Introduction to

LIGAND FIELD THEORY

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Introduction to
LIGAND FIELD THEORY

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INTRODUCTION TO LIGAND FIELD THEORY

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Preface

I have tried to give an introduction to that field of chemistry which deals with the spectral and magnetic features of inorganic complexes. It has been my intention not to follow the theory in all its manifestations, but merely to describe the basic ideas and applications. This has been done with an eye constantly aimed at the practical and experimental features of the chemistry of the complex ions. The book is thus primarily intended for the inorganic chemist, but it is true that, in order to follow the exposition, a course in basic quantum mechanics is needed.

Simple examples are nearly always used to illustrate the arguments, but the quoted experimental evidence must of necessity be limited. Nevertheless, in the last chapter an attempt has been made to cover most of the important work so far performed that lies within the scope of the book. However, the field is advancing so rapidly that a complete survey would be outdated before long.

Since I am a chemist writing for chemists, my emphasis and notation will probably appear clumsy to the physicists primarily responsible for the theory. For this I make no excuse. Elegant derivations and condensed notation are in my opinion not desirable in an introduction to a field.

Nothing is more dangerous than to force every observation into a fixed framework of ideas. I have tried to present the case for the ligand field theory as it is now understood. It is my personal view that there are really only a few places where we need to revise part of the theory in order to understand the sundry phenomena. It must always be remembered, however, that the ligand field theory offers only a model of nature, with all the inherent limitations of models.

I want particularly to thank, among many others, Dr. Andrew D. Liehr, Mellon Institute, Dr. Max Wolfsberg, Brookhaven National Laboratories, and Dr. Harry B. Gray, Columbia University, for numerous discussions and for help with the manuscript. I am also greatly indebted to Mrs. Lise Seifert for her assistance in preparing the manuscript. Finally, I want to thank the editors of *Annual Review of Physical Chemistry* for permission to draw from the 1956 paper written by the late Prof. W. Moffitt and myself.

Carl J. Ballhausen

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CHAPTER 1

Introduction

1-a. History of Complexes

The name "complex" was first used in the chemical literature late in the nineteenth century. Thanks primarily to the pioneering works of C. W. Blomstrand and S. M. Jørgensen,† a series of compounds for which no explanation could be given in terms of the classical valence picture was characterized. These two investigators and their pupils were especially interested in the compounds containing either trivalent chromium, trivalent cobalt, or divalent platinum and the seemingly irrational products obtained when these elements were treated with ammonia, chlorine, etc.

Most baffling was the existence of isomers; e.g., the compound $CoCl_3 \cdot 4NH_3$ could exist in two forms, a violet one and a green one. In retrospect it is, of course, easy to see why the above-mentioned workers failed to reach an understanding of these and similar phenomena; "stereochemistry" was at that time a completely new field.

The complete failure of the classical valence picture to account for the chemistry of what we now call the transition groups was first realized by Werner (1893). Proceeding mostly on the basis of work performed by Jørgensen, he proposed, for instance, that the yellow "luteo salt" $Co(NH_3)_6Cl_3$ was built in the shape of a regular octahedron, the Co(III) ion being placed in the center and the six ammonia molecules being located at the corners of the polyhedron. Werner introduced two different kinds of valence forces in order to account for the chemistry of these compounds: the "primary valence," which equals three in the luteo salt, and the "secondary valence," which equals six in this example. In other words, the compound should, in a modern language, be formulated as $[Co(NH_3)_6]^{3+}Cl_3^{3-}$. The explanation of the previously mentioned puzzle is then clear; the green and violet compounds $[Co(NH_3)_4Cl_2]Cl$ are the *cis*- and *trans*-dichlorotetrammine cobalt(III) chloride.

The study of the isomers of the platinum(II) complexes further led Werner to postulate a square planar configuration for these compounds, an assumption which modern X-ray work has proved to be correct. Time has thus shown that Werner's view on the stereochemistry of the complex

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† See, for example, Ref. 1 for an account of the early development of the theory.

molecules was completely right, but it is only in recent years that an understanding of why the complexes form and behave as they do has been reached.

The conception of a coordination or complex molecule has in modern times been extended to be any compound containing a central ion surrounded by a cluster of ions or molecules. Such a compound may be more or less chemically stable; $SO_4^{=}$, for instance, is a very stable complex, whereas $Ni(NH_3)_6^{++}$ is not. It is customary to call the ions or molecules surrounding the central ion "ligands." The central ion or atom may accommodate a certain number of ligands, and this number is called the "coordination number." In the case of $SO_4^{=}$, for example, it is four.

In some cases a central atom or ion exhibits a different coordination number toward different ligands. A well-known example is Ni(II), because this ion can be either hexa- or tetracoordinated. We say that Ni(II) has the characteristic coordination numbers six and four. The question of the actual coordination number of a certain ion is usually investigated in the solid state by means of an X-ray analysis and in solution by means of an analysis of the consecutive complexity constants. This latter subject has in modern times been especially investigated by J. Bjerrum. Since it is not intended to follow the subsequent development of the history of the coordination compounds here, however, we shall refer the reader to Bailar's book[1]† for a broad outline of the subject.

We shall in this book be concerned only with the electronic structures of the transition series, i.e., the elements having unfilled *d* or *f* electronic shells. These are the *first transition series* (Sc → Cu), where the 3*d* shell is being filled up; the *second transition series* (Y → Ag), where the 4*d* shell is being filled up; and the *third transition series* involving 5*d* electrons (La → Au). In addition, we have the *rare earths* (Ce → Lu) and the *actinides* (Th →   ), where the 4*f* and the 5*f* shells, respectively, are being filled.

We shall be primarily interested in the chemistry and electronic structures of the elements containing *d* electrons. Furthermore, since most work has been done with the elements of the first 3*d* transition series, nearly all of the examples given in the following chapters are taken from there. It must, however, be realized that this limitation is of a practical rather than of a theoretical nature, because the theory which we shall outline applies to complexes of all the transition elements.

1-b. Theories of Bonding

The all-important question for the coordination compounds of the transition metals is this: How does one describe and characterize the bonding between the central ion and the ligands in terms of some electronic theory? In modern times three methods have been used to solve the problems of the nature of these bonds and to account for the other properties of the complexes. They are:

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† Superscript numbers are those of references listed at the end of the chapter.

1. The molecular-orbital method
2. The valence-bond theory
3. The crystal or ligand field theory

Until recently, most chemists working with the complexes of the transition metal ions have been mainly interested in the application of the valence-bond theory as exemplified by Pauling[2] in his famous book "The Nature of the Chemical Bond." Special emphasis was there laid upon the magnetic properties of the complexes, and a seemingly successful theory was built upon those features.

However, more than twenty years have passed since Van Vleck[3–5] demonstrated the superiority of the crystal field approach in the discussion of the magnetic properties of inorganic complexes. Now, it must at once be said that for the complexes under discussion both the valence-bond picture and the crystal field picture can be considered as a specialization of the molecular-orbital method.[5,7] Indeed, the most useful approach to these compounds is now called the ligand field theory, which is really nothing more than a hybridization of the ideas of Bethe[6] and Van Vleck[3,4] with those of Mulliken.[7,5] Thus the best features of both the valence-bond picture and the crystal field theory are incorporated in the ligand field theory, and it is this theory with which we shall be mostly concerned. As we shall not in this book follow the historical line of development, it is perhaps of some value to scan briefly through the most important papers from which the present theory has emerged.

1-c. History of the Crystal Field Approach

The basic idea of the crystal field theory, namely, that the metal ion in the complexes is subjected to an electric field originating from the ligands, is due to Becquerel[8] (1929). The same year saw this proposal formulated into an exact theory by Bethe.[6] In a now classic paper, Bethe investigated, by means of symmetry concepts, how the symmetry and strength of a crystalline field affect the electronic levels of the gaseous metal ions. In doing so, he laid down the foundation for all further work in this field.

Nearly simultaneous with the work of Bethe was the work of Kramers.[9] In 1930, the latter succeeded in proving the very important result that the electronic levels in molecules containing an odd number of electrons must remain at least twofold degenerate, provided that no magnetic field is present. This so-called "Kramers degeneracy" is again closely related to the existence of the "double groups" (Bethe).

The first application of the new theory to chemistry was made by Van Vleck (1932). By realizing that the quenching of the "orbital momentum" would be a consequence of the crystalline field model, he succeeded in explaining why the paramagnetism of the complexes of the first transition series corresponds to a "spin-only" value.[10] Furthermore, the crystalline field model was able to predict in which cases there would be small deviations from this empirical rule.[11]

These predictions were completely justified by the calculations of Schlapp and Penney[12] and of Jordahl,[13] who showed that both the anisotropy and the variation of the magnetic susceptibility with temperature could be exactly predicted and calculated. Their very important papers directly confirmed the basic idea in the crystal field approach, namely, that the crystal field reduces the degeneracy of the electronic levels of the gaseous metal atom. A note by Gorter,[14] in which it is shown that the crystal field of a regular tetrahedron will produce the same levels as those produced by a regular octahedron but with the level order inverted, concludes the pioneer papers.

In the years preceding the war the efforts were mostly concentrated on explaining and calculating the detailed magnetic behavior of the complex ions. It soon turned out, however, that the theory was hampered because of insufficient experimental data. This period could be called "the period of Van Vleck," because nearly all the important contributions were due to him and his school. As some examples we cite Van Vleck and Penney's[15] treatment of the Mn(II) ion, the proof that the crystal field theory and the theory of Pauling both were special cases of the molecular-orbital theory,[3] the definitions of the "strong" and "weak" crystal field,[4] the investigation of the $K_3Fe(CN)_6$ system,[16] and the research into the magnetic behavior of the vanadium, titanium, and chromium alums.[17]

The means by which the absorption bands of inorganic complexes acquire intensity was another problem first treated by Van Vleck.[18] He pointed out that it is necessary to couple the electronic wave functions with the odd vibrations of the molecule in order to get band intensities different from zero, if one assumes that the absorption bands are due to transitions between the various split $3d^n$ or $4f^n$ configurations. To the same period belong Van Vleck's investigations into the Jahn-Teller theorem as applied to octahedral molecules.[19] Jahn and Teller had shown in 1937 that no nonlinear molecule could be stable in a degenerate state (apart, of course, from a Kramers degeneracy). If, therefore, a certain configuration is predicted to give rise to an electronic degeneracy, such a configuration must immediately distort, via nuclear displacements in the molecule, in such a way that the degeneracy is removed. Van Vleck calculated the Jahn-Teller distortions for molecules of the form XY_6 and showed how this configurational instability affected the magnetic moment of the molecules.

The subsequent paper on the complete energy levels of chrome alum by Finkelstein and Van Vleck[20] laid down the method of calculation employed in nearly all the inquiry that followed. A few other papers, as, for example, Polder's[21] calculation of the magnetic anisotropy of the Cu(II) salts, mark the close of the second period in the history of crystal field theory.

The development after the war of the spectrophotometer and of the paramagnetic resonance technique brought new life into the theoretical and experimental development of the crystal field theory, and the consequence has been a steadily increasing flood of papers dealing with these subjects. References to most of this work can be found in seven review papers, Refs. 22–28. Since we have now reached a point at which the developments cease to be history, we shall leave the subject here.

Before we close this chapter, it may perhaps be appropriate to make a few remarks concerning the nomenclature we shall use. By the name "crystal field theory" we shall understand the original theory of Bethe and Van Vleck, i.e., the theory which does not consider the role played by the ligands further than to credit them with producing a steady "crystalline field." On the other hand, the name "ligand field theory" indicates a hybridization of the pure crystal field theory with the molecular-orbital theory of Mulliken. The ligand field theory incorporates the best features of both the pure crystal field theory and the molecular-orbital theory, and as such is the superior tool for dealing with the complexes. Nearly all the results of the crystal field theory are also valid in the ligand field theory. However, since the former theory in some ways is the easier to understand, we shall start by treating that case. In the following chapter we shall accordingly proceed to recapitulate some important features of the theory of atomic spectra because that theory is the starting point of the crystal field theory.

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CHAPTER 2

Theory of Atomic Spectra

2-a. Orbitals and States

In this chapter we shall treat the problem of how to find the energy states of n equivalent electrons moving in a central field. We shall do so by assuming the single-electron approximation. This approximation scheme distributes the n electrons among the single-electron orbitals, paying due regard to the spin properties of the final states. Our treatment will follow closely the classic book of Condon and Shortley,[1] "Theory of Atomic Spectra."

The basic orbitals we shall use are those of the hydrogen-like atom, as usual characterized as 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d* and so forth.† Each of these orbitals has a characteristic degeneracy and energy. As is well known, *s* orbitals are nondegenerate, *p* orbitals are threefold degenerate, and *d* orbitals are fivefold degenerate, meaning that there are, for instance, five different *d* orbitals, all with the same energy. A further degeneracy is provided by the spin property of the electron. Every electron can have either an α or β spin, and the Pauli exclusion principle tells us that no two electrons having the same set of quantum numbers may be found in a system. Consequently, only two electrons can be accommodated in each single orbital. The various *s*, *p*, *d* sets of orbitals can thus contain respectively 2, 6, and 10 electrons.

The orbitals *s*, *p*, *d*, etc. are solutions to the Schrödinger equation $\mathcal{H}\psi = E\psi$, where

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \tag{2-1}$$

Z being the "effective" charge of the center. If we have an atom containing j electrons, the approximate Hamiltonian function is

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_j \nabla_j^2 - \sum_j \frac{Z_j e^2}{r_j} + \sum_{j>k} \frac{e^2}{r_{jk}} \tag{2-2}$$

with ∇_j^2 the Laplacian operator for electron number j and r_{jk} the distance

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† Small letters are used throughout this book to indicate one-electron functions, and capital letters are used to indicate state functions.

between the jth and kth electrons. For the present we shall neglect the interaction between the orbitals and the spins (*vide infra*). In what follows we shall regard the term $\sum_{j>k} \frac{e^2}{r_{jk}}$ as a perturbation upon the single-electron functions. In the atoms the various orbitals have different energies, and we can make use of the "aufbau principle" for constructing multielectronic structures. Consider the one-electron orbitals arranged in order of increasing energy. In order to build up the electronic structures, we feed the electrons one by one into these orbitals, beginning with the orbital having the lowest energy. Proceeding in this way, we must, of course, take care of the exclusion principle by placing only two electrons into each single orbital. The total energy of an atomic configuration containing n electrons is thus the sum of the energies of all the occupied orbitals corrected for the additional energy due to the mutual repulsion between the electrons. This latter effect is due to the Coulomb repulsion term $1/r_{jk}$ present in the Hamiltonian.

We can now proceed to build up the periodic system of the elements in the well-known way, hydrogen being represented in its ground state by $(1s)$, helium by $(1s)^2$, lithium by $(1s)^2(2s)$, and, say, argon by $(1s)^2(2s)^2(2p)^6$-$(3s)^2(3p)^6$. This latter atomic configuration is designated as [A] throughout the rest of the book.

We have now arrived at the transition elements, since the electronic structure of Ti^{3+} is $[A](3d)^1$, that of V^{3+} is $[A](3d)^2$, that of Cr^{3+} is $[A](3d)^3$, and so forth. Owing to the degeneracy of the $3d$ orbitals, it now becomes a question how to "drop" the electrons down into the five d orbitals in order to obtain the lowest energy. This question would be trivial if there were no repulsion between the electrons (all the d orbitals have a priori the same energy), but because of this repulsion certain arrangements of the electrons are going to be more favorable energetically than others. In what follows we can completely neglect the closed argon 18-electron shell, since there is no freedom left there, and concentrate upon the $(3d)^n$ part. This approximation then neglects core–outer shell exchange.

A brief recapitulation of the nomenclature for atomic states is perhaps not out of order at this place. For most atoms we assume the existence of the so-called Russel-Saunders or LS coupling. This implies that we can characterize an atomic configuration by means of the two quantum numbers L and S, specifying respectively the total orbital momentum and the total spin momentum. Thus in an LS coupling scheme L and S are good quantum numbers. For a single electron, $\mathbf{L}$ is, of course, equal to $\mathbf{l}$, the orbital momentum of a single electron, but for more than one electron, $\mathbf{L}$ is given by the vector addition $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 + \cdots + \mathbf{l}_n$. The same holds true for $\mathbf{S}$. By analogy with the nomenclature for one particle, the projections of $\mathbf{L}$ and $\mathbf{S}$ upon the z axis are called M_L and M_S. Since both $\mathbf{L}$ and $\mathbf{S}$

are measures of orbital momentum, they must be positive, but M_L and M_S can take all integer values from $+L$ to $-L$ and from $+S$ to $-S$, again as is the case in the single-particle theory.

Because of the restrictions imposed by the Pauli principle, however, not all combinations of **L** and **S** can be obtained in a many-particle system and we shall now show by means of an example how to determine the possible states of a given system. As our example we choose the $(3d)^2$ configuration, but the method is applicable to all possible systems.[1]

In the $(3d)^2$ system both electrons have the same main quantum number $n = 3$ and both have $l = 2$.

It is thus necessary that the two electrons should differ in either m_l or m_s. Let us write down the various possibilities, and let us write $m_s = \frac{1}{2}$ as a $+$ superscript and $m_s = -\frac{1}{2}$ as a $-$ superscript. We shall further arrange them in a scheme of classification according to the value of $M_L = \Sigma m_l$ and $M_S = \Sigma m_s$. The notation $(2^+,1^-)$ means that electron 1 has $m_s = \frac{1}{2}$ and $m_l = 2$ and that electron 2 has $m_s = -\frac{1}{2}$ and $m_l = 1$. Our scheme is then as shown in the following table.

M_L \ M_S	1	0	-1
4		$(2^+,2^-)$	
3	$(2^+,1^+)$	$(2^+,1^-)$ $(2^-,1^+)$	$(2^-,1^-)$
2	$(2^+,0^+)$	$(2^+,0^-)$ $(2^-,0^+)$ $(1^+,1^-)$	$(2^-,0^-)$
1	$(2^+,-1^+)$ $(1^+,0^+)$	$(2^+,-1^-)$ $(2^-,-1^+)$ $(1^+,0^-)$ $(1^-,0^+)$	$(2^-,-1^-)$ $(1^-,0^-)$
0	$(2^+,-2^+)$ $(1^+,-1^+)$	$(2^+,-2^-)$ $(2^-,-2^+)$ $(1^+,-1^-)$ $(1^-,-1^+)$ $(0^-,0^+)$	$(2^-,-2^-)$ $(1^-,-1^-)$

Since it is obvious that the table is going to repeat itself for negative values of M_L, we shall not bother to write that part out. All in all, we must get $10 \cdot 9/1 \cdot 2 = 45$ different "micro states" distributed in the various M_L and M_S boxes of the scheme, since we have 10 places in which to put two equivalent electrons.

Starting at the top of the scheme, we notice the micro state $(2^+,2^-)$ having $M_L = 4$, $M_S = 0$. Since $M_L = 4$, this must come from a G ($L = 4$) state, and since $M_S = 0$, it must have $S = 0$. It is customary to write the multiplicity $2S + 1$ as an upper subscript placed to the left of the orbital-momentum quantum number; here we get a singlet G state written ${}^1G$. Since M_L can take all values from $+4$ to -4, this means that the ${}^1G$ state uses a micro state in all the M_L boxes with $M_S = 0$, a total of nine micro states. There is now no micro state having $M_L = 4$ left over, and we turn next to $M_L = 3$ and pick out $(2^+,1^+)$. As before, this indicates an F ($L = 3$) state, but since $M_S = 1$, this tells us that $S = 1$. In other words, $(2^+,1^+)$ belongs to a ^3F state.

Now in a ^3F state M_S can take the values 1, 0, −1 regardless of the values of M_L, so it makes use of $3 \times 7 = 21$ micro states. Thus we must pick out one micro state in each of the columns in the table for each row where $|M_L| \leq 3$. Since the micro state left over with the highest M_L is one having $M_L = 2$ and $M_S = 0$, we get a ^1D state, and by continuing this procedure, we find that the possible states in a d^2 system are ^1G, ^3F, ^1D, ^3P, and ^1S. This example illustrates the rule that, for equivalent electrons, $L + S$ must be even for any given state by the Pauli exclusion principle.

We have so far neglected the interaction between the magnetic dipoles connected with the spin of the electron and the magnetic dipoles produced by the electrons by moving in their orbits. This interaction is usually called the spin-orbit coupling, and it has the effect of splitting the LS terms up into various levels characterized by their total angular momentum $\mathbf{J}$. The collection of levels in an LS term is called a multiplet, and the splittings of the multiplets for the $(3d)^n$ configurations owing to the spin-orbit coupling are of the order of magnitude of a hundred wave numbers. For $\mathbf{J}$ we have $\mathbf{J} = \mathbf{L} + \mathbf{S}$, and we notice that the individual levels are $(2J + 1)$-fold degenerate.

For the present, however, we shall concentrate on evaluating the energies of the LS terms and postpone the treatment of the spin-orbit coupling until later in this chapter. But even before we can calculate energies, we must know the wave functions, and a brief treatment of this subject is consequently given next.

2-b. Atomic Wave Functions

The Pauli principle stating that no two electrons can occupy identical orbitals (including spin) is translated into the following statement: All wave functions must be antisymmetrical in every pair of electrons; i.e., an interchange of two electrons must change the sign of the wave function.

Since all electrons are identical, no physical quantity must depend on how we choose to number our electrons. Given, therefore, two orbitals ψ_1 and ψ_2, where ψ_1 and ψ_2 include both the space and spin coordinates, the wave function $\Psi_{\mathrm{I}} = \psi_1(1)\,\psi_2(2)$ is consequently just as good as $\Psi_{\mathrm{II}} = \psi_1(2)\,\psi_2(1)$, and, of course, it has the same energy. Any linear combination, for instance, $\Psi = \psi_1(1)\,\psi_2(2) \pm \psi_1(2)\,\psi_2(1)$, will therefore do. However, the Pauli principle tells us that we must choose the minus sign, because only in that case does the total wave function change sign by interchanging electrons 1 and 2. Therefore,

$$\Psi = \psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)$$

or, written as a determinant,

$$\Psi = \begin{vmatrix} \psi_1(1) & \psi_1(2) \\ \psi_2(1) & \psi_2(2) \end{vmatrix}$$

Such "Slater determinants" are the simplest, and in the one-electron approximation the only, many-electron wave functions which obey the antisymmetry properties nature demands. It is wave functions of this type that we shall use in our work. In general, the wave function Ψ is normalized to 1, that is, $\int \Psi^* \Psi \, d\tau = 1$. If the individual orbitals are normalized and orthogonal on each other, we get for the normalization factor $N = 1/\sqrt{n!}$, where n is the number of electrons in the system. For short we shall often write a determinantal antisymmetrized, normalized wave function as $|(\psi_1)(\psi_2) \cdots (\psi_n)|$ in this book. This term corresponds to the diagonal element in the expansion of the determinantal wave function where electron 1 is placed in ψ_1, electron 2 is placed in ψ_2, and so forth. In the complete expanded wave function, however, we have, of course, all possible permutations of electrons. We notice immediately that, if two electrons had the same set of quantum numbers, two of the columns in the determinant would be identical, and consequently the wave function would be zero. Thus the old way of formulating the Pauli principle is contained in the statement that the wave function shall be antisymmetrical with regard to exchange of two electrons, which justifies our statement at the beginning of this section. Usually, we separate the orbital- and spin-dependent parts of the wave function, and, as before, indicate the spin properties of the single electrons in the various orbitals by putting a plus or minus sign (standing for $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$) above the orbitals as, for example, $|(\overset{+}{\psi_1})(\overset{-}{\psi_2}) \cdots (\overset{-}{\psi_n})|$. If the wave function is written in this way, we must remember that, owing to the properties of determinants, an interchange of the orbitals may change the phase of the wave function. An even permutation will leave the sign of the wave function the same, and an odd permutation will change the sign. This follows from the fact that by changing two rows or columns in a determinant the sign is reversed.

2-c. The Raising and Lowering Operators

The following question now arises: Are the micro states in the scheme on page 9 eigenfunctions† of $\hat{L}$ and $\hat{S}$? The answer is that this is true only where there is only one state in a certain labeled box. Thus the state $(2^+,2^-)$ is an eigenstate belonging to ^1G (with $M_L = 4$) and $(2^+,1^+)$ is an eigenstate belonging to ^3F (with $M_L = 3$). However, for cases with more than one micro state in the scheme we must develop a technique for picking out

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† Where there is possibility of confusion, we shall distinguish between an operator and its eigenvalues by means of a circumflex placed above the operator; for example, $\hat{x}$ = operator and x = eigenvalue.

suitable linear combinations of these micro states in order to form eigenfunctions for $\hat{L}$ and $\hat{S}$. To do so, we shall now briefly study some useful properties of angular momentum.

The operators of the total electronic angular momentum $\hat{L}$ with respect to the three axes are called $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$, and these operators are defined as the sum of the operators for the single electrons

$$\begin{aligned}\hat{L}_x &= l_{1x} + l_{2x} + \cdots + l_{nx}\\ \hat{L}_y &= l_{1y} + l_{2y} + \cdots + l_{ny}\\ \hat{L}_z &= l_{1z} + l_{1z} + \cdots + l_{nz}\end{aligned}$$

As usual, $l_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$, and the expressions for l_y and l_z are analogous. Similarly, we have for the commutation rules

$$\begin{aligned}l_xl_y - l_yl_x &= i\hbar l_z\\ l_yl_z - l_zl_y &= i\hbar l_x\\ l_zl_x - l_xl_z &= i\hbar l_y\end{aligned} \tag{2-3}$$

These expressions also hold true for systems of particles, in which case $\hat{L}_i$ is substituted for l_i.

Further, we have for the square of the orbital angular momentum

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

and we have similar expressions for the spin operators $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$, and $\hat{S}^2$. Then for a state characterized by L, M_L, S, M_S, which we may denote by (L,M_L,S,M_S), the following relations hold true[1,2]:

$$\begin{aligned}\hat{L}^2(L,M_L,S,M_S) &= L(L+1)\hbar^2(L,M_L,S,M_S)\\ \hat{L}_z(L,M_L,S,M_S) &= M_L\hbar(L,M_L,S,M_S)\end{aligned} \tag{2-4}$$

and

$$\begin{aligned}\hat{S}^2(L,M_L,S,M_S) &= S(S+1)\hbar^2(L,M_L,S,M_S)\\ \hat{S}_z(L,M_L,S,M_S) &= M_S\hbar(L,M_L,S,M_S)\end{aligned} \tag{2-5}$$

Since the expressions for $\hat{L}^2$ and $\hat{L}_z$ are analogous to the expressions for $\hat{S}^2$ and $\hat{S}_z$, we shall limit ourselves in investigating only one set, (L,M_L). Our problem is to calculate $(\hat{L}_x \pm i\hat{L}_y)$ operating upon a set (L,M_L). By using the commutation rules, we have

$$\begin{aligned}(\hat{L}_x \pm i\hat{L}_y)\hat{L}_z &= \hat{L}_z\hat{L}_x - i\hbar\hat{L}_y \pm i(i\hbar\hat{L}_x + \hat{L}_z\hat{L}_y)\\ &= \hat{L}_z(\hat{L}_x \pm i\hat{L}_y) \mp \hbar(\hat{L}_x \pm i\hat{L}_y)\end{aligned} \tag{2-6}$$

We then, by using the above, obtain

$$(\hat{L}_z \mp \hbar)(\hat{L}_x \pm i\hat{L}_y)(L,M_L) = (\hat{L}_x \pm i\hat{L}_y)\hat{L}_z(L,M_L) = \hbar M_L(\hat{L}_x \pm i\hat{L}_y)(L,M_L)$$

By rearranging, we have

$$\hat{L}_z(\hat{L}_x \pm i\hat{L}_y)(L,M_L) = \hbar(M_L \pm 1)(\hat{L}_x \pm i\hat{L}_y)(L,M_L)$$

In other words,

$$(\hat{L}_x \pm i\hat{L}_y)(L,M_L) = \hbar a_{L,M_L}(L, M_L \pm 1) \tag{2-7}$$

The constant a_{L,M_L} can be calculated in the following way, for example, for the operator $(\hat{L}_x + i\hat{L}_y)$. We assume that both (L,M_L) and $(L, M_L + 1)$ are normalized, and we make use of the fact that $\hat{L}_x$ and $\hat{L}_y$ [but not $(\hat{L}_x + i\hat{L}_y)$] are Hermitian operators.[1,2] For an Hermitian operator $\hat{k}$ we have for the matrix element† $(a|k|b)$ the identity $(a|k|b) = (b|k|a)^*$, where an asterisk indicates the complex conjugate quantity. Then

$$\int(\hat{L}_x + i\hat{L}_y)^*(L,M_L)^*(\hat{L}_x + i\hat{L}_y)(L,M_L)\,d\tau = \hbar^2|a_{L,M_L}|^2$$

$$\int(\hat{L}_x + i\hat{L}_y)^*(L,M_L)^*\hat{L}_x(L,M_L)\,d\tau + i\int(\hat{L}_x + i\hat{L}_y)^*(L,M_L)^*\hat{L}_y(L,M_L)\,d\tau = \hbar^2|a_{L,M_L}|^2$$

$$\int(L,M_L)\hat{L}_x^*(\hat{L}_x + i\hat{L}_y)^*(L,M_L)^*\,d\tau + i\int(L,M_L)\hat{L}_y^*(\hat{L}_x + i\hat{L}_y)^*(L,M_L)^*\,d\tau = \hbar^2|a_{L,M_L}|^2$$

By taking the complex conjugate and collecting the terms again, we find

$$\int(L,M_L)^*(\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y)(L,M_L)\,d\tau = \hbar^2|a_{L,M_L}|^2$$

$$\int(L,M_L)^*[\hat{L}^2 - \hat{L}_z^2 + i(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x)](L,M_L)\,d\tau = \hbar^2|a_{L,M_L}|^2$$

$$L(L + 1) - M_L^2 - M_L = |a_{L,M_L}|^2 \tag{2-8}$$

In this way we find the two results

$$\hat{L}_+(L,M_L) \equiv (\hat{L}_x + i\hat{L}_y)(L,M_L) = \hbar\sqrt{(L + M_L + 1)(L - M_L)}\,(L, M_L + 1) \tag{2-9}$$

$$\hat{L}_-(L,M_L) \equiv (\hat{L}_x - i\hat{L}_y)(L,M_L) = \hbar\sqrt{(L - M_L + 1)(L + M_L)}\,(L, M_L - 1) \tag{2-10}$$

Similar expressions hold for $(\hat{S}_x \pm i\hat{S}_y)$. For an α spin having $S = \frac{1}{2}$ and $M_S = \frac{1}{2}$ we notice that $(\hat{S}_x + i\hat{S}_y)(\frac{1}{2},\frac{1}{2}) = 0$ and

$$(\hat{S}_x - i\hat{S}_y)(\tfrac{1}{2},\tfrac{1}{2}) = \hbar(\tfrac{1}{2}, -\tfrac{1}{2})$$

By writing $\hat{S}_+ = \hat{S}_x + i\hat{S}_y$ and $\hat{S}_- = \hat{S}_x - i\hat{S}_y$, we have in general

$$\begin{aligned} \hat{S}_+\alpha &= 0 & \hat{S}_+\beta &= \hbar\alpha \\ \hat{S}_-\alpha &= \hbar\beta & \hat{S}_-\beta &= 0 \end{aligned} \tag{2-11}$$

Finally, we are interested in the matrix elements of $\hat{L}^2$. Expanding, we obtain, omitting $\hbar^2$ in this and immediately following equations,

$$\hat{L}^2 = \Big(\sum_i \hat{l}_i\Big)^2 = \sum_i \hat{l}_i^2 + 2\sum_{i>j} \hat{l}_i \cdot \hat{l}_j$$

Thus:

$$\hat{L}^2 = \sum_i \hat{l}_i^2 + 2\sum_{i>j} \hat{l}_{i_z}\hat{l}_{j_z} + \sum_{i>j} (\hat{l}_{i_+}\hat{l}_{j_-} + \hat{l}_{i_-}\hat{l}_{j_+}) \tag{2-12}$$

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† $(a|k|b)$ stands for $\int\psi_a^*\hat{k}\psi_b\,d\tau$.

and by operating upon a determinantal wave function, we get

$$\begin{aligned}\hat{L}^2|(l_1m_{l_1})\cdots(l_im_{l_i})\cdots(l_nm_{l_n})| \\ &= \Big[\sum_i l_i(l_i+1) + 2\sum_{i>j} m_{l_i}m_{l_j}\Big]\,|(l_1m_{l_1})\cdots(l_im_{l_i})\cdots(l_nm_{l_n})| \\ &\quad + \sum_{i\neq j}\sqrt{(l_i+m_{l_i}+1)(l_i-m_{l_i})}\,\sqrt{(l_j-m_{l_j}+1)(l_j+m_{l_j})} \\ &\qquad |(l_1m_{l_1})\cdots(l_i,m_{l_i}+1)\cdots(l_j,m_{l_j}-1)| \qquad (2\text{-}13)\end{aligned}$$

It must be remembered that the orbitals in the wave functions must always be brought back to the standard order and that an odd permutation will change the sign of the wave function.

We may now return to our example on page 9:

$$\begin{aligned}\hat{L}^2(2^+,2^-) &= (2\cdot3+2\cdot3+2\cdot2\cdot2)(2^+,2^-) = 4\cdot5\cdot(2^+,2^-) \\ \hat{S}^2(2^+,2^-) &= (\tfrac{1}{2}\cdot\tfrac{3}{2}+\tfrac{1}{2}\cdot\tfrac{3}{2}+2\cdot\tfrac{1}{2}(-\tfrac{1}{2}))(2^+,2^-)+(2^-,2^+) \\ &= (\tfrac{3}{2}-\tfrac{1}{2}-1)(2^+,2^-) = 0 \qquad (2\text{-}14)\end{aligned}$$

Therefore, for ${}^1G$ (as we have observed previously)

$$\Psi(L,M_L,S,M_S) = \Psi(4,4,0,0) = (2^+,2^-)$$

Then

$$\hat{L}_-\Psi(4,4,0,0) = \sqrt{1\cdot8}\,\Psi(4,3,0,0) \qquad (2\text{-}15)$$

and also

$$\hat{L}_-(2^+,2^-) = \sqrt{4}\,(1^+,2^-) + \sqrt{4}\,(2^+,1^-) \qquad (2\text{-}16)$$

In other words,

$$\Psi(4,3,0,0) = \sqrt{\tfrac{1}{2}}\,[(2^+,1^-) - (2^-,1^+)] \qquad (2\text{-}17)$$

By operating again with L_- upon (2-17),

$$\begin{aligned}\sqrt{2\cdot7}\,\Psi(4,2,0,0) &= \sqrt{\tfrac{1}{2}}\,[\sqrt{6}\,(0^+,2^-) + \sqrt{4}\,(1^+,1^-) \\ &\qquad - \sqrt{6}\,(0^-,2^+) - \sqrt{4}\,(1^-,1^+)] \\ \Psi(4,2,0,0) &= \sqrt{\tfrac{3}{14}}\,(2^+,0^-) + \sqrt{\tfrac{8}{14}}\,(1^+,1^-) \\ &\qquad - \sqrt{\tfrac{3}{14}}\,(2^-,0^+) \qquad (2\text{-}18)\end{aligned}$$

A check is continuously provided by the requirement that the wave function shall appear normalized. For ${}^3F$

$$\begin{aligned}\Psi(L,M_L,S,M_S) &= \Psi(3,3,1,1) = (2^+,1^+) \\ \hat{L}_-\Psi(3,3,1,1) &= \sqrt{6}\,\Psi(3,2,1,1) \\ &= \sqrt{4}\,(1^+,1^+) + \sqrt{2\cdot3}\,(2^+,0^+) \qquad (2\text{-}19)\end{aligned}$$

Since $(1^+,1^+)$ is zero because of the Pauli principle, we get (as of course could be anticipated since there is only one micro state for $M_L = 2$ and $M_S = 1$)

$$\Psi(3,2,1,1) = (2^+,0^+) \qquad (2\text{-}20)$$

Let us now find $\hat{S}_{-}\Psi(3,2,1,1)$. Here

$$\begin{aligned} \hat{S}_{-}\Psi(3,2,1,1) &= \sqrt{2}\,\Psi(3,2,1,0) \\ &= (2^{-},0^{+}) + (2^{+},0^{-}) \\ \Psi(3,2,1,0) &= \frac{1}{\sqrt{2}}[(2^{+},0^{-}) + (2^{-},0^{+})] \end{aligned} \tag{2-21}$$

Because the wave function for ${}^{1}D,\Psi(2,2,0,0)$ is made up of $(2^{+},0^{-})$, $(2^{-},0^{+})$, $(1^{+},1^{-})$, we must take that combination of these micro states which is orthogonal to $\Psi(3,2,1,0)$ and $\Psi(4,2,0,0)$. Consequently,

$$ {}^{1}D,\Psi(2,2,0,0) = a(2^{+},0^{-}) + b(2^{-},0^{+}) + c(1^{+},1^{-}) \tag{2-22}$$

and we get

$$\begin{aligned} a\sqrt{3} - b\sqrt{3} + c\sqrt{8} &= 0 \\ a + b &= 0 \end{aligned} \tag{2-23}$$

with the normalizing condition $a^2 + b^2 + c^2 = 1$. Solving, we get

$$ {}^{1}D,\Psi(2,2,0,0) = \sqrt{2/7}\,(2^{+},0^{-}) - \sqrt{2/7}\,(2^{-},0^{+}) - \sqrt{3/7}\,(1^{+},1^{-}) \tag{2-24}$$

Let us now find the wave function for ${}^{3}P(1,1,1,1)$. Operating with $\hat{L}_{-}$ upon ${}^{3}F(3,2,1,1)$, we get

$$ {}^{3}F,\Psi(3,1,1,1) = \sqrt{3/5}\,(2^{+},-1^{+}) + \sqrt{2/5}\,(1^{+},0^{+}) \tag{2-25}$$

Since ${}^{3}P(1,1,1,1)$ must be orthogonal to ${}^{3}F(3,1,1,1)$, we get

$$ {}^{3}P(1,1,1,1) = \sqrt{2/5}\,(2^{+},-1^{+}) - \sqrt{3/5}\,(1^{+},0^{+}) \tag{2-26}$$

In this way we could continue and construct all the wave functions which are diagonal in the (L,M_L,S,M_S) scheme. The method will always work, but it is not unique if more than one state of a given designation is present.[1,5] As we shall see, it is not in general necessary to construct the wave functions in order to find the term energies except for special cases.

2-d. Matrix Elements

Let us now investigate how to calculate some matrix elements for various kinds of operators, and let us start out with a one-electron operator, e.g. the transition probability operator $\hat{R}$ of an n-electron system. The expectation value of R is proportional to the dipole moment of the system, and we have

$$\hat{R} = \sum_{n} \hat{r}_n = \hat{r}_1 + \hat{r}_2 + \cdots + \hat{r}_n \tag{2-27}$$

$\hat{r}_n$ being the displacement of electron number n from the origin. We are interested in the matrix element

$$(A|R|B) = \int \Psi^{*}(A) R \Psi(B)\, d\tau \tag{2-28}$$

where A is an antisymmetrized one-electron product wave function

$$\Psi(A) = \frac{1}{\sqrt{n!}} \sum_{P} (-1)^{P} P_A \psi\{(a_1) \cdots (a_n)\} \tag{2-29}$$

with a similar expression for B. Here $1/\sqrt{n!}$ is the normalization factor if the single orbitals $a_1 \cdots a_n$ are normalized individually. P is the number of permutations. This is really only another way of writing down the determinantal wave function

$$\Psi(A) = \frac{1}{\sqrt{n!}} \begin{vmatrix} a_1(1) & a_2(1) & \cdots & a_n(1) \\ a_1(2) & a_2(2) & \cdots & a_n(2) \\ \cdots & \cdots & \cdots & \cdots \\ a_1(n) & \cdots & \cdots & a_n(n) \end{vmatrix} \tag{2-30}$$

We have before used the shortened notation $\Psi = |(a_1)(a_2) \cdots (a_n)|$ for such a determinantal wave function.

The matrix $(A|R|B)$ is then expanded:

$$(A|R|B) = \frac{1}{n!} \sum_i \sum_P \sum_{P'} (-1)^{P+P'} \int P\Psi^*(A) r_i P'\Psi(B)\, d\tau \tag{2-31}$$

It is now immaterial whether we look at P as permuting the electrons or the orbitals. Looking at the term for r_i, we get

$$\int Pa_1^*(1)P'b_1(1)\, d\tau_1 \cdots \int Pa_i^*(i) r_i P'b_i(i)\, d\tau_i \cdots \int Pa_n^*(n)P'b_n(n)\, d\tau_n \tag{2-32}$$

Thus each of the integral factors will vanish, with the exception of the ith, unless $Pa_m = P'b_m$. Therefore, at least $(n - 1)$ sets of orbitals in A and in B must be identical. It follows that the selection rule is $(A|R|B) = 0$ and, in general, $(A|F|B) = 0$, where F is any one-electron operator, defined $F = \sum_i f_i$, if A and B differ by more than one orbital.

In order to calculate $(A|F|B)$, we must establish a certain standard ordering of the orbitals in A and B. If this conventional order is not found, the determinantal wave functions must be so rearranged that the same orbital always occurs in the same place. Such a standard order may, of course, always be obtained by interchanging the columns of the determinantal wave function. During this process, the sign of the wave function will change according to the number of permutations.

Suppose then that A is equal to B except for one individual set, which is the a_k of A when A is arranged in conventional order. We can then form a set B':

$$B' = a_1 a_2 \cdots a_{k-1} b_k a_{k+1} \cdots a_n$$

This may not be the conventional order for B, but it may be brought to the conventional order by permutations. Thus $\Psi(B') = \pm\Psi(B)$. The plus sign applies if B' differs from B by an even number of interchanges; the minus sign applies if the permutation is an odd one. Then

$$(A|F|B) = \pm(A|F|B') \tag{2-33}$$

We may now calculate $(A|F|B')$ quite simply. In order that the product of integrals should not vanish, P' must be the same permutation as P so as to keep corresponding functions together. Since P' then equals P, the sign $(-1)^{p+p}$ of each term must be positive. Further, P must be such a permutation as to bring the function a_k to the ith position. For a given i we can do this in $(n-1)!$ ways, and since this should be done for each i, the final result is multiplied by n.

The final result for the summation over P, P', and i is thus

$$\begin{aligned}(A|F|B) &= \pm \frac{n(n-1)!}{n!} \int a_k^*(1)f(1)b_l(1)\,d\tau_1 \\ &= \pm \int a_k^*(1)f(1)b_l(1)\,d\tau_1 \qquad (2\text{-}34)\end{aligned}$$

where the plus or minus sign is determined by whether an even or odd permutation is necessary to bring a_k and b_l into the same order.

For diagonal elements the argument runs along quite similar lines. Since the two sets are identical, we need not worry about the plus or minus sign, and further, since $P = P'$, we have

$$(A|F|A) = \frac{1}{n!} \sum_i \sum_P \int Pa_i^*(i)f(i)Pa_i(i)\,d\tau_i \qquad (2\text{-}35)$$

For each of the n values of i there are $(n-1)!$ ways of permutating the indices different from i, and with the summation carried out we finally get

$$(A|F|A) = \sum_{i=1}^{n} \int a_i^*(1)f(1)a_i(1)\,d\tau_1 \qquad (2\text{-}36)$$

Thus the expectation value of F is simply the sum of the expectation values of f over the various orbitals.

It is further seen that if the one-electron operator is independent of the spin coordinates, we must have $\sum_1^n m_s$ for A equal to $\sum_1^n m_s$ for B if the matrix element is not going to vanish because of spin orthogonality. Furthermore, we must, of course, have states with the same value of S if $(A|F|B)$ is going to be different from zero.

2-e. Two-electron Operators

The most important two-electron operator is the Coulomb repulsion term $g(i,j) = \sum_{i>j=1} (e^2/r_{ij})$. We note that written in this form care has been taken to count each interaction only once. As previously mentioned, this term is responsible for the separations of the different groups of multiplets in the spectrum of the atom. With two determinantal wave functions A and B written in the shortened notation $A = |(a_1)(a_2) \cdots (a_n)|$ and $B = |(b_1)(b_2) \cdots (b_n)|$ we notice immediately that the matrix element

$(A|g(i,j)|B)$ will be equal to zero if the two wave functions differ in more than two sets of orbitals. We must then consider the three possible cases: (1) A and B differ in two orbitals, (2) A and B differ in one orbital, and, finally, (3) the diagonal term.

Case 1. Given the two wave functions $A = |(a_1)(a_2)(a_3) \cdots (a_n)|$ and $B = |(b_1)(b_2)(a_3) \cdots (a_n)|$, where for simplicity we have moved the two different orbitals to the first two columns in the determinantal wave function. This condition imposes, of course, no limitations in the following, since it is only a matter of the phase. In the matrix element $(A|g(i,j)|B)$ we can then at once integrate out all of the a_3 to a_n orbitals. This follows from the fact that it is necessary to take $g(i,j)$ as $g(1,2)$, since otherwise the whole matrix element would vanish because of orthogonality between a_1 and b_1 or a_2 and b_2. For this reason a_1 and a_2 must be mated with b_1 and b_2, and by performing the same type of summation over the permutation operators P and P' as before, it is easily seen that we get

$$(A|g(i,j)|B) = \int\int a_1^*(1)a_2^*(2)g(1,2)b_1(1)b_2(2)\,d\tau_1\,d\tau_2 - \int\int a_1^*(1)a_2^*(2)g(1,2)b_1(2)b_2(1)\,d\tau_1\,d\tau_2 \tag{2-37}$$

In the generalized case we get

$$(A|g(i,j)|B) = \pm[\int\int a_j^*(1)a_k^*(2)g(1,2)b_i(1)b_l(2)\,d\tau_1\,d\tau_2 - \int\int a_j^*(1)a_k^*(2)g(1,2)b_i(2)b_l(1)\,d\tau_1\,d\tau_2] \tag{2-38}$$

where the plus or minus sign in front of the expression as before is determined by the parity of the permutation necessary to bring the wave functions into the standard order.

Case 2. If the two wave functions A and B differ in only one orbital, we can match the corresponding orbitals in A and B by a suitable permutation

$$\begin{aligned} A &= |(a_1)(a_2) \cdots (a_k) \cdots (a_n)| \\ B &= |(a_1)(a_2) \cdots (b_k) \cdots (a_n)| \end{aligned} \tag{2-39}$$

and by exactly similar arguments as previously we get

$$(A|g(1,2)|B) = \pm \sum_t \Big[\int\int a_k^*(1)a_t^*(2)g(1,2)b_l(1)a_t(2)\,d\tau_1\,d\tau_2 - \int\int a_k^*(1)a_t^*(2)g(1,2)b_l(2)a_t(1)\,d\tau_1\,d\tau_2\Big] \tag{2-40}$$

where t runs over the $n - 1$ sets of orbitals common to A and B.

Case 3. Finally, we have for the diagonal elements

$$(A|g(1,2)|A) = \sum_{k>t=1}^{n} \Big[\int\int a_k^*(1)a_t^*(2)g(1,2)a_k(1)a_t(2)\,d\tau_1\,d\tau_2 - \int\int a_k^*(1)a_t^*(2)g(1,2)a_t(1)a_k(2)\,d\tau_1\,d\tau_2\Big] \tag{2-41}$$

In this last case the integrals with a plus sign are called "Coulomb integrals" and the integrals with negative signs "exchange integrals."

If $g(i,j)$ is independent of the spin coordinates, the integration over these coordinates can be carried out at once, and we simply get a factor of +1 in the Coulomb integral and a delta function $\delta(m_s^k, m_s^l)$ in the exchange integral. This means that only for electrons with parallel spins do we get an exchange integral.

2-f. Evaluation of the Matrix Elements $(ab|1/r_{12}|cd)$.

We are now in a position to calculate the matrix elements resulting from the Coulomb repulsion term $g(i,j) = \sum_{i>j=1}^{n} (e^2/r_{ij})$.

As our wave functions we take hydrogen-like wave functions characterized by the set (n,l,m_l,m_s). As shown above, the most general integral which can occur is

$$\left(ab\left|\frac{e^2}{r_{12}}\right|cd\right) = \iint a^*(1)b^*(2)\frac{e^2}{r_{12}}c(1)\,d(2)\,d\tau_1\,d\tau_2 \qquad (2\text{-}42)$$

where the single-electron wave functions are the usual solutions to the hydrogen-like atom

$$a(1) = R_{nl}(r_1)Y_l^{m_l}(\Theta_1,\varphi_1) \qquad (2\text{-}43)$$

where $Y_l^{m_l}$ is a normalized spherical harmonic.† We notice immediately that the spin components of a and c and of b and d must be the same if the integral is not to be zero.

Further, we must expand $1/r_{12}$ in spherical harmonics:[1,2]

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty}\sum_{m=-k}^{k}\frac{4\pi}{2k+1}\frac{r_<^k}{r_>^{k+1}}Y_k^m(\Theta_1,\varphi_1)Y_k^{m*}(\Theta_2,\varphi_2) \qquad (2\text{-}44)$$

where $r_<$ is the lesser and $r_>$ is the greater of r_1 and r_2.

$$Y_l^m(\Theta,\varphi) = P_l^m(\cos\Theta)\frac{1}{\sqrt{2\pi}}e^{im\varphi}$$

where $P_l^m(\cos\Theta)$ is a normalized Legendre function. We then collect the part of the integral dependent upon φ:

$$\begin{aligned}\cdots\int_0^{2\pi}\frac{1}{\sqrt{2\pi}}e^{-im_a\varphi_1}\frac{1}{\sqrt{2\pi}}e^{im\varphi_1}\frac{1}{\sqrt{2\pi}}e^{im_c\varphi_1}\,d\varphi_1 \\ \int_0^{2\pi}\frac{1}{\sqrt{2\pi}}e^{-im_b\varphi_2}\frac{1}{\sqrt{2\pi}}e^{-im\varphi_2}\frac{1}{\sqrt{2\pi}}e^{im_d\varphi_2}\,d\varphi_2 \\ = \cdots\frac{1}{8\pi^3}\int_0^{2\pi}e^{i(m-m_a+m_c)\varphi_1}\,d\varphi_1\int_0^{2\pi}e^{i(m_d-m-m_b)\varphi_2}\,d\varphi_2\end{aligned}$$

† A very important point is the choice of phase for the spherical harmonics $Y_l^{m_l}$. We shall always use the Condon-Shortley "natural choice of phrase"; a factor of -1 for positive odd values of m_l or, for short, just written m. Thus $Y_l^m = (-1)^m Y_l^{-m}$. This is a point to be carefully checked every time a formula from a different book is used; many hours of work have been spent in order to find mistakes in signs due to such errors.

Only if $(m - m_a + m_c) = 0$ and $(m_d - m - m_b) = 0$ do we get a value different from zero; therefore,

$$m_a - m_c = m_d - m_b \equiv m$$

or

$$m_a + m_b = m_c + m_d \tag{2-45}$$

With this condition the integrals over φ_1 and φ_2 reduce to $1/2\pi$. Defining the quantity c^k as

$$c^k(lm_l, l'm_l') = \sqrt{\frac{2}{2k+1}} \int_0^\pi P_k^{m_l - m_l'}(\cos\Theta)\, P_l^{m_l}(\cos\Theta)\, P_{l'}^{m_l'}(\cos\Theta) \sin\Theta\, d\Theta \tag{2-46}$$

and

$$R^k(abcd) = e^2 \int_0^\infty \int_0^\infty \frac{r_<^{\,k}}{r_>^{\,k+1}} R_1(a)R_2(b)R_1(c)R_2(d) r_1^2\, dr_1\, r_2^2\, dr_2 \tag{2-47}$$

we get as final result

$$(ab|1/r_{12}|cd) = \delta(m_s^a, m_s^c)\delta(m_s^b, m_s^d) \cdot \delta(m_l^a + m_l^b, m_l^c + m_l^d) \times \sum_{k=0}^{\infty} c^k(l^a m_l^a, l^c m_l^c) c^k(l^d m_l^d, l^b m_l^b) \cdot R^k(abcd) \tag{2-48}$$

For the diagonal elements in particular we define

$$J(a,b) = (ab|1/r_{12}|ab) \tag{2-49}$$

and

$$K(a,b) = (ab|1/r_{12}|ba) \tag{2-50}$$

TABLE 2-1

$c^k(lm_l, l'm_l')$ for $l,l' = 2,2$

m_l	m_l'	$k = 0$	$k = 2$	$k = 4$
± 2	± 2	$+1$	$-\frac{\sqrt{4}}{7}$	$+\frac{1}{21}$
± 2	± 1	0	$+\frac{\sqrt{6}}{7}$	$-\frac{\sqrt{5}}{21}$
± 2	0	0	$-\frac{\sqrt{4}}{7}$	$+\frac{\sqrt{15}}{21}$
± 1	± 1	$+1$	$+\frac{1}{7}$	$-\frac{\sqrt{16}}{21}$
± 1	0	0	$+\frac{1}{7}$	$+\frac{\sqrt{30}}{21}$
0	0	$+1$	$+\frac{\sqrt{4}}{7}$	$+\frac{\sqrt{36}}{21}$
± 2	∓ 2	0	0	$+\frac{\sqrt{70}}{21}$
± 2	∓ 1	0	0	$-\frac{\sqrt{35}}{21}$
± 1	∓ 1	0	$-\frac{\sqrt{6}}{7}$	$-\frac{\sqrt{40}}{21}$

where the J integral is called the Coulomb integral and the K integral is called the exchange integral. Further definitions include

$$a^k(l^a m_l^a, l^b m_l^b) = c^k(l^a m_l^a, l^a m_l^a) \cdot c^k(l^b m_l^b, l^b m_l^b) \tag{2-51}$$

$$b^k(l^a m_l^a, l^b m_l^b) = [c^k(l^a m_l^a, l^b m_l^b)]^2 \tag{2-52}$$

and for equivalent electrons

$$F^k = R^k(n^a l^a n^b l^b, n^a l^a n^b l^b) \tag{2-53}$$

There now remains only the evaluation of the c^k coefficients. These integrals of three Legendre functions have been calculated and are given in Condon and Shortley.[1] Since we are mostly interested in d electrons, we give below tables for the a^k, b^k, and c^k coefficients for these electrons. Following Condon and Shortley,[1] we shall in the text use $F_k = F^k/D_k$, where D_k is the denominator of the corresponding a's and b's. Thus $F_2 = F^2/49$ and $F_4 = F^4/441$.

TABLE 2-2

$a^k(lm_l, l'm_l') = a^k(l'm_l', lm_l)$

$\lvert m_l \rvert$	$\lvert m_l' \rvert$	$k = 2$	$k = 4$
2	2	$4/49$	$1/441$
2	1	$-2/49$	$-4/441$
2	0	$-4/49$	$6/441$
1	1	$1/49$	$16/441$
1	0	$2/49$	$-24/441$
0	0	$4/49$	$36/441$

Because of the phase choice, $c^k(l'm_l', lm_l) = (-1)^{m_l - m_{l'}} c^k(lm_l, l'm_l')$. Since $b^k = [c^k]^2$, we get $b^k(lm_l, l'm_l') = b^k(l'm_l', lm_l)$. Further, $F_k = F^k/D_k$, D_k being the denominator given in Table 2-2.

2-g. Term Energies

We can now calculate the first-order perturbation energy for the various terms in a $(d)^n$ configuration. To do so, we can either utilize wave functions constructed in the manner prescribed in Sec. 2-c or we can make use of a method devised by Slater. This latter method utilizes the fact that the sum of the roots in a secular equation is equal to the sum of the diagonal elements occurring in the determinant.[†] Since there are no matrix elements

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[†]

$$\begin{vmatrix} H_{11} - E & H_{12} & \cdots & H_{1n} \\ H_{21} & H_{22} - E & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ H_{n1} & \cdots & \cdots & H_{nn} - E \end{vmatrix} = 0$$

gives by expanding

$$E^n - E^{n-1}(H_{11} + H_{22} + \cdots + H_{nn}) + E^{n-2}(\cdots) = 0$$

with

$$E_1 + E_2 + \cdots + E_n = H_{11} + H_{22} + \cdots + H_{nn}$$

connecting states of different M_L and M_S, and since the energies of the terms are independent of M_L and M_S in an LS coupling scheme, this rule allows us to set up a set of linear equations for each box in a set as given in Sec. 2-*a*, and to solve for the energies. The method is best illustrated by an example. We shall take the example of d^2 given in Sec. 2-*a*. Then we have for the energies of the states

$$\begin{aligned}
E(^1G) &= E(2^+,2^-) \\
E(^3F) &= E(2^+,1^+) \\
E(^3F) + E(^1G) &= E(2^+,1^-) + E(2^-,1^+) \\
E(^3F) + E(^1G) + E(^1D) &= E(2^+,0^-) + E(2^-,0^+) \\
&\quad + E(1^+,1^-) \\
E(^3F) + E(^3P) &= E(2^+,-1^+) \\
&\quad + E(1^+,0^+) \\
E(^1S) + E(^3P) + E(^1D) + E(^3F) + E(^1G) &= E(2^+,-2^-) \\
&\quad + E(2^-,-2^+) + E(1^+,-1^-) + E(1^-,-1^+) + E(0^+,0^-)
\end{aligned} \tag{2-54}$$

and so forth. Equations of this type can be readily solved for the term energies, viz.:

$$\begin{aligned}
E(^1G) &= E(2^+,2^-) \\
E(^3F) &= E(2^+,1^+) \\
E(^1D) &= E(2^+,0^-) + E(2^-,0^+) + E(1^+,1^-) - E(2^+,2^-) - E(2^+,1^+) \\
E(^3P) &= E(2^+,-1^+) + E(1^+,0^+) - E(2^+,1^+) \\
E(^1S) &= E(2^+,-2^-) + E(2^-,-2^+) + E(1^+,-1^-) + E(1^-,-1^+) \\
&\quad + E(0^+,0^-) - E(2^+,1^-) - E(2^-,1^+) - E(1^+,0^-) - E(1^-,0^+)
\end{aligned} \tag{2-55}$$

and in these equations the term energies are given as the sum of the various single diagonal elements.

For the diagonal elements we have from Sec. 2-*f*:

$$(A|1/r_{12}|A) = \sum_{a>b=1}^{n} [J(ab) - K(ab)]$$

with the summation extending over all pairs of individual sets. One disregards the closed shells which only give a common additive factor. Then

$$\begin{aligned}
E(^1G) &= J(2,2) = F_0 + 4F_2 + F_4 \\
E(^3F) &= J(2,1) - K(2,1) = F_0 - 8F_2 - 9F_4 \\
E(^1D) &= J(2,0) + J(2,0) + J(1,1) - J(2,2) - J(2,1) + K(2,1) \\
&= F_0 - 3F_2 + 36F_4 \\
E(^3P) &= J(2,-1) - K(2,-1) + J(1,0) - K(1,0) - J(2,1) + K(2,1) \\
&= F_0 + 7F_2 - 84F_4 \\
E(^1S) &= J(2,-2) + J(2,-2) + J(1,-1) + J(1,-1) + J(0,0) - J(2,1) \\
&\quad - J(2,1) - J(1,0) - J(1,0) \\
&= F_0 + 14F_2 + 126F_4
\end{aligned}$$

Only if there is more than one of a certain term type do we need to solve a secular equation in order to find the energy of the levels, because the method then will only give the *sum* of the energies of the like terms. It is here necessary to go back to the wave functions constructed to be eigenstates of LS and to set up the secular equation.

It is, of course, always possible to get the energies of the terms in this way, but usually this involves more labor, even if no secular equation needs to be solved. As an example, we shall take d^2, ^3P, the wave function of which we have found in Sec. 2-*c*.

$$^3P(1,1,1,1) = \sqrt{2/5}\,(2^+,-1^+) - \sqrt{3/5}\,(1^+,0^+)$$

$$\begin{aligned}
E(^3P) &= \frac{2}{5}J(2,-1) - \frac{2}{5}K(2,-1) + \frac{3}{5}J(1,0) - \frac{3}{5}K(1,0) \\
&\quad - \frac{2\sqrt{6}}{5}\left((2^+,-1^+)\left|\frac{1}{r_{12}}\right|(1^+,0^+)\right) + \frac{2\sqrt{6}}{5}\left((2^+,-1^+)\left|\frac{1}{r_{12}}\right|(0^+,1^+)\right) \\
&= \frac{2}{5}(F_0 - 2F_2 - 4F_4) - \frac{2}{5}(35F_4) + \frac{3}{5}(F_0 + 2F_2 - 24F_4) \\
&\quad - \frac{3}{5}(F_2 + 30F_4) - \frac{2\sqrt{6}}{5}(-\sqrt{6}\,F_2 + 5\sqrt{6}\,F_4) \\
&\qquad + \frac{2\sqrt{6}}{5}(2\sqrt{6}\,F_2 - 10\sqrt{6}\,F_4) = F_0 + 7F_2 - 84F_4 \qquad (2\text{-}56)
\end{aligned}$$

This result is, of course, identical with the one previously found.

Usually F_2 and F_4 are taken as semiempirical parameters; i.e., we do not attempt to calculate them, but instead fit the results with the term values known from experiment. Such term values are collected, for instance, in C. Moore, Ref. 3. In the case of $(3d)^2$ V(III) we find[†] the values tabulated below. Unfortunately, ^1S has still not been found experimentally. Regarding F_2 and F_4 as adjustable parameters and taking the two energy differences $^3P - {}^3F$ and $^1D - {}^3F$ from experiment, we get, as an example,

	J	cm^{-1}		J	cm^{-1}
$E(^3F)$	2	0	$E(^3P)$	0	13,121
	3	318		1	13,238
	4	730		2	13,435
$E(^1D)$	2	10,960	$E(^1G)$	4	18,389

$$\begin{aligned}
E(^3P - {}^3F) &= 15F_2 - 75F_4 = 13{,}000\ \text{cm}^{-1} \\
E(^1D - {}^3F) &= \ \ 5F_2 + 45F_4 = 10{,}600\ \text{cm}^{-1} \qquad (2\text{-}57)
\end{aligned}$$

[†] Note that the metal ion V(III)— that is, the ion in oxidation state 3 in our nomenclature—is designated by V(IV) in Ref. 3 and similar spectroscopic tables. This nomenclature is due to the fact that the nonionized state of an element E is labeled E(I) by the spectroscopists.

Table 2-3

d^2: (Ref. 1)

$$\begin{aligned}
E({}^1S) &= F_0 + 14F_2 + 126F_4\\
E({}^1G) &= F_0 + 4F_2 + F_4\\
E({}^3P) &= F_0 + 7\mathrm{F}_2 - 84F_4\\
E({}^1D) &= F_0 - 3F_2 + 36F_4\\
E({}^3F) &= F_0 - 8F_2 - 9F_3
\end{aligned}$$

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d^3: (Ref. 1)

$$\begin{aligned}
E({}^2P) &= 3F_0 - 6F_2 - 12F_4\\
E({}^2_{\pm}D) &= 3F_0 + 5F_2 + 3F_4 \pm \sqrt{193F_2{}^2 - 1650F_2F_4 + 8325F_4{}^2}\\
E({}^2F) &= 3F_0 + 9F_2 - 87F_4\\
E({}^2G) &= 2F_0 - 11F_2 + 13F_4\\
E({}^2H) &= 3F_0 - 6F_2 - 12F_4\\
E({}^4P) &= 3F_0 - 147F_4\\
E({}^4F) &= 3F_0 - 15F_2 - 72F_4
\end{aligned}$$

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d^4: (Ref. 4)

$$\begin{aligned}
E({}^1_{\pm}S) &= 6F_0 + 10F_2 + 6F_4 \pm \tfrac{1}{2}\sqrt{3088F_2{}^2 - 26{,}400F_2F_4 + 133{,}200F_4{}^2}\\
E({}^1_{\pm}D) &= 6F_0 + 9F_2 - 76.5F_4 \pm \tfrac{1}{2}\sqrt{1296F_2{}^2 - 10{,}440F_2F_4 + 30{,}825F_4{}^2}\\
E({}^1F) &= 6F_0 - 48\ F_4\\
E({}^1_{\pm}G) &= 6F_0 - 5F_2 - 6.5F_4 \pm \tfrac{1}{2}\sqrt{708F_2{}^2 - 7500F_2F_4 + 30{,}825F_4{}^2}\\
E({}^1I) &= 6F_0 - 15F_2 - 9\ F_4\\
E({}^3_{\pm}P) &= 6F_0 - 5F_2 - 76.5F_4 \pm \tfrac{1}{2}\sqrt{912F_2{}^2 - 9960F_2F_4 + 38{,}025F_4{}^2}\\
E({}^3D) &= 6F_0 - 5F_2 - 129\ F_4\\
E({}^3_{\pm}F) &= 6F_0 - 5F_2 - 76.5F_4 \pm \tfrac{1}{2}\sqrt{612F_2{}^2 - 4860F_2F_4 + 20{,}025F_4{}^2}\\
E({}^3G) &= 6F_0 - 12F_2 - 94\ F_4\\
E({}^3H) &= 6F_0 - 17F_2 - 69\ F_4\\
E({}^5D) &= 6F_0 - 21F_2 - 189\ F_4
\end{aligned}$$

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d^5: (Ref. 5)

$$\begin{aligned}
E({}^2S) &= 10F_0 - 3F_2 - 195F_4\\
E({}^2P) &= 10F_0 + 20F_2 - 240F_4\\
E({}^2_{\pm}D) &= 10F_0 - 3F_2 - 90F_4 \pm \sqrt{513F_2{}^2 - 4500F_2F_4 + 20{,}700F_4{}^2}\\
E({}^2D) &= 10F_0 - 4F_2 - 120F_4\\
E({}^2_{\pm}F) &= 10F_0 - 9F_2 - 165F_4\\
E({}^2F) &= 10F_0 - 25F_2 - 15F_4\\
E({}^2_{\pm}G) &= 10F_0 - 3F_2 - 155F_4\\
E({}^2G) &= 10F_0 - 13F_2 - 145F_4\\
E({}^2H) &= 10F_0 - 22F_2 - 30F_4\\
E({}^2I) &= 10F_0 - 24F_2 - 90F_4\\
E({}^4P) &= 10F_0 - 28F_2 - 105F_4\\
E({}^4D) &= 10F_0 - 18F_2 - 225F_4\\
E({}^4F) &= 10F_0 - 13F_2 - 180F_4\\
E({}^4G) &= 10F_0 - 25F_2 - 190F_4\\
E({}^6S) &= 10F_0 - 35F_2 - 315F_4
\end{aligned}$$

From this $F_2 \sim 1900\ \text{cm}^{-1}$, $F_4 \sim 210\ \text{cm}^{-1}$, and $F_2/F_4 = 9.0$.

For the d shell a calculation of F_2 and F_4 assuming hydrogenic wave functions can be performed by evaluating the integrals

$$F_k = \frac{e^2}{D_k} \int_0^\infty \int_0^\infty \frac{r_<{}^k}{r_>{}^{k+1}} [R_1(d)]^2 r_1{}^2\, dr_1{}^2\, [R_2(d)]^2 r_2{}^2\, dr_2 \qquad (2\text{-}58)$$

With

$$R_1 = R_2 = -\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} r^2 e^{-(Z/3a_0)r}$$

the result is

$$F_2 = 203Z \quad \text{cm}^{-1} \qquad \text{and} \qquad F_4 = 14.7Z \quad \text{cm}^{-1} \tag{2-59}$$

with $F_2/F_4 = 13.8$.

Owing to the well-known equivalence of electrons and "holes" the electronic configurations d^n and d^{10-n} will produce identical multiplet terms, and furthermore the energy difference between the various terms is the same for the d^n and d^{10-n} configurations. In Table 2-3 we have collected the values of the term energies for the d^2, d^3, d^4, and d^5 electronic configurations as expressed in the Condon-Shortley-Slater approximation scheme.

2-h. General Remarks on the Method

The definition of the F_k integrals, as well as the actual evaluation, shows clearly that all of these quantities are positive. The actual calculation of the various $(3d)^n$ terms then confirms the validity of Hund's rule, viz., of the terms given by equivalent electrons those with greatest multiplicity lie deepest, and the lowest is that with the greatest L. The theory will usually also predict the ordering and energy of the excited terms with fair accuracy. The reasons for occasional discrepancies are not difficult to find; examples are breakdown of the one-electron description and admixture via the presence of the $1/r_{12}$ term in the Hamiltonian of higher terms such as $(3d)^{n-1}(4s)$ into the configuration. We may, however, have sufficient faith in our approximation scheme as it stands to use it as the starting point in our further considerations with regard to spin-orbit coupling.

Of course, there exist other methods of finding the term energies than the ones just outlined. In particular, the work of Racah[6-8] and Löwdin[9] has shown us both more powerful and more elegant ways of doing so. However, we may remark that, because we are here primarily interested in d electrons as contrasted to f electrons, no real advantage can be obtained by using the methods of Racah. On the other hand, if we were interested in the terms arising from $(4f)^n$ configurations, the method of Condon, Shortley, and Slater would be impossibly cumbersome and Racah's formalism would be the only practical one. It is always wise to remember that simple problems ought to be solved by simple means, and the heavy artillery spared until it is needed. A uniform treatment of angular momentum can be found in Refs. 8 and 10. In the latter reference a bibliography is given.

2-i. Spin-Orbit Coupling in a Hydrogen-like System

The spin of an electron gives rise to a magnetic dipole. On the other hand, a magnetic dipole is also produced by the movement of the electron in its orbit. Thus an interaction between these two magnetic dipoles is possible, and this effect is called the spin-orbit interaction. This feature is closely connected with relativistic effects; considerations of Dirac show that the magnetic perturbation energy of the spin in a central field can be expressed as

$$\mathcal{H}^{(1)} = \xi(r)\mathbf{l}\cdot\mathbf{s} \qquad \text{with } \xi(r) = \frac{\hbar^2}{2m^2c^2}\frac{1}{r}\frac{\partial U(r)}{\partial r} \tag{2-60}$$

where $U(r)$ is the potential in which the electron moves.

In this approximation the Hamiltonian for a hydrogen-like system is

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + \xi(r)\mathbf{l}\cdot\mathbf{s} \tag{2-61}$$

We have in the preceding sections classified the solutions to the Hamiltonian with no inclusion of spin-orbit coupling in an (l,m_l,s,m_s) scheme, and we shall here treat the spin-orbit operator as a perturbation, using these sets as the unperturbed wave functions. Then

$$E^{(1)} = (n,l,m_l,m_s)|\mathcal{H}^{(1)}|(n',l',m_l',m_s') \tag{2-62}$$

Separating the angular part from the radial part of the integral

$$E^{(1)} = (n,l)|\xi(r)|(n',l')\cdot(l,m_l,m_s)|\hat{l}_z\hat{s}_z + \tfrac{1}{2}\hat{l}_+\hat{s}_- + \tfrac{1}{2}\hat{l}_-\hat{s}_+|(l',m',m_s') \tag{2-63}$$

where as usual $\hat{l}_+ = \hat{l}_x + i\hat{l}_y$, etc.

Looking back to the formulas given on page 13 for the matrix elements of $\hat{L}_z$ and $\hat{L}_\pm$, we see that, since both $\hat{l}_z$ and $\hat{l}_x \pm i\hat{l}_y$ are diagonal in l, we must have $l = l'$. But, further, for $\hat{l}_z$ and $\hat{s}_z$

$$m_l = m_l' \qquad \text{and} \qquad m_s = m_s'$$

For $\hat{l}_\pm$ and $\hat{s}_\mp$ $\quad m_l = m_l' \pm 1 \quad$ and $\quad m_s = m_s' \mp 1$

Therefore, $m_l + m_s = m_l' + m_s'$ in order for the matrix element not to vanish. We have then that n,l and $m_j = m_l + m_s$ are good quantum numbers, but that m_l and m_s are not. This suggests that the total angular momentum $\mathbf{j} = \mathbf{l} + \mathbf{s}$ is a good quantum number. Since the Hamiltonian operator commutes with $\hat{l}^2$, $\hat{s}^2$, $\hat{j}^2$, and $\hat{j}_z$, we can choose these quantum numbers to characterize our states here labeled as (n,l,j,m_j).

From the definition of $\mathbf{j}$ we have the identity $\mathbf{j}^2 = (\mathbf{l} + \mathbf{s})^2$

$$\mathbf{j}^2 = \mathbf{l}^2 + \mathbf{s}^2 + 2\mathbf{l}\cdot\mathbf{s} \qquad \text{or} \qquad \hat{l}\cdot\hat{s} = \tfrac{1}{2}(\hat{j}^2 - \hat{l}^2 - \hat{s}^2) \tag{2-64}$$

Knowing that $\hat{j}^2$, $\hat{l}^2$, and $\hat{s}^2$ are diagonal and using the above identity, we get

$$E(n,l,j,m_j) = E(n,l) + \xi_{nl}(n,l,j,m_j)|\hat{l}\cdot\hat{s}|(n,l,j,m_j)$$

$$E(n,l,j,m_j) = E(n,l) + \frac{\xi_{nl}}{2}[j(j+1) - l(l+1) - s(s+1)] \tag{2-65}$$

with

$$\xi_{nl} = \hbar^2\int_0^\infty [R(n,l)]^2\xi(r)r^2\,dr \tag{2-66}$$

For a single electron we have $s = \frac{1}{2}$ with $j = l \pm \frac{1}{2}$. In this case

$$E(n,l,j,m_j) = E(n,l) + \xi_{nl} \begin{Bmatrix} l/2 \\ -(l+1)/2 \end{Bmatrix} \quad \begin{matrix} j = l + \frac{1}{2} \\ j = l - \frac{1}{2} \end{matrix} \tag{2-67}$$

Since ξ_{nl} is positive, the state with the lower j lies lowest. The doublet separation is $(l + \frac{1}{2})\xi_{nl}$. The levels into which each configuration is split by the inclusion of the spin-orbit term are designated according to the l value of the configuration from which they spring. The value of j is added as a subscript, with the spin multiplicity being given in its usual place. In the case just treated the two levels would then be designated ${}^2l_{l+\frac{1}{2}}$ and ${}^2l_{l-\frac{1}{2}}$. The same nomenclature is, of course, used with capital letters for many-electron systems.

Assuming a Coulomb potential $U(r) = -Ze^2/r$, and by use of a hydrogenic radial wave function, we can calculate

$$\xi_{nl} = \frac{e^2\hbar^2}{2m^2c^2a_0^3} \frac{Z^4}{n^3l(l+\frac{1}{2})(l+1)} \tag{2-68}$$

with Z "the effective charge" in the wave function and a_0 the Bohr radius. For $3d$ electrons

$$\xi_{3d} = 1.44 \times 10^{-2}\, Z^4 \qquad \text{cm}^{-1} \tag{2-69}$$

2-j. Spin-Orbit Coupling in a Many-electron Case

If more than one electron is present, we get

$$\mathcal{H}^{(1)} = \sum_i \xi(r_i)\mathbf{l}_i \cdot \mathbf{s}_i \tag{2-70}$$

thus neglecting the interaction of the spins with other orbits than their own. This is a valid approximation so long as the central field is stronger than the interelectronic interactions. Using our (L,M_L,S,M_S) scheme, we get for a term diagonal in L and S treating $\mathcal{H}^{(1)}$ as a perturbation:

$$E^{(1)} = (L,M_L,S,M_S)|\mathcal{H}^{(1)}|(L,M'_L,S,M'_S) \tag{2-71}$$

The calculation of this matrix element is complicated by the fact that $\mathcal{H}^{(1)}$ is expressed as a sum of single-electron vector operators, whereas the (L,S) scheme is characterized by the total value of L and S. However, it can be proved,[1] and is indeed intuitively clear, that we must have

$$E^{(1)} = \lambda(L,M_L,S,M_S)|\mathbf{L} \cdot \mathbf{S}|(L,M'_L,S,M'_S) \tag{2-72}$$

where the constant λ is a radial integral depending only upon L and S.

We see that *within* a given LS term the matrix elements of

$$\mathcal{H}^{(1)} = \sum_i \xi(r_i)\mathbf{l}_i \cdot \mathbf{s}_i$$

are proportional to the matrix elements of $\mathbf{L} \cdot \mathbf{S}$. In the same way as before we find that the matrix elements of $\hat{L} \cdot \hat{S}$

$$(L,M_L,S,M_S)|\hat{L} \cdot \hat{S}|(L,M'_L,S,M'_S) \tag{2-73}$$

are different from zero only if

$$M_L + M_S = M'_L + M'_S = M_J \tag{2-74}$$

This is, of course, true for the term diagonal in M_L and M_S, but we notice that $\mathbf{L} \cdot \mathbf{S}$ is able to couple terms together, provided they have the same value of J. Thus the spin-orbit coupling can, for example, mix together states which differ in their S values by $\Delta S = 1$. A word of caution is, however, not out of place here as regards the value of the proportionality factor λ, and for elements off diagonal in L and S it is recommended to go back and use the single orbital operator $\sum_i \xi(r_i)\mathbf{l}_i \cdot \mathbf{s}_i$. Usually, however, we ignore the admixtures of other L and S terms by the spin-orbit coupling and consider only the diagonal term.

Just as for the one-electron case we have

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$
$$\mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L} \cdot \mathbf{S} \quad \text{or} \quad \mathbf{L} \cdot \mathbf{S} = \tfrac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) \tag{2-75}$$

and with the above approximation of neglecting off-diagonal terms the energy of a state (L,S,J,M) is given by

$$E = E(L,S) + \lambda\tfrac{1}{2}[J(J + 1) - L(L + 1) - S(S + 1)] \tag{2-76}$$

Then the energy difference between the level J and $J - 1$ is

$$\Delta E = E(L,S,J,M) - E(L, S, J - 1, M) = \lambda J$$

This is the Landé interval rule.

As an example we shall in Table 2-4 take the ^3F state for V(III)d^2. It is seen that the theory holds rather well, the numbers in the last column of the table being nearly equal.

TABLE 2-4. ^3F STATE IN V(III)d^2

Level	Energy, cm^{-1}	Interval ΔE	$\lambda = \Delta E/J$
$^3F_2$	0		
$^3F_3$	318	318	106
$^3F_4$	730	412	103

Values are taken from the compilation of C. Moore.[3]

We have for the total width $\Delta E(\lambda)$ of a given multiplet:

$$\Delta E(\lambda) = \lambda \sum_{L-S+1}^{L+S} x = \lambda \sum_{0}^{L+S} x - \lambda \sum_{0}^{L-S} x \tag{2-77}$$

Since
$$\sum_{0}^{n} x = \tfrac{1}{2}n(n+1) \tag{2-78}$$
we get
$$\Delta E(\lambda) = \lambda \cdot S \cdot (2L+1) \tag{2-79}$$

2-k. Absolute Term Intervals

In this section we shall investigate the connection between λ, the splitting factor for a many-electron system, and ξ_{nl}, the one-electron parameter. We have for the *diagonal* element:

$$(L,M_L,S,M_S)|\sum_i \xi(r_i)\mathbf{l}_i \cdot \mathbf{s}_i|(L,M_L,S,M_S) = \lambda M_L \cdot M_S \tag{2-80}$$

On the other hand, since the state (L,M_L,S,M_S) is a determinantal wave function built up of single orbitals, we get

$$(L,M_L,S,M_S)|\sum_i \xi(r_i)\mathbf{l}_i \cdot \mathbf{s}_i|(L,M_L,S,M_S) = \sum_i \xi_{nl} m_l^i m_s^i \tag{2-81}$$

By equating these two expressions, we have

$$\lambda = \frac{1}{M_L M_S} \sum_i \xi_{nl} m_l^i m_s^i \tag{2-82}$$

If there is more than one determinantal wave function with a certain M_L and M_S, we use the same method of the invariance of the diagonal sum that we used in evaluating term energies to get

$$M_L M_S \sum_{\text{Terms}} \lambda(L,S) = \sum_{\substack{\text{Determi-}\\\text{nants}}} \sum_i \xi_{nl} m_l^i m_s^i \tag{2-83}$$

In this way we can evaluate $\lambda(L,S)$ in a stepwise fashion with the same limitation as previously: that if more than one term with a given (L,S) is present, we can only get the sum of the λ's.

Going back to the d^2 case, we thus have as an example

$$\begin{aligned} {}^3F\ (M_L = 3) &= (2^+,1^+) \\ \lambda({}^3F) &= \frac{1}{3\cdot 1}(\xi_{3d}\cdot 2\cdot \tfrac{1}{2} + \xi_{3d}\cdot 1 \cdot \tfrac{1}{2}) \\ \lambda({}^3\mathrm{F}) &= \tfrac{1}{2}\xi_{3d} \end{aligned} \tag{2-84}$$

and for ${}^3P$ we get as

$$\begin{aligned} {}^3F\ (M_L = 1) + {}^3P\ (M_L = 1) &= (2^+,-1^+) + (1^+,0^+) \\ \lambda({}^3F) + \lambda({}^3P) &= \xi_{3d}(2\cdot\tfrac{1}{2} - 1\cdot\tfrac{1}{2} \\ &\qquad + 1\cdot\tfrac{1}{2} + 0\cdot\tfrac{1}{2}) \\ \lambda({}^3P) &= \tfrac{1}{2}\xi_{3d} \end{aligned} \tag{2-85}$$

The ratio of the total widths of ${}^3F$ and ${}^3P$ is therefore

$$\frac{\tfrac{1}{2}\xi_{3d}\cdot 1\cdot 7}{\tfrac{1}{2}\xi_{3d}\cdot 1 \cdot 3} = \frac{7}{3} = 2.33\cdots$$

Experiments yield 2.2.

For the *ground state* only we have, according to Hund's rule for a shell less than half full, $\Sigma m_l = M_L = L$ and $\Sigma m_s = M_S = S$. Then

$$L \cdot S \cdot \lambda = \xi_{nl} \cdot \tfrac{1}{2}\Sigma m_l = \xi_{nl} \cdot \tfrac{1}{2} \cdot L$$

$$\lambda = \frac{\xi_{nl}}{2S} \tag{2-86}$$

and for a shell more than half full

$$L \cdot S \cdot \lambda = \xi_{nl}\left[\tfrac{1}{2}\sum_{-l}^{l} m_l - \tfrac{1}{2}\sum m_l\right] = -\xi_{nl} \cdot \tfrac{1}{2}L$$

$$\lambda = \frac{-\xi_{nl}}{2S} \tag{2-87}$$

We notice that the sign of λ changes as we go to a more than half-filled shell. This means again that for shells that are more than half-filled, the state with the highest value of J has the lowest energy in contrast to the case for a less than half-filled shell.

So far we have completely neglected spin-spin interactions. Usually they will not be important and may be neglected. However, in special cases they may have an appreciable effect on the multiplet intervals. See Ref. 11 for a treatment of this effect.

2-1. Zeeman Splitting

Since the energy in the spin-orbit approximation does not depend upon M_J (or simply written M), we have still a $2J + 1$ degeneracy to reckon with. However, the presence of a magnetic field completely removes this last degeneracy. Since the experimental identification of a level means a determination of J, we see that by simply counting the sublevels into which a given level splits upon inclusion of a magnetic field, we get the J value for the level in question.

The energy operator associated with the Zeeman effect is

$$\mathcal{H}^{(2)} = \mu_B(\hat{L} + 2\hat{S})\mathbf{H} \tag{2-88}$$

where L and S are measured in units of $\hbar$. Here μ_B is the Bohr magneton $\mu_B = e\hbar/2mc$, **H** is the magnetic field present, and the factor 2 before $\hat{S}$ is due to the magnetic anomaly of the spin. We shall treat only the case where $\mathcal{H}^{(2)}$ is small compared to the spin-orbit perturbation $\mathcal{H}^{(1)}$. This allows us to start with the sets (L,S,J,M) as our unperturbed wave functions.

Since all directions are equivalent, we take the z-axis as the direction of **H** and get for the perturbation

$$\mathcal{H}^{(2)} = \mu_B H_Z(\hat{L}_Z + 2\hat{S}_Z) \tag{2-89}$$

Now $$J_Z = L_Z + S_Z$$

so $$\mathcal{H}^{(2)} = \mu_B H_Z(\hat{J}_Z + \hat{S}_Z) \tag{2-90}$$

Taking a diagonal element, we get

$$E^{(2)} = (L,S,J,M)\,|\mu_B H_Z(\hat{J}_Z + \hat{S}_Z)|\,(L,S,J,M) = \mu_B H_Z M g$$

with
$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \tag{2-91}$$

the Landé factor. This follows from the fact that

$$(L,S,J,M)|J_Z|(L,S,J,M) = M$$

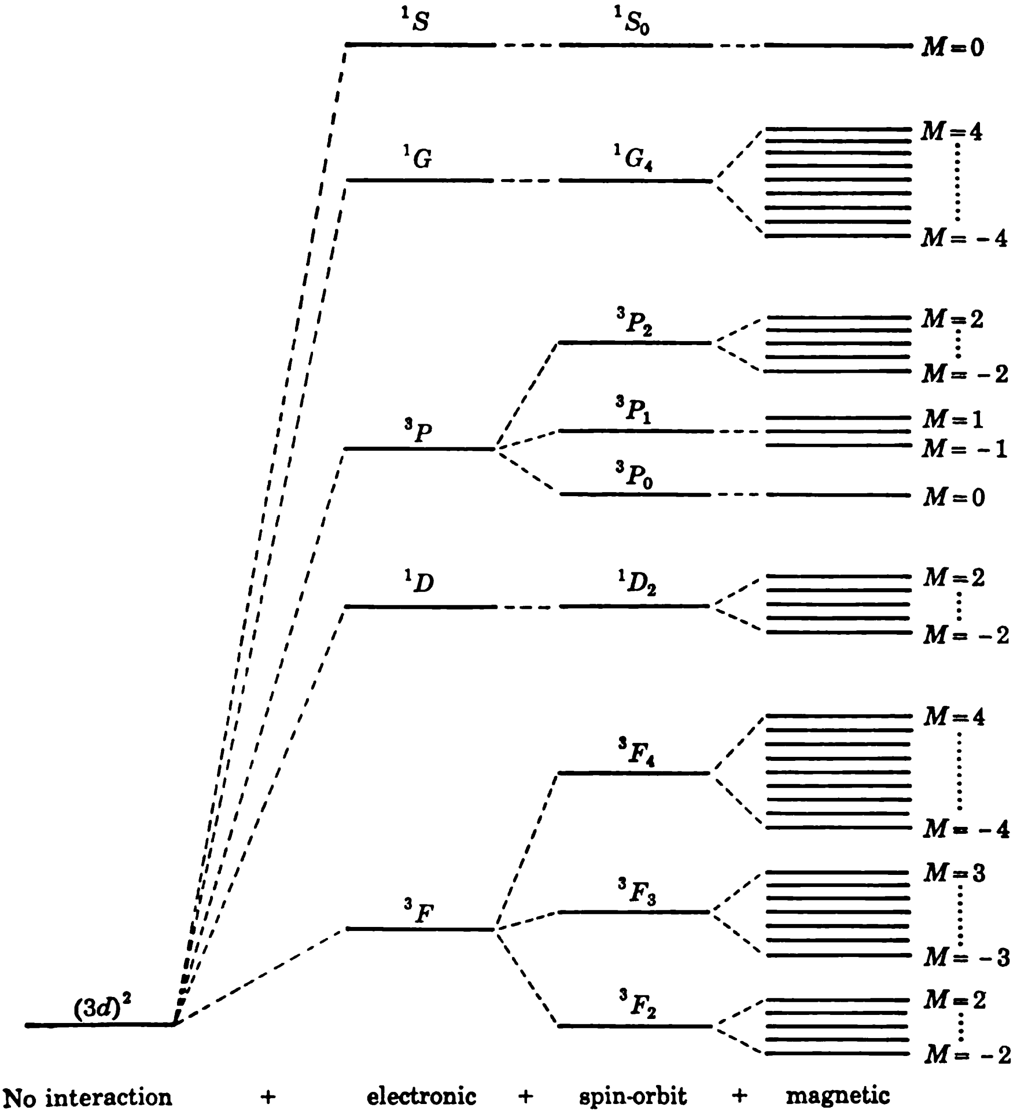

FIG. 2-1. Energy-level diagram for $(3d)^2$, not drawn to scale. Altogether there are $10 \cdot 9/1 \cdot 2 = 45$ various levels.

and (see Condon and Shortley, Ref. 1)

$$(L,S,J,M)|S_Z|(L,S,J,M) = \frac{M}{J(J+1)}(L,S,J,M)|\hat{S}\cdot\hat{J}|(L,S,J,M)$$
$$= \frac{M}{J(J+1)}\cdot\frac{1}{2}[J(J+1) - L(L+1) + S(S+1)] \quad (2\text{-}92)$$

We notice that a level with a certain quantum number J is split up into $2J + 1$ sublevels upon the application of a magnetic field. The spacing between these sublevels is constant and equals $g\mu_B H$, and, further the lowest sublevel is seen to be the one with $M = -J$.

Figure 2-1 illustrates the various degrees of approximations for our $(3d)^2$ example.

2-m. Selection Rules

A transition between two states a and b can occur as an electric dipole radiation only if the integral $\int\psi_a\mathbf{r}\psi_b\,d\tau$ is different from zero. We are here especially interested in the states coming from d^n configurations, and it follows immediately that transitions between the various d^n levels are forbidden as electric dipole transitions. This is due to the fact that a d orbital is an "even" function, i.e., it does not change sign upon inversion in its center whereas $\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$ does change sign upon an inversion. The whole integral therefore changes its sign upon reflection in the nucleus, but since the value of the integral must be independent of the choice of the coordinate system, it follows that it must vanish. These remarks prove a special case of Laporte's rule: Only transitions between an even state and an odd state are allowed as electric dipole transitions. Since this rule depends solely upon the *symmetry properties* of the wavefunctions, and does not depend upon the actual analytical form of the wave functions, it is of a very general nature. A closer analysis of this and related features is given in the next chapter.

From what has been said previously, it follows further that, as long as we take our wave functions to be one-electron determinantal wave functions, the matrix element $(\Psi_A|\mathbf{r}|\Psi_B)$ will differ from zero only if (1) Ψ_A and Ψ_B differ at most in *one* of the orbitals and if (2) the spin quantum numbers S and M_S are the same for Ψ_A and Ψ_B.

Another kind of transition, namely, the so-called magnetic dipole transitions, are of importance in the case of the Zeeman splittings. The transition probabilities between levels characterized by the quantum number M_J depend upon the existence of nonvanishing matrix elements of the form

$$(\Psi_A|\mathbf{r}\times\mathbf{p}|\Psi_B) = (\Psi_A|\mathbf{l}|\Psi_B) \quad (2\text{-}93)$$

Since $\mathbf{r}\times\mathbf{p}$ is an even operator, we notice that magnetic dipole transitions can take place within a given d^n configuration, and inspection of the matrix elements immediately gives the selection rule $\Delta M_J = 0$ or ± 1. However, in general the probability of a magnetic dipole transition is much less than the probability of an electric dipole transition.[1,2]

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CHAPTER 3

Symmetry

3-a. Concept of Symmetry Operators

The aim of this chapter is to outline a very powerful method for selecting wave functions suitable for the elucidation of the electronic properties of molecules. The importance of the method is due to the fact that the application of it is based solely upon the knowledge of the geometry of the investigated molecule. The subject is usually approached through the formal theory of groups, but we shall at least partly try to treat the problem by the more intuitive approach of symmetry operators. Our treatment of the subject will be by no means exhaustive; indeed we shall mostly proceed by using simple examples to illustrate the strength of the method, with the appropriate generalizations being indicated. More rigorous treatments of the problem can be found in Refs. 1 to 7 and 13.

Let us take a molecule possessing a certain geometrical shape. In order to describe this molecule, a coordinate system is needed; it is, of course, obvious that such a coordinate system can be chosen in a great many ways. Thus while the *description* of the molecule must depend upon the chosen coordinate system, it must follow that no *physical importance* can be attached to any particular coordinate system. In other words, when calculating observable quantities of a molecule, it must turn out to be immaterial how the original coordinate system was chosen.

Consider benzene as an example. In order to describe the molecule, we place a coordinate system with the z axis perpendicular to the plane of the molecule and number the carbon atoms from one to six. Into this molecular skeleton an electron is dropped. The Hamiltonian $\mathcal{H}$ for the system, assuming a positive charge Ze on each carbon atom, is

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 - Ze^2\left(\frac{1}{r_1} + \frac{1}{r_2} + \cdots + \frac{1}{r_6}\right) \tag{3-1}$$

r_1 to r_6 being the distances from the appropriate carbon atoms to the electron.

We define a symmetry operator as any coordinate transformation which leaves the Hamiltonian invariant. Such a coordinate transformation is equivalent to a symmetry operation which brings the molecule back "into itself." In the case of the benzene molecule one symmetry operation would be, for instance, to rotate the molecule 60° around the z axis. This operation would only change the numbering of the carbon atoms, and since the energy of the system surely cannot depend upon a purely artificial numbering, it must remain invariant upon this operation. Inspection of the Hamiltonian (3-1) shows that this is indeed the case.

Now suppose that we have solved the Schrödinger equation for a given molecule and obtained a set of corresponding eigenvalues E_n and eigenfunctions ψ_n, where

$$E_n = \int \psi_n^* \mathcal{H} \psi_n \, d\tau \tag{3-2}$$

Let us apply a symmetry operation upon the molecule. Since by definition such an operation will leave $\mathcal{H}$ invariant, the transformed eigenfunctions belonging to an original eigenvalue E_n must still correspond to the same E_n. Denoting a symmetry operation by $\hat{S}$ and calling $\hat{S}\psi_n = \varphi_n$,

$$\hat{S}\int \psi_n^* \mathcal{H} \psi_n \, d\tau = \int \varphi_n^* \mathcal{H} \varphi_n \, d\tau = E_n$$

If we now first look upon a nondegenerate eigenfunction ψ, it follows immediately that $\hat{S}\psi$ can at most differ from ψ by a phase factor. When the corresponding eigenvalue is evaluated, this phase factor cancels out, since $\hat{S}\psi_n^*\psi_n = \psi_n^*\psi_n$.

More interesting is the case of a truly degenerate set of orthonormal eigenfunctions $\psi_1 \cdots \psi_n$ all corresponding to an eigenvalue E_n. In this case any normalized linear combination of $\psi_1 \cdots \psi_n$ will also have the eigenvalue of E_n:

$$E_n = \int \Psi_{\mathrm{I}}^* \mathcal{H} \Psi_{\mathrm{I}} \, d\tau \tag{3-3}$$

with

$$\Psi_{\mathrm{I}} = a_1\psi_1 + a_2\psi_2 + \cdots + a_n\psi_n$$

and

$$a_1^2 + a_2^2 + \cdots + a_n^2 = 1$$

There are, of course, n possible linear orthogonal combinations. By applying a symmetry operation to one of the wave functions, it is again possible that it will go into itself with or without a shift of phase, but it is more likely that it will go into a linear combination of the ψ_n's. In general, with a given *complete* set of degenerate wavefunctions $\psi_1 \cdots \psi_n$, performing a symmetry operation on the molecule will yield

$$\hat{S}\begin{pmatrix} \psi_1 \\ \psi_2 \\ \cdots \\ \psi_n \end{pmatrix} = \begin{pmatrix} a_{11}\psi_1 + a_{12}\psi_2 + \cdots + a_{1n}\psi_n \\ a_{21}\psi_1 + a_{22}\psi_2 + \cdots + a_{2n}\psi_n \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ a_{n1}\psi_1 + a_{n2}\psi_2 + \cdots + a_{nn}\psi_n \end{pmatrix} \tag{3-4}$$

Since the sets $\psi_1 \cdots \psi_n$ are orthogonal to each other, the transformed sets are orthogonal to each other too. This follows from the fact that all we have done is to rotate the coordinate system and express the rotated functions in terms of the old functions. New ψ's cannot get into the linear combinations in (3-4), because the set $\psi_1 \cdots \psi_n$ was a complete set of degenerate functions. The above statement is of course only a clarification of what is meant by the concept "truly degenerate."

Consequently, if for a given molecule all possible symmetry operations leave an initial starting function unaltered, except for immaterial phase changes, we have found a function transforming like a nondegenerate solution to the Schrödinger equation. If on the other hand, new linearly independent functions are created by the application of the symmetry operators, the initial function transforms like a member of a degenerate set of solutions to the Schrödinger equation. By further operating upon the newly created functions with the symmetry operators, we can obtain a complete set of functions transforming like the degenerate wavefunctions. The completeness will manifest itself in that no possible symmetry operation will create additional linearly independent functions.

3-b. Nomenclature of Symmetry Operators

The symmetry of a certain molecule can be expressed by collecting all the various symmetry operations which leave the molecule unaltered. For a single molecule these operations are of two kinds: rotations and reflections.

If a molecule is left unaltered by the rotation around an axis through an angle $2\pi/n$, such an axis is called a C_n symmetry axis. A fourfold axis is denoted C_4, a twofold axis C_2, etc. In general, a symmetry operator $\hat{C}_n$ is defined as the operator which rotates the molecule an angle $2\pi/n$ around a given axis. It is therefore immediately obvious that, for example, two successive operations by $\hat{C}_4$ written $\hat{C}_4 \cdot \hat{C}_4 = \hat{C}_4^2$ are equal to $\hat{C}_2$. Furthermore, if the molecule is rotated n times around a C_n symmetry axis, it returns to the starting position. The complete set of operations is then equal to the identity operation E. Thus

$$\hat{C}_n^n = \hat{E} \tag{3-5}$$

A molecule may be left unaltered by reflection in a plane of symmetry. If this plane is *perpendicular* to the main symmetry axis, i.e., the axis with the highest index, such a symmetry operation is denoted σ_h. If the plane contains the symmetry axis, the symmetry operation is called σ_d or σ_v. Some molecules may have a center of symmetry. A reflection in such a center is denoted i. Here $\hat{\imath}$ is called the inversion operator with $\hat{\imath}^2 = \hat{E}$.

A performance first of a given rotation C_n followed by σ_h is called improper rotation and is denoted by the symbol S_n. Obviously,

$$\hat{S}_n = \hat{\sigma}_h\hat{C}_n \tag{3-6}$$

Further,

$$\hat{C}_2\hat{\sigma}_h = \hat{\imath} \tag{3-7}$$

Usually, the result of the performance of two successive symmetry operations is not independent of the order in which they are applied. In some cases, however, the order is immaterial and we say that the symmetry operators commute. It is immediately obvious, for example, that two rotations about the same axis commute, but that two rotations about different axis need not commute.

3-c. Representations

For a given molecule the complete set of h symmetry operators comprise the point group for the molecule, where h is the order of the group. Since the wave functions for the molecule must be of such a nature as to leave the energy of the system unaltered during the symmetry operations, we can see that in some loose way the wave functions must conform to the point group in question.

Our problem is just how to utilize the known symmetry properties of the molecule in order to build these "boundary conditions" into the wave functions of the molecule. This is important because of the fact that usually we cannot solve the Schrödinger equation for the complicated molecules in question. We can, however, guess at the wave functions and at least make the wave functions behave according to the given molecular geometry.

The concept and treatment of symmetry is so very important for the illustration of the molecular wave functions because a wave function behaving according to the symmetry properties of the molecule in many ways is a "better" and more convenient wave function than one which does not have these features built in.

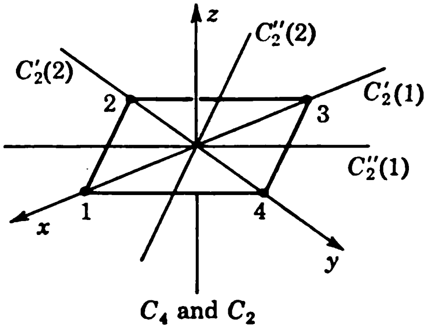

Fig. 3-1. Symmetry axes for a molecule belonging to the group D_4.

As an example let us take the point group D_4. A molecule belonging to this symmetry group is shown in Fig. 3-1. Considering the various different symmetry operations which make the molecule go into itself, we notice that the z axis contains a twofold axis and a fourfold axis. The z axis contains in reality *two* fourfold axes, since we can turn the molecule both clockwise and counterclockwise by an angle of 90° and get different configurations. The first symmetry operation is called $C_4(1)$, and the second $C_4(2)$. It is further seen from the figure that there are four other twofold axes. The corresponding symmetry operators are called respectively $\hat{C}'_2(1)$, $\hat{C}'_2(2)$, $\hat{C}''_2(1)$, and $\hat{C}''_2(2)$. Furthermore, we have as always the identity operator $\hat{E}$. In this case the order of the group h consequently equals eight. All of these eight symmetry operations alter the numbering of the four corners of the square in Fig. 3-1 in a unique way. However, applying two of them in succession is always equivalent to the use of a single symmetry operator. This feature is due to the general property of groups that the product of two elements is contained in the group.

