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ENERGY LEVELS OF PLATINUM(II) COMPLEXES
ON THE BASIS OF LIGAND FIELD THEORY

by

Richard Ferdinand Fenske

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I. INTRODUCTION

A. Nature and Purpose of the Problem

In the past decade, no single aspect of inorganic chemistry from an interpretive point of view has received wider interest than the use of ligand field theory to explain the physical properties of the transition metal, rare earth, and actinide complexes. Such characteristics as magnetic susceptibility, stability, ionic radii, and absorption spectra have been satisfactorily explained by application of this theory.

Ligand field theory, or crystal field theory as it is often called, has the advantage of not only giving excellent agreement when used in quantitative calculations but in being easily conceivable from a qualitative point of view. Thus it maintains, within the limits of the assumptions made, its quantum mechanical validity, while lending itself to pictorial representations which are readily grasped.

Applications of this theory have been greatest in regard to the transition metal complexes. These complexes consist of the metal ion, which possess one or more d-electrons, surrounded by several other ions or molecules, each called a ligand group or simply ligand. These ligands are arranged more or less symmetrically around the central transition metal. In most applications of the theory, it is only these

nearest ligands which affect the energy levels of the central atom.

The theory makes the simplifying assumption that the effect of the symmetric ligands on the energy levels of the central atom can be explained by considering the ligands as point charges or point dipoles. The resultant electrostatic interaction between the point charges (or dipoles) and the originally degenerate d-electron orbitals causes a splitting of the levels and hence a partial or complete removal of the degeneracy. The type of splitting which results is dependent upon the symmetry arrangement of the ligands. The degree of splitting is dependent upon the intensity of the electrostatic interaction. An understanding of the absorption spectra of the complexes can then be obtained by considering the energy required for electronic transitions to take place between these levels.

In most of the studies reported in the literature, the symmetry required was either tetrahedral or octahedral. However, certain complexes, including those of platinum(II), have been shown to possess square-planar symmetry. The effect on the energy levels is, of course, quite different. It is the purpose of this thesis to present quantitative calculations of the energy levels of platinum(II) complexes, and from them obtain an explanation of the absorption spectra observed for these compounds.

B. Organization of the Thesis

In organizing a theoretical thesis of this type, a two-fold purpose must be served. The fundamental principles of the approach and the results of their application to the problem must be compactly presented without burdening the reader with involved derivations which would only distract his attention. In some instances, however, the reader might wish to apply these techniques to a similar problem of his own. In such a case, a simple presentation of the end results without some of the details of their derivation places him at a distinct disadvantage. To overcome the above difficulties, it has been decided to include a rather extensive appendix section which will contain detailed derivations or calculations which will be used in the main body of the text.

C. Symbolism

It is convenient to be able to express certain mathematical terms as concisely as possible. To avoid confusion, the following is an annotated list of the symbols employed.

- 1). $\psi_{n,l,m}$ Single electron spatial wave functions of the atomic orbital type with principal quantum number, n , orbital angular momentum, l , and magnetic quantum number, m .
- 2). $\psi_{5,l,m}$ Same as 1, but with $n = 5$ understood.

- 3). $|S, M_S, L, M_L\rangle$ Many electron wave function which is a sum of antisymmetrized product functions such that it is an eigenfunction of J^2 , L^2 , M_J , and M_L . See Section V and Appendix A.
- 4). $|S, L, J, M_J\rangle = {}^{2S+1}L_J(M_J)$ Many electron wave function which is a sum of $|S, M_S, L, M_L\rangle$ functions such that it is an eigenfunction of J^2 , L^2 , J^2 , and M_J , but not of M_L and M_S . See Section V and Appendix A.
- 5). (m, m') A two-electron product function of the type, $|l, m\rangle^{(1)} |l', m'\rangle^{(2)}$, with $l = l' = 2$ and the order, electron one-electron two understood.
- 6). α, β The spin z-component quantum numbers, α referring to $+\frac{1}{2}$, β to $-\frac{1}{2}$.
- 7). $(m, m')\alpha\beta$ $[1l, m]\alpha^{(1)} [1l', m']\beta^{(2)}$, that is, α belongs to electron one and β belongs to electron two.
- 8). $(z^2), (x^2-y^2), (xy), (xz), (yz)$ The single electron d-wave functions in real form. See Table 19.
- 9). δ_{ab} The Kroneker delta. $\delta = 1$, when $a=b$
 $\delta = 0$, when $a \neq b$
- 10). $Y_{lm}(\theta\phi) = Y(lm)$ The spherical harmonics. See Appendix B-1.

- 11). $P_l^m(\cos \Theta)$ The associated Legendre functions.
See Appendix B-1.
- 12). $Y(J, M_J)$ Notation indicating that the function $|S, L, J, M_J\rangle$ has the same symmetry property as the spherical harmonic with equivalent numerical values.
See Appendix C-6-ii.
- 13). V^{LF} The ligand Field Potential. See Section IV-B.
- 14). $Q_2, Q_1, Q_0, B_2, -2$ Single-electron matrix elements due to the ligand field potential. See Table 4.
- 15). F_2 and F_4 Slater-Condon parameters for electronic interaction. See Sections V-B-1, V-D, and Appendix D-4.
- 16). D_{lm} Coefficients in the expansion of the ligand field potential in terms of spherical harmonics. See equations 67 and 73 in Section IV-B.
- 17). K_{lm} Coefficients in the expansion of the product of two spherical harmonics in a sum of spherical harmonics. See equation 96, Section IV-C-3-ii, and Appendix B-2.
- 18). $J_{lm}(\ell_a^m \ell_b^m)$ $Y^*(\ell_a^m) Y(\ell_b^m) Y(\ell^m) d\tau_{\Theta\Phi}$. See

Section IV-C-i.

19). $G_l(a,b)$

The radial integral = $-q N^2 \int R_a(r) R_b(r) R_l(r) r^2 dr$. See Section IV-C-3-ii and Appendix B-3.

20). $G_l(X)$

An integral defined by the relation:

$$G_l(a,b) = \frac{q f}{78.75} G_l(X). \text{ See Section}$$

IV-C-3-ii and Appendix B-3.

21). $B_l(a,b)$

$$\frac{\mu f^2}{78.75} \frac{d}{dX} G_l(X); \text{ where } X = fR, \text{ and}$$

R is the effective radial distance;
and μ is the effective dipole moment.

See Section IV-C-3-ii and Appendix B-3.

II. LIGAND FIELD THEORY: FUNDAMENTAL CONCEPTS, LITERATURE REVIEW, QUALITATIVE APPROACH

A. Model for Electronic Structure

1. General principles

The basic principles of ligand field theory were developed by Bethe (1) in 1929. His classic paper considered the effects on a "free ion" which would result when that ion was placed in an electric field of a given symmetry. Bethe originally conceived the theory as being applicable to energy levels of ions in a crystal and hence applied the term "Crystal Field Theory". This term, while still popular, is being replaced by that of "Ligand Field Theory", particularly since many of the applications are concerned, not with crystals, but with metal complexes in solution. Furthermore, some qualitative discussions include the effect of π -bonding garnered from molecular orbital theory, in addition to the simple electrostatic picture. Hence, the term "Crystal" seems inappropriate.

In any initial discussion of ligand field theory, it would do well to consider first a transition metal ion which contained a single d-electron, for example scandium(II). In the free ion, this d-electron is considered to be in a spherically symmetric potential field due to the electrons in the lower shells of the atom. Without going into detail at this point, it may be stated that under these conditions, the

wave functions expressing the motion of the electron are similar to those obtained for a hydrogen atom. That is, the spatial part of the wave function consists of a radial part and an angular part, the latter being expressible in analytic form. For the single d-electron under consideration, there are five possible spatial functions which would give the same energy value for the state. These orbitals can be expressed in real form by the equations:

$$d_{z^2} = R(r) \cdot r^2 \cdot (3 \cos^2 \theta - 1), \quad (1)$$

$$d_{(x^2-y^2)} = R(r) \cdot r^2 \cdot (\sin^2 \theta \cdot \cos 2\phi), \quad (2)$$

$$d_{xy} = R(r) \cdot r^2 \cdot (\sin^2 \theta \cdot \sin 2\phi), \quad (3)$$

$$d_{xz} = R(r) \cdot r^2 \cdot (\sin \theta \cos \theta \cos \phi), \quad (4)$$

$$d_{yz} = R(r) \cdot r^2 \cdot (\sin \theta \cos \theta \sin \phi), \quad (5)$$

$[R(r) \cdot r^2]$ represents the radial dependence of the functions; θ and ϕ are the usual spherical polar angles. See Figure 1. It is presumed that the appropriate normalization factors for the functions are included in the $R(r)$ terms. The subscripts on the d-orbitals come from the expressions which would result when r^2 times the angular expressions are changed to Cartesian coordinates.

For simplicity of reproduction, in this thesis the real d-orbitals are expressed in the forms (z^2) , (x^2-y^2) , (xy) , (xz) , and (yz) ; the correspondence with the usual forms being:

$$(z^2) = d_{z^2} \quad (6)$$

$$(x^2-y^2) = d_{x^2-y^2} \quad (7)$$

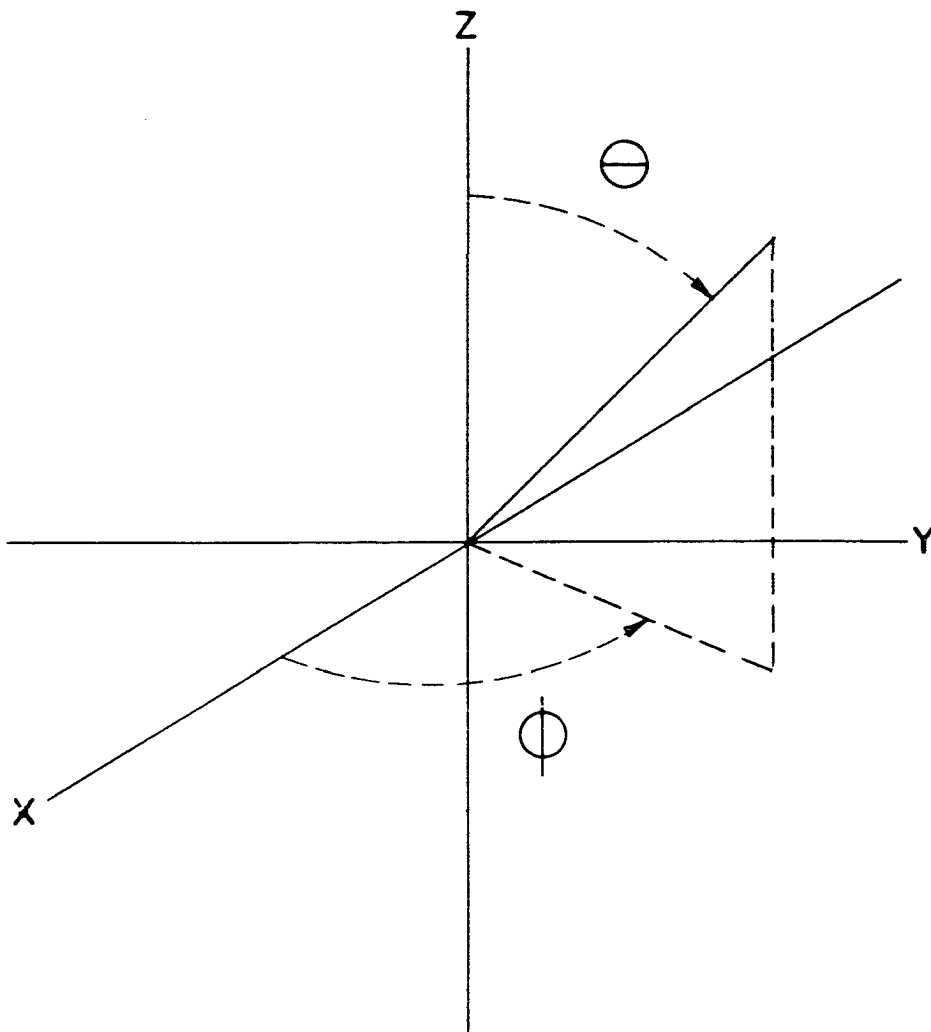


Figure 1. The spherical polar angles

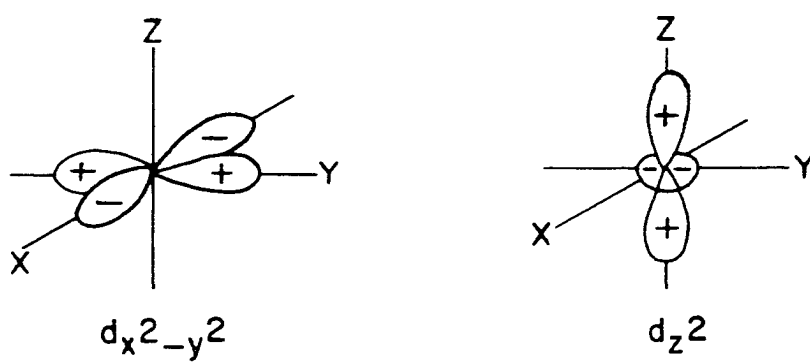
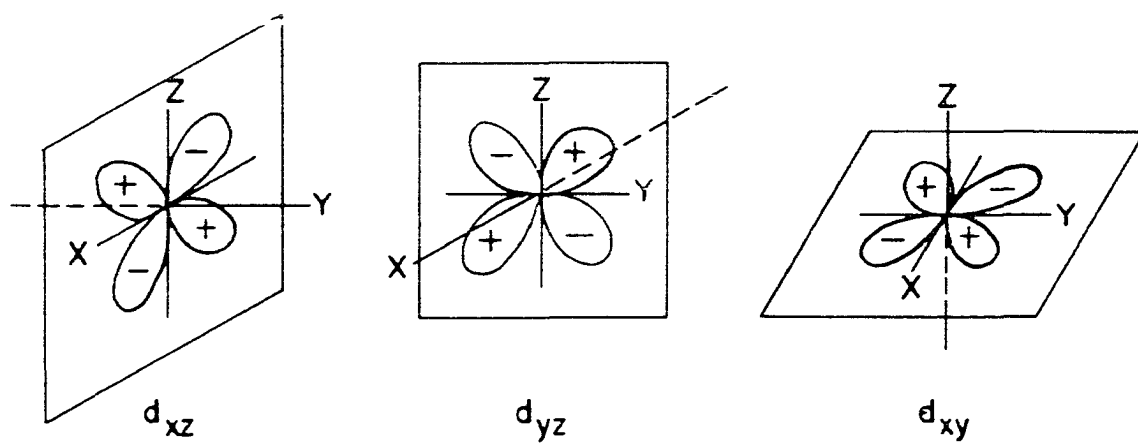
$$(xy) = d_{xy} \quad (8)$$

$$(xz) = d_{xz} \quad (9)$$

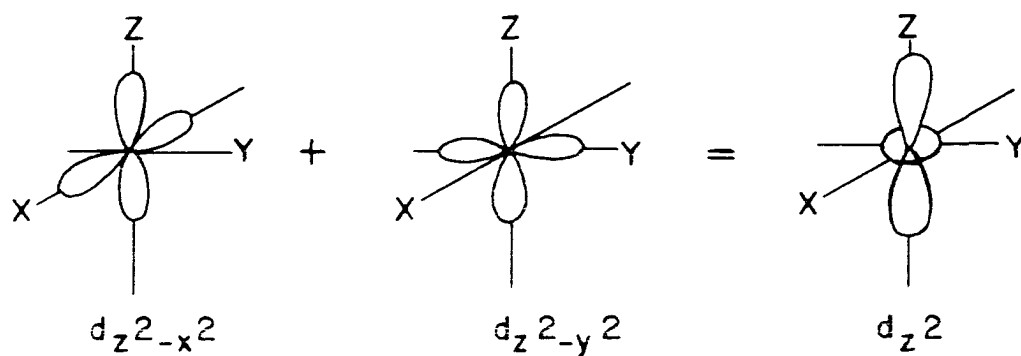
$$(yz) = d_{yz} \quad (10)$$

Figure 2a shows the conventional boundary contours for the five orbitals. These contours indicate roughly the region in space which will contain almost all of the electronic charge of an electron in such an orbital. The (+) and (-) signs refer to the algebraic sign of the wave function which describes the orbital. The (z^2) orbital can also be considered as a sum of two orbitals; $(z^2 - x^2)$ plus $(z^2 - y^2)$ whose contours would be analogous to that of $(x^2 - y^2)$. See Figure 2b.

In the spherically symmetric potential of the free ion, the five orbitals are degenerate and the wave function of the single d-electron will be a linear combination of these orbitals. Following Bethe's argument, if the free ion is now considered to be placed in an ionic crystal of a particular symmetry, the degeneracy of the orbitals will be partially or completely removed. For example, if the free ion were surrounded by six negative charges, one placed along each positive and negative axis at equal distances from the origin (i.e., octahedral symmetry) electronic repulsion would take place between these charges and the electron. Qualitatively, it is obvious that the interaction of the charges with the electron in either the (xy) , (xz) , or (yz) orbitals will be



(a)



(b)

Figure 2. Boundary contours of the d-orbitals

identical and will be less than that due to the interaction between the charges and the $(x^2 - y^2)$ and (z^2) orbitals. See Figure 3a. The latter two orbitals would be directed toward the charges while the other three are directed between the charges. Furthermore the degree of splitting will certainly depend upon the magnitude of the charges and upon the distances between the charges and the central ion.

If the charges along the z-axis are of different magnitude and/or different distances from the origin than those along the x and y axes, a "distorted octahedron" or tetragonal symmetry results. In such a case, the degeneracy of the orbitals is split even further. Only the (xz) and (yz) orbitals remain degenerate. If the distortion along the z-axis is slight, the energy levels will be those given in Figure 3b.

As the distance to the z-axis ligands is imagined to become greater and greater until finally the ligands can be considered to be completely removed, the (xy) and (z^2) levels will cross and the energy levels will be those given in Figure 3c. From a qualitative standpoint, it would be difficult to decide whether or not the (z^2) level would also cross below that of the degenerate set, (xz) , (yz) . See Figure 3d. This latter situation has been postulated by Chatt et al. (2) as the energy levels in platinum(II) complexes. This possibility is discussed in detail in a later section of the thesis.

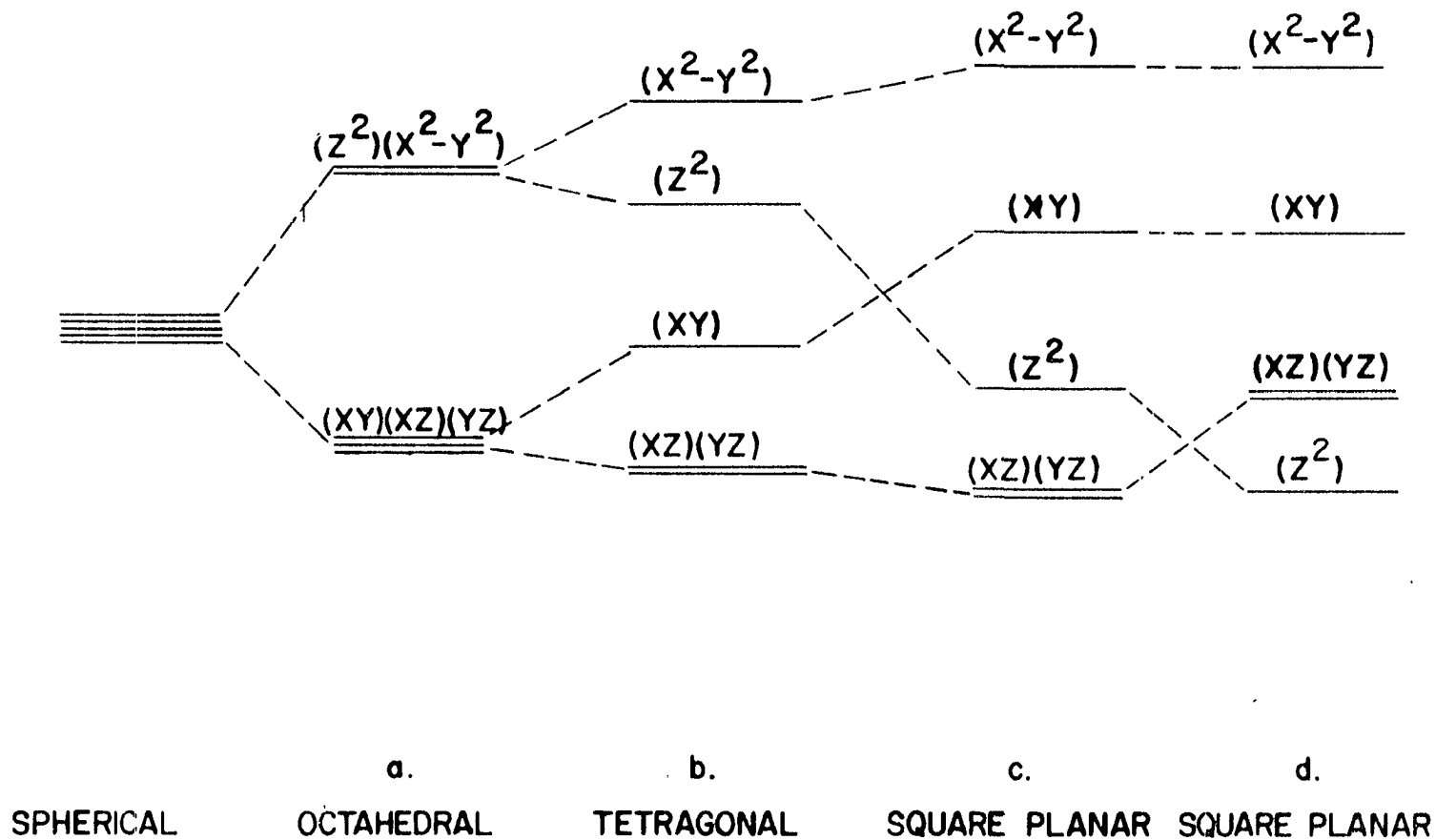


Figure 3. Energy levels of d-orbitals in various symmetries

When the metal ion contains only a single d-electron in its outer shell, the previous considerations hold regardless of the strength of the ligand field. However, when there is more than one d-electron present, it is necessary to distinguish between three cases, commonly referred to as the weak field, strong field, and intermediate field. In qualitative discussions, the inclusion of spin-orbit coupling of the electrons is seldom considered. That is, the assumption is made that the ligand field strength is great enough to overcome the spin-orbit effect.

2. Weak field

In the weak field case, the ligand field strength is considered as being small and hence acts as a perturbation on the various multiplets of the free ion. In this situation, the ground state and excited states of the free ion are first determined in terms of the total angular momentum states and the effect on these states as a result of the ligand field is considered.

For example, for an ion with two d-electrons, such as vanadium(III), the possible states are: 1G , 1D , 1S , 3P , and 3F . For derivation of these states, see Appendix A. According to Hund's Rule, the ground state is that state with the greatest multiplicity, and if there are more than one with that multiplicity, the state with the highest orbital

angular momentum (L) is the ground state. In this case, 3F is the ground state. Other considerations and experimental evidence suggest that 1D would be the first excited state, then 3P , 1G , 1S .

Just as the ligand field split the degeneracy of the d-electron wave functions, so now it removes the degeneracy of the wave functions associated with these various states. In the case of single d-electrons, the degeneracy was in the magnetic quantum number, m_l , belonging to the orbital angular momentum, l . In this case, one is dealing with the degenerate axial component, M_L , of the total orbital angular momentum, L .

It can be shown, for example, that in an octahedral field the 7-fold spatially degenerate state, 3F splits into two 3-fold states and one non-degenerate state. Techniques for obtaining these states are given in the section on Group Theory. The 5-fold degenerate 1D state, whose wave functions have the same angular dependence as the d-electrons themselves, follow the identical pattern as given for the d-electron, i.e., one 3-fold and one 2-fold degenerate state is obtained. The degeneracy of the 3P state is not removed by the octahedral field. This is apparent when one considers that the angular dependence of the wave functions is the same as that of p-electrons. Contour diagrams of the p-electron functions show that the three functions, p_x , p_y , p_z , have orbitals

directed along the X-, Y-, Z-, axes respectively. Hence with equal charges along all three axes, the electronic interaction will be the same for all three orbitals. The 9-fold degenerate 1G state will result in two states with 3-fold degeneracy, one state with 2-fold and one non-degenerate state. The 1S state is non-degenerate in any case.

Figure 4 is a qualitative diagram of the effects that the octahedral ligand field would have on the various states considered. The left hand column are the states of the free ion. The right hand column shows the splitting of the states by the octahedral field. The labeling of the ligand field states by ${}^1A_{1g}$, 1E_g , etc., corresponds to the group theory representations of Mulliken (3). The degeneracy of each state is given in the parentheses following the group symbol. It should be noted that the degeneracy of each state is given only in terms of the spatial degeneracy. The true degeneracy is the spatial degeneracy times the multiplicity.

The effect of any ligand field on the energy levels of a cation is expressible as the sum of two terms, one of which is spherically symmetric (V_r) and the other is dependent upon the symmetry of the ligands. For example, in an octahedral field, the ligand potential can be expressed as:

$$V = V_r + V_o \quad (11)$$

where V_o is the electronic potential which has the properties of the octahedral group O_h . The effect of the spherically

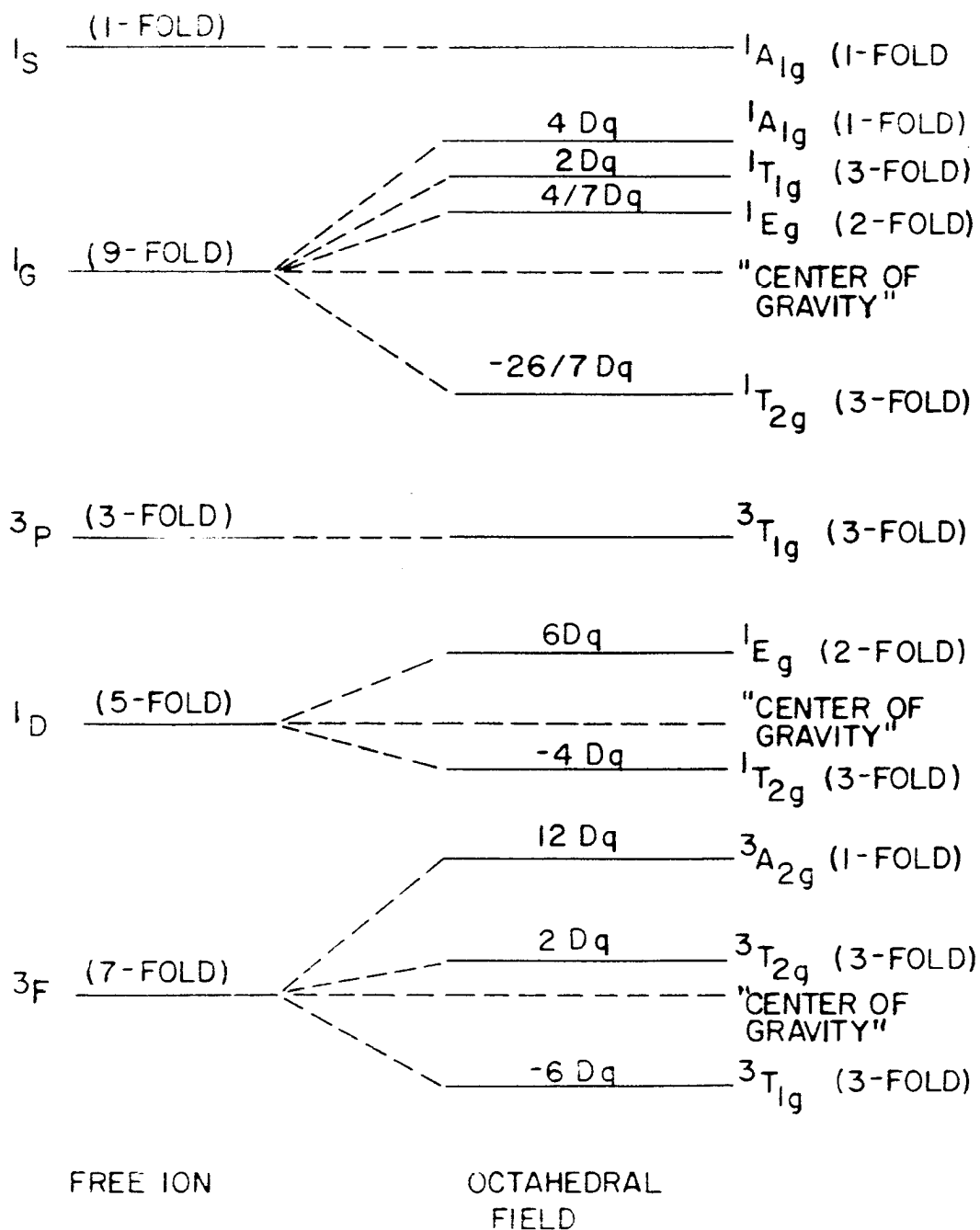
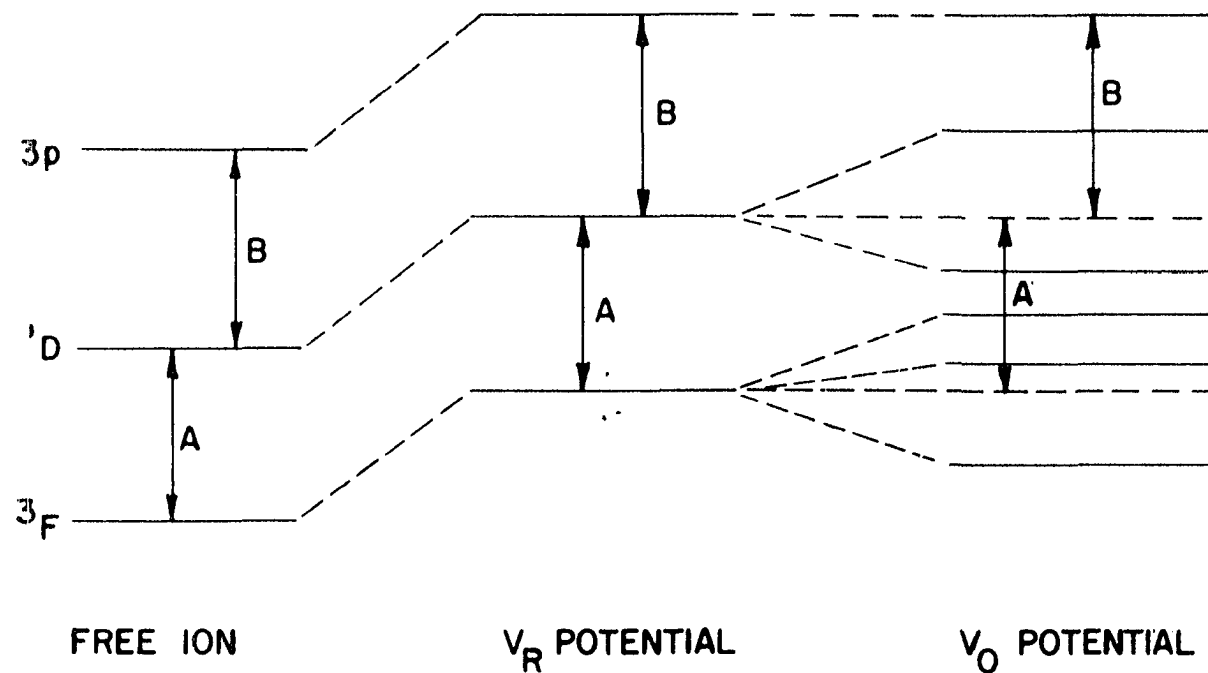


Figure 4. Effects of a weak octahedral ligand field potential on the d^2 energy levels

symmetric term, V_L , is simply to shift all levels with the same number of d-electrons by a uniform amount. This is illustrated in Figure 5. Thus, as a result of V_L , the absolute values of the energy levels change, but the separations of the states relative to each other are unaffected. In Figure 5, the relative separations, A and B, between the states remains the same. It is the application of the symmetry dependent potential, V_O , which affects the relative separations of the energy levels. The diagrams in Figure 4 ignore the effect of the V_L term since the absorption spectra depends only on the relative separation of the energy levels.

In Figure 4, the energy of each state, relative to its initial energy in the free ion, but ignoring the V_L contribution, is given in terms of a single parameter, Dq . The energy parameter, Dq , was originally employed by Schlapp and Penney (4) and is defined in terms of the energy of a single d-electron in an octahedral field. Ten Dq equals the difference in energy between the triplet, t_{2g} , and doublet, e_g , state of a single d-electron in the octahedral field. The derivation of Dq is discussed more fully in Appendix B-4.

It is noteworthy that the over-all "center of gravity" of the weak field levels relative to one another is unchanged by the symmetry potential, V_O , of the ligand field. For example, while the 3-fold degenerate state of 1D is lowered by $4Dq$ units, the 2-fold degenerate state is raised by $6 Dq$ units.



A AND B ARE THE ENERGY DIFFERENCES BETWEEN THE STATES AS INDICATED

Figure 5. Effects of the spherical and non-spherical portions of the octahedral potential on the energy levels

Thus:

$$3x(-4Dq) + 2x(6Dq) = 0 \quad (12)$$

The relative positions of the levels in Figure 4 presumes that the ligands are represented as negative charges, or as dipoles whose negative ends are directed toward the cation. If they were positive charges, the energy levels that would result can be obtained by mirroring of the levels in Figure 4 through their respective centers of gravity, that is, the values of Dq change sign.

There is a well-known reciprocity relation in atomic spectroscopy between electrons and "holes". (See for example, Pauling and Wilson (5), Condon and Shortley (6), etc.) The terms arising from d^n electrons, where $n \leq 5$, are the same as those arising from d^{10-n} . Thus it is possible to obtain the terms for d^8 by considering it as having two "holes" instead of the eight electrons. The coulombic interaction between the holes is the same as between the electrons and hence the terms are in the same order for both d^2 and d^8 ; i.e., 3F , 1D , 3P , 1G , 1S . However, just as the multiplet structure within each multiplet is inverted in atomic spectroscopy when the hole formalism is employed, so a similar inversion takes place in the ligand field levels. This is quite acceptable from a qualitative point of view since the holes would be attracted toward the negative ligands, whereas repulsion would take place in the case of the electrons.

Figure 6 illustrates the differences for d^2 and d^8 electrons for the 3F ground state in an octahedral field. Moffitt and Ballhausen (7) have listed the octahedral states and their energies in Dq units which result from the ligand field acting on the ground states of the free ion having d^1 and d^9 electrons.

3. Strong field

In the strong field case, the interaction between the individual d-electrons and the ligands is greater than the interaction between the electrons themselves. Qualitatively speaking, the character which the wave functions assume is that of the ligand field. Thus in the case of the d-electrons in a strong octahedral field, one speaks of (t_{2g}) and (e_g) electrons, depending upon which symmetry orbital the electrons occupy. The discussion concerning the single d-electron previously given applies, in the first approximation, to all the d-electrons of the central atom.

In quantum mechanical terms, the wave functions used as basis functions for the energy matrices are such that the matrices are diagonal in the ligand field terms, while the electronic interaction between the electrons are considered as perturbations on the ligand field. The single electron wave functions used to obtain the product wave functions are characterized by the "quantum numbers", (t_{2g}) and (e_g), rather

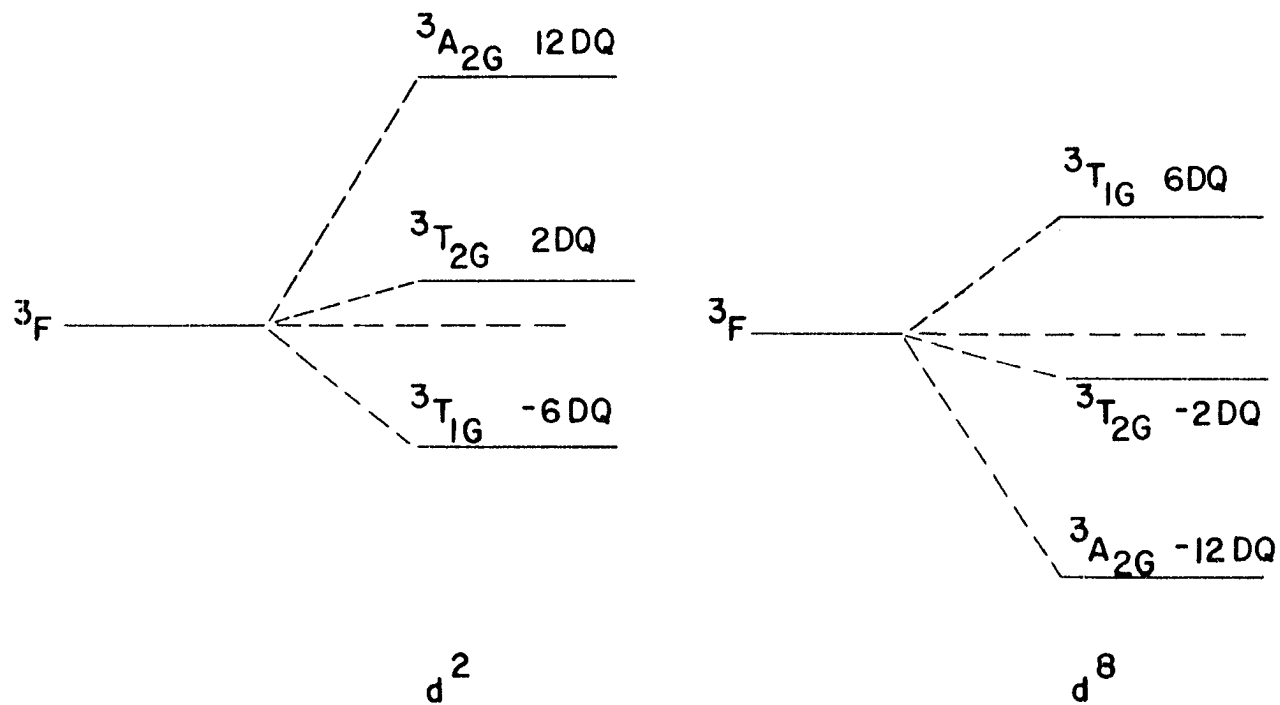


Figure 6. Comparison of the d^2 and d^8 configurations in an octahedral potential field

than the spherical quantum number, (l). The Pauli Exclusion Principle and Hund's Rule still apply, of course, but in this case they concern the number of electrons which can occupy a particular symmetry orbital. For example, a maximum of six electrons can occupy the (t_{2g}) orbital, and four can occupy the (e_g) orbital.

The symmetry of the ground and excited states are determined most easily by means of the "direct product" of group theory. Hence, discussion of the derivation of these symmetries is deferred to the section of this thesis on group theory.

4. Intermediate fields

The intermediate field, as the name implies, is that situation between the two extremes given previously. The ligand field interaction and the electronic interaction between the electrons are roughly comparable, hence approximations in either direction are invalid. As a result, the intermediate field does not lend itself as readily to qualitative discussion but requires actual calculations based upon the resultant matrix elements in order to obtain correlation with experimental data.

The differences between the three cases can be illustrated by consideration of the electron distribution for an ion containing four or more electrons. For example, Griffeth

(8) points out that $\text{Fe}(\text{H}_2\text{O})^{+2}$ is strongly paramagnetic, indicating unpaired d-electrons, whereas $\text{Fe}(\text{CN})_6^{-4}$ is diamagnetic, indicating all six d-electrons are paired. Orgel (9), as well as Griffith (8), correlate the tendency toward spin pairing in complexes with the ligand field necessary to overcome the loss in "exchange energy" which results when electrons are paired. Orgel (9) has calculated the increase in electron repulsion which results from pairing electrons in an octahedral field. For example, in terms of the Slater-Condon parameters (6) for the electronic interaction between the electrons, the ground state energies are:

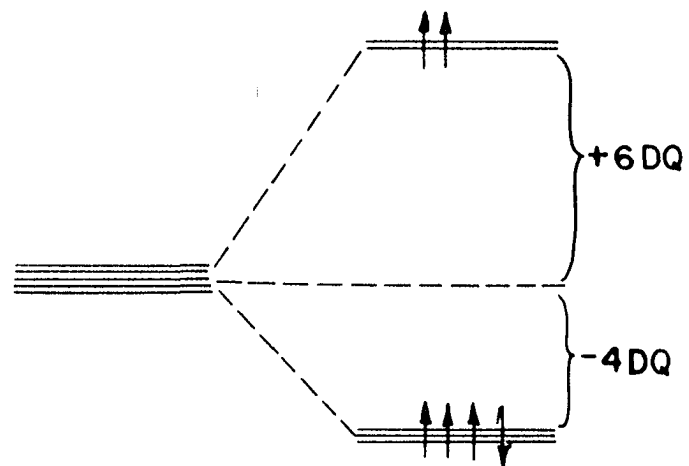
$$\text{Fe(II) free ion or weak field:} \quad -35F_2 - 315F_4$$

$$\text{Fe(II) strong field:} \quad -30F_2 - 60F_4$$

$$\text{Increase in electron repulsion:} \quad 5F_2 + 255F_4$$

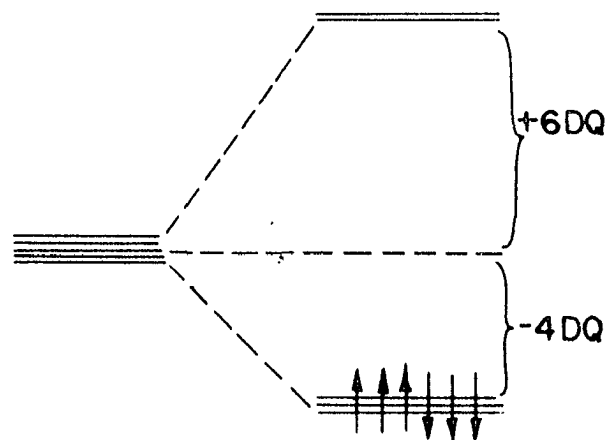
The increase in electron repulsion is termed by Orgel (9) as "promotional energy" or "loss in exchange energy". The techniques for calculating these energies are given in Appendix C. Spectroscopic values for Fe(II), as tabulated by Orgel (9), for F_2 and F_4 are 1540 cm^{-1} and 120 cm^{-1} respectively. Hence the promotional energy is estimated as 38300 cm^{-1} .

The free ion, when placed in a weak octahedral field, has an over-all lowering of energy equal to $4 Dq$, see Figure 7a. In a strong octahedral field, the lowering is equal to $24 Dq$, that is $20 Dq$ more than for the weak field. See Figure 7b.



$$2 \times (+6DQ) + 4 \times (-4DQ) = -4DQ$$

a. WEAK FIELD



$$6 \times (-4DQ) = -24DQ$$

b. STRONG FIELD

Figure 7. Comparison of the d^6 configuration in weak and strong octahedral fields

Therefore, in order that the ligand field be strong enough for spin pairing to take place, Dq must be equal to or greater than approximately 1900 cm^{-1} . If Dq is much less than this value, the field is weak. If it is much greater than 1900 cm^{-1} , the field is strong. If Dq is approximately equal to 1900 cm^{-1} , the field is of intermediate strength.

B. Applications to Experiment

The title of this section is somewhat misleading in the sense that all applications must be quantitatively sound. However, certain generalizations and conclusions can be seen to be valid without recourse to actual calculations.

1. Absorption spectra

The first use of ligand field theory to solution chemistry, was made by Ilse and Hartmann (10) in interpreting the absorption spectra of $\text{Ti}(\text{H}_2\text{O})_6^{+3}$. The free ion, Ti^{+3} , has a single d-electron, hence its ground state is 2D and its first excited state is 2S . Emission spectra indicate that the energy of this transition in wave numbers is $8 \times 10^4\text{ cm}^{-1}$. The hexaquo species, however, displays a single absorption peak at $1.7 \times 10^4\text{ cm}^{-1}$. From the discussion of the d-electron energy levels in an octahedral field (Section II-1) the low energy absorption peak is seen to be a transition from the $^2T_{2g}$ ground state to the 2E_g excited state. This simple

application awakened the interests of chemists to the possibilities of the theory in regard to the absorption spectra of transition metal complexes. Within five years, the theory was applied to dozens of complexes, including manganese(II), (11); chromium(III), (12); cobalt(III), (13); and nickel(II), (14). By 1955, the essential principles of the sources of the colors of transition metal complexes had been developed, including the explanation of the spectrochemical series.

2. The spectrochemical series

As early as 1923, Fajans (15) noticed that successive replacement of certain ligands surrounding the cation by other ligands shifted the maxima of the prominent band systems to progressively shorter wavelengths. This led to the construction of the spectrochemical series, an example of which is: $I^- < Br^- < Cl^- < OH^- < F^- < H_2O < NH_3 < \text{ethylene diamine} < CN^-$. The trend seemed to be more or less independent of the cation, except for certain conspicuous failures. A very satisfying interpretation of the trend and the reason for the anomalous behavior of cations having d^4 , d^5 , d^6 , and d^7 electrons is given by Orgel (9, 16, 17). Each of the ligands given above results in a successively stronger ligand field, thus increasing the separation of the T_{2g} and the E_g states. (It is presumed that the discussion concerns octahedral complexes.) In those cases, for example d^1 , where the ground

state multiplicity in both the weak field and strong field is the same, the spectrochemical shift follows a smooth trend. In situations which involve changes in the multiplicity of the ground state, although the energy levels shift as a continuous function of Dq , the selection rules for the preferred transitions change. For example, the weak field ground state for d^6 is $^5T_{2g}$, and hence quintuplet-quintuplet transitions will give the prominent bands. In the strong field, the ground state is $^1A_{1g}$ as a result of complete filling of the (t_{2g}) level, and singlet-singlet transitions take preference.

3. Magnetic behavior

In the discussion of the three types of ligand fields, section II-3, the differences in the number of paired electrons which resulted in the strong field, as compared to the weak field, was illustrated. The changes in paramagnetic behavior should therefore coincide with the changes in multiplicity associated with increasing field strength as discussed with reference to the spectrochemical series. Thus, having estimated Dq from absorption spectra, it is possible for one to predict the magnetic properties of the complex, or conversely the magnetic properties should help to predict the qualitative features of the spectra.

4. Miscellaneous applications

In addition to the applications already mentioned, ligand field theory has been successfully applied to explanations of heats of hydration (17, 18), ionic radii (19), and spectral band widths (20). Early work in the field involved explanations of the paramagnetic behavior of rare earth complexes (21,22). Several excellent reviews of the qualitative and quantitative aspects of the theory have been written. Among those to be recommended are the reports by Moffitt and Ballhausen (7), McClure (23), and Basolo and Pearson (18).

III. GROUP THEORY APPLIED TO QUANTUM MECHANICS

A. Basis Functions for Group Representations

The following discussion assumes a general familiarity of the principles of group theory on the part of the reader. However, for purposes of completeness, a review of the concepts of group theory which are used in this thesis is given in Appendix C.

Quantum mechanics is concerned with eigenstates of a Hamiltonian operator, \mathcal{H} , which may be defined in a coordinate system, \vec{x} . The operator is denoted, $\mathcal{H}(\vec{x})$, though in general it is a function of derivatives with respect to the coordinates as well as the coordinates themselves. Schroedinger's equation expresses the relationship for the energy eigenvalues:

$$\mathcal{H}(\vec{x}) \psi_i(\vec{x}) = E_i \psi_i(\vec{x}). \quad (13)$$

If both sides of the equation are subject to some transformation, R , one obtains:

$$R \mathcal{H}(\vec{x}) \psi_i(\vec{x}) = R E_i \psi_i(\vec{x}). \quad (14)$$

In those cases, and they are the cases of interest, where the operator, $\mathcal{H}(\vec{x})$, is invariant under the transformation, the operators $\mathcal{H}(\vec{x})$ and R commute, i.e.,

$$R \mathcal{H}(\vec{x}) = \mathcal{H}(\vec{x}) R, \quad (15)$$

and since E_i is a numerical value, R commutes with it. Hence it is possible to write:

$$\mathcal{H}(\vec{x}) (R \psi_i(\vec{x})) = E_i (R \psi_i(\vec{x})). \quad (16)$$

But this requires that the function $(R \psi_i)$ be a solution of the Schroedinger equation with the eigenvalue E_i .

