1   Ligand Field Theory and the Properties of Transition Metal Complexes

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1 GENERAL INTRODUCTION

From the early days of studying transition metal complexes, researchers have been intrigued by their intense colors and unusual magnetic behavior. In recent years the spectroscopic methodology available to rigorously study these and other properties has become extremely sophisticated and covers more than 10 orders of magnitude in photon energy. Different energy regions provide complementary insight into the electronic structure properties of a transition metal complex; and by utilizing the appropriate combination of methods one can address and solve essentially any spectroscopic problem. This can be of importance on a fundamental level (high resolution spectroscopy at 2 K on single crystals of high symmetry complexes) or in application to problems of wide general interest to the scientific community (Bioinorganic Chemistry, Materials Science, Environmental Chemistry, etc.). Ligand field theory provides a basis for understanding many of the wide range of spec-

troscopic observables in terms of the electronic structures of transition metal complexes.

The roots of ligand field theory are in group theory and geometry and indeed the parameters of the model to be developed in Section 2 are best viewed as defined by the symmetry of the complex. Often real systems have little or no symmetry; however, significant insight can still be achieved by viewing these complexes as low symmetry perturbations on a higher "effective symmetry" system. In 1929 Hans Bethe described the energy splitting of a many electron metal ion in a crystal lattice site and developed much of the formalism of the method.[1] This is a pure electrostatic model (negative point charge ligands having a repulsive interaction with electrons on the metal ion) and allows for no overlap (i.e., no covalent bonds). It was eventually recognized that a quantitative evaluation of the key parameter of crystal field theory, $10 Dq$ (see Section 2), gives a value that is an order of magnitude smaller than is experimentally observed and does not predict correct trends in $10 Dq$ with ligand variation. Van Vleck demonstrated that the problem with crystal field theory is its neglect of overlap with the ligand valence orbitals.[2]

Covalency is included in crystal field theory by recognizing that the parameters of the model are dictated by symmetry and by the interelectronic repulsion which is well defined in the free ion. These can then be adjusted to fit the experiment and the resultant parameters can be interpreted in terms of bonding interactions with the ligands. This is known as ligand field theory which has great utility in describing a large number of experimental observables in terms of a few experimental parameters.

Ligand field theory (and the related angular overlap model) provides much of the basis for our understanding of the magnetic, EPR and $d \rightarrow d$ spectroscopic properties of a transition metal complex. However, when one considers higher energy states, more covalent ligands, and the effects of covalency on the parameters of any spectroscopic region, one must utilize the most general description of bonding, molecular orbital theory.

In Section 2, we develop the different models for describing the energy splittings of the d orbitals of the metal ion in any ligand environment: crystal field theory, ligand field theory, the angular overlap model, and molecular orbital theory. In Section 3, we allow for more than one negative electron or positive hole in these d orbitals. One of the powers of ligand field theory is its ability to incorporate the experimental electron repulsion parameters of atomic theory into the bonding description of transition metal complexes. This is developed from both the weak field and strong field approaches, the latter being used to generate the ligand field energy level diagrams for transition metal complexes. In Section 4 we consider how these diagrams and the more general molecular orbital description of bonding relate to key physical properties of metal complexes: geometry, magnetism, spectroscopy and covalency. This chapter provides the basis for understanding the spectroscopy and covalency developed in detail in the following chapters. The modern molecular orbital methods for describing the electronic structure of transition metal complexes are presented in Chapters 10 and 11.

2 ONE-ELECTRON ORBITAL ENERGIES IN TRANSITION METAL COMPLEXES

2.1 Crystal and Ligand Field Theory

A metal ion in the gas phase, that is, a free ion, has five degenerate d orbitals which are defined in Eqn. (1). R_{nl} is the radial function of the electron with quantum numbers n and l, and the remaining component of each orbital is a spherical harmonic (Y_n^m) which is dependent on the quantum number m_l and is described using the polar coordinates of the electron as defined in Figure 1.

$$d(m_l = 0) = R_{nl}\sqrt{(1/2\pi)}\sqrt{(5/8)}(3\cos^2\theta - 1)$$
$$d(m_l = \pm 1) = R_{nl}\sqrt{(1/2\pi)}\sqrt{(15/4)}\cos\theta\sin\theta \cdot e^{\pm i\phi}$$
$$d(m_l = \pm 2) = R_{nl}\sqrt{(1/2\pi)}\sqrt{(15/16)}\sin^2\theta \cdot e^{\pm 2i\phi} \qquad (1)$$

From group theory, when the metal ion is placed in a ligand environment of octahedral (O_h) or lower symmetry, these d orbitals must split in energy as the highest dimension irreducible representation in O_h symmetry is three (T_1 or T_2). It is the goal of this section to determine this energy splitting quantitatively. In the crystal field model one treats the ligands as negative point charges and evaluates their repulsive interactions with the electron in the d orbitals assuming that there is no overlap of the ligand with the metal d orbitals.

The energy of an orbital Φ_i is given by the matrix element:

$$E = \langle \Phi_i | \mathbf{V} | \Phi_i \rangle \qquad (2)$$

where, in crystal field theory, $\mathbf{V}$ is a Hamiltonian operator describing the symmetry (geometry) of the environment.

In our case the Φ_i are fivefold degenerate in the free ion and one must solve a secular determinant to extract the energies of the set of wavefunctions in the crystal field. Assuming a general crystal field $\mathbf{V}$ perturbing the d orbitals, the general secular
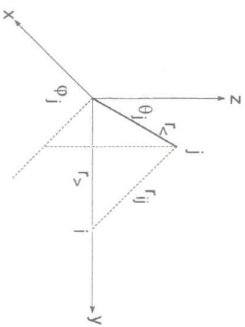

Figure 1. Polar coordinates for electron j and ligand i in the point charge model.

determinant shown in Eqn. (3), is obtained.

m_l	2	1	0	-1	-2	
2	$\langle 2|V|2\rangle - E$	$\langle 2|V|1\rangle$	$\langle 2|V|0\rangle$	$\langle 2|V|-1\rangle$	$\langle 2|V|-2\rangle$	
1	$\langle 1|V|2\rangle$	$\langle 1|V|1\rangle - E$	$\langle 1|V|0\rangle$	$\langle 1|V|-1\rangle$	$\langle 1|V|-2\rangle$	$= 0$ (3)
0	$\langle 0|V|2\rangle$	$\langle 0|V|1\rangle$	$\langle 0|V|0\rangle - E$	$\langle 0|V|-1\rangle$	$\langle 0|V|-2\rangle$	
-1	$\langle -1|V|2\rangle$	$\langle -1|V|1\rangle$	$\langle -1|V|0\rangle$	$\langle -1|V|-1\rangle - E$	$\langle -1|V|-2\rangle$	
-2	$\langle -2|V|2\rangle$	$\langle -2|V|1\rangle$	$\langle -2|V|0\rangle$	$\langle -2|V|-1\rangle$	$\langle -2|V|-2\rangle - E$	