By applying the various symmetry operators of the point group, we see, for example, that

$$\hat{C}'_2(1) \cdot \hat{C}''_2(2) = \hat{C}_4(1) \tag{3-8}$$

As before, such equations should be understood in the following sense: first apply $\hat{C}''_2(2)$ to the molecule and then $\hat{C}'_2(1)$. The result is equivalent to the application of $\hat{C}_4(1)$ to the molecule, Fig. 3-2.

The concept of a *class* is now introduced in the following way. A symmetry operator $\hat{S}'$ is said to belong to the same class as another symmetry operator $\hat{S}''$ if the relation $\hat{T}^{-1}\hat{S}'\hat{T} = \hat{S}''$ is satisfied. Here $\hat{T}$ is a symmetry operator of the group and $\hat{T}^{-1}$ is the inverse symmetry operator defined by $\hat{T} \cdot \hat{T}^{-1} = \hat{E}$.

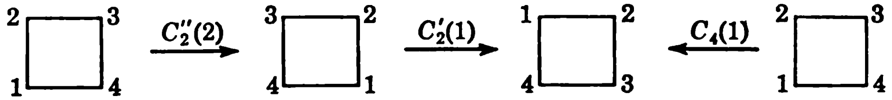

FIG. 3-2. Application of symmetry operators to a D_4 point group molecule.

Let us take an example using the point group D_4. As $\hat{T}$ we take the rotation around the fourfold axis $\hat{C}_4(1)$, as $\hat{S}'$ we take $\hat{C}'_2(1)$, and as $\hat{S}''$ we take $\hat{C}'_2(2)$. Then

$$\hat{T}^{-1}\hat{S}'\hat{T}\,{}^2_1\square^3_4 = \hat{T}^{-1}\hat{S}'\,{}^1_4\square^2_3 = \hat{T}^{-1}\,{}^3_4\square^2_1 = {}^2_3\square^1_4$$

$$\hat{S}''\,{}^2_1\square^3_4 = {}^2_3\square^1_4$$

In other words, $\hat{C}'_2(1)$ and $\hat{C}'_2(2)$ belong to the same class. In the above example we find the five classes $[E]$, $[C_4(1), C_4(2)]$, $[C_2]$, $[C'_2(1), C'_2(2)]$, and $[C''_2(1), C''_2(2)]$. It is seen that a class is indeed only a set of operators which are of the same physical kind.

Our aim is now to construct a set of "numbers" in such a way that they reflect the symmetry properties of the molecule. In order to do so, we write down the complete multiplication table for the group elements as, for example, $\hat{C}'_2(1)\hat{C}''_2(2) = \hat{C}_4(1)$. Each symmetry element is then identified with a certain matrix, and the complete set of matrices, using matrix multiplication, must be chosen in such a way that they multiply according to the multiplication table of the group. Such a set of matrices is called a *representation of the group;* it can always be chosen in a great many ways. In the above example we see that by representing $\hat{C}_4(1)$ by $\{1\}$, $\hat{C}'_2(1)$ by $\{1\}$, and $\hat{C}''_2(2)$ by $\{1\}$, we get $\{1\} \cdot \{1\} = \{1\}$.

One way of representing all symmetry operations would clearly be to put all of the matrices equal to 1. This representation of the group is called Γ_1. But there exist other sets of matrices chosen in such a way that the group multiplication table is fulfilled. Some representations for D_4 can be seen in Table 3-1. The representation Γ_5 is an example of a two-dimensional representation.

Notice that the representations are orthogonal to each other, for example,

TABLE 3-1. REPRESENTATIONS FOR THE POINT GROUP D_4

	E	$C_4(1)$	$C_4(2)$	C_2	$C_2'(1)$	$C_2'(2)$	$C_2''(1)$	$C_2''(2)$
Γ_1	$\{1\}$	$\{1\}$	$\{1\}$	$\{1\}$	$\{1\}$	$\{1\}$	$\{1\}$	$\{1\}$
Γ_2	$\{1\}$	$\{1\}$	$\{1\}$	$\{1\}$	$\{-1\}$	$\{-1\}$	$\{-1\}$	$\{-1\}$
Γ_3	$\{1\}$	$\{-1\}$	$\{-1\}$	$\{1\}$	$\{1\}$	$\{1\}$	$\{-1\}$	$\{-1\}$
Γ_4	$\{1\}$	$\{-1\}$	$\{-1\}$	$\{1\}$	$\{-1\}$	$\{-1\}$	$\{1\}$	$\{1\}$
Γ_5	$\begin{Bmatrix}1 & 0\\ 0 & 1\end{Bmatrix}$	$\begin{Bmatrix}0 & 1\\ -1 & 0\end{Bmatrix}$	$\begin{Bmatrix}0 & -1\\ 1 & 0\end{Bmatrix}$	$\begin{Bmatrix}-1 & 0\\ 0 & -1\end{Bmatrix}$	$\begin{Bmatrix}0 & 1\\ 1 & 0\end{Bmatrix}$	$\begin{Bmatrix}0 & -1\\ -1 & 0\end{Bmatrix}$	$\begin{Bmatrix}1 & 0\\ 0 & -1\end{Bmatrix}$	$\begin{Bmatrix}-1 & 0\\ 0 & 1\end{Bmatrix}$

$\Gamma_1 \cdot \Gamma_2 = 1 + 1 + 1 + 1 - 1 - 1 - 1 - 1 = 0$. For the many-dimensional representations this holds true for each equivalent set of numbers in the matrices, e.g., for the $\Gamma_5(a_{12})$ component

$$\Gamma_4 \cdot \Gamma_5(a_{12}) \\ = 1 \cdot 0 - 1 \cdot 1 - 1(-1) + 1 \cdot 0 - 1 \cdot 1 - 1(-1) + 1 \cdot 0 + 1 \cdot 0 = 0$$

An n-dimensional representation is said to be reducible if there exists a linear transformation that will decompose all of the matrices of the representation into a block form as, for instance, shown in Eq. (3.9).

$$\left\{\begin{array}{cc} a_{11}\cdots\cdots a_{1i} & \\ \vdots \qquad \vdots & \\ \vdots \qquad \vdots & \\ a_{i1}\cdots\cdots a_{ii} & \\ & a_{jj}\cdots\cdots a_{jn} \\ & \vdots \qquad \vdots \\ & \vdots \qquad \vdots \\ & a_{nj}\cdots\cdots a_{nn} \end{array}\right\} \tag{3-9}$$

If, on the other hand, the representation cannot be reduced to a block form by a linear transformation, it is said to be *irreducible*. Calling the irreducible representations $\Gamma_1, \Gamma_2, \ldots, \Gamma_n$, we say that the reducible representation is composed of the irreducible representations $\Gamma_i + \Gamma_j + \cdots$. It can be shown that there are always the same number of irreducible representations in a group as there are classes.

In the above example (point group D_4) there are thus five irreducible representations. These are just the five representations given in Table 3-1.

The following relation is of great value in finding the dimensions l of the irreducible representations. With c classes we get c irreducible representations each of dimension l_n. Then

$$l_1^2 + l_2^2 + \cdots + l_c^2 = h \tag{3-10}$$

where h is the order of the group.

In the above example $c = 5$ and $h = 8$. Thus

$$l_1^2 + l_2^2 + l_3^2 + l_4^2 + l_5^2 = 8$$

This relation is fulfilled only for $l_1 = l_2 = l_3 = l_4 = 1$ and $l_5 = 2$.

By *the character* χ of an element of a representation we understand the trace of the matrix. Noticing in our example that the trace is the same for matrices in the same class, we have, for example, for Γ_5:

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
χ:	2	0	−2	0	0

Matrices in the same class are called equivalent, and we can prove that they will always have the same character. This is also intuitively clear, since different elements belonging to the same class differ only in the choice of coordinate systems used and are physically the same process.

For two equivalent representations A and B we have by definition

$$\mathsf{T}^{-1}\mathsf{A}\mathsf{T} = \mathsf{B} \tag{3-11}$$

That is, there is a matrix T which relates A to B by means of a similarity transformation. For the special case of a real unitary matrix T we have $\mathsf{T}^{-1} = \tilde{\mathsf{T}}$, where T^{-1} is the inverse and $\tilde{\mathsf{T}}$ is the transposed matrix. Writing Tr for the trace we have:

$$\mathrm{Tr}\ (\mathsf{T}^{-1}\mathsf{A}\mathsf{T}) = \mathrm{Tr}\ (\tilde{\mathsf{T}}\mathsf{A}\mathsf{T})$$

and since a unitary transformation preserves the trace,

$$\mathrm{Tr}\ (\mathsf{A}) = \mathrm{Tr}\ (\mathsf{B}) \tag{3-12}$$

We have thus proved what we noticed to be true in our example, that elements of representations belonging to the same class have identical characters. Since the character of a representation is unchanged by a similarity transformation, we can characterize a certain representation by means of its character system.

The character of a reducible representation is equal to the sum of the characters of the irreducible representations which together compose the reducible representation. How many times n a certain irreducible representation occurs in a given reducible representation can be determined uniquely, given the character of the reducible representation χ_R and the character table of the group $\chi_R^{(i)}$. We have

$$n^{(i)} = \frac{1}{h} \sum_R \chi_R^{(i)} \cdot \chi_R \tag{3-13}$$

where *h* is the order of the group and the sum is over *all* of the *h* operations in the group. Another way of obtaining *n* is, of course, by adding the characters of the irreducible representations together in a trial-and-error way until the sum is equal to the found character set of the reducible representation.

As an example of a character table we give Table 3-2, the character table for D_4.† We notice that the characters form a set of five orthogonal vectors spanning the D_4 group. Such character tables for all possible symmetry classes can be found in many textbooks.[1,4]

TABLE 3-2. CHARACTER TABLE FOR D_4

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
B_1	1	−1	1	1	−1
B_2	1	−1	1	−1	1
E	2	0	−2	0	0

3-d. Important Point Groups Occurring in Inorganic Complexes

1. O_h. The most common molecular structure for inorganic complexes is the regular octahedron possessing an inversion center, Fig. 3-3. This

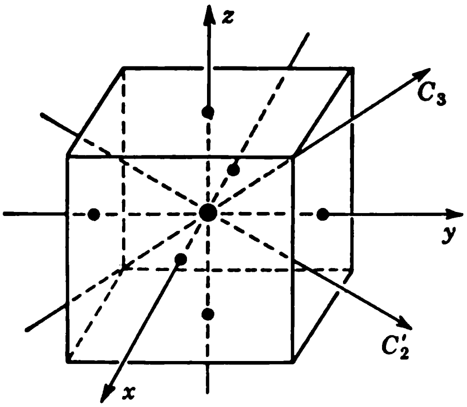

FIG. 3-3. Regular octahedron. Point group O_h.

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† One-dimensional representations are designated with the letters *A* and *B*. Those having a character +1 under the principal rotation are the *A* representations; those with a character −1 are the *B* representations. Two-dimensional representations are labeled with the letter *E*, three-dimensional representations with the letter *T*, and four-dimensional representations with the letter *G*. Within the various one-, two-, three-, or four-dimensional groups we distinguish between the representations by means of a number put down as a subscript. In addition, we shall use the subscripts *g* and *u*. They stand for the behavior of the representation when the inversion operator $\hat{\imath}$ is applied. If the representation does not change sign, we designate it by a subscript *g*; if it does change sign, the subscript is *u*.

molecule has the following symmetry operations:

E, the identity operation.
8 C_3 axes. (One of them is shown in the figure. There are eight threefold axes because there are four body diagonals, and we can rotate the molecule around one of these either plus or minus 120°.)
3 C_2 axes (the "coordinate axis" in the figure).
6 C_4 axes (the "coordinate axis" with a rotation plus or minus 90°).
6 C_2' axes (the six axes bisecting the coordinate axis).

To these symmetry operations must be added the application of the inversion operation $\hat{\imath}$. Thus the classes are augmented by $\hat{E} \cdot \hat{\imath} = \hat{\imath}$, $8\hat{C}_3 \cdot \hat{\imath}$, $3\hat{C}_2 \cdot \hat{\imath}$, $6\hat{C}_4 \cdot \hat{\imath}$, and $6\hat{C}_2 \cdot \hat{\imath}$. The point group of the regular octahedron is characterized by the letter O_h.

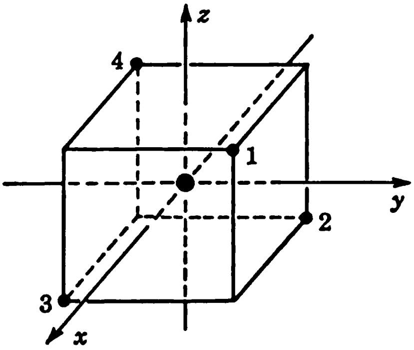

FIG. 3-4. Regular tetrahedron. Point group T_d.

2. T_d. The regular tetrahedron belongs to the point group T_d, Fig. 3-4. The molecule has the following symmetry operations:

E, the identity operation
8 C_3, as in O_h
3 C_2, as in O_h
6 $S_4 = 6C_4\sigma_h$ the C_4 axis as in O_h
6 $\sigma_d = 6C_2'i$ the C_2' axis as in O_h

The symmetry operations for a T_d molecule are thus very closely related to those of an O_h molecule, the most important difference being that a T_d molecule does *not* possess a symmetry center and thus has no inversion operation.

3. D_{4h}. This point group is characterized as follows:

E, the identity operatior
2 C_4 axes
1 C_2 axis
2 C_2' axes
2 C_2'' axes

Furthermore, we have the inversion operator $\hat{\imath}$ operating upon all the previous symmetry operations

$$\hat{E} \cdot \hat{\imath} = \hat{\imath} \qquad 2\hat{C}_4 \cdot \hat{\imath} = 2\hat{S}_4 \qquad \hat{\imath}\hat{C}_2 = \hat{\sigma}_h$$
$$2\hat{C}_2'\hat{\imath} = 2\hat{\sigma}_v \qquad \text{and} \qquad 2\hat{C}_2''\hat{\imath} = \hat{\sigma}_d$$

Examples of molecules possessing D_{4h} symmetry are $Ni(CN)_4^-$ and *trans*-$[Co(NH_3)_4Cl_2]^-$, Fig. 3-5*a* and *b*.

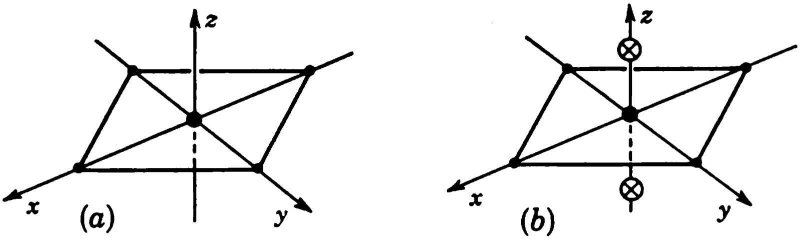

FIG. 3-5. Molecules with D_{4h} symmetry.

4. D_3. The last point group we shall mention specifically is D_3. An example of a molecule in this point group is $Co(en)_3^{3+}$, where en stands for the chelate $H_2N—CH_2—CH_2—NH_2$, Fig. 3-6. The symmetry operations here are

$$E \qquad 2C_3 \qquad \text{and} \qquad 3C_2$$

Again the molecule does not possess a symmetry center.

We shall not give any other examples of actual "molecules," because the structures treated here are the most important ones found in the stereochemistry of inorganic complexes. For a full description of all the possible point groups actually occurring, an excellent reference book is Wilson, Decius, and Cross, Ref. 1.

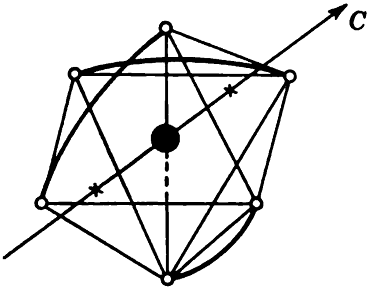

FIG. 3-6. D_3 symmetry $M(en)_3$.

3-e. Representations and Wave Functions

In order to construct suitable wave functions for a given molecule, consider a set of orthogonal functions $\psi_1 \cdots \psi_n$. Let us in turn perform all of the h different symmetry operations of the molecule. These symmetry operations change the coordinate system, and our basic functions $\psi_1 \cdots \psi_n$ are then subjected to a linear transformation. As an example

$$\hat{S}\begin{pmatrix} \psi_1 \\ \psi_2 \\ \cdots \\ \psi_n \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ a_{n1} & \cdots & \cdots & a_{nn} \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \\ \cdots \\ \psi_n \end{pmatrix} \tag{3-14}$$

In other words, the functions $\psi_1 \cdots \psi_n$ provide a basis for a set of matrices. *These matrices describing symmetry operations are a representation of the group.* Such representations are often reducible, so that different combinations of the basic functions will mix and belong to different irreducible representations.

Usually we are not so much interested in the set of representations as we are in the number and kind of irreducible representations contained in the basic set of functions. These features can be investigated by utilizing the characters of the representation of the group, because formula (3-13) tells us how to find the number and kind of the irreducible representations given the characters of the reducible representation. For the irreducible representations the character below E is equal to the degeneracy of the electronic state. This number is, of course, also the dimension of the irreducible representation.

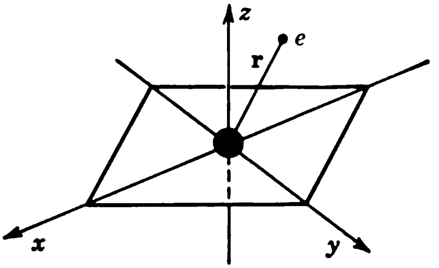

FIG. 3-7. Metal electron in a D_{4h} molecule.

It may happen in rare cases that there is "accidental degeneracy" in the system, but for most molecules the dimension of the irreducible representation is equal to the actual degree of degeneracy.

In some cases we are interested in the combinations of the basic functions which provide a basis for the various irreducible representations. Usually this is an easy thing to get directly from the transformation properties of the basic functions. In special cases, however, it pays to use the following procedure: Consider a transformation scheme

	E	$C_4(1)$	$C_4(2)$	$C_2(1)$	$C_2(2)$	$C_2(3)$	$\cdots$
ψ_1	ψ_1	ψ_2	ψ_3	ψ_3	ψ_2	ψ_1	$\cdots$
ψ_2	ψ_2	ψ_8	ψ_7	ψ_2	ψ_1	ψ_2	$\cdots$
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$

Then the combinations of basic functions transforming like Γ_i will be the sum of the functions in a row multiplied with the characters of Γ_i.

In order to clarify our ideas, let us consider a specific example, that of a d electron centered in the middle of a square configuration as in Fig. 3-7. The d orbitals are $2 \cdot l + 1 = 2 \cdot 2 + 1 =$ fivefold degenerate and the orbitals are

$$\psi_{3,2,m_l} = R_{3,2}(r) P_2^{m_l} (\cos \Theta) \frac{e^{im_l\varphi}}{\sqrt{2\pi}} \tag{3-15}$$

with $|m_l| \leq 2$.

We take these five orthogonal functions as our basic set $\psi_1 \cdots \psi_5$ and investigate how the functions transform under operations of the point group D_4. The most general rotation is that around an arbitrary axis through the angle Φ. The simplest way of investigating how the five d orbitals behave is by always quantizing $\psi_1 \cdots \psi_5$ with respect to the axis about which we rotate. If this is the case, our rotation will carry φ over in $\varphi + \Phi$ and take

$$\psi_{3,2,m_l} = R_{3,2}(r)P_2^{m_l}(\cos\Theta)\frac{e^{im_l\varphi}}{\sqrt{2\pi}}$$

over into

$$R_{3,2}(r)P_2^{m_l}(\cos\Theta)\frac{e^{im_l(\varphi+\Phi)}}{\sqrt{2\pi}}$$

The rotation is thus given by the matrix

$$\begin{pmatrix} e^{il\Phi} & 0 & 0 \\ 0 & e^{i(l-1)\Phi} & \cdots \\ \cdots & \cdots & \cdots \\ 0 & \cdots & e^{-il\Phi} \end{pmatrix} \tag{3-16}$$

that is, the character of a rotation $\chi(\Phi)$ is given by

$$\chi(\Phi) = e^{il\Phi} + e^{i(l-1)\Phi} + \cdots + e^{-il\Phi} \tag{3-17}$$

$$= e^{-il\Phi}\sum_{n=0}^{2l}(e^{i\Phi})^n = \frac{\sin(l+\frac{1}{2})\Phi}{\sin(\Phi/2)} \tag{3-18}$$

For $\Phi = \pi \qquad \chi(C_2) = (-1)^l$

$$\Phi = \frac{\pi}{2} \qquad \chi(C_4) = \begin{cases} 1 & l = 0,1,4,5, \ldots \\ -1 & l = 2,3,6,7, \ldots \end{cases}$$

The characters of the representations spanned by the five *d* orbitals in the point group D_4 are then

E	$2C_4$	C_2	$2C_2'$	$2C_2''$
5	-1	1	1	1

Using the formula (3-13), we have

$$\begin{aligned}
n(a_1) &= \tfrac{1}{8}(5\cdot 1\cdot 1 + 2(-1)\cdot 1 + 1\cdot 1\cdot 1 + 2\cdot 1\cdot 1 + 2\cdot 1\cdot 1) = 1\\
n(a_2) &= \tfrac{1}{8}(5\cdot 1\cdot 1 + 2(-1)\cdot 1 + 1\cdot 1\cdot 1 + 2(1)(-1) + 2(1)(-1)) = 0\\
n(b_1) &= \tfrac{1}{8}(5\cdot 1\cdot 1 + 2(-1)(-1) + 1\cdot 1\cdot 1 + 2(1)(1) + 2(1)(-1)) = 1\\
n(b_2) &= \tfrac{1}{8}(5\cdot 1\cdot 1 + 2(-1)(-1) + 1\cdot 1\cdot 1 + 2(1)(-1) + 2(1)(1)) = 1\\
n(e) &= \tfrac{1}{8}(5\cdot 2\cdot 1 + 2(-1)\cdot 0 + (-2)\cdot 1\cdot 1 + 1\cdot 2\cdot 0 + 1\cdot 2\cdot 0) = 1
\end{aligned}$$

In other words, the representation spanned by the five *d* orbitals is a reducible representation made up by the irreducible representation a_1, b_1, b_2, and *e*. The fivefold degeneracy of the *d* orbitals is removed in the D_4 point group, and we get three nondegenerate levels and one twofold degenerate level.

If the system under consideration has a symmetry center, the symmetry operation "inversion in the center" can be added to all the rotational operators previously described. This will simply double the order of the group; in our previous example, D_4 becomes D_{4h} and we will get Table 3-3 for the character table.

TABLE 3-3. COMPLETE CHARACTER TABLE FOR POINT GROUP D_{4h}

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2iC_4$	iC_2	$2iC_2'$	$2iC_2''$
a_{1g}	1	1	1	1	1	1	1	1	1	1
a_{2g}	1	1	1	−1	−1	1	1	1	−1	−1
b_{1g}	1	−1	1	1	−1	1	−1	1	1	−1
b_{2g}	1	−1	1	−1	1	1	−1	1	−1	1
e_g	2	0	−2	0	0	2	0	−2	0	0
a_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
a_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1
b_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1
b_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1
e_u	2	0	−2	0	0	−2	0	2	0	0

The representations for which the characters remain unaltered during the inversion are called even (g) representations, and those which change sign during this operation are called odd (u) representations. The letters g and u are added as a subscript to the name of the representation. In many cases one need not bother with the "complete" character table, because it is possible to tell beforehand whether we will get odd or even representations. For example, since all d orbitals are "even" under reflection in their symmetry center, we can get only "even" representations by using the d orbitals as our basic functions. Thus the five d orbitals taken as basic functions span the four irreducible representations a_{1g}, b_{1g}, b_{2g}, and e_g in the D_{4h} point group. This is, of course, also found by utilizing the full character table (Table 3-3) together with the formula (3-13).

3-f. The Direct Product

Consider a certain symmetry operation $\hat{S}$ in a group. Let us now operate with $\hat{S}$ upon two sets of functions both of which form bases for irreducible representations in the group

$$\hat{S}\begin{pmatrix}\psi_1\\ \cdot\\ \cdot\\ \cdot\\ \psi_i\end{pmatrix} = \mathbf{A}\begin{pmatrix}\psi_1\\ \cdot\\ \cdot\\ \cdot\\ \psi_i\end{pmatrix} \tag{3-19}$$

$$\hat{S}\begin{pmatrix}\varphi_1\\ \cdot\\ \cdot\\ \cdot\\ \varphi_j\end{pmatrix} = \mathbf{B}\begin{pmatrix}\varphi_1\\ \cdot\\ \cdot\\ \cdot\\ \varphi_j\end{pmatrix} \tag{3-20}$$

The trace of the matrix $\mathbf{A}$ is by definition equal to the character of the representation under the symmetry operation S, and the same holds true for the trace of $\mathbf{B}$.

With the two sets of functions (ψ_i) and (φ_j) we can form the products $(\psi_i)(\varphi_j)$ and obtain a new system of functions which can be used as basic functions for a new representation. Such a representation is called the *direct-product* representation. It is easy to prove that the characters of the direct-product representation are equal to the products of the characters for the component representations. We have

$$\mathrm{Tr}\,(\mathbf{A}) \cdot \mathrm{Tr}\,(\mathbf{B}) = \mathrm{Tr}\,(\mathbf{A} \times \mathbf{B}) \tag{3-21}$$

This is simply a consequence of the rules for forming the direct product of two matrices, since $\mathbf{A} \times \mathbf{B}$ contains on its diagonal all products of all a_{ii}'s with all b_{jj}'s. The character of a direct-product representation is therefore the product of the characters:

$$\chi(A) \cdot \chi(B) = \chi(A \times B) \tag{3-22}$$

The dimension of $\chi(A \times B)$ will clearly be equal to the product of the dimensions of $\mathbf{A}$ and $\mathbf{B}$. Therefore, there is no a priori reason that $(\mathbf{A} \times \mathbf{B})$ should be an irreducible representation even if $\mathbf{A}$ and $\mathbf{B}$ are irreducible.

Let us take an example using the group D_4. Suppose that we want to find the direct-product representation using the two irreducible representations E and B_2 as the component representations. Then the character of the direct product is the products of the characters of $E \times B_2$:

$$\{2 \quad 0 \quad -2 \quad 0 \quad 0\} = \chi(E)$$

In this way we see that the direct-product representation of B_2 and E will be an irreducible representation with E symmetry properties. Let us now calculate

$$E \times E = \{4 \quad 0 \quad 4 \quad 0 \quad 0\}$$

Clearly, this is a reducible representation; by use of the formula (3-13) or simply by adding the characters together, we find

$$E \times E = A_1 + A_2 + B_1 + B_2 \tag{3-23}$$

The complete multiplication table for D_4 is given in Table 3-4. Notice that the representation A_1 occurs only in the diagonal of the table. This holds true for *all* tables of direct products.

TABLE 3-4. MULTIPLICATION TABLE FOR D_4

	A_1	A_2	B_1	B_2	E
A_1	A_1	A_2	B_1	B_2	E
A_2	A_2	A_1	B_2	B_1	E
B_1	B_1	B_2	A_1	A_2	E
B_2	B_2	B_1	A_2	A_1	E
E	E	E	E	E	$A_1 + A_2 + B_1 + B_2$

Consider now the case when the two sets of functions (ψ_i) and (φ_j) are identical. The reducible representation of the products $(\psi_i)(\varphi_j)$ can then be decomposed into two representations of smaller dimension. One set is of the type $(\psi_i)(\varphi_j) + (\psi_j)(\varphi_i)$; the other is of the form $(\psi_i)(\varphi_j) - (\psi_j)(\varphi_i)$ $(i \neq j)$. The first set is a *symmetric product* because it does not change sign by permutating the electronic coordinates, whereas the second combination does change sign and is therefore called the *antisymmetric product.* The characters of the symmetric product are denoted by the symbol $[\chi^2](\hat{S})$, and the characters of the antisymmetric product are called $\{\chi^2\}(\hat{S})$.

It is then easy to show[3] that

$$[\chi^2](\hat{S}) = \tfrac{1}{2}([\chi(\hat{S})]^2 + \chi(\hat{S}^2))$$

and

$$\{\chi^2\}(\hat{S}) = \tfrac{1}{2}([\chi(\hat{S})]^2 - \chi(\hat{S}^2))$$

Let us take an example. Consider the t_2 representation in O_h symmetry. The set of characters is found to be

$\hat{E}$	$\hat{C}_3$	$\hat{C}_2$	$\hat{C}_4$	$\hat{C}'_2$
3	0	−1	−1	1

Hence

$$[\chi(\hat{S})]^2 = 9 \quad 0 \quad 1 \quad 1 \quad 1$$

We have further the equations

$$\hat{E}^2 = \hat{E} \qquad \hat{C}_3{}^2 = \hat{C}_3 \qquad \hat{C}_2{}^2 = \hat{E} \qquad \hat{C}_4{}^2 = \hat{C}_2 \qquad \text{and} \qquad \hat{C}'^2_2 = \hat{E}$$

Hence

$$\chi(\hat{S}^2) = 3 \quad 0 \quad 3 \quad -1 \quad 3$$

By applying the formulas for the symmetric and antisymmetric product, we then get

$$[\chi^2](\hat{S}) = 6 \quad 0 \quad 2 \quad 0 \quad 2$$

and

$$\{\chi^2\}(\hat{S}) = 3 \quad 0 \quad -1 \quad 1 \quad -1$$

The symmetric representations are then found to be A_1, E, and T_2 and the antisymmetric representation is found to be T_1. If we also consider the spin functions, we have that the electronic configuration $(t_{2g})^2$ can produce the states ${}^3T_{1g}$ and ${}^1A_{1g}$, ${}^1E_g$, and ${}^1T_{2g}$. This latter result follows from the fact that the total wave function will be antisymmetric.

The calculation of the direct products is of special importance when evaluating molecular integrals. We want in such cases to evaluate integrals of the form $\int \psi_A^* \hat{Q} \psi_B \, d\tau$, where the wave functions ψ_A and ψ_B have been chosen in such a way as to form bases for the irreducible representations of the point group of the molecule. The integral is then different from zero only if it is invariant under all symmetry operations of the group. But this means that the direct product $\Gamma_A \cdot \Gamma_Q \cdot \Gamma_B$ must contain at least one completely invariant term.

$\Gamma_A \cdot \Gamma_Q \cdot \Gamma_B$ will in general be reducible:

$$\Gamma_A\Gamma_Q\Gamma_B = \sum_i a_i\Gamma_i \tag{3-24}$$

where the Γ_i are irreducible representations of the group. Our matrix element will then be different from zero if the totally symmetric representation A_{1g} is found in the expansion (3-24). For an arbitrary operator $\hat{Q}$ we must have $\Gamma_Q = \Gamma_A\Gamma_B$ in order for the matrix element to be different from zero.

If $\hat{Q}$ is equal to the Hamiltonian of the molecule, we know it to be invariant under all symmetry operations of the molecule. It then follows from the tables of characters that $\int\psi_A^*\mathcal{H}\psi_B\,d\tau$ is different from zero only if $\Gamma_A = \Gamma_B$. This ensures that no matter how high a perturbation treatment is carried, the symmetry designations will always remain "good" quantum numbers, so long as we stay in the same group. A perturbation calculation carried "one step further" is thus unable to split up any true degeneracies found by means of simple symmetry considerations. Because of the foregoing considerations it must therefore be recommended to start a calculation with wave functions transforming correctly according to the group of the molecule.

3-g. Double Groups

The atomic wave functions are in general made up by both an orbital and a spin part. Whereas the orbital part is always characterized by having integer values of l, this is not so for the spin part. In a state system characterized by the quantum number J we have

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{3-25}$$

The two possible spin states are the $\alpha(\frac{1}{2},\frac{1}{2})$ and the $\beta(\frac{1}{2},-\frac{1}{2})$ states, and the spin of an electron, no matter how we choose our axis of quantization, can always be described by a linear combination of the two functions α and β. Since $s = \frac{1}{2}$ for an electron, J is a half-integer in systems with an odd number of electrons. The question that then arises is how to treat the transformation properties for systems with a half-integer angular momentum.

Consider formula (3-18) for the character of a rotation through an angle Φ:

$$\chi(\Phi) = \frac{\sin\,(j + \frac{1}{2})\Phi}{\sin\,\frac{1}{2}\Phi} \tag{3-26}$$

Then for j integer $\quad \chi(\Phi) = \chi(\Phi + 2\pi)$
but for j half-integer $\quad \chi(\Phi) = -\chi(\Phi + 2\pi)$

A rotation of 2π brings any physical system back to itself, so the transformation matrix and characters for the rotations Φ and $\Phi + 2\pi$ ought to be equal. However, we have just seen that for j half-integer the signs of the representations are double-valued in the rotation group; they are not true representations. Every character changes sign when we perform a rotation of 2π, but we notice that a rotation by 4π is equivalent to the identity operator $\hat{E}$.

For $\Phi = 0$ and 2π we have, by using l'Hospital's rule,

$$\chi(0) = \frac{(j + \frac{1}{2}) \cos (j + \frac{1}{2})0}{\frac{1}{2} \cdot \cos \frac{1}{2} \cdot 0} = 2j + 1 \tag{3-27}$$

$$\chi(2\pi) = \frac{(j + \frac{1}{2}) \cos (j + \frac{1}{2})2\pi}{\frac{1}{2} \cos \pi} \qquad \begin{array}{ll} j \text{ integer} & \chi(2\pi) = 2j + 1 \\ j \text{ half-integer} & \chi(2\pi) = -(2j + 1) \end{array} \tag{3-28}$$

The only character with a unique value is the character for a rotation by π for j half-integer:

$$\chi(\pi) = \chi(3\pi) = 0$$

In order to obtain the double-valued representations, we introduce with Bethe[6] the fiction that a molecule is to go into itself not upon a rotation 2π around an axis, but only upon a rotation of 4π. This, of course, makes no difference in a *physical* sense and is to be considered only a mathematical device.

A new group element R, the rotation by 2π, is now defined and the elements of the single-valued group are expanded by means of multiplication by R. The double group thus contains more classes than the single group, but not twice as many. This stems from the fact that the rotations by π are unique. All of the classes that contain rotations by π accordingly correspond to one class each of the double group, whereas all others correspond to two classes each.

In our previous example, D_4, we have the following symmetry operations

$$E \quad R \quad 2C_4 \quad 2C_4R \quad C_2 \quad C_2R \quad 2C_2' \quad 2C_2'R \quad 2C_2'' \quad 2C_2''R$$

However, since the twofold rotations are single-valued, we really only have the following symmetry operations:

$$(E) \quad (R) \quad \begin{pmatrix} C_4 \\ C_4{}^3R \end{pmatrix} \begin{pmatrix} C_4{}^3 \\ C_4R \end{pmatrix} \begin{pmatrix} C_2 \\ C_2R \end{pmatrix} \begin{pmatrix} 2C_2' \\ 2C_2'R \end{pmatrix} \begin{pmatrix} 2C_2'' \\ 2C_2''R \end{pmatrix}$$

seven classes with h the order of the group equal to 16. Then

$$16 = 1^2 + 1^2 + 1^2 + 1^2 + 2^2 + 2^2 + 2^2 \tag{3-29}$$

It follows that in the double group we have seven irreducible representations: the first five identical with those met previously in the single group, the last two double-valued representations appearing as a consequence of the augmented order of the group.

Some authors use a nomenclature for the various representations of the double group identical to the one used for representations[3] of the single group and distinguish the double groups by primes put as subscripts to the symbols of the ordinary groups. We shall, however, usually reserve the Mulliken nomenclature for the ordinary groups and use the gamma notation of Bethe[6] for the double groups. Hence, we shall, for instance, write $\Gamma_5(^3T_{2g})$ indicating the Γ_5 component coming from $^3T_{2g}$. In the direct-product tables 3-7 and 3-8 we have, however, used the extended Mulliken notation in order to facilitate their use for the single groups.

Table 3-5 is the character table for the D_{4h} double group D_4'. Such character tables can be found in the usual way by construction and use of the group multiplication table.[6]

TABLE 3-5. CHARACTER TABLE FOR D_4'

	E	R	C_4 $C_4{}^3R$	C_4R $C_4{}^3$	C_2 C_2R	$2C_2'$ $2C_2'R$	$2C_2''$ $2C_2''R$	Bethe's nomenclature
A_1'	1	1	1	1	1	1	1	Γ_1
A_2'	1	1	1	1	1	-1	-1	Γ_2
B_1'	1	1	-1	-1	1	1	-1	Γ_3
B_2'	1	1	-1	-1	1	-1	1	Γ_4
E_1'	2	2	0	0	-2	0	0	Γ_5
E_2'	2	-2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0	Γ_6
E_3'	2	-2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0	Γ_7

In the octahedral case we have the following classes:

$$E \quad R \quad 8C_3 \quad 8C_3R \quad 6C_2 \quad 6C_4 \quad 6C_4R \quad 12C_2'$$

8 classes with 48 elements. Then

$$48 = 1^2 + 1^2 + 2^2 + 3^2 + 3^2 + x_1{}^2 + x_2{}^2 + x_3{}^2 \qquad (3\text{-}30)$$

$$24 = x_1{}^2 + x_2{}^2 + x_3{}^2$$

$$24 = 2^2 + 2^2 + 4^2 \qquad (3\text{-}31)$$

In other words, we must add three representations to the single group of order 2, 2, and 4 in order to obtain all the irreducible representations of the double group, Table 3-6.

TABLE 3-6. CHARACTER TABLE FOR THE DOUBLE GROUP O'

	E	R	$4C_3$ $4C_3{}^2R$	$4C_3R$ $4C_3{}^2$	$3C_2$ $3C_2R$	$3C_4$ $3C_4{}^3R$	$3C_4R$ $3C_4{}^3$	$6C_2'$ $6C_2'R$	Bethe's nomenclature
A_1'	1	1	1	1	1	1	1	1	Γ_1
A_2'	1	1	1	1	1	-1	-1	-1	Γ_2
E_1'	2	2	-1	-1	2	0	0	0	Γ_3
T_1'	3	3	0	0	-1	1	1	-1	Γ_4
T_2'	3	3	0	0	-1	-1	-1	1	Γ_5
E_2'	2	-2	1	-1	0	$\sqrt{2}$	$-\sqrt{2}$	0	Γ_6
E_3'	2	-2	1	-1	0	$-\sqrt{2}$	$\sqrt{2}$	0	Γ_7
G'	4	-4	-1	1	0	0	0	0	Γ_8

The direct products of the double group are obtained in exactly the same way as in the case of the single groups. Tables 3-7 and 3-8 are the multiplication tables for the tetragonal and octahedral double group. The direct products for the five "single-valued" representations in both the tetragonal and octahedral groups are, of course, identical with the ones given for the double groups. Furthermore, what has previously been said concerning the use of the direct products in the evaluating of matrix elements holds true in the double groups also.

TABLE 3-7. DIRECT PRODUCTS OF THE IRREDUCIBLE REPRESENTATIONS IN D'_4

	A'_1	A'_2	B'_1	B'_2	E'_1	E'_2	E'_3
A'_1	A'_1	A'_2	B'_1	B'_2	E'_1	E'_2	E'_3
A'_2	A'_2	A'_1	B'_2	B'_1	E'_1	E'_2	E'_3
B'_1	B'_1	B'_2	A'_1	A'_2	E'_1	E'_3	E'_2
B'_2	B'_2	B'_1	A'_2	A'_1	E'_1	E'_3	E'_2
E'_1	E'_1	E'_1	E'_1	E'_1	$A'_1 + A'_2 + B'_1 + B'_2$	$E'_2 + E'_3$	$E'_2 + E'_3$
E'_2	E'_2	E'_2	E'_3	E'_3	$E'_2 + E'_3$	$A'_1 + A'_2 + E'_1$	$B'_1 + B'_2 + E_1$
E'_3	E'_3	E'_3	E'_2	E'_2	$E'_2 + E'_3$	$B'_1 + B'_2 + E'_1$	$A'_1 + A'_2 + E'_1$

TABLE 3-8. DIRECT PRODUCTS OF THE IRREDUCIBLE REPRESENTATIONS IN O'

	A'_1	A'_2	E'_1	T'_1	T'_2	E'_2	E'_3	G'
A'_1	A'_1	A'_2	E'_1	T'_1	T'_2	E'_2	E'_3	G'
A'_2	A'_2	A'_1	E'_1	T'_2	T'_1	E'_3	E'_2	G'
E'_1	E'_1	E'	$A'_1 + A'_2 + E'$	$T'_1 + T'_2$	$T'_1 + T'_2$	G'	G'	$E'_2 + E'_3 + G'$
T'_1	T'_1	T'_2	$T'_1 + T'_2$	$A'_1 + E' + T'_1 + T'_2$	$A'_2 + E' + T'_1 + T_2$	$E'_2 + G'$	$E'_3 + G'$	$E'_2 + E'_3 + 2G$
T'_2	T'_2	T'_1	$T'_1 + T'_2$	$A'_2 + E' + T'_1 + T'_2$	$A'_1 + E' + T'_1 + T'_2$	$E'_3 + G'$	$E'_2 + G'$	$E'_2 + E'_3 + 2G'$
E'_2	E'_2	E'_3	G'	$E'_2 + G'$	$E'_3 + G'$	$A'_1 + T'_1$	$A'_2 + T'_2$	$E' + T'_1 + T'_2$
E'_3	E'_3	E'_2	G'	$E'_3 + G'$	$E'_2 + G'$	$A'_2 + T'_2$	$A'_1 + T'_1$	$E' + T'_1 + T'_2$
G'	G'	G'	$E'_2 + E'_3 + G'$	$E'_2 + E'_3 + 2G'$	$E'_2 + E'_3 + 2G'$	$E'_1 + T'_1 + T'_2$	$E' + T'_1 + T'_2$	$A' + A'_2 + E' + 2T'_1 + 2T'_2$

As usual, let us illustrate the foregoing with an example. We take the 10 basic functions obtained by multiplying the five d orbitals (3-15) with either an α-spin function or a β-spin function. Our aim is to find the irreducible representations contained in the 10 basic functions in a D_4' point group. In order to use formula (3-18), we notice that for the d orbitals $l = 2$ and $s = \frac{1}{2}$. Consequently, j is equal to either $\frac{5}{2}$ or $\frac{3}{2}$. The characters are then given by (3-18):

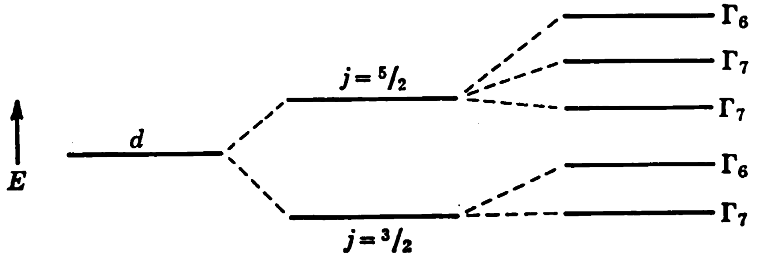

FIG. 3-8. A d electron with "j-j coupling" in tetragonal symmetry.

	E	R	C_4	C_4R	C_2	C_2'	C_2''
$j = \frac{3}{2}$	4	−4	0	0	0	0	0
$j = \frac{5}{2}$	6	−6	$-\sqrt{2}$	$\sqrt{2}$	0	0	0

These reducible character sets reflect the presence of the irreducible representations Γ_6 and Γ_7. By means of formula (3-13), we obtain

$$\Gamma\,(j = \tfrac{3}{2}) = \Gamma_6 + \Gamma_7 \qquad \text{and} \qquad \Gamma\,(j = \tfrac{5}{2}) = \Gamma_6 + 2\Gamma_7 \tag{3-32}$$

For the point group O' we get, on the other hand, for $j = \frac{3}{2}$ and $\frac{5}{2}$ the following character set:

	E	R	C_3	C_3R	C_2	C_4	C_4R	C_2'
$j = \frac{3}{2}$	4	−4	−1	1	0	0	0	0
$j = \frac{5}{2}$	6	−6	0	0	0	$-\sqrt{2}$	$\sqrt{2}$	0

The reducible representations are reduced to a sum of irreducible representations:

$$\Gamma\,(j = \tfrac{3}{2}) = \Gamma_8 \qquad \text{and} \qquad \Gamma\,(j = \tfrac{5}{2}) = \Gamma_7 + \Gamma_8 \tag{3-33}$$

There is another way of finding the irreducible representations contained in the 10 basic functions of a d electron with spin equal to $\frac{1}{2}$. For, say, a cubic group we take the direct product of the irreducible representations spanned by the five d orbitals, with the irreducible representation spanned by the α- and β-spin functions. Thus for the point group O_h:

	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
$l = 2$					
$\chi =$	5	−1	1	−1	1

$$\Gamma\,(l = 2) = e_1 + t_2 \tag{3-34}$$

Further,

	E	R	C_3	C_3R	C_2	C_4	C_4R	C_2'
$l = \frac{1}{2}$								
$\chi =$	2	-2	1	-1	0	$\sqrt{2}$	$-\sqrt{2}$	0

$$\Gamma\,(l = \tfrac{1}{2}) = \Gamma_6 \tag{3-35}$$

The direct product $\Gamma\,(l = 2)\,\Gamma\,(l = \frac{1}{2})$ then gives (see Table 3-8) the result

$$\Gamma\,(l = 2)\,\Gamma\,(l = \tfrac{1}{2}) = (\Gamma_3 + \Gamma_5)\Gamma_6 = \Gamma_8 + \Gamma_7 + \Gamma_8 \tag{3-36}$$

exactly as found previously.

A point to note is that the double-valued representations all are of even dimension. All levels having half-integer values of j are therefore at least twofold degenerate. This result has been shown by Kramers[8] to be true in general for all half-integer values of j in any symmetry, provided that no magnetic field is present. Such a degeneracy is accordingly called a Kramers degeneracy.

For a full treatment of the double groups, Refs. 3, 5, 6, and 8 to 11 ought to be consulted.

3-h. The Eulerian Angles

Performing a symmetry operation usually means to rotate a coordinate system. This can, of course, be done in a great many ways; here we shall carry out the transformation from one cartesian coordinate system to another by means of three rotations performed in a certain specified order. The angles so defined are called the "Eulerian angles."

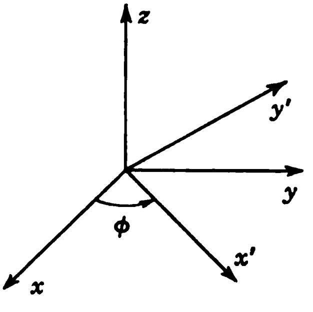

FIG. 3-9. Counterclockwise rotation of coordinate system.

There are in the literature many definitions of Eulerian angles. We shall utilize the one used by Goldstein;[12] look however in his book for a description of the various systems used by other authors. The first rotation is a rotation by an angle ϕ counterclockwise (right-handed screw) about the z axis of the initial coordinate system, Fig. 3-9. The second rotation is a counterclockwise rotation by an angle Θ about the *new* x axis. Finally, we rotate the system counterclockwise by an angle ψ about the *new* z axis. Note that the second and third rotations are defined only when the earlier rotation(s) have been performed.

In describing the rotation, we can either keep a point fixed in space or rotate the function. We shall here always keep a point fixed in space. This is particularly to be kept in mind when rotating two functions simultaneously.

Rotating the coordinate system about a z axis is described by the transformation matrix

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{3-37}$$

A further rotation about the new a axis is described by

$$\begin{pmatrix} d \\ e \\ f \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\Theta & \sin\Theta \\ 0 & -\sin\Theta & \cos\Theta \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} \tag{3-38}$$

Finally, a rotation around the new f axis is described by

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} d \\ e \\ f \end{pmatrix} \tag{3-39}$$

The complete rotation is then described by the matrix product

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\Theta & \sin\Theta \\ 0 & -\sin\Theta & \cos\Theta \end{pmatrix} \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{3-40}$$

Example: For a rotation by $2\pi/3$ around the axis passing through the center of the coordinate system and the point (1,1,1) we have $\phi = \pi/2$, $\Theta = \pi/2$, $\psi = 0$. Then

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{3-41}$$

It is more difficult to find the transformation matrix in terms of ϕ, Θ, and ψ for α and β spin. We shall not develop the necessary formalism to do so; instead, we merely state the appropriate transformation matrix without proof. A derivation can be found, for example, in Refs. 3 and 12.

Let us represent α and β spin with the matrices

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{3-42}$$

A rotation by ϕ around the z axis is then given by the matrix

$$\begin{pmatrix} e^{\frac{1}{2}i\phi} & 0 \\ 0 & e^{-\frac{1}{2}i\phi} \end{pmatrix} \tag{3-43}$$

and a rotation by Θ around the x axis is given by

$$\begin{pmatrix} \cos\frac{1}{2}\Theta & i\sin\frac{1}{2}\Theta \\ i\sin\frac{1}{2}\Theta & \cos\frac{1}{2}\Theta \end{pmatrix} \tag{3-44}$$

The rotation by ψ around the new z axis is similar to (3-43). As before, the matrix of the complete transformation is equal to the product of the three transformations. The transformation matrix is then

$$\begin{pmatrix} e^{i(\psi+\phi)/2}\cos\frac{\theta}{2} & ie^{i(\psi-\phi)/2}\sin\frac{\theta}{2} \\ ie^{-i(\psi-\phi)/2}\sin\frac{\theta}{2} & e^{-i(\psi+\phi)/2}\cos\frac{\theta}{2} \end{pmatrix} \tag{3-45}$$

Example: Rotation by $2\pi/3$ around a threefold axis as before gives

$$\hat{C}_3\alpha = \begin{pmatrix} e^{i\pi/4}\cos\frac{\pi}{4} & ie^{-i\pi/4}\sin\frac{\pi}{4} \\ ie^{i\pi/4}\sin\frac{\pi}{4} & e^{-i\pi/4}\cos\frac{\pi}{4} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{3-46}$$

$$= \frac{1}{\sqrt{2}}\begin{pmatrix} e^{i\pi/4} \\ ie^{i\pi/4} \end{pmatrix} = \frac{e^{i\pi/4}}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} = \frac{e^{i\pi/4}}{\sqrt{2}}(\alpha + i\beta) \tag{3-47}$$

In the same way

$$\hat{C}_3\beta = \frac{e^{-i\pi/4}}{\sqrt{2}}(i\alpha + \beta) \tag{3-48}$$

We now leave the introductory theory and generalizations in order to concentrate upon our initial objective, the electronic structures of complexes. We shall, however, see that the theory of atomic spectra and the theory of groups are indispensable tools if we want to attack our main problem in a both elegant and powerful way.

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CHAPTER 4

The Crystal Field Theory: I. Fields of Octahedral Symmetry

4-a. Formalism

The crystal field theory treats an inorganic complex as if such a compound could be regarded as an "ionic" molecule. It is then evident that the central metal atom in the complex is subjected to an electric field originating from the surrounding atoms or molecules, analogously to what would take place if the atom were located in a little cavity inside a crystalline lattice. Such a "crystalline field" would, of course, destroy the spherical symmetry of the free atom, and the consequences of this situation are dealt with by the crystal field theory. The model considers an isolated molecule, and it handles the electrons of the central metal ion as if they were subjected to an electric field originating from the surrounding molecules, called ligands.

The electrons on the ligands are not allowed to overlap and mix with the electrons of the metal ion; as a result, the role played by the ligands is rather limited. Of course they can be polarized by the metal ion of the complex, but the motions of their electrons are assumed to remain unaffected by such factors as whether the electrons of the metal ion are in an excited state or not. Thus the ligands are only supposed to provide a constant electric potential possessing the symmetry of the arrangement of the ligand nuclei, in which the electrons of the metal ion can move.[1]

It was realized later that this point of view does not constitute as serious a limitation of the theory as might be supposed. Indeed, Van Vleck[2] showed that the theory of molecular orbitals gives a justification to the above point of view. It must only be remembered that the word "ionic" as used in the crystal field theory is not to be taken in any way to represent the truth.

The quantal treatment for such a model is therefore easily formulated.[3,4] The Hamiltonian for the electrons of the metal ion consists of two terms

$$\mathcal{H} = \mathcal{H}_F + \mathcal{V} \tag{4-1}$$

Here $\mathcal{H}_F$ is the Hamiltonian for the free ion and $\mathcal{V}$ is the potential provided by its ligands. It is supposed that the eigenfunctions and eigenvalues of

$\mathcal{H}_F$ are known.[5] Accordingly, the potential $\mathcal{V}$ is regarded as a perturbation which determines the electronic motions and term values of the metal ion in the complex. We notice that the whole problem could be regarded as a sort of intramolecular Stark effect.

Written out in greater detail, we have for the Hamiltonian:

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{r_i} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{r_{ij}} + \sum_i \xi_i(r)\mathbf{l}_i \cdot \mathbf{s}_i + \mathcal{V} \tag{4-2}$$

With the exception of the term in $\mathcal{V}$, the Hamiltonian (4-2) is exactly the Hamiltonian for the free ion. The solution to this problem was treated in Chap. 2. However, when we are going to perturb the eigenvalues for the free ions with $\mathcal{V}$, it is, of course, very important to known how $\mathcal{V}$ compares in order of magnitude with the two other perturbing quantities in (4-2), the electronic repulsion term $\Sigma(e^2/r_{ij})$ and the spin-orbit term $\Sigma\xi_i(r)\mathbf{l} \cdot \mathbf{s}$. It is seen that three cases can be realized:

1. $\mathcal{V} < \xi(r)\mathbf{l} \cdot \mathbf{s}$	complexes of the rare earths
2. $\xi(r)\mathbf{l} \cdot \mathbf{s} < \mathcal{V} < e^2/r_{ij}$	complexes of the first transition group
3. $\mathcal{V} > e^2/r_{ij}$	"covalent" complexes

It is customary to call the second case "the weak crystalline field case" and the third case "the strong crystalline field case." Of course, there is no real distinction between the three cases; analytically they go over into each other. The reason we distinguish between them is simply in order to specify our starting point. In actual cases the complexes of the rare earths are found in case 1, while the complexes of the first transition group are found somewhere in between cases 2 and 3 and can be described starting from either point of view. On the other hand, virtually all of the complexes of the second and third transition series are best approximated as "covalent" complexes.

Since the unperturbed functions, being eigenfunctions to the Hamiltonian

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \tag{4-3}$$

are solutions to a problem with full spherical symmetry, it is convenient to expand $\mathcal{V}$ in a series of normalized spherical harmonics:

$$\mathcal{V} = \sum_i \sum_l \sum_m Y_l^m(\Theta_i,\varphi_i)R_{nl}(r_i) \tag{4-4}$$

the first summation being over the i electrons of the cation. It now becomes important to know the symmetry of ligands around the cation, because $\mathcal{V}$ must transform as the totally symmetric representation in the symmetry group of the molecule. This is due to the fact that the Hamilton function for the molecule must remain totally symmetric under all symmetry operations.

By far the most important term in the expansion of $\mathcal{V}$ is the spherically symmetric term having $l = 0$:

$$\mathcal{V}_R = \sum_i \frac{1}{\sqrt{4\pi}} R_0(r_i) \tag{4-5}$$

$\mathcal{V}_R$ is responsible for the greater part of the lattice energy or heat of solution of a given cation. On the other hand, it has little effect on the electronic properties of the molecule since, to a first approximation, it will only give rise to a uniform shift of all levels with the same number of electrons.

This first approximation supposes that the radius of the free cation is the same in its ground and lower excited states; i.e., it supposes that the radial parts of the d orbitals are the same for both the ^3F and ^3P states of V^{3+}. In that case the influence of $\mathcal{V}_R$ will be felt only in the second approximation as the result of second-order interactions with highly excited configurations in which, say, a $3d$ electron is promoted to a $4d$ orbital. Now, within our framework of approximation we can neglect these effects as being small. That they are not completely negligible can be observed in very accurate work by the measurement of the absorption spectra of the complexes. It is found[6] that the term distances for the metal ion are less (extrapolated from the crystalline field theory) than what is observed for the free ion. This could be a result of the presence of $\mathcal{V}_R$ in the complete Hamiltonian,[17,48,49] but it could also be due to the mixing of configurations of the type $3d^{n-1}4s$ into $3d^n$ via the $1/r_{12}$ term or to the migration of charge from the ligands to the central ion.[15,43,47]

Of the remaining terms in the expansion of $\mathcal{V}$ many may be neglected. For example, if the effects to be described arise from degeneracies in incomplete d or f shells, all harmonics of odd order are ineffective, since any matrix representation of an odd-order potential in a basis of orbitals with the same parity vanishes identically. Further, when only d electrons are involved, all potentials after the fourth-order terms exert no influence, because the direct product of two d-orbital sets spans no representations of the rotation group of order higher than 4. And finally, as already mentioned, the potential $\mathcal{V}$ must have the same symmetry as the cationic site: if this is octahedral, $\mathcal{V}$ must remain invariant under all operations of O_h.

It is worth noticing that to good approximation $\mathcal{V}_R$ is the only component of $\mathcal{V}$ that is operative on S states in general, and therefore on closed shells and half-filled shells of maximum multiplicity in particular. Rather crudely, one may regard $\mathcal{V}_R$ as providing a spherical hole of constant potential outside which it offers an infinite potential barrier to cationic electrons. This view has the merit that it emphasizes the dependence of $\mathcal{V}_R$ on the effective ionic radius.

4-b. Octahedral Fields

Many of the principal features of the transition-metal ions emerge from the following simple model. The ions whose lower electronic states all arise from the configurations [A] $(3d)^n$ are situated in fields of perfect octahedral symmetry. The question then arises as to the form of $\mathcal{V}$. Putting

$$\mathcal{V} = \mathcal{V}_R + \mathcal{V}_0 \tag{4-6}$$

we have already seen that $\mathcal{V}_R$ spans the a_{1g} representation in the group O_h. To find the proper expansion for $\mathcal{V}_0$, we consider, for reasons stated earlier, the even harmonics of order 2 and 4.

For the set $Y_2^m(\Theta,\varphi)$ $|m| \leq 2$ we have, using the formulas (3-18), that the characters in O_h symmetry are

	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
$\chi =$	5	-1	1	-1	1

The irreducible components of Y_2^m are seen to be e_g and t_{2g}.

For the set $Y_4^m(\Theta,\varphi)$ $|m| \leq 4$ we get for the characters:

	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
$\chi =$	9	0	1	1	1

By use of the character table for O_h and the formula (3-13), we obtain

$$\begin{aligned}
n_{a_{1g}} &= \tfrac{1}{24}(9\cdot 1\cdot 1 + 0\cdot 8\cdot 1 + 1\cdot 3\cdot 1 + 1\cdot 6\cdot 1 + 1\cdot 6\cdot 1) = 1\\
n_{a_{2g}} &= \tfrac{1}{24}(9\cdot 1\cdot 1 + 0\cdot 8\cdot 1 + 1\cdot 3\cdot 1 - 1\cdot 6\cdot 1 - 1\cdot 6\cdot 1) = 0\\
n_{e_g} &= \tfrac{1}{24}(9\cdot 1\cdot 2 - 0\cdot 8\cdot 1 + 1\cdot 3\cdot 2 + 1\cdot 6\cdot 0 + 1\cdot 6\cdot 0) = 1\\
n_{t_{1g}} &= \tfrac{1}{24}(9\cdot 1\cdot 3 + 0\cdot 8\cdot 0 - 1\cdot 3\cdot 1 + 1\cdot 6\cdot 1 - 1\cdot 6\cdot 1) = 1\\
n_{t_{2g}} &= \tfrac{1}{24}(9\cdot 1\cdot 3 + 0\cdot 8\cdot 0 - 1\cdot 3\cdot 1 - 1\cdot 6\cdot 1 + 1\cdot 6\cdot 1) = 1
\end{aligned}$$

The irreducible components are thus a_{1g}, e_g, t_{1g}, and t_{2g}. In other words, one linear combination of the $Y_4^m(\Theta,\varphi)$ will transform as an a_{1g} representation in O_h. In order to find this linear combination of spherical harmonics, we will look upon their transformation properties. A choice must now be made: about what axis are we going to quantize the system? Let us first take the C_4 axis, this being at the same time our z axis, Fig. 3-3. Then $\hat{C}_4$ implies

$$\hat{C}_4\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} y \\ -x \\ z \end{pmatrix} \tag{4-7}$$

By operating upon the spherical harmonics of order 4 (Appendix I) with

$\hat{C}_4$, we have, using the phases prescribed by Condon and Shortley,[5]

$$\hat{C}_4 \begin{pmatrix} Y_4^4 \\ Y_4^3 \\ Y_4^2 \\ Y_4^1 \\ Y_4^0 \\ Y_4^{-1} \\ Y_4^{-2} \\ Y_4^{-3} \\ Y_4^{-4} \end{pmatrix} = \begin{pmatrix} Y_4^4 \\ iY_4^3 \\ -Y_4^2 \\ -iY_4^1 \\ Y_4^0 \\ iY_4^{-1} \\ -Y_4^{-2} \\ -iY_4^{-3} \\ Y_4^{-4} \end{pmatrix} \tag{4-8}$$

Since $\mathcal{V}_0$ must transform as a_{1g}, we have $\hat{C}_4\mathcal{V}_0 = \mathcal{V}_0$, and the transformation properties (4-8) then make it obvious that we can only have

$$\mathcal{V}_0 = aY_4^4 + bY_4^0 + cY_4^{-4} \tag{4-9}$$

or, paying no attention to normalization,

$$\mathcal{V}_0 = Y_4^0 + dY_4^4 + eY_4^{-4} \tag{4-10}$$

We observe further that $\hat{C}_2'Y_4^4 = Y_4^{-4}$ and that $\hat{C}_2'Y_4^{-4} = Y_4^4$. Since $\hat{C}_2'Y_4^0 = Y_4^0$, it is seen that $d = e$ in order for the trace under C_2' to be 1.

$$\mathcal{V}_0 = Y_4^0 + d(Y_4^4 + Y_4^{-4}) \tag{4-11}$$

Finally, the three harmonics will mix under $\hat{C}_3$. Since the trace again shall be 1, we must have

$$\begin{aligned} \mathcal{V}_0 = \hat{C}_3\mathcal{V}_0 &= \tfrac{1}{8}(35x^4 - 30x^2r^2 + 3r^4) + d\sqrt{35/128}\,[(y+iz)^4 + (y-iz)^4] \\ &= \tfrac{1}{8}(35z^4 - 30z^2r^2 + 3r^4) + d\sqrt{35/128}\,[(x+iy)^4 + (x-iy)^4] \end{aligned} \tag{4-12}$$

leaving out the common factor $\sqrt{9/4\pi}$. Collecting terms in z^4, we get

$$\tfrac{3}{8} + 2d\sqrt{35/128} = 1 \qquad \text{or} \qquad d = \sqrt{5/14} \tag{4-13}$$

Then

$$\mathcal{V}_0 = Y_4^0 + \sqrt{5/14}\,(Y_4^4 + Y_4^{-4}) \tag{4-14}$$

In cartesian coordinates we have

$$\mathcal{V}_0 = x^4 + y^4 + z^4 - \tfrac{3}{5}r^4 \tag{4-15}$$

Notice that Laplace's equation $\nabla^2\mathcal{V}_0 = 0$ holds true for $\mathcal{V}_0$.

Instead of taking the fourfold axis to be the z axis, we might just as well take the threefold axis to be our axis of quantization, Fig. 3-3. We want $\mathcal{V}_0$ to be diagonal under the operation $\hat{C}_3$. Looking at the form of the spherical harmonics, we have

$$Y_l^m = P_l^m \frac{e^{im\varphi}}{\sqrt{2\pi}} \tag{4-16}$$

with

$$\hat{C}_3Y_l^m = P_l^m \frac{e^{im(\varphi+2\pi/3)}}{\sqrt{2\pi}} \tag{4-17}$$

that is, only for $m = 0$ or ± 3 do we get

$$\hat{C}_3 Y_l^m = Y_l^m \tag{4-18}$$

Consequently, with the threefold axis acting as the axis of quantization

$$\mathcal{V}_0 = Y_4^0 + aY_4^3 + bY_4^{-3} \tag{4-19}$$

Since one of the operations $\hat{C}_2'$ makes $x \to -x$, $z \to -z$, and $y \to y$,

$$\hat{C}_2'\mathcal{V}_0 = Y_4^0 - aY_4^{-3} + bY_4^{+3} \tag{4-20}$$

or

$$\mathcal{V}_0 = Y_4^0 + a(Y_4^3 - Y_4^{-3}) \tag{4-21}$$

Rotating around the C_2 axis we get, by using formula (3-40),

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \frac{1}{3} & 0 & \frac{2\sqrt{2}}{3} \\ 0 & -1 & 0 \\ \frac{2\sqrt{2}}{3} & 0 & -\frac{1}{3} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{4-22}$$

Further, since $\hat{C}_2\mathcal{V}_0 = \mathcal{V}_0$, the final result is

$$\mathcal{V}_0 = Y_4^0 + \sqrt{10/7}\,(Y_4^3 - Y_4^{-3}) \tag{4-23}$$

Although (4-14) and (4-23) look different because of the different choice of axis of quantization, they are, of course, identical.

Neglecting spin-orbit forces for the present, we see that the crystal field $\mathcal{V}$ can be split up in two parts, $\mathcal{V}_R$ and $\mathcal{V}_0$. $\mathcal{V}_R$ is very large and corresponds to the replacement of the six ligands by a spherically symmetric field. The potential $\mathcal{V}_0$, on the other hand, is more specific stereochemically and reflects the existence of the six negatively charged ligands located at the vertices of the octahedron. It will remove the orbital degeneracy of the *d* electrons, since these will prefer to avoid regions where the electronic density of the ligands is greatest. The extent to which the orbital alignments are determined by $\mathcal{V}_0$ will therefore depend upon the number of electrons present and their correlating interactions with one another.

4-c. Single *d* Electron in a Cubic Field

The effect of the octahedral field is most clearly shown by considering[7] the Ti^{3+} ion, possessing a single 3*d* electron outside the argon shell [A]. If higher configurations are ignored, $\mathcal{V}_0$ has no effect on the closed shell, but simply splits the fivefold orbital degeneracy of the ion. We have seen in Chap. 3, page 53, that the reducible representation spanned by the five *d* orbitals contains the irreducible representations e_g and t_{2g} of the octahedral group O_h, the former being doubly degenerate and the latter threefold degenerate.

Let us find the five linear combinations of the *d* orbitals transforming as

e_g and t_{2g} in the group O_h. We first take the fourfold axis as the axis of quantization, and we further indicate by a subscript to the d orbitals the value of m_l. Then $d_{m_l} = R(r)Y_2^{m_l}$. Using the phase convention of Condon and Shortley[5] and dropping the common factors of $R(r)$ and $\sqrt{5/4\pi}$, we have

$$\begin{aligned} d_{\pm 2} &= Y_2^{\pm 2} = \sqrt{3/8}\,(x \pm iy)^2 \\ d_1 &= Y_2^1 = -\sqrt{3/2}\,(x+iy)z \\ d_0 &= Y_2^0 = \tfrac{1}{2}(3z^2 - r^2) \\ d_{-1} &= Y_2^{-1} = \sqrt{3/2}\,(x - iy)z \end{aligned} \tag{4-24}$$

TABLE 4-1. TRANSFORMATION PROPERTIES OF d ORBITALS IN O_h

	E	$C_3\begin{pmatrix} x \to y \\ y \to z \\ z \to x \end{pmatrix}$	$C_2\begin{pmatrix} z \to z \\ x \to -x \\ y \to -y \end{pmatrix}$	$C_4\begin{pmatrix} z \to z \\ x \to y \\ y \to -x \end{pmatrix}$	$C_2'\begin{pmatrix} z \to -z \\ x \to y \\ y \to x \end{pmatrix}$
d_2	d_2	$-\sqrt{6/16}\,d_0 - \sqrt{1/16}\,d_2 - \sqrt{1/16}\,d_{-2} - \sqrt{4/16}\,d_1 - \sqrt{4/16}\,d_{-1}$	d_2	$-d_2$	$-d_{-2}$
d_1	d_1	$+\frac{i}{2}d_2 - \frac{i}{2}d_{-2} + \frac{i}{2}d_1 - \frac{i}{2}d_{-1}$	$-d_1$	$-id_1$	id_{-1}
d_0	d_0	$-\sqrt{2/8}\,d_0 + \sqrt{3/8}\,d_2 + \sqrt{3/8}\,d_{-2}$	d_0	d_0	d_0
d_{-1}	d_{-1}	$-\frac{i}{2}d_2 + \frac{i}{2}d_{-2} + \frac{i}{2}d_1 - \frac{i}{2}d_{-1}$	$-d_{-1}$	id_{-1}	$-id_1$
d_{-2}	d_{-2}	$-\sqrt{6/16}\,d_0 - \sqrt{1/16}\,d_2 - \sqrt{1/16}\,d_{-2} + \sqrt{4/16}\,d_1 + \sqrt{4/16}\,d_{-1}$	d_{-2}	$-d_{-2}$	$-d_2$
χ	5	-1	1	-1	1

In Table 4-1 we notice first of all that the reducible representation χ is composed of the irreducible representations e_g and t_{2g}, as of course it must be. Since the system has been quantized along the fourfold axis, it would be natural to demand that the wave functions be diagonal with respect to this axis. This is seen to be the case, and d_1, d_0, and d_{-1} are further seen to be "pure" orbitals, whereas d_2 and d_{-2} can mix under a fourfold rotation. Then

$$\psi_\pm = ad_2 \pm bd_{-2} \tag{4-25}$$

By the application of $\hat{C}_2'$ we get $a = b = 1$, and with the normalization factor of $1/\sqrt{2}$ included:

$$\psi_\pm = \frac{1}{\sqrt{2}}\,(d_2 \pm d_{-2}) \tag{4-26}$$

Then

	E	C_3	C_2	C_4	C_2'
ψ_+	ψ_+	$-\sqrt{3/4}\;d_0 - \sqrt{1/4}\;\psi_+$	ψ_+	$-\psi_+$	$-\psi_+$
ψ_-	ψ_-	$-\sqrt{1/2}\;d_1 - \sqrt{1/2}\;d_{-1}$	ψ_-	$-\psi_-$	ψ_-

We notice that ψ_+ mixes with d_0 and that ψ_- mixes with d_1 and d_{-1} under $\hat{C}_3$. Since the trace under $\hat{C}_4$ of both e_g and t_{2g} is rational, we must group d_1 and d_{-1} together. Our final result is then

$$
\begin{aligned}
&t_{2g}^{0} = \frac{1}{\sqrt{2}}(d_2 - d_{-2}) \qquad t_{2g}^{-} = d_{-1} \qquad t_{2g}^{+} = d_1 \\
&e_g^{a} = d_0 \qquad e_g^{b} = \frac{1}{\sqrt{2}}(d_2 + d_{-2})
\end{aligned}
\tag{4-27}
$$

For many purposes it is nice to operate with real positive wave functions. Such orbitals can easily be obtained, although they are no longer eigenfunctions of the $\hat{C}_4$ operator. We notice that the e_g orbitals are real and transform like

$$
e_g \begin{cases} d_{x^2-y^2} = \dfrac{1}{\sqrt{2}}(d_2 + d_{-2}) = \dfrac{\sqrt{3}}{2}(x^2 - y^2) \\ d_{z^2} = d_0 = \tfrac{1}{2}(3z^2 - r^2) \end{cases}
\tag{4-28}
$$

By taking linear combinations of d_{-1} and d_1, we get the real wave functions

$$
t_{2g} \begin{cases} d_{xy} = \dfrac{1}{i\sqrt{2}}(d_2 - d_{-2}) = \sqrt{3}\,(xy) \\ d_{xz} = -\dfrac{1}{\sqrt{2}}(d_1 - d_{-1}) = \sqrt{3}\,(xz) \\ d_{yz} = -\dfrac{1}{i\sqrt{2}}(d_1 + d_{-1}) = \sqrt{3}\,(yz) \end{cases}
\tag{4-29}
$$

The two ways of writing the orbitals are, of course, equivalent and supplementary to each other.

Notice that the densities of the e_g electrons are directed toward the vertices of the octahedron, i.e., toward the ligands, whereas those of the t_{2g} electrons avoid these regions, Fig. 4-1. Since the ligands are either anions or molecules the negative ends of whose dipoles are directed toward the cation, it is evident that the t_{2g} orbitals are more stable than the e_g orbitals. Explicitly, their energies may be written

$$
\begin{aligned}
E(e_g) &= \epsilon_0 + \int \phi^*(e_g^a)\mathcal{V}_0\phi(e_g^a)\,d\tau = \epsilon_0 + x \\
E(t_{2g}) &= \epsilon_0 + \int \phi^*(t_{2g}^0)\mathcal{V}_0\phi(t_{2g}^0)\,d\tau = \epsilon_0 + y
\end{aligned}
\tag{4-30}
$$

By convention,[4] the overall splitting of a single d electron under $\mathcal{V}_0$ is set equal to $10Dq$, where $Dq > 0$. Then

$$
10Dq = x - y \tag{4-31}
$$

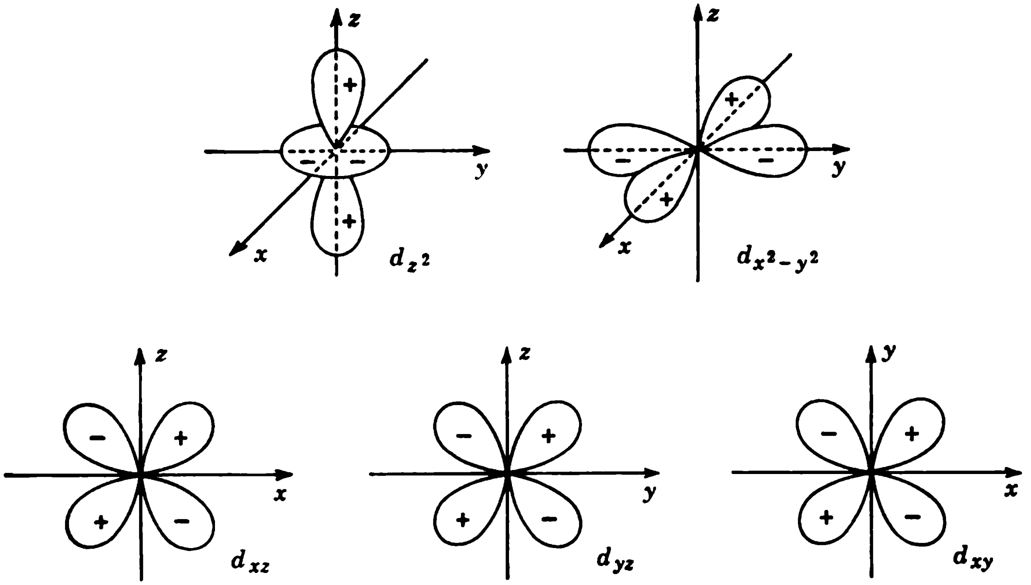

FIG. 4-1. e_g and t_{2g} electronic densities.

x and y may be determined by noting that $\mathcal{V}_0$ makes no contribution to S states—such as that found by filling all d orbitals with electrons. Then

$$\begin{aligned} 10Dq &= x - y \\ 0 &= 4x + 6y \end{aligned} \tag{4-32}$$

or

$$x = 6Dq \qquad \text{and} \qquad y = -4Dq \tag{4-33}$$

$$6Dq = \int \phi^*(e_g{}^a)\mathcal{V}_0\phi(e_g{}^a)\, d\tau$$

or

$$-4Dq = \int \phi^*(t_{2g}^{\circ})\mathcal{V}_0\phi(t_{2g}^{\circ})\, d\tau \tag{4-34}$$

The situation is pictured in Fig. 4-2. The original fivefold degenerate d orbitals are split up by the inclusion of the octahedral field $\mathcal{V}_0$. The quantity Dq is usually treated as a semiempirical parameter; i.e., it is taken from experiments.

The ligands are sometimes replaced by supposedly equivalent point charges, dipoles, and so forth, in which case the integrations can be performed.[7–9] Dq turns out in this simple crystalline field model to be a function of Z, the "effective charge" of the metal ion, the bond distance from the metal ion to the ligands, and the value of the formal charges, dipoles,

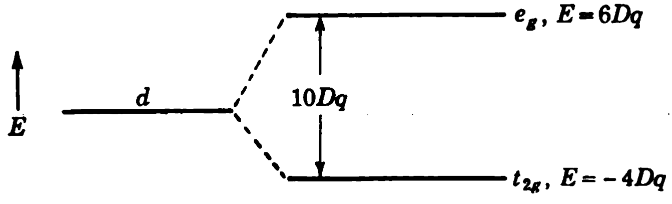

FIG. 4-2. Splitting of the d orbitals in an octahedral field.

etc., found upon the ligands. By taking suitable values of these new parameters, a reasonable value of Dq can be obtained, but it is clear that such a procedure only tries to avoid the issue: a calculation of Dq based on the complete Hamiltonian of the molecule. This is, however, not an easy thing to do,[10,11] but it has been successfully achieved by Shulman and Sugano.[52] The specific performance of the integration of Dq is, for practical use of the crystal field theory, of little importance, since Dq is always to be determined semiempirically.

Instead of quantizing along the fourfold axis, one might of course just as well use the threefold axis as the axis of quantization. Here we get that the wave functions are diagonal along the threefold axis C_3:

$$\begin{array}{c|l} & C_3 \\ \hline d_2 & \left(-\frac{1}{2} - i\frac{\sqrt{3}}{2}\right) d_2 \\ d_1 & \left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right) d_1 \\ d_0 & \quad d_0 \\ d_{-1} & \left(-\frac{1}{2} - i\frac{\sqrt{3}}{2}\right) d_{-1} \\ d_{-2} & \left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right) d_{-2} \end{array} \tag{4-35}$$

Notice that d_2 and d_{-1} transform in the same way under $\hat{C}_3$ and therefore can mix together. The same holds true for d_1 and d_{-2}. d_0, on the other hand, transforms in a unique way. We then pick out d_0 and operate upon it with $\hat{C}_2$. Hence by the use of formula (3-40) $x \rightarrow \frac{1}{3}x + \frac{2\sqrt{2}}{3}z$, $y \rightarrow -y$, and $z \rightarrow \frac{2\sqrt{2}}{3}x - \frac{1}{3}z$, and with $d_0 = d_{z^2}$

$$d_{z^2} \xrightarrow{C_2} -\frac{1}{3}d_{z^2} + \frac{2\sqrt{2}}{3}\left[\sqrt{\frac{2}{3}}\,d_{x^2-y^2} - \sqrt{\frac{1}{3}}\,d_{xz}\right] \tag{4-36}$$

where for simplicity we use the real wave functions (4-29). Now

$$\sqrt{\frac{2}{3}}\,d_{x^2-y^2} - \sqrt{\frac{1}{3}}\,d_{xz} = \sqrt{\frac{2}{3}}\frac{1}{\sqrt{2}}(d_2 + d_{-2}) - \sqrt{\frac{1}{3}}\left(-\frac{1}{\sqrt{2}}\right)(d_1 - d_{-1}) \tag{4-37}$$

$$= \left(\sqrt{\frac{1}{3}}\,d_2 - \sqrt{\frac{1}{6}}\,d_{-1}\right) + \left(\sqrt{\frac{1}{3}}\,d_2 + \sqrt{\frac{1}{6}}\,d_{+1}\right) \tag{4-38}$$

where the d orbitals are collected according to how they are able to mix together. Demanding that the two combinations are to be normalized to unity, e.g.,

$$\int a^*(\sqrt{1/3}\,d_2 - \sqrt{1/6}\,d_{-1})^*\,a(\sqrt{1/3}\,d_2 - \sqrt{1/6}\,d_{-1})\,d\tau = 1 \tag{4-39}$$

TABLE 4-2. TRANSFORMATION PROPERTIES OF t_{2g} AND e_g ORBITALS

	E	C_3	C_2	C_4	C_2'
$t_{2g}^{\circ} = d_0$	t_{2g}°	t_{2g}°	$-\frac{1}{3}t_{2g}^{\circ} + \frac{2}{3}t_{2g}^{a} + \frac{2}{3}t_{2g}^{b}$	$-\frac{1}{3}t_{2g}^{\circ} - \left(\frac{1}{3} - \frac{\sqrt{3}}{3}i\right)t_{2g}^{a} - \left(\frac{1}{3} + \frac{\sqrt{3}}{3}i\right)t_{2g}^{b}$	t_{2g}°
$t_{2g}^{a} = \sqrt{\frac{2}{3}}\,d_2 - \sqrt{\frac{1}{3}}\,d_{-1}$	t_{2g}^{a}	$\left(-\frac{1}{2} - i\frac{\sqrt{3}}{2}\right)t_{2g}^{a}$	$\frac{2}{3}t_{2g}^{\circ} - \frac{1}{3}t_{2g}^{a} + \frac{2}{3}t_{2g}^{b}$	$-\left(\frac{1}{3} + i\frac{\sqrt{3}}{3}\right)t_{2g}^{a} - \frac{1}{3}t_{2g}^{b} - \left(\frac{1}{3} - \frac{\sqrt{3}}{3}i\right)t_{2g}^{\circ}$	t_{2g}^{b}
$t_{2g}^{b} = \sqrt{\frac{2}{3}}\,d_{-2} + \sqrt{\frac{1}{3}}\,d_1$	t_{2g}^{b}	$\left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right)t_{2g}^{b}$	$\frac{2}{3}t_{2g}^{\circ} + \frac{2}{3}t_{2g}^{a} - \frac{1}{3}t_{2g}^{b}$	$-\frac{1}{3}t_{2g}^{a} - \left(\frac{1}{3} + \frac{\sqrt{3}}{3}i\right)t_{2g}^{\circ} + \left(-\frac{1}{3} + \frac{\sqrt{3}}{3}i\right)t_{2g}^{b}$	t_{2g}^{a}
χ	3	0	−1	−1	1
$e_g^{a} = \sqrt{\frac{1}{3}}\,d_2 + \sqrt{\frac{2}{3}}\,d_{-1}$	e_g^{a}	$\left(-\frac{1}{2} - i\frac{\sqrt{3}}{2}\right)e_g^{a}$	e_g^{a}	e_g^{b}	e_g^{b}
$e_g^{b} = \sqrt{\frac{1}{3}}\,d_{-2} - \sqrt{\frac{2}{3}}\,d_1$	e_g^{b}	$\left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right)e_g^{b}$	e_g^{b}	e_g^{a}	e_g^{a}
χ	2	−1	2	0	0

we get that both a and b equal $\sqrt{2}$. By multiplying the $\sqrt{2}$ inside the parentheses in (4-38), we obtain

$$d_0 \xrightarrow{C_3} -\tfrac{1}{3}\,d_0 + \tfrac{2}{3}\left(\sqrt{\tfrac{2}{3}}\,d_2 - \sqrt{\tfrac{1}{3}}\,d_{-1}\right) + \tfrac{2}{3}\left(\sqrt{\tfrac{2}{3}}\,d_{-2} + \sqrt{\tfrac{1}{3}}\,d_1\right) \tag{4-40}$$

We know that the d orbitals span one threefold t_{2g} level and one twofold e_g level in an octahedral field. Consequently, we try

$$t_{2g} = \begin{cases} d_0 \\ \sqrt{\tfrac{2}{3}}\,d_2 - \sqrt{\tfrac{1}{3}}\,d_{-1} \\ \sqrt{\tfrac{2}{3}}\,d_{-2} + \sqrt{\tfrac{1}{3}}\,d_1 \end{cases} \tag{4-41}$$

and since the e_g level must be orthogonal upon the t_{2g} orbitals,

$$e_g = \begin{cases} \sqrt{\tfrac{1}{3}}\,d_2 + \sqrt{\tfrac{2}{3}}\,d_{-1} \\ \sqrt{\tfrac{1}{3}}\,d_{-2} - \sqrt{\tfrac{2}{3}}\,d_1 \end{cases} \tag{4-42}$$

The transformation properties of (4-41) and (4-42) are collected in Table 4-2.

If instead we take combinations of the real d orbitals with the threefold axis as the axis of quantization, we get

$$t_{2g} = \begin{cases} \sqrt{\tfrac{2}{3}}\,d(x^2 - y^2) - \sqrt{\tfrac{1}{3}}\,d(xz) & = t_{2g}^{+} \\ \sqrt{\tfrac{2}{3}}\,d(xy) + \sqrt{\tfrac{1}{3}}\,d(yz) & = t_{2g}^{-} \\ d(z^2) & = t_{2g}^{\circ} \end{cases} \tag{4-43}$$

$$e_g = \begin{cases} \sqrt{\tfrac{1}{3}}\,d(x^2 - y^2) + \sqrt{\tfrac{2}{3}}\,d(xz) & = e_g^{+} \\ \sqrt{\tfrac{1}{3}}\,d(xy) - \sqrt{\tfrac{2}{3}}\,d(yz) & = e_g^{-} \end{cases} \tag{4-44}$$

The transformation scheme of (4-43) and (4-44) is found in Table 4-3.

TABLE 4-3. TRANSFORMATION PROPERTIES OF t_{2g} AND e_g ORBITALS

	E	C_3	C_2	C_4	C_2'
t_{2g}^{+}	t_{2g}^{+}	$-\frac{1}{2}t_{2g}^{+} - \frac{\sqrt{3}}{2}t_{2g}^{-}$	$\frac{1}{3}t_{2g}^{+} + \frac{2\sqrt{2}}{3}t_{2g}^{\circ}$	$-\frac{2}{3}t_{2g}^{+} + \frac{\sqrt{3}}{3}t_{2g}^{-} - \frac{\sqrt{2}}{3}t_{2g}^{\circ}$	t_{2g}^{+}
t_{2g}^{-}	t_{2g}^{-}	$-\frac{1}{2}t_{2g}^{-} + \frac{\sqrt{3}}{2}t_{2g}^{+}$	$-t_{2g}^{-}$	$-\frac{\sqrt{3}}{3}t_{2g}^{+} + \frac{\sqrt{6}}{3}t_{2g}^{\circ}$	$-t_{2g}^{-}$
t_{2g}°	t_{2g}°	t_{2g}°	$-\frac{1}{3}t_{2g}^{\circ} + \frac{2\sqrt{2}}{3}t_{2g}^{+}$	$-\frac{1}{3}t_{2g}^{\circ} - \frac{\sqrt{2}}{3}t_{2g}^{+} - \frac{\sqrt{6}}{3}t_{2g}^{-}$	t_{2g}°
χ	3	0	-1	-1	1
e_g^{+}	e_g^{+}	$-\frac{1}{2}e_g^{+} - \frac{\sqrt{3}}{2}e_g^{-}$	e_g^{+}	e_g^{+}	e_g^{+}
e_g^{-}	e_g^{-}	$-\frac{1}{2}e_g^{-} + \frac{\sqrt{3}}{2}e_g^{+}$	e_g^{-}	$-e_g^{-}$	$-e_g^{-}$
χ	2	-1	2	0	0

The electronic spectrum of, say, the $Ti(H_2O)_6^{3+}$ ion would be described[7] as arising from the transition $t_{2g} \rightarrow e_g$, with an excitation energy of $10Dq$. If the symmetry is close to octahedral, we should expect a single weak band, since no change in parity occurs. Such a band is indeed found for the ion with a maximum at 4900 A corresponding to $Dq = 2040\ \text{cm}^{-1}$.

In atomic spectroscopy it is found that the terms arising from n (≤ 5) d electrons outside an argon shell are the same as those arising from $10 - n$ electrons outside the same shell or, equivalently, of n holes in the completed d^{10} shell. Since the interaction between two holes yields the same repulsive Coulombic term as between two electrons, the terms are in the same order for both d^n and d^{10-n} configurations. However, since the magnetic moment due to the circulation of a positron is the opposite of that due to an electron, the multiplet structure is inverted.[5]

A similar reciprocity exists in crystal field theory, say, between Ti^{3+} and Cu^{++}, whose configuration is d^9. It is clear that the ^2D state of Cu^{++} also splits into ^2E_g and $^2T_{2g}$ terms. But the order of the levels is now inverted because the electrostatic field due to the ligands has an effect on electrons opposite to that it has on holes.[12]

The spectrum of the Cu^{++} aquo complex should then consist of a single weak band, in exact analogy with the Ti^{3+} aquo complex. Such a very broad band is also found[13] with a maximum around 8000 A. In order to explain the finer details of this band system, we must invoke considerable contribution from fields of lower symmetry;[9,14,15] the hydrated ion is a distorted octahedron. These effects will be treated in Chap. 5.

4-d. Weak Fields

In dealing with systems with more than one electron or one hole the classification on page 58 is convenient. The case we shall pursue first is the weak-field limit,[2] where $\xi(r)\mathbf{l} \cdot \mathbf{s} < \mathcal{V} < e^2/r_{12}$, that is, the crystal field $\mathcal{V}$ is small with respect to the separation of different groups of multiplets in the atomic spectra of the gaseous metal ion.

In the weak-field case the quantum numbers L and S of the central ion retain their validity, and we have only to determine how a given (L,S) scheme is split by the octahedral field, without considering the possibility that the different levels may interact under it. The nonvanishing matrix elements of the d electrons quantized along the fourfold axis with $\mathcal{V}_0$ are seen from (4-27) and (4-33) to be

$$\begin{aligned}
(d_{\pm2}|\mathcal{V}_0|d_{\pm2}) &= Dq \\
(d_{\pm2}|\mathcal{V}_0|d_{\mp2}) &= 5Dq \\
(d_{\pm1}|\mathcal{V}_0|d_{\pm1}) &= -4Dq \\
(d_0|\mathcal{V}_0|d_0) &= 6Dq
\end{aligned} \tag{4-45}$$

If instead the axis of quantization is the threefold axis, we get by using

(4-41), (4-42) and Table 2-1,

$$\begin{aligned}
(d_{\pm 2}|\mathcal{V}_0|d_{\pm 2}) &= -{}^{2}\!/_{3}Dq \\
(d_{\pm 1}|\mathcal{V}_0|d_{\pm 1}) &= {}^{8}\!/_{3}Dq \\
(d_0\,|\mathcal{V}_0|d_0) &= -4Dq \\
(d_{\pm 2}|\mathcal{V}_0|d_{\mp 1}) &= (d_{\mp 1}|\mathcal{V}_0|d_{\pm 2}) = \pm\, {}^{10}\!/_{3}\sqrt{2}\,Dq
\end{aligned} \tag{4-46}$$

The qualitative features of the crystalline field splittings due to a cubic field are most simply obtained by group theory. Thus by applying (3-18) to the states composed by the (d^n) electrons:

$$\begin{aligned}
S &\rightarrow A_1 \\
P &\rightarrow T_1 \\
D &\rightarrow E + T_2 \\
F &\rightarrow A_2 + T_1 + T_2 \\
G &\rightarrow A_1 + E + T_1 + T_2 \\
H &\rightarrow E + 2T_1 + T_2
\end{aligned} \tag{4-47}$$

and so forth.

As usual, the states labeled S, P, D, F, G, and H have the values of L equal to 0, 1, 2, 3, 4, and 5. If we want to find the linear combinations of orbitals transforming correctly, we proceed by using group theory. For instance, for an F state we can construct the full transformation scheme for the set of spherical harmonics $Y_3^3 \rightarrow Y_3^{-3}$ and then find the linear combinations which transform as A_2, T_1, and T_2, by using the scheme indicated on page 44. There is, however, a shortcut which can be used.

The cubic field $\mathcal{V}_0$ Eq. (4-14), contains only terms having $M_L = 0$ or ± 4. Using this property of $\mathcal{V}_0$, we then see that, in the set $L = 3$ and $M_L = (3,2,1,0,-1,-2,-3)$, $M_L = 0$ can only have a matrix element with itself, because there are no states present with $M_L = \pm 4$. $M_L = 0$ is therefore an eigenstate. Calling the state $L = 3$, $M_L = M$ Ψ_M, we have the general expression for the wanted matrix elements

$$(\Psi_M|\mathcal{V}_0|\Psi_{M'}) \neq 0 \tag{4-48}$$

or in analogy with (2-45)

$$M' - M = 0 \text{ or } \pm 4 \tag{4-49}$$

Hence, Ψ_1 can be coupled to Ψ_{-3} via the crystalline field. An eigenstate to $\mathcal{V}_0$ can then be made by a proper linear combination of Ψ_1 and Ψ_{-3}.

For $L = 3$ it is seen that the eigenstates divide up into groups, Ψ_0 being in a group all by itself and (Ψ_1,Ψ_{-3}), (Ψ_{-1},Ψ_3), and (Ψ_2,Ψ_{-2}) being the other groups.

Operating with $\hat{C}_3$ upon Ψ_0, we get

$$\hat{C}_3\Psi_0 = \frac{1}{i\sqrt{2}}\left[\sqrt{\frac{3}{8}}\,\Psi_1 + \sqrt{\frac{5}{8}}\,\Psi_{-3}\right] + \frac{1}{i\sqrt{2}}\left[\sqrt{\frac{3}{8}}\,\Psi_{-1} + \sqrt{\frac{5}{8}}\,\Psi_3\right]$$

A set of three linearly independent states can be taken as

$$\begin{gathered}\sqrt{3/8}\,\Psi_1 + \sqrt{5/8}\,\Psi_{-3}\\ \sqrt{3/8}\,\Psi_{-1} + \sqrt{5/8}\,\Psi_3\\ \Psi_0\end{gathered} \tag{4-50}$$

It is further easy to see, by use of the transformation properties and the character table for the group O_h, that the set (4-50) transforms like T_1. Two other states must then be

$$\begin{gathered}\sqrt{5/8}\,\Psi_1 - \sqrt{3/8}\,\Psi_{-3}\\ \sqrt{5/8}\,\Psi_{-1} - \sqrt{3/8}\,\Psi_3\end{gathered} \tag{4-51}$$

Operating with $\hat{C}_3$ upon one of these functions yields

$$\begin{aligned}\hat{C}_3\left(\sqrt{\frac{5}{8}}\Psi_1 - \sqrt{\frac{3}{8}}\Psi_{-3}\right) = &-\frac{i}{2}\left(\sqrt{\frac{5}{8}}\Psi_1 - \sqrt{\frac{3}{8}}\Psi_{-3}\right)\\ &+\frac{i}{2}\left(\sqrt{\frac{5}{8}}\Psi_{-1} - \sqrt{\frac{3}{8}}\Psi_3\right) + \frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}(\Psi_2 + \Psi_{-2})\end{aligned}$$

As before, we find that the set

$$\begin{gathered}\sqrt{5/8}\,\Psi_1 - \sqrt{3/8}\,\Psi_{-3}\\ \sqrt{5/8}\,\Psi_{-1} - \sqrt{3/8}\,\Psi_3\\ \frac{1}{\sqrt{2}}(\Psi_2 + \Psi_{-2})\end{gathered} \tag{4-52}$$

transforms like T_2. The only set left is then

$$\frac{1}{\sqrt{2}}(\Psi_2 - \Psi_{-2}) \tag{4-53}$$

and inspection of the transformation properties soon reveals that the function (4-53) indeed transforms like A_2. A table of proper eigenfunctions can be found in Appendix II.

Now let us calculate the energies of the states ${}^3A_{2g}$, ${}^3T_{2g}$, and ${}^3T_{1g}$ in the $(3d)^2$ system coming from ${}^3F$ in the weak-field limit. From Eqs. (2-19), (2-20), and (2-25) we have

$$\Psi(3,3,1,1) = \Psi_3 = |2^+,1^+| \tag{4-54}$$

$$\Psi(3,2,1,1) = \Psi_2 = |2^+,0^+| \tag{4-55}$$

$$\Psi(3,1,1,1) = \Psi_1 = \sqrt{3/5}\,|2^+,-1^+| + \sqrt{2/5}\,|1^+,0^+| \tag{4-56}$$

By operating with Eq. (2-20) upon the last function, we obtain

$$\Psi(3,0,1,1) = \Psi_0 = \sqrt{1/5}\,|2^+,-2^+| + \sqrt{4/5}\,|1^+,-1^+| \tag{4-57}$$

and by further application of Eq. (2-10), we get

$$\Psi(3,-2,1,1) = \Psi_{-2} = |0^+,-2^+| \tag{4-58}$$

The energy of the state $^3A_{2g}$ is then

$$\begin{aligned} E(^3A_{2g}) &= \int \frac{1}{\sqrt{2}} (\Psi_2 - \Psi_{-2})^* \mathcal{V}_0 \frac{1}{\sqrt{2}} (\Psi_2 - \Psi_{-2})\, d\tau \\ &= \frac{1}{2} \int |2^+,0^+|\mathcal{V}_0|2^+,0^+|\, d\tau - \frac{1}{2} \int |2^+,0^+|\mathcal{V}_0|0^+,-2^+|\, d\tau \\ &\quad - \frac{1}{2} \int |0^+,-2^+|\mathcal{V}_0|2^+,0^+|\, d\tau + \frac{1}{2} \int |0^+,-2^+|\mathcal{V}_0|0^+,-2^+|\, d\tau \end{aligned} \tag{4-59}$$

By expanding the determinants and using (4-45), we get

$$\begin{aligned} E(^3A_{2g}) &= (d_2|\mathcal{V}_0|d_2) + (d_0|\mathcal{V}_0|d_0) + (d_2|\mathcal{V}_0|d_{-2}) \\ &= Dq + 6Dq + 5Dq = 12Dq \end{aligned} \tag{4-60}$$

For the $^3T_{2g}$, using the third wave function in the set (4-52), the energy is

$$\begin{aligned} E(^3T_{2g}) &= \int |2^+,0^+|\mathcal{V}_0|2^+,0^+|\, d\tau + \int |2^+,0^+|\mathcal{V}_0|0^+,-2^+|\, d\tau \\ &= Dq + 6Dq - 5Dq = 2Dq \end{aligned} \tag{4-61}$$

and finally for the $^3T_{1g}$ using the Ψ_0 function:

$$\begin{aligned} E(^3T_{1g}) &= \tfrac{1}{5} \int |2^+,-2^+|\mathcal{V}_0|2^+,-2^+|\, d\tau + \tfrac{4}{5} \int |1^+,-1^+|\mathcal{V}_0|1^+,-1^+|\, d\tau \\ &= \tfrac{1}{5}(2Dq) + \tfrac{4}{5}(-8Dq) = -6Dq \end{aligned} \tag{4-62}$$

For the terms coming from the $(3d)^2$ ^1D term we have from Eq. (2-24):

$$\Psi_2 = \Psi(2,2,0,0) = \sqrt{2/7}\, |2^+,0^-| - \sqrt{2/7}\, |2^-,0^+| - \sqrt{3/7}\, |1^+,1^-| \tag{4-63}$$

Operating upon (4-63) with (2-10) gives us

$$\begin{aligned} \Psi_1 = \Psi(2,1,0,0) &= \sqrt{3/7}\, |2^+,-1^-| - \sqrt{3/7}\, |2^-,-1^+| - \sqrt{1/14}\, |1^+,0^-| \\ &\quad + \sqrt{1/14}\, |1^-,0^+| \end{aligned} \tag{4-64}$$

$$\begin{aligned} \Psi_0 = \Psi(2,0,0,0) &= \sqrt{2/7}\, |2^+,-2^-| - \sqrt{2/7}\, |2^-,-2^+| - \sqrt{2/7}\, |0^+,0^-| \\ &\quad + \sqrt{1/14}\, |1^+,-1^-| - \sqrt{1/14}\, |1^-,-1^+| \end{aligned} \tag{4-65}$$

Since Ψ_1 transforms like one of the components of T_{2g} and Ψ_0 like one of the components of ^1E_g, we get

$$E(^1E_g) = \int \Psi_0^* \mathcal{V}_0 \Psi_0\, d\tau = 24/7\, Dq \tag{4-66}$$

$$E(^1T_{2g}) = \int \Psi_1^* \mathcal{V}_0 \Psi_1\, d\tau = -16/7\, Dq \tag{4-67}$$

For the $^3T_{1g}$ term coming from the $^3P(3d)^2$ in the weak-field limit we have, from (2-26),

$$\Psi_1 = {}^3P(1,1,1,1) = \sqrt{2/5}\, |2^+,-1^+| - \sqrt{3/5}\, |1^+,0^+| \tag{4-68}$$

Since Ψ_1 is an eigenfunction for $\mathcal{V}_0$ (see Appendix II), we have

$$\begin{aligned} E({}^3T_{1g}, {}^3P) &= \int \Psi_1^* \mathcal{V}_0 \Psi_1 \, d\tau \qquad (4\text{-}69) \\ &= \tfrac{2}{5}(Dq - 4Dq) + \tfrac{3}{5}(-4Dq + 6Dq) = 0 \end{aligned}$$

a result which ought not to surprise us if we remember that a P state does not split in a cubic crystalline field.[1]

A list of spherical harmonics up to the order 5, together with the linear combinations transforming correctly in O_h symmetry, can be found in Appendixes I and II. Tables of wave functions for the various d^n configurations are listed by Fieschi and Löwdin.[16]

A check upon the correctness of the energy values which have been found is provided by the requirement that the "center of gravity" for the split atomic levels shall be preserved.[1] We have already used this principle in order to obtain Eq. (4-33), and the expansion of the principle to more involved systems is straightforward. The "center-of-gravity" rule may be proved by noting that $\mathcal{V}_0$ makes no contribution to S states such as that found by filling all of the single electronic levels with electrons. Take for instance an f electron in a cubic field. Here we get three levels, the a_2 level being single-orbital degenerate, the t_1 and t_2 levels each being threefold degenerate. By filling the levels up with 14 electrons, we get

$$2E(a_2) + 6E(t_2) + 6E(t_1) = 0 \qquad (4\text{-}70)$$

or

$$E(a_2) + 3E(t_2) + 3E(t_1) = 0 \qquad (4\text{-}71)$$

That is, the center-of-gravity rule states: Multiply the energy of the split levels by their degeneracy factor and the result adds up to zero. This holds true too for splittings of the atomic states made up by $(3d)^n$ electrons, since the crystalline field energies of the split $D, F, G, \ldots$ states are proportional to the split states of the $d, f, g, \ldots$ electrons.

