LIGAND-FIELD PARAMETERS

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Published by the Syndics of the Cambridge University Press
Bentley House, 200 Euston Road, London NW1 2DB
American Branch: 32 East 57th Street, New York, N.Y.10022

Library of Congress Catalogue Card Number: 72–93139

ISBN: 0 521 20137 3

Printed in Great Britain
at the University Printing House, Cambridge
(Brooke Crutchley, University Printer)

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PREFACE

Most books on ligand-field theory are concerned with the symmetry-determined aspects of the subject. The assignment of d-d spectra and the construction of crystal-field correlation diagrams form the stuff of most conventional texts, whilst the differences between various books in this area usually reflect only different degrees of mathematical sophistication. In the main, the discipline and rigour such books describe refer only to quantities which depend on the angular properties of wavefunctions, radial properties being sequestered into 'proportionality constants'. From an heuristic point of view, such approaches are obviously sensible in that a qualitative understanding of phenomena must always precede a quantitative one. On being confronted with a succession of transition-metal electronic spectra, for example, it is clearly desirable to establish qualitative relationships between them and to assign electronic transitions to experimental bands before commenting upon 'crystal-field strengths'. All this is to say that the usual approach to ligand-field theory is *via* symmetry and group theory. However mathematical, such an approach is essentially qualitative; although a semi-quantitative understanding of spectra and magnetism readily follows.

The principles of crystal-field theory are usually illustrated by reference to systems with cubic symmetry, and Dq as the only scaling parameter: but few transition-metal complexes are exactly octahedral or tetrahedral. In general such distorted molecules display anisotropy in their electronic, or other, properties as evidenced, for example, by magnetic anisotropy and spectral polarization studies of single crystals. Molecules involving coordination numbers other than four or six may be anisotropic without there being distortion from some ideal symmetry: five-coordinate trigonal bipyramidal complexes typify such cases. Less tractable are molecules with rhombic or lower symmetry, though many may be described as axially distorted from an appropriate cubic symmetry precursor. In all cases, departure from cubic symmetry means less information can be had from group theory alone. Crystal-field parameters proliferate in these circumstances, $Dq, Ds, Dt, Cp, D\sigma, D\tau, \rho_2, \rho_4$, being some of the symbols used to label them throughout the literature. The parameters used vary from coordination number to coordination number, from symmetry to symmetry and from author to author. It is not always clear whether any or all of these parameters are, or can be, related to one another. Nor is it clear how the parameter values deduced from the spectra or magnetism of 'distorted' systems reflect geometrical distortions as opposed to some radial properties which may be related to bonding in some way analogous to the behaviour of $10\,Dq$.

The present book has been written to describe and explore the nature of the purely non-symmetry-determined part of ligand-field theory. Discussion of symmetry properties is only made to introduce and define ligand-field parameters. Accordingly an elementary knowledge of the usual approaches to ligand-field theory is assumed, together with a similar acquaintance with elementary group theory. It is hoped that the subject matter of this book will draw the attention of those already expert in the general area of ligand-field theory. However, the detailed presentation of the material has also been made with final year honours students and young researchers in mind. Some of the ideas described are well-established and some are new. The subject of ligand-field parameters is not closed and to some extent this book presents a progress report which includes commentary of some current areas of disagreement in the literature.

The plan of the book is roughly as follows. The introductory chapter outlines the role of symmetry in ligand-field theory and contrasts it with the function of splitting parameters. Interpretations and predictions of the simplest crystal-field and molecular-orbital approaches to the Spectrochemical Series are reviewed to focus attention on those aspects of ligand-field theory which are not determined by symmetry. Chapter 2 describes the crystal-field formalism, introducing potentials, angular and radial integrals and the multipole expansion. The expansion of the $1/r_{ij}$ operator in terms of spherical harmonics is written in various different ways in order to clarify its use. The significance of $1/r_{ij}$ as a two-electron operator, and hence the fundamental character of the crystal-field model, is elaborated in the third chapter where it is discussed in the more general context of interelectron repulsion parameters. This chapter also presents a simple discussion of interelectron repulsion parameters as determined by group theory and describes some of the approximations involved in their definition. A brief resumé of Trees' correction is included here.

Radial parameters which arise in angularly-distorted systems are described in chapter 4 and the second-order radial parameter Cp is introduced. Separation of angular distortion from radial parameters is emphasized here and several recent results of magnetic and spectral studies of single crystals are reviewed in this spirit. A similar treatment of D_{4h} symmetry molecules is made in chapter 5 where Ds and Dt parameters are defined. It is shown how values for these parameters may be recast in terms of Cp and Dq, thus possibly leading to interesting, and apparently general, trends in the ratio Cp/Dq. Throughout both chapters, the philosophy of crystal-field parameterization is discussed and the dangers of a too-literal interpretation of the definitions of Ds, Dt, Cp and Dq are emphasized.

Interpretations of radial parameters begin in chapter 6 which reviews the nature and calculation of $10\,Dq$, ranging from the most elementary point-charge model to the latest all-electron, *ab initio*, molecular-orbital calculations. The chapter aims to identify the assumptions and problems of the various methods which have been employed to calculate $10\,Dq$ and so give an insight into the various factors which really determine this quantity. No attempt is made to provide a basis for actual computation. The difficulties of *ab initio* calculations are such that simpler models must generally be used for understanding splitting parameters for a wide range of compounds and in chapter 7, a fresh appraisal of the unrealistic point-charge model is described, largely in a spirit of exploration. Simple trends in the relative behaviour of Cp and Dq as functions of bond length, effective nuclear charge and ligand charge are deduced which indicate an, albeit temporary, utility for the approach described. Semi-empirical molecular-orbital models, especially the angular overlap method, are alternatives favoured by some authors and these are reviewed in chapter 8. The chapter ends with a comparison of the parameterized point-charge model and the angular overlap method applied to low-symmetry ligand-field parameters.

The Nephelauxetic effect is discussed in chapter 9. The various formalisms used to describe the effect are outlined and the apparently opposing views about evidence for differential orbital expansion are reviewed. The discussion thus centres round parameters conventionally symbolized by $B, C, F_2, F_4, \beta_{33}, \beta_{35}, \beta_{55}$. As in the discussion of the low-symmetry crystal-field parameters, some of the current areas of ignorance and the need for further research are pointed out.

To some extent each chapter may be read independently and in this form may commend itself as a 'teaching review'. All but one chapter end with a listing of particularly relevant and useful texts which are cited by a lower case letter. All other references are cited numerically and listed numerically and alphabetically at the end of the book.

We are most grateful for the time and effort given us by Professors A. D. Buckingham and J. Lewis in numerous discussions and in critically reading much of the manuscript. We should also like to thank Drs D. J. Mackey, E. D. McKenzie, P. N. Quested and W. R. Smail and Professor D. P. Craig for various constructive comments in the earlier stages. Dr Mackey also performed the calculations described in the appendix to chapter 7. Finally we wish to thank Mrs Thora Saunders who greatly simplified the later stages by preparing an accurate typescript so quickly.