The magnitudes of these elements must be evaluated numerically and then the determinant is solved to extract the energies of the five d orbitals in the field described by $\mathbf{V}$. Except in situations of extremely low symmetry, we can expect that many, if not most, of the off-diagonal elements in determinant (3) will be zero. Fortunately, it is possible to determine that an element is zero without the need to actually evaluate it, as will be demonstrated below. Once all the numerical magnitudes are available, the determinant is diagonalized. This involves matrix manipulation such that all the off-diagonal elements are zero. The numbers remaining on the diagonal of the matrix are then the five (in this case) solutions of the determinant. They represent the energies of the 5 d orbitals in the field $\mathbf{V}$. This secular determinant is simply the matrix form of a set of five simultaneous equations in five unknowns. Note that the sum of the diagonal elements of this determinant equals the sum of the energies of the roots and the wavefunctions which diagonalize the matrix are the appropriate one-electron d orbitals, that is, they are the symmetry-adapted wavefunctions for the ligand environment of the complex (e.g., see development in Eqns. (27–29)).

2.1.1 Construction of a Crystal Field Hamiltonian

The potential associated with an electron, j, at a distance r_{ij} from a negatively charged ligand, i, of charge Z_i is given by (Figure 1):

$$V_i = Z_i e / r_{ij} \qquad (4)$$

By summing this potential over all ligands, the total energy of each electron in the field can be derived. The potential, $1/r_{ij}$, experienced by an electron in a crystal field, can be expanded in terms of spherical harmonics $Y_n^m(\theta, \phi)$ centered at the origin. Since the d orbitals (in (1)) are also described in terms of spherical harmonics centered at the metal nucleus as origin, the harmonics describing $1/r_{ij}$ can also be centered at the metal nucleus. The potential then takes the form:

$$\sum_i \frac{Z_i e}{r_i - r_j} = \sum_{k=0}^{\infty} \sum_{q=-k}^{k} (4\pi/(2k+1)) \\ \times \sum_i Z_i e Y_k^{q*}(\theta_i, \Phi_i) \cdot (r_<^k/(r_>^{k+1})) \cdot Y_k^q(\theta_j, \Phi_j) \qquad (5)$$

where $Y_k^q(\theta_i, \phi_i)$ refers to the ligand, and $Y_k^q(\theta_j, \phi_j)$ refers to the electron. The distances $r_<$ and $r_>$ are the shorter and longer of the radial vectors connecting the origin to the electron and to the charge (ligand). Usually it is assumed that the electron does not move far from the metal nucleus so that $r_<$ refers to the electron–nucleus distance, and $r_>$ the metal–ligand bond.

The first spherical harmonic in (5) describes the angular coordinates of the ligand (charge) and is defined by their polar coordinates $(r_>, \theta_i, \phi_i)$. The second spherical harmonic in (5) describes the angular coordinates of the electron, defined by its polar coordinates $(r_<, \theta_j, \phi_j)$. We decide which Y_k^q functions to use for a particular stereochemistry by using group theory. Since the geometry of a molecule is intrinsic and independent of its orientation, in that it is not changed by any symmetry operation such as rotation or reflection, the Hamiltonian operator must be totally symmetric, such that whatever geometry is described by these harmonics, their linear combination must transform as the totally symmetric representation in the molecular point group.

The group theoretical transformation properties of the Y_l^m functions are determined by their L value, which is their angular momentum quantum number (vide infra, Eqn. (80)). In an octahedral environment, angular momentum transforms as:

$$L = 0 \rightarrow A_{1g}; \quad L = 1 \rightarrow T_{1u}; \quad L = 2 \rightarrow E_g + T_{2g};$$
$$L = 3 \rightarrow A_{2u} + T_{2u} + T_{1u}; \quad L = 4 \rightarrow A_{1g} + E_g + T_{1g} + T_{2g} \quad (6)$$

Thus in an octahedral environment only harmonics with $L = 0$ and 4 span A_{1g} and can then contribute to the Hamiltonian. For d orbitals we need only consider $L \leq 4$. We shall see that matrix element (2) can be constructed as the coupling of angular momenta in a vector sense. A property of such coupling is that the three components must be capable of forming a triangle. Thus to couple two d functions, each of $l = 2$, we cannot use harmonics greater than $L = 4$ since otherwise we would not be able to form this triangle. Similarly to couple f functions ($l = 3$) together we can use harmonics up to $L = 6$. For lower point groups, one should take the representations listed in (6) and determine which representations are spanned by these functions in the lower group. For example, in D_{4h} we still exclude $L = 1, 3$ since they are odd in any group with a center of symmetry. However $L = 2$ functions now contribute since $E_g(O_h)$ correlates with $A_{1g} + B_{1g}$ in D_{4h}.

As an example, consider the generation of the Hamiltonian for a square planar (D_{4h}) complex using, in Eqn. (5), the $k = 2, 4$ harmonics as noted above ($k = 0$ can be ignored since it will affect all the d orbitals to the same extent). In the usual polar coordinate representation (Figure 1), the four ligands lie in the xy plane at $90°$ to the z axis (i.e., $\theta = 90°$). The ϕ values (angle with the x axis when the ligand is projected into the xy plane) for the four ligands, 1–4, will be $0°$, $90°$, $180°$ and $270°$, respectively. A completely general Hamiltonian using $L = 2$ and 4 harmonics can be written

$$V = \sum_i Z_i e / r_{ij} = c_2^0 \cdot R_2(r) \cdot Y_2^0 + c_2^2 \cdot R_2(r)(Y_2^2 + Y_2^{-2})$$
$$+ c_4^0 \cdot R_4(r) \cdot Y_4^0 + c_4^2 \cdot R_4(r)(Y_4^2 + Y_4^{-2}) + c_4^4 \cdot R_4(r)(Y_4^4 + Y^{-4}) \quad (7a)$$

where

$$c_k^q = \left(\frac{4\pi}{2k+1} \right) Z_i e \sum_i Y_k^q(\theta_i, \phi_i) \quad (7b)$$

$$R_k(r) = r_<^k / r_>^{k+1}$$

with the equivalent contributions from the components $(-2, +2)$ and $(-4, +4)$ grouped together. Note that the $c_4^{\pm 1}$ and $c_4^{\pm 3}$ terms are omitted since they do not contribute to fourfold group geometries. They may be needed for threefold axis groups, or if wavefunctions quantized along a threefold axis were required[3].