In the above example ${}^3F(d^2)$ we get

$$1E({}^3A_{2g}) + 3E({}^3T_{2g}) + 3E({}^3T_{1g}) = 0 \qquad (4\text{-}72)$$

$$12Dq + 3\,(2Dq) + 3(-6Dq) = 0 \qquad (4\text{-}73)$$

and for ${}^1D(d^2)$

$$2E({}^1E_g) + 3E({}^1T_{2g}) = 0 \qquad (4\text{-}74)$$

$$2(\tfrac{24}{7}Dq) + 3(-\tfrac{16}{7}Dq) = 0 \qquad (4\text{-}75)$$

The above considerations are valid for all crystal field calculations, so long as we do not include configuration interaction with higher terms. It is consequently always good in the *weak-field* case. If configuration interaction is included, account must be taken of the fact that the interacting levels will repel each other.

In Table 4-4 we have listed the symmetries of states into which the ground level of the free ion splits.[17] These states are listed in increasing order of excitation. Thus the ground state of the Cr^{3+} ion in the field is the orbital nondegenerate $^4A_{2g}$ state. The numbers that are given in parentheses following such term symbols assess the energies due to $\mathcal{V}_0$ in terms of the parameter Dq for a single electron; the Cr^{3+} ion, for example, is stabilized by some $12Dq$ in the limit of weak fields.

It is interesting to find how many electrons, on the average, occupy the t_{2g} orbitals and how many the e_g orbitals in the various states of the crystalline ions.[18] In general, these numbers will not be integers because, in weak fields, the tendency for maximum field stabilization, namely, the preferential filling of the t_{2g}, still is subordinate to the forces of correlation between the electronic motions. The expectation values for these occupation numbers are most easily determined from Table 4-4. With the total number of electrons equal to N and the occupation number of t_{2g} electrons equal to n, we have with XDq equal to the total energy of the term

TABLE 4-4. STATES AND ENERGIES IN WEAK OCTAHEDRAL FIELDS[17]

Ground state of Free ion	*Octahedral states and energies in Dq units*
$d\ {}^2D$	$^2T_{2g}(-4)$, $^2E_g(+6)$
$d^2\ {}^3F$	$^3T_{1g}(-6)$, $^3T_{2g}(+2)$, $^3A_{2g}(+12)$
$d^3\ {}^4F$	$^4A_{2g}(-12)$, $^4T_{2g}(-2)$, $^4T_{1g}(+6)$
$d^4\ {}^5D$	$^5E_g(-6)$, $^5T_{2g}(+4)$
$d^5\ {}^6S$	$^6A_{1g}(0)$
$d^6\ {}^5D$	$^5T_{2g}(-4)$, $^5E_g(+6)$
$d^7\ {}^4F$	$^4T_{1g}(-6)$, $^4T_{2g}(+2)$, $^4A_{2g}(+12)$
$d^8\ {}^3F$	$^3A_{2g}(-12)$, $^3T_{2g}(-2)$, $^3T_{1g}(+6)$
$d^9\ {}^2D$	$^2E_g(-6)$, $^2T_{2g}(+4)$

$$-4n + (N - n)6 = X \tag{4-76}$$

or

$$n = \frac{6N - X}{10} \tag{4-77}$$

Thus for the ground state of $(3d)^2\ T_{1g}$ with $E(T_{1g}) = -6Dq$ it is found that, on the average, nine-fifths of the two electrons must be found in the stable t_{2g} shell and only one-fifth in the unstable e_g shell. For three, four, . . . , eight electrons, the pairs of occupation numbers for the ground state are (3,0), (3,1), (3,2), (4,2), $({}^{24}\!/_{5},{}^{11}\!/_{5})$, and (6,2), respectively. In the excited states, of course, electron density is transferred from the t_{2g} to the e_g levels. Indeed, such numbers are entirely equivalent to prescriptions of energies.[18]

4-e. Strong Fields

We now turn our attention toward the third case, the "strong" crystalline field case. Here the crystal field splitting parameter Dq is large enough so that the torques exerted on the orbital motions of the electrons are determined by the lattice site symmetry, rather than by the correlative interactions between the electrons. The forces tending to repel the electrons of the central ion from the ligands cause a complete "Paschen-Back effect" which destroys the (L,S) coupling of the ion. In place of the quantum numbers L and S we now have the occupation numbers of the t_{2g} and e_g orbitals. The lowest group of states arises by filling first the t_{2g} shell and only then, when six electrons have been accommodated, the less stable e_g levels. Such an assignment of electronic configuration will in cases of degeneracy subsume a number of different states whose splitting is due to the Coulomb repulsions of the electrons. These same repulsions are, of course, responsible for the separations of the different groups of multiplets in the spectrum of the free ion.

The evaluation of appropriate energies in the limit of strong fields is quite straightforward. The energy of a term is just obtained by counting the number of electrons in the t_{2g} and e_g orbitals with $E(t_{2g}) = -4Dq$ and $E(e_g) = 6Dq$. To this must be added the intraatomic energies in terms of Slater's F_2 and F_4 parameters. This is done by the same methods used in atomic spectroscopy, because the set of orbitals t_{2g}, e_g is just another way of listing the usual atomic d orbitals. In other words, in order to evaluate the "strong-field" energies we must know the Coulomb (J) and exchange (K) integrals using a t_{2g}, e_g basis. For instance,

$$J(xz,yz) = \int (xz)^*(1)\ (yz)^*(2)\ \frac{1}{r_{12}}\ (xz)(1)\ (yz)(2)\ d\tau \tag{4-78}$$

By substituting for (xz) and (yz), we obtain

$$J(xz,yz) = \frac{1}{4}\int (d_1 - d_{-1})^*(1)\ (d_1 + d_{-1})^*(2)\ \frac{1}{r_{12}}\ (d_1 - d_{-1})(1)\ (d_1 + d_{-1})(2)\ d\tau$$

By expanding and by using Eqs. (2-45), (2-49), and (2-50), we get

$$\begin{aligned} J(xz,yz) &= \tfrac{1}{2}[J(1,1) + J(1,-1) - K(1,-1)] \\ &= F_0 - 2F_2 - 4F_4 \end{aligned} \tag{4-79}$$

Similarly for $K(xz,yz)$:

$$K(xz,yz) = \int (xz)^*(1)\ (yz)^*(2)\ \frac{1}{r_{12}}\ (yz)(1)\ (xz)(2)\ d\tau \tag{4-80}$$

By substituting and expanding,

$$K(xz,yz) = \tfrac{1}{2}K(1,-1) = 3F_2 + 20F_4 \tag{4-81}$$

In this way Tables 4-5 and 4-6 have been constructed.[19,50]

TABLE 4-5. COULOMB INTEGRALS (J) AND EXCHANGE INTEGRALS (K) OF THE SET $t_{2g}(xz,yz,xy)$ AND $e_g(x^2 - y^2, z^2)$ (REF. 19)

$$J(z^2,z^2) = J(x^2 - y^2, x^2 - y^2) = J(xy,xy) = J(xz,xz) = J(yz,yz)$$
$$= F_0 + 4F_2 + 36F_4$$
$$J(x^2 - y^2, xz) = J(x^2 - y^2, yz) = J(xy,yz) = J(xy,xz)$$
$$= J(xz,yz) = F_0 - 2F_2 - 4F_4$$
$$J(z^2,xz) = J(z^2,yz) = F_0 + 2F_2 - 24F_4$$
$$J(z^2,xy) = J(z^2,x^2 - y^2) = F_0 - 4F_2 + 6F_4$$
$$J(x^2 - y^2, xy) = F_0 + 4F_2 - 34F_4$$
$$K(xy,yz) = K(xy,xz) = K(xz,yz) = K(x^2 - y^2, xz) = K(x^2 - y^2, yz)$$
$$= 3F_2 + 20F_4$$
$$K(z^2, x^2 - y^2) = K(z^2,xy) = 4F_2 + 15F_4$$
$$K(z^2,xz) = K(z^2,yz) = F_2 + 30F_4$$
$$K(x^2 - y^2, xy) = 35F_4$$

TABLE 4-6. VALUES OF THE MATRIX ELEMENTS $(ab|1/r_{12}|cd)$ DIFFERENT FROM ZERO

a	b	c	d	$(ab\|1/r_{12}\|cd)$
(xz)	(z^2)	(xz)	$(x^2 - y^2)$	$-2\sqrt{3}\,F_2 + 10\sqrt{3}\,F_4$
(yz)	(z^2)	(yz)	$(x^2 - y^2)$	$2\sqrt{3}\,F_2 - 10\sqrt{3}\,F_4$
(xz)	(xz)	(z^2)	$(x^2 - y^2)$	$\sqrt{3}\,F_2 - 5\sqrt{3}\,F_4$
(yz)	(yz)	(z^2)	$(x^2 - y^2)$	$-\sqrt{3}\,F_2 + 5\sqrt{3}\,F_4$
(z^2)	(xy)	(xz)	(yz)	$\sqrt{3}\,F_2 - 5\sqrt{3}\,F_4$
(z^2)	(xy)	(yz)	(xz)	$\sqrt{3}\,F_2 - 5\sqrt{3}\,F_4$
(z^2)	(xz)	(xy)	(yz)	$2\sqrt{3}\,F_2 - 10\sqrt{3}\,F_4$
$(x^2 - y^2)$	(xy)	(xz)	(yz)	$3F_2 - 15F_4$
$(x^2 - y^2)$	(xy)	(yz)	(xz)	$-3F_2 + 15F_4$

As an example of a strong-field calculation we shall treat the electronic $(t_{2g})^2$ configuration. For $S = 1$ we have the following determinantal wave functions all consistent with the Pauli principle:

$$\psi_1 = |\overset{+}{(xz)}\overset{+}{(yz)}| \qquad \psi_2 = |\overset{+}{(xz)}\overset{+}{(xy)}| \qquad \psi_3 = |\overset{+}{(yz)}\overset{+}{(xy)}| \tag{4-82}$$

For $S = 0$ we get the wave functions

$$\Theta_1 = \frac{1}{\sqrt{2}}\,[|\overset{+}{(xz)}\overset{-}{(yz)}| - |\overset{-}{(xz)}\overset{+}{(yz)}|] \tag{4-83}$$

$$\Theta_2 = \frac{1}{\sqrt{2}}\,[|\overset{+}{(xz)}\overset{-}{(xy)}| - |\overset{-}{(xz)}\overset{+}{(xy)}|] \tag{4-84}$$

$$\Theta_3 = \frac{1}{\sqrt{2}}\,[|\overset{+}{(yz)}\overset{-}{(xy)}| - |\overset{-}{(yz)}\overset{+}{(xy)}|] \tag{4-85}$$

$$\Theta_4 = |\overset{+}{(xz)}\overset{-}{(xz)}| \tag{4-86}$$

$$\Theta_5 = |\overset{+}{(yz)}\overset{-}{(yz)}| \tag{4-87}$$

$$\Theta_6 = |\overset{+}{(xy)}\overset{-}{(xy)}| \tag{4-88}$$

For the triplet state ($S = 1$) the transformation properties are

	E	C_3	C_2	C_4	C_2'
ψ_1	ψ_1	ψ_3	ψ_1	ψ_1	$-\psi_1$
ψ_2	ψ_2	$-\psi_1$	$-\psi_2$	ψ_3	$-\psi_3$
ψ_3	ψ_3	$-\psi_2$	$-\psi_3$	$-\psi_2$	$-\psi_2$
χ	3	0	−1	1	−1

The character of the transformation tells us that the set ψ_1, ψ_2, and ψ_3 transforms like ${}^3T_{1g}$.

For the singlet states (4-83) to (4-88) ($S = 0$) the transformation properties are

	E	C_3	C_2	C_4	C_2'
Θ_1	Θ_1	Θ_3	Θ_1	$-\Theta_1$	Θ_1
Θ_2	Θ_2	Θ_1	$-\Theta_2$	Θ_3	$-\Theta_3$
Θ_3	Θ_3	Θ_2	$-\Theta_3$	$-\Theta_2$	$-\Theta_2$
Θ_4	Θ_4	Θ_5	Θ_4	Θ_5	Θ_5
Θ_5	Θ_5	Θ_6	Θ_5	Θ_4	Θ_4
Θ_6	Θ_6	Θ_4	Θ_6	Θ_6	Θ_6
χ	6	0	2	0	2

By use of (2-13) we see that the above reducible representation can be reduced to the sum of the irreducible representations $A_{1g} + E_g + T_{2g}$. In other words, the set Θ_1 to Θ_6 comprises a basis for three sets of wave functions transforming like ${}^1A_{1g}$, ${}^1E_g$, and ${}^1T_{2g}$.

If the direct product $t_{2g} \times t_{2g}$ is taken, we get

$$\chi: \{9 \quad 0 \quad 1 \quad 1 \quad 1\}$$

Clearly this is a reducible representation; by use of (2-13) we see that

$$t_{2g} \times t_{2g} = A_{1g} + E_g + T_{1g} + T_{2g}$$

in agreement with what is found above. This latter procedure does not tell us that it is the T_{1g} state which is the triplet state, but this can be seen by taking the antisymmetric direct product as outlined in Chap. 3.

A table giving the complete distribution of d^n levels in strong cubic crystalline field is for convenience given in Appendix III.

By inspecting the transformation table for Θ_1 to Θ_6, we notice (as indeed is obvious) that Θ_1 to Θ_3 does not mix with Θ_4 to Θ_5. Further,

	E	C_3	C_2	C_4	C_2'
Θ_1	Θ_1	Θ_3	Θ_1	$-\Theta_1$	Θ_1
Θ_2	Θ_2	Θ_1	$-\Theta_2$	Θ_3	$-\Theta_3$
Θ_3	Θ_3	Θ_2	$-\Theta_3$	$-\Theta_2$	$-\Theta_2$
χ	3	0	−1	−1	1

Hence, Θ_1, Θ_2, Θ_3 form the basis for the ${}^1T_{2g}$ state. In order to find the linear combinations of Θ_4, Θ_5, and Θ_6 transforming like E_g and A_{1g}, we diagonalize under, say, $\hat{C}_4$ and, since Θ_6 already is diagonal,

$$\hat{C}_4 \begin{pmatrix} \Theta_4 \\ \Theta_5 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \Theta_4 \\ \Theta_5 \end{pmatrix} \tag{4-89}$$

Then

$$\begin{vmatrix} 0 - \lambda & 1 \\ 1 & 0 - \lambda \end{vmatrix} = 0 \tag{4-90}$$

or

$$\lambda = \pm 1$$

Hence

$$\hat{C}_4 \begin{pmatrix} \frac{1}{\sqrt{2}} (\Theta_4 + \Theta_5) \\ \frac{1}{\sqrt{2}} (\Theta_4 - \Theta_5) \\ \Theta_6 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} (\Theta_4 + \Theta_5) \\ \frac{1}{\sqrt{2}} (\Theta_4 - \Theta_5) \\ \Theta_6 \end{pmatrix} \tag{4-91}$$

Because the characters of E_g and A_{1g} under C_4 are respectively zero and one, we can take $(1/\sqrt{2})(\Theta_4 - \Theta_5)$ as *one* component of E_g, $E_g{}^a$. On the other hand, for the ${}^1A_{1g}$ level

$$\hat{C}_3 \left(a \frac{1}{\sqrt{2}} (\Theta_4 + \Theta_5) + b\Theta_6 \right) = (1) \left[a \frac{1}{\sqrt{2}} (\Theta_4 + \Theta_5) + b\Theta_6 \right] \tag{4-92}$$

giving us a relation to evaluate a and b.

$$\hat{C}_3 \left(a \frac{1}{\sqrt{2}} (\Theta_4 + \Theta_5) + b\Theta_6 \right)$$

$$= a \frac{1}{\sqrt{2}} (\Theta_5 + \Theta_6) + b\Theta_4 \equiv a \frac{1}{\sqrt{2}} (\Theta_4 + \Theta_5) + b\Theta_6 \tag{4-93}$$

or

$$a = \sqrt{2}\, b \tag{4-94}$$

Further, because $a^2 + b^2 = 1$, we get

$$\psi({}^1A_{1g}) = \sqrt{\tfrac{1}{3}}\, \Theta_4 + \sqrt{\tfrac{1}{3}}\, \Theta_5 + \sqrt{\tfrac{1}{3}}\, \Theta_6 \tag{4-95}$$

The last component of ${}^1E_g$ must then be orthogonal upon $\psi({}^1A_{1g})$ and $(1/\sqrt{2})(\Theta_4 - \Theta_5)$, that is:

$$\psi({}^1E_g{}^b) = \sqrt{\tfrac{1}{6}}\, \Theta_4 + \sqrt{\tfrac{1}{6}}\, \Theta_5 - \sqrt{\tfrac{4}{6}}\, \Theta_6 \tag{4-96}$$

Having determined the wave functions, we find the energies by the use of the formalism in Sec. 2-*g* and Tables 4-5 and 4-6.

$$\begin{aligned} E(^3T_{1g}) &= E(\psi_1) = J(xz,yz) - K(xz,yz) \\ &= F_0 - 5F_2 - 24F_4 \end{aligned} \tag{4-97}$$

$$\begin{aligned} E(^1T_{2g}) &= E(\Theta_1) = J(xz,yz) + K(xz,yz) \\ &= F_0 + F_2 + 16F_4 \end{aligned} \tag{4-98}$$

$$\begin{aligned} E(^1E_g) &= E\left(\frac{1}{\sqrt{2}}(\Theta_4 - \Theta_5)\right) = \frac{1}{2}J(xz,xz) + \frac{1}{2}J(yz,yz) - K(xz,yx) \\ &= F_0 + F_2 + 16F_4 \end{aligned} \tag{4-99}$$

$$\begin{aligned} E(^1A_{1g}) &= E(\sqrt{1/3}\,\Theta_4 + \sqrt{1/3}\,\Theta_5 + \sqrt{1/3}\,\Theta_6) \\ &= 1/3 J(xz,xz) + 1/3 J(yz,yz) + 1/3 J(xy,xy) + 2/3 K(xz,yz) \\ &\qquad + 2/3 K(xz,xy) + 2/3 K(yz,xy) \\ &= F_0 + 10F_2 + 76F_4 \end{aligned} \tag{4-100}$$

To all these energies we must add $2E(t_{2g}) = -8Dq$, and the final result is then

$$E(t_{2g}{}^2, {}^1A_{1g}) = F_0 + 10F_2 + 76F_4 - 8Dq + 2\epsilon_0 \tag{4-101}$$

$$E(t_{2g}{}^2, {}^1E_g, {}^1T_{2g}) = F_0 + 16F_4 - 8Dq + 2\epsilon_0 \tag{4-102}$$

$$E(t_{2g}{}^2, {}^3T_{1g}) = F_0 - 5F_2 - 24F_4 - 8Dq + 2\epsilon_0 \tag{4-103}$$

We notice that in the strong-field approximation ^1E_g and $^1T_{2g}$ are accidentally degenerate.

In Table 4-7 we list the lowest configurations and the crystal field states into which they are split by the correlative interactions. The energies are listed for the ground states of the free ions and for the ground states of the ions in a strong crystalline field of O_h symmetry. In general, the crystalline states in the strong-field case are *not* stationary states of the free ion, but rather linear combinations of these, called valence states. The energy differences between the valence states and the ground states of the free ions are called "promotional energies."

Values for the parameters F_2 and F_4 are obtained from the spectra of the free ions.[19,22] Values of Dq which depend upon both the nature of the ligands and the ions with which they complex are, as usual, determined semiempirically.

It will be noticed that, in every case, there is only one state of maximum multiplicity which, by Hund's principle, is therefore also the ground state. The multiplicities and symmetries predicted for the ground states are the same, in both the weak- and strong-field limits, for all cases except d^4, d^5, d^6, and d^7. This is due to the fact that the occupation numbers in the former limit differ appreciably from those in the latter only for these numbers of electrons. Since in these cases the transition from the weak to the strong crystalline field corresponds to a transfer of electrons from the e_g shell to the t_{2g} shell, the total spin quantum number S will be lower in the crystal state as compared to the gaseous state. The octahedral stabilization energy is greater, however, because we gain $10Dq$ by every electron transferring from the e_g shell to the t_{2g} shell.

From Table 4-7 quantitative criteria may be given to distinguish the weak- from the strong-field cases.[19–21] For example, in the former limit the field stabilization for d^6 ions is only $4Dq$; in the latter, however, it is as much as $24Dq$. This stabilization has, however, been achieved at the expense of some $5(F_2 + 51F_4)$ in promotional energy. When the last quantity is much greater than $20Dq$, the complex is paramagnetic; conversely, when it is much less, the complex is diamagnetic. Very frequently, the two crucial quantities are of comparable magnitude, and these situations are treated in terms of intermediate coupling.

TABLE 4-7. STATES AND ENERGIES IN STRONG OCTAHEDRAL FIELDS[17,19]

Atomic configuration	Crystal configuration	Symmetry of ground state	Octahedral stabilization
d^1	(t_{2g})	${}^2T_{2g}$	$4Dq$
d^2	$(t_{2g})^2$	${}^3T_{1g}$	$8Dq$
d^3	$(t_{2g})^3$	${}^4A_{2g}$	$12Dq$
d^4	$(t_{2g})^4$	${}^3T_{1g}$	$16Dq$
d^5	$(t_{2g})^5$	${}^2T_{2g}$	$20Dq$
d^6	$(t_{2g})^6$	${}^1A_{2g}$	$24Dq$
d^7	$(t_{2g})^6(e_g)$	${}^2E_g$	$18Dq$
d^8	$(t_{2g})^6(e_g)^2$	${}^3A_{2g}$	$12Dq$
d^9	$(t_{2g})^6(e_g)^3$	${}^2E_g$	$6Dq$

Atomic configuration	Energy of crystal ground state	Energy of atom ground state	Promotional energies	Symmetry of other states
d^1	0	0	0	
d^2	$-5F_2 - 24F_4$	$-8F_2 - 9F_4$	$3F_2 - 15F_4$	${}^1A_{1g}, {}^1E_g, {}^1T_{2g}$
d^3	$-15F_2 - 72F_4$	$-15F_2 - 72F_4$	0	${}^2E_g, {}^2T_{1g}, {}^2T_{2g}$
d^4	$-15F_2 - 44F_4$	$-21F_2 - 189F_4$	$6F_2 + 145F_4$	${}^1A_{1g}, {}^1E_g, {}^1T_{2g}$
d^5	$-20F_2 - 40F_4$	$-35F_2 - 315F_4$	$15F_2 + 275F_4$	
d^6	$-30F_2 - 60F_4$	$-35F_2 - 315F_4$	$5F_2 + 255F_4$	
d^7	$-36F_2 - 219F_4$	$-43F_2 - 324F_4$	$7F_2 + 105F_4$	
d^8	$-50F_2 - 387F_4$	$-50F_2 - 387F_4$	0	${}^1A_{1g}, {}^1E_g$
d^9	$-56F_2 - 504F_4$	$-56F_2 - 504F_4$	0	

4-f. Fields of Intermediate Strength

As has been indicated, there may be discontinuities in the symmetries and multiplicities of the ground states of ions on going from the weak- to the strong-field case. The important thing, however, is that the crystal field theory treats the transition domain in terms of the same physical picture, without explicitly invoking any discontinuous change in bond type. The fields of intermediate strength are the ones where $\mathcal{V}_0$ and e^2/r_{12} are of the same order of magnitude. In order to reach that region, we can of course make the approach either from the weak-field or from the strong-field limit. Since the two sets of basis functions are connected by a unitary transformation, they must yield identical results if each problem is solved exactly.

We shall illustrate the appropriate analysis which deals with the intermediate coupling for the simple case of two d electrons.[23] For simplicity we confine our attention to triplet states.

1. Weak-field Treatment. $(3d)^2$ produces two triplet states ^3P and ^3F with the energy difference between them (Sec. 2-*g*)

$$^3P - {}^3F = 15F_2 - 75F_4 \tag{4-104}$$

Under the influence of a weak field, ^3F yields $^3A_{2g}$, $^3T_{2g}$, and $^3T_{1g}$ components, whereas the ^3P state is not split and transforms under $^3T_{1g}$. Since these are the solely occurring triplets, we see that only the two $^3T_{1g}$ components may interact in stronger fields. That they will, in fact, do so is clear because the crystal field energy of the ground $^3T_{1g}$ state of d^2 is different in the two limits.

Writing down the perturbation matrix for the two $^3T_{1g}$ under $\mathcal{V}_0$, using Sec. 2-*c*,

$$({}^3T_{1g}{}^a(F)) = Y_3^\circ = \sqrt{1/5}\,|2^+, -2^+| + \sqrt{4/5}\,|1^+, -1^+| \tag{4-105}$$
$$({}^3T_{1g}{}^a(P)) = Y_1^\circ = \sqrt{4/5}\,|2^+, -2^+| - \sqrt{1/5}\,|1^+, -1^+| \tag{4-106}$$

From (4-45)

$$({}^3T_{1g}{}^a(\mathrm{F})|\mathcal{V}_0|{}^3T_{1g}{}^a(F)) = -6Dq \tag{4-107}$$
$$({}^3T_{1g}{}^a(P)|\mathcal{V}_0|{}^3T_{1g}{}^a(P)) = 0Dq \tag{4-108}$$
$$({}^3T_{1g}{}^a(F)|\mathcal{V}_0|{}^3T_{1g}{}^a(P)) = 4Dq \tag{4-109}$$
$$\begin{vmatrix} -6Dq - E & 4Dq \\ 4Dq & 15F_2 - 75F_4 - E \end{vmatrix} = 0 \tag{4-110}$$

Further,

$$E({}^3T_{2g}) = 2Dq \tag{4-111}$$
$$E({}^3A_{2g}) = 12Dq \tag{4-112}$$

Notice that for $Dq = 0$, the weak-field limit, we get $E(^3F) = 0$ and $E(^3P) = 15F_2 - 75F_4$, the correct separation between ^3P and ^3F. On the other hand, for $Dq \gg 15F_2 - 75F_4$ we get

$$E({}^3T_{1g},F) = -8Dq \quad \text{and} \quad E({}^3T_{1g},P) = 2Dq \tag{4-113}$$

These are the strong-field limits.

2. Strong-field Treatment. As previously seen, $(t_{2g})^2$ produces a $^3T_{1g}$ component. From $(t_{2g})(e_g)$ comes

$$t_{2g} \times e_g = t_{1g} + t_{2g} \tag{4-114}$$

and since the two electrons differ in their symmetry quantum number, we can get both triplets and singlets. The configuration $(t_{2g})(e_g)$ hence produces a ${}^3T_{1g}$ and a ${}^3T_{2g}$ component. Finally, $(e_g)^2$ produces a ${}^3A_{2g}$ component, Fig. 4-3. Previously we have found

$$E((t_{2g})^2\,{}^3T_{1g}) = F_0 - 5F_2 - 24F_4 - 8Dq \tag{4-115}$$

For the triplet components springing from the subshell configuration $(t_{2g})(e_g)$ we get the transformation properties in D_{4h} symmetry, Table 4-8.

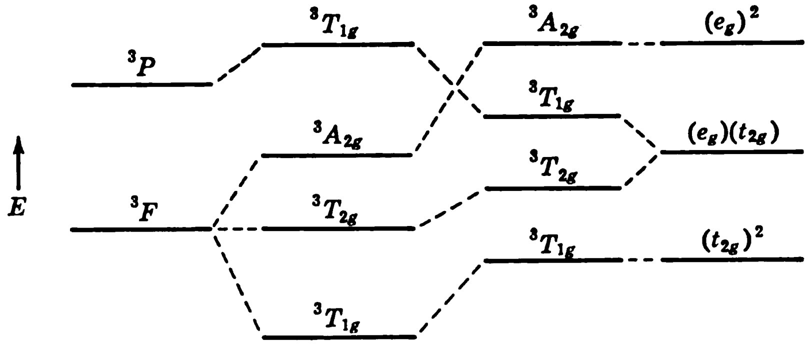

FIG. 4-3. Level scheme d^2 in octahedral field.

TABLE 4-8. TRANSFORMATION PROPERTIES OF $(e_g)(t_{2g})$ IN D_{4h} SYMMETRY

E	$2C_4$	C_2	$2C_2'$	$2C_2''$
$\psi_1 = \lvert\overset{+}{(xy)}\overset{+}{(x^2-y^2)}\rvert$	ψ_1	ψ_1	$-\psi_1$	$-\psi_1$
$\psi_2 = \lvert\overset{+}{(xz)}\overset{+}{(x^2-y^2)}\rvert$	$-\psi_3$	$-\psi_2$	$-\psi_2$	ψ_3
$\psi_3 = \lvert\overset{+}{(yz)}\overset{+}{(x^2-y^2)}\rvert$	ψ_2	$-\psi_3$	ψ_3	ψ_2
$\psi_4 = \lvert\overset{+}{(xy)}\overset{+}{(z^2)}\rvert$	$-\psi_4$	ψ_4	$-\psi_4$	ψ_4
$\psi_5 = \lvert\overset{+}{(xz)}\overset{+}{(z^2)}\rvert$	ψ_6	$-\psi_5$	$-\psi_5$	$-\psi_6$
$\psi_6 = \lvert\overset{+}{(yz)}\overset{+}{(z^2)}\rvert$	$-\psi_5$	$-\psi_6$	ψ_6	$-\psi_5$

Notice that ψ_1 transforms like A_{2g} while ψ_4 transforms like B_{2g}. From the character tables in Wilson, Decius, and Cross[24] we see that a descent in symmetry from O_h to D_{4h} causes the splittings

$$\begin{aligned} T_{2g} &\rightarrow E_g + B_{2g} \\ T_{1g} &\rightarrow E_g + A_{2g} \\ E_g &\rightarrow B_{1g} + A_{1g} \\ A_{2g} &\rightarrow B_{1g} \\ A_{1g} &\rightarrow A_{1g} \end{aligned} \tag{4-116}$$

Hence, the B_{2g} component in D_{4h} comes from the T_{2g} component in O_h and the A_{2g} component in D_{4h} comes from the T_{1g} component in O_h. Consequently,

$$^3T_{1g}{}^a(t_{2g}e_g) = |\overset{+}{(xy)}\overset{+}{(x^2 - y^2)}| \tag{4-117}$$

and

$$^3T_{2g}{}^a(t_{2g}e_g) = |\overset{+}{(xy)}\overset{+}{(z^2)}| \tag{4-118}$$

By the use of Table 4-5,

$$\begin{aligned} E(^3T_{1g}(t_{2g}e_g)) &= J(xy,\, x^2 - y^2) - K(xy,\, x^2 - y^2) + 2Dq \\ &= F_0 + 4F_2 - 69F_4 + 2Dq \end{aligned} \tag{4-119}$$

$$\begin{aligned} E(^3T_{2g}(t_{2g}e_g)) &= J(xy,z^2) - K(xy,z^2) + 2Dq \\ &= F_0 - 8F_2 - 9F_4 + 2Dq \end{aligned} \tag{4-120}$$

Finally, for the $^3A_{2g}$ component

$$\begin{aligned} E(^3A_{2g}(e_g)^2) &= J(x^2 - y^2,\, z^2) - K(x^2 - y^2,\, z^2) + 12Dq \\ &= F_0 - 8F_2 - 9F_4 + 12Dq \end{aligned} \tag{4-121}$$

As before, a configuration interaction takes place between the two $^3T_{1g}$ components. Taking care to use the A_{2g} component in D_{4h} of $^3T_{1g}(t_{2g})^2$, we get

$$\begin{aligned} &(^3T_{1g}{}^a(t_{2g})^2|e^2/r_{12}|^3T_{1g}{}^a(t_{2g},e_g)) \\ &\quad = (|(xz)(yz)|e^2/r_{12}|(xy)(x^2 - y^2)|) \\ &\quad = ((xz)(yz)|e^2/r_{12}|(xy)(x^2 - y^2)) - ((xz)(yz)|e^2/r_{12}|(x^2 - y^2)(xy)) \end{aligned} \tag{4-122}$$

By use of Table 4-6,

$$(^3T_{1g}{}^a(t_{2g})^2|e^2/r_{12}|^3T_{1g}{}^a(t_{2g})(e_g)) = -6F_2 + 30F_4 \tag{4-123}$$

Hence for the $^3T_{1g}$ components,

$$\begin{vmatrix} F_0 - 5F_2 - 24F_4 - 8Dq - E & -6F_2 + 30F_4 \\ -6F_2 + 30F_4 & F_0 + 4F_2 - 69F_4 + 2Dq - E \end{vmatrix} = 0 \tag{4-124}$$

Further,

$$E(^3T_{2g}) = F_0 - 8F_2 - 9F_4 + 2Dq \tag{4-125}$$

$$E(^3A_{2g}) = F_0 - 8F_2 - 9F_4 + 12Dq \tag{4-126}$$

Notice again that for $Dq = 0$, the weak-field limit, we get the correct separation $E(^3P) - E(^3F) = 15F_2 - 75F_4$. The strong-field limit is, of course, also reflected in (4-125) and (4-126).

What takes place during the transition from the weak- to the strong-field limit is that a continuous change, with increasing Dq, occurs during which the initial pure $^3F(T_{1g})$ and $^3P(T_{1g})$ functions are progressively contaminated by each other. Finally, in the strong-field limit, the eigenfunctions arise instead from the pure configurations $(t_{2g})^2$ and $(t_{2g})(e_g)$.

We see that the transition between the two cases really reflects the compromise between the correlative interactions, which are the basis of Hund's principle, and the tendency to minimize the crystal field energy. Further, that a singlet state of d^6 should cross over several triplets, and the ${}^5T_{2g}$ component of the quintuplet ${}^5D$, which it usurps as the ground state of, for example, most Co^{3+} complexes, is no longer surprising.[19,21] All that is required is a strong crystalline potential $\mathcal{V}_0$.

The complete secular equations for the series d^1 to d^9 have been published by Orgel[25] as calculated from the weak-field point of view and by Tanabe and Sugano,[26,27] reproduced by McClure,[28] as seen from the strong-field point of view. We shall have occasion to return to the individual energy schemes later in this book when discussing specific examples, and we shall postpone further discussion until then.

4-g. Computation Aids

In the foregoing sections we have outlined two of the possible ways of finding the crystal field energies in the weak and the strong limit. These methods are, of course, by no means the only possible ones; indeed, taking as a starting point the original paper by Penney and Schlapp,[3] a very powerful and elegant method, the so-called operator equivalent method, has been developed. The method is based on the fact that in calculating matrix elements $(A|Q|B)$ we can substitute the operator Q with another, more easily calculable operator P, provided that the two operators transform in the same way within our group.[29–33] The two matrix elements are, of course, not going to be identical, but within a given manifold they will be proportional. For instance, in the weak-field case we want to find the various matrix elements of $\mathcal{V}_0$ within the manifold spanned by the $(2L + 1)$ orbital states of given L, S, and M_S. Here

$$\mathcal{V}_0 = \Sigma(x_i^4 + y_i^4 + z_i^4 - \tfrac{3}{5}r_i^4) \qquad (4\text{-}127)$$

As shown by Stevens,[29] by replacing x, y, and z in (4-127) by L_x, L_y, and L_z, an *operator expression* for $\mathcal{V}_0$ which is easier to handle than (4-127) is obtained. In performing this change we must only remember that, whereas x_i and y_i commute, L_x and L_y do not. The way to handle this is to replace, say, x_iy_i by $\tfrac{1}{2}\{L_xL_y + L_yL_x\}$ and similarly for more complicated expressions.[30] Then

$$\begin{aligned}\hat{\mathcal{V}}_0 &= \hat{L}_x^4 + \hat{L}_y^4 + \hat{L}_z^4 - \tfrac{1}{5}(L + 1)[3L(L + 1) - 1] \\ &= \tfrac{1}{20}[35\hat{L}_z^4 - 30L(L + 1)\hat{L}_z^2 + 25\hat{L}_z^2 - 6L(L + 1) \\ &\qquad + 3L^2(L + 1)^2] + \tfrac{1}{8}(\hat{L}_+^4 + \hat{L}_-^4) \qquad (4\text{-}128)\end{aligned}$$

The proportionality constant between $\mathcal{V}_0$ and $\hat{\mathcal{V}}_0$ is determined by evaluating a single matrix element, chosen for its simplicity, in both perturbation matrices. As an example we shall treat the now well-known case of the weak crystalline field splitting of ${}^3F(d^2)$.

The perturbation matrix $^3F(d^2)$ is, with $\mathcal{H}^{(1)} = \mathcal{V}_0$ and by the use of $\hat{L}_-^4\,(3,3) = 24\sqrt{15}\,(3,-1)$ and so forth, easily seen to be

$$\begin{array}{ccccccc} \psi_3 & \psi_2 & \psi_1 & \psi_0 & \psi_{-1} & \psi_{-2} & \psi_{-3} \\ \hline 9 & 0 & 0 & 0 & 3\sqrt{15} & 0 & 0 \\ 0 & -21 & 0 & 0 & 0 & 15 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 & 3\sqrt{15} \\ 0 & 0 & 0 & 18 & 0 & 0 & 0 \\ 3\sqrt{15} & 0 & 0 & 0 & 3 & 0 & 0 \\ 0 & 15 & 0 & 0 & 0 & -21 & 0 \\ 0 & 0 & 3\sqrt{15} & 0 & 0 & 0 & 9 \end{array} \qquad (4\text{-}129)$$

The solutions are immediately found to be

$$E = \begin{cases} 18 & \text{threefold degenerate} \\ -6 & \text{threefold degenerate} \\ -36 & \text{onefold degenerate} \end{cases}$$

The proportionality constant is evaluated, for example, from the eigenfunction for the $L_z = 3$, $S_z = 1$ component of $^3F(d^2)$ $|2^+, 1^+|$. By the use of (4-45) we get for the diagonal matrix element

$$(2^+, 1^+|\mathcal{V}_0|2^+, 1^+) = -3Dq$$

By comparison with (4-129), where this matrix element is $9x$, we see that the proportionality factor between $\mathcal{V}_0$ and $\hat{\mathcal{V}}_0$ is $-\frac{1}{3}Dq$. The final result is then

$$E(^3F,d^2) = \begin{cases} -6Dq & \text{threefold degenerate} \\ 2Dq & \text{threefold degenerate} \\ 12Dq & \text{onefold degenerate} \end{cases}$$

Knowing that a ^3F state splits into the components $^3A_{2g}$, $^3T_{1g}$, and $^3T_{2g}$, we know further that $E(^3A_{2g}) = -12Dq$, but we cannot in this way decide between $^3T_{1g}$ and $^3T_{2g}$.

In many cases the "complete" energy scheme can be obtained with even less work. In order to illustrate, let us again use the triplet components of the d^2 system. The possible electronic configurations in the *strong* field are

$(t_{2g})^2$ giving rise to a $^3T_{1g}$ component
$(t_{2g})(e_g)$ giving rise to a $^3T_{1g}$ and a $^3T_{2g}$ component
$(e_g)^2$ giving rise to a $^3A_{2g}$ component

Consequently, since there is no correlation between the $^3T_{2g}$ and $^3A_{2g}$ components, we immediately get

$$E(^3A_{2g}) = 6Dq + 6Dq = 12Dq \qquad (4\text{-}130)$$
$$E(^3T_{2g}) = 6Dq - 4Dq = 2Dq \qquad (4\text{-}131)$$

and the perturbation matrix for the ${}^3T_{1g}$ components will be of the form:

$$\begin{array}{c} \begin{array}{cc} (t_2)^2 & (t_{2g})(e_g) \end{array} \\ \begin{vmatrix} -8Dq - E & y \\ y & 2Dq - E \end{vmatrix} = 0 \end{array} \tag{4-132}$$

Seen from the weak-field point of view, both ${}^3P$ and ${}^3F$ produce a ${}^3T_{1g}$ component, but we know further that $E({}^3P) = 0Dq$ because a P state does not split in a cubic field. Since the trace of the perturbation matrix (the sum of the roots) is invariant, we get for the weak-field case

$$E({}^3P, {}^3T_{1g}) + E({}^3F, {}^3T_{1g}) = -8Dq + 2Dq = -6Dq \tag{4-133}$$

and

$$E({}^3P, {}^3T_{1g}) = 0Dq \tag{4-134}$$

Hence

$$E({}^3F, {}^3T_{1g}) = -6Dq \tag{4-135}$$

Still another way of obtaining this result is by use of the center-of-gravity rule for the components of ${}^3F$:

$$E({}^3A_{2g}) + 3E({}^3T_{1g}) + 3E({}^3T_{2g}) = 0 \tag{4-136}$$

$$12Dq + 3E({}^3T_{1g}) + 3(2Dq) = 0 \tag{4-137}$$

$$E({}^3T_{1g}) = -6Dq \tag{4-138}$$

Even the interaction term between the two ${}^3T_{1g}$ components can be obtained in this special case without involving wave functions. The diagonal elements of the ${}^3T_{1g}$ part of the energy matrix whose rows and columns refer to the weak-field case are clearly $\epsilon - 6Dq$ and $\epsilon + 15(F_2 - 5F_4)$, where ϵ is just the energy of the free ${}^3F$ ion in the spherically symmetric field $\mathcal{V}_R$. The off-diagonal elements are found by noting that, as F_2, F_4 tend to zero, the eigenvalues must become those of the strong-field limit, namely, $-8Dq$ and $2Dq$. Then

$$\begin{vmatrix} -6Dq - E & X \\ X & -E \end{vmatrix} = 0 \tag{4-139}$$

$$E^2 + 6EDq - X^2 = 0 \tag{4-140}$$

must produce the roots $-8Dq$ and $2Dq$. Hence

$$X^2 = 16(Dq)^2 \tag{4-141}$$

$$X = 4Dq \tag{4-142}$$

where we have chosen the plus sign as the phase.

A method for obtaining the energies of the levels in crystal fields of high symmetry has been given by Judd.[34] In the process of finding the roots of the secular determinant the degenerate solutions will turn up many times. This is, of course, a waste of time and effort. Judd describes a method which is a natural extension of Slater's method used in atomic spectroscopy but which has the same disadvantage: when two or more components of a level correspond to the same irreducible representation, Judd's method, as well as Slater's method, will give only their mean energy. Since the methods depend upon the utilization of the various possible "spur" relations already treated above, and upon the "descent in symmetry" method treated below, the reader is referred to Ref. 34 for a fuller description.

To summarize the "rules of thumb":

1. No levels possessing the same symmetry designation may cross in the energy-level diagram.
2. Within a manifold spanned by the $(2L + 1)$ orbital states of given L, S, and M_L the "center of gravity" is preserved.
3. The crystal field energies in the weak and in the strong field are equal when there is only one component of a given symmetry designation present.
4. S and P terms do not split up, and in the weak-field case

$$E(S) = E(P) = 0Dq$$

5. If more than one component of a given symmetry designation is present, the trace of the perturbation matrix is equal to the sum of the energies of the roots.

4-h. Descent in Symmetry

Still another very powerful method that is available, namely, the "descent in symmetry" method, allows us to specify the energy spectrum of a given system. It was by this method that Bethe[1] originally distinguished between the various electronic levels, and since it still is extremely useful in nearly all calculations, we shall give a brief outline of it.

In a molecule possessing a high degree of symmetry, many of the electronic components are of high degeneracies. These degeneracies can be removed by going down in symmetry. Suppose we have a threefold degenerate level in O_h symmetry. By going down to D_{4h} symmetry, we find that the threefold symmetry is done away with and that we have instead one nondegenerate level and one twofold degenerate level. In the lower symmetry the nondegenerate level transforms like an irreducible component of the sub group. Hence, by constructing a wave function which transforms correctly in the lower symmetry group, we know that this is a component of the threefold degenerate level in the higher symmetry group. The remaining two components in the high symmetry can then be generated by the application of a symmetry operator, not present in the low symmetry, to the constructed wave function.

That the energy can be calculated immediately both in the high and in the low symmetry is evident. But, further, when a configurational interaction is possible, we know that if the constructed wave functions transform correctly in the point group of the molecule, it is only the *same symmetry species which can interact.* . Still further, it is only the same *subspecies* within a symmetry classification which can interact. In other words, if we in O_h, say, have two levels both with the symmetry T_{1g} and want to know the interaction term, we go down to D_{4h} symmetry, pick out the two A_{2g} components, and write down the configuration interaction matrix in O_h symmetry using the two A_{2g} components.

In most of the cases occurring in O_h symmetry, a descent in symmetry to D_{4h} is enough to characterize a certain level. However, a further descent may sometimes be necessary. Full tables correlating the species of a group with its subgroups may be found in Wilson, Decius, and Cross.[24] We shall give only the correlation table $O_h \rightarrow D_{4h}$. For the single orbitals t_{2g} and e_g we have of course $t_{2g} \rightarrow e_g + b_{2g}$ and $e_g \rightarrow a_{1g} + b_{1g}$.

TABLE 4-9. DESCENT IN SYMMETRY FROM O_h TO D_{4h}

$O_h \rightarrow D_{4h}$		$O_h \quad D_{4h}$
$A_{1g} \rightarrow A_{1g}$	(xz)	$t_{2g}{}^a \rightarrow e_g{}^a$
$A_{2g} \rightarrow B_{1g}$	(yz)	$t_{2g}{}^b \rightarrow e_g{}^b$
$E_g \rightarrow A_{1g} + B_{1g}$	(xy)	$t_{2g}{}^c \rightarrow b_{2g}$
$T_{1g} \rightarrow A_{2g} + E_g$	(z^2)	$e_g{}^a \rightarrow a_{1g}$
$T_{2g} \rightarrow B_{2g} + E_g$	$(x^2 - y^2)$	$e_g{}^b \rightarrow b_{1g}$

As an example, we shall treat the electronic configuration $(t_{2g})^2$. By the use of Appendix III, we get

$$(t_{2g})^2 \rightarrow {}^3T_{1g},\ {}^1A_{1g},\ {}^1E_g, \text{ and } {}^1T_{2g} \tag{4-143}$$

The triplet state is trivial; we find immediately that $|\overset{+}{(xz)}\overset{+}{(yz)}|$ transforms like ${}^3A_{2g}$ in D_{4h}. Then

$$\begin{aligned} E({}^3T_{1g}) &= J(xz,yz) - K(xz,yz) \\ &= F_0 - 5F_2 - 24F_4 \end{aligned} \tag{4-144}$$

The singlet states are produced by the distribution, Table 4-10, of the electrons on the three different orbitals $e_g{}^a$, $e_g{}^b$, and b_{2g}. From this

$$\psi({}^1E_g{}^+) = \sqrt{1/2}\,\{|\overset{+}{(xz)}\overset{-}{(xy)}| - |\overset{-}{(xz)}\overset{+}{(xy)}|\} \tag{4-145}$$

$$\begin{aligned} E({}^1E_g{}^+) &= J(xz,xy) + K(xz,xy) \\ &= F_0 + F_2 + 16F_4 = {}^1T_{1g}(O_h) \end{aligned} \tag{4-146}$$

TABLE 4-10. DISTRIBUTION OF TWO ELECTRONS IN D_{4h} SYMMETRY, SINGLET STATES

(xz) $e_g{}^a$	(yz) $e_g{}^b$	(xy) b_{2g}	Symmetry in D_{4h}
×	×		${}^1B_{2g}$
××	××		${}^1B_{1g}$ and ${}^1A_{1g}{}^{(1)}$
		××	${}^1A_{1g}{}^{(2)}$
	×	×	${}^1E_g{}^-$
×		×	${}^1E_g{}^+$

since ${}^1E_g(D_{4h})$ only can arise from ${}^1T_{2g}(O_h)$. Defining $\phi_1 = |(\overset{+}{xz})(\overset{-}{xz})|$ and $\phi_2 = |(\overset{+}{yz})(\overset{-}{yz})|$, we get in D_{4h} symmetry

	E	C_4	C_2	C_2'	C_2''
$\phi_1 + \phi_2$	$\phi_1 + \phi_2$	$\phi_1 + \phi_2$	$\phi_1 + \phi_2$	$\phi_1 + \phi_2$	$\phi_1 + \phi_2$
$\phi_1 - \phi_2$	$\phi_1 - \phi_2$	$-(\phi_1 - \phi_2)$	$\phi_1 - \phi_2$	$\phi_1 - \phi_2$	$-(\phi_1 - \phi_2)$

By a comparison with the character table for D_{4h}, we see that

$$\frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \text{ transforms like } {}^1A_{1g}$$

$$\frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \text{ transforms like } {}^1B_{1g}$$

Then

$$\begin{aligned} E({}^1B_{1g}) &= \tfrac{1}{2}J(xz,xz) + \tfrac{1}{2}J(yz,yz) - K(xz,yz) \\ &= F_0 + F_2 + 16F_4 = {}^1E_g(O_h) \end{aligned} \tag{4-147}$$

since ${}^1B_{1g}(D_{4h})$ only can arise from ${}^1E_g(O_h)$. Furthermore,

$$\begin{aligned} E({}^1A_{1g})(1) &= \tfrac{1}{2}J(xz,xz) + \tfrac{1}{2}J(yz,yz + K(xz,yz) \\ &= F_0 + 7F_2 + 56F_4 \end{aligned} \tag{4-148}$$

$$\begin{aligned} E({}^1A_{1g})(2) &= J(xy,xy) \\ &= F_0 + 4F_2 + 36F_4 \end{aligned} \tag{4-149}$$

Finally, because of the invariance of the trace for the ${}^1A_{1g}$ components,

$$\begin{aligned} E({}^1A_{1g})O_h &= E({}^1A_{1g})(1) + E({}^1A_{1g})(2) - E({}^1B_{1g}) \\ &= F_0 + 10F_2 + 76F_4 \end{aligned} \tag{4-150}$$

These results are, of course, identical with the ones found previously, but they are perhaps obtained with somewhat less labor.

4-i. Equivalence of t_{2g} and p Electrons

Finally, we shall point out a useful analogy between t_{2g} and p electrons.[35–39,51] Writing p_1, p_0, and p_{-1} for p electrons having $m_l = 1, 0$, and -1, we have by the use of Eqs. (2-9) and (2-10)

$$\mathcal{L}_z\begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} \qquad \mathcal{L}_x\begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix}$$

and

$$\mathcal{L}_y\begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} = \frac{i}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}\begin{pmatrix} p_1 \\ p_0 \\ p_{-1} \end{pmatrix} \tag{4-151}$$

The set $\phi_1 = d_{-1}$, $\phi_0 = \dfrac{1}{\sqrt{2}}(d_2 - d_{-2})$, and $\phi_{-1} = -d_1$, where we have used a similar nomenclature as that for the p electrons, can be taken as a representation for t_{2g}. So long as we stay *inside* these orbitals, we have

$$\hat{L}_z\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} = -\begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} \quad \hat{L}_x\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} = -\frac{1}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix}$$

and

$$\hat{L}_y\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} = -\frac{i}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ -1 & 0 & 1\\ 0 & -1 & 0\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} \tag{4-152}$$

Formally, we can also treat the t_{2g} electrons as "pseudo" p electrons, i.e., in particular $l^2 = 1(1 + 1) = 2$. From the table of group characters we see that $\chi(t_{2g})^2 = \chi(t_{1u})^2$. Hence, we have

$$(t_{2g})^2 \equiv p^2 \tag{4-153}$$

The electronic configuration p^2 produces the following terms: ${}^3P$, ${}^1D$, and ${}^1S$. These will in an octahedral field produce the following levels: ${}^3T_{1g}$, $({}^1T_{2g}, {}^1E_g)$, and ${}^1A_{1g}$. [Notice that in our previous example $(t_{2g})^2$ we found ${}^1T_{2g}$ and ${}^1E_g$ to have the same energy.] Furthermore,

$$\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 \tag{4-154}$$

$$\mathbf{L}^2 = \mathbf{l}_1^2 + \mathbf{l}_2^2 + 2\mathbf{l}_1 \cdot \mathbf{l}_2 \tag{4-155}$$

or

$$\mathbf{l}_1 \cdot \mathbf{l}_2 = \tfrac{1}{2}[L(L + 1) - \Sigma l(l + 1)] \tag{4-156}$$

Similarly

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \tfrac{1}{2}[S(S + 1) - \Sigma s(s + 1)] \tag{4-157}$$

In order to find the energies for the $(t_{2g})^n$ configurations, we first consider $(t_{2g})^2$, for which we use L and S as good quantum numbers. The energies of the individual states are then [see the example $(t_{2g})^2$ on page 88], with

$$B = 3F_2 + 20F_4 \tag{4-158}$$

and

$$E_0 = F_0 - 5F_2 - 24F_4 \tag{4-159}$$

$$E({}^3P) = E_0 \qquad \mathbf{s}_1 \cdot \mathbf{s}_2 = \tfrac{1}{4} \qquad \mathbf{l}_1 \cdot \mathbf{l}_2 = -1 \tag{4-160}$$

$$E({}^1D) = E_0 + 2B \qquad \mathbf{s}_1 \cdot \mathbf{s}_2 = -\tfrac{3}{4} \qquad \mathbf{l}_1 \cdot \mathbf{l}_2 = 1 \tag{4-161}$$

$$E({}^1S) = E_0 + 5B \qquad \mathbf{s}_1 \cdot \mathbf{s}_2 = -\tfrac{3}{4} \qquad \mathbf{l}_1 \cdot \mathbf{l}_2 = -2 \tag{4-162}$$

The Hamiltonian may therefore be written[38,39] in a $(t_{2g})^n$ type of configuration

$$\mathcal{H}_{12} = E_0 - (\mathbf{l}_1 \cdot \mathbf{l}_2 + 4\mathbf{s}_1 \cdot \mathbf{s}_2)B \tag{4-163}$$

whatever the coupling scheme, i.e., whatever the states of the two electrons, stationary or complex. The n-electron Hamiltonian is therefore

$$\begin{aligned}\mathcal{H} = \sum_i \sum_{j>i} \mathcal{H}_{ij} &= \tfrac{1}{2}n(n - 1)E_0 - B\sum_i \sum_{j>i} (\mathbf{l}_i \cdot \mathbf{l}_j + 4\mathbf{s}_i \cdot \mathbf{s}_j)\\ &= \tfrac{1}{2}n(n - 1)E_0 - B\left[\tfrac{1}{2}\left(\mathbf{L}^2 - \sum_i \mathbf{l}_i^2\right) + 2\left(\mathbf{S}^2 - \sum_i \mathbf{s}_i^2\right)\right]\\ &= \tfrac{1}{2}n(n - 1)E_0 + \tfrac{5}{2}nB - B[\tfrac{1}{2}\mathbf{L}^2 + 2\mathbf{S}^2]\end{aligned} \tag{4-164}$$

The energy eigenvalues are therefore just

$$E = \tfrac{1}{2}n(n-1)E_0 + \tfrac{5}{2}nB - B[\tfrac{1}{2}L(L+1) + 2S(S+1)] \quad (4\text{-}165)$$

We shall have occasion to return to this formalism in the treatment of spin-orbit coupling effects.

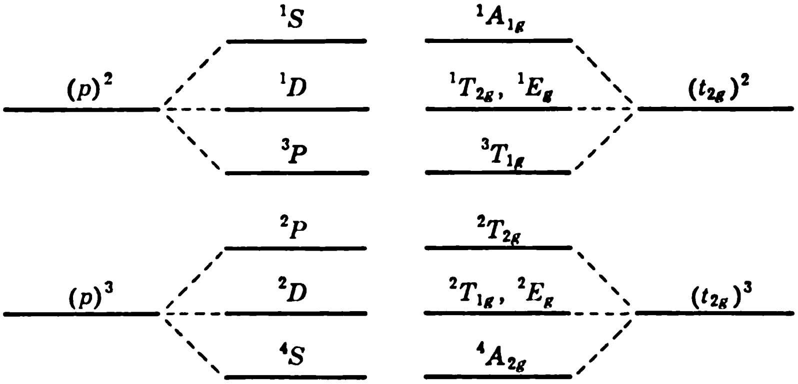

FIG. 4-4. The t_{2g}-p equivalence. Notice the reversal for the D terms T_{1g} and T_{2g}.

4-j. The Spectrochemical Series[17]

Many regularities in the spectra of octahedral complexes had been noted some time before the advent of crystal field theory. It was observed, for example, that the successive replacement of I^- by Br^-, Cl^-, and H_2O as the ligands surrounding a particular cation shifted the maxima of prominent band systems to progressively shorter wavelengths. Similar effects were noticed with other ligands, and it appeared possible to classify these on the basis of their spectral effects. This led to the construction of the spectrochemical series (Fajans[44] and Tsuchida[45]) $I^- < Br^- < Cl^- < OH^- < F^- < H_2O <$ pyridine $< NH_3 <$ ethylenediamine $< CN^-$. Minor variants arose, depending mainly on the particular cation in conjunction with which they were developed. But the general trend of the ligands appeared to be roughly independent of the central ion. The spectra concerned, it should be remarked, were those diffuse systems which we now classify as spin-allowed. With certain conspicuous exceptions, the qualitative features of a given cation could be systematized very satisfactorily in this way. Those ligand replacements which did not fall into line were accompanied by radical changes in stereochemistry or a change in multiplicity of the central ion.

By applying the spectrochemical series to, for example, the d^9 (Cu^{++}, say) case, we see that we may rationalize the ligand sequence as one of increasing Dq. The excitation energy is $10Dq$ here, and the hypsochromic shifts must therefore correspond to increases in this parameter. More generally, let us suppose that the series represents a succession of increasing octahedral fields $\mathfrak{V}_0$ when the relevant ligands are associated with a given central ion, whatever that may be. Let us further agree to consider only spin-allowed band systems. Then it may be proved that unless the multiplicity of the ground state changes, the spectrum of a given octahedral ion is shifted to shorter wavelengths on replacing its ligands by others lying above it in the spectrochemical series.

This "existence theorem" is easily established for magnetically normal complexes whose symmetry and spin for the ground states are those of the weak-field limit. For the configurations d^4, d^5, and d^6, as well as for d^1 and d^9, there is no distinction between the weak- and strong-field cases, since the free ions have only one term, namely, their ground term of maximum multiplicity. Their lower and upper states both arise from this term, and their separation is linear in Dq. The remaining ions, d^2, d^3, d^7, and d^8, have two terms of maximum multiplicity, of which ^3F or ^4F is the ground state and ^3P or ^4P the excited state. In the weak-field limit, the P states are not split but yield T_{1g} states. Their interactions with the ground states of d^2, d^7 for intermediate or strong fields can only depress the latter, so that the intervals, which increase linearly in both limits, increase more rapidly with Dq in the intermediate domain. And finally, for d^3 and d^8, whose ground states are the same in fields of all sizes, we have only to note that the excitation energies increase linearly in both limiting cases.

In those cases, namely, d^4, d^5, d^6, and d^7, where the ground-state multiplicity is different in the strong- and weak-field limits, two quite distinct types of spectral behavior may occur. For although the energy levels all move continuously as functions of Dq, as soon as, for example, the $^1A_{1g}$ state of Co^{3+} supplants its $^5T_{2g}$ state as the ground state, the selection rules change. No longer are the prominent bands in the spectrum due to quintuplet-quintuplet transitions but singlet-singlets take their place. It is an entirely different set of states that is now "visible." A simplifying factor in this magnetically "anomalous" case arises from the fact that, in the strong-field limit, the ground state is the only state of its total spin which arises from the lowest configuration. In this limit, or near it—and for present purposes all these "anomalous" cases fall into this category—it is clear that an increase in Dq removes the ground state yet further from all other states of the same multiplicity which must arise from excited crystal configurations. The existence of the spectrochemical series has been demonstrated for such complexes also.

It may be observed that the spectral shifts of different bands are governed by the same factor which accounts for their breadths.[46] Analytically, both depend upon the quantity $d(\Delta E)/d(Dq)$. Thus the absence of narrow spin-allowed bands and the existence of the spectrochemical series are closely related. Indeed, it is clear that the broader the band, the more it should be shifted on replacing the ligands by others near them in the spectrochemical series. It is only for the spin-allowed bands, however, that the direction of the displacement is always the same. $d(\Delta E)/d(Dq)$ may be zero, or even negative, and reverse this for the spin-forbidden bands.

So far we have dealt exclusively with crystalline fields possessing O_h symmetry and with no spin-orbit interaction included. In the next chapter we shall consider fields of lower symmetry.

APPENDIX I

SPHERICAL HARMONICS IN RECTANGULAR COORDINATES NORMALIZED TO ONE

(Phases as prescribed by Condon and Shortley[5])

$$Y_0^0 = \sqrt{\frac{1}{4\pi}}$$

$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}}\,\frac{x - iy}{r}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\,\frac{z}{r}$$

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}}\,\frac{x + iy}{r}$$

$$Y_2^{-2} = \sqrt{\frac{5}{4\pi}}\sqrt{\frac{3}{8}}\,\frac{(x - iy)^2}{r^2}$$

$$Y_2^{-1} = \sqrt{\frac{5}{4\pi}}\sqrt{\frac{3}{2}}\,\frac{z(x - iy)}{r^2}$$

$$Y_2^0 = \sqrt{\frac{5}{4\pi}}\sqrt{\frac{1}{4}}\,\frac{3z^2 - r^2}{r^2}$$

$$Y_2^1 = -\sqrt{\frac{5}{4\pi}}\sqrt{\frac{3}{2}}\,\frac{z(x + iy)}{r^2}$$

$$Y_2^2 = \sqrt{\frac{5}{4\pi}}\sqrt{\frac{3}{8}}\,\frac{(x + iy)^2}{r^2}$$

$$Y_3^{-3} = \sqrt{\frac{7}{4\pi}}\sqrt{\frac{5}{16}}\,\frac{(x - iy)^3}{r^3}$$

$$Y_3^{-2} = \sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{8}}\,\frac{z(x - iy)^2}{r^3}$$

$$Y_3^{-1} = \sqrt{\frac{7}{4\pi}}\sqrt{\frac{3}{16}}\,\frac{(x - iy)(5z^2 - r^2)}{r^3}$$

$$Y_3^0 = \sqrt{\frac{7}{4\pi}}\sqrt{\frac{1}{4}}\,\frac{z(5z^2 - 3r^2)}{r^3}$$

$$Y_3^1 = -\sqrt{\frac{7}{4\pi}}\sqrt{\frac{3}{16}}\,\frac{(x + iy)(5z^2 - r^2)}{r^3}$$

$$Y_3^2 = \sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{8}}\,\frac{z(x + iy)^2}{r^3}$$

$$Y_3^3 = -\sqrt{\frac{7}{4\pi}}\sqrt{\frac{5}{16}}\,\frac{(x + iy)^3}{r^3}$$

$$Y_4^{-4} = \sqrt{\frac{9}{4\pi}}\sqrt{\frac{35}{128}}\frac{(x-iy)^4}{r^4}$$

$$Y_4^{-3} = \sqrt{\frac{9}{4\pi}}\sqrt{\frac{35}{16}}\frac{z(x-iy)^3}{r^4}$$

$$Y_4^{-2} = \sqrt{\frac{9}{4\pi}}\sqrt{\frac{5}{32}}\frac{(x-iy)^2}{r^4}(7z^2-r^2)$$

$$Y_4^{-1} = \sqrt{\frac{9}{4\pi}}\sqrt{\frac{5}{16}}\frac{(x-iy)}{r^4}(7z^3-3zr^2)$$

$$Y_4^{0} = \sqrt{\frac{9}{4\pi}}\sqrt{\frac{1}{64}}\frac{35z^4-30z^2r^2+3r^4}{r^4}$$

$$Y_4^{1} = -\sqrt{\frac{9}{4\pi}}\sqrt{\frac{5}{16}}\frac{(x+iy)}{r^4}(7z^3-3zr^2)$$

$$Y_4^{2} = \sqrt{\frac{9}{4\pi}}\sqrt{\frac{5}{32}}\frac{(x+iy)^2}{r^4}(7z^2-r^2)$$

$$Y_4^{3} = -\sqrt{\frac{9}{4\pi}}\sqrt{\frac{35}{16}}\frac{z(x+iy)^3}{r^4}$$

$$Y_4^{4} = \sqrt{\frac{9}{4\pi}}\sqrt{\frac{35}{128}}\frac{(x+iy)^4}{r^4}$$

$$Y_5^{-5} = \sqrt{\frac{11}{4\pi}}\sqrt{\frac{63}{256}}\frac{(x-iy)^5}{r^5}$$

$$Y_5^{-4} = \sqrt{\frac{11}{4\pi}}\sqrt{\frac{315}{128}}\frac{z(x-iy)^4}{r^5}$$

$$Y_5^{-3} = \sqrt{\frac{11}{4\pi}}\sqrt{\frac{35}{256}}\frac{(x-iy)^3}{r^5}(9z^2-r^2)$$

$$Y_5^{-2} = \sqrt{\frac{11}{4\pi}}\sqrt{\frac{105}{32}}\frac{(x-iy)^2}{r^5}(3z^3-zr^2)$$

$$Y_5^{-1} = \sqrt{\frac{11}{4\pi}}\sqrt{\frac{15}{128}}\frac{(x-iy)}{r^5}(21z^4-14z^2r^2+r^4)$$

$$Y_5^{0} = \sqrt{\frac{11}{4\pi}}\,\frac{1}{8}\,\frac{63z^5-70z^3r^2+15zr^4}{r^5}$$

$$Y_5^{1} = -\sqrt{\frac{11}{4\pi}}\sqrt{\frac{15}{128}}\frac{x+iy}{r^5}(21z^4-14z^2r^2+r^4)$$

$$Y_5^{2} = \sqrt{\frac{11}{4\pi}}\sqrt{\frac{105}{32}}\frac{(x+iy)^2}{r^5}(3z^3-zr^2)$$

$$Y_5^{3} = -\sqrt{\frac{11}{4\pi}}\sqrt{\frac{35}{256}}\frac{(x+iy)^3}{r^5}(9z^2-r^2)$$

$$Y_5^{4} = \sqrt{\frac{11}{4\pi}}\sqrt{\frac{315}{128}}\frac{z(x+iy)^4}{r^5}$$

$$Y_5^{5} = -\sqrt{\frac{11}{4\pi}}\sqrt{\frac{63}{256}}\frac{(x+iy)^5}{r^5}$$

APPENDIX II

Linear Combinations of Spherical Harmonics Classified according to Their Transformation Properties[1,40] in Point-group Symmetry O_h
(The four-fold axis is taken as the z axis. For other symmetries, see Bell.[41])

S	A_1	Y_0^0
P	T_1	Y_1^{-1} Y_1^0 $-Y_1^1$
D	T_2	$\frac{1}{\sqrt{2}}(Y_2^2 - Y_2^{-2})$ Y_2^1 Y_2^{-1}
	E	$\frac{1}{\sqrt{2}}(Y_2^2 + Y_2^{-2})$ Y_2^0
F	T_1	$\sqrt{3/8}\,Y_3^1 + \sqrt{5/8}\,Y_3^{-3}$ $\sqrt{3/8}\,Y_3^{-1} + \sqrt{5/8}\,Y_3^3$ Y_3^0
	T_2	$\sqrt{5/8}\,Y_3^1 - \sqrt{3/8}\,Y_3^{-3}$ $\sqrt{5/8}\,Y_3^{-1} - \sqrt{3/8}\,Y_3^3$ $\frac{1}{\sqrt{2}}(Y_3^2 + Y_3^{-2})$
	A_2	$\frac{1}{\sqrt{2}}(Y_3^2 - Y_3^{-2})$
G	T_2	$\frac{1}{\sqrt{2}}(Y_4^2 - Y_4^{-2})$ $\sqrt{1/8}\,Y_4^{-1} - \sqrt{7/8}\,Y_4^3$ $\sqrt{1/8}\,Y_4^1 - \sqrt{7/8}\,Y_4^{-3}$
	A_1	$\sqrt{\frac{7}{12}}Y_4^0 + \sqrt{\frac{5}{12}}(Y_4^4 + Y_4^{-4})\frac{1}{\sqrt{2}}$
	E	$\frac{1}{\sqrt{2}}(Y_4^2 + Y_4^{-2})$ $\sqrt{\frac{5}{12}}\,Y_4^0 - \sqrt{\frac{7}{12}}(Y_4^4 + Y_4^{-4})\frac{1}{\sqrt{2}}$
	T_1	$\frac{1}{\sqrt{2}}(Y_4^4 - Y_4^{-4})$ $\sqrt{7/8}\,Y_4^{-1} + \sqrt{1/8}\,Y_4^3$ $\sqrt{7/8}\,Y_4^1 + \sqrt{1/8}\,Y_4^{-3}$

H	E	$\frac{1}{\sqrt{2}}(Y_5^2 - Y_5^{-2})$
		$\frac{1}{\sqrt{2}}(Y_5^4 - Y_5^{-4})$
	T_2	$\frac{1}{\sqrt{2}}(Y_5^2 + Y_5^{-2})$
		$-\frac{\sqrt{120}}{16} Y_5^{-5} + \frac{\sqrt{112}}{16} Y_5^{-1} + \frac{\sqrt{24}}{16} Y_5^3$
		$-\frac{\sqrt{120}}{16} Y_5^5 + \frac{\sqrt{112}}{16} Y_5^1 + \frac{\sqrt{24}}{16} Y_5^3$
	T_1	Y_5^0
		$\frac{\sqrt{126}}{16} Y_5^{-5} + \frac{\sqrt{60}}{16} Y_5^{-1} + \frac{\sqrt{70}}{16} Y_5^3$
		$\frac{\sqrt{126}}{16} Y_5^5 + \frac{\sqrt{60}}{16} Y_5^1 + \frac{\sqrt{70}}{16} Y_5^{-3}$
	T_1	$\frac{1}{\sqrt{2}}(Y_5^4 + Y_5^{-4})$
		$\frac{\sqrt{10}}{16} Y_5^{-5} + \frac{\sqrt{84}}{16} Y_5^{-1} - \frac{\sqrt{162}}{16} Y_5^3$
		$\frac{\sqrt{10}}{16} Y_5^5 + \frac{\sqrt{84}}{16} Y_5^1 - \frac{\sqrt{162}}{16} Y_5^{-3}$

Tables of wave functions for the d^n configurations may be found in Fieschi and Löwdin.[16]

APPENDIX III

DISTRIBUTIONS OF d^n LEVELS IN STRONG CRYSTALLINE FIELDS OF CUBIC SYMMETRY AFTER JØRGENSEN[42]

			Total sum of degeneracy numbers
d	e	${}^2E$	4
	t_2	${}^2T_2$	6
d^2	e^2	${}^1A_1 + {}^3A_2 + {}^1E$	6
	et_2	${}^1T_1 + {}^3T_1 + {}^1T_2 + {}^3T_2$	24
	$(t_2)^2$	${}^1A_1 + {}^1E + {}^3T_1 + {}^1T_2$	15
d^3	e^3	${}^2E$	4
	e^2t_2	$2\,{}^2T_1 + {}^4T_1 + 2\,{}^2T_2$	36
	$e(t_2)^2$	${}^2A_1 + {}^2A_2 + 2\,{}^2E + 2\,{}^2T_1 + {}^4T_1 + 2\,{}^2T_2 + {}^4T_2$	60
	$(t_2)^3$	${}^4A_2 + {}^2E + {}^2T_1 + {}^2T_2$	20
d^4	e^4	${}^1A_1$	1
	e^3t_2	${}^1T_1 + {}^3T_1 + {}^1T_2 + {}^3T_2$	24
	$e^2(t_2)^2$	$2\,{}^1A_1 + {}^1A_2 + {}^3A_2 + 3\,{}^1E + {}^3E + {}^1T_1 + 3\,{}^3T_1 + 3\,{}^1T_2 + 2\,{}^3T_2 + {}^5T_2$	90
	$e(t_2)^3$	${}^1A_1 + {}^3A_1 + {}^1A_2 + {}^3A_2 + {}^1E + 2\,{}^3E + {}^5E + 2\,{}^1T_1 + 2\,{}^3T_1 + 2\,{}^1T_2 + 2\,{}^3T_2$	80
	$(t_2)^4$	${}^1A_1 + {}^1E + {}^3T_1 + {}^1T_2$	15

d^5	t_2e^4	${}^2T_2$	6
	$(t_2)^2e^3$	${}^2A_1 + {}^2A_2 + 2\,{}^2E + 2\,{}^2T_1 + {}^4T_1 + 2\,{}^2T_2 + {}^4T_2$	60
	$(t_2)^3e^2$	$2\,{}^2A_1 + {}^4A_1 + {}^6A_1 + {}^2A_2 + {}^4A_2 + 3\,{}^2E + 2\,{}^4E + 4\,{}^2T_1 + {}^4T_1 + 4\,{}^2T_2 + {}^4T_2$	120
	$(t_2)^4e$	${}^2A_1 + {}^2A_2 + 2\,{}^2E + 2\,{}^2T_1 + {}^4T_1 + 2\,{}^2T_2 + {}^4T_2$	60
	$(t_2)^5$	${}^2T_2$	6

The configurations d^6 to d^9 can be formed from the table by use of the relation $d^n = d^{10-n}$.

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CHAPTER 5

The Crystal Field Theory: II. Fields of Tetrahedral and of Lower Symmetry

5-a. Tetragonal Fields

There are, of course, many complexes whose symmetry is not octahedral. Indeed, the more sensitive one's measurements, the rarer it becomes to find a perfectly octahedral system. Even when the six ligands are identical, there are many factors tending to destroy their most regular arrangement about the cation. Complexes show, to a greater or lesser degree, both optical and magnetic anisotropies. This makes it very important to discuss the effects of departures from octahedral symmetry. Deviations from the octahedral symmetry are usually treated as perturbations upon the higher symmetry. The most common distortion of the octahedral crystalline field is the presence of a tetragonal or a trigonal field component. We shall treat the tetragonal distortion first.[1–7] In this case the complex may contain four identical ligands arranged in a square at whose center the cation is located. Above and below this plane two other ligands could be placed, the formula for the complex being *trans*-MX_4Y_2. The symmetry is now that of a distorted octahedron, namely, D_{4h}.

The Hamiltonian for a problem possessing tetragonal symmetry is easily seen to be

$$\mathcal{H} = \mathcal{H}_F + \mathcal{V}_R + \mathcal{V}_0 + \mathcal{V}_T \tag{5-1}$$

where $\mathcal{H}_F$, $\mathcal{V}_R$, and $\mathcal{V}_0$ have been defined previously and $\mathcal{V}_T$ is the tetragonal perturbation. In the point group D_{4h} the spherical harmonics of order less than 5 span the identity representation a_{1g} for $n = 2$ and $n = 4$. Hence, disregarding $\mathcal{V}_R$, the complete tetragonal crystalline field potential is

$$\mathcal{V} = aY_2^0 + bY_4^0 + c(Y_4^4 + Y_4^{-4}) \tag{5-2}$$

Treating the tetragonal field as a perturbation upon a cubic field $\mathcal{V}_0$, where $\mathcal{V}_0$ is given in Eq. (4-14),

$$\mathcal{V}_0 = Y_4^0 + \sqrt{5/14}\,(Y_4^4 + Y_4^{-4}) \tag{5-3}$$

we notice that the tetragonal potential (5-2) can be written as

$$\mathcal{V} = \mathcal{V}_0 + \mathcal{V}_T \tag{5-4}$$

where

$$\mathcal{V}_T = AR_2(r)Y_2^0 + BR_4'(r)Y_4^0 \tag{5-5}$$

The elimination of the term $(Y_4^4 + Y_4^{-4})$ in (5-2) by means of (5-3) can be explained on physical grounds as a conservation of the field in the xy plane of the molecule. In other words, the bonding of the four ligands in the plane is left unaltered by the substitution on the z axis. The tetragonal distortion is thus regarded as a perturbation which does not distort the orbitals, but only changes their energies.

We shall thus study the complex MX_4Y_2 as if it were octahedral, say, MX_6, and then add the tetragonal perturbation $\mathcal{V}_T$, whose effect is generally small with respect to that of $\mathcal{V}_0$. $\mathcal{V}_T$ will have the sense either of attracting or of repelling electrons in the neighborhood of the ligands Y. If Y lies below X in the spectrochemical series, we would expect this to be an attraction.

As in the case of an O_h field, we can perform the perturbation by using either the weak-field or the strong-field wave functions. The various matrix elements of the axially symmetric perturbation term $\mathcal{V}_T$ are most easily calculated by using an operator technique. Substituting l_z for z in (5-5), we get

$$\mathcal{V}_T = f_2(r)\tfrac{1}{2}\{3l_z^2 - l(l+1)\} + f_4'(r)\tfrac{1}{8}\{35l_z^4 - 30l(l+1)l_z^2 + 25l_z^2 - 6l(l+1) + 3l^2(l+1)^2\} \tag{5-6}$$

As for d electrons $l = 2$,

$$\mathcal{V}_T = \tfrac{3}{2}f_2(r)(l_z^2 - 2) + \tfrac{3}{2}f_4'(r)(\tfrac{35}{12}l_z^4 - \tfrac{155}{12}l_z^2 + 6) \tag{5-7}$$

Calling the radial integrals Ds and Dt defined as

$$Ds = \int[R_{3d}(r)]^2\,\tfrac{3}{2}f_2(r)\,d\tau \tag{5-8}$$

$$Dt = \int[R_{3d}(r)]^2\,\tfrac{3}{2}f_4'(r)\,d\tau \tag{5-9}$$

and choosing the sign of the latter part of the operator (5-7) to be minus in order to stabilize the axial orbital d_0 the most (see Appendix II), we have

$$\mathcal{V}_T = Ds(l_z^2 - 2) - Dt(\tfrac{35}{12}l_z^4 - \tfrac{155}{12}l_z^2 + 6) \tag{5-10}$$

Ds and Dt are splitting parameters for Y_2^0 and Y_4^0, respectively, in the same way that Dq is for $\mathcal{V}_0$. The expected splitting of the octahedral levels due to the descent in symmetry is given in Table 4-9.

The signs and relative magnitudes of Ds, Dt naturally depend upon the nature of the tetragonal distortion undergone by the octahedron[22] and must be determined by experiments analogous to what is the case for Dq.

In the weak field we get for the matrix elements of $\mathcal{V}_T$

$$\begin{aligned}(d_{\pm 2}|\mathcal{V}_T|d_{\pm 2}) &= 2Ds - Dt\\(d_{\pm 1}|\mathcal{V}_T|d_{\pm 1}) &= -Ds + 4Dt\\(d_0|\mathcal{V}_T|d_0) &= -2Ds - 6Dt\end{aligned} \tag{5-11}$$

With $\hat{Y}_4^0 = \hat{\mathcal{V}}_4$ and $\hat{Y}_2^0 = \mathcal{V}_2$ we have, by using the operator form given in Eq. (5-10), $\hat{\mathcal{V}}_T = \hat{\mathcal{V}}_2 + \hat{\mathcal{V}}_4$. Then from Appendix I:

$$\begin{aligned}\mathcal{V}_4\begin{pmatrix}xz\\yz\end{pmatrix} &= 4\begin{pmatrix}xz\\yz\end{pmatrix}\\\mathcal{V}_4(xy) &= -(xy)\\\mathcal{V}_4(x^2 - y^2) &= -(x^2 - y^2)\\\mathcal{V}_4(z^2) &= -6(z^2)\end{aligned} \tag{5-12}$$

and

$$\begin{aligned}\mathcal{V}_2\begin{pmatrix}xz\\yz\end{pmatrix} &= -\begin{pmatrix}xz\\yz\end{pmatrix}\\\mathcal{V}_2(xy) &= 2(xy)\\\mathcal{V}_2(x^2 - y^2) &= 2(x^2 - y^2)\\\mathcal{V}_2(z^2) &= -2(z^2)\end{aligned} \tag{5-13}$$

For the strong field, since $e_g(O_h) \to (a_{1g} + b_{1g})(D_{4h})$,

$$\begin{aligned}E(b_{1g}) &= (d_{x^2-y^2}|\mathcal{V}_T|d_{x^2-y^2}) = 2Ds - Dt\\E(a_{1g}) &= (d_{z^2}|\mathcal{V}_T|d_{z^2}) = -2Ds - 6Dt\end{aligned} \tag{5-14}$$

Further, since $t_{2g}(O_h) \to (b_{2g} + e_g)(D_{4h})$,

$$\begin{aligned}E(b_{2g}) &= (d_{xy}|\mathcal{V}_T|d_{xy}) = 2Ds - Dt\\E(e_g) &= (d_{xz}|\mathcal{V}_T|d_{xz}) = -Ds + 4Dt\end{aligned} \tag{5-15}$$

Notice that the center-of-gravity rule holds for the Ds elements inside the e_g and t_{2g} levels but for the Dt elements only for the whole configuration. This is due to the fact that Y_2^0 terms do not occur in $\mathcal{V}_0$ but that Y_4^0 terms do.

Let us find the tetragonal splitting in the excited strong-field states of d^3, ${}^4T_{2g}(t_{2g})^2e_g$ and ${}^4T_{1g}(t_{2g})^2e_g$. By descent in symmetry to D_{4h}, we see that

$$\psi_1 = |\overset{+}{(xz)}\overset{+}{(yz)}\overset{+}{(x^2 - y^2)}| \qquad \text{and} \qquad \phi_1 = |\overset{+}{(xx)}\overset{+}{(yz)}\overset{+}{(z^2)}|$$

transform like B_{2g} and A_{2g}, respectively. Hence, ψ_1 is a component of ${}^4T_{2g}$ in O_h and ϕ_1 is a component of ${}^4T_{1g}$ in O_h.

The complete wave functions for ${}^4T_{2g}$ and ${}^4T_{1g}$ in O_h symmetry are then constructed by the application of the operator $\hat{C}_3$ upon ψ_1 and ϕ_1.

$$\begin{aligned}\psi_1 &= |\overset{+}{(xz)}\overset{+}{(yz)}\overset{+}{(x^2 - y^2)}|\\\psi_2 &= -\frac{1}{2}|\overset{+}{(yz)}\overset{+}{(xy)}\overset{+}{(x^2 - y^2)}| + \frac{\sqrt{3}}{2}|\overset{+}{(yz)}\overset{+}{(xy)}\overset{+}{(z^2)}|\\\psi_3 &= -\frac{1}{2}|\overset{+}{(xy)}\overset{+}{(xz)}\overset{+}{(x^2 - y^2)}| - \frac{\sqrt{3}}{2}|\overset{+}{(xy)}\overset{+}{(xz)}\overset{+}{(z^2)}|\end{aligned} \tag{5-16}$$

and

$$\phi_1 = |\overset{+}{(xz)}\overset{+}{(yz)}\overset{+}{(z^2)}|$$

$$\phi_2 = -\frac{1}{2}|\overset{+}{(yz)}\overset{+}{(xy)}\overset{+}{(z^2)}| - \frac{\sqrt{3}}{2}|\overset{+}{(yz)}\overset{+}{(xy)}\overset{+}{(x^2 - y^2)}| \qquad (5\text{-}17)$$

$$\phi_3 = -\frac{1}{2}|\overset{+}{(xy)}\overset{+}{(xz)}\overset{+}{(z^2)}| + \frac{\sqrt{3}}{2}|\overset{+}{(xy)}\overset{+}{(xz)}\overset{+}{(x^2 - y^2)}|$$

Hence,

$$(\psi_1|\mathcal{V}_T|\psi_1) = 7Dt \qquad (5\text{-}18)$$

$$(\psi_2|\mathcal{V}_T|\psi_2) = (\psi_3|\mathcal{V}_T|\psi_3) = -\tfrac{7}{4}Dt \qquad (5\text{-}19)$$

or

$$\Delta E(^4T_{2g},O_h) = \tfrac{35}{4}Dt$$

$$(\phi_1|\mathcal{V}_T|\phi_1) = -4Ds + 2Dt \qquad (5\text{-}20)$$

$$(\phi_2|\mathcal{V}_T|\phi_2) = (\phi_3|\mathcal{V}_T|\phi_3) = 2Ds + \tfrac{3}{4}Dt \qquad (5\text{-}21)$$

or

$$\Delta E(^4T_{1g}O_h) = 6Ds - \tfrac{5}{4}Dt$$

In deriving these results the configuration interaction that takes place between the split ^4E_g components of the $^4T_{1g}$ and $^4T_{2g}$ has not been considered. They are thus valid only in first order.

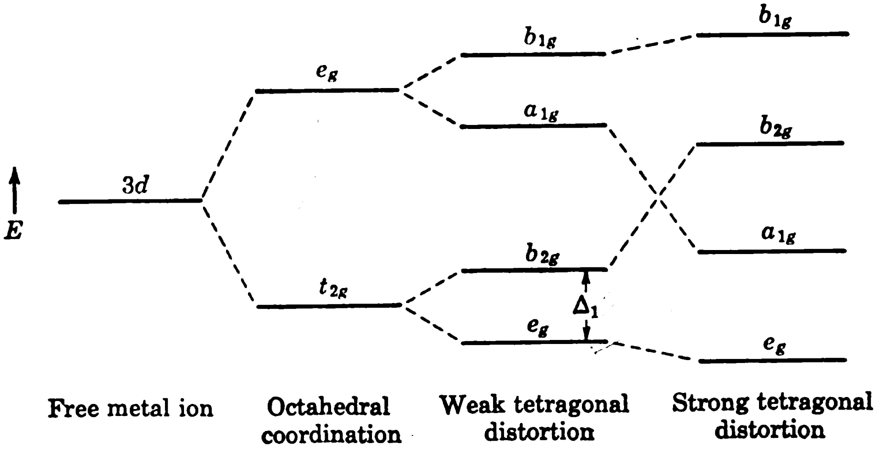


FIG. 5-1. Energy-level diagram for a tetragonal distorted metal complex.

The lowering of the symmetry from O_h to D_{4h} causes, as we have seen, a splitting of the cubic orbitals t_{2g} and e_g (Fig. 5-1). These further splittings may give rise to a situation entirely analogous to the one responsible for the low-spin complexes of Fe(III), Co(III), etc., Sec. 4-*g*.

As the most simple example consider a tetragonally distorted Cr(III) complex. In the cubic field the ground state would be $\psi(^4A_{2g}) = (t_{2g})^3$. In the tetragonal case, however, the ground state could be either (see Fig. 5-1) $\psi(^2E_g) = (e_g)^3$ or $\psi(^4B_{1g}) = (e_g)^2(b_{2g})$. We have found that the energy difference Δ between b_{2g} and e_g is $3Ds - 5Dt$. On the other hand, the energy required to couple the spin in a $(e_g)^3$ configuration is seen from Eq. (4-165) to be $3(3F_2 + 20F_4)$. Hence, the complex will exhibit three unpaired spins if

$$3(3F_2 + 20F_4) > 3Ds - 5Dt \qquad (5\text{-}22)$$

but if the opposite holds true, it will have only one unpaired spin.

In tetragonal Cr(III) complexes the latter case has not been realized, but a situation similar to the one described above occurs for tetragonal Ni(II) complexes, especially for square planar complexes such as $Ni(CN)_4^{-}$. Since Ni(II) has the electronic configuration $[A](3d)^8$, the competition is here (see Fig. 5-1) between the electronic configurations $(e_g)^4(b_{2g})^2(a_{1g})(b_{1g})$ or $(e_g)^4(b_{2g})^2(a_{1g})$ (weak tetragonal) or $(e_g)^4(a_{1g})^2(b_{2g})(b_{1g})$ or $(e_g)^4(a_{1g})^2(b_{2g})^2$ (strong tetragonal) giving either paramagnetic ($S = 1$) or diamagnetic ($S = 0$) ground states. For a closer mathematical analysis of this case see Ref. 20.

A pronounced tetragonal splitting of the excited electronic states has been observed only for complexes of Cr^{3+} and Co^{3+}. The theory for the Co^{3+} complexes especially has received a great deal of attention,[6,23,24] but it can easily be seen that the Cr^{3+} complexes behave both qualitatively and quantitatively like the Co^{3+} compounds. The discussion of the experimental details will be given later.

5-b. Trigonal Fields

If the octahedron is distorted along the trigonal axis, a splitting of the octahedral levels quite similar to what is found in the tetragonal case takes place. The symmetry of the molecule is lowered from O_h to D_{3d} or C_{3v}; in both cases the threefold degenerate levels in O_h, T_{1g}, and T_{2g} split into one single and one twofold degenerate level. The twofold level E_g, however, remains degenerate in contrast to what takes place in going from O_h to D_{4h}. The correlation scheme for O_h to D_{3d} is shown in Table 5-1.

TABLE 5-1. CORRELATION BETWEEN O_h AND D_{3d}

O_h	D_{3d}
A_1	A_1
A_2	A_2
E	E
T_1	$A_2 + E$
T_2	$A_1 + E$

In the trigonal case it is most convenient to start out with octahedral wave functions quantized along the threefold axis. As before, we take the crystalline field to be made up by a cubic and an axial field:

$$\mathcal{V} = \mathcal{V}_0 + \mathcal{V}_r \tag{5-23}$$

with Eq. (4-23)

$$\mathcal{V}_0 = Y_4^0 + \sqrt{10/7}\,(Y_4^3 - Y_4^{-3}) \tag{5-24}$$

and

$$\mathcal{V}_r = aR_2(r)Y_2^0 + bR_4'(r)Y_4^0 \tag{5-25}$$

Notice that the perturbing potential $\mathcal{V}_r$ is identical in form to $\mathcal{V}_T$, the tetragonal perturbation, but the orbital set that $\mathcal{V}_r$ must operate upon is (4-41) to (4-44) and not (4-27) to (4-29).

Again we choose the sign of Y_4^0 to be minus in order to stabilize the d_{z^2} orbital the most, and we obtain the following equations by using the operator technique upon the cubic orbital set (4-43), (4-44) and calling $\hat{Y}_4^0 = \hat{\mathcal{V}}_4$ and $\hat{Y}_2^0 = \hat{\mathcal{V}}_2$ as in the tetragonal case.

$$
\begin{aligned}
\hat{\mathcal{V}}_4 t_{2g}^{\pm} &= \frac{2}{3} t_{2g}^{\pm} - \frac{5\sqrt{2}}{3} e_g^{\pm} \\
\hat{\mathcal{V}}_4 t_{2g}^{0} &= -6 t_{2g}^{0} \\
\mathcal{V}_4 e_g^{\pm} &= \frac{7}{3} e_g^{\pm} - \frac{5\sqrt{2}}{3} t_{2g}^{\pm}
\end{aligned}
\qquad (5\text{-}26)
$$

$$
\begin{aligned}
\hat{\mathcal{V}}_2 t_{2g}^{\pm} &= t_{2g}^{\pm} + \sqrt{2}\, e_g^{\pm} \\
\hat{\mathcal{V}}_2 t_{2g}^{0} &= -2 t_{2g}^{0} \\
\hat{\mathcal{V}}_2 e_g^{\pm} &= \sqrt{2}\, t_{2g}^{\pm}
\end{aligned}
\qquad (5\text{-}27)
$$

Contrary to what is found for a tetragonal perturbation, we see that a trigonal field scrambles the t_{2g} and e_g orbitals. Analogously to Ds and Dt, we designate[25] the trigonal splitting parameters $D\sigma$ and $D\tau$. The nonvanishing matrix elements are then for the weak-field case

$$
\begin{aligned}
(d_{\pm 2}|\mathcal{V}_\tau|d_{\pm 2}) &= 2D\sigma - D\tau \\
(d_{\pm 1}|\mathcal{V}_\tau|d_{\pm 1}) &= -D\sigma + 4D\tau \\
(d_0\ |\mathcal{V}_\tau|\ d_0) &= -2D\sigma - 6D\tau
\end{aligned}
\qquad (5\text{-}28)
$$

and for the strong-field case

$$
\begin{aligned}
(t_{2g}^{\pm}|\mathcal{V}_\tau|t_{2g}^{\pm}) &= D\sigma + \tfrac{2}{3} D\tau \\
(t_{2g}^{0}\ |\mathcal{V}_\tau|t_{2g}^{0}) &= -2D\sigma - 6D\tau \\
(e_g^{\pm}\ |\mathcal{V}_\tau|e_g^{\pm}) &= \tfrac{7}{3} D\tau \\
(t_{2g}^{\pm}|\mathcal{V}_\tau|e_g^{\pm}) &= \sqrt{2}\, D\sigma - \frac{5\sqrt{2}}{3} D\tau
\end{aligned}
\qquad (5\text{-}29)
$$

As pointed out by Pryce and Runciman,[12] it may sometimes be advantageous when considering a trigonal distortion to use the linear combinations (5-30)

$$
\begin{aligned}
t_0 &= +\frac{1}{\sqrt{3}}[(xy) + (yz) + (xz)] \\
t_+ &= -\frac{1}{\sqrt{3}}[(xy) + \omega(yz) + \omega^2(xz)] \\
t_- &= +\frac{1}{\sqrt{3}}[(xy) + \omega^{-1}(yz) + \omega^{-2}(xz)] \\
e_+ &= -\frac{1}{\sqrt{2}}[(z^2) + i(x^2 - y^2)] \\
e_- &= +\frac{1}{\sqrt{2}}[(z^2) - i(x^2 - y^2)]
\end{aligned}
\qquad (5\text{-}30)
$$

where $\omega = e^{2\pi i/3}$. The unitary transformation

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} & 0 \\ \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & -\sqrt{\frac{2}{3}} \\ \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \tag{5-31}$$

will direct the z axis along the (111) direction and transform $\mathcal{V}_r$, Eq. (5-25), to

$$\mathcal{V}_r = A_2[xy + yz + xz] + A_4[yz(r^2 - 7x^2) + xz(r^2 - 7y^2) + xy(r^2 - 7z^2)] \tag{5-32}$$

Both the terms in brackets are the sum of three functions transforming like the cubic representation T_2. Taking the direct product, it is easy to see that the matrix element $(e|\mathcal{V}_r|e)$ is equal to zero but that the matrix elements $(t|\mathcal{V}_r|t)$ and $(t|\mathcal{V}_r|e)$ are different from zero. Demanding that the center of gravity shall be preserved inside the $(t_{2g})^n$ configuration, and calling the suitable linear combinations of the splitting parameters $D\sigma$ and $D\tau$ for $\mathcal{V}$ and $\mathcal{V}'$, respectively, we can put

$$(t_\pm|\mathcal{V}_r|t_\pm) = -\tfrac{1}{3}\mathcal{V} \tag{5-33}$$

$$(t_0|\mathcal{V}_r|t_0) = \tfrac{2}{3}\mathcal{V} \tag{5-34}$$

and

$$(t_\pm|\mathcal{V}_r|e_\pm) = \mathcal{V}' \tag{5-35}$$

all other matrix elements being zero. This form of a trigonal perturbation has the advantage over the previous treatment that to a good approximation $\mathcal{V}'$ can be put equal to zero,[12] at least in so far as energy calculations are concerned, retaining only $\mathcal{V}$ as the trigonal parameter. However, the mixing of $t_\pm$ and $e_\pm$ is important where band-intensity calculations are concerned.[21]

A special case of a trigonal field component is presented by complexes possessing three bidentate rings such as $\mathrm{Cr(en)_3}^{+3}$, where en stands for ethylenediamine. Such complexes can only possess the symmetry D_3, but to a high approximation their behavior follows the patterns to be expected for molecules of full octahedral symmetry. For instance, the spectra of *tris*-ethylenediamine complexes bear a very close resemblance to those of the hexamines. Since, however, no center of symmetry is present in these molecules, d and p orbitals may be mixed via the crystalline field.

The possible additional terms in the crystalline field potential capable of scrambling the d and p orbitals are

$$Y_1^0 \qquad Y_3^0 \qquad Y_3^3 + Y_3^{-3} \qquad \text{and} \qquad Y_3^3 - Y_3^{-3}$$

where the trigonal axis in D_3 has been taken as z axis. The transformation properties in D_3 are given in the following table.

	E	C_3	C_2	
Y_1^0	Y_1^0	Y_1^0	$-Y_1^0$	A_2
Y_3^0	Y_3^0	Y_3^0	$-Y_3^0$	A_2
$Y_3^3 + Y_3^{-3}$	$Y_3^3 + Y_3^{-3}$	$Y_3^3 + Y_3^{-3}$	$Y_3^3 + Y_3^{-3}$	A_1
$Y_3^3 - Y_3^{-3}$	$Y_3^3 - Y_3^{-3}$	$Y_3^3 - Y_3^{-3}$	$-(Y_3^3 - Y_3^{-3})$	A_2

(5-36)

In other words, the crystalline field potential can be augmented with a term of the form $Y_3^3 + Y_3^{-3}$. Such an additional potential has been used by Moffitt[11] in a vain attempt to account for the optical rotatory dispersion spectra of Co(en)_3^{+3} and Cr(en)_3^{+3}.

On the other hand, all the terms in (5-36) which transform like A_2 in D_3 transform like A_1 in C_{3v}. Hence, we would expect a great amount of scrambling of d and p orbitals to take place in this latter symmetry. In general, however, these terms are neglected and the molecules are treated as if their electronic configurations were made up of pure d orbitals.

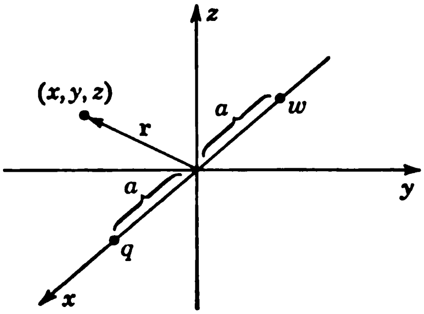


Fig. 5-2. Point charges in a linear molecule.

5-c. Cis, Trans and Rhombic Fields

In order to clarify some peculiarities about the crystalline field potential, we shall look a bit closer at the point-charge model, Fig. 5-2. Two point charges q and w are placed in the x axis at a distance $\pm a$ from the center of the coordinate system. The resulting potential at the point (x,y,z) is then

$$\mathcal{V} = \frac{w}{\sqrt{(x+a)^2 + y^2 + z^2}} + \frac{q}{\sqrt{(x-a)^2 + y^2 + z^2}} \tag{5-37}$$

$$= \frac{1}{a}\left[w\left(1 + 2\frac{x}{a} + \frac{r^2}{a^2}\right)^{-1/2} + q\left(1 - 2\frac{x}{a} + \frac{r^2}{a_2}\right)^{-1/2}\right] \tag{5-38}$$

Expanding $\mathcal{V}$ around $\mathbf{r} = 0$ inside a sphere with radius $r = a$, we have by use of the formula[14]

$$(1 - 2r\cos\Theta + r^2)^{-1/2} = \sum_{n=0}^{\infty} r^n P_n(\cos\Theta) \tag{5-39}$$

$$\mathcal{V} = \frac{1}{a}\left[w\left\{1 - \frac{r}{a}P_1(x) + \left(\frac{r}{a}\right)^2 P_2(x) - \left(\frac{r}{a}\right)^3 P_3(x) + \left(\frac{r}{a}\right)^4 P_4(x) - \cdots\right\}\right.$$
$$\left. + q\left\{1 + \frac{r}{a}P_1(x) + \left(\frac{r}{a}\right)^2 P_2(x) + \left(\frac{r}{a}\right)^3 P_3(x) + \left(\frac{r}{a}\right)^4 P_4(x) + \cdots\right\}\right] \tag{5-40}$$

Since we are operating inside a manifold of d orbitals, we throw the odd

Legendre functions away and cut off the series after the P_4 term. Hence,

$$\mathcal{V} = \frac{1}{a}(w + q)\left[1 + \left(\frac{r}{a}\right)^2 P_2(x) + \left(\frac{r}{a}\right)^4 P_4(x)\right] \tag{5-41}$$

Notice that only the *sum* of w and q is of importance for the crystalline field potential. In other words, the crystalline potential for an octahedron can be written as the sum of three contributions, each of them containing the sum of the axial electric charges. By adding the contributions of all three axes together and putting all the point charges equal, the cubic potential (4-15) is of course obtained.