July 1972

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1

SYMMETRY VERSUS SPLITTING PARAMETERS

Symmetry plays a central role in the interpretation of transition metal *d–d* spectra. The information contained in these spectra may conveniently be considered under the three headings of splitting patterns, absolute energy differences, and intensities and polarizations. Only absolute energy differences are independent of symmetry. Intensities, though largely determined by non-symmetry factors, do have a qualitative aspect insofar as selection rules, derived from group theory, may be involved. Spectral splitting patterns, especially of highly symmetrical molecules, are very largely symmetry-based features. In a similar way, the orders of magnitude for magnetic moments successfully predicted by the 'spin-only' formula and the principles of crystal-field orbital quenching derive largely from group-theoretical considerations. Even early qualitative estimates of the magnitudes of magnetic anisotropies were made directly from a knowledge of formal ground term degeneracies.

Our understanding of the *magnitudes* of spectral splittings and of the detailed behaviours of magnetic moments and anisotropies, however, rests on theories owing little or nothing directly to symmetry. The size of the spectral splitting factor Dq, for instance, is not determined by group theory. Also, interpretations of the electronic properties of molecules with less than cubic symmetry involve many more such parameters, of which Cp, Dt, Ds, $D\sigma$ and $D\tau$ are perhaps the best known. The nature and use of such quantitative parameters form the subject matter of this book.

The origin and first examples of the use of crystal-field theory concerned magnetic moments and their dependence on the quenching of orbital angular momentum.[e] Thus, while it was realized that lanthanide ions in crystal lattices cannot be completely indifferent to their environment, it was found empirically in the late 1920s that Hund's formula,

$$\mu_{\text{eff}} = g\sqrt{[J(J+1)]}, \tag{1.1}$$

where

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}, \tag{1.2}$$

---

[e] References marked with a letter are to be found at the end of the chapter.

a formula derived for free-ions, satisfactorily explained the observed magnetic moments in lanthanide compounds. Crystal-field theory grew out of the discovery that this simplicity did not extend to the magnetic properties of compounds of the main transition block. Van Vleck had derived a complementary formula to (1.1), describing the magnetic moments of free-ions of the first-row transition series where, in first order, spin–orbit coupling effects might reasonably be ignored:

$$\mu_{\text{eff}} = \sqrt{[L(L+1)+4S(S+1)]}. \tag{1.3}$$

Accordingly, the magnetic moments of ions with a Russell–Saunders ^3F ground term, Ni^{2+} for example, should have values of $\sqrt{20} = 4.47$ Bohr magnetons. Experimental values for octahedral compounds of nickel(II), however, are typically *ca.* 3.2 Bohr magnetons. The explanation of these and similar discrepancies came independently in general terms from Stoner and in comprehensive detail from Bethe.[7]

It was recognized that, in compounds, the metal electrons are no longer subject only to the attractive nuclear and the repulsive inter-electron coulombic (and exchange) forces, but also to the influence of neighbouring atoms in the molecule or crystal lattice. Without specifying the nature of this influence, electrostatic or covalent bonding for example, some important conclusions may be made by recourse only to symmetry. Thus we know that eigenstates transforming as F terms in spherical symmetry transform as $A_2+T_2+T_1$ terms in cubic symmetry. As discussed below, we also know the relative ordering of the energies of these terms, barring a sign, from symmetry considerations alone. In its most elementary form, crystal-field theory serves to establish this sign by depicting the influencing ligands as negative charges. So it is that crystal-field theory, but mostly group theory, establishes a $^3A_{2g}$ ground term for octahedral nickel(II) compounds, for example. The orbital non-degeneracy of this ground term reduces Van Vleck's formula (1.3) to the well-known 'spin-only' formula,[81]

$$\mu_{\text{eff}} = \sqrt{[4S(S+1)]} = \sqrt{[n(n+2)]}, \tag{1.4}$$

where n is the number of unpaired electrons, and the phrase 'orbital quenching' was coined. We do not make it part of our task to further discuss aspects of crystal-field theory which are the substance of most conventional text-books in the subject: a few are listed at the end of this chapter. While assuming familiarity with these matters, we wish to highlight some important development points in crystal-field theory and to emphasize the differing roles played by group theory on the one hand and 'quantitative' theories on the other.

---

[7] References marked with a number are to be found on pages 229–32.

The 'spin-only' formula and its embellishments with 'orbital contributions' [which are only a reverse way of describing a situation intermediate between those of (1.3) and (1.4)] go far in explaining room-temperature average magnetic moments. Also based on the symmetry-predicted ground state orbital degeneracies is Van Vleck's early explanation[112] of the sizes of magnetic anisotropies observed in transition-metal complexes. Magnetic anisotropies are concerned with spatial anisotropy in molecules (as opposed to spin anisotropy) and so, in first order at least, with the orbital part of the ground term wavefunctions. A slight departure from cubic symmetry removes the degeneracy of an orbital-triplet or doublet term, different components being associated with different spatial directions in the molecule. In molecules with formal orbital-triplet ground terms, then, unequal thermal population of these components may lead to large magnetic anisotropies. Ions with orbital-singlet ground terms, however, should display no magnetic anisotropy, at least in first order, as distortion has no orbital degeneracy to remove. This purely symmetry-based theory satisfactorily explains, for example the $< 1\,\%$ anisotropy† for high-spin iron(III) compounds with formal $^6A_{1g}$ ground terms and the typically 30 % anisotropy for near octahedral ions of cobalt(II) with $^4T_{1g}$ ground terms. It is, however, the business of the quantitative side of crystal-field or other theories to explain why these cobalt(II) compounds exhibit 30 % anisotropies rather than, say, 80 %. It is the basis of the quantitative aspects of these theories that we shall be discussing.

We mentioned above how symmetry rules dictate more than just which term may arise for an ion in a molecular or crystal environment. It is instructive to examine this powerful use of symmetry further. The free-ion ground terms in the transition metals are ^2D ^3F ^4F ^5D ^6S ^5D ^4F ^3F and ^2D for the d^1 to d^9 configurations, respectively. The group-theoretical transformation rules of lowering the symmetry from spherical to octahedral give

$$D \to E_g+T_{2g}, \quad F \to A_{2g}+T_{2g}+T_{1g}, \quad S \to A_{1g}$$

and are well known. The relative ordering of these terms for the lowest energy Russell–Saunders free-ion terms are shown in figure 1.1. Let us remind ourselves of the basic steps in the argument which allows group theory to derive most of the information in figure 1.1.

In octahedral symmetry a set of five d orbitals splits into a triplet

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† Expressed say, as anisotropy of susceptibility versus mean susceptibility, i.e. $\Delta\chi/\bar{\chi}$.