The c_k^q values are evaluated as follows, using Y_k^q harmonics from Appendix 1, by summation over the ligands

$$c_2^0 = \sum_{i=0}^4 Z e(4\pi/5)\sqrt{(5/8)}\sqrt{(1/2\pi)}(3\cos^2\theta - 1)$$
$$= Z e(4\pi/5)\sqrt{(5/8)}\sqrt{(1/2\pi)}(-4)$$
$$= -4Z e\sqrt{(\pi/5)} \quad (8)$$

where the (-4) is the sum of $(3\cos^2\theta - 1)$ over the four ligands for which $\cos(90) = 0$.

The remaining components can be obtained from Table 1. The $c_2^{\pm 2}$ and $c_4^{\pm 2}$ sum to zero in this geometry. Considering c_4^0 and $c_4^{\pm 4}$, we find:

$$c_4^0 = \sum_{i=0}^4 Z e(4\pi/9)\sqrt{(9/128)}\sqrt{(1/2\pi)}(35\cos^4\theta_i - 30\cos^2\theta_i + 3)$$
$$= Z e(4\pi/9)\sqrt{(9/128)}\sqrt{(1/2\pi)}(+12) = Z e(\sqrt{\pi})$$

$$c_4^4 = \sum_{i=0}^4 Z e(4\pi/9)\sqrt{(315/256)}\sqrt{(1/2\pi)}\sin^4\theta_i e^{\pm 4i\phi}$$
$$= Z e(4\pi/9)\sqrt{(315/256)}\sqrt{(1/2\pi)}(+4) = Z e(\sqrt{\pi})\sqrt{35/18} \quad (9)$$

Ligand	θ_i	ϕ_i	c_2 $\sin^2\theta e^{\pm 2i\phi}$ ($c_2^{\pm 2}$)	c_4 $35\cos^4\theta_i - 30\cos^2\theta_i + 3$ (c_4^0)	$\sin^2\theta(7\cos^2\theta - 1)e^{\pm 4i\phi}$ ($c_4^{\pm 2}$)	$\sin^4\theta e^{\pm 4i\phi}$ ($c_4^{\pm 4}$)
1	90	0	1	3	1	1
2	90	90	-1	3	1	1
3	90	180	1	3	-1	1
4	90	270	-1	3	-1	1
Total			0	12	0	4

Table 1

Collecting the terms and incorporating into Eqn. (7) generates the Hamiltonian suitable for a square planar D_{4h} complex, ML_4:

$$V_{sq.pl.} = Ze(\sqrt{\pi})\left[-4(1/\sqrt{5})(r^2/a^3)Y_2^0 \right.$$
$$\left. + (r^4/a^5)(Y_4^0 + \sqrt{(35/18)}(Y_4^4 + Y_4^{-4}))\right] \quad (10)$$

where the in-plane metal-ligand distance, r, is a.

The inclusion of two additional equivalent ligands, L, along the z axis, to the square plane (i.e., at $(\theta, \phi) = (0, 0)$ and $(180, 0)$-generates the Hamiltonian for an octahedral complex. The reader should prove that the addition of these two equivalent ligands will indeed cause the Y_2^0 terms to disappear. The addition of two ligands, X, ($\neq L$) generates the tetragonal complex ML_4X_2, also of D_{4h} symmetry. This is most simply treated in this formalism by assuming that these ligands lie at a distance "b" instead of "a". It does not matter if, in reality, these are chemically different ligands; the methodology will simply generate semiempirical parameters which will reflect the difference in "field" generated by L and by X.

$$V_{D_{4h}} = V_{O_h} + V_{tetrag}$$

This Hamiltonian will give (10) if the "b" terms are omitted and generate the O_h Hamiltonian if "b" = "a". The first line in (11) is the octahedral Hamiltonian.

In this fashion, crystal field Hamiltonians for any geometry can be constructed by inserting the angular coordinates of the ligands into the general equation (5) and summing the results. The actual c_k^q (or Y_k^q) which are required are most easily derived by noting which of the $L = 1, 2, 3, 4$ terms span A_1 (or A_{1g}) in the molecular symmetry group concerned. If the molecule does not have a center of symmetry, then harmonics with $L = 1$ and 3 may also contribute. These then are added to the general Hamiltonian (7).

$$V(D_{4h}) = \sqrt{(49/18)}\sqrt{(2\pi)}(Zer^4/a^5)[Y_4^0 + \sqrt{5/14}(Y_4^4 + Y_4^{-4})]$$
$$- 2Ze\sqrt{(2\pi)}[\sqrt{(2/5)}((r^2/a^3) - (r^2/b^3))Y_2^0]$$
$$- 2Ze\sqrt{(2\pi)}[\sqrt{(2/9)}((r^4/a^5) - (r^4/b^5))Y_4^0] \quad (11)$$

2.1.2 *Evaluation of One-Electron Crystal Field Matrix Elements*   Several rather different procedures exist to derive the matrix elements of the crystal field Hamiltonian.

2.1.2.1 *Manual Integration*   To develop methods to evaluate the magnitudes of the matrix elements of these Hamiltonians consider first that a d orbital may be expressed in terms of spherical harmonics according to its m_l value as given in Eqn. (1).

Suppose we evaluate the energy of the $m_l = 0$ orbital, which corresponds with d_{z^2}, in an octahedral field. If the octahedral Hamiltonian is broken down into the Y_4^0 and $Y_4^{\pm 4}$ components, then the Y_4^0 component may be written $\langle lm|V|lm \rangle =$

$\langle 20|Y_4^0|20 \rangle$ and expanded as:

$$\langle 20|Y_4^0|20 \rangle$$
$$= \int R_{nl}\sqrt{(1/2\pi)}\sqrt{(5/8)}\sqrt{(49/18)}\sqrt{(2\pi)}(Ze^2r^4/a^5)R_{nl}\sqrt{(1/2\pi)}\sqrt{(5/8)}r^2\,dr$$
$$\times \sqrt{(1/2\pi)}\sqrt{(9/128)}\int(35\cos^4\theta - 30\cos^2\theta + 3)(3\cos^2\theta - 1)^2\sin\theta\,d\theta$$
$$= \alpha_4(5/8)\sqrt{(49/18)}\sqrt{(9/128)}(1/\sqrt{2\pi})\int(35\cos^4\theta - 30\cos^2\theta + 3)$$
$$\times (3\cos^2\theta - 1)^2\sin\theta\,d\theta \quad (12)$$

where, for 3d electrons:

$$\alpha_2 = Ze^2\int R_{3d}(r^2/a^3)R_{3d}\cdot r^2\,dr = Ze^2\overline{(r^2/a^3)}$$
$$\alpha_4 = Ze^2\int R_{3d}(r^4/a^5)R_{3d}\cdot r^2\,dr = Ze^2\overline{(r^4/a^5)} \quad (13)$$

Two alternate general procedures exist to evaluate the magnitudes of these matrix elements $\langle m_l|V|m_l' \rangle$ in (12). The right-hand side of (12) signifies integration over all space of a triple product of functions. This can be handled in a standard mathematical way but becomes extremely cumbersome for complicated Hamiltonians with many components. We do not develop this classical procedure here.