Calling the sum of the charges on the x, y, and z axes respectively μ_1, μ_2, and μ_3, the complex is said to have a cubic crystalline field if $\mu_1 = \mu_2 = \mu_3$. If $\mu_1 = \mu_2 \neq \mu_3$, the crystal field has tetragonal symmetry, and finally, if $\mu_1 \neq \mu_2 \neq \mu_3$, the crystalline field has rhombic symmetry. This latter case is seen to be the lowest symmetry possible in an octahedral complex.

It is thus possible[15] to define a tetragonal contribution to the octahedral crystalline field as

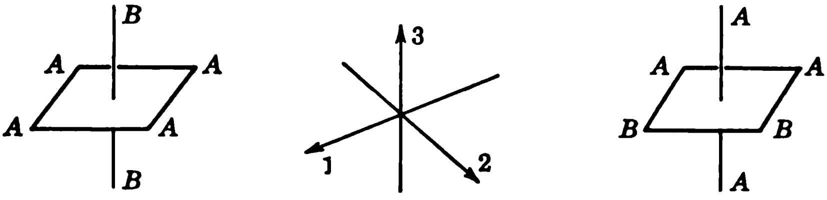
$$\mathcal{V}_T = \left(\frac{\mu_1 + \mu_2}{2} - \mu_3\right) f(x,y,z) \tag{5-42}$$

and as

$$\mu_1 = \mu_2 \neq \mu_3$$

$$\mathcal{V}_T = (\mu_1 - \mu_3) f(x,y,z) \tag{5-43}$$

Owing to the fact that only the sum of the charges on each axis determines the electronic structure of a given complex where all distances are equal, the symmetry groups of a cis and trans complex are both in practice D_{4h}, tetragonal (Fig. 5-3), even if formally the symmetry group of the cis complex only is C_{2v}. Hence for the tetragonality parameter $(\mu_1 - \mu_3)$



trans-MA_4B_2
$\mu_1 = \mu_2 \neq \mu_3$

cis-MA_4B_2
$\mu_1 = \mu_2 \neq \mu_3$

FIG. 5-3. Cis and trans configurations.

$$\begin{array}{rlcrl}
\multicolumn{2}{c}{\textit{trans}\text{-}\mathrm{MA_4B_2}} & \qquad & \multicolumn{2}{c}{\textit{cis}\text{-}\mathrm{MA_4B_2}} \\
\mu_1 &= 2q_A & & \mu_1 &= q_A + q_B \\
\mu_3 &= 2q_B & & \mu_3 &= 2q_A \\
\mu_1 - \mu_3 &= 2(q_A - q_B) & & \mu_1 - \mu_3 &= -(q_A - q_B)
\end{array}$$

In other words, we should expect a trans complex to exhibit a tetragonal splitting, being twice the splitting of a cis complex, and with the level order inverted.[15,24]

It must, however, be borne in mind that the result is derived by using the crudest of approximations, and too much reliance cannot be placed in it. Nevertheless, it offers a simple explanation for the well-known fact that the absorption bands of a trans complex usually are split more than those of the corresponding cis complex.

We shall not have much to say concerning the rhombic crystalline field case. Very few calculations have been made with such a potential since the classic work of Schlapp and Penney[16] concerned with the lower electronic states of Co(II). Usually it is more important to include other terms in the Hamiltonian, such as the spin-orbit coupling, or dynamical effects (Jahn-Teller) than it is to augment the crystalline field potential with a rhombic field component. The incorporation of these latter effects will be dealt with later.

5-d. Tetrahedral Fields

As already mentioned in Sec. 3-*d*, the regular tetrahedron (point group T_d) belongs to a cubic point group. The symmetry operations are $\hat{E}$, $8\hat{C}_3$, $3\hat{C}_2$, $6\hat{S}_4$, and $6\hat{\sigma}_d$. So long as we stay inside the manifold spanned by the d orbitals, the crystalline field potential $\mathcal{V}$ is identical with that of $\mathcal{V}_0$ and the d orbitals split up in a threefold degenerate t_2 level and a twofold degenerate e level. In order to prove this, we look at the transformation scheme for d orbitals in T_d symmetry,[17] Fig. 3-4.

TRANSFORMATION SCHEME FOR d ORBITALS IN T_d

	E	C_3	C_2	S_4	σ_d
d_{xy}	d_{xy}	d_{xz}	d_{xy}	$-d_{xy}$	d_{xy}
d_{yz}	d_{yz}	d_{xy}	$-d_{yz}$	d_{xz}	$-d_{xz}$
d_{xz}	d_{xz}	d_{yz}	$-d_{xz}$	$-d_{yz}$	$-d_{yz}$
χ	3	0	-1	-1	1
$d_{x^2-y^2}$	$d_{x^2-y^2}$	$-\frac{1}{2}d_{x^2-y^2} + \frac{\sqrt{3}}{2} d_{z^2}$	$d_{x^2-y^2}$	$-d_{x^2-y^2}$	$-d_{x^2-y^2}$
d_{z^2}	d_{z^2}	$-\frac{1}{2}d_{z^2} - \frac{\sqrt{3}}{2} d_{x^2-y^2}$	d_{z^2}	d_{z^2}	d_{z^2}
χ	2	-1	2	0	0

A comparison with the character table[17] for T_d reveals that the set (xy), (yz), and (xz) transforms as t_2 and $(x^2 - y^2)$ and (z^2) as e. Notice that we have dropped the subscript g in the orbital designations because of the lack of a center of symmetry in the molecule. However, the d orbitals used to describe the tetrahedral orbitals have, of course, still an inherent center of inversion.

In order to compare the magnitude of the splitting in a tetrahedral molecule with the splitting found in an octahedral molecule, we shall again look at the point-charge models of the molecules, Fig. 5-1. If q_i point charges are placed around the center of the coordinate system, the resulting potential is

$$\mathcal{V} = e^2 \sum_i \frac{q_i}{|\mathbf{r}_k - \mathbf{a}_i|} \tag{5-44}$$

Expanding[14] $\mathcal{V}$ around the center of the coordinate system in a series of normalized spherical harmonics, we have

$$\mathcal{V} = e^2 \sum_i \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi q_i}{2l+1} \frac{r_<^{\,l}}{r_>^{\,l+1}} Y_l^{m*}(\Theta,\varphi) Y_l^m(\Theta_i,\varphi_i) \tag{5-45}$$

where $r_<$ is the smaller and $r_>$ is the larger of the two distances $|\mathbf{r}_k|$ and $|\mathbf{a}_i|$ and Θ_i, φ_i are the angular coordinates for a_i.

The crystalline field energy for the $d_{z^2} = R(r)Y_2^0$ orbital having $m_l = 0$ and $l = 2$ is

$$E(d_{z^2}) = (R(r)Y_2^0|\mathcal{V}|Y_2^0R(r)) \tag{5-46}$$

Hence in the matrix element (5-46) only $m_l = 0$ gives a contribution, and with the further knowledge that only fourth-order terms occur in $\mathcal{V}$ we have

$$E(d_{z^2}) = \left(R(r)Y_2^0 \left| e^2 \sum_i \frac{4\pi q_i}{9} \frac{r_<^{\,4}}{r_>^{\,5}} Y_4^0(\Theta,\varphi) Y_4^0(\Theta_i,\varphi_i) \right| Y_2^0 R(r)\right) \tag{5-47}$$

By comparing the energy of the d_{z^2} orbital in an octahedral and in a tetrahedral crystalline field we get, because the radial parts cancel out and because Y_4^0 is equal to a constant times the Legendre polynomial $P_4(\cos\Theta)$,

$$\frac{E(d_{z^2})\text{ oct.}}{E(d_{z^2})\text{ tet.}} = \frac{\sum_{i=1}^{6} q_i P_4(\cos\Theta_i)}{\sum_{i=1}^{4} q_i P_4(\cos\Theta_i)} \tag{5-48}$$

In an octahedral field we have, with q_1 and q_6 located upon the z axis,

$$|\cos\Theta_1| = |\cos\Theta_6| = 1 \tag{5-49}$$

and for the q's in the xy plane

$$\cos\Theta_i = 0 \qquad i = 2, 3, 4, 5 \tag{5-50}$$

For a tetrahedral field:

$$|\cos\Theta_i| = \frac{\sqrt{3}}{3} \qquad i = 1, 2, 3, 4 \tag{5-51}$$

Hence
$$\frac{E(d_{z^2})\text{ oct.}}{E(d_{z^2})\text{ tet.}} = -\frac{9}{4} \tag{5-52}$$

If we had placed eight point charges at the corners of the cube, the ratio (5-49) would have been $-9/8$.

For a point-charge model the following relations are thus found to be valid.

$$-\tfrac{9}{4}Dq\text{ tet.} = Dq\text{ oct.} = -\tfrac{9}{8}Dq\text{ cube} \tag{5-53}$$

Notice that the level order is inverted in going from an octahedron to a tetrahedron. This reversal was first pointed out by Gorter.[18]

As proved above, we can take over all of the theory developed in the preceding chapter for the O_h point group and apply it to the T_d molecules. The only necessary change is that the sign of Dq must be reversed. This holds strictly true so long as we stay inside the d orbitals, but a complication arises in that the tetrahedral molecule does not have a center of symmetry. As we shall show next, the expansion of $\mathcal{V}$ contains an odd (third-order) potential in T_d, in contrast to what is found in O_h. This term cannot, of course, have matrix elements between two d orbitals, but it may scramble the d and p states.

Of the possible odd-order potentials we see immediately that the set Y_1^1, Y_1^0, and Y_1^{-1} transform like T_1 in T_d. This leaves the set Y_3^{-3} to Y_3^3. Constructing the real functions

$$\begin{aligned}
\psi_1 &= \frac{1}{i\sqrt{2}}(Y_3^3 + Y_3^{-3}) & \psi_5 &= \frac{1}{i\sqrt{2}}(Y_3^1 + Y_3^{-1}) \\
\psi_2 &= \frac{1}{\sqrt{2}}(Y_3^3 - Y_3^{-3}) & \psi_6 &= \frac{1}{\sqrt{2}}(Y_3^1 - Y_3^{-1}) \\
\psi_3 &= \frac{1}{\sqrt{2}}(Y_3^2 + Y_3^{-2}) & \psi_7 &= Y_3^0 \\
\psi_4 &= \frac{1}{i\sqrt{2}}(Y_3^2 - Y_3^{-2}) & &
\end{aligned} \tag{5-54}$$

We have that the transformation scheme in T_d is as follows:

	E	C_3	C_2	S_4	σ_d
ψ_1	ψ_1	$\frac{\sqrt{15}}{4}\psi_6 - \frac{1}{4}\psi_2$	$-\psi_1$	ψ_2	ψ_2
ψ_2	ψ_2	$-\sqrt{5/8}\,\psi_7 + \sqrt{3/8}\,\psi_3$	$-\psi_2$	$-\psi_1$	ψ_1
ψ_3	ψ_3	$-\frac{\sqrt{10}}{4}\psi_5 + \frac{\sqrt{6}}{4}\psi_1$	ψ_3	ψ_3	$-\psi_3$
ψ_4	ψ_4	ψ_4	ψ_4	ψ_4	ψ_4
ψ_5	ψ_5	$-\frac{1}{4}\psi_6 - \frac{\sqrt{15}}{4}\psi_2$	$-\psi_5$	$-\psi_6$	$-\psi_6$
ψ_6	ψ_6	$\sqrt{3/8}\,\psi_7 + \sqrt{5/8}\,\psi_3$	$-\psi_6$	ψ_5	$-\psi_5$
ψ_7	ψ_7	$\sqrt{5/8}\,\psi_1 + \sqrt{3/8}\,\psi_5$	ψ_7	$-\psi_7$	ψ_7

(5-55)

Inspection of (5-55) reveals that $\psi_4 = (1/i\sqrt{2})(Y_3^2 - Y_3^{-2})$ transforms like a_1 in T_d symmetry. In cartesian coordinates

$$\psi_4 = \mathcal{V} = kxyz \tag{5-56}$$

where k is a constant.

The p orbitals are located ~10^5 cm^{-1} above the d orbitals for the first-row transition elements. The correct "3d" wave functions to use in the construction of the tetrahedral states are then given by first-order perturbation theory as

$$\psi(3d) = \psi^\circ(3d) - \sum_p \frac{(\psi^\circ(3d)|\mathcal{V}|\psi^\circ(4p))}{E_p^\circ - E_d^\circ}\,\psi^\circ(4p) \tag{5-57}$$

or written out

$$\left.\begin{aligned} \psi_{xy} &= (3d_{xy}) - \omega(4p_z) \\ \psi_{xz} &= (3d_{xz}) - \omega(4p_y) \\ \psi_{yz} &= (3d_{yz}) - \omega(4p_x) \end{aligned}\right\} \quad t_2 \tag{5-58}$$

$$\left.\begin{aligned} \psi_{x^2-y^2} &= (3d_{x^2-y^2}) \\ \psi_{z^2} &= (3d_{z^2}) \end{aligned}\right\} \quad e \tag{5-59}$$

with

$$\omega = \frac{k}{E_p^\circ - E_d^\circ}\,(3d_{xy}|xyz|4p_z) \tag{5-60}$$

Using a point-charge model,[19] the value of ω is about 8×10^{-2}. The intermixing of 3d and 4p orbitals is thus about 10 per cent in this approximation. In a molecular-orbital scheme,[19] however, this mixing is insignificant in comparison with the effect produced by the scrambling of the ligand and metal orbitals (see later). Hence, there is a good theoretical reason for the experimental fact that a point-charge model for a tetrahedral molecule does not work nearly as well as for an octahedral molecule.

All in all, it may be concluded that the crystal field theory gives the most satisfactory results for cubic octahedral complexes. This is mainly due to the fact that the lower the symmetry the more parameters are required in order to specify the electronic states. These additional parameters can usually never be unambiguously assigned, owing to the lack of sufficient experimental data. The further discussion of the features dealt with in this chapter will be postponed to Chap. 10, where the electronic properties of individual ions will be elucidated.

APPENDIX I

Application of Tetragonal Operators upon the Set of d Orbitals

$$(\ell_z^2 - 2)\begin{cases} d_2 = 2d_2 \\ d_1 = -d_1 \\ d_0 = -2d_0 \\ d_{-1} = -d_{-1} \\ d_{-2} = 2d_{-2} \end{cases}$$

$$(^{35}\!/_{12}\,\ell_z^4 - {}^{155}\!/_{12}\,\ell_z^2 + 6)\begin{cases} d_2 = d_2 \\ d_1 = -4d_1 \\ d_0 = 6d_0 \\ d_{-1} = -4d_{-1} \\ d_{-2} = d_{-2} \end{cases}$$

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CHAPTER 6

Spin-Orbit Coupling

6-a. Importance of Spin-Orbit Coupling

The influence of the spin-orbit coupling upon the electronic properties of the complex ions is, of course, to a great extent governed by the order of magnitude of the coupling constant. Owing to the fact that the crystal field splitting for the $(3d)^n$ systems is large compared to the small *LS* splitting, we have so far been able to neglect this latter effect in our treatment. It follows that, at least in the weak-field approximation scheme, the validity of the quantum numbers *L* and *S* is not seriously impaired for the $(3d)^n$ complexes.

On the other hand, for complexes of the rare earths and actinides the crystal field splitting is small compared to the *LS* splitting, and for the complexes possessing $(4d)^n$ and $(5d)^n$ electronic configurations the crystal field splitting and the spin-orbit coupling are of the same order of magnitude. Consequently, for the electronic configurations $(4f)^n$ and $(5f)^n$ *J* is a good quantum number, whereas for $(4d)^n$ and $(5d)^n$ configurations neither *L* nor *J* is a good quantum number. These latter cases must accordingly be treated in an intermediate coupling scheme.

Even though the spin-orbit coupling is small in the $(3d)^n$ systems, its presence has important consequences for the magnetic properties and also, to a certain extent, for the spectral features of these complexes. Magnetically, its presence can be felt in the departure from the spin-only value of the magnetic susceptibility of the complex[1] and in the zero-field splitting[2] found, for instance, by paramagnetic resonance methods. Optically it has been possible in only a few cases to detect a spin-orbit splitting of the absorption bands for $(3d)^n$ complexes.[3] This is due to the fact that usually the multiplet structure is very poorly resolved in these bands.

The presence of the spin-orbit coupling is perhaps most clearly revealed by the existence of the so-called "spin-forbidden" absorption bands. These bands are due to transitions between states which differ in their spin quantum number *S*. Since without spin-orbit coupling *S* would be a rigorous quantum number, these transitions are observed only because the spin-orbit coupling scrambles together states which differ by $\Delta S = 1$.

As we move from 3*d* to 4*d* and further to 5*d* electrons, the value of the spin-orbit coupling constant ξ increases. Hence Moffitt et al.[4] are forced to treat the $(5d)^n$ electronic configurations by using *jj* coupling. Or rather, by using this coupling as a starting point, they find that these compounds are located midway between the *jj* and *LS* coupling schemes. This situation is parallel to the one encountered in Chap. 4 in the treatment of the intermediate crystalline field.

Although, as indicated, the spin-orbit coupling plays a dominant role in the theory of f^n configurations, we shall not have much to say about these compounds, even though many of the historical developments in crystal field theory are due to studies of the rare earths.[5–9] From a chemical point of view, however, these complexes are less interesting than those of the first, second, and third transition series. Chemically, their properties are a more or less continuous reflection of the lanthanide contraction with the anticipated singularities at or near the xenon structure, the half-completed 4*f* shell, and the completed 4*f* shell.

The 4*f* electrons are shielded from their ligands by the completed 5*s* and 5*p* shells, so that the crystalline field of a given (L,S,J) term only is about 100 cm^{-1}. The crystal field which further has a rather low symmetry (C_{3h} or even C_{3v}) is consequently of much less importance than the spin-orbit couplings, the latter being mostly of the order of a couple of thousand wave numbers for these ions. Accordingly, the electronic features of the complexes of the rare earths are affected very little by their environment. Spectral studies of their salts in the infrared, visible, and ultraviolet are of interest because they yield, effectively, the atomic line spectra of the ions in a specific oxidation state. The interpretation of these spectra is mostly a problem in atomic spectroscopy, however, and at that a very difficult and tricky one. Chemically, perhaps, the main interest of these studies would lie in getting information about local site symmetries in crystals. We shall therefore leave this subject here by giving a few references to past and current work in this field.[10–20,83–85] Two excellent review papers are also listed.[21,22]

6-b. Spin-Orbit Coupling for One *d* Electron in Octahedral Fields

The interaction of the spins of a system of *d* electrons with their own orbital motions in a central force field may, as treated in Chap. 2, be written

$$\mathcal{H}_\xi = \xi_d \sum_i \mathbf{l}_i \cdot \mathbf{s}_i \tag{6-1}$$

where ξ_d is a characteristic of the radial part of the *d* orbitals and of the central field and $\mathbf{l}_i$ and $\mathbf{s}_i$ are expressed in units of $\hbar$. For a many-electron, many-atom system one could then use an expression of the form[86]

$$\mathcal{H}_\xi = \sum_j \left(\xi_i \sum_i \mathbf{l}_i \cdot \mathbf{s}_i\right)_j$$

where j is the number of centers. However, the simple form (6-1) of the spin-orbit interaction operator will also be used for the crystalline ions, but the justification of this necessitates a few comments.

The spin-orbit interactions (6-1) are valid only when the field in which the electron moves has spherical symmetry.[23] This is, of course, not so for a complex, but the difficulty is that a complete relativistic treatment of a many-electron system cannot be given at the present time, and hence the spin-dependent part of the Hamiltonian must be approximated. It would be expected that for the point group O_h the spin-orbit interaction should take the form

$$\xi_d \sum_i \mathbf{t}_i \cdot \mathbf{s}_i \tag{6-2}$$

Since $\hat{s}_x$, $\hat{s}_y$, and $\hat{s}_z$ transform like T_1, $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ must likewise transform like T_1 in order for (6-2) to transform like the total-symmetry representation. Or put in another way, l_x, l_y, and l_z transform like T_1 (*vide infra*). Then, because of symmetry reasons, $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ must transform like l_x, l_y, and l_z. For pure d orbitals, $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ are, of course, identical with l_x, l_y, and l_z.

In order to incorporate the effect of the crystalline field $\mathcal{V}$, we could expand $\mathcal{V}$ around the center and perform the appropriate analysis.[24] The additional term such a calculation[25] would introduce is very small, however. This is due to the fact that the "crystalline field" is only a small fraction of the central field found in the gaseous ion. It is, of course, this feature which enables us to treat $\mathcal{V}$ as a perturbation upon the spectroscopic ions.

We shall thus in what follows consider only (6-1) and incorporate deviations from the central-field model in the adjustable parameter ξ_d. In principle this quantity could be taken over from atomic spectroscopy, but it has been observed, by Owen[26] among others, that the spin-orbit coupling parameter ξ_d appears to be smaller for ions in complexes than for free ions. Hence, exactly as we handle the spectroscopic parameters F_2 and F_4, ξ_d will be treated as a parameter having about the order of magnitude found for the free ions.[27]

We have for the three components l_x, l_y, and l_z of the angular momentum l:

$$\begin{aligned} l_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ l_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ l_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned} \tag{6-3}$$

The transformation properties in O_h are given in the following table. From the character tables for O_h we see that the set l_x, l_y, and l_z transforms like the irreducible representation t_{1g}.

	E	$C_3\begin{pmatrix}x \to y\\ y \to z\\ z \to x\end{pmatrix}$	$C_2\begin{pmatrix}z \to z\\ x \to -x\\ y \to -y\end{pmatrix}$	$C_4\begin{pmatrix}z \to z\\ x \to y\\ y \to -x\end{pmatrix}$	$C_2'\begin{pmatrix}x \to y\\ y \to x\\ z \to -z\end{pmatrix}$	i
l_x	l_x	l_y	$-l_x$	l_y	l_y	l_x
l_y	l_y	l_z	$-l_y$	$-l_x$	l_x	l_y
l_z	l_z	l_x	l_z	l_z	$-l_z$	l_z
χ	3	0	-1	1	-1	3

It is now easy to see by means of symmetry arguments which crystal states will show first-order multiplet separations.[28,29] A term whose orbital symmetry is Γ, say, will exhibit properties for spin-orbit coupling only if the direct-product representation $\Gamma \cdot T_{1g} \cdot \Gamma$ contains the identity representation A_{1g}. It follows from the group multiplication table 3-8 that the multiplet structure is expected to be pronounced only for those octahedrally coordinated ions with either T_1 or T_2 ground states.

In order to illustrate the very striking changes which may occur on first tying **L** to the octahedral lattice, and only afterward allowing it to couple with **S**, we take the case of a single d electron. The free ion has the states ${}^2D_{3/2}$, ${}^2D_{5/2}$ with the spin-orbit energies (2-67) of $-\frac{3}{2}\xi_d$ and ξ_d, respectively. On the other hand, by placing ${}^2D$ in a cubic crystalline field, we obtain the sixfold degenerate ${}^2T_{2g}$ and fourfold degenerate ${}^2E_g$ levels. From (3-36) we know that the inclusion of the spin will make ${}^2E_g$ transform like $\Gamma_8({}^2E_g)$ in the octahedral double group and that ${}^2T_{2g}$ will split up into $\Gamma_8({}^2T_{2g})$ and $\Gamma_7({}^2T_{2g})$. It is then evident that $\Gamma_8({}^2E_g)$ may interact, though of course it cannot be split, in second order of $\mathcal{H}_\xi$ with $\Gamma_8({}^2T_{2g})$ but not with $\Gamma_7({}^2T_{2g})$.

The wave functions for $\Gamma_8({}^2E_g)$ are immediately found to be, using the orientations of Liehr,[45]

$$\begin{aligned}
\Gamma_8{}^a\,({}^2E_g) &= \frac{1}{\sqrt{2}}(d_2 + d_{-2})\beta &&= \overset{-}{(x^2 - y^2)}\\
\Gamma_8{}^b\,({}^2E_g) &= -\frac{1}{\sqrt{2}}(d_2 + d_{-2})\alpha &&= -\overset{+}{(x^2 - y^2)} \qquad (6\text{-}4)\\
\Gamma_8{}^c\,({}^2E_g) &= d_0\beta &&= \overset{-}{(z^2)}\\
\Gamma_8{}^d\,({}^2E_g) &= -d_0\alpha &&= -\overset{+}{(z^2)}
\end{aligned}$$

which are the four different combinations of α and β spin with the d orbitals $(x^2 - y^2)$ and (z^2) with appropriate phases.

The proper zero-order wave functions for $\Gamma_8({}^2T_{2g})$ and $\Gamma_7({}^2T_{2g})$ are a bit more difficult to obtain. In order to find them, we shall utilize the set (3-27) for the t_{2g} orbitals, invest them with spin, and look at their transformation properties, first under $\hat{C}_4$.

Keeping a point fixed in space, and using Table 4-1, we get for $\hat{C}_4$ operating upon α and β spin from (3-45)

$$\hat{C}_4\alpha = e^{-\omega}\alpha \qquad \hat{C}_4\beta = e^{\omega}\beta \tag{6-5}$$

with $\omega = i\pi/4$.

Hence, by writing down the six orbitals and operating upon them with $\hat{C}_4$, we obtain a diagonal matrix

$$\hat{C}_4\begin{pmatrix} t^{\circ}_{2g}\alpha \\ t^{\circ}_{2g}\beta \\ t_{2g}^-\alpha \\ t_{2g}^-\beta \\ t_{2g}^+\alpha \\ t_{2g}^+\beta \end{pmatrix} = \begin{pmatrix} -e^{-\omega} & 0 & 0 & 0 & 0 & 0 \\ 0 & -e^{\omega} & 0 & 0 & 0 & 0 \\ 0 & 0 & e^{\omega} & 0 & 0 & 0 \\ 0 & 0 & 0 & -e^{-\omega} & 0 & 0 \\ 0 & 0 & 0 & 0 & -e^{\omega} & 0 \\ 0 & 0 & 0 & 0 & 0 & e^{-\omega} \end{pmatrix}\begin{pmatrix} t^{\circ}_{2g}\alpha \\ t^{\circ}_{2g}\beta \\ t_{2g}^-\alpha \\ t_{2g}^-\beta \\ t_{2g}^+\alpha \\ t_{2g}^+\beta \end{pmatrix} \tag{6-6}$$

It is seen that both $t_{2g}^-\alpha$ and $t_{2g}^+\beta$ transform in a unique way, whereas $t^{\circ}_{2g}\alpha$ can couple together with $t_{2g}^-\beta$ and $t^{\circ}_{2g}\beta$ can couple together with $t_{2g}^+\alpha$. We know that the six functions will provide a basis for a fourfold degenerate Γ_8 level and a twofold degenerate Γ_7 level. Because the trace, as seen from Table 3-6, is real under $\hat{C}_4$, $t_{2g}^-\alpha$ and $t_{2g}^+\beta$ must either both belong to Γ_8 or be the basis functions for Γ_7. If they comprise the Γ_7, we know that they must stay inside themselves when operating upon them with any symmetry operator in the double group. An application of, say, $\hat{C}_3$ soon reveals that this is not so. Consequently, $t_{2g}^-\alpha$ and $t_{2g}^+\beta$ are two of the orbitals which span Γ_8.

We are now in a position to find the linear combinations of the orbitals which span Γ_7. Consider the linear combination

$$at^{\circ}_{2g}\alpha + bt_{2g}^-\beta$$

and let us perform the symmetry operation $\hat{C}_3$ upon it. By using the $\hat{C}_3$ operation utilized in Table 4-1 and keeping a point fixed in space, we get from Eq. (3-46)

$$\begin{aligned} \hat{C}_3\alpha &= \frac{1}{\sqrt{2}}e^{-\omega}(\alpha + \beta) \\ \hat{C}_3\beta &= \frac{1}{\sqrt{2}}e^{\omega}(-\alpha + \beta) \qquad \omega = \frac{i\pi}{4} \end{aligned} \tag{6-7}$$

Then

$$\hat{C}_3[at^{\circ}_{2g}\alpha + bt_{2g}^-\beta] = \frac{e^{-\omega}}{\sqrt{2}}\left[a\frac{1}{\sqrt{2}}(-t_{2g}^+\alpha - t_{2g}^+\beta - t_{2g}^-\alpha - t_{2g}^-\beta) + b\frac{1}{\sqrt{2}}\left(-t^{\circ}_{2g}\alpha + t^{\circ}_{2g}\beta + \frac{1}{\sqrt{2}}t_{2g}^+\alpha - \frac{1}{\sqrt{2}}t_{2g}^-\alpha - \frac{1}{\sqrt{2}}t_{2g}^+\beta + t_{2g}^-\beta\right)\right] \tag{6-8}$$

Since $t_{2g}^{-}\alpha$ and $t_{2g}^{+}\beta$ must not occur in Γ_7, we have

$$-a\frac{1}{\sqrt{2}} - \frac{1}{2}b = 0 \tag{6-9}$$

or $b = -\sqrt{2}\,a$. Hence one of the normalized Γ_7 orbitals is

$$\sqrt{1/3}\,[t_{2g}^{0}\alpha - \sqrt{2}\,t_{2g}^{-}\beta] \tag{6-10}$$

The other one is found from (6-8) to be

$$\sqrt{1/3}\,[t_{2g}^{0}\beta + \sqrt{2}\,t_{2g}^{+}\alpha] \tag{6-11}$$

Two of the compounds of Γ_8 having already been found, the other two are constructed to be orthogonal upon (6-10) and (6-11). Our final result is thus, again with appropriate phases[45]

$$\begin{aligned}
\Gamma_8^{a}(t_{2g}) &= \sqrt{1/3}\,(-\sqrt{2}\,t_{2g}^{0}\beta + t_{2g}^{+}\alpha)\\
\Gamma_8^{b}(t_{2g}) &= \sqrt{1/3}\,(-\sqrt{2}\,t_{2g}^{0}\alpha - t_{2g}^{-}\beta)\\
\Gamma_8^{c}(t_{2g}) &= t_{2g}^{-}\alpha\\
\Gamma_8^{d}(t_{2g}) &= -t_{2g}^{+}\beta
\end{aligned} \tag{6-12}$$

$$\begin{aligned}
\Gamma_7^{a}(t_{2g}) &= \sqrt{1/3}\,(t_{2g}^{0}\beta + \sqrt{2}\,t_{2g}^{+}\alpha)\\
\Gamma_7^{b}(t_{2g}) &= \sqrt{1/3}\,(-t_{2g}^{0}\alpha + \sqrt{2}\,t_{2g}^{-}\beta)
\end{aligned} \tag{6-13}$$

$$\begin{aligned}
\Gamma_8^{a}(e_g) &= e_g^{b}\beta\\
\Gamma_8^{b}(e_g) &= -e_g^{b}\alpha\\
\Gamma_8^{c}(e_g) &= e_g^{a}\beta\\
\Gamma_8^{d}(e_g) &= -e_g^{a}\alpha
\end{aligned} \tag{6-14}$$

By using these wave functions, we can now find the energy under the spin-orbit perturbation. With

$$\mathcal{H}_\xi = \xi\mathbf{l}\cdot\mathbf{s} = \xi(l_z\hat{s}_z + \tfrac{1}{2}l_+\hat{s}_- + \tfrac{1}{2}l_-\hat{s}_+) \tag{6-15}$$

where as usual $l_+ = l_x + il_y$, etc., we find with $n = a, b, c, d$

$$\mathcal{H}_\xi\Gamma_8^{n}(t_{2g}) = -\tfrac{1}{2}\xi_d\Gamma_8^{n}(t_{2g}) + \sqrt{3/2}\,\xi_d\Gamma_8^{n}(e_g) \tag{6-16}$$

$$\mathcal{H}_\xi\Gamma_7^{n}(t_{2g}) = \xi_d\Gamma_7^{n}(t_{2g}) \tag{6-17}$$

$$\mathcal{H}_\xi\Gamma_8^{n}(e_g) = \xi_d\sqrt{3/2}\,\Gamma_8^{n}(t_{2g}) \tag{6-18}$$

Hence we get for the energy spectrum, Fig. 6-1.

$$E(\Gamma_7) = -4Dq + \xi_d \tag{6-19}$$

and for the two Γ_8 levels

$$\begin{vmatrix} -4Dq - \tfrac{1}{2}\xi_d - E & \sqrt{3/2}\,\xi_d \\ \sqrt{3/2}\,\xi_d & 6Dq - E \end{vmatrix} = 0 \tag{6-20}$$

The solutions of (6-20) are†

$$E = \begin{cases} 6Dq + \sqrt{3/2}\,\xi_d \cot \Theta \\ -4Dq - \tfrac{1}{2}\xi_d - \sqrt{3/2}\,\xi_d \cot \Theta \end{cases} \tag{6-21}$$

with

$$\tan 2\Theta = \frac{-\sqrt{6}\,\xi_d}{10Dq + \tfrac{1}{2}\xi_d} \tag{6-22}$$

The form of (6-21) and (6-22) is due to Moffitt et al.[4] The left side of Fig. 6-1 pictures the case where $10Dq \gg \xi_d$. When the spin-orbit coupling becomes stronger, however, it eventually supplants the octahedral field in directing **L**. This is manifested by the interaction between the $^2T_{2g}$ state and the ^2E_g states under $\mathcal{H}_\xi$. The two Γ_8 states in question have the off-diagonal element $\sqrt{3/2}\,\xi_d$. When ξ_d gets bigger, a uniform displacement of the two Γ_8 levels takes place until, finally, when ξ_d overwhelms Dq, the free-ion functions are recovered and J is a good quantum number again. This situation is found to the extreme right in Fig. 6-1.

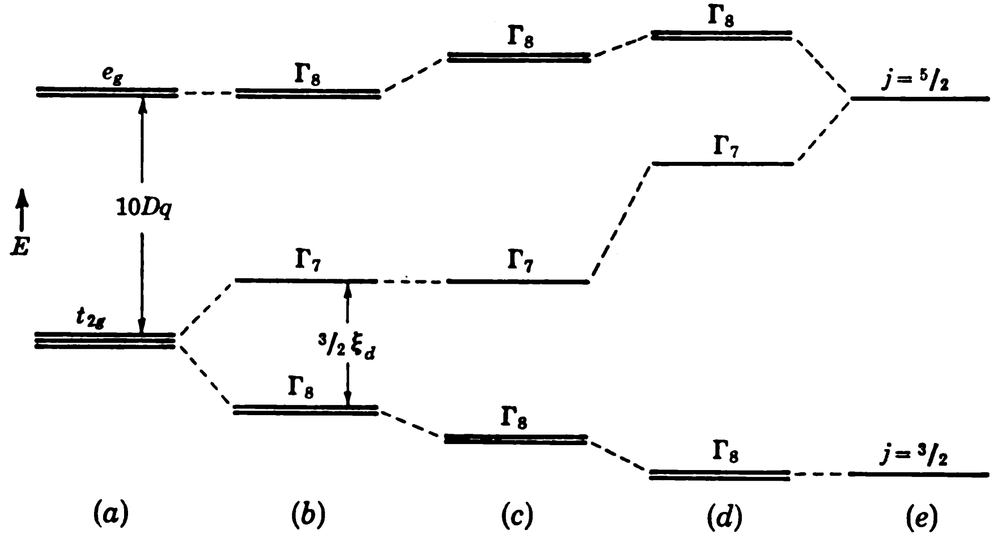

FIG. 6-1. Term splittings for a single d electron. (a) Levels in a strong octahedral field; (b) levels with weak spin-orbit coupling; (c) levels with intermediate spin-orbit coupling; (d) levels with strong spin-orbit coupling; (e) levels for the free ion in jj coupling.

To the first order in the parameter $\xi_d/10Dq$ the perturbed functions for

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† The solutions to the determinantal equation

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} = 0$$

are by taking $\tan 2\Theta = 2H_{12}/(H_{11} - H_{22})$ equal to

$$E = \begin{cases} H_{11} - H_{12}\cot\Theta & \Psi = \sin\Theta\psi_1 - \cos\Theta\psi_2 \\ H_{22} + H_{12}\cot\Theta & \Psi = \cos\Theta\psi_1 + \sin\Theta\psi_2 \end{cases}$$

the lowest multiplet Γ_8 are typified by

$$\psi = \Gamma_8{}^n\,(t_{2g}) - \sqrt{3/2}\,\frac{\xi_d}{10Dq}\,\Gamma_8{}^n\,(e_g) \tag{6-23}$$

The second-order energy correction for this level is just

$$\Delta E = -\frac{3}{2}\,\frac{\xi_d{}^2}{10Dq} \tag{6-24}$$

6-c. Spin-Orbit Coupling for d^n Configurations in Octahedral Fields

In principle the elucidation of the energy spectrum for a d^n system, assuming both a spin-orbit coupling and a crystalline field to be present, presents no difficulties. The Hamiltonian for the system is

$$\mathcal{H} = \sum_i \left\{ -\frac{\hbar^2}{2m}\nabla_i{}^2 - \frac{Ze^2}{|\mathbf{r}_i|} + \xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i \right\} + \sum_{j>i}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \mathcal{V} \tag{6-25}$$

and as usual the solutions to the Schrödinger equation are obtained by a perturbation technique. To obtain the eigenvalues, we can use either the weak or the strong crystalline field functions as a basis for the perturbation by the spin-orbit term present in $\mathcal{H}$. A third possibility is to build the electronic configurations up by using the orbital set (6-12) to (6-14) and then perturb with the electronic correlation $1/|\mathbf{r}_i - \mathbf{r}_j|$. This latter procedure is seen to be an extension of the methods used in the strong-field problem without spin-orbit coupling.

Whatever scheme we use, the result should be the same if each problem is solved exactly. This follows from the fact that the three sets of basis functions are connected by a unitary transformation. However, and this is usually the case, if we have no inclination to solve the spin-orbit problem "exactly," we must choose the basis orbitals to be used in the perturbation to be as close as possible to the actual case.

The interest in the spin-orbit coupling is generally centered around the energy spectrum of the lowest states. The reason for this is simply that these are the levels which determine the magnetic properties of the compound. So far, "complete" calculations have been performed[30] only for d^2 and d^8 in octahedral and tetrahedral crystalline fields. In Ref. 30 the problem was solved by using both "weak" and "strong" wave functions. However, an application of these methods to d^3, d^4, and d^5 is, to say the least, going to be very cumbersome. In these latter cases it seems much more feasible to find the secular equations by using either the tensor method developed by Tanabe and Kamimura[31] or the technique developed by, among others, Griffith.[32] The latter author uses the fact proved in Chap. 4 that the t_{2g} orbitals can be treated as pseudo p orbitals. We shall not treat the procedure of Tanabe and Kamimura here; instead, we shall look a bit closer at Griffith's method and see how to utilize the formal equation $t_{2g} = p$ in the calculation of spin-orbit energies.

For a single t_{2g} electron we have, by using Eq. (4-152)

$$\xi_{3d}\mathbf{l}_{t_{2g}}\cdot\mathbf{s} = -\xi_{3d}\mathbf{l}_p\cdot\mathbf{s} \tag{6-26}$$

and

$$\mathbf{l}_p + \mathbf{s} = \mathbf{j} \tag{6-27}$$

Then

$$\xi_{3d}\mathbf{l}_{t_{2g}}\cdot\mathbf{s} = -\tfrac{1}{2}\xi_{3d}[j(j+1) - l_p(l_p+1) - s(s+1)] \tag{6-28}$$

$$= \xi_{3d}[\tfrac{11}{8} - \tfrac{1}{2}j(j+1)]$$

$$= \begin{cases} -\tfrac{1}{2}\xi_{3d} & j = \tfrac{3}{2} \\ \xi_{3d} & j = \tfrac{1}{2} \end{cases} \tag{6-29}$$

as found previously.

This analogy can be applied to the $(t_{2g})^n$ electronic systems, for instance, $(t_{2g})^2$, (Fig. 6-2).

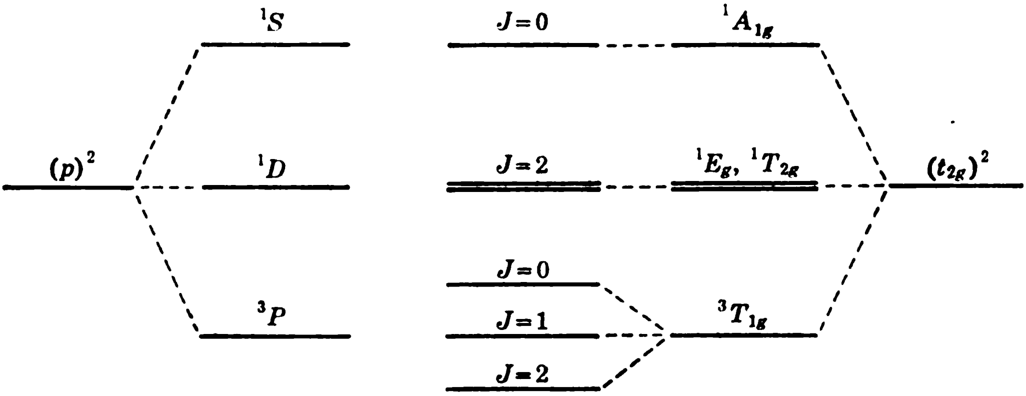

FIG. 6-2. Spin-orbit splittings in the $(t_{2g})^2$ electronic configuration.

From Condon and Shortley[33] we have $\lambda(^3P) = \tfrac{1}{2}\xi_p$. This yields using Landé's formula (2-65)

$$E = -\tfrac{1}{2}\xi_d\tfrac{1}{2}[J(J+1) - L(L+1) - S(S+1)] \tag{6-30}$$

for

^1S	$J = 0$	$L = 0$	$S = 0$	$E_\xi = 0$
^1D	$J = 2$	$L = 2$	$S = 0$	$E_\xi = 0$
^3P	$J = 0$	$L = 1$	$S = 1$	$E_\xi = \xi_{3d}$
	$J = 1$	$L = 1$	$S = 1$	$E_\xi = \tfrac{1}{2}\xi_{3d}$
	$J = 2$	$L = 1$	$S = 1$	$E_\xi = -\tfrac{1}{2}\xi_{3d}$

In the strong-field limit the ground state of cubic vanadium(III) compounds will thus exhibit a spin-orbit splitting of $\tfrac{3}{2}\xi_{3d} \simeq 300$ cm^{-1}. Notice that the $^3P_2$ level is accidentally degenerate because $J = 2$ spans the irreducible components Γ_3 and Γ_5 in the double group. It can be shown that this is a general feature[32] and that $^{2S+1}T_1$ and $^{2S+1}T_2$ states each split into three levels with degeneracies $2S - 1$, $2S + 1$, and $2S + 3$. These levels satisfy in this approximation (neglect of off-diagonal terms) a Landé interval rule. The proportionality factor in front of (6-30) is, however, not easy to calculate for the excited states of the $(t_{2g})^n(e_g)^m$ configurations, and we shall refer to Griffith's papers[29,32] for the actual evaluation. The more limited case of the spin-orbit coupling in $(t_{2g})^n$ configurations has been exhaustively treated by Moffitt et al.[4]

Usually, the spin-orbit splittings are small compared with the bandwidth of the absorption bands. For instance, for the excited $^4T_{2g}(t_{2g})^2(e_g)$ state found in Cr^{3+} complexes we get, either by the use of Griffith's method or simply by writing down the 12 wave functions and solving the perturbation matrix, $E = \frac{3}{4}\lambda$ (sixfold degenerate), $E = -\frac{1}{2}\lambda$ (fourfold degenerate), and $E = -\frac{5}{4}\lambda$ (twofold degenerate). λ is, as usual, the spin-orbit coupling constant for the ^4F state of the free ion.

Inasmuch as the total width of $^4F(d^3)$ equals 956 $cm^{-1} = \lambda S(2L + 1)$, we get[27] $\lambda = 91$ cm^{-1}. The total splitting of the $^4T_{2g}(d^3)$ term is therefore $2\lambda = 182$ cm^{-1}. The fact that this quantity is only about one-tenth of the bandwidth implies that it will be impossible to observe the spin-orbit coupling in the absorption spectra of solutions. The same splitting of 2λ is incidentally found for the other excited Cr^{3+} state, the $^4T_{1g}(t_{2g})^2(e_g)$.

As an example for future reference, let us just sketch the use of symmetry considerations to classify the spin-orbit energy spectrum of two states in Ni(II) complexes. We shall treat the $(3d)^8$ system as the hole equivalent $(3d)^2$ system and consequently have for the orbital part of the ground state in the strong-field approximation

$$\psi(A_{2g}) = |(x^2 - y^2)(z^2)| \tag{6-31}$$

With $S = 1$ we see from Table 3-8 that such a state will produce a $T_1 \cdot A_2 = T_2'$ (equals Γ_5 level) in the double group O'. The three states comprising Γ_5 are easily seen to be

$$^3A_{2g}(\Gamma_5) = \begin{cases} \Theta_1 = |\overset{+}{(x^2 - y^2)}\overset{+}{(z^2)}| \\ \Theta_2 = \dfrac{1}{\sqrt{2}}|\overset{+}{(x^2 - y^2)}\overset{-}{(z^2)}| + \dfrac{1}{\sqrt{2}}|\overset{-}{(x^2 - y^2)}\overset{+}{(z^2)}| \\ \Theta_3 = |\overset{-}{(x^2 - y^2)}\overset{-}{(z^2)}| \end{cases} \tag{6-32}$$

The first excited triplet state is a $^3T_{2g}$ state. The orbital parts are here

$$\begin{aligned} \phi_1 &= |(xy)(z^2)| \\ \phi_2 &= \frac{1}{2}|(xz)(z^2)| + \frac{\sqrt{3}}{2}|(xz)(x^2 - y^2)| \\ \phi_3 &= \frac{1}{2}|(yz)(z^2)| - \frac{\sqrt{3}}{2}|(yz)(x^2 - y^2)| \end{aligned} \tag{6-33}$$

(These functions are most easily found by going down in symmetry to D_{4h}, picking out the B_{2g} state ϕ_1, and operating upon ϕ_1 with $\hat{C}_3$.) In the double group O' we get, as again $S = 1$ transforms like T_1,

$$T_1 \cdot T_2 = A_2' + E' + T_1' + T_2' \tag{6-34}$$

In O' the ninefold degenerate ${}^3T_{2g}$ state is evidently going to produce Γ_2, Γ_3, Γ_4, and Γ_5 states. For the Γ_5 states a mixing of ${}^3A_{2g}(\Gamma_5)$ and ${}^3T_{2g}(\Gamma_5)$ can accordingly take place via the spin-orbit coupling. The three spin states are

$$\psi_1 = \alpha\alpha \qquad \psi_0 = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \qquad \psi_{-1} = \beta\beta \tag{6-35}$$

and out of the nine possible combinations $\phi_1\psi_1$, $\phi_1\psi_0$, etc., we want to pick out the three linear combinations transforming like Γ_5 in O'. Operating with $\hat{C}_4$ upon the set ψ_1, ψ_0, and ψ_{-1}, we find by the use of (3-43)

$$\hat{C}_4\begin{pmatrix}\psi_1\\ \psi_0\\ \psi_{-1}\end{pmatrix} = \begin{pmatrix} i & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -i\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_0\\ \psi_{-1}\end{pmatrix} \tag{6-36}$$

and since, further,

$$\hat{C}_4\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\end{pmatrix} = \begin{pmatrix} -1 & 0 & 0\\ 0 & 0 & -1\\ 0 & 1 & 0\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\end{pmatrix} \tag{6-37}$$

it is practical to take linear combinations of ϕ_1, ϕ_2, and ϕ_3 which are diagonal under $\hat{C}_4$. These are easily seen to be the set

$$\Psi_1 = \phi_1 \qquad \Psi_2 = \frac{1}{\sqrt{2}}(\phi_2 - i\phi_3) \qquad \Psi_3 = \frac{1}{\sqrt{2}}(i\phi_2 - \phi_3) \tag{6-38}$$

since

$$\hat{C}_4\begin{pmatrix}\Psi_1\\ \Psi_2\\ \Psi_3\end{pmatrix} = \begin{pmatrix} -1 & 0 & 0\\ 0 & -i & 0\\ 0 & 0 & i\end{pmatrix}\begin{pmatrix}\Psi_1\\ \Psi_2\\ \Psi_3\end{pmatrix}$$

Then for the whole set

$$\hat{C}_4\begin{pmatrix}\Psi_1\psi_1\\ \Psi_1\psi_0\\ \Psi_1\psi_{-1}\\ \Psi_2\psi_1\\ \Psi_2\psi_0\\ \Psi_2\psi_{-1}\\ \Psi_3\psi_1\\ \Psi_3\psi_0\\ \Psi_3\psi_{-1}\end{pmatrix} = \begin{pmatrix} -i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & i & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & -i & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & i & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\Psi_1\psi_1\\ \Psi_1\psi_0\\ \Psi_1\psi_{-1}\\ \Psi_2\psi_1\\ \Psi_2\psi_0\\ \Psi_2\psi_{-1}\\ \Psi_3\psi_1\\ \Psi_3\psi_0\\ \Psi_3\psi_{-1}\end{pmatrix} \tag{6-39}$$

Going down in symmetry from O' to D'_4, we find, in the usual way, that B'_2 in D'_4 is a component of Γ_5 in O'. The trace of $B'_2(D'_4)$ under $\hat{C}_4$ is -1.

Consequently

$$\psi(\Gamma_5{}^a) = a\Psi_1\psi_0 + b\Psi_2\psi_{-1} + c\Psi_3\psi_1 \tag{6-40}$$

The trace of B_2' under C_2'' is 1. Since

$$\hat{C}_2''\begin{pmatrix}\Psi_1\psi_0\\ \Psi_2\psi_{-1}\\ \Psi_3\psi_1\end{pmatrix} = \begin{pmatrix}-1 & 0 & 0\\ 0 & 0 & i\\ 0 & -i & 0\end{pmatrix}\begin{pmatrix}\Psi_1\psi_0\\ \Psi_2\psi_{-1}\\ \Psi_3\psi_1\end{pmatrix} \tag{6-41}$$

we have immediately that $a = 0$ and

$$\psi(\Gamma_5{}^a) = \frac{1}{\sqrt{2}}\,[\Psi_2\psi_{-1} + i\Psi_3\psi_1] \tag{6-42}$$

as $\hat{C}_2''\psi(\Gamma_5{}^a) = \psi(\Gamma_5{}^a)$. Operation upon (6-42) with $\hat{C}_3$ yields the two other components of $\Gamma_5(O')$

$$\begin{aligned}\psi(\Gamma_5{}^b) &= \frac{1}{\sqrt{2}}\,[\Psi_2\psi_0 + i\Psi_1\psi_1]\\ \psi(\Gamma_5{}^c) &= \frac{1}{\sqrt{2}}\,[\Psi_3\psi_0 - \Psi_1\psi_{-1}]\end{aligned} \tag{6-43}$$

the traces under $\hat{C}_4$ being respectively $-i$ and i.

Since the eigenvalues of ${}^3A_{2g}(\Gamma_5)$ under $\hat{C}_4$ are

$$\hat{C}_4\begin{pmatrix}\Theta_1\\ \Theta_2\\ \Theta_3\end{pmatrix} = \begin{pmatrix}-i & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & i\end{pmatrix}\begin{pmatrix}\Theta_1\\ \Theta_2\\ \Theta_3\end{pmatrix} \tag{6-44}$$

we know further that the spin-orbit coupling mixes $\Gamma_5{}^a$ (${}^3T_{2g}$) with Θ_2, $\Gamma_5{}^b$ (${}^3T_{2g}$) with Θ_1, and $\Gamma_5{}^c$ (${}^3T_{2g}$) with Θ_3.

Since

$$(\Gamma_5{}^n\,({}^3A_{2g})|\lambda\mathbf{L}\cdot\mathbf{S}|\Gamma_5{}^n\,({}^3T_{2g})) = 2\sqrt{2}\,\lambda \tag{6-45}$$

and with $E({}^3T_{2g}) - E({}^3A_{2g}) = 10Dq$, we have in the first order for the wave functions of the ground state

$$\Phi(\Gamma_5{}^n) = \Gamma_5{}^n\,({}^3A_{2g}) - \frac{2\sqrt{2}\,\lambda}{10Dq}\,\Gamma_5{}^n\,({}^3T_{2g}) \tag{6-46}$$

with $n = a, b, c$.

6-d. Spin-Orbit Splittings Calculated by the Method of Abragam and Pryce

A very elegant method for the calculation of spin-orbit splittings has been developed by Abragam and Pryce.[34,35] Their procedure depends in essence upon the setting up of "pseudo" atomic state functions and then taking over the appropriate features from the theory of atomic spectra. As an example showing the power of the method we shall treat an F state in a cubic crystalline field.

An orbital F state in O_h can be represented by the following wave functions for a single particle in an f state (cf. Appendix II, Chap. 4).

$$T_2 \quad \begin{cases} \psi_x = \dfrac{\sqrt{105}}{2}\, x(y^2 - z^2) \\ \psi_y = \dfrac{\sqrt{105}}{2}\, y(z^2 - x^2) \\ \psi_z = \dfrac{\sqrt{105}}{2}\, z(x^2 - y^2) \end{cases} \tag{6-47}$$

$$T_1 \quad \begin{cases} \phi_x = \dfrac{\sqrt{7}}{2}\, x(2x^2 - 3y^2 - 3z^2) \\ \phi_y = \dfrac{\sqrt{7}}{2}\, y(2y^2 - 3z^2 - 3x^2) \\ \phi_z = \dfrac{\sqrt{7}}{2}\, z(2z^2 - 3x^2 - 3y^2) \end{cases} \tag{6-48}$$

and
$$A_2 \qquad \chi = \sqrt{105}\, xyz \tag{6-49}$$

These wave functions are normalized and transform in the cubic point group as indicated. We now form the new linear combinations

$$T_2 \quad \begin{cases} \psi_1 = -\dfrac{1}{\sqrt{2}}(\psi_x + i\psi_y) \\ \psi_0 = \psi_z \\ \psi_{-1} = \dfrac{1}{\sqrt{2}}(\psi_x - i\psi_y) \end{cases} \tag{6-50}$$

$$T_1 \quad \begin{cases} \phi_1 = -\dfrac{1}{\sqrt{2}}(\phi_x + i\phi_y) \\ \phi_0 = \phi_z \\ \phi_{-1} = \dfrac{1}{\sqrt{2}}(\phi_x - i\phi_y) \end{cases} \tag{6-51}$$

If we take the total set of the seven orbitals (6-49) to (6-51) comprising the F state, we have, for instance,

$$\begin{aligned} \mathcal{L}_z\phi_1 &= -\tfrac{3}{2}\phi_1 - \frac{\sqrt{15}}{2}\psi_{-1} \\ \mathcal{L}_z\phi_0 &= -\frac{6i}{\sqrt{15}}\chi \\ \mathcal{L}_z\phi_{-1} &= \tfrac{3}{2}\phi_{-1} + \frac{\sqrt{15}}{2}\psi_1 \end{aligned} \tag{6-52}$$

By further operating upon the set T_1 with $\mathcal{L}_x$, $\mathcal{L}_y$, and $\mathcal{L}_z$, we get if we do not consider any admixture of other states,

$$\hat{L}_z\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} = -\frac{3}{2}\begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} \tag{6-53}$$

$$\hat{L}_y\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} = -\frac{3}{2}\frac{i}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ -1 & 0 & 1\\ 0 & -1 & 0\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} \tag{6-54}$$

$$\hat{L}_x\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} = -\frac{3}{2}\frac{i}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_0\\ \phi_{-1}\end{pmatrix} \tag{6-55}$$

In other words, the set ϕ_1, ϕ_0, and ϕ_{-1} behaves as an atomic P state having $L = 1$, but with an effective orbital Landé factor equal to $-\frac{3}{2}$ (cf. Sec. 4-*i*). The advantage of defining the orbitals in this way is that $L'_z + S'$ is a constant of the motion and its eigenvalues M can be used to classify the various states, just as is the case in the theory of atomic spectra.

Let us with Low[36] calculate the spin-orbit splitting of the ground state of a Co^{++} ion in a cubic crystalline field by using the above method. The lowest atomic state is a ^4F state, the ground level in O_h being a $^4T_{1g}$ state. Then

$$\begin{aligned}\mathcal{H}_\lambda &= \lambda\mathbf{L}\cdot\mathbf{S} = \alpha\lambda\mathbf{L}'\cdot\mathbf{S}\\ &= \alpha\lambda(\hat{L}'_z\hat{S}_z + \tfrac{1}{2}\hat{L}'_+\hat{S}_- + \tfrac{1}{2}\hat{L}'_-\hat{S}_+)\end{aligned} \tag{6-56}$$

By using M as a good quantum number, we now calculate the fine-structure matrices. We use a notation (L'_z, M_s) to characterize a given state. For $M = \pm\frac{1}{2}$ we get the secular equation

$$\begin{array}{r|ccc|l} & (\mp 1, \pm\frac{3}{2}) & (0, \pm\frac{1}{2}) & (\pm 1, \mp\frac{1}{2}) & \\ (\mp 1, \pm\frac{3}{2}) & -\frac{3}{2}\alpha\lambda - E & \sqrt{\frac{3}{2}}\,\alpha\lambda & 0 & \\ (0, \pm\frac{1}{2}) & \sqrt{\frac{3}{2}}\,\alpha\lambda & 0 - E & \sqrt{2}\,\alpha\lambda & = 0\\ (\pm 1, \mp\frac{1}{2}) & 0 & \sqrt{2}\,\alpha\lambda & -\frac{1}{2}\alpha\lambda - E & \end{array} \tag{6-57}$$

For $M \pm \frac{3}{2}$ we get

$$\begin{array}{r|cc|l} & (0, \pm\frac{3}{2}) & (\pm 1, \pm\frac{1}{2}) & \\ (0, \pm\frac{3}{2}) & 0 - E & \sqrt{\frac{3}{2}}\,\alpha\lambda & = 0\\ (\pm 1, \pm\frac{1}{2}) & \sqrt{\frac{3}{2}}\,\alpha\lambda & \frac{1}{2}\alpha\lambda - E & \end{array} \tag{6-58}$$

and finally for $M = \pm\frac{5}{2}$ the only state is given by $(\pm 1, \pm\frac{3}{2})$ with an energy

$$E = \tfrac{3}{2}\alpha\lambda \tag{6-59}$$

Solutions of (6-57) to (6-59), putting $\alpha = -\frac{3}{2}$, yields the following roots:

$$E = \begin{cases} \frac{15}{4}\lambda & M = \pm\frac{1}{2}\\ \frac{6}{4}\lambda & M = \pm\frac{1}{2}, \pm\frac{3}{2}\\ -\frac{9}{4}\lambda & M = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}\end{cases}$$

Since the spin-orbit coupling constant λ is negative (we are in the second half of the d shell), the $^{15}\!/_4\lambda$ is the lowest level. The total width of the multiplet is hence approximately 6λ. It is only approximate because we have neglected configurational mixing with higher states. With[27] $|\lambda| = 178\ \mathrm{cm}^{-1}$ the total width is $1066\ \mathrm{cm}^{-1}$. Experiments show[37] that the splitting in $\mathrm{CoBr_2}$ is $1150\ \mathrm{cm}^{-1}$.

Putting $E = {}^{15}\!/_4\lambda$ back into (6-57), we obtain the wave function of the doublet Γ_6

$$\Gamma_6 \left\{ \begin{aligned} \psi_{1/2} &= \frac{1}{\sqrt{2}}\,\phi_{-1,3/2} - \frac{1}{\sqrt{3}}\,\phi_{0,1/2} + \frac{1}{\sqrt{6}}\,\phi_{1,-1/2} \\ \psi_{-1/2} &= \frac{1}{\sqrt{2}}\,\phi_{1,-3/2} - \frac{1}{\sqrt{3}}\,\phi_{0,-1/2} + \frac{1}{\sqrt{6}}\,\phi_{-1,1/2} \end{aligned} \right. \tag{6-60}$$

We knew, of course, beforehand that the ground state would have a Kramers degeneracy because the system possesses an odd number of electrons.

6-e. *g* Factors in an Octahedral Field

Some of the most interesting features of the spin-orbit splittings appear when we consider the Zeeman effect. In a magnetic field **H** the term $\mathcal{H}^{(2)}$ giving the magnetic energy

$$\mathcal{H}^{(2)} = \beta\mathbf{H}\cdot\sum_i(\mathbf{l}_i + 2\mathbf{s}_i) = \beta\mathbf{H}\cdot(\mathbf{L} + 2\mathbf{S}) \tag{6-61}$$

must be added to the Hamiltonian. Here β is the Bohr magneton. The separations within a given multiplet due to a field along some axis κ, say, may be expressed in the form

$$h\nu = g_\kappa\beta H_\kappa \tag{6-62}$$

where g_κ is the so-called spectroscopic splitting factor. The theory for the atomic Landé g factors was briefly treated in Sec. 2-1, where it was found that for free ions g was given by

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \tag{6-63}$$

whenever Russel-Saunders coupling holds.

For an octahedral complex the g factors are isotropic; i.e., they have the same value regardless of whether $\kappa = x$, y, or z. However, their values differ widely from those given by the Landé formula.

Let us evaluate the Zeeman splittings for a single d electron in an octahedral field. For the ground state Γ_8, by using the wave functions (6-12), we get

$$(\Gamma_8{}^n\,(t_{2g})|\beta H_z(l_z + 2s_z)|\Gamma_8{}^n\,(t_{2g})) = 0 \tag{6-64}$$

with $n = a, b, c, d$.

Hence the $\Gamma_8(t_{2g})$ quartet is not split by any field at all, using zeroth-order functions. It is, however, possible for this state to couple to the $\Gamma_8(e_g)$ states via the spin-orbit coupling. The wave functions in first-order approximation are given in (6-21)

$$\psi(\Gamma_8{}^n) = \Gamma_8{}^n\,(t_{2g}) - \sqrt{\frac{3}{2}}\,\frac{\xi_d}{10Dq}\,\Gamma_8{}^n\,(e_g)$$

Evaluating the matrix elements

$$(\psi(\Gamma_8{}^n)|\beta H_z(\hat{l}_z + 2\hat{s}_z)|\psi(\Gamma_8{}^n))$$

we get

$$\begin{aligned} E^a &= \frac{4\xi_d}{10Dq}\beta H_z & m &= +\frac{3}{2} \\ E^b &= 0 & m &= \frac{1}{2} \\ E^c &= 0 & m &= -\frac{1}{2} \\ E^d &= \frac{-4\xi_d}{10Dq}\beta H_z & m &= -\frac{3}{2} \end{aligned} \tag{6-65}$$

In other words, we get an undisplaced doublet and two singlets. The only good quantum number is $m = m_s + m_l$, and by the selection rule for magnetic dipole transitions we must have $\Delta m = \pm 1$ in order for the transition to be allowed. Then from (6-62) and (6-65)

$$g_z\beta H_z = \frac{4\xi_d}{10Dq}\beta H_z \tag{6-66}$$

$$g = \frac{4\xi_d}{10Dq} \tag{6-67}$$

It is seen that the g factor for the $\Gamma_8(t_{2g})$ state differs from zero by virtue of its "high-frequency" terms. For Ti^{3+} complexes we have $\xi_d \simeq 100\ \text{cm}^{-1}$ and $10Dq \simeq 20{,}000\ \text{cm}^{-1}$; the g factor is only $\simeq 1/50$.

For the excited states we get, upon evaluating $(\hat{l}_z + 2\hat{s}_z)$ by using the unperturbed wave functions (6-13) and (6-14), that for $\Gamma_7(t_{2g})$ the two levels are separated by $2\beta H_z$ and therefore that $g = 2$. Similarly, the $\Gamma_8(e_g)$ levels are split into two doublets of energy $\pm\beta H_z$; once again $g = 2$. By comparison, the g factors for the ${}^2D_{3/2}$ and ${}^2D_{5/2}$ levels of the free ion are $4/5$ and $6/5$.

Let us further calculate the g factor for the ground state of cubic Ni^{++} complexes. The wave functions are given in Eq. (6-30). By evaluating $\hat{L}_z + 2\hat{S}_z$, we get

$$\begin{aligned} (\Theta_1|\hat{L}_z + 2\hat{S}_z|\Theta_1) &= 2 \\ (\Theta_2|\hat{L}_z + 2\hat{S}_z|\Theta_2) &= 0 \\ (\Theta_3|\hat{L}_z + 2\hat{S}_z|\Theta_3) &= -2 \end{aligned}$$

The g factor is thus 2 in the first approximation. If, on the other hand, we take account of the fact that the ground state can mix with the level $\Gamma_5({}^3T_{2g})$

via the spin-orbit coupling, we see that by use of the wave functions given in Eq. (6-46) a correction to the g factor of 2 is obtained. In order to estimate this correction, we must evaluate $(\psi(\Gamma_5{}^n)|\hat{L}_z + 2\hat{S}_z|\psi(\Gamma_5{}^n))$ to the first order in λ. With

$$\psi(\Gamma_5{}^n) = \Gamma_5{}^n\,({}^3A_{2g}) - \frac{2\sqrt{2}\,\lambda}{10Dq}\,\Gamma_5{}^n\,({}^3T_{2g}) \tag{6-68}$$

where the components are as given in Sec. 6-c, we get

$$\begin{aligned} (\psi(\Gamma_5{}^1)|\hat{L}_z + 2\hat{S}_z|\psi(\Gamma_5{}^1)) &= 2 - \frac{8\lambda}{10Dq} \\ (\psi(\Gamma_5{}^2)|\hat{L}_z + 2\hat{S}_z|\psi(\Gamma_5{}^2)) &= 0 \\ (\psi(\Gamma_5{}^3)|\hat{L}_z + 2\hat{S}_z|\psi(\Gamma_5{}^3)) &= -\left(2 - \frac{8\lambda}{10Dq}\right) \end{aligned}$$

Hence, to the first order in λ the Landé g factor is equal to

$$g = 2 - \frac{8\lambda}{10Dq} \tag{6-69}$$

From resonance spectra we get $g = 2.25$ for $Ni(H_2O)_6{}^{++}$, in admirable accord with the theory if $-8\lambda/10Dq = 0.25$. On a quantitative basis, and this is rather typical, the agreement is less satisfactory. Taking $\lambda = -324\ \text{cm}^{-1}$, the value given by atomic spectroscopy,[27] one would predict $10Dq$ to be 10,700 cm^{-1}. In fact the first broad maximum found in the spectrum of $Ni(H_2O)_6{}^{++}$ which directly gives $10Dq$ is located[39] at 8500 cm^{-1}.

It appears, therefore, that in order to account for the g factors, one must assume that the spin-orbit coupling constant is diminished from its free-ion value to only about $-270\ \text{cm}^{-1}$ for the crystalline ion. A closer analysis of this and related effects has been performed by Owen,[26] and we shall return to this point when discussing the molecular orbital approach.

As a final example of a calculation of the spectroscopic g factor we shall take the case of a cubic Co^{++} complex. The wave functions for the Γ_6 ground state have been found by the method of Abragam and Pryce and are given in Eq. (6-60). Since, after (6-52), $\hat{L}_z\phi_m = m\alpha\phi_m$ with $\alpha = -3/2$, we have

$$\begin{aligned} (\psi_{1/2}|\hat{L}_z + 2\hat{S}_z|\psi_{1/2}) &= -1/3\,\alpha + 5/3 \\ (\psi_{-1/2}|\hat{L}_z + 2\hat{S}_z|\psi_{-1/2}) &= 1/3\,\alpha - 5/3 \end{aligned}$$

Hence the g factor is

$$g = -2/3\,\alpha + 10/3 \tag{6-70}$$

and since $\alpha = -3/2$, $g = 4.333$ to the first order.

In the second order the spin-orbit coupling mixes in a slight amount of the excited ${}^4T_{2g}(\Gamma_6)$ state to the ground state, similarly to the situation found for Ni^{++} complexes. We must then find the combination of the spin functions and orbital functions given in Eq. (6-50) transforming like the excited state Γ_6.

By operating upon $\psi_{1,3/2}, \psi_{1,1/2} \cdots$ with $\hat{C}_4$ and $\hat{C}_2$, it is easy to find that the two orbitals

$$a\psi_{1,3/2} + b\psi_{0,-3/2} + c\psi_{-1,-1/2}$$
$$a\psi_{-1,-3/2} + b\psi_{0,3/2} + c\psi_{1,1/2}$$

span the Γ_6 level. Application of the operator $\hat{C}_3$ yields $a = \sqrt{1/6}$, $b = \sqrt{1/3}$, and $c = -\sqrt{1/2}$ by the now well-known procedure. Hence

$$\Gamma_6(^4T_{2g}) \begin{cases} \sqrt{1/6}\,\psi_{1,3/2} + \sqrt{1/3}\,\psi_{0,-3/2} - \sqrt{1/2}\,\psi_{-1,-1/2} \\ \sqrt{1/6}\,\psi_{-1,-3/2} + \sqrt{1/3}\,\psi_{0,3/2} - \sqrt{1/2}\,\psi_{1,1/2} \end{cases} \tag{6-71}$$

The mixing parameter $(\Gamma_6(^4T_{2g})|\lambda\mathbf{L}\cdot\mathbf{S}|\Gamma_6(^4T_{1g}))$ is evaluated to be $3\sqrt{5}\,\lambda/4$, and the wave function for the ground state is, to the first order in λ, given by

$$\Gamma_6(^4T_{1g}) - \frac{3\sqrt{5}\,\lambda}{40Dq}\,\Gamma_6(^4T_{2g}) \tag{6-72}$$

Calculation of the g factor then yields a value

$$g = \frac{10}{3} - \frac{2}{3}\alpha - \frac{15}{2}\frac{\lambda}{10Dq} \tag{6-73}$$

This calculation has neglected the contribution to the $^4T_{1g}(F)$ state from the $^4T_{1g}(P)$ state; i.e., we have not considered the mixing of these two states due to the crystalline field. This effect is easy to include,[35,36] because the orbital part of the ground state can be written

$$\Psi = \epsilon\phi + \tau\pi \tag{6-74}$$

where ϵ and τ are defined as the coefficients to the orbital functions of the ground state $T_{1g}(^4F)$ and of the excited $T_{1g}(^4P)$ state. Then

$$(\Psi|\hat{L}_z|\Psi) = (\alpha\epsilon^2 + \tau^2)M \tag{6-75}$$

and we see that any admixture of the P state will reduce the effective value of α. Hence

$$\alpha' = -\tfrac{3}{2}\epsilon^2 + \tau^2 \tag{6-76}$$

and

$$g = \frac{10}{3} + \left(\epsilon^2 - \frac{2}{3}\tau^2\right) - \frac{15}{2}\frac{\lambda}{10Dq} \tag{6-77}$$

Experiments yield[30] a value of $g = 4.278$ for Co^{++} ions in a MgO crystal. With $Dq = 1000$ cm^{-1} and a separation between the ^4F and ^4P state of 14,400 cm^{-1} we find $\epsilon = 0.981$ and $\tau = -0.194$. Since λ for Co^{++} is -180 cm^{-1}, we get $g = 4.406$.

The discrepancy between experiment and theory can be removed by the introduction[40] of a so-called "orbital reduction factor" k. This factor takes account of the deviations of the orbitals from the atomic orbitals (see next chapter). The final result for the g factor is then

$$g = \frac{10}{3} + k\left(\epsilon^2 - \frac{2}{3}\tau^2\right) - \frac{15}{2}\frac{\lambda}{10Dq} \tag{6-78}$$

If there is some covalent bonding present, k will be less than 1. We notice that theory and experiment agree in the above example for a value of $k = 0.86$. The orbitals are thus nearly—but not completely—described by the atomic wave functions. We shall later return to this point.

6-f. g Factors in a Tetragonal or Trigonal Field

It often happens that a paramagnetic resonance experiment reveals that the spectroscopic g factor is anisotropic. In that case the experiments cannot be explained by assuming a cubic crystalline field to be present; such a result definitely indicates that a lower crystalline field than cubic is operative upon the metal ion. Indeed, owing to a remarkable theorem of Jahn and Teller[41,42] (*vide infra*) we know that all possible degeneracies, both orbital and spin, are removed from the ground state of any molecule. The only kind of degeneracy unaffected by the Jahn and Teller theorem is a Kramers degeneracy.[43,44] Kramers' theorem tells us that a system containing an odd number of electrons and with no magnetic field present always will leave all levels with an even degeneracy. Hence we see that the combined Jahn-Teller-Kramers theorems will make the ground state a singlet if the number of electrons is even and a doublet if the number is odd.

Very little attention has been paid toward the behavior of the higher excited states when both a tetragonal or trigonal field and a spin-orbit coupling is operative. Liehr[45] has published the perturbation matrices for the d^1 and d^9 case and Sugano and Tanabe[64] have treated the absorption spectra of Cr^{3+} in Al_2O_3 by assuming both a spin-orbit coupling and a trigonal field to be present. Apart from that and unpublished results for d^3 by Low,[46] nothing appears to have been done. We shall therefore confine our analysis to the behavior of the lowest electronic states. Here, on the other hand, a true abundance of work has been done. But since this research is mostly concerned with the explanation of paramagnetic resonance experiments, and since this is a topic exhaustively dealt with in many excellent recent monographs[47,48] and review papers,[12,38,76] we shall only outline the pertinent features.

In order to illustrate the calculation of the g factors of ions in a trigonal field, we shall first look upon the case of a single d electron. The ground state of a Ti^{3+} ion which in octahedral symmetry is a $^2T_{2g}$ term is in a trigonal field split by an amount [see (5-29)] $\Delta = 3D\sigma + 6\tfrac{2}{3}D\tau$, which quantity we take to be positive. Hence, of the three orbital levels arising from the octahedral $^2T_{2g}$, a_{1g} is the lowest and the doubly degenerate e_g level is lying some Δ above it, Fig. 6-3. When the spin-orbit coupling is switched on, the $^2A_{1g}$ term transforms like the twofold degenerate Γ_6 in the double group[49] and ^2E transforms like $\Gamma_6 + \Gamma_4 + \Gamma_5$, Γ_4 and Γ_5 being nondegenerate. Owing to the theorem of Kramers,[43,44] Γ_4 and Γ_5 must remain degenerate in the absence of a magnetic field (see too Liehr, Ref. 45, footnote 35). The zero-order wave functions for the ground Γ_6 doublet with $\Delta \gg \xi_d$ would then be $t^{\circ}_{2g}\alpha$ and $t^{\circ}_{2g}\beta$. Finding expectation values for $(\hat{L}_z + 2\hat{S}_z)$ and for $(\hat{L}_x + 2\hat{S}_x)$, their Zeeman splittings may be written $g_{\parallel}\beta H_z$ and $g_{\perp}\beta H_x$,

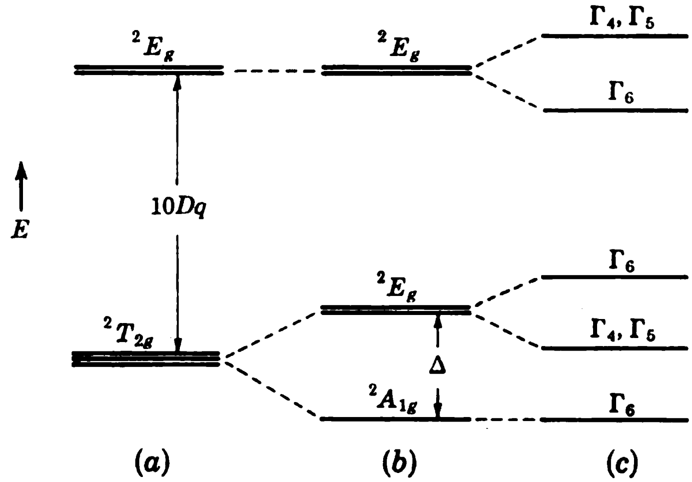

FIG. 6-3. Trigonal and spin-orbit splittings. (a) Octahedral symmetry without spin-orbit coupling; (b) trigonal symmetry without spin-orbit coupling; (c) trigonal symmetry with spin-orbit coupling.

respectively, for magnetic fields directed along, or normal to the threefold axis. By using the above wave functions, we obtain

$$g_{\parallel} = 2 \qquad g_{\perp} = 2 \tag{6-79}$$

Experimentally it is found[50] that $g_{\parallel} = 1.25$ and $g_{\perp} = 1.14$. The theory must then be reconsidered.

Next we shall look at the case where ξ_d and Δ are comparable (about 100 cm^{-1}), though both are small with respect to $10Dq$. Using the orbital set (4-41) we find an off-diagonal element in $\mathcal{H}_\xi$ between $t^{\circ}_{2g}\beta$ and $t_{2g}{}^a\alpha$ equal to $\sqrt{1/2}\,\xi_d$. The resulting eigenfunctions for the perturbed ground state, a Kramers spin doublet, take the form

$$\begin{aligned} \psi_{1/2} &= ad_0\alpha + b(\sqrt{2/3}\, d_{-2} + \sqrt{1/3}\, d_1)\beta \\ \psi_{-1/2} &= ad_0\beta - b(\sqrt{2/3}\, d_2 - \sqrt{1/3}\, d_{-1})\alpha \end{aligned} \tag{6-80}$$

where a and b are simple functions of ξ_d, Δ. By finding the resulting energy separation with a magnetic field present, we obtain

$$g_{\parallel} = 2(a^2 - 2b^2) \qquad g_{\perp} = 2(a^2 + \sqrt{2}\, ab) \tag{6-81}$$

and by inserting the values of a and b, we obtain[51]

$$g_{\parallel} = -1 + \frac{3(\Delta + \frac{1}{2}\xi_d)}{\sqrt{(\Delta + \frac{1}{2}\xi_d)^2 + 2\xi_d^2}} \qquad g_{\perp} = 1 + \frac{\Delta - \frac{3}{2}\xi_d}{\sqrt{(\Delta + \frac{1}{2}\xi_d)^2 + 2\xi_d^2}} \tag{6-82}$$

These expressions reduce to zero, of course, when $\xi_d \gg \Delta$, because the trigonal perturbation is then suppressed and the effective symmetry is octahedral again; the levels reduce to components of ${}^2T_{2g}(\Gamma_8)$. On the other hand, if $\Delta \gg \xi_d$, $g_{\parallel}$ and $g_{\perp}$ both become 2, as found previously. The expressions for $g_{\parallel}$ and $g_{\perp}$ given in (6-82) are still not quite sufficient to explain the experimentally found values $g_{\parallel} = 1.25$ and $g_{\perp} = 1.14$. The low figures are to be expected on the basis of (6-82), but their actual values require a more detailed discussion in which second-order corrections arising from the excited octahedral ${}^2E_g$ state are taken into account. See further Kamimura[52] and Stevens.[40]

Let us with Pryce[53,54] look a bit more at the theory for the g factor when an orbital singlet is the ground state. We are interested in the energy values of the crystalline field system when these levels are perturbed with

$$\mathcal{H}^{(1)} = \lambda\mathbf{L}\cdot\mathbf{S} + \beta\mathbf{H}\cdot(\mathbf{L} + 2\mathbf{S}) \tag{6-83}$$

By applying first-order perturbation theory, we get for the ground state ψ_0

$$(\psi_0|\mathcal{H}^{(1)}|\psi_0) = 2\beta\mathbf{H}\cdot\mathbf{S} \tag{6-84}$$

since the terms $(\psi_0|\hat{L}_x|\psi_0)$, $(\psi_0|\hat{L}_y|\psi_0)$, and $(\psi_0|\hat{L}_z|\psi_0)$ vanish because a singlet orbital state carries no angular momentum. In the second order we get, calling the excited states ψ, a correction to the energy

$$\begin{aligned} E^{(1)} &= -\sum_{n\neq 0} \frac{|(\psi_0|\lambda\mathbf{L}\cdot\mathbf{S} + \beta\mathbf{H}\cdot(\mathbf{L} + 2\mathbf{S})|\psi_n)|^2}{E_n - E_0} \\ E^{(1)} &= -\sum_{n\neq 0} \frac{|(\psi_0|\lambda\mathbf{L}\cdot\mathbf{S} + \beta\mathbf{H}\cdot\mathbf{L}|\psi_n)|^2}{E_n - E_0} \end{aligned} \tag{6-85}$$

Since we are only interested in the terms linear in $\lambda\beta H$, we get, by collecting the terms from the first- and second-order perturbation,

$$E^{(1)} = 2\beta(\delta_{ij} - \lambda\Lambda_{ij})S_iH_j \tag{6-86}$$

where Λ_{ij} is a real, symmetrical, positive definite tensor defined in terms of the matrix elements of the orbital angular momentum $\hat{L}$ by

$$\Lambda_{ij} = \sum_{n\neq 0} \frac{(\psi_0|\hat{L}_i|\psi_n)(\psi_n|\hat{L}_j|\psi_0)}{E_n - E_0} \tag{6-87}$$

Hence the general anisotropic g factor is given by

$$g_{ij} = 2(\delta_{ij} - \lambda\Lambda_{ij}) \tag{6-88}$$

This whole calculation is, of course, valid only provided $E_n - E_0 \gg \lambda$.

Let us calculate the g factors for a Cu^{++} ion in a field corresponding to tetragonal D_{4h} symmetry as an example for the use of the formula (6-88). The octahedron is supposed to be elongated along the fourfold axis. We shall use the hole formalism for the d^9 system; the energy levels are then as pictured in Fig. 5-1 as seen upside down. An elongated octahedron should stabilize electrons in the d_{z^2} orbital; consequently, a hole should be repelled. Hence we would expect the $d_{x^2-y^2}$ to be the ground state in d^9. Let us, however, calculate the g factors in both cases.

1. **Ground State** d_{z^2}. With $j = z, \hat{L}_z d_{z^2} = 0$; with $j = x, \hat{L}_x d_{z^2} = -i\sqrt{3}\, d_{yz}$. We get $\psi_n = d_{yz}$ in order for Λ_{ij} to be different from zero. Inspection then gives $i = x$, and hence by (6-88),

$$g_{\parallel} = 2 \qquad g_{\perp} = 2\left(1 - \frac{3\lambda}{\Delta_1}\right) \tag{6-89}$$

where $\Delta_1 = E(e_g) - E(a_{1g})$.

2. **Ground State** $d_{x^2-y^2}$. With $j = z$, $\hat{L}_z d_{x^2-y^2} = 2id_{xy}$. Only with $i = z$ do we get a value of Λ_{ij} different from zero. With $j = x$, $\hat{L}_x d_{x^2-y^2} = -id_{yz}$ and, further, $i = x$. Then

$$g_{\parallel} = 2\left(1 - \frac{4\lambda}{\Delta_2}\right) \qquad g_{\perp} = 2\left(1 - \frac{\lambda}{\Delta_3}\right) \tag{6-90}$$

where $\Delta_2 = E(b_{2g}) - E(b_{1g})$ and $\Delta_3 = E(e_g) - E(b_{1g})$. For a more accurate calculation see Abragam and Pryce.[63]

It is seen that measurements of the g factors can decide which ground state the complex has. Experiments on $Cu(NH_3)_4SO_4 \cdot H_2O$ showed[55] $g_{\parallel} = 2.22$ and $g_{\perp} = 2.05$ agreeing with the second possibility, exactly as expected.

The combined effects of a noncubic field and the spin-orbit coupling will in many cases lead to a so-called zero-field splitting of the ground state. Consider as an example $[Ni(H_2O)_6]SiF_6$. The ground state of $(3d)^8$ is in a cubic field ${}^3A_{2g}(\Gamma_5)$, that is, an orbital nondegenerate state but a threefold degenerate spin level. The next excited triple state is a ${}^3T_{2g}$. A tetragonal or trigonal field will split the orbital degenerate states, in particular the excited ${}^3T_{2g}$ state, into a twofold orbital degenerate level and a single one. The spin-orbit energy may then be regarded as a perturbation which couples the ground state together with the excited states. Hence, the spin multiplet of the ground state will feel the splitting of the excited states indirectly. These spin levels will therefore undergo a small splitting, the zero-field splitting. Without the influence of the excited states the spin triplet would be degenerate, since the deepest orbital levels is nondegenerate.

In order to illustrate the effect, we shall estimate the zero-field splitting for a trigonal Ni^{++} complex under the simplified assumption that the only excited state present is the $^3T_{2g}$ state. The calculation will be performed by using the "strong" wave functions (6-43) and (6-44).

For the cubic $^3A_{2g}(\Gamma_5)$ and $^3T_{2g}(\Gamma_5)$ wave functions we have found, Eq. (6-45), that the interaction term under $\mathcal{H}^{(1)} = \lambda \mathbf{L} \cdot \mathbf{S}$ equals $2\sqrt{2}\,\lambda$. Under the influence of a trigonal field the threefold degenerate $^3T_{2g}(\Gamma_5)$ will split up into a singlet and a doublet, whereas the $^3A_{2g}(\Gamma_5)$ ground level will not exhibit any splitting, Fig. 6-4.

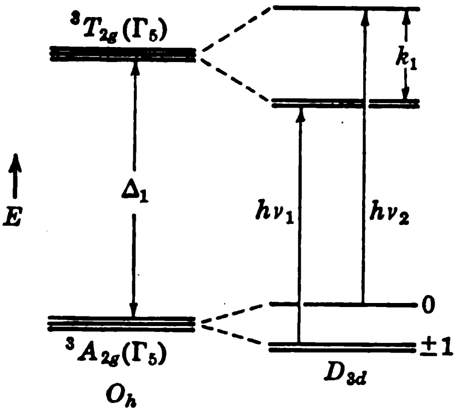

FIG. 6-4. Trigonal splittings of Γ_5 states for d^8.

By using second-order perturbation with $\mathcal{H}^{(1)} = \lambda \mathbf{L} \cdot \mathbf{S}$, we get with $h\nu_1$ and $h\nu_2$ as defined in Fig. 6-4

$$E^{(2)}_{(\pm 1)} = -\frac{8\lambda^2}{h\nu_1} \tag{6-91}$$

$$E^{(2)}_{(0)} = -\frac{8\lambda^2}{h\nu_2} \tag{6-92}$$

Hence

$$\delta = E^{(2)}_{(0)} - E^{(2)}_{(\pm 1)} = 8\lambda^2\left(\frac{1}{h\nu_1} - \frac{1}{h\nu_2}\right) \tag{6-93}$$

With $k_1 \approx h\nu_2 - h\nu_1 \ll \Delta_1$ this may be written

$$\delta \approx \frac{8k_1\lambda^2}{\Delta_1{}^2} \tag{6-94}$$

A more general calculation taking the $^1T_{2g}(\Gamma_5)$ contribution into account[30] yields

$$\delta \approx \frac{9k_1\lambda^2}{\Delta_1{}^2} \tag{6-95}$$

Notice that the theory demands the singlet level to have higher energy than the doublet if k_1 is positive. A positive k_1 is what we should expect from the considerations in Sec. 5-*b*, provided the octahedron is elongated along the threefold axis.

Inclusion of a magnetic field then yields the further splitting indicated in Fig. 6-5. We observe that for a given frequency $h\nu$ two resonance absorption lines will occur for such values of H that

$$h\nu = g_{\|}\beta H_{\|} \pm \delta \tag{6-96}$$

Experiments[56,57] yield a (temperature-dependent) value of $\delta \simeq 0.50$ cm^{-1} for $[\mathrm{Ni(H_2O)_6}]\mathrm{SiF_6}$. Since λ is -275 cm^{-1} for this complex[26] and Δ_1 is $\sim$9000 cm^{-1}, we see that the splitting of the excited state can be calculated via (6-95) to be in the neighborhood of 50 cm^{-1}.

The paramagnetic resonance experiment does not tell us the order of the split levels in the ground state. It is true that the theory as outlined above predicts the singlet to be placed above the doublet, but, after all, this prediction is dependent upon the sign of the trigonal splitting parameter D_T. It was realized quite early,[58] however, that only for the above splitting of the ground state was it possible to account for the bulk magnetic behavior of the complex at very low temperatures (*vide infra*).

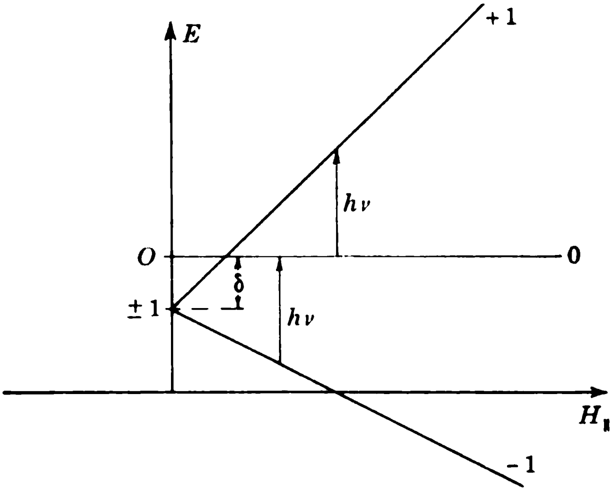

FIG. 6-5. Zeeman splitting of ground state $\Gamma_5(3d)^8$ with H parallel to the trigonal axis.

In cases where the crystalline field in Ni^{++} complexes is of lower symmetry than trigonal (or tetragonal) the doubly degenerate $E_{(\pm 1)}$ level will split up, and consequently Γ_5 will be made up of three singly degenerate levels in zero field. This is, for instance, the case in $\mathrm{Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O}$. For a closer discussion of these cases see Ollom and Van Vleck[59] and Griffiths and Owen.[60]

The reason we can get singly degenerate states for Ni^{++} complexes is, of course, that the number of electrons is even, and hence Kramers' degeneracy is not operative. In complexes of Cr^{3+}, on the other hand, where the ground state in a cubic field is $d^3\ {}^4A_{2g}(\Gamma_8)$, a lower field can only split the fourfold degenerate ground state into two Kramers doublets. A calculation of Van Vleck,[61] as corrected by Meijer and Gerritsen,[62] yields

$$\delta = E_{\pm 1/2} - E_{\pm 3/2} = \frac{152}{9}\frac{k_1\lambda^2}{\Delta_1{}^2} \tag{6-97}$$

where, as in Fig. 6-4, Δ_1 is the energy difference, $\simeq 10Dq$, $E(^4T_{2g}) - E(^4A_{2g})$ and k_1 is $E(^4T_{2g}(A)) - E(^4T_{2g}(E))$. Resonance experiments[38] for the alum $CsCr(SO_4)_2 \cdot 12H_2O$ yield that, at $T = 290°K$, $\delta = 2 \times 0.073 = 0.146$ cm^{-1}. Since[39] $\Delta_1 = 17{,}400$ cm^{-1} and[26] $\lambda = 58$ cm^{-1}, we get $k_1 \approx 800$ cm^{-1}.

In the foregoing we have tacitly assumed that all of the zero-field splitting is due to the presence of a spin-orbit coupling in connection with a low symmetry. At the same time spin-spin interactions may also play a role, again, of course, only where the symmetry of the complex permits a splitting of the ground state. However, this effect is usually small in comparison with the spin-orbit splitting, just as in the case of atomic spectra. If the system is treated by a so-called spin Hamiltonian (*vide infra*), both effects are incorporated into the measurable quantity D.

6-g. The Spin Hamiltonian

In our cursory discussion of paramagnetic resonance phenomena in the complexes of the transition groups we must not forget to introduce the spin Hamiltonian. It is true that this concept has its greatest advantage in discussing the interaction of the nuclear spin with the electronic spin, a topic with which we will not be concerned for the simple reason that so many excellent review papers and books deal with these aspects.[12,38,47,48] The spin Hamiltonian concept is mostly due to Abragam and Pryce and their collaborators.[12,34,35,38,53]

In order to derive the spin Hamiltonian, we shall look again upon the perturbation treatment with $\mathcal{H}^{(1)} = \lambda\mathbf{L}\cdot\mathbf{S} + \beta\mathbf{H}(\mathbf{L} + 2\mathbf{S})$ given in Eqs. (6-83) to (6-87). Carried through to the second order in λ and β, we have

$$E^{(2)} = 2\beta(\delta_{ij} - \lambda\Lambda_{ij})S_iH_j - \lambda^2\Lambda_{ij}S_iS_j - \beta^2\Lambda_{ij}H_iH_j \qquad (6\text{-}98)$$

where the tensor Λ_{ij} is as previously defined. Dropping the last term (which gives rise to a uniform displacement of the levels and is responsible for an induced paramagnetic moment, *vide infra*), and already having seen that the first term is the g factor, we shall concentrate upon the second term in (6-98).

This term is the one responsible for the splitting of the spin multiplet in zero magnetic field. In order to study the effect, we shall as an example take a crystalline field possessing axial symmetry (trigonal or tetragonal). In that case we can write $\Lambda_{xx} = \Lambda_{yy} = \Lambda_\perp$ and $\Lambda_{zz} = \Lambda_\parallel$, the other tensor components being zero.[34,54] Then

$$-\lambda^2\Lambda_{ij}\hat{S}_i\hat{S}_j = -\lambda^2[\Lambda_\perp(\hat{S}_x^2 + \hat{S}_y^2) + \Lambda_\parallel S_z^2] \qquad (6\text{-}99)$$

Since

$$\hat{S}_x^2 + \hat{S}_y^2 = S(S+1) - \hat{S}_z^2 \qquad (6\text{-}100)$$

we get

$$-\lambda^2\Lambda_{ij}\hat{S}_i\hat{S}_j = -\lambda^2[\Lambda_\perp S(S+1) - (\Lambda_\perp - \Lambda_\parallel)\hat{S}_z^2] \qquad (6\text{-}101)$$

Calling

$$D = (\Lambda_\perp - \Lambda_\parallel)\lambda^2 \qquad (6\text{-}102)$$

and rearranging (6-101), the final result is

$$-\lambda^2\Lambda_{ij}\hat{S}_i\hat{S}_j = D[\hat{S}_z^2 - \tfrac{1}{3}S(S+1)] - \tfrac{1}{3}\lambda^2 S(S+1)(2\Lambda_\perp + \Lambda_\parallel) \tag{6-103}$$

For example, we see that the energy difference of the spin multiplet for $Ni^{++}(3d)^8$ with $S = 1$ and $M_s = \pm 1, 0$ is just the quantity D.

By substituting (6-103) into (6-98) and dropping all constant terms, we get for the spin Hamiltonian in axial symmetry:

$$\mathcal{H} = g_\parallel\beta H_z\hat{S}_z + g_\perp\beta(H_x\hat{S}_x + H_y\hat{S}_y) + D\hat{S}_z^2 \tag{6-104}$$

Departures from axial symmetry can be described by adding the term $E(\hat{S}_x^2 - \hat{S}_y^2)$ and changing the second term in (6-102) as follows:

$$\mathcal{H} = \beta(g_zH_z\hat{S}_z + g_xH_x\hat{S}_x + g_yH_y\hat{S}_y) + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) \tag{6-105}$$

Let us try to find the eigenvalues of (6-105) with $S = 1$. For H parallel to the axis of quantization z, and writing $(\hat{S}_x^2 - \hat{S}_y^2)$ as $\tfrac{1}{2}(\hat{S}_+^2 + \hat{S}_-^2)$ with $\hat{S}_+$ and $\hat{S}_-$ having their usual meaning, we get

$$\mathcal{H} = \beta g_zH_z\hat{S}_z + D\hat{S}_z^2 + \tfrac{1}{2}E(\hat{S}_+^2 + \hat{S}_-^2) \tag{6-106}$$

The perturbation matrix is then taking $M_S = 1, 0, -1$

$$\begin{array}{cc} M_S = & \begin{array}{ccc} \quad 1 \quad & \quad 0 \quad & \quad -1 \quad \end{array} \\ & \boxed{\begin{array}{ccc} g_z\beta H + D & 0 & E \\ 0 & 0 & 0 \\ E & 0 & -g_z\beta H + D \end{array}} \end{array} \tag{6-107}$$

with eigenvalues

$$E^{(1)} = \begin{cases} 0 \\ D \pm \sqrt{g_z^2\beta^2H_z^2 + E} \end{cases} \tag{6-108}$$

For H parallel to x the spin Hamiltonian is

$$\mathcal{H} = \beta g_xH_xS_x + DS_z^2 + \tfrac{1}{2}E(S_+^2 + S_-^2) \tag{6-109}$$

The perturbation matrix is for $S = 1$, $M_S = \pm 1, 0$

$$\begin{array}{cc} M_S = & \begin{array}{ccc} \quad 1 \quad & \quad 0 \quad & \quad -1 \quad \end{array} \\ & \boxed{\begin{array}{ccc} D & \frac{\sqrt{2}}{2}\beta g_xH_x & E \\ \frac{\sqrt{2}}{2}\beta g_xH_x & 0 & \frac{\sqrt{2}}{2}\beta g_xH_x \\ E & \frac{\sqrt{2}}{2}\beta g_xH_x & D \end{array}} \end{array} \tag{6-110}$$

with eigenvalues

$$E^{(1)} = \begin{cases} D - E & (6\text{-}111) \\ \dfrac{D+E}{2} \pm \sqrt{\left(\dfrac{D+E}{2}\right)^2 + \beta^2 g_x^2 H_x^2} & (6\text{-}112) \end{cases}$$

Finally, for H parallel to y

$$E^{(1)} = \begin{cases} D + E & (6\text{-}113) \\ \dfrac{D-E}{2} \pm \sqrt{\left(\dfrac{D-E}{2}\right)^2 + \beta^2 g_y^2 H_y^2} & (6\text{-}114) \end{cases}$$

The importance of the spin Hamiltonian lies in the fact that it offers a simple theoretical framework for inserting the various measurable quantities g, D, and E. These constants can then in turn be related to the electronic configuration of the ion. Hence, knowing the experimental results, we can substitute back into our theoretical expressions and in this way critically test our initial assumptions about the orbitals, the energy states, and the bonding.

6-h. Magnetic Susceptibilities

Measurement and interpretation of the magnetic susceptibilities was the first field in which the crystal field theory showed its power. From the time of Van Vleck's now-classic work "Electric and Magnetic Susceptibilities"[1] an enormous amount of labor has been done in order to interpret the finer points of the experimental results. A classic magnetochemist was usually content with measuring the magnetic susceptibility of a complex at one temperature and then converting the result to "number of Bohr magnetons" or "number of unpaired spins" by means of Curie's formula. Sad to say, most of this work is now completely outdated. Only measurements done over a wide range of temperature can be subjected to a thorough theoretical test; when that is done, it is usually seen that the Curie law is not so universal as one would have liked.

The reason that the measurements of magnetic susceptibilities fell into decline during and after the war is just the difficulty in interpreting the results. Whereas measurements of the spectroscopic g factor give information about a single electronic level, the magnetic susceptibility only tells us about the average population of the various electronic levels. Nevertheless, a good deal of information was obtained about the electronic ground states in the complexes by magnetic methods, even though some of it had to be revised with the coming of the paramagnetic resonance method.

In this section we shall briefly treat some typical cases by means of the crystal field theory, the alternative method of Pauling now having mostly historical interest. We shall give below a brief derivation of the basic formula due to Van Vleck[1] for calculating the magnetic susceptibility.