If E_i is k -fold degenerate, the Schroedinger equation is:

$$c_{ml} = \sum_{j=1}^k b_{mj} a_{jl} . \quad (28)$$

But this is simply the notation for the process for matrix multiplication:

$$C = (B) (A) . \quad (29)$$

Thus the collection of all coordinate transformations which leave the Hamiltonian invariant forms a group and the matrices obtained from the coefficients in the expansion of $R \psi_i$, etc., form a representation of the group. It can be shown that all such matrices which result from rotation operations are unitary matrices.

The set of degenerate eigenfunctions, $\psi_{i1}, \psi_{i2}, \dots, \psi_{ik}$ is said to form a basis for the representation of the group, since the representation is generated by the application of the group operations, R, S , etc. The dimension of the representation is equal to the degeneracy of the corresponding eigenvalue.

Of particular importance are the irreducible representations of the group. The definition of an irreducible representation is given in Appendix C. For each group of interest, these irreducible representations are known. They are useful in choosing the approximate wave functions in an efficient manner, since a set of functions which transform among each other according to an irreducible representation necessarily possess the degeneracy of the irreducible representation. Two sets of functions, each of which transforms in itself accord-

$$\mathcal{H}(\vec{x}) \psi_{ik}(\vec{x}) = E_i \psi_{ik}(\vec{x}) \quad (17)$$

Then any linear combination of the functions $\psi_{i1}, \psi_{i2}, \dots, \psi_{ik}$, is a solution of the Schroedinger equation and hence:

$$R \psi_{i\ell} = \sum_{j=1}^k \psi_{ij} a_{j\ell}, \quad (18)$$

where:

$$\sum_{j=1}^k a_{j\ell}^2 = 1. \quad (19)$$

If there is another transformation operation S applicable to the equation, i.e., S and $\mathcal{H}(\vec{x})$ also commute, then:

$$S \mathcal{H}(\vec{x}) R \psi_{ik}(\vec{x}) = S E_i (R \psi_{ik}), \quad (20)$$

$$\text{and} \quad \mathcal{H}(\vec{x}) (S R \psi_{ik}(\vec{x})) = E_i (S R \psi_{ik}), \quad (21)$$

$$\text{also:} \quad \mathcal{H}(\vec{x}) (S \psi_{ik}) = E_i (S \psi_{ik}). \quad (22)$$

$$\text{Therefore:} \quad S \psi_{ij} = \sum_{m=1}^k \psi_{im} b_{mj}, \quad (23)$$

$$\text{and hence} \quad S R \psi_{i\ell} = \sum_{j=1}^k a_{j\ell} S \psi_{ij} = \sum_{j=1}^k \sum_{m=1}^k \psi_{im} b_{mj} a_{j\ell}. \quad (24)$$

The product of the two transformation S and R may be denoted by

$$S \cdot R = T. \quad (25)$$

Then T is also a transformation of the group and:

$$\mathcal{H}(\vec{x}) (T \psi_{i\ell}) = E_i (T \psi_{i\ell}), \quad (26)$$

$$\text{hence:} \quad T \psi_{i\ell} = \sum_{m=1}^k \psi_{im} c_{m\ell}. \quad (27)$$

From this it is obvious that:

ing to an irreducible representation, have, in general, different eigenvalues.¹

Therefore, if Γ_j is an irreducible representation of dimension k , and if $\psi_{j1}, \psi_{j2}, \dots, \psi_{jk}$ is the set of degenerate eigenfunctions which form a basis for the j^{th} irreducible representation of the group, then the eigenfunctions transform according to the operations of the group. For example, two of the d-electron wave functions expressed in real form can be written:

$$\psi_1 = C_1 \cdot R(r) \cdot (xz)$$

$$\psi_2 = C_2 \cdot R(r) \cdot (yz),$$

where C_1 and C_2 are constants, $R(r)$ is the radial function, and (xz) and (yz) are the angular parts of the wave functions expressed in terms of Cartesian coordinates. In square-planar or tetragonal symmetry, these two functions are the basis functions for the representation E_g .²

The matrix table for the E_g representation is given in Table 1. By application of these matrices to the row matrix of ψ_1 and ψ_2 , one obtains, for example:

$$E(\psi_1 \ \psi_2) = (\psi_1 \ \psi_2) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = (\psi_1 \ \psi_2) \quad (30)$$

$$C_4(\psi_1 \ \psi_2) = (\psi_1 \ \psi_2) \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = (-\psi_2 \ \psi_1) \quad (31)$$

etc.

¹If they happen to have the same eigenvalue, the degeneracy of the two sets is called accidental degeneracy.

²In the same symmetry, the other three orbitals whose angular parts are expressible as $(3z^2-r^2)$, (x^2-y^2) , and (xy) , belong to the Groups A_{1g} , B_{1g} , and B_{2g} , respectively.

Table 1. Matrices for representation E_g of the group D_{4h} ^a

E	C_4	C_4^3	C_2
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
$C_2'(x)$	$C_2'(y)$	$C_2''(xy)$	$C_2''(-xy)$
$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
i	σ_h	S_4	S_4^3
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$
$\sigma_d'(x)$	$\sigma_d'(y)$	$\sigma_d''(xy)$	$\sigma_d''(-xy)$
$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$

^aThe meaning of the group elements is given in Appendix C.

The validity of these relationships may be checked by consideration of what happens to the functions, (xz) and (yz) , under the various operations. For example, under C_4 : x is replaced by $-y$, y is replaced by x , and z is replaced by z . Therefore, (xz) is replaced by $(-yz)$, and (yz) is replaced by

(xz). The replacement operations mentioned consider the transformations which keep the functions fixed in space and redefines the coordinates in terms of which the functions are expressed. Thus:

$$C_4(\psi_1 \ \psi_2) = (-\psi_2 \ \psi_1), \quad (32)$$

which is exactly the result given by the corresponding matrix multiplication. Hence, ψ_1 and ψ_2 are said to be basis functions for the E_g representation.

B. The Direct Product

A detailed account of the derivation of the direct product of group theory is given in Appendix C-8. One of the most important applications of the direct product involves the evaluation of integrals composed of functions which are bases for representations of the group. If F is any function which transforms according to an irreducible representation of a group, then the integral

$$I = \int F \, d\tau,$$

will be different from zero only if this irreducible representation is the totally symmetric representation, $\Gamma_1 = A_{1g}$ of the group. That is,

$$R F = F, \text{ for all operations, } (R), \text{ of the group. } (33)$$

Consider the integral of the type:

$$\int \phi_A \phi_B \, d\tau.$$

The integrand belongs to the representation:

$$\Gamma_{\text{integrand}} = \Gamma_A \times \Gamma_B \quad (34)$$

where $\Gamma_A \times \Gamma_B$ is the direct product of the representations of ϕ_A and ϕ_B . In general, the direct product is reducible, that is,

$$\Gamma_{\text{integrand}} = \sum_i a_i \Gamma_i \quad (35)$$

where Γ_i are irreducible representations of the group, and a_i is the number of times the i^{th} irreducible representation is contained in the direct product. As a consequence, the integral can be written as a sum of functions,

$$\phi_A \phi_B = \sum_i a_i F_i \quad (36)$$

where F_i belongs to the irreducible representation Γ_i . Consequently, the integral will be different from zero only if the direct product contains the totally symmetric representation, $\Gamma_1 = A_{1g}$. For groups whose characters, i.e., the sum of the diagonal elements, are real this requires that $\Gamma_A = \Gamma_B$.

Similarly, if an operator, f , is the basis function of an irreducible representation, in order that integrals of the type:

$$\int \phi_A f \phi_B d\tau$$

be different from zero, it is necessary that at least one of the irreducible components of $\Gamma_A \times \Gamma_B$ be the same irreducible representation as Γ_f .

Since the Hamiltonian is invariant under all operations of the group, it belongs to the totally symmetric representation, $\Gamma_1 = A_{1g}$. Therefore, for the integral

$$\int \phi_A H \phi_B d\tau ,$$

to be different from zero, it is necessary that one of the irreducible representations of $\Gamma_A \times \Gamma_B$ be Γ_1 . This requires that $\Gamma_A = \Gamma_B$.

Thus if one constructs functions which are symmetry adapted, that is, are basis functions for the irreducible representations, it is known that there will exist no off-diagonal matrix elements connecting functions belonging to different irreducible representations. For example, if there are three irreducible representations for a particular group, Γ_1 , Γ_2 , and Γ_3 , then the functions can be arranged in such a manner so that the matrix of the elements $\int \phi_A H \phi_B d\tau$ will have the general form:

$$\begin{array}{c} \Gamma_1 \\ \Gamma_2 \\ \Gamma_3 \end{array} \left(\begin{array}{ccc} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \boxed{} & & \bigcirc \\ & \boxed{} & \\ \bigcirc & & \boxed{} \end{array} \right)$$

C. The Irreducible Representations of the Full Rotation Group under D_{4h} Symmetry

In atomic systems, it is possible to consider many types of energy degeneracies. For example, there is the degeneracy associated with the orbital angular momentum, ℓ , of a single electron. This degeneracy is $(2\ell + 1)$ -fold and the states associated with it have m_ℓ values between $+\ell$ and $-\ell$. Similarly, the degeneracy of the states which are the results of products of two or more electrons can be characterized as having a total orbital angular momentum, L , which is the sum of the orbital angular momenta of the individual electrons. The degeneracy of such a state is $(2L + 1)$ and the wave functions associated with the state are characterized by M_L values. It is also possible to consider states of a particular J value, where J is the total angular momentum and is equal to $S + L$. The degeneracy of a particular J state is $(2J + 1)$ and the wave functions associated with it are characterized by M_J values.

The discussion that is to follow is equally applicable to all such degeneracies, since in each case the wave functions associated with the states form basis functions for a group representation. That is, in a field of non-spherical symmetry, the reduction of the states associated with a particular value of total angular momentum, J , will correspond to the reduction of the states associated with the orbital angular momentum,

l , having the same value. For example, if the single electron function:

$$\psi_1 = N \cdot R(r) \cdot 1/\sqrt{2} [Y(2,2) + Y(2,-2)], \quad (37)$$

is the basis function for an irreducible representation of the non-spherical rotation group under consideration, then a function which also is a basis function for the same representation is given by:

$$\psi = 1/\sqrt{2} [|2,2 \rangle + |2,-2 \rangle] \quad (38)$$

where $|J, M_J \rangle$ indicates the wave function associated with the state having total angular momentum J and z -component M_J .

When two groups have such a one to one correspondence they are said to be isomorphic. The validity of these considerations is indicated in Appendix C.

An analogous situation exists for the spin states, s , of a single electron, and for the product of two or more electrons, S . A set of matrices corresponding to the group representation can be constructed by the methods outlined in Appendix C. Such matrices give the corresponding transformations in complex space that are associated with the given transformations in real space. Hence the arguments for the reduction of the matrices corresponding to a given angular momentum, l , also hold for the spin functions.

With the above statements in mind, it is necessary to consider the reduction of only one type of degenerate state.

It is convenient to follow the example of Bethe (1) and use the orbital angular momentum of a single electron.

In the spherical symmetry of the free ion, the degeneracy of a state with orbital angular momentum, l , is $2l + 1$. In spherical symmetry, the representation corresponding to this degenerate state is irreducible. However, in the field of lower symmetry which results from the ligands of the complex, the representation is reducible. In order to effect the reduction, use is made of a fundamental theorem of group theory: each reducible representation of a group can be separated in only one fashion into its irreducible parts. Furthermore, the "character", that is, the sum of the diagonal elements of the matrix representation, of each group element in the reducible representation equals the sum of the characters which belong to the element in the irreducible representations. Therefore, knowledge of the character of the reducible representation for each symmetry operation of the ligand field, together with the table of characters of the irreducible representations, enables the reduction of the l -state to be made.

As shown in Appendix C, the character associated with the rotation of the basis functions by a particular angle ϕ about a chosen axis is given by:

$$\chi(E) = 2l + 1 \quad (39)$$

$$\chi(\phi) = \frac{\sin(l + \frac{1}{2})\phi}{\sin \frac{1}{2}\phi} \quad \text{when } \phi \neq 0 \quad (40)$$

For the d-electrons in a square planar field, for example, the symmetry classes are E, C₄, C₂, C₂['], and C₂^{''}; with $l = 2$.

$$\chi(E) = 2l + 1 = 5$$

$$\chi(C_4) = \frac{\sin(5/2)\pi/2}{\sin \pi/4} = \frac{-\sin \pi/4}{\sin \pi/4} = -1 \quad (42)$$

$$\chi(C_2) = \chi(C_2') = \chi(C_2'') = \frac{\sin(5/2)\pi}{\sin \pi/2} = 1 \quad (43)$$

Table 2 gives the characters for the irreducible representations for the Group D₄. By use of the table, it is apparent that the irreducible representations which are the components of the reducible representation for $l = 2$ are: A₁ + B₁ + B₂ + E. Since all states with $l = \text{even}$ are unchanged as a result of inversion through the origin, the d-electron states in the D_{4h} symmetry are A_{1g} + B_{1g} + B_{2g} + E_g.

By similar applications, the irreducible components of any reducible representation may be obtained. Table 3 gives the number of times a particular irreducible representation is contained in the reducible representation of a given l in square-planar or tetragonal symmetry. For example, for a state with $l = 3$, one uses the fourth column ($4\lambda + 3$) with $\lambda = 0$, and the irreducible representations are A₂ + B₁ + B₂ + E

Table 2. Irreducible representations for group D_4

Representation	Operation				
	E	C_2	$2C_4$	$2C_2'$	$2C_2''$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	1	-1	1	-1
B_2	1	1	-1	-1	1
E	2	-2	0	0	0

Table 3. The irreducible representations in D_4 of the states with angular momentum l

$l =$	4λ	$4\lambda + 1$	$4\lambda + 2$	$4\lambda + 3$
A_1	$\lambda + 1$	λ	$\lambda + 1$	λ
A_2	λ	$\lambda + 1$	λ	$\lambda + 1$
B_1	λ	λ	$\lambda + 1$	$\lambda + 1$
B_2	λ	λ	$\lambda + 1$	$\lambda + 1$
E	2λ	$2\lambda + 1$	$2\lambda + 1$	$2\lambda + 2$

IV. LIGAND FIELD THEORY: QUANTITATIVE APPROACH

A. The Schroedinger Equation and Its Solution

The determination of the energy levels of the central ion requires the solution of Schroedinger's equation:

$$\hat{H}\psi = E\psi \quad (44)$$

where

$$\hat{H} = \sum_i \left\{ -\frac{\hbar^2}{2m_i} \nabla_i^2 - \frac{Ze^2}{r_i} + \xi(r_i) \vec{L} \cdot \vec{S} \right\} + \sum_{i > j} \frac{e^2}{r_{ij}} + \sum_i V^{LF}(r_i) \quad (45)$$

The first four terms in the Hamiltonian, \hat{H} , are the usual atomic Hamiltonian operator for the free ion; the last term, $V^{LF}(r_i)$ expresses the effects of the non-spherical potential field of the surrounding ligands on an electron of the central ion. Prior to consideration of the effects of this latter term, some remarks concerning the atomic Hamiltonian for the free ion are in order.

1. The Free Ion

In all approaches to the solution of the Schroedinger equation for a many electron atomic system, it has been necessary to make some approximation in order to solve the problem. One of the most common involves the "Central Field Approximation" in which the interaction of the electrons with the nucleus and a large part of the mutual interaction of the electrons are combined in a potential, U , which is dependent

upon the radial distance only. That is, one starts with an approximate Hamiltonian,

$$\mathcal{H}_0 = \sum_i \left[-\frac{\hbar^2}{2m_i} \nabla_i^2 + U(r_i) \right] \quad (46)$$

and considers the remaining terms of the true Hamiltonian as a perturbation:

$$\mathcal{H}' = \sum_i \left[\left(-\frac{Ze^2}{r_i} - U(r_i) + \xi(r_i) \vec{L} \cdot \vec{J} \right) \right] + \sum_{i>j} \frac{e^2}{r_{ij}} \quad (47)$$

The zero order wave functions, i.e., the wave functions, ψ_0 , that are solutions of the equation:

$$\mathcal{H}_0 \psi_0 = E_0 \psi_0, \quad (48)$$

can be expressed as products of single electron wave functions because \mathcal{H}_0 is the sum of one electron operators. The single electron functions are very similar in form to the wave functions of the hydrogen atom in that they are products of a radial function and an angular function expressible in terms of the spherical harmonics. It is beyond the intent of this thesis to reproduce in detail the solution of the atomic problem particularly since the solution is well surveyed in such standard texts as those by Condon and Shortley (6), Pauling and Wilson (5) and Eyring et al. (24). The following principles of the approach should be mentioned:

(i) The zero order basis functions are constructed as linear combinations of antisymmetrized products of single electron functions arising from one configuration.

(ii) In cases where spin-orbit coupling is important, it is convenient that a zero order function, ψ , be characterized by the quantum numbers, S , L , J , and M_J . That is, ψ is an eigenfunction of the operators J^2 , L^2 , S^2 , and M_J , such that

$$J^2 \psi = \hbar^2 S(S+1) \psi \quad (49)$$

$$L^2 \psi = \hbar^2 L(L+1) \psi$$

$$S^2 \psi = \hbar^2 J(J+1) \psi$$

$$M_J \psi = \hbar M_J \psi$$

where: J^2 is the total angular momentum operator

L^2 is the total orbital angular momentum operator

S^2 is the total spin momentum operator

M_J is the z-component operator of the total angular momentum.

Such a function, ψ , may be written as $|S, L, J, M_J\rangle$.

A particular function, $|S, L, J, M_J\rangle$, is an appropriate linear combination of the functions, $|S, M_S, L, M_L\rangle$, which are eigenfunctions of L^2 , M_L , S^2 , M_S , that is:

$$L^2 \phi = \hbar^2 L(L+1) \phi \quad (50)$$

$$S^2 \phi = \hbar^2 S(S+1) \phi$$

$$M_S \phi = \hbar M_S \phi$$

$$M_L \phi = \hbar M_L \phi$$

where M_L and M_S are the z-component operators of the total orbital angular momentum and the total spin momentum, and ϕ is an $|S, M_S, L, M_L\rangle$ function. These $|S, M_S, L, M_L\rangle$ functions are themselves linear combinations of antisymmetrized products

(determinants) of single electron wave functions,

(l, m_l, s, m_s) .³ Thus for example,

$$|S, M_S, L, M_L\rangle = |1, 1, 3, 3\rangle = 1/\sqrt{2} [(2, 2, \frac{1}{2}, \frac{1}{2})^{(1)} (2, 1, \frac{1}{2}, \frac{1}{2})^{(2)} - (2, 1, \frac{1}{2}, \frac{1}{2})^{(1)} (2, 2, \frac{1}{2}, \frac{1}{2})^{(2)}] \quad (51)$$

where the superscripts (1) and (2) refer to electrons one and two respectively. Since it is the d-electrons that are of interest, $l = 2$ and $S = \frac{1}{2}$, always. Furthermore, if one represents $m_s = +\frac{1}{2}$ by α and $m_s = -\frac{1}{2}$ by β and one always writes the one electron functions in the order: electron one, electron two, then the expression for $|1, 1, 3, 3\rangle$ may be written:

$$|1, 1, 3, 3\rangle = 1/\sqrt{2} [(2, \alpha)(1, \alpha) - (1, \alpha)(2, \alpha)] \quad (52)$$

or alternatively:

$$|1, 1, 3, 3\rangle = 1/\sqrt{2} [(2, 1) - (1, 2)] [\alpha\alpha] \quad (53)$$

and similarly for the other $|S, M_S, L, M_L\rangle$ functions.

The derivation and construction of the $|S, M_S, L, M_L\rangle$ and the $|S, L, J, M_J\rangle$ functions, including the consistent choice of phase factors, is considered in Appendix A.

(iii) The single electron functions are separable into radial and angular parts. Thus:

$$\phi = R(r) \cdot Y(l, m_l) \quad (54)$$

where $Y(l, m_l)$ are the spherical harmonics.

³The notation, $| \quad \rangle$, is used to denote a function $|S, L, J, M_J\rangle$. The notation, $| \quad)$, is used to denote a function $|S, M_S, L, M_L\rangle$. The notation, (\quad) , is used to denote the product of the single electron space functions associated with electron one and electron two in that order.

(iv) Since it is only the relative energy levels within the chosen configuration that are of interest, the mixing of the zero order basis functions is found by the diagonalization of the matrix corresponding to the operator:

$$H'' = \sum_i \xi(r_i) \mathcal{L}_i \cdot \mathcal{S}_i + \sum_{i>j} e^2/r_{ij} \quad (55)$$

and this operator need be applied only to those electrons outside closed shells and subshells. This means that the zero order wave functions which constitute the basis functions are constructed only from consideration of the electrons outside of closed shells and subshells. The relative energy levels are obtained by diagonalization of a matrix of the general form:

$$\begin{pmatrix} H''_{11} & H''_{12} & H''_{13} & \cdots & H''_{1n} \\ H''_{21} & H''_{22} & H''_{23} & \cdots & H''_{2n} \\ \vdots & & & & \\ \vdots & & & & \\ H''_{n1} & H''_{n2} & H''_{n3} & \cdots & H''_{nn} \end{pmatrix}$$

where $H''_{\alpha\beta} = \int \psi_{\alpha} H'' \psi_{\beta} d\tau$

2. Ion in the ligand field

The basic assumption in ligand field theory is that the field potential perturbs the atomic levels only in such a way as to modify the mixing of the zero order functions within a given configuration. This means that one proceeds exactly as

the free ion problem except that the operator H is replaced by the operator H'' :

$$H'' = \sum_i \xi(r_i) \mathbf{L}_i \cdot \mathbf{S}_i + \sum_{i > j} e^2/r_{ij} + \sum_i V_i^{LF} \quad (56)$$

Within the framework of the simplification of the central field approximation and the considerations concerning the ligand potential to be discussed, diagonalization results in an exact solution in the sense that all effects are considered. In many applications it is possible to neglect spin-orbit coupling, which results in an appreciable reduction in the number of wave functions which need be considered. However, the spin-orbit coupling effect in platinum is appreciable and must be included in the calculations.

Two extreme cases can be considered in constructing the zero order basis functions. In the so-called weak field case, the ligand field effect is much smaller than the electronic interaction effect. In this situation, it is convenient to use the free atom basis functions in terms of the quantum numbers, S , L , J , and M_J . As is shown later, this choice results in the matrix elements being diagonal in the electronic interaction parameters. The ligand field will result in non-zero values for both diagonal and off-diagonal elements, but the off-diagonal elements will be small in comparison to the diagonal elements. Consequently, only weak mixing of the free atom states result. In a sense, one can

consider the ligand potential as a perturbation of those atomic states in which the electronic interaction has already been taken into account.

In the strong field case, the ligand field effect is much greater than the electronic interaction. In this situation, it is convenient to consider that the zero order Hamiltonian, H_0^{LF} , be expressed as:

$$H_0^{LF} = H_0 + \sum_i V_i \quad (57)$$

Consequently, the strong field zero order functions, ψ_0 , are antisymmetric product functions of new one electron functions, ψ_i . These one electron functions have the symmetry of the ligand field. It is assumed that they can be expressed as linear combinations of the free-ion one-electron functions, (l, m_l, s, m_s) . The proper linear combination are those which diagonalize the one electron matrix: $(\psi_i | V^{LF} | \psi_k)$. Thus the basis functions are constructed so that the matrix elements are diagonal in the ligand field parameters. In this case, the electronic interaction term contributes to both diagonal and off-diagonal elements and again, the off-diagonal elements are small and the mixing of the ligand field states is slight. Hence the electron interaction can be considered as a perturbation on the ligand field states.

For the case of intermediate fields, the off-diagonal elements are not small in either basis and the choice of basis

functions is arbitrary. This is true since it is possible to express the weak field basis in terms of the strong field basis by a unitary transformation. By means of this transformation the expressions for the wave functions associated with the weak field are related to the expressions for the wave functions for the strong field. The eigenvalues which result upon diagonalization must be the same regardless of which basis is used.

B. The Ligand Field Potential in the Hamiltonian

Thus far the exact form of the ligand potential, V^{LF} , has not been specified. Several expressions are possible (7, 8, 14, 21) all of which are essentially equal. For conceptual simplicity, none is more satisfying than the point of view that the effect of the ligands can be approximated by considering them as point charges or point dipoles. In this thesis, the ligands are considered as point dipoles. For mathematical reasons, it is convenient to initially consider the case of point charges and to carry out the calculations in atomic units, namely:

Unit charge: e = the charge of the electron

Unit length: $a_0 = \hbar^2/me^2$ = Bohr radius = 0.529A

Unit energy: e^2/a_0 = twice the ionization potential of the hydrogen atom = 27.2 electron volts.

Then by use of these units,

$e = -1$, for an electron

$e = +1$, for a "hole"

$q > 0$ = charge of positive ligand in atomic units

$q < 0$ = charge of negative ligand in atomic units

Figure 8 gives a simple schematic diagram of the arbitrary location of a single ligand charge, q_k , and an electron, $e = -1$, with respect to the origin. The electron is located at $P(r, \theta, \phi)$ and the ligand at $Q(r_k, \theta_k, \phi_k) = Q_k$. Then the potential at P due to the charge q_k at Q_k is given by:

$$V_k(r, \theta, \phi) = -q_k / r_{pk}$$

where r_{pk} is the distance from Q_k to P. As shown in Eyring et al. (24), it is possible to expand $V_k(r, \theta, \phi)$ in terms of spherical harmonics, as follows:

$$V_k(r, \theta, \phi) = -q_k \sum_{l=0}^{\infty} \sum_{m=-l}^l Y_{lm}(\theta, \phi) B_{l,m}^k(r), \quad (59)$$

where

$$B_{l,m}^k(r) = \frac{r_{<}}{r_{>+1}} \frac{4\pi}{2l+1} [Y_{lm}(\theta_k, \phi_k)]^*, \quad (60)$$

$Y_{lm}(\theta, \phi)$ = the spherical harmonic at the location of the electron,

$Y_{lm}(\theta_k, \phi_k)$ = the spherical harmonic at the location of the ligand,

$r_{>}$ = the larger of the distances r and r_k ,

$r_{<}$ = the smaller of the distances r and r_k .

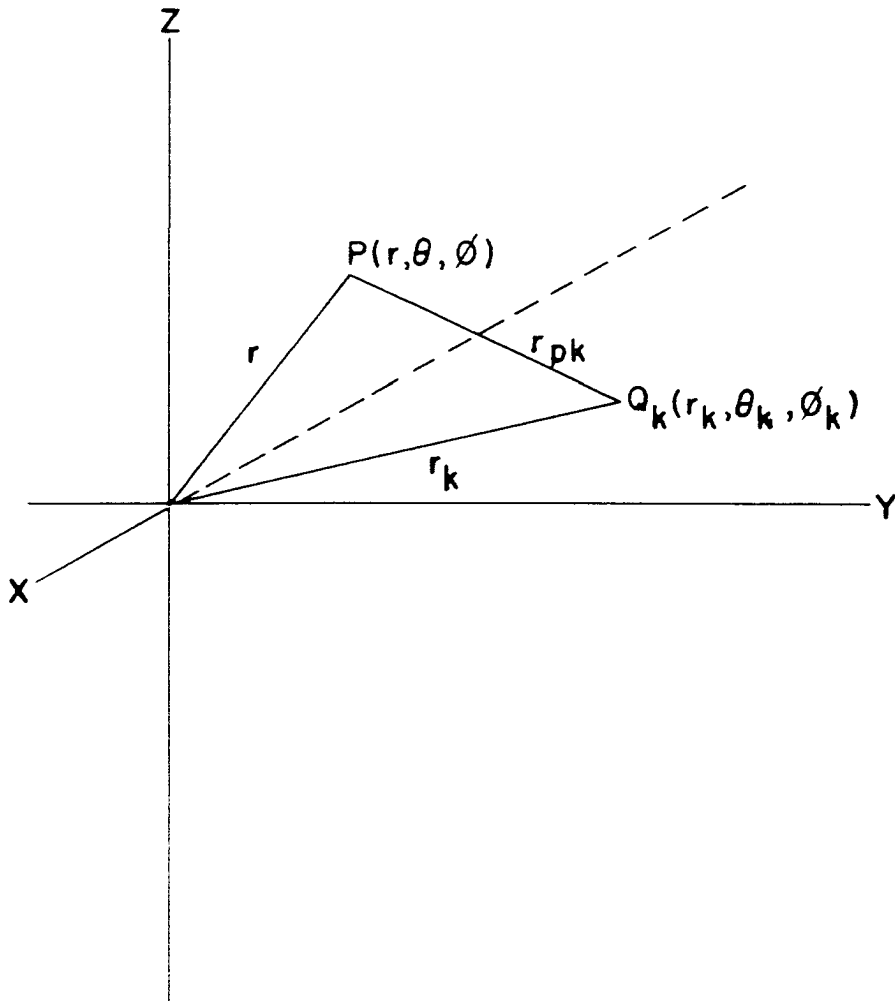


Figure 8. Generalized locations of the ligand point charge and an electron of the central ion

Alternatively:

$$B_{\ell, m}^k(r) = \frac{r^{\ell}}{r^{\ell+1}} \left[\frac{4\pi}{2\ell+1} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{\frac{1}{2}} P_{\ell}^{|m|}(\cos \theta_k) e^{-im\phi_k}, \quad (61)$$

where

$$P_{\ell}^{|m|}(\cos \theta_k) = \text{an associated Legendre Function,}$$

$$= \frac{\sin^{|m|} \theta}{2^{\ell} \ell!} \frac{d^{\ell+|m|}}{d \cos \theta^{\ell+|m|}} (\cos^2 \theta - 1)^{\ell}. \quad (62)$$

The foregoing formula describes the potential at $P(r)$ due to one ligand. For several ligands:

$$V^{LF} = \sum_k (r, \theta, \phi), \quad (63)$$

the summation being over the ligands. By substitution, one obtains:

$$V^{LF} = - \sum_{\ell, m} Y(\ell, m) \sum_k q_k B_{\ell m}^k(r) \quad (64)$$

In the square-planar symmetry, it is convenient to locate the ligand point charges, (q_1, q_2, q_3, q_4) , along the $\pm X$ and $\pm Y$ axes. Consequently the following relations hold:

$$q_1 = q_2 = q_3 = q_4 = q,$$

$$r_1 = r_2 = r_3 = r_4$$

$$\theta_1 = \theta_2 = \theta_3 = \theta_4 = \pi/2, \text{ hence } \cos \theta_k = 0,$$

$$\phi_1 = 0,$$

$$\phi_2 = \pi/2,$$

$$\phi_3 = \pi,$$

$$\phi_4 = 3\pi/2.$$

Therefore,

$$B_{\ell m}^k(r) = \left\{ r \left\langle \frac{(\ell - |m|)!}{(\ell + |m|)!} \left[\frac{4\pi}{2\ell + 1} \right]^{\frac{1}{2}} P_{\ell}^{|m|}(0) \right\rangle \right\} q \cdot e^{-im\phi_k}, \quad (65)$$

and

$$V^{LF} = -q \sum_{\ell, m} D_{\ell m} \cdot R_{\ell}(r) \cdot Y_{\ell m}(\theta, 0), \quad (66)$$

where

$$D_{\ell m} = \left[\frac{(\ell - m)!}{(\ell + m)!} \left[\frac{4\pi}{2\ell + 1} \right]^{\frac{1}{2}} \cdot P_{\ell}^{|m|}(0) \sum_k e^{-im\phi_k} \right], \quad (67)$$

and

$$R_{\ell}(r) = r \left\langle \frac{r^{\ell}}{r^{\ell+1}} \right\rangle.$$

A restriction on the possible values of m can be obtained by consideration of the fact that in square-planar symmetry the potential at a point $S(r, \theta, \phi)$ must be the same as that at a point $T(r, \theta, \phi + \pi/2)$. Then,

$$Y_{\ell m}(\theta, \phi) = Y_{\ell m}(\theta, \phi + \pi/2). \quad (68)$$

Therefore:

$$e^{im\phi} = e^{im(\phi + \pi/2)} = e^{im\phi} \cdot e^{im\pi/2} \quad (69)$$

$$1 = e^{im\pi/2}. \quad (70)$$

But this requires that

$$m = 0, \pm 4, \pm 8, \dots, \text{etc.} \quad (71)$$

Furthermore, values for $P_{\ell}^m(0)$ can be found in standard texts; for example, Jahnke and Emde (25). Since Legendre functions are either even or odd in their arguments, it follows that $P_{\ell}^m(0)$ vanishes for $\ell - m = \text{odd}$. Substituting

the formula for $P_l^m(0)$ in the case $l - m = \text{even}$, and also $e^{im\phi_k} = 1$ for all ϕ_k , one finds:

$$V^{LF} = -q \sum_{l=0}^{\infty} \sum_{m=-l}^l D_{lm} \cdot R_l(r) \cdot Y_{lm}(\theta, \phi) \quad (72)$$

$$D_{lm} = \frac{(-1)^{\frac{1}{2}(l-m)}}{2^l} \left(\frac{64\pi}{2l+1} \right)^{\frac{1}{2}} \frac{[(l-m)! (l+m)!]^{\frac{1}{2}}}{[\frac{1}{2}(l-m)! [\frac{1}{2}(l+m)!]} \quad (73)$$

where l and m are restricted to:

$$l = 0, 2, 4, 8, \dots; \quad m = 0, 4, 8, \dots$$

Furthermore, it is shown in Appendix B-2 that in the expansion of Equation 72 only the terms with $l \leq 4$ contribute to the matrix elements which are needed in conjunction with d-electrons. With the previous restrictions on m and the fact that $m \leq l$, always, the "effective" ligand potential for square-planar symmetry becomes

$$\begin{aligned} V^{LF} = -q \{ & D_{00} \cdot R_0(r) \cdot Y_{00}(\theta, \phi) + D_{20} \cdot R_2(r) \cdot Y_{2,0}(\theta, \phi) \\ & + D_{40} \cdot R_4(r) \cdot Y_{40}(\theta, \phi) + D_{4,4} \cdot R_4(r) \cdot Y_{4,4}(\theta, \phi) \\ & + D_{4,-4} \cdot R_4(r) \cdot Y_{4,-4}(\theta, \phi) \} \end{aligned} \quad (74)$$

Evaluating the D 's from Equation 73, one obtains:

$$\begin{aligned} V^{LF} = -q \{ & 8\sqrt{\pi} \cdot R_0 Y(0,0) - 4\sqrt{\pi}/\sqrt{5} \cdot R_2 Y(2,0) \\ & + \sqrt{\pi} \cdot R_4 Y(4,0) + \sqrt{35\pi}/3\sqrt{2} \cdot R_4 [Y(4,4) + Y(4,-4)] \} \end{aligned} \quad (75)$$

In this potential, the terms associated with the spherical

harmonic, $Y(0,0)$, is spherically symmetric and hence does not affect the relative separations between the energy levels (7). Another way of expressing this is to say that the $Y(0,0)$ term contributes equally to each diagonal matrix element and does not contribute to the off-diagonal elements. Since only the relative separations are of interest, this term may be neglected and the effective potential in its final form is:

$$V^{LF} = -q \left\{ -4 \sqrt{\pi} / \sqrt{5} R_2 Y(2,0) + \sqrt{\pi} R_4 Y(4,0) + \sqrt{35\pi} / 3 \sqrt{2} R_4 [Y(4,4) + Y(4,-4)] \right\} \quad (76)$$

C. Matrix Elements Due to the Ligand Field

1. Two electron integrals as a sum of one electron integrals

For the ligand field effect in both the weak and strong field cases, the matrix elements to be evaluated are of the form:

$$H_{jk} = \int \psi_j^* V^{LF} \psi_k d\tau \quad (77)$$

where the ψ functions are a linear combination of product functions, ϕ_i , that is,

$$\psi_j = \sum_j \phi_j ; \quad \psi_k = \sum_k \phi_k \quad (78)$$

For the d^2 or d^8 configuration, the "basic" product function, ϕ_i , is a product of two one-electron functions, that is,

$$\phi_i = |l, m\rangle^{(1)} |l', m'\rangle^{(2)} \quad (79)$$

where (1) and (2) refer to electrons one and two. Thus

$$H_{jk} = \int \sum_j \phi_j^* v^{LF} \sum_k \phi_k d\tau = \sum_j \sum_k \int \phi_j^* v^{LF} \phi_k d\tau \quad (80)$$

The two electron integral, $\int \phi_j^* v^{LF} \phi_k d\tau$, may be simplified to a sum of one-electron integrals. For example, consider the integral

$$\int [\ell_a^{m_a}(1) \ell_b^{m_b}(2)]^* v^{LF} [\ell_c^{m_c}(1) \ell_d^{m_d}(2)] d\tau$$

where $v^{LF} = v^{LF}(1) + v^{LF}(2)$.

Then the above integral may be written as:

$$\begin{aligned} & \int |\ell_a^{m_a}\rangle^* v^{LF} |\ell_c^{m_c}\rangle d\tau_1 \int |\ell_b^{m_b}\rangle |\ell_d^{m_d}\rangle d\tau_2 \\ & + \int |\ell_b^{m_b}\rangle^* v^{LF} |\ell_d^{m_d}\rangle d\tau_2 \int |\ell_a^{m_a}\rangle^* |\ell_c^{m_c}\rangle d\tau_1 \end{aligned}$$

This total process may be illustrated by a simple example.

Consider the matrix element,

$$H_{11} = \int \psi_1^* v^{LF} \psi_1 d\tau \quad (81)$$

where ψ_1 is a linear combination of a product of two one-electron functions, such as,

$$\begin{aligned} \psi_1 = 1/\sqrt{2} [& |2,2\rangle^{(1)} |2,2\rangle^{(2)} \\ & + |2,-2\rangle^{(1)} |2,-2\rangle^{(2)}] \end{aligned} \quad (82)$$

Then one obtains the matrix element:

$$H_{11} = \int \psi_1^* V \psi_1 d\tau \quad (83)$$

$$= \int \psi_1^* (V(1) + V(2)) \psi_1 d\tau \quad (84)$$

$$= \frac{1}{2} \int [|2,2\rangle^{(1)} |2,2\rangle^{(2)} + |2,-2\rangle^{(1)} |2,-2\rangle^{(2)}]^* (V(1) + V(2)) [|2,2\rangle^{(1)} |2,2\rangle^{(2)} + |2,-2\rangle^{(1)} |2,-2\rangle^{(2)}] d\tau_1 d\tau_2 \quad (85)$$

$$= \frac{1}{2} \int [|2,2\rangle^{*(1)} |2,2\rangle^{*(2)}] V(1) + V(2) [|2,2\rangle^{(1)} |2,2\rangle^{(2)}] d\tau_1 d\tau_2 \\ + \int [|2,2\rangle^{*(1)} |2,2\rangle^{*(2)}] V(1)+V(2) [|2,-2\rangle^{(1)} |2,-2\rangle^{(2)}] d\tau_1 d\tau_2 \\ + \int [|2,-2\rangle^{*(1)} |2,-2\rangle^{*(2)}] V(1)+V(2) [|2,2\rangle^{(1)} |2,2\rangle^{(2)}] d\tau_1 d\tau_2 \\ + \int [|2,-2\rangle^{*(1)} |2,-2\rangle^{*(2)}] V(1)+V(2) [|2,-2\rangle^{(1)} |2,-2\rangle^{(2)}] d\tau_1 d\tau_2 \quad (86)$$

For the first term:

$$\int [|2,2\rangle^{*(1)} |2,2\rangle^{*(2)}] V(1)+V(2) [|2,2\rangle^{(1)} |2,2\rangle^{(2)}] d\tau_1 d\tau_2 = \\ \int |2,2\rangle^{*(1)} V(1) |2,2\rangle^{(1)} d\tau_1 \int |2,2\rangle^{*(2)} |2,2\rangle^{(2)} d\tau_2 \\ + \int |2,2\rangle^{*(2)} V(2) |2,2\rangle^{(2)} d\tau_2 \int |2,2\rangle^{*(1)} |2,2\rangle^{(1)} d\tau_1 \quad (87) \\ = \int |2,2\rangle^{*(1)} V(1) |2,2\rangle^{(1)} d\tau_1 + \int |2,2\rangle^{*(2)} V(2) |2,2\rangle^{(2)} d\tau_2$$

where N is the normalization factor, $R_m(r)$ is the radial part, and $Y(l,m)$, the angular part in terms of the spherical harmonics.

In some applications of ligand field theory (4, 23, 26) the radial parts of the zero order basis functions remain unspecified when dealing with both the ligand field and the electronic interaction effects. It has been decided that in this thesis, the same procedure will be followed in regard to the electronic interaction. However, for the ligand field effect, it is convenient to follow the examples of Ballhausen (27) and Maki (28, 29) and to express the single electron wave functions in terms of Slater orbitals (30). These orbitals can be expressed as:

$$|n,l,m\rangle = N \cdot r^{(n^*-1)} \cdot e^{-Z^*r/n^*a_0} \cdot Y(l,m) \quad (90)$$

where: N is the normalization constant for the radial portion

$Y(l,m)$ are the spherical harmonics

n^* is the effective principal quantum number

a_0 is the Bohr radius equal to one atomic unit

Z^* is the effective nuclear charge.

For the (5d) orbitals of the platinum(II) complexes, $n^* = 4$ and $Z^* = 7.55$. If one defines $f = Z^*/n^*$, then $f = 1.8875$. Normalization of the wave function, as shown in Appendix B, yields:

$$|5,2,m\rangle = \left[\frac{2^9 f^9}{8!} \right]^{1/2} r^3 \cdot e^{-fr} \cdot Y(2,m) \quad (91)$$

Since this thesis deals only with the 5d orbitals, it is

Similarly, for the last term one obtains:

$$\int |2,-2\rangle^{*(1)} v(1) |2,-2\rangle^{(1)} d\tau_1 + \int |2,-2\rangle^{*(2)} v(2) |2,-2\rangle^{(2)} d\tau_2$$

while for the middle two terms, one obtains such expressions as:

$$\int |2,2\rangle^{(1)} v(1) |2,-2\rangle^{(1)} d\tau_1 \underbrace{\int |2,2\rangle^{(2)} |2,-2\rangle^{(2)} d\tau_2}_0 = 0.$$

Hence:

$$\begin{aligned} H_{11} = \frac{1}{2} [& \int |2,2\rangle^{*(1)} v(1) |2,2\rangle^{(1)} d\tau_1 \\ & + \int |2,2\rangle^{*(2)} v(2) |2,2\rangle^{(2)} d\tau_2 \\ & + \int |2,-2\rangle^{*(1)} v(1) |2,-2\rangle^{(1)} d\tau_1 \\ & + \int |2,-2\rangle^{*(2)} v(2) |2,-2\rangle^{(2)} d\tau_2] \end{aligned} \quad (88)$$

Thus, the initial matrix element is reduced to the sum of one electron integrals.

2. The single electron functions

The zero order basis functions, ϕ_i , are products of single electron wave functions. A single electron function can be expressed as a product of a radial part and an angular part. That is, a single electron function has the form:

$$\psi_{n,l,m} = N \cdot R_m(r) \cdot Y(l,m) \quad (89)$$

convenient to symbolize the single electron wave function as $|l, m\rangle$. Furthermore, in the case of a product of two one-electron functions, $|l, m\rangle^{(1)} |l', m'\rangle^{(2)}$, since $l = 2$ for both, it is convenient to write this product as (m, m') where the first value in the parenthesis refers to electron one and the second to electron two.

3. One electron integrals

From the discussion in section IV-C-3, it is apparent that a matrix element involving the ligand field resolves into a sum of one-electron matrix elements of the form:

$$\int |l_a m_a\rangle^* V^{LF} |l_b m_b\rangle d\tau$$

Upon substitution of the functions:

$$|l_a m_a\rangle = N \cdot R_a(r) \cdot Y(l_a m_a)$$

$$|l_b m_b\rangle = N \cdot R_b(r) \cdot Y(l_b m_b),$$

as given by equation 91, and the potential, V^{LF} , as given by Equation 66, one obtains,

$$\int |l_a m_a\rangle^* V^{LF} |l_b m_b\rangle d\tau = \sum_{l, m} D_{lm} \cdot G_l(a, b) \cdot J_{lm}(l_a m_a l_b m_b) \quad (92)$$

where $J_{lm}(l_a m_a l_b m_b)$ = the angular integral =

$$\int Y^*(l_a m_a) Y(l_b m_b) Y(l m) d\tau \quad (93)$$

$G_l(a, b)$ = the radial integral =

$$-qN^2 \int R_a(r) \cdot R_b(r) \cdot R_l(r) \cdot d\tau_r \quad (94)$$

D_{lm} = ligand field coefficients, see Equation 73.

a. The angular integral, $J_{lm}(\ell_a m_a \ell_b m_b) = J_{lm}$ In or-

der to evaluate the angular integral, recourse is made to the fact that the product of two spherical harmonics can be expanded in terms of a sum of spherical harmonics. Thus:

$$Y^*(\ell_a m_a) Y(\ell_b m_b) = \sum_{\ell', m'} K_{\ell', m'} \cdot Y^*(\ell', m')$$

and the angular integral becomes:

$$\int Y^*(\ell_a m_a) \cdot Y(\ell_b m_b) \cdot Y(\ell m) d\tau_{\theta\phi} = \sum_{\ell', m'} K_{\ell', m'} \int Y^*(\ell', m') \cdot Y(\ell m) d\tau_{\theta\phi} \quad (96)$$

Because of the orthogonality relations of the spherical harmonics, the integrals on the right hand side vanish unless $\ell = \ell'$ and $m = m'$. Hence the angular integral, $J_{lm}(\ell_a m_a \ell_b m_b)$, is seen to be identical with the expansion coefficient, $K_{\ell m}$, of Equation 95.

A procedure for determination of these coefficients is given in Section 4.6 of the text by Edmonds (31) and is discussed in detail in Appendix B-2. In particular, it is found that:

$$\ell_a + \ell_b \geq \ell$$

$$K_{\ell m} = 0, \text{ unless } m_a + m_b = m$$

$$\ell_a + \ell_b + \ell = \text{even}$$

Since $l_a = l_b = 2$ for d-electrons, and since it was previously established that $m = 0, \pm 4$, the only terms needed in the expansion of v^{LF} are those with $l = 0, 2, 4$, as in the formula for the effective potential given by Equation 76. Furthermore, explicit application of these same restrictions shows that the single electron integrals given in Table 4 are the only ones which are different from zero.

Therefore, there are only seven products of spherical harmonics that need be evaluated by the techniques given in Appendix B-2. The expansions for these seven are given in Table 5. Actually, the harmonic, $Y(0,0)$, and its coefficient, appearing in this table are not needed for reasons discussed in section IV-B.