Before considering an efficient procedure to evaluate these integrals, note that the magnitudes of these d matrix elements are expressed in terms of radial integrals, α_n, usually called, for example for fourfold groups, D_s, D_t, and Dq, where:

$$Dq = (1/6)Ze^2\overline{(r^4/a^5)} = (1/6)\alpha_4(a)$$
$$Ds = (2/7)Ze^2[\overline{r^2/a^3} - \overline{r^2/b^3}] = (2/7)[\alpha_2(a) - \alpha_2(b)]$$
$$Dt = (2/21)Ze^2[\overline{r^4/a^5} - \overline{r^4/b^5}] = (2/21)[\alpha_4(a) - \alpha_4(b)]$$
$$Dt = (4/7)[Dq(Eq) - Dq(Ax)] \quad (14)$$

where $Dq(Eq)$ and $Dq(Ax)$ are the equatorial and axial crystal field strengths. These radial integrals are treated as empirical parameters and evaluated by solving the electronic spectrum (see Section 2.1.4).

The left-hand side of Eqn. (12), written in the Dirac formulation in momentum space, signifies the coupling of two angular momenta to give a resultant angular momentum. This more modern approach is especially adaptable to computer evaluation, and will be developed here.

2.1.2.2 *Tensor Methods and the Wigner–Eckart Theorem* [4-11]   Given that both the operators and the wavefunctions can each be expressed in terms of spherical harmonics, which are themselves measures of angular momentum, the fundamental element

which needs evaluation is of the form $(Y_a|V_b|Y_c)$. Scalars (simple numbers with no direction) and vectors (magnitude and direction) are well known. These are subsets of the more general *tensor* which may be written C_k^q where k is the rank of the tensor and q is its component. For example k and q may relate to the quantum numbers L and M_L. Scalars are tensors of rank zero and vectors are tensors of rank 1. A C_k^q tensor has $(2k+1)$ components in parallel fashion to the $(2L+1)$ values for M_L. These tensors are related to the spherical harmonics via:

$$C_k^q = (4\pi/(2k+1))^{1/2} Y_k^q \tag{15}$$

Some common C_k^q are:

$$C_0^0 = 1; \quad C_1^0 = \cos\theta; \quad C_1^{\pm1} = \mp(1/2)^{1/2}\sin\theta\, e^{\pm i\phi}$$

$$C_2^0 = \frac{1}{2}(3\cos^2\theta - 1); \quad C_2^{\pm1} = \mp\left(\frac{3}{2}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$$

$$C_2^{\pm2} = \left(\frac{3}{8}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi} \tag{16}$$

Substituting Eqns. (14) and (15) into our D_{4h} Hamiltonian (11), as an example, yields the rather simple form:

$$V_{D4h} = 21Dq[C_4^0 + \sqrt{(5/14)}(C_4^4 + C_4^{-4})] - 21Dt\,C_4^0 - 7Ds\,C_2^0 \tag{17}$$

Any other ligand field Hamiltonian can be similarly constructed using Dq, Ds, and Dt or α_2, α_4 etc. as appropriate. The one-electron matrix elements (2) of these ligand field operators then collapse to a series of sums of $\langle d_i|C_k^q|d_j\rangle$ involving the tensor operators C_k^q. Now we explore how they are evaluated.

Two one-electron functions $|j, m_j\rangle$ (where j may be l, s, or j) can be coupled by a general tensor operator, C_k^q, via:

$$\langle jm|C_k^q|j'm'\rangle = (-1)^{j-m}\begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix}\langle j\|C_k\|j'\rangle \tag{18}$$

where $\langle j\|C_k\|j'\rangle$ is a reduced matrix element of the tensor operator, obviously independent of component m, and the term in parentheses which is a Wigner $3-j$ symbol, contains all component dependence. These are available in a tabulation (see Appendix 2) or readily calculated. The beauty of the Wigner–Eckart theorem[12] is that it separates those aspects relating to the symmetry of the molecule (the $3-j$ symbol) and the physical properties of the system contained within the reduced matrix element. The procedure is also elegant because one can solve for the reduced matrix element using a simple case and then use the same value for much more complex situations.[10,11]

This expression (18) is an extremely powerful procedure for evaluating integrals arising from the coupling of any wavefunctions by any operator capable of being

written in angular momentum terms. The reader should look closely at how the $3-j$ symbol is written in terms of the various components of the matrix element on the left. The numerical values of these $3-j$ symbols have all been evaluated and are available in various sources;[5,7,10,11,13] see Appendix 2.

The reader should exercise caution in using these $3-j$ symbols especially with respect to their sign. They have fundamental properties which should be clearly understood before they are routinely employed. These properties include:

i) They vanish (are equal to zero) if j, k, and j' do not form a 'triangle' in their number space. This is the aforementioned triangle rule; this may also be written that $j + j' \geq k \geq |j - j'|$. Thus if say, $j = 2$, $j' = 2$, then k can only be equal to 0, 1, 2, 3, 4.

ii) The sum of the components in the bottom row must equal zero;

iii) If all three components in the bottom row are multiplied by -1, then the $3-j$ symbol changes sign if the sum of the top row, $j + k + j'$ is odd;

iv) if the columns are permuted, then the $3-j$ symbol is invariant if $j + k + j'$ is even; otherwise it changes sign under the influence of an odd number of permutations.