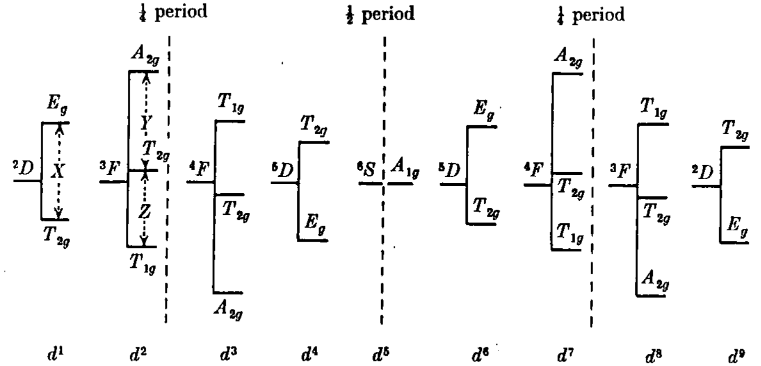


Figure 1.1. Splitting diagrams for d^n configurations in O_h crystal fields, showing inversions in ½ and ¼ periods.

and a doublet – the t_{2g} and e_g sets – and these are energetically separated by a quantity we call Δ_{oct} or $10Dq$. In that 'the energy of the t_{2g} set' refers to the energy of a single electron placed in that set, the energy separation of the E_g and T_{2g} *terms* which arise from the d^1 (^2D) configuration is also $10Dq$. The situation for the d^1 configuration is straightforward and well-known. With one exception, all that is involved is group theory. The exception is the *sign* of the orbital or term splittings. In crystal-field terms the metal orbitals are variously repelled by negative ligands and the familiar result in octahedral geometry is that the t_{2g} orbitals lie lower than the e_g orbitals. Insofar as we are concerned with energy *splittings*, a 'baricentre rule' may be invoked such that a d^5 configuration is unshifted energetically on forming a spin-free octahedral complex.[c] Thus, relative to the d^1 configuration, we place the t_{2g} orbitals at $-4Dq$ in energy and the e_g orbitals at $+6Dq$: the same figures pertain for the T_{2g} and E_g terms relative to ^2D.

Conventional crystal-field text-books are extensively concerned with the more complex situation occurring for d configurations involving more than one electron.[b,c] Figure 1.2 shows part of the weak-field/strong-field correlation diagram for octahedral d^2 ions. Only spin-triplet terms are shown. On the left side of figure 1.2 interelectron repulsion effects split the d^2 configuration into Russell–Saunders terms, Hund's rules leaving ^3F lowest. The nature of these terms, that is their quantum labelling as opposed to their absolute energy separations, is determined entirely by coupling coefficients which in turn derive from the commutation relations between angular momentum operators. Group theory of a slightly different kind tells us that, on lowering the symmetry from free-ion spherical to complex octahedral, the Russell–Saunders terms split into the component terms shown in the figure. At this stage, the ordering and relative energies of the terms arising, say, from ^3F are unknown. As we are considering energy splittings only, the neglect of crystal-field terms possessing full spherical symmetry means that the energy of the $^3T_{1g}(P)$ term should be the same as its parent ^3P term, in first order. Group theory alone has therefore established the qualitative nature of the left-hand side of figure 1.2.

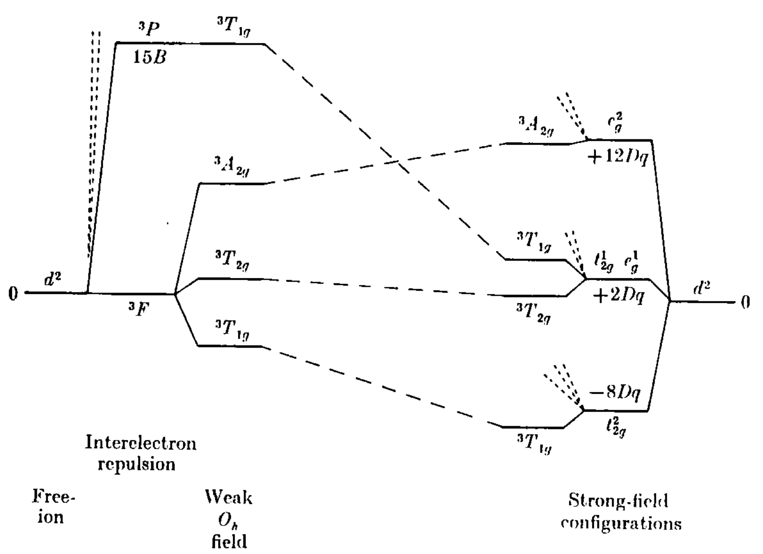


Figure 1.2. Partial correlation diagram for d^2 configuration in O_h crystal field, showing spin-triplet terms only.

On the right-hand side are represented the strong-field configurations in O_h symmetry, corresponding to placing two electrons in the t_{2g} orbital set, one in t_{2g} and one in e_g, or both in the e_g set. At this strong-field limit, we are supposing that there is no interaction between the pair of metal electrons. Such interaction would involve two-electron operators so that the strong-field representations as one-electron wavefunctions implicitly require the neglect of any electron *interactions*. The ordering of these strong-field configurations derives directly from the ordering of the t_{2g} and e_g orbitals used in the d^1 case: not only the ordering but also the energy values with respect to the free-ion spherical distribution represented by d^2. If electron interaction of any sort is included, the degeneracies of the strong-field configurations are lost, but in a way determined by group theory. The t_{2g}^2 configuration, for example, gives rise to the terms

$$^1A_{1g}+{}^1E_g+{}^1T_{2g}+{}^3T_{1g}.$$

Figure 1.2 shows the spin-triplet terms which arise in this way. The next step in the argument is to correlate the terms on the two sides of the diagrams. This is straightforward for the $^3A_{2g}$ and $^3T_{2g}$ terms as these occur only once each. There are two $^3T_{1g}$ terms, however, and these must be correlated with due regard to the 'non-crossing rule' (ref. 17, p. 200). If the abscissa in figure 1.2 is taken to measure free-ion electron interaction effects, the crystal-field or one-electron operator effects being held constant, then the energy separation between the $^3A_{2g}$ and $^3T_{2g}$ terms stays constant throughout the figure as $10Dq$ – the energy separation of the parent strong-field configurations. The two $^3T_{1g}$ terms, however, have a variable separation due to a fixed, finite crystal-field matrix element between these terms separated by (assumed) variable interelectron repulsions. The calculation of the off-diagonal crystal-field matrix element x may be made without recourse to the specific nature of the crystal-field operator. The process involves the setting up of the $^3T_{1g}$ energy matrix, as follows:

$$\begin{array}{c|cc} & {}^3T_{1g}(F) & {}^3T_{1g}(P) \\ \hline {}^3T_{1g}(F) & -6Dq-E & x \\ {}^3T_{1g}(P) & x & 15B-E \end{array} \tag{1.5}$$

where $15B$ is the $^3F-{}^3P$ energy separation due to interelectron repulsion and E is the energy of either $^3T_{1g}$ term under the combined perturbation of crystal-field and interelectronic repulsions. The diagonal elements are taken with respect to the energy of the ^3F term. In the limit of no interaction between $^3T_{1g}$ terms, the baricentre rule fixes the energy of the $^3T_{1g}(F)$ term as $-6Dq$, relative to ^3F. The interaction between the two $^3T_{1g}$ terms is represented by the off-diagonal element x. This matrix represents the situation anywhere across the abscissa in figure 1.2 as both crystal-field and electron interaction effects are involved. In order to solve this general secular problem, we consider the special case where we know the solutions already; namely, the strong-field limit. Thus, at the right-hand side of the figure, interelectron repulsions are assumed to vanish and hence also B in (1.5). This leads to the quadratic equation:

$$E^2+6DqE-x^2 = 0. \tag{1.6}$$

In the strong-field limit, however, we know the roots to be $-8Dq$ and $+2Dq$. Putting E equal to either of these values in (1.6) gives

$$x = \pm 4Dq. \tag{1.7}$$

In summary then, we see how the ordering of the A_{2g}, T_{2g} and T_{1g} terms arising from a free-ion F term and their relative energy separations are determined by group-theoretical considerations. Symmetry even tells us that, relative to X in figure 1.1 being $10Dq$, Y and Z for the d^2 case are $10Dq$ and $8Dq$ respectively. Further, symmetry also relates the splitting patterns for all the d^n configurations, giving rise to the familiar inversions in the half and quarter periods as shown in figure 1.1. These inversion rules may be arrived at *via* the hole formalism. Thus, being concerned here with terms of maximum spin multiplicity, we note that six d electrons will arrange themselves with one electron of one spin per orbital plus a single electron of the other spin. The distribution of this 'extra' electron amongst the five orbitals of 'other spin' will be identical to the distribution of the single electron of the d^1 configuration. The splitting patterns for a d^{5+n} configuration should be identical, therefore, to those for a d^n configuration. In addition, the arrangements of 10-n electrons in the whole d spin-orbital set will be like the arrangements of n electrons but inverted energetically, as arrangements of 10-n electrons are equivalent to arrangements of n holes, i.e. particles of opposite charge. Accordingly, the splitting patterns for d^{10-n} configurations are the inverse of those for d^n. This rule is responsible for the inversion in the half period of figure 1.1 and, in conjunction with the similarity of d^n to d^{5+n}, for the inversions in the quarter period. An alternative way of deriving the d^2-d^3 inversion, for example, would be to set up a correlation diagram like figure 1.2. The left-hand side would be qualitatively identical, in that symmetry alone at first does not appear to determine the relative orderings of A_{2g}, T_{2g} and T_{1g} terms. But, on approaching the problem from the strong-field side, we note that the ordering of strong-field configurations, with the usual single assumption of negatively charged (or dipolar) ligands, is

$$(t_{2g})^3 < (t_{2g})^2(e_g)^1 < (t_{2g})^1(e_g)^2 \text{ etc.}$$

The group-theoretical transformation of these configurations on recognizing electron interactions then determines the ordering of the terms, $^4A_{2g}$ being lowest.

We have reviewed the construction of splitting patterns and correlation diagrams in some detail, partly to provide a basis for later discussions, but mainly to re-emphasize the role of symmetry in these 'crystal-field' arguments. There is one more well-known feature of these diagrams which is neither group-theoretical nor a quantitative feature like Δ_{oct} or $10Dq$. It is the famous $-\frac{4}{9}$ relationship between the theoretical magnitudes of the splitting parameters in octahedral and tetrahedral geometries. At the most elementary level, the inversion implied by the minus sign is conventionally demonstrated by inscribing an octahedron and a tetrahedron in cubes with common axes and examining the relative proximity of d_ϵ (t_2 or t_{2g}) and d_γ(e or e_g) orbital sets to negatively charged ligands. The $\frac{4}{9}$ factor assumes identical natures for the metal and ligands in the two geometries and equal 'bond lengths'. Although the origin of the $-\frac{4}{9}$ factor is not directly group theoretical, it does derive from geometry. It may be seen as due partly to a change in coordination number and partly to the change in size of the cubes in which one inscribes tetrahedra or octahedra with equal bond lengths. As discussed later in this book, the $-\frac{4}{9}$ factor is not a quantitative factor on the same footing as the splitting parameters Dq etc., and as such may be referred to as a geometrical factor.

So we appreciate the strength of simple crystal-field theory. In cubic symmetry, a single parameter is sufficient, in first order at least, to represent the splitting patterns of all d configurations in octahedral, tetrahedral (or other cubic) geometries and to establish orders of magnitude for magnetic properties which are consequential on ground term multiplicities. This power largely derives from group theory. However, when we are interested in absolute energy splittings, in correlations between spectra, magnetism, chemistry and structure, our attention turns to the magnitudes of the splitting factors for which symmetry and group theory have nothing to say.

Perhaps the most celebrated of early discussions on the magnitude of crystal-field splittings was that concerning high- and low-spin iron(III) compounds. Pauling[81] had described his hybridization scheme for octahedral compounds in which six directed covalent bonds could be formed involving overlap of ligand (σ) orbitals with central metal d^2sp^3 hybrids. Six pairs of electrons donated by the ligands fill these directed orbitals. Any further electrons, equal in number to the number of d electrons on the corresponding metal free-ion, had to fit into the remaining, unhybridized d orbitals if possible. So, for iron(III) complexes with the d^5 configuration, six covalent bonds implied five electrons in three d orbitals and hence one unpaired electron. The low magnetic moment of the $Fe(CN)_6^{3-}$ ion was in general agreement with this idea. On the other hand, the high moment of FeF_6^{3-} ions, corresponding to five unpaired electrons, implied the non-involvement of the iron $3d$ orbitals in hybridization. Pauling therefore considered the bonding in the complex fluoride to be weaker than in the hexacyanide, more 'ionic' in character and, following the later ideas of Huggins, to involve sp^3d^2 hybrids in which the outer, rather than inner, d orbitals participate. In Pauling's view, the change in spin-multiplicity implied a change of bond type.

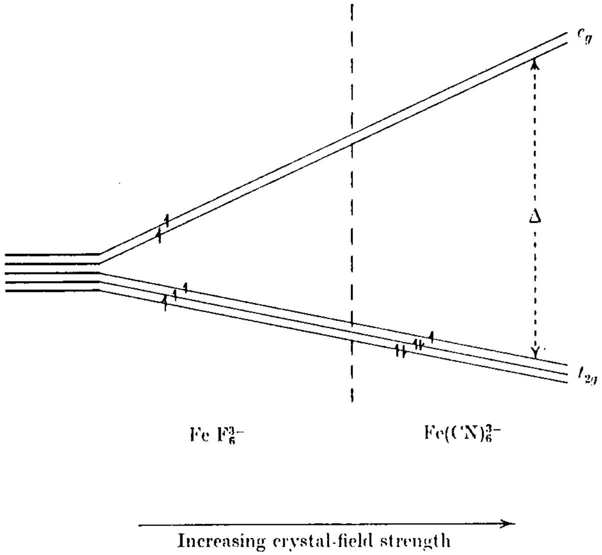


Figure 1.3. Relationship between spin-pairing and Δ in crystal-field model.