Evaluation of the non-zero single electron integrals, given in Table 4, by means of equations 92, 76, and the values in Table 5, leads to the results:

$$Q_0 = \int |2, \pm 2\rangle^* v^{LF} |2, \pm 2\rangle d\tau = -\frac{4}{7} G_2(a, b) + \frac{3}{7} G_4(a, b). \quad (97)$$

$$Q_1 = \int |2, \pm 1\rangle^* v^{LF} |2, \pm 1\rangle d\tau = -\frac{2}{7} G_2(a, b) - \frac{2}{7} G_4(a, b). \quad (98)$$

$$Q_2 = \int |2, 0\rangle^* v^{LF} |2, 0\rangle d\tau = \frac{4}{7} G_2(a, b) + \frac{1}{14} G_4(a, b). \quad (99)$$

$$B_{2, -2} = \int |2, \pm 2\rangle^* v^{LF} |2, \mp 2\rangle d\tau = \frac{5}{6} G_4(a, b). \quad (100)$$

It is seen that only two radial integrals, $G_2(a, b)$ and $G_4(a, b)$ need be evaluated.

Table 4. Allowed values of m and l for non-zero single electron matrix elements

Allowed values of m			l values required in expansion		Integral	Designation
m_a	m_b	m				
0	0	0	0,	2, 4	$ 2,0\rangle^* v^{LF} 2,0\rangle d\tau$	Q_0
± 1	± 1	0	0,	2, 4	$ 2,\pm 1\rangle^* v^{LF} 2,\pm 1\rangle d\tau$	Q_1
± 2	± 2	0	0,	2, 4	$ 2,\pm 2\rangle^* v^{LF} 2,\pm 2\rangle d\tau$	Q_2
± 2	∓ 2	± 4		4	$ 2,\pm 2\rangle^* v^{LF} 2,\mp 2\rangle d\tau$	$B_{2,-2}$

Table 5. Expansion of products of spherical harmonics

Product	Expansion
$Y^*(2,2)Y(2,2) = Y^*(2,-2)Y(2,-2)$	$\frac{1}{14\sqrt{\pi}} Y^*(4,0) - \frac{\sqrt{5}}{7\sqrt{\pi}} Y^*(2,0)$ $+ \frac{1}{2\sqrt{\pi}} Y^*(0,0)$
$Y^*(2,1)Y(2,1) = Y^*(2,-1)Y(2,-1)$	$-\frac{2}{7\sqrt{\pi}} Y^*(4,0) + \frac{\sqrt{5}}{14\sqrt{\pi}} Y^*(2,0)$ $+ \frac{1}{2\sqrt{\pi}} Y^*(0,0)$
$Y^*(2,0)Y(2,0) =$	$\frac{3}{7\sqrt{\pi}} Y^*(4,0) + \frac{\sqrt{5}}{7\sqrt{\pi}} Y^*(2,0)$ $+ \frac{1}{2\sqrt{\pi}} Y^*(0,0)$
$Y^*(2,2)Y(2,-2)$	$\frac{\sqrt{5}}{\sqrt{14\pi}} Y^*(4,-4)$
$Y^*(2,-2)Y(2,2)$	$\frac{\sqrt{5}}{\sqrt{14\pi}} Y^*(4,4)$

b. The radial integrals, $G_l(a,b)$ and $B_l(a,b)$ Explicit-

it forms for the radial integrals, $G_l(a,b)$ are obtained by substitution of the radial parts, $NR_a(r)$ and $NR_b(r)$, from Equation 91 into the definition given by Equation 94. Such substitution yields:

$$G_l(a,b) = -q \frac{2^9 f^9}{8!} \int_0^\infty (r^3 e^{-fr}) (r^3 e^{-fr}) (r \langle \frac{1}{r} \rangle^{l+1}) r^2 dr \quad (101)$$

As indicated above, the only values of l which need be considered are $l = 2$ and $l = 4$. These integrals are most easily evaluated by a change of variable from r to x , where $x = fr$. It is thus possible to define two integrals, $G_2(X)$ and $G_4(X)$, such that:

$$G_l(a,b) = \frac{-qf}{78.75} \cdot G_2(X) \quad (102)$$

$$G_l(a,b) = \frac{-qf}{78.75} \cdot G_4(X) \quad (103)$$

The techniques for evaluating these integrals are outlined in Appendix B-3. The resultant expressions, given in Table 6, are in terms of $X = fR$, where R is the "effective radial distance", in atomic units, from the charge q to the electron.

In this thesis, the ligands are considered as point dipoles and not point charges. If one specifies that the dipoles are oriented such that the negative ends are directed toward the central ion, as shown in Appendix B-3, one must substitute $-B_l(a,b)$ for $G_l(a,b)$ in equations 97-100, where:

Table 6. Radial integrals for point charges and point dipoles

Point charge integrals	
$G_2(X)$	$= \frac{1}{X^3} [1771.875 - e^{-2X}(1.25X^9 + 8.75X^8 + 41.25X^7$ $+ 470.625X^5 + 153.75X^6 + 1181.25X^4 + 2362.5X^3$ $+ 3543.75X^2 + 3543.75X + 1171.875)]$
$G_4(X)$	$= \frac{1}{X^5} [58471.75 - e^{-2X}(2.25X^{11} + 15.75X^{10} + 82.125X^9$ $+ 371.25X^8 + 1485X^7 + 5197.5X^6 + 15592.5X^5$ $+ 38981.25X^4 + 77962.5X^3 + 116943.75X^2$ $+ 116943.75X + 58471.875)]$
Point dipole integrals	
$B_2(X)$	$= \frac{1}{X^4} [-5315.625 + (e^{-2X})(25X^{10} + 10X^9 + 38.75X^8$ $+ 142.5X^7 + 480X^6 + 1421.25X^5 + 3543.75X^4$ $+ 7087.5X^3 + 10631.25X^2 + 10631.25X + 5315.625)]$
$B_4(X)$	$= \frac{1}{X^6} [-292359.75 + (e^{-2X})(4.5X^{12} + 18X^{11} + 85.5X^{10}$ $+ 414X^9 + 1856.25X^8 + 7425X^7 + 25987.5X^6$ $+ 77926.5X^5 + 194906.25X^4 + 389812.5X^3$ $+ 584718.75X^2 + 584718.75X + 292359.75)]$

$$-B_l(a,b) = \frac{-\mu f^2}{78.75} \cdot B_l(X) = \frac{-\mu f^2}{78.75} \cdot \frac{d}{dX} G_l(X) \quad (104)$$

with $X = fR$ and R is the "effective radial distance", and μ is the "effective dipole moment". The expressions for $B_2(X)$ and $B_4(X)$ are given in Table 6.

Since this thesis concerns the d^8 configuration, it is the potential with respect to "electron holes" that are of interest. Therefore, the sign of the potential changes and one must now substitute $+B_l(a,b)$ for $G_l(a,b)$ in Equations 97-100, where

$$B_l(a,b) = \frac{\mu f^2}{78.75} \cdot B_l(X), \quad (105)$$

with

$$B_l(X) = \frac{d}{dX} G_l(X).$$

From Equations 97-100, the non-zero single-electron integrals for the d^8 configuration in point dipole square-planar symmetry are given in Table 7. From this table, it is seen that the integrals are functions of two parameters; the effective dipole moment, μ , and $X = fR = 1.8875R$, where R is the effective radial distance.

Table 7. The non-zero single electron matrix elements^a

Designation	Integral	Matrix element
Q_0	$\int 2,0\rangle^* V^{LF} 2,0\rangle d\tau \frac{uf^2}{78.75}$	$[\frac{3}{7} B_4(X) - \frac{4}{7} B_2(X)]$
Q_1	$\int 2,\pm 1\rangle^* V^{LF} 2,\pm 1\rangle d\tau \frac{uf^2}{78.75}$	$[-\frac{2}{7} B_4(X) - \frac{2}{7} B_2(X)]$
Q_2	$\int 2,\pm 2\rangle^* V^{LF} 2,\pm 2\rangle d\tau \frac{uf^2}{78.75}$	$[\frac{1}{14} B_4(X) + \frac{4}{7} B_2(X)]$
$B_{2,-2}$	$\int 2,\pm 2\rangle^* V^{LF} 2,\mp 2\rangle d\tau \frac{uf^2}{78.75}$	$[\frac{5}{6} B_4(X)]$

^aThese integrals are for the d^8 configuration for point dipoles whose negative ends are directed toward the central ion.

V. SYMMETRY ADAPTED FUNCTIONS AND THE MATRIX ELEMENTS FOR SQUARE-PLANAR SYMMETRY

A. Weak Field Functions

1. Wave functions of the free ion

As has been indicated, in the weak field case the basis functions are constructed in terms of the quantum numbers S, L, J, M_J from the antisymmetric products of the single electron functions. Prior to consideration of the ligand field potential, the derivation of the wave functions follows the techniques for the wave functions of the free ion. For a d^2 or d^8 system the possible states are, 1G_4 , 3F_4 , 3F_3 , 3F_2 , 1D_2 , 3P_2 , 3P_1 , 3P_0 , and 1S_0 . The methods for deriving these states and the wave functions associated with them are given in Appendix A. The wave functions for the states are given in Table 8. As is seen from the table, the degeneracy of each J-state is $2J + 1$.

2. Wave functions for ion in the ligand field

If the wave functions of the free ion were used directly as basis functions for the ligand field problem, a single 45 by 45 matrix would result. It has been shown by group theory that placement of the free ion in the potential of the ligand field removes the $2J + 1$ degeneracy of the states. Furthermore, it was indicated that the irreducible representations

Table 8. d^2 free ion wave functions

$2S+1$ $L_J(M_J)$ function	Two-electron product function
${}^1G_4:$	
${}^1G_4(4) = \frac{1}{\sqrt{2}} [(2,2)][\alpha\beta-\beta\alpha]$	
${}^1G_4(3) = \frac{1}{2} [(1,2)+(2,1)][\alpha\beta-\beta\alpha]$	
${}^1G_4(2) = \frac{1}{\sqrt{28}} [\sqrt{3}(2,0)+\sqrt{8}(1,1)+\sqrt{3}(0,2)][\alpha\beta-\beta\alpha]$	
${}^1G_4(1) = \frac{1}{\sqrt{28}} [(2,-1)+\sqrt{6}(1,0)+\sqrt{6}(0,1)+(-1,2)][\alpha\beta-\beta\alpha]$	
${}^1G_4(0) = \frac{1}{2\sqrt{35}} [(2,-2)+4(1,-1)+6(0,0)+4(-1,1)+(-2,2)][\alpha\beta-\beta\alpha]$	
${}^1G_4(-1) = \frac{1}{\sqrt{28}} [(1,-2)+\sqrt{6}(0,0)+\sqrt{6}(-1,0)+(-2,1)][\alpha\beta-\beta\alpha]$	
${}^1G_4(-2) = \frac{1}{\sqrt{28}} [\sqrt{3}(-2,0)+\sqrt{8}(-1,-1)+\sqrt{3}(0,-2)][\alpha\beta-\beta\alpha]$	
${}^1G_4(-3) = \frac{1}{2} [(-2,-1)+(-1,-2)][\alpha\beta-\beta\alpha]$	
${}^1G_4(-4) = \frac{1}{\sqrt{2}} [(-2,-2)][\alpha\beta-\beta\alpha]$	
${}^1D_2:$	
${}^1D_2(2) = \frac{1}{\sqrt{14}} [\sqrt{2}(2,0)-\sqrt{3}(1,1)+\sqrt{2}(0,2)][\alpha\beta-\beta\alpha]$	
${}^1D_2(1) = \frac{1}{\sqrt{28}} [\sqrt{6}(2,-1)-(1,0)-(0,1)+\sqrt{6}(-1,2)][\alpha\beta-\beta\alpha]$	
${}^1D_2(0) = \frac{1}{\sqrt{28}} [2(2,-2)+(1,-1)-2(0,0)+(-1,1)+2(-2,2)][\alpha\beta-\beta\alpha]$	
${}^1D_2(-1) = \frac{1}{\sqrt{28}} [\sqrt{6}(-2,1)-(-1,0)-(0,0)+\sqrt{6}(1,-2)][\alpha\beta-\beta\alpha]$	
${}^1D_2(-2) = \frac{1}{\sqrt{14}} [\sqrt{2}(-2,0)-\sqrt{3}(-1,-1)+\sqrt{2}(0,-2)][\alpha\beta-\beta\alpha]$	

Table 8. (Continued)

$2S+1L_J(M_J)$ function	Two-electron product function
<u>$1S_0$:</u>	
$1S_0(0)$	$= \frac{1}{\sqrt{10}} [(2,-2)-(1,-1)+(0,0)-(-1,1)+(-2,2)][\alpha\beta-\beta\alpha]$
<u>$3F_4$:</u>	
$3F_4(4)$	$= \frac{1}{\sqrt{2}} [(2,1)-(1,2)][\alpha\alpha]$
$3F_4(3)$	$= \sqrt{\frac{3}{8}} [(2,0)-(0,2)][\alpha\alpha] + \frac{1}{4} [(2,1)-(1,2)][\alpha\beta+\beta\alpha]$
$3F_4(2)$	$= \sqrt{\frac{3}{56}} [\sqrt{3}(2,-1)-\sqrt{2}(0,1)+\sqrt{2}(1,0)-\sqrt{3}(-1,2)][\alpha\alpha]$ $+ \sqrt{\frac{3}{28}} [(2,0)-(0,2)][\alpha\beta+\beta\alpha] + \frac{1}{2\sqrt{14}} [(2,1)-(1,2)][\beta\beta]$
$3F_4(1)$	$= \frac{1}{\sqrt{28}} [(2,-2)+2(1,-1)-2(-1,1)-(-2,2)][\alpha\alpha]$ $+ \frac{1}{\sqrt{112}} [3(2,-1)+\sqrt{6}(1,0)-\sqrt{6}(0,1)-3(-1,2)][\alpha\beta+\beta\alpha]$ $+ \frac{\sqrt{3}}{\sqrt{56}} [(2,0)-(0,2)][\beta\beta]$
$3F_4(0)$	$= \frac{1}{\sqrt{140}} [3(1,-2)+\sqrt{6}(0,0)-\sqrt{6}(-1,0)-3(-2,1)][\alpha\alpha]$ $+ \frac{1}{\sqrt{35}} [(2,-2)+2(1,-1)-2(-1,1)-(-2,2)][\alpha\beta+\beta\alpha]$ $+ \frac{1}{\sqrt{140}} [3(2,-1)+\sqrt{6}(1,0)-\sqrt{6}(0,1)-3(-1,2)][\beta\beta]$

Table 8. (Continued)

$2S+1L_J(M_J)$ function	Two-electron product function
${}^3F_4(-1)$	$= \sqrt{\frac{3}{56}} [(0,-2) - (-2,0)] [\alpha\alpha]$ $+ \frac{1}{\sqrt{112}} [3(1,-2) + \sqrt{6}(0,01) - \sqrt{6}(-1,0) - 3(-2,1)] [\alpha\beta + \beta\alpha]$ $+ \frac{1}{\sqrt{28}} [(2,-2) + 2(1,-1) - 2(-1,1) - (-2,2)] [\beta\beta]$
${}^3F_4(-2)$	$= \frac{1}{\sqrt{56}} [(-1,-2) - (-2,-1)] [\alpha\alpha]$ $+ \frac{\sqrt{3}}{\sqrt{28}} [(0,-2) - (-2,0)] [\alpha\beta + \beta\alpha]$ $+ \frac{\sqrt{3}}{\sqrt{56}} [\sqrt{3}(1,-2) + \sqrt{2}(0,-1) - \sqrt{2}(-1,0) -$ $\sqrt{3}(-2,1)] [\beta\beta]$
${}^3F_4(-3)$	$= \frac{1}{4} [(-1,-2) - (-2,-1)] [\alpha\beta + \beta\alpha] + \frac{\sqrt{3}}{\sqrt{8}} [(0,-2) - (-2,0)] [\beta\beta]$
${}^3F_4(-4)$	$= \frac{1}{\sqrt{2}} [(-1,-2) - (-2,-1)] [\beta\beta]$
${}^3F_3:$	
${}^3F_3(3)$	$= \frac{1}{\sqrt{8}} [(2,0) - (0,2)] [\alpha\alpha] + \frac{\sqrt{3}}{4} [(1,2) - (2,1)] [\alpha\beta + \beta\alpha]$
${}^3F_3(2)$	$= \frac{1}{\sqrt{24}} [\sqrt{3}(2,-1) + \sqrt{2}(1,0) - \sqrt{2}(0,1) - \sqrt{3}(-1,2)] [\alpha\alpha]$ $+ \frac{1}{\sqrt{12}} [(0,2) - (2,0)] [\alpha\beta + \beta\alpha] + \frac{1}{\sqrt{8}} [(1,2) - (2,1)] [\beta\beta]$

Table 8. (Continued)

$2S+1$ function	$L_J(M_J)$ Two-electron product function
${}^3F_3(1)$	$= \frac{1}{\sqrt{20}} [(2,-2)+2(1,-1)-2(-1,1)-(-2,2)][\alpha\alpha]$ $+ \frac{1}{\sqrt{240}} [\sqrt{3}(-1,2)+\sqrt{2}(0,1)-\sqrt{2}(1,0)-\sqrt{3}(2,-1)]$ $[\alpha\beta+\beta\alpha] + \frac{\sqrt{5}}{\sqrt{24}} [(0,2)-(2,0)][\beta\beta]$
${}^3F_3(0)$	$= \frac{1}{\sqrt{20}} [\sqrt{3}(1,-2)+\sqrt{2}(0,0)-\sqrt{2}(-1,0)-\sqrt{3}(2,1)][\alpha\alpha]$ $+ \frac{1}{\sqrt{20}} [\sqrt{3}(-1,2)+\sqrt{2}(0,1)-\sqrt{2}(1,0)-\sqrt{3}(2,-1)][\beta\beta]$
${}^3F_3(-1)$	$= \frac{\sqrt{5}}{\sqrt{24}} [(0,-2)-(-2,0)]\alpha\alpha$ $+ \frac{1}{\sqrt{240}} [\sqrt{3}(1,-2)+\sqrt{2}(0,0)-\sqrt{2}(-1,0)-\sqrt{3}(-2,1)]$ $[\alpha\beta+\beta\alpha] + \frac{1}{\sqrt{20}} [(-2,2)+2(-1,1)-2(1,-1)-(-2,-2)][\beta\beta]$
${}^3F_3(-2)$	$= \frac{1}{\sqrt{8}} [(-1,-2)-(-2,-1)][\alpha\alpha] + \frac{1}{\sqrt{12}} [(0,-2)-(-2,0)][\alpha\beta+\beta\alpha]$ $+ \frac{1}{\sqrt{24}} [\sqrt{3}(-2,1)+\sqrt{2}(0,0)-\sqrt{3}(1,-2)][\beta\beta]$
${}^3F_3(-3)$	$= \frac{\sqrt{3}}{4} [(-1,-2)-(-2,-1)][\alpha\beta+\beta\alpha] + \frac{1}{\sqrt{8}} [(-2,0)-(0,-2)][\beta\beta]$
${}^3F_2:$	
${}^3F_2(2)$	$= \frac{1}{\sqrt{210}} [\sqrt{3}(2,-1)+\sqrt{2}(1,0)-\sqrt{2}(0,1)-\sqrt{3}(-1,2)][\alpha\alpha]$

Table 8. (Continued)

$2S+1$ $L_J(M_J)$ function	Two-electron product function
${}^3F_2(2)$ (Continued)	
	$+ \frac{\sqrt{5}}{\sqrt{84}} [(0,2) - (2,0)] [\alpha\beta + \beta\alpha]$
	$+ \frac{\sqrt{5}}{\sqrt{14}} [(2,1) - (1,2)] [\beta\beta]$
${}^3F_2(1)$	$= \frac{1}{\sqrt{70}} [(2,-2) + 2(1,-1) - 2(-1,1) - (-2,2)] [\alpha\alpha]$
	$+ \frac{1}{\sqrt{105}} [\sqrt{6} (-1,2) + 2(0,1) - 2(1,0) - \sqrt{6}(2,-1)] [\alpha\beta + \beta\alpha]$
	$+ \frac{\sqrt{5}}{\sqrt{21}} [(2,0) - (0,2)] [\beta\beta]$
${}^3F_2(0)$	$= \frac{1}{\sqrt{70}} [\sqrt{6} (1,-2) + 2(0,-1) - 2(-1,0) - \sqrt{6}(-2,1)] [\alpha\alpha]$
	$+ \frac{\sqrt{3}}{\sqrt{140}} [(-2,2) + 2(-1,1) - 2(1,-1) - (2,-2)] [\alpha\beta + \beta\alpha]$
	$+ \frac{\sqrt{3}}{\sqrt{105}} [\sqrt{3} (2,-1) + \sqrt{2}(1,0) - \sqrt{2}(0,1) - \sqrt{3}(-1,2)] [\beta\beta]$
${}^3F_2(-1)$	$= \frac{\sqrt{5}}{\sqrt{21}} [(0,-2) - (-2,0)] [\alpha\alpha]$
	$+ \frac{1}{\sqrt{105}} [\sqrt{6} (-2,1) + 2(-1,0) - 2(0,-1) - \sqrt{6}(1,-2)] [\alpha\beta + \beta\alpha]$

Table B. (Continued)

$2S+1$ $L_J(M_J)$ function	Two-electron product function
${}^3F_2(-2)$	$= \frac{\sqrt{5}}{\sqrt{14}} [(-1, -2) - (-2, -1)] [\alpha\alpha]$ $+ \frac{\sqrt{5}}{\sqrt{84}} [(-2, 0) - (0, -2)] [\alpha\beta + \beta\alpha]$ $+ \frac{1}{\sqrt{210}} [\sqrt{3}(1, -2) + \sqrt{2}(0, -1) - \sqrt{2}(-1, 0) - \sqrt{3}(-2, 1)] [\beta\beta]$
3P_2	
${}^3P_2(2)$	$= \frac{1}{\sqrt{10}} [\sqrt{2}(2, -1) + \sqrt{3}(0, 1) - \sqrt{3}(1, 0) - \sqrt{2}(-1, 2)] [\alpha\alpha]$
${}^3P_2(1)$	$= \frac{1}{\sqrt{20}} [2(2, -2) + (-1, 1) - (1, -1) - 2(-2, 2)] [\alpha\alpha]$ $+ \frac{1}{\sqrt{40}} [\sqrt{2}(2, -1) + \sqrt{3}(0, 1) - \sqrt{3}(1, 0) - \sqrt{2}(-1, 2)] [\alpha\beta + \beta\alpha]$
${}^3P_2(0)$	$= \frac{1}{\sqrt{60}} [\sqrt{2}(1, -2) + \sqrt{3}(-1, 0) - \sqrt{3}(0, -1) - \sqrt{2}(-2, 1)] [\alpha\alpha]$ $+ \frac{1}{\sqrt{30}} [2(2, -2) + (-1, 1) - (1, -1) - 2(-2, 2)] [\alpha\beta + \beta\alpha]$ $+ \frac{1}{\sqrt{60}} [\sqrt{2}(2, -1) + \sqrt{3}(1, 0) - \sqrt{2}(-1, 2)] [\beta\beta]$
${}^3P_2(-1)$	$= \frac{1}{\sqrt{40}} [\sqrt{2}(1, -2) + \sqrt{3}(-1, 0) - \sqrt{3}(0, -1) - \sqrt{2}(-2, 1)] [\alpha\beta + \beta\alpha]$ $+ \frac{1}{\sqrt{20}} [2(2, -2) + (-1, 1) - (1, -1) - 2(-2, 2)] [\beta\beta]$

Table 2. (Continued)

$2S+1_{LJ}(M_J)$ function	Two-electron product function
$^3P_2(-2)$	$= \frac{1}{\sqrt{10}} [\sqrt{2}(1,-2) + \sqrt{3}(-1,0) - \sqrt{3}(0,-1) - \sqrt{2}(-2,1)] [\beta\beta]$
$^3P_1:$	
$^3P_1(1)$	$= \frac{1}{\sqrt{20}} [2(2,-2) + (-1,1) - (1,-1) - 2(-2,2)] [\alpha\alpha]$ $+ \frac{1}{\sqrt{40}} [\sqrt{2}(-1,2) + \sqrt{3}(1,0) - \sqrt{3}(0,1) - \sqrt{2}(2,-1)] [\alpha\beta + \beta\alpha]$
$^3P_1(0)$	$= \frac{1}{\sqrt{20}} [\sqrt{2}(1,-2) + \sqrt{3}(-1,0) - \sqrt{3}(0,-1) - \sqrt{2}(-2,1)] [\alpha\alpha]$ $+ \frac{1}{\sqrt{20}} [\sqrt{2}(-1,2) + \sqrt{3}(1,0) - \sqrt{3}(0,1) - \sqrt{2}(2,-1)] [\beta\beta]$
$^3P_1(-1)$	$= \frac{1}{\sqrt{40}} [\sqrt{2}(1,-2) + \sqrt{3}(-1,0) - \sqrt{3}(0,-1) + \sqrt{2}(-2,1)] [\alpha\beta + \beta\alpha]$ $+ \frac{1}{\sqrt{20}} [2(-2,2) + (1,-1) - (-1,1) - 2(2,-2)] [\beta\beta]$
$^3P_0:$	
$^3P_0(0)$	$= \frac{1}{\sqrt{30}} [\sqrt{2}(1,-2) + \sqrt{3}(-1,0) - \sqrt{3}(0,-1) - \sqrt{2}(-2,1)] [\alpha\alpha]$ $+ \frac{1}{\sqrt{60}} [2(-2,2) + (1,-1) - (-1,1) - 2(2,-2)] [\alpha\beta + \beta\alpha]$ $+ \frac{1}{\sqrt{30}} [\sqrt{2}(2,-1) + \sqrt{3}(0,1) - \sqrt{3}(1,0) - \sqrt{2}(-1,2)] [\beta\beta]$

one considers the spherical harmonics in terms of cartesian coordinates and takes such linear combinations of them as to obtain elements which transform according to the irreducible representations of the group. Then the combinations of the $|S, L, J, M_J\rangle$ functions which correspond to those spherical harmonics will be basis functions for the same irreducible representations.

There are five irreducible representations of the rotation group D_4 . Hence, by suitable choice of the wave functions, the single large matrix can be reduced to five smaller matrices. The five irreducible representations are: $\Gamma_1 = A_1$; $\Gamma_2 = A_2$; $\Gamma_3 = B_1$; $\Gamma_4 = B_2$; and $\Gamma_5 = E$, where the notation follows that of Bethe(1) and the A,B,E, notation follows that of Mulliken (2). The Γ_5 or E irreducible representation is doubly degenerate; the other four are non-degenerate.

As shown in the section on group theory, the $2J + 1$ degenerate representations can be reduced to their irreducible representations by means of Table 3. The irreducible representations for the various J values of interest are given in Table 9. Thus, for example, linear combinations of the wave functions associated with the state 1D_2 , with $J = 2$, can be made such that one combination is the basis function for Γ_1 , another combination transforms according to Γ_3 , another according to Γ_4 , and the remaining pair are basis functions

into which the states are reduced can be determined from the characters of the reducible $2J + 1$ representation. And finally, if ψ_A and ψ_B are basis functions for irreducible representations, since the ligand potential, V , must belong to the irreducible representation A_1 , the matrix element

$\int \psi_A^* V \psi_B d\tau = 0$ unless $\Gamma_A = \Gamma_B$, that is, unless ψ_A and ψ_B are basis functions for the same irreducible representation.

Thus, it is possible to reduce the size of the matrix which needs to be diagonalized by taking such linear combinations of the $2J + 1$ functions associated with each J -state so that the combinations form basis functions for the irreducible representations of the group. Such functions are frequently termed "symmetry adapted" functions. The functions given in Table 8 are, in general, not symmetry adapted.

3. Construction of symmetry adapted functions

There are several ways of obtaining the proper linear combinations for symmetry adapted functions (32, 33). Appendix C shows that a convenient approach is to consider the $|S, L, J, M_J\rangle$ functions as having an angular dependence which corresponds to a spherical harmonic $Y(J, M_J)$. That is, the appropriate linear combination of $|S, L, J, M_J\rangle$ functions required to form a basis function for an irreducible representation corresponds to that combination of spherical harmonics, $Y(J, M_J)$, which form a basis for the irreducible representation. Hence,

Table 9. Irreducible representations of the J-states in D_4

J-value	Irreducible representations	
	Bethe notation	Mulliken notation
$J = 0$	Γ_1	A_1
$J = 1$	$\Gamma_2 + \Gamma_5$	$A_2 + E$
$J = 2$	$\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$	$A_1 + B_1 + B_2 + E$
$J = 3$	$\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5 + \Gamma_5$	$A_2 + B_1 + B_2 + E + E$
$J = 4$	$\Gamma_1 + \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$ $+ \Gamma_5 + \Gamma_5$	$A_1 + A_1 + A_2 + B_1 + B_2$ $+ E + E$

for the doubly degenerate Γ_5 .

By application of the techniques outlined in Appendix C it is a simple matter to show that the transformation properties of the coordinates x , y , and z , and the products of coordinates such as xy , xz , yz , x^2-y^2 , etc., conform to certain irreducible representations. For example, in square-planar symmetry, the coordinate z belongs to the irreducible representation Γ_1 . Similarly, the pair x and y , or the pair xz and yz , belong to the representation Γ_5 . The product xy belongs to Γ_4 , and the product x^2-y^2 to Γ_3 , and so on. A sample set of such functions is given in Table 10.

It is possible to present the spherical harmonics in terms of cartesian coordinates just as easily as in terms of spherical coordinates. Table 11 lists the normalized

spherical harmonics up to $J = 4$, in terms of spherical and cartesian coordinates. Comparison of the representation of the spherical harmonics with $J = 2$ with the sample set in Table 10 shows that $Y(2,0)$ should be the basis function for Γ_1 . Similarly,

$$1/\sqrt{2} [Y(2,2) + Y(2,-2)] = \sqrt{15}/\sqrt{64\pi} [x^2 - y^2]$$

and hence this combination should transform according to Γ_3 .

In like fashion:

$$1/i\sqrt{2} [Y(2,2) - Y(2,-2)] = \sqrt{15}/\sqrt{64\pi} [xy], \text{ hence } \Gamma_4.$$

And finally,

$$1/\sqrt{2} [Y(2,-1) - Y(2,1)] = \sqrt{15}/\sqrt{16\pi} [xz] \\ 1/\sqrt{2} [Y(2,-1) + Y(2,1)] = \sqrt{15}/\sqrt{16\pi} [yz] \quad \text{hence, } \Gamma_5.$$

Therefore, the linear combinations of the $|S, L, J, M_J\rangle$ functions which yield symmetry adapted functions belonging to the appropriate irreducible representations for 1D_2 are:

Table 10. Coordinate functions which are bases for the D_4 irreducible representations

Function	Corresponding irreducible representation
$[3(z)^2 - 1]$	Γ_1
$[x^2 - y^2]$	Γ_3
$[xy]$	Γ_4
$[(xz), (yz)]$	Γ_5
$[xyz]$	Γ_3
$[5z^3 - 3z]$	Γ_2

Table 11. Normalized spherical harmonics^a

Spherical harmonic	Spherical coordinates	Cartesian coordinates
$Y(0,0)$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{2\sqrt{\pi}}$
$Y(1,\pm 1)$	$\mp \frac{\sqrt{3}}{\sqrt{8\pi}} \sin \theta e^{\pm i\phi}$	$\mp \frac{\sqrt{3}}{\sqrt{8\pi}} \frac{(x \pm iy)}{r}$
$Y(1,0)$	$\frac{\sqrt{3}}{\sqrt{4\pi}} \cos \theta$	$\frac{\sqrt{3}}{\sqrt{4\pi}} \frac{z}{r}$
$Y(2,\pm 2)$	$\frac{\sqrt{15}}{\sqrt{32\pi}} \sin^2 \theta e^{\pm i2\phi}$	$\frac{\sqrt{15}}{\sqrt{32\pi}} \left(\frac{x \pm iy}{r} \right)^2$
$Y(2,\pm 1)$	$\mp \frac{\sqrt{15}}{\sqrt{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$	$\mp \frac{\sqrt{15}}{\sqrt{8\pi}} \frac{(x \pm iy)z}{r^2}$
$Y(2,0)$	$\frac{\sqrt{5}}{\sqrt{16\pi}} (3 \cos^2 \theta - 1)$	$\frac{\sqrt{5}}{\sqrt{16\pi}} \left[3 \left(\frac{z}{r} \right)^2 - 1 \right]$
$Y(3,\pm 3)$	$\mp \frac{\sqrt{35}}{\sqrt{64\pi}} \sin^3 \theta e^{\pm i3\phi}$	$\mp \frac{\sqrt{35}}{\sqrt{64\pi}} \left(\frac{x \pm iy}{r} \right)^3$
$Y(3,\pm 2)$	$\frac{\sqrt{105}}{\sqrt{32\pi}} \sin^2 \theta \cos \theta e^{\pm i2\phi}$	$\frac{\sqrt{105}}{\sqrt{32\pi}} \frac{(x \pm iy)^2 z}{r^3}$
$Y(3,\pm 1)$	$\mp \frac{\sqrt{21}}{\sqrt{64\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$	$\mp \frac{\sqrt{21}}{\sqrt{64\pi}} \frac{(x \pm iy)}{r} \left[5 \left(\frac{z}{r} \right)^2 - 1 \right]$
$Y(3,0)$	$\frac{\sqrt{7}}{\sqrt{16\pi}} (5 \cos^3 \theta - 3 \cos \theta)$	$\frac{\sqrt{7}}{\sqrt{16\pi}} \left[5 \left(\frac{z}{r} \right)^3 - 3 \left(\frac{z}{r} \right) \right]$

^aThe spherical harmonics employed in Table 11 correspond to those used by Wigner (30) and Condon and Shortley (6). There are several ways to define the spherical harmonics and caution must be exercised in comparing the symmetry adapted functions used by various authors. Detailed comments covering the spherical harmonics are given in Appendix B-1.

Table 11. (Continued)

Spherical harmonic	Spherical coordinates	Cartesian coordinates
$Y(4, \pm 4)$	$\sqrt{\frac{315}{512\pi}} \sin^4 \theta e^{\pm i4\phi}$	$\sqrt{\frac{315}{512\pi}} \left(\frac{x \pm iy}{r} \right)^4$
$Y(4, \pm 3)$	$\mp \sqrt{\frac{315}{64\pi}} \sin^3 \theta \cos \theta e^{\pm i3\phi}$	$\mp \sqrt{\frac{315}{64\pi}} \left(\frac{x \pm iy}{r} \right)^3 \frac{z}{r}$
$Y(4, \pm 2)$	$\sqrt{\frac{45}{128\pi}} (7 \cos^2 \theta - 1) \sin^2 \theta e^{\pm i2\phi}$	$\sqrt{\frac{45}{128\pi}} \left(\frac{x \pm iy}{r} \right)^2 \left[7 \left(\frac{z}{r} \right)^2 - 1 \right]$
$Y(4, \pm 1)$	$\mp \sqrt{\frac{45}{64\pi}} (7 \cos^3 \theta - 3 \cos \theta) \sin \theta e^{\pm i\phi}$	$\mp \sqrt{\frac{45}{64\pi}} \left(\frac{x \pm iy}{r} \right) \frac{z}{r} \left[7 \left(\frac{z}{r} \right)^2 - 3 \right]$
$Y(4, 0)$	$\frac{3}{16} (35 \cos^4 \theta - 30 \cos^2 \theta + 1)$	$\frac{3}{16} \left[35 \left(\frac{z}{r} \right)^4 - 30 \left(\frac{z}{r} \right)^2 + 1 \right]$

$$\Gamma_1 = {}^1D_2(0) = |0,2,2,0\rangle$$

$$\Gamma_3 = 1/\sqrt{2} [{}^1D_2(2) + {}^1D_2(-2)] = 1/\sqrt{2} [|0,2,2,2\rangle + |0,2,2,-2\rangle]$$

$$\Gamma_4 = 1/i\sqrt{2} [{}^1D_2(2) - {}^1D_2(-2)] = 1/i\sqrt{2} [|0,2,2,2\rangle - |0,2,2,-2\rangle]$$

$$\Gamma_5 = 1/\sqrt{2} [{}^1D_2(-1) - {}^1D_2(1)] = 1/\sqrt{2} [|0,2,2,-1\rangle - |0,2,2,1\rangle]$$

$$i/\sqrt{2} [{}^1D_2(-1) + {}^1D_2(1)] = i/\sqrt{2} [|0,2,2,-1\rangle + |0,2,2,1\rangle]$$

It is important to notice that all states with $J = 2$ have analogous combinations. For example, for the 3F_2 state:

$$\Gamma_1 = {}^3F_2(0) = |1,3,2,0\rangle$$

$$\Gamma_3 = 1/\sqrt{2} [{}^3F_2(2) + {}^3F_2(-2)] = 1/\sqrt{2} [|1,3,2,2\rangle + |1,3,2,-2\rangle]$$

$$\Gamma_4 = 1/i\sqrt{2} [{}^3F_2(2) - {}^3F_2(-2)] = 1/i\sqrt{2} [|1,3,2,2\rangle - |1,3,2,-2\rangle]$$

$$\Gamma_5 = 1/\sqrt{2} [{}^3F_2(-1) - {}^3F_2(1)] = 1/\sqrt{2} [|1,3,2,-1\rangle - |1,3,2,1\rangle]$$

$$i/\sqrt{2} [{}^3F_2(-1) + {}^3F_2(1)] = i/\sqrt{2} [|1,3,2,-1\rangle + |1,3,2,1\rangle]$$

A similar set is obtained for the 3P_2 states.

Table 12 gives the appropriate combinations of the spherical harmonics which belong to the irreducible representations of the group D_4 . From this table, the correct combination of the states given in Table 7 can be made which yield the symmetry adapted weak field functions. It is important that in constructing the elements of the sets belonging to degenerate representations such as Γ_5 that one heed the precautions given in Appendix D-3. The weak field basis functions are given in Table 13.

Table 12. Combination of spherical harmonics which form basis functions for the irreducible representations of D_4

J value	Represent- ation	Corresponding spherical harmonic	Coordinate function
J = 0	1	$Y(0,0)$	a constant
J = 1	2	$Y(1,0)$	$(\frac{z}{r})$
	5	$\frac{i}{\sqrt{2}} [Y(1,1)+Y(1,-1)]$	$\frac{y}{r}$
		$\frac{1}{\sqrt{2}} [Y(1,1)-Y(1,-1)]$	$-\frac{x}{r}$
J = 2	1	$Y(2,0)$	$[3(\frac{z}{r})^2-1]/r^2$
	3	$\frac{1}{\sqrt{2}} [Y(2,2)+Y(2,-2)]$	$[x^2-y^2]/r^2$
	4	$\frac{1}{i\sqrt{2}} [Y(2,2)-Y(2,-2)]$	xy/r^2
	5	$\frac{1}{\sqrt{2}} [Y(2,-1)-Y(2,1)]$	xz/r^2
		$\frac{i}{\sqrt{2}} [Y(2,-1)+Y(2,1)]$	yz/r^2
J = 3	2	$Y(3,0)$	$[5(\frac{z}{r})^3 - 3(\frac{z}{r})]$
	3	$\frac{1}{i\sqrt{2}} [Y(3,2)-Y(3,-2)]$	xyz/r^3
	4	$\frac{1}{\sqrt{2}} [Y(3,2)+Y(3,-2)]$	$z(x^2-y^2)/r^3$
	5 ^I	$\frac{1}{i\sqrt{2}} [Y(3,3)+Y(3,-3)]$	$y(y^2-3x^2)/r^3$
		$\frac{1}{\sqrt{2}} [Y(3,3)-Y(3,-3)]$	$x(3y^2-3x^2)/r^3$
	5 ^{II}	$\frac{i}{\sqrt{2}} [Y(3,1)+Y(3,-1)]$	$y[5(\frac{z}{r})^2-1]/r$
		$\frac{1}{\sqrt{2}} [Y(3,1)-Y(3,-1)]$	$x[1-5(\frac{z}{r})^2]/r$

Table 12. (Continued)

J value	Represent- ation	Corresponding spherical harmonic	Coordinate function
J = 4	1^I	$\frac{1}{\sqrt{2}} [Y(4,4)+Y(4,-4)]$	$[x^4-6x^2y^2+y^4]/r^4$
	1^{II}	$Y(4,0)$	$[35(\frac{z}{r})^4-30(\frac{z}{r})^2+3]$
	2	$\frac{1}{i\sqrt{2}} [Y(4,4)-Y(4,-4)]$	$xy[x^2-y^2]/r^4$
	3	$\frac{1}{\sqrt{2}} [Y(4,2)+Y(4,-2)]$	$[x^2-y^2][7(\frac{z}{r})^2-1]/r^2$
	4	$\frac{1}{i\sqrt{2}} [Y(4,2)-Y(4,-2)]$	$[xy][7(\frac{z}{r})^2-1]/r^2$
	5^I	$\frac{1}{\sqrt{2}} [Y(4,-3)-Y(4,3)]$	$[xz][x^2-3y^2]/r^4$
		$\frac{1}{i\sqrt{2}} [Y(4,-3)+Y(4,3)]$	$[yz][y^2-3x^2]/r^4$
	5^{II}	$\frac{1}{\sqrt{2}} [Y(4,-1)-Y(4,1)]$	$[xz][7(\frac{z}{r})^2-3]/r^2$
		$\frac{1}{i\sqrt{2}} [Y(4,-1)+Y(4,1)]$	$[yz][7(\frac{z}{r})^2-3]/r^2$

Table 13. Weak field basis function

Symmetry adapted free ion functions	
<u>Γ_1 matrix</u>	
$^1\Gamma_1(^1G_4I)$	$= \frac{1}{\sqrt{2}} [^1G_4(4) + ^1G_4(-4)]$
$^1\Gamma_1(^1G_4II)$	$= G_4(0)$
$^1\Gamma_1(^1D_2)$	$= ^1D_2(0)$
$^1\Gamma_1(^1S_0)$	$= ^1S_0(0)$
$^3\Gamma_1(^3F_4I)$	$= \frac{1}{\sqrt{2}} [^3F_4(4) + ^3F_4(-4)]$
$^3\Gamma_1(^3F_4II)$	$= ^3F_4(0)$
$^3\Gamma_1(^3F_2)$	$= ^3F_2(0)$
$^3\Gamma_1(^3P_2)$	$= ^3P_2(0)$
$^3\Gamma_1(^3P_0)$	$= ^3P_0(0)$
<u>Γ_2 matrix</u>	
$^1\Gamma_2(^1G_4)$	$= \frac{1}{i\sqrt{2}} [^1G_4(4) - ^1G_4(-4)]$
$^3\Gamma_2(^3F_4)$	$= \frac{1}{i\sqrt{2}} [^3F_4(4) - ^3F_4(-4)]$
$^3\Gamma_2(^3F_3)$	$= ^3F_3(0)$
$^3\Gamma_2(^3P_1)$	$= ^3P_1(0)$

Table 13. (Continued)

Symmetry adapted free ion functions	
<u>Γ_3 matrix</u>	
$1\Gamma_3(^1G_4)$	$= \frac{1}{\sqrt{2}} [^1G_4(2) + ^1G_4(-2)]$
$1\Gamma_3(^1D_2)$	$= \frac{1}{\sqrt{2}} [^1D_2(2) + ^1D_2(-2)]$
$3\Gamma_3(^3F_4)$	$= \frac{1}{\sqrt{2}} [^3F_4(2) + ^3F_4(-2)]$
$3\Gamma_3(^3F_2)$	$= \frac{1}{\sqrt{2}} [^3F_2(2) + ^3F_2(-2)]$
$3\Gamma_3(^3P_2)$	$= \frac{1}{\sqrt{2}} [^3P_2(2) + ^3P_2(-2)]$
$3\Gamma_3(^3F_3)$	$= \frac{1}{i\sqrt{2}} [^3F_3(2) - ^3F_3(-2)]$
<u>Γ_4 matrix</u>	
$1\Gamma_4(^1G_4)$	$= \frac{1}{i\sqrt{2}} [^1G_4(2) - ^1G_4(-2)]$
$1\Gamma_4(^1D_2)$	$= \frac{1}{i\sqrt{2}} [^1D_2(2) - ^1D_2(-2)]$
$3\Gamma_4(^3F_4)$	$= \frac{1}{i\sqrt{2}} [^3F_4(2) - ^3F_4(-2)]$
$3\Gamma_4(^3F_2)$	$= \frac{1}{i\sqrt{2}} [^3F_2(2) - ^3F_2(-2)]$
$3\Gamma_4(^3P_2)$	$= \frac{1}{i\sqrt{2}} [^3P_2(2) - ^3P_2(-2)]$
$3\Gamma_4(^3F_3)$	$= \frac{1}{\sqrt{2}} [^3F_3(2) + ^3F_3(-2)]$

Table 13. (Continued)

Symmetry adapted free ion functions	
Γ_5 matrix	
${}^1\Gamma_5({}^1G_4\text{I})$	$\frac{1}{\sqrt{2}} [{}^1G_4(-3) - {}^1G_4(3)]$ $\frac{1}{i\sqrt{2}} [{}^1G_4(-3) + {}^1G_4(3)]$
${}^1\Gamma_5({}^1G_4\text{II})$	$\frac{1}{\sqrt{2}} [{}^1G_4(-1) - {}^1G_4(1)]$ $\frac{1}{i\sqrt{2}} [{}^1G_4(-1) + {}^1G_4(1)]$
${}^1\Gamma_5({}^1D_2)$	$\frac{1}{\sqrt{2}} [{}^1D_2(-1) - {}^1D_2(1)]$ $\frac{1}{i\sqrt{2}} [{}^1D_2(-1) + {}^1D_2(1)]$
${}^3\Gamma_5({}^3F_4\text{I})$	$\frac{1}{\sqrt{2}} [{}^3F_4(-3) - {}^3F_4(3)]$ $\frac{1}{i\sqrt{2}} [{}^3F_4(-3) + {}^3F_4(3)]$
${}^3\Gamma_5({}^3F_4\text{II})$	$\frac{1}{\sqrt{2}} [{}^3F_4(-1) - {}^3F_4(1)]$ $\frac{1}{i\sqrt{2}} [{}^3F_4(-1) + {}^3F_4(1)]$
${}^3\Gamma_5({}^3F_2)$	$\frac{1}{\sqrt{2}} [{}^3F_2(-1) - {}^3F_2(1)]$ $\frac{1}{i\sqrt{2}} [{}^3F_2(-1) + {}^3F_2(1)]$

Table 13. (Continued)

Symmetry adapted free ion functions	
${}^3\Gamma_5({}^3P_2)$	$\frac{1}{\sqrt{2}} [{}^3P_2(-1) - {}^3P_2(1)]$ $\frac{1}{i\sqrt{2}} [{}^3P_2(-1) + {}^3P_2(1)]$
${}^3\Gamma_5({}^3F_3\text{I})$	$\frac{1}{i\sqrt{2}} [{}^3F_3(3) + {}^3F_3(-3)]$ $\frac{1}{\sqrt{2}} [{}^3F_3(3) - {}^3F_3(-3)]$
${}^3\Gamma_5({}^3F_3\text{II})$	$-\frac{1}{i\sqrt{2}} [{}^3F_3(1) + {}^3F_3(-1)]$ $\frac{1}{\sqrt{2}} [{}^3F_3(1) - {}^3F_3(-1)]$
${}^3\Gamma_5({}^3P_1)$	$\frac{1}{\sqrt{2}} [{}^3P_1(1) + {}^3P_1(-1)]$ $\frac{1}{\sqrt{2}} [{}^3P_1(1) - {}^3P_1(-1)]$

B. The Weak Field Matrix Elements

As has been indicated, the formation of the symmetry adapted functions results in five matrices in the case of square planar symmetry. Γ_1 has nine basis functions, Γ_2 has four, Γ_3 has six, Γ_4 has six, and Γ_5 has ten. Because of the inclusion of spin-orbit coupling, there are off-diagonal elements connecting the singlet and triplet states. This is the reason for the large size of the five matrices.