Matrix elements of the C_k^q operator (in Eqn. (17) for example) can be evaluated in this formalism ($j = j$, l, or s) simply as a product of the function shown in (18) and the component independent reduced matrix element which can be evaluated using:

$$\langle j\|C_k\|j'\rangle = (-1)^j[2j+1)(2j'+1)]^{1/2}\begin{pmatrix} j & k & j' \\ 0 & 0 & 0 \end{pmatrix} \tag{19}$$

Thus, knowing the values of the $3-j$ symbols, and the reduced matrix elements, the evaluation of $\langle jm|C_k^q|j'm'\rangle$ becomes straightforward and rapid.

$$\langle jm|C_k^q|j'm'\rangle$$
$$= (-1)^{-m}[(2j+1)(2j'+1)]^{1/2}\begin{pmatrix} j & k & j' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \tag{20}$$

Thus, for example, to evaluate $\langle 22|C_2^0|22\rangle$;

$$\langle 22|C_2^0|22\rangle = (-1)^{-2}[(2*2+1)]\begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 2 & 2 & 2 \\ -2 & 0 & 2 \end{pmatrix} \tag{21}$$

$$\langle 22|C_2^0|22\rangle = +1 \times 5 \times (-\sqrt{(2/35)}) \times \sqrt{(2/35)} = -2/7 \tag{22}$$

For ease of text expression in the following discussion, we use a condensed form of the $3-j$ symbol, namely $(j_1j_2j_3/m_1m_2m_3)$ (i.e., for the right-hand $3-j$ symbol in Eqn. (21), $(222/-202)$. Similarly for the nonzero C_4^0 matrix elements:

$$\langle 20|C_4^0|20\rangle = (-1)^0 \times 5 \times \sqrt{(2/35)} \times \sqrt{(2/35)} = 2/7$$

$$\langle 21|C_4^0|21\rangle = \langle 2-1|C_4^0|2-1\rangle = (-1)^{-1} \times 5 \times \sqrt{(2/35)} \times \sqrt{(8/315)} = -4/21$$

$$\langle 22|C_4^0|22\rangle = \langle 2 - 2|C_4^0|2 - 2\rangle = (-1)^{-2} \times 5 \times \sqrt{(2/35)} \times \sqrt{(1/630)} = 1/21$$
$$\langle 22|C_4^4|2 - 2\rangle = \langle 2 - 2|C_4^{-4}|22\rangle = (-1)^{-2} \times 5 \times \sqrt{(2/35)} \times (1/3)$$
$$= \sqrt{(10/63)} \tag{23}$$

The Wigner–Eckart theorem and this tensor methodology provide a rapid procedure for evaluating the matrix elements of crystal field operators.

The octahedral Hamiltonian is simply (from (17), $Ds = Dt = 0$):

$$V_{\text{oct}} = 21Dq\left[C_4^0 + \sqrt{(5/14)}(C_4^4 + C_4^{-4})\right]$$

Then:

$$\langle 20|V_{\text{oct}}|20\rangle = 21Dq\left[\langle 0|C_4^0|0\rangle + \sqrt{(5/14)}\langle 0|C_4^4 + C_4^{-4}|0\rangle\right]$$
$$= 21Dq[(2/7) + \sqrt{(5/14)}(0)] = 6Dq$$
$$\langle 22|V_{\text{oct}}|22\rangle = \langle -2|V_{\text{oct}}| - 2\rangle = 21Dq[(1/21) + \sqrt{(5/14)}(0)] = Dq$$
$$\langle 21|V_{\text{oct}}|21\rangle = \langle -1|V_{\text{oct}}| - 1\rangle = 21Dq[(-4/21) + \sqrt{(5/14)}(0)] = -4Dq$$

and finally:

$$\langle 22|V_{\text{oct}}|2 - 2\rangle = 21Dq[0 + \sqrt{(5/14)}(\sqrt{(10/63)})] = 5Dq \tag{25}$$

yielding the secular determinant (26).

V_{oct}	$|2, 2\rangle$	$|2, 1\rangle$	$|2, 0\rangle$	$|2, -1\rangle$	$|2, -2\rangle$	
$|2, 2\rangle$	$Dq - E$	0	0	0	$5Dq$	
$|2, 1\rangle$	0	$-4Dq - E$	0	0	0	
$|2, 0\rangle$	0	0	$6Dq - E$	0	0	$= 0$ (26)
$|2, -1\rangle$	0	0	0	$-4Dq - E$	0	
$|2, -2\rangle$	$5Dq$	0	0	0	$Dq - E$	

The solution to this secular determinant generates the well-known octahedral splitting energies $+ 6Dq$ (twofold degenerate e_g set) and $-4Dq$ (threefold degenerate t_{2g} set).

If an element of the form $\langle\theta_i|V|\theta_j\rangle$ is nonzero, this implies that the basis orbital θ_i is mixed with the basis orbital θ_j by the operator V. Thus the symmetry-adapted wavefunction (i.e., a wavefunction which transforms properly as one of the irreducible representations of the point group concerned) will be a linear combination of θ_i and θ_j. To obtain the correct form of this wavefunction, or generally of all the wavefunctions described by the secular determinant, we utilize the energies of the wavefunctions to solve the set of simultaneous equations which the matrix represents. Thus for secular determinant (26), we can write, from the top line of the determinant:

$$(Dq - E)x + 5Dqy = 0 \tag{27}$$

where x is the coefficient required for $|2, 2\rangle$ and y is the coefficient required for $|2, -2\rangle$. Further, because of normalization, $x^2 + y^2 = 1$. Inserting the solution $E = +6Dq$ into (27) and solving yields $x = y = 1/\sqrt{2}$ and therefore the wavefunction with the energy $+ 6Dq$ is of the form:

$$1/\sqrt{2}[|2, 2\rangle+|2, -2\rangle] \quad \text{(which corresponds with the real } d(x^2 - y^2) \text{ orbital)} \tag{28}$$

Similarly, inserting $E = -4Dq$, then $x = -y = 1/\sqrt{2}$ and the wavefunction is:

$$1/\sqrt{2}[|2, 2\rangle - |2, -2\rangle] \quad \text{(which corresponds with the real } d(xy) \text{ orbital)} \tag{29}$$

The remaining three orbitals, $|1\rangle$, $|0\rangle$, and $|-1\rangle$ are already eigenstates of the octahedral operator, which is to say they are diagonal with no off-diagonal elements between themselves or with any other d orbital. The orbital $|0\rangle$ corresponds with $d(z^2)$ lying at $+6Dq$, and is degenerate with the $d(x^2 - y^2)$ orbital forming the e_g set of orbitals in the octahedral field. The orbitals $|1\rangle$ and $|-1\rangle$ are degenerate at $-4Dq$ and thus one can take their in and out-of-phase normalized combinations to form the real $d(yz)$ and $d(xz)$ orbitals respectively. Together with $d(xy)$ these form the threefold degenerate t_{2g} set of orbitals in the octahedral field. The e_g and t_{2g} orbitals are said to be symmetry-adapted to the octahedral field.

