) R. SAITO and M. MORITA, Progr. Theoret. Phys. (Tokyo) **13**, 540 [1955]; (c) A. P. YUTSIS, I. B. LEVINSON, and V. V. VANAGAS, "Theory of Angular Momentum", Translated from Russian, published for the National Science Foundation, Washington, D. C., by the Israel Program for Scientific Translation, Jerusalem 1962.

[21] $R_4(r_i)$ in a six coordinate octahedral ligand fields is given by $R_4(r_i) = \text{eq.} \frac{7}{2}\sqrt{\frac{4\pi}{9}} \cdot \frac{r_<^4}{r_>^5}$ and $R_2(r_i)$ and $R_4'(r_i)$ in a two coordinate cylindrical ligand field are given by $R_2(r_i) = \text{eq. } 2\sqrt{\frac{4\pi}{5}} \cdot \frac{r_<^2}{r_>^3}$ and $R_4'(r_i) = \text{eq. } 2\sqrt{\frac{4\pi}{9}} \frac{r_<^4}{r_>^5}$. In these equations[4a], e and q are the charges of the electron and the ligand, respectively, and $r_<$ is the lesser of the r coordinate of the electron and the metal-ligand bond distance, $r_>$ being the greater of the two.

[22] The $D\sigma$ and $D\tau$ parameters are related to the trigonal splitting parameters v and v' of PRYCE and RUNCIMAN [(a) M. H. L. PRYCE and W. A. RUNCIMAN, Discussions Faraday Soc. **26**, 34 [1958]] and to K and K' of SUGANO and TANABE [(b) S. SUGANO and Y. TANABE, J. Phys. Soc. Japan **13**, 880 [1958]] by the equations: $v' = K' = \sqrt{2}/3\,(3D\sigma - 5D\tau)$ and $v = -3K = 1/3\,(9D\sigma + 20D\tau)$.

[23] The A_2 and A_4 parameters of HOUGEN et al. [J. T. HOUGEN, G. E. LEROI, and T. C. JAMES, J. Chem. Phys. **34**, 1670 [1961]] are just half of the $D\mathfrak{s}$ and $D\mathfrak{t}$ parameters, respectively.

[24] The many electron spin-orbit parameter λ of a d^n ion is related to the one electron spin-orbit coupling constant ζ by the formula $\zeta = 2S|\lambda|$, where S is the spin of the ion.

[25] (a) Racah's A, B, C parameters and the F_0, F_2, F_4 parameters of Condon and Shortley are connected by the equations: $A = F_0 - 49F_4$, $B = F_2 - 5F_4$, and $C = 35F_4$; (b) A being a constant additive energy term in the diagonal elements, it will not be included in further discussion.

[26] Since the electron correlation parameters are being used as adjustable parameters (and not as the free-ion parameters), it is not necessary to take into account the orbit-orbit interaction. Inclusion of this perturbation [(a) R. E. TREES, Phys. Rev. **83**, 756 [1951]; (b) Ibid. **84**, 1089 [1951]; (c) Ibid. **85**, 382 [1952]; (d) G. RACAH, ibid. **85**, 381 [1952]] in the Hamiltonian results in an additive energy term $\alpha \cdot L(L+1)$, where α is the Trees parameter, in the diagonal elements of the weak-field energy matrices. The corresponding correction in the energy matrices of any other representation can be easily obtained from the weak-field secular determinants containing the Trees constant and the unitary transformations connecting the two schemes.

[27] Note that the electron correlation is diagonal in this representation. The necessary matrix elements are: ${}^3F = -8B$, ${}^3P = 7B$, ${}^1G = 4B + 2C$, ${}^1D = -3B + 2C$ and ${}^1S = 14B + 7C$.

[28] (a) L. E. ORGEL, J. Chem. Phys. **23**, 1819 [1955]; (b) H. YAMATERA, Bull. Chem. Soc. Japan **31**, 95 [1958].

[29] (a) The trigonal wave functions can be laboriously transformed into their tetragonal Cartesian equivalents [Eq. (2)] or expanded in terms of the free-ion functions which in turn can be employed to calculate the electron correlation elements as described in the quadrate case; (b) Because of the importance of these integrals in any therory based on symmetry, including molecular orbital theory, the have been derived here once and for all. These integrals have been checked and verified by expanding the trigonal orbitals into their tetragonal equivalents and calculating the elements from them.