Each matrix element is the sum of three effects; i.e.,

$$\begin{aligned} \int \psi_A^* H \psi_B d\tau &= \int \psi_A^* \left(\sum_{i>j} e^2/r_{ij} \right) \psi_B d\tau \\ &+ \int \psi_A^* \sum_i \mathcal{L}_i \cdot \mathcal{S}_i \psi_B d\tau + \int \psi_A^* V^{LF} \psi_B d\tau \end{aligned} \quad (110)$$

1. Electronic interaction

It would be possible to evaluate the matrix elements of the electronic interaction in terms of the Slater-Condon parameters by the methods outlined in Appendix D. Or, since the weak field functions were chosen so that the matrix elements are diagonal in the electronic interaction terms, the methods outlined in section 27 of Condon and Shortley (6) could be used. Even this is not necessary, since the results for the d^2 configuration are listed on page 206 in Condon and Shortley (6).

The electronic interaction elements are given in terms of two parameters, F_2 and F_4 , known as the Slater-Condon parameters. These parameters are actually integrals very similar in form to the integrals G_2 and G_4 which result from the ligand field. However, the values of F_2 and F_4 are frequently determined from experimental data, particularly from emission spectra. In this thesis, F_2 and F_4 are considered as parameters to be determined.

2. Spin-orbit coupling

The coupling operator may be written:

$$\sum_i \xi(r_i) \vec{L}_i \cdot \vec{S}_i = \xi(r_1) \vec{L}_1 \cdot \vec{S}_1 + \xi(r_2) \vec{L}_2 \cdot \vec{S}_2 \quad (111)$$

and, assuming the parameter $\xi(r)$ is the same for both electrons:

$$\begin{aligned} \sum_i \xi(r_i) \vec{L}_i \cdot \vec{S}_i = & \alpha [\mathcal{L}_+(1) \mathcal{S}_-(1) + \mathcal{L}_-(1) \mathcal{S}_+(1) + \mathcal{L}_+(2) \mathcal{S}_-(2) \\ & + \mathcal{L}_-(2) \mathcal{S}_+(2)] + 2\alpha [\mathcal{L}_z(1) \mathcal{S}_z(1) + \mathcal{L}_z(2) \mathcal{S}_z(2)] \end{aligned} \quad (112)$$

where $\alpha = \xi/2$

\mathcal{L}_+ = The "step up" operator for orbital angular momentum

$$= \mathcal{L}_x + i\mathcal{L}_y$$

\mathcal{L}_- = The "step down" operator for orbital angular momentum

$$= \mathcal{L}_x - i\mathcal{L}_y$$

$$\begin{aligned} \mathcal{J}_+ &= \text{The "step up" operator for spin angular momentum} \\ &= \mathcal{J}_x + i\mathcal{J}_y \end{aligned}$$

$$\begin{aligned} \mathcal{J}_- &= \text{The "step down" operator for spin angular momentum} \\ &= \mathcal{J}_x - i\mathcal{J}_y \end{aligned}$$

However, the tedious calculations for the weak field functions are not necessary since the matrix elements for d^2 are given in Table 1¹¹ of Condon and Shortley (6).

3. Ligand field effect

As has been stated, the ligand field matrix elements can be expressed as sums of four single electron integrals, Q_2 , Q_1 , Q_0 , and $B_{2,-2}$. The process of obtaining the correct combinations is somewhat lengthy and there have been methods evolved which circumvent the actual construction of the wave functions. One such method, developed by Bleaney and Stevens (21) is discussed in Appendix B. However, the method itself is somewhat involved and in the case of the two electron functions, it was felt that the more direct approach was just as rapid.

Because of the differences in spin between the singlet and triplet states, there are no ligand field elements connecting these states. For an element that is non-zero, the off-diagonal element between the 1D_2 and 1S_0 basis functions for the Γ_1 matrix has been chosen to illustrate the calcula-

tion involved. With the help of Tables 8 and 13.

$$\begin{aligned}
 \int \psi_A^* V^{LF} \psi_B d\tau &= \int \psi^* 1_{D_2}(0) V^{LF} \psi 1_{S_0}(0) d\tau \\
 &= \int \frac{1}{\sqrt{28}} [2(2,-2) + (1,-1) - 2(0,0) + (-1,1) \\
 &\quad + 2(-2,2)] [\alpha\beta - \beta\alpha]^* \cdot V^{LF} \\
 &\quad \cdot \frac{1}{\sqrt{10}} [(2,-2) - (1,-1) + (0,0) - (-1,1) \\
 &\quad + (-2,2)] [\alpha\beta - \beta\alpha] d\tau. \tag{113}
 \end{aligned}$$

The spin terms simply double the space results. Hence:

$$\begin{aligned}
 \int \psi_A^* V^{LF} \psi_B d\tau &= \frac{2}{\sqrt{280}} [2 \int (2,-2)^* V^{LF}(2,-2) d\tau \\
 &\quad - \int (1,-1)^* V^{LF}(1,-1) d\tau - 2 \int (0,0)^* V^{LF}(0,0) d\tau \\
 &\quad - \int (-1,1)^* V^{LF}(-1,1) d\tau + 2 \int (-2,2)^* V^{LF}(-2,2) d\tau] \tag{114}
 \end{aligned}$$

All other possible combinations result in integrals whose values are zero. The first integral term can be expanded as:

$$\begin{aligned}
 2 \int (2,-2)^* V^{LF}(2,-2) d\tau &= 2 \left[\int (2)_1^* V_1^{LF}(2)_1 d\tau \right. \\
 &\quad \left. + \int (-2)_2^* V_2^{LF}(-2)_2 d\tau \right] = 2[Q_2 + Q_2] = 4Q_2. \tag{115}
 \end{aligned}$$

The same result is obtained for the fifth integral term. For the second and fourth integrals:

$$\begin{aligned}
- \int (1, -1)^* v^{LF}(1, -1) d\tau &= - \left[\int (1)_1^* v_1^{LF}(1)_1 d\tau \right. \\
&\quad \left. + \int (-1)_2^* v_2^{LF}(-1)_2 d\tau_2 \right] = - [Q_1 + Q_1] = -2Q_1 \quad (116)
\end{aligned}$$

And the third term yields:

$$2 \int (0, 0)^* v^{LF}(0, 0) d\tau = 4Q_0 \quad (117)$$

Hence:

$$\begin{aligned}
\int \psi^* \left(\frac{1}{D_2}(0) \right) v^{LF} \psi \left(\frac{1}{S_0}(0) \right) d\tau &= \frac{2}{\sqrt{280}} [8Q_2 - 4Q_1 + 4Q_0] \\
&= \frac{4}{\sqrt{70}} [2Q_2 - Q_1 + Q_0] \quad (118)
\end{aligned}$$

By similar processes, all matrix elements due to the ligand potential may be evaluated.

4. The complete matrices

The final tabulation of all the weak field matrix elements are given in Tables 14 through 18.

C. Strong Field Functions

The strong field functions are chosen so that the matrix elements are diagonal in the ligand field parameters. This is attained by use of basis functions which are symmetry adapted with regard to both spin and space. The method for construction of such functions may be outlined as follows:

Table 14a. Weak field matrix elements, d^8 configuration in square-planar symmetry. Γ_1 matrix^a

	$1G_4$	$1G_4$	$1D_2$	$1S_0$	$3F_4$	$3F_4$	$3F_2$	$3P_2$	$3P_0$
	(I)	(II)			(I)	(II)			
$1G_4(I)$	a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	0	0	0	0
$1G_4(II)$	a_{21}	a_{22}	a_{23}	a_{24}	0	a_{26}	0	0	0
$1D_2$	a_{31}	a_{32}	a_{33}	a_{34}	0	0	a_{37}	a_{38}	0
$1S_0$	a_{41}	a_{42}	a_{43}	a_{44}	0	0	0	0	a_{49}
$3F_4(I)$	a_{51}	0	0	0	a_{55}	a_{56}	a_{57}	a_{58}	a_{59}
$3F_4(II)$	0	a_{62}	0	0	a_{65}	a_{66}	a_{67}	a_{68}	a_{69}
$3F_2$	0	0	a_{73}	0	a_{75}	a_{76}	a_{77}	a_{78}	a_{79}
$3P_2$	0	0	a_{83}	0	a_{85}	a_{86}	a_{87}	a_{88}	a_{89}
$3P_0$	0	0	0	a_{94}	a_{95}	a_{96}	a_{97}	a_{98}	a_{99}

^aThe non-zero a_{ij} matrix elements, where the first index is the row and the second is the column, are given in Table 14b.

Table 14b. Non-zero values of Γ_1 weak field matrix elements

Matrix elements	Values
a_{11}	$= 2Q_2 + 4F_2 + F_4$
$a_{21} = a_{12}^*$	$= 2/\sqrt{35} B_{2-2}$
a_{22}	$= 2/35 [Q_2 + 16Q_1 + 18Q_0] + 4F_2 + F_4$
$a_{31} = a_{13}^*$	$= 4/\sqrt{7} B_{2-2}$

Table 14b. (Continued)

Matrix elements	Values
$a_{32} = a_{23}^*$	$= 4/7 \sqrt{5} [Q_2 + 2Q_1 - 3Q_0]$
a_{33}	$= 2/7 [4Q_2 + Q_1 + 2Q_0] - 3F_2 + 36F_4$
$a_{41} = a_{14}^*$	$= 4/\sqrt{10} B_{2-2}$
$a_{42} = a_{24}^*$	$= 4/5 \sqrt{14} [Q_2 - 4Q_1 + 3Q_0]$
$a_{43} = a_{34}^*$	$= 4/\sqrt{70} [2Q_2 - Q_1 - Q_0]$
a_{44}	$= 2/5 [2Q_2 + 2Q_1 + Q_0] + 14F_2 + 126F_4$
$a_{51} = a_{15}^*$	$= -2\alpha$
a_{55}	$= [Q_2 + Q_1] - 3\alpha - 8F_2 - 9F_4$
$a_{62} = a_{26}^*$	$= -2\alpha$
$a_{65} = a_{56}^*$	$= -3/\sqrt{35} B_{2-2}$
a_{66}	$= 1/35 [17Q_2 + 47Q_1 + 6Q_0] - 3\alpha - 8F_2 - 9F_4$
$a_{73} = a_{37}^*$	$= 4\sqrt{3}/\sqrt{5} \alpha$
$a_{75} = a_{57}^*$	$= -2\sqrt{3}/\sqrt{35} B_{2-2}$
$a_{76} = a_{67}^*$	$= 2\sqrt{3}/35 [Q_2 - 3Q_1 + 2Q_0]$
a_{77}	$= 2/35 [9Q_2 + 22Q_1 + 4Q_0] + 4\alpha - 8F_2 - 9F_4$

Table 14b. (Continued)

Matrix elements	Values
$a_{83} = a_{38}^*$	$= -42/\sqrt{5} \alpha$
$a_{85} = a_{58}^*$	$= -\sqrt{2}/\sqrt{15} B_{2-2}$
$a_{86} = a_{68}^*$	$= 2/5 \sqrt{42} [11Q_2 - 8Q_1 - 3Q_0]$
$a_{87} = a_{78}^*$	$= 4/5 \sqrt{14} [-Q_2 + 2Q_1 - Q_0]$
a_{88}	$= 1/5 [6Q_2 + 3Q_1 + Q_0] - \alpha + 7F_2 - 84F_4$
$a_{94} = a_{49}^*$	$= 2/\sqrt{6} \alpha$
$a_{95} = a_{59}^*$	$= -2/\sqrt{15} B_{2-2}$
$a_{96} = a_{69}^*$	$= 2/5 \sqrt{21} [-Q_2 + 4Q_1 - 3Q_0]$
$a_{97} = a_{79}^*$	$= 4/5 \sqrt{7} [2Q_2 - Q_1 - Q_0]$
$a_{98} = a_{89}^*$	$= \sqrt{2}/5 [-2Q_2 + 2Q_1 + Q_0]$
a_{99}	$= 2/5 [2Q_2 + 2Q_1 + Q_0] + 2\alpha + 7F_2 - 84F_4$

Table 15a. Weak field matrix elements, Γ_2 matrix^a

	$1G_4$	$3F_4$	$3F_3$	$3P_1$
$1G_4$	b_{11}	b_{12}	0	0
$3F_4$	b_{21}	b_{22}	b_{23}	b_{24}
$3F_3$	0	b_{32}	b_{33}	b_{34}
$3P_1$	0	b_{42}	b_{43}	b_{44}

^aThe non-zero matrix elements, b_{ij} , are given in Table 15b.

Table 15b. Non-zero values of Γ_2 weak field matrix elements

Matrix elements	Value
b_{11}	$2Q_2 + 4F_2 + F_4$
$b_{21} = b_{12}^*$	-2α
b_{22}	$Q_2 + Q_1 - 3\alpha - 8F_2 - 9F_4$
$b_{32} = b_{23}^*$	$i \sqrt{3}/\sqrt{5} B_{2-2}$
b_{33}	$1/5 [3Q_2 + 5Q_1 + 2Q_0] + \alpha - 8F_2 - 9F_4$
$b_{42} = b_{24}^*$	$i \sqrt{2}/\sqrt{5} B_{2-2}$
$b_{43} = b_{34}^*$	$\sqrt{6}/5 [Q_2 - Q_0]$
b_{44}	$1/5 [2Q_2 + 5Q_1 + 3Q_0] + \alpha + 7F_2 - 84F_4$

Table 16a. Weak field matrix elements, Γ_3 matrix^a

	1G_4	1D_2	3F_4	3F_3	3F_2	3P_2
1G_4	c_{11}	c_{12}	c_{13}	0	0	0
1D_2	c_{21}	c_{22}	0	0	c_{25}	c_{26}
3F_4	c_{31}	0	c_{33}	c_{34}	c_{35}	c_{36}
3F_3	0	0	c_{43}	c_{44}	c_{45}	c_{46}
3F_2	0	c_{52}	c_{53}	c_{54}	c_{55}	c_{56}
3P_2	0	c_{62}	c_{63}	c_{64}	c_{65}	c_{66}

^aThe non-zero matrix elements, c_{ij} , are given in Table 17a, on page 99.

Table 16b. Weak field matrix elements, Γ_4 matrix^a

	1G_4	1D_2	3F_4	3F_3	3F_2	3P_2
1G_4	d_{11}	d_{12}	d_{13}	0	0	0
1D_2	d_{21}	d_{22}	0	0	d_{25}	d_{26}
3F_4	d_{31}	0	d_{33}	d_{34}	d_{35}	d_{36}
3F_3	0	0	d_{43}	d_{44}	d_{45}	d_{46}
3F_2	0	d_{52}	d_{53}	d_{54}	d_{55}	d_{56}
3P_2	0	d_{62}	d_{63}	d_{64}	d_{65}	d_{66}

^aThe non-zero matrix elements, d_{ij} , are given in Table 17b, on page 100.

Table 17a Non-zero values of Γ_3 weak field matrix elements

Matrix elements	Value
c_{11}	$1/7[3Q_2 + 8Q_1 + 3Q_0 + 3B_{2-2}] + 4F_2 + F_4$
$c_{21} = c_{12}^*$	$2\sqrt{3}/7 [Q_2 - 2Q_1 + Q_0 + B_{2-2}]$
c_{22}	$2/7[2Q_2 + 3Q_1 + 2Q_0 + 2B_{2-2}] - 3F_2 + 36F_4$
$c_{31} = c_{13}^*$	-2α
c_{33}	$1/14[11Q_2 + 8Q_1 + 9Q_0 - 9B_{2-2}] - 3\alpha - 8F_2 - 9F_4$
$c_{43} = c_{34}^*$	$i/2\sqrt{7} [-Q_2 + 2Q_1 - Q_0 + 3B_{2-2}]$
c_{44}	$1/6[5Q_2 + 4Q_1 + 3Q_0 + B_{2-2}] + \alpha - 8F_2 - 9F_4$
$c_{52} = c_{25}^*$	$4\sqrt{3}/\sqrt{5} \alpha$
$c_{53} = c_{35}^*$	$1/7\sqrt{5}[-Q_2 + 5Q_1 - 4Q_0 - 3B_{2-2}]$
$c_{54} = c_{45}^*$	$i/3\sqrt{35} [Q_2 + 5Q_1 - 6Q_0 + 11B_{2-2}]$
c_{55}	$1/105[103Q_2 + 80Q_1 + 27Q_0 - 55B_{2-2}] + 4\alpha - 8F_2 - 9F_4$
$c_{62} = c_{26}^*$	$-\sqrt{42}/\sqrt{5} \alpha$
$c_{63} = c_{36}^*$	$1/\sqrt{70} [3Q_2 - 3Q_0 - B_{2-2}]$
$c_{64} = c_{46}^*$	$i/\sqrt{10} [-Q_2 + Q_0 - B_{2-2}]$
$c_{65} = c_{56}^*$	$2/5\sqrt{14} [Q_2 - Q_0 - 5B_{2-2}]$
c_{66}	$1/5[2Q_2 + 5Q_1 + 3Q_0] - \alpha + 7F_2 - 84F_4$

Table 17b. Non-zero values of Γ_4 matrix elements

Matrix elements	Values
d_{11}	$1/7[3Q_2 + 8Q_1 + 3Q_0 - 3B_{2-2}] + 4F_2 + F_4$
$d_{21} = d_{12}^*$	$2\sqrt{3}/7[Q_2 - 2Q_1 + Q_0 - B_{2-2}]$
d_{22}	$2/7[2Q_2 + 3Q_1 + 2Q_0 - 2B_{2-2}] - 3F_2 + 36F_4$
$d_{31} = d_{13}^*$	-2α
d_{33}	$1/14[11Q_2 + 8Q_1 + 9Q_0 + 9B_{2-2}] - 3\alpha - 8F_2 - 9F_4$
$d_{43} = d_{34}^*$	$i/\sqrt{28}[Q_2 - 2Q_1 + Q_0 + 3B_{2-2}]$
d_{44}	$1/6[5Q_2 + 4Q_1 + 3Q_0 - B_{2-2}] + \alpha - 8F_2 - 9F_4$
$d_{52} = d_{25}^*$	$4\sqrt{3}/\sqrt{5}\alpha$
$d_{53} = d_{35}^*$	$1/7\sqrt{5}[-Q_2 + 5Q_1 - 4Q_0 + 3B_{2-2}]$
$d_{54} = d_{45}^*$	$i/3\sqrt{35}[-Q_2 - 5Q_1 + 6Q_0 + 11B_{2-2}]$
d_{55}	$1/105[103Q_2 + 80Q_1 + 27Q_0 + 55B_{2-2}] + 4\alpha - 8F_2 - 9F_4$
$d_{62} = d_{26}^*$	$-\sqrt{42}/\sqrt{5}\alpha$
$d_{63} = d_{36}^*$	$1/\sqrt{70}[3Q_2 - 3Q_0 + B_{2-2}]$
$d_{64} = d_{46}^*$	$i/\sqrt{10}[Q_2 - Q_0 - B_{2-2}]$
$d_{65} = d_{56}^*$	$1/5\sqrt{14}[2Q_2 - 2Q_0 + 5B_{2-2}]$
d_{66}	$1/5[2Q_2 + 5Q_1 + 3Q_0] - \alpha + 7F_2 - 84F_4$

Table 18a. Weak field matrix elements, Γ_5 matrix^a

	1G_4 (I)	1G_4 (II)	1D_2	3F_4 (I)	3F_4 (II)	3F_2	3P_2	3F_3 (I)	3F_3 (II)	3P_1
1G_4 (I)	e_{11}	e_{12}	e_{13}	e_{14}	0	0	0	0	0	0
1G_4 (II)	e_{21}	e_{22}	e_{23}	0	e_{25}	0	0	0	0	0
1D_2	e_{31}	e_{32}	e_{33}	0	0	e_{36}	e_{37}	0	0	0
3F_4 (I)	e_{41}	0	0	e_{44}	e_{45}	e_{46}	e_{47}	e_{48}	e_{49}	e_{4x}
3F_4 (II)	0	e_{52}	0	e_{54}	e_{55}	e_{56}	e_{57}	e_{58}	e_{59}	e_{5x}
3F_2	0	0	e_{63}	e_{64}	e_{65}	e_{66}	e_{67}	e_{68}	e_{69}	e_{6x}
3P_2	0	0	e_{73}	e_{74}	e_{75}	e_{76}	e_{77}	e_{78}	e_{79}	e_{7x}
3F_3 (I)	0	0	0	e_{84}	e_{85}	e_{86}	e_{87}	e_{88}	e_{89}	e_{8x}
3F_3 (II)	0	0	0	e_{94}	e_{95}	e_{96}	e_{97}	e_{98}	e_{99}	e_{9x}
3P_1	0	0	0	e_{x4}	e_{x5}	e_{x6}	e_{x7}	e_{x8}	e_{x9}	e_{xx}

^aThe non-zero matrix elements, e_{ij} , are given in Table 18b. The tenth row and tenth column are indicated by the letter, x.

Table 18b. The non-zero values of Γ_5 weak field matrix elements

Matrix elements	Value
e_{11}	$Q_2 + Q_1 + 4F_2 + F_4$
$e_{21} = e_{12}^*$	$-1/\sqrt{7} B_{2-2}$
e_{22}	$1/7 [Q_2 + 7Q_1 + 6Q_0] + 4F_2 + F_4$
$e_{31} = e_{13}^*$	$-\sqrt{6}/7 B_{2-2}$
$e_{32} = e_{23}^*$	$\sqrt{6}/7 [Q_2 - Q_0]$
e_{33}	$1/7 [6Q_2 + 7Q_1 + Q_0] - 3F_2 + 36F_4$
$e_{41} = e_{14}^*$	-2α
e_{44}	$1/4 [4Q_2 + Q_1 + 3Q_0] - 3\alpha - 8F_2 - 9F_4$
$e_{52} = e_{25}^*$	-2α
$e_{54} = e_{45}^*$	$3/2 \sqrt{7} B_{2-2}$
e_{55}	$1/28 [16Q_2 + 31Q_1 + 9Q_0] - 3\alpha - 8F_2 - 9F_4$
$e_{63} = e_{36}^*$	$4 \sqrt{3}/\sqrt{5} \alpha$
$e_{64} = e_{46}^*$	$3/\sqrt{70} B_{2-2}$
$e_{65} = e_{56}^*$	$1/7 \sqrt{10} [Q_2 - 2Q_1 + Q_0]$
e_{66}	$1/105 [80Q_2 + 64Q_1 + 66Q_0] + 4\alpha - 8F_2 - 9F_4$
$e_{73} = e_{37}^*$	$-\sqrt{42}/\sqrt{5} \alpha$
$e_{74} = e_{47}^*$	$1/\sqrt{20} B_{2-2}$
$e_{75} = e_{57}^*$	$1/2 \sqrt{35} [7Q_2 - 4Q_1 - 3Q_0]$
$e_{76} = e_{67}^*$	$4/5 \sqrt{14} [-Q_1 + Q_0]$
e_{77}	$1/10 [10Q_2 + 7Q_1 + 3Q_0] - \alpha + 7F_2 - 84F_4$
$e_{84} = e_{48}^*$	$i \sqrt{3}/4 [Q_1 - Q_0]$

Table 18b. (Continued)

Matrix elements	Value
$e_{85} = e_{58}^*$	$i \sqrt{3} / 2 \sqrt{7} B_{2-2}$
$e_{86} = e_{68}^*$	$-11 i / \sqrt{210} B_{2-2}$
$e_{87} = e_{78}^*$	$i \sqrt{3} / 2 \sqrt{5} B_{2-2}$
e_{88}	$1/4 [4Q_2 + 3Q_1 + Q_0] + \alpha - 8F_2 - 9F_4$
$e_{94} = e_{49}^*$	$-3i/2 \sqrt{5} B_{2-2}$
$e_{95} = e_{59}^*$	$i/4 \sqrt{35} [-4Q_2 + 11Q_1 - 7Q_0]$
$e_{96} = e_{69}^*$	$i/15 \sqrt{14} [-13Q_2 + 34Q_1 - 21Q_0]$
$e_{97} = e_{79}^*$	$i/10 [3Q_2 - 4Q_1 + Q_0]$
$e_{98} = e_{89}^*$	$1/2 \sqrt{15} B_{2-2}$
e_{99}	$1/60 [40Q_2 + 53Q_1 + 27Q_0] + \alpha - 8F_2 - 9F_4$
$e_{x4} = e_{4x}^*$	$-i/2 \sqrt{5} B_{2-2}$
$e_{x5} = e_{5x}^*$	$i/2 \sqrt{35} [Q_2 - 4Q_1 + 3Q_0]$
$e_{x6} = e_{6x}^*$	$4i/5 \sqrt{14} [2Q_2 - Q_1 - Q_0]$
$e_{x7} = e_{7x}^*$	$3i/10 [2Q_2 - Q_1 - Q_0]$
$e_{x8} = e_{8x}^*$	$-\sqrt{3} / \sqrt{20} B_{2-2}$
$e_{x9} = e_{9x}^*$	$1/10 [5Q_2 - 4Q_1 - Q_0]$
e_{xx}	$1/10 [10Q_2 + 7Q_1 + 3Q_0] + \alpha + 7F_2 - 84F_4$

1). Construct symmetry adapted single electron space functions by linear combinations of the single electron functions $|\ell, m_\ell, s, m_s\rangle$.

2). Construct symmetry adapted product functions of the spatial functions by taking all possible combinations of the single electron symmetry adapted functions. In the case of d^2 or d^8 systems, these product functions are two electron functions. For d^3 systems they would be three electron functions, and so on. The symmetry of a particular product function is obtained by means of the direct product theorem of group theory.

3) Construct symmetry adapted spin functions by means of the two by two complex matrices corresponding to the rotation operations of the group.

4). Construct the symmetry adapted basis functions from all possible combinations of the symmetry adapted spin functions and the symmetry adapted space functions. Pauli's exclusion principle applies to the possible combinations. The symmetry of the final function can again be determined by the direct product theorem.

1. Single electron symmetry adapted functions

Since the single electron space functions are expressed as:

$$|\ell, m_\ell\rangle = N \cdot R(\) \cdot Y(\ell, m_\ell), \quad (119)$$

the construction of the symmetry adapted single electron functions follows identically the technique used to construct the symmetry adapted $|JM_J\rangle$ functions in the weak field. Thus, the single electron functions are obtained by use of Table 11 with $l = 2$ corresponding to $J = 2$. The functions are listed in Table 19. It is again noted that the combinations of the $|lm_l\rangle$ functions depend upon the definition of the spherical harmonics and care should be exercised when comparing the expressions of various authors. To distinguish between the symmetry of the final basis functions and the symmetry of the single electron functions, it is convenient to follow the example of Liehr and Ballhausen (26). They denote the over-all symmetry of the basis functions by the Bethe (1) notation: Γ_1 , Γ_2 , etc.; and denote the symmetry of the single electron functions using lower case letters of the Mulliken (2) notation: a_1 , a_2 , b_1 , b_2 , and e . Table 18 gives the symmetry in both notations, but the Mulliken notation is used.

2. Symmetry adapted spatial product functions

By application of the direct product theorem of group theory, the irreducible representation(s) to which the products of two symmetry adapted single electron functions belong can be obtained. Table 20 lists the resultant irreducible product representations for the D_4 group. Of course since none of the five symmetry adapted d-orbitals belongs to

Table 19. Symmetry adapted single electron functions

Symmetry group Bethe Mulliken	Function	Usual designa- tion of the orbital	Designation in this thesis
$\Gamma_1 = a_1$	$ 2,0\rangle$	dz^2	(z^2)
$\Gamma_3 = b_1$	$\frac{1}{\sqrt{2}} [2,2\rangle + 2,-2\rangle]$	$dx^2 - y^2$	$(x^2 - y^2)$
$\Gamma_4 = b_2$	$\frac{1}{i\sqrt{2}} [2,2\rangle - 2,-2\rangle]$	dxy	(xy)
$\Gamma_5 = e$	$\frac{1}{\sqrt{2}} [2,-1\rangle - 2,1\rangle]$	dxz	(xz)
	$\frac{i}{\sqrt{2}} [2,-1\rangle + 2,1\rangle]$	dyz	(yz)

Table 20. Direct products of D_{4h} irreducible representation

Direct product	Irreducible repre- sentation(s)	Direct product	Irreducible representa- tion(s)
$a_1 \times a_1$	$= a_1$	$a_2 \times a_2$	$= a_1$
$a_1 \times a_2 = a_2 \times a_1$	$= a_2$	$a_2 \times b_1 =$	
		$b_1 \times a_2$	$= b_2$
$a_1 \times b_1 = b_1 \times a_1$	$= b_1$	$a_2 \times b_2 =$	
		$b_2 \times a_2$	$= b_1$
$a_1 \times b_2 = b_2 \times a_1$	$= b_2$	$a_2 \times e = e \times a_2$	$= e$
$b_1 \times b_1$	$= a_1$	$b_2 \times b_2$	$= a_1$
$a_1 \times e = e \times a_1$	$= e$	$b_2 \times e = e \times b_2$	$= e$
$b_1 \times b_2 = b_2 \times b_1$	$= a_2$	$e \times e$	$= a_1 + a_2 +$
			$b_1 + b_2$
$b_1 \times e = e \times b_1$	$= e$		

the irreducible representation, a_2 , those direct products involving this representation are not required for the spatial product functions. However, as is seen in the following section, one of the symmetry adapted spin functions for the triplet state does form a basis function for the a_2 representation, and hence it is included in Table 20.

The details of constructing the symmetry adapted two electron product functions for the D_4 group are outlined in Appendix D. The functions which result are not tabulated since the procedure is quite straightforward. A final tabulation which includes the symmetry adapted spin functions is given in Table 21. To quickly illustrate the procedure, one can consider the products of the two functions (x^2-y^2) and (xy) . Since (x^2-y^2) is a basis function for b_1 , and (xy) is a basis function for b_2 , then both product functions, $(x^2-y^2)^{(1)} \cdot (xy)^{(2)}$ and $(xy)^{(1)} \cdot (x^2-y^2)^{(2)}$ are basis functions for the irreducible representation a_2 , since $b_1 \times b_2 = a_2$. Generally, it is convenient to construct linear combinations of the two functions, one symmetric and the other antisymmetric. Thus:

$$\phi_1 = 1/\sqrt{2} [(x^2-y^2)(xy) + (xy)(x^2-y^2)] \text{ (symmetric)}$$

$$\phi_2 = 1/\sqrt{2} [(x^2-y^2)(xy) - (xy)(x^2-y^2)] \text{ (anti-symmetric)}$$

where $(x^2-y^2)(xy)$ means that (x^2-y^2) is the wave function associated with electron 1, and (xy) is the wave function associated with electron 2.

Table 21. Strong field basis functions, coordinate form

Symmetry adapted product functions in terms of Cartesian
coordinates

Γ_1 matrix:

$${}^1A_1(a_1a_1) = \frac{1}{\sqrt{2}} [(z^2)(z^2)][\alpha\beta - \beta\alpha]$$

$${}^1A_1(b_1b_1) = \frac{1}{\sqrt{2}} [(x^2-y^2)(x^2-y^2)][\alpha\beta - \beta\alpha]$$

$${}^1A_1(b_2b_2) = \frac{1}{\sqrt{2}} [(xy)(xy)][\alpha\beta - \beta\alpha]$$

$${}^1A_1(ee) = \frac{1}{2} [(xz)(xz) + (yz)(yz)][\alpha\beta - \beta\alpha]$$

$${}^3A_2(ee) = \frac{1}{2} [(xz)(yz) - (yz)(xz)][\alpha\beta + \beta\alpha]$$

$${}^3A_2(b_1b_2) = \frac{1}{2} [(x^2-y^2)(xy) - (xy)(x^2-y^2)][\alpha\beta + \beta\alpha]$$

$$\begin{aligned} {}^3E(a_1e) &= \frac{1}{\sqrt{8}} [(xz)(z^2) - (z^2)(xz)][\alpha\alpha + \beta\beta] \\ &\quad - [(yz)(z^2) - (z^2)(yz)][i][\alpha\alpha - \beta\beta] \end{aligned}$$

$$\begin{aligned} {}^3E(b_1e) &= \frac{1}{\sqrt{8}} [(xz)(x^2-y^2) - (x^2-y^2)(xz)][\alpha\alpha + \beta\beta] \\ &\quad + [(yz)(x^2-y^2) - (x^2-y^2)(yz)][i][\alpha\alpha - \beta\beta] \end{aligned}$$

$$\begin{aligned} {}^3E(b_2e) &= \frac{1}{\sqrt{8}} [(xz)(xy) - (xy)(xz)][i][\alpha\alpha - \beta\beta] \\ &\quad - [(yz)(xy) - (xy)(yz)][\alpha\alpha + \beta\beta] \end{aligned}$$

Γ_2 matrix:

$${}^1A_2(b_1b_2) = \frac{1}{2} [(x^2-y^2)(xy) + (xy)(x^2-y^2)][\alpha\beta - \beta\alpha]$$

$$\begin{aligned} {}^3E(a_1e) &= \frac{1}{\sqrt{8}} [(xz)(z^2) - (z^2)(xz)][i][\alpha\alpha - \beta\beta] \\ &\quad + [(yz)(z^2) - (yz)(z^2)][\alpha\alpha + \beta\beta] \end{aligned}$$

Table 21. (Continued)

Symmetry adapted product functions in terms of Cartesian
coordinates

Γ_2 matrix (continued):

$${}^3E (b_1e) = \frac{1}{\sqrt{8}} [(x^2-y^2)(xz) - (xz)(x^2-y^2)][i][\alpha\alpha - \beta\beta] \\ - [(x^2-y^2)(yz) - (yz)(x^2-y^2)][\alpha\alpha + \beta\beta]$$

$${}^3E (b_2e) = \frac{1}{\sqrt{8}} [(xz)(xy) - (xy)(xz)][\alpha\alpha + \beta\beta] \\ + [(yz)(xy) - (xy)(yz)][i][\alpha\alpha - \beta\beta]$$

Γ_3 matrix:

$${}^1B_1(a_1b_1) = \frac{1}{2} [(z^2)(x^2-y^2) + (x^2-y^2)(z^2)][\alpha\beta - \beta\alpha]$$

$${}^1B_1 (ee) = \frac{1}{2} [(xz)(xz) - (yz)(yz)][\alpha\beta - \beta\alpha]$$

$${}^3B_2(a_1b_2) = \frac{1}{2} [(z^2)(xy) - (xy)(z^2)][\alpha\beta + \beta\alpha]$$

$${}^3E (a_1e) = \frac{1}{\sqrt{8}} [(xz)(z^2) - (z^2)(xz)][\alpha\alpha + \beta\beta] \\ + [(yz)(z^2) - (z^2)(yz)][i][\alpha\alpha - \beta\beta]$$

$${}^3E (b_1e) = \frac{1}{\sqrt{8}} [(xz)(x^2-y^2) - (x^2-y^2)(xz)][\alpha\alpha + \beta\beta] \\ - [(yz)(x^2-y^2) - (x^2-y^2)(yz)][i][\alpha\alpha - \beta\beta]$$

$${}^3E (b_2e) = \frac{1}{\sqrt{8}} [(xz)(xy) - (xy)(xz)][i][\alpha\alpha - \beta\beta] \\ + [(yz)(xy) - (xy)(yz)][\alpha\alpha + \beta\beta]$$

Γ_4 matrix:

$${}^1B_2(a_1b_2) = \frac{1}{2} [(z^2)(xy) + (xy)(z^2)][\alpha\beta - \beta\alpha]$$

$${}^1B_2 (ee) = \frac{1}{2} [(xz)(yz) + (yz)(xz)][\alpha\beta - \beta\alpha]$$

Table 21. (Continued)

Symmetry adapted product functions in terms of Cartesian
coordinates

Γ_4 matrix (continued):

$${}^3B_1 (a_1b_1) = \frac{1}{2} [(z^2)(x^2-y^2) - (x^2-y^2)(z^2)][\alpha\beta + \beta\alpha]$$

$$\begin{aligned} {}^3E (a_1e) &= \frac{1}{\sqrt{8}} [(xz)(z^2) - (z^2)(xz)][i][\alpha\alpha - \beta\beta] \\ &\quad - [(yz)(z^2) - (z^2)(yz)][\alpha\alpha + \beta\beta] \end{aligned}$$

$$\begin{aligned} {}^3E (b_1e) &= \frac{1}{\sqrt{8}} [(xz)(x^2-y^2) - (x^2-y^2)(xz)][i][\alpha\alpha - \beta\beta] \\ &\quad + [(yz)(x^2-y^2) - (x^2-y^2)(yz)][\alpha\alpha + \beta\beta] \end{aligned}$$

$$\begin{aligned} {}^3E (b_2e) &= \frac{1}{\sqrt{8}} [(xz)(xy) - (xy)(xz)][\alpha\alpha + \beta\beta] \\ &\quad - [(yz)(xy) - (xy)(yz)][i][\alpha\alpha - \beta\beta] \end{aligned}$$

Γ_5 matrix:

$$\begin{aligned} {}^1E(a_1e) &= (1) = \frac{1}{2} [(z^2)(xz) + (xz)(z^2)][\alpha\beta - \beta\alpha] \\ &\quad (2) = \frac{1}{2} [(z^2)(yz) + (yz)(z^2)][\alpha\beta - \beta\alpha] \end{aligned}$$

$$\begin{aligned} {}^1E(b_1e) &= (1) = \frac{1}{2} [-(x^2-y^2)(xz) - (xz)(x^2-y^2)][\alpha\beta - \beta\alpha] \\ &\quad (2) = \frac{1}{2} [(x^2-y^2)(yz) + (yz)(x^2-y^2)][\alpha\beta - \beta\alpha] \end{aligned}$$

$$\begin{aligned} {}^1E(b_2e) &= (1) = \frac{1}{2} [(xy)(yz) + (yz)(xy)][\alpha\beta - \beta\alpha] \\ &\quad (2) = \frac{1}{2} [(xy)(xz) + (xz)(xy)][\alpha\beta - \beta\alpha] \end{aligned}$$

$$\begin{aligned} {}^3E(a_1e) &= (1) = \frac{1}{2} [(z^2)(yz) - (yz)(z^2)][\alpha\beta + \beta\alpha] \\ &\quad (2) = \frac{1}{2} [-(z^2)(xz) + (xz)(z^2)][\alpha\beta + \beta\alpha] \end{aligned}$$

Table 21. (Continued)

Symmetry adapted product functions in terms of Cartesian
coordinates

Γ_5 matrix continued:

$${}^3E(b_1e) = \begin{aligned} (1) &= \frac{1}{2} [(x^2-y^2)(yz) - (yz)(x^2-y^2)][\alpha\beta + \beta\alpha] \\ (2) &= \frac{1}{2} [(x^2-y^2)(xz) - (xz)(x^2-y^2)][\alpha\beta + \beta\alpha] \end{aligned}$$

$${}^3E(b_2e) = \begin{aligned} (1) &= \frac{1}{2} [(xy)(xz) - (xz)(xy)][\alpha\beta + \beta\alpha] \\ (2) &= \frac{1}{2} [-(xy)(yz) + (yz)(xy)][\alpha\beta + \beta\alpha] \end{aligned}$$

$${}^3B_1(a_1b_1) = \begin{aligned} (1) &= \frac{1}{2} [(z^2)(x^2-y^2) - (x^2-y^2)(z^2)][\alpha\alpha + \beta\beta] \\ (2) &= \frac{1}{2} [(z^2)(x^2-y^2) - (x^2-y^2)(z^2)][i][\alpha\alpha - \beta\beta] \end{aligned}$$

$${}^3B_2(a_1b_2) = \begin{aligned} (1) &= \frac{1}{2} [(z^2)(xy) - (xy)(z^2)][i][\alpha\alpha - \beta\beta] \\ (2) &= \frac{1}{2} [-(z^2)(xy) + (xy)(z^2)][\alpha\alpha + \beta\beta] \end{aligned}$$

$${}^3A_2(b_1b_2) = \begin{aligned} (1) &= \frac{1}{2} [(x^2-y^2)(xy) - (xy)(x^2-y^2)][i][\alpha\alpha - \beta\beta] \\ (2) &= \frac{1}{2} [(x^2-y^2)(xy) - (xy)(x^2-y^2)][\alpha\alpha + \beta\beta] \end{aligned}$$

$${}^3A_2(ee) = \begin{aligned} (1) &= \frac{1}{2} [(xz)(yz) - (yz)(xz)][i][\alpha\alpha - \beta\beta] \\ (2) &= \frac{1}{2} [(xz)(yz) - (yz)(xz)][\alpha\alpha + \beta\beta] \end{aligned}$$

3. Symmetry adapted spin functions

The spin functions, α and β , may be considered to be basis vectors for a two dimensional complex space. Therefore, in order to construct symmetry adapted spin functions one makes use of a transformation property inherent in the definition of the spin components, namely, that for every symmetry operation matrix in real space there is a corresponding matrix in complex space having the same group properties. The derivation of such matrices is discussed in Appendix D. The important conclusions to be considered from the appendix are:

A. Just as the weak field functions may be characterized by certain irreducible representations according to their values of total orbital angular momentum, J , so the spin functions can be characterized by their values of spin, S . Thus, for the integral spins, $S = 1$ and $S = 0$ in the D_4 symmetry, one obtains from Table 3:

$$S = 1 \text{ belongs to } A_2 + E$$

$$S = 0 \text{ belongs to } A_1.$$

In the case of half-integral spins, recourse to the "double groups" is necessary. See the article by Bethe (1) or McClure (23).

B. The spin basis functions corresponding to the irreducible representations are:

$$A_1: \quad \xi_1 = 1/\sqrt{2} \quad [\alpha\beta - \beta\alpha] \quad ; \text{ for singlet states, } S = 0. \quad (120)$$

$$A_2: \quad \xi_2 = 1/\sqrt{2} \quad [\alpha\beta + \beta\alpha] \quad ; \text{ for triplet states, } S = 1 \quad (121)$$

$$E: \quad \begin{array}{l} \xi_3 = 1/\sqrt{2} \quad [\alpha\alpha + \beta\beta] \\ \xi_4 = 1/\sqrt{2} \quad [\alpha\alpha - \beta\beta] \end{array} \quad ; \text{ for triplet states, } S = 1 \quad (122)$$

4. Strong field symmetry adapted functions

Combining the symmetry adapted space and spin functions to obtain the final form of the basis functions for the strong field matrices follows the same "direct product approach".

For example, consider the direct product function:

$$\psi = \phi \times \xi_2 \quad (123)$$

where $\phi = 1/\sqrt{2} [(x^2 - y^2)(xy) - (xy)(x^2 - y^2)]$, which belongs to a_2 ,

and $\xi_2 = 1/\sqrt{2} [\alpha\beta + \beta\alpha]$, which belongs to A_2 .

ψ is the basis function for the irreducible representation

$$\Gamma_1 = A_1 \text{ since } a_2 \times A_2 = A_1.$$

By similar processes all possible combinations of the spin and space functions are taken. Of course, full cognizance of the Pauli Exclusion Principle must be made. Thus, the combination of ϕ , given above, with the spin function, $\xi_1 = \frac{1}{\sqrt{2}} [\alpha\beta - \beta\alpha]$ is not allowed since both space and spin parts are antisymmetric and the total function would be symmetric.

The strong field basis functions which result for square-

planar symmetry are given in Table 21. The states are labelled $^{2S+1}\Gamma_i(u,v)$, where S is the spin of the state, Γ_i is the representation to which the spatial product function belongs, and u,v are the symmetry representations of the single electron space functions from which the function is composed.

Thus, for example, the function

$$\psi = \frac{1}{2} [(x^2-y^2)(xy) - (xy)(x^2-y^2)] [\alpha\beta + \beta\alpha] \quad (124)$$

would be ${}^3A_2(b_1b_2)$.

D. Strong Field Matrix Elements

In calculating the matrix elements of the strong field, it is convenient to convert the (z^2) , (xz) , etc., notation back to the $|l, m_l, s, m_s\rangle$ notation. Thus:

$$\begin{aligned} 1/2 [(xz)(yz) - (yz)(xz)] [\alpha\beta + \beta\alpha] &= \\ &= 1/2 \quad i/2 [| -1\rangle - | 1\rangle] [| -1\rangle + | 1\rangle] \\ &\quad - [| -1\rangle + | 1\rangle] [| -1\rangle - | 1\rangle] \{ \alpha\beta + \beta\alpha \} \\ &= 1/2i [(1, -1) - (-1, 1)] [\alpha\beta + \beta\alpha] \end{aligned} \quad (125)$$

Table 22 lists the strong field matrix elements in the $|l, m_l, s, m_s\rangle$ form. Then the ligand field matrix elements are calculated in the same way as for the weak field functions. Of course, ligand field terms appear only in the diagonal elements of the matrices.