It should now be evident that if we had used the set of 5 symmetry-adapted wavefunctions themselves, instead of the $|m_l\rangle$ basis set, the resulting secular determinant would already have been diagonal, that is, all the off-diagonal elements would be zero because the field V is totally symmetric (i.e., transforms as the totally symmetric representation of the group) and they therefore would not mix wavefunctions with different symmetry representations. This can be seen by noting that:

$$\langle 1/\sqrt{2}(|2, 2\rangle - |2, -2\rangle)|V|1/\sqrt{2}(|2, 2\rangle - |2, -2\rangle)\rangle$$
$$= 1/2\{2\langle2|V|2\rangle + \langle-2|V| - 2\rangle - 2\langle2|V| - 2\rangle\}$$
$$= 1/2\{1Dq + 1Dq + 2 \times 5Dq\} = +6Dq \tag{30}$$

and similarly:

$$\langle 1/\sqrt{2}(|2, 2\rangle + |2, -2\rangle)|V|1/\sqrt{2}(|2, 2\rangle + |2, -2\rangle)\rangle = -4Dq$$

and:

$$\langle 1/\sqrt{2}(|2, 2\rangle - |2, -2\rangle)|V|1/\sqrt{2}(|2, 2\rangle + |2, -2\rangle)\rangle = 0 \tag{31}$$

In the octahedral case (determinant in (26)) the diagonal energies of both $|2, 2\rangle$ and $|2, -2\rangle$ (θ_i and θ_j) are the same which then requires an equal mix ($1/\sqrt{2}$) of each function leading to the in and out-of-phase coupling represented in Eqns. (28,29). Where the diagonal energies are different, a non-equal mix will occur, leading in the

two-orbital mixing situation, to the two general wavefunctions:

$$\alpha\theta_1 + \sqrt{(1-\alpha^2)}\theta_2 \quad \text{and} \quad \alpha\theta_2 - \sqrt{(1-\alpha^2)}\theta_1 \quad (32)$$

Finally, we evaluate one of the elements for the tetragonal D_{4h} Hamiltonian (17) [see (21–23)].

Hence:

$$\langle 20|V_{D4h}|20\rangle = 21Dq[\langle 0|C_4{}^0|0\rangle + \sqrt{(5/14)}[\langle 0|C_4{}^4|0\rangle + \langle 0|C_4{}^{-4}|0\rangle]]$$
$$- 21Dt\langle 0|C_4{}^0|0\rangle - 7Ds\langle 0|C_2{}^0|0\rangle$$
$$= 21Dq(2/7) + \sqrt{(5/14)}(0)] - 21Dt(2/7) - 7Ds(2/7)$$

$$\langle 20|V_{D4h}|20\rangle = 6Dq - 2Ds - 6Dt$$

The other terms can be obtained similarly:

$$\langle 22|V_{D4h}|22\rangle = \langle 2-2|V_{D4h}|2-2\rangle = Dq + 2Ds - Dt$$
$$\langle 21|V_{D4h}|21\rangle = \langle 2-1|V_{D4h}|2-1\rangle = -4Dq - Ds + 4Dt$$
$$\langle 20|V_{D4h}|20\rangle = 6Dq - 2Ds - 6Dt$$
$$\langle 22|V_{D4h}|2-2\rangle = 5Dq \quad (33)$$

The absence of any Ds or Dt contribution in this last off-diagonal element is seen to be due to the inability of a $C_2{}^0$ or $C_4{}^0$ operator to couple $|2, 2\rangle$ with $|2, -2\rangle$ (sum of the bottom row of $3-j$ symbols must equal zero).

For the real d-orbitals (Eqn. (34)):

$$d(x^2 - y^2) = (1/\sqrt{2})[|2, 2\rangle + |2, -2\rangle]$$
$$d(z^2) = |2, 0\rangle$$
$$d(xy) = (1/i\sqrt{2})[|2, 2\rangle - |2, -2\rangle]$$
$$d(xz) = -(1/\sqrt{2})[|2, 1\rangle - |2, -1\rangle]$$
$$d(yz) = -(1/i\sqrt{2})[|2, 1\rangle + |2, -1\rangle] \quad (34)$$

these energies are (from (33) and (34)):

$$\langle x^2 - y^2|V_{D4h}|x^2 - y^2\rangle = 6Dq + 2Ds - Dt$$
$$\langle z^2|V_{D4h}|z^2\rangle = 6Dq - 2Ds - 6Dt$$
$$\langle xy|V_{D4h}|xy\rangle = -4Dq + 2Ds - 6Dt$$
$$\langle xz|V_{D4h}|xz\rangle = -4Dq - Ds + 4Dt \quad (35)$$

These methods are totally general for generating the d^1 matrix elements of any crystal field Hamiltonian. The energy splitting of the d-orbitals for octahedral, tetrago-
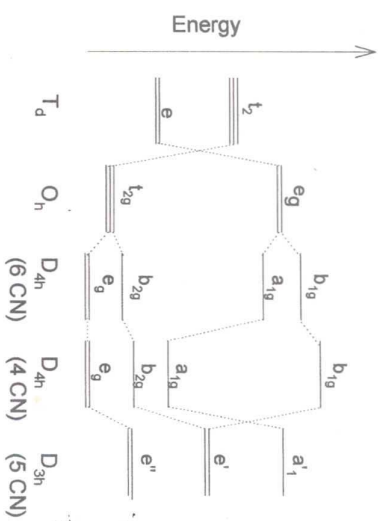

Figure 2. A d-orbital splitting pattern for tetrahedral (T_d), octahedral (O_h), tetragonal six-coordinate (D_{4h}, 6 CN), square (D_{4h}, 4 CN) and trigonal bipyramidal (D_{3h}, 5 CN) fields. The relative energy of the a_{1g} ($d(z^2)$), orbital in a square species is arbitrarily shown. It may lie below the b_{2g} or e_g levels depending on the molecule concerned.

nal, square planar, and tetrahedral fields obtained in this manner are given in Figure 2.

2.1.3 *Companion and Komarynsky Method*

There may well be instances where one is interested in the d orbital energies and wavefunctions, but not in the actual form of the crystal field Hamiltonian, which, in the case of a low symmetry species, may be quite complicated. Companion and Komarynsky[14] (CK) published a formalism which yields these energies, based upon the polar coordinates of the ligands, without independently deriving the actual Hamiltonian. Tables 2 and 3 give the ligand and position functions D_{lm} and G_{lm} and H_{ab} integrals, in terms of these ligand position functions. H_{ab} (a, b 1–5) are a shorthand notation for entries in the 5 × 5 real d orbital crystal field matrix.

$$\langle x^2 - y^2|V|x^2 - y^2\rangle = H_{11}$$
$$\langle xz|V|xz\rangle = H_{22}$$
$$\langle z^2|V|z^2\rangle = H_{33}$$
$$\langle yz|V|yz\rangle = H_{44}$$
$$\langle xy|V|xy\rangle = H_{55}$$

and off-diagonal elements such as:

$$\langle x^2 - y^2|V|z^2\rangle = H_{13} \quad \text{etc.}$$

Four steps are followed to generate the required energies:

i) identify the polar coordinates of the ligand positions in terms of the angle θ_i and Φ_i, in Figure 1.