[30] Instead of writing down the complete secular determinants we have listed here the matrix elements for convenience. The matrix elements include the diagonal and only half of the off-diagonal elements. The other half are the complex conjugates of the corresponding off-diagonals listed. As an example $\langle x|y\rangle = \langle x^*|y\rangle$ and $\langle y|x\rangle = \langle y^*|x\rangle = \langle x^*|y\rangle^* = \langle x|y\rangle^*$.

[31] (a) Y. TANABE and S. SUGANO, J. Phys. Soc. Japan **9**, 753 [1954]; (b) Ibid. **9**, 766 [1954]; (c) S. SUGANO, Y. TANABE, and H. KAMIMURA, "Multiplets of Transition-Metal Ions in Crystal", Academic Press, New York 1970.

[32] The free-ion values for V^{3+} and Ni^{2+}, respectively, are: ${}^{3c}\zeta = 210, 666\ \text{cm}^{-1}$, $B = 860, 1042\ \text{cm}^{-1}$, and $C = 3605, 4060\ \text{cm}^{-1}$.

[33] The energy matrices were solved and the energy levels were plotted on the IBM 7090 computer at the University of Pittsburgh Computer Center. Energy diagrams were plotted on a Calcomp Plotter through IBM 1401, which is fed by a magnetic tape from IBM 7090. The energy matrices are being presently programmed at the Computer Center of the Florida Atlantic University with the assistance of Mr. D. GATSINOS.

[34] (a) J. R. PERUMAREDDI, J. Phys. Chem. **71**, 3155 [1967]; (b) This relation which is applicable only in the limit of crystalline field formalism is being used here merely to simplify the construction of the energy diagrams, although it has not been definitely established yet. In contrast, the theoretical relation between the Dq's of octahedral and tetrahedral ligand fields seems to agree with the available experimental data.

[35] (a) These values were chosen as representative examples after a survey had been made of the optical spectral data of all the known tetragonal and trigonal complexes of nickel(II) and vanadium(III); (b) The choice of both Ds, Dt or $D\sigma$, $D\tau > 0$ corresponds to a pure tetragonal or trigonal axial compression of the initially cubic system, the choice of both Ds, Dt or $D\sigma$, $D\tau < 0$ corresponds to a pure axial elongation, and the choice of mixed signed magnitudes (i. e., Ds and Dt or $D\sigma$ and $D\tau$ of opposite signs) to more complex situations of variable covalency effects. Note that for the trigonal system the compression is one which forces (squeezes) the ligands towards the threefold axis and the elongation one which forces (releases) them from it. Note also that for the tetragonal system substitution by ligands of stronger ligand field strength along the four-old axis (octahedron) can be viewed as equivalent to a distortion of compression and similarly substitution by ligands of weaker ligand field strength to an elongation.

[36] The $D\mu$ parameter, either by itself or expressed in terms of $\varkappa$ which is the ratio of $D\mu$ to $D\nu$, is the least understood parameter at the present time. In the limit of crystalline field formalism, it is expected to have the same sign and a few orders of magnitude greater than $D\nu$. On the other hand in a symmetry based parametric theory such as the ligand field theory, it may be positive or negative of $D\nu$ and may assume any value. Thus, as low a value as close to zero and as high a value as 9 had been used [5, 4] for $\varkappa$ in interpreting the optical spectral data of quadrate, trigonal, and cylindrical complexes of nickel(II) and vanadium(III). We have chosen -5 and 5 as representative of a low and a high value of $\varkappa$, respectively.

[37] The superscripts on the energy labels in the Figures refer to the percentage content of that eigenvector component of the eigenfunction. The various symbols have the following meaning:

§, 75±2.5%; ‡, 70±2.5%; ‡‡, 65±2.5%;
~~S~~, 60±2.5%; ¢, 55±2.5%; P, 50±2.5%;
~~Y~~, 45±2.5%; ‡‡, 40±2.5%; ~~Y~~, 35±2.5%;
~~D~~, 30±2.5%; ~~T~~, 25±2.5%; ~~N~~, 20±2.5%.