For the LS coupling elements and the electrostatic interaction terms there are no convenient tables, as existed for the weak field functions. Hence, they are calculated from the

Table 22. Strong field basis functions, $|l, m_l, s, m_s\rangle$ formSymmetry adapted product functions in $|l, m_l, s, m_s\rangle$ form Γ_1 matrix:

$$^1A_1(a_1a_1) = \frac{1}{\sqrt{2}} [(0,0)][\alpha\beta - \beta\alpha]$$

$$^1A_1(b_1b_1) = \frac{1}{\sqrt{8}} [(2,2)+(2,-2) + (-2,2) + (-2,-2)][\alpha\beta - \beta\alpha]$$

$$^1A_1(b_2b_2) = \frac{1}{\sqrt{8}} [-(2,2) + (2,-2) + (-2,2) - (-2,-2)][\alpha\beta - \beta\alpha]$$

$$^1A_1(ee) = \frac{1}{2} [(1,-1) + (-1,1)][\alpha\beta - \beta\alpha]$$

$$^3A_2(ee) = \frac{1}{2i} [(-2,2) - (2,-2)][\alpha\beta + \beta\alpha]$$

$$^3A_2(b_1b_2) = \frac{1}{2i} [(-2,2) - (2,-2)][\alpha\beta + \beta\alpha]$$

$$^3E(a_1e) = \frac{1}{2} [(-1,0) - (0,-1)][\alpha\alpha] + [(0,1)-(1,0)][\beta\beta]$$

$$^3E(b_1e) = \frac{1}{\sqrt{8}} [(2,1) + (-2,1) - (1,2) - (1,-2)][\alpha\alpha] \\ + [(-1,2) + (-1,-2) - (2,-1) - (-2,-1)][\beta\beta]$$

$$^3E(b_2e) = \frac{1}{\sqrt{8}} [(2,1) - (-2,1) - (1,2) + (1,-2)][\alpha\alpha] \\ + [-(-1,2) + (-1,-2) + (2,-1) - (-2,-1)][\beta\beta]$$

 Γ_2 matrix:

$$^1A_2(b_1b_2) = \frac{1}{2i} [(2,2) - (-2,-2)][\alpha\beta - \beta\alpha]$$

$$^3E(a_1e) = \frac{1}{2i} [(0,-1) - (-1,0)][\alpha\alpha] + [(0,1) - (1,0)][\beta\beta]$$

$$^3E(b_1e) = \frac{1}{i\sqrt{8}} [(2,1)-(-2,1)-(1,2)+(1,-2)][\alpha\alpha] \\ + [(2,-1)-(-2,-1)+(-1,2)-(-1,-2)][\beta\beta]$$

Table 22. (Continued)

Symmetry adapted product function in $|l, m_l, s, m_s\rangle$ form

Γ_2 matrix continued:

$${}^3E(b_2e) = \frac{1}{i\sqrt{8}} [(2,1) - (-2,1) - (1,2) + (1,-2)][\alpha\alpha] \\ + [(2,-1) - (-2,-1) + (-1,2) - (-1,-2)][\beta\beta]$$

Γ_3 matrix:

$${}^1B_1(a_1b_1) = \frac{1}{\sqrt{8}} [(2,0) + (-2,0) + (0,2) + (0,-2)][\alpha\beta + \beta\alpha]$$

$${}^1B_1(ee) = \frac{1}{2} [(1,1) + (-1,-1)][\alpha\beta - \beta\alpha]$$

$${}^3B_2(a_1b_2) = \frac{1}{i\sqrt{8}} [(0,2) - (0,-2) - (2,0) + (-2,0)][\alpha\beta + \beta\alpha]$$

$${}^3E(a_1e) = \frac{1}{2} [(0,1) - (1,0)][\alpha\alpha] + [(-1,0) - (0,-1)][\beta\beta]$$

$${}^3E(b_1e) = \frac{1}{\sqrt{8}} [(-1,2) + (-1,-2) - (2,-1) - (-2,-1)][\alpha\alpha] \\ + [-(1,2) - (1,-2) + (2,1) + (-2,1)][\beta\beta]$$

$${}^3E(b_2e) = \frac{1}{\sqrt{8}} [(-1,2) - (-1,-2) - (2,-1) + (-2,-1)][\alpha\alpha] \\ + [(1,2) - (1,-2) - (2,1) + (-2,1)][\beta\beta]$$

Γ_4 matrix:

$${}^1B_2(a_1b_2) = \frac{1}{i\sqrt{8}} [(0,2) - (0,-2) + (2,0) - (-2,0)][\alpha\beta - \beta\alpha]$$

$${}^1B_2(ee) = \frac{1}{i2} [(1,1) - (-1,-1)][\alpha\beta - \beta\alpha]$$

$${}^3B_1(a_1b_1) = \frac{1}{\sqrt{8}} [(0,2) + (0,-2) - (2,0) - (-2,0)][\alpha\beta + \beta\alpha]$$

$${}^3E(a_1e) = \frac{1}{i2} [(1,0) - (0,1)][\alpha\alpha] + [(-1,0) - (0,-1)][\beta\beta]$$

Table 22. (Continued)

Symmetry adapted product function in $\{l, m_l, s, m_s\}$ form

Γ_4 matrix continued:

$${}^3E (b_1e) = \frac{1}{i\sqrt{8}} [-(-1,2) - (-1,-2) + (2,-1) + (-2,-1)] [\alpha\alpha] \\ + [-(1,2) - (1,-2) + (2,1) + (-2,1)] [\beta\beta]$$

$${}^3E (b_2e) = \frac{1}{i\sqrt{8}} [(-1,2) - (-1,-2) - (2,-1) + (-2,-1)] [\alpha\alpha] \\ + [-(1,2) + (1,-2) + (2,1) - (-2,1)] [\beta\beta]$$

Γ_5 matrix:

$${}^1E (a_1e) = \begin{aligned} (1) &= \frac{1}{\sqrt{8}} [(0,-1) - (0,1) + (-1,0) - (1,0)] [\alpha\beta - \beta\alpha] \\ (2) &= \frac{1}{i\sqrt{8}} [-(0,-1) - (0,1) - (-1,0) - (1,0)] [\alpha\beta - \beta\alpha] \end{aligned}$$

$${}^1E (b_1e) = \begin{aligned} (1) &= \frac{1}{4} [-(2,-1) - (-2,-1) + (2,1) + (-2,1) - (-1,2) \\ &\quad - (-1,-2) + (1,2) + (1,-2)] [\alpha\beta - \beta\alpha] \\ (2) &= \frac{1}{i4} [-(2,-1) - (-2,-1) - (2,1) - (-2,1) - (-1,2) \\ &\quad - (-1,-2) - (1,2) - (1,-2)] [\alpha\beta - \beta\alpha] \end{aligned}$$

$${}^1E (b_2e) = \begin{aligned} (1) &= \frac{1}{4} [(2,-1) - (-2,-1) + (2,1) - (-2,1) + (-1,2) \\ &\quad - (-1,-2) + (1,2) - (1,-2)] [\alpha\beta - \beta\alpha] \\ (2) &= \frac{1}{i4} [(2,-1) - (-2,-1) - (2,1) + (-2,1) + (-1,2) \\ &\quad - (-1,-2) - (1,2) + (1,-2)] [\alpha\beta - \beta\alpha] \end{aligned}$$

$${}^1E (a_1e) = \begin{aligned} (1) &= \frac{1}{i\sqrt{8}} [-(0,-1) - (0,1) + (-1,0) + (1,0)] [\alpha\beta + \beta\alpha] \\ (2) &= \frac{1}{\sqrt{8}} [-(0,-1) + (0,1) + (-1,0) - (1,0)] [\alpha\beta + \beta\alpha] \end{aligned}$$

Table 22. (Continued)

Symmetry adapted product function in $|l, m_l, s, m_s\rangle$ form

Γ_5 matrix continued:

$$\begin{aligned}
 {}^1E (b_1e) = \quad (1) &= \frac{1}{4i} [-(2,-1) - (-2,-1) - (2,1) - (-2,1) + (-1,2) \\
 &\quad + (-1,-2) + (1,2) + (1,-2)] [\alpha\beta + \beta\alpha] \\
 (2) &= \frac{1}{4} [(2,-1) + (-2,-1) - (2,1) - (-2,1) - (-1,2) \\
 &\quad - (-1,-2) + (1,2) + (1,-2)] [\alpha\beta + \beta\alpha]
 \end{aligned}$$

$$\begin{aligned}
 {}^1E (b_2e) = \quad (1) &= \frac{1}{4i} [(2,-1) - (-2,-1) - (2,1) + (-2,1) - (-1,2) \\
 &\quad + (-1,-2) + (1,2) - (1,-2)] [\alpha\beta + \beta\alpha] \\
 (2) &= \frac{1}{4} [-(2,-1) + (-2,-1) - (2,1) - (-2,1) + (-1,2) \\
 &\quad - (-1,-2) + (1,2) + (1,-2)] [\alpha\beta + \beta\alpha]
 \end{aligned}$$

$$\begin{aligned}
 {}^3B_1(a_1b_1) = \quad (1) &= \frac{1}{\sqrt{8}} [(0,2) + (0,-2) - (2,0) - (-2,0)] [\alpha\alpha + \beta\beta] \\
 (2) &= \frac{i}{\sqrt{8}} [(0,2) + (0,-2) - (2,0) - (-2,0)] [\alpha\alpha - \beta\beta]
 \end{aligned}$$

$$\begin{aligned}
 {}^3B_2(a_1b_2) = \quad (1) &= \frac{1}{\sqrt{8}} [(0,2) - (0,-2) - (2,0) + (-2,0)] [\alpha\alpha - \beta\beta] \\
 (2) &= \frac{1}{i\sqrt{8}} [-(0,2) + (0,-2) + (2,0) - (-2,0)] [\alpha\alpha + \beta\beta]
 \end{aligned}$$

$$\begin{aligned}
 {}^3A_2(b_1b_2) = \quad (1) &= \frac{1}{2} [(-2,2) - (2,-2)] [\alpha\alpha - \beta\beta] \\
 (2) &= \frac{1}{i2} [(-2,2) - (2,-2)] [\alpha\alpha + \beta\beta]
 \end{aligned}$$

$$\begin{aligned}
 {}^3A_2 (ee) = \quad (1) &= \frac{1}{2} [(1,-1) - (-1,1)] [\alpha\alpha - \beta\beta] \\
 (2) &= \frac{1}{i2} [(1,-1) - (-1,1)] [\alpha\alpha + \beta\beta]
 \end{aligned}$$

operator expressions. For the LS coupling terms:

$$\begin{aligned} \sum_i \tilde{s}(r_i) \tilde{L}_i \tilde{S}_i = & a(l_+(1) s_-(1) + l_-(1) s_+(1) + l_+(2) s_-(2) \\ & + l_-(2) s_+(2)) + 2a(l_j(1) s_j(1) + l_j(2) s_j(2)) \end{aligned} \quad (126)$$

For the electronic interaction terms, the general expression for two electron wave functions has been given by Condon and Shortley (6):

$$\begin{aligned} (ab|e^2/r_{ij}|cd) = & \delta(m_s^a, m_s^c) \delta(m_s^b, m_s^d) \delta(m_l^a + m_l^b, m_l^c + m_l^d) \cdot \\ & \sum_{k=0}^{\infty} c^k(l^a m_l^a, l^c m_l^c) c^k(l^d m_l^d, l^b m_l^b) F_k(n^a l^a n^b l^b, n^c l^c n^d l^d) \end{aligned} \quad (127)$$

where the F_k are the Slater-Condon Parameters and the c^k are coefficients. The methods for evaluating the c^k are outlined in Appendix D.

Application of the three operators to the functions listed in Table 22 yields the strong field matrix elements given in Tables 23 through 27.

Table 23b. Non-zero values of Γ_1 strong field matrix elements

Matrix elements	Value
v_{11}	$2Q_0 + 4F_2 + 36F_4$
$v_{21} = v_{12}^*$	$4F_2 + 15F_4$
$v_{22} -$	$2[Q_2 + B_{2-2}] + 4F_2 + 36F_4$
$v_{31} = v_{13}^*$	$4F_2 + 15F_4$
$v_{32} = v_{23}^*$	$35F_4$
v_{33}	$2[Q_2 - B_{2-2}] + 4F_2 + 36F_4$
$v_{41} = v_{14}^*$	$\sqrt{2} [F_2 + 30F_4]$
$v_{42} = v_{24}^*$	$\sqrt{2} [3F_2 + 20F_4]$
$v_{43} = v_{34}^*$	$\sqrt{2} [3F_2 + 20F_4]$
v_{44}	$2Q_1 + 7F_2 + 56F_4$
$v_{54} = v_{45}^*$	$-2 i \alpha$
v_{55}	$2Q_1 - 5F_2 - 24F_4$
$v_{62} = v_{26}^*$	$i \sqrt{8} \alpha$
$v_{63} = v_{36}^*$	$i \sqrt{8} \alpha$
$v_{65} = v_{56}^*$	$6F_2 - 30F_4$
v_{66}	$2Q_2 + 4F_2 - 69F_4$
$v_{71} = v_{17}^*$	$2 \sqrt{3} \alpha$
$v_{74} = v_{47}^*$	$-\sqrt{6} \alpha$
$v_{75} = v_{57}^*$	$-i \sqrt{6} \alpha$

Table 23a. Strong field matrix elements, d^8 configuration in square-planar symmetry, f_1 matrix^a

	1A_1 (a_1a_1)	1A_1 (b_1b_1)	1A_1 (b_2b_2)	1A_1 (ee)	3A_2 (ee)	3A_2 (b_1b_2)	3E (a_1e)	3E (b_1e)	3E (b_2e)
$^1A_1(a_1a_1)$	v_{11}	v_{12}	v_{13}	v_{14}	0	0	v_{17}	0	0
$^1A_1(b_1b_1)$	v_{21}	v_{22}	v_{23}	v_{24}	0	v_{26}	0	v_{28}	0
$^1A_1(b_2b_2)$	v_{31}	v_{32}	v_{33}	v_{34}	0	v_{36}	0	0	v_{39}
$^1A_1(ee)$	v_{41}	v_{42}	v_{43}	v_{44}	v_{45}	0	v_{47}	v_{48}	v_{49}
$^3A_2(ee)$	0	0	0	v_{54}	v_{55}	v_{56}	v_{57}	v_{58}	v_{59}
$^3A_2(b_1b_2)$	0	v_{62}	v_{63}	0	v_{65}	v_{66}	0	v_{68}	v_{69}
$^3E(a_1e)$	v_{71}	0	0	v_{74}	v_{75}	0	v_{77}	v_{78}	v_{79}
$^3E(b_1e)$	0	v_{82}	0	v_{84}	v_{85}	v_{86}	v_{87}	v_{88}	v_{89}
$^3E(b_2e)$	0	0	v_{93}	v_{94}	v_{95}	v_{96}	v_{97}	v_{98}	v_{99}

^aThe non-zero matrix elements, v_{ij} , where the first index is the row and the second is the column, are given in Table 23b.

Table 23b. (Continued)

Matrix elements	Value
v_{77}	$Q_1 + Q_0 + F_2 - 54F_4 + \alpha$
$v_{82} = v_{28}^*$	-2α
$v_{84} = v_{48}^*$	$\sqrt{2} \alpha$
$v_{85} = v_{58}^*$	$-i \sqrt{2} \alpha$
$v_{86} = v_{68}^*$	$i \sqrt{2} \alpha$
$v_{87} = v_{78}^*$	$3 \sqrt{3} [-F_2 + 5F_4]$
v_{88}	$Q_2 + Q_1 + B_{2-2} - \alpha - 5F_2 - 24F_4$
$v_{93} = v_{39}^*$	2α
$v_{94} = v_{49}^*$	$-\sqrt{2} \alpha$
$v_{95} = v_{59}^*$	$i \sqrt{2} \alpha$
$v_{96} = v_{69}^*$	$-i \sqrt{2} \alpha$
$v_{97} = v_{79}^*$	$3 \sqrt{3} [F_2 - 5F_4]$
$v_{98} = v_{89}^*$	$2\alpha - 3F_2 + 15F_4$
v_{99}	$Q_2 + Q_1 - B_{2-2} - \alpha - 5F_2 - 24F_4$

Table 24a. Strong field matrix elements, Γ_2 matrix^a

	1A_2 (b_1b_2)	3E (b_1e)	3E (b_2e)	3E (a_1e)
$^1A_2(b_1b_2)$	w_{11}	w_{12}	w_{13}	0
$^3E(b_1e)$	w_{21}	w_{22}	w_{23}	w_{24}
$^3E(b_2e)$	w_{31}	w_{32}	w_{33}	w_{34}
$^3E(a_1e)$	0	w_{42}	w_{43}	w_{44}

^aThe non-zero matrix elements, w_{ij} , are given in Table 24b.

Table 24b. Non-zero values of Γ_2 strong field matrix elements

Matrix elements	Values
w_{11}	$2Q_2 + 4F_2 + F_4$
$w_{21} = w_{12}^*$	$-\sqrt{2} \alpha$
w_{22}	$Q_2 + Q_1 + B_{2-2} - \alpha - 5F_2 - 24F_4$
$w_{31} = w_{13}^*$	$-\sqrt{2}\alpha$
$w_{32} = w_{23}^*$	$-2\alpha - 3F_2 + 15F_4$
w_{33}	$Q_2 + Q_1 - B_{2-2} - \alpha - 5F_2 - 24F_4$
$w_{42} = w_{24}^*$	$3\sqrt{3} [F_2 - 5F_4]$
$w_{43} = w_{34}^*$	$-3\sqrt{3} [F_2 - 5F_4]$
w_{44}	$Q_1 + Q_0 + \alpha + F_2 - 54F_4$

Table 25a. Strong field matrix elements, Γ_3 matrix^a

	1B_1 (a_1b_1)	1B_1 (ee)	3E (a_1e)	3E (b_1e)	3E (b_2e)	3B_2 (a_1b_2)
${}^1B_1(a_1b_1)$	x_{11}	x_{12}	x_{13}	x_{14}	0	x_{16}
${}^1B_1(ee)$	x_{21}	x_{22}	x_{23}	x_{24}	x_{25}	0
${}^3E(a_1e)$	x_{31}	x_{32}	x_{33}	x_{34}	x_{35}	x_{36}
${}^3E(b_1e)$	x_{41}	x_{42}	x_{43}	x_{44}	x_{45}	0
${}^3E(b_2e)$	0	x_{52}	x_{53}	x_{54}	x_{55}	x_{56}
${}^3B_2(a_1b_2)$	x_{61}	0	x_{63}	0	x_{65}	x_{66}

^aThe non-zero matrix elements, x_{ij} , are given in Table 25b.

Table 25b. Non-zero values of Γ_3 strong field matrix elements

Matrix elements	Values
x_{11}	$Q_2 + Q_0 + B_{2-2} + 21F_4$
$x_{21} = x_{12}^*$	$2\sqrt{3} [F_2 - 5F_4]$
x_{22}	$2Q_1 + F_2 + 16F_4$
$x_{31} = x_{13}^*$	$-\sqrt{2} \alpha$
$x_{32} = x_{23}^*$	$\sqrt{6} \alpha$
x_{33}	$Q_1 + Q_0 - \alpha + F_2 - 54F_4$
$x_{41} = x_{14}^*$	$\sqrt{6} \alpha$
$x_{42} = x_{24}^*$	$-\sqrt{2} \alpha$
$x_{43} = x_{34}^*$	$3\sqrt{3} [-F_2 + 5F_4]$
x_{44}	$Q_2 + Q_1 + B_{2-2} + \alpha - 5F_2 - 24F_4$
$x_{52} = x_{25}^*$	$\sqrt{2} \alpha$
$x_{53} = x_{35}^*$	$3\sqrt{3} [-F_2 + 5F_4]$
$x_{54} = x_{45}^*$	$-2\alpha + 3F_2 - 15F_4$
x_{55}	$Q_2 + Q_1 - B_{2-2} + \alpha - 5F_2 - 24F_4$
$x_{61} = x_{16}^*$	$2i \alpha$
$x_{63} = x_{36}^*$	$-i\sqrt{2} \alpha$
$x_{65} = x_{56}^*$	$-i\sqrt{6} \alpha$
x_{66}	$Q_2 + Q_0 - B_{2-2} - 8F_2 - 9F_4$

Table 26a. Strong field matrix elements, Γ_4 matrix^a

	$^1B_2(a_1b_2)$	$^1B_2(ee)$	$^3E(a_1e)$	$^3E(b_1e)$	$^3E(b_2e)$	$^3B_1(a_1b_1)$
$^1B_2(a_1b_2)$	y_{11}	y_{12}	y_{13}	0	y_{15}	y_{16}
$^1B_2(ee)$	y_{21}	y_{22}	y_{23}	y_{24}	y_{25}	0
$^3E(a_1e)$	y_{31}	y_{32}	y_{33}	y_{34}	y_{35}	y_{36}
$^3E(b_1e)$	0	y_{42}	y_{43}	y_{44}	y_{45}	y_{46}
$^3E(b_2e)$	y_{51}	y_{52}	y_{53}	y_{54}	y_{55}	0
$^3B_1(a_1b_1)$	y_{61}	0	y_{63}	y_{64}	0	y_{66}

^aThe non-zero matrix elements, y_{ij} , are given in Table 26b.

Table 26b. Non-zero values of Γ_4 strong field matrix elements

Matrix elements	Values
Y_{11}	$Q_2 + Q_0 - B_{2-2} + 21F_4$
$Y_{21} = Y_{12}^*$	$2\sqrt{3} [F_2 - 5F_4]$
Y_{22}	$2Q_1 + F_2 + 16F_4$
$Y_{31} = Y_{13}^*$	2α
$Y_{32} = Y_{23}^*$	$-\sqrt{6} \alpha$
Y_{33}	$Q_1 + Q_0 - \alpha + F_2 - 54F_4$
$Y_{42} = Y_{24}^*$	-2α
$Y_{43} = Y_{34}^*$	$3\sqrt{3} [-F_2 + 5F_4]$
Y_{44}	$Q_2 + Q_1 + B_{2-2} + \alpha - 5F_2 - 24F_4$
$Y_{51} = Y_{15}^*$	$\sqrt{6} \alpha$
$Y_{52} = Y_{25}^*$	$-\sqrt{2} \alpha$
$Y_{53} = Y_{35}^*$	$3\sqrt{3} [F_2 - 5F_4]$
$Y_{54} = Y_{45}^*$	$-3F_2 + 15F_4 + 2\alpha$
Y_{55}	$Q_2 + Q_1 - B_{2-2} + \alpha - 5F_2 - 24F_4$
$Y_{61} = Y_{16}^*$	$-2i \alpha$
$Y_{63} = Y_{36}^*$	$-i\sqrt{2} \alpha$
$Y_{64} = Y_{46}^*$	$-i\sqrt{6} \alpha$
Y_{66}	$Q_2 + Q_0 + B_{2-2} - 8F_2 - 9F_4$

Table 27a. Strong field matrix elements, Γ_5 matrix^a

	1E (a_1e)	1E (b_1e)	1E (b_2e)	3E (a_1e)	3E (b_1e)	3E (b_2e)	3B_1 (a_1b_1)	3B_2 (a_1b_2)	3A_2 (b_1b_2)	3A_2 (ee)
$^1E(a_1e)$	z_{11}	z_{12}	z_{13}	z_{14}	0	0	z_{17}	z_{18}	0	z_{1X}
$^1E(b_1e)$	z_{21}	z_{22}	z_{23}	0	z_{25}	z_{26}	z_{27}	0	z_{29}	0
$^1E(b_2e)$	z_{31}	z_{32}	z_{33}	0	z_{35}	z_{36}	0	z_{38}	0	z_{3X}
$^3E(a_1e)$	z_{41}	0	0	z_{44}	z_{45}	z_{46}	z_{47}	z_{48}	0	z_{4X}
$^3E(b_1e)$	0	z_{52}	z_{53}	z_{54}	z_{55}	z_{56}	z_{57}	0	z_{59}	z_{5X}
$^3E(b_2e)$	0	z_{62}	z_{63}	z_{64}	z_{65}	z_{66}	0	z_{68}	z_{69}	z_{6X}
$^3B_1(a_1b_1)$	z_{71}	z_{72}	0	z_{74}	z_{75}	0	z_{77}	z_{78}	0	0
$^3B_2(a_1b_2)$	z_{81}	0	z_{83}	z_{84}	0	z_{86}	z_{87}	z_{88}	0	0
$^3A_2(b_1b_2)$	0	z_{92}	0	0	z_{95}	z_{96}	0	0	z_{99}	z_{9X}
$^3A_2(ee)$	z_{X1}	z_{X2}	z_{X3}	z_{X4}	z_{X5}	z_{X6}	0	0	z_{X9}	z_{XX}

^aThe non-zero matrix elements, z_{ij} , are given in Table 27b. The tenth row and tenth column are indicated by the Roman numeral, X.

Table 27b. Non-zero values of Γ_5 strong field matrix elements

Matrix elements	Values
z_{11}	$Q_1 + Q_0 + 3F_2 + 6F_4$
$z_{21} = z_{12}^*$	$\sqrt{3} [F_2 - 5F_4]$
z_{22}	$Q_2 + Q_1 + B_{2-2} + F_2 + 16F_4$
$z_{31} = z_{13}^*$	$\sqrt{3} [-F_2 + 5F_4]$
$z_{32} = z_{23}^*$	$3F_2 - 15F_4$
z_{33}	$Q_2 + Q_1 - B_{2-2} + F_2 + 16F_4$
$z_{41} = z_{14}^*$	$i\alpha$
z_{44}	$Q_1 + Q_0 + F_2 - 54F_4$
$z_{52} = z_{25}^*$	$-i\alpha$
$z_{53} = z_{35}^*$	$2i\alpha$
$z_{54} = z_{45}^*$	$3\sqrt{3} [F_2 - 5F_4]$
z_{55}	$Q_2 + Q_1 + B_{2-2} - 5F_2 - 24F_4$
$z_{62} = z_{26}^*$	$2i\alpha$
$z_{63} = z_{36}^*$	$-i\alpha$
$z_{64} = z_{46}^*$	$-3\sqrt{3} [F_2 - 5F_4]$
$z_{65} = z_{56}^*$	$-3F_2 + 15F_4$
z_{66}	$Q_2 + Q_1 - B_{2-2} - 5F_2 - 24F_4$
$z_{71} = z_{17}^*$	$-\alpha$
$z_{72} = z_{27}^*$	$\sqrt{3}\alpha$
$z_{74} = z_{47}^*$	$-i\alpha$
$z_{75} = z_{57}^*$	$i\sqrt{3}\alpha$

Table 27b. (Continued)

Matrix elements	Values
z_{77}	$Q_2 + Q_0 + B_{2-2} - 8F_2 - 9F_4$
$z_{81} = z_{18}^*$	α
$z_{83} = z_{38}^*$	$\sqrt{3} \alpha$
$z_{84} = z_{48}^*$	$i\alpha$
$z_{86} = z_{68}^*$	$i \sqrt{3} \alpha$
$z_{87} = z_{78}^*$	-2α
z_{88}	$Q_2 + Q_0 - B_{2-2} - 8F_2 - 9F_4$
$z_{92} = z_{29}^*$	$-\alpha$
$z_{95} = z_{59}^*$	$i\alpha$
$z_{96} = z_{69}^*$	$-i\alpha$
z_{99}	$2Q_2 + 4F_2 - 69F_4$
$z_{x1} = z_{1x}^*$	$\sqrt{3} \alpha$
$z_{x2} = z_{2x}^*$	$-\alpha$
$z_{x3} = z_{3x}^*$	α
$z_{x4} = z_{4x}^*$	$i \sqrt{3} \alpha$
$z_{x5} = z_{5x}^*$	$-i\alpha$
$z_{x6} = z_{6x}^*$	$i\alpha$
$z_{x9} = z_{9x}^*$	$-6F_2 + 30F_4$
z_{xx}	$2Q_1 - 5F_2 - 24F_4$

VI. COMPUTER TECHNIQUES

A. Over-all Program

From the previous considerations, it is clear that the determination of the energy levels of the platinum(II) complexes consists in the diagonalization of the five matrices: Γ_1 , Γ_2 , Γ_3 , Γ_4 , Γ_5 . The matrix elements are functions of five parameters: F_2 , F_4 , α , μ , and X , where F_2 and F_4 are the electronic interaction (Slater-Condon) parameters, α is the spin-orbit coupling parameter, μ is the "effective dipole moment" of the ligands, and $X = 1.8875 R$, where R is the "effective radial distance" of the ligands.

The over-all method for determination of the "correct" combination of the parameters was to fix the values of four of them by reasonable physical considerations and vary the fifth parameter to obtain a set of curves which describe the changes in the theoretical energy levels as a function of that parameter. When "near correlation" of the differences in the theoretical energy levels with the experimental absorption spectra was obtained, the effects of changes in the other four parameters on the energy levels were determined. By repeated adjustment of the parameters the choice of the best set was made. This repetitive approach, indeed the diagonalization of five large matrices for even one set of parameters, would have been essentially impossible without a computer.

All the calculations made in connection with this thesis

were done by means of the Cyclone Digital Computer at Iowa State University of Science and Technology. The "Cyclone" is a digital computer having a random access electronic memory, employing a perforated tape input and a tape or Teletype printer output. A detailed description of the nature and operation of the computer can be found in the programming manual (34).

At the time the computations were made, the memory of the Cyclone was limited to 1024 storage positions. For this reason, it was necessary to separate the calculations of the energy levels into two parts: 1) the calculation of the matrix elements, and 2) the diagonalization of the matrices. As this is being written, a program for the expansion of the memory of the Cyclone is being considered. Since this will result in changes in the coding of commands, subroutines, etc., the detailed programs will not be included in this thesis. However, a copy of the sequence of commands, as well as tape copies, of the programs used are on file at the computer facility.

B. Calculation of the Matrix Elements

For the most part, the calculation of the matrix elements for a particular set of the five parameters consisted of simple multiplication and addition. However, in order to evaluate the ligand field integrals, $B_2(X)$ and $B_4(X)$ given

in Table 6, without loss of significant figures, it was necessary to employ a "floating decimal routine". This is a subroutine for the computer such that all numbers could be manipulated in the form $A \times 10^p$, where p is either a positive or negative integer.

In general terms, the first computer program was designed so that upon entry of the chosen values of the five parameters in the floating decimal form, the computer would calculate the ligand field integrals $B_2(X)$ and $B_4(X)$. Their values were both stored in the memory and printed on the output tape. The single-electron ligand field matrix elements, Q_2 , Q_1 , Q_0 , and $B_{2,-2}$, were then calculated from the values of the B_2 and B_4 integrals and the chosen value of μ . These values were stored and printed. The complete matrix elements were then calculated from the single-electron matrix elements and the chosen values of the parameters F_2 , F_4 , and α . These values were then printed in the sequence required for the diagonalization program so that the output tape from this first program could be used as the data input tape of the diagonalization program. All output data were printed in the floating decimal format, the matrix elements for all five matrices, Γ_1 , Γ_2 , etc., being printed in turn.

The tremendous advantage achieved by use of the computer to calculate the matrix elements is illustrated by the fact that a sample computation which took the computer two minutes

to carry out, required eight hours when the calculations were made by means of a desk calculator.

C. Diagonalization of the Matrices

The computer programming required for the diagonalization of the matrices was greatly simplified by the availability of a subroutine. This subroutine calculated the eigenvalues and eigenvectors of the matrices by utilizing the Jacobi iteration technique as outlined in the text by Bodewig (35). This method requires that the matrix elements be scaled such that $\sum_{i=1} m_i^2 < \frac{1}{2}$, where m is an element of the matrix, and the summation is over all the elements of the matrix. This was another reason why it was convenient to have the calculations separated into two parts. Inspection of the answers from the first program allowed the inclusion of appropriate scaling factors into the second program to be made.

One comment concerning the diagonalization of the matrices involving complex numbers is in order. Since the computer handles only real numbers, it is necessary to expand the matrix. Bodewig (35) points out that if the hermetian matrix, \underline{A} , contains complex numbers, that is if

$$\underline{A} = \underline{M} + i\underline{N} \quad (128)$$

then the complex system of order n can be replaced by a real system of order $2n$ by the matrix:

$$\underline{B} = \begin{pmatrix} \underline{M} & -\underline{N} \\ \underline{N} & \underline{M} \end{pmatrix} \quad (129)$$

Upon diagonalization of the matrix \underline{B} , the eigenvalues of \underline{A} will appear twice.

This requires, for example, that the 6 x 6 matrix for the weak field Γ_3 matrix given in Table 16 be expanded to a 12 x 12 matrix, and the matrix elements in the first program be calculated accordingly.

Generally, the total computer time required for evaluation of all the energy levels for one set of the five parameters took approximately twelve minutes.

VII. RESULTS AND DISCUSSION

A. Experimental Results

1. Absorption spectra

The transitions of the electrons of the central ion from the ground state to the excited states, as indicated in section II-B-1, give rise to the absorption spectrum of the transition metal complex. The absorption maxima correspond to the energies involved in the transitions.

The absorption spectra of the platinum(II) complexes studied were obtained by means of a Cary recording spectrophotometer, model 12, manufactured by Applied Physics Corp., Pasadena, California. Some of the spectra were available as a result of previous investigations carried out at Iowa State University of Science and Technology (36, 37). The original spectra obtained in these investigations were available for study. All such spectra were in essential agreement with the results obtained by Chatt, et al. (2). The values of the frequencies of the absorption maxima and their extinction coefficients for the complexes considered by Chatt, et al. (2) appear in Table 28. Some of these assignments should be taken with reservation, as indicated by the following section on Gaussian analysis.

Since the absorption spectra with which this thesis is concerned are those which Chatt et al. (2) studied, and hence

Table 28. Absorption maxima of platinum(II) complexes^a

Complex	$\nu \times 10^4 \text{cm}^{-1}$	ϵ_{max}^b	$\nu \times 10^4 \text{cm}^{-1}$	ϵ_{max}
	Peak 1		Peak 2	
$[\text{PtCl}_4]^{=}$	3.02	64	2.55	59
$[\text{Pt}(\text{NH}_3)\text{Cl}_3]^{-}$	3.33	74	2.89	118
trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	3.67	75	3.17	60
trans- [$(\text{C}_5\text{H}_{11})_2\text{NH}_2\text{PtCl}_2$]	3.71	97	3.12	67
cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	3.72	69	3.31	128
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]^{+}$	3.92 ^c	117	3.60	40
	Peak 3		Peak 4 ^d	
$[\text{PtCl}_4]^{=}$	2.10	15.0	1.77	2.6
$[\text{Pt}(\text{NH}_3)\text{Cl}_3]^{-}$	2.41	19.8	2.07	2.8
trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	2.68	21.4	--	--
trans- [$(\text{C}_5\text{H}_{11})_2\text{NH}_2\text{PtCl}_2$]	2.64	21.8	2.26	2.2
cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	2.73	23.0	2.40	3.2
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]^{+}$	3.10	32.5	--	--

^aTaken from Chatt et al. (2) and confirmed by repetition of the curve analysis.

^b ϵ_{max} is the extinction coefficient of the peak maxima in units of $\text{cm}^{-1} \times (\text{Moles of complex ion/liter})^{-1}$.

^cThis value, which differs from that given by Chatt et al. (2), is the result of a recent analysis of the spectra by Ferruccio Aprile, Department of Chemistry, Iowa State University of Science and Technology. Data from spectra analysis. Private communication. 1961.

^dPeak 4 is the assignment given by Chatt et al. (2). Its contribution, if included in Peak 3, would be so small that it would not change the frequency of the maxima of Peak 3.

are already available, reproduction of all the curves will not be included. A typical absorption spectrum, that of an aqueous solution of $[\text{PtCl}_4]^-$ ion, is given in Figure 9. At first glance, three absorption maxima are apparent. In addition, for each complex, there appears to be an intense peak at a relatively high frequency, $> 4.5 \times 10^4 \text{ cm}^{-1}$, whose maximum extinction coefficient is greater than 2000. This maximum is beyond the range of the detectable frequencies of the spectrophotometer.

When one, two, or more NH_3 molecules are substituted for Cl^- ions in the $[\text{PtCl}_4]^-$ complex, appreciable changes take place in the extinction coefficients of the maxima. However, as illustrated by Figure 10 and the values in Table 28, the absorption maxima appear to shift to higher and higher frequencies in a rather uniform fashion. This is in keeping with the spectrochemical series discussed in section II-B-2. Chatt et al. (2) consider such a trend as indicative that despite the decrease in symmetry which results when the NH_3 molecules are introduced into the complexes the transitions involved in the absorption spectra remain unchanged. For example, if Peak 2 in the $[\text{PtCl}_4]^-$ spectra arises from the singlet-to-singlet transition $(xy) \rightarrow (x^2-y^2)$, then the corresponding peak in the $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$ spectra is due to the same transition. In effect, such an assumption, which is not without precedent in theoretical ligand field studies (27, 28), simplifies the

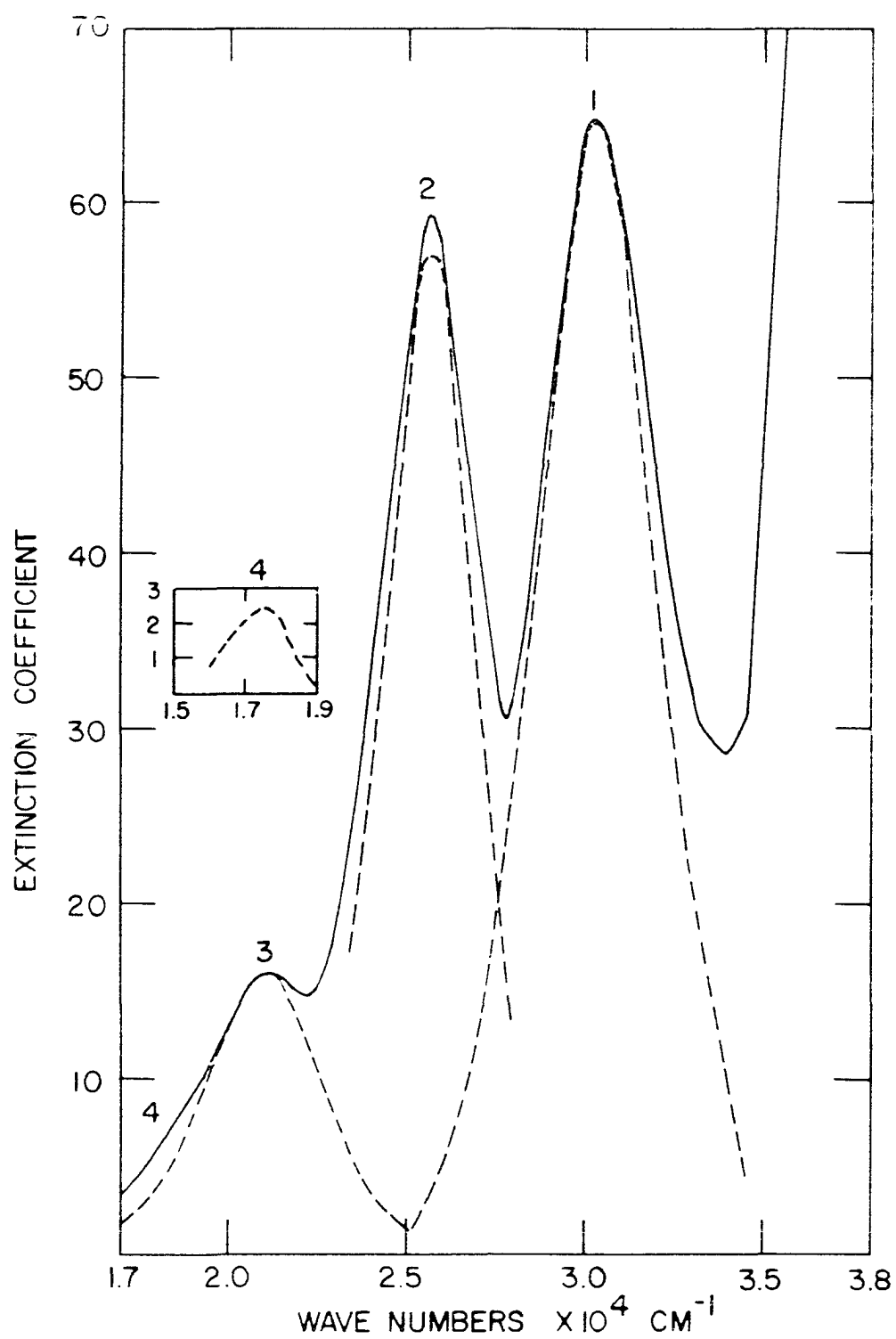


Figure 9. Absorption spectra of $[\text{PtCl}_4]^{2-}$ in aqueous solution

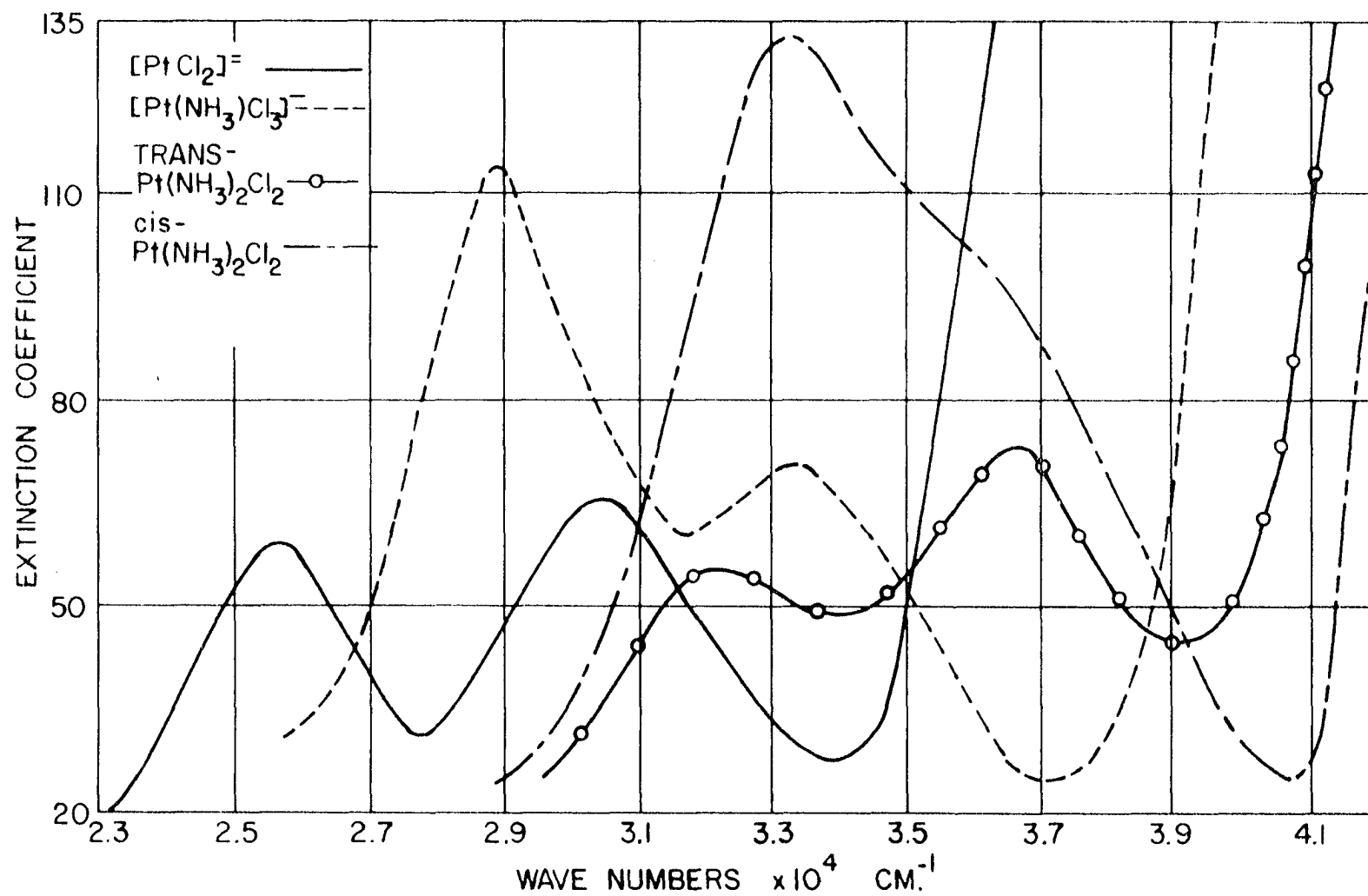


Figure 10. The two main peaks of the absorption spectra of several platinum(II) complexes

calculations by assigning to the substituted complexes a symmetry, D_{4h} , which is greater than that which they actually possess. This assumption is also applied in this thesis. As a consequence, a single radial distance, R , is used and assumed to be reasonably applicable to all central ion to ligand distances. As a result an effective ligand dipole moment, μ' , which is actually a weighted average of the individual ligand dipoles, can be assigned to each complex.

2. Gaussian analysis of the spectra

In order to assign suitable frequency values to the absorption maxima, the absorption curves were analyzed by the technique outlined by Jorgensen (38). This method assumes that the absorption peaks follow a Gaussian distribution given by the equation:

$$\epsilon = (\epsilon_0) \exp [-a(\nu - \nu_0)^2],$$

where ν = frequency of the light being absorbed,

ϵ = extinction coefficient for the frequency, ν ,

ϵ_0 = maximum extinction coefficient,

ν_0 = frequency of the maximum ϵ_0

a = constant

Application of this technique to the absorption spectra of $[\text{PtCl}_4]^-$ in aqueous solution results in the dotted-line curves given in Figure 9. The values of ϵ_0 , ν_0 , and a , are those given by Chatt et al. (2). Notice that as a result of such an

analysis, those authors obtained a fourth absorption maxima at a frequency of $1.77 \times 10^4 \text{ cm}^{-1}$. That is, they contend that the third maxima is actually the result of two transitions which are fairly close to each other in energy and hence appear as one peak.

It is certainly possible that the third absorption maxima could be the result of two transitions rather than one. However, to make the rather arbitrary analysis given in Figure 9 and to assign the energies of the two transitions, see Table 28, on the basis of the small residual extinction coefficient of Peak 4 seems to be somewhat unjustified. This point is considered again in the following section.

B. Qualitative Interpretation

It is quite well known (39) that complexes of platinum(II) are diamagnetic and square-planar. This suggests that a strong field description for the energy levels is reasonable, since the electrons must be paired. Figure 11 gives the two possible energy level assignments. Figure 11a indicates the levels as given by Chatt et al. (2). Figure 11b gives the choice preferred as a result of the calculations reported in this thesis. The difference between the two lies in the positions of the (z^2) and the $(xz)(yz)$ orbitals.

In either assignment, the ground state requires that the (x^2-y^2) orbital be empty. It is reasonable then that the

—————(x^2-y^2)

↑↓ ———(xy)

↑↓ ↑↓ ———(xz)(yz)

↑↓ ———(z^2)

SUGGESTED BY CHATT. *et. al.*(2)

a.

—————(x^2-y^2)

↑↓ ———(xy)

↑↓ ———(z^2)

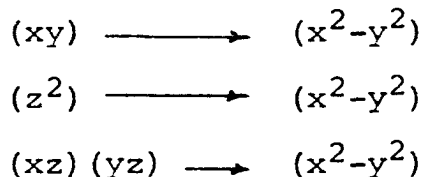
↑↓ ↑↓ ———(xz)(yz)

SUGGESTED BY THIS THESIS

b.

Figure 11. Alternative energy level assignments for square-planar platinum(II) complexes

excited states consist of configurations in which an electron has been promoted from one of the lower orbitals to the (x^2-y^2) orbital. One could expect then that the absorption peaks would appear as a result of the transitions:



A hasty conclusion might be that the three absorption maxima given in Figure 9 could be assigned to these transitions. Such a judgement overlooks the fact that Peak 3 in the figure differs appreciably in its maximum extinction coefficient from those of Peaks 1 and 2. Furthermore, Chatt et al. (2) have given strong arguments that Peak 2 must be due to the transition, $(xy) \longrightarrow (x^2-y^2)$, since Peak 2 is not shifted by changes in solvent. But this transition must be lower in energy than either of the other two possibilities. The question as to the nature of Peak 3 then arises.

The foregoing discussion assumed that the transitions were from a singlet ground state to a singlet excited state. Indeed in elements where the spin-orbit coupling is small, such an assumption is justified since electronic transitions of the type, singlet-to-triplet, are forbidden. However, platinum has appreciable spin-orbit coupling (23) and hence mixing of the singlet and triplet states result. One can view this, in a sense, as imparting singlet "character" to the triplet state.

Thus, singlet-to-triplet transitions may be possible, although one would expect such a transition to be less probable, and hence its extinction coefficient would be less than that for singlet-to-singlet transitions. But this is exactly what is evident in the case of Peak 3 in Figure 9. Therefore, it is reasonable to assign to this peak the singlet-to-triplet transitions corresponding to the singlet-to-singlet transitions given by Peaks 1 and 2, the latter being assigned to the transition, $(xy) \rightarrow (x^2-y^2)$.

Since Peaks 1 and 2 are nearly equivalent in intensity, it seems reasonable to assume that their singlet-to-triplet transitions would be the same. This would not be the case if one accepted the Gaussian analysis of Chatt et al. (2). It seems more appropriate to assign the frequency of Peak 3 as an average value of the frequencies of the two singlet-to-triplet transitions.

Because of the near equality of intensities of Peaks 1 and 2, the former can be designated as a singlet-to-singlet transition. However, whether this transition is from the (z^2) orbital or the $(xz)(yz)$ orbitals depends upon the choice between the energy level schemes in Figures 11a or 11b.

Note that in either case, one singlet-to-singlet transition is presumed to be absent in the absorption spectra. This situation is understandable when one realizes that all the transitions under discussion are transitions within the d^8

configuration. Such transitions are usually forbidden and become allowed only as a result of vibrational interactions (7, 26). Consequently, if one of these transitions involves an energy requirement which approaches the energy of an allowed transition, for example, the transition of an electron from 5d to 6p, the absorption peak due to the "forbidden" transition will be lost in the absorption peak which appears as a result of the allowed transition. By reason of its apparently high extinction coefficient, the unassigned peak with $\nu_0 > 3.5 \times 10^4 \text{ cm}^{-1}$ which appears in Figure 9, is assumed to be such a d-to-p transition. The third expected singlet-to-singlet transition is presumed to be "buried" under this transition.