Suppose that we have the energy of the level E_n of a molecule developed in a series in the applied field H

$$E_n = E_n^\circ + HE_{n,m}^{(1)} + H^2E_{n,m}^{(2)} + \cdots \tag{6-115}$$

where n and m specify quantum numbers and E_n° is the energy in zero field. The magnetic moment μ of the molecule *in the direction of the applied field* is then

$$\mu = -\frac{\partial E}{\partial H} \tag{6-116}$$

In the presence of the magnetic field there is a thermal distribution of aligned dipoles in the various energy levels. The total magnetic moment P is then found as the statistical mean over all the stationary states, using a Boltzmann distribution.

$$P = N\frac{\sum\limits_{n,m} \mu_{n,m}\, e^{-E_n/kT}}{\sum\limits_{n} e^{-E_n/kT}} \tag{6-117}$$

where N is Avogadro's number. With

$$e^{-E_n/kT} = \exp\left[-\frac{E_n^\circ + HE_{n,m}^{(1)} + \cdots}{kT}\right] \simeq e^{-E_n^\circ/kT}\left(1 - \frac{HE_{n,m}^{(1)}}{kT}\right) \tag{6-118}$$

and

$$\mu_{n,m} = -\frac{\partial E_{n,m}}{\partial H} = -E_{n,m}^{(1)} - 2HE_{n,m}^{(2)} - \cdots \tag{6-119}$$

we get in this approximation for P

$$P = N\frac{\sum\limits_{n,m} (-E_{n,m}^{(1)} - 2HE_{n,m}^{(2)})\left(1 - H\frac{E_{n,m}^{(1)}}{kT}\right)e^{-E_n^\circ/kT}}{\sum\limits_{n} e^{-E_n^\circ/kT}} \tag{6-120}$$

If, as is always supposed, the compound does not have a permanent polarization in zero magnetic field, the following equation holds true:

$$\sum_{n,m} -E_{n,m}^{(1)}e^{-E_n^\circ/kT} = 0$$

Hence, retaining only terms linear in H,

$$P = N\frac{H\sum\limits_{n,m}\left(\frac{[E_{n,m}^{(1)}]^2}{kT} - 2E_{n,m}^{(2)}\right)e^{-E_n^\circ/kT}}{\sum\limits_{n} e^{-E_n^\circ/kT}} \tag{6-121}$$

The susceptibility χ_i in a given direction ($i = x,y,z$) is given by $\chi_i = P_i/H_i$.

Equation (6-121) then gives for the susceptibility

$$\chi_i = N \frac{\sum\limits_{n,m} \left(\frac{[E^{(1)}_{n,m}]^2}{kT} - 2E^{(2)}_{n,m} \right) e^{-E_n^\circ/kT}}{\sum\limits_{n} e^{-E_n^\circ/kT}} \tag{6-122}$$

For the case where the separation of the levels of the ground state is small compared to kT, and the next excited level has an energy that is large compared to kT, Van Vleck[1] has shown that the susceptibility is given by

$$\chi_i = N \left[\sum_{n,m} \frac{[E^{(1)}_{0,m}]^2}{j_m kT} - 2 \sum_{n,m} \frac{E^{(2)}_{0,m}}{j_m} \right] \tag{6-123}$$

Here

$$E^{(1)}_{0,m} = (\psi_{0,m}|\mu_i|\psi_{0,m}) \tag{6-124}$$

$$E^{(2)}_{0,m} = \frac{\sum\limits_{n,m} |(\psi_{0,m}|\mu_i|\psi_{n,m})|^2}{E_0 - E_n} \tag{6-125}$$

with

$$\mu_i = \beta(\hat{L}_i + 2\hat{S}_i) \tag{6-126}$$

and j_m is the multiplicity of the ground state. The first and second terms in (6-123) are respectively called the low- and the high-frequency terms.

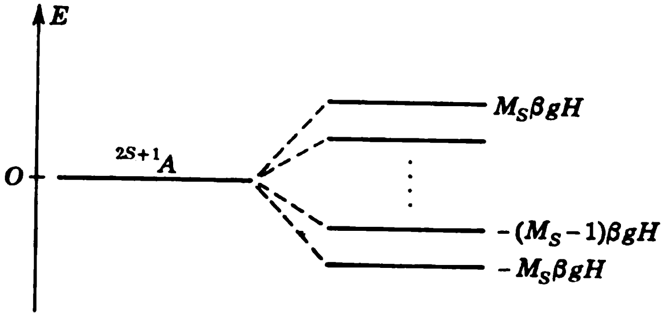

FIG. 6-6. Splitting of spin degeneracy in a magnetic field.

We shall now calculate the magnetic susceptibility of a complex assuming an orbital singlet, having $2S + 1$ spin degeneracy, to be the ground state. By the inclusion of the magnetic field, the spin degeneracy will be removed and the splitting pictured in Fig. 6-6 will occur.

Neglecting high-frequency terms, we have that $E^{(2)}_{0,m} = 0$. Thus by using (6-123), we obtain, because $\beta gH \ll kT$,

$$\chi = \frac{Ng^2\beta^2}{kT} \frac{(-S)^2 + (-S+1)^2 + \cdots + (S)^2}{2S+1} \tag{6-127}$$

$$= \frac{N\beta^2}{3kT} g^2 S(S+1) \tag{6-128}$$

This is then the temperature-dependent part of the gram susceptibility calculated under the assumption that only the ground state is populated. Experimentally, the "effective magnetic moment" μ_{eff} is obtained from the observed susceptibilities according to Curie's formula

$$\chi = \frac{N\mu_{\text{eff}}^2}{3kT} \tag{6-129}$$

By comparison with (6-128) we see that

$$\mu_{\text{eff}}^2 = \beta^2 g^2 S(S+1) \tag{6-130}$$

Let us take an example. In an octahedral Ni^{++} complex an orbital singlet lies lowest and we have previously found, Eq. (6-69), the Landé g factor to be $2(1 - 4\lambda/10Dq)$. With $S = 1$ we then have for the low-frequency term

$$\chi_{\text{lf}} = \frac{8N\beta^2}{3kT}\left(1 - \frac{4\lambda}{10Dq}\right)^2 \tag{6-131}$$

The high-frequency term presents no difficulties either. The orbital ground state is $|(x^2 - y^2)(z^2)|$. Because of orthogonality, it is only the angular part of $\beta(\hat{L}_i + 2\hat{S}_i)$ which is operative in the $E^{(2)}$ term; we find

$$\hat{L}_z|(x^2 - y^2)(z^2)| = 2i|(xy)(z^2)|$$

The latter orbital state belongs to the ${}^3T_{2g}$ level, being located some $10Dq$ above the ground state. Hence, by summing over $M_s = 1, 0, -1$, we get

$$\chi_{\text{hf}} = N\beta^2(-2)\frac{4+4+4}{3(-10Dq)} \tag{6-132}$$

and the total formula for the susceptibility of a cubic octahedral Ni(II) compound then becomes

$$\chi = \frac{8N\beta^2}{3kT}\left(1 - \frac{4\lambda}{10Dq}\right)^2 + \frac{8N\beta^2}{10Dq} \tag{6-133}$$

We have in the derivation of (6-132) omitted the effect of the mixing of ${}^3A_{2g}$ and ${}^3T_{2g}$ via the spin-orbit coupling. This is, however, not important here.

By an odd coincidence, the value of $8N\beta^2/3k$ is very near to 1. Hence, by inserting[26] for $Ni(NH_3)_6Br_2$ that $Dq = 1080\ \text{cm}^{-1}$ and $\lambda = -200\ \text{cm}^{-1}$, we have

$$\chi_{Ni(NH_3)_6^{++}} = \frac{1.1536}{T} + 193 \times 10^{-6} \tag{6-134}$$

For $T = 291°\text{K}$, $\chi = 4157 \times 10^{-6}$, which is in close agreement with the experimental value,[67] corrected for the diamagnetism of $2Br^-$, of 4099×10^{-6}.

Suppose now that the Ni^{++} complex possesses only axial symmetry. For H parallel to the axis of quantization, z, the spin Hamiltonian is [see Eqs.

(6-105) to (6-108)],

$$\mathcal{H} = \beta g_{\parallel} H_z S_z + D S_z^2 \tag{6-135}$$

with eigenvalues $E^{(1)} = 0$ and $E^{(1)} = D \pm g_{\parallel}\beta H$, Fig. 6-7. The "low-frequency" part of the susceptibility is then given by

$$\chi_{\parallel} = N \frac{\dfrac{0^2}{kT} e^{-0/kT} + 2 \dfrac{g_{\parallel}^2\beta^2}{kT} e^{-D/kT}}{1 + 2e^{-D/kT}}$$

$$\chi_{\parallel} = \frac{2Ng_{\parallel}^2\beta^2}{kT} \cdot \frac{1}{2 + e^{D/kT}} \tag{6-136}$$

At temperatures where $kT \gg D$ the susceptibility may be evaluated in ascending powers of $1/T$. With $e^{D/kT} \simeq 1 + D/kT$, Eq. (6-136) yields

$$\chi_{\parallel} = \frac{2N\beta^2 g_{\parallel}^2}{3kT}\left(1 - \frac{D}{3T}\right) \tag{6-137}$$

where D is measured in degrees Kelvin. We notice that measurements of the susceptibility over a suitable temperature range decide the sign of D.

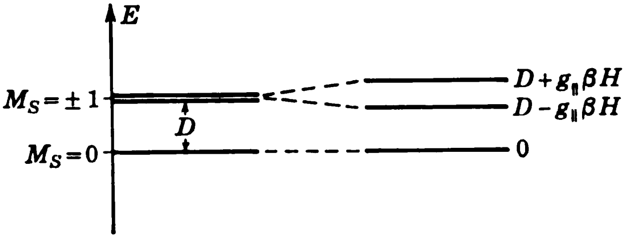

FIG. 6-7. The Zeeman splitting of the ground state of an axial Ni^{++} complex.

As mentioned in Sec. 6-*f*, D is usually negative, corresponding to a reversal of the levels in Fig. 6-7.

Another way of expanding (6-136) if $kT \gg D$ is

$$\chi_{\parallel} = \frac{2Ng_{\parallel}^2\beta^2}{3k} \frac{1}{T + \Theta} \tag{6-138}$$

with $\Theta = \frac{1}{3}D$ (D in degrees Kelvin). This latter expression shows that if the ground state is split in zero field, the susceptibility will follow a Curie-Weiss law for $kT > D$. General formulas for the magnetic susceptibilities of the $(t_{2g})^n$ electronic configurations in lower symmetry than O_h have been given by Kamimura.[52]

Let us now treat the case of one d electron in a cubic field. First we shall assume that $Dq \gg \lambda \simeq kT$. Hence, we shall, like Kotani,[68] look at the levels springing from the $(t_{2g})^1$ configuration. The wave functions for the Γ_8 and Γ_7 coming from t_{2g} in the double group have been given in Eqs. (6-12) and (6-13).

With $\mathcal{H} = \lambda \mathbf{l} \cdot \mathbf{s} + \beta H_z(l_z + 2s_z)$ we get for the secular equation using (6-12) and (6-13)

$$(\Gamma_8^{c,d}\,(t_{2g})|\mathcal{H}|\Gamma_8^{c,d}) = -\tfrac{1}{2}\lambda \tag{6-139}$$

$$\begin{array}{cccc} \Gamma_{8a} & \Gamma_{7a} & \Gamma_{8b} & \Gamma_{7b} \\ \left| \begin{array}{c} -\frac{1}{2}\lambda - E \\ \sqrt{2}\,\beta H_z \\ 0 \\ 0 \end{array} \right. & \begin{array}{c} \sqrt{2}\,\beta H_z \\ \beta H_z + \lambda - E \\ 0 \\ 0 \end{array} & \begin{array}{c} 0 \\ 0 \\ -\frac{1}{2}\lambda - E \\ \sqrt{2}\,\beta H_z \end{array} & \left. \begin{array}{c} 0 \\ 0 \\ \sqrt{2}\,\beta H_z \\ \lambda - \beta H_z - E \end{array} \right| \end{array} = 0 \tag{6-140}$$

If the solutions to the secular equation are expanded in powers of H_z, the eigenvalues are:

$$E = \begin{cases} -\dfrac{1}{2}\lambda & \text{twofold degenerate} \\ -\dfrac{1}{2}\lambda - \dfrac{4}{3}\dfrac{\beta^2}{\lambda}H_z^2 & \text{twofold degenerate} \\ \lambda - \beta H_z + \dfrac{4}{3}\dfrac{\beta^2}{\lambda}H_z^2 & \text{nondegenerate} \\ \lambda + \beta H_z + \dfrac{4}{3}\dfrac{\beta^2}{\lambda}H_z^2 & \text{nondegenerate} \end{cases} \tag{6-141}$$

Direct application of Van Vleck's formula (6-122) then yields (here we drop the "parallel" because all directions are equal)

$$\chi = \frac{2\left(\dfrac{0^2}{kT} - 2\cdot 0\right)e^{\lambda/2kT} + 2\left(\dfrac{0^2}{kT} + 2\dfrac{4}{3}\dfrac{\beta^2}{\lambda}\right)e^{\lambda/2kT} + 2\left(\dfrac{\beta^2}{kT} - 2\dfrac{4}{3}\dfrac{\beta^2}{\lambda}\right)e^{-\lambda/kT}}{2e^{\lambda/2kT} + 2e^{\lambda/2kT} + 2e^{-\lambda/kT}} \tag{6-142}$$

With $x = \lambda/kT$ this expression reduces to

$$\chi = \frac{N\beta^2}{3kT}\,\frac{8 + (3x - 8)e^{-3x/2}}{x(2 + e^{-3x/2})} \tag{6-143}$$

The "effective" number of Bohr magnetons to put into Curie's formula is thus

$$n_{\text{eff}}^2 = \frac{8 + (3x - 8)e^{-3x/2}}{x(2 + e^{-3x/2})} \tag{6-144}$$

This expression is seen to be strongly dependent upon T, a clear indication that Curie's law does not hold. For $T \rightarrow \infty$, n_{eff} converges to $\sqrt{5}$; but for $T \rightarrow 0$, n_{eff} goes to zero. Such behavior might appear very surprising at first sight. After all, there is an unpaired spin! However, the reason for the result is due to the action of spin-orbit coupling on the ground state. This is a so-called nonmagnetic state; i.e., the spin part and the orbital part of the magnetism cancel each other.

Next, with Moffitt et al.[4] and Liehr,[45] we shall look at a single *d* electron in a cubic field; only this time we assume that $\lambda \simeq Dq \gg kT$. This case is found,[4] for instance, in ReF_6. Direct application of (6-144) yields a value of n_{eff}^2 very close to zero. However, (6-144) has been derived under the assumption that no mixing occurs between $t_{2g}(\Gamma_8)$ and $e_g(\Gamma_8)$, and the inclusion of this scrambling will alter the situation appreciably. Furthermore, since $t_{2g}(\Gamma_7)$ now is placed high over $t_{2g}(\Gamma_8)$, we shall treat the matrix elements involving $t_{2g}(\Gamma_7)$ as high-frequency magnetic terms.

In this case it is permissible to use (6-123), and we get

$$\chi = \frac{N\beta^2}{3kT}\left[\frac{3}{4}\sum_{s=a}^{d} |(\Gamma_8{}^s\,|l_z + 2\hat{s}_z|\Gamma_8{}^s)|^2 + 3kT\alpha\right] \tag{6-145}$$

with

$$\alpha = \frac{2}{4}\sum_{s=a}^{d} \frac{|(\Gamma_8{}^s\,|l_z + 2\hat{s}_z|\Gamma_7{}^s)|^2}{h\nu_1} \tag{6-146}$$

The wave functions for the ground state $t_{2g}(\Gamma_8)$ with the mixing of $e_g(\Gamma_8)$ included have been found in the footnote, page 119, to be

$$\Gamma_8{}^s = \sin\varphi\,\Gamma_8{}^s\,(t_{2g}) - \cos\varphi\,\Gamma_8{}^s\,(e_g) \tag{6-147}$$

with $s = a, b, c, d$ and $\tan 2\varphi = \dfrac{-\sqrt{6}\,\lambda}{10Dq + \frac{1}{2}\lambda}$

With μ_z equal to $l_z + 2s_z$ we have

$$(\Gamma_8{}^s\,|\mu_z|\Gamma_8{}^s) = \sin^2\varphi(\Gamma_8{}^s\,(t_{2g})|\mu_z|\Gamma_8{}^s\,(t_{2g}) + \cos^2\varphi(\Gamma_8{}^s\,(e_g))|\mu_z|\Gamma_8{}^s\,(e_g)) - 2\sin\varphi\cos\varphi(\Gamma_8{}^s\,(t_{2g})|\mu_z|\Gamma_8{}^s\,(e_g))$$

By use of the orbitals (6-12) and (6-14), we find

$$(\Gamma_8{}^a\,|\mu_z|\Gamma_8{}^a) = -\cos^2\varphi + 8\sqrt{\tfrac{1}{6}}\sin\varphi\cos\varphi \tag{6-148}$$
$$(\Gamma_8{}^b\,|\mu_z|\Gamma_8{}^b) = \cos^2\varphi - 8\sqrt{\tfrac{1}{6}}\sin\varphi\cos\varphi \tag{6-149}$$
$$(\Gamma_8{}^c\,|\mu_z|\Gamma_8{}^c) = -\cos^2\varphi \tag{6-150}$$
$$(\Gamma_8{}^d\,|\mu_z|\Gamma_8{}^d) = \cos^2\varphi \tag{6-151}$$

By inserting (6-148) to (6-151) in (6-145), we get for the susceptibility

$$\chi = \frac{N\beta^2}{3kT}[\tfrac{1}{4}(1 + \cos 2\varphi)(19 - 13\cos 2\varphi - 4\sqrt{6}\sin 2\varphi) + 3kT\alpha] \tag{6-152}$$

On the other hand, in the calculation of the high-frequency term (6-146) we neglect the mixing of the two Γ_8 states. Direct computation using (6-12) and (6-13) or placing the terms containing the exponential factor in (6-143) equal to zero then yields

$$\alpha \approx \frac{2}{h\nu_1} = \frac{4}{3\lambda} \tag{6-153}$$

For ReF_6 we have[4] $Dq = 3000\ \text{cm}^{-1}$ and $\lambda = 3400\ \text{cm}^{-1}$. Then $2\varphi = 165.28°$ and

$$\mu_{\text{eff}}^2 = 0.24 + T\cdot 8.2\cdot 10^{-4} \tag{6-154}$$

Notice that the temperature-dependent part of χ differs from zero only because of the scrambling of $\Gamma_8(t_{2g})$ and $\Gamma_8(e_g)$. This is, of course, not unexpected in view of our previous result for the g factor of this system. It is of further interest to see that, although $10Dq$ is much larger than λ, the mixing brings μ_{eff} from a value of zero to a value of about one-half. General formulas for the magnetic susceptibilities of $(t_{2g})^n$ electronic configurations have been given by Kotani[65,68] and Figgis.[69]

The next example we shall treat in some detail is the case where the ground state is a nonmagnetic singlet. Two different mechanisms may here give rise to a feeble paramagnetism. A temperature-dependent susceptibility may arise if there is a thermally accessible state placed not too high above the magnetically inert ground state, and a temperature-independent contribution to the paramagnetic susceptibility may spring from the "high-frequency" term in Van Vleck's formula.

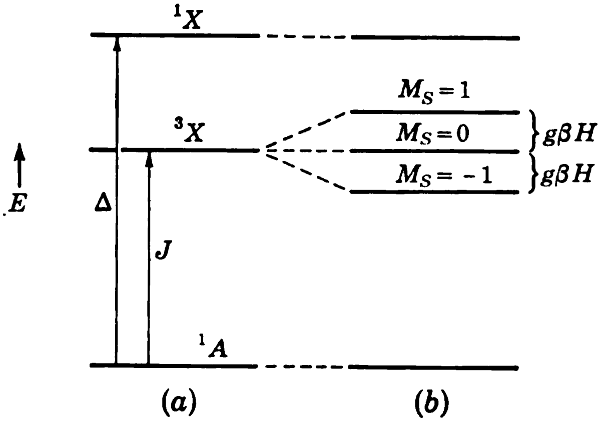

FIG. 6-8. System with a singlet ground state. (a) Zero magnetic field; (b) magnetic field present.

Let us first consider case 1. As pictured in Fig. 6-8, the first excited state is a triplet. By switching the magnetic field on, the triplet will show a Zeemann splitting as indicated. The magnetic susceptibility of the system is then, disregarding the term in H^2,

$$\chi = N \frac{2 \dfrac{g^2\beta^2}{kT} e^{-J/kT}}{1 + 3e^{-J/kT}} \tag{6-155}$$

$$\chi = \frac{2g^2N\beta^2}{3kT} \frac{1}{1 + \frac{1}{3}e^{J/kT}} \tag{6-156}$$

or, with $N\beta^2/3k = \frac{1}{8}$ and $g = 2$ to the first approximation,

$$\chi = \frac{1}{T} \frac{1}{1 + \frac{1}{3}e^{J/kT}} \tag{6-157}$$

Both for T going toward zero and toward infinity χ tends to zero. Clearly,

χ must have a maximum; by a simple differentiation this is found to occur when

$$\frac{J}{kT} = 1.193 \simeq \tfrac{6}{5} \tag{6-158}$$

or χ has its maximum value for $T = \tfrac{5}{6}J$ (J in degrees Kelvin). For $kT \gg J$ the susceptibility follows a Curie-Weiss law $\chi = \tfrac{3}{4}\frac{1}{T + \Theta}$ with $\Theta = \tfrac{1}{4}J$ (J in degrees Kelvin). Examples of compounds which follow the above formulas are certain "diamagnetic" Ni(II) complexes.[71]

As already mentioned, the temperature-independent susceptibility is due to the scrambling via $\hat{L}$ of the ground state with a high-lying excited state. Consider, for example, a diamagnetic cubic Co(III) complex.[72,75] The ground state in the strong-field approximation is given by

$$\psi = |\overset{+}{(xz)}\overset{-}{(xz)}\overset{+}{(yz)}\overset{-}{(yz)}\overset{+}{(xy)}\overset{-}{(xy)}|$$

a ${}^1A_{1g}$ state carrying neither spin nor angular momentum. In the point group O_h $\mathbf{L}$ transforms like T_{1g}. Hence, the ground state can be mixed with excited states transforming like ${}^1T_{1g}$. Further, since $\mathbf{L} = \sum_i \mathbf{l}_i$ is a sum of one electron term, the excited ${}^1T_{1g}$ states can differ from the ground state only in the assignment of a single electron.

The only state fulfilling the above conditions is the state responsible for the "first" spin-allowed band in Co(III) complexes, Fig. 6-8. In $\text{Co(NH}_3)_6{}^{3+}$, for instance, it is located 21,000 cm^{-1} above the ground state; an energy more than sufficient to fulfill the conditions of a high-frequency term. A component of this ${}^1T_{1g}$ state is given by

$$\Theta = \frac{1}{\sqrt{2}}\left[|\overset{+}{(xz)}\overset{-}{(xz)}\overset{+}{(yz)}\overset{-}{(yz)}\overset{+}{(xy)}(x^2 \overset{-}{-} y^2)| - |\overset{+}{(xz)}\overset{-}{(xz)}\overset{+}{(yz)}\overset{-}{(yz)}\overset{-}{(xy)}(x^2 \overset{+}{-} y^2)|\right] \tag{6-159}$$

found by the usual symmetry arguments going down to D_{4h}. Hence,

$$(\Theta|L_z|\psi) = -2\sqrt{2}\,i \tag{6-160}$$

and from formulas (6-123) and (6-125) we get

$$\chi_{hf} = 2N\beta^2\frac{8}{\Delta} \qquad \chi_{hf} = \frac{4.170}{\Delta(\text{cm}^{-1})} \tag{6-161}$$

For $\text{Co(NH}_3)_6{}^{3+}$ we then have $\chi_{hf} = 198 \times 10^{-6}$. The high-frequency term found in a "normal" paramagnetic substance, as, for instance, $\text{Ni(NH}_3)_6{}^{++}$, has been given in Eq. (6-132).

We remark in passing that the same matrix element which governs the value of the high-frequency term in (6-123) is also responsible for the paramagnetic contribution to the "chemical screening constant" in nuclear magnetic resonance. The interested reader is referred to Refs. 72, 74, and

75, where the relative value of this constant for diamagnetic cobalt(III) is related to the energy separation ${}^1A_{1g} - {}^1T_{1g}$.

Finally, we shall look very briefly upon the magnetic properties of polynuclear complexes. Consider a binuclear compound where both the metal atoms if left alone would possess a spin angular momentum. It is then clear that these two may interact, and this feature can formally be accounted for by a spin-spin coupling between the ions of the form

$$\mathcal{H}^{(1)} = -J\mathbf{S}_1 \cdot \mathbf{S}_2 \tag{6-162}$$

J is the exchange coupling constant.[1] Let us define

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 \tag{6-163}$$

Then

$$2\mathbf{S}_1 \cdot \mathbf{S}_2 = S(S+1) - S_1(S_1+1) - S_2(S_2+1) \tag{6-164}$$

and

$$\mathcal{H}^{(1)} = -\tfrac{1}{2}J[S(S+1) - S_1(S_1+1) - S_2(S_2+1)] \tag{6-165}$$

where the allowed values of S are obtained by the addition rule of two spin vectors

$$S = S_1 + S_2,\ S_1 + S_2 - 1,\ \ldots,\ |S_1 - S_2|$$

If $S_1 = S_2$, then

$$S = 2S_1,\ 2S_1 - 1,\ \ldots,\ 1,\ 0$$

Disregarding the constant terms in S_1 and S_2 of (6-165) and taking J to be negative (corresponding to an antiferromagnetic interaction[1,87]) the level scheme using (6-165) as a perturbation will be

$$E^{(1)} = -\tfrac{1}{2}JS(S+1)$$

each level being $2S + 1$ degenerate. For $S = \tfrac{1}{2}$, which case is realized in copper(II) acetate,[70] the situation is exactly as pictured in Fig. 6-8; a low-lying singlet and a triplet placed at a distance J above it. Hence, the analysis of the susceptibility of copper(II) acetate runs parallel to the previous case and the formulas (6-155) to (6-158) are valid, even if the origin of the separation between the singlet and triplet is quite different in this latter case.

A beautiful example of antiferromagnetism is found in the complexes of iridium. The discussion of $IrCl_6^-$ given in Refs. 77 to 79 is very elegant and clarifying and should be consulted for further details concerning the phenomenon. In some cases the exchange between the metal atoms is so strong that the triplet is a very high lying level. This occurs, for instance, in the diamagnetic complex $Ru_2Cl_{10}O^{4-}$ treated by Dunitz and Orgel.[80]

For complexes containing three metallic ions the papers by Kambe[81] and Yvon et al.[82] should be consulted. We shall, however, take leave of the subject here, because a further discussion would take us far into the domain of solid-state physics.

Even though many of the results quoted in this chapter have been obtained from measurements upon crystals, we believe them to be valid also for a single molecule. On the other hand, the interesting spectral and magnetic phenomena due to the interactions in a lattice structure again lie outside the scope of this book.

APPENDIX I

APPLICATION OF THE OPERATORS $\hat{L}_z$ AND $(\hat{L}_x \pm i\hat{L}_y)$ UPON THE SET (xz), (yz), (xy), $(x^2 - y^2)$, AND (z^2)

$$
\begin{aligned}
\hat{L}_z(z^2) &= 0 \\
\hat{L}_z(xz) &= i(yz) \\
\hat{L}_z(yz) &= -i(xz) \\
\hat{L}_z(xy) &= -2i(x^2 - y^2) \\
\hat{L}_z(x^2 - y^2) &= 2i(xy) \\
(\hat{L}_x \pm i\hat{L}_y)(xz) &= \mp(x^2 - y^2) - i(xy) \pm \sqrt{3}\,(z^2) \\
(\hat{L}_x \pm i\hat{L}_y)(yz) &= i(x^2 - y^2) \mp (xy) + i\sqrt{3}\,(z^2) \\
(\hat{L}_x \pm i\hat{L}_y)(xy) &= \pm (yz) + i(xz) \\
(\hat{L}_x \pm i\hat{L}_y)(z^2) &= \mp \sqrt{3}\,(xz) - i\sqrt{3}\,(yz) \\
(\hat{L}_x + i\hat{L}_y)(x^2 - y^2) &= \pm(xz) - i(yz)
\end{aligned}
$$

APPENDIX II

THE OPERATOR $\mathbf{l}\cdot\mathbf{s}$ OPERATING UPON THE CUBIC ORBITAL SET (xz), (yz), (xy), $(x^2 - y^2)$, AND (x^2)

$$
\begin{aligned}
\mathbf{l}\cdot\mathbf{s}\overset{+}{(z^2)} &= -\frac{\sqrt{3}}{2}\overset{-}{(xz)} - \frac{i\sqrt{3}}{2}\overset{-}{(yz)} \\
\mathbf{l}\cdot\mathbf{s}\overset{-}{(z^2)} &= \frac{\sqrt{3}}{2}\overset{+}{(xz)} - \frac{i\sqrt{3}}{2}\overset{+}{(yz)} \\
\mathbf{l}\cdot\mathbf{s}(x^2 \overset{+}{-} y^2) &= i\overset{+}{(xy)} - \frac{i}{2}\overset{-}{(yz)} + \frac{1}{2}\overset{-}{(xz)} \\
\mathbf{l}\cdot\mathbf{s}(x^2 \overset{-}{-} y^2) &= -i\overset{-}{(xy)} - \frac{i}{2}\overset{+}{(yz)} - \frac{1}{2}\overset{+}{(xz)} \\
\mathbf{l}\cdot\mathbf{s}\overset{+}{(xy)} &= -i(x^2 \overset{+}{-} y^2) + \frac{1}{2}\overset{-}{(yz)} + \frac{i}{2}\overset{-}{(xz)} \\
\mathbf{l}\cdot\mathbf{s}\overset{-}{(xy)} &= i(x^2 \overset{-}{-} y^2) - \frac{1}{2}\overset{+}{(yz)} + \frac{i}{2}\overset{+}{(xz)} \\
\mathbf{l}\cdot\mathbf{s}\overset{+}{(xz)} &= \frac{i}{2}\overset{+}{(yz)} - \frac{1}{2}(x^2 \overset{-}{-} y^2) - \frac{i}{2}\overset{-}{(xy)} + \frac{\sqrt{3}}{2}\overset{-}{(z^2)} \\
\mathbf{l}\cdot\mathbf{s}\overset{-}{(xz)} &= -\frac{i}{2}\overset{-}{(yz)} + \frac{1}{2}(x^2 \overset{+}{-} y^2) - \frac{i}{2}\overset{+}{(xy)} - \frac{\sqrt{3}}{2}\overset{+}{(z^2)} \\
\mathbf{l}\cdot\mathbf{s}\overset{+}{(yz)} &= -\frac{i}{2}\overset{+}{(xz)} + \frac{i}{2}(x^2 \overset{-}{-} y^2) - \frac{1}{2}\overset{-}{(xy)} + \frac{i\sqrt{3}}{2}\overset{-}{(z^2)} \\
\mathbf{l}\cdot\mathbf{s}\overset{-}{(yz)} &= \frac{i}{2}\overset{-}{(xz)} + \frac{i}{2}(x^2 \overset{+}{-} y^2) + \frac{1}{2}\overset{+}{(xy)} + \frac{i\sqrt{3}}{2}\overset{+}{(z^2)}
\end{aligned}
$$

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CHAPTER 7

Molecular Orbitals

7-a. General Discussion

So far, the only role of the ligands has been to produce a "crystalline" field causing the splitting of the various orbitals of the metal atom. Now, such a point of view is equivalent to regarding a complex molecule as held together by purely ionic forces, replacing any inherent bonding by point charges attracting and repulsing each other. However, we know from Earnshaw's theorem of electrostatics that no system of charges can be in stable equilibrium while at rest. Obviously, a modification in our view of the bonding is needed in order to save the situation. It is true that in the preceding chapters we have very seldom utilized any specific features of the orbitals; for the most part it was only their symmetry properties that we used. However, the crux of the matter is this: will the inclusion of a more realistic bonding scheme produce a splitting of the orbitals in the way the crystal field theory demands? As we shall see the answer is, fortunately, yes.

As mentioned in the introduction, we call this second approximation the ligand field theory because it acknowledges the presence of the ligands to a much greater extent than the pure crystal field theory does. Hence, the ligand field method differs from the crystalline field procedure in that the structural unit for the wave function is the whole complex ion, rather than the single central atom. In order to construct suitable wave functions, we introduce the so-called linear combination of atomic orbitals (LCAO) method. In this connection the use of symmetry considerations will prove to be extremely useful. Such an approach is due to Van Vleck, and for a beautiful exposition of the ideas behind the theory, his classical papers, Refs. 1 to 3, should be consulted.

A question which naturally arises here is this: What proof do we have for the claimed superiority of the molecular-orbital description over the pure crystalline field model? Quite apart from the more indirect evidence such as the impossibility of fitting certain magnetic experiments[4] and absorption-band intensities[5] without use of the molecular-orbital scheme, a very direct proof for the "covalency" of certain complexes has been given by Owen and Stevens.[6] They found that the paramagnetic resonance spectrum of $IrCl_6^-$ showed a hyperfine structure which could only be interpreted as originating from the Cl^- ions. Similar experiments yielding identical results have since been performed by Tinkham[7] on the complexes MnF_2, FeF_2, and CoF_2. These experiments give us a clear proof that the magnetic electrons move in a molecular orbital extending over the entire complex, and hence that an MO scheme is closer to the truth than a crystalline field description is.

The LCAO method may, as stated, be used to construct orbitals for the complex. These orbitals are of the form

$$\Psi = \psi(\Gamma) + \sum_i a_i\psi_i \tag{7-1}$$

where $\psi(\Gamma)$ is a wave function of the central atom transforming in the molecular point group as the irreducible representation Γ and $\sum_i a_i\psi_i$ is a linear combination of ligand wave functions transforming as the same irreducible representation Γ. Only if this is the case is it possible to have any "smearing out" of the electronic orbital over the whole molecular unit, since only then can we have any cross terms between the two parts of (7-1).

Let us first consider the so-called σ bonds in an octahedral complex, Fig. 7-1. These orbitals are symmetric about the line joining the ligand and the central atom. They can consequently be either s, p_z, d_{z^2}, . . . orbitals.† There are six such bonds; consequently, we can construct six linearly independent orbitals using these wave functions. The question of how to construct combinations transforming under one of the representations of the group then arises.

To determine the irreducible representations, we may proceed in a way similar to that used for the determination of molecular vibrations.[8] The character χ_S for any symmetry operation $\hat{S}$ is simply equal to q, where q is the number of "bonds" left "upon the same atom" by the application of $\hat{S}$. This result is true, because only if a certain bond is not "shifted" will it appear on the diagonal in the transformation matrix. Since the character

---

† The reader may possibly wonder about the way the six coordinate systems centered on the ligands are numbered and oriented. The seemingly confusing picture is not due to a random distribution of arrows; the coordinate systems are constructed in such a fashion that the following principles are fulfilled:

1. The numbering of the ligands follows Van Vleck.[1]
2. The z axis is always pointing toward the metal atom. Hence, all of the σ bonds are described by using the z coordinate, and the π bonds by using the x and y coordinates.
3. All of the ligand coordinate systems are left-handed coordinate systems. This choice has been made because of the fact that two center integrals usually are evaluated by using one right- and one left-handed coordinate system.
4. The positive ends of the twelve x and y axis have been chosen in such a way that only positive signs appear in the linear combinations of the ligand orbitals making up the t_{2g} π orbitals. This is, of course, by no means necessary; any combination of signs would do. However, since the most important π bond is the t_{2g} bond, it is convenient to use only plus signs.

Conditions 2, 3, and 4 then fix the coordinate systems as shown in Fig. 7-1.

is the sum of the diagonal elements, the above rule has been proved. Hence, for the σ bonds in O_h, Fig. 7.1,

	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8iC_3$	$3iC_2$	$6iC_4$	$6iC_2$
χ_σ	6	0	2	2	0	0	0	4	0	2

Using (3-13), we then find that this reducible representation can be decomposed into the irreducible representations a_{1g}, e_g, and t_{1u}. It is thus possible to construct linear combinations of ligand orbitals transforming as a_{1g}, e_g, and t_{1u}. Furthermore, in the O_h symmetry the central ion's s orbitals transform under a_{1g}, the p orbitals under t_{1u}, and the d orbitals under e_g and t_{2g}. Thus we get the well-known result that the bonding scheme is a d^2sp^3 hybridization.[10] The two d orbitals to be used are therefore the e_g orbitals.

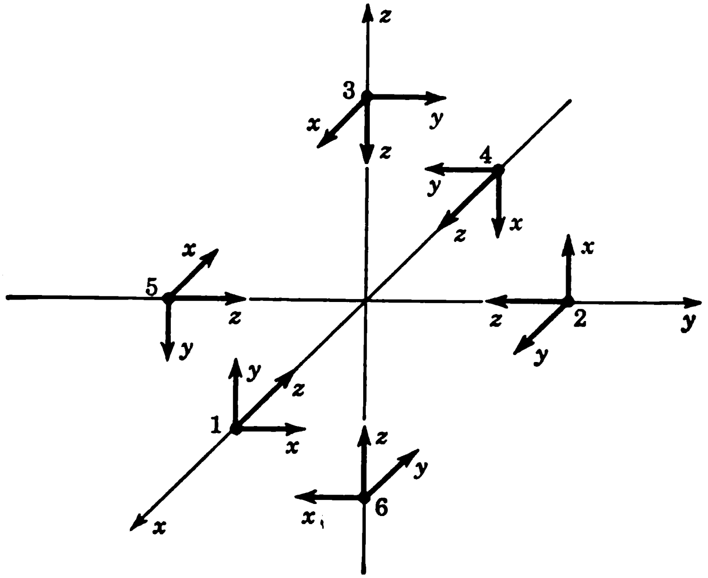


FIG. 7-1. σ and π bonds in an octahedral complex.

The exact form of the ligand orbitals can be found either by inspection or by use of the procedure outlined upon page 44. It is easy to see that the (normalized) linear combination

$$a_{1g} = \frac{1}{\sqrt{6}}(z_1 + z_2 + z_3 + z_4 + z_5 + z_6) \qquad (7\text{-}2)$$

will transform like a_{1g}. But what about the e_g orbitals?

For this case we construct the following transformation table for the symmetry operations having a character different from zero. By multiply-

	E	$C_3(1)$	$C_3(2)$	$C_3(3)$	$C_3(4)$	$C_3(5)$	$C_3(6)$	$C_3(7)$	$C_3(8)$	$C_2(1)$	$C_2(2)$	$C_2(3)$
z_1	z_1	z_3	z_2	z_6	z_2	z_3	z_5	z_5	z_6	z_1	z_4	z_4
z_2	z_2	z_1	z_3	z_6	z_3	z_4	z_3	z_4	z_6	z_2	z_5	z_5

ing each entry in the table with the appropriate character, we get the two linear combinations

$$2z_1 - z_3 - z_2 - z_6 - z_2 - z_3 - z_5 - z_5 - z_6 + 2z_1 + 2z_4 + 2z_4$$
$$= 4z_1 + 4z_4 - 2z_2 - 2z_3 - 2z_5 - 2z_6$$
$$2z_2 - z_1 - z_3 - z_6 - z_3 - z_4 - z_3 - z_4 - z_6 + 2z_2 + 2z_5 + 2z_5$$
$$= 4z_2 + 4z_5 - 2z_1 - 2z_3 - 2z_4 - 2z_6$$

Hence, we could take the two linear combinations

$$\psi_1 = 2z_1 - z_2 - z_3 + 2z_4 - z_5 - z_6 \qquad (7\text{-}3)$$
$$\psi_2 = -z_1 + 2z_2 - z_3 - z_4 + 2z_5 - z_6 \qquad (7\text{-}4)$$

as the two e_g orbitals. It is, however, much more convenient to construct two new orbitals following the two e_g orbitals d_{z^2} and $d_{x^2-y^2}$. We have under C_4 for the e_g orbitals

$$\hat{C}_4\begin{pmatrix} d_{z^2} \\ d_{x^2-y^2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} d_{z^2} \\ d_{x^2-y^2} \end{pmatrix} \qquad (7\text{-}5)$$

Hence, we must demand

$$\hat{C}_4(a\psi_1 + b\psi_2) = \pm(a\psi_1 + b\psi_2) \qquad (7\text{-}6)$$

and substituting (7-3) and (7-4) into (7-6) then yields

$$a = \pm b \qquad (7\text{-}7)$$

Our new orbitals are thus

$$\psi_1 + \psi_2 = z_1 + z_2 - 2z_3 + z_4 + z_5 - 2z_6 \qquad (7\text{-}8)$$
$$\psi_1 - \psi_2 = 3z_1 - 3z_2 + 3z_4 - 3z_5 \qquad (7\text{-}9)$$

or, changing the sign and normalizing,

$$\psi_{z^2} = \frac{1}{3\sqrt{2}}(2z_3 + 2z_6 - z_1 - z_2 - z_4 - z_5) \qquad (7\text{-}10)$$
$$\psi_{x^2-y^2} = \tfrac{1}{2}(z_1 - z_2 + z_4 - z_5) \qquad (7\text{-}11)$$

A similar procedure could be used to find the linear combinations of the σ orbitals transforming like t_{1u}. However, if we remember that the three p orbitals transform like t_{1u} we see immediately from Fig. 7-2 that the orbitals producing the maximum amount of overlap with the central ion are

$$\psi_x = \frac{1}{\sqrt{2}}(z_3 - z_6) \qquad (7\text{-}12)$$
$$\psi_y = \frac{1}{\sqrt{2}}(z_2 - z_5) \qquad (7\text{-}13)$$
$$\psi_z = \frac{1}{\sqrt{2}}(z_1 - z_4) \qquad (7\text{-}14)$$

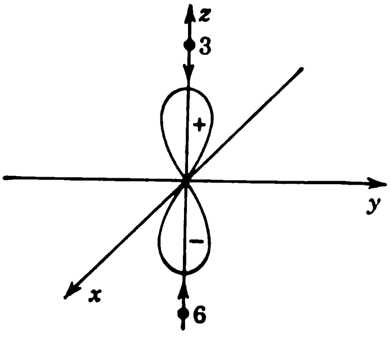


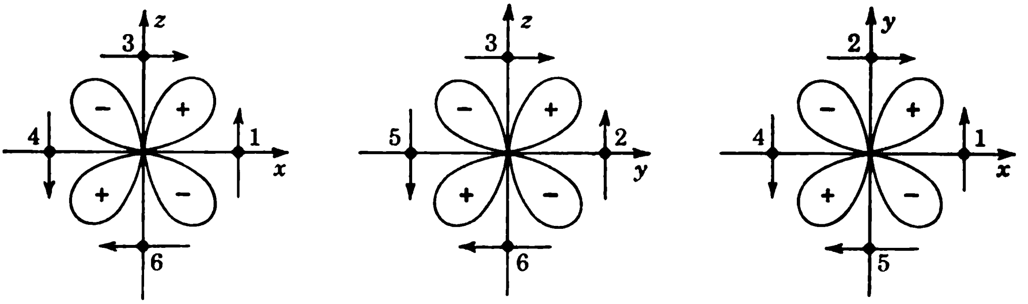
FIG. 7-2. A t_{1u} σ bond in O_h.

These three orbitals transform under t_{1u}. Thus we have in Eqs. (7-2) and (7-10) to (7-14) found the six combinations of the ligand orbitals constituting the possible σ bonds.

Let us next consider the π bonds. These are made up of a pair of orbitals perpendicular to the bond[9] as shown in Fig. 7-1. In order to determine the linear combinations of such orbitals transforming under the irreducible representations of the point group of the molecule, we proceed as before. The character of the reducible representation is in O_h given by

	E	$8C_3$	$3C_2$	$6C_4$	$6C_2$	i	$8iC_3$	$3iC_2$	$6iC_2$	$6iC_4$	$6iC_2'$
χ_π:	12	0	-4	0	0	0	0	0	0	0	0

This reducible representation can be decomposed into the irreducible representations t_{1g}, t_{1u}, t_{2g}, and t_{2u}. Hence we can make linear combinations of ligand orbitals which will span the above-mentioned irreducible representations.



(xz) (yz) (xy)

FIG. 7-3. The molecular t_{2g} orbitals.

The analytical form of the linear combinations of ligand orbitals transforming like t_{2g} follows from the principles outlined previously. We remember that the d orbitals (xy), (xz), and (yz) transform like t_{2g}, and in Fig. 7-3 we have pictured the three orbitals together with the ligand π orbitals having the same symmetry as the individual t_{2g} orbitals. From inspection of Fig. 7-3 we see immediately that

$$t_{2g}\quad\left\{\begin{aligned}\psi_{xz} &= x_3 + y_1 + x_4 + y_6\\ \psi_{yz} &= x_2 + y_3 + x_6 + y_5\\ \psi_{xy} &= x_1 + y_2 + x_5 + y_4\end{aligned}\right. \tag{7-15}$$

In the same way we can find the sets transforming like t_{1u} and t_{1g} by remembering[8] that the p orbitals transform like t_{1u} and the rotations of the O_h molecule like t_{1g}.

$$t_{1u}\quad\left\{\begin{aligned}\psi_{x} &= x_3 + y_2 - x_5 - y_6\\ \psi_{y} &= x_1 + y_3 - x_6 - y_4\\ \psi_{z} &= x_2 + y_1 - x_4 - y_5\end{aligned}\right. \tag{7-16}$$

$$t_{1g} = \begin{cases} x_3 - y_1 - x_4 + y_6 \\ x_2 - y_3 - x_6 + y_5 \\ x_1 - y_2 - x_5 + y_4 \end{cases} \tag{7-17}$$

The last set of orbitals is then constructed to be orthogonal upon the above sets. Hence

$$t_{2u} = \begin{cases} x_3 - y_2 + x_5 - y_6 \\ x_1 - y_3 + x_6 - y_4 \\ x_2 - y_1 + x_4 - y_5 \end{cases} \tag{7-18}$$

It would, of course, also have been possible to apply here the methods used to find the $\sigma(e_g)$ orbitals. However, the above method illustrates how we can utilize our "physical intuition" and escape some tedious algebra.

Having found the various linear combinations of ligand orbitals transforming like the irreducible representations of the point group of the molecule, our next task is to find the irreducible representations spanned by the various types of central orbitals. These are, of course, the representations the crystal field theory works with. We have previously found the scheme

Orbitals	s	p	d	f
Representations	a_{1g}	t_{1u}	e_g, t_{2g}	a_{2u}, t_{1u}, t_{2u}

Then, taking a linear combination of ligand and central orbitals, we get (7-19) for one of the components of the molecular orbital having e_g symmetry

$$\psi_{x^2-y^2} = \alpha d_{x^2-y^2} + \beta \tfrac{1}{2}(z_1 - z_2 + z_4 - z_5) \tag{7-19}$$

and *mutatis mutandis* for the other e_g component.

In (7-19) α and β are the mixing coefficients, which in principle are obtained by the usual variational calculation.[9] If we neglect the overlap between the central and ligand orbitals (*vide infra*), the following relation holds for the mixing coefficients α and β:

$$\alpha^2 + \beta^2 = 1 \tag{7-20}$$

or

$$\beta = \sqrt{1 - \alpha^2} \tag{7-21}$$

In order for the electron to be shared equally between the two orbitals, α must be equal to β. The solution of (7-21) then yields $\alpha = \beta = \pm\sqrt{\tfrac{1}{2}}$. This case corresponds to Pauling's covalent orbitals.[10]

We see that the transition from the crystal field theory to the ligand field theory depends upon the value of α. If α is equal to 1, we have the crystal field case. Furthermore, the smaller the value of α the more the complex deviates from strict crystalline field theory. The Pauling theory assumes $\alpha = \sqrt{\tfrac{1}{2}}$, corresponding to complete mixing of metal and ligand orbitals, but this assumption is usually farther from the truth than the assumption $\alpha \approx 1$, the "ionic case."

In Table 7-1 we have collected the various possibilities for molecular-orbital formation using the s, p, and d orbitals of the metal atom. It should be noted that so long as we do not consider f orbitals as involved in the bonding, the π orbitals of symmetry t_{2u} are nonbonding. The t_{1g} π orbitals, on the other hand, require g orbitals in order to form bonding orbitals.

TABLE 7-1. POSSIBLE MOLECULAR-ORBITAL COMBINATIONS IN O_h SYMMETRY
(The numbering of the ligand orbitals is shown in Fig. 7-1)

Symmetry	Central atom	Ligand orbitals σ orbitals	Ligand orbitals π orbitals
a_{1g}	s	$\frac{1}{\sqrt{6}}(z_1 + z_2 + z_3 + z_4 + z_5 + z_6)$	
e_g	$d_{x^2-y^2}$	$\frac{1}{2}(z_1 - z_2 + z_4 - z_5)$	
	d_{z^2}	$\frac{1}{3\sqrt{2}}(2z_3 + 2z_6 - z_1 - z_2 - z_4 - z_5)$	
t_{1u}	p_x	$\frac{1}{\sqrt{2}}(z_1 - z_4)$	$\frac{1}{2}(x_3 + y_2 - x_5 - y_6)$
	p_y	$\frac{1}{\sqrt{2}}(z_2 - z_5)$	$\frac{1}{2}(x_1 + y_3 - x_6 - y_4)$
	p_z	$\frac{1}{\sqrt{2}}(z_3 - z_6)$	$\frac{1}{2}(x_2 + y_1 - x_4 - y_5)$
t_{2g}	d_{xz}		$\frac{1}{2}(x_3 + y_1 + x_4 + y_6)$
	d_{yz}		$\frac{1}{2}(x_2 + y_3 + x_6 + y_5)$
	d_{xy}		$\frac{1}{2}(x_1 + y_2 + x_5 + y_4)$

It is very important to realize that the solving of the quadratic secular equation associated, for instance, with the determination of the mixing coefficients for the a_{1g} orbital yields two solutions. The lower root represents a lower energy than is found in the separated system; hence, we call it a bonding orbital. The upper root, on the other hand, yields a higher energy than found for the free atoms; hence, we call it an antibonding orbital. The antibonding orbital is usually distinguished from the bonding orbital by means of an asterisk; this should not be confused with the sign for complex conjugation. We may picture the bonding as shown in Fig. 7-4. By convention, the signs of α and β are both taken to be positive for the *bonding* orbital, whereas they differ for the antibonding orbital. In the octahedral symmetry there is only one case (the t_{1u} orbital) where we obtain a 3 by 3 secular equation. The solution to this will, of course, give us three roots, usually one bonding, one nearly nonbonding, and one antibonding orbital.

Since the π orbitals do not point toward the central atom, they usually give a much weaker bonding than the σ orbitals give. In many cases it is even possible to neglect the π bonds and consider only the σ bonds in the bonding scheme. If this is done, the π orbitals are treated as nonbonding.

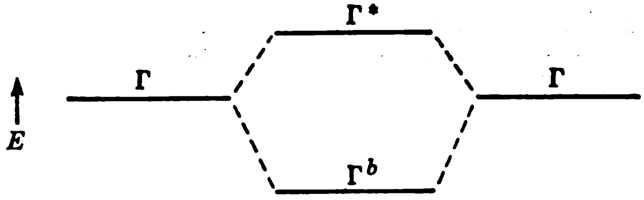


FIG. 7-4. Bonding and antibonding levels in LCAO theory. To the left and right are presented the energy levels for the separated complex, while the levels for the resulting compound are in the center.

7-b. Bonding Scheme for an Octahedral Complex

Let us now consider the bonding scheme in a complex possessing O_h symmetry, first assuming that only σ bonding is operative, Fig. 7-5. On the left we place the energy levels of the gaseous metal ion, on the right the energy levels of the free ligand. In the middle of the figure we then place the levels for the combined molecular orbital of the complex.

Each of the ligand's σ orbitals contains two electrons. Consequently, we must accommodate 12 electrons plus the electrons coming from the central ion in our bonding scheme. For instance, for $Ti(H_2O)_6^{3+}$ one lone pair of electrons on each water molecule are taken to be the σ electrons; the metal atom, on the other hand, has one 3*d* electron. The molecular electronic configuration for this complex is thus $(a_{1g}^b)^2(t_{1u}^b)^6(e_g^b)^4(t_{2g})$. Notice that the 12 σ electrons occupy all of the bonding orbitals, placing a single electron in the nonbonding t_{2g} orbital.

The level above the t_{2g} orbital is the antibonding e_g orbital. In the crystal field theory the energy difference between the e_g and the t_{2g} orbital is taken as $10Dq$; here we notice that $10Dq$ must be interpreted as the energy difference between the *antibonding* e_g and the t_{2g} level. Formally, therefore, this case is not distinguishable from the "ionic" bonding pattern. However, the magnitude of $10Dq$ in the ligand field theory depends entirely upon how strong the bonding is. If π bonding is present, the value of $10Dq$ will be modified further because the t_{2g} orbital can now participate in the bonding. Quantitatively, therefore, $10Dq$ is immoderately sensitive to changes in the bonding situation.

The important problem must then be how to calculate the quantity $10Dq$ from basic principles. This is not an easy task; indeed, in the first attempt made, Kleiner[11] obtained a value for chrome alum of $Dq = -550\ \text{cm}^{-1}$, the experimental value being $Dq = 1750\ \text{cm}^{-1}$. Tanabe and Sugano[12] obtained $Dq = 4750\ \text{cm}^{-1}$ for the same compound. Both of these results are thus in serious disagreement with experiments. The reason for Kleiner's bad result is the neglect in his calculation of the exchange forces between the

3*d* orbitals of the central ion and the ligand orbitals. The inclusion of this effect will, as shown by Tanabe and Sugano, correct the sign of *Dq*. In order to take into account the deformation of the electronic cloud of the Cr^{3+} ion by complex formation, the latter authors made the central ion and ligand orbitals orthogonal to each other. As in Kleiner's calculation, their model is thus a purely ionic one differing from the procedure outlined above.

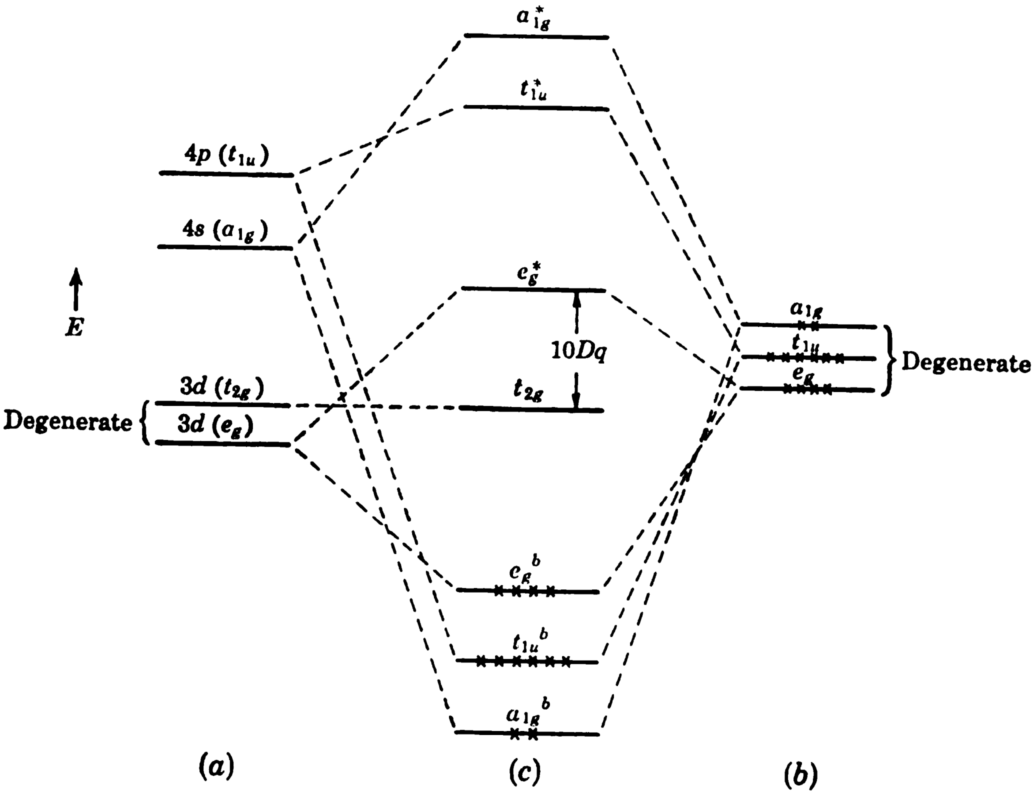


FIG. 7-5. Bonding scheme for an octahedral complex. (*a*) Energy levels for the gaseous metal ion; (*b*) energy levels for the ligands; (*c*) energy levels for the combined metal and ligand orbitals.

The triumph of calculating 10*Dq* from first principles was left to Shulman and Sugano.[49] Using molecular wave functions, and evaluating all of the necessary integrals on an electronic computer, they succeeded in obtaining 10*Dq* for $KNiF_3$. It turned out that it is the cross terms of the wave function with the Hamilton operator which determine the sign of *Dq*. This calculation thus opens up a quite new view upon the basic origin of the crystal field splitting.

The formal solution to a molecular-orbital calculation has been given by Jarrett.[13] Starting from antisymmetrized molecular orbitals, he has shown that the crystal field splitting parameter can have a different term value for each irreducible representation. There is, of course, nothing surprising in this result, since it is intuitively clear that the contribution to *Dq* from the "exchange" between the ligands and the metal atom depends to some extent upon the total electronic configuration of a certain state.

There are, however, one or two points which still remain rather mysterious. We have mentioned earlier that the Condon-Slater integrals F_n and the spin-orbit coupling parameter ξ are somewhat reduced in the complexes from their free-ion values. Even if the reduction of the term distances may be rationalized by using a purely crystal field approximation, the reduction of ξ cannot be explained in this way, since it requires a withdrawing of charge from the central ion. This effect has been taken as a clear indication that "covalent" bonds are operative. Unfortunately, however, neither the calculation of Tanabe and Sugano[12] nor that of Shulman and Sugano[49] led to diminished values of ξ and F_n. All in all, it may be stated that a complete theoretical explanation of these phenomena is badly needed.

A much less rigorous scheme for the calculation of Dq than the one utilized by the Japanese authors[12] has been put forward by Wolfsberg and Helmholz.[14] These authors were interested in the energy levels of the tetrahedral molecules MnO_4^- and $CrO_4^=$, but their procedure may just as well be applied to octahedral complexes.

Starting with the linear combinations of the ligand and metal orbitals which transform correctly in the point group of the molecule, the calculations of the molecular-orbital energies is, as usual, made by the solution of a secular determinant. Since we have already selected the molecular orbitals transforming like the irreducible representations, we can write the secular equation for each irreducible representation as follows:

$$|H_{ij} - S_{ij}E| = 0 \tag{7-22}$$

The quantities H_{ij} and S_{ij} are defined below.

The molecular orbital to use for the E_g level in O_h (Table 7-1) is

$$\Psi = N(\psi_1 + \lambda\psi_2) \tag{7-23}$$

with

$$\psi_1 = d_{x^2-y^2} \tag{7-24}$$

$$\psi_2 = \tfrac{1}{2}(z_1 - z_2 + z_4 - z_5) \tag{7-25}$$

A molecular orbital with $\lambda \ll 1$ may, as mentioned previously, be considered as a nearly pure metal orbital, whereas a value of $\lambda \gg 1$ indicates a nearly pure ligand orbital.

For the normalizing constant N we have

$$N^{-2} = 1 + 2\lambda S + \lambda^2 \tag{7-26}$$

where S, the so-called overlap integral, is defined as

$$S = \int \psi_1^* \psi_2 \, d\tau \tag{7-27}$$

The secular equation is then

$$\begin{vmatrix} H_{11} - E & H_{12} - ES \\ H_{21} - ES & H_{22} - E \end{vmatrix} = 0 \tag{7-28}$$

with

$$H_{ii} = \int \psi_i^* \mathcal{H} \psi_i \, d\tau \tag{7-29}$$

$$H_{ij} = H_{ji} = \int \psi_i^* \mathcal{H} \psi_j \, d\tau \tag{7-30}$$

$\mathcal{H}$ is the Hamiltonian for the system.

The values of H_{ii}, that is, the energies of an electron in the ith orbital in the field of the nuclear skeleton and the remaining valence electrons, are taken as the experimentally known ionization energies of any inorganic complexes which resemble the compound under discussion. They are hence treated as semiempirical parameters, because a nonempirical calculation of these quantities would lead us straight back to the difficulties encountered by Tanabe and Sugano.[12] The H_{ij} integral is approximated by setting it proportional to the corresponding overlap integral S according to the relation

$$H_{ij} = FS\frac{H_{ii} + H_{jj}}{2} \tag{7-31}$$

The overlap integral S is finally computed by using either Slater functions as orbitals or, if available, Hartree-Fock solutions. (For the evaluation of S, see Appendix 1.) The proportionality constant F is usually assigned a value of about 2.

By applying the above scheme, Kuroda and Ito[15] and Yamatera[17] both found $10Dq \simeq 20{,}000$ cm^{-1} for $Co(NH_3)_6^{3+}$. This is in rather good agreement with the experimental value[29] of $10Dq = 23{,}500$ cm^{-1}. Yamatera's results[17] clearly show that the strongest bonding orbital is the a_{1g}, followed by e_g and t_{1u}. The calculated values of λ in the trial LCAO are given together with the values of the group overlap integrals in Table 7-2.

TABLE 7-2. ELECTRONIC PARAMETERS FOR THE COMPLEX $Co(NH_3)_6^{3+}$ (After Yamatera[17])

Values of group overlap integral	$S(d,\sigma_d) = 0.3$ $S(s,\sigma_s) = 0.72$ $S(p,\sigma_p) = 0.6$
Computed values of λ's; the asterisk indicates an antibonding orbital	$\lambda^* a_{1g} = -0.93$ $\lambda^* t_{1u} = -0.76$ $\lambda^* e_g = -0.65$ $\lambda t_{1u} = 3.49$ $\lambda e_g = 2.23$ $\lambda a_{1g} = 1.61$

From the wave function given in Eq. (7-23) it is apparent that the fraction of electronic charge on the metal atom is given by N^2 for each singly occupied orbital. If after Mulliken[30] we add to this quantity exactly half of the overlap population, we get, by summing over the n ($n = 12$) bonding electrons plus the 6 nonbonding electrons, that the net electronic charge upon the metal atom is

$$9 - 6 - \sum_i \left(\frac{1 + \lambda_i S_i}{1 + 2\lambda_i S_i + \lambda_i^2} \right) n_i$$
$$= 3 - 6 \times 0.18 - 4 \times 0.22 - 2 \times 0.37 = 0.30$$

In other words, whereas in the ionic model the cobalt ion carries a charge of three positive units of electricity, these are now smeared out over the whole complex, and the metal atom is nearly neutral. This result is in accord with the charge-neutrality principle of Pauling,[31] which states that the central atom in a complex carries a residual charge very close to zero.

All in all, we may conclude that the method of Wolfsberg and Helmholz yields fairly reliable results even if the approximations used in the secular equations are very extreme. Furthermore, it is found that if complexes having a lower symmetry than O_h (or T_d) are treated in the same way,[16,19] a reasonable account of the properties of the electrons in these complexes can be given. Some minor questions may arise; for instance, does the method yield the exact location of some of the bonding and antibonding levels?[5] Such questions may be answered by a closer analysis of the experimental facts.[32,33] However, approximate models such as the one outlined above do not, of course, answer the previously mentioned principal questions.

In closing this section we notice that the MO bonding scheme may give an indication of why coordination numbers of six are more common for the transition elements than are coordination numbers of eight.[1,34] When eight ligands are placed at the corners of a regular cube and σ bonding is assumed, we find that eight linearly independent orbitals can be constructed. These orbitals transform under the following irreducible representations of the O_h point group: a_{1g}, a_{2u}, t_{1u}, and t_{2g}. Since the 4s orbital transforms like a_{1g}, the 4p like t_{1u}, and the 3d like t_{2g} and e_g, we see that unless we include the 4f orbitals in our bonding scheme we cannot utilize the bonding power of the a_{2u} σ orbital. On the other hand, in an octahedral symmetry all of the σ bonds may be used for bonding purposes. The inclusion of the 4f orbitals in the bonding scheme will depend upon their energies. For the elements of the first transition series the f orbitals will have too high an energy to be available for bonding, and hence we would expect these elements to avoid eight coordination. But in the later series where the f orbitals become more available, eight coordination should be able to occur.

7-c. Estimation of Wave Functions in an MO Scheme

As we have seen in the last section, the calculation of the "mixing coefficients" in the LCAO MO description of the electronic orbitals in a complex from basic principles is rather difficult. It has been found, however, that it is feasible to estimate the mixing of metal and ligand orbitals by using certain experimental results, or in other words to achieve our goal by using a semiempirical theory. Since the full description of some of these methods would lead us far afield into the theory of nuclear magnetic resonance and, furthermore, since some of the problems involved are not fully understood at the time of writing, we shall give only a cursory discussion of some of the most important features.

The first procedure for the evaluation of the mixing coefficients is due to Stevens[35] and Owen.[36] Their method depends upon the fact that the orbital magnetic moment of an unpaired d electron is reduced if the magnetic electron is spread out in a molecular orbital over the entire molecule. As the first example[36] we shall treat an octahedral Ni^{++} complex.

Assuming only σ bonding to be present, and using the hole formalism, the wave function for the ground state (6-34) may be written

$$^3A_{2g} = |\phi_{x^2-y^2}\phi_{z^2}| \tag{7-32}$$

where $\phi_{x^2-y^2}$ and ϕ_{z^2}, the antibonding e_g orbitals, are given by

$$\phi_{x^2-y^2} = \alpha d_{x^2-y^2} - \sqrt{1-\alpha^2}\,\tfrac{1}{2}(z_1 - z_2 + z_4 - z_5) \tag{7-33}$$

$$\phi_{z^2} = \alpha d_{z^2} - \sqrt{1-\alpha^2}\,\frac{1}{2\sqrt{3}}\,(2z_3 + 2z_6 - z_1 - z_2 - z_4 - z_5) \tag{7-34}$$

To the first order we then have for the g factor

$$g = \left(|\phi_{x^2-y^2}\phi_{z^2}| \sum_i (l_z + 2\hat{s}_z)|\phi_{x^2-y^2}\phi_{z^2}|\right) \tag{7-35}$$

leading to a value of $g = 2$ if the overlap terms between the metal atom and the ligands are neglected.

To the second order, by taking the first excited level (6-35) into account, we get

$$g = 2 - \frac{\left|\left(|\phi^+_{x^2-y^2}\phi^+_{z^2}| \sum_i \xi_d l_z\hat{s}_z + \beta H_z(l_z + 2\hat{s}_z)|d^+_{xy}\phi^+_{z^2}|\right)\right|^2}{10Dq} \tag{7-36}$$

$$g = 2 - \frac{|(\phi^+_{x^2-y^2}|\xi_d l_z\hat{s}_z + \beta H_z l_z|d^+_{xy})|^2}{10Dq} \tag{7-37}$$

$$g = 2 - \frac{\alpha^2}{10Dq}\,(\xi_d + 2\beta H_z)^2 \tag{7-38}$$

With $\xi_d = 2\lambda$, where λ is the LS coupling constant for the ^3F term of the nickel ion, we finally get, by retaining only terms linear in H,

$$g = 2 - \frac{8\alpha^2\lambda}{10Dq} \tag{7-39}$$

In Chap. 6 we have quoted the experimental values for $Ni(H_2O)_6^{++}$: $g = 2.25$, $10Dq = 8500\ cm^{-1}$, and $\lambda = -324\ cm^{-1}$. Inserting these into (7-39), we find $\alpha^2 = 0.82$, and thus $\alpha \simeq 0.9$. In other words, the antibonding e_g orbital is mostly made up of the metal ion $3d$ wave function.

The second example deals with the complex $IrCl_6^{=}$ as treated by Stevens.[35] This compound has the electronic configuration $(5d)^5$, and in the octahedral strong-field limit the ground state is $(t_{2g})^5$. Using the hole formalism, and with spin-orbit coupling included, the ground state will be the doublet Γ_7 [see Eq. (6-13)]

$$\Gamma_7 \begin{cases} \sqrt{\tfrac{1}{3}}\,(t^\circ_{2g}\beta + \sqrt{2}\,t_{2g}{}^+\alpha) \\ \sqrt{\tfrac{1}{3}}\,(-t^\circ_{2g}\alpha + \sqrt{2}\,t_{2g}{}^-\beta) \end{cases} \tag{7-40}$$

The energy separation to the next state, Γ_8, will be $\tfrac{3}{2}\xi$. Since

$$t_{2g}{}^+ = d_1 = -\frac{1}{\sqrt{2}}(d_{xz} + id_{yz}) \tag{7-41}$$

$$t_{2g}{}^- = d_{-1} = \frac{1}{\sqrt{2}}(d_{xz} - id_{yz}) \tag{7-42}$$

$$t^\circ_{2g} = id_{xy} \tag{7-43}$$

we find

$$l_z\begin{pmatrix} t_{2g}{}^+ \\ t_{2g}{}^- \\ t^\circ_{2g} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} t_{2g}{}^+ \\ t_{2g}{}^- \\ t^\circ_{2g} \end{pmatrix} \tag{7-44}$$

We shall now make allowance for the fact that the orbitals used in Γ_7 are not pure *d* orbitals but are instead molecular orbitals of the form given in Eq. (7-23). The molecular orbital will *transform* like the angular part of the pure *d* orbital, and we shall designate these new orbitals by means of a tilde. Hence for the Γ_7 orbitals

$$\Gamma_7 \begin{cases} \sqrt{\tfrac{1}{3}}\,(\tilde{t}^\circ_{2g}\beta + \sqrt{2}\,\tilde{t}_{2g}{}^+\alpha) & (7\text{-}45) \\ \sqrt{\tfrac{1}{3}}\,(-\tilde{t}^\circ_{2g}\alpha + \sqrt{2}\,\tilde{t}_{2g}{}^-\beta) & (7\text{-}46) \end{cases}$$

with

$$\tilde{t}_{2g}{}^+ = -\frac{1}{\sqrt{2}}(\tilde{d}_{xz} + i\tilde{d}_{yz}) \tag{7-47}$$

$$\tilde{t}_{2g}{}^- = \frac{1}{\sqrt{2}}(\tilde{d}_{xz} - i\tilde{d}_{yz}) \tag{7-48}$$

$$\tilde{t}^\circ_{2g} = i\tilde{d}_{xy} \tag{7-49}$$

Applying the operator l_z, we have

$$l_z\begin{pmatrix} \tilde{t}_{2g}{}^+ \\ \tilde{t}_{2g}{}^- \\ \tilde{t}^\circ_{2g} \end{pmatrix} = k\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \tilde{t}_{2g}{}^+ \\ \tilde{t}_{2g}{}^- \\ \tilde{t}^\circ_{2g} \end{pmatrix} \tag{7-50}$$

where the "orbital reduction factor k" accounts for the fact that the orbitals are not pure *d* orbitals. For a *d* electron we have, of course, $k = 1$. We have had occasion to use a reduction factor before when we treated the paramagnetic resonance of Co^{++} in Chap. 6.

If the Zeeman splitting of Γ_7 is evaluated by using the modified orbitals (7-47) to (7-49), we get

$$g = \tfrac{2}{3}(2k + 1) \tag{7-51}$$

a result which, of course, gives $g = 2$ if $k = 1$. This was found previously.

Let us now try to calculate k. We have

$$(\tilde{t}_{2g}{}^{+}|l_z|\tilde{t}_{2g}{}^{+}) = k \tag{7-52}$$

with

$$\tilde{t}_{2g}{}^{+} = -\frac{1}{\sqrt{2}}(\tilde{d}_{xz} + i\,\tilde{d}_{yz}) \tag{7-53}$$

$$\tilde{d}_{xz} = N(d_{xz} + \lambda\tfrac{1}{2}(\pi_{x_3} + \pi_{y_1} + \pi_{x_4} + \pi_{y_6})) \tag{7-54}$$

$$\tilde{d}_{yz} = N(d_{yz} + \lambda\tfrac{1}{2}(\pi_{x_2} + \pi_{y_3} + \pi_{x_6} + \pi_{y_5})) \tag{7-55}$$

The normalizing factor N is given by

$$N^{-2} = 1 + \lambda^2 + 2\lambda S \tag{7-56}$$

with the group overlap integral S equal to

$$S = \int d_{xz}\tfrac{1}{2}(\pi_{x_3} + \pi_{y_1} + \pi_{x_4} + \pi_{y_6})\, d\tau \tag{7-57}$$

Then

$$l_z\tilde{t}_{2g}{}^{+} = -\frac{N}{\sqrt{2}}\left[d_{xz} + id_{yz} + \frac{\lambda}{2}\,l_z(\pi_{y_1} + i\pi_{x_2} + \pi_{x_4} + i\pi_{y_5}) + \frac{\lambda}{2}\,l_z(\pi_{x_3} + i\pi_{y_3}) + \frac{\lambda}{2}\,l_z(\pi_{y_6} + i\pi_{x_6})\right] \tag{7-58}$$

l_z is taken with the metal atom as the center, and since

$$l_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

the last two terms yield, being centered upon the z axis, Fig. 7-2,

$$l_z(\pi_{x_3} + i\pi_{y_3}) = l_z^{(3)}(\pi_{x_3} + i\pi_{y_3}) \tag{7-59}$$

$$l_z(\pi_{y_6} + i\pi_{x_6}) = -\,l_z^{(6)}(\pi_{y_6} + i\pi_{x_6}) \tag{7-60}$$

where the origin of l_z has been moved to the ligand sites 3 and 6. We now obtain for k:

$$k = \frac{N^2}{2}\left[2 + \frac{\lambda}{2}\int (d_{xz} + id_{yz})^* l_z(\pi_{y_1} + i\pi_{x_2} + \pi_{x_4} + i\pi_{y_5})\, d\tau + 3\lambda S + \lambda^2\right] \tag{7-61}$$

The second term in the above expression is evaluated by using the hermitian properties of l_z:

$$\begin{aligned}&\frac{\lambda}{2}\int (d_{xz} + id_{yz})^* l_z(\pi_{y_1} + i\pi_{x_2} + \pi_{x_4} + i\pi_{y_5})\, d\tau\\ &= \frac{\lambda}{2}\int (\pi_{y_1} + i\pi_{x_2} + \pi_{x_4} + i\pi_{y_5})l_z^*(d_{xz} + id_{yz})^*\, d\tau\\ &= \lambda S\end{aligned}$$

Hence

$$k = \frac{1 + 2\lambda S + \tfrac{1}{2}\lambda^2}{1 + 2\lambda S + \lambda^2} = 1 - \frac{1}{2}\lambda^2 N^2 \tag{7-62}$$

The experimental value of the isotropic g factor for $IrCl_6^-$ is 1.8. This gives a value of $k = 0.85$, and by calculating S we can get an estimation of λ. The above simple theory neglects the presence of the high-frequency terms in the formulas for the g factor. For this reason our calculation is to be regarded as more illustrative than significant.

The second way of estimating the wave functions for the magnetic electrons utilizes a possible anomalous hyperfine structure in the electron paramagnetic resonance spectrum. Once more looking at the paramagnetic resonance spectrum of $IrCl_6^-$, Griffiths, Owen, and Ward[37,38] found, for instance, a hyperfine structure which could only be explained as arising from the interaction of the magnetic spin of the electron with the nuclear spin of the chlorine ion. Later, Tinkham[7,39] obtained similar results in the paramagnetic resonance of the diluted iron-group fluorides, a case of special interest being the MnF_2 compound. For an excellent discussion of this latter system the reader is referred to Clogston et al.[40] Briefly, the theory is as follows:

The observed hyperfine structure (hfs) is due to the interaction of the F^{19} nuclei spin with the nonlocalized electronic spins of the complex. This may be described by adding to the spin Hamiltonian a term of the form

$$\sum_i \mathbf{S} \cdot A^i \cdot \mathbf{I}_i \tag{7-63}$$

where the summation is to be taken over the F^{19} nuclei, each possessing a nuclear spin I. From the spacing of the resonance lines one can experimentally estimate the parameter A^i. The hyperfine interaction is different from zero because the orbitals of the unpaired electrons contain a certain amount of fluoride ion character. In the case of σ bonding this fraction has been given in Eq. (7-23).

If the σ bond is made up of $2s$ and $2p\sigma$ fluoride orbitals, the hyperfine interaction is[39]

$$A = A_{2s} + A_{2p}(3 \cos^2 \Theta - 1) \tag{7-64}$$

where Θ is the angle between the axis of the p function and the axis of the applied magnetic field. The numerical values of A_{2s} and A_{2p} have been calculated by Moriya[41] to be

$$A_{2s} = 1.57 \text{ cm}^{-1} \tag{7-65}$$

$$A_{2p} = 0.044 \text{ cm}^{-1} \tag{7-66}$$

With the above values of the hyperfine interaction for the individual atomic states it is now possible to determine the parameters of the wave functions for the magnetic electron. For example, the ratio between the *observed* isotropic hyperfine interaction and the above value of $A_{2s} = 1.57 \text{ cm}^{-1}$ simply gives the fraction of the $2s$ fluoride orbital present in the wave function.

The third way of estimating the "covalent" character of the bonding is very closely related to the above method. Instead of looking at the paramagnetic resonance of the electron, we look at the nuclear magnetic resonance of the ligands. This technique, due to Shulman et al.,[42] is certainly the most direct way possible of measuring the electronic density at a point removed from the center of the cation.

The initial experiment of Shulman et al.[42] was performed upon a crystal of MnF_2. It was found that the nuclear F^{19} resonance frequency was shifted from the free-ion F^- value by a surprisingly large internal field. As is true in the case of the electronic spin resonance condition, the relation for the nuclear resonance frequency ω is

$$\omega = \gamma_N H_0 \tag{7-67}$$

where H_0 is the magnetic field strength and γ_N, a constant, is the "gyromatic ratio" for an F^{19} nucleus. Shulman's experiments then showed that the resonance condition could be expressed by the relation

$$\omega = \gamma_N(H_0 + \Delta H) \tag{7-68}$$

and after some corrections the final result[42] for the shift was given as

$$\frac{\Delta H}{H_0} = 0.0735 \tag{7-69}$$

This large shift was explained as due to the mixing of the fluoride orbitals with the manganese orbitals.[42,43] What takes place is a so-called spin polarization. Owing to the presence of the unpaired Mn^{++} electrons, the F^- nuclei, which usually have an equal amount of α and β spin electrons surrounding them, are left with an electronic cloud where the α and β electrons are no longer exactly paired off. This results in a net internal magnetic field at the F^{19} nuclei, and hence a shift in the resonance condition takes place. If ΔH is positive, we speak of a paramagnetic shift; if it is negative, the shift is called diamagnetic.

The isotropic shift is given by the fractional probability density of α and β spin evaluated at the fluorine nucleus, where (SD) stands for spin density:

$$f_s = \left[\frac{(\mathrm{SD})_\alpha - (\mathrm{SD})_\beta}{(\mathrm{SD})_\beta}\right]_{\text{nucleus}} \tag{7-70}$$

Experimentally, this quantity can be calculated[43,44] from the measured resonance shift, parallel to the situation in the electronic resonance experiment dealt with earlier.

The above quantity f_s can be related to the bonding parameters as follows. Let us for simplicity look at a diatomic molecule AB, with the atomic wave functions ψ and φ centered at A and B, respectively, Fig. 7-6. The bonding orbital is constructed as

$$\Psi_{\text{bonding}} = N(\lambda\psi + \varphi) \tag{7-71}$$

and the antibonding orbital is given by

$$\Phi = N^*(\psi + a\varphi) \tag{7-72}$$

Here, owing to orthogonality and normalization properties, we have

$$N^{-2} = \lambda^2 + 1 + 2\lambda S \tag{7-73}$$
$$(N^*)^{-2} = a^2 + 1 + 2aS \tag{7-74}$$
$$\lambda + a\lambda S + a + S = 0 \tag{7-75}$$

with the overlap integral S defined as

$$S = \int \psi^* \varphi \, d\tau \tag{7-76}$$

If the bonding orbital is mostly made up of the φ wave function, we have

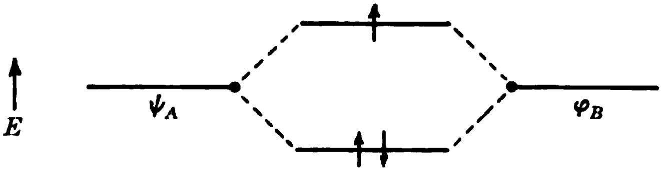


FIG. 7-6. Bonding and antibonding orbitals containing three electrons.

$\lambda \ll 1$. It then follows that in the antibonding orbital the greatest contribution comes from ψ and that, consequently, $a \ll 1$. With these conditions and if S is much less than 1, the above equations reduce to

$$N^{-2} \simeq 1 \tag{7-77}$$
$$(N^*)^{-2} \simeq 1 \tag{7-78}$$
$$a = -(\lambda + S) \tag{7-79}$$

The total wave function for a three-electron system is, to the zero order, given by

$$|\overset{+}{\Psi_b}\overset{-}{\Psi_b}\overset{+}{\Phi}| \tag{7-80}$$

The α and β spin densities in the *bonding* orbital pair each other off, and what is left is an unpaired α spin density located in the antibonding orbital:

$$(\mathrm{SD})_\alpha = \int |\Phi|^2 \, d\tau \tag{7-81}$$

The spin density of ψ evaluated at B is negligible, or, in other words, both of the wave functions ψ and φ are very localized. Then the unbalanced spin density as evaluated at B is

$$(N^*)^{+2} a^2 |\varphi(0)|^2 \tag{7-82}$$

and the fractional probability charge f_s is

$$f_s = \frac{(N^*)^2 a^2 |\varphi(0)|^2}{N^2 |\varphi(0)|^2} = (\lambda + S)^2 \tag{7-83}$$

This whole procedure is directly applicable to MnF_2, if we interpret ψ as the wave function for the Mn^{++} ion and φ as the fluoride $2s$ wave function.[43] Experiments yield a value of $f_s = 0.50 \times 10^{-2}$. If S, calculated from Hartree Fock wave functions, is equal to 0.05, we obtain $\lambda \simeq 0.02$. Hence, we notice that the antibonding magnetic electrons mostly move in the metal e_g orbitals.

It is even possible to sort out the σ and π contributions to the bonding. Reference is here made to the papers by Shulman and Knox.[44,45] These authors estimated the fraction of unpaired $2s$ together with $f_\sigma - f_\pi$, the difference between the fraction of unpaired $2p_\sigma$ and $2p_\pi$, for a series of compounds. This and similar work is very important, because it will in the end enable us to "map" the electronic density of the magnetic electrons. However, since we have, in the last section, moved rather deeply into the domain of solid-state physics, we shall leave the subject here.

7-d. Band Intensities in Parity Allowed Transitions

In special cases it is sometimes possible to estimate the mixing parameter for the molecular orbitals of a complex by making use of band intensity measurements. The idea behind the scheme is as follows. Consider an electronic transition between the ground state and an excited state in a complex. The "oscillator strength" f of such a transition can be obtained experimentally from the integrated band intensity

$$f = 4.32 \times 10^{-9} \int \epsilon_\nu \, d\nu \tag{7-84}$$

where ϵ_ν is the measured molar extinction coefficient as a function of the frequency ν. ν is measured in wave numbers, centimeters^{-1}.

Theoretically, this quantity is given by the following expression,[46] if we limit our considerations to electric dipole transitions:

$$f = 1.085 \times 10^{-5} \times \nu \times \text{av}_{\text{I}} \sum_{\text{II}} |\Psi_{\text{I}}^* \mathbf{r} \Psi_{\text{II}} \, d\tau|^2 \tag{7-85}$$

Here Ψ_{I} and Ψ_{II} are the wave functions for the initial and final states between which the transition takes place, ν is the frequency of the band in centimeters^{-1}, and $\mathbf{r}$ is the "dipole vector," in angstroms.

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z \tag{7-86}$$

As indicated, we need further to sum the expression over the excited states and average this sum over the initial states in order to calculate f.

The important quantity to be evaluated in (7-85) is the transition moment integral $P = \int \Psi_{\text{I}}^* \mathbf{r} \Psi_{\text{II}} \, d\tau$ between the two states Ψ_{I} and Ψ_{II}. Now if Ψ_{I} and Ψ_{II} are determinantal wave functions composed of d orbitals, application of the inversion operator $\hat{\imath}$ immediately tells us that P is zero. Or, in other words, the dipole vector spans odd representations in a point group possessing an inversion center. Consequently, for the direct-product representation to contain the identity representation, we need a direct product of the form $\Gamma_u \times \Gamma_u(r) \times \Gamma_g$. This is, of course, only another way of stating Laporte's rule that only transitions from odd to even states are allowed as electric dipole transitions. Furthermore, taking the single orbitals in Ψ_{I} and Ψ_{II} to be molecular orbitals, as discussed in the preceding sections, will not help us to get a value of P different from zero if the molecule has a center of symmetry and the transition takes place between two states of the same parity.†

However, for molecules which do not possess a center of symmetry, the above considerations must be modified. It is, of course, true that some components of a molecular orbital may possess an "inherent" center of inversion, while the molecular orbitals for the entire molecule do not. A tetrahedral molecule such as $CoCl_4^-$ admirably falls into the above category. The molecular orbitals used in the bonding scheme are made up of $3d$ orbitals centered upon the Co^{++} ion and σ orbitals centered upon the Cl^- ions. The d orbitals are, of course, "even" under i; the σ orbitals, on the other hand, are not.

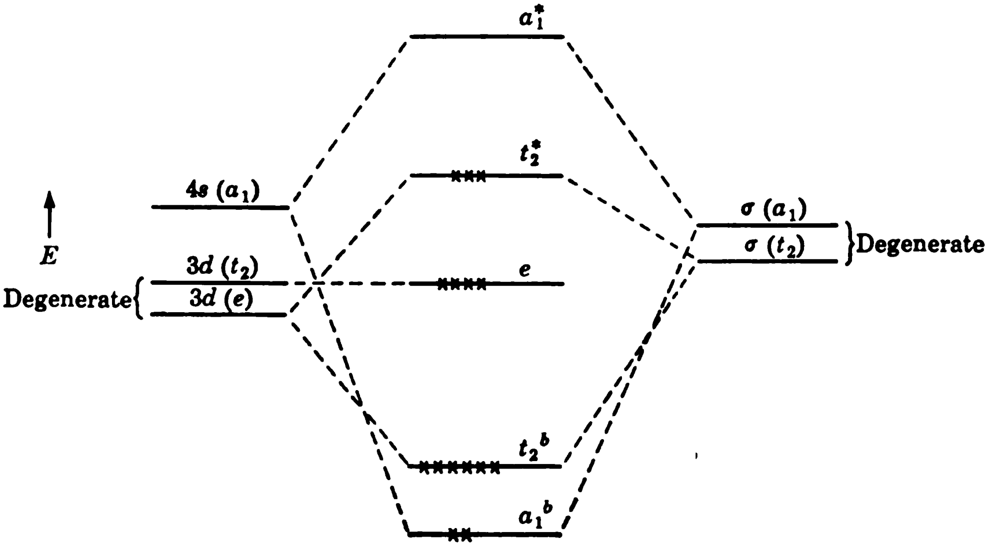


FIG. 7-7. Energy-level scheme for the complex $CoCl_4^-$. The superscripts b and $*$ are used to distinguish the bonding and antibonding orbitals, respectively.

In order to illustrate our method, we shall consider the $CoCl_4^-$ complex more carefully. Upon performing the usual group theoretical reductions, we soon find that the irreducible representations of the σ bonds in T_d symmetry transform under a_1 and t_2, and similarly that the d and s electrons transform under t_2, e, and a_1, respectively. Our bonding scheme is pictured in Fig. 7-7.

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† Actually, in a polyatomic molecule possessing a symmetry center we can couple the vibrational motion to the electronic structure in such a way as to do away with the symmetry center and induce some intensity into the absorption bands. This so-called "vibronic" problem will be treated in the next chapter.

The transition giving rise to the lowest absorption band is due to an electron being promoted from the nonbonding e orbital to the antibonding t_2 orbital. The e orbitals are taken as the pure d orbitals d_{z^2} and $d_{x^2-y^2}$; the t_2 antibonding orbitals are of the following form:[5]

$$t_2 = N \begin{pmatrix} \alpha(3d_{yz}) - \sqrt{1-\alpha^2}\,\tfrac{1}{2}(\sigma_1 + \sigma_3 - \sigma_2 - \sigma_4) \\ \alpha(3d_{xz}) - \sqrt{1-\alpha^2}\,\tfrac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4) \\ \alpha(3d_{xy}) - \sqrt{1-\alpha^2}\,\tfrac{1}{2}(\sigma_1 + \sigma_4 - \sigma_2 - \sigma_3) \end{pmatrix} \tag{7-87}$$

The numbering of the orbitals used here is the same as that in Fig. 3-4 and N is a normalization factor with which we include the overlap effects.

The one-electron transitions in which we are interested for the ligand field model are the six $e \rightarrow t_2$ transitions. The transition moment matrix then contains the elements $(e|\mathbf{r}|t_2^*)$ which can be reduced to the form

$$-N\sqrt{1-\alpha^2}\int e\mathbf{r}\left(\tfrac{1}{2}\sum_{i=1}^{4}\sigma_i\right)d\tau \tag{7-88}$$

because $(d|\mathbf{r}|d) = 0$.

At this stage of the calculation the reader may possibly wonder from which point $\mathbf{r}$ is going to be measured. It is, however, very easy to see that the value of the computed intensity does not depend upon the choice of coordinate system for $\mathbf{r}$ (as of course it must not do). Usually $\mathbf{r}$ is therefore centered on the same coordinate system as the d orbitals.

As shown in Appendix II, the transition moment elements are given by

$$(3d_{x^2-y^2}|\mathbf{r}|(\widetilde{yz})) = -N\sqrt{1-\alpha^2}\,\frac{4}{\sqrt{3}}\,A\mathbf{i} \tag{7-89}$$

$$(3d_{x^2-y^2}|\mathbf{r}|(\widetilde{xz})) = N\sqrt{1-\alpha^2}\,\frac{4}{\sqrt{3}}\,A\mathbf{j} \tag{7-90}$$

$$(3d_{x^2-y^2}|\mathbf{r}|(\widetilde{xy})) = 0 \tag{7-91}$$

$$(3d_{z^2}|\mathbf{r}|(\widetilde{yz})) = N\sqrt{1-\alpha^2}\,\tfrac{4}{3}A\mathbf{i} \tag{7-92}$$

$$(3d_{z^2}|\mathbf{r}|(\widetilde{xz})) = N\sqrt{1-\alpha^2}\,\tfrac{4}{3}A\mathbf{j} \tag{7-93}$$

$$(3d_{z^2}|\mathbf{r}|(\widetilde{xy})) = -N\sqrt{1-\alpha^2}\,\tfrac{8}{3}A\mathbf{k} \tag{7-94}$$

where **i**, **j**, and **k** are the unit vectors and A is a number. Thus for a given set of "effective charges" and bond distances we know all of the quantities in formula (7-85) with the sole exception of α, "the degree of covalency." Hence we can use the experimental value of f to estimate α. In $CoCl_4^=$ the above method yields[5] a value of $\alpha \simeq \sqrt{\tfrac{1}{2}}$, or, in other words, the complex is fully covalent-bonded.

Notice that by using the above matrix elements for the dipole transition in a T_d molecule, we obtain the required isotropy for the transition $e \rightarrow t_2$, even if the various matrix elements are polarized differently. However, in a lower symmetry the levels would split and we should expect the molecule to exhibit dichroism.

It is evident that of the methods outlined in this chapter for the estimation of the degree of covalency present in the complexes, the above procedure is by far the most uncertain. However, in the only case where a comparison between various methods has so far been made, namely, for $CoCl_4^=$, the estimate of α from a paramagnetic resonance measurement agrees quite satisfactorily with the value of α obtained from intensity measurements. Nevertheless, for complexes which do not possess an electric spin magnetic moment, and where consequently the methods based upon a resonance technique break down, the method based on intensities seems at present to be the only feasible way open. Examples which come to mind[5] are MnO_4^- and $CrO_4^=$, even though the situation in these compounds is confused owing to the presence of π bonding and the resultant uncertainty with regard to the bonding scheme.[14]

If we broaden our investigation to include the so-called "change transfer bands," the above method can also be used for centrosymmetric complexes. Nearly all complexes, even those possessing an inversion center, have in addition to their "ligand field bands" some very intense absorption bands placed in the near ultraviolet region of the spectrum.[47,48] Indeed, the intensity of these bands is so high that we must assume that they are due to even-odd transitions. Looking at the bonding scheme given in Fig. 7-5, we see that a transition of an electron from an e_g or t_{2g} orbital to the antibonding t_{1u} orbital produces an allowed transition. By writing down the various determinantal wave functions of the system, it is easy to see by means of group theory which transitions can take place. For instance, in O_h symmetry $\mathbf{r}$ transforms like T_{1u}. Hence only the transitions

$$\begin{aligned} A_{1g} &\rightarrow T_{1u} \\ A_{2g} &\rightarrow T_{2u} \\ E_g &\rightarrow T_{1u},\ T_{2u} \\ T_{1g} &\rightarrow A_{1u},\ E_u,\ T_{1u},\ \text{and}\ T_{2u} \\ T_{2g} &\rightarrow A_{2u},\ E_u,\ T_{1u},\ \text{and}\ T_{2u} \end{aligned}$$

can take place as electric dipole transitions.

If the single electron transition formally takes place from a nonbonding t_{2g} d orbital to a t_{1u} molecular orbital, and if we know the wavelength and intensity of the transition, we can calculate the "degree of covalency" for the t_{1u} molecular orbital with the methods outlined above. On the other hand, if the transition starts from an antibonding e_g orbital, we can only get the product of the "covalency factors" of the two orbitals. Because of a complete lack of exact experimental spectral knowledge in this part of the spectrum, there have, however, so far been no investigations pursuing this aspect of the theory.

We have seen that the basic features of the pure crystal field theory are included in and justified by the approach of molecular orbitals. The ligand field method has the advantage of possessing a greater flexibility than the crystal field method; for indeed the latter arises as a specialization of the former simply by putting the "covalency factor" in the ligand field orbitals equal to zero. We may now ask ourselves: How does it come about that the crystal field method really works as well as it does?

The reason it works is twofold. First, both the crystal field model and the ligand field model are in essence methods which are governed by the *symmetry* of the molecule. So long as we utilize only the symmetry properties of the molecule, meaningful results can be obtained without excessive calculations. Second, in many applications we can neglect to the first order the mixing of ligand and metal orbitals because of the relative smallness of the scrambling. However, and this point must always be kept in mind, any basic understanding of the sundry phenomena occurring in the chemistry of the complexes can be obtained only by use of the ligand field theory in its widest sense.

APPENDIX I

Evaluation of the "Group Overlap" Integrals

The group overlap integrals S are of the general form

$$S = \int \Big(\sum_i a_i\psi_i\Big)^* \varphi_{\text{cent}}\, d\tau$$

where ψ_i are the ligand wave functions and φ_{cent} is the orbital for the central atom. The group overlap integrals may be evaluated in terms of the simple diatomic overlap[20] S_{ij} by expressing the central atom orbital in terms of linear combinations of equivalent orbitals oriented relative to the coordinate system chosen at the ligand sites. As an example we shall treat the group overlap integral

$$S(e_g) = \int \tfrac{1}{2}(z_1 - z_2 + z_4 - z_5)^* 3d_{x^2-y^2}\, d\tau \tag{A-1}$$

encountered on page 161.

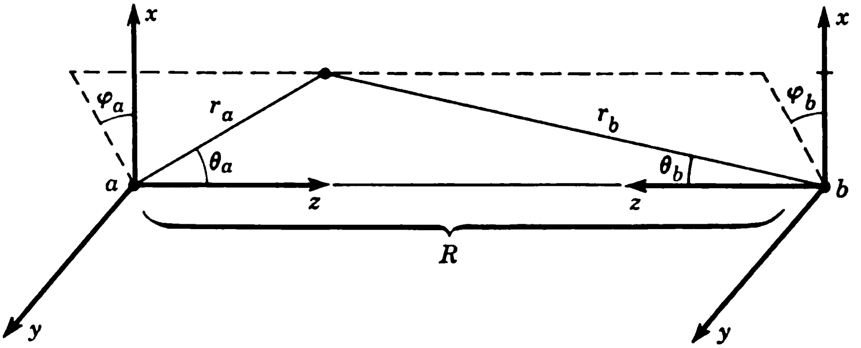

FIG. A-1. Spheroidal coordinate system.

We want to express S by using the formulas given by Mulliken et al.[20] These authors use the spheroidal coordinates ζ, η, φ defined by

$$\zeta = \frac{r_a + r_b}{R} \qquad \eta = \frac{r_a - r_b}{R} \qquad \varphi = \varphi_a = \varphi_b$$

$$1 \le \zeta \le \infty \qquad -1 \le \eta \le 1 \qquad 0 \le \varphi \le 2\pi$$

where r_a, r_b, and $\varphi_a(=\varphi_b)$ are pictured in Fig. A-1. Notice that coordinate system b is left-handed. Expanding (A-1), we have:

$$S(e_g) = \tfrac{1}{2}\int z_1^* d_{x^2-y^2}\,d\tau - \tfrac{1}{2}\int z_2^* d_{x^2-y^2}\,d\tau + \tfrac{1}{2}\int z_4^* d_{x^2-y^2}\,d\tau - \tfrac{1}{2}\int z_5^* d_{x^2-y^2}\,d\tau \qquad \text{(A-2)}$$

Let us start by calculating the first integral in (A-2). It is now necessary to express the d orbital in a coordinate system pointing toward the ligand coordinate system, Fig. A-1. In the old coordinate system we have with **i**, **j**, and **k** as unit vectors:

$$\mathbf{r} = \sin\Theta\cos\varphi\,\mathbf{i} + \sin\Theta\sin\varphi\,\mathbf{j} + \cos\Theta\,\mathbf{k} \qquad \text{(A-3)}$$

By using α and β in the same way as Θ and φ, we have in the *new*, rotated system

$$\mathbf{r} = \sin\alpha\cos\beta\,\mathbf{i}' + \sin\alpha\sin\beta\,\mathbf{j}' + \cos\alpha\,\mathbf{k}' \qquad \text{(A-4)}$$

Hence

$$\mathbf{r}\cdot\mathbf{k} = \cos\Theta = \sin\alpha\cos\beta(\mathbf{i}'\cdot\mathbf{k}) + \sin\alpha\sin\beta(\mathbf{j}'\cdot\mathbf{k}) + \cos\alpha(\mathbf{k}'\cdot\mathbf{k}) \qquad \text{(A-5)}$$

$$\mathbf{r}\cdot\mathbf{j} = \sin\Theta\sin\varphi = \sin\alpha\cos\beta(\mathbf{i}'\cdot\mathbf{j}) + \sin\alpha\sin\beta(\mathbf{j}'\cdot\mathbf{j}) + \cos\alpha(\mathbf{k}'\cdot\mathbf{j}) \qquad \text{(A-6)}$$

$$\mathbf{r}\cdot\mathbf{i} = \sin\Theta\cos\varphi = \sin\alpha\cos\beta(\mathbf{i}'\cdot\mathbf{i}) + \sin\alpha\sin\beta(\mathbf{j}'\cdot\mathbf{i}) + \cos\alpha(\mathbf{k}'\cdot\mathbf{i}) \qquad \text{(A-7)}$$

In other words, we express $\cos\Theta$, $\sin\Theta\sin\varphi$, and $\sin\Theta\cos\varphi$ by means of the new variables $\cos\alpha$, $\sin\alpha\sin\beta$, and $\sin\alpha\cos\beta$. In our example

$$3d_{x^2-y^2} = \frac{1}{81\sqrt{2}}\left(\frac{Z}{a_0}\right)^{7/2} r^2 e^{-(Z/3a_0)r}\sin^2\Theta\cos 2\varphi \qquad \text{(A-8)}$$

or

$$3d_{x^2-y^2} = f(r)\sin^2\Theta\,(\cos^2\varphi - \sin^2\varphi) \qquad \text{(A-9)}$$

By turning the original coordinate system of the central atom into the position indicated in Fig. A-1, we get

$$(\mathbf{j}'\cdot\mathbf{k}) = (\mathbf{i}'\cdot\mathbf{j}) = (\mathbf{k}'\cdot\mathbf{i}) = 1 \qquad \text{(A-10)}$$

all other scalar products being zero.
Hence

$$\sin\Theta\cos\varphi = \cos\alpha \qquad \text{(A-11)}$$

$$\sin\Theta\sin\varphi = \sin\alpha\cos\beta \qquad \text{(A-12)}$$

and

$$d_{x^2-y^2} = f(r)[\cos^2\alpha - \sin^2\alpha\cos^2\beta] \qquad \text{(A-13)}$$

The first integral in (A-2) is in this way transformed to

$$\int\psi_\sigma f(r)[\cos^2\alpha - \sin^2\alpha\cos^2\beta]\,d\tau \qquad \text{(A-14)}$$

Similarly, for the remaining three integrals

$$\int\psi_\sigma f(r)[\sin^2\alpha\cos^2\beta - \cos^2\beta]\,d\tau \qquad \text{(A-15)}$$

$$\int\psi_\sigma f(r)[\cos^2\alpha - \sin^2\alpha\sin^2\beta]\,d\tau \qquad \text{(A-16)}$$

$$\int\psi_\sigma f(r)[\sin^2\alpha\cos^2\beta - \cos^2\alpha]\,d\tau \qquad \text{(A-17)}$$

By inserting these four integrals back into Eq. (A-2) and collecting the four terms together, we obtain

$$S(e_g) = \int\psi_\sigma f(r)[3\cos^2\alpha - 1]\,d\tau \qquad \text{(A-18)}$$

and finally since

$$3d_{z^2} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{7/2} r^2 e^{-(Z/3a_0)r}(3\cos^2\Theta - 1) \qquad \text{(A-19)}$$

Eq. (A-18) can be reduced to the form

$$S(e_g) = \sqrt{3}\int\psi_\sigma\cdot 3d_{z^2}\,d\tau \qquad \text{(A-20)}$$

The σ orbital need not, of course, be a pure atomic orbital; it could, for example, be a hybrid orbital of the form

$$\psi_\sigma = a\psi_{2s} + \sqrt{1 - a^2}\,\psi_{2p_z} \qquad \text{(A-21)}$$

where

$$0 \leq a \leq 1$$

The corresponding group overlap integrals for the orbitals a_{1g} and t_{1u} in octahedral symmetry are given by

$$S(a_{1g}) = \sqrt{6}\int \psi_\sigma 4s\, d\tau \qquad \text{(A-22)}$$

$$S(t_{1u}) = \sqrt{2}\int \psi_\sigma 4p_z\, d\tau \qquad \text{(A-23)}$$

The two center overlap integrals have been extensively tabulated.[20-24]

The evaluation of the two center overlap integrals follows the procedure given by Mulliken et al.[20] As an example, we shall sketch the computation of $S(2p_\sigma, 3d_\sigma)$.