Van Vleck's[111] approach to the problem was to consider the cyanide ligands as producing a stronger crystal-field than the fluorides, so much so that the ground state involved paired electrons even at the cost of increased interelectron repulsion energy, as in figure 1.3. Pauling[81] found this view unappealing in that fluorine, being the most electronegative element, might be expected to provide a greater electrostatic crystal-field perturbation. However, Van Vleck chose to regard Δ, the splitting factor, as a *parameter* of the system, not necessarily determined solely or largely by purely electrostatic effects. At the same time he showed[111] the relationships between Pauling's hybridization valence-bond method, Bethe's crystal-field model, and Mulliken's molecular-orbital approach,[71] and we shall have more to say about this shortly. The important concept to emerge from the

$FeF_6^{3-}/Fe(CN)_6^{3-}$ work is that all ligand influences, whether electrostatic or covalent, could be parameterized within the crystal-field framework by the splitting factor, Δ. Actually, this does not need to be within a crystal-field framework specifically, i.e. electrostatic, for as discussed earlier, octahedral symmetry requires only one parameter to describe spectral term splittings (neglecting second-order effects involving interelectron repulsion parameters) so that the idea of parameterizing all forms of ligand influence by a single Δ factor is no more than a statement of symmetry. The notion has permeated the chemical literature, however, that electrostatic and covalent bonding effects are somehow both 'surprisingly' compatible with crystal field theory. We shall return to this point also.

And so we come to that remarkable collection of data called the 'Spectrochemical Series'. This is an empirical ordering of metals and ligands according to the size of Δ values their spectra possess.[d] For a given metal it is found that Δ values increase along the series

$$I^- < Br^- < \underline{S}CN^- < Cl^- < F^- < H_2O < \underline{N}CS^- < NH_3 < en < dipy < CN^-, \quad (1.8)$$

where en = ethylenediamine and dipy = dipyridyl, and that this series is approximately independent of the central metal ion. A second series, approximately independent of the ligand is:

$$\text{Mn(II)} < \text{Ni(II)} < \text{Co(II)} < \text{V(II)} < \text{Fe(III)} < \text{Cr(III)} < \text{Co(III)} < \text{Ru(III)} < \text{Mo(III)} < \text{Rh(III)} < \text{Pd(IV)} < \text{Ir(III)} < \text{Pt(IV)}. \quad (1.9)$$

The way these two series may be written in terms of only ligands or only metals may be put in the more revealing and remarkable way expressing Δ as a product of a purely ligand function f and a purely metal function g:

$$\Delta \sim f(\text{ligands}) . g(\text{metal}). \quad (1.10)$$

Empirical values of f and g, derived from a large number of observed spectra of octahedral compounds are given in table 1.1. There are irregularities, but the values in the table are widely applicable.

One feature of series (1.8) noted earlier, is the way Δ values increase with decreasing size of the donor atom on the ligand:

$$I < Br < Cl < S < F < O < N < C. \quad (1.11)$$

TABLE 1.1. *Factorizability of the Spectrochemical Series*

Ligands	f	Metal	$g/10^3\,cm^{-1}$
$6F^-$	0.90	V(II)	12.3
$6H_2O$	1.00	Cr(III)	17.4
6 urea	0.91	Mn(II)	8.0
$6NH_3$	1.25	Mn(IV)	23.0
3 en	1.28	Fe(III)	14.0
3 ox^{2-}	0.98	Co(III)	19.0
$6Cl^-$	0.80	Ni(II)	8.9
$6CN^-$	1.70	Mo(III)	24.0
$6Br^-$	0.76	Rh(III)	27.0
		Re(IV)	35.0
		Ir(III)	32.0
		Pt(IV)	36.0

This seems reasonable on the basis of a simple electrostatic origin for the splitting Δ, as smaller ligands imply smaller bond lengths. On a simple electrostatic model, involving no penetration of metal orbitals into the ligand, a charged sphere appears to a point outside to set up an electrostatic potential equal to that if the total charge were at the centre of the sphere. Thus net charge and distance (bond length) are the important factors. What seems less clear from this simple picture is why OH^- and H_2O ligands give very similar crystal-field splittings. Similarly MnF_2 and $Mn(H_2O)_6^{2+}$ have nearly identical spectra. Thus empirically bond lengths appear relevant, as expected from a simple electrostatic model, but net charge does not. These points have been emphasized repeatedly by Jørgensen.[d,57,58] He also points out that the increase of Δ values with increasing metal charge, summarized by the empirical inequalities,

$$\Delta \quad \text{for} \quad \text{M(II)} \ll \text{M(III)} < \text{M(IV)}, \quad (1.12)$$

'can hardly be explained by any reasonable electrostatic model'.[d] This statement is based on the idea of increasingly contracted metal orbitals with increased nuclear charge which then interact decreasingly with the negative or dipolar ligands. The further empirical summation of series (1.9), that

$$\Delta \quad \text{for} \quad 3d \ll 4d < 5d \quad (1.13)$$

seems qualitatively compatible with the electrostatic model on the basis of increasing d orbital size, if not of increasing diffuseness.

It is clear, not only from questions stated or implied in earlier paragraphs but also from general chemical knowledge about electrovalent and covalent character, that a purely electrostatic explanation of spectral splitting factors in general and the Spectrochemical Series in particular in unrealistic. The origin of Δ within a *molecular-orbital*

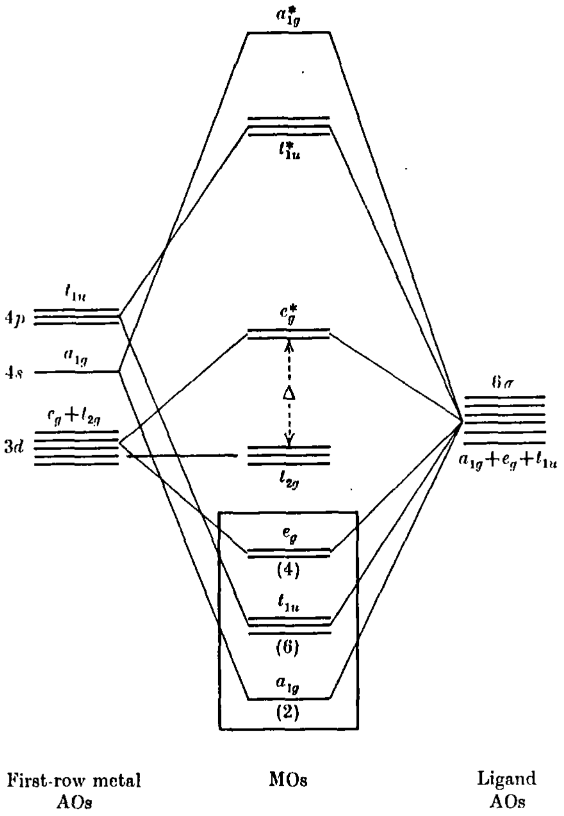
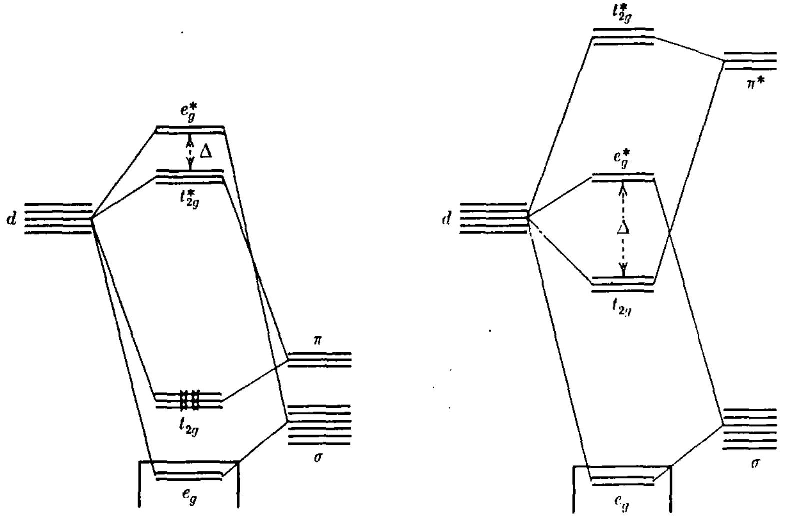