Table 2   Ligand Position Function, D_m and G_m [14]

$D_{00}^i = \alpha_0^i$

$D_{20}^i = \alpha_2^i(\cos^2\theta_i - 1)$

$D_{40}^i = \alpha_4^i(35/3\cos^4\theta_i - 10\cos^2\theta_i + 1)$

$D_{21}^i = \alpha_2^i \sin\theta_i \cos\theta_i \cos\phi_i$

$D_{22}^i = \alpha_2^i \sin^2\theta_i \cos 2\phi_i$

$D_{41}^i = \alpha_4^i \sin\theta_i \cos\theta_i (7/3\cos^2\theta_i - 1)\cos\phi_i$

$D_{42}^i = \alpha_4^i \sin^2\theta_i (7\cos^2\theta_i - 1)\cos 2\phi_i$

$D_{43}^i = \alpha_4^i \sin^3\theta_i \cos\theta_i \cos 3\phi_i$

$D_{44}^i = \alpha_4^i \sin^4\theta_i \cos 4\phi_i$

$G_{21}^i = \alpha_2^i \sin\theta_i \cos\theta_i \sin\phi_i$

$G_{22}^i = \alpha_2^i \sin^2\theta_i \sin 2\phi_i$

$G_{41}^i = \alpha_4^i \sin^2\theta_i \cos\theta_i (7/3\cos^2\theta_i - 1)\sin\phi_i$

$G_{42}^i = \alpha_4^i \sin^2\theta_i (7\cos^2\theta_i - 1)\sin 2\phi_i$

$G_{43}^i = \alpha_4^i \sin^3\theta_i \cos\theta_i \sin 3\phi_i$

$G_{44}^i = \alpha_4^i \sin^4\theta_i \sin 4\phi_i$

ii) calculate the ligand position functions D_{lm}^i and G_{lm}^i, for each ligand, and sum over all ligands to generate D_{lm} and G_{lm}. These will be associated with a set of α_n terms for each non-equivalent ligand in the complex. These functions relate directly to the Y_l^m functions in Eqn. (5). Where d orbitals are concerned, only functions with $l = 0, 2,$ or 4 are required (odd Y_l^m cannot couple even d orbitals). We ignore the $l = 0$ function which only raises all d orbitals by the same degree, and hence need consider only terms in the radial parameter α_2 and α_4;

iii) use these D_{lm} and G_{lm} values to generate the H_{ab} secular determinant using Tables 2 and 3; and

iv) solve this determinant for the desired energies.

For example, for a trigonal bipyramid, distinguishing the axial and equatorial ligands using $\alpha_n(Ax)$ and $\alpha_n(Eq)$, then $\theta_i = 90°$ for the equatorial ligands and $\theta_i = 0°$ for the axial ligands, summing over all five ligands to generate:

$$D_{20} = 4\alpha_2(Ax) - 3\alpha_2(Eq)$$
$$D_{40} = (16/3)\alpha_4(Ax) + 3\alpha_4(Eq) \qquad (37)$$

Using $\Phi_i = 0°$ for the axial ligands, and $\Phi_i = 0, 120,$ and 240° for the three equatorial ligands, all other D_{lm} and G_{lm} values are seen to sum to zero. Then, neglecting terms in D_{22}, D_{42} and D_{44}, which all sum to zero, from Table 3:

$$H_{11} = H_{55} \ (E(x^2 - y^2, xy))$$
$$= -(1/7)D_{20} + (1/56)D_{40}$$

tion Functions — ...

$H_{11} = D_{00} - 1/7 D_{20} + 1/56 D_{40} + 5/24 D_{44}$

$H_{22} = D_{00} + 1/14 D_{20} - 1/14 D_{40} + 3/14 D_{22} + 5/42 D_{42}$

$H_{33} = D_{00} + 1/7 D_{20} + 3/28 D_{40}$

$H_{44} = D_{00} + 1/14 D_{20} - 1/14 D_{40} - 3/14 D_{22} - 5/42 D_{42}$

$H_{55} = D_{00} - 1/7 D_{20} + 1/56 D_{40} - 5/24 D_{44}$

$H_{12} = 3/7 D_{21} - 5/28 D_{41} + 5/12 D_{43}$

$H_{13} = -\sqrt{3/7} D_{22} + 5\sqrt{3}/84 D_{42}$

$H_{14} = -3/7 D_{21} + 5/28 G_{41} + 5/12 G_{43}$

$H_{15} = 5/24 G_{44}$

$H_{23} = \sqrt{3/7} D_{21} + 5\sqrt{3}/14 D_{41}$

$H_{24} = 3/14 G_{22} + 5/42 G_{42}$

$H_{25} = 3/7 G_{21} - 5/28 G_{41} + 5/12 G_{43}$

$H_{34} = \sqrt{3/7} G_{21} + 5\sqrt{3}/14 G_{41}$

$H_{35} = -\sqrt{3/7} G_{22} + 5\sqrt{3}/84 G_{42}$
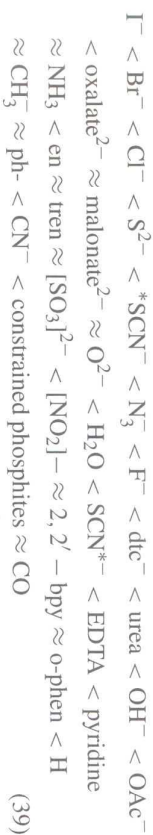
$H_{45} = 3/7 D_{21} - 5/28 D_{41} - 5/12 D_{43}$

$$= (3/7)\alpha_2(Eq) - (4/7)\alpha_2(Ax) + (3/56)\alpha_4(Eq) + (2/21)\alpha_4(Ax)$$

$$H_{22} = H_{44} \ (E(xz, yz))$$
$$= (1/14)D_{20} - (1/14)D_{40}$$
$$= -(3/14)\alpha_2(Eq) + (2/7)\alpha_2(Ax) - (3/14)\alpha_4(Eq) - (8/21)\alpha_4(Ax)$$

$$H_{33} = E(z^2)$$
$$= (1/7)D_{20} + (3/28)D_{40}$$
$$= (4/7)\alpha_2(Ax) - (3/7)\alpha_2(Eq) + (9/28)\alpha_4(Eq) + (4/7)\alpha_4(Ax) \qquad (38)$$

Since there are no nonzero off-diagonal H_{ab} elements, in this example, the H_{nn} energies accord directly with the real d orbital energies also included in Figure 2. The CK method provides a facile procedure to generate these one-electron d-orbital energies and associated wavefunctions through diagonalization of the secular determinant from Table 3, for any stereochemistry. It would be relatively easy to extend the tables of functions to make this also useful for other electron configurations.