In order to assign the transition which results in Peak 1, it is necessary to turn to quantitative calculations. Such calculations should require that having set the value of a ligand field parameter from the experimental value of the singlet-to-singlet transitions, $(xy) \rightarrow (x^2-y^2)$, that is, from Peak 2, one can predict values for the other transitions which agree with the experimental results for Peaks 1 and 3.

C. Theoretical Calculations

1. Initial choice of parameter values

In essence, the calculations of the theoretical energy levels depend upon the five parameters, F_2 and F_4 from the electronic interaction; α from the spin-orbit coupling; and μ

and R from the ligand field potential. A reasonable approach seemed to be to fix as many of these parameters as possible from independent data and to vary the remaining parameter or parameters to obtain approximate solutions. Then one could vary the originally fixed parameters to ascertain whether small changes in these values would improve the solutions.

It was felt that the electronic interaction parameters, F_2 and F_4 , and the spin-orbit parameter, α , could be estimated from atomic spectra and atomic theory, while the radial distance, R , could be obtained from internuclear distances determined by x-ray diffraction techniques. Thus, the only really "free" parameter would be the effective dipole moment, u .

a. The electronic interaction parameters, F_2 and F_4

It was initially hoped that the differences in the energy levels, 3F , 3P , 1D , etc., for the weak field calculations could be directly obtained from empirical data from atomic spectroscopy. However, while the energy levels of platinum and platinum(I) are available (40), work on the platinum(II) emission spectra has not been initiated.⁴ However, values for these parameters can be reasonably estimated from atomic theory.

It has been fairly well established (6) that the relation

⁴Sitterly, Charlotte Moore. National Bureau of Standards, Washington, D. C. Atomic energy levels program. Private communication. 1960.

between F_2 and F_4 can be approximated by: $F_2 \approx 11 F_4$. By use of this relation and the energy level tables (40) for platinum(I), one can estimate that the value of F_4 should be approximately 4.0×10^{-4} atomic units.⁵ The estimate made by Chatt et al. (2) for F_4 in the complex was 3.92×10^{-4} atomic units. This latter value has been chosen as the fixed value for F_4 , since a decrease in the electronic interaction parameter seems to result on passing from the free ion to the complex (41).

b. The spin-orbit coupling parameter, α McClure (23) has listed the spin-orbit coupling values, $\alpha = 1/2 \xi$, for many of the elements. From this tabulation, α for platinum has been fixed at 9.4×10^{-3} atomic units. However, it is convenient initially to keep the singlet and triplet states separate so that one can follow the course of the "preferred" transitions, that is, the singlet-to-singlet transitions for the strong field case. Therefore, in the first approximation of the appropriate parameter values, the spin-orbit coupling parameter was kept at zero. The final values must include appreciable spin-orbit coupling, however, since appreciable coupling takes place in platinum and the justification of the intensity of the singlet-to-triplet transition depends upon it.

⁵This estimate was based on the experimental difference between the $4F_{9/2} 5d^8 ({}^3F)6s$ level and the $4P_{5/2} 5d^8 ({}^3P)6s$ level. For the theoretical difference, in terms of Slater-Condon parameters see p. 203 of the text by Condon and Shortley (6).

c. The effective radial distance, R

If one can pre-

sume that the internuclear distances in a complex do not change appreciably from the solid to the solution, an estimate of the radial distance, R, can be made from x-ray diffraction data. Dickinson (42) has determined the platinum to chlorine distance in K_2PtCl_4 to be $2.33 \pm .05 \text{ \AA}$, while the platinum to ammonia distance, measured in mixed complexes (43, 44), is approximately 2.2 \AA . These distances give values of X equal to 8.5 a.u. and 8.0 a.u. respectively. The value of 8.0 a.u. was initially chosen for X since it had been the experience of certain authors (27, 28) that a distance somewhat smaller than the internuclear distance resulted in better agreement between theory and experiment.

d. The use of point dipoles in comparison with point

charges

Ballhausen (27) points out that in dealing with halide complexes one should consider that the perturbation on the central ion energy levels is due both to the charge of the halide ion and the induced dipole moment of the latter caused by the influence of the central ion. Chatt et al. (2) suggest that in halo-platinum complexes, some $d\pi-d\pi$ bonding takes place. Such interaction would further tend to distort the charge distribution about the halide ions to make them appear more like dipoles than spherical charges. Furthermore, the substituted groups are ammonia molecules and hence should be considered as dipoles in ligand field terms. Therefore, in

order to keep the calculations as simple as possible, it was decided to use the dipole expressions for all the ligand species. This simplification has also been employed by Maki (29) in certain applications.

2. Energy levels as a function of dipole moment

To summarize the foregoing discussions, the initial choices of parameters were:

$$\begin{aligned}
 F_4 &= 3.92 \times 10^{-4} \text{ atomic units (a.u.)} \\
 F_2 &= 14 F_4 = 5.488 \times 10^{-3} \text{ a.u.} \\
 \alpha &= 0 \\
 X &= fR = 8.0 \text{ a.u.} \\
 \mu &= \text{variable}
 \end{aligned}$$

The values of μ ranged from 0 to 3.5 a.u. A plot of the resultant energy levels is given in Figure 12. To avoid confusion, only those levels which might be relevant are drawn in detail. While the group notations, 1A_1 , 1A_2 , etc., are no longer completely valid because of the mixing of the states, the eigenfunctions indicate that the states are essentially those given and it is convenient to retain them in order to discuss the transitions qualitatively.

The figure clearly illustrates the difference between the weak and strong field cases. When μ is less than 1.0 a.u., the ground state is seen to be a triplet state resulting from the 3F state, and the "allowed" transitions within the d^2

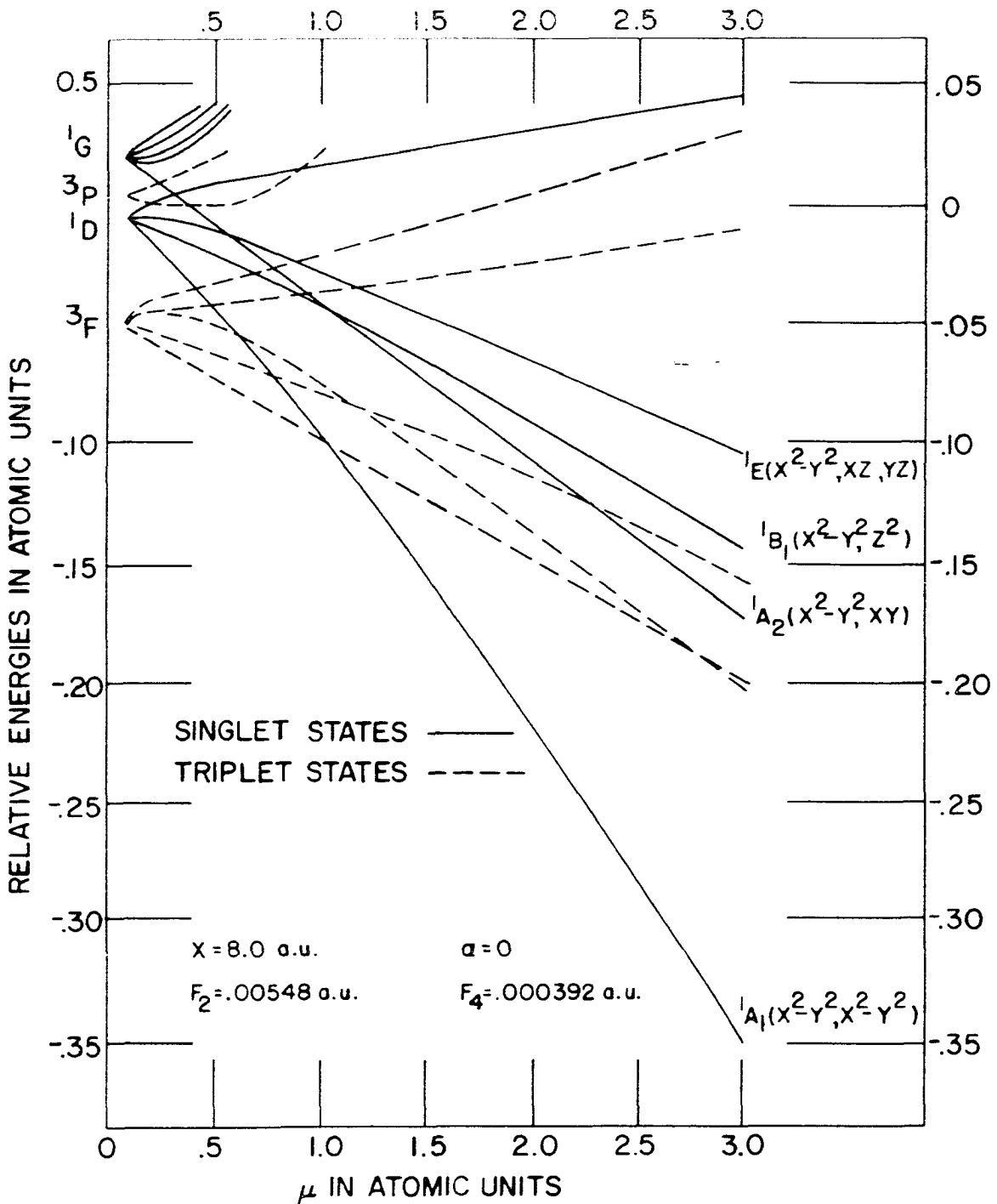


Figure 12. Relative energy levels, initial choice of parameters [The zero point energy level is below absolute zero energy by an amount equal to the integrals $E_0 + F_0$. See Condon and Shortley (6).]

configuration would be triplet-to-triplet transitions, particularly within the 3F states split by the ligand field. When μ is greater than 1.0 a.u., the ground state is a singlet state whose original source is the 1D state. The electrons in such a case are all paired and the complex would be diamagnetic. The preferred transitions in the strong field case are singlet-to-singlet transitions. The most likely transitions are between the 1A_1 ground state and the states given at the right hand of Figure 12. For convenience, the unoccupied orbitals are listed in parentheses following the group theory notation. The following observations concerning the levels are noteworthy:

1. In accordance with the qualitative discussion, the lowest energy singlet-to-singlet transition in the strong field case, for example $\mu > 2.0$ a.u. is to the 1A_2 state, that is, the electron transition is from the (xy) orbital to the (x^2-y^2) orbital.
2. The next lowest singlet-to-singlet transition is from 1A_1 to 1B_1 , that is the electron transition is from the (z^2) to the (x^2-y^2) orbital, while the transition from the doublet, (xz)(yz) orbital to the (x^2-y^2) orbital requires greater energy. If energies are involved in the transitions from the 1A_1 to 1A_2 and 1B_1 which give agreement with the experimental absorption spectra, it would appear that the (z^2) orbital is above the (xz)(yz) doublet,

that is, Figure 11b is preferable to that suggested by Chatt et al. (2), Figure 11a.

3. The three lowest triplet levels which originate from the 3F state follow a pattern favorable to the interpretation given in the qualitative discussion. At dipole moments greater than 2.0 a.u., the highest of the three is "lost" in the preferred singlet-to-singlet transition. The two lower levels have energy values which are nearly equal and hence transitions to them would appear as one absorption peak.

If one plots the differences in energy between the 1A_1 ground state and the excited states, 1A_2 , 1B_1 , 1E , and the two lowest triplet states given in Figure 12, as a function of dipole moment, one obtains the curves given in Figure 13. For convenience, the energies in the figure are given in terms of wave numbers so that direct comparison of the theoretical transition energies with the results given in Table 28 may be made.

From the previous discussion, it has been indicated that absorption Peak 2 of Table 28 is a result of the transition, singlet-to-singlet $(xy) \longrightarrow (x^2-y^2)$, or in group theory notation, $^1A_1 \longrightarrow ^1A_2$. By using the values of this peak as a standard, one can fix the corresponding effective dipole moments for the complexes and predict the theoretical values for Peaks 1 and 3. By this procedure, the results given in Table 29 have been obtained. While agreement between experi-

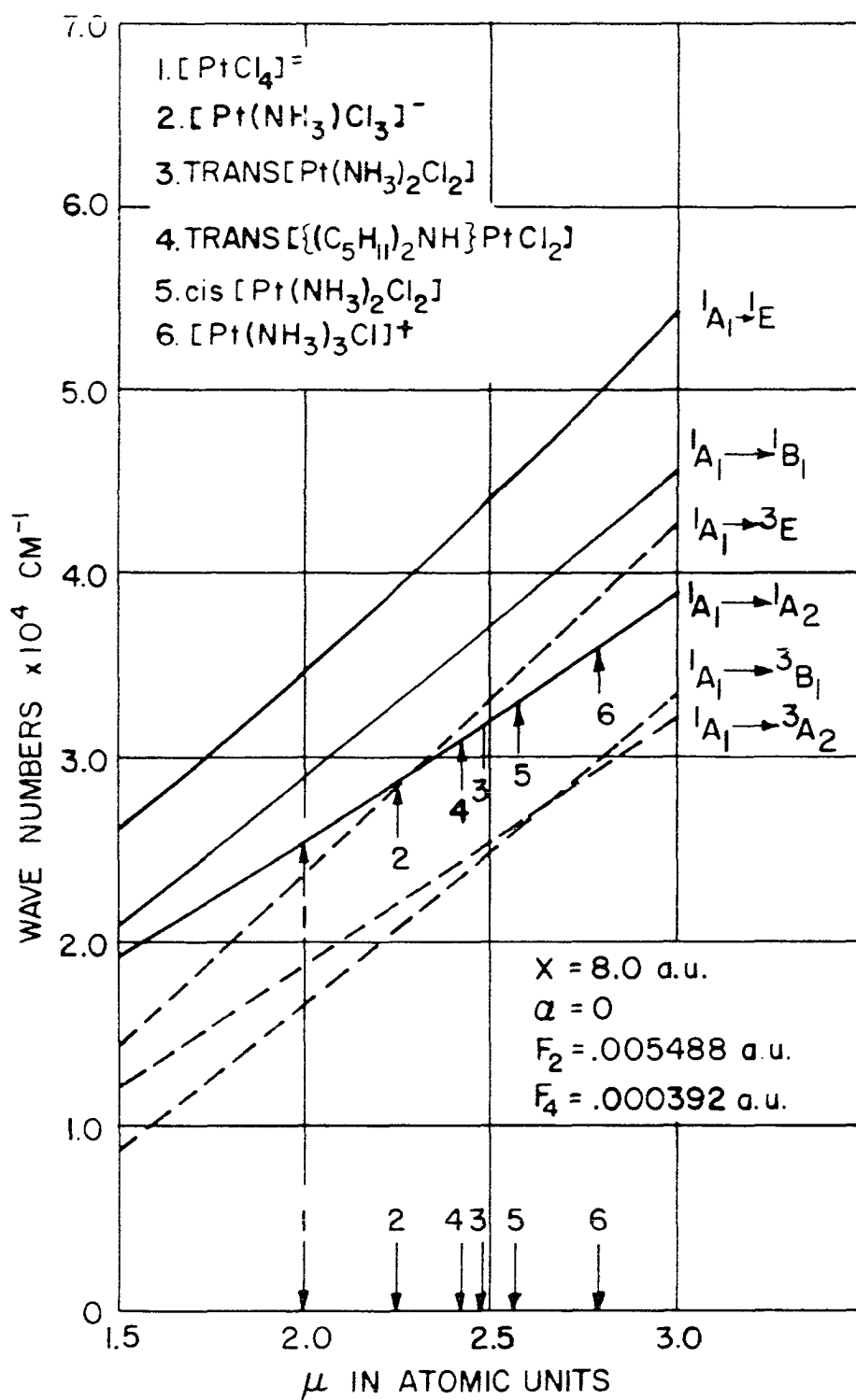


Figure 13. Transition energies as a function of dipole moment for the initial choice of the parameters

Table 29. Comparison of calculated and experimental transition energies from initial parameter choices^a

Compound	Std. Peak 2 and 1A_1 to 1A_2	Exp. Peak 1	Theory 1A_1 to 1B_1	Exp Peak 3	1A_1 to 3A_2	Theory 1A_1 to 3B_1	Av.
$[PtCl_4]^{=}$	2.55	3.02	2.90	2.10	1.90	1.60	1.75
$[Pt(NH_3)Cl_3]$	2.89	3.33	3.31	2.41	2.22	2.11	2.17
trans- $Pt(NH_3)_2Cl_2$	3.17	3.67	3.67	2.68	2.47	2.40	2.44
trans- [$\{(C_5H_{11})_2NH\}_2PtCl_2]$	3.12	3.71	3.61	2.64	2.52	2.47	2.50
cis- $[Pt(NH_3)_2Cl_2]$	3.31	3.72	3.84	2.73	2.66	2.64	2.65
$[Pt(NH_3)_3Cl]^+$	3.60	3.92	4.20	3.10	2.96	3.00	2.98

^a $\chi = 8.0$ a.u., $F_2 = 5.488 \times 10^{-4}$ a.u., $F_2 = 3.92 \times 10^{-5}$ a.u., $\alpha = 0$.

mental and theoretical singlet-to-singlet values are not bad, it should be remembered that these results have been obtained with the spin-orbit coupling parameter equal to zero whereas in platinum it is appreciable. However, the results do tend to indicate that with introduction of the spin-orbit coupling, agreement between theory and experiment should be possible with but minor adjustments in the parameters.

3. Effects of changes in the electronic interaction parameters on the transition energies

Prior to the inclusion of the spin-orbit coupling parameter, it was deemed advisable to investigate the effect of changes in the electronic interaction parameters, F_2 and F_4 , on the transition energies, since the parameters had to be obtained somewhat indirectly. For this study, the parameters were:

$$\mu = 2.0 \text{ a.u.}$$

$$x = 8.0 \text{ a.u.}$$

$$\alpha = 0$$

$$F_2 = 14 F_4$$

$$F_4 = \text{variable}$$

The energy levels were obtained for four values of F_4 :

$$1) \quad F_4 = 3.92 \times 10^{-4} \text{ a.u.,}$$

$$2) \quad F_4 = 3.60 \times 10^{-4} \text{ a.u.,}$$

$$3) \quad F_4 = 3.40 \times 10^{-4} \text{ a.u.,}$$

$$1) F_4 = 3.00 \times 10^{-4} \text{ a.u.}$$

For these values the transition energies between the various states were obtained. Rather than present all of them, only those transitions which would lead to absorption peaks of interest are given in Table 30. As is seen from the table, the transition energies are only slightly affected by rather large changes in the electronic interaction values. This indicates that the energy levels are primarily a function of the ligand field; that is, the ligands impart a strong field

Table 30. Effect of electronic interaction on the transition energies^a

Transition	Transition energy ^b for a given F_4 value ^c			
	$F_4 =$ 3.0	$F_4 =$ 3.4	$F_4 =$ 3.6	$F_4 =$ 3.92
$^1A_1 \text{ — } ^1A_2$	2.58	2.56	2.56	2.56
$^1A_1 \text{ — } ^1B_1$	3.00	2.95	2.93	2.91
$^1A_1 \text{ — } ^3A_2$	2.10	2.01	1.97	1.90
$^1A_1 \text{ — } ^3B_1$	2.08	1.90	1.84	1.71

^a $\chi = 8.0 \text{ a.u.}$, $F_2 = 5.488 \times 10^{-4} \text{ a.u.}$, $F_2 = 3.92 \times 10^{-5} \text{ a.u.}$, $\alpha = 0$.

^bTransition energies given in wave numbers $\times 10^4 \text{ cm}^{-1}$.

^cAll values of F_4 are $F_4 \times 10^{-4} \text{ a.u.}$

effect on the platinum ion. It also suggests that any adjustment of the theoretical energy levels to give better agreement with experiment should be accomplished by means of the ligand field parameters, R and μ . Finally, it was felt that on the basis of the results obtained, the original choice for the parameters F_2 and F_4 should be retained.

4. Final choice of parameters after inclusion of the experimental spin-orbit coupling value

Upon inclusion of the spin-orbit coupling value given by McClure (23), it was found that except for the theoretical results involving the $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Pt}(\text{NH}_3)_3\text{Cl}^+$ complexes, somewhat poorer agreement with experimental values was obtained. Trial calculations with various values of the radial distance parameter $X = fR$, indicated that reasonable agreement was achieved for these other complexes if one used the experimental Pt-Cl distance from $\text{PtCl}_4^{=}$; that is, $X = 8.5$ a.u. Thus, the final choices of parameters for these complexes are given in Group I of Table 31. It is interesting to note that the effective dipoles are reasonably self-consistent. For example, the effective dipole for $[\text{NH}_3\text{PtCl}_3]^-$ should be:

$$\mu' = [3/4 \mu_{\text{Cl}} + 1/4 \mu_{\text{NH}_3}] \quad (131)$$

Then, from $[\text{PtCl}_4]^{=}$, $\mu_{\text{Cl}} = 2.89$, and

Table 31. Final choice of parameters

Compound	Effective dipole moment ^a
Group I ^b	
$[\text{PtCl}_4]^-$	2.89 a.u.
$[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$	3.14 a.u.
trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	3.38 a.u.
trans- $[(\text{C}_5\text{H}_{11})_2\text{NH}_2\text{PtCl}_2]$	3.34 a.u.
cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	3.51 a.u.
$[\text{Pt}(\text{H}_2\text{O})\text{Cl}_3]$	2.96 a.u.
$\text{Pt}(\text{H}_2\text{O})_2\text{Cl}_2$	3.07 a.u.
$[\text{Pt}(\text{OH})\text{Cl}_3]^-$	3.02 a.u.
$[\text{Pt}(\text{OH})_2\text{Cl}_2]^-$	3.16 a.u.
Group II ^c	
cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	2.74 a.u.
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$	2.92

^aDipole moment fixed on the basis that absorption Peak 2 corresponds to the $^1A_1 \rightarrow ^1A_2$ transition.

^bFixed parameters: $X = 8.5$ a.u., $F_2 = 5.488 \times 10^{-3}$ a.u., $F_4 = 3.92 \times 10^{-4}$ a.u., and $\alpha = 9.42 \times 10^{-3}$ a.u.

^cFixed parameters: $X = 8.0$ a.u., $F_2 = 5.488 \times 10^{-3}$ a.u., $F_4 = 3.92 \times 10^{-4}$ a.u., and $\alpha = 9.42 \times 10^{-3}$ a.u.

$$3.14 \text{ a.u.} = [3/4 (2.89) + 1/4 \mu_{\text{NH}_3}]. \quad (132)$$

Thus,

$$\mu_{\text{NH}_3} = 3.84 \text{ a.u.}$$

By use of these values, one can estimate the dipole for $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$:

$$\mu'' = [1/2 \mu_{\text{Cl}} + 1/2 \mu_{\text{NH}_3}] = 3.38 \text{ a.u.} \quad (133)$$

which is exactly that for the trans-complex. By similar processes the average dipole for the di-aquo and di-hydroxy species can be predicted. The results are 3.00 a.u. and 3.12 a.u. respectively, which compare fairly well with the values listed in Table 31.

The resultant transition energies vs. effective dipole moment, with $X = 8.5 \text{ a.u.}$, are given in Figure 14. Comparison between the experimental and theoretical transition energies are given in Group I in Table 32. This group also includes preliminary results from a study of the absorption peaks of aquo-substituted and hydroxy-substituted chlorocomplexes. These results are incomplete since the singlet-to-triplet peaks have not been experimentally determined as yet. The singlet-to-singlet transitions agree rather well.

Estimates of the transition energies in the $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ complex based upon the energy levels given in Figure 14 result in poor agreement with the experimental values. However, it was possible that in this case, the platinum to nitrogen distance for the complex would better represent the central

Table 32. Comparison of final theoretical transition energies with experimental results^a

Cmp. ^b	Std.	Exp.	Theory	% Error	Exp.	Theory			
	Peak 2		¹ A ₁			¹ A ₁	¹ A ₁	Ave.	% Error
	to ¹ A ₂		to ¹ B ₁			to ³ A ₂	to ³ B ₁		
Group I									
A	2.55	3.02	2.92	3.3%	2.10	2.20	2.16	2.18	3.8%
B	2.89	3.33	3.28	1.5%	2.41	2.48	2.50	2.49	3.3%
C	3.17	3.67	3.53	3.3%	2.68	2.74	2.83	2.79	4.6%
D	3.12	3.71	3.61	2.7%	2.64	2.70	2.76	2.73	3.4%
E	3.33	3.72	3.81	2.4%	2.73	2.88	3.00	2.94	7.7%
F	2.64	3.14	3.02	3.8%	-	2.28	2.26	2.27	-
G	2.78	3.22	3.18	1.2%	-	2.41	2.41	2.41	-
H	2.72	3.18	3.11	2.2%	-	2.34	2.34	2.34	-
I	2.90	3.33	3.31	0.6%	-	2.51	2.53	2.52	-
Group II									
J	3.31	3.72	3.68	1.1%	2.73	2.90	2.80	2.85	4.4%
K	3.60	3.92	3.99	1.8%	3.10	3.10	3.16	3.13	1.0%

^aAll results are in wave numbers $\times 10^4 \text{ cm}^{-1}$.

^bThe complexes are as follows: A = $[\text{PtCl}_4]^-$; B = $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$; C = trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$; D = trans- $[\{(\text{C}_5\text{H}_{11})_2\text{NH}\}_2\text{PtCl}_2]$; E = cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$; F = $[\text{Pt}(\text{H}_2\text{O})\text{Cl}_3]^-$; G = $[\text{Pt}(\text{H}_2\text{O})_2\text{Cl}_2]$; H = $[\text{Pt}(\text{OH})\text{Cl}_3]^-$; I = $[\text{Pt}(\text{OH})_2\text{Cl}_2]^-$; J = cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$; and K = $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$.

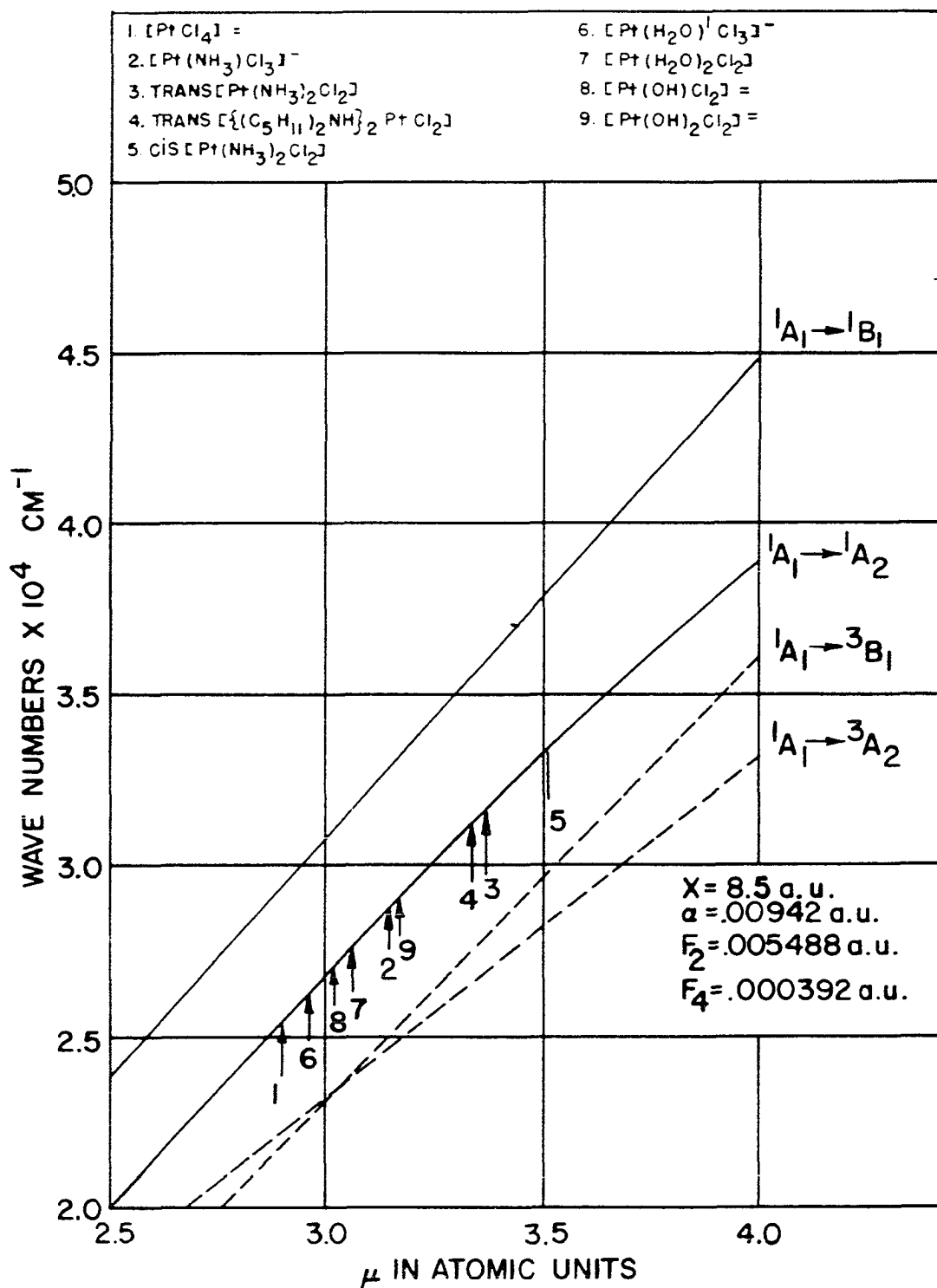


Figure 14. Transition energies as a function of dipole moment for the final choice of the parameters

ion to ligand distance than the platinum to chloride distance. Therefore, a value of X equal to 8.0 a.u. was employed which, when used with an appropriate value of u' given in Group II of Table 31, resulted in good agreement between experimental and theoretical energy levels. The results are given in Group II of Table 32, along with a second evaluation of cis-
[Pt(NH₃)₂Cl₂] made by use of the same radial distance.

D. Discussion

The calculations and results presented in this thesis support an alternative assignment of energy levels to that given by Chatt et al. (2). Some discussion about the reasons for the two assignments seems to be in order.

The main difference between the two assignments is in the relative positions of the (z^2) and the (xz), (yz) orbitals. All the features of the spectra, save one, which are noted by Chatt et al. (2) to be consistent with the assignment of Peak 1 to the transition from the degenerate (xz), (yz) state to the (x^2-y^2) state, are equally consistent with the alternative assignment of the transition from the (z^2) state. Without going into detail, this single feature concerns the absorption spectra of the solid complexes, and the presumption is made that the energy levels in the solid are the same as those of the complexes in solution. However, in order to be sure of this, one would expect that the absorption peaks in the two

situations would be identical. as they were in certain Ni(II) complexes investigated by Maki (29). This is not the case with the platinum complexes under discussion. For example, the three peaks of the solution spectra of K_2PtCl_4 are at 331 mμ, 392 mμ, and 476 mμ, while the spectra of the solid, the peaks are at 340 mμ, 375 mμ, and 500 mμ. While these are somewhat close, it should be noted that the shifts are not all in the same direction. Furthermore, Dickinson (42) has shown that in the solid K_2PtCl_4 the platinum atoms appear in chains above one another, whereas it is to be expected that in aqueous solution, the water molecules would be oriented such that the negative end of the dipole would be directed toward the platinum ion. In view of the fact that in crystals the complex ions of platinum frequently form metal-metal bonds, (44), it is possible that the solution and solid spectra are not analogous. In ligand field terms, positive charges on the z-axes due to the platinum ions could alter the positions of the energy levels.

Furthermore, if Peak 1 were due to the transition from the (xz), (yz) orbitals, one would expect a splitting of this peak in the spectra of the lower symmetry complexes, for example, in $trans-[Pt(NH_3)_2Cl_2]$. Chatt et al. (2) explain the fact that no apparent splitting takes place as due to the fact that the (x^2-y^2) orbital is much more sensitive to the nature of the ligands than those of the (xz) and (yz) orbitals.

However, in terms of the energy level assignment of this thesis, no splitting would be expected since the transition is from the single (z^2) orbital in all the complexes.

The energy level assignment supported by the present work is in accord with the assignment applied to Ni(II) complexes (14). The effects of configuration interaction and spin-orbit coupling, which were not exploited in the previous treatment of platinum(II), have been included. However, it should be noted that in view of present theories of bonding in complexes, ligand field calculations which employ a point charge or point dipole model are perhaps oversimplifications and will accordingly remain suspect. Nevertheless, within the framework of the dipole model, the complete ligand field calculations in this thesis result in an unambiguous assignment of the levels which gives reasonable agreement with experimental values.

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IX. BIBLIOGRAPHY

1. Bethe, H. Ann. Physik Ser. 5, 3: 133. 1929.
2. Chatt, J., Gamlen, G. A., and Orgel, L. E. J. Chem. Soc. (London): 486. 1958.
3. Mulliken, R. S. Phys. Rev. 43: 279. 1932.
4. Schlapp, R. and Penney, W. G. Phys. Rev. 42: 666. 1932.
5. Pauling, L. and Wilson, E. B. Introduction to Quantum Mechanics. New York, N. Y., McGraw-Hill Book Co., Inc. 1935.
6. Condon, E. U. and Shortley, G. H. The Theory of Atomic Spectra. London, Cambridge University Press. 1959.
7. Moffitt, W. E. and Ballhausen, C. J. Ann. Rev. Phys. Chem. 7: 107. 1956.
8. Griffeth, J. S. J. Inorg. and Nuclear Chem. 2: 1. 1956.
9. Orgel, L. E. J. Chem. Physics 23: 1819. 1955.
10. Ilse, F. E. and Hartmann, H. Zeits. Phys. Chem. 197: 239. 1951.
11. Schläfer, H. L. Zeits. Phys. Chem. 4: 116. 1955.
12. Hartmann, H. and Kruse, H. H. Zeits. Phys. Chem. 5: 9. 1955.
13. Basolo, F., Ballhausen, C. J., and Bjerrum, J. Acta Chem. Scand. 9: 810. 1955.
14. Ballhausen, C. J. Kgl. Danske Videnskab Selskab. Mat. fys. Medd. 29: No. 8. 1955.
15. Fajans, K. Naturwissenschaften 11: 165. 1923.
16. Orgel, L. E. J. Chem. Physics 23: 1004. 1955.
17. _____. J. Chem. Soc. (London): 4756. 1955.
18. Basolo, F. and Pearson, R. G. Mechanisms of Inorganic Reactions. New York, N. Y., John Wiley and Sons, Inc. 1958.

19. Santen, J. H. and Wieringen, J. S. Rev. trav. chim.
71: 420. 1952.
20. Orgel, L. E. J. Chem. Physics 23: 1824. 1955.
21. Bleaney, B. and Stevens, K. W. H. Repts. Prog. Physics
16: 108. 1953.
22. Van Vleck, J. H. Electric and Magnetic Susceptibilities.
London, Oxford University Press. 1932.
23. McClure, D. S. Solid State Physics 9: 399. 1959.
24. Eyring, H., Walter, J., and Kimball, G. Quantum Chemistry.
New York, N. Y., John Wiley and Sons, Inc. 1944.
25. Jahnke, E. and Emde, F. Tables of Functions. 4th ed.
New York, N. Y., Dover Publications, Inc. 1945.
26. Liehr, A. D. and Ballhausen, C. J. Ann. of Physics 6:
134. 1959.
27. Ballhausen, C. J. Kgl. Danske Videnskab Selskab. Mat.-
fys. Medd. 29: No. 4. 1955.
28. Maki, G. J. Chem. Physics 23: 651. 1958.
29. _____. Ibid. 29: 162. 1958.
30. Slater, J. C. Phys. Rev. 36: 57. 1930.
31. Edmonds, A. R. Angular Momentum in Quantum Mechanics.
Princeton, N. J., Princeton University Press. 1957.
32. Richardson, J. W. A Theoretical Study of the Electronic
Structure of Transition Metal Complexes. Unpublished
Ph. D. Thesis. Ames, Iowa, Library, Iowa State
University of Science and Technology. 1956.
33. Melvin, M. A. Rev. Mod. Physics 28: 18. 1956.
34. Iowa State University of Science and Technology. Com-
puter Laboratory. Cyclone Programming Manual No. 1.
Ames, Iowa, Author. 1959.
35. Bodewig, E. Matrix Calculus. 2nd ed. Amsterdam, North-
Holland Publishing Co. 1959.

36. Elleman, T. S. Kinetics of the Acid Hydrolysis - (aquation) and Isotopic Exchange of Chloride with Trichloroammineplatinate(II) Complex in Aqueous Solution. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.
37. Reishus, J. W. Aquation and Isotope Exchange of the Chloride Ligands of the Cis-dichlorodiammine-platinum(II) Complex. Unpublished Ph. D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.
38. Jorgensen, C. K. Acta Chem. Scand. 8: 1495. 1954.
39. Keinberg, J., Argersinger, W. J., Jr., and Griswold, E. Inorganic Chemistry. Boston, D. C. Heath and Co. 1960.
40. Moore, C. Atomic Energy Levels. U. S. National Bureau of Standards. Circular 467. 1958.
41. Owen, J. Proc. Roy. Soc. of London. Ser. A, 227: 183. 1955.
42. Dickinson, R. G. J. Am. Chem. Soc. 44: 2404. 1922.
43. Porai-Koshits, M. A. Trudy. Inst. Krist., Akad. Nauk. S.S.S.R. 9: 229. 1954. (Original not available for examination; abstracted in Chem. Abstracts 48: 13325d. 1954).
44. Atoji, M., Richardson, J. W. and Rundle, R. E. J. Am. Chem. Soc. 79: 3017. 1957.
45. Rotenberg, M., Bivins, R., Metropolis, N., and Wooten, J. K., Jr. The 3-j and 6-j Symbols. Cambridge, Mass., The Technology Press, Massachusetts Institute of Technology. 1959.
46. Mandl, F. Quantum Mechanics. 2nd ed. New York, N. Y., Academic Press, Inc. 1957.
47. Larsen, H. D. Rinehart Mathematical Tables. New York, N. Y., Rinehart and Co., Inc. 1948.
48. Maki, G. J. Chem. Phys. 29: 1129. 1958.
49. Liehr, A. D. J. Phys. Chem. 64: 43. 1960.

50. Stevens, M. E. H. Proc. Phys. Soc. (London) A65: 209. 1952.
51. Wigner, E. P. Group Theory. (translated from German by Griffin, J. J.) New York, N. Y., Academic Press, Inc. 1959.
52. Goldstein, H. Classical Mechanics. Cambridge, Mass., Addison-Wesley Publishing Co., Inc. 1953.
53. Tisza, L. Zeits. f. Physik 82: 48. 1933.
54. Finkelstein, R. and Van Vleck, J. H. J. Chem. Physics 8: 790. 1940.

V. APPENDICES

A. Appendix A: Derivation of the Wave Functions
of the Free Ion

In order to construct the wave functions associated with the energy levels of the free platinum(II) ion, one must be careful in the choice of phase factors. For example, if

$${}^3F_4(3) = \sqrt{3}/\sqrt{8} [(2,0)-(0,2)]\alpha\alpha + 1/4 [(2,1)-(1,2)][\alpha\beta + \beta\alpha], \quad (134)$$

then either

$${}^3F_3(3) = 1/\sqrt{8} [(2,0)-(0,2)]\alpha\alpha + \sqrt{3/4} [-(2,1)+(1,2)][\alpha\beta+\beta\alpha], \quad (135)$$

or

$${}^3F_3(3) = 1/\sqrt{8} [-(2,0)+(0,2)]\alpha\alpha + \sqrt{3/4} [(2,1)-(1,2)][\alpha\beta + \beta\alpha], \quad (136)$$

will be orthogonal to ${}^3F_4(3)$. The choice of phase factors, both within a particular J value and between different J values, must be consistent. To assure this, it has been decided to employ the systematic approach given by Condon and Shortley (6) in which the wave functions $|S, M_S, L, M_L\rangle$ are derived first and then the $|S, L, J, M_J\rangle$ wave functions are obtained from appropriate combinations of the $|S, M_S, L, M_L\rangle$ functions. However, in the derivation of the $|S, L, J, M_J\rangle$ functions, the procedure that will be followed is the one given by Rotenberg et al. (45).

1. The free ion states

To obtain the states of the free ion, the method outlined in section 1⁷ of Condon and Shortley's text (6) is particularly advantageous, not only because of its simplicity, but also because of the useful information derivable from the table that is constructed in the process of deriving the states. To obtain the states which result from two equivalent d-electrons, one considers all possible combinations of M_L and M_S which can be obtained with the restriction of the Pauli exclusion principle. Now $M_L = \sum m_l$ and $M_S = \sum m_s$, where m_l and m_s are the magnetic and spin quantum numbers for the d-electrons. Since $m_l = \pm 2, \pm 1, 0$, and $m_s = \pm 1/2$ for each electron, the possible M_L and M_S values are:

$$M_L = \pm 4, \pm 3, \pm 2, \pm 1, 0,$$

$$M_S = \pm 1, 0.$$

One then proceeds to construct a table of all possible combinations of the m_l and m_s value which will give a particular M_L and M_S . Such a listing for the d^2 case is given in Table 33.

Since there is a state with $M_L = 4$, $M_S = 0$, there must exist a state with $L = 4$, $S = 0$, that is, 1G . Now 1G will have M_L values from 4 to -4, with $M_S = 0$. Similarly, since there is a state with $M_L = 3$, $M_S = 1$, there must exist a 3F state, that is a state with $L = 3$, $S = 1$. Now in the cell, $M_L = 2$, $M_S = 0$, one of the terms is accounted for by the 1G state and another by the 3F state. Since there is a third

Table 33. M_C and M_L values for d^2 or d^8 configuration^a

M_S M_L	1	0	-1
4	--	(2 ⁺ 2 ⁻)	--
3	(2 ⁺ 1 ⁺)	(2 ⁺ 1 ⁻) (2 ⁻ 1 ⁺)	(2 ⁻ 1 ⁻)
2	(2 ⁺ 0 ⁺)	(2 ⁺ 0 ⁻) (2 ⁻ 0 ⁺) (1 ⁺ 1 ⁻)	(2 ⁻ 0 ⁻)
1	(2 ⁺ -1 ⁺) (1 ⁺ 0 ⁺)	(2 ⁺ -1 ⁻) (2 ⁻ -1 ⁺) (1 ⁺ 0 ⁻) (1 ⁻ 0 ⁺)	(2 ⁻ -1 ⁻) (1 ⁻ 0 ⁻)
0	(2 ⁺ -2 ⁺) (1 ⁺ -1 ⁺)	(2 ⁺ -2 ⁻) (2 ⁻ -2 ⁺) (1 ⁺ -1 ⁻) (1 ⁻ -1 ⁺) (0 ⁺ 0 ⁻)	(2 ⁻ -2 ⁻) (1 ⁻ -1 ⁻)
-1	(-2 ⁺ 1 ⁺) (-1 ⁺ 0 ⁺)	(-2 ⁺ 1 ⁻) (-2 ⁻ 1 ⁺) (-1 ⁺ 0 ⁻) (-1 ⁻ 0 ⁺)	(-2 ⁻ 1 ⁺) (-1 ⁻ 0 ⁻)
-2	(-2 ⁺ 0 ⁺)	(-2 ⁺ 0 ⁻) (-2 ⁻ 0 ⁺) (-1 ⁺ -1 ⁻)	(-2 ⁻ 0 ⁻)
-3	(-2 ⁺ -1 ⁺)	(-2 ⁺ -1 ⁻) (-2 ⁻ -1 ⁺)	(-2 ⁻ -1 ⁻)
-4	--	(-2 ⁺ -2 ⁻)	--

^aIn this table, (A⁺B⁻) is a representation such that A and B are the m_l values of the two electrons and the superscripts, (+) and (-), represent the m_s values, with (+) = $\alpha = \frac{1}{2}$ and (-) = $\beta = -\frac{1}{2}$. The entire expression represents the antisymmetric product function. Thus, (2⁺1⁺) = $1/\sqrt{2} [(2,1) - (1,2)]\alpha\alpha$.

term in the cell, there must exist a state with $L = 2$, $S = 0$, that is 1D . Similarly from the cell $M_L = 1$, $M_S = 1$, one obtains the 3P state; and from $M_L = 0$, $M_S = 0$, the 1S state is derived. Hence the states associated with d^2 or d^8 are 1G , 1D , 1S , 3F , and 3P .

2. The $|S, M_S, L, M_L\rangle$ functions by means of step operators

If the function for a particular state is represented by $|n, m\rangle$ where n is the angular momentum quantum number and m is the z -component quantum number, then one can define an operator, A_- , such that:

$$A_- |n, m\rangle = \hbar [(n-m)(n-m+1)]^{\frac{1}{2}} |n, m-1\rangle. \quad (137)$$

A_- is called the "step down" operator. If, for example, n is the orbital angular momentum operator, l , and m is m_l , then,

$$A_- = l_- = l_x - il_y. \quad (138)$$

An introduction to the concept of "step down" and "step up" operators is given in Chapter VI of the text by Mandl (46). Suffice it to say that the step operators are not limited to the orbital angular momentum, l , but that analogous definitions apply for the total angular momentum, j , the spin, s , etc.

Since,

$$\mathcal{L} = l_{(1)} + l_{(2)}, \quad (139)$$

and

$$S = s_{(1)} + s_{(2)}, \quad (140)$$

where the (1) and (2) refer to electrons one and two, one can define:

$$\mathcal{L}_- = l_{-(1)} + l_{-(2)}, \quad (141)$$

$$S_- = s_{-(1)} + s_{-(2)}. \quad (142)$$

Therefore, if one could obtain a function $|S, M_S, L, M_L\rangle$ which

was expressed in terms of the appropriate single electron product functions, one could find, for example, $|S, M_S, L, M_L-1\rangle$, $|S, M_S, L, M_L-2\rangle$, etc., or $|S, M_S-1, L, M_L\rangle$, $|S, M_S-2, L, M_L\rangle$, etc., by repeated applications of the appropriate operators. For example, from Table 33, it is obvious that the wave function for the state $|S, M_S, L, M_L\rangle = |1, 1, 3, 3\rangle$ is given by

$$|1, 1, 3, 3\rangle = 1/\sqrt{2} [(2, 1) - (1, 2)]\alpha\alpha. \quad (143)$$

Then,

$$\mathcal{L}_- |1, 1, 3, 3\rangle = \{\mathcal{L}_-(1) + \mathcal{L}_-(2)\} 1/\sqrt{2} [(2, 1) - (1, 2)]\alpha\alpha. \quad (144)$$

Hence,

$$\begin{aligned} \hbar [(3+3)(3-3+1)]^{\frac{1}{2}} |1, 1, 3, 2\rangle = \\ \hbar/\sqrt{2} [(2+1)(2-1+1)]^{\frac{1}{2}} [(2, 0) - (0, 2)]\alpha\alpha. \end{aligned} \quad (145)$$

Therefore,

$$|1, 1, 3, 2\rangle = 1/\sqrt{2} [(2, 0) - (0, 2)]\alpha\alpha. \quad (146)$$

By a similar process:

$$\mathcal{S}_- |1, 1, 3, 3\rangle = \{\mathcal{S}_-(1) + \mathcal{S}_-(2)\} 1/\sqrt{2} [(2, 1) - (1, 2)]\alpha\alpha. \quad (147)$$

$$\hbar \sqrt{2} |1, 0, 3, 3\rangle = \hbar/\sqrt{2} [(2, 1) - (1, 2)][\alpha\beta + \beta\alpha]. \quad (148)$$

$$|1, 0, 3, 3\rangle = 1/2 [(2, 1) - (1, 2)][\alpha\beta + \beta\alpha]. \quad (149)$$

By such a step down procedure, the $|S, M_S, L, M_L\rangle$ functions for all M_S and M_L values associated with $S = 1$ and $L = 3$ may be obtained. This technique assures that the proper relative phases for all states are obtained. The $|S, M_S, L, M_L\rangle$ functions required for the 3F states are given in Table 34.