Figure 1.4. Schematic MO diagram for σ-bonding in O_h symmetry.

framework has also been considered for a long time. In very general terms we may look at MO diagrams for octahedral complexes involving first, just σ-bonding and then, with π-bonding also. Schematically the diagram for a σ-bonded octahedral compound is as shown in figure 1.4. Six σ-bonding ligand atomic orbital combinations transform[4] in O_h symmetry as $a_{1g}+t_{1u}+e_g$. These may combine with the metal atomic orbitals transforming as a_{1g}, t_{1u} and e_g for *s*, *p* and *d* orbitals, respectively. No σ-bonding therefore involves the t_{2g} metal orbitals. The diagram, though qualitative, is constructed with the assumption that bonding between ligand and metal *s*, *p* or *d* orbitals are sufficiently similar to leave the e_g^* as the first antibonding orbital above the non-bonding t_{2g} set. Twelve electrons σ-donated by the six ligands fill the lowest three levels (i.e. the six lowest molecular orbitals) whose



(*a*) π-donor ligands (*b*) π-acceptor ligands

Figure 1.5. Schematic MO diagrams for π-bonding in O_h symmetry.

ordering is therefore unimportant in the present context. These levels are indicated within the box in figure 1.4 and show the analogy with Pauling's valence-bond d^2sp^3 hybrids. The three t_{2g} metal *d* orbitals are non-bonding both in Pauling's scheme and in the present MO scheme. They house the 'metal' electrons if possible: if not, some electrons go into the antibonding e_g^* level. The non-bonding t_{2g} orbital set with the antibonding e_g^* set above it, thus 'mimic' the t_{2g}–e_g splitting referred to in pure crystal-field theory. The inter-relationship of these three approaches, Pauling's valence-bond method, Bethe's crystal-field approach and Mulliken's molecular-orbital model is clear. In the MO scheme, Δ increases with increased σ-donor 'strength'; i.e. the more the bonding e_g level is depressed in energy, the more the e_g^* antibonding is raised. Δ is associated with the transition $t_{2g}\rightarrow e_g^*$.

It proves convenient to consider the addition of a π-bonding interaction under the separate headings of π-donor and π-acceptor ligands.[f] When discussing π-donor ligands we should consider fairly low-lying filled ligand π-bonding orbitals in contrast to high-lying empty π-antibonding orbitals for π-acceptor ligands. In either case the π-bonding ligand combinations transform as t_{2g} and hence interact with the metal t_{2g} *d* orbitals. The extreme cases are represented schematically in figure 1.5 in which the low energy σ-bonding a_{1g}

and t_{1u} orbitals and high energy σ-antibonding a_{1g}^* and t_{1u}^* orbitals are omitted for clarity. For both cases of π-donor and π-acceptor ligands the diagrams assume similar σ-bonding characteristics so that the bonding e_g levels and antibonding e_g^* levels are taken at the same energies. The π-bonding interaction in both cases leaves a t_{2g} bonding MO level lower than a t_{2g} antibonding set, as usual. In the case of the π-donor ligands, the t_{2g} bonding level is filled by ligand electrons but not in the π-acceptor case. As a result, and allowing for the different energies of ligand π-donor and π-acceptor orbitals, the 'crystal-splitting' Δ is to be associated with the transition $t_{2g}^* \to e_g^*$ for π-donors and with $t_{2g} \to e_g^*$ for π-acceptors. As shown in the figure, this means larger Δ values for π-acceptors than π-donors. A better statement in general is that Δ increases with ligand π-acceptor ability. Such is the generally accepted explanation of the high place cyanide enjoys in the Spectrochemical Series.

It has been suggested[60] that the Spectrochemical Series need only be correlated with ligand π-bonding function. Although this can be misleading and doctrinaire, there is a sense in which it is true. Ideas about the so-called synergic effect of σ-bonding and π-back-bonding are well-known and respected in transition-metal theoretical chemistry (see, for example, ref. *f*). The potential violation of Pauling's electroneutrality principle by increased ligand σ-(or other) donation is offset by the removal of metal negative charge by ligand π-(or other) vacant orbitals. Each mode of bonding facilitates the other to a point of equilibrium. Thus, other things being equal, improved π-acceptor properties in a ligand may be associated with improved σ-donor properties. But as discussed above, increased π-acceptor and σ-donor effects both act together to increase the splitting factor Δ. So, insofar that the effects of ligand π-acceptor and σ-donor properties on Δ are inseparable, one could regard the Spectrochemical Series as governed by one or other alone if one so chose. Such an approach would be at odds with conventional ideas on the variable possibilities of σ-bonding throughout the series of ligands but perhaps not of π-bonding. In any case the separation is indefensible. In tetrahedral symmetry, of course, σ- and π-bonding contributions to Δ are even less separable than in octahedral ones.

There are, then, two main approaches to an understanding of spectral splitting parameters – crystal-field theory with electrostatic potentials, and molecular-orbital theory. It is also well to remember here that there is only one splitting factor in cubic symmetry but many more in molecules of lower symmetry: we are interested in all of them. While we prefer to leave a critical comparison of the two approaches till later, it is convenient here to consider some 'pros and cons'.

Jørgensen has little regard for the utility of crystal-field theory. Considering the *f.g* 'factorizability' of the Spectrochemical Series and other similar matters, he says (ref. *d*, p. 132):

> While all these features justify the greatest optimism regarding the usefulness of ligand-field theory as a *semi-empirical theory*... we must also conclude that the parameter Δ is nearly impossible to predict within a factor of 2 or 5 (as it is impossible to predict most other quantities in theoretical chemistry also) except by the very successful interpolation of empirical series. We may consider Δ as consisting of mainly four contributions:
>
> $$\Delta \sim +\text{electrostatic first-order perturbation} + \sigma(\mathrm{L}\to\mathrm{M}) - \pi(\mathrm{L}\to\mathrm{M}) + \pi(\mathrm{L}\leftarrow\mathrm{M}). \qquad [1.14]$$

In the preface of his recent book,[57] *Modern Aspects of Ligand-Field Theory*, he is more strident still.