2.1.4   Ligand Field Theory and the Spectrochemical Series   While crystal field theory has made a critical contribution to inorganic spectroscopy through its ability to correctly predict the d-orbital splitting diagrams and rationalize and assign the observed spectroscopy in terms of parameters such as Dq, Ds, Dt, and α_n, it fails to provide reliable information about the nature of the metal–ligand chemical bond since it ignores covalency and treats the ligand as a point charge. Its success arises because it is firmly grounded in symmetry.

The approach generally taken is to obtain, experimentally, numerical values for these parameters from fits to spectra; this is known as ligand field theory. Innumer-

able attempts have been made to extract chemical information from the magnitudes of these parameters. The most important parameter, Dq, varies with the bonding interaction of the ligand with the metal center. Good π-acceptors have high Dq values, while good π-donors have low Dq values. This trend in Dq is known as the Spectrochemical Series:

$$I^- < Br^- < Cl^- < S^{2-} < {}^*SCN^- < N_3^- < F^- < dtc^- < urea < OH^- < OAc^-$$
$$\approx oxalate^{2-} \approx malonate^{2-} \approx O^{2-} < H_2O < SCN^{-*} < EDTA < pyridine$$
$$\approx NH_3 < en \approx tren \approx [SO_3]^{2-} < [NO_2]^- \approx 2, 2' - bpy \approx o\text{-phen} < H$$
$$\approx CH_3^- \approx ph\text{-} < CN^- < constrained\ phosphites \approx CO \qquad (39)$$

Its origin in molecular orbital theory is developed in Section 2.3.1. The Dt parameter is a derivative parameter in that it is a measure of the difference between axial and equatorial Dq values (Eqn. (14)), while the Ds parameter has not been reliably shown to have chemical significance.

Thus the next step is to recognize that there is covalency in the metal–ligand bond. This can be done through employment of a variety of molecular orbital methodologies which will be addressed in Section 2.3. First, however, we present an early, but still widely used attempt to include covalency—namely the Angular Overlap Model (AOM).

2.2 Angular Overlap Model

2.2.1 *General Approach*

This theory[15–17] is also well founded in symmetry, resting on earlier work by McClure,[18] and Yamatera[19] who, independently, began the idea of a two-dimensional spectrochemical series by factoring the effects of a ligand field into σ- and π-components. The AOM theory recognizes that the d orbitals can be perturbed in a σ, π, or δ-fashion by the ligand orbitals and generates a series of parameters distinguished by these bonding classifications. The connection between the magnitudes of these parameters and the actual σ- or π-bond strengths (free energies) of the chemical bond remains dubious, but their relative values do seem to agree with intuitive expectations concerning the ordering of a metal–ligand bond in terms of the extent of σ- or π-bonding. The numbers thus obtained are therefore more easily linked to chemical information than are the ligand field parameters. These AOM parameters are still semiempirical and are indeed linked to the ligand field parameters by simple mathematical manipulation. More sophisticated MO methods must be employed to obtain rigorous information or insight (vide infra).

Consider an $M–L_z$ bond fragment lying along the z axis. The AOM theory defines a σ-bonding interaction labeled $e_\sigma(L)$ for interaction of the lone pair σ-electrons on the ligand with a $d\sigma$ orbital lying along the z axis and $e_\pi(L)$ for interaction of the (equivalent) ligand p_x and p_y ($p\pi$) orbitals lying along the ligand local x and y axes, such that:

$$E(z^2) = e_\sigma(L); \quad E(x^2 - y^2) = E(xy) = 0; \quad E(xz) = E(yz) = e_\pi(L) \quad (40)$$

Technically these definitions are considered relative to the δ-interaction being regarded as zero. Thus each of the five d orbitals is perturbed by its specific interaction with ligand σ- and π-symmetry orbitals. Based upon the electron density in each orbital along each coordinate axis, if a σ-interaction with the doughnut of charge in the xy plane of a $d(z^2)$ orbital is $(1/4)e_\sigma(L)$ and the interaction with each of the four lobes of a $d(x^2 - y^2)$ orbital is $(3/4)e_\sigma(L)$. Then, for example, the specific $M–L_x$ fragment, being $M–L$ along the x axis, yields the contributions:

$$E(z^2) = (1/4)e_\sigma(L); \quad E(x^2 - y^2) = (3/4)e_\sigma(L);$$
$$E(xz) = E(xy) = e_\pi(L); \quad E(yz) = 0 \quad (41)$$

To obtain the energies for a species, such as ML_6, one simply sums all the perturbations along each axis, to obtain:

$$E(z^2) = E(x^2 - y^2) = 3e_\sigma(L); \quad E(xz) = E(xy) = E(yz) = 4e_\pi(L) \quad (42)$$

This generates the expected splitting into t_{2g} and e_g with an energy separation of $10Dq = 3e_\sigma(L) - 4e_\pi(L)$. In analogous fashion, if we consider a $trans$-ML_4Z_2 (Z on z axis) species and assume that both L and Z possess lone pairs of π-symmetry along their local x, y axis (each $M–L$, $M–Z$ bond uses the ligand local z axis), then one can again simply sum the energy contributions from each ligand. This is easily constructed when realizing, for example, that the $d(xz)$ orbital interacts with a π-lone pair on each of two L ligands and with a π-lone pair on each of two Z ligands, thus:

$$E(z^2) = e_\sigma(L) + 2e_\sigma(Z); \quad E(x^2 - y^2) = 3e_\sigma(L);$$
$$E(xz) = E(yz) = 2e_\pi(Z) + 2e_\pi(L); \quad E(xy) = 4e_\pi(L) \quad (43)$$

2.2.2 *More Rigorous Approach*

The above analysis is trivial when the ligands occupy the regular axis positions of an octahedron. For almost all other systems and especially for low symmetry systems, we should look more closely into the theoretical basis for this procedure.

Following the Wolfsberg–Helmholz approximation (see Section 2.3), the interaction of a d orbital, initial energy H_M, with a ligand orbital, initial energy H_L, and overlap S_{ML} yields the final energies E_d and E_l according to:[20]

$$E_d - H_M = (H_M + H_L)^2 \cdot (S_{ML})^2/(H_M - H_L) = e_\sigma(L)$$
$$E_l - H_L = -(H_M + H_L)^2 \cdot (S_{ML})^2/(H_M - H_L) = -e_\sigma(L) \quad (44)$$

Thus the metal orbital is destabilized by a σ-antibonding interaction, and the ligand orbital is correspondingly stabilized; $e_\sigma(L)$ is always positive. The AOM parameter is then proportional to the square of the overlap between metal and ligand orbital. The overlap contribution may be factored into a radial part which depends upon the metal, the ligand, and their distance apart; and an angular contribution which is