Table 34. (S, M_S, L, M_L) functions for 3P states

$ S, M_S, L, M_L\rangle$	Two-electron product functions
$ 1, 1, 3, 3\rangle$	$1/\sqrt{2}[(2, 1) - (1, 2)][\alpha\alpha]$
$ 1, 0, 3, 3\rangle$	$1/2[(2, 1) - (1, 2)][\alpha\beta + \beta\alpha]$
$ 1, -1, 3, 3\rangle$	$1/\sqrt{2}[(2, 1) - (1, 2)][\beta\beta]$
$ 1, 1, 3, 2\rangle$	$1/\sqrt{2}[(2, 0) - (0, 2)][\alpha\alpha]$
$ 1, 0, 3, 2\rangle$	$1/2[(2, 0) - (0, 2)][\alpha\beta + \beta\alpha]$
$ 1, -1, 3, 2\rangle$	$1/\sqrt{2}[(2, 0) - (0, 2)][\beta\beta]$
$ 1, 1, 3, 1\rangle$	$1/\sqrt{10}[\sqrt{2}(1, 0) - \sqrt{2}(0, 1) + \sqrt{3}(2, -1) - \sqrt{3}(-1, 2)][\alpha\alpha]$
$ 1, 0, 3, 1\rangle$	$1/\sqrt{20}[\sqrt{2}(1, 0) - \sqrt{2}(0, 1) + \sqrt{3}(2, -1) - \sqrt{3}(-1, 2)][\alpha\beta + \beta\alpha]$
$ 1, -1, 3, 1\rangle$	$1/\sqrt{10}[\sqrt{2}(1, 0) - \sqrt{2}(0, 1) + \sqrt{3}(2, -1) - \sqrt{3}(2, -1) - \sqrt{3}(-1, 2)][\beta\beta]$
$ 1, 1, 3, 0\rangle$	$1/\sqrt{10}[(2, -2) - (-2, 2) + 2(1, -1) - 2(-1, 1)][\alpha\alpha]$
$ 1, 0, 3, 0\rangle$	$1/\sqrt{20}[(2, -2) - (-2, 2) + 2(1, -1) - 2(-1, 1)][\alpha\beta + \beta\alpha]$
$ 1, -1, 3, 0\rangle$	$1/\sqrt{10}[(2, -2) - (-2, 2) + 2(1, -1) - 2(-1, 1)][\beta\beta]$
$ 1, 1, 3, -1\rangle$	$1/\sqrt{10}[\sqrt{2}(0, -1) - \sqrt{2}(-1, 0) + \sqrt{3}(1, -2) - \sqrt{3}(-2, 1)][\alpha\alpha]$
$ 1, 0, 3, -1\rangle$	$1/\sqrt{20}[\sqrt{2}(0, -1) - \sqrt{2}(-1, 0) + \sqrt{3}(1, -2) - \sqrt{3}(-2, 1)][\alpha\beta + \beta\alpha]$
$ 1, -1, 3, -1\rangle$	$1/\sqrt{10}[\sqrt{2}(0, -1) - \sqrt{2}(-1, 0) + \sqrt{3}(1, -2) - \sqrt{3}(-2, 1)][\beta\beta]$
$ 1, 1, 3, -2\rangle$	$1/\sqrt{2}[(0, 02) - (-2, 0)][\alpha\alpha]$
$ 1, 0, 3, -2\rangle$	$1/2[(0, -2) - (-2, 0)][\alpha\beta + \beta\alpha]$

$$+1)^{1/2} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} |j_1, m_1, j_2, m_2\rangle. \quad (150)$$

In the case of the wave functions being considered, $j_1 = S$; $j_2 = L$; $j = J$; $m_1 = M_S$; $m_2 = M_L$; and $m = M_J$. The equation would be difficult to handle were it not for the fact that a complete set of values for the 3-j symbol,

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix},$$

have been determined and tabulated by Rotenberg et al. (45). The text is self explanatory and quite easy to follow. A more detailed discussion of the 3-j symbol, its properties and uses, is given by Edmonds (31).

An illustration of the use of the foregoing equation might prove helpful. In constructing the wave function for the state $|S, L, M, M_J\rangle = |1, 3, 4, 3\rangle$, by means of the $|S, M_S, L, M_L\rangle$ functions, one obtains the expression:

$$|1, 3, 4, 3\rangle = (-1)^{3-1-3} \sum_{m_1, m_2} (8+1)^{1/2} \begin{pmatrix} 1 & 3 & 4 \\ m_1 & m_2 & -3 \end{pmatrix} |1, m_1, 3, m_2\rangle \quad (151)$$

Now since $j_1 = S = 1$, then $m_1 = m_S = \pm 1, 0$. It can be shown (31) that the 3-j symbol is zero unless $m_1 + m_2 = m$. Therefore when:

$$\begin{aligned} m_1 &= 1, m_2 \text{ must equal } 2, \\ m_1 &= 0, m_2 \text{ must equal } 3, \end{aligned}$$

Table 34. (Continued)

$ S, M_S, L, M_L\rangle$	Two-electron product functions
$ 1, -1, 3, -2\rangle$	$1/\sqrt{2} [(0, -2) - (-2, 0)][\beta\beta]$
$ 1, 1, 3, -3\rangle$	$1/\sqrt{2} [(-1, -2) - (-2, -1)][\alpha\alpha]$
$ 1, 0, 3, -3\rangle$	$1/2 [(-1, -2) - (-2, -1)][\alpha\beta + \beta\alpha]$
$ 1, -1, 3, -3\rangle$	$1/\sqrt{2} [(-1, -2) - (-2, -1)][\beta\beta]$

3. The $|S, L, J, M_J\rangle$ functions

In section 5⁸, Condon and Shortley (6) point out that the states of different terms have no particular phase relation. That is, the highest M_L value for any one of the states, 1G_4 , 1D_2 , 1S_0 , 3F_4 , and 3P_2 , can be constructed simply on the basis of their orthogonality relationships. However, the phase relation does become important between the 3F states; i.e., between 3F_4 , 3F_3 , and 3F_2 , and between the three 3P states; i.e., between 3P_2 , 3P_1 , and 3P_0 .

In order to construct the $|S, L, J, M_J\rangle$ functions from the $|S, M_S, L, M_L\rangle$ functions, while guaranteeing the consistency of the phase relations, one can make use of the relationship between the functions in terms of the 3-j symbol. The general relation is given by:

$$|j_1, j_2, j, m\rangle = (-1)^{j_2 - j_1 - m} \sum_{m_1, m_2} (2j + 1) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \quad \text{(Continued next page)}$$

$m_1 = -1$, m_2 must equal 4.

But in the latter case m_2 would exceed $j_2 = 3$, and since it is required that $m_2 \leq j_2$, this last combination is not allowed.

Thus the wave function becomes:

$$|1,3,4,3\rangle = -3 \begin{pmatrix} 1 & 3 & 4 \\ 1 & 2 & -3 \end{pmatrix} |1,1,3,2\rangle - 3 \begin{pmatrix} 1 & 3 & 4 \\ 0 & 3 & -3 \end{pmatrix} |1,0,3,3\rangle \quad (152)$$

From Rotenberg, et al. (45), one obtains:

$$\begin{pmatrix} 1 & 3 & 4 \\ 1 & 2 & -3 \end{pmatrix} = \frac{-1}{2\sqrt{3}}; \text{ and } \begin{pmatrix} 1 & 3 & 4 \\ 0 & 3 & -3 \end{pmatrix} = \frac{-1}{6}.$$

Hence:

$$\begin{aligned} |1,3,4,3\rangle &= \sqrt{3/2} |1,1,3,2\rangle + 1/2 |1,0,3,3\rangle, \\ &= \sqrt{3/2} \quad 1/\sqrt{2} [(2,0)-(0,2)]\alpha\alpha \\ &\quad + 1/2 \quad 1/2 [(2,1)-(1,2)] [\alpha\beta + \beta\alpha] \\ &\quad + \sqrt{3} / \sqrt{8} [(2,0)-(0,2)] [\alpha\alpha] \\ &\quad + 1/4 [(2,1)-(1,2)] [\alpha\beta + \beta\alpha] \end{aligned} \quad (153)$$

Such techniques are required to insure the consistency between the 3F states as well as between the 3P states. It is not necessary to employ the above method in order to determine all the $|S, L, J, M_J\rangle$ wave functions. For example, the wave functions for $^1G_4(4)$ and $^3F_4(4)$ may be written directly from consideration of the antisymmetry requirements and the values given in Table 33, since there is only one possible $|S, M_S, L, M_L\rangle$ function belonging to each of them. Thus:

$$^1G_4(4) = |0,0,4,4\rangle = |0,0,4,4\rangle = 1/\sqrt{2} [(2,2)] [\alpha\beta - \beta\alpha]. \quad (154)$$

One notes that all the singlet functions will be antisymmetric in their spin parts and hence must be symmetric in their space parts. Similarly, all triplet states will be symmetric with respect to spin and antisymmetric with respect to space. Thus:

$${}^3F_4(4) = |1,3,4,4\rangle = |1,1,3,3\rangle = 1/\sqrt{2} [(2,1)-(1,2)]\alpha\alpha \quad (155)$$

To obtain the other wave functions belonging to 1G_4 and 3F_4 , that is, the wave functions with different M_J values, one can use the step down operators:

$$J_- |S, L, J, M_J\rangle = \hbar [(J+M)(J-M+1)]^{1/2} |S, L, J, M_J-1\rangle, \quad (156)$$

for the left hand side; and

$$J_- = L_- + S_- = s_-(1) + s_-(2) + l_-(1) + l_-(2), \quad (157)$$

for the right hand side. The procedure is then analogous to that given for the step operators of the $|S, M_S, L, M_L\rangle$ functions.

Furthermore, since the phase factor for different L terms is unimportant, one can derive the first term of the singlets, ${}^1D_2(2)$ and ${}^1S_0(0)$, from orthogonality considerations, examples of which are given in the text by Mandl (46).

Regardless of whether the 3-j symbol technique is employed throughout, or only used in those cases where the phase factor is important, one can construct the wave functions in a straightforward, though tedious, manner. The free ion wave functions for the d^2 or d^8 configuration are given in Table 8.

B. Appendix B: The Ligand Field Derivations.

Weak Field

1. The spherical harmonics

Because of their importance in this thesis and the fact that the choice of the phase factor is often a source of confusion, some discussion of the spherical harmonics is in order. The spherical harmonics, as employed in this thesis, follow the definition given by Condon and Shortley (6):

$$Y_{\ell, m}(\theta, \phi) = (-1)^m \left[\frac{(2\ell+1)}{2} \frac{(\ell-m)!}{(\ell+m)!} \right]^{\frac{1}{2}} \frac{1}{\sqrt{2\pi}} P_{\ell}^{|m|}(\cos \theta) e^{im\phi} \quad (158)$$

$$Y_{\ell, -m}(\theta, \phi) = + \left[\frac{(2\ell+1)}{2} \frac{(\ell-m)!}{(\ell+m)!} \right]^{\frac{1}{2}} \frac{1}{\sqrt{2\pi}} P_{\ell}^{|m|}(\cos \theta) e^{-im\phi}, \quad (159)$$

where:

$$P_{\ell}^{|m|}(x) = \frac{(1-x^2)^{m/2}}{2^{\ell} \ell!} \frac{d^{\ell+|m|}}{dx^{\ell+|m|}} (x^2-1)^m \quad (160)$$

Frequently, in this report, a spherical harmonic has been expressed as $Y(\ell, m)$ for simplicity of reproduction. In such cases, the dependence of the function on θ and ϕ is meant to be understood.

It is particularly important to note the phase factor, $(-1)^m$, when comparison with similar expressions of the spherical harmonics is made. The inclusion of this factor by some authors and its omission by others has led to slightly different expressions for the d-electron orbitals.

Explicit expressions for the normalized spherical

harmonics are given in Table 11. They are presented both as functions of the angles, θ and ϕ , and as functions of the coordinates, x, y, z , and the radial distance, r . Correspondence between the two sets is indicated by the relationships:

$$x = r \cdot \sin \theta \cos \phi, \quad (161)$$

$$y = r \cdot \sin \theta \sin \phi, \quad (162)$$

$$z = r \cdot \cos \theta, \quad (163)$$

$$\exp(im\phi) = \cos(m\phi) + i \cdot \sin(m\phi). \quad (164)$$

Three properties of the spherical harmonics should be kept in mind:

$$1. \quad Y(l, m) = 0, \text{ if } |m| > l, \quad (165)$$

$$2. \quad Y^*(l, m) = (-1)^m Y(l, -m), \text{ where } (*) \text{ indicates the complex conjugate.} \quad (166)$$

$$3. \quad \int Y^*(l, m) Y(l', m') d\tau = \delta(l, l') \cdot \delta(m, m'), \quad (167)$$

that is, the integral equals one if l equals l' and m equals m' , and is equal to zero if l does not equal l' or m does not equal m' .

Proofs of these relations, as well as an excellent review of the properties of the spherical harmonics and the different phase conventions used by various authors can be found in section 2.5 of the text by Edmonds (31).

2. Expansion of a product of spherical harmonics

In the course of determining the matrix elements due to the ligand field, one finds it necessary to evaluate integrals

of the type:

$$\int Y^*(l_a, m_a) Y(l_b, m_b) Y(l, m) d\tau.$$

Section 4.6 of the text by Edmonds (31) contains a procedure for the expansion of the product of two spherical harmonics in terms of a sum of spherical harmonics,

$$Y^*(l_a, m_a) Y(l_b, m_b) = \sum_{l, m} K_{l, m} Y^*(l, m). \quad (168)$$

By use of the expansion and the orthogonality relationship of the spherical harmonics, the above integral can be evaluated.

According to Edmonds (31), the general expression for the expansion is given by:

$$Y(l_a, m_a) \cdot Y(l_b, m_b) = \sum_{l, m} \left[\frac{(2l_a+1)(2l_b+1)(2l+1)}{4\pi} \right] \begin{pmatrix} l_a & l_b & l \\ m_a & m_b & m \end{pmatrix} \times \begin{pmatrix} l_a & l_b & l \\ 0 & 0 & 0 \end{pmatrix} \cdot Y^*(l, m) \quad (169)$$

Thus, the coefficient, $K_{l, m}$, corresponds to the terms preceding the spherical harmonic, $Y^*(l, m)$, on the right hand side of Equation 169. The terms in the large parentheses are the same 3-j symbols introduced in Appendix A.

Certain properties of the 3-j symbol limit the number of terms which need to be considered in the expansion. Rotenberg et al. (45) indicate that the 3-j symbol is equal to zero unless:

$$l \leq l_a + l_b$$

$$-m = m_a + m_b$$

Furthermore, the particular 3-j symbol, $\begin{pmatrix} l_a & l_b & l \\ 0 & 0 & 0 \end{pmatrix}$,

equals zero if $l_a + l_b + l = \text{odd number}$. Hence, the expansion must have either all odd or all even spherical harmonics for given values of l_a and l_b , and the highest order harmonic has $l = l_a + l_b$.

Rather than employ the fundamental definition for the 3-j symbol, as given by Edmonds (31), it can be evaluated by use of the tables compiled by Rotenberg et al. (45). An actual example might clarify the calculations. Consider the product, $Y^*(2,1) Y(2,1)$. Since $Y^*(l,m) = (-1)^m Y(l,-m)$, then:

$$Y^*(2,1) Y(2,1) = (-1) Y(2,-1) Y(2,1) \quad (170)$$

$$= - \sum_{l=0}^4 \left[\frac{(5)(5)(2l+1)}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} 2 & 2 & l \\ -1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 2 & 2 & l \\ 0 & 0 & 0 \end{pmatrix} Y^*(l,0) \quad (171)$$

$$\begin{aligned} Y^*(2,1) Y(2,1) &= - \left[\frac{25}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} 2 & 2 & 0 \\ -1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 2 & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \cdot Y^*(0,0) \\ &\quad - \left[\frac{125}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} 2 & 2 & 2 \\ -1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} \cdot Y^*(2,0) \\ &\quad - \left[\frac{225}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} 2 & 2 & 4 \\ -1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 2 & 2 & 4 \\ 0 & 0 & 0 \end{pmatrix} \cdot Y^*(4,0). \end{aligned} \quad (172)$$

Evaluation of the 3-j symbols from the tables given by Rotenberg et al. (45) leads to the result:

$$Y^*(2,1) Y(2,1) = \frac{1}{2\sqrt{\pi}} Y^*(0,0) + \frac{5}{7\sqrt{\pi}} Y^*(2,0) - \frac{2}{7\sqrt{\pi}} Y^*(4,0). \quad (173)$$

3. Evaluation of the radial integral

a. Normalization of the Slater orbital The d-electron wave function for platinum(II), approximated by means of a Slater orbital (30), has the form:

$$\phi = (N r^3 e^{-fr}) Y(2,m), \quad (174)$$

where: N = normalization constant,

$$f = Z^*/n^* = 7.55/4 = 1.89,$$

Z^* = the effective nuclear charge,

n^* = the effective principal quantum number.

It is required that:

$$\int \phi^* \phi d\tau = 1. \quad (175)$$

Therefore, since the spherical harmonics are already normalized,

$$N^2 \int (r^3 e^{-fr}) (r^3 e^{-fr}) r^2 dr = 1. \quad (176)$$

From standard tables of integrals (47), one finds that:

$$\int_0^{\infty} x^{m-1} e^{-ax} dx = \frac{1}{a^m} \Gamma(m), \quad (177)$$

where $\Gamma(m) = (m-1)!$

In the case of the integral under consideration, $m = 9$, $a = 2f$. Therefore,

$$N^2 \int r^8 e^{-2fr} dr = \frac{N^2}{(2f)^9} (8!) = 1. \quad (178)$$

Hence:

$$N = \left[\frac{f^9}{78.75} \right]^{1/2}. \quad (179)$$

b. The radial integral, $G_l(a,b)$ In the process of the evaluation of the one-electron matrix elements, the angular integral, $G_l(a,b)$, was obtained, where:

$$G_l(a,b) = -q N^2 \int_0^{\infty} R_a(r) R_b(r) R_l(r) r^2 dr \quad (180)$$

with $N^2 = f^9/78.75$,

$$R_a(r) = R_b(r) = r^3 e^{-fr}$$

$$R_l(r) = r^{\frac{l}{2}} / r^{\frac{l+1}{2}}$$

In order to evaluate this integral, it is convenient to make a change of variable such that $x = fr$ and $X = fR$, and then to consider the integral as the sum of two integrals, the first from zero to X and the second from X to infinity. Thus,

$$G_l(a,b) = -\frac{qf}{78.75} \left[\frac{1}{X^{\frac{l+1}{2}}} \int_0^X x^8 e^{-2x} x^{\frac{l}{2}} dx + \frac{X^{\frac{l}{2}}}{1} \int_X^{\infty} \frac{x^8 e^{-2x}}{x^{\frac{l+1}{2}}} dx \right] \quad (181)$$

$$= -\frac{qf}{78.75} G_l(X) \quad (182)$$

where $G_l(X)$ are the terms in the bracketts in Equation 181.

The only integrals of interest in a square-planar potential field are those with $l = 2$ and 4. Therefore:

$$G_2(X) = \frac{1}{X^3} \int_0^X x^{10} e^{-2x} dx + X^2 \int_X^{\infty} x^5 e^{-2x} dx \quad (183)$$

$$G_4(X) = \frac{1}{X^5} \int_0^X x^{12} e^{-2x} dx + X^4 \int_X^{\infty} x^3 e^{-2x} dx \quad (184)$$

In standard tables of integrals (47) one finds:

$$\int_0^{\infty} x^p e^{-ax} dx = \frac{a^{-p-1}}{p+1} [(ax)^p - p(ax)^{p-1} + p(p-1)(ax)^{p-2} - \cdots (-1)^p p!] \quad (185)$$

where p is an integer. By use of this relation, one can evaluate the integrals in Equations 183 and 184 in terms of the variable X . The resultant expressions are given in Table 6 in section IV-D-3.

The $G_l(a,b)$ integrals result from the fact that the ligands are considered to be point charges. In order to determine the expression for point dipoles, one considers the potential due to a negative charge, $-q$, at a distance R from the central ion and a positive charge, $+q$, at a distance $R + \Delta R$. The radial expression then becomes:

$$-B_l(a,b) = + \frac{qf}{78.75} G_l(X) - \frac{qf}{78.75} G_l(X + \Delta X) \quad (186)$$

Since $\Delta X = f\Delta R$, and the point dipole is defined as

$$\mu = \lim_{\Delta R \rightarrow 0} q\Delta R \quad (187)$$

then:

$$-B_l(a,b) = \frac{\mu f^2}{78.75} \lim_{\Delta X \rightarrow 0} \left[\frac{G_l(X+\Delta X) - G_l(X)}{\Delta X} \right] \quad (188)$$

$$= - \frac{\mu f^2}{78.75} B_l(X), \quad (189)$$

where

$$B_l(X) = \frac{d}{dX} G_l(X). \quad (190)$$

The $G_l(a,b)$ and $B_l(a,b)$ integrals in the foregoing discussion were for the interaction of the ligand field with

an electron. If, as is the case in this thesis, one employs the "electron hole" formalism, the signs of all the integrals change. Thus, the appropriate radial integrals for the interaction of the point dipoles with the "electron holes" of the d^8 configuration are:

$$B_2(a,b) = \frac{uf^2}{78.75} B_2(X) \quad (191)$$

$$B_4(a,b) = \frac{uf^2}{78.75} B_4(X) \quad (192)$$

where:

$$B_2(X) = \frac{d}{dX} G_2(X) \quad (193)$$

$$B_4(X) = \frac{d}{dX} G_4(X) \quad (194)$$

The expressions for $B_2(X)$ and $B_4(X)$ are given in Table 6 in section IV-D-3.

4. Correlation of the ligand field matrix elements as given by various authors

To the tyro in ligand field, one of the most confusing aspects is the array of equations and symbols used by various authors to express the ligand potential and the resultant matrix elements. The confusion is compounded when one deals with square-planar symmetry which is a special case of the more general tetragonal symmetry group, D_{4h} .

a. The ligand potential To exemplify the possible methods of representing the ligand potential, the forms given by four authors will be compared with the equation used in

this thesis.

(1) Ballhausen The potential for square-planar symmetry used in this thesis is identical with that given by Ballhausen (27):

$$V^{LF} = -q \left\{ -4 \sqrt{\pi} / \sqrt{5} R_2 Y(2,0) + \sqrt{\pi} R_4 Y(4,0) + \sqrt{35\pi} / 3 \sqrt{2} R_4 [Y(4,4) + Y(4,-4)] \right\} \quad (195)$$

where

$$R_l = r_{<}^l / r_{>}^{l+1} . \quad (196)$$

This expression, which is derived in section IV, is for the interaction of point charges, q , with electrons of the central ion.

(2) Maki The potential employed by Maki (28, 29, 48) for square-planar symmetry is very similar to the one used in this thesis:

$$V^{LF} = -q \left\{ 8 \sqrt{\pi} R_0 Y(0,0) - 4 \sqrt{\pi} R_2 Y(2,0) + \sqrt{\pi} R_4 Y(4,0) - \sqrt{35\pi} / 3 \sqrt{2} R_4 [Y(4,4) + Y(4,-4)] \right\} \quad (197)$$

where R_l is defined by Equation 196. The initial term, $8 \sqrt{\pi} R_0 Y(0,0)$, is relatively unimportant since it simply results in the addition of the same value to each diagonal element in the matrices and hence does not affect the relative separations between the energy levels. Indeed, Maki (28) discards this term in her calculations. The important difference in the two expressions is in the sign of the coefficient which precedes the $Y(4,4)$ and $Y(4,-4)$ spherical

harmonics. This difference arises as a result of the choice of locations of the ligand with respect to the coordinate axes. Maki (28) chose to locate the ligands along the $\pm xy$ axes while in this thesis they are considered to be along the $\pm x$ and $\pm y$ axes. Maki's choice not only changes the sign of the appropriate matrix element but also results in an interchange in the interpretation of the symmetry representations, B_1 and B_2 .

(3) Liehr Liehr (49), following the methods outlined by Moffitt and Ballhausen (7), arrives at an expression for tetragonal symmetry through consideration of the tetragonal field as a sum of an octahedral field and an axial field. The axial field, which may be due to different ligands or a different ligand distance, is considered to be along the $\pm z$ -axes. The potential expression is:

$$V_T = V_O + V_A \quad (198)$$

where V_T = tetragonal potential

V_O = octahedral potential⁶

$$= \{Y(4,0) + \sqrt{5}/\sqrt{14} [Y(4,4) + Y(4,-4)]\} D_4(r) \quad (199)$$

V_A = axial potential

$$= Y(2,0) D_2(r') + Y(4,0) D_4(r') \quad (200)$$

The methods of this thesis, when applied to the same two

⁶Actually, Liehr (49) uses $R_4(r)$ rather than $D_4(r)$, but this could lead to confusion when comparison with the form of this thesis is made.

potentials, V_0 and V_A , result in the following expressions in terms of point charges and electrons:

$$V_0 = -q \left\{ 7 \sqrt{\pi} / 3 Y(4,0) R_4(r) + \sqrt{35\pi} / 3 \sqrt{2} R_4(r) [Y(4,4) + Y(4,-4)] \right\} \quad (201)$$

$$= -q 7 \sqrt{\pi} / 3 R_4(r) \left\{ Y(4,0) + 5 / \sqrt{14} [Y(4,4) + Y(4,-4)] \right\} \quad (202)$$

$$V_A = -q' \left\{ 4 \sqrt{\pi} / \sqrt{5} R_2(r') Y(2,0) + 4 \sqrt{\pi} 3 R_4(r') Y(4,0) \right\} \quad (203)$$

where q and r do not necessarily equal q' and r' . Comparison of Equations 199 and 200 with Equations 202 and 203 lead to the relationships:

$$D_4(r) = -q 7 \sqrt{\pi} / 3 R_4(r) \quad (204)$$

$$D_2(r') = -q' 4 \sqrt{\pi} / \sqrt{5} R_2(r') \quad (205)$$

$$D_4(r') = -q' 4 \sqrt{\pi} / 3 R_4(r') \quad (206)$$

In order to obtain the expression for square-planar symmetry, from the $V_T = V_0 + V_A$ approach, one considers the axial potential, V_A as being due to charges which are equal in magnitude but opposite in sign to those due to the octahedral field, and located such that the radial distances involved in V_0 and V_A are the same. That is, for Equations 202 and 203:

$$q' = -q \quad (207)$$

$$R_2(r') = R_2(r) \quad (208)$$

$$R_4(r') = R_4(r) \quad (209)$$

The resultant expression for the square-planar potential, V_{Sq} , is then identical with that given in Equation 195.

A corresponding application to Liehr's expression (49), given in Equations 199 and 200, cannot be made directly since $D_4(r)$ and $D_4(r')$ contain certain coefficients within them which are not the same, as can be seen from Equations 204 and 206. Actually, in the square-planar case:

$$D_4(r) = 7/4 D_4(r'), \quad (210)$$

and hence the square-planar potential in Liehr's notation is:

$$V_{Sq} = -Y(2,0) D_2(r) + 3/7 Y(4,0) D_4(r) + 5/\sqrt{14} [Y(4,4) + Y(4,-4)] D_4(r) \quad (211)$$

Equation 211 presumes that, $V_{Sq} = V_0 - V_A$, in order to make the same cancellation of potential accomplished by Equation 207.

(4) Bleaney and Stevens Bleaney and Stevens

(21) present three possible expressions for the ligand potential in tetragonal symmetry. The first form is simply the expansion of the potential with unspecified coefficients, that is:

$$V = \sum A_l^m r^{-l} Y(l,m) \quad (212)$$

$$V = A_2^0 r^{-2} Y(2,0) + A_4^0 r^{-4} Y(4,0) + A_4^{4-4} r^{-4} Y(4,4) + A_4^{-4-4} r^{-4} Y(4,-4), \quad (213)$$

where $A_4^4 = A_4^{-4}$. In Equation 213, the radial term, r^l , and the coefficients, A_l^m , roughly correspond to the radial term, $R_l(r)$ and the numerical coefficients respectively, in Equation 195.

The second expression given by Bleaney and Stevens (21)

simply presents the first expression in terms of cartesian coordinates instead of spherical harmonics. Thus:

$$V = B_2^0 \bar{r}^{-2} (3z^2 - r^2) + B_4^0 (35z^2 - 30r^2 z^2 + 3r^4) \bar{r}^{-4} + B_4^4 (x^4 - 6x^2 y^2 + y^4) \bar{r}^{-4} \quad (214)$$

where the A_l^m and B_l^m coefficients are related by:

$$\begin{aligned} B_2^0 &= 5/4 \sqrt{\pi} A_2^0 \\ B_4^0 &= 3/16 \sqrt{\pi} A_4^0 \\ B_4^4 &= 3 \sqrt{35}/8 \sqrt{2\pi} A_4^4 \end{aligned}$$

The third form of the potential, to be given in Equation 215, is actually the most useful. The potential is expressed as a function of angular momentum operators. Stevens (50) has shown that the matrix elements expressed as a function of x , y , and z are proportional to the matrix elements of a similar operator in which x , y , and z are everywhere replaced by the total angular momentum operators, J_x , J_y , and J_z , respectively. The only precaution in the substitution is that whereas x , y , and z commute, J_x , J_y , and J_z do not. Therefore, a term such as xz would be replaced by $1/2 (J_x J_z + J_z J_x)$. Thus, from the expression given by Equation 214, one obtains:

$$V = B_2^0 \alpha \bar{r}^{-2} (3J_z^2 - J^2) + B_4^0 \beta \bar{r}^{-4} (35J_z^2 - 30J^2 J_z^2 + 25J_z^2 - 6J^2 + 3(J^2)^2) + B_4^4 \beta \bar{r}^{-4} / 2 [J_+^4 + J_-^4], \quad (215)$$

where α and β are the proportionality constants to be considered and determined. The details of this approach are carefully and exhaustively covered by Stevens (50) and need

not be reproduced here. The advantage of the method is that it is not necessary to obtain the specific forms for all the wave functions for the weak field in terms of products of single electron functions. However, the method is complex enough, because of the necessity of obtaining the appropriate proportionality factors, α and β , for each g and λ value, that it is just as convenient, in the two electron case, to obtain the wave functions. In situations which involve more than two electrons, however, the technique would be very helpful.

b. The single electron matrix elements Two main systems for presentation of the ligand field parameters are found in the literature. One involves the use of the variable, "effective dipole moment", μ , and "effective radial distance", R ; the other employs parameters denoted by Dq , Ds , and Dt . The former approach is used in this thesis, as well as by Maki (28) and Ballhausen (14, 27). The Dq , etc., symbolism is used by Liehr (49) and others (7, 23, 26).

The single electron matrix elements, Q_2 , Q_1 , Q_0 , and B_{2-2} , for square-planar symmetry, have been derived in detail in this thesis in terms of μ and the "B" integrals, which are functions of R . Their values are repeated in Table 35. Table 35 also contains expressions for the matrix elements in tetragonal and square-planar potentials in terms of Dq , Ds , and Dt .

The historic definition (4) of Dq is given in terms of a

Table 35. Single electron matrix elements in analogous forms

Matrix element	Function of μ and R square-planar ^b	Function of Dq, Ds, and Dt ^a tetragonal	Square-planar
Q_2	$1/14 B_4 + 4/7 B_2$	$Dq + 2Ds - Dt$	$3/7 Dq - 2Ds$
Q_1	$-2/7 B_4 - 2/7 B_2$	$-4Dq - Ds + 4Dt$	$-12/7 Dq + Ds$
Q_0	$3/7 B_4 - 4/7 B_2$	$6Dq - 2Ds - 6Dt$	$18/7 Dq + 2Ds$
B_{2-2}	$5/6 B_4$	$5 Dq$	$5 Dq$

^aThe parameters Dq, Ds, and Dt are defined by Equations 216, 218, and 220 respectively. They are related to the "B" integrals in column two by Equations 227, 228, and 229.

^bThe B integrals in this column represent the $B_l(a,b)$ integrals defined by Equation 105 and expressed as functions of $X = fR$ in Table 6. Maki's results (28) differ in the sign preceding the B_{2-2} matrix element because of her choice of ligand locations.

matrix element for an octahedral field, namely:

$$Dq = \int |2, \pm 2\rangle^* V_0 |2, \pm 2\rangle d\tau, \quad (216)$$

where V_0 is the octahedral ligand field potential as given by Equations 199 and 202.

Use of Equation 199 and the appropriate expansion of the spherical harmonics associated with the single electron wave functions leads to the result:

$$Dq = 1/14 \sqrt{\pi} \langle D_4(r) \rangle \quad (217)$$

where $\langle D_4(r) \rangle$ is the radial integral, $\int R(a) R(b) D_4(r) r^2 dr$.

In an analogous fashion, Moffitt and Ballhausen (7) and

Liehr (49) define D_s by the relation:

$$D_s = - \int |2, \pm 1\rangle^* V_A^{(2)} |2, \pm 1\rangle d\tau, \quad (218)$$

where $V_A^{(2)} = D_2(r') Y(2,0)$, that is, $V_A^{(2)}$ is the first term in the axial potential given by Equation 200. Therefore:

$$D_s = - 5/14 \sqrt{\pi} \langle D_2(r') \rangle, \quad (219)$$

where $\langle D_2(r') \rangle$ is the corresponding radial integral.

Similarly, D_t is defined by the relation:

$$D_t = - \int |2, \pm 2\rangle V_A^{(4)} |2, \pm 2\rangle d\tau, \quad (220)$$

where $V_A^{(4)} = D_4(r') Y(4,0)$, that is, it is the second term in the axial potential given by Equation 200. Therefore:

$$D_t = -1/14 \sqrt{\pi} \langle D_4(r') \rangle. \quad (221)$$

In terms of the approach used by Liehr (49), the single electron matrix element, Q_2 , in a tetragonal field is given by:

$$Q_2 = \int |2, \pm 2\rangle^* V_T |2, \pm 2\rangle d\tau, \quad (222)$$

where V_T is defined by Equation 198, 199, and 200. Then:

$$Q_2 = 1/14 \sqrt{\pi} \langle D_4(r) \rangle - 5/7 \sqrt{\pi} \langle D_2(r') \rangle + 1/14 \sqrt{\pi} \langle D_4(r') \rangle, \quad (223)$$

which, from the definitions of D_q , D_s , and D_t , can be expressed as:

$$Q_2 = D_q + 2D_s - D_t. \quad (224)$$

In an analogous fashion, the other single electron integrals for the tetragonal field can be evaluated. Similarly, the expressions for square-planar symmetry can be obtained by application of Equation 211 and the definitions of D_q and D_s .

Both sets are given in Table 35.

To obtain correspondence between the various sets given in the table, it is necessary to evaluate Dq , Ds , and Dt in terms of the approach used in this thesis, given by Equations 202 and 203. Thus, for point charges and electrons in tetragonal symmetry:

$$Dq = \int |2, \pm 2\rangle^* V_0 |2, \pm 2\rangle d\tau \quad (225)$$

$$= 1/6 G_4(a,b) = 1/6 [-q \int R_a(r) R_b(r) R_4(r) r^2 dr], \quad (226)$$

where $G_4(a,b)$ is the radial integral defined by Equation 94.

For point dipoles and "electron holes", the expression for Dq is:

$$Dq = 1/6 [\mu f^2 / 78.75 B_4(X)] = 1/6 B_4(a,b). \quad (227)$$

Analogously:

$$Ds = -2/7 [\mu f^2 / 78.75 B_2(X')] = -2/7 B_2(a,b), \quad (228)$$

$$Dt = -2/21 [\mu f^2 / 78.75 B_4(X')] = -2/21 B_4(a,b). \quad (229)$$

C. Appendix C: Group Theory

The following is not meant to be an all inclusive treatise on the theory of groups. It is assumed that the reader is familiar with the general concepts as outlined in texts such as that by Eyring, et al. (24). Proofs of the validity of various relationships and applications are generally omitted since they are available in such standard texts as that by Wigner (51). Certain concepts are worth special consideration because of their applicability to the ligand field theory calculations.

1. Basis functions

A set of functions, $\psi_1, \psi_2 \dots \psi_k$, is said to form a basis for a representation of a group if the application of the group operations on the functions generate the group representation. That is, the set of functions, under the operation of some element of the group, go into linear combinations of one another. Mathematically:

$$R \psi_i = \sum_{j=1}^k \Gamma(R)_{ji} \psi_j, \quad (230)$$

where R is a group operation,

$\Gamma(R)_{ji}$ is an element of the matrix representation corresponding to the group operation.

2. D_{4h} group operations

Square-planar complexes of platinum(II), such as $[\text{PtCl}_4]^{2-}$, belong to the rotation group D_{4h} . This symbol is most easily defined after examination of the group elements. They are:

- 1) E = the identity operator
- 2a) C_4 = counterclockwise rotation by $2\pi/4$ about the z-axis, which is the principal axis
- 2b) C_4^3 = counterclockwise rotation by $3(2\pi/4)$ or clockwise by $2\pi/4$ about the z-axis
- 3) C_2 = rotation about the z-axis by $2\pi/2$
- 4a) $C_2(x)$ = rotation about the x-axis by $2\pi/2$

- 4b) $C_2'(y)$ = rotation about the y-axis by $2\pi/2$
- 5a) $C_2''(xy)$ = rotation about the (xy)-axis by $2\pi/2$
- 5b) $C_2''(-xy)$ = rotation about the (-xy)-axis by $2\pi/2$
- 6) i = inversion through the origin
- 7) σ_h = reflection in the xy-plane
- 8a) S_4 = counterclockwise rotation about the z-axis by $2\pi/4$ followed by reflection in the (xy) plane
- 8b) S_4^3 = clockwise rotation about the z-axis by $2\pi/4$ followed by reflection in the (xy) plane
- 9a) $\sigma_d(x)$ = reflection in the (xz) plane
- 9b) $\sigma_d(y)$ = reflection in the (yz) plane
- 10a) $\sigma_d'(xy)$ = reflection in the plane defined by the (xy)-axis and the (z)-axis
- 10b) $\sigma_d'(-xy)$ = reflection in the plane defined by the (-xy)-axis and the (z)-axis

Those operations which belong to the same class, that is, whose matrix representations are connected by similarity transformations are grouped together. For example, C_4 and C_4^3 belong to the same class.

In the symbol, D_{4h} , the (4) indicates that the principle axis is a 4-fold axis. D_4 means that there are four 2-fold axes perpendicular to the principle 4-fold axis. The subscript, (h), indicates that the symmetry operations σ_h and σ_d are elements of the representation. The operations for the D_{4h} group, together with their "characters", which will be

discussed in Appendix C, are given in Table 36.

3. Matrix representation of a group

Matrices are able to form representations of groups since it is possible to obtain matrices which have a one-to-one correspondence to the group elements and which have the same multiplication table. Obviously, the matrices which describe rotation operators fall into this category.

In constructing the matrices corresponding to the group elements, one must use a consistent approach, since it is possible to use one of two techniques. This is most easily

Table 36. Character table for the symmetry group, D_{4h}

Irr. Rep. ^a	Group operation									
	E	C_2	$2C_4$	$2C_2'$	$2C_2''$	i	σ_h	$2S_4$	$2\sigma_v'$	$2\sigma_v''$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1g}	1	1	-1	1	-1	1	1	-1	1	-1
B_{1u}	1	1	-1	1	-1	-1	-1	1	-1	1
B_{2g}	1	1	-1	-1	1	1	1	-1	-1	1
B_{2u}	1	1	-1	-1	1	-1	-1	1	1	-1
E_g	2	-2	0	0	0	2	-2	0	0	0
E_u	2	-2	0	0	0	-2	-2	0	0	0

^aIrr. Rep. stands for irreducible representation.

seen by consideration of a vector,

$$\vec{r} = x_1 \vec{i} + y_1 \vec{j} + z_1 \vec{k} \quad (231)$$

where x_1 , y_1 , and z_1 are the coordinates of the vector and \vec{i} , \vec{j} , \vec{k} , are the orthogonal unit vectors, which define the 3-dimensional space. See Figure 15. The components of a vector can be expressed in terms of the Euler angles, θ and ϕ , and the length of the vector, r . Thus:

$$x_1 = r \cdot \sin\theta \cos\phi$$

$$y_1 = r \cdot \sin\theta \sin\phi$$

$$z_1 = r \cdot \cos\theta$$

a. Rotation of the vector

If one considers the situation in which the group operations act upon the vector, then it is possible to describe the new vector which results in terms of the original coordinate system,

$$\vec{r}' = x_2 \vec{i}' + y_2 \vec{j}' + z_2 \vec{k}' \quad (232)$$

For example, consider a counterclockwise rotation about the z -axis by an angle α operating on the original vector. Then θ is unaffected, but ϕ changes to $\phi + \alpha$. Then the coordinates of the new vector, \vec{r}' , are given by:

$$x_2' = r \sin\theta \cos(\phi + \alpha) = r \cdot \sin\theta [\cos\alpha \cos\phi - \sin\alpha \sin\phi] \quad (233)$$

$$y_2' = r \sin\theta \sin(\phi + \alpha) = r \cdot \sin\theta [\sin\alpha \cos\phi + \cos\alpha \sin\phi] \quad (234)$$

$$z_2 = r \cos\theta \quad (235)$$

Hence:

$$x_2 = (\cos\alpha)x_1 - (\sin\alpha)y_1 \quad (236)$$

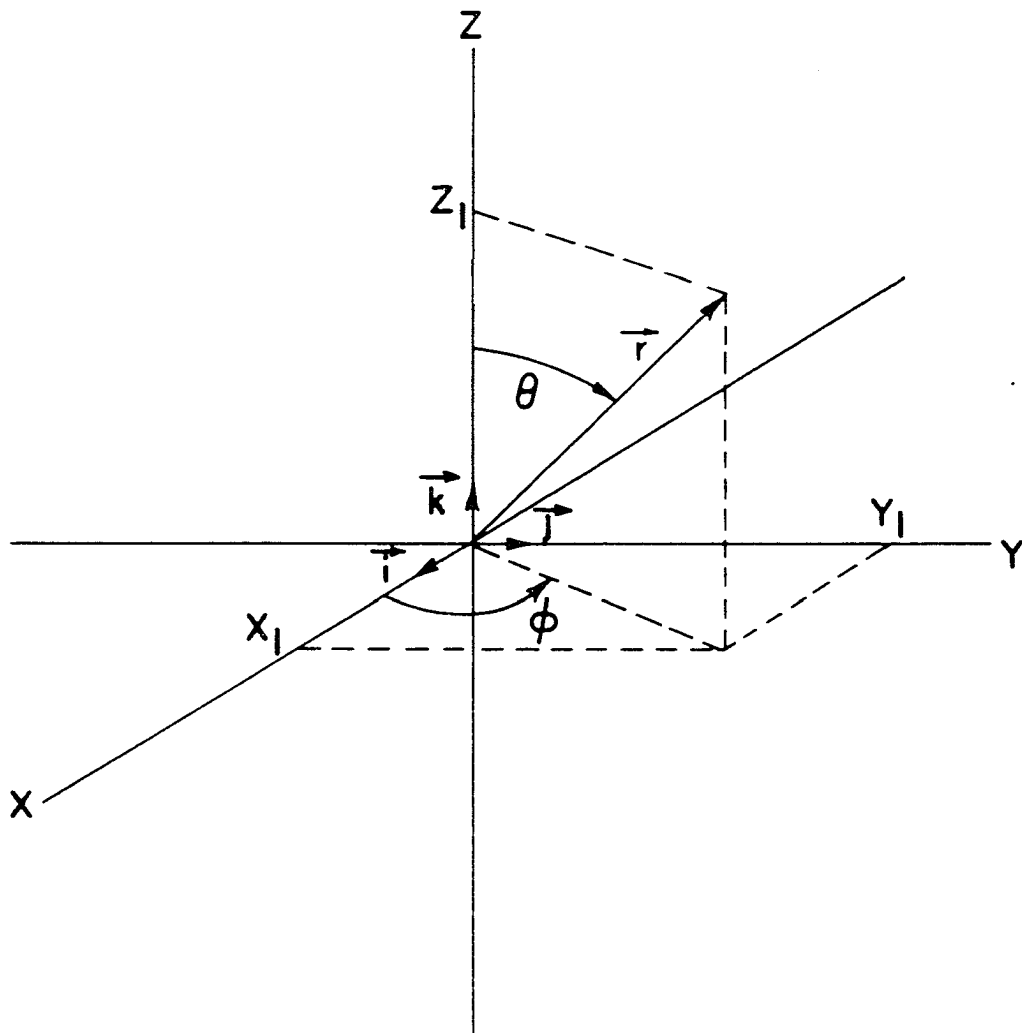


Figure 15. Coordinates of a vector

$$y_2 = (\sin\alpha)x_1 + (\cos\alpha)y_1 \quad (237)$$

$$z_2 = z_1 \quad (238)$$

Expressing the same relations in matrix form, one obtains:

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} \quad (239)$$

If $\alpha = 90^\circ$, as in the case of C_4 of the D_{4h} group:

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} \quad (240)$$

b. Rotation of the coordinate system of the vector

If one considers that the group operations act, not on the vector, but on the coordinate system, then it is possible to define the vector in terms of the new coordinate system.

Thus, the vector, \vec{r} , in the new coordinate system is given by:

$$\vec{r} = x'\vec{i}' + y'\vec{j}' + z'\vec{k}' \quad (241)$$

Consider the same rotation operation, counterclockwise rotation about the z-axis by an angle α , this time acting on the coordinate system. That is, the group operations act on the basis vectors, \vec{i} , \vec{j} , \vec{k} , to give new basis vectors, \vec{i}' , \vec{j}' , \vec{k}' . The relation between the old basis vectors and the new basis vectors is obtained by the methods given in the previous section.

The vector, \vec{r} , in the new basis, has new coordinates, x' , y' , z' . It is easily shown that:

$$x' = (\cos\alpha)x_1 + (\sin\alpha)y_1 \quad (242)$$

$$y' = (-\sin\alpha)x_1 + (\cos\alpha)y_1 \quad (243)$$

$$z' = z_1 \quad (244)$$

In matrix notation, this is

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} \quad (245)$$

It is seen that the matrix corresponding to the operation is the inverse of that given for the rotation of the vector. It is important to note, however, that the coordinates of the vector in the original basis are related to the coordinates in the new basis by:

$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \quad (246)$$

which is identical to the matrix for the rotation of the vector.

c. Effect of change of coordinates on the basis functions Symmetry groups are of interest in this thesis, not because of their effect on vectors but because of their usefulness in choosing appropriate basis functions. Hence, the effects of the group elements on functions are of importance. Here again, one has the choice of "rotating the function" or of "rotating the coordinate system in which the function is defined". The latter method is chosen in order to be

consistent with the use of the spin transformation matrices given by Goldstein (52).