However, crystal-field theory still enjoys much popularity in the introduction of ligand-field theory at elementary levels. This stems partly from the agreement between crystal-field and molecular-orbital theories with regard to the *qualitative* splitting of the *d*-orbital set. It is because much of ligand-field theory is concerned with qualitative questions, such as the role of symmetry, that the apparently simpler electrostatic model has long been retained as a framework within which such questions may be answered. While molecular-orbital theory undoubtedly provides a more satisfying basis by which metal–ligand interactions may be discussed, it does not necessarily follow that molecular-orbital calculations lead to better quantitative predictions. Indeed, the semi-empirical MO methods most favoured by chemists involve gross approximations which lead inevitably to theoretical predictions of questionable significance.

In the quantitative description of the energy levels of metal complexes severe problems exist with both approaches. We can simplify to some extent and say that these problems may be associated with the lack of reality in crystal-field theory and the approximate nature of semi-empirical MO methods. It is pertinent to enquire whether utility is a better judge than reality in deciding between semi-empirical methods.

In the simplest crystal-field model the metal orbitals are supposed to be repelled by the negative part of the ligands which are represented either by point-charges or point-dipoles. There is no penetration of the ligand by the metal orbital and no possibility of electron exchange effects. Objections to the model range from Pauling's comment on FeF$_6^{3-}$/Fe(CN)$_6^{3-}$ to Jørgensen's remarks on the dependence of Δ on metal oxidation state. The attractions of the model, however, are the simplicity in calculating detailed spectral or magnetic quantities and also the ease in conception. Objections to semi-empirical molecular-orbital models are the increased complexity of calculations and the requirement of such data as valence state ionization potentials or the like, overlap integrals and so on. Further, at the present time, results of calculations on one system (metal, say) do not carry over to others in an obvious way as do those of the crystal-field model. This may change, however. The obvious attraction of MO methods, of course, is their conceptual realism.

The previous paragraph contains many bald statements. We hope to justify our remarks in later chapters. Most work in this area has been done using crystal-field theory and most parameters in magnetochemistry and spectral studies are expressed in these terms. We shall, therefore, study the crystal-field model in detail first and return to molecular-orbital approaches later. At this stage we do not wish to comment further on which approach is 'best'. We are interested in the spectral and magnetic properties of molecules with less than cubic symmetry and hence in the whole array of crystal-field parameters like *Cp*, *Ds* and *Dt*. In discussing these, we develop a 'crystal-field point of view' which seems qualitatively compatible with most experimental observations.

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2

THE CRYSTAL-FIELD FORMALISM

EXPANSION OF FUNCTIONS

The crystal-field model considers isolated molecules or complex ions in which the central metal electrons are subject to an electric field originating from the surrounding ligands. Earlier papers in the subject used to refer to 'interatomic Stark effects'. The electric field results from a potential V at any point and the effect of V on a metal electron at that point is described quantum mechanically by the energy operator, the Hamiltonian,

$$\mathscr{H}' = -eV. \qquad (2.1)$$

Energy calculations of crystal-field splittings require evaluation of matrix elements of the form

$$\int \psi_i^*.eV.\psi_j.d\tau \equiv \langle\psi_i|eV|\psi_j\rangle, \qquad (2.2)$$

in which ψs represent metal wavefunctions. In order to proceed we must know how to operate on ψ_j with V. For this we must know the explicit form of the potential operator V. The form of V is established using a most important mathematical theorem called the *expansion theorem*. It is worth while reviewing this theorem, but we do so in an informal way.

Without heed to mathematicians' rigour, the expansion theorem may be stated as follows:

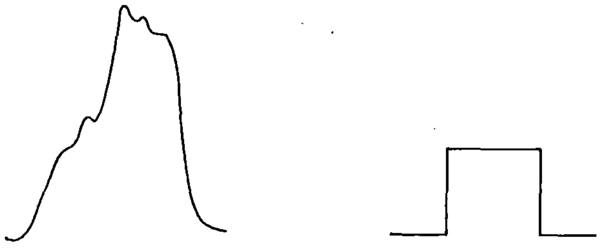
'*Almost any* function of a set of variables may be expressed as a linear combination of a *complete* set of eigenfunctions, of the same variables, of *any* operator.'

We shall comment particularly on the italicized words. Symbolically:

$$f(x_1, x_2, \ldots) = a_1\phi_1(x_1, x_2, \ldots) + a_2\phi_2(x_1, x_2, \ldots) + \ldots + a_n\phi_n(x_1, x_2, \ldots) + \ldots, \qquad (2.3)$$

where f is a function of the variables $(x_1, x_2, \ldots)$, expanded in terms of the ϕs, with expansion coefficients a_i, where the ϕs form a complete set of eigenfunctions of some operator Ω:

$$\Omega\phi_i = \lambda_i\phi_i. \qquad (2.4)$$



(a) (b)

Figure 2.1.

Consider the function of a single variable x. This may look as unappealing as those in figure 2.1. There are limitations on the sorts of functions which may be expanded as in (2.3) but we should be all right if we avoid those which are not single-valued, have infinite discontinuities or, over the variable range to be expanded, have an infinite number of finite discontinuities.

We may choose *any* operator according to the theorem, let us choose $\partial^2/\partial x^2$. Eigenfunctions of an operator are those which satisfy (2.4) in that they are unchanged by the operator except for a numerical multiplicative factor. For $\partial^2/\partial x^2$ we could choose the set of functions $\sin nx$:

$$\frac{\partial^2}{\partial x^2}(\sin nx) = -n^2(\sin nx). \tag{2.5}$$

The proper definition of 'completeness' is a complicated matter but for our purposes it means all possible variations of the type of function (here all n in $\sin nx$) which form an orthogonal set, i.e. are independent of one another. In the present example, we take $\sin nx$ for all positive integer n. According to the expansion theorem, therefore, we may write a general function of x as:

$$\begin{aligned} f(x) &= a_1 \sin x + a_2 \sin 2x + \ldots + a_n \sin nx + \ldots \\ &= \sum_k^\infty a_k \sin kx. \end{aligned} \tag{2.6}$$

Notice that the complete set is infinitely large. We could equally well have taken the eigenfunctions of $\partial^2/\partial x^2$ as $\cos nx$ or indeed the combination $(\cos nx + i \sin nx) \equiv e^{inx}$. These are all examples of Fourier series which are thus special cases of the expansion theorem. In practice it is helpful to choose a basis set, i.e. a set of eigenfunctions, such that the expansion coefficients a_k tend to vanish as n increases giving a (rapidly) convergent series. Such is the hope, for example, in perturbation theory. It is worth remembering, however, that this is a matter of convenience rather than of necessity.