We have, by using Slater orbitals,[25]

$$(2p_\sigma) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z^*}{a_0}\right)^{5/2} r e^{-(Z^*/2a_0)r} \cos\Theta \qquad \text{(A-24)}$$

The expression for $3d_\sigma$ is given in (A-19).

We follow Mulliken et al.[20] and define

$$\mu = \frac{Z^*}{n} \qquad \text{(A-25)}$$

and

$$p = \tfrac{1}{2}(\mu_a + \mu_b)\frac{R}{a_0} \qquad \text{(A-26)}$$

$$t = \frac{\mu_a - \mu_b}{\mu_a + \mu_b} \qquad \text{(A-27)}$$

We follow the usual conventions[20] that if the two atomic orbitals have a different principal quantum number n, the one with the *smaller* n is identified with atom a. If the principal quantum numbers of the two atomic orbitals are equal, the atom with the larger μ will be identified with atom a. Here

$$\mu_a = \tfrac{1}{2}z_p \qquad \text{(A-28)}$$

$$\mu_b = \tfrac{1}{3}z_d \qquad \text{(A-29)}$$

By using spheroidal coordinates, we get

$$r_a = \frac{R}{2}(\zeta + \eta) \qquad \text{(A-30)}$$

$$r_b = \frac{R}{2}(\zeta - \eta) \qquad \text{(A-31)}$$

and

$$\exp\left[-(\mu_a r_a + \mu_b r_b)\frac{1}{a_0}\right] = e^{-\zeta p} \times e^{-\eta p t} \qquad \text{(A-32)}$$

Further,

$$r_a \cos\Theta_a = \frac{R}{2}(1 + \zeta\eta) = R - r_b\cos\Theta_b \qquad \text{(A-33)}$$

and

$$d\tau = \left(\frac{R}{2}\right)^3 (\zeta^2 - \eta^2)\, d\zeta\, d\eta\, d\varphi \qquad \text{(A-34)}$$

By making use of the auxiliary functions defined in (A-35) and (A-36), we get

$$A_n(p) = \int_1^\infty e^{-px} x^n\, dx \qquad \text{(A-35)}$$

$$B_n(pt) = \int_1^{-1} e^{-ptx} x^n\, dx \qquad \text{(A-36)}$$

$$S = \frac{(1 - t^2)^{5/2}(1 - t)p^6}{96\sqrt{2}}\,[A_0(-3B_2 + B_4) + A_1(B_3 + B_5) + A_2(3B_0 + B_4)$$
$$+ A_3(-B_1 - 3B_3) + A_4(-B_0 - B_2) + A_5(-B_1 + 3B_3)] \qquad \text{(A-37)}$$

The A and B integrals are tabulated in Refs. 26 to 28. The overlap integral S is tabulated by Jaffé and Doak.[31]

APPENDIX II

The evaluation of the transition moment integral for σ bonds in a regular tetrahedron proceeds along lines similar to those in the evaluation of the group overlap integral S in Appendix I. The evaluation of the matrix element $(d_{x^2-y^2}|\mathbf{r}|\tilde{d}_{yz})$ is given as an example below. We have in the original coordinate system

$$3d_{x^2-y^2} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z_d}{a_0}\right)^{7/2} r_1{}^2 e^{-(Z_d/3a_0)r_1}\,(\sin^2\Theta_1\cos^2\varphi_1 - \sin^2\Theta_1\sin^2\varphi_1)$$

If the coordinate transformation scheme outlined in Appendix 1 is used and the $3d_{x^2-y^2}$ orbital is rotated in such a way that the new z axis points toward ligand 1, while the new x axis occupies the plane defined by the old and new z axes, we find

$$3d_{x^2-y^2} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z_d}{a_0}\right)^{7/2} r_a{}^2 e^{-(Z_d/3a_0)r_a}\left(-\frac{2}{\sqrt{3}}\sin^2\Theta_a\sin\varphi_a\cos\varphi_a + 2\sqrt{2/3}\,\sin\Theta_a\cos\Theta_a\sin\varphi_a\right) \qquad \text{(A-38)}$$

Furthermore,

$$x = r_a(-\sqrt{1/6}\,\sin\Theta_a\cos\varphi_a + \sqrt{1/2}\,\sin\Theta_a\sin\varphi_a + \sqrt{1/3}\,\cos\Theta_a) \qquad \text{(A-39)}$$
$$y = r_a(-\sqrt{1/6}\,\sin\Theta_a\cos\varphi_a - \sqrt{1/2}\,\sin\Theta_a\sin\varphi_a + \sqrt{1/3}\,\cos\Theta_a) \qquad \text{(A-40)}$$
$$z = r_a(\sqrt{2/3}\,\sin\Theta_a\cos\varphi_a + \sqrt{1/3}\,\cos\Theta_a) \qquad \text{(A-41)}$$

By multiplying the consecutive rotated d functions with the appropriate rotated vector $\mathbf{r}$ and summing according to the phases of $\sigma_1 \cdots \sigma_4$, we get

$$P = (3d_{x^2-y^2}|\mathbf{r}|\tilde{d}_{yz}) \qquad \text{(A-42)}$$
$$P = (3d_{x^2-y^2}|\mathbf{r}|\tfrac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)) \qquad \text{(A-43)}$$

leading to

$$P = \frac{4}{\sqrt{3}}A\cdot\mathbf{i} + 0\cdot\mathbf{j} + 0\cdot\mathbf{k} \qquad \text{(A-44)}$$

where

$$A = \int \frac{1}{81\sqrt{2\pi}}\left(\frac{Z_d}{a_0}\right)^{7/2} r_a{}^3 e^{-(Z_d/3a_0)r_a}\sin^2\Theta_a\cos\Theta_a\cos^2\varphi_a\,\sigma_b\,d\tau \qquad \text{(A-45)}$$

In some cases this transition moment integral can be expressed as an overlap integral If, for instance, σ_b is taken to be a $2p_z$ function and we set $\mu_a = Z_d/3$ and $\mu_b = Z_p/2$, we obtain

$$A = \int \frac{1}{\sqrt{6\pi}}\left(\frac{\mu_a}{a_0}\right)^{7/2} r_a{}^2 e^{-\mu_a r_a/a_0}\sin\Theta_a\cos\Theta_a\cos\varphi_a\sqrt{\frac{1}{\pi}}\left(\frac{\mu_b}{a_0}\right)^{5/2} r_b{}^2 e^{-\mu_b r_b/a_0}\cos\Theta_b\sin\Theta_b\cos\varphi_b\,d\tau \qquad \text{(A-46)}$$

or by substituting the relevant orbitals

$$A = \frac{\sqrt{3}}{2\sqrt{2}}\frac{a_0}{\mu_b}S(3d_{z^2}{}^{\mu_a}, 3d_{z^2}{}^{\mu_b}) \qquad \text{(A-47)}$$

The transition moment integral is hence reduced to an overlap integral. S may be evaluated by the methods outlined in Appendix I, but in most cases the overlap integral in question will be found tabulated in Refs. 20 to 24.

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CHAPTER 8

Vibronic Interactions

8-a. Vibrational Spectra

So far, no account has been taken of the fact that the nuclear framework of the complex is not stationary, but exhibits vibrations around some average position. The complete wave function for such a system is, after Born and Oppenheimer,[1] given by the adiabatic approximation as

$$\Psi = \psi_{\text{el}}\psi_{\text{vib}} \tag{8-1}$$

The electronic wave function ψ_{el} is, of course, a function of both the electronic coordinates and the nuclear parameters. The vibrational wave function ψ_{vib} depends only upon the relative positions of the nuclei.

Designating the electronic coordinates by $\mathbf{r}_i$ and the nuclear coordinates by $\mathbf{s}_a$, we are then interested[77] in the solutions to the Schrödinger equation

$$\mathcal{H}(\mathbf{r}_i,\mathbf{s}_a)\Psi_k(\mathbf{r}_i,\mathbf{s}_a) = E_k(\mathbf{s}_a)\Psi_k(\mathbf{r}_i,\mathbf{s}_a) \tag{8-2}$$

where Ψ_k is an electronic eigenfunction for the state k of the molecule possessing a nuclear configuration specified as $\mathbf{s}_a$.

The usual way of solving such problems is to calculate the electronic energy for an assumed equilibrium configuration $\mathbf{s}_a = 0$ and then to include a change in the nuclear configuration by means of a perturbation technique. It is obvious that the electronic energy and wave functions may be altered by such a coupling to the vibrations of the nuclei, and we talk about a vibrational electronic ("vibronic") interaction.

Two types of phenomena are very closely related to the vibronic interactions, viz., the intensity of the spectral transitions in the complex ions and the stability of their molecular configurations. These phenomena are in some ways the most interesting features in the theory of the electronic structures of complex ions. Before we proceed to outline the theory of the vibronic interactions, however, we shall look briefly at the solutions to the pure vibrational problems.

It is well known[2] that for an n-atomic nonlinear molecule there will be $3n - 6$ normal vibrational motions and that these may be characterized by means of their symmetry properties. In order to find the possible vibrational symmetry species for a molecule, every atom in the molecule is given three displacement coordinates. These are usually taken as either cartesian coordinates or internal coordinates. The various symmetry operations of the point group are then applied. To find the character of the transformation, we need only consider those atoms which are not shifted by the application of the symmetry operations, since only in those cases will the displacement coordinates still be on the diagonal of the transformation matrix. The situation is then exactly parallel to the one encountered in finding the various σ and π bonding combinations. Indeed, the sum of the vibrational symmetry modes and the rotational symmetry coordinates is for a complex equal to the sum of the σ and π symmetry combinations for the ligands.

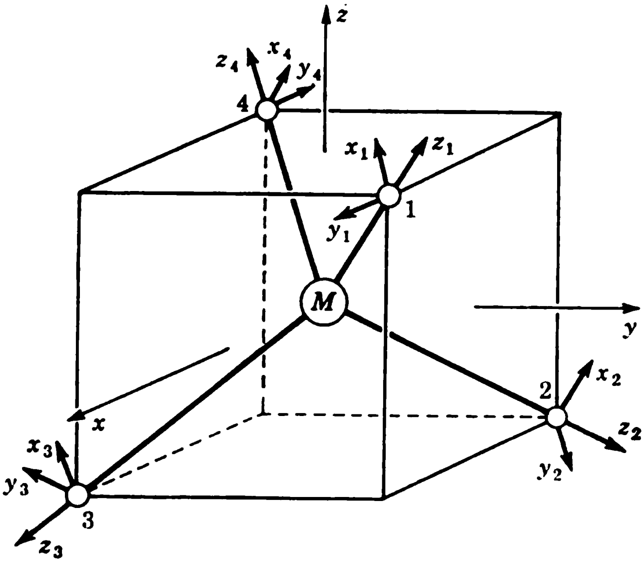

FIG. 8-1. Numbering and coordinate systems for a tetrahedral molecule. The z axis for any ligand is the bond-stretching coordinate; the x axis is in the plane defined by the z axis of the metal atom and the radius vector to the ligand.

On the other hand, the central atom σ and π combinations transform as the nuclear translations.

Let us take two examples. First for a regular octahedron (point group O_h) we have the symmetry species for σ bonds a_{1g}, t_{1u}, and e_g and for π bonds t_{1g}, t_{1u}, t_{2g}, and t_{2u}. With the rotational symmetry coordinates transforming like[2] t_{1g} in O_h the vibrational modes will be† α_{1g}, ϵ_g, $2\tau_{1u}$, τ_{2g}, and τ_{2u}. For a regular tetrahedron we get in the same way the vibrational modes α_1, ϵ, and $2\tau_2$. The construction of the corresponding linear combination of displacement coordinates transforming according to the vibrational symmetry modes proceeds exactly as the construction of the corresponding linear combinations of atomic orbitals; from the above they are seen to be identical.

As an example of the treatment of a vibrational problem we shall take a tetrahedral molecule. The orientation and numbering of the ligands are shown in Fig. 8-1, and calling the rotational and translational coordinates

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† We use Greek letters to designate the vibrational symmetry modes in order not to confuse them with the electronic symmetry designations.

R and *T*, respectively, we get the following expressions for the various symmetry coordinates.

	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4	z_1	z_2	z_3	z_4	x_M	y_M	z_M
S_1									$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$			
S_{2a}	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$											
S_{2b}					$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$							
S_{3a}									$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$			
S_{3b}									$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$			
S_{3c}									$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$			
S_{4a}	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$											
S_{4b}	$-\frac{1}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{\sqrt{3}}{4}$	$\frac{\sqrt{3}}{4}$	$-\frac{\sqrt{3}}{4}$	$-\frac{\sqrt{3}}{4}$							
S_{4c}	$-\frac{1}{4}$	$\frac{1}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$	$-\frac{\sqrt{3}}{4}$	$\frac{\sqrt{3}}{4}$	$-\frac{\sqrt{3}}{4}$	$\frac{\sqrt{3}}{4}$							
R_a					$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$							
R_b	$-\frac{\sqrt{3}}{4}$	$-\frac{\sqrt{3}}{4}$	$\frac{\sqrt{3}}{4}$	$\frac{\sqrt{3}}{4}$	$-\frac{1}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$							
R_c	$\frac{\sqrt{3}}{4}$	$-\frac{\sqrt{3}}{4}$	$\frac{\sqrt{3}}{4}$	$-\frac{\sqrt{3}}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$							
T_a															1
T_b														1	
T_c													1		

Using a set of internal coordinates[2] for the bending modes we get, denoting the bending of the valence angle (ligand *N*, metal atom, ligand *M*) α_{NM}, the following set of symmetry coordinates:

	α_{12}	α_{13}	α_{14}	α_{23}	α_{24}	α_{36}
S_1^*	$\sqrt{1/6}$	$\sqrt{1/6}$	$\sqrt{1/6}$	$\sqrt{1/6}$	$\sqrt{1/6}$	$\sqrt{1/6}$
S_{2a}^*	$-\sqrt{1/12}$	$-\sqrt{1/12}$	$\sqrt{4/12}$	$\sqrt{4/12}$	$-\sqrt{1/12}$	$\sqrt{1/12}$
S_{2b}^*	$-1/2$	$1/2$	0	0	$1/2$	$-1/2$
S_{4a}^*	0	0	$\sqrt{1/2}$	$-\sqrt{1/2}$	0	0
S_{4b}^*	$\sqrt{1/2}$	0	0	0	0	$-\sqrt{1/2}$
S_{4c}^*	0	$\sqrt{1/2}$	0	0	$-\sqrt{1/2}$	0

S_1^* is a redundant coordinate equal to zero,[2] because the sum of the angle bends vanishes identically. However, in order to preserve the unitary transformation properties of the above matrix, we shall carry it along for a while.

It is now only a matter of geometry to see that

$$S_{2n}^* = \sqrt{3}\,S_{2n} \qquad n = a, b, c \tag{8-3}$$

$$S_{4n}^* = \sqrt{2}\,S_{4n} \qquad n = a, b, c \tag{8-4}$$

Furthermore, we define new symmetry coordinates $\tilde{S}$ with the metal ion included, to subtract out the translations, and get

$$\tilde{S}_1 = S_1 \tag{8-5}$$
$$\tilde{S}_{2n} = S_{2n} \tag{8-6}$$
$$\tilde{S}_{3n} = S_{3n} - 2\sqrt{1/3}\, T_n \qquad n = a, b, c \tag{8-7}$$
$$\tilde{S}_{4n} = S_{4n} - 2\sqrt{2/3}\, T_n \tag{8-8}$$

The equations of motion are given by

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{Q}_k} + \frac{\partial V}{\partial Q_k} = 0 \tag{8-9}$$

where Q_k is a normal coordinate and T and V are the kinetic and potential energy, respectively. The solution of these equations yields

$$Q_k = K_k \cos\,(\lambda_k t + \epsilon_k) \tag{8-10}$$

With a valence field potential[2] for the tetrahedron equal to

$$2T = \sum_{j=1}^{4} (\dot{x}_j^2 + \dot{y}_j^2 + \dot{z}_j^2)m + (\dot{x}_M^2 + \dot{y}_M^2 + \dot{z}_M^2)M \tag{8-11}$$

and

$$2V = k \sum_{j=1}^{4} (\Delta r_j)^2 + k_\alpha \sum_{i<j=2}^{6} (r\alpha_{ij})^2 \tag{8-12}$$

we get the solutions to the vibrational problem

$$m\lambda_1 = k \tag{8-13}$$
$$m\lambda_2 = 3k_\alpha \tag{8-14}$$

together with the secular equation[2]

$$\begin{array}{ccc} S_{4a} & S_{3a} & T_a \\ \left|\begin{array}{c} 2k_\alpha - \lambda m \\ 0 \\ -4\sqrt{2/3}\, k_\alpha \end{array}\right. & \begin{array}{c} 0 \\ k - \lambda m \\ -2\sqrt{1/3}\, k \end{array} & \left.\begin{array}{c} -4\sqrt{2/3}\, k_\alpha \\ -2\sqrt{1/3}\, k \\ 4/3 k + 16/3 k_\alpha - \lambda M \end{array}\right| \end{array} = 0 \tag{8-15}$$

This latter gives the solutions (besides $\lambda = 0$, the translation)

$$\lambda_3 + \lambda_4 = \frac{k}{m}\left(1 + \frac{4}{3}\frac{m}{M}\right) + \frac{2k_\alpha}{m}\left(1 + \frac{8}{3}\frac{m}{M}\right) \tag{8-16}$$
$$\lambda_3 \times \lambda_4 = \frac{2k_\alpha k}{m^2}\left(1 + 4\frac{m}{M}\right) \tag{8-17}$$

The α_1 and ϵ symmetry coordinates occur only once in the transformation from rectangular internal coordinates to symmetry coordinates. After being mass-normalized[2] they are therefore also normal coordinates. The two normal coordinates of symmetry species τ_2 can, however, first be determined by putting the solutions λ_3 and λ_4 back into the secular determinant (8-15) and solving the appropriate linear equations.

With a valence force potential containing two constants we can thus find k and k_α from a knowledge of λ_1 and λ_2 as

$$k = 4\pi^2 mc^2 \nu_1^2 \qquad (8\text{-}18)$$

$$3k_\alpha = 4\pi^2 mc^2 \nu_2^2 \qquad (8\text{-}19)$$

ν is here given in centimeters^{-1} and c is the velocity of light. Knowing k and k_α, ν_3 and ν_4 may then be computed. A typical example here is $TiCl_4$. Experiments yield[3] $\nu_1 = 386$ cm^{-1}, $\nu_2 = 120$ cm^{-1}, $\nu_3 = 495$ cm^{-1}, $\nu_4 = 141$ cm^{-1}, and by using ν_1 and ν_2, we calculate $\nu_3 = 545$ cm^{-1} and $\nu_4 = 135$ cm^{-1}. For the force constants we get $k = 3.11 \times 10^5$ dyne/cm and $k_\alpha = 0.10 \times 10^5$ dyne/cm.

The solutions to the vibrational problem in O_h symmetry are,[4,5] with a valence field potential of the form

$$2V = K \sum_{i=1}^{6} (\Delta r_i)^2 + 2K_1 \sum_{\substack{i,j=1 \\ i \neq j}}^{6} (\Delta r_i)(\Delta r_j) + K_\alpha \sum_{i<j=2}^{6} (r\alpha_{ij})^2 \qquad (8\text{-}20)$$

found to be

$$m\lambda_1 = K + 10K_1 \qquad (8\text{-}21)$$

$$m\lambda_2 = (K - 2K_1) \qquad (8\text{-}22)$$

$$m^2\lambda_3\lambda_4 = \frac{M + 6m}{M} 2K_\alpha(K - 2K_1) \qquad (8\text{-}23)$$

$$m(\lambda_3 + \lambda_4) = \frac{M + 4m}{M} 2K_\alpha + \frac{M + 2m}{M} (K - 2K_1) \qquad (8\text{-}24)$$

$$m\lambda_5 = 4K_\alpha \qquad (8\text{-}25)$$

$$m\lambda_6 = 2K_\alpha \qquad (8\text{-}26)$$

Experimental values of the various vibrational frequencies are so far very scarce. Lafont,[6] who measured the Raman spectrum of $Zn(H_2O)_6^{++}$, found $\nu_1(\alpha_{1g}) = 394$ cm^{-1}, $\nu_2(\epsilon_g) = 200$ cm^{-1}, and $\nu_5(\tau_{2g}) = 239$ cm^{-1}. From these values we calculate $\nu_3(\tau_{1u}) = 218$ cm^{-1} $\nu_4(\tau_{1u}) = 505$ cm^{-1}, and $\nu_6(\tau_{2u}) = 169$ cm^{-1}.

For $\nu_4(\tau_{1u})$ in $Co(NH_3)_6^{3+}$ Basolo et al.[7] report a value of 330 cm^{-1}, in very close agreement with the value of $\nu_4 = 328$ cm^{-1} later found by Bertin et al.[8] On the other hand, Powell and Sheppard[15] find a value of this frequency equal to 502 cm^{-1}, which agrees with the value of 490 cm^{-1} found by Block.[16] These latter values are comparable to the above calculated value.

Mostly from combination bands Caglioti et al.[9] found the following frequencies for the complex $Cr(CN)_6^{3-}$: $\nu_1(\alpha_{1g}) = 374$ cm^{-1}, $\nu_2(\epsilon_g) = 336$ cm^{-1}, $\nu_3(\tau_{1u}) = 124$ cm^{-1}, $\nu_4(\tau_{1u}) = 457$ cm^{-1}, and $\nu_5(\tau_{2g}) = 106$ cm^{-1}. By using ν_1, ν_2, and ν_5 to estimate K, K_1, and K_α in (8-21), we calculate $\nu_3(\tau_{1u}) = 200$ cm^{-1}, $\nu_4(\tau_{1u}) = 503$ cm^{-1}, and $\nu_6(\tau_{2u}) = 75$ cm^{-1}. The agreement between the observed and calculated values is seen not to be very good.

All in all we must conclude that a great deal of experimental work is needed in order to obtain a reliable force potential for the complexes of the iron group. On the other hand, the information with regard to carbonyls[10] and hexafluorides of the heavier elements[11–17] is somewhat more abundant.

8-b. Absorption Band Intensities for Centrosymmetric Complexes

By many standards the electronic absorption bands responsible for the colors of the octahedral transition metal complexes would be regarded as very weak: the broad spin-allowed systems have molar extinction coefficients which rarely exceed 100. On the other hand, many of these complexes appear to have centers of symmetry and, since no change in parity accompanies the excitations, these should be strongly forbidden, orbitally, in electric dipole radiation fields. Seen from this point of view, it is perhaps even surprising that the oscillator strengths f of the main bands in the hexammines of Cr^{3+} and Co^{3+}, for example, should be as high as the 10^{-3} or so which are observed.

To account for this manifestation, two theories have been advanced. If it is agreed that the molecule has a center of symmetry, the band intensity may be due to either magnetic dipole or electric quadruple radiation.[18] Alternatively, it is supposed that the odd vibrations of the ligands destroy the center of symmetry, thereby invalidating Laporte's rule.[4,19–30,43–46]

The former set is easily rejected in the present case, though it may be important in the spectra of the rare-earth salts. In O_h the orbital magnetic moment transforms under T_{1g}. Therefore, if we consider a diamagnetic Co^{3+} complex where the two crystal field bands are due to the transitions from the ground state ${}^1A_{1g}$ to the ${}^1T_{1g}$ and ${}^1T_{2g}$ states, respectively, we see that the ${}^1A_{1g} \to {}^1T_{1g}$ transition is permitted as magnetic dipole transition, while the ${}^1A_{1g} \to {}^1T_{2g}$ transition is not. Furthermore, the electric quadruple tensor spans the irreducible representations E_g and T_{2g} in O_h. In this case we thus find that the second transition will be permitted, but not the first.

Neither of these effects may then separately account for the intensity of both band systems. Both are also too weak. For the magnetic dipole emission we have[18]

$$f_n = \frac{8\pi^2 mc\nu}{3he^2} \left| \left(n \middle| \frac{e}{2mc} \mathbf{r} \times \mathbf{p} \middle| m \right) \right|^2 \qquad (8\text{-}27)$$

or

$$f_n = \frac{h\nu}{6mc} \sum |\mathbf{L}|^2 \qquad (8\text{-}28)$$

where m and e are the electronic mass and charge, c is the velocity of light, ν is the band frequency in wave numbers, and $\Sigma|\mathbf{L}|^2$ refers to the sum of the squares of the changes in angular momentum (in units of $\hbar^2$) on going from the nondegenerate ground state to each of the components of the excited state.

For diamagnetic Co^{3+} complexes we have for the excitation corresponding to the first spin-allowed band

$$\Sigma|\mathbf{L}|^2 = |({}^1A_{1g}|\hat{L}|{}^1T_{1g})|^2 \tag{8-29}$$

which by descent in symmetry to D_{4h} (sec. 4-*h*) is seen to be equal to

$$\Sigma|\mathbf{L}|^2 = 3|({}^1A_{1g}|\hat{L}_z|{}^1A_{2g})|^2 \tag{8-30}$$

By using determinantal wave functions and the strong-field approximation, we get $\Sigma|\mathbf{L}|^2 = 24$. With $\nu({}^1A_{1g} \rightarrow {}^1T_{1g}) = 21{,}000\ \mathrm{cm}^{-1}$ we calculate $f({}^1A_{1g} \rightarrow {}^1T_{1g}) \simeq 2 \times 10^{-5}$. The experimentally found value of $\sim 10^{-3}$ therefore simply cannot be explained by assuming magnetic dipole radiation, and matters become even worse when we consider the electric quadruple radiation. Both of these proposals must then be discarded, and this means that the hypothesis that the molecule has a center of symmetry must be given up.

If we next compare the absorption spectra of, for example, *cis*- and *trans*-$\mathrm{Co(en)_2Cl_2^+}$, we see that the bands are somewhat stronger for the cis compound, where there is no center of symmetry, than they are for the trans compound.[31] This certainly shows that a static dissymmetric field is a major factor in promoting the band intensities. But it seems unlikely to be the only factor, as shown by the spectra of monosubstituted luteo $\mathrm{Co^{3+}}$ complexes, which differ only very slightly from the pure luteo spectra.

Let us finally compare the spectrum of Co(III) *tris*-ethylenediamine with the spectrum of Co(III) hexammine. The intensities of the bands are nearly equal; the *tris*-ethylenediamine being slightly more intense than the hexamine. We may now think that the source of intensity in both cases is the presence of a static distortion. However, from optical rotatory dispersion data we can estimate the *f*(static) values for the *tris*-ethylenediamine complex[32] in solution. It turns out that the *f*(static) value is a factor of 10^{-4} or so too small to account for the observed oscillator strengths of a solution of the complex (see Chap. 9).

It remains to investigate the influence of asymmetrical ligand vibrations on the wave functions of the complex. The argument is as follows: Let us suppose that Q represents an asymmetrical vibrational coordinate of species Γ_u. Let us then expand the crystalline field potential in this coordinate

$$\mathcal{V} = \mathcal{V}_0 + Q\left(\frac{\partial \mathcal{V}}{\partial Q}\right)_0 + \cdots \tag{8-31}$$

Since $\mathcal{V}$ must transform like the totally symmetric representation and Q transforms like an odd representation Γ_u, we get immediately that $(\partial\mathcal{V}/\partial Q)_0$ must transform like Γ_u in order for the product to transform like Γ_{1g}. We can then mix some odd functions into our even function by means of first-order perturbation theory.

$$\psi = \psi_g - \frac{Q \int \psi_g \left(\frac{\partial \mathcal{V}}{\partial Q}\right)_0 \psi_u \, d\tau}{E_u - E_g}\, \psi_u \tag{8-32}$$

If ψ_g represents the unperturbed "crystal field" wave functions, we see that an odd vibration of the ligands can cause ψ_g to interact with excited states ψ_u of odd parity—particularly those corresponding to one-electron jumps, e.g., $(t_{2g})^{-1}(t_{1u})$. For simplicity, let us suppose Q to represent the only vibrational mode, the corresponding harmonic oscillator functions being χ_p, χ_q for quantum numbers p, q, respectively. Then the electronic and vibrational, i.e., vibronic, state of the octahedral complex is represented by a function $\Psi_p = \psi\chi_p$.

Let us further assume that the force constants and equilibrium position are the same both in the electronic ground state N and in an excited state V. The probability of a transition from Np to Vq is proportional to

$$|R_{Np,Vq} = \int\int \Psi^*_{Np}\mathbf{r}\Psi_{Vq}\, d\tau_{\text{elec}}\, d\tau_{\text{vib}}|^2 \tag{8-33}$$

with $\mathbf{r}$ being the electric dipole vector. We find that

$$R_{Np,Vq} = \int (c_N^*\psi^*_{Nu}\mathbf{r}\psi_{Vg} + c_V\psi^*_{Ng}\mathbf{r}\psi_{Vu})\, d\tau_{\text{elec}} \int \chi^*_{Np}Q\chi_{Vq}\, d\tau_{\text{vib}} \tag{8-34}$$

from which we see that transitions are allowed only if the vibrational states p, q differ by 1 quantum.† At low temperatures, therefore, the spectrum will correspond to the 1-0 band, the 0-0 band being absent.

It may be noted that the vibrational integral is proportional to the square root of p or q, whichever is the greater.[2] At higher temperatures, therefore, the stronger $2 - 1$, $3 - 2$, . . . bands appear, corresponding to larger amplitudes of vibration and greater distortions. The total intensity of these electronically forbidden systems therefore increases with temperature.

In order to calculate the variation of the intensity with the temperature, we assume a Boltzmann distribution in the vibrational levels of the ground state.[4,49,50] The transition probability from the nth vibrational level is then proportional to

$$|(n|Q|n+1)|^2 e^{-nh\nu/kT} + |(n|Q|n-1)|^2 e^{-nh\nu/kT}$$

and summing over all levels, calling $e^{-h\nu/kT} = x$

$$f \simeq |(0|Q|1)|^2 \frac{\sum_{n=0}^{\infty} (n+1)x^n + \sum_{n=1}^{\infty} nx^n}{\sum_{n=0}^{\infty} x^n} \tag{8-35}$$

$$f \simeq |(0|Q|1)|^2 \frac{1+x}{1-x} \tag{8-36}$$

The band intensity is thus proportional to coth $(h\nu/2kT)$. The agreement

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† In the derivation[33] of (8-34) use is made of a relationship which connects the dipole length matrix element $(\psi_N|\mathbf{r}|\psi_V)$ with the dipole velocity matrix element $(\psi_N|\nabla|\psi_V)$. The relation[33] is derived under the assumption that the wave functions are exact solutions to Schrödinger's equation; this is, of course, not true in most instances. For calculational purposes one should then preferably use dipole velocity matrix elements. See Shull[34] and Wolfsberg.[35]

with experiments[49,68] is not bad, but it must of course be borne in mind that for an octahedral complex the variation of the oscillator strength f with temperature is given theoretically[4] as a sum of three hyperbolic cotangent terms.

Let us for a moment return to Eq. (8-32) in order to sketch briefly the final form of the formula for the oscillator strength. With[42] the oscillator strength f for an even-even transition equal to

$$f = 1.085 \times 10^{11}\,\Delta E\,(d^n)|(\psi_{1g}|\mathbf{r}|\psi_{2g})|^2 \tag{8-37}$$

we get by substituting (8-32) for, for example, ψ_{2g}

$$f = 1.085 \times 10^{11}\,\Delta E\,(d^n)\,\frac{a^2}{(E_u - E_{2g})^2}\,|(\psi_{1g}|\mathbf{r}|\psi_u)|^2 \tag{8-38}$$

But we have for the oscillator strength f' of the even-odd transition

$$f' = 1.085 \times 10^{11}(E_u - E_{1g})|(\psi_{1g}|\mathbf{r}|\psi_u)|^2 \tag{8-39}$$

Hence if E_u is high above E_{1g} and E_{2g},

$$f \simeq f'\,\frac{\Delta E\,(d^n)}{(E_u - E_g)^3}\,a^2 \tag{8-40}$$

to be multiplied, of course, with the temperature factor. We observe that the $g \rightarrow g$ transition "borrows" intensity from the $g \rightarrow u$ transition. The actual amount is seen to be very sensitive to the separation of the even and odd states in question.

The expansion (8-31) is, of course, also valid for an inherent small crystal distortion. In that case Q is simply the constant before the additional potential in the Hamiltonian, but it is clear that in order to break off the expansion so fast, the complex must be very nearly centrosymmetric. We remark that in this latter case symmetry considerations require that the band envelope contain only the totally symmetric vibrational progression.

Ordinarily, the bands with which we are concerned are very broad. This applies especially to the bands that are due to transitions between states arising from the same free-ion level. If we ignore the broadening attributable to thermal fluctuations, the main part of the spectrum will consist of a totally symmetric vibrational progression superposed on one vibrational quantum of an asymmetric vibration. Clearly, if the vibrational constants (by which we mean to include the equilibrium internuclear distances) in the ground and excited states are the same, a single sharp set of lines would be observed. The greater the difference in these constants, however, the broader will the overall spectrum appear.

Now, the major factor responsible for differences in the interactions of a given ion with its ligands is the relative number of its e_g and t_{2g} electrons. Bands for which both upper and lower states have the same number of t_{2g} electrons are therefore expected to be sharp, but those for which this number changes may be very broad.[36] For example, the lowest quartet-quartet transition of the $Cr(H_2O)_6^{3+}$ ion lies at 17,000 cm^{-1} and has a half-width[37] of some 1625 cm^{-1}. The excitation is due to a transition $(t_{2g})^3 \rightarrow (t_{2g})^2(e_g)$. By contrast, certain doublet states due to transitions $(t_{2g})^3 \rightarrow (t_{2g})^3$ may also be seen in the same spectrum. They are so sharp that when observed in a crystal, Zeeman splittings of only 1 cm^{-1} may be observed.[38,39]

The analysis of the band envelopes of the absorption spectra found in inorganic complexes is furthermore complicated by the fact that all of the absorption bands are due to transitions between states at least one of which is subjected to a configurational distortion of the Jahn-Teller type (*vide infra*). If, say, the excited state of the complex has a different configuration than that of the ground state, vibrational frequencies which in the ground state are non-totally symmetric may be totally symmetric in the excited state. Hence, the absorption band may show a simple progression in single quanta of such modes.[40,41]

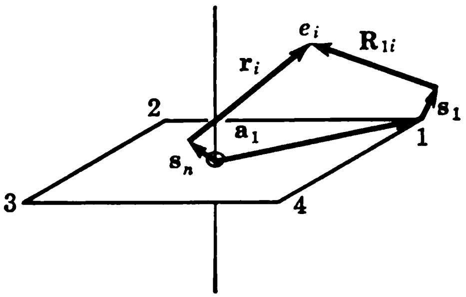

FIG. 8-2. Displacement vectors used in the vibronic potential.

The actual calculation[4,23–27] of band intensities differs from the procedure previously outlined only so far as we have to take account of all the odd vibrations of the centrosymmetric complex and assume a specific form of the Hamiltonian. Using the crystal field approximation, we have for the electronic potential energy $\mathcal{V}_0$ that

$$\mathcal{V}_0(\mathbf{r}_i,\mathbf{a}_j) = -\sum_{i,j} \frac{q_je^2}{|\mathbf{r}_i - \mathbf{a}_j|} \tag{8-41}$$

$\mathbf{r}_i$ being the radius vector of electron number i (of charge $-e$) and $\mathbf{a}_j$ being the position vector of ligand number j, which carries a charge of $+q_je$.

Calling the displacement vector of the central ion $\mathbf{s}_n$ and that of a ligand $\mathbf{s}_j$, Fig. 8-2, we have for $\mathcal{V}$:

$$\mathcal{V} = -\sum_{i,j} \frac{q_je^2}{|\mathbf{r}_i - \mathbf{s}_j - \mathbf{a}_j + \mathbf{s}_n|} \tag{8-42}$$

Expanding (8-42) and retaining only linear terms in the nuclear displacement vectors $\mathbf{s}_n$ and $\mathbf{s}_j$, we get

$$\mathcal{V} = -\sum_{i,j} \frac{q_je^2}{|\mathbf{r}_i - \mathbf{a}_j|} \left\{1 - \frac{(\mathbf{s}_n - \mathbf{s}_j)\cdot(\mathbf{r}_i - \mathbf{a}_j)}{|\mathbf{r}_i - \mathbf{a}_j|^2}\right\} \tag{8-43}$$

or

$$\mathcal{V} = \mathcal{V}_0 + \sum_j (\mathbf{s}_j - \mathbf{s}_n)\,\nabla_{\mathbf{a}_j}\,\mathcal{V}_0 \tag{8-44}$$

The evaluation of the matrix elements connecting the odd and even states is now easy to perform by using the last term in (8-44) as the perturbation operator. The elements are then differentiated with respect to the ligand coordinates and summed over the j ligands, and vibrational symmetry coordinates are substituted in for the various sums in $(\mathbf{s}_j - \mathbf{s}_n)$. The remainder of the calculation is now straightforward, although rather tedious.[4]

It is sometimes maintained that only the odd stretching frequency ν_4 is really effective in promoting intensity. That this is, however, not entirely so can be seen from Table 8-1, where the intensity distribution, at absolute zero, is given[30] for the various vibrational levels of the complexes of Ti^{3+}, V^{3+}, Ni^{++}, and Cu^{++}. In the ionic approximation these ratios are independent of the ligand field and the $(e_g,t_{2g}) - t_{1u}$ separation, and they are dependent only upon the bond distance and the effective charges used.

TABLE 8-1. INTENSITY RATIOS AMONG THE VIBRATIONAL LEVELS

M	Transition	$\nu_4(\tau_{1u}):\nu_3(\tau_{1u})$	$\nu_4(\tau_{1u}):\nu_6(\tau_{2u})$
Ti^{3+}	${}^2T_{2g} \rightarrow {}^2E_g$	1.3:1	1.4:1
V^{3+}	${}^3T_{1g} \rightarrow {}^3T_{2g}$	5.6:1	31:1
	${}^3T_{1g} \rightarrow {}^3T_{1g}$	2.4:1	24:1
	${}^3T_{1g} \rightarrow {}^3A_{2g}$	1:1.5	364:1
Ni^{++}	${}^3A_{2g} \rightarrow {}^3T_{2g}$	3.1:1	2.9:1
	${}^3A_{2g} \rightarrow {}^3T_{1g}$	1:6.5	1.7:1
	${}^3A_{2g} \rightarrow {}^3T_{1g}$	1:6.5	1.7:1
Cu^{++}	${}^2E_g \rightarrow {}^2T_{2g}$	2.0:1	16:1

In order to render the actual calculation of the oscillator strengths more feasible, use is sometimes made of the closure properties of the eigenfunctions.[24,25,43,44] This, however, means that rather serious errors can creep into the calculation.[28,30]

So far, we have considered only transitions between two states which (1) have the same spin component and (2) differ in occupancy number by no more than one orbital if the states are approximated as single antisymmetrized product functions. In such an approximation one should observe only spin-allowed transitions corresponding to one-electron jumps. It is, however, very often true that a configurational interaction under the Hamiltonian removes the last restriction, and bands which formally might be thought of as corresponding to two-electron jumps[47] may be seen.

The restriction imposed upon the transitions by the selection rule $\Delta S = 0$, valid in Russel-Saunders coupling, is broken down by the inclusion of the spin-orbit operator in the Hamiltonian, because, as we have seen previously, this operator couples together states which differ by $\Delta S = 1$. The amount of mixing is, of course, determined by the value of the spin-orbit coupling parameter and how close the two interacting states approach each other.

Suppose that a triplet state (T) is placed above the ground state (O), which we also take to be a triplet state, and that above (T) we have a singlet state (S). Neglecting the mixing of the singlet state with the ground state, we have that the singlet state will have an amount of triplet character equal to

$$|a| = \frac{(\psi_T|\mathcal{H}_{\text{spin-orbit}}|\psi_S)}{E_S - E_T} \tag{8-45}$$

and hence that the oscillator strength f_{OS} for a transition from the ground state to the singlet will be

$$f_{OS} = 1.085 \times 10^{11}(E_S - E_O)a^2|(\psi_O|\mathbf{r}|\psi_T)|^2 \tag{8-46}$$

But with an oscillator strength f_{OT} for the triplet-triplet transition

$$f_{OT} = 1.085 \times 10^{11}(E_T - E_O)|(\psi_O|\mathbf{r}|\psi_T)|^2 \tag{8-47}$$

we get

$$f_{OS} = f_{OT}\frac{E_S - E_O}{E_T - E_O}\,\frac{|(\psi_T|\mathcal{H}_{\text{spin-orbit}}|\psi_S)|^2}{(E_S - E_T)^2} \tag{8-48}$$

In this way, the spin-orbit perturbation which scrambles the excited triplet state (T) with an excited singlet state (S) allows the spin-forbidden transition (O) → (S) to steal intensity from the spin-allowed (O) → (T) transition.

A case where it has been thought[57] that a spin-forbidden transition borrowed a great deal of intensity from a nearby spin-allowed transition is found for the second, doubly peaked $\text{Ni(H}_2\text{O)}_6^{++}$ band, placed at about 14,000 cm^{-1}. Explicit calculations[23] seem, however, to reveal that the doublet structure of this band is due to a spin-orbit fine structure and not to a superimposed spin-forbidden state. This latter interpretation is, however, dependent upon the choice of the electron repulsion term F_4 to be 110 cm^{-1} (see Chap. 10).

The best-investigated system where spin-forbidden transitions take place is the d^5 configuration found for instance in $\text{Mn(H}_2\text{O)}_6^{++}$. The ground state has $S = \frac{5}{2}$, but all of the excited states have either $S = \frac{3}{2}$ or $S = \frac{1}{2}$. Hence spin-orbit coupling can mix some $S = \frac{3}{2}$ character into the ground state. Exact calculations of the intensities of these spin-forbidden bands have been carried out by Koide and Pryce,[24] who assume a vibronic scrambling. They find oscillator strengths of about 5×10^{-8} in excellent agreement with the experimental values.[48] However, for spin-forbidden transitions, magnetic dipole transitions yield oscillator strengths which are close to those of the vibronic electric dipole transitions.[44] The electric and magnetic dipole transitions may in a crystal be distinguished experimentally quite simply[51,52] by a comparison of the axial and transverse spectra.

8-c. Dichroism

As we have seen, the validity of Laporte's rule for centrosymmetric complexes is released both by presence of inherent odd crystalline fields and by odd vibrations of the ligands. Assuming the transitions to be due to electric dipole transitions, we may often distinguish between the two cases by means of the different polarizations of the absorption bands.

Consider, for instance, the complex *trans*-$Co(NH_3)_4Cl_2^+$. Let us assume that there is no center of symmetry present and that the point group of the molecule is C_{4v}. The "first" absorption band in O_h, which is due to ${}^1A_{1g} \rightarrow {}^1T_{1g}$, is now split up (see Fig. 8.3) into two bands, ${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow {}^1A_2$.

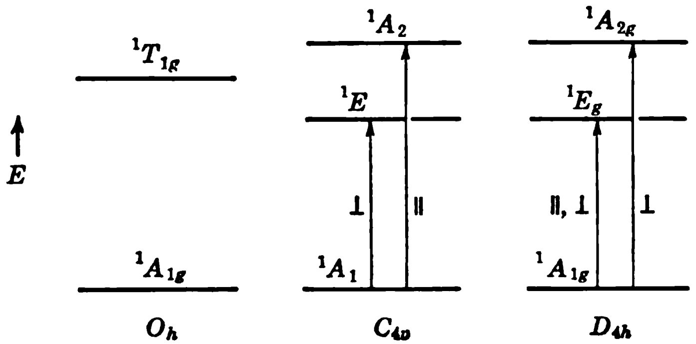

FIG. 8-3. "Visible" transitions for a cobalt(III) complex without and with a center of symmetry.

With the electric dipole vector transforming in C_{4v} as A_2 (parallel) and E (perpendicular) we find that the transition ${}^1A_1 \rightarrow {}^1A_2$ can be seen only with the electric vector parallel to the C_4 axis, while the transition ${}^1A_1 \rightarrow {}^1E$ can be seen only when the electric vector is perpendicular to the C_4 axis. If, on the other hand, a symmetry center is present, the molecule belongs to the D_{4h} point group. In D_{4h} symmetry, the electric dipole vector parallel to the z axis transforms as A_{2u}, while the electric dipole vector perpendicular to the z axis transforms as E_u. The ground state of the complex transforms under A_{1g}. It is therefore necessary that the final orbitals contain either some A_{2u} or E_u symmetry properties in order for the bands to appear in absorption. We hence write for the wave functions of the separated components of ${}^1T_{1g}$:

$$\psi(E_g) + \lambda_1\phi(E_u) + \lambda_2\phi(A_{2u})$$
$$\psi(A_{2g}) + \lambda_3\phi(E_u) + \lambda_4\phi(A_{2u})$$

The odd normal vibrations for the complex having D_{4h} symmetry are found in the usual way. They are $2\alpha_{2u}$, β_{2u}, and $3\epsilon_u$. Since there is no normal vibration of α_{1u} symmetry, and since no other vibration can couple $\psi(A_{2g})$ with $\phi(A_{2u})$, the wave functions are reduced to

$$\psi(E_g) + \lambda_1\phi(E_u) + \lambda_2\phi(A_{2u})$$
$$\psi(A_{2g}) + \lambda_3\phi(E_u)$$

In other words, the ${}^1A_{1g} \rightarrow {}^1E_g$ band will be seen both parallel and perpendicular, while the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ band will be seen perpendicular only.

A series of complexes where the major intensity-giving factor is found to be[53] an inherent odd crystalline field are the *tris*-oxalato-metallates. The "second band" in octahedral Cr^{3+} complexes is due to the transition ${}^4A_{2g} \rightarrow {}^4T_{1g}$. Going down in symmetry to D_3, the excited state splits up into ${}^4A_2 + {}^4E$ and the ground state transforms like ${}^4A_2$. With the electric dipole vector transforming like A_2 ($\|$) and $E(\perp)$ with respect to the three-fold axis we notice that we can see the transition ${}^4A_2 \rightarrow {}^4E$ only with the light polarized perpendicularly, but that no transition will occur for a parallel polarization. Experimentally[53] $\epsilon_\| : \epsilon_\perp = 0.06$. On the other hand, if the intensity were vibronic in character, all of the transitions—parallel as well as perpendicular—would be seen. Quite similar results have been obtained by Yamada and Tsuchida[76] for crystals of $Co(en)_3{}^{3+}$. Also, here it seems that the major intensity-giving factor is an inherent odd crystalline field. If this result is compared with our previous results for a solution of this complex, it indicates, strangely enough, that the major intensity-giving factors differ in the two cases.

On the other hand, the absorption spectrum[54] of *trans*-$Co(en)_2Cl_2{}^+$ is an example of a complex where the major part of the band intensity is vibronic in character.[22] Although the actual symmetry of the complex ion cannot be higher than D_{2h}, other work shows that the effective symmetry is D_{4h}. The situation with regard to the first band is then as pictured in Fig. 8.3. Since the experiments[54] show that the transition ${}^1A_{1g} \rightarrow {}^1E_g$ is seen both parallel and perpendicular, whereas ${}^1A_{1g} \rightarrow {}^1A_{2g}$ is seen only perpendicular, we must conclude that the intensity is due to a vibrational perturbation.[22]

For complexes imbedded in a strong crystalline lattice, such as vanadium corundum ($Al_2O_3:V^{3+}$) and chromium corundum ($Al_2O_3:Cr^{3+}$), it has been found[44] that nearly all of the band intensity arises from a lack of a center of symmetry. These systems present some very interesting features, but the treatment is unfortunately highly complex. We shall therefore only give some appropriate references.[44,55,56]

8-d. Jahn-Teller Configurational Instability

As a general rule, it is found that those transition metal ions whose ground states in octahedral fields are orbitally degenerate form complexes whose symmetry is lower, say, tetragonal or rhombic. This may be due to many causes: crystal packing considerations for the complex within a lattice, repulsions between neighboring ligands, and so forth. It is, however, also to be expected on very general grounds. According to a theorem by Jahn and Teller,[58] when the orbital state of an ion is degenerate for symmetry reasons, the ligands will experience forces distorting the nuclear framework until the ion assumes a configuration both of lower symmetry and of lower energy, thereby resolving the degeneracy.

For obvious reasons, structural anomalies are best detected for the ground states of the molecules; X-ray, electron- and neutron-diffraction, and paramagnetic and nuclear magnetic resonance experiments are certainly more easily performed in this case. However, even if a molecule should distort because of a Jahn-Teller effect, and even if such a distortion is found, for example, by X-ray measurements, we cannot be absolutely certain that the observed deformation is not due to the packing in the crystalline lattice. Hence, caution must be exercised in the interpretation of experimental facts.

Most generally, the Jahn and Teller theorem[58] as extended by Jahn[59] can be formulated as follows: A molecule possessing a degenerate state in either orbit or spin must distort in order to remove as much degeneracy as possible. This statement does not mean that the molecule is formed possessing a degenerate state, immediately discovers this, and then proceeds to distort. On the contrary, after visualizing that certain molecules may have a regular configuration, we find that the predicted structure is an impossible one owing to the very general nature of the Jahn-Teller theorem.

The discussion naturally falls into two parts, namely, the static and the dynamical aspects of the Jahn-Teller theorem. In the first part we investigate how the electronic energy of the system varies when the parameters specifying the nuclear framework of the system are varied. The stable molecular configuration is then obtained by minimizing the electronic energy with respect to these parameters. The dynamic problem, on the other hand, consists of an investigation of the ensuing coupling of the motions of the nuclei with the low-frequency electronic motions. These so-called vibronic couplings lead to very interesting quantum-mechanical effects.

In order to clarify the nature of the Jahn-Teller distortions, we shall consider a tetrahedral molecule possessing a twofold degenerate ground state. We can take this ground state to transform under the irreducible representation E in the point group T_d. The angular parts of the orbitals will then transform[2] like the polynomials $(3z^2 - r^2)$ and $(x^2 - y^2)$.

We have found that a tetrahedral molecule possesses a degenerate vibrational mode of symmetry species ϵ. The two symmetry coordinates spanning this irreducible representation will be called S_{2a} and S_{2b}. As S_{2a} we take the linear combination of cartesian displacement coordinates which transform like the polynomial $(3z^2 - r^2)$ and as S_{2b} the one transforming like $(x^2 - y^2)$.

The Hamiltonian for the regular configuration of the tetrahedron is designated $\mathcal{H}_0$, and we consequently have

$$\int \psi^*_{x^2-y^2} \mathcal{H}_0 \psi_{x^2-y^2}\, d\tau = \int \psi^*_{z^2} \mathcal{H}_0 \psi_{z^2}\, d\tau = E \tag{8-49}$$

$$\int \psi^*_{x^2-y^2} \mathcal{H}_0 \psi_{z^2}\, d\tau = 0 \tag{8-50}$$

Let us consider now an expansion of the Hamiltonian with respect to

S_{2a} and S_{2b}

$$\mathcal{H} = \mathcal{H}_0 + S_{2a}\frac{\partial \mathcal{H}_0}{\partial S_{2a}} + S_{2b}\frac{\partial \mathcal{H}_0}{\partial S_{2b}} + \cdots \tag{8-51}$$

In order for $\mathcal{H}$ to be totally symmetric under all symmetry operations of T_d, $\partial\mathcal{H}_0/\partial S_{2a}$ must transform like S_{2a} and $\partial\mathcal{H}_0/\partial S_{2b}$ like S_{2b}. We can then write

$$\mathcal{H} = \mathcal{H}_0 + S_{2a}k_1\frac{1}{\sqrt{3}}(3z^2 - r^2) + S_{2b}k_1(x^2 - y^2) \tag{8-52}$$

Taking as our zero-order functions $d_{x^2-y^2}$ and d_{z^2} and $\mathcal{H}^{(1)}$ as $\mathcal{H} - \mathcal{H}_0$, first-order perturbation theory yields the secular equation

$$\begin{vmatrix} H_{11} - \Delta E & H_{12} \\ H_{21} & H_{22} - \Delta E \end{vmatrix} = 0 \tag{8-53}$$

Here

$$H_{11} = \int d^*_{x^2-y^2}\mathcal{H}^{(1)}d_{x^2-y^2}\,d\tau \tag{8-54}$$

$$H_{22} = \int d^*_{z^2}\mathcal{H}^{(1)}d_{z^2}\,d\tau \tag{8-55}$$

$$H_{12} = H_{21} = \int d^*_{x^2-y^2}\mathcal{H}^{(1)}d_{z^2}\,d\tau \tag{8-56}$$

Transforming $\mathcal{H}^{(1)}$ to an operator form, we have

$$\mathcal{H}^{(1)} = S_{2a}k_2\sqrt{3}\,(l_z^2 - 2) + S_{2b}k_2\tfrac{1}{2}(l_+^2 + l_-^2) \tag{8-57}$$

where we have written l_+ for $l_x + il_y$ and l_- for $l_x - il_y$. The secular equation then gives

$$\begin{vmatrix} \frac{c}{2}S_{2a} - \Delta E & \frac{c}{2}S_{2b} \\ \frac{c}{2}S_{2b} & -\frac{c}{2}S_{2a} - \Delta E \end{vmatrix} = 0 \tag{8-58}$$

$$\Delta E = \pm\frac{c}{2}\sqrt{S_{2a}^2 + S_{2b}^2} \tag{8-59}$$

A quasi-elastic potential energy must now be added to the perturbation energy. This is taken as $\frac{1}{2}k(S_{2a}^2 + S_{2b}^2)$, the harmonic potential. Then we get the two potential surfaces

$$E = \frac{1}{2}k(S_{2a}^2 + S_{2b}^2) \pm \frac{c}{2}\sqrt{S_{2a}^2 + S_{2b}^2} \tag{8-60}$$

Defining the two polar coordinates r and φ by

$$S_{2a} = r\cos\varphi \qquad S_{2b} = r\sin\varphi \tag{8-61}$$

and substituting into (8-60), we have

$$E = \frac{1}{2} kr^2 \pm \frac{cr}{2} \tag{8-62}$$

Hence, we see that the original twofold degenerate potential surface is now split up into an upper (plus sign) and a lower (minus sign) potential surface. The minimum value of the energy can easily be found from (8-62) as

$$E_{\min} = -\frac{|c|^2}{8k} \qquad \text{for } r_0 = \frac{|c|}{2k} \tag{8-63}$$

The wave function corresponding to the lower potential surface is then found to be

$$\psi = \sin \tfrac{1}{2}\varphi d_{x^2-y^2} - \cos \tfrac{1}{2}\varphi d_{z^2} \tag{8-64}$$

If the energy separation between the upper and the lower surface is large compared to the zero-point vibrational energy, the Born-Oppenheimer approximation is valid; the system will remain on the lower potential surface. φ is seen to be a cyclic coordinate. Semiclassically we will have $\varphi/2 = \nu t$, a frequency multiplied by the time. Hence, the charge density $|\psi|^2$ will vary periodically with time and it is impossible to specify which of the original wave functions the system is in. The upper and lower potential sheets are pictured in Fig. 8-4.

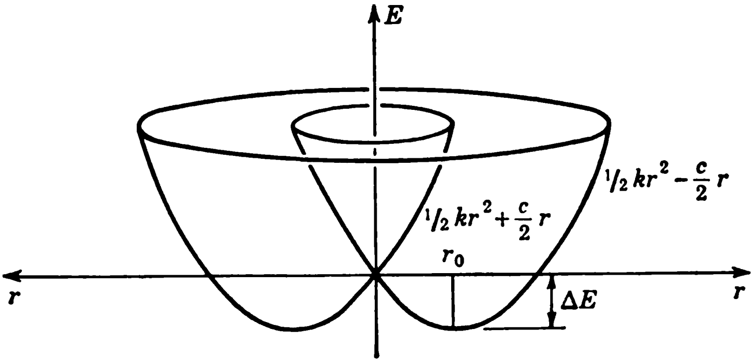

FIG. 8-4. The electronic energy potential surfaces for a twofold degenerate electronic level.

If, however, the stability gain ΔE is approximately equal to the zero-point energy of the vibrational mode, we cannot expect the motion to be confined to the lower electronic potential energy surface, and a coupling between the electronic and nuclear motions will arise. This latter situation is the one encountered in the dynamical Jahn-Teller effect.

Let us now perform an actual calculation (using an electrostatic model) for VCl_4. If π bonding is neglected, we find that the one unpaired electron present is placed in the σ nonbonding, doubly degenerate, metal orbital e. If we compare VCl_4 with $TiCl_4$, we see that the only difference is the presence of one more electron in the former compound. We get[64]

$$H_{x^2-y^2,x^2-y^2} = \left(2B_0 - \frac{2}{9}B_4\right)S_1 - \frac{\alpha}{2}S_{2a} \tag{8-65}$$

$$H_{z^2,z^2} = \left(2B_0 - \frac{2}{9}B_4\right)S_1 + \frac{\alpha}{2}S_{2a} \tag{8-66}$$

$$H_{x^2-y^2,z^2} = H_{z^2,x^2-y^2} = -\frac{\alpha}{2}S_{2b} \tag{8-67}$$

where

$$\alpha = \frac{8\sqrt{2}}{r_0}\left(G_2 - \frac{5}{9}G_4\right) \tag{8-68}$$

with r_0 being the bond distance V—Cl. The radial integrals G_l and B_l are defined as

$$G_l = \int_0^\infty R^2(r)f_l(r,r_0)r^2\,dr \tag{8-69}$$

and

$$B_l = \frac{dG_l}{dr_0} \tag{8-70}$$

The quantities B_l and G_l are tabulated in Ballhausen and Ancmon.[69]

E is again found to be

$$E = \left(2B_0 - \frac{2}{9}B_4\right)S_1 \pm \frac{\alpha}{2}\sqrt{S_{2a}^2 + S_{2b}^2} \tag{8-71}$$

The total potential surface of VCl_4 is then given by

$$E = \mathcal{V}_0 + E \tag{8-72}$$

We now assume that the potential surfaces of $TiCl_4$ and VCl_4 are the same except for the terms due to ligand field effects, i.e., the terms in α and B_4. By making the substitutions

$$S_1 = q_1 \qquad S_{2a} = q_2\cos\varphi_2 \qquad S_{2b} = q_2\sin\varphi_2 \tag{8-73}$$

the potential surface for VCl_4 may be written

$$E = \frac{1}{2}k_1q_1^2 - \frac{2}{9}B_4q_1 + \frac{1}{2}k_2q_2^2 \pm \frac{\alpha q_2}{2} \tag{8-74}$$

where k_1 and k_2 are the force constants for the harmonic vibrations of symmetry α_1 and ϵ, respectively.

As before, we minimize with respect to q_1 and q_2. This leads to the result:

$$q_1 = \frac{{}^2\!/_9B_4}{k_1} \qquad q_2 = \frac{\mp\alpha}{2k_2} \tag{8-75}$$

Let us first consider the implications of the q_1 term. By definition[69] the quantity B_4 is negative, and hence, in the absence of Jahn-Teller distortions, Eq. (8-75) predicts that the system will undergo a contraction relative to $TiCl_4$. This is borne out by experiments.[64]

This and similar results for the octahedral configuration were obtained in 1952 by Van Santen and Wieringen.[70] It has since been reformulated by Hush and Pryce[71] and Liehr and Ballhausen.[5]

The configurational instability of the Jahn-Teller type is apparent from the q_2 terms in Eq. (8-74). A positive α results in a splitting of the electronic degeneracy, and also in a continuous set of minima, found at $q_2 = \alpha/2k_2$. The energy gain ΔE is $-\alpha^2/8k_2$. The apparent independence of φ_2 which this result shows is due to the neglect of the second-order terms in Eq. (8-51). If these are included, a more refined potential surface of the form[64]

$$E = \tfrac{1}{2}k_1q_1^2 - \tfrac{2}{9}B_4q_1 + \tfrac{1}{2}k_2q_2^2 \pm \tfrac{1}{2}q_2(\alpha^2 + \beta^2q_2^2 + \gamma^2q_1^2 - 2\beta\gamma q_1q_2\cos 3\varphi_2 - 2\alpha\beta q_2\cos 3\varphi_2 + 2\alpha\gamma q_1)^{1/2} \quad (8\text{-}76)$$

is obtained, where β and γ are constants involving derivatives of the potential. The appearance of the cos $3\varphi_2$ term in (8-76) makes it clear that the molecule will have a threefold potential barrier.

The minimization of the expression (8-76) for the lower potential sheet with respect to φ_2 gives the condition

$$\sin 3\varphi_2 = 0$$

$$\varphi_2 = \frac{n\pi}{3} \qquad n = 0, 1, 2, 3, 4, 5 \quad (8\text{-}77)$$

Three of these points will give identical potential minima and the other three will yield identical saddle points, but the identification of which is dependent upon the sign of β. The height of the potential barrier is found[5,64] for most complexes to be a few hundred reciprocal centimeters.

The situation can thus be described as follows: At low temperatures the molecule will be frozen into one of the three potential traps, and it will assume the shape of a compressed tetrahedron. At temperatures so high that the molecule has sufficient energy to override the barriers the complex will exhibit a sort of pseudo rotation: all of the ligands are forced to perform a coupled rotation around the regular bond angles.

The original derivation of the theorem was given by Jahn and Teller in 1937. The theorem has since been reformulated by Clinton and Rice[78,79] on the basis of the Hellmann-Feynman theorem. This latter formulation is, however, subjected to the limitations imposed by the use of Hellmann-Feynman's theorem for approximate wave functions. In what follows we shall therefore give a short outline of the original proof.

Given an orthonormal set of degenerate wave functions $\psi_1^\circ \cdots \psi_n^\circ$ as solutions to the Schrödinger equation for the symmetric state of the molecule. Then

$$\mathcal{H}_0\psi_i^\circ = E_0\psi_i^\circ \qquad i = 1 \cdots n \quad (8\text{-}78)$$

The Hamiltonian $\mathcal{H}$ for the stationary electronic states of a molecule contains as parameters the various nuclear coordinates. We now look at small displacements of the nuclei and describe these displacements by means of the vibrational symmetry coordinates S_j of the molecule. Expanding $\mathcal{H}$ in a Taylor series around the symmetrical configuration we have

$$\mathcal{H} = \mathcal{H}_0 + \sum_j S_j\mathcal{V}_j + \frac{1}{2}\sum_{j,k} S_jS_k\mathcal{V}_j\mathcal{V}_k + \cdots \tag{8-79}$$

Here S_j is a function of the nuclear displacement coordinates and $\mathcal{V}_j$ is a function of only the electronic coordinates. Since the Hamiltonian must be invariant under all symmetry operations, we get immediately that S_j and $\mathcal{V}_j$ must transform in the same way.

Taking the set $\psi_i^0(i = 1 \cdots n)$ as our zero-order wave functions and $\mathcal{H}^{(1)} = \sum_j S_j\mathcal{V}_j$ as the perturbation matrix, we must now evaluate matrix elements of the form

$$V_{in} = S_j(i|\mathcal{V}_j|n) \tag{8-80}$$

In order for the initial degeneracy to be retained, all of the matrix elements V_{in} must vanish; if this is not the case, a splitting of the degeneracy will occur. The energy expression will further contain terms linear in S_j, and hence the initial configuration cannot be stable. Since the S_j can be chosen at will, V_{in} will vanish only if the matrix element (8-80) is zero.

The degenerate set $\psi_i^0(i = 1 \cdots n)$ span the irreducible representation Γ in the point group of the molecule, and $\mathcal{V}_j$ transforms like S_j. The condition for a nonvanishing matrix element $(i|\mathcal{V}_j|n)$ is therefore that the symmetric direct product $[\Gamma]^2$ must contain a representation also found in the normal vibrational modes. $[\Gamma]^2$ will, of course, always contain the unit representation, which, taken together with the totally symmetric vibrational mode, will yield values of (8-80) different from zero. However, since the totally symmetric vibration cannot by its very nature destroy the symmetry of the molecule, we may assume without loss of generality that the system is stable with respect to such displacements.

Jahn and Teller were able to show, by going through all of the possible 34 molecular point groups, that in all the cases where a degenerate electronic state can occur there will always exist a vibrational mode which will destroy the degeneracy. The nuclei will be displaced in such a way as to remove the degeneracy; the symmetry of the molecule is lowered. The only exceptions to the above rule are linear molecules, where it was found that only quadratic terms in the expansion (8-79) can take away the degeneracy[67] ("Renner effects").

Even in the absence of linear terms in the energy expression, the degeneracy may be partially removed owing to the nonequivalent quadratic terms present in the expansion of $\mathcal{H}$. However, these effects, of which the Renner effect is a special case, are usually small compared with the effects induced by the linear terms (Jahn-Teller effects).

Thus far the discussion has neglected the presence of spin-orbit forces. Jahn[59] has shown, however, that a symmetric configuration of the nuclei again cannot be stable if there is spin degeneracy. The only exceptions are linear molecules and spin levels possessing a twofold Kramers degeneracy. A result of this is that a large spin-orbit coupling may stabilize a symmetric configuration otherwise expected to distort.[59,61–63] The condition for stability is simply that the ground state in a spin-orbit representation ("the double groups") shall be either a singlet or a Kramers doublet. Furthermore, the next excited state capable of interacting under a vibrational mode with the ground state must have an energy higher than the zero-point vibration; if not, a "pseudo Jahn-Teller effect" will take place.

The question of how in the general case to predict the stable configuration of a complex subjected to a Jahn-Teller distortion is a rather tricky one, and the elucidation of this problem has occupied many authors. We shall state the problem as follows: Given a certain degenerate state and a certain degenerate vibrational mode, is it then possible to predict the stable configuration of the molecule? In what follows we shall assume that the various potential surfaces are well separated and that we can neglect spin-orbit coupling. Furthermore, we shall treat only octahedral and tetrahedral configurations.

TABLE 8-2. DEGENERATE ELECTRONIC AND VIBRATIONAL STATES FOR OCTAHEDRAL AND TETRAHEDRAL MOLECULES

	Possible degenerate electronic functions	Symmetric products	Vibrational symmetry coordinates
O_h	E	$[E]^2 = A_1 + E$	α_{1g}, ϵ_g, $2\tau_{1u}$, τ_{2g}, τ_{2u}
	T_1	$[T_1]^2 = A_1 + E + T_2$	
	T_2	$[T_2]^2 = A_1 + E + T_2$	
T_d	E	$[E]^2 = A_1 + E$	α_1, ϵ, $2\tau_2$
	T_1	$[T_1]^2 = A_1 + E + T_2$	
	T_2	$[T_2]^2 = A_1 + E + T_2$	

In Table 8-2 we have collected the possible degenerate electronic levels found in O_h and T_d together with the symmetry species of the vibrational modes. Looking apart from the totally symmetric vibrational mode, we notice that in both O_h and T_d the doubly degenerate mode is the only active mode for a doubly degenerate electronic level. On the other hand, the degenerate levels of species T_1 and T_2 are split up by both ϵ and τ_2 vibrational modes. We shall now develop the individual cases.

Tetrahedron; Electronic State E; Vibrational Mode ϵ. As previously, the tetrahedron will distort in such a way as to preserve its fourfold rotation reflection axis. The distorted compound will have axial symmetry with an infinite number of distortions which in the S_{2a} and S_{2b} space will lie on a circle with radius $r_0 = |c|/2k$. At three points on this circle the symmetry will be D_{2d}; otherwise, it will only be D_2. The three special points correspond to an elongated or compressed tetrahedron.

Octahedron; Electronic State E; Vibrational Mode ϵ. The analysis very closely follows the tetrahedral case. Again we have cylindrical symmetry, and the minimum energy is found on a circle with a radius as of above. The three special points have symmetry D_{4h} corresponding to an elongated (or compressed) octahedron; all other configurations have only D_{2h} symmetry.

Tetrahedron; Electronic State T_2 or T_1; Vibrational Mode ϵ. As our perturbing potential we take again

$$\mathcal{H}^{(1)} = c_1 S_{2a} \sqrt{3}\,(l_z^2 - 2) + c_1 S_{2b} \tfrac{1}{2}(l_+^2 + l_-^2)$$

and for the threefold degenerate level the orbitals d_{xz}, d_{yz}, and d_{xy}. The perturbation matrix can then be written

$$c_\epsilon S_{2a} \frac{1}{2} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & +2 \end{pmatrix} + c_\epsilon S_{2b} \frac{\sqrt{3}}{2} \begin{pmatrix} -1 & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{8-81}$$

or

$$c_\epsilon \begin{pmatrix} -\frac{1}{2} S_{2a} - \frac{\sqrt{3}}{2} S_{2b} & 0 & 0 \\ 0 & -\frac{1}{2} S_{2a} + \frac{\sqrt{3}}{2} S_{2b} & 0 \\ 0 & 0 & S_{2a} \end{pmatrix} \tag{8-82}$$

The solutions are easily seen to represent three equivalent distortions corresponding to an elongation or compression along the three fourfold axes. The symmetry of the molecule will be D_{2d}. For the potential surface we find in S_{2a}, S_{2b} space

$$E = \tfrac{1}{2} k_1 r^2 - c_\epsilon r \cos \varphi \tag{8-83}$$

Minimizing E with respect to r and φ, we find an energy gain equal to

$$\Delta E = \frac{c_\epsilon^2}{2k_1} \tag{8-84}$$

Octahedron; Electronic State T_2 or T_1; Vibrational Mode ϵ. The analysis follows the preceding case. We obtain three equivalent tetragonal distortions, the symmetry going down to D_{4h}. The energy gain as before is equal to

$$\Delta E = \frac{c_\epsilon^2}{2k_1} \tag{8-85}$$

Tetrahedron; Electronic State T_2 or T_1; Vibrational Mode τ_2. Representing the threefold vibrational mode by the set (x,y,z), we obtain a perturbing potential

$$\mathcal{H}^{(1)} = c_\tau'(S_{5a}x + S_{5b}y + S_{5c}z) \tag{8-86}$$

with the perturbation matrix obtained as before

$$c_\tau S_{5a}\begin{pmatrix}0 & 0 & 0\\0 & 0 & 1\\0 & 1 & 0\end{pmatrix} + c_\tau S_{5b}\begin{pmatrix}0 & 0 & 1\\0 & 0 & 0\\1 & 0 & 0\end{pmatrix} + c_\tau S_{5c}\begin{pmatrix}0 & 1 & 0\\1 & 0 & 0\\0 & 0 & 0\end{pmatrix} \tag{8-87}$$

The solutions to the secular equation are then given by the equation

$$-E^3 + E(S_{5a}^2 + S_{5b}^2 + S_{5c}^2) + 2S_{5a}S_{5b}S_{5c} = 0 \tag{8-88}$$

Setting

$$\begin{aligned} S_{5a} &= r \sin\Theta \cos\varphi \\ S_{5b} &= r \sin\Theta \sin\varphi \\ S_{5c} &= r \cos\Theta \end{aligned} \tag{8-89}$$

we have

$$E^3 - r^2E - r^3 \sin^2\Theta \cos\Theta \sin 2\varphi = 0 \tag{8-90}$$

The potential energy surfaces are given as the solutions to (8-90) plus, of course, the quasi-elastic term $\frac{1}{2}k_2r^2$. Hence,

$$E = c_\tau E'(\Theta,\varphi,r) + \tfrac{1}{2}k_2r^2 \tag{8-91}$$

where E' are the solutions to (8-90). Extremizing with respect to Θ and φ, we have the conditions

$$\frac{\partial E}{\partial\Theta} = \frac{\partial E'}{\partial\Theta} = 0 \tag{8-92}$$

$$\frac{\partial E}{\partial\varphi} = \frac{\partial E'}{\partial\varphi} = 0 \tag{8-93}$$

yielding the simultaneous equations

$$\sin\Theta \sin 2\varphi(2\cos^2\Theta - \sin^2\Theta) = 0 \tag{8-94}$$

$$\sin\Theta \sin 2\Theta \cos 2\varphi = 0 \tag{8-95}$$

possessing the nontrivial solution

$$\cos\Theta = \sqrt{\frac{1}{3}} \qquad \varphi = \frac{\pi}{4} \tag{8-96}$$

The molecule is seen to distort along the threefold axis. Substituting these values into (8-90), we obtain

$$E' = \frac{2}{\sqrt{3}}r \qquad \text{onefold degenerate} \tag{8-97}$$

and

$$E' = -\frac{1}{\sqrt{3}}r \qquad \text{twofold degenerate} \tag{8-98}$$

Minimizing (8-91) with respect to r in the form

$$E = -c_\tau\frac{2}{\sqrt{3}}r + \frac{1}{2}k_2r^2 \tag{8-99}$$

we obtain an energy gain equal to

$$\Delta E = \frac{2}{3}\frac{c_\tau^2}{k_2} \tag{8-100}$$

Octahedron; Electron State T_2 or T_1; Vibrational Mode τ_2. The analysis is equivalent to the one above. The octahedron will distort along one of the threefold axes, the resulting symmetry being D_{3d}. The energy gain is as before

$$\Delta E = \frac{2}{3}\frac{c_\tau^2}{k_2} \tag{8-101}$$

For a threefold degenerate electronic state we have seen that both of the vibrational modes of symmetry ϵ and τ_2 may cause a Jahn-Teller splitting. The resulting potential energy surface will have three points corresponding to equivalent tetragonal distortions and four points corresponding to equivalent trigonal distortions. The combination of both modes yields six further solutions to the secular equation. These represent a very low symmetry of the complex. However, Öpik and Pryce[61] have shown that the six intermediate points cannot represent a minimum.

The trigonal and tetragonal configurations are thus the only stable ones. The trigonal one is stable if and only if

$$\frac{2}{3}\frac{c_\tau^2}{k_2} > \frac{1}{2}\frac{c_\epsilon^2}{k_1} \tag{8-102}$$

or

$$\frac{c_\tau^2 k_1}{c_\epsilon^2 k_2} > \frac{3}{4} \tag{8-103}$$

and the tetragonal configuration is stable if and only if

$$\frac{c_\tau^2 k_1}{c_\epsilon^2 k_2} < \frac{3}{4} \tag{8-104}$$

If by accident the two stabilization energies (8-85) and (8-101) are equal, the complex will oscillate back and forth between a tetragonal and a trigonal configuration.

For a twofold degenerate E level we find an expression for the energy gain which, expressed in $S_{2a} - S_{2b}$ space, is independent of φ. However, by taking account of the quadratic terms in the expansion (8-79) of the Hamiltonian, this result is no longer true. A closer analysis[5,61] shows that the resulting potential surface will possess a threefold barrier comprising a weak restriction to the preferred values of φ. Depending upon the actual sign of the second-order interaction,[5] the minima will correspond to either an "elongated" or a "compressed" molecule.

It may happen that the barrier height is comparable with the vibrational motions. The molecule may now override or tunnel through the barrier, going from one potential minima to the next. In that case φ is again more or less cyclic, whereas r_0 still is strongly determined. The motion will take the molecule through a continuous series of configurations; i.e., we may regard the molecule as undergoing a but feebly hindered "internal rotation" or "inversion."†

If, on the other hand, the vibrational motions are unable to surmount the saddle points in the barrier, the molecule is best described as having a static lower symmetry. In a certain sense we can speak of the "effective" vibrational nuclear mass being so heavy that the nuclei are held near the potential minima and only exhibit harmonic vibrations.

Finally, we shall make a few remarks on the dynamical Jahn-Teller problem for complexes.[72-75] One case which has been treated is the coupling between the electronic and nuclear motions found in a doubly degenerate electronic state whose degeneracy is removed by the interaction of a doubly degenerate vibration. We have just seen that in this case the energy separation between the two potential sheets is $\Delta E = \alpha^2/8k_2$.

Suppose now that the zero-order vibrational energy $h\nu$ for the doubly degenerate vibration is of such a magnitude that

$$\frac{\alpha^2}{8k_2} \approx h\nu = \hbar\sqrt{\frac{k_2}{\mu}} \tag{8-105}$$

where μ is the "effective nuclear mass." It is then clear that the motion cannot be confined to the lowest potential sheet, and a vibronic coupling takes place between the electronic and vibrational motions.

The expression for the energy of the two potential surfaces A and B can be written

$$E = V_0 + \tfrac{1}{2}k(q_1{}^2 + q_2{}^2) \pm a\sqrt{q_1{}^2 + q_2{}^2} \tag{8-106}$$

The eigenfunctions corresponding to these solutions are called $\psi_A(\tau,q_1,q_2)$ and $\psi_B(\tau,q_1,q_2)$, where τ stands for the electronic space and spin coordinates.

For the vibronic case the eigenfunctions must take the form[74]

$$\Psi(\tau,q_1,q_2) = \psi_A(\tau,q_1,q_2)\alpha(q_1,q_2) + \psi_B(\tau,q_1,q_2)\beta(q_1,q_2) \tag{8-107}$$

where $\alpha(q_1,q_2)$ and $\beta(q_1,q_2)$ are the vibrational functions on the potential sheets A and B.

The perturbation matrix for the potential sheets can in the above case be written in the form ($q_1 = r\cos\varphi$, $q_2 = r\sin\varphi$)

$$\begin{pmatrix} V_0 + \tfrac{1}{2}k(q_1{}^2 + q_2{}^2) & a(q_1 - iq_2) \\ a(q_1 + iq_2) & V_0 + \tfrac{1}{2}k(q_1{}^2 + q_2{}^2) \end{pmatrix}$$

With p_1 and p_2 being the canonically conjugated momenta to q_1 and q_2 we find that $\alpha(q_1,q_2)$ and $\beta(q_1,q_2)$ are given as the solutions to the coupled

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† In analogy with the ammonia inversion. It may be remarked in passing that this behavior should produce some interesting features in the heat capacity of such a system.

equations

$$\left[\frac{1}{2\mu}(p_1^2 + p_2^2) + \frac{1}{2}k(q_1^2 + q_2^2) - E\right]\alpha + a[q_1 - iq_2]\beta = 0 \quad (8\text{-}108)$$

$$a[q_1 + iq_2]\alpha + \left[\frac{1}{2\mu}(p_1^2 + p_2^2) + \frac{1}{2}k(q_1^2 + q_2^2) - E\right]\beta = 0 \quad (8\text{-}109)$$

It is obvious that the functions α and β are not the usual functions for a twofold degenerate vibrational mode.

The solutions to these equations cannot be obtained in closed form. We notice that if a were equal to zero, (8-108) and (8-109) would reduce to the Schrödinger equation for a two-dimensional isotropic harmonic oscillator. The wave function for this is, in r and φ space,

$$\psi(m,n) = N(n,m)e^{\pm im\varphi}e^{-r^2/2}r^m L_t^m(r^2) \quad (8\text{-}110)$$

where

$$t = \frac{m+n}{2} \quad (8\text{-}111)$$

m may assume values $m = n, n-2, n-4, \ldots, 0$, or 1, and $L_t^m(r^2)$ is an associated Laguerre polynomial. $N(n,m)$ is a normalizing constant. The energy levels are

$$E_n = (n+1)h\nu \quad (8\text{-}112)$$

the degeneracy of each level being $n + 1$. It is not difficult to show[75,77] that by treating $q_1 \pm iq_2$ as a perturbation, the degeneracy will split up so that all of the levels become doubly degenerate. Equations (8-108) and (8-109) may then be solved by using various perturbation techniques depending upon the strength of the perturbation.[73] We shall not pursue this subject further; instead, we refer the interested reader to the already quoted papers by Moffitt, Liehr, Longuet-Higgins, and others.

Finally, we remark that even if we confine the motion to the lower potential sheet, the vibrational levels are split up by the possibilities of tunneling from one to another of the possible valleys found on the potential surface. Again the situation is closely parallel to the phenomena of the ammonia inversion.

8-e. Experimental Evidence of the Jahn-Teller Effect

We shall now examine some typical features related to the Jahn-Teller effect and see what experimental proofs are available. It is tempting to quote Van Vleck:[65] "It is a great merit of the J-T effect that it disappears when not needed." Alas, it is also true that the effect is very difficult to find when it should manifest itself! The following is to be taken not as a complete list of references, but only as an indication of the types of work performed.

1. Structural Evidence. A Jahn-Teller structural instability should be operative for octahedral Cu^{++} complexes, because in O_h the ground state would be ^2E_g. A list of references given by Orgel and Dunitz[80] indicates that nearly all known octahedrally coordinated Cu^{++} complexes possess the D_{4h} structure, and this is taken as proof of the operation of the Jahn-Teller effect. However, extreme caution is needed in the interpretation. As mentioned, Coulombic forces having nothing to do with the Jahn-Teller forces may also cause a distortion.

Calculations show[5] that, assuming an ionic bonding scheme, one should expect the compressed octahedron to be stable, in contrast to what is found in the majority of cases. Only one example of a compressed octahedron is so far known,[81] and that is the case of K_2CuF_4. This is, of course, a compound which would be likely to possess a high degree of ionic bonding.

The tetrahedral molecule Cs_2CuCl_4 is, on the other hand, an example of a "distorted" Cu^{++} complex[82] in which the distortion is unconnected with the Jahn-Teller forces. The orbital ground state would be of T_2 symmetry, but the spin-orbit coupling removes this degeneracy and leaves the complex in a Jahn-Teller resistant Kramers doublet.[66] The observed distortion must then be connected with the Coulombic repulsion between the chloride ions.[83]

The MnF_2 compound should possess an E_g ground state if the complex had a regular octahedral structure. Again in this case a lower structure is found.[84] As for the copper complexes, we should expect three equivalent ions per unit cell, corresponding to the three possible minima in the molecular potential. From perusal of the wave function for the lower potential surface we see, however, that it is impossible to specify the d orbital the electron should be in. This prediction is borne out by the nuclear magnetic resonance experiments reported by Shulman and Jaccarino.[85]

It may happen that the theory demands a distortion take place but that the structural measurements fail to reveal it because of the very nature of the method.[86] This is, for example, demonstrated in the case of the VCl_4 molecule.[64]

2. Resonance Methods. The only well-documented case for the existence of a Jahn-Teller effect is found for the $Cu(H_2O)_6SiF_6$ complex.[5,87–90] Paramagnetic resonance measurements revealed that the g factor was isotropic at room temperature but anisotropic at low temperatures. The explanation of this effect is found in the form of the wave function (8-64) for the lower potential sheet. The discussion of this phenomenon is given in Chap. 10 under the section dealing with Cu(II) complexes.

The possibility that the nuclei may "tunnel" through the potential barriers also affects the value of the coupling term between the electronic and nuclear spins. This effect has been treated in some detail by Avvakumov.[90]

Contrary to what is usually believed, octahedral Co^{++} complexes should not experience a Jahn-Teller configurational instability, because the ground state is a Kramers doublet.[63,91] The possibility exists, however, that a small "pseudo" Jahn-Teller splitting may take place, since the nearest level with which the ground state may mix under a vibrational perturbation is only placed some 400 cm^{-1} above.

In octahedral Fe^{++} the inclusion of the spin-orbit coupling yields a threefold degenerate ground state.[92] Some Jahn-Teller splitting must then occur. However, Van Vleck has shown[63] that the spin triplet should only give a splitting of about one-tenth of the value one would get for an orbital triplet. This indicates that the Jahn-Teller stabilization would be a hundred times smaller, and hence virtually inoperative.

3. Vibrational Analysis. The study of infrared spectra, as well as the study of fine structure found in the ultraviolet absorption spectra, may yield significant information concerning the Jahn-Teller effect. By comparing the infrared spectra of Jahn-Teller resistant acetylacetonate complexes with the spectrum of manganic acetylacetonate, Forman and Orgel[93] concluded that a Jahn-Teller effect was operative in the manganic compound.

Similar indirect evidence has been accumulated by Weinstock et al.[13,14,94] for the complexes ReF_6, OsF_6, and IrF_6. The theory concerning the influence of the Jahn-Teller mechanism upon the ordinary selection rules for vibrational modes has been given by Thorson.[95]

The vibrational fine structure of the absorption bands of V^{3+} in a corundum lattice has been studied by Pryce and Runciman.[40] Similar studies on Cr^{3+} have been reported by Ford and Hill.[96] In both cases the first allowed absorption band showed a simple progression in a doubly degenerate mode. This leads to the conclusion that the excited state is distorted in such a way that the formerly degenerate vibrational mode in the lower symmetry transforms like the totally symmetric mode. The presence of such a progression in single quanta is therefore clear evidence of a strong Jahn-Teller distortion of the excited state.

4. Absorption Spectra. Neglecting π bonding, we have that in octahedral symmetry the t_{2g} electrons are nonbonding, whereas the e_g electrons are highly antibonding. A violent Jahn-Teller distortion would then be expected to take place for E_g states, but only a relatively small configurational instability should occur for electronic states of T_{2g} or T_{1g} symmetry.

Consider, for instance, the absorption spectrum of $Ti(H_2O)_6{}^{3+}$ being due to the transition $T_{2g} \rightarrow E_g$. With a Jahn-Teller configurational distortion of the E_g state we would expect the spectrum to exhibit a double peaked band. Such a band is indeed also found,[97] but a closer analysis is at present impossible.

The analysis of the band envelopes of the absorption spectra found in inorganic complexes is usually a nearly impossible task, since all the absorption bands are due to transitions between states at least one of which is subjected to a Jahn-Teller distortion. Furthermore, we see the enormous difficulties if we remember that, because of the parity restriction, a vibronic scrambling of an odd and even electronic state must take place in order to make the electronic transition allowed for a molecule possessing a center of symmetry. Consequently, apart from very qualitative suggestions, very little work has so far been done.

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CHAPTER 9

Some Further Aspects

9-a. The Faraday Effect

If we apply a magnetic field parallel to the direction of propagation of an incident plane-polarized light wave traveling in some medium, the plane of polarization will be changed. This is the so-called Faraday effect. The theory of Maxwell tells us that a plane-polarized light wave may be regarded as a superposition of a right and a left circularly polarized wave of the same frequency. Under normal circumstances these two waves would travel at the same speed, but in the presence of a magnetic field this will no longer be true; as a consequence the resultant vector, though still plane-polarized,[1] will be rotated through some angle Θ.

The derivation of the appropriate formula is not difficult; it follows once the expression for the dispersion of light is known.[44] However, since this formula can be derived only by the use of time-dependent perturbation theory, with which we have not so far been concerned, and since an excellent exposition of the theory behind the Faraday effect is given by Born and Jordan,[2] we shall refer to their monograph for a strict derivation.

As first shown by Kramers,[3] we have the following expression for the rotation Θ of the plane of polarization per unit length:

$$\Theta = \frac{4\pi\nu^2 Ni}{hc\bar{n}S} \sum_{g,n} \frac{[(g|X|n)(n|Y|g)]}{\nu^2 - \nu_{ng}{}^2} \exp\left(\frac{-h\nu_g}{kT}\right) \tag{9-1}$$

where ν is the frequency of the incident light, N is Avogadro's number, $\bar{n}$ is the average refractive index, and S is the partition function. $(g|X|n)$ and $(n|Y|g)$ are the components of the total electronic dipole moment along the x and y axes, respectively, in the *presence of the magnetic field*, and the square brackets have the meaning of a vector product:

$$[(g|X|n)(n|Y|g)] = (g|X|n)(n|Y|g) - (g|Y|n)(n|X|g) \tag{9-2}$$

The summation g goes over all the occupied states, each of which is weighted with its appropriate Boltzmann factor, and the summation n is over all excited states, Fig. 9-1.

Suppose now that the situation is as pictured in Fig. 9-1a, where the ground state is a Kramers doublet split under the influence of the magnetic field. If all of the ions were in the state g_1, the rotation of the plane of polarization would be ρ_∞, and, similarly, if they all were in the state g_2, the rotation would be $-\rho_\infty$. The assumption is now made that we cannot resolve spectroscopically the difference in energy separation between the two ground states and the excited states. Weighing each of the two states with its appropriate Boltzmann factor, we get for the observed rotation

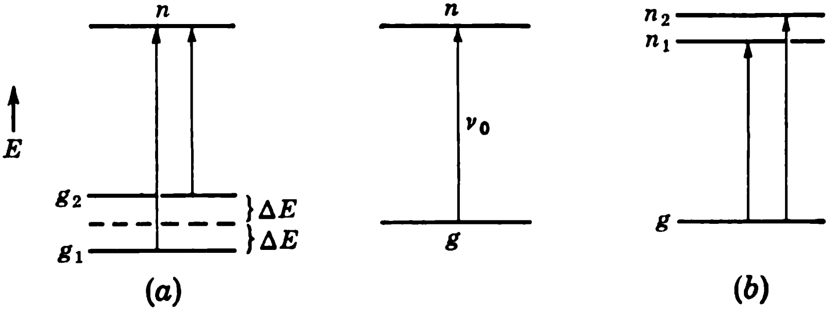

FIG. 9-1. Energy-level diagrams giving rise to (*a*) paramagnetic and (*b*) diamagnetic Faraday rotation.

$$\Theta = \frac{\rho_\infty e^{\Delta E/kT} - \rho_\infty e^{-\Delta E/kT}}{e^{\Delta E/kT} + e^{-\Delta E/kT}} = \rho_\infty \tanh \frac{\Delta E}{kT} \tag{9-3}$$

Since

$$2\Delta E = g\mu_B H \tag{9-4}$$

where g is the spectroscopic splitting factor and μ_B the Bohr-magneton, we get approximately[4] by an expansion

$$\Theta = \frac{\rho_\infty g\mu_B}{2kT} H$$

where

$$\rho_\infty = \frac{4\pi Ni}{\hbar c\bar{n}} \frac{\nu^2}{\nu^2 - \nu_{ng}{}^2} [(g_1|X|n)(n|Y|g_1)] \tag{9-5}$$

The above expressions are valid for the paramagnetic Faraday effect, so called because it depends upon the temperature in the same way as does the paramagnetic susceptibility.

On the other hand, if the situation is as pictured in Fig. 9-1*b*, it is necessary to consider the different frequency dependences of the multiplet components. Writing

$$\nu_{gn} = \nu_0 + H\nu_0{}^{(1)} \tag{9-6}$$

because the splitting of the levels in a magnetic field (the Zeeman effect) is proportional to the field, we get for the so-called diamagnetic part of the Faraday rotation

$$\Theta = \frac{8\pi Ni}{\hbar c\bar{n}} \frac{\nu^2 \nu_0 \nu_0{}^{(1)}}{(\nu^2 - \nu_0{}^2)^2} [(g|X|n_1)(n_1|Y|g)]H \tag{9-7}$$

The diamagnetic part of the Faraday rotation is seen to be temperature independent. The distinction between the diamagnetic and paramagnetic parts of Eq. (9-1) is due to Rosenfeld,[6] who developed the theory of the Faraday effect for atoms. Usually the situation is of course a mixture of the two cases *a* and *b*. However, for molecules a third kind of frequency dependence may also appear as has been shown by Serber.[7]

The rotation Θ in a cell of length l is in general seen to be given by a formula of the form $\Theta = VHl$, where the factor of proportionality is called the Verdet constant. It can be shown[5] (as is indeed trivial in the above simple case) that, calling the paramagnetic susceptibility χ, we have in many cases

$$V = A\chi + K \tag{9-8}$$

Use has been made[5] of this relation to connect the magnetic and rotational data for tysonite, a rare-earth mineral containing Ce^{3+}.

The application of Eq. (9-1) to calculate the rotational properties of complexes using a crystal field level scheme is seen to lead to a value of zero for the contribution of the "crystal field bands" to the rotation. The reason for this is of course the same as found in the band intensity calculations: nonzero values of the matrix elements appearing in Eq. (9-1) require transitions between even and odd states. Nevertheless, experimentally the crystal field bands are seen to yield a contribution.[8] Hence, once more we need to consider the mixing of even and odd states if we want to do a thorough calculation. We may, however, also set up a semiempirical theory as follows.

As shown by Stephen[9] among others, Eq. (9-1) can be put in a more convenient form for calculation by using the commutation relation

$$L_zX - XL_z = i\hbar Y \tag{9-9}$$

Substituting (9-9) into (9-1) we get, assuming L to be a good quantum number:

$$\Theta = \frac{8\pi\nu^2N}{\hbar^2c\bar{n}S}\sum_{g,n}\frac{|(g|X|n)|^2}{\nu^2 - \nu_{ng}{}^2}\{(n|L_z|n) - (g|L_z|g)\}\exp\left(\frac{-h\nu_g}{kT}\right) \tag{9-10}$$

Strictly speaking, L is of course a good quantum number only in the weak-field limit. However, as discussed by Stephen,[9] Eq. (9-10) is a good approximation in nearly all cases of interest. Furthermore, neglecting the influence of the static magnetic field upon the amplitudes of the matrix elements $(g|X|n)$ and assuming isotropy for the transition $g \rightarrow n$, we have for the oscillator strength[10] $f_{g\rightarrow n}$:

$$f_{g\rightarrow n} = \frac{8\pi^2mc}{h}\nu_{ng}|(g|X|n)|^2 \tag{9-11}$$

where ν_{ng} is the frequency of the transition $g \rightarrow n$ and m is the electronic mass. By substituting (9-11) into (9-10), we finally get

$$\Theta = \frac{2\nu^2 N}{hc\bar{n}mS} \sum_{g,n} \frac{f_{g\to n}}{\nu_{ng}(\nu^2 - \nu_{ng}{}^2)} \{(n|L_z|n) - (g|L_z|g)\} \exp\left(\frac{-h\nu_g}{kT}\right) \qquad (9\text{-}12)$$

This formula has been used by Stephen[9] to calculate the Faraday rotation for a solution of $Co(H_2O)_6{}^{++}$. The agreement between the theory and the experiments was seen to be quite satisfactory, and a similar conclusion was reached by Stone[43] in his work on $MnO_4{}^-$ and $TiCl_4$.

Measurements and calculations of the Faraday effect for complexes had previously, before the advent of paramagnetic resonance methods, been used to investigate the zero-order field splittings of the electronic ground states. Examples of such calculations are the Van Vleck and Penney[11] investigations into the paramagnetic rotations of manganous and ferric salts and the similar work of Becquerel and Opechowski[12] concerned with the behavior of $Ni(H_2O)_6 \cdot SiF_6$. The latter authors found that the zero-order field splitting for the nickel fluosilicate was 0.301 cm^{-1} with the singlet placed above the doublet. This result is in excellent accord with the results obtained from paramagnetic resonance. By the use of a crystalline field with a trigonal component included, they could further deduce a Dq value of 1069 cm^{-1} from their measurements of the paramagnetic rotation. However, even if these results were very good, more direct evidence produced by resonance and spectral measurements have made these ingenious methods obsolete.

9-b. Optical Rotatory Dispersion

The theory for the optical rotatory dispersion of complex ions has been given by Moffitt,[13] and we shall follow his exposition of the subject. As is well known[14] a fundamental requirement for optical activity is that the molecule possess neither a plane nor a center of symmetry. This condition is fulfilled for complexes whose ligands consist of three symmetrical bidentate groups as exemplified by the complex ions $Co(en)_3{}^{3+}$ and $Cr(ox)_3{}^{3-}$, whose ligands are respectively ethylenediamine and the oxalate ion. The study of these ions is simplified by the fact that they possess one threefold axis and three twofold axes, their point group symmetry being D_3.

When the ground states g of our systems are separated by an energy large with respect to kT from their first excited states, then the optical activity of their solutions is given by the molecular rotation[14]

$$[M] = \sum_n [M_n] \qquad (9\text{-}13)$$

$$[M_n] = \left(\frac{96\pi N}{hc}\right)\left(\frac{\bar{n}^2 + 2}{3}\right)\left(\frac{\nu^2 R_n}{\nu_{ng}{}^2 - \nu^2}\right) \qquad (9\text{-}14)$$

where the excited states have been labeled n.

If a marked dispersion is present, one can then separate out the partial rotation $[M_n]$ due to the nth absorption band and then, by means of (9-14), calculate R_n, the rotational strength.

The quantum-mechanical expression for R_n has been given by Condon;[14] it is

$$R_n = \frac{e^2}{2mc}\,\mathrm{Im}\,(\mathbf{P}_{gn} \cdot \mathbf{L}_{ng}) \tag{9-15}$$

where the vectors

$$\mathbf{P}_{gn} = \int \Psi_g^* \mathbf{R} \Psi_n \, d\tau \tag{9-16}$$

$$\mathbf{L}_{gn} = \int \Psi_g^* \mathbf{L} \Psi_n \, d\tau \tag{9-17}$$

represent the electric and magnetic dipole moments associated with the transition $g \rightarrow n$ occurring at ν_{ng} wave numbers. Finally, Im stands for the imaginary part of the dotted product. The aim of any electronic theory is therefore the calculation of R_n.

In the point group D_3 the parallel components of both the electric and the magnetic moment operators transform under A_2, whereas the perpendicular components span the irreducible representation E. Taking the direct product we then have the polarizations for the electric and magnetic transitions given below.

	A_1	A_2	E
A_1	—	$\parallel$	$\perp$
A_2	$\parallel$	—	$\perp$
E	$\perp$	$\perp$	$\parallel, \perp$

The fact that the magnetic dipole and the electric dipole vectors both have the same transformation properties in D_3 can be used to give a simple relation between the rotational strength R_n of a transition, its intensity, and its magnetic moment. This is useful, because the magnetic moment of a transition using the crystal field theory is easy to calculate, whereas the calculation of the corresponding electric moment, as seen previously, is difficult.

We are interested in calculating the rotational strengths for *tris*-ethylenediamine Cr^{3+} and Co^{3+} complexes. Now, although these complexes have symmetry D_3, their absorption spectra show that their "effective" symmetry approximates O_h. This is interpreted by saying that the Hamiltonian consists of two terms, the usual $\mathcal{V}_0$ term spanning the identical representation in O_h and a very small term $\mathcal{V}_D$ which is invariant under those symmetry operations of O_h which survive in D_3. The first-order corrections arising from $\mathcal{V}_D$ enable us to write the perturbed octahedral wave functions as

$$\psi = \psi_g^\circ + \lambda(\varphi_u + \varphi_g) \tag{9-18}$$

We want to calculate the rotatory strength R_n to the first order in λ. Our zero-order wave functions ψ_g° are all even wave functions, and the electric moment operator transforms under T_{1u} in O_h, whereas the magnetic moment operator transforms under T_{1g}. Hence if a given transition is magnetically allowed, its rotational strength appears in first order of λ. If, on the other hand, it is forbidden in magnetic dipole radiation fields, R_n will be of order λ^2.

Turning our attention back to $\mathrm{Cr(en)_3^{3+}}$ and $\mathrm{Co(en)_3^{3+}}$ once more, we see that for the chromium complex which has a ${}^4A_{2g}$ ground state only the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition should be optically active to the first order and that the cobalt complex should show optical rotation only in the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition.

It is found that the magnetic moments of the allowed transitions are essentially isotropic. This is, of course, due to the fact that they are evaluated by using cubic wave functions. On the other hand, the electric moments evaluated with the perturbed wave functions will not share this property and will differ in magnitude as well as in direction.