In order to illustrate the effects on the functions which result when the rotation operators act on the coordinate system, consider the function,

$$F = f(x, y, z).$$

If a change of basis is made by rotation, then the relation between the old and new coordinates is given by

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} & & \\ & A & \\ & & \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (247)$$

where (A) is the matrix obtained by the considerations given in the previous section. One can then define R to be that operator which changes f in such a way that,

$$g(x', y', z') = Rf(x', y', z'),$$

evaluated for (x', y', z') has the same value as f evaluated for (x, y, z) . Hence:

$$Rf(x', y', z') = f(x, y, z) = f[A^{-1}(x', y', z')] \quad (248)$$

It is typical for an operation that if $F_k(k = 1, 2, \dots)$ form a basis for a representation of a group to which R belongs then the algebraic form of each RF_k is such that it can be expressed in a linear combination of all F_k , that is,

$$RF_k(x, y, z) = F_k[A^{-1}(x, y, z)] = F_j(x, y, z)R_{jk} \quad (249)$$

where R_{jk} is the matrix typical for R, independent of (x, y, z) .

For example, consider the two functions:

$$F_1 = f_1(x, y, z) = r \cdot (xz) \quad (250)$$

$$F_2 = f_2(x, y, z) = r \cdot (yz) \quad (251)$$

If the coordinate bases are rotated by 90° counterclockwise about the z -axis, it can be shown that:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -y' \\ x' \\ z' \end{pmatrix} \quad (252)$$

Then, F_1 and F_2 in the new basis have the forms:

$$F_1 = Rf_1(x', y', z') = r \cdot (-y'z') \quad (253)$$

$$F_2 = Rf_2(x', y', z') = r \cdot (x'z') \quad (254)$$

From this, it is possible to define the matrix corresponding to the operator, R . Dropping the prime notation as superfluous, one can write:

$$R(f_1 \quad f_2) = \begin{pmatrix} r(xz) & r(yz) \end{pmatrix} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} r(-yz) & r(xz) \end{pmatrix} \quad (255)$$

The simplest way to construct the appropriate matrices corresponding to the group operations as given above is to consider the operations as "replacement" operations. For example, in the foregoing case of C_4 rotation about the z -axis, the coordinate (x) was replaced by $(-y)$, (y) was replaced by (x) , and (z) was replaced by (z) . Hence, these replacements are carried out in the functions and:

$$f_1 = r \cdot (xz) \text{ becomes } r \cdot (-yz) = -f_2 \quad (256)$$

$$f_2 = r \cdot (yz) \text{ becomes } r \cdot (xz) = f_1 \quad (257)$$

It is understood, of course, that the function remains the

same but the form of the function changes.

To show that the resultant matrix is not the same as in the case in which the function is rotated, consider the operator, R' , where R' is the same C_4 rotation but acting on the functions, f_1 and f_2 , themselves. If one expresses the new functions in the same basis, (x,y,z) , it is clear that

$$R' \begin{pmatrix} r(xz) & r(yz) \end{pmatrix} = \begin{pmatrix} r(yz) & r(-xz) \end{pmatrix} \quad (258)$$

Hence, in matrix notation:

$$\begin{pmatrix} r(xz) & r(yz) \end{pmatrix} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} r(yz) & r(-xz) \end{pmatrix} \quad (259)$$

Comparison of the rotation matrices in the two cases shows that one is the inverse of the other.

4. Reducible and irreducible representations of the group

If three matrices, A , A' and B , are related by the equation:

$$A' = BAB^{-1}$$

then A' is called the transform of A by B . B is called the transformation matrix, and the process of constructing A' from A and B is called a similarity transformation. These transformations imply that it is possible to choose a new co-ordinate system in which one operation is replaced by the other. If the matrix B is unitary, i.e., if $B^{-1} = B^*$, where B^* is the hermetian conjugate matrix of B , then the transformation is called a unitary transformation.

A matrix representation, $\Gamma(R)$, of a group, where (R) is an element of the group, is called reducible if all the matrices of the group can, by one similarity transformation be put in the form, $\Gamma'(R)$ given by

$$\Gamma'(R) = S^{-1} \Gamma(R) S = \begin{pmatrix} \boxed{1(R)} & & & \\ & \boxed{2(R)} & & \\ & & \boxed{3(R)} & \\ & & & \ddots \\ & & & & \boxed{i(R)} \end{pmatrix} \quad (260)$$

where $\Gamma_1(R)$, $\Gamma_2(R)$, etc., are irreducible representations of the group. By irreducible representations is meant, of course, that other similarity transformations cannot be found which further decrease the size of the matrix blocks. This implies that the basis functions can be grouped into several sets, each of which, by itself, generates one of the irreducible representations, $\Gamma_i(R)$.

The diagram makes no attempt to estimate the number of elements in each irreducible representation, and the zeroes indicate that all other elements outside the blocks are zero. Since the total size of the matrix is unchanged, the number of rows and columns in the irreducible matrices equals the number of rows and columns of the original reducible matrix. Furthermore, $\Gamma_1(R)$ need not necessarily be different from $\Gamma_2(R)$, etc.

Since the original reducible matrix was unitary, the

transformation was a unitary transformation and the irreducible matrices are unitary. Any such reduction of reducible matrices is unique, that is, the reducible representation is composed of one particular set of irreducible representations.

For the group of interest, D_{4h} , there exist five irreducible representations which are not equivalent. By equivalence is meant that two representations are simply the same operations with respect to different coordinate systems.

The matrices in Table 37 are good examples of a reducible representation of the D_{4h} group. These matrices were obtained from the relationships between old and new coordinates as a result of the group operations on the coordinates, that is,

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} R \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}, \quad (261)$$

as outlined in the previous section. The dotted lines indicate the division of the matrices into two irreducible representations. Fortunately, the matrices are already in reduced form and a similarity transformation is not required. As is indicated later, the upper 2 X 2 set belongs to the irreducible representation, E_u , the lower belongs to the representation, A_{2u} . If the reducible representation of Table 37 is called, Γ , then one writes symbolically:

$$\Gamma = E_u + A_{2u} \quad (262)$$

Table 37. Example of a reducible representation of the D_{4h} group

Operation			
\underline{E}	$\underline{C_4}$	$\underline{C_4^3}$	$\underline{C_2}$
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ \hline 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ \hline 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ \hline 0 & 0 & 1 \end{pmatrix}$
$\underline{C_2'(x)}$	$\underline{C_2'(y)}$	$\underline{C_2''(xy)}$	$\underline{C_2''(-xy)}$
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ \hline 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ \hline 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ \hline 0 & 0 & -1 \end{pmatrix}$
\underline{i}	$\underline{\sigma_h}$	$\underline{S_4}$	$\underline{S_4^3}$
$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ \hline 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ \hline 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ \hline 0 & 0 & -1 \end{pmatrix}$
$\underline{\sigma_v'(x)}$	$\underline{\sigma_v'(y)}$	$\underline{\sigma_v''(xy)}$	$\underline{\sigma_v''(-xy)}$
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ \hline 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ \hline 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ \hline 0 & 0 & 1 \end{pmatrix}$

5. Character or trace of a matrix

The trace of a matrix is defined as the sum of the diagonal elements of a matrix, i.e., for the matrix A:

$$\text{trace (A)} = \sum_i A_{ii} \quad (263)$$

The traces of matrices representing a group are denoted by $\chi(R)$ and are called the characters of the representation, i.e.,

$$\chi(R) = \sum_i \Gamma(R)_{ii} \quad (264)$$

The trace of a matrix has the property that its value is unchanged if the matrix undergoes a similarity transformation. Thus:

$$\begin{aligned} \text{trace } (A') &= \sum A'_{ii} = \text{trace } (S^{-1}AS) \\ &= \sum_{ijk} S^{-1}_{ij} A_{jk} S_{ki} \\ &= \sum_{jK} [SS^{-1}]_{kj} A_{jk} \\ &= \sum_{jK} \delta_{kj} A_{jk} = A_{jj} \end{aligned} \quad (265)$$

$$\text{trace } (A') = \text{trace } (A) \quad (266)$$

A class of elements in a group is defined as all members of the group which are connected by those similarity transformations in which the transforming matrix is one of the group elements. All class members have the same character. Table 36 is the character table for the irreducible representations of the D_{4h} group. It combines the operations into classes.

There are several useful properties of the characters:

- a. A necessary and sufficient condition for a representation to be irreducible is $\sum_R |\chi(R)|^2 = g$, where g is the order of the group, i.e., the number of

group operations.

- b. A necessary and sufficient condition for the equivalence of two irreducible representations is the equality of their character systems.
- c. If a reducible representation, Γ , is decomposed into its irreducible representations, that is,

$$\Gamma = \sum_i c_i \Gamma_i \quad (267)$$

then for each group element, (R) , the character, $\chi(R)$ in the representation Γ is related to its characters, $\chi_i(R)$, in the representations Γ_i by

$$\chi(R) = \sum_i c_i \chi_i(R). \quad (268)$$

- d. The number of times an irreducible representation, $\Gamma_i(R)$, or a representation equivalent to it, appears in a reducible representation, $\Gamma(R)$, is given by:

$$c = 1/g \sum_R [\chi(R)][\chi_i(R)]^* \quad (269)$$

6. The full 3-dimensional rotation-reflection group

a. Nature of the full rotation-reflection group The

continuous group which is formed from the set of all real orthogonal 3-dimensional matrices is called the full 3-dimensional rotation group. The pure rotation group includes only orthogonal matrices with determinant +1, while the rotation-reflection group also includes those with determinant -1.

Basis functions for irreducible representations of the

full rotation-reflection group are the spherical harmonics, $Y_l^m(\theta, \phi)$. This can be understood by consideration of an application of the full rotation group to a physical situation, namely, an electron in a spherically symmetric potential as encountered in consideration of single electron hydrogen-like atoms. It will be recalled that the wave functions, with principle quantum number n , associated with hydrogen-like atoms can be grouped into degenerate sets according to the orbital quantum number, l . The degeneracy of each set is $2l + 1$. The angular dependence of the wave functions in a set is given in terms of the spherical harmonics, $Y(l, m)$, ranging from $Y(l, m)$ to $Y(l, -m)$ in integers of m . Wave functions associated with states which are degenerate, other than those states which are accidentally degenerate, are basis functions for irreducible representations of the group. Hence the spherical harmonics, $Y(l, m)$ are basis functions for the irreducible representations of the full rotation-reflection group.

From consideration of the group operations acting on the basis functions, the general expression for the characters of the group can be obtained. In the full rotation group, all rotations by an angle, α , about any axis are members of the same class. Since members of the same class have the same character, it is convenient to find the character, $\chi(\alpha)$, by consideration of a rotation about the z -axis.

Apart from unimportant coefficients, the spherical harmonics are given by:

$$\begin{aligned}
 Y(l, l) &= P_l^l(\cos\theta) e^{il\phi} \\
 Y(l, l-1) &= P_l^{l-1}(\cos\theta) e^{i(l-1)\phi} \\
 &\vdots \\
 Y(l, -l) &= P_l^{-l}(\cos\theta) e^{-il\phi}
 \end{aligned} \tag{270}$$

Rotation about the z-axis does not affect θ , but changes ϕ to $\phi + \alpha$. Hence:

$$\begin{aligned}
 Y'(l, l) &= P_l^l(\cos\theta) e^{il(\phi+\alpha)} \\
 &\vdots \\
 Y'(l, -l) &= P_l^{-l}(\cos\theta) e^{-il(\phi+\alpha)}
 \end{aligned} \tag{271}$$

Thus the rotation can be represented by the matrices:

$$\begin{aligned}
 &\left(\begin{array}{cccc} Y(l, l) & Y(l, l-1) & \cdots & Y(l, -l) \end{array} \right) \begin{pmatrix} e^{il\alpha} & & & \\ & e^{i(l-1)\alpha} & & \\ & & \ddots & \\ & & & e^{-il\alpha} \end{pmatrix} = \\
 &= (Y'(l, l) \ Y'(l, l-1) \ \cdots \ Y'(l, -l)) \tag{272}
 \end{aligned}$$

Hence the representation for the $Y(l, m)$ in the full rotation group is:

$$(\alpha) = \begin{pmatrix} e^{il\alpha} & & & \\ & e^{i(l-1)\alpha} & & \\ & & \ddots & \\ & & & e^{-il\alpha} \end{pmatrix} \tag{273}$$

The character of this representation is, therefore:

$$\chi(\alpha) = e^{i\ell\alpha} + e^{i(\ell-1)\alpha} + \dots + e^{-i\ell\alpha} \quad (274)$$

$$= e^{i\ell\alpha} \sum_{n=0}^{2\ell} [e^{-i\alpha}]^n \quad (275)$$

This is a geometrical series, the summation of which is given by:

$$\chi(\alpha) = \frac{\sin(\ell+1/2)\alpha}{\sin 1/2\alpha} \quad (276)$$

b. Isomorphism of the $|J, M_J\rangle$ and $|\ell, m_\ell\rangle$ representations in the full rotation group It has been indicated above that the spherical harmonics, $Y(\ell, m)$, are basis functions for irreducible representations of the full rotation group. It is possible to show that the functions $|J, M_J\rangle$ also form basis for the full rotation group.

If there are two representations of a group such that there exists a unique one-to-one correspondence between group elements so that their multiplication table is the same, then the two representations are essentially identical and are called isomorphic. It is desirable to indicate that the $|J, M_J\rangle$ and $|\ell, m_\ell\rangle$ functions form basis functions for representations which are isomorphic, if the numerical values of J and M_J are identical with those of ℓ and m , respectively.

$|J, M_J\rangle$ functions have three properties:

1. They are eigenfunctions of angular momentum operators.
2. They are basis functions for irreducible repre-

sentations of the full rotation reflection group.

3. They can be constructed with the help of the step-up and step-down operators, which are made up from angular momentum operators.

These properties are intrinsically related to each other because angular momentum operators are the infinitesimal operators of the rotation group.

Such $|J, M_J\rangle$ functions exist in the one-electron as well as the many-electron case. The above mentioned properties are basic consequences of the representation and are valid in all cases.

Let $|J, M_J\rangle^n$, a set of n -electron functions, be the basis functions for a representation, and let $|J, M_J\rangle^m$ be a set of m -electron functions which form a basis for the same representation. Hence, the $|J, M_J\rangle^n$ and $|J, M_J\rangle^m$ have the same transformation properties under any rotation. As a consequence, any linear combination of the $|J, M_J\rangle^n$ functions has the same transformation properties as the analogous linear combination of the $|J, M_J\rangle^m$ functions, that is, the appropriate combinations are independent of the values of m and n .

Furthermore, it should be noted that the isomorphism of the representations corresponding to the $|J, M_J\rangle^n$ and $|J, M_J\rangle^m$ functions holds in rotation groups of lower symmetry than that of the full rotation group, since such groups are sub-groups of the full rotation group.

It is easiest to construct those linear combinations which form the basis for irreducible representations from one-electron functions, that is, $m = 1$. Analogous linear combinations of n -electron functions will then form bases for the same irreducible representations.

Since the angular dependence of one-electron functions, $|\ell, m_\ell\rangle$, and hence their symmetry properties, are given in terms of the spherical harmonics, $Y(\ell, m)$, it is convenient to fashion the symmetry properties of the $|J, M_J\rangle$ functions after those of the "spherical harmonics", $Y(J, M_J)$.

7. The irreducible representations of the $(2\ell+1)$ -fold representation in fields of lower symmetry

It has been shown that the spherical harmonics are the basis functions for the $(2\ell+1)$ -fold irreducible representations of the full rotation group. This group has spherical symmetry. In fields of lower symmetry, as in D_{4h} for example, the representations are no longer irreducible but reducible. This means that each matrix can be block partitioned into matrices of lower dimension which furnish the irreducible representations. The reduction of the $2\ell+1$ representation can be carried out by recollection of two facts:

1. The character of the now reducible representation is unchanged by the lower symmetry. This means that the character for a given element of the

reducible representation is obtained by the same equation given for the irreducible representation of the full rotation group, namely:

$$\chi(\alpha) = \frac{\sin(l + 1/2)\alpha}{\sin 1/2\alpha} \quad (277)$$

where α is the angle of rotation for the element. Note that this means that all rotations by 180° for example, have the same character since they belong to the same class in the full rotation group even though they may belong to different classes in the lower symmetry group.

2. Once having determined the characters of the reducible representation, use is made of the property of the characters,

$$\chi(R) = \sum C_i \chi_i(R) \quad (278)$$

that is, for each element, (R) , the character of the reducible representation equals the sum of the characters of all irreducible representations contained in the reducible representation.

An example of the reduction of the representation for $l = 2$ is given in the main body of this thesis.

8. The direct product

From two representations of the group, $\Gamma'(R)$ and $\Gamma''(R)$, it is possible to construct a new representation of the group. This new representation, called the Kronecker or Direct

Product representation. is written as:

$$\Gamma(R) = \Gamma'(R) \times \Gamma''(R). \quad (279)$$

Although it is usually unnecessary to calculate the matrix elements, they can be obtained by taking all possible products of the matrix elements of $\Gamma'(R)$ and $\Gamma''(R)$ according to the formula:

$$\Gamma(R)_{(ij)(kl)} = \Gamma'(R)_{ik} \Gamma''(R)_{jl}. \quad (280)$$

$\Gamma(R)_{(ij)(kl)}$ is the element in the $(ij)^{\text{th}}$ row and the $(kl)^{\text{th}}$ column of $\Gamma(R)$. The index (ij) is taken in the dictionary sense so that (ij) precedes $(i'j')$ when $i < i'$, or if $i = i'$ when $j < j'$. If $\Gamma'(R)$ is of dimension m and $\Gamma''(R)$ is of dimension n , then $\Gamma(R)$ is of dimension mn . For example, if $\Gamma'(R)$

$$\text{is } \begin{pmatrix} A & B \\ C & D \end{pmatrix} \text{ and } \Gamma''(R) = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix}$$

then:

$$\Gamma(R) = \begin{pmatrix} Aa & Ab & Ac & Ba & Bb & Bc \\ Ad & Ae & Af & Bd & Be & Bf \\ Ag & Ah & Ai & Bg & Bh & Bi \\ Ca & Cb & Cc & Da & Db & Dc \\ Cd & Ce & Cf & Dd & De & Df \\ Cg & Ch & Ci & Dg & Dh & Di \end{pmatrix} \quad (281)$$

The characters of the direct product are given by the products of the characters entering into the direct product, that is:

$$\chi(R) = \chi'(R) \chi''(R) \quad (282)$$

Generally speaking the direct product will be a reducible representation. This reduction can be made by use of the

characters of the irreducible representations and the properties of the characters of the reducible representation given in section 5 of this appendix. Frequently the reduction can be made by inspection. For more complicated cases, if $\Gamma_\alpha(R)$ and $\Gamma_\beta(R)$ are the irreducible representations whose direct product is desired then

$$\Gamma(R) = \Gamma_\alpha(R) \times \Gamma_\beta(R) = \sum_{\lambda=1}^n \phi_{\alpha\beta\lambda} \Gamma_\lambda(R) \quad (283)$$

where $\phi_{\alpha\beta\lambda}$ is the number of times the λ irreducible representation occurs in the product of the Γ_α and Γ_β representations. $\phi_{\alpha\beta\lambda}$ is calculated from the relation:

$$\phi_{\alpha\beta\lambda} = \frac{1}{g} \sum_R \chi_\alpha(R) \chi_\beta(R) [\chi_\lambda(R)]^* \quad (284)$$

As an example, consider the direct product of the E_u representation in D_{4h} symmetry with itself. From the characters in Table 36 and the relation $\chi(R) = \chi_{E_u}(R) \chi_{E_u}(R)$, one obtains:

$$\chi(E) = \chi(E) \cdot \chi(E) = 2 \cdot 2 = 4 \quad (285)$$

$$\chi(C_2) = \chi(C_2) \chi(C_2) = (-2) \cdot (-2) = 4 \quad (286)$$

$$\chi(2C_4) = \chi(2C_4) \chi(2C_4) = 0 \cdot 0 = 0 \quad (287)$$

etc.

Inspection of the character table and the property

$$\chi(R) = \sum c_i \chi_i(R)$$

shows that

$$\chi(R) = \chi_{A_{1g}}(R) + \chi_{A_{2g}}(R) + \chi_{B_{1g}}(R) + \chi_{B_{2g}}(R). \quad (288)$$

Therefore:

$$\Gamma(R) = \Gamma_{E_u}(R) \times \Gamma_{E_u}(R) = \Gamma_{A_{1g}} + \Gamma_{A_{2g}} + \Gamma_{B_{1g}} + \Gamma_{B_{2g}} \quad (289)$$

Or more simply:

$$E_u \times E_u = A_{1g} + A_{2g} + B_{1g} + B_{2g} \quad (290)$$

D. Appendix D: Ligand Field Derivations, Strong Field

1. Symmetry adapted spin functions

In construction of the strong field matrix elements, it is possible to obtain wave functions such that the ligand field terms appear only in the diagonal elements of the matrices. However, when spin-orbit coupling is included, it is necessary that the wave functions be symmetry adapted with respect to both spin and space functions.

In order to construct the symmetry adapted spin functions, one makes use of a transformation property inherent in the definition of the spin components, namely, that for every symmetry operation matrix in real space there is a corresponding matrix in the complex space having the same group properties. In chapter 4, section 5, of the text by Goldstein (52), the construction of such a set of 2×2 complex unitary matrices is described. For reasons of space limitations, only the final result will be given.

The complex matrix for the rotations in square-planar

symmetry, described in terms of the Euler angles, θ and ϕ , is:

$$Q = \begin{pmatrix} (\cos\frac{\phi}{2} + i\sin\frac{\phi}{2}) \cos\frac{\theta}{2} & (i\cos\frac{\phi}{2} + \sin\frac{\phi}{2}) \sin\frac{\theta}{2} \\ (i\cos\frac{\phi}{2} - \sin\frac{\phi}{2}) \sin\frac{\theta}{2} & (\cos\frac{\phi}{2} - i\sin\frac{\phi}{2}) \cos\frac{\theta}{2} \end{pmatrix} \quad (291)$$

Although there are actually fifteen group operations in the D_{4h} group, it is often sufficient to use just five of them to obtain the group representation of a particular set of functions. The five are:

- 1) the identity operation, E ,
- 2) rotation about the z -axis by 180° , C_2 ,
- 3) counterclockwise rotation about the z -axis by 90° ,
 C_4 ,
- 4) rotation about the x -axis by 180° , $C_2'(x)$,
- 5) rotation about the xy -axis by 180° , $C_2''(xy)$.

In order to obtain correspondence between the complex matrices, Q , and the rotations, it is necessary to consider the real space operations as replacement operations. For example, in the rotation about the z -axis by 90° , $\theta = 0^\circ$, and $\phi = 90^\circ$, then:

$$Q(C_4) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1+i & 0 \\ 0 & 1-i \end{pmatrix}, \quad (292)$$

while the corresponding C_4 operation in real space is such that a function of x , y , and z is replaced by a function of $-y$, x , and z . These replacement operations are discussed in detail in Appendix C.

Table 38 lists the results of the five operations. The first row of matrices are the Q matrices corresponding to the five group operations. The second row lists the five 2×2 real matrices which are isomorphic, that is, have the same group relationships, as the complex matrices. Application of this latter group will be illustrated later in Appendix D.3.

The effect of the various group operations on the spinor matrices, α and β are, of course,

$$\alpha = \begin{pmatrix} 1 & \\ & 0 \end{pmatrix}, \text{ and } \beta = \begin{pmatrix} 0 & \\ & 1 \end{pmatrix}. \quad (293)$$

Thus, for example:

$$C_4\alpha = \frac{1}{\sqrt{2}} \begin{pmatrix} 1+i & 0 \\ 0 & 1-i \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1+i \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} [\alpha + i\alpha]. \quad (294)$$

$$C_4\beta = \frac{1}{\sqrt{2}} \begin{pmatrix} 1+i & 0 \\ 0 & 1-i \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1-i \end{pmatrix} = \frac{1}{\sqrt{2}} [\beta - i\beta]. \quad (295)$$

Therefore:

$$C_4(\alpha\alpha) = \frac{1}{2}[\alpha + i\alpha][\alpha + i\alpha] = i\alpha\alpha \quad (296)$$

$$C_4(\beta\beta) = \frac{1}{2}[\beta - i\beta][\beta - i\beta] = -i\beta\beta \quad (297)$$

$$C_4(\alpha\beta) = \frac{1}{2}[\alpha + i\alpha][\beta - i\beta] = \alpha\beta \quad (298)$$

$$C_4(\beta\alpha) = \frac{1}{2}[\beta - i\beta][\alpha + i\alpha] = \beta\alpha \quad (299)$$

By similar means, the effects of the symmetry operations on the spin parts of the two electron functions can be obtained. The results are tabulated in Table 39.

The two possible spin states which result from the two

Table 38. Matrix representations in complex and real space for some of the operations of the D_{4h} group

Matrix	Operation ^a				
	E	C_4	C_2	C_2'	C_2''
Complex matrix	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1+i & 0 \\ 0 & 1-i \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$	$\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & i+1 \\ i-1 & 0 \end{pmatrix}$
Real matrix	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

^aThe operations used are explained in the text immediately following Equation 291.

Table 39. Effect of the rotation operations on the spin functions

Initial function	Operation ^a				
	E	C_4	C_2	C_2'	C_2''
$(\alpha\alpha)$	$(\alpha\alpha)$	$i(\alpha\alpha)$	$-(\alpha\alpha)$	$-(\beta\beta)$	$-i(\beta\beta)$
$(\beta\beta)$	$(\beta\beta)$	$-i(\beta\beta)$	$-(\beta\beta)$	$-(\alpha\alpha)$	$i(\alpha\alpha)$
$(\alpha\beta)$	$(\alpha\beta)$	$(\alpha\beta)$	$(\alpha\beta)$	$-(\beta\alpha)$	$-(\beta\alpha)$
$(\beta\alpha)$	$(\beta\alpha)$	$(\beta\alpha)$	$(\beta\alpha)$	$-(\alpha\beta)$	$-(\alpha\beta)$

^aThe rotation operations of this table are the same as those of Table 38.

electron product functions are the singlet and triplet states, with $S = 0$, and $S = 1$, respectively. Just as the space functions may be characterized by certain irreducible group representations according to their values of total orbital angular momentum, J , in the weak field case, so the spin functions can be characterized by their values of S . Thus, for example, the singlet spin function belongs to the representation A_1 since all the group operations leave the wave function invariant. From Table 3, it is seen that the irreducible representations for $S = 1$ are $A_2 + E$. This means that the three triplet functions, $\alpha\alpha$, $\beta\beta$, and $1/\sqrt{2} [\alpha\beta + \beta\alpha]$, can be combined in some linear fashion such that one of the functions belongs to the representation A_2 and the other two functions belong to the representation E . Intuition alone predicts that $1/\sqrt{2} [\alpha\beta + \beta\alpha]$ would belong to the representation A_2 , and this is confirmed by application of the group operations to the function.

Because certain of the group operations change $\alpha\alpha$ into $\beta\beta$ and others involve the complex number, i , the appropriate linear combinations for the doublet, E , is seen to be:

$$1/\sqrt{2} [\alpha\alpha + \beta\beta]$$

$$i/\sqrt{2} [\alpha\alpha - \beta\beta]$$

The group operations on the above matrix give the same results as those obtained by application of the real 2×2 matrices given in the second row of Table 38. Therefore, the symmetry

adapted spin functions may be tabulated as:

$$\begin{array}{ll}
 \text{Singlet } \xi_1 = 1/\sqrt{2} [\alpha\beta - \beta\alpha] & \text{belongs to } A_1 \\
 \text{Triplet } \xi_2 = 1/\sqrt{2} [\alpha\beta + \beta\alpha] & \text{belongs to } A_2 \\
 \text{Triplet } \xi_3 = 1/\sqrt{2} [\alpha\alpha + \beta\beta] & \left. \vphantom{\begin{array}{l} \text{Triplet } \xi_3 \\ \text{Triplet } \xi_4 \end{array}} \right\} \text{ belong to } E \\
 \text{Triplet } \xi_4 = i/\sqrt{2} [\alpha\alpha - \beta\beta] &
 \end{array} \quad (300)$$

Knowledge of the representations to which the spin functions belong, that is, for which they are basis functions, is valuable since the complete symmetry adapted functions can be quickly assembled once the symmetry adapted space functions are known. The complete functions are constructed, and the representations to which they belong obtained, by means of the direct product of group theory. Specific examples of the construction are presented in the next section of this thesis.

2. Construction of the strong field wave functions

A linear combination of the d-electron wave functions in their complex form may be taken such that five real functions may be written. Furthermore, the five real functions are symmetry adapted, that is, they are basis functions for the symmetry group operations. Thus:

- (z^2) belongs to the representation a_1 ,
- (x^2-y^2) belongs to the representation b_1 ,
- (xy) belongs to the representation b_2 ,
- $(xz), (yz)$ belong to e .

When the product functions of two single electron wave

functions are constructed, the symmetry group to which they belong are given directly by the direct product of the symmetry representations. For example, the product functions:

$$\phi_1 = (x^2 - y^2)(xy) \quad (301)$$

$$\phi_2 = (xy)(x^2 - y^2), \quad (302)$$

belong to the symmetry representation, a_2 , since group theory shows that $b_1 \times b_2 = a_2$. Actually, it is possible to construct a symmetric and antisymmetric function by linear combinations of ϕ_1 and ϕ_2 . Thus:

$$\chi_1 = 1/\sqrt{2}[\phi_1 + \phi_2] = 1/\sqrt{2} [(x^2 - y^2)(xy) + (xy)(x^2 - y^2)], \quad (303)$$

$$\chi_2 = 1/\sqrt{2}[\phi_1 - \phi_2] = 1/\sqrt{2} [(x^2 - y^2)(xy) - (xy)(x^2 - y^2)]. \quad (304)$$

Both χ_1 and χ_2 belong to the group a_2 . The validity of the direct product conclusion can be readily checked by determination of the effects of the rotations on the functions.

The inclusion of spin follows the same simple scheme. All that need be remembered is that the singlet function requires that the space part be a symmetric function and that the triplet state has an antisymmetric space part. Thus, from appropriate combinations of Equations 303 and 304 with the spin functions given by Equation 300:

$$\begin{aligned} \text{Singlet state: } \psi_1 &= \chi_1 \times \xi_1; \text{ belongs to } a_2 \times A_1 = A_2 \\ &= \Gamma_2 \end{aligned}$$

$$\begin{aligned} \text{Triplet state: } \psi_2 &= \chi_2 \times \xi_2; \text{ belongs to } a_2 \times A_1 = A_1 \\ &= \Gamma_1 \end{aligned}$$

$$\left. \begin{aligned} \psi_3 &= \chi_2 \times \xi_3 \\ \psi_4 &= \chi_2 \times \xi_4 \end{aligned} \right\} \text{ belong to } a_2 \times E = E = \Gamma_5 \quad (305)$$

It is convenient to use the representation of Bethe (1) to denote the final irreducible representation to which the complete function, space and spin, belongs, and to use the notation of Liehr and Ballhausen (26) for identification of the space part of the functions. Thus, $\psi_2 = \chi_2 \times \xi_2$ above, belongs to Γ_1 and the basis function is denoted by ${}^3A_2(b_1b_2)$. The superscript on the capital letter symmetry group symbol represents the fact that the function is a triplet. The A_2 part indicates the symmetry representation of the direct product of the space functions. The representations in parenthesis are the individual space representations of the two electron functions which make up the direct product.

Thus, the space functions that are required are constructed from all possible combinations of the four states, a_1 , b_1 , b_2 , and e . Inclusion of the spin follows the same pattern. Some complexity arises in connection with the functions which result from $e \times e$, since:

$$e \times e = a_1 + a_2 + b_1 + b_2. \quad (306)$$

There are two cases to be considered; 1) when both e representations are space functions, and 2) when one is a space function and the other a spin function.

In the first case, the two space functions which belong

to e are (xz) and (yz). There are four combinations of the two electron product that are possible:

$$\chi_1 = 1/\sqrt{2} [(xz)(xz) + (yz)(yz)] \quad (307)$$

$$\chi_2 = 1/\sqrt{2} [(xz)(xz) - (yz)(yz)] \quad (308)$$

$$\chi_3 = 1/\sqrt{2} [(xz)(yz) + (yz)(xz)] \quad (309)$$

$$\chi_4 = 1/\sqrt{2} [(xz)(yz) - (yz)(xz)] \quad (310)$$

It is apparent that the first three functions are symmetric and the last is antisymmetric. Thus χ_1 , χ_2 , χ_3 will result in singlet states and χ_4 belongs to triplet states. Furthermore, application of the group operations to the four functions shows that:

χ_1 belongs to A_1 ,

χ_2 belongs to B_1 ,

χ_3 belongs to B_2 ,

χ_4 belongs to A_2 .

Appropriate combinations of the χ functions with the spin functions given in Equation 300 lead to the results:

$$\psi_5 = \chi_1 + \xi_1 = A_1 \times a_1, \text{ belongs to } \Gamma_1 \quad (311)$$

$$\psi_6 = \chi_2 \times \xi_1 = B_1 \times a_1, \text{ belongs to } \Gamma_3 \quad (312)$$

$$\psi_7 = \chi_3 \times \xi_1 = B_2 \times a_1, \text{ belongs to } \Gamma_4 \quad (313)$$

$$\psi_8 = \chi_4 \times \xi_1 = A_2 \times a_2, \text{ belongs to } \Gamma_1 \quad (314)$$

$$\left. \begin{aligned} \psi_9 &= \chi_4 \times \xi_3 \\ \psi_{10} &= \chi_4 \times \xi_4 \end{aligned} \right\} = A_2 \times e, \text{ belongs to } \Gamma_5. \quad (315)$$

In situations of other symmetries, or when more than two electrons need be considered, it becomes more difficult to

determine which states that result from the direct product will be symmetric and which will be antisymmetric. In such cases, recourse may be made to the methods outlined by Tisza (53) for obtaining the symmetric portion of the direct product. An example of its application to a specific problem has been given by Finkelstein and Van Vleck (54).

The second case in which two E representations result is that in which one is due to the space part and the other due to the spin part of the wave function. For example, consider the two electron combination of the (z^2) orbital with the (xz) , (yz) doublet. Then:

$$\phi_1 = 1/\sqrt{2} [(z^2)(xz) + (xz)(z^2)], \text{ symmetric,} \quad (316)$$

$$\phi_2 = 1/\sqrt{2} [(z^2)(xz) - (xz)(z^2)], \text{ antisymmetric,} \quad (317)$$

$$\phi_3 = 1/\sqrt{2} [(z^2)(yz) + (yz)(z^2)], \text{ symmetric,} \quad (318)$$

$$\phi_4 = 1/\sqrt{2} [(z^2)(yz) - (yz)(z^2)], \text{ antisymmetric.} \quad (319)$$

The two symmetric functions belong to the E symmetry representation, and upon combination with the antisymmetric spin function, $\xi_1 = 1/\sqrt{2}[\alpha\beta - \beta\alpha]$, which belongs to a_2 , result in a degenerate pair:

$$\left. \begin{aligned} \psi_{11} &= \phi_1 \times \xi_1 \\ \psi_{12} &= \phi_3 \times \xi_1 \end{aligned} \right\}, \text{ which belong to } \Gamma_5.$$

The state would be denoted as ${}^1\Gamma_5 ({}^1E(a_1e))$.

Similarly, the ${}^3E(a_1e)$ functions can be readily formed by combination of the two antisymmetric space functions with the symmetric spin function, $\xi_2 = 1/\sqrt{2} [\alpha\beta + \beta\alpha]$. Thus:

$$\left. \begin{aligned} \psi_{12} &= \phi_2 \times \xi_2 \\ \psi_{13} &= \phi_4 \times \xi_2 \end{aligned} \right\} \text{ belong to } \Gamma_5,$$

and are designated ${}^3\Gamma_5 E(a_1 e)$.

But the combination of the antisymmetric space functions, ϕ_2 and ϕ_4 with the symmetric spin functions, ξ_3 and ξ_4 , result in triplet functions which belong, not to Γ_5 , but to Γ_1 , Γ_2 , Γ_3 , and Γ_4 , since $E \times e = \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$. There are four simple combinations of ϕ_2 and ϕ_4 with ξ_3 and ξ_4 :

- 1) $\phi_2 \times \xi_3$
- 2) $\phi_2 \times \xi_4$
- 3) $\phi_4 \times \xi_3$
- 4) $\phi_4 \times \xi_4$.

Obviously, they will not be symmetry adapted in themselves, but linear combinations of them will be. Thus:

$$\psi_{14} = 1/\sqrt{2} [(\phi_2 \xi_3 - \phi_4 \xi_4)], \text{ belongs to } \Gamma_1 \quad (320)$$

$$\psi_{15} = 1/\sqrt{2} [(\phi_2 \xi_4 + \phi_4 \xi_3)], \text{ belongs to } \Gamma_2 \quad (321)$$

$$\psi_{16} = 1/\sqrt{2} [(\phi_2 \xi_3 + \phi_4 \xi_4)], \text{ belongs to } \Gamma_3 \quad (322)$$

$$\psi_{17} = 1/\sqrt{2} [(\phi_2 \xi_4 - \phi_4 \xi_3)], \text{ belongs to } \Gamma_4. \quad (323)$$

That these functions are appropriately symmetry adapted can be checked by application of the group operations on both the spin and space parts of the functions.

There is one further precaution that must be exercised in the construction of the wave functions and that is in regard

to the phases and order of presentation of the two wave functions associated with the Γ_5 representation. These factors are discussed in the next section of this appendix.

3. Phase factors and order of the Γ_5 representation functions

The following discussion applies equally to the strong field and weak field functions, but because of the "tangibility" of the strong field functions when dealing with basis function rotations they will be used to illustrate the situation.

Consider the two sets of strong field functions which belong to the Γ_5 representation:

$${}^3E(a_1e) \begin{cases} \psi_1 = 1/2 [(z^2)(yz) - (yz)(z^2)][\alpha\beta + \beta\alpha] \\ \psi_2 = 1/2 [-(z^2)(xz) + (xz)(z^2)][\alpha\beta + \beta\alpha] \end{cases} \quad (324)$$

$${}^3E(b_1e) \begin{cases} \phi_1 = 1/2 [(xy)(xz) - (xz)(xy)][\alpha\beta + \beta\alpha] \\ \phi_2 = 1/2 [-(xy)(yz) + (yz)(xy)][\alpha\beta + \beta\alpha] \end{cases} \quad (325)$$

By the techniques discussed in Appendix D.4, it is possible to show that the matrix element: —

$$\int \psi_1^* Q \phi_1 d\tau = 3\sqrt{3} [F_2 - 5F_4], \quad (326)$$

where Q is the electronic interaction operator, and F_2 and F_4 are the Slater-Condon parameters for the electronic interaction.

Similarly, the matrix element:

$$\int \psi_2^* Q \phi_2 d\tau = -3\sqrt{3} [F_2 - 5F_4]. \quad (327)$$

But if one uses the other possible combinations as the non-diagonal matrix element, the incorrect value of zero is obtained. That is:

$$\int \psi_1^* Q \phi_2 d\tau = \int \psi_2^* Q \phi_1 d\tau = 0 \quad (328)$$

In order to avoid the pitfall of choosing the wrong pair with which to calculate the matrix element, it is necessary to carefully order the members of each set of degenerate functions and to calculate the matrix element from corresponding members of the set. The way to do this is to arbitrarily choose one particular ordered set as a standard, study the effect of the rotation operations on the standard set, and order the remaining sets such that their wave functions follow the same pattern.

For example, in this thesis, the set arbitrarily chosen as standard was:

$$\begin{aligned} {}^1E(a_1e) = \psi_1 &= 1/2 [(z^2)(xz) + (xz)(z^2)][\alpha\beta - \beta\alpha] \\ \psi_2 &= 1/2 [(z^2)(yz) + (yz)(z^2)][\alpha\beta - \beta\alpha] \end{aligned} \quad (329)$$

By use of the replacement operators and the corresponding spin operators it can be shown that:

$$E (\psi_1 \ \psi_2) = (\psi_1 \ \psi_2) \quad (330)$$

$$C_4 (\psi_1 \ \psi_2) = (-\psi_2 \ \psi_1) \quad (331)$$

$$C_2 (\psi_1 \ \psi_2) = (-\psi_1 \ -\psi_2) \quad (332)$$

$$C_2' (\psi_1 \quad \psi_2) = (-\psi_1 \quad \psi_2) \quad (333)$$

$$C_2'' (\psi_1 \quad \psi_2) = (-\psi_2 \quad -\psi_1), \quad (334)$$

where E and the C operators are the same as those given in Table 38 and the corresponding matrices are those given by the second row of the same table. Thus:

$$C_4 (\psi_1 \quad \psi_2) = (\psi_1 \quad \psi_2) \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = (-\psi_2 \quad \psi_1). \quad (335)$$

A "possible" choice for another set belonging to the $_5$ representation might be:

$$\begin{aligned} {}^3E(b_1e) = \quad x_1 &= 1/2[(xy)(yz) - (yz)(xz)][\alpha\beta + \beta\alpha] \\ x_2 &= 1/2[(xy)(xz) - (xz)(xy)][\alpha\beta + \beta\alpha] \end{aligned} \quad (336)$$

On application of the replacement operators and the corresponding spin operators, one obtains:

$$E \quad (x_1 \quad x_2) \quad (x_1 \quad x_2) \quad (337)$$

$$C_4 \quad (x_1 \quad x_2) \quad (-x_2 \quad x_1) \quad (338)$$

$$C_2 \quad (x_1 \quad x_2) \quad (-x_1 \quad -x_2) \quad (339)$$

$$C_2' \quad (x_1 \quad x_2) \quad (x_1 \quad -x_2) \quad (340)$$

$$C_2'' \quad (x_1 \quad x_2) \quad (x_2 \quad x_1) \quad (341)$$

Note that the spin changes from Table 39 influence the signs preceding the functions. With the choice of functions given by Equation 336, differences appear in regard to the C_2' and C_2'' rotations, that is Equations 340 and 341 do not correspond to Equations 333 and 334 as they should. However, if the functions:

$${}^3E(b_1e) = \begin{matrix} \tilde{\epsilon}_1 = x_2 \\ \tilde{\epsilon}_2 = -x_1 \end{matrix}, \quad (342)$$

are used, the group operations have the same results as those of the standard set. This is the situation with all the functions constructed by the methods outlined in Appendix D.2. That is, they will either be proper choices or will become the proper choices by a simple re-order and/or change of sign. Consistency of the signs preceding the matrix elements can be obtained by calculation of the matrix element from the first function of the ordered pair.

4. Electronic interaction terms for strong field matrix elements

In the case of the weak field matrix elements, the electronic interaction between electrons outside of closed shells resulted in non-zero values only for the diagonal matrix elements. This was the result of construction of the symmetry adapted functions for the weak field from wave functions of the type $|S, L, J, M_J\rangle$ which are already diagonalized with respect to the electronic interaction. The expressions for the diagonal terms were obtained from tabulations available in the text by Condon and Shortley (6).

In the strong field case, however, the matrix elements are diagonal with respect to the ligand field parameters and will have non-zero electronic interaction values for both

diagonal and off-diagonal elements. The general form for the calculation of electronic interaction terms has been given in section 8⁶ of Condon and Shortley (6). The problem is quite similar to that involving the interaction of the ligand point charge with the electrons of the central atom in that the matrix element of interest is of the form:

$$(a \ b \mid Q \mid c \ d) = \int u_a^*(1) u_b^*(2) (e^2/r_{12}) u_c(1) u_d(2) d\tau, \quad (343)$$

where u_i are the single electron wave functions, with (1) and (2) referring to electron one and electron two respectively; e is the charge of the electron, r_{12} is the distance between the electrons. By expressing the single electron functions in terms of radial and angular parts and expanding the potential, Q , in terms of the spherical harmonics, one can show that the matrix element becomes:

$$(a \ b \mid Q \mid c \ d) = \delta(m_s^a, m_s^c) \delta(m_s^b, m_s^d) \delta(m_l^a + m_l^b, m_l^c + m_l^d) \times \sum_{k=m} c^k(l^a m_l^a, l^c m_l^c) c^k(l^d m_l^d, l^b m_l^b) F_k, \quad (344)$$

where the F_k are radial functions usually left as parameters to be evaluated and the c^k coefficients are obtained from the expression:

$$c^k(l m_l, l' m_l') = \sqrt{2} \sqrt{2k+1} \int_0^\pi \Theta(k, m_l - m_l') \Theta(l, m) \Theta(l', m_l') \sin\theta d\theta \quad (345)$$

where the Θ functions are the associated Legendre functions.

Values of the c^k coefficients have been tabulated by Condon and Shortley (6) and can be found in Table 1⁶ of their text. In the use of this table, it is important to note the dependence of the c^k coefficients, namely, $c^k(\underline{a}, \underline{c})$ and $c^k(\underline{d}, \underline{b})$, and to know that:

$$c^k(l m_l, l' m_{l'}) = (-1)^{m_l - m_{l'}} c^k(l' m_{l'}, l m_l). \quad (346)$$

For example, to evaluate the d-electron interaction element:

$$(1^+ 0^- | Q | 2^+ -1^-),$$

where a, b, c, and d are given in terms of the m_l value and the superscripts (+) and (-) refer to the spin values. One notes that the Kronecker delta requirements are fulfilled, particularly the one which deals with the m_l values. Therefore:

$$\begin{aligned} (1^+ 0^- | Q | 2^+ -1^-) \\ = c^2(1, 2) c^2(-1, 0) F_2 + c^4(1, 2) c^4(-1, 0) F_4 \end{aligned} \quad (347)$$

$$= -c^2(2, 1) c^2(-1, 0) F_2 - c^4(2, 1) c^4(-1, 0) F_4 \quad (348)$$

The form in Equation 348 is due to the relation given by Equation 346. From Table 1⁶ of Condon and Shortley (6):

$$c^2(2, 1) = +\sqrt{6}$$

$$c^2(-1, 0) = +1$$

$$c^4(2, 1) = -\sqrt{5}$$

$$c^4(-1, 0) = +\sqrt{30}$$

Hence:

$$(1^+ 0^- | Q | 2^+ -1^-) = \sqrt{6} F_2 - 5 \sqrt{6} F_4 \quad (349)$$

To evaluate the matrix elements of the strong field

functions, it is necessary to sum all possible two electron interactions. For example, for the matrix element:

$$(A | Q | B),$$

where:

$$\begin{aligned} A &= 1/2 [(xz)(yz) - (yz)(xz)][\alpha\beta + \beta\alpha] \\ &= 1/2i [(1,-1) - (-1,1)][\alpha\beta + \beta\alpha] \end{aligned} \quad (350)$$

$$\begin{aligned} B &= 1/2 [(x^2-y^2)(xy) - (xy)(x^2-y^2)][\alpha\beta + \beta\alpha] \\ &= 1/2i [(-2,2) - (2,-2)][\alpha\beta + \beta\alpha], \end{aligned} \quad (351)$$

one can ignore the spin Kronecker deltas since they are satisfied, and multiply the space results by two to account for the two spin states, $\alpha\beta$ and $\beta\alpha$. Therefore:

$$(A | Q | B) = 2/4 [(1,-1) - (-1,1) | Q | (-2,2) - (2,-2)], \quad (352)$$

$$\begin{aligned} &= 1/2 [(1,-1 | Q | -2,2) - (1,-1 | Q | 2,-2) \\ &\quad - (-1,1 | Q | -2,2) + (-1,1 | Q | 2,-2)] \end{aligned} \quad (353)$$

From the same techniques illustrated by Equations 347, 348, and 349, the matrix element can be shown to be:

$$\begin{aligned} (A | Q | B) &= 1/2 [(-35 F_4) - (-6F_2 - 5F_4) - (6F_2 - 5F_4) \\ &\quad + (-35F_4)], \end{aligned} \quad (354)$$

$$= 6F_2 - 30F_4. \quad (355)$$

Similar procedures result in the evaluation of all the diagonal and off-diagonal elements due to the electronic interaction.