Another way of looking at the expansion theorem is by noting the close mathematical analogy between quantum-mechanical functions and vectors.[27] We may write a vector A as a linear combination of the base vectors x_1, x_2, x_3:

$$A = a_1x_1 + a_2x_2 + a_3x_3 = \sum_k^3 a_k x_k. \tag{2.7}$$

Note the independence, or orthogonality, of the base vectors x_k. The coefficients a_k tell us how much of each base vector is in A. They are the projections of A on the base vectors. The dot products

$$a_k = x_k . A, \tag{2.8}$$

and so (2.7) may be written:

$$A = \sum_k^3 x_k(x_k . A). \tag{2.9}$$

We could equally well express A in terms of the base vectors y_j: these will be related to the base vectors x_k by some transformation – a rotation perhaps:

$$A = \sum_j^3 y_j(y_j . A). \tag{2.10}$$

The expansion coefficients $b_j = (y_j . A)$ (2.11)

are now different as we have expanded A in terms of a different set of basis vectors. All this has a formal analogy in the expansion of functions. Writing

$$f(x) = a_1\phi_1(x) + a_2\phi_2(x) + \ldots + a_n\phi_n(x) + \ldots \tag{2.12}$$

we have expressed the function $f(x)$ in terms of the basis functions $\phi(x)$. We could equally well expand them in terms of another basis, e.g.

$$f(x) = b_1\psi_1(x) + b_2\psi_2(x) + \ldots + b_n\psi_n(x) + \ldots. \tag{2.13}$$

The bases must be complete. In the case of vectors in three-dimensional space we require three base vectors. There may be many more, even an infinite number, in the many-dimensional Hilbert space, as it is called, in which we choose to expand $f(x)$. The analogy between vectors and functions extends also to the coefficients a_k or b_j. Thus if we premultiply (2.12) by $\phi_n^*(x)$ and integrate, we get

$$\int \phi_n^*(x).f(x).dx = a_1 \int \phi_n^*(x).\phi_1(x).dx + \ldots + a_n \int \phi_n^*(x).\phi_n(x).dx + \ldots \tag{2.14}$$

so that, by orthogonality of the basis functions ϕ,

$$a_n = \int \phi_n^*(x) . f(x) . dx \equiv \langle \phi_n | f \rangle. \tag{2.15}$$

The integral $\langle \phi_n | f \rangle$ corresponds to the dot product of the vectors x_k and A in (2.8): $\langle \phi_n | f \rangle$ tells us how much of $\phi_n(x)$ is in $f(x)$. From (2.12) and (2.15) we have:

$$f(x) = \sum_k^n |\phi_k\rangle \langle \phi_k | f \rangle. \tag{2.16}$$

There are, of course, many more facets of the vector-function analogy. While they are fascinating, we do not require them for the present task. We have presented this discussion in order to give two ways of looking at the expansion theorem. It is a discussion which might well precede an exposition of perturbation theory or of the variational principle. The expansion theorem is used throughout quantum mechanics. We wish to use it now to determine the crystal-field potential eV.

THE CRYSTAL-FIELD POTENTIAL AS AN EXPANSION

The potential eV set up by an arrangement of ligands around a central metal immediately presents us with a problem. We wish to operate with eV, which is produced by ligands at various origins in space, on metal electronic wavefunctions which are referred to a single origin – the central metal ion. It is therefore convenient (though not necessary) to express eV in a form referred to the same single origin. The usual way of doing this is to expand the potential eV as a series of spherical harmonics centred on the metal ion. Thus we might normally regard a ligand as a point-charge or collection of point charges and so express the electrostatic potential it sets up as inversely proportional to the distance of the charges. Instead we express the potential, or rather the sum of potentials from all the ligands, in terms of a coordinate frame whose origin lies elsewhere – on the metal ion. That we can do this follows from the expansion theorem. The potential occurs in the three spatial dimensions and so we require three coordinates for the basis functions in our expansion. It is particularly convenient, though again not essential, to deal with polar coordinates and express V as:

$$V = \sum_k \sum_q c_k^q . R_k(r) . Y_k^q(\theta, \phi). \tag{2.17}$$

By analogy with (2.12), c_k^qs are expansion coefficients of V with respect to the basis functions $R_k(r) Y_k^q(\theta, \phi)$. Note that the basis functions involve all three coordinates r, θ, ϕ even though we have separated them as spherical harmonics $Y_k^q(\theta, \phi)$ and radial functions $R_k(r)$. Note also that at this point we need specify nothing about the radial functions $R_k(r)$. To be quite clear, we write the early part of (2.17) *in extenso*:

$$V = c_0^0 R_0 Y_0^0 + c_1^1 R_1 Y_1^1 + c_1^0 R_1 Y_1^0 + c_1^{-1} R_1 Y_1^{-1} + c_2^2 R_2 Y_2^2 + \ldots. \tag{2.18}$$

Clearly (2.17) includes harmonics from Y_0^0 to Y_∞^∞ and as such would be comparatively useless: but symmetry and group theory are able to impose an early series termination.

The power of group theory is only realized in the present problem when the operator is viewed in the context in which it is to be used. Matrix elements are the observable quantities, not operators. The matrix elements we must evaluate, in (2.2), may be factorized into radial and angular parts. Let $R(\psi)$ and $A(\psi)$ stand for the radial and angular parts of ψ: similarly $R(V)$ and $A(V)$ for the radial and angular parts of V. Then a typical matrix element in the series is

$$\begin{aligned} M &= \langle \psi_i | V | \psi_j \rangle \\ &= \langle R(\psi_i) | R(V) | R(\psi_j) \rangle . \langle A(\psi_i) | A(V) | A(\psi_j) \rangle. \end{aligned} \tag{2.19}$$

Substituting (2.18) we have:

$$\begin{aligned} M = {} & c_0^0 \langle R(\psi_i) | R_0 | R(\psi_j) \rangle \langle A(\psi_i) | Y_0^0 | A(\psi_j) \rangle \\ & + c_1^1 \langle R(\psi_i) | R_1 | R(\psi_j) \rangle \langle A(\psi_i) | Y_1^1 | A(\psi_j) \rangle + \ldots \\ & + c_k^q \langle R(\psi_i) | R_k | R(\psi_j) \rangle \langle A(\psi_i) | Y_k^q | A(\psi_j) \rangle + \ldots. \end{aligned} \tag{2.20}$$

Now we have not specified the radial parts of either the potential or the metal wavefunctions so we cannot expect to say anything about the radial integrals

$$\langle R(\psi_i) | R_k | R(\psi_j) \rangle.$$

But the angular integrals

$$\langle A(\psi_i) | Y_k^q | A(\psi_j) \rangle$$

are specified. If in our particular problem any of these angular integrals vanish identically, i.e. by virtue of symmetry, then there is no point in knowing the associated radial integral and more important, no point in knowing the associated expansion coefficient c_k^q. In other words, by looking at the group-theoretical behaviour of the angular parts of the matrix elements of V we can hope to identify those terms in the expansion of V which are relevant.

SERIES TERMINATORS

A most useful series terminator is derived from the specification of the wavefunctions ψ. If ψ_i, ψ_j are metal d orbitals, the angular matrix elements of (2.20) vanish for Y_k^q with $k > 4$; if metal f orbitals, they