Since the molecule does not possess a center of symmetry, there will be an electronically allowed part of the transition $g \rightarrow n$. Calling this contribution of the oscillator strength $f_{gn}^{(e)}$, we have as usual

$$f_{gn}^{(e)} = \frac{8\pi^2 mc}{3h} \nu_{ng} \sum_r |\mathbf{P}_{gn}^{(r)}|^2 \tag{9-19}$$

if the upper level is r-fold degenerate.

As pointed out by Moffitt,[13] it is very important to distinguish between the "electronically allowed" part of the oscillator strength and the total oscillator strength. The reason for this is straightforward. We have seen that the main part of the intensity of an absorption band in the crystal field approximation is due to a vibronic transition $g\chi_p \rightarrow n\chi_q$, where the vibrational states χ_p and χ_q differ by 1 quantum. On the other hand, the magnetic dipole transition takes place between two states having the same vibrational state. Since for R_n we are then forced to use

$$R_n = \mathrm{Im}\,(g\chi_p|\mathbf{r}|n\chi_p)(n\chi_p|\mathbf{l}|g\chi_p)$$

we see that in order for the summation over the excited states n to be different from zero, only the electronically allowed part of the electric dipole transition will make a contribution to R_n. Hence we only consider the intensities of the 0-0 band and totally symmetric progressions as contributing to the $f_{gn}^{(e)}$ curve.

A possible way of obtaining an upper limit of the value of $f_{gn}^{(e)}$ for the *tris*-ethylenediamine complexes would be by comparing the measured total oscillator strength for a certain transition with the measured oscillator strength for the hexammine complex. The intensities of the latter are entirely due to asymmetric vibrational modes and solvent fluctuations. Hence we may tentatively estimate, by taking the difference of the intensities, how much the presence of the static dissymmetry due to the presence of the ligand bridges gives in intensity. This difference ought then to be a very rough measure of $f_{gn}^{(e)}$. It is found, however, that the values of $f_{gn}^{(e)}$ obtained in this way are much too large (*vide infra*).

We are now able to make an order-of-magnitude calculation of R_n for a magnetically allowed transition. For the transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$ in $Co(en)_3^{3+}$ we found in Chap. 8, for instance, $\Sigma|L|^2 = 24\hbar^2$. We then get for $|R_n|$ with $n = {}^1T_{1g}$ and by using (9-19):

$$|R_n| \simeq \frac{e^2}{2mc} |\mathbf{P}_{gn}||\mathbf{L}_{gn}| = \sqrt{\frac{3he^4}{32\pi^2m^3c^3}} \sqrt{\frac{f_{gn}^{(e)}}{\nu_{ng}}} \sqrt{24\hbar^2} \tag{9-20}$$

Using the "reduced" rotational strength $\overline{R_n}$ defined by Moffitt[13] by measuring **P** in Debye units and **L** in Bohr magnetons, we obtain

$$|\overline{R_n}| = 3 \times 10^{18} \sqrt{\frac{he^2}{mc\pi^2}} \sqrt{\frac{f_{gn}^{(e)}}{\nu_{ng}}} \tag{9-21}$$

$$|\overline{R_n}| \simeq 7.1 \times 10^3 \sqrt{\frac{f_{gn}^{(e)}}{\nu_{ng}}} \tag{9-22}$$

where ν_{ng} is expressed in centimeters^{-1}.

Experimentally, the transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$ in $Co(en)_3^{3+}$ is found at 21,000 cm^{-1} and the value of $|\overline{R_n}|$ is estimated[15] to be of the order of magnitude of 10^{-2}. Using these numbers, we can then get $f_{gn}^{(e)} \simeq 4 \times 10^{-8}$. On the other hand, the estimation of $f_{gn}^{(e)}$ directly from the absorption spectra as of above yields $f_{gn}^{(e)} \simeq 10^{-4}$. The "inherent" dissymmetry produced by the bridges is thus found to have very little influence upon the intensity of the spectral transition, most of which must be due to a vibrational progression. This result is strangely enough not in agreement with the measurements of the dichroism of these complexes, as outlined in Sec. 8-c. We emphasize, however, that the above considerations have value only as an order-of-magnitude calculation.

Moffitt[13] tried further to compute the rotational strengths from first principles by using a specific potential for $\mathcal{V}_D$. However, Sugano[16] has shown that this model is incorrect, since the complexes cannot attain optical rotatory power using Moffitt's expression for the potential.

The approximate selection rules telling us the orders of magnitude to be expected for rotational strengths are, then, the most important of Moffitt's work.[13] Constructed as they are upon which states combine magnetically, they should be very general. Also, all existing experiments have so far substantiated them; even Ni^{++} placed in an asymmetric lattice obeys[47] Moffitt's simple selection rules. It is, however, obvious that the inclusion of such refinements as spin-orbit interaction and configurational interaction may impair their validity slightly.

9-c. "Sandwich" Compounds

On the border line between inorganic and organic chemistry stand the metalloorganic compounds. Especially in recent years, a vast number of such complexes have been made; see for instance Fischer[17] and Wilkinson and Cotton.[18] The bonding between the metal and the organic ligands is mostly due to the donating properties of the π orbitals found on the unsaturated hydrocarbons.[19] Usually, the molecular symmetry of these complexes is rather low and thus not well-suited to a theoretical treatment. However, a special group of metalloorganic compounds, the so-called "sandwich compounds," forms an exception to this rule, and it is with this group that we shall be especially concerned.

A typical example of a sandwich compound is ferrocene. This is the trivial name for the compound $Fe(C_5H_5)_2$; iron di-π-cyclopentadiene, usually written $Fe(Cp)_2$. The structure is known[20,21] to consist of two planar C_5H_5 rings with an iron atom sandwiched in between. The two rings have a staggered configuration; the molecular point group symmetry is D_{5d}, Fig. 9-2.

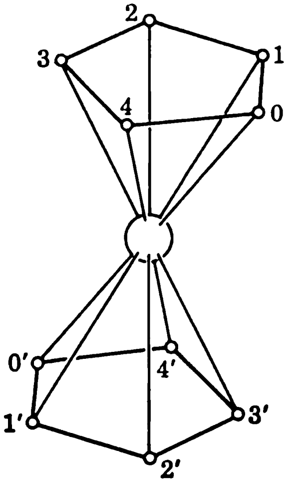

FIG. 9-2. Molecular geometry of ferrocene.

The electronic structure of ferrocene and the similar compounds which can be made with other transition metals has been discussed many times in the literature; for an excellent survey of the existing theories the Wilkinson and Cotton paper[18] ought to be consulted. It is here sufficient to mention that the basic features of the bonding present in these compounds have been given by Moffitt[22] and Dunitz and Orgel,[23] while more quantitative calculations have been performed by Shustorovich and Dyatkina[24–26] and Dahl and Ballhausen.[27,28]

All of the investigations so far performed have made use of the molecular-orbital theory. The reason for this is clear; consider ferrocene, for example. With only 18 valence electrons (10 from the rings and 8 from the iron atom) we must in a valence-bond theory make 10 equivalent bonds from the metal atom to the 10 carbon atoms. Ferrocene is therefore an electron-deficient compound, and it is consequently best treated in a molecular-orbital scheme. The basic features in the bonding theory for sandwich compounds are obtained by writing down the linear combinations of ring π orbitals transforming correctly in the point group symmetry D_{5d} and combining these with the appropriate metal orbitals.

Consider first ring A only, Fig. 9-2. Denoting a carbon $2p\pi$ orbital π_r with $r = 0, 1, \ldots 4$, we can construct the following five orbitals:

$$\begin{aligned}
\varphi_A(a_2) &= \sqrt{1/5}\,(\pi_0 + \pi_1 + \pi_2 + \pi_3 + \pi_4)\\
\varphi_A(e_1{}^+) &= \sqrt{1/5}\,(\pi_0 + \omega\pi_1 + \omega^2\pi_2 + \omega^3\pi_3 + \omega^4\pi_4)\\
\varphi_A(e_1{}^-) &= \sqrt{1/5}\,(\pi_0 + \omega^{-1}\pi_1 + \omega^{-2}\pi_2 + \omega^{-3}\pi_3 + \omega^{-4}\pi_4)\\
\varphi_A(e_2{}^+) &= \sqrt{1/5}\,(\pi_0 + \omega^2\pi_1 + \omega^4\pi_2 + \omega^6\pi_3 + \omega^8\pi_4)\\
\varphi_A(e_2{}^-) &= \sqrt{1/5}\,(\pi_0 + \omega^{-2}\pi_1 + \omega^{-4}\pi_2 + \omega^{-6}\pi_3 + \omega^{-8}\pi_4)\\
\omega &= e^{2\pi/5}
\end{aligned} \tag{9-23}$$

A similar set of linear combinations exists, of course, for ring B. The symmetry orbitals for the two rings together are then simply given as

$$\begin{aligned}
\varphi(a_{1g}) &= \sqrt{\tfrac{1}{2}}\,[\varphi_A(a_2) + \varphi_B(a_2)] & \varphi(a_{2u}) &= \sqrt{\tfrac{1}{2}}\,[\varphi_A(a_2) - \varphi_B(a_2)] \\
\varphi(e_{1g}{}^{\pm}) &= \sqrt{\tfrac{1}{2}}\,[\varphi_A(e_1{}^{\pm}) + \varphi_B(e_1{}^{\pm})] & \varphi(e_{1u}{}^{\pm}) &= \sqrt{\tfrac{1}{2}}\,[\varphi_A(e_1{}^{\pm}) - \varphi_B(e_1{}^{\pm})] \\
\varphi(e_{2g}{}^{\pm}) &= \sqrt{\tfrac{1}{2}}\,[\varphi_A(e_2{}^{\pm}) + \varphi_B(e_2{}^{\pm})] & \varphi(e_{2u}{}^{\pm}) &= \sqrt{\tfrac{1}{2}}\,[\varphi_A(e_2{}^{\pm}) - \varphi_B(e_2{}^{\pm})]
\end{aligned} \tag{9-24}$$

Let us next look at the metal orbitals. In the point group D_{5d} we easily find the following transformation properties:

$3d_0$	$3d_{\pm 1}$	$3d_{\pm 2}$	$4s$	$4p_0$	$4p_{\pm 1}$
a_{1g}	e_{1g}	e_{2g}	a_{1g}	a_{2u}	e_{1u}

The bonding molecular orbitals for the ferrocene molecule are then made up of linear combinations of the type

$$\psi(a_{1g}) = c_1(3d_0) + c_2(4s) + c_3\varphi(a_{1g}) \tag{9-25}$$

$$\psi(a_{2u}) = c_4(4p_0) + c_5\varphi(a_{2u}) \tag{9-26}$$

and so forth. The problem now consists in the calculation of the various mixing coefficients $c_1, \ldots, c_N$. This is as usually done by a variational procedure. Because of the symmetry properties, we see that we obtain one three-dimensional, one one-dimensional, and four two-dimensional secular equations to solve. All in all, we will obtain 19 orbitals, some bonding, some nonbonding, and some antibonding. The 18 valence electrons occupy 9 of these molecular orbitals, the remaining 10 orbitals being used for the construction of excited states.

In order to gain some insight into the bonding capacities of the various orbitals, we first look at the overlap. Within themselves the metal orbitals and the ring orbitals are, of course, orthogonal to each other. On the other hand, there are overlap integrals, different from zero, between those of the orbitals which transform in the same way. Using Watson's[29] self-consistent orbitals for iron, and a radial $2p$ carbon orbital with an "effective charge" $\xi = 1.59$ after Zener,[30] we obtain[27] with the Seibold and Sutton[21] structural parameters.

$S(a_{1g})$	$S(a'_{1g})$	$S(e_{1g})$	$S(e_{2g})$	$S(a_{2u})$	$S(e_{1u})$
0.527	0.030	0.148	0.079	0.236	0.468

Here we have defined

$$S(a_{1g}) = \int \psi^*(4s)\varphi(a_{1g})\,d\tau \tag{9-27}$$

$$S(a'_{1g}) = \int \psi^*(3d_0)\varphi(a_{1g})\,d\tau \tag{9-28}$$

and similarly for the other overlap integrals.

Taking the numerical values of the overlap as a rough and ready measure of the strength of the bonding in ferrocene, we would expect the strongly bonding orbitals to be a_{1g}, e_{1u}, a_{2u}, and e_{1g} followed by the weakly, or nonbonding, orbitals e_{2g} and a'_{1g}. This is also found by explicit calculations.[27] The electronic structure for the ground state of ferrocene using 18 valence electrons can then be written

$$^1A_{1g}: \quad (a_{1g})^2(e_{1u})^4(a_{2u})^2(e_{1g})^4(e_{2g})^4(a'_{1g})^2$$

By the solutions of the secular equations for the orbitals in question we obtain, of course, the energies of the antibonding orbitals as well.[27] The lowest empty orbitals in ferrocene turn out to be (e_{2u}) and (e^*_{2g}). We can then construct low excited states for the molecule by the excitation of the (e_{1g}) or (e_{2g}) electrons to the (e_{2u}) or (e^*_{2g}) antibonding orbitals. Using the nomenclature $(a \rightarrow b)$ to indicate that an electron has been excited from orbital (a) to orbital (b), it is easy to see by means of the group characters that an excitation $(e_{2g}) \rightarrow (e_{2u})$ will produce the excited states $^1A_{1u}$, $^1A_{2u}$, and $^1E_{1u}$. With the ground state transforming like $^1A_{1g}$, and with the electric dipole vector transforming like $A_{2u}(\|)$ and $E_{1u}(\perp)$ with respect to the fivefold symmetry axis, the excitation $(e_{2g}) \rightarrow (e_{2u})$ should produce two "allowed" bands: $^1A_{1g} \rightarrow {}^1A_{2u}$ $(\|)$ and $^1A_{1g} \rightarrow {}^1E_{1u}$ $(\perp)$. Numerically,[27] these transitions are found to be placed at 7.06 ev and 5.75 ev, respectively. The agreement with experiment is as good as can be expected.

If one is allowed to extrapolate the results gained for the ground state of ferrocene to the other sandwich compounds, one obtains the following picture. The neutral dicyclopentadienyl metal complexes possess a closed electronic system of 12 electrons, $(a_{1g})^2(e_{1u})^4(a_{2u})^2(e_{1g})^4$. The "sandwiches" of the first transition series then differ only in the occupancy number of the a'_{1g} and e_{2g} orbitals. Further use of the e_{2u} (or e^*_{2g}) orbital allow one to write down the electronic ground state for the Co and Ni compounds and to account for the spectral features. For the various ground states we then have the following electronic structures, consistent with the magnetic data:

$Ti(Cp)_2$	$(12)(a'_{1g})^2$	$S = 0$
$V(Cp)_2$	$(12)(a'_{1g})^1(e_{2g})^2$	$S = 3/2$
$Cr(Cp)_2$	$(12)(a'_{1g})^2(e_{2g})^2$	$S = 1$
$Fe(Cp)_2$	$(12)(a'_{1g})^2(e_{2g})^4$	$S = 0$
$Co(Cp)_2$	$(12)(a'_{1g})^2(e_{2g})^4(e_{2u})^1$	$S = 1/2$
$Ni(Cp)_2$	$(12)(a'_{1g})^2(e_{2g})^4(e_{2u})^2$	$S = 1$

The reason for the sudden jump to three unpaired electrons in going from $Ti(Cp)_2$ to $V(Cp)_2$ has been explained by Orgel[19] as due to the great gain in exchange energy for this configuration. The argument is then the same as the one used previously to explain the change in the magnetism of octahedrally coordinated Co^{3+} complexes.

It has been pointed out that the orbitals in a sandwich compound resemble to a great extent those of an octahedral complex with a trigonal distortion.[19,31] Since the d orbitals in a D_{5d} molecular point group transform as a_{1g}, e_{1g}, and e_{2g} and in the point group D_{3d} as a_{1g}, e_{1g}, and e_{1g}, this is hardly surprising. This similarity between the sandwich molecules and the octahedral complexes has been used in an attempt to calculate the electronic levels of the cyclopentadienyl complexes using a crystal field model for the compounds.[32] With the exception of the placement of the antibonding orbitals such a model proved quite successful.

Whereas in a "normal" sandwich compound the two rings will be parallel to each other, there are good reasons to expect that the making of a protonated species as, for example, $(C_5H_5)_2FeH^+$ will alter this structure.[28] (See, however, Ref. 42 for a different view upon this compound.) If the two Cp rings are twisted in such a way that the radius vectors from the metal atom to the centers of the rings make an angle less than 180°, the six principal bonding molecular orbitals will, of course, be changed. However, the total bonding energy is supposedly only very slightly affected. It is then possible to construct three nonbonding hybrids, sticking out in between the rings. These orbitals can then be used for bonding purposes, for example, the taking up of protons or hydrogens. The agreement between experiment and theory is most satisfactory.[28]

Another class of sandwich compounds has two benzene rings instead of the cyclopentadienyl rings. The best characterized complex of this type is $Cr(C_6H_6)_2$. The absorption spectrum and the bonding of the compounds of chromium and benzene have been elucidated by Berry.[45,46]

9-d. Stability of Complex Ions

A question which has occupied many authors is the following: Is it possible to correlate the available thermodynamic data for the complex ions such as complexity constants and heats of formation with the spectral and magnetic data for the same complexes? Usually, this is not an easy thing to do. What would, for instance, be more natural than to suppose that the spectrochemical series, being as it is a measure of the "crystal field strength," would also be the series one would arrive at if the ligands were arranged in order of increasing complexity constants? Yet this is not so. Such a series can indeed be constructed, but it will differ not insignificantly from the spectrochemical series. In order to treat this question, let us for the moment return to the absorption spectra of the complexes.

As pointed out earlier, it is nearly always found that in order to fit the absorption bands of the complex ions to the various theoretical level schemes, we need to diminish the Condon-Shortley-Slater parameters F_2 and F_4 from the values obtained from atomic spectroscopy. This corresponds to a reduction of the term distances found by extrapolating the crystal field strength to zero. If a sufficient number of bands can be identified, we then have the possibility of calculating Dq as well as the apparent term distances. We now want to arrange the ligands in a series which is based upon their power of diminishing the term distances.[33] For instance, we find for Cr(III) that $E(^4P - {}^4F) = 15(F_2 - 5F_4) = 14{,}200\ \text{cm}^{-1}$. By calculating the apparent term distance $x = ({}^4P - {}^4F)$ from the absorption spectra and forming the ratio $\beta = x/14{,}200$, we get the following series[33] in order of smaller values of β.

$$F^- > H_2O > NH_3 > \text{en} > \text{ox}^= > SCN^- > Cl^- > CN^-$$

This series, which is seen to differ appreciably from the spectrochemical series, is called the nephelauxetic series.[33] It is found to be valid for many metal ions. The remarkable thing is that this series is very close to the one a chemist working with complexity constants would draw up in order to illustrate the increasing power of the ligands for complexing. Why this should be so is still an open question.

Other factors influencing the stability of transition metal ions are (1) the decrease of the ionic radii expected within a period parallel to the contraction found for the rare earths and (2) the crystal field stabilization. This latter stabilization can really be divided into two effects, the first one being the influence of the crystalline field upon the "ionic radii" of the cation as explained in the Jahn-Teller section in the preceding chapter.

The second manifestation of the crystal field stabilization is simply given by the energy gain in units of Dq for the ground state. An energy gain of magnitude $4Dq$ is, for instance, obtained by making an octahedral Ti^{3+} complex. The corresponding stabilization energies for other octahedral systems are given in Table 4-4 in the weak-field limit. The strong-field limit stabilization can be seen from Table 4-7.

TABLE 9-1. CRYSTAL FIELD STABILIZATION

Atomic configuration	Stabilization energy for octahedral complexes	
	Weak field	Strong field
d^1	$4Dq$	$4Dq$
d^2	$6Dq$	$8Dq - (3F_2 - 15F_4)$
d^3	$12Dq$	$12Dq$
d^4	$6Dq$	$16Dq - (6F_2 + 145F_4)$
d^5	$0Dq$	$20Dq - (15F_2 + 275F_4)$
d^6	$4Dq$	$24Dq - (5F_2 + 255F_4)$
d^7	$6Dq$	$18Dq - (7F_2 + 105F_4)$
d^8	$12Dq$	$12Dq$
d^9	$6Dq$	$6Dq$

After correction for ligand field stabilization, we should then expect, for example, the heat of formation to follow a smooth rising curve inside a given period of the periodic system, Fig. 9-3.

The above expected behavior is in fact also observed; it was first theoretically explained by Penney[41] and later elaborated upon by Orgel.[34] If, however, one tries to correlate the above phenomena with values of the complexity constants or the kinetic behavior of complexes, difficulties appear. It is quite clear that for a single molecule the bonding energy is equal to the total gain in the electronic energy. Consider now the two complexes $Cr(NH_3)_6^{3+}$ and CrF_6^{3-}. The gain in crystal field stabilization is given by

$$12(Dq(NH_3) - Dq(F^-))$$

but if we use this energy difference to calculate the difference in complexity constants by means of the well-known thermodynamic formulas, we will arrive at quite incorrect results. The reason is straightforward: the difference in the relative bonding energies exemplified in the electronic configuration for the σ bonding electrons $(a_{1g})^2(t_{1u})^6(e_g)^4$ for the two complexes has not been taken into account.

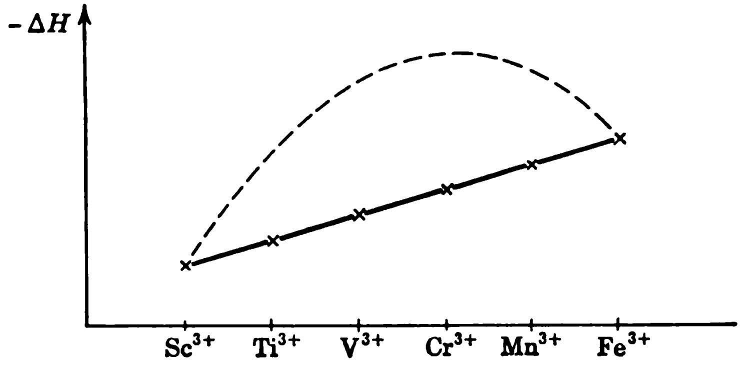

FIG. 9-3. Heat of formation for trivalent complexes of the first transition series. Straight line: expected heat of formation due to contracting effects. Dashed line: above function corrected for crystal field stabilizations.

This difference is by definition connected with the concept of electronegativities of the ligands or, what amounts to the same thing, the electron affinities of the metal ions. It is clear that a "complete" calculation of the electronic structures could answer questions as to the relative gain of energy going from one ligand to another. We have seen, however, that this is very difficult. We are then forced to use semiempirical ideas such as electron affinities and the like.[35] Another difficulty is, of course, that the calculation of complexity constants and kinetic behavior[36] from "first principles" requires the theory of statistical mechanics. Such an analysis has not been performed as yet for any but the most simple of gas phase reactions.

Even though the above questions are of the greatest interest for the chemist working with the reactions of the complex ions, we shall not have anything further to say about this topic. We leave it reluctantly, however, and only because a great many excellent books and review papers[19,35–40] have dealt very exhaustively with the above aspects of the ligand field theory.

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CHAPTER 10

Electronic Structures of Selected Inorganic Complexes

In this last chapter we shall try to discuss the most important features of our knowledge related to the electronic structures of inorganic complexes. For reasons stated earlier we shall not treat complexes of the rare earths or actinides, but shall deal only with the transition metals. To try to cover all work done here is, of course, impossible and perhaps even undesirable. For instance, the number of papers dealing in some way with the absorption spectra of Ni^{++} complexes would alone require about 1000 references. Clearly, a quotation of this order is out of the question in a book of this size.

Each element will be treated separately, and the various oxidation steps of an element will be found under the heading of the element in question. We have not attempted a uniform classification of the sundry phenomena; rather we do not hesitate to digress a bit if we feel that this would clarify a certain point.

We are indebted to the following six volumes of references.

For the paramagnetic resonance measurements:

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COMPLEXES CONTAINING 3*d* ELECTRONS

10-a. Scandium

Scandium has the electronic structure [A](3*d*)(4*s*)^2, where [A] stands for a closed argon configuration. Sc^{++} has the electronic configuration [A](3*d*), but no compounds of scandium with this oxidation number are known.

10-b. Titanium

Titanium has the electronic structure [A](3*d*)^2(4*s*)^2. Divalent titanium complexes can be made, but they are very unstable. Of greatest interest is the oxidation number 3, where the electronic configuration is [A](3*d*).

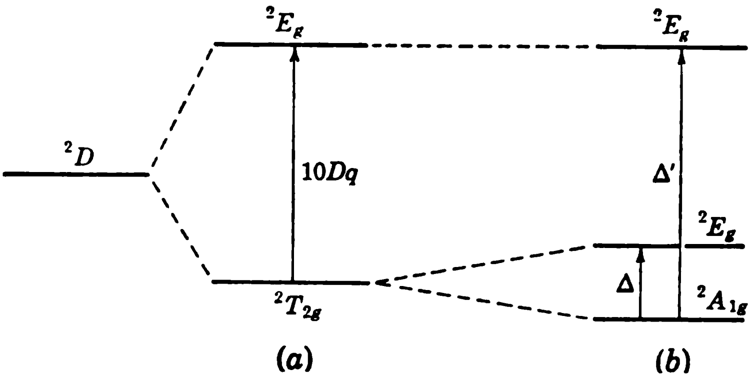


FIG. 10-1. Electronic states of Ti^{3+} complexes. (*a*) Octahedral field; (*b*) trigonal field of D_{3d} symmetry.

Ti^{3+} forms octahedral complexes. In water solution we have the violet ion $Ti(H_2O)_6{}^{3+}$ possessing a crystal field absorption band[1,2] at 20,300 cm^{-1} with a shoulder at 17,400 cm^{-1}. The maximum at 20,300 cm^{-1} is also found[3] in the crystal $CsTi(SO_4)_2 \cdot 12H_2O$ at room temperature. No displacement is found to occur by cooling the alum down to −192°C. The absorption band is interpreted as the crystal field band $^2T_{2g} \rightarrow {}^2E_g$. Since the energy difference of this transition is equal to $10Dq$, we get $Dq = 2030$ cm^{-1} for the $Ti(H_2O)_6{}^{3+}$ complex, Fig. 10-1. Further spectral studies of Ti^{3+} in various solvents have been made by Hartmann[4] and Jørgensen.[5]

The appearance of the double peak has been identified[6] as the manifestation of a Jahn-Teller effect in the excited ^2E_g state, since Van Vleck[7] has proved that the ground state $^2T_{2g}$ of Ti^{3+} is only slightly split under Jahn-Teller distortions. The oscillator strength[2] of the band, Fig. 10-1, $^2T_{2g} \rightarrow {}^2E_g$ is 1×10^{-4}. This value has been shown by Liehr and Ballhausen[8] to be consistent with a vibronic intensity mechanism.

Measurements of relaxation phenomena,[9,10] paramagnetic susceptibility,[11,12,51] and spectroscopic splitting factors[13–15] show that a trigonal field is superimposed upon the octahedral field in the titanium alum. This, together with the spin-orbit forces, causes a splitting of the ground state into a low-lying orbital singlet and a higher-lying doublet. As to the value of this splitting there is some doubt. Bleaney et al.[14] favor a value of some 30 cm^{-1}, whereas Dutta-Roy et al.[12] point out that the susceptibility values can be fitted with any value of Δ from 200 to 30 cm^{-1}.

The values of the g factors are[14] $g_{\parallel} = 1.25$ and $g_{\perp} = 1.14$. The theory of the splitting factors is given in Sec. 6-*f*. It is worthwhile to point out that the actual values can be fitted with some success to the formulas given there if a covalency factor $k \simeq 0.7$ is assumed.

The paramagnetic resonance spectrum has also been measured[16] for the brownish-red compound $\mathrm{KTi(C_2O_4)_2{\cdot}2H_2O}$. It is found that $g_{\parallel} = 1.86$ and $g_{\perp} = 1.96$. The complex cannot, however, possess a regular octahedral structure, and with an unknown structure no interpretation of these values is possible.

10-c. Vanadium

Vanadium has the electronic structure $[\mathrm{A}](3d)^3(4s)^2$. We are here interested in tetra-, tri-, and divalent vanadium with respectively one, two, and three $3d$ electrons.

Tetravalent Vanadium. The tetravalent vanadium ion is isoelectronic with the trivalent titanium. The best-known compound is probably the brown $\mathrm{VCl_4}$ possessing a tetrahedral structure.[17] Assuming only σ bonding to be present, the ground state will be a nonbonding ^2E state. As shown in Chap. 8, this molecule is subjected to a Jahn-Teller distortion, and an interesting comparison between $\mathrm{VCl_4}$ and $\mathrm{TiCl_4}$ can be made.[18] The ground state is, because of the Jahn-Teller effect, an orbital singlet. It is now found that the molecule is stabilized by some 0.7 kcal/mole and that the stable molecular configuration at low temperatures corresponds to an elongated tetrahedron. At higher temperatures the molecule can interconvert through a series of configurations.[18] It is, however, rather odd that no splitting[432] of the vibrational levels due to the symmetry lower than T_d is observed for $\mathrm{VCl_4}$.

The molecule has an absorption[19] band at 9000 cm^{-1} with a maximum molar extinction equal to 110. If this band is attributed[20] to the transition $^2E \rightarrow {}^2T$, we get $Dq = 900\ \mathrm{cm}^{-1}$. Since in the ionic approximation $Dq\ (\text{tet.}) = -\frac{4}{9}\ Dq\ (\text{oct.})$, we would expect a hypothetical Dq for an octahedral V^{4+} compound to be about 2000 cm^{-1}.

Tetravalent vanadium in an octahedral configuration is found in the blue $\mathrm{VO_2}$. The structure[27] is very much like the rutile ($\mathrm{TiO_2}$) structure but highly distorted, with one V—O bond much shorter than the rest. This seems to have some significance if we compare the tendency of V(IV) to form VO^{++} ions. V(IV) ions can replace titanium ions in rutile, and the paramagnetic resonance of the ion can be measured[21] in a diluted crystal. Each V(IV) ion is probably here subjected to a crystalline field of a compressed tetragonal character.

The g values are found to be

$$g_\perp = 1.914 \qquad g_\parallel = 1.957$$

With a spin-orbit coupling factor $\xi_d = 248\ \mathrm{cm}^{-1}$ found from atomic spectroscopy[22] but reduced to $\xi_d' = 150\ \mathrm{cm}^{-1}$ after Owen[23] we find, using formulas (6-82), that Δ, the tetragonal splitting of the lower triplet, is of the order of magnitude of $5000\ \mathrm{cm}^{-1}$. This means that it will be incorrect not to consider the mixing between t_{2g} and e_g. Assuming $\Delta' > \Delta \gg \xi_d'$ (see Fig. 10-1), we then get

$$g_\parallel = 2\left(1 - \frac{4\xi_d'}{\Delta'}\right) \qquad g_\perp = 2\left(1 - \frac{\xi_d'}{\Delta}\right)$$

By solving the equations for Δ' and Δ and using the above values of $g_\parallel$, $g_\perp$, and ξ_d', we get $\Delta' = 28{,}000\ \mathrm{cm}^{-1}$ and $\Delta = 3500\ \mathrm{cm}^{-1}$.

Tetravalent vanadium is also found in the blue vanadyl ion VO^{++}. This ion, and the complexes which can be made from it, also contains one unpaired electron. Some results from measurements of paramagnetic resonance can be found in the review paper by Bowers and Owen.[16] The g factors are all very close to 2, and measurements of the magnetic susceptibility[24,25] likewise indicate that the odd electron is in an orbital singlet.

An average g value of 1.962 has been reported[26] for solutions of VO^{++} but the spectra show small anisotropy in both the g tensor and in the hyperfine interaction. This indicates that the complex should be written $VO(H_2O)_n{}^{2+}$. As pointed out by Lundgren,[28] the metal ion in $VOSO_4(H_2O)_5$ seems to form VO_6 octahedra, and hence we take $n = 5$.

The spectrum of the blue solutions of $VO(H_2O)_5{}^{++}$ has been measured many times.[5,29–31] There is one band system in the visible with a maximum at $13{,}000\ \mathrm{cm}^{-1}$ and a shoulder at $16{,}000\ \mathrm{cm}^{-1}$. In the near ultraviolet a second band system appears with a shoulder at $41{,}700\ \mathrm{cm}^{-1}$. The interpretation of the first band system has been considered by Jørgensen,[5] who treats the molecule as a strongly tetragonally distorted octahedron, and by Furlani,[31] who considers only $C_{\infty v}$ point group symmetry. Of these two suggestions it seems to us that the point of view adopted by Jørgensen is by far the more realistic.

The bonding scheme will in our opinion probably look as follows,[418] Fig. 10-2. A very strong σ bond will be formed between the $(2p_z + 2s)$ hybrid of the oxygen and the $(3d_{z^2} + 4s)$ hybrid of the vanadium ion. Since, furthermore, the $2p_x$ and $2p_y$ orbitals on the oxygen will make a strong π bond with the $3d_{xz}$, $3d_{yz}$ orbitals on the metal ion, we need not wonder why VO^{++} is such a stable complex. The $(3d_{z^2} - 4s)$ hybrid, together with the orbitals $3d_{x^2-y^2}$ and $4p_x$, $4p_y$, and $4p_z$, are then just capable of five σ bonds directed in a tetragonal pyramid with the V^{4+} ion located at its base.

The first band system in VO^{++} is in our opinion due to the transitions $b_2 \rightarrow e_\pi^*$ and $b_2 \rightarrow b_1^*$. This is supported by intensity calculations[418] and band polarization measurements. The first intense ultraviolet band is further due to the transition $e_\pi{}^b \rightarrow b_2$. It is seen to be a perpendicularly polarized charge transfer band.[418,419] This is borne out by experiments.

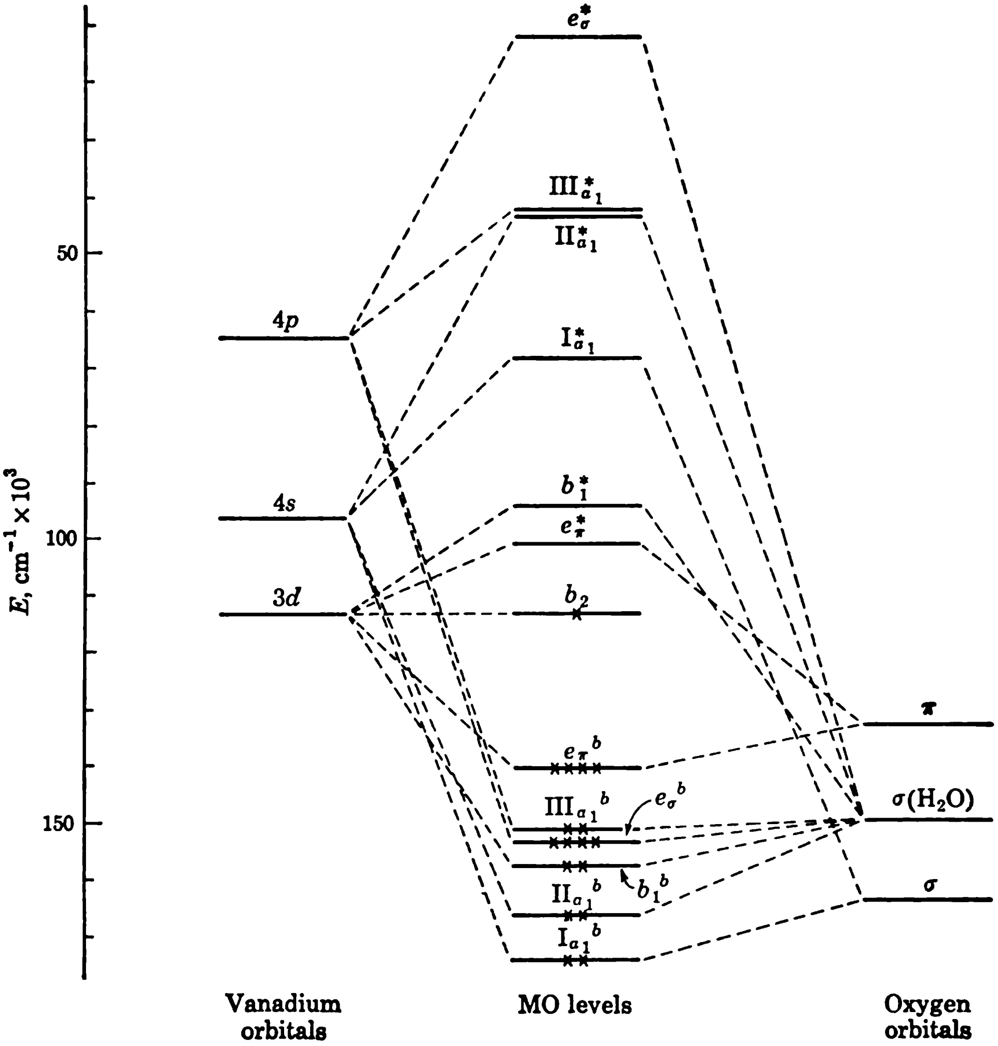


Fig. 10-2. Bonding diagram[418] for VO^{++}. In C_{4v} the σ orbitals from the water ligands transform as $2a_1$, b_1, and e. Of the oxygen orbitals the σ orbital transforms as a_1 and the π orbitals as e. The vanadium orbitals transform as $3d$ (a_1,b_1,b_2, and e), $4p$ (a_1,e), and $4s$ (a_1).

Trivalent Vanadium. The electronic configuration of V(III) is $[A](3d)^2$. The triplet terms are ^3F and ^3P. The various levels in a cubic crystal field can be seen schematically in Fig. 10-3.

The best-investigated system containing $(3d)^2$ in an octahedral coordination is undoubtedly vanadium corundum, made by substituting V^{3+} into Al_2O_3. The absorption spectrum of this complex has been investigated by Low[32] and by Pryce and Runciman.[33] Low found three strong bands located at 17,400 cm^{-1}, 25,200 cm^{-1}, and 34,500 cm^{-1}, which he interpreted[34,35] as the transitions ${}^3T_{1g} \rightarrow {}^3T_{2g}$, ${}^3T_{1g} \rightarrow {}^3T_{1g}$, and ${}^3T_{1g} \rightarrow {}^3A_{2g}$, that is, the strong-field assignments. In addition he also reported[32] weak bands at 21,000 cm^{-1}, 25,400 cm^{-1}, 29,300 cm^{-1}, and 30,150 cm^{-1}. These were assigned as transitions from the ground state ${}^3T_{1g}$ to the split components of the singlet states. In other words, they correspond to spin-forbidden transitions.

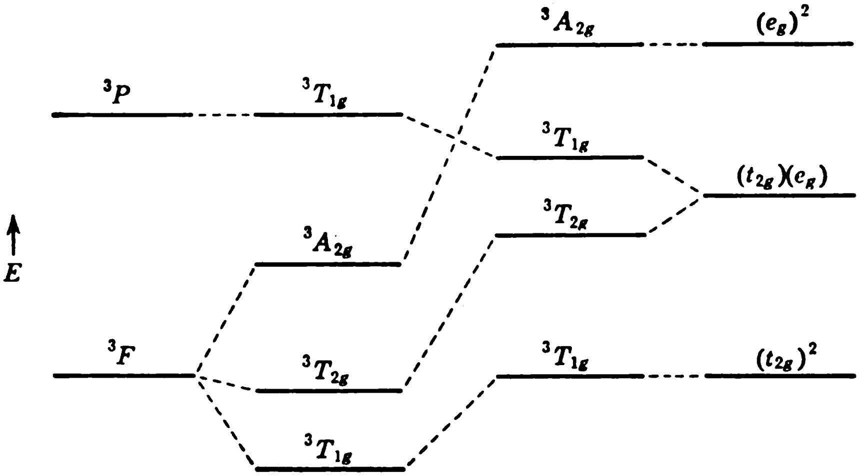


FIG. 10-3. Triplet terms of $(3d)^2$ in O_h field. To the left, the weak-field ordering of the levels; to the right, the strong-field levels.

In order to fit these latter bands to a theoretical crystal field scheme, Liehr and Ballhausen[36] performed a "complete" calculation of the energy levels including spin-orbit coupling and with full configuration interaction. The agreement between theory and experiment was found to be quite good.

The mechanism by which the "third" band ${}^3T_{1g} \rightarrow {}^3A_{2g}$ acquires intensity is treated by Ballhausen.[48] In the strong crystal field approximation this transition corresponds to a two-electron excitation and therefore ought (apart, of course, from parity restrictions) to be forbidden. However, it was shown that the presence of a trigonal field makes a configuration interaction possible with the result that the transition in question may "borrow" intensity from the ${}^3T_{1g} \rightarrow {}^3T_{1g}$ transition.

The excellent work of Pryce and Runciman[33] modifies the above assignments somewhat. Whereas the previously mentioned authors used a crystal field of O_h symmetry in their calculations, Pryce and Runciman included an additional trigonal component. Neglecting the spin-orbit coupling, they were able to account for the observed bands with reasonable accuracy. The presence of the trigonal field, of course, causes some of the crystal field levels to split up further. Let us for instance look at the ground state, Fig. 10-4. The trigonal field causes a large splitting of about 1200 cm^{-1} between $^3A_2$ and ^3E. The combined action of the trigonal field and of the spin-orbit coupling will split $^3A_2$ further up into two components with a separation of some 8 cm^{-1}. The presence of a magnetic field will finally split the upper doublet some tenths of a wave number. Pryce and Runciman[33] were able to measure directly the separation of the levels $M = 0$ and $M = \pm 1$, Fig. 10-4, in the absorption spectra, and a value of about 8 cm^{-1} was found. The polarization of some of the bands was also studied.[33,175] Furthermore, a g value slightly less than 2 was found for the level $M = \pm 1$. The paramagnetic resonance measurements of Zverev and Prokhorov[37] have confirmed that $g = 1.92$ and that the separation of the levels $M = 0$ and $M = \pm 1$ is some 10 cm^{-1}. The theory for the paramagnetic resonance in the V(III) complexes is given by Abragam and Pryce.[52]

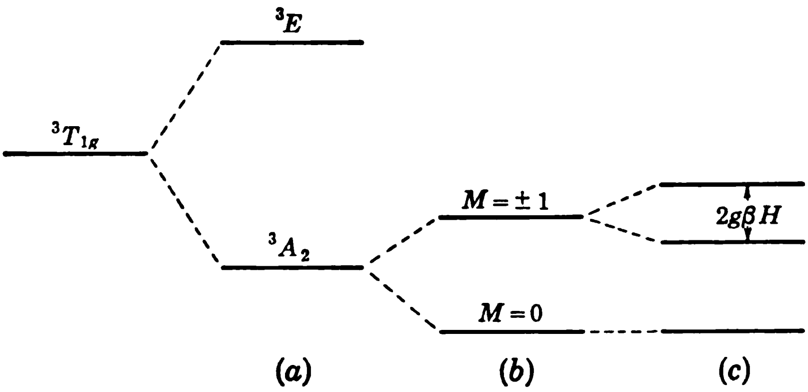


FIG. 10-4. Splitting of ground state of $(3d)^2$ in a trigonal field. (a) Trigonal splitting; (b) trigonal splitting with spin-orbit coupling included; (c) splitting in a magnetic field.

The only other vanadium(III) compound which has been thoroughly investigated is the vanadium alum. The absorption spectrum of the blue ion $V(H_2O)_6^{3+}$ has been extensively investigated by Hartmann et al.[38-42] The first two spin-allowed transitions corresponding to the excitations[35] $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g} \rightarrow {}^3T_{1g}$ were found at 12,400 cm^{-1} and 26,200 cm^{-1}, respectively. With a term separation $^3P - {}^3F$ equal to[22] 13,200 cm^{-1} we calculate[35] $Dq = 1785$ cm^{-1}. The third spin-allowed band should then be located at 34,100 cm^{-1}. It is not seen, however, owing to the strong charge transfer in the ultraviolet part of the spectrum. The values of the intensities for the absorption spectrum have been calculated by Ballhausen and Liehr.[49]

The magnetic properties of V(III) alum have likewise received some attention.[12,43-46,51] Mostly because of the difficulties of preparing and measuring the susceptibility of the vanadium alum, the exact values of the parameters occurring in the theory are still in some doubt. With a level scheme as given in Fig. 10-4 we will have (6-137)

$$\chi_{\parallel} = \frac{N\beta^2 2g_{\parallel}^2}{3kT}\left(1 - \frac{D}{3kT}\right)$$

for the temperature-dependent part of the susceptibility. The separation D between the levels $M = 0$ and $M = \pm 1$ is fitted with $D = 4.8$ cm^{-1}. There is also considerable doubt concerning the value of the temperature-independent term. The separation between ^3E and $^3A_2$, Fig. 10-4, appears to be some 1500 cm^{-1}.

Absorption spectra of other V(III) compounds include[42] $V(CON_2H_4)_6^{3+}$, $V(C_3H_2O_4)_3^{3-}$, and some vanadium(III) fluorides.[47] In this latter case it was found necessary to include a trigonal field in order to account for the spin-forbidden band $^3T_{1g} \rightarrow {}^1E_g$ found for VF_6^{3-} at 10,200 cm^{-1}. The spectrum of V^{3+} in a tetrahedral configuration is given by Gruen and Gut.[50]

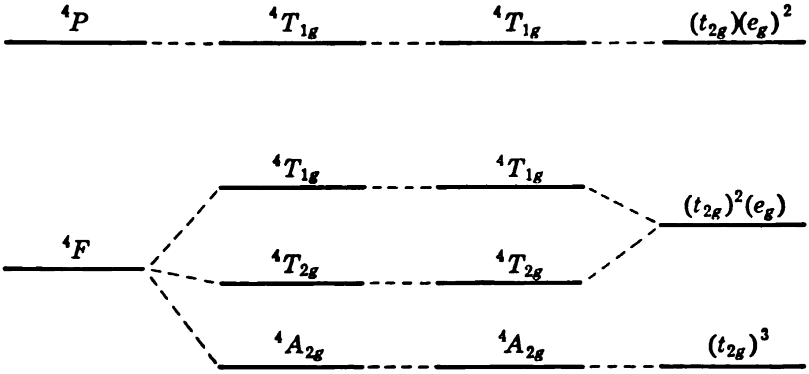


FIG. 10-5. Quartet terms of $(3d)^3$ in O_h field.

Divalent Vanadium. The electronic structure is $[A](3d)^3$. The quartet terms are ^4F and ^4P. In a cubic crystal field the various levels can be seen schematically in Fig. 10-5. The ground state is seen to be an orbital singlet. In the octahedral double group it will transform as Γ_8. However, because of the combined effect of the spin-orbit coupling and a small trigonal field component, it will split up in two Kramers doublets characterized by $S_z = \pm 3/2$ and $S_z = \pm 1/2$.

The paramagnetic resonance of the violet $V(NH_4)_2(SO_4)_2 \cdot 6H_2O$ has been measured by Bleaney et al.[53] The Tutton salt was diluted with the isomorphous Zn(II) salt, and the electronic parameters were fitted to a spin Hamiltonian

$$\mathcal{H} = g\beta HS + D(S_z^2 - \tfrac{1}{3}S(S+1)) + E(S_x^2 - S_y^2)$$

g_z was found to be 1.951 with $D = 0.158$ cm^{-1} and $E = 0.049$ cm^{-1}. The

g factor in a cubic field is given by

$$g = 2\left(1 - \frac{4\lambda}{10Dq}\right)$$

With[22] the spin-orbit coupling parameter $\lambda = 55\ \text{cm}^{-1}$ we get $10Dq \simeq 9000\ \text{cm}^{-1}$. The magnetic susceptibility for the field parallel to the z axis, Fig. 10-6, is given by

$$\chi_\parallel = N\,\frac{2\,\frac{9}{4}\,\frac{\beta^2 g_\parallel{}^2}{kT}\,e^{-D/kT} + 2\,\frac{1}{4}\,\frac{\beta^2 g_\parallel{}^2}{kT}\,e^{D/kT}}{2e^{-D/kT} + 2e^{D/kT}}$$

or

$$\chi_\parallel = \frac{N\beta^2 g_\parallel{}^2}{4kT}\left(5 - \frac{4D}{kT}\right)$$

For V^{++} dissolved in MgO Low[64] found $g = 1.980$.

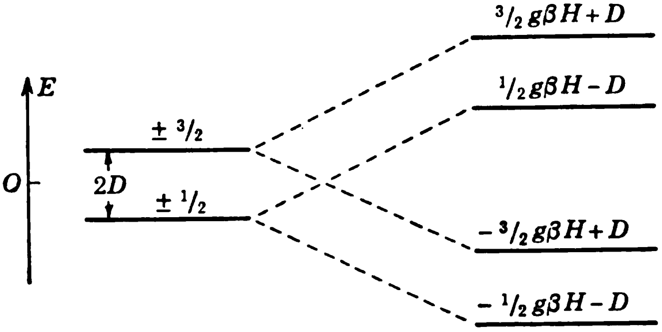


FIG. 10-6. Splitting of $^4A_{2g}$ in a magnetic field.

The absorption spectrum of the violet ion $V(H_2O)_6{}^{++}$ has been studied by Holmes and McClure,[65] Jørgensen,[178] and Bennett and Holmes.[146] Holmes and McClure showed that the previous interpretation of the spectrum by Owen[23] based upon older measurements was wrong. Two bands with extraordinarily small extinction coefficients ($\sim$0.5) were found at 11,800 cm^{-1} and 17,500 cm^{-1}.

The energies of the states are easy to find by the methods of Chap. 4.

$$\begin{aligned} E(^4A_{2g}) &= 3(-4Dq) = -12Dq \\ E(^4T_{2g}) &= 2(-4Dq) + 6Dq = -2Dq \end{aligned}$$

$$\begin{array}{c} ^4T_{1g}(F) \\ ^4T_{1g}(P) \end{array} \begin{vmatrix} 6Dq - E & 4Dq \\ 4Dq & x - E \end{vmatrix} = 0$$

where x is the separation between ^4F and ^4P. Taking the first band to represent the transition $^4A_{2g} \rightarrow {}^4T_{2g}$, we get $10Dq = 11{,}800\ \text{cm}^{-1}$. This value is of the same order of magnitude as found from the magnetic measurements. The transition $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ is then calculated to occur at 18,100 cm^{-1} if $x = E(^4P) - E(^4F)$ is taken to be[22] 11,300 cm^{-1}.

The transition $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ is thus expected to occur at 28,500 cm^{-1}. This was not observed because of charge transfer. Study of the crystal $VSO_4 \cdot 7H_2O$ revealed, however,[146] that for this system $Dq = 1200$ cm^{-1} with $E(^4P) - E(^4F)$ equal to 10,000 cm^{-1}. The third band $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ was observed at 27,800 cm^{-1}.

10-d. Chromium

Chromium has the electronic structure $[A](3d)^5(4s)$. By far the most interesting oxidation state is Cr(III) possessing the electronic structure $[A](3d)^3$; indeed, the amount of work done with this ion is quite staggering. Let us first consider the absorption spectra of Cr(III) with various ligands.

Trivalent Chromium. Assuming a cubic octahedral field to be present, the electronic ground state will be a $^4A_{2g}$ state arising from the strong-field configuration $(t_{2g})^3$. Other states springing from this configuration are ^2E_g, $^2T_{1g}$, and $^2T_{2g}$. The next strong-field configuration is $(t_{2g})^2(e_g)$, producing the quartet states $^4T_{2g}$ and $^4T_{1g}$. The energies of these states are easily calculated to be

$(t_{2g})^3\ {}^4A_{2g}$	$3F_0 - 15F_2 - 72F_4 - 12Dq$
$(t_{2g})^3\ {}^2E_g,\ {}^2T_{1g}$	$3F_0 - 6F_2 - 12F_4 - 12Dq$
$(t_{2g})^3\ {}^2T_{2g}$	$3F_0 + 28F_4 - 12Dq$
$(t_{2g})^2\ (e_g)\ {}^4T_{2g}$	$3F_0 - 15F_2 - 72F_4 - 2Dq$
$(t_{2g})^2\ (e_g)\ {}^4T_{1g}$	$3F_0 - 3F_2 - 132F_4 - 2Dq$

The energy scheme of the quartet levels is pictured in Fig. 10-5; it is, of course, equivalent to that of the isoelectronic V(II) ion.

The absorption spectrum of the violet hexaquo chromium(III) ions shows[56] two "strong" absorption bands with $\epsilon \simeq 15$ placed at 17,400 cm^{-1} and 24,500 cm^{-1}. Interpreting these as the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, we get

$$\Delta E(^4T_{2g} - {}^4A_{2g}) = 10Dq = 17{,}400 \text{ cm}^{-1}$$
$$\Delta E(^4T_{1g} - {}^4A_{2g}) = 10Dq + 12(F_2 - 5F_4) = 24{,}500 \text{ cm}^{-1}$$

and we have immediately that for $Cr(H_2O)_6^{3+}$ $Dq = 1740$ cm^{-1} and $F_2 - 5F_4 = 590$ cm^{-1}.

The measurements by Spedding and Nutting[57,58] on the absorption spectrum of the violet chrome alum $KCr(SO_4)_2 \cdot 12H_2O$ showed further two series of sharp lines at low temperatures. One series was placed at 15,000 cm^{-1}, the other at 22,000 cm^{-1}. These lines [the first set of which can also be seen in an aqueous solution of Cr(III)] are taken to represent the spin-forbidden transition $^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}$ and $^4A_{2g} \rightarrow {}^2T_{2g}$. With

$$\Delta E(^2E_g, {}^2T_{1g} - {}^4A_{2g}) = 3(3F_2 + 20F_4) = 15{,}000 \text{ cm}^{-1}$$

and $$\Delta E(^2T_{2g} - {}^4A_{2g}) = 5(3F_2 + 20F_4) = 22{,}000 \text{ cm}^{-1}$$

we get respectively

$$3F_2 + 20F_4 = 5000 \text{ cm}^{-1}$$
$$3F_2 + 20F_4 = 4400 \text{ cm}^{-1}$$

The results are seen to be fairly consistent. By taking an average value of $3F_2 + 20F_4 = 4700 \text{ cm}^{-1}$ together with the value of $F_2 - 5F_4 = 590 \text{ cm}^{-1}$ we obtain the numbers $F_2 = 1000 \text{ cm}^{-1}$ and $F_4 = 80 \text{ cm}^{-1}$. We have here only considered the diagonal elements in the strong perturbation matrix of $(3d)^3$. The inclusion of the nondiagonal elements will alter the above numerical estimates somewhat, though not significantly. The complete perturbation matrices for $(3d)^3$ in O_h have been given by Finkelstein and Van Vleck.[59] This paper is remarkable because it was the first attempt to explain the absorption spectrum of a complex ion by using a crystal field model, and it was just the spin-forbidden transition found at 15,000 cm^{-1} which was discussed. Preceding this paper Van Vleck considered[60] the Zeeman effect of these lines, using the data provided by Spedding and Nutting.[58] Van Vleck showed conclusively that the lines observed by Spedding and Nutting were due to quartet-doublet transitions.

In the pure strong O_h crystalline field we notice that ^2E_g and $^2T_{1g}$ are degenerate. This, however, does not hold true when we consider that spin-orbit forces, not to speak of lower crystalline fields, are present. At low temperatures $KCr(SO_4)_2 \cdot 12H_2O$ shows[57,58] three strong absorption lines placed at 14,926 cm^{-1}, 14,932 cm^{-1}, and 14,858 cm^{-1}. The number of lines changes both with temperature and with the composition of the alum; the $RbCr(SO_4)_2 \cdot 12H_2O$ possesses, for example, only two sharp lines.

The theoretical explanation of these facts is by no means clear. The states ^2E_g and $^2T_{1g}$ yield five Kramers doublets, all presumed to occur around 15,000 cm^{-1}. In an electric dipole field we would then expect fifteen lines if the transition was made allowed by exciting a quantum of the three odd vibrations τ_{1u}, τ_{1u}, and τ_{2u}. Since no such number is observed, we must conclude that the lines are either allowed electric dipole transitions or magnetic dipole transitions.

Assuming that the transitions to ^2E_g and $^2T_{1g}$ "steal" all of their intensity from the first spin-allowed transition $^4A_{2g} \rightarrow {}^4T_{2g}$ we get, using (8-48),

$$\frac{f(^4A_{2g} \rightarrow {}^2E_g)}{f(^4A_{2g} \rightarrow {}^2T_{1g})} = \frac{|(^4T_{2g}|\mathcal{H}_{\text{spin-orbit}}|^2E_g)|^2}{|(^4T_{2g}|\mathcal{H}_{\text{spin-orbit}}|^2T_{1g})|^2} = \frac{16\xi^2}{6\xi^2} = \frac{8}{3}$$

This calculation has utilized the strong-field wave functions. We therefore expect[69] that the ^2E_g levels would be about twice as strong as the $^2T_{1g}$ levels in case they lie close together.

Hartmann and Schmidtke[68] have tried to explain the chrome doublets as due solely to the splitting of $^2T_{1g}$. However, since their calculations are dependent on their choice of the "weak" wave functions for $^2T_{1g}$ and ^2E_g, the validity of their results is open to question.

To add to the confusion, the Zeeman splitting of the three levels, as reported by Spedding and Nutting,[58] yields an isotropic g factor close to 2. This cannot be explained[70] by assuming the levels to be ^2E_g. We have thus apparently arrived at a dead end.

The way out is, however, nearly certain to be a consideration of the vibronic problem.[67] Hence, in order to connect the Jahn-Teller effect of the excited states with the optical transitions to said states, one must treat the dynamical Jahn-Teller problem as described by Longuet-Higgins et al.[71,183,187,251] This is not going to be an easy task.

If next we look at the quartet energy levels as seen from the intermediate-field point of view, we get the following expressions for the energy levels:[59]

$$E(^4A_{2g}) = -12Dq \qquad E(^4T_{2g}) = -2Dq$$

$$E(^4T_{1g}) = \begin{vmatrix} 6Dq - E & 4Dq \\ 4Dq & x - E \end{vmatrix} = 0$$

where x is the separation of the ^4F and ^4P levels within the Cr(III) complex. Dq for the complex $Cr(H_2O)_6{}^{3+}$ is, of course, still 1740 cm^{-1}, and by using this value together with the value of 24,500 cm^{-1} for the second band, we can calculate x. This has been done by Owen,[23] who finds $x = 10{,}200$ cm^{-1}. This is considerably less than the value of a some 13,800 cm^{-1} found by atomic spectroscopy[22] for the gaseous ion. This reduction of term distances is very characteristic, and, as shown in the preceding chapter, has been interpreted as due to the presence of some degree of covalency.[23,61]

The "third" spin-allowed transition due to the transition $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ can now be calculated. It should occur at some 38,000 cm^{-1}, and experimentally it is found[62] at 38,000 cm^{-1}. This fact is thus a very good confirmation of the theory.

The variation of the band intensity with temperature for the spin-allowed bands in chrome alum has been investigated by Holmes and McClure.[65] The effect of substitution of D_2O for H_2O in $Cr(H_2O)_6{}^{3+}$ has been considered by Halpern and Harkness[63] and Bigeleisen.[64] Both the position of the maxima and the intensity of the spin-allowed bands are found to undergo minor changes.[63] These are explained[64] by the change of the vibrational levels due to the heavier ligand. The attempts which have been made to calculate $10Dq$ from first principles for chrome alum have been described in Sec. 7-*b*.

Turning our attention toward the magnetic features of chrome alum, we get of course the same g factor formulas as found for V^{++}, again assuming a crystal field of symmetry O_h: $g = 2(1 - 4\lambda/10Dq)$. The $^4A_{2g}$ ground state will likewise split under the combined effect of a spin-orbit coupling and a small trigonal field component into the pairs $M_s = (\pm\frac{1}{2})$ and $(\pm\frac{3}{2})$. This effect has been treated in some detail in Sec. 6-*g*. The classic work dealing with the bulk magnetic susceptibility of chrome alum is that of

Schlapp and Penney.[65] For the paramagnetic resonance features reference is made to Davis and Strandberg.[66]

The absorption (and emission) spectra of Cr^{3+} dissolved in Al_2O_3 and MgO have been investigated very thoroughly.[67,70,72–83] In these lattices Cr^{3+} is surrounded by six $O^{=}$ ions. The color of the crystal is red. The field is predominantly octahedral, but a strong trigonal field component is present. The absorption spectrum of ruby (Cr^{3+}, Al_2O_3) is therefore quite similar to that of the Cr alum. Two broad bands found[74] at 18,000 cm^{-1} and 25,000 cm^{-1} are attributed to the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, respectively. These bands are remarkably anisotropic; spectral measurements using polarized light showed[83] that each band is composed of two broad bands, one of the components being perpendicularly polarized with respect to the trigonal axis.

The polarizations show that the $^4T_{1g}$ and $^4T_{2g}$ bands each are split into a ^4E and a ^4A state; the ^4A state is in both cases found at the shorter wavelength side of the corresponding perpendicular transition.[72] The splitting amounts to some 500 cm^{-1}. The polarizations of these bands show that a static asymmetric field of T_{1u} symmetry is the main intensity-giving factor.[72] The $^4T_{2g}$ state shows further evidence for a vibronic coupling. Both Greschushnikov and Feofilov[80] and Ford and Hill[76] have found a simple progression of the ϵ_u vibrational mode of the corundum lattice superimposed upon the ^4E band. This is a clear indication of a Jahn-Teller distortion of the ^4E state of Cr^{3+} in ruby.

Sharp lines are found in the ruby spectrum at 24,418 cm^{-1}. The first doublet is interpreted[72,73] as the $^4A_{2g} \rightarrow {}^2E_g$ transitions, the second group of lines being assigned to $^4A_{2g} \rightarrow {}^2T_{2g}$. These assignments were made certain by the calculations of their intensity ratios as well as their Zeeman features.[70] The $^4A_{2g} \rightarrow {}^2T_{1g}$ transition is very illusive. It is calculated to appear around 15,000 cm^{-1}, but Ford,[77] among others, could find no evidence for such a transition; the lines which are observed in this region of the spectrum were assigned to be vibrational satellites of the ^2E_g state. This opinion is not shared by Low,[81] who identified the same lines as the missing $^4A_{2g} \rightarrow {}^2T_{1g}$. Some of the lines may also be due to a spin-spin coupling between the Cr^{3+} ions.[430] Clearly, more work is needed in order to clarify the situation. The spectral shift toward the blue found in ruby as compared to the spectrum of chrome alum has been interpreted by Orgel[82] as due to the compression of the Cr^{3+} ion by the corundum lattice.

Direct measurements of the g factor of the ^2E_g state in ruby have been reported by Geschwind et al.[88] The transition probabilities between the Zeeman components of this state have been treated by Clogston.[89]

The absorption spectrum of Cr^{3+} in a MgO lattice shows much the same features as the ruby spectrum.[84] The three spin-allowed bands are found at 16,200 cm^{-1}, 22,700 cm^{-1}, and 29,700 cm^{-1}, with a spin-forbidden line at some 14,319 cm^{-1}. This line has been shown[85] to be due to a magnetic dipole transition. Both the paramagnetic resonance spectrum and the absorption spectrum of Cr^{3+} in a spinel structure have likewise been investigated.[86,87]

Turning our attention to the absorption spectra of Cr^{3+} complexes in solution, both Schläfer[90] and Schäffer[91] have collected appropriate references. We quote[90] that for the yellow $Cr(NH_3)_6^{3+}$ the "doublet" band is found at 15,300 cm^{-1} with the first two spin-allowed bands located at 21,500 cm^{-1} and 28,500 cm^{-1}. The g factor is found to be[92] $g = 1.97$.

$Cr(en)_3^{3+}$, where en stands for ethylenediamine, is yellow and has[90] two spin-forbidden bands at 15,100 cm^{-1} and 15,600 cm^{-1}. The first two spin-allowed bands occur at 21,880 cm^{-1} and 28,490 cm^{-1}. The g value of the complex[93] is very close to 2, the zero-field splitting being $\sim$0.3 cm^{-1}. The dichroism has been measured by Yamada and Tsuchida.[94] As discussed in Chap. 8, this is consistent with the assumption of a crystalline field of D_3 symmetry.

For the reddish-violet ion $Cr(ox)_3^{3-}$ we find a pattern similar to that for $Cr(en)_3^{3+}$. Dq is about[95] 1750 cm^{-1}, and the small spin-forbidden band is located at 14,350 cm^{-1}. The zero-field splitting is[93] $\sim$0.9 cm^{-1}. Cr(III) *tris*-acetylacetone is a very interesting compound. The g factor is found to be[93] 1.983, the zero-field splitting being some 1.18 cm^{-1}. With $g = 2.002 - 8\lambda/10Dq$ and with[97] $10Dq \simeq 17{,}500$ cm^{-1} we get a value of $\lambda \simeq 40$ cm^{-1}. Using the formula for the zero-field splitting given in Sec. 6-*f*, we then find that the $^4T_{2g}$ state should be split some 12,000 cm^{-1}. This is a quite fantastic number, especially since measurements on a crystal using polarized light[97] indicate that the absorption band found at some 17,500 cm^{-1} is split only some 900 cm^{-1}. Obviously something is wrong since without doubt the band at 17,500 cm^{-1} is due to the transition $^4A_{2g} \rightarrow {}^4T_{2g}$. The reddish-violet Cr(III) hexafluoroacetylacetonate has, finally, an even larger zero-field splitting[98] of 1.40 cm^{-1}, but a g factor similar to that of Cr(III) acetylacetonate. Consequently, a closer study seems to be called for here.

The absorption spectra of Cr(III) complexes with lower symmetry than O_h have been investigated by Hartmann and Kruse.[99] *Trans*- and *cis*-CrX_4Y_2 complexes were considered. As noticed in Sec. 5-*c*, the symmetry groups of cis and trans complexes are both in practice D_{4h}, and we expect the splitting of a trans complex to be twice that of a cis complex. This is very nearly what the experiments show.[100,101]

Divalent Chromium. The electronic structure of the ion is $[A](3d)^4$, and the ground state is ^5D. This is the only quintet state.

In a weak octahedral crystal field this level will split into a ^5E_g and a $^5T_{2g}$ state, the $^5E_g(t_{2g})^3(e_g)$ state being the lowest. However, in a strong crystalline field of octahedral symmetry the ground state will be $^3T_{1g}(t_{2g})^4$.

The energies of the two different ground states are

$$E(^5E_g) = -6Dq - 21F_2 - 189F_4$$
$$E(^3T_{1g}) = -16Dq - 15F_2 - 44F_4$$

Thus for $10Dq < 6F_2 + 145F_4$ we will have the quintet ground state, but if the reverse holds true, the $^3T_{1g}$ will be lowest. This latter case has been realized[25] in $K_4Cr(CN)_6{\cdot}3H_2O$.

The blue complex $Cr(H_2O)_6^{++}$ shows one absorption band[65,104] located at 14,000 cm^{-1}. This is attributed to the transition $^5E_g \rightarrow {}^5T_{2g}$, Fig. 10-7.

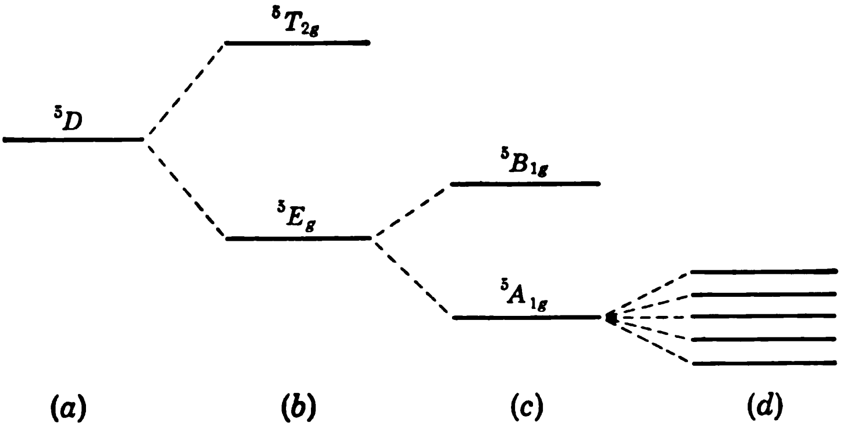


FIG. 10-7. Schematic energy levels of $(3d)^4$ in a weak field. (a) Gaseous ion; (b) cubic crystalline field; (c) tetragonal crystalline field; (d) spin-orbit coupling included.

With the ground state an orbital doublet in O_h, we would expect a strong Jahn-Teller distortion to take place. The evidence for this is also convincing; Pecsok and Bjerrum[102] found that only two molecules of ethylenediamine could be taken up in aqueous solution. This was interpreted as due to a strong tetragonal distortion. The crystal structure of CrF_2 shows[103] also that the structure is highly tetragonally distorted, four Cr—F bonds being some 2.0 A and the last two being some 2.4 A. A rough calculation of the Jahn-Teller splitting of the ^5E_g state indicates[6] that it is some 6000 cm^{-1}.

The magnetic features of various Cr(II) complexes have been studied by Asmussen.[25] The effective number of Bohr magnetons in the dark-blue $Cr(CN)_6^{4-}$ is, for example, found to be 3.22. This is, of course, somewhat higher than the "spin-only" value of 2.83, but Kotani[105] has shown that this is due to a large orbital contribution. The number of Bohr magnetons found in the high-spin complexes is, on the other hand, close to the spin-only value, since all of the orbital momentum is quenched. The susceptibility of $CrSO_4{\cdot}6H_2O$, for instance,[106] shows that the Weiss law is obeyed with an effective Bohr number of 4.82. With a spin Hamiltonian of the form

$$\mathcal{H} = D(\hat{S}_z^2 - \tfrac{1}{3}S(S+1)) + (g_\parallel H_\parallel \hat{S}_z + g_\perp H_\perp \hat{S}_x + g_\perp H_\perp \hat{S}_y)\beta$$

we get for the principal susceptibilities (putting $N\beta^2/3k = \tfrac{1}{8}$)

$$\chi_\parallel = \frac{3g_\parallel^2}{4T}\left(1 - \frac{7D}{5kT}\right) \qquad \chi_\perp = \frac{3g_\perp^2}{4T}\left(1 - \frac{7D}{10kT}\right)$$

From measurements of the paramagnetic resonance spectrum of $CrSO_4 \cdot 5H_2O$ Ono[107] found $D = 2.24$ cm^{-1}, $g_\perp = 2.00$, and $g_\parallel = 1.96$. The theoretical values for the g factors have been given by Abragam and Pryce.[52]

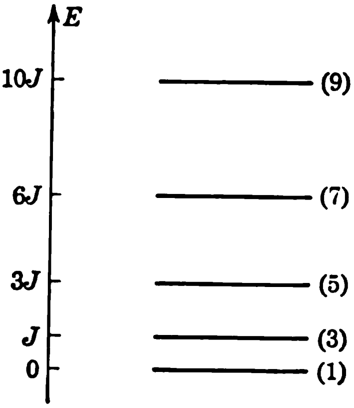


FIG. 10-8. Schematic level scheme for a spin-spin interaction of the form $\mathcal{H}^{(1)} = -J\mathbf{S}_1 \cdot \mathbf{S}_2$ with $S_1 = S_2 = 2$. The numbers give the degeneracy of the levels.

The case of the red chromous acetate is extremely interesting. King and Garner[108] found that the compound contained no unpaired electrons, and they concluded from this that the Cr(II) ion was tetrahedrally coordinated. This was incorrect, however, since Van Niekerk and Schoening[109] showed by X-ray measurements that chromous acetate monohydrate is a binuclear complex held together by acetate bridges, each Cr^{++} having sixfold coordination. The short Cr—Cr distance indicated the existence of a strong interaction between adjacent Cr atoms, and an explanation along these lines was soon given by Furlani[110] and Figgis and Martin.[111]

With a spin-spin interaction of the form $\mathcal{H}^{(1)} = -J\mathbf{S}_1 \cdot \mathbf{S}_2$ we have found the level scheme in Sec. 6-*h*. With $S_1 = S_2 = 2$ we get five levels placed as in Fig. 10-8. The magnetic susceptibility calculated per Cr(II) ion is easily found to be

$$\chi = \frac{N}{2}\frac{2g^2\beta^2}{3kT}\frac{1}{1 + \tfrac{1}{3}e^{J/kT}}$$

where g is the g factor for the first excited state ($E = J$) and where we have neglected all other excited states. This is permissible, since J is found to some 700 cm^{-1}; i.e., with[110] $\chi = 113 \times 10^{-6}$ at $T = 300$°K and assuming that to the first approximation $g = 2$, we get $J = 770$ cm^{-1}.

Monovalent Chromium. The electronic structure of this ion is $[A](3d)^5$ with a ground state of ^6S. Cr(I) presumably occurs in crystals of NaF where Cr^{3+} ions have been added to the melt and irradiated. The ground state would be a $^6A_{1g}$ state.[112] Griffith, Lewis, and Wilkinson[113] have further made the bright-green compound $K_3[Cr(CN)_5NO]H_2O$. From the magnetic susceptibility, which corresponds to one unpaired electron, they concluded that the compound contains Cr^+ and NO^+. The optical spectrum and the electron spin resonance have been measured by Bernal and Harrison.[114] The g value was found to be very close to 2. The absorption spectrum showed three optical transitions located at 13,700 cm^{-1}, 22,000 cm^{-1}, and at 30,000 cm^{-1}. Their[114] assignments of these transitions differ, however, from what one would expect;[115] a more realistic calculation indicates the following ordering of the bands in the C_{4v} symmetry

$$^2B_2(e)^4(b_2)^1 \rightarrow {}^2B_1(e)^4(b_1)^1 \qquad 14{,}000 \text{ cm}^{-1}$$
$$^2B_2(e)^4(b_2)^1 \rightarrow {}^2E(e)^3(b_2)^1(b_1)^1 \qquad 22{,}000 \text{ cm}^{-1}$$

There are several excited states which could account for the observed absorption at 30,000 cm^{-1}; a possible assignment has been given by Gray et al.[433] The level scheme is identical to that of VO^{++}, Fig. 10-2, only with e_π^* placed above $1a_1^*$. This reversal is due to the presence of the empty antibonding π(NO) level.

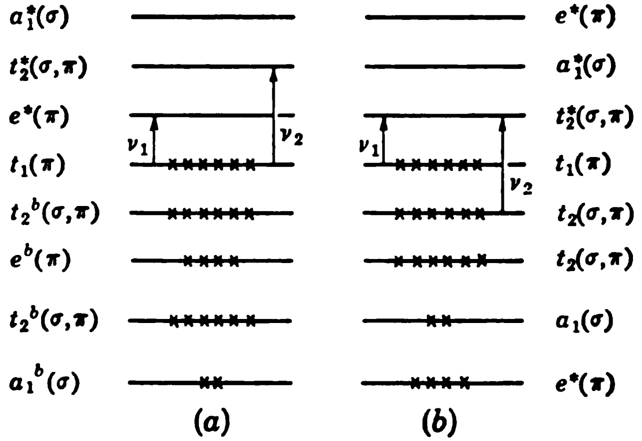


FIG. 10-9. Level schemes for the tetrahedral CrO$_4^-$ complex. (a) Proposal of Ballhausen and Liehr;[117] (b) proposal of Wolfsberg and Helmholz.[116]

Tetrahedral and Binuclear Chromium Complexes. Tetrahedral chromium complexes are known only for chromium in the oxidation state six. The best-known compound is the yellow chromate ion CrO$_4^-$. The electronic structure of this ion has been considered by Wolfsberg and Helmholz[116] and by Ballhausen and Liehr.[117] Wolfsberg and Helmholz performed a simplified MO calculation and proposed the following electronic assignment for the ground state, Fig. 10-9:

$$^1A_1\text{:} \quad (e)^4(t_2)^6(a_1)^2(t_2)^6(t_1)^6$$

The first excited orbital should be of symmetry (t_2).

This result has been criticized by Ballhausen and Liehr[117] on the grounds that the stabilization due to π bonding of the e orbital is too great to be reasonable. Instead, they proposed the following electronic ground state:

$$^1A_1\text{:} \quad (a_1)^2(t_2)^6(e)^4(t_2)^6(t_1)^6$$

The first excited orbitals in their level scheme are of (e) and (t_2) symmetry.

The chromate ion exhibits two absorption bands in the visible placed at 27,000 and 36,500 cm^{-1}, respectively.[118] Since these bands are fairly strong with oscillator strengths $f \simeq 0.1$, they must be assigned to the only orbitally allowed transition $^1A_1 \rightarrow {}^1T_2$. In both level schemes excited states of symmetry $^1T_2$ are available, and the calculation of oscillator strengths cannot decide between the possibilities, since both assignments lead to reasonable results. Experimental work on the isoelectronic complex MnO_4^- shows however,[119] that by adding one electron to MnO_4^-, to obtain $MnO_4^{=}$, the extra electron is accommodated in an e state. This makes it likely that the Ballhausen and Liehr level scheme is also the one found in $CrO_4^{=}$. The calculation of the band intensities shows in both cases that π bonding is of great importance for $CrO_4^{=}$. From a chemical point of view this is, of course, extremely reasonable.

Level diagrams have likewise been given[120] for CrO_3F^- and CrO_2Cl_2. The lower symmetry of these molecules, however, makes the assignments more tentative than is the case for $CrO_4^{=}$.

We next turn our attention toward the binuclear chromium complexes. There are essentially two ways of describing the electronic features of these molecules. One is a molecular orbital description similar to the one given by Dunitz and Orgel[121] for the complex anion $[Cl_5Ru—O—RuCl_5]^{4-}$.

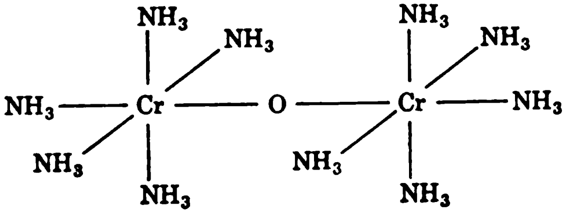


FIG. 10-10. Assumed molecular geometry for $Cr_2O(NH_3)_{10}^{4+}$.

Consider the blue complex $[(NH_3)_5Cr—O—Cr(NH_3)_5]^{4+}$ called decammine-μ-oxo-dichromium(III) or "basic rhodo chromium." Let us assume that the Cr—O—Cr grouping is linear, Fig. 10-10. Each Cr^{3+} is then in a crystal field of C_{4v} symmetry; using the σ bonds from all six ligands, only the metal orbitals d_{xz}, d_{yz}, and d_{xy} are nonbonding. In C_{4v} these orbitals transform as E and B_2. With two chromium ions in D_{4h} we can then form the orbitals E_u, E_g, B_{2g}, B_{2u}, and since the chromium atoms are rather far removed from each other, we would expect these orbitals to be nearly degenerate, pair by pair.

However, interaction with the π orbitals on the oxygen which transform as E_u removes this state of affairs for the E_u, E_g pair, and we get a strong bonding and antibonding E_u orbital:

$$(E_u^b)[(E_g)(B_{2g})(B_{2u})](E_u^*)$$

With 10 valence electrons (4 from the oxygen and 6 from the two chromium ions) we would then expect an electronic configuration $(E_u{}^b)^4[(E_g)^4(B_{2g})^1(B_{2u})^1]$; that is, the complex should have two unpaired spins. It is, however, found to be nearly diamagnetic at room temperature.[91,122–124] The susceptibility of the complex as a function of temperature shows, furthermore, an extremum point at some 80°K. This is a clear indication of the fact that the ground state is not the only occupied state, but that other states with energies comparable to kT are present. If this is the case, we cannot, of course, expect the susceptibility to follow a Curie-Weiss law. One of these low-lying states could, for instance, be $(E_u{}^b)^4[(E_g)^4(B_{2g})^2(B_{2u})^0]$, but there are, of course, many other possibilities. Furthermore, we have assumed the complex to have D_{4h} symmetry, and any deviation from this symmetry could also alter our level scheme.

The other way of treating the magnetism of these compounds is to assume a spin-spin interaction of the form $-J\mathbf{S}_1 \cdot \mathbf{S}_2$, where S_1 and S_2 are the spins on the two chromium ions, respectively. If we take χ_M to be the molar susceptibility of the complex which contains two gram ions of Cr^{3+}, we get very easily, (see Sec. 6-*h*)

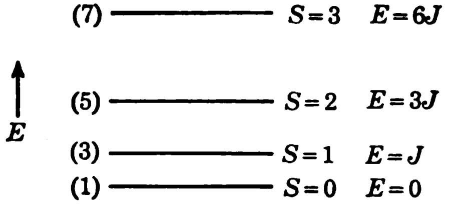


FIG. 10-11. Spin-spin coupling with $S_1 = S_2 = \frac{3}{2}$. Numbers in parentheses give the degeneracies.

$$\chi_M = \frac{N\beta^2 g^2}{3kT}\,\frac{6x^5 + 30x^3 + 84}{x^6 + 3x^5 + 5x^3 + 7}$$

with $x = e^{J/kT}$. Putting $g = 2$ and $N\beta^2/3k = \frac{1}{8}$ we finally have

$$\chi_M = \frac{1}{T}\,\frac{3x^5 + 15x^3 + 42}{x^6 + 3x^5 + 5x^3 + 7}$$

In order to account for the experimental results for the basic rhodo chromium, Kobayashi et al.[123] found that J should be greater than 140 cm^{-1}. This is a very large spin-spin interaction, since other single-bridged binuclear chromium compounds usually have[124] a value of J of about 20 cm^{-1}. As suggested by Earnshaw and Lewis,[124] the small interaction may be associated with a metal-oxygen-metal bond angle of the order of 120°, rather than 180° as may occur in the basic rhodo salt. The main point in their argument is that a linear system, owing to stronger π bonding in the bridge, should exhibit a greater spin-spin interaction.

The spectral features of binuclear chromium complexes seem to support the above point of view. Whereas the spectrum[91] of the red compound $[(NH_3)_5CrOHCr(NH_3)_5]^{5+}$ is quite analogous to the spectra of its constituents, the blue basic salt $[(NH_3)_5CrOCr(NH)_3)_5]^{4+}$ shows[91] four very sharp peaks in the ultraviolet region. Even though some of these peaks may be "hot," i.e., originating from an excited state, the absorption spectra of the "acid" and "basic" rhodo salt are quite different. Thus both the spectral and the magnetic evidence points to two different structures for the compounds under discussion, and the most likely interpretation seems then to be the nonidentity of the metal-oxygen-metal bond angles.

10-e. Manganese

Manganese has the electronic structure $[A](3d)^5(4s)^2$. We shall consider Mn^{++}, Mn^{3+}, Mn^{4+}, and Mn^{7+}, the last oxidation state occurring formally in MnO_4^-.

Divalent Manganese. The electronic ground state of the Mn^{++} ion is ^6S. No other sextet levels are present. In the weak-field limit, assuming octahedral configuration, the ground state will be $(t_{2g})^3(e_g)^2$, possessing five unpaired spins. In the strong-field limit it will be $(t_{2g})^5$ with only one unpaired spin. One could now ask if a configuration like $(t_{2g})^4(e_g)^1$ with three unpaired spins could be a ground state in some "intermediate" field. Explicit calculations, as reflected in the level diagram given by Tanabe and Sugano[125–127] show, however, that this will never take place.

In a tetrahedral crystal field, the ground state will, of course, again be $(e)^2(t_2)^3$ in the weak-field limit, and in the strong tetrahedral field it will be $(e)^4(t_2)^1$, again possessing one unpaired spin. This latter situation has, however, not yet been reported.

In a high-spin octahedrally coordinated Mn^{++} complex the lowest configuration $(t_{2g})^3(e_g)^2$ gives rise to the ground state $^6A_{1g}$. Since this is the only sextet level present, all of the absorption bands must therefore be spin-forbidden transitions. This fact is reflected in the very low extinction coefficients observed for these bands.

Consider for instance the absorption spectrum of[55,96,128–131,148] the pink $Mn(H_2O)_6^{++}$. Table 10-1 gives the measured and calculated values for the absorption peaks of Mn^{++} dissolved in perchloric acid.[131]

The assignments of the bands can, of course, be made only after the level diagram for d^5 has been calculated. The perturbation matrices for the various states are found to contain no diagonal terms, and the splitting of the various levels are therefore solely determined by the nondiagonal terms.

TABLE 10-1. CALCULATED AND EXPERIMENTAL VALUES FOR THE ABSORPTION BANDS OF $Mn(H_2O)_6^{++}$
(After Heidt et al.[131])

State	Calculated energy, cm^{-1}	Experimental energy, cm^{-1}
$^4T_{1g}(^4G)$	19,400	18,870
$^4T_{2g}(^4G)$	22,800	23,120
$^4E_g, ^4A_{1g}(^4G)$	25,200	24,960, 25,275
$^4T_{2g}(^4D)$	28,200	27,980
$^4E_g(^4D)$	29,900	29,750
$^4T_{1g}(^4P)$	35,000	32,960
$^4A_{2g}(^4F)$	40,700	40,820
$^4T_{1g}(^4F)$	41,900	

This is not surprising if we remember that the d^5 electronic configuration is its own hole equivalent. Level diagrams have been given by Orgel[20] and Tanabe and Sugano.[125]

The complete level diagram is as usual a function of three parameters: $10Dq$ and the Slater integrals F_2 and F_4. For the gaseous ion $F_2 = 1327\ \text{cm}^{-1}$ and $F_4 = 108\ \text{cm}^{-1}$. The absorption bands of $Mn(H_2O)_6^{++}$ can best be fitted with $F_2 = 1200\ \text{cm}^{-1}$ and $F_4 = 106\ \text{cm}^{-1}$, together with a value of $10Dq = 8480\ \text{cm}^{-1}$. The assignments based upon these values differ somewhat from the assignments given by Jørgensen[129] and Tanabe and Sugano.[125] It was pointed out by Jørgensen that since the energy differences ${}^4E_g({}^4D) - {}^6A_{1g}({}^6S)$ and ${}^4A_{2g}({}^4F) - {}^6A_{1g}({}^6S)$ are independent of the value of Dq, the corresponding absorption bands are particularly suited for the investigation of the values of F_2 and F_4 found in the complex.

A study of the intensity to be expected in the optical absorption spectrum of hydrated Mn^{++} salts has been given by Koide and Pryce.[132] The results seem very gratifying, but they are open to a number of objections as pointed out earlier.

The absorption lines in the antiferromagnetic states of $MnCl_2 \cdot 4H_2O$ and $MnBr_2 \cdot 4H_2O$ have been investigated by Tsujikawa.[144] These salts have a Neél temperature of 1.6°K and 2.2°K, respectively, and when the salts become antiferromagnetic, one would expect polarization and energy shifts of the absorption spectrum. Tsujikawa looked at the violet doublet absorption band ${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}({}^4G)$ and found considerable shifts in the polarization properties.

Besides the $Mn(H_2O)_6^{++}$ ion the absorption spectra of the octahedrally coordinated pink compounds MnF_2, $MnCl_2$, and $MnBr_2$ have been extensively studied.[133–136] The conclusions are quite similar to those obtained for the hydrated complex, with, of course, appropriate changes in the parameters. It is found that whereas the positions of the band maxima can be accounted for very nicely, other properties, such as the observed oscillator strengths,[134] do not agree with the theory of Koide and Pryce.[132]

Both the electron paramagnetic resonance[137–139,143] and the nuclear magnetic resonance[140,141] of MnF_2 have been looked into very closely. The reason for this is, as explained in Chap. 7, that these experimental techniques open the way for an elucidation of the form of the wave functions for the magnetic electrons. The related phenomenon of antiferromagnetism in $KMnF_3$ has among others been studied by Ogawa.[145] Finally, Watson[142] has investigated the form of the wave functions for Mn^{++} in a crystalline field of cubic symmetry and obtained a measure of the Dq value for a Mn^{++} ion embedded in a crystalline lattice.

Turning our attention toward the ground state ${}^6A_{1g}$, we find that the magnetic susceptibility at not too low temperatures is given with great accuracy by the spin-only value:[147]

$$\chi = \frac{4N\beta^2 S(S+1)}{3kT} = \frac{30N\beta^2}{3kT} \simeq \frac{3.75}{T}$$

This is, of course, not surprising, since neither any crystal fields nor the spin-orbit coupling alone can remove the sixfold degeneracy of the ground state. However, since the highest degeneracy possible in the cubic double group is four, higher-order perturbations involving crystal fields and spin-orbit coupling simultaneously must be operative. A very small ground state splitting will then take place. So long as the temperature is high, this can, however, not be of importance in the measurements of the susceptibility.

Paramagnetic resonance experiments have shown that in actual cases the ground state is split into three Kramers doublets[149,150] separated by some 0.1 cm^{-1}. This indicates definitely that the symmetry of the complex is less than cubic. The behavior of the energy levels in a magnetic field of arbitrary direction with respect to the axes is difficult to evaluate; an exposition of this subject is given by Low.[151]

The elucidation of the exact nature of the zero-order field splitting is still needed. Van Vleck and Penney[147] did some order-of-magnitude calculations assuming only the spin-orbit coupling and a cubic field to be present. Meijer[152] introduced an additional field of trigonal symmetry and obtained an overall splitting of 0.15 cm^{-1} of the three Kramers doublets.

Pryce,[52,153] on the other hand, considered in addition a spin-spin interaction and argued that this latter mechanism could be the dominating factor. Some modifications of his theory were given by Watanabe,[154] who listed some additional possibilities. The most recent paper dealing with these questions has been published by Powell et al.[155] These authors pointed out that omitting the spin doublets of d^5, as done by Watanabe, reduces the calculated splittings by almost two orders of magnitude and that spin-spin interactions are of considerably lesser importance than spin-orbit interactions. Evidence for the sign of the crystalline cubic field splitting parameter for an S state has been collected by Low.[151,156]

The paramagnetic resonance spectrum of many Mn^{++} complexes has been investigated in great detail. Reference is here given to the review paper by Low.[151] The g values are always found to be very close to 2, but the coefficients D and E in the spin Hamiltonian have been found to be extremely sensitive to the surroundings of the Mn^{++} ion. We quote here only some recent work: Low and Suss[159] considered Mn^{++} in Al_2O_3, and Kikuchi and Matarrese looked upon Mn^{++} in calcite.[160,161] Friedman and Low[162] have again looked more closely into the resonance spectrum of Mn^{++} in $ZnSiF_6{\cdot}6H_2O$.

Considerable interest is also connected with the behavior of the ${}^4T_{1g}({}^4G)$ state. This is due to the fact that this is the state which is responsible for the fluorescence[157] found in many manganous compounds; especially beautiful fluorescence is, for instance, found in the yellow-green tetraethylammonium manganese(II) bromide.[129] This complex is presumably tetrahedrally coordinated.

Since the energy of the ${}^4T_{1g}$ state is highly sensitive to both the reduction of the term interval ${}^6S - {}^4G$ and to the value of Dq, variations in the emitted light from one phosphor to another may be considerable. This is clearly demonstrated in the work of Klasens et al.,[163] who investigated the position of the emission of Mn^{++} embedded in different perovskite crystal structures. The authors found that a linear relation existed between the maximum of the transition and the space available to the Mn^{++} ion. This latter quantity is again expected to be proportional to the Dq value. Thus when Dq becomes greater, the energy difference ${}^4T_{1g} - {}^6A_{1g}$ decreases and the emission moves to lower wave numbers.

The splitting of the twelvefold degenerate ${}^4T_{1g}$ state under the combined influence of spin-orbit coupling and interactions with higher states has been considered by Clogston.[158] Spin resonance observations in this state would be expected to be of considerable interest.

There are only a few examples of tetrahedrally coordinated Mn^{++} complexes. Besides the already mentioned $[N(C_2H_5)_4]_2MnBr_4$, we know, for instance,[164] that the manganese in Cs_3MnCl_5 possesses a tetrahedral coordination of chlorine. However, the balance between octahedral and tetrahedral coordination is extremely fine, as shown by the octahedrally coordinated manganese in Cs_2MnCl_4. The spectrum of the species $MnCl_4^-$ is given by Buffagnie and Dunn,[258] and Cotton et al.[318,324] have further published spectra of the manganous halides and phosphine oxide complexes.

An example of a "low-spin" complex possessing the ground state ${}^2T_{2g}(t_{2g})^5$ is the dark-violet $K_4Mn(CN)_6{\cdot}3H_2O$. No absorption spectrum seems so far to have been reported, but the magnetic features have been well documented. Both Kamimura[165] and Figgis[166] have given theoretical expressions for the variation of the susceptibility with the temperature. Kamimura assumed the crystal field, besides the cubic part, to have a component of trigonal or tetragonal symmetry comparable in magnitude with the spin-orbit interaction. In addition to these factors, Figgis, building upon the work of Bleaney and O'Brien,[167] also considered the delocalization of the t_{2g} electrons to the ligand orbitals, as discussed in Chap. 7.

The splitting of the ${}^2T_{2g}$ due to a tetragonal crystalline field was called $\Delta\ (= 3Ds - 5Dt)$. The orbital singlet was assumed to be lowest, and the magnetic moment operator taken to be $(k\hat{L} + 2\hat{S})\beta$. The measurements of Figgis[168] of the magnetic susceptibility of $K_4Mn(CN)_6{\cdot}3H_2O$ then indicated that a very good fit of the experimental points could be obtained with $k = 0.75$, $\Delta = 400\ \text{cm}^{-1}$, and λ, the spin-orbit coupling constant, equal to $-200\ \text{cm}^{-1}$.

The values of the g factors found by Baker, Bleaney, and Bowers[169] were 2.624, 2.182, and 0.63. The value of $k = 0.74$ corresponds to an overall splitting of the orbital levels[167] of about 500 cm^{-1}. The paramagnetic resonance measurements and the values of the susceptibility must therefore be said to support the proposed model.

Trivalent Manganese. The ground state of the gaseous ion is ${}^5D[A](3d)^4$. This is the only quintet state present. Under the influence of a weak crystal field of O_h symmetry it splits up in the usual fashion, a low ^5E_g state and an excited $^5T_{2g}$ state placed at $10Dq$. The complex is seen to be isoelectronic with Cr^{++} complexes and just as is the case for the latter, we would expect Mn^{3+} complexes possessing four unpaired spins to be subjected to a violent Jahn-Teller distortion. The separation of the two potential surfaces is calculated[6] to be some 4000 cm^{-1}.

Evidence for the Jahn-Teller distortion is presumably observed in the asymmetry of the $Mn^{3+}(F^-)$ octahedra[170,171] found in MnF_3. It is, however, well worth remembering that if a real Jahn-Teller mechanism is operating, it is impossible to specify the atomic orbital of the odd electron. The nuclear magnetic resonance measurements of Shulman and Jaccarino[172] on the red MnF_3 confirm this theoretical prediction.

The absorption spectrum of the red ion MnF_6^{-3} has been measured by Furlani and Ciana.[174] A single band is found to occur at 21,700 cm^{-1}. With the band assignment $^5E_g \rightarrow {}^5T_{2g}$ we then get $Dq = 2170$ cm^{-1}. The red-violet alum $CsMn(SO_4)_2 \cdot 12H_2O$ has a similar band[173,174] placed at 21,000 cm^{-1}. For the oxalate[174] $Mn(C_2O_4)_3^{-3}$ this band is found at 20,050 cm^{-1}. In this latter complex a weak band is further found at 9600 cm^{-1}, being presumably the $^5E_g \rightarrow {}^3T_{1g}$ transition. The effective magnetic moment of the red-violet compound $Mn(C_2O_4)_3K_3 \cdot 3H_2O$ is[25] 4.96, a value very characteristic of high-spin Mn^{3+} complexes.

When the octahedral crystal field gets stronger, the ground state eventually becomes $^3T_{1g}(t_{2g})^4$. This state of affairs is found in $K_3Mn(CN)_6$. The condition for a low-spin complex is seen from Table 9-1 to be

$$10Dq > 6F_2 + 145F_4$$

From the term values[22] and Table 3-3 we get $F_2 = 11.3F_4 = 1470$ cm^{-1}. The inequality then yields $10Dq$ greater than 27,670 cm^{-1} or $Dq \gtrsim 2800$ cm^{-1}.

The near-infrared absorption spectrum of the dark-red crystalline $K_3Mn(CN)_6$ has been measured by Jones and Runciman.[175] They recorded a number of parallel and perpendicular polarized lines at some 9500 cm^{-1}. The absorption spectrum in solution was found[176] to have a weak peak located at 21,000 cm^{-1} just before the charge transfer bands set in.

The configuration $(t_{2g})^4$ gives rise to the ground state $^3T_{1g}$ as well as the degenerate pair $(^1E_g, {}^1T_{2g})$ and $^1A_{1g}$ placed respectively at an energy $2(3F_2 + 20F_4)$ and $5(3F_2 + 20F_4)$ above the ground state. Allowing for a reduction of F_2 and F_4 due to complex formation and using the reasonable values $F_2 = 1000$ cm^{-1} and $F_4 = 100$ cm^{-1}, we have $3F_2 + 20F_4 \approx 5000$ cm^{-1}. This places the transitions $^3T_{1g} \rightarrow (^1T_{2g}, {}^1E_g)$ at 10,000 cm^{-1} and $^3T_{1g} \rightarrow {}^1A_{1g}$ at 25,000 cm^{-1}.

The next configuration $(t_{2g})^3(e_g)$ gives rise, among others, to the following two low-lying levels; ^5E_g placed at $10Dq - 6F_2 - 145F_4$ and ^3E_g located at $10Dq + 2F_2 - 45F_4$. With the above values of F_2 and F_4 and a tentative value of $Dq = 3000\ \text{cm}^{-1}$, being a little more than the Dq value for Cr(CN)_6^{3-}, we get $E(^5E_g) = 9500\ \text{cm}^{-1}$ and $E(^3E_g) = 27{,}500\ \text{cm}^{-1}$.

It thus seems impossible to make any definite assignments of the observed bands, since the low-lying absorption band may be due to $^3T_{1g} \rightarrow {^5E_g}$ equally well as to $^3T_{1g} \rightarrow (^1T_{2g}, {^1E_g})$. Also, the band at 21,000 cm⁻¹ may be due to either $^3T_{1g} \rightarrow {^1A_{1g}}$ or $^3T_{1g} \rightarrow {^3E_g}$. However, both from an energetic point of view and from the low intensity, the first assignment of this band seems at the present time the most reasonable.

The magnetic susceptibility of $\text{K}_3\text{Mn(CN)}_6$ has been studied by Cooke and Duffus[177] and by Kamimura.[165] The spin-orbit coupling splits the ground state $^3T_{1g}$ into three levels; the lowest level being a singlet. This level is diamagnetic, and consequently the magnetic moment will go to zero by cooling. This result is not altered by the inclusion of a tetragonal or trigonal field component.[165]

The variation with temperature of the effective Bohr magneton number can be described[177] rather well with a value of the spin-orbit coupling factor $\lambda = 340\ \text{cm}^{-1}$. The total width of the $^3T_{2g}$ spin multiplet is then $\frac{3}{2}\lambda = 510\ \text{cm}^{-1}$. The inclusion of a lower field component equal to $-200\ \text{cm}^{-1}$ in addition to a value of $\lambda = 285\ \text{cm}^{-1}$ improves the agreement with experiment. Since the ground state is a singlet, no paramagnetic resonance should occur for this state, and none is observed.

Tetravalent Manganese. The ground state of the gaseous ion is $^4F[\text{A}](3d)^3$, with a ^4P state located at some 16,000 cm⁻¹. The spectra and magnetic behavior of Mn(IV) complexes should therefore resemble these of Cr(III). The absorption spectrum of the yellow ion $\text{MnF}_6^{=}$ has been studied by Jørgensen.[179] From the two spin-allowed bands $^4A_{2g} \rightarrow {^4T_{2g}}$ and $^4A_{2g} \rightarrow {^4T_{1g}}$ he concluded that $10Dq = 21{,}750\ \text{cm}^{-1}$ and that

$$F_2 - 5F_4 = 600\ \text{cm}^{-1}$$

Four weak spin-prohibited bands were further observed at 16,400 cm⁻¹ to 15,800 cm⁻¹. These correspond to the "ruby" lines of Cr(III).

The heteropolymolybdate complex of Mn(IV) has also been prepared,[180] and the spectrum has been measured. This and similar compounds are phosphors, and the absorption and fluorescence in $\text{Mn}^{4+}(\text{O}^{=})_6$ have been studied by Kemeny and Haake.[421]

Hepta-, Hexa-, and Pentavalent Manganese. Since heptavalent manganese has a closed argon shell with no outer electrons, its complexes are isoelectronic with the corresponding Cr(VI) compounds. As a result, MnO_4^- and $\text{CrO}_4^{=}$ exhibit exactly the same electronic features, and we shall therefore, as far as the theory is concerned, refer to what has already been said about $\text{CrO}_4^{=}$.

The purple permanganate ion shows two absorption bands located at some 19,000 cm⁻¹ and 32,000 cm⁻¹.[181] The assignments of these two bands are as in $\text{CrO}_4^{=}$, Fig. 10-9*a*. The ground state is $^1A_1(t_1)^6$, and the two excited configurations $(t_1)^5(e)$ and $(t_1)^5(t_2)$ both give rise to one $^1T_2$ state. With the electric dipole vector transforming as T_2 in T_d it is natural to assign[117] the two spin-allowed bands to the transitions $^1A_1 \rightarrow {}^1T_2(1,2)$.

The permanganate ion exhibits a weak temperature-independent paramagnetism with a value[182] of the magnetic susceptibility χ equal to about 58×10^{-6}. Carrington[422] has used Van Vleck's formula for the temperature-independent paramagnetism (6-125) of a crystalline powder

$$\chi = \tfrac{2}{3}N\beta^2 \sum_{n \neq 0} \frac{|(0|\hat{L}|n)|^2}{E_n - E_0}$$

to calculate χ. By writing down the determinantal wave functions for the excited states using the orbitals shown in Fig. 10-9 and by making reasonable assumptions for the energy differences and the mixing coefficients in the molecular orbitals, he arrived at a value of $\chi = 63.1 \times 10^{-6}$. No attempt was made to calculate the diamagnetic part of the susceptibility.

$MnO_4^{=}$ is made from MnO_4^- by adding one electron to the molecule. This electron is expected to go into the first excited orbital of MnO_4^-. The question then arises: what is the symmetry of this orbital? As seen from Fig. 10-9, Wolfsberg and Helmholz[116] assumed this state to be of t_2 symmetry, whereas Ballhausen and Liehr[117] took it to be an e state.

Using both assignments, the absorption spectrum[181] of the dark-green ion $MnO_4^{=}$ has been discussed by Furlani, Ciana, and Batticci.[118] However, Carrington et al.[184,185] gave a tentative explanation of the spectrum using the fact that electron resonance studies of $MnO_4^{=}$ quite unambiguously showed[119,186] the unpaired electron to be in a doubly degenerate e level. The magnetic moment of the complex has been measured by Jensen and Klemm.[188]

MnO_4^{3-} has also been considered.[118,185,186] As expected from the above results the ground state turned out to be a $^3A_2 \cdots (t_1)^6(e)^2$ state. The absorption spectrum is fairly complicated, and only qualitative suggestions have so far been given for the interpretation.

10-f. Iron

Iron has the electronic structure $[A](3d)^6(4s)^2$. We shall consider Fe^{++}, Fe^{3+}, and Fe^{6+}, the last oxidation state occurring formally in $FeO_4^{=}$.

Divalent Iron. The electronic ground state of Fe^{++} is ^5D. No other quintet state is present. In the weak-field limit, and with octahedral configuration, the ground state is then $(t_{2g})^4(e_g)^2$, with the spin quantum number $S = 2$. In the strong-field limit the ground state will be $(t_{2g})^6$ with $S = 0$. The criterion for low spin has been given in Sec. 4-f to be $20Dq < 5(F_2 + 51F_4)$. The schematic level scheme will look as shown in Fig. 10-12. From the usual rule of thumb we have $F_2 = 10F_4 = 1000\ \mathrm{cm}^{-1}$. The crossover point is then expected to occur at $10Dq \approx 15{,}000\ \mathrm{cm}^{-1}$.

The absorption spectrum of the pale-green ion $Fe(H_2O)_6^{++}$ has been studied, among others, by Jørgensen,[96] Furlani,[189] and Cotton and Meyers.[249] A double peak is found at some 10,000 cm^{-1}, with a number of very small peaks beginning at 20,000 cm^{-1} and upwards. The double peak is identified as the transition ${}^5T_{2g} \rightarrow {}^5E_g$ split, approximately 2000 cm^{-1}, due to a Jahn-Teller effect.[6] The small peaks are supposedly the transitions ${}^5T_{2g} \rightarrow {}^3T_{1g}$, ${}^3T_{2g}$, ... These have, however, not been identified with certainty. The absorption spectra of some other "weak-field" Fe^{++} complexes as recorded by Furlani[189] are seen to exhibit quite analogous features.

The complete matrices for the energy-level splittings of the d^6 configuration in weak octahedral and tetrahedral fields have been given by Low and Weger.[191] The paramagnetic resonance splittings of Fe^{++} have also been theoretically[191] and experimentally investigated.[192] The g value observed for Fe^{++} in octahedral coordination in MgO is $g = 3.428$.

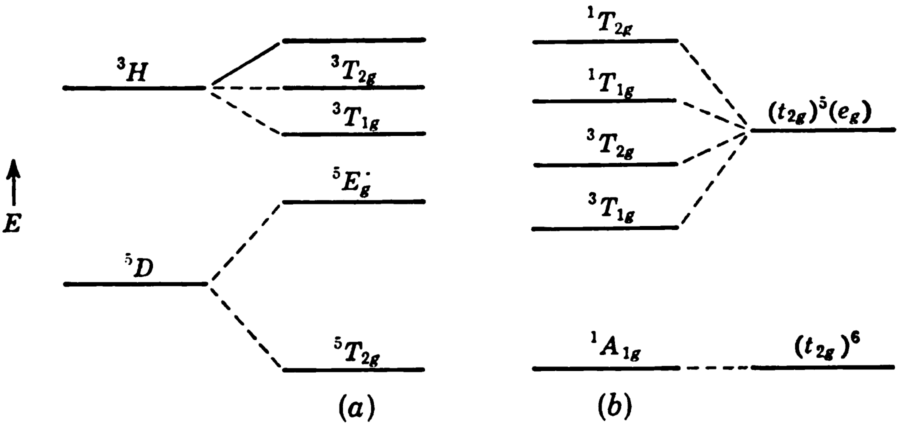


FIG. 10-12. Splitting scheme for $(3d)^6$ in an octahedral field. (a) Weak field; (b) strong field. Crossover point of ${}^5T_{2g}$ and ${}^1A_{1g}$ at $20Dq \approx 5(F_2 + 51F_4)$.

Bloomfield, Lawson, and Rey[193] have used a point-charge model and Slater free-ion orbital wave functions to calculate the crystal field splitting in $Fe_3Al_2(SiO_4)_3$, the ferrous silicate garnet. Agreement with experiment was obtained by varying the charge distribution. The nuclear magnetic resonance of the white paramagnetic FeF_2 has been measured by Stout and Shulman,[194] and the hyperfine interactions found were used to evaluate the fraction of unpaired 2s spins in the F^- orbitals. The magnetic anisotropy of FeF_2 has been considered by Moriya et al.[195]

The magnetic susceptibility of the green ferrous ammonium sulfate has been investigated by several authors.[196–199] With a trigonal distortion present the level scheme for the lowest levels will look as pictured in Fig. 10-13.

The splitting δ is found[197] to be some 1200 cm^{-1}, and ϵ is equal to 10.9 cm^{-1}. On the other hand, for $FeSiF_6 \cdot 6H_2O$ ϵ is evaluated to be[200] -10.4 cm^{-1}. The g factors in this latter case are $g_{\parallel} = 2.00$ and $g_{\perp} = 2.14$.

In the strong-field limit the complex will be diamagnetic and the first spin-allowed transition will be due to the transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$, Fig. 10-12*b*. The yellow $Fe(CN)_6{}^{4-}$ shows one shoulder at 31,000 cm^{-1} before the charge-transfer spectrum sets in. It thus seems reasonable to assign this band to the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition. The spectrum of the yellow-green ion $[Fe(CN)_5NO]^-$ containing divalent iron and NO^+ has been measured by Cotton et al.[326] and interpreted by Gray and Ballhausen.[115]

Trivalent Iron. The electronic ground state of Fe^{3+} is ${}^6S$. Since this metal ion is isoelectronic with Mn^{++}, we shall refer to what has been said there concerning the general features of d^5.

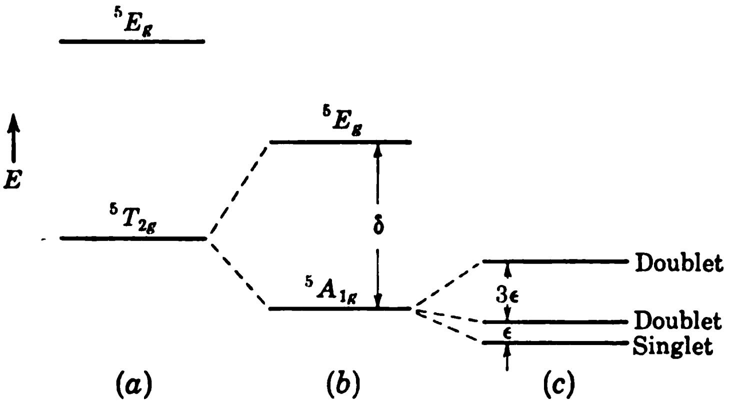


FIG. 10-13. Splitting of ground state ${}^5T_{2g}$ for $(3d)^6$. (*a*) Cubic field; (*b*) trigonal field included; (*c*) spin-orbit included.

The spectrum of the high-spin violet iron complex $Fe(H_2O)_6{}^{3+}$ has been measured a few times,[96,201,202] even though the presence of brown hydroxy complexes of the type $[Fe(H_2O)_5OH]^{++}$ or even the formation of bimolecular complexes (*vide infra*) makes the spectrum hard to measure. The absorption spectrum of Fe^{3+} in beryl, where Fe^{3+} is coordinated to six oxygens, has been investigated by Dvir and Low.[203] This spectrum seems to be the most reliable so far reported, and we give the numbers in Table 10-2 together with their likely assignments. It must, however, be realized that the assignments given here are by no means certain and that there exist various opinions among the quoted authors.

TABLE 10-2. SPECTRUM OF Fe^{3+} COORDINATED WITH SIX O^-

	Experimental
${}^6A_{1g} \rightarrow {}^4T_{1g}(t_{2g})^4(e_g)$	12,300 cm^{-1}
	14,200 cm^{-1}
${}^6A_{1g} \rightarrow {}^4T_{2g}(t_{2g})^4(e_g)$	17,500 cm^{-1}
	20,000 cm^{-1}
${}^6A_{1g} \rightarrow {}^4E_g(t_{2g})^3(e_g)^2$ ${}^6A_{1g} \rightarrow {}^4A_{1g}(t_{2g})^3(e_g)^2$	23,000 cm^{-1}
${}^6A_{1g} \rightarrow {}^4T_{1g}(t_{2g})^3(e_g)^2$	26,500 cm^{-1}

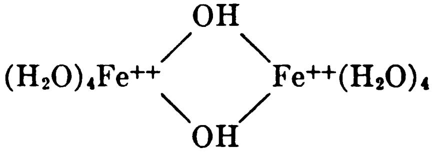
The zero-order splitting of the ground ${}^6S$ level, owing to the combined influence of the spin-orbit coupling and the presence of lower fields, is exactly as found for Mn^{++}. The early investigations by Meijer[152] and Kronig and Bouwkamp[204] were especially concerned with the behavior of iron alum. More recent work includes the thermal and magnetic properties of ferric methylammonium sulfate at low temperatures as investigated by Cooke et al.[205] These authors concluded that the $M_s = \pm 1/2$ level was the lowest.

Furthermore, Bleaney and Trenam[206] have looked into the paramagnetic resonance of the ferric alums and have evaluated the various constants in the spin Hamiltonian.

The electron spin resonance of Fe^{3+} in various surroundings has attracted some attention. Fe^{3+} in rutile was investigated by Carter and Okaya,[207] and Geschwind[423] looked at the resonance of the ion in both octahedral and tetrahedral sites in yttrium gallium garnet. Finally, a test of the spin Hamiltonian for Fe^{3+} in strontium titanate was carried out by Aisenberg, Statz, and Koster.[208] Other Fe^{3+} compounds which have been investigated by means of paramagnetic resonance methods include the colorless FeF_6^{3-}, which was looked into by Helmholz,[209] and ferrihemoglobin.[210–213]

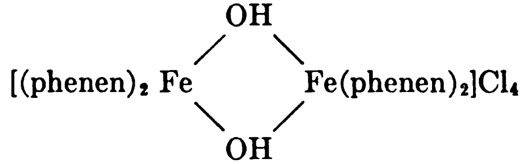
The iron complexes so far discussed have all been octahedrally coordinated. From spectral measurements Friedman[214] has, however, concluded that a tetrahedral species $FeCl_4^-$ is present in concentrated HCl with some added $FeCl_3$. The absorption spectrum looks very complicated, and so far no assignments of the various peaks have been given.

In basic perchlorate solutions of Fe^{3+} Mulay and Selwood[215] have found magnetic and spectroscopic evidence for the presence of a brown diamagnetic dimer which they write as



$$\begin{array}{ccc} & OH & \\ (H_2O)_4Fe^{++} & & Fe^{++}(H_2O)_4 \\ & OH & \end{array}$$

Another dimeric ferric compound is the brown



$$\begin{array}{ccc} & OH & \\ [(\text{phenen})_2\,Fe & & Fe(\text{phenen})_2]Cl_4 \\ & OH & \end{array}$$

where phenen stands for *o*-phenantholine. The magnetism of this compound has been investigated by Earnshaw and Lewis[124,426] and by Elliott.[427] The theory behind the magnetism of a dimer is given in the section dealing with the corresponding Cr^{3+} complexes.

The best characterized of all low-spin complexes containing Fe^{3+} is undoubtedly the red $K_3Fe(CN)_6$. The ground state is ${}^2T_{2g}(t_{2g})^5$, and the behavior is analogous to that of the low-spin complexes of Mn^{++}. The principal magnetic susceptibilities of $K_3Fe(CN)_6$ were calculated by Howard[216] in a now classic work. The overall features of the susceptibility could be explained by using a cubic crystalline field with the superposition of a small rhombic field. Another set of parameter values for this complex has been given by Kamimura.[165] As shown by Ohtsuka,[217] there is a spin-spin interaction effect in $K_3Fe(CN)_6$; the spins of $S = \frac{1}{2}$ on two ions combine to give a total spin of 1 or 0. This antiferromagnetic effect in the susceptibility was not taken into account by the former theories, and it may conceivably improve the agreement with experiment. Measurements of the g values in the undiluted $K_3Fe(CN)_6$ have been performed by Baker, Bleaney, and Bowers,[169] but the interpretation is very uncertain.

The absorption spectrum of $Fe(CN)_6^{3-}$ has been given by Kiss et al.[218] and by Jørgensen.[219] An attempt toward a theoretical explanation has been published by Naiman.[220] Using values of $Dq = 3500\ \text{cm}^{-1}$, $F_2 = 1190\ \text{cm}^{-1}$, and $F_4 = 94\ \text{cm}^{-1}$, he was able to reproduce the crystal field bands. However, the complex possesses in addition some extremely strong charge-transfer bands which make the identification rather uncertain. The color and electronic configuration of Prussian blue $KFe(III)[Fe(II)(CN)_6]$ has been investigated by Robin.[428] The absorption spectrum is tentatively interpreted as due to charge transfer between the $Fe(CN)_6^{4-}$ and Fe^{3+} ions.

Hexavalent Iron. Hexavalent iron occurs in the red ferrate ion, $FeO_4^{=}$. This ion is isoelectronic with MnO_4^{3-}, and the ground state configuration is thus $^3A_2(t_1)^6(e)^2$ (see Manganese). The resultant spin is $S = 1$, and this is confirmed both by measurements of the paramagnetic susceptibility[221,222] and by the g factor.[186]

The absorption spectrum of $FeO_4^{=}$ has been measured and interpreted by, among others, Carrington et al.[184,185,223] and by Furlani.[118] Two broad bands with some fine structure are observed at some 12,720 cm^{-1} and 19,600 cm^{-1}. They are assigned to the transitions $^3A_2 \rightarrow {}^3T_1$ and $^3A_2 \rightarrow {}^3T_1$, respectively.[184] Their oscillator strengths have been interpreted[185] as due mainly to electronic transitions among the ligand orbitals, and not to charge transfer from the metal orbitals to the ligands as suggested by Ballhausen and Liehr.[117]

10-g. Cobalt

The oxidation states of interest are Co^{++} and Co^{3+}. Co^{++} possesses the electronic structure $[A](3d)^7$ and occurs in both octahedral and tetrahedral coordination. Co^{3+}, on the other hand, is always hexacoordinated, except for the case of heteropoly tungstocobaltate anions containing Co(II) and Co(III) in tetrahedral coordination.[348]

Divalent Cobalt. In octahedral coordination the ground state can be either $^4T_{1g}(t_{2g})^5(e_g)^2$ or $^2E_g(t_{2g})^6(e_g)$ depending upon the strength of the crystal field. We get that the condition for low spin is $12Dq > 7(F_2 + 15F_4)$, or, with $F_2 = 1000\ \text{cm}^{-1}$ and $10F_4 = F_2$, $Dq > 1500\ \text{cm}^{-1}$. This is a very high Dq value for a doubly ionized ion of the first transition series, and consequently we would expect only the cyanide complex to fulfill this requirement.

Adamson[224] has, however, shown that the violet species formed from Co^{++} and KCN is $K_3Co(CN)_5$, a diamagnetic solid. In excess of aqueous cyanide it turns paramagnetic corresponding to one unpaired electron. Nevertheless, all evidence indicates that this ion is $Co(CN)_5^{3-}$ rather than $Co(H_2O)(CN)_5^{3-}$. So far no truly hexacoordinated Co(II) complex with $S = \frac{1}{2}$ has thus been reported.

The gaseous Co^{++} ion has the ground state ^4F with the excited state ^4P located at some 14,500 cm^{-1}. Under the influence of a cubic field these levels will split up into $^4T_{1g}(F)$, $^4T_{2g}(F)$, $^4A_{2g}(F)$, and $^4T_{1g}(P)$ arranged in order of increasing energy. This level scheme was first given by Abragam and Pryce[225] and used by them to interpret the optical absorption of $Co(H_2O)_6^{++}$.

Located just a bit higher than the ^4P is a ^2G state which, of course, is also split under the influence of a crystal field. One of the split components is the ^2E_g state which eventually, at the limit of strong crystalline fields, becomes the ground state. As seen from the level diagram given by Tanabe and Sugano,[126] the ^2E_g crosses all the quartet levels on its way down. The features connected with the crossing are, however, more complicated than indicated by the above authors, since spin-orbit coupling effects have been neglected in the calculation.

The "visible" absorption spectrum of the pink $Co(H_2O)_6^{++}$ consists of one band located[65] at 8350 cm^{-1} and a band system found at some 20,000 cm^{-1}. Measuring at low temperatures, Pappalardo[226] gave evidence for some narrow lines scattered from 19,000 cm^{-1} to 26,000 cm^{-1} in $CoCl_2{\cdot}6H_2O$. The X-ray structure of the complex performed by Mizuno[229] shows, however, this complex to be *trans*-$[CoCl_2(H_2O)_4]$.

The absorption band found at 8350 cm^{-1} is identified, with the transition $^4T_{1g} \rightarrow {}^4T_{2g}$, and the one at 20,000 cm^{-1} with $^4T_{1g} \rightarrow {}^4T_{1g}(P)$. The energy matrix for the two $^4T_{1g}$ levels is

$$\begin{vmatrix} -6Dq - E & 4Dq \\ 4Dq & x - E \end{vmatrix} = 0$$

with $E(^4T_{2g}) = 2Dq$ and $E(^4A_{2g}) = 12Dq$.

To fit the two absorption bands, we use Dq and $x = E(^4P - {}^4F)$ as parameters and obtain $Dq = 950$ cm^{-1} with $x = 12{,}800$ cm^{-1}. The absorption band corresponding to the transition $^4T_{1g} \rightarrow {}^4A_{2g}$ is then placed at 17,850 cm^{-1}. Only a very small absorption is seen at this position in the spectrum[55,56] indicating that, if our theory is correct, the band $^4T_{1g} \rightarrow {}^4A_{2g}$ can only possess a very small intensity. Fortunately, this is also found theoretically. As pointed out by Koide,[227] the above transition corresponds to a two-electron jump, and as such should have an oscillator strength of only $f = 4.8 \times 10^{-6}$, while the ${}^4T_{1g} \rightarrow {}^4T_{1g}$ transition should possess an f value of 1.7×10^{-4}.

The double peak found in this last absorption band is, after Koide,[227] due to the spin-orbit splitting of the ${}^4T_{1g}(P)$ state. A comparison of the calculated and experimental absorption spectrum of the red $CoBr_2 \cdot 6H_2O$ shows very clearly that this is the case. The spin-orbit splitting of the ground state ${}^4T_{1g}$ has further been observed by Newman and Chrenko,[228] as already mentioned in Sec. 6-*d*.

The variation with temperature of the intensities for the bands of $CoSO_4 \cdot 7H_2O$ has been studied by Holmes and McClure[55] and for CoO by Pratt and Coelho.[230] The hyperbolic cotangent dependence found earlier seems to give a good fit of the experimental results. The transitions are thus vibronic in character.

Some further work dealing with the spectra of the red octahedral complexes $Co(NH_3)_6^{++}$ and $Co(en)_3^{++}$ has been performed by Ballhausen and Jørgensen.[231] The work of Ferguson,[416] who investigated the visible polarized crystal spectrum of the violet form of *trans*-$[CoCl_2(H_2O)_4](H_2O)_2$ and $Co(py)_2Cl_2$, where py stands for pyridine, is a good example of the type of spectral work which will gain greater and greater importance. The absorption spectrum of Co^{++} in various lattices has been investigated by Low[232,233] and that of CoO by Pratt and Coelho.[230]

The theory of paramagnetic resonance in cobalt(II) salts has been given by Abragam and Pryce[225] and Low.[232] The ground state will, as mentioned earlier, be a Kramers doublet; the value of the g factor assuming cubic octahedral configuration has been given in Sec. 6-*e*. Experimental values of g for the red $CoSiF_6 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ can be found in the work of Bleaney and Ingram.[234]

The theory of the paramagnetic susceptibility of the red octahedrally coordinated Co(II) complexes has occupied many authors, starting with the classic work of Schlapp and Penney.[65] In order to account for the susceptibility of $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$, Schlapp and Penney were forced to conclude that only rhombic symmetry was present in the crystal. However, the magnetic resonance behavior of the ions in this salt shows perfect axial symmetry. The anisotropy of the magnetic susceptibility must then be explained by assuming the presence of both a tetragonal crystal field and a magnetic coupling between the two ions per unit cell.[225]

The testing of the above idea was performed by Kambe et al.[417] and Uryû.[235] Using the wave functions of Abragam and Pryce,[225] Uryû obtained an excellent fit of the experimental points by using a tetragonal splitting of 1090 cm^{-1} and a spin-orbit coupling constant of $\lambda = -180\ cm^{-1}$. Of great interest is also the work of Haseda and Kanda,[236,237] who studied the already-mentioned system $CoCl_2 \cdot 6H_2O$. Here an antiferromagnetic transition takes place at about 3°K.

Chakravarty and Chatterjee[238] have further given a few magnetic data on various Co(II) complexes, and Cossee[239] has studied the magnetic properties of Co(II) ions in the octahedral interstices of close-packed oxide lattices. General considerations as to the behavior of the magnetic susceptibilities of Co(II) complexes in various surroundings have been given by Figgis and Nyholm.[240]

Tetrahedral complexes containing Co(II) ions are usually formed with the halogens, an example being the blue $CoCl_4^-$. Since the level order is inverted in going from octahedral to tetrahedral coordination, the ground state is here ${}^4A_2(e)^4(t_2)^3$. No low-spin complex of Co(II) can then occur in tetrahedral coordination.

The energy-level diagram of the quartet states for tetrahedral Co(II) complexes will look as pictured in Fig. 10-14. Three quartet-quartet transitions should occur. Dq for $Co(H_2O)_6^{++}$ is equal to 950 cm^{-1}. Since Cl^- is below water in the spectrochemical series and a point-charge model of the complex yields $Dq(\text{tet.}) = \frac{4}{9}\, Dq(\text{oct.})$, we would expect Dq for $CoCl_4^-$ to be about 400 cm^{-1}.

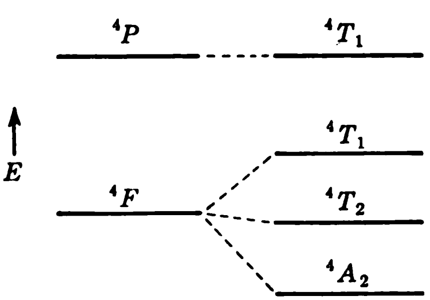


FIG. 10-14. Energy-level diagram for the quartet states of tetrahedral Co(II) complexes.

Experimentally, Dreisch and Trommer[241] found a band at 6300 cm^{-1} and Ballhausen and Jørgensen[231] reported a very intense band located at about 15,000 cm^{-1}. With a Dq value of 400 cm^{-1}, and using a weak crystalline field model, the transition ${}^4A_2 \rightarrow {}^4T_2$ should occur at $10Dq = 4000$ cm^{-1}. The next transition ${}^4A_2 \rightarrow {}^4T_1(F)$ should be found at $18Dq = 7200$ cm^{-1}, and, finally, the transition ${}^4A_2 \rightarrow {}^4T_1(P)$ should occur at

$$12Dq + 14{,}500 \text{ cm}^{-1} = 19{,}300 \text{ cm}^{-1}$$

Fitting the last two bands to the above transitions, and taking the configuration interaction between the two ${}^4T_1$ states into account, we get $Dq = 360$ cm^{-1} and $E({}^4P - {}^4F) = 10{,}400$ cm^{-1}. Some doubt has, however, been raised as to the location of the infrared band,[258] which we have taken to be 6300 cm^{-1}. The whole question of spectral assignments has been discussed in a very detailed way by Cotton et al.[352]

The intensity of the band ${}^4A_2 \rightarrow {}^4T_1(P)$ has been calculated by Ballhausen and Liehr.[117] It was found that a model of the complex using only σ bonding gave an adequate description of the observed intensity.

Magnetic moments of $CoCl_4^-$, $CoBr_4^-$, and CoI_4^- and values of Dq have been reported by Holm and Cotton.[242,243] Their results are in excellent agreement with the measurements of Bowers and Owen[16] of the g factors in the blue Cs_3CoCl_5. The paramagnetic resonance of Co^{++} with fourfold coordination has also been treated by Hall and Hayes.[244]

The crystal spectra of some tetrahedrally coordinated Co(II) complexes have been obtained by Ferguson.[245] Using polarized light, he obtained the spectrum of, for example, the blue $Co(py)_2Br_2$. All of these spectra show considerable dichroism due first of all to the symmetry of the complex but due also to interactions between the complexes in the crystal.

Cotton and Holm[246,247] have postulated the existence of high-spin four-coordinated planar Co(II) complexes. Provided the crystal field is not too strong, this is, of course, possible, but a conclusive proof for such a structure has not yet been given. It is only with very complicated ligands that this situation should be observed, but this, of course, makes it difficult to conclude anything with certainty. Nevertheless, the magnetic measurements make it highly probable that structural changes occur rather easily for Co(II) if the ion is complexed with large chelate ligands.

Trivalent Cobalt. The Co^{3+} ion is isoelectronic with divalent iron, and we shall therefore refer to the introduction concerned with this latter ion. The only paramagnetic complexes so far reported are the blue CoF_6^{3-} and $CoF_3(H_2O)_3$ having an effective moment of $\bar{\mu} = 5.2\beta$ and 4.47β, respectively.[248] New measurements by Cotton and Meyers,[249] however, gave somewhat higher values of $\bar{\mu}$. In order for the complex to be paramagnetic, we must have $20Dq < 5(F_2 + 51F_4)$.

The absorption spectrum of CoF_6^{3-} should then consist of one broad band corresponding to the transition ${}^5T_{2g} \rightarrow {}^5E_g$ (see Fig. 10-12*a*), and such a band has been observed by Cotton and Meyers[249] placed at about 13,000 cm^{-1}. The absorption band is very broad and split into two distinct peaks. This has been taken as evidence for the operation of a Jahn-Teller effect in the excited ${}^5E_g$ state.[6]

Two of the infrared vibrational frequencies are also known[250] for CoF_6^{3-}: $\nu_3 = 475$ cm^{-1} and $\nu_4 = 310$ cm^{-1}. These numbers are somewhat dependent upon the lattice parameters.

The greater part of the Co(III) complexes do not, however, contain any unpaired spins, and the situation is then as pictured in Fig. 10-12*b*. The absorption spectra of diamagnetic octahedrally coordinated Co(III) complexes should hence be made up of two strong bands corresponding to the transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$. In addition, some singlet-triplet bands could appear.

By using the descent-in-symmetry method, it is easy to find that in the strong-field approximation we have

$$\Delta E({}^1T_{1g} - {}^1A_{1g}) = -35F_4 + 10Dq$$
$$\Delta E({}^1T_{2g} - {}^1A_{1g}) = 16F_2 - 115F_4 + 10Dq$$

and for the singlet-triplet bands

$$\Delta E({}^3T_{1g} - {}^1A_{1g}) = -105F_4 + 10Dq$$
$$\Delta E({}^3T_{2g} - {}^1A_{1g}) = 8F_2 - 245F_4 + 10Dq$$

It is in this connection interesting to observe that Cr^{3+} complexes and diamagnetic Co^{3+} complexes exhibit the same spectral behavior. All other things being equal the only difference is that the distance between the first two principal bands for a given Co^{3+} complex will be some $\frac{4}{3}$ times the corresponding distance for the equivalent Cr^{3+} complex.

Let us for instance consider the spectrum[56] of the yellow "luteo" complex $Co(en)_3^{3+}$. Two strong bands appear at 21,400 cm^{-1} and 29,600 cm^{-1}, respectively, and a very broad spin-prohibited band can be detected[96] at approximately 14,000 cm^{-1}. Identifying this last band with the first singlet to triplet transition ${}^1A_{1g} \rightarrow {}^3T_{1g}$ and the others with the singlet-singlet transitions, we get $Dq = 2510\ cm^{-1}$, $F_2 = 975\ cm^{-1}$, and $F_4 = 105\ cm^{-1}$.

All other Co^{3+} complexes with O_h or pseudo O_h symmetry behave in the same way, and we shall give only a very few references: the dark-green $Co(ox)_3^{3-}$, Ref. 95, and the yellow $Co(NH_3)_6^{3+}$, Ref. 252, together with the extensive measurements of Shimura and Tsuchida.[253] The dichroism of $Co(en)_3^{3+}$ has been measured by Yamada and Tsuchida.[94]

Other features of the Co(III) compounds include the electronic distribution within the complex. Kamimura et al.[254] have used the Thomas-Fermi equation, and by means of a trial function of spherical symmetry, they have calculated the charge distribution for the valence and core electrons in $Co(NH_3)_6^{3+}$. The residual paramagnetism of cobaltic complexes due to the high-frequency term in Van Vleck's formula has been considered by Ballhausen and Asmussen[255] and by Griffith and Orgel.[256] With the matrix element $|({}^1A_{1g}|\hat{L}|{}^1T_{1g})|^2 = 24\hbar^2$ we get, depending upon the energy separation $E({}^1T_{1g} - {}^1A_{1g})$, that the high-frequency terms yield a temperature-independent paramagnetism χ_{hf} of the order of magnitude $\chi_{hf} \simeq 200 \times 10^{-6}$ eu.

It should also be mentioned here that the variation of the chemical screening constant in the nuclear magnetic resonance spectra of Co(III) complexes can be explained in a way that is similar to the explanation of variation in the high-frequency susceptibility term.[256,257]

Owing to the fact that most of the substituted Co(III) complexes are very stable, many measurements have been made of the absorption spectra of Co(III) complexes with a lower symmetry than O_h. We have shown in Sec. 5-*c* that the splitting of the bands in a trans complex should be approximately twice the splitting in a cis complex. The measurements of Basolo, Ballhausen, and Bjerrum[259] show this to be approximately true for a variety of substituted Co(III) complexes. Similar results have been reached by Yamatera[260] and by Nakamoto et al.[261]

The dichroism of the green *trans*-$[Co(en)_2Cl_2]^+$ as measured by Yamada et al.[262] has been interpreted by Ballhausen and Moffitt[263] as due to the selection rules imposed upon the complex by the vibronic couplings present. For further details reference is given to Sec. 8-*c*.

Binuclear Cobalt Complexes. Very few structures of complexes containing more than one cobalt atom per structural unit are known. The best investigated complexion of this type is undoubtedly $[(NH_3)_5Co—O_2—Co(NH_3)_5]^{5+}$. As is to be expected from its odd number of charges, it has one unpaired electron.[264] Paramagnetic resonance absorption measurements have shown[265] that the single unpaired electron interacts equally with both cobalt nuclei. Any formulation of the structure must therefore assume that the two cobalt atoms are equivalent.

The complex structure does not seem to be established, however. An investigation by Okaya quoted in Ref. 265 reaches the result that the structure is as shown in Fig. 10-15*a*, whereas Brosset and Vannerberg[266] obtained the result pictured in Fig. 10-15*b*. Structure *b* is in accordance with a proposal, based on the molecular-orbital theory, by Vlček.[267] However, the structural question evidently needs further work in order to be settled.

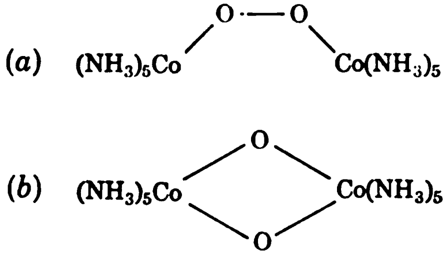


FIG. 10-15. Proposed structures for $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$. (*a*) Ref. 265; (*b*) Ref. 266.

The crystal spectrum of the deep-green $[(NH_3)_5Co—O_2—Co(NH_3)_5](NO_3)_5$ has been obtained by Yamada, Shimura, and Tsuchida,[268] together with the spectrum of the brown $[(NH_3)_5Co—O_2—Co—(NH_3)_5](NO_3)_4 \cdot 2H_2O$. As is to be expected, these show a strong dichroism, but no assignments of the bands have as yet been done.

10-h. Nickel

Nickel has the electronic structure $[A](3d)^8(4s)^2$. We shall consider only divalent Ni, possessing eight 3*d* electrons. The complex structure can be either octahedral, square planar, or tetrahedral, and we shall treat the possibilities in that order.

Octahedral nickel complexes are by far the most common; indeed, it is only quite recently that the existence of tetrahedral nickel complexes was finally proved.[311] The ground state of nickel(II) in octahedral coordination is ${}^3A_{2g}(t_{2g})^6(e_g)^2$; it is seen from the level diagram in Fig. 10-16 that Ni(II) in octahedral coordination will always possess two unpaired spins. Three absorption bands corresponding to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ should then be observed.[20,126,270] In addition, some spin-forbidden triplet to singlet bands could appear.

The observed spectra of octahedral Ni(II) complexes have indeed just the above features. We quote some results from the studies of Jørgensen.[271,272] For the pale green $Ni(H_2O)_6^{++}$ the three spin-allowed absorption bands are located at 8500 cm^{-1}, 13,500 cm^{-1}, and 25,300 cm^{-1}, respectively, and for the violet $Ni(NH_3)_6^{++}$ they are found at 10,700 cm^{-1}, 17,500 cm^{-1}, and

28,200 cm^{-1}. As seen from the diagram, the energy separation between $^3T_{2g}(F)$ and $^3A_{2g}(F)$ is equal to $10Dq$, and therefore Dq for $Ni(H_2O)_6^{++}$ and $Ni(NH_3)_6^{++}$ is 850 cm^{-1} and 1070 cm^{-1}, respectively. A great many more Dq values for various Ni(II) complexes may be found in the already-mentioned work of Jørgensen.

The usual phenomenon of the apparent reduction of the term distance $^3F - {}^3P$ is again observed for Ni(II) complexes.[23,273] We shall not elaborate the argument that "covalency" may be responsible for this effect, but only observe that at least some of the reduction may be accounted for by calculating the configuration interaction between the states coming from the configurations[274] $(3d)^8$, $(3d)^7(4s)$, $(3d)^6(4p)^2$, etc.

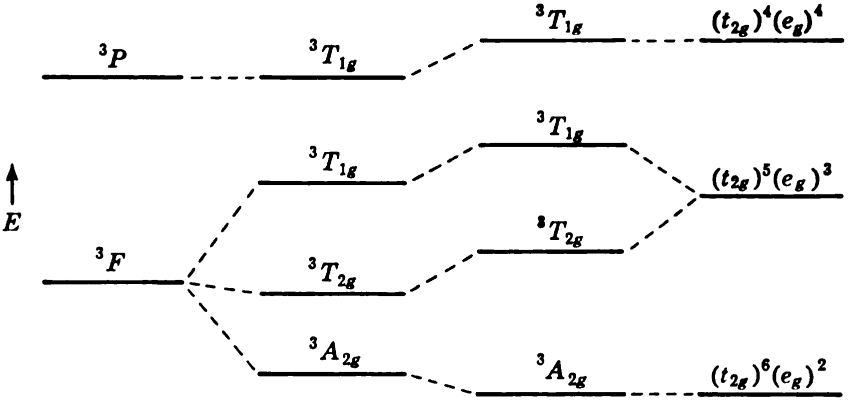


FIG. 10-16. Level scheme for the triplet states in octahedrally coordinated Ni(II) complexes.

If the spectrum of $Ni(H_2O)_6^{++}$ is compared with the spectrum of, say, $Ni(NH_3)_6^{++}$, it is noticed that the "second" absorption band, corresponding formally to the transition $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, is a double-peaked band in the former but not in the latter complex. Two different explanations have been put forward to account for this phenomenon. Jørgensen[271] is of the opinion that the double peak is due to the closeness of a ^1E_g state coming from ^1D. At just the Dq value of water the two states $^3T_{1g}(F)$ and $^1E_g(D)$ should be very close together; the spin-orbit coupling should then couple the two states, dividing the intensity between them. At other values of Dq the two states should be so far removed from each other that the mixing under the spin-orbit coupling can be neglected.

In order to test the above theory, Liehr and Ballhausen[86] calculated and solved the complete energy-level diagram for $(3d)^8$ with spin-orbit coupling included. The resulting energy-level diagram is seen in Fig. 10-17, the labeling being that appropriate to the double group. It is seen that the $^1E_g(\Gamma_3)$ level never does approach very closely to any "triplet" Γ_3 level, making the assignment of Jørgensen somewhat doubtful. It must immediately be admitted that the above conclusion is strongly dependent upon the

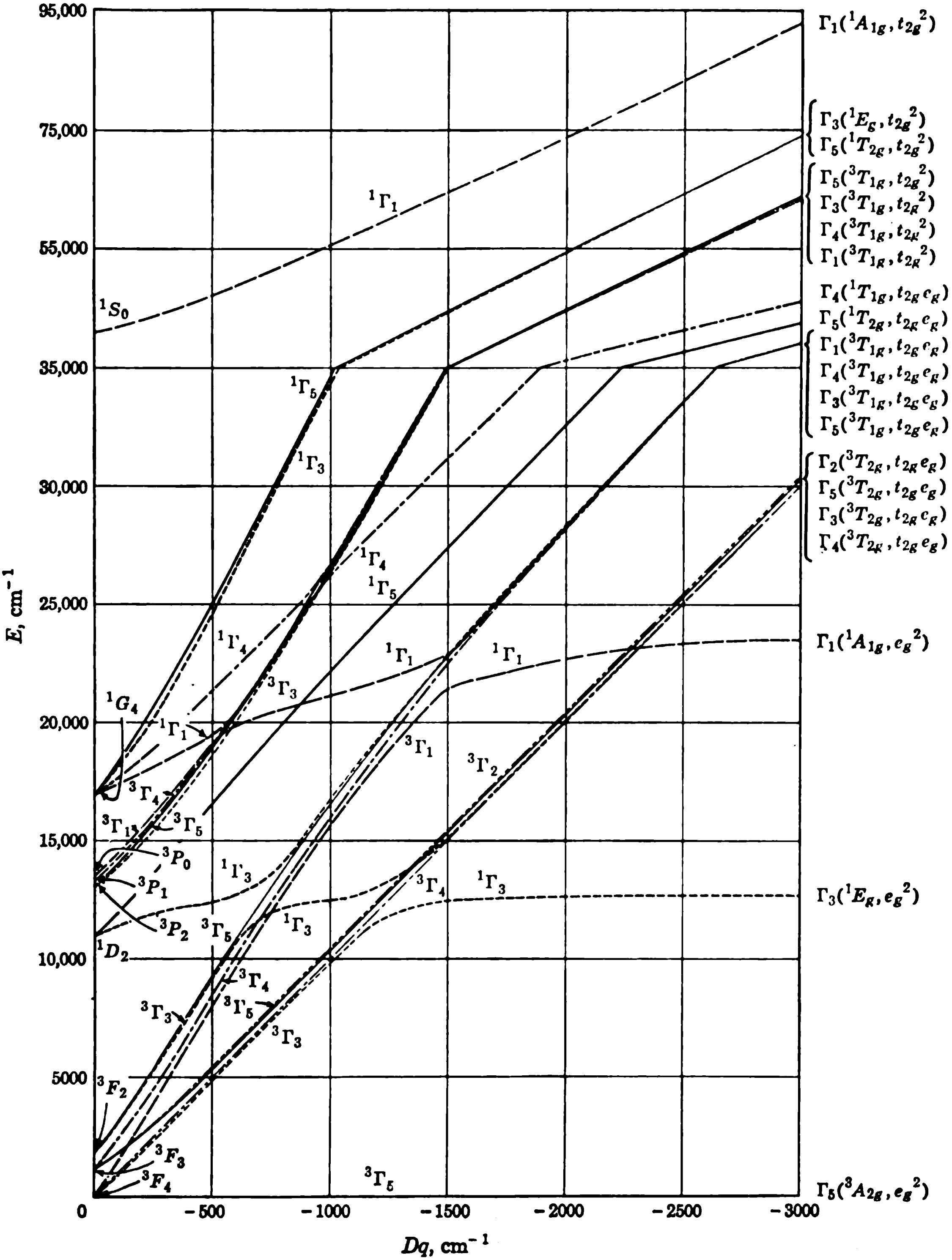


FIG. 10-17. Energy-level diagram for $(3d)^8$ with spin-orbit coupling included. The labeling is that of the double group. The hole formalism has been used.

initial choice of the values of F_2, assumed equal to $14F_4$, and the spin-orbit coupling parameter λ. This latter parameter was, however, taken from the paramagnetic resonance experiments,[23] and the value of $F_2 = 14F_4$ was varied until the best overall picture of the spectrum of $Ni(H_2O)_6^{++}$ was obtained. Hence, some reliance can be put in the level diagram given in Fig. 10-17.

Calculations of the band intensities[49] using the wave functions calculated for the above parameters also indicate that the double peak is not due to a mixing with ${}^1E_g$. Since the values of the spin-orbit parameter λ is dependent[23] upon the crystal field parameter Dq, the energy calculations predict a wider spread of the spin-orbit components of the ${}^3T_{1g}(F)$ state for $Ni(H_2O)_6^{++}$ than for $Ni(NH_3)_6^{++}$; see Fig. 10-18 for numerical results. We must now remember that the intensity is produced by means of a vibronic coupling, and since there exist no vibrational frequencies large enough to fill the 612-cm^{-1} gap appearing in the spin-orbit structure of ${}^3T_{1g}(F)$ in $Ni(H_2O)_6^{++}$, a double-peaked band should appear. On the other hand, since there are vibrations[8] which may close the 372-cm^{-1} cleft found in $Ni(NH_3)_6^{++}$, this ion should possess a single-peaked band, at least at room temperatures. The calculated numbers for the oscillator strengths f of the relevant transitions turn out to be[49] for $Ni(H_2O)_6^{++}$ $f({}^3A_{2g} \rightarrow {}^3T_{1g}(F)) = 4.3 \times 10^{-5}$ and $f({}^3A_{2g} \rightarrow {}^1E_g) = 0.1 \times 10^{-5}$, again confirming that the mixing via the spin-orbit coupling of ${}^1E_g$ and ${}^3T_{1g}$ is not strong enough to explain the appearance of the double peak.

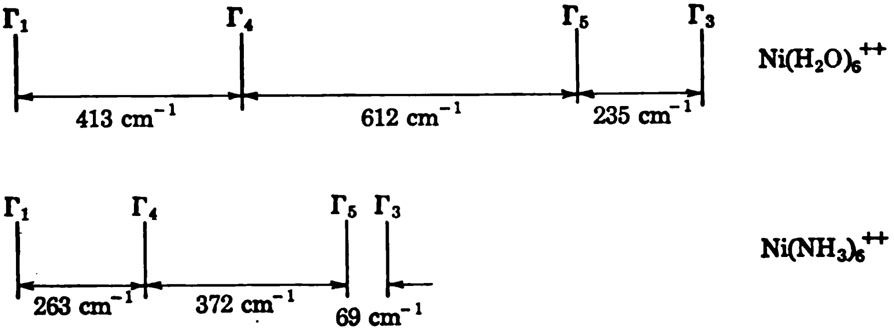


FIG. 10-18. Predicted spin-orbit fine structure for the ${}^3T_{1g}(F)$ level. For $Ni(H_2O)_6^{++}$ we have taken $Dq = 900$ cm^{-1}, $\lambda = -275$ cm^{-1}, $F_4 = 90$ cm^{-1}, and $F_2 = 14F_4$. For $Ni(NH_3)_6^{++}$, $Dq = 1100$ cm^{-1}, $\lambda = -200$ cm^{-1}, $F_4 = 90$ cm^{-1}, and $F_2 = 14F_4$.

The variation of the band intensity of this "red band" of $Ni(H_2O)_6^{++}$ has been studied by Holmes and McClure,[55] who found that the intensity variation was indeed that of a vibronic transition. Further studies of the band intensities of Ni(II) complexes has been performed by Englman.[275]

Very illuminating studies of the optical spectrum of the ion $Ni(H_2O)_6^{++}$ at low temperatures have been performed by Pappalardo,[276] Piper and Koertge,[277] and Hartmann and Müller.[278] Specifically it was found[277] that a series of weak bands at about 19,000 cm^{-1} were due to simultaneous electronic and vibrational excitations involving the H—O stretching vibration. This assignment was confirmed by the study of the isotopic shift upon changing the hydrogen to deuterium.

The optical spectrum of Ni(II) in cubic MgO has been investigated by Low.[279] As expected, it was found to resemble the spectrum of $Ni(H_2O)_6^{++}$ a great deal. The effect of pressure on the spectra of several Ni(II) complexes was looked into by Stephens and Drickamer.[280] Recently, Shulman and Sugano[425] have calculated the crystal field splitting parameter $10Dq$ for $KNiF_3$, using molecular-orbital theory with atomic Hartree-Fock functions. Their results for this complex show that it is possible to calculate $10Dq$ from first principles.

The magnetic features of Ni(II) complexes have been studied extensively, starting with the work of Schlapp and Penney.[65] Their formula for the magnetic susceptibility of octahedral Ni(II) complexes has been given in Sec. 6-*h*, Eq. (6-133). The magnetic anisotropy of a number of hydrated Ni(II) salts such as the green $NiSO_4 \cdot 6H_2O$ and Tutton salts of the composition $K_2Ni(SO_4)_2 \cdot 6H_2O$ in the temperature range from 90 to about 370°K has been investigated by Bose, Mitra, and Datta[282] and by Haseda and Date.[283,284]

The green nickel salt $NiCl_2 \cdot 6H_2O$ has received special attention. The structure is most likely[285] *trans*-$[NiCl_2(H_2O)_4]2H_2O$, and the magnetic properties indicate that an antiferromagnetic transition takes place at about 6°K.[283,284] Specific-heat measurements on the system $NiCl_2 \cdot 6H_2O$ confirm the above point of view.[287]

It was mentioned in Sec. 6-*h* that Cu(II) acetate forms dimers and exhibits an antiferromagnetic coupling. For the sake of the record we mention here that the hydrated acetates of Ni(II) and Co(II) do not exhibit such a behavior.[288]

We next turn our attention toward the paramagnetic resonance found in octahedral Ni(II) complexes. The appropriate theory for this phenomenon was given in Chap. 6. A great many papers have dealt with this subject, some of the more important being the work of Holden et al.,[289] Penrose and Stevens,[290,291] and Griffiths and Owen.[292] The g factor for the octahedral Ni(II) complexes is given by the usual formula: $g = 2 - 8\lambda/10Dq$. The value of the g factor and the zero-order field splitting[294] of the ground state ${}^3A_{2g}$ (see Chap. 6) are of course the quantities the paramagnetic resonance experiments can reveal.

Typical values are $g = 2.25$ for a number of $Ni(H_2O)_6^{++}$ complexes. Notice that a measurement of g, together with the position of the first absorption band, enables us to calculate λ, the "effective" spin-orbit coupling parameter, within the crystal. It is for instance found[23] that λ in $Ni(H_2O)_6^{++}$ is reduced from its free-ion value of $-324\ \text{cm}^{-1}$ to a value of $-270\ \text{cm}^{-1}$. This latter value was the one used in the "complete" calculation of the level scheme in Ni(II) previously referred to.

The value of the zero-order splitting is very dependent upon the crystal structure of the complex. It is, furthermore, pressure[293] and temperature dependent.[16] The values vary from a few wave numbers down to zero. Other ways of estimating zero-order field splittings include measurements of the Faraday effect[295] and heat-capacity.[296]

By elongating one of the axes of an octahedral complex, the limiting structure of the complex will be a square planar configuration. It was earlier postulated that this structure automatically would produce a diamagnetic Ni(II) complex. However, as shown by Ballhausen[269,270] and Maki,[297–299] this is by no means certain. A very weak square planar crystal field will still produce a paramagnetic complex. Similar conclusions have been reached independently by Hartmann and Fischer-Wasels.[300] Conditions for dia- and paramagnetism of square planar Ni(II) complexes have been given by Ballhausen and Liehr[301] as seen from a "strong" crystalline field point of view. The relevant discussion of this phenomenon is given in Sec. 5-*a*.

The absorption spectra of diamagnetic and paramagnetic square planar Ni(II) complexes are difficult to interpret. A beginning has been made with the work of Maki,[298,299] but many details are as yet uncertain. One of the troubles is that, most probably, π bonding effects are far from negligible in these cases. The simple crystal field picture is therefore expected to break down. Furthermore, equilibria between dia- and paramagnetic forms are often found,[303] not to speak of a change in magnetism of the complex in various solvents.[302,307]

If the triplet state is placed not too high in energy over the singlet ground state, there is a possibility that it may be populated at ordinary temperatures. Hence, the complex should exhibit a "weak" temperature-dependent paramagnetism.[301] The theory for this case is given in Sec. 6-*h*. By investigating the paramagnetism of the olive-green nickel complexes with *n*-alkyl-salicylaldimines, Sacconi et al.[304] succeeded in proving that the variation of the magnetic susceptibility with temperature was due to the above mechanism, and not to an equilibrium square planar to tetrahedral configuration as had previously been postulated.[305]

The crystal spectra of Ni(II) complexes with salicylaldehyde and its imides have been recorded, by using polarized light, by Ferguson.[306] The orthorhombic form of bis-(*n*-methylsalicylaldimine)-Ni(II) is strongly dichroic and appears red or green in different polarizations. The two visible absorption bands were assigned to the transitions ${}^1A_g \rightarrow {}^1B_{1g}$ and ${}^1A_g \rightarrow {}^1B_{2g}$. Now, neither the theory of Maki[297] nor that of Ballhausen and Liehr[301] is in complete agreement with these assignments, so obviously the matter needs closer study. The trouble with these investigations is that so very few structures of square planar nickel(II) complexes are known, one of the few being the crystal structure of the diamagnetic green bis-(*n*-methylsalicylaldimine)-nickel(II) complex.[308]

The spectra and magnetism of the so-called "Lifschitz complexes" have attracted a good deal of attention.[301,309] These Ni(II) complexes with the ligands 1,2 diphenyl ethylene diamine, abbreviated "stien," have the composition $Ni(stien)_2^{++}$. Depending on the nature of the anion, these compounds form either blue (paramagnetic) or yellow (diamagnetic) crystals, which in many cases are interconvertible. With the anion of a weak acid such as acetate and the like there is in addition the possibility of having a dimer possessing an antiferromagnetic coupling between the metal atoms.[301] A closer study of the magnetic and structural properties of these complexes is highly desirable.

A borderline case between the planar and octahedral structure is found for the green Ni(II) bis-acetylacetone. Previously thought to be tetrahedral, this complex has now been shown to be a trimer in the solid state.[310] As for the structure in solution, Cotton and Fackler[377] have shown that we probably have a monomer-polymer equilibrium. This latter phenomenon seems to be found for many of the solutions of $Ni(chelate)_2$ complexes.

The last structure of Ni(II) with which we shall be concerned is the tetrahedral configuration. For a long time the tetrahedral configuration for Ni(II) was believed to be nonexistent, but now some examples have finally been brought to light. The first complex of Ni(II) which was shown for certain to be tetrahedrally coordinated[311] was the blue $NiCl_2(P\varphi_3)_2$, where φ stands for C_6H_5. Spectral and magnetic studies of this compound have been carried out by Cotton, Faut, and Goodgame.[312] The effective number of Bohr magnetons were found to be about 3.40 at room temperature; the spectrum showed absorption maxima at 10,800 cm^{-1}, 16,300 cm^{-1}, and 17,600 cm^{-1}. Other tetrahedral Ni(II) complexes can be made with phosphine oxide, arsine oxide, and various halides as ligands.[313]

Of even greater theoretical interest are the tetrahedral halide complexes $NiX_4^=$ with X = Cl, Br, and I. The colors of these complexes are respectively blue, blue, and red. The tetrahedral structure of $NiCl_4^=$ in fused salts of LiCl and KCl was demonstrated by Gruen and McBeth.[314] Preliminary spectral studies of this ion were made by various authors.[258,315] It was, however, left to Goodgame, Goodgame, and Cotton,[316] and independently to Furlani and Morpurgo,[317] to perform a fuller analysis of the spectral data. It was then found[316] that the optical features could be satisfactorily interpreted only by the use of the "complete" spin-orbit treatment of the electronic $(3d)^8$ configuration.[36] The results indicate that $10Dq$ for $NiCl_4^=$ is some 380 cm^{-1} and that the term distance $^3F - {}^3P$ is reduced about 25 per cent. The Dq value is in reasonable agreement with the ionic model theoretical value of $Dq(\text{tet.}) = \frac{4}{9}Dq(\text{oct.})$ in going from an octahedral to a tetrahedral complex.

The values of $10Dq$ further suggest that the spectro-chemical series for tetrahedral Ni(II) complexes is $I^- \sim Br^- < Cl^-$. The nephelauxetic series on the other hand is Cl < Br < I. The measurements of the magnetic moments[316] of NiI_4^- seem to indicate that a considerable distortion of the complex from the tetrahedral structure takes place. Such a distortion cannot be attributed to a Jahn-Teller effect, since the spin-orbit forces will remove the degeneracy of the ${}^3T_{1g}$ state and leave a Jahn-Teller resistant singlet as the ground state.[36] The possibility of a pseudo Jahn-Teller effect is, however, not excluded, Sec. 8-*d*. Nevertheless, the deformation of the complex is most likely due to the surroundings in the crystal.

10-i. Copper

Copper has the electronic structure $[A](3d)^{10}(4s)^1$. We shall consider only divalent copper, which has the electronic configuration $[A](3d)^9$. The structure of the complex can be either a distorted octahedron, which in the limit goes to the square planar configuration, or a tetrahedron.

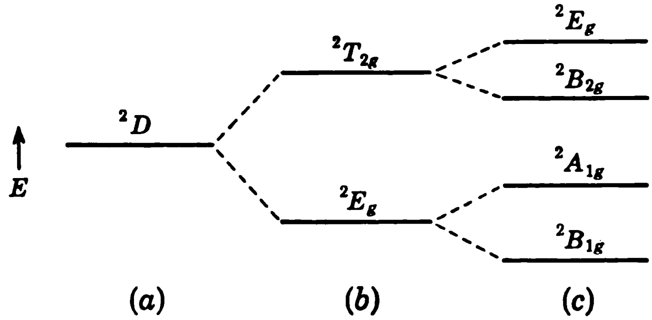


FIG. 10-19. Energy-level diagram for sixfold coordinated Cu(II) ions. (*a*) State of free ion; (*b*) splitting in cubic field; (*c*) splitting in tetragonal field.

The ground state of a cubic octahedrally coordinated Cu(II) ion is ${}^2E_g(t_{2g})^6(e_g)^3$. The only excited state should then be ${}^2T_{2g}(t_{2g})^5(e_g)^4$; the energy difference being $10Dq$. Stated in other words, with Cu(II) possessing one hole in the filled *d* shell, the spectral behavior of the complex should be as found in Ti^{3+} complexes, only with the level order inverted.

This inversion of the level order has important consequences because, as pointed out in Sec. 8-*d*, the ${}^2E_g$ state should be highly susceptible to a Jahn-Teller configurational instability. We would then expect that no regular octahedrally coordinated Cu(II) complex should exist, and this is in accord with the experimental findings.[170]

The absorption spectra of octahedrally coordinated Cu(II) ions confirm the structural data. Consider, for instance, the crystal spectrum of the blue $CuSO_4 \cdot 5H_2O$. The crystal structure has been reported by Beevers and Lipson.[319] Each copper(II) ion is surrounded by four water molecules arranged in an approximate square planar configuration, with two polar sulfate oxygens in trans position. The crystal field is hence of D_{4h} symmetry, and the electronic levels should be as shown in Fig. 10-19. The doubly degenerate ground state ${}^2E_g$ is split into two components, and the upper state ${}^2T_{2g}$ is split into two other components. Analysis of the polarized absorption spectrum as performed by Holmes and McClure[55] shows just three transitions located from 10,000 cm^{-1} to 14,000 cm^{-1}.

The theory for the absorption bands of octahedrally coordinated copper(II) complexes has been given by Polder,[319] Ballhausen,[320] and Belford et al.[321] Spectral data for many copper(II) complexes in solution have been given by Bjerrum et al.[322] and by Jørgensen.[272] The absorption spectrum of the blue crystalline $CuSiF_6 \cdot 6H_2O$ has been given and interpreted by Pappalardo,[323] who assumed a regular octahedral configuration with spin-orbit coupling included. (See also Liehr, Ref. 424.) This effect will broaden the ${}^2E_g \rightarrow {}^2T_{2g}$ transition because the upper ${}^2T_{2g}$ state will be split in this approximation. Assuming the spin-orbit constant λ to have essentially the free-ion value, a value of $Dq = 1120\ \text{cm}^{-1}$ was deduced. This value is in good agreement with the Dq values for the other divalent aquo complexes of the first transition group. The intensity of the vibronically allowed transition has been treated by Liehr and Ballhausen.[8]

The absorption spectrum of $Cu(H_2O)_6^{++}$ in solution shows, on the other hand, a very unsymmetric band which can be resolved into at least two peaks.[322] The reason for this is probably, as already mentioned, that the Jahn-Teller effect produces a distortion of the octahedral coordination of water, Sec. 8-*d*. Calculations show[6,7,325] that, by assuming an ionic bonding scheme, one should expect the compressed octahedron to be stable. This is in contradiction to what is found in the majority of cases. Only one example of a compressed octahedron, namely,[327] K_2CuF_4, is so far known. This is, of course, a compound which would be likely to possess a high degree of ionic bonding.

It must, however, be said that the only well-documented case for the existence of a Jahn-Teller effect in Cu(II) complexes is found in $Cu(H_2O)_6 \cdot SiF_6$. Paramagnetic resonance measurements[328,329] revealed that the g factor was isotropic at room temperature but anisotropic at low temperatures. The explanation for this is found in the form of the wave function for the ground state of the complex.[330] If we remember the similar discussion of VCl_4 in Sec. 8-*d*, we notice that the electronic wave function for the lowest potential sheet can be written

$$\psi = \sin \tfrac{1}{2}\varphi d_{x^2-y^2} - \cos \tfrac{1}{2}\varphi d_{z^2}$$

By evaluating the three g factors using this wave function, we get

$$g_x = 2 + \frac{2\lambda}{10Dq} (\sin \tfrac{1}{2}\varphi + \sqrt{3} \cos \tfrac{1}{2}\varphi)^2$$
$$g_y = 2 + \frac{2\lambda}{10Dq} (\sin \tfrac{1}{2}\varphi - \sqrt{3} \cos \tfrac{1}{2}\varphi)^2$$
$$g_z = 2 + \frac{2\lambda}{10Dq} (0 \times \cos \tfrac{1}{2}\varphi - 2 \sin \tfrac{1}{2}\varphi)^2$$

where, as usual, λ is the spin-orbit coupling parameter.

At high temperatures where φ can be considered cyclic, the g factors must be averaged over φ. For each vibrational state we then obtain an isotropic g factor:

$$g_x = g_y = g_z = 2 + \frac{4\lambda}{10Dq}$$

For low temperatures, on the other hand, a trapping takes place; φ assumes a definite value, and the g factors can be fitted to experiments by taking $\varphi = \pi/3$, π, or $5\pi/3$. Then

$$g_x = g_y = g_\perp = 2 + \frac{2\lambda}{10Dq}$$

$$g_z = g_\parallel = 2 + \frac{8\lambda}{10Dq}$$

The observed values[329] are $g_\perp = 2.11$ and $g_\parallel = 2.46$, which are seen to agree remarkably well with the theory.[6] This result is the more interesting since it definitely indicates that the "stable" configuration of the copper complex is an elongated octahedron. The reverse situation (where $\varphi = 0$, $2\pi/3$, or $4\pi/3$) would lead to values

$$g_x = g_y = g_\perp = 2 + \frac{6\lambda}{10Dq}$$

$$g_z = g_\parallel = 2$$

These values are not supported by experiments. The discussion here should be compared with the one given in Sec. 6-*f*.

The complete theory for the paramagnetic resonance spectra of copper salts has been given by Abragam and Pryce[331] and others.[332,333] Experimental results are plentiful; we quote only the measurements of Bagguley and Griffiths,[334,335] respectively concerned with the resonance found in copper sulfate and the copper Tutton salts. The paramagnetic resonance of a single crystal of copper(II) acetylacetonate has further been studied by McGarvey.[336] Writing down the molecular orbitals and evaluating the g factors using these wave functions,[23] he obtained evidence for a strong π bonding in this complex. The proof that the unpaired electron is not in a $4p$ orbital has been given by Okamura and Date.[337]

The magnetic susceptibility of copper(II) complexes has also been studied extensively since the work of Jordahl.[338] Using a predominantly cubic field including a small rhombic component, a rather good fit could be obtained for the susceptibility of the blue copper Tutton salt $K_2Cu(SO_4)_2 \cdot 6H_2O$. Jordahl's work was carried further by Polder,[339] who gave explicit formulas for the magnetic susceptibility of the tetragonally distorted copper(II) complexes, viz.,

$$\chi_\parallel = \frac{0.376}{T}\left(1 - \frac{4\lambda}{\Delta_1}\right)^2 + \frac{2.1}{\Delta_1}$$

$$\chi_\perp = \frac{0.376}{T}\left(1 - \frac{\lambda}{\Delta_2}\right)^2 + \frac{0.53}{\Delta_2}$$

where $\Delta_1 = E(^2B_{2g}) - E(^2B_{1g})$ and $\Delta_2 = E(^2E_g) - E(^2B_{1g})$. The last term in these formulas is of course the high-frequency term. The anisotropic magnetic behavior of a series of hydrated copper(II) salts has been extensively studied by Bose, Mitra, and Datta.[340] Other copper complexes whose susceptibilities have been studied over a temperature range include a number of "planar" copper chelates.[341]

The blue complex $Cu(NH_3)_4SO_4 \cdot H_2O$ has received a great deal of attention. The paramagnetic resonance has been studied by Abe and Ôno[342] and by Carlson and Spence.[343] Their results yield $g_\parallel = 2.22$ and $g_\perp = 2.05$ as expected from the theory. However, the picture shifts[344] if we turn to the measurements of the susceptibility at liquid-helium temperatures. An antiferromagnetic coupling sets in, and the susceptibility has a maximum at a few degrees Kelvin. The theoretical explanation has been given by Eisenstein.[345] The structure of $Cu(NH_3)_4SO_4 \cdot H_2O$ can best be described as a distorted *trans*-$[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex, and by assuming a spin-spin coupling between the two copper ions per unit cell, both the magnetic and thermal properties can be explained.

The most famous example of antiferromagnetism in a copper(II) complex is found in the green cupric acetate. The susceptibility for this compound passes through a maximum at room temperature and then decreases rapidly.[346] The paramagnetic resonance shows that the magnetic state is an excited state with $S = 1$, and that consequently the resonance vanishes[347] by cooling.

This overall picture is consistent with a strong spin-spin coupling as previously discussed in Sec. 6-*h*. The coupling constant J can, of course, be obtained from susceptibility measurements as outlined earlier. However, it can also be obtained from the variation of the intensity of the paramagnetic resonance spectrum with temperature. This is done in the following way. With a level picture as given in Fig. 6-8 the intensity P is proportional to the difference in population between the two Stark levels, separated by $g\beta H$, between which the transition occurs. In the excited ^3X state we have a fraction x of the total population. The value of x is, after Boltzmann,

$$x = \frac{3e^{-J/kT}}{1 + 3e^{-J/kT}}$$

When the magnetic field is applied, this fraction is distributed among the three Stark levels as follows:

$$n_{-1} = \tfrac{1}{3}e^{g\beta H/kT} \qquad n_0 = \tfrac{1}{3} \qquad n_1 = \tfrac{1}{3}e^{-g\beta H/kT}$$

The difference in population between adjacent levels is therefore

$$\frac{x}{3}\left(1 - e^{-g\beta H/kT}\right) \simeq x\,\frac{g\beta H}{3kT}$$

The signal intensity will hence vary as

$$P \approx \frac{e^{-J/kT}}{1 + 3e^{-J/kT}} \frac{g\beta H}{kT} \approx \frac{1}{T} \frac{e^{-J/kT}}{1 + 3e^{-J/kT}}$$

Bleaney and Bowers[347] found in this way a value of $J = 260$ cm^{-1}. The susceptibility curve indicates, on the other hand, that $J = 315$ cm^{-1}. It is probably true that the exchange energy between the two copper ions in the acetate increases with temperature.[349]

Because of this behavior it was concluded that cupric acetate monohydrate was a dimer, and the actual structure of $Cu_2(ac)_4 \cdot 2H_2O$, as solved by Van Niekerk and Schoening,[109] proved this conclusively. The two copper atoms have only a distance of 2.64 A and are held together with four acetate bridges.

The more detailed mechanism of the exchange interaction has been investigated by Stevens[350] and Ross,[351] and a great amount of experimental work has been carried out on the acetate and related copper complexes.[111,353–357] Spectra and dichroism of the crystals have been reported by Yamada et al.,[358–360] but no detailed assignments have as yet been given.

The copper(II) chlorides are rather interesting. The structure of the garnet-red $CsCuCl_3$ was shown by Wells[361] to consist of a copper ion surrounded by six chlorine ions in an octahedral arrangement. On the other hand, the yellow Cs_2CuCl_4 was shown by Helmholz and Kruh[362] and Morosin and Lingafelter[363] to contain tetrahedrally coordinated copper(II) units. However, these units are not regular tetrahedra, but are found to be somewhat flattened. Finally, the red-brown compound $LiCuCl_3 \cdot 2H_2O$ contains[429] planar $Cu_2Cl_6^{=}$ ions with symmetrical Cu—Cl—Cu bridges; the ions are weakly linked by larger Cu···Cl bonds to form chains. The ground state seems to be a spin triplet.

The electronic structure of the tetrahedrally coordinated copper(II) complexes should be exactly as found for the octahedrally coordinated complexes, except with the level order inverted. The *Dq* value is as usual decreased[320] by a factor of $4/9$. The distorted structure of the yellow $CuCl_4^{=}$ has been explained by Felsenfeld[364] as a compromise between the mutual coulombic repulsions of the Cl^- ions and the crystal field stabilization of the Cu^{++} ion. It is worthwhile to mention that the distorted structure is not due to a Jahn-Teller mechanism.[424]

The absorption spectrum of $CuCl_4^{=}$ is difficult to interpret,[320] since it mostly consists of charge-transfer bands. The absorption band found[362] at some 13,000 cm^{-1} has been identified as[117] the transition $^2T_2 \rightarrow {}^2E$. The oscillator strength of the band is about 2×10^{-3}. However, since *Dq* for $CoCl_4^{=}$ is ~360 cm^{-1}, it does not look likely that *Dq* for $CuCl_4^{=}$ should be 1300 cm^{-1}. Hence, the band in question must be a charge-transfer band. Crystal spectra of the compound using polarized light have been reported by

Yamada and Tsuchida.[365] These measurements are in accord with a structure consisting of a slightly compressed tetrahedron. The magnetic susceptibility over a range of temperatures has been measured by Figgis and Harris,[341] without revealing anything of particular interest. On the other hand, the absorption spectrum of Cu^{++} in ZnO shows a band at 5800 cm^{-1}. This is in excellent agreement with the predictions of the crystal field theory,[323] and we therefore propose that the crystal field band of $CuCl_4^{=}$ should be found at some 6000 cm^{-1}.

The most puzzling of all Cu(II) complexes is undoubtedly the blue anhydrous $Cu(NO_3)_2$. In the crystal each copper ion is reported to be octacoordinated, the structure being a hexagonal bipyramid.[366] In the gas phase, on the other hand, each copper ion is surrounded by two nitrate groups, with four oxygens forming a trigonal pyramid.[367] No explanation of the electronic structures has at present been given.

COMPLEXES CONTAINING 4*d* AND 5*d* ELECTRONS

Rather large differences exist between the complexes of the first transition series and those of the latter. This is due to the fact that the 4*d* and 5*d* electrons are less tightly bonded to the metal atom than their sister 3*d* electrons are. As a result, molecular-orbital formation occurs readily; 10*Dq* becomes great, and the "charge-transfer" states have lower energies than most "crystal field" states. Furthermore, the problem of spin-orbit coupling becomes much more important; to treat it as a small and rather unimportant perturbation is not allowed any more. All this means that we observe either too much or too little, with the result that the interpretation becomes very difficult. In what follows we shall very briefly indicate some of the most important features for these complexes, and since much less work has been done here than is the case for the first transition elements, the discussion will be rather brief.

10-j. Niobium

Niobium has the electronic configuration $[Kr](4d)^4(5s)$, where [Kr] stands for the closed krypton configuration. Nb(II) is therefore expected to have the electronic structure $[Kr](4d)^3$ and should resemble Cr(III). The spectrum of the yellow Nb(II) ions in strong HCl has been investigated by Cozzi and Vivarelli,[368] who find evidence for the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition at 22,700 cm^{-1}. Hence, Dq would be 2270 cm^{-1} as compared to the Dq value of 1740 cm^{-1} for $Cr(H_2O)_6^{3+}$. No magnetic data seem to be available.

Nb(III) seems likewise to have some crystal field bands, but no interpretation has been given. The spectrum of Nb(IV) was found[368] to have a maximum at 13,500 cm^{-1} in 13-molar HCl and at 14,300 cm^{-1} in 8-molar HCl, the colors of the solutions being respectively red-orange and blue.

10-k. Molybdenum

Molybdenum has the electronic configuration $[Kr](4d)^5(5s)$. Mo(III) has, then, the structure $[Kr](4d)^3$, and again we would expect the features of its complexes to be analogous to those of Cr(III).

The absorption spectra of the red ions $MoCl_6^{3-}$, $MoBr_6^{3-}$, and the green ion $Mo(H_2O)_6^{3+}$ have been recorded by Hartmann and Schmidt.[369] It is, for example, found that $MoCl_6^{3-}$ has a spin-forbidden band located at 15,000 cm^{-1} and two allowed bands situated at 19,000 cm^{-1} and 24,000 cm^{-1}. These bands can then be correlated with the transitions ${}^4A_{2g} \rightarrow {}^2E_g$, ${}^4T_{2g}$, and ${}^4T_{1g}$. We get immediately $Dq = 1900$ cm^{-1} and from the other energy differences $F_2 \approx 1100$ cm^{-1} and $F_4 \simeq 85$ cm^{-1}.

The paramagnetic resonance measurements yield[16,370] a g value for the deep-red complex K_3MoCl_6 of 1.96. With $g = 2 - 8\lambda/10Dq$ we get $\lambda = 95$ cm^{-1}. This is a considerable reduction from the free-ion value of about 270 cm^{-1}. On the other hand, a "complete" treatment[431] including spin-orbit coupling of the $(4d)^3$ system gave the parameter set $F_2 = 710$ cm^{-1}, $F_4 = 56$ cm^{-1}, and $\lambda = 183$ cm^{-1}. The magnetic susceptibility of the compound has been investigated by Epstein and Elliott[371] from 77 to 295°K. They found $\chi = 1.82/T$, corresponding to a magnetic moment of 3.83 Bohr magnetons.

Mo(IV) has two $4d$ electrons. The best-known complex is probably the yellow $K_4[Mo(CN)_8]$. The Mo(IV) ion is eight-coordinated, the structure being a duodecahedron.[372] In this structure the $4d$ orbitals will split up into three orbital singlets and one doublet,[370] with one of the singlets placed far below the other levels. In a strong crystal field we should then expect the ground state for $Mo(CN)_8^{4-}$ to be a spin-paired ${}^1A_{1g}$ state, and this expectation is found to be justified.

The various orbitals which could be used in the bonding have been discussed by Penney and Anderson,[373] Racah[374] and Duculot.[375] It was shown[374] that an s–p–d hybrid would account nicely for the found bond angles. No absorption spectrum seems so far to have been published.

Mo(V) is found in the green complex $[MoOCl_5]^-$. With one $4d$ electron this complex should resemble VO^{++}, and some similarities are found by Jørgensen.[5] The bands at 14,050 cm^{-1} and 22,500 cm^{-1} were tentatively ascribed to "crystal field" bands, the other bands of the complex being probably charge-transfer bands. The theory for the crystal field bands has been given by Liehr.[424] The complete molecular energy level diagram has been indicated by Gray and Hare.[434] In addition to the crystal field bands, these authors also identified some of the charge-transfer bands. The level scheme is identical to that of VO^{++}, Fig. 10-2.

The yellow $K_3Mo(CN)_8$ has been shown[370] to have a g factor of 2.005. If we assume that the structure of the complex is identical with that of $K_4Mo(CN)_8$, the single electron should be found in a $d_{x^2-y^2}$ orbital with a large energy jump to the next levels. The value of g should then be close to 2, but the fact that it is greater than the free-spin value shows that the crystal field model is not sufficient to give a complete description of the magnetic properties. The effective number of Bohr magnetons is 1.66.

Finally, we mention that the magnetic properties of the dark-colored $MoCl_5$ have been investigated by Knox and Coffey.[376] The effective moment is found to be 1.52 Bohr magnetons, and $\mu_{eff} = 2.83 \sqrt{\chi(T + \Delta)}$, with $\Delta = -23°$. Since the structure is unknown, no interpretation can be given. The spectrum of $MoCl_5$ in the gas phase, where the molecule presumably has the structure of a trigonal bipyramid, has been published by Bader and Westland.[435] It is, however, most likely that their spectrum is that of $MoOCl_3$.

10-l. Technetium

Technetium has the electronic structure $[Kr](4d)^5(5s)^2$. Nothing much is known of its chemistry, except for the fact that $TcCl_4$ forms small blood-red crystals. The magnetic properties[376] of $TcCl_4$ are not consistent with the magnetic moment of d^3; the observed moment being $\mu_{eff} = 3.44$ with $\mu_{eff} = 2.83 \sqrt{\chi(T + \Delta)}$ and $\Delta = -57°$. However, the plot of the susceptibility versus $1/T$ is not a straight line. Since the structure is unknown, no interpretation can be offered.

10-m. Ruthenium

Ruthenium has the electronic structure $[Kr](4d)^7(5s)$. Complexes with the metal in the oxidation states two to six are found. Ru(II) has the structure $[Kr](4d)^6$; it should, then, be analogous to Co(III). $Ru(CN)_6^{4-}$ is colorless and presumably diamagnetic. Some blue chloro complexes are also known. They are often assumed[219] to be $RuCl_4^-$. No structural data are known.

Ru(III) complexes, on the other hand, are fairly well characterized. The electronic structure corresponds to d^5, and hence Ru^{3+} should resemble Mn^{++}. Spectra of the red species $RuCl_6^{3-}$ and $RuBr_6^{3-}$ have been given by Jørgensen.[219] The work of Hartmann and Buschbeck[378] contains some very nice spectra of $RuCl_6^{3-}$ and the colorless $Ru(NH_3)_6^{3+}$ and also, for instance, the spectra of the red-violet complex $[Ru(NH_3)_5I]^{++}$.

The magnetism of the compounds corresponds to a spin quantum number $S = \frac{1}{2}$, as is to be expected for the configuration $(t_{2g})^5$. The ground state is thus ${}^2T_{2g}(t_{2g})^5$, and the first excited doublet levels will be ${}^2A_{2g}(t_{2g})^4(e_g)$ and ${}^2T_{1g}(t_{2g})^4(e_g)$. We are thus tempted to ascribe the "first" band of $RuCl_6^{3-}$, found at 19,200 cm^{-1}, to the transition ${}^2T_{2g} \rightarrow {}^2A_{2g}$. The energy difference between these two states is, assuming pure $(t_{2g}),(e_g)$ quantization, $10Dq - 3F_2 - 20F_4$. With $F_2 = 10F_4 = 1000\ cm^{-1}$ we then get a value of $Dq = 2400\ cm^{-1}$, which seems very reasonable.

The magnetic properties of Ru(III) complexes have been studied by

Figgis et al.[379,380] An order-of-magnitude estimation of $\lambda = 1000$ cm^{-1} was obtained. Finally, Epstein and Elliott[371] have given the paramagnetic susceptibility of $RuCl_3$ as a function of temperature and have found that Curie's law is obeyed for this compound. Paramagnetic resonance measurements on $Ru(NH_3)_6Cl_3$ have been performed by Griffiths, Owen, and Ward.[370]

Ru(IV) possesses the electronic configuration $[Kr](4d)^4$. The absorption spectra show only[381] charge-transfer bands. The magnetic properties have been rather well investigated. The susceptibility of the green complex K_2RuCl_6 has been measured by Earnshaw et al.[379] over a wide temperature range and interpreted by Figgis et al.[380] and Griffith.[382] Calculations[382] of the relevant matrix elements within the $(t_{2g})^4$ subshell in intermediate coupling yields a closed formula for the magnetic susceptibility. The estimation of χ using free-ion parameters produced a good fit of the experimental data. The high-frequency term was further calculated to be some 60×10^{-6} eu.

Results quite similar to the ones quoted above were obtained by Kamimura et al.[383] For K_2RuCl_6 a value of the spin-orbit coupling factor $\xi_{4d} = 1400$ cm^{-1} was deduced. The quantity $3F_2 + 20F_4$ was further found to be 3500 cm^{-1}. The reported value[370] of $g = 1.92$ seems to be somewhat uncertain.

Ru(VI) should possess two unpaired electrons, and magnetic measurements on the tetrahedral compound $RuO_4^{=}$ show[384] a g factor equal to 2.0, which is in accord with the electronic $(e)^2$ structure of the ground state. (See Fig. 10-9 with the level scheme for $CrO_4^{=}$.) The magnetic susceptibility is also in accord with this structure.

The spectrum of the black $RuO_4^{=}$ has been given by Connick and Hurley.[386] It shows a broad band with a shoulder toward the blue. Similarities to the spectra of MnO_4^{3-} and $FeO_4^{=}$ are to be expected. The spectra of RuO_4^- and RuO_4 are likewise given.[386]

The dimeric red compound $[Ru_2Cl_{10}O]^{4-}$ is known to exist in the crystal. It is diamagnetic, and the probable reason for this has been given by Dunitz and Orgel[121] by using a molecular-orbital description. We refer to our previous remarks concerned with binuclear Cr complexes.

10-n. Rhodium

The most stable oxidation state of this metal is Rh(III), which has the electronic configuration $[Kr](4d)^6$. Rh(III) complexes should then resemble the Co(III) complexes. The ground state of the octahedral Rh(III) complexes is thus ${}^1A_{1g}(t_{2g})^6$, and the singlet excited states are ${}^1T_{1g}$ and ${}^1T_{2g}$, belonging to the configuration $(t_{2g})^5(e_g)$, Fig. 10-12*b*. Since these complexes are diamagnetic, no paramagnetic resonance can, of course, be detected. The high-frequency term in the formulas of Van Vleck has been estimated[255] to be some 130×10^{-6} eu.

The compounds containing Rh(III) are usually formulated as containing only one formula unit. This seems, however, to be oversimplified in some cases. Consider, for instance, the red compound with the apparent formula $K_3Rh(ox)_3 \cdot 4\frac{1}{2}H_2O$, where ox stands for the oxalate ion $C_2O_4^{=}$. The proton magnetic resonance study of Porte, Gutowsky, and Harris[387] indicates that the true structure for the compound should be formulated as $K_6[Rh(ox)_3][Rh(ox)_2(Hox)(OH)]8H_2O$.

Extensive studies of the absorption spectra for Rh(III) complexes have been carried out by Jørgensen.[388,389] We quote some numbers. For the red $RhCl_6^{3-}$: ${}^1A_{1g} \rightarrow {}^1T_{1g}$ at 19,300 cm^{-1} and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ at 24,300 cm^{-1}, with ${}^1A_{1g} \rightarrow {}^3T_{1g}$ found at 14,700 cm^{-1}. For the colorless $Rh(NH_3)_6^{3+}$: ${}^1A_{1g} \rightarrow {}^1T_{1g}$ at 32,700 cm^{-1} and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ at 39,100 cm^{-1}. For the orange *tris*-oxalato complex in solution: ${}^1A_{1g} \rightarrow {}^1T_{1g}$ at 25,100 cm^{-1} and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ at 30,000 cm^{-1}. The spin-forbidden band ${}^1A_{1g} \rightarrow {}^3T_{1g}$ is found at 19,200 cm^{-1}. In addition to the spectra of the complexes with six identical ligands, a great number of spectra of monosubstituted and *cis*- and *trans*-Rh(III) complexes have been recorded.[388,389]

These data make it possible to calculate Dq, F_2, and F_4 values for these complexes similarly to what has been done for Co(III) complexes. We find, for instance, for $RhCl_6^{3-}$ that $Dq = 2160$ cm^{-1}, $F_2 = 640$ cm^{-1}, and $F_4 = 70$ cm^{-1}. From the measurements[389] of the orange *cis*- and the yellow *trans*-$Rh(ox)_2Cl_2^{3-}$ it should further be possible to estimate the values of the Ds and Dt splitting parameters.

10-o. Palladium

Palladium has the electronic structure $[Kr](4d)^{10}$. We shall be most interested in Pd(II), possessing eight $4d$ electrons. However, we remark in passing that palladium complexes containing Pd(IV) exist and that the absorption spectrum of $PdF_6^{=}$ has been predicted by Jørgensen.[179] It is also possible to make the black compound PdF_3. The magnetic moment[393] of the complex is 2.05 Bohr magnetons.

Pd(II) forms square planar complexes which are, as expected, diamagnetic.[390] For the yellow aqueous solution of Pd^{++} and Cl^- Sundaram and Sandell[391] have found one absorption band at 23,800 cm^{-1}, which presumably is due to the complex $PdCl_4^{=}$, and another band at 21,200 cm^{-1}, which they think is due to the $PdCl_6^{4-}$ species. The dichroism of a number of Pd(II) complexes has been studied by Yamada,[392] but no interpretation has so far been given.

10-p. Tungsten

Tungsten has the electronic structure $[Xe](5d)^4(6s)^2$, where [Xe] stands for a closed xenon electronic configuration. This metal has an unusual tendency to form polynuclear complexes. These are of unknown molecular structure, and consequently only very little is known about the electronic states of tungsten complexes.

W(V) should possess one $5d$ electron.[424] Jørgensen[5] is of the opinion that the blue monomer $WOCl_5^-$ exists in strong HCl. The solution has a single band with the maximum placed at 15,300 cm^{-1}. However, more than one species could exist in the solution. With cyanide, wolfram forms the orange-yellow complex $W(CN)_8^{3-}$. The paramagnetic resonance has been measured,[394] yielding a g value of 1.972. The colorless complexes $NaWF_6$ and KWF_6 both show antiferromagnetism.[395]

W(IV) contains two $5d$ electrons. The best-known complex is the yellow diamagnetic $K_4[W(CN)_8]2H_2O$. This seems to indicate that the structure is identical with the corresponding molybdenum complex.

W(III) is found in the yellow-green dimer $W_2Cl_9^{3-}$. The spectrum does not resemble[5] that of Mo(III). The magnetic properties[396] show that there is a very strong spin-spin coupling between the two wolfram atoms.

10-q. Rhenium

With the electronic structure $[Xe](5d)^5(6s)^2$, rhenium should resemble Mn, and this expectation is found to be justified. The greatest difference between the two elements is that Re^{++} is nearly unknown.

Re(III) is found in the reddish-black $ReCl_3$. The ion should have the electronic structure $[Xe](3d)^4$. The magnetic susceptibility has been measured by Knox and Coffey.[376] An effective moment of 2.04 Bohr magnetons was found, but the evaluation of Δ using the formula $\mu_{eff} = 2.83\sqrt{\chi(T + \Delta)}$ yielded a value of $\Delta = 985°$. Such a value has no meaning, and a closer theoretical analysis should be performed.

The optical and magnetic features of the green K_2ReCl_6 have been thoroughly studied.[398,399] Some preliminary spectral assignments were made by Jørgensen,[397] but it was left to Eisenstein[398,399] to give the full interpretation. Re(IV) is a $(5d)^3$ system. With a large spin-orbit coupling present all of the levels can be classified as Γ_6, Γ_7, and Γ_8 in the octahedral double group. The ground state is ${}^4A_{2g}(\Gamma_8)$. In order to understand the spectrum, Eisenstein[399] calculated all of the relevant matrix elements for the d^3 configuration in the octahedral double group, as well as the matrix elements for the magnetic moment operator.

The absorption spectrum between 7000 cm^{-1} and 17,000 cm^{-1} consists of four band systems, some of them with superimposed vibrational structure. All of these bands are due to transitions within the $(t_{2g})^3$ configuration. The first excited state at ~7700 cm^{-1} is ${}^2T_{1g}(\Gamma_8)$. The next two states are ${}^2E_g(\Gamma_8)$ found at 9105 cm^{-1} and ${}^2T_{1g}(\Gamma_6)$ at 9574 cm^{-1}. The excited state at 14,180 cm^{-1} can be attributed to ${}^2T_{2g}(\Gamma_7)$, and the peak at 15,385 cm^{-1} to ${}^2T_{2g}(\Gamma_8)$.

In order to calculate the above energy levels, suitable values of the sundry parameters were chosen and put into the perturbation matrices. These values were then varied until the best fit of the spectrum was obtained. The Dq value was found to be 3350 cm^{-1} with $\xi_{5d} = 2300$ cm^{-1}. For the $(t_{2g})^3$ configuration it was further found that $F_2 = 630$ cm^{-1} and $F_4 =$ 50 cm^{-1}.

Using the above set of parameters, the susceptibility of the complex K_2ReCl_6 was calculated[399] by means of the formula of Van Vleck. By introducing an "orbital reduction factor" k equal to 0.7, a very reasonable fit of the experimental data was obtained. In addition, some evidence was found that the complex shows antiferromagnetism at low temperatures.

Re(V) is, for instance, found in the blackish-brown $ReCl_5$. The magnetic susceptibility has been measured over a temperature range by Knox and Coffey.[376] No spectral or structural data are available.

Re(VI) forms the pale-yellow compound ReF_6. The system possesses the electronic configuration $[Xe](5d)^1$, and the coupling scheme for a single d electron in an octahedral field has been given by Moffitt et al.[400] and Liehr.[424] Formally, it is, of course, identical with the $3d$ case pictured in Fig. 6-1. The absorption spectrum of ReF_6 shows two bands located at 5200 cm^{-1} and 32,500 cm^{-1}. The first transition is attributed to an excitation $\Gamma_8(t_{2g}) \rightarrow \Gamma_7(t_{2g})$, while the second is due to the transition $\Gamma_8(t_{2g}) \rightarrow \Gamma_8(e_g)$. These numbers imply that the ligand field is very strong, and by using this approximation, we get $Dq = 3200$ cm^{-1} and $\xi_{5d} = 3500$ cm^{-1}. However, by taking the configuration interaction between the two Γ_8 levels into account and by taking $Dq = 3000$ cm^{-1} and $\xi_{5d} = 3200$ cm^{-1}, Eisenstein[401] could account for the experimental values.

Even these latter values may be too high, however. The ground state Γ_8 in a regular octahedral configuration should experience a configurational instability of the Jahn-Teller type. Eisenstein[401] has made a rough estimate of the effect, and he has shown that as low a value of ξ_{5d} as 2500 cm^{-1}, together with a $Dq = 2950$ cm^{-1} and a tetragonal field of 187 cm^{-1}, may account for the experimental facts. Since for ReF_6 the vibrational frequencies and force constants are all known,[402] it should be possible to perform an "exact" Jahn-Teller calculation.

10-r. Osmium

The electronic structure of Os is $[Xe](5d)^6(6s)^2$. Important metal oxidation states are four, five, and six. Os(IV) has the structure $[Xe](5d)^4$. The magnetic susceptibility of complexes containing Os^{4+} has received a great deal of attention. The calculations of Griffith[382] and Kamimura et al.[383] are relevant here. The measurements of Earnshaw et al.[379] on the red salt K_2OsCl_6 can be explained by assuming a value of $\xi_{5d} = 3600$ cm^{-}. The ground state would be $(\gamma_8)^4$, producing a Γ_1 level. Other excited states are pictured in Fig. 10-20.

$OsCl_6^{=}$ has an extremely narrow band at 17,240 cm^{-1} which Jørgensen[403] interprets as the $\Gamma_1 \rightarrow \Gamma_1$ transition, Fig. 10-20. By using this value, Griffith[382] was able to calculate the magnetic susceptibility $\chi = 848 \times 10^{-6}$ for $OsCl_6^=$, in good accord with the experimental value.

A great many electron transfer bands are further observed[403] in $OsCl_6^=$. Some tentative considerations as to the origin of these and similar charge-transfer bands have been given by Jørgensen in the already quoted reference.

The magnetic susceptibility of Os^{5+} in the colorless complex $KOsF_6$ has been measured by Figgis et al.[380] With the electronic configuration of $(5d)^3$ the ground state is a $^4A_{2g}(\Gamma_8)$ state and few irregularities should be observed. The $\bar{\mu}_{\rm eff} = 3.30$ shows some reduction from the spin-only value, but this is presumably due only to the usual interaction with the $^4T_{2g}$ excited level, since $\bar{\mu}_{\rm eff} \simeq 3.88(1 - 4\lambda/10Dq)$.

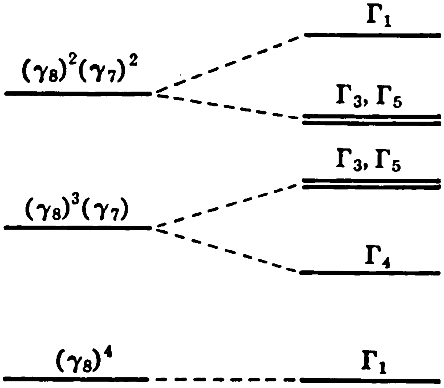


FIG. 10-20. Schematic energy scheme for the lowest levels of $(t_{2g})^4$ in the octahedral double group.[382,400]

Os(VI) is found in the pale-green OsF_6. The coupling scheme for the $(t_{2g})^2$ configuration has been given by Moffitt et al.[400] As is to be expected from the level scheme, Fig. 6-1, the configuration for the ground state is $(\gamma_8)^2$ containing two unpaired spins. This is confirmed by the measurements of the susceptibility.[404] Tentative assignments of the transitions found in OsF_6 were given by Moffitt et al.[400] The full discussion of the optical absorption spectrum and the susceptibility of this molecule was later presented by Eisenstein.[405]

First of all, it was pointed out that, in analogy with ReF_6, OsF_6 should experience a configurational instability of the Jahn-Teller type. Indeed, Weinstock, Claassen, and Malm[406] state that the behavior found for the vibrational frequency of ϵ_g symmetry is a direct consequence of the operation of a Jahn-Teller effect. For simplicity, however, the model used by Eisenstein does not consider this complication.

Using a full configuration interaction in the double group of O_h, and a procedure[405] analogous to the one given by Liehr and Ballhausen,[36] the two-electron problem was solved. The effects of covalent bonding on the Racah parameters and the nonequivalence of the t_{2g} and e_g electron radial functions were, however, taken explicitly into account.[405] The spectrum of OsF_6 could then be reproduced with a Dq value of 3554 cm^{-1}, $F_2 = 615$ cm^{-1}, $F_4 = 43$ cm^{-1}, and a spin-orbit coupling constant for the $(t_{2g})^2$ configuration of 3200 cm^{-1} and for the $(t_{2g})(e_g)$ configuration of 1900 cm^{-1}.

The susceptibility was further evaluated[405] by using the formula of Van Vleck. The above-mentioned measurements[404] could be accounted for by using an orbital reduction factor $k = 0.5$ together with the parameters evaluated from the spectral data.

10-s. Iridium

The electronic structure of Ir is $[\mathrm{Xe}](5d)^7(6s)^2$, and the oxidation states we shall consider are Ir(III), Ir(IV), Ir(V), and Ir(VI).

Ir(III) has the electronic configuration $[\mathrm{Xe}](5d)^6$. It should thus behave very similarly to Rh(III) and Co(III), and this is found to be the case. The ground state is, for an octahedrally coordinated Ir(III) ion, the usual $^1A_{1g}(t_{2g})^6$ level, and the first excited singlet states are $^1T_{1g}$ and $^1T_{2g}$. The absorption spectra of most known Ir(III) complexes have been given by Jørgensen.[388,389,407] For instance, for the olive-green $\mathrm{IrCl_6}^{3-}$ the transition $^1A_{1g} \rightarrow {}^1T_{1g}$ is found at 34,100 $\mathrm{cm^{-1}}$ and the transition $^1A_{1g} \rightarrow {}^1T_{2g}$ at 28,100 $\mathrm{cm^{-1}}$. The spin-forbidden transitions $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$ are found at 16,300 $\mathrm{cm^{-1}}$ and 17,900 $\mathrm{cm^{-1}}$, respectively. From these values we calculate in the usual way (see trivalent cobalt) that $Dq = 2800\ \mathrm{cm^{-1}}$, $F_2 = 740\ \mathrm{cm^{-1}}$, and $F_4 = 112\ \mathrm{cm^{-1}}$. Absorption spectra of complexes possessing lower symmetry than O_h are also given.[407]

Ir(IV) is, for instance, found in the dark-red $\mathrm{K_2IrCl_6}$. The metal ion has the electronic structure $(5d)^5$, and we would then expect the ground state to be $^2T_{2g}(t_{2g})^5$. However, the spin-orbit coupling will split this state and leave a Kramers spin-doublet as the lowest level. (See Fig. 6-1; the figure should be inverted.)

The absorption spectrum of $\mathrm{IrCl_6}^-$ has been given by Jørgensen.[219] A number of bands can be seen, but it is doubtful whether any of them can be assigned as crystal field bands. The same situation is found for the deep-blue $\mathrm{IrBr_6}^-$.

Measurements of the paramagnetic resonance of $\mathrm{K_2IrCl_6}$ show[370] an isotropic g value equal to 1.82. The spectrum further exhibits a considerable amount of hyperfine structure. The value of g is 1.82 instead of 2.00, the number we expect (Sec. 6-*e*) for a cubic complex. Since the g factor is isotropic, it must be concluded that the structure is cubic. The theoretical value can be brought down below 2 only if the effective orbital angular momentum is slightly reduced. As discussed earlier in Sec. 7-*c*, such a reduction might be the result of the magnetic electrons spending their time in molecular orbitals instead of atomic orbitals.

Since, furthermore, a hyperfine structure which could only come from the interaction of the electronic spin with the chlorine nuclei was observed, a direct proof was given for the first time for the presence of π bonding in a complex.[408] From the measured size of the hyperfine structure, and from the observed value of $g = 1.8$, it was estimated that the five t_{2g} electrons are in the iridium orbitals about 80 per cent of the time.

Measurements of the signal intensity for the paramagnetic resonance spectrum of the red crystals of $\mathrm{(NH_4)_2IrCl_6}$ revealed further that there is an antiferromagnetic exchange between the iridium atoms in the crystal.[409] The theory for the evaluation of the coupling constant J is given in the section dealing with copper acetate; for $(NH_4)_2IrCl_6$ it was estimated that $J \simeq 5$ cm^{-1}.

The effective spin-orbit coupling parameter ξ_{5d} has finally been deduced to be some 2100 cm^{-1}. The value is found[410] by measuring the temperature-independent paramagnetism χ_{hf}, since

$$\chi_{hf} = \frac{N\beta^2(2 + g)^2}{6\xi}$$

In this expression g is the g value of the ground-state doublet. The magnetic susceptibilities of K_2IrCl_6, $(NH_4)_2IrCl_6$, and other Ir(IV) compounds have been measured by Norman and Morrow.[411]

Ir(V) complexes are not very common, and only some magnetic susceptibility measurements have been reported.[380] The white $KIrF_6$ was, for instance, found at room temperature to have an effective number of Bohr magnetons equal to 1.26. The electronic configuration is $(t_{2g})^4$ for the ground state, and the level diagram for the first excited states is given in Fig. 10-20. The theory for the magnetic susceptibility of this configuration has been given by Griffith.[382]

The level scheme for the pale-yellow solid IrF_6, possessing the configuration d^3, has also been treated by Moffitt et al.[400] Again using an intermediate coupling scheme, these authors succeeded in accounting for all of the "visible" crystal field bands. The infrared spectrum of IrF_6 has been recorded by Mattraw et al.,[412] and the force constants have been calculated by Claassen.[402]

10-t. Platinum

Platinum has the electronic configuration $[Xe](5d)^9(6s)$. We shall here concentrate upon the oxidation states Pt(II), Pt(IV), and Pt(VI) possessing the electronic configurations $(5d)^8$, $(5d)^6$, and $(5d)^4$, respectively.

Many four-coordinated Pt(II) complexes are known. Like Ni(II) and Pd(II), these complexes have a square planar configuration, but unlike nickel, Pt(II) never forms octahedral complexes. A typical example is the colorless $[Pt(NH_3)_4]Cl_2$. It is diamagnetic[390] with $\chi = -126 \times 10^{-6}$. This is, of course, to be expected for a planar configuration.

The spectra of some Pt(II) complexes are given and interpreted by Chatt, Gamlen, and Orgel.[413] The level scheme for a d electron in a field of D_{4h} is given in Fig. 5-1. The ground state would be ${}^1A_{1g}(e_g)^4(a_{1g})^2(b_{2g})^2$, and the first absorption band of $PtCl_4^-$ is assigned as a transition to the triplet state ${}^3A_{2g}(e_g)^4(a_{1g})^2(b_{2g})(b_{1g})$. By similar excitations, a variety of singlet and triplet states can be made.[413] The interpretation of the spectrum is made difficult by the fact that the large spin-orbit coupling destroys the usefulness of the spin quantum number.

The absorption spectrum of the red crystals of K_2PtCl_4 using polarized light has been investigated by Yamada.[392] Two absorption bands appeared at 26,600 cm^{-1} ($\perp$) and 29,400 cm^{-1} ($\parallel$). These bands do not directly correspond to the solution spectrum. Assuming the usual vibronic mechanism for producing band intensity, we must associate an electronic $g \rightarrow g$ transition with the excitation of one odd vibrational quantum. The stretching mode of species ϵ_u should be by far the most active in promoting intensity.[413] By taking the symmetric direct product, it is then easy to see that a transition to an A_{2g} or B_{1g} state should behave as found experimentally for the band located at 26,600 cm^{-1}.

Orgel[414] has given an explanation of the trans effect found in platinous complexes which relates the kinetics of the reaction to the electronic structure of the molecule. This effect shows itself in the way certain ligands tend to labilize the groups trans to themselves in planar Pt(II) complexes. A bimolecular reaction mechanism which involved a transition state with a geometry closely related to that of a trigonal bipyramid was proposed. According to Orgel, the ligands with the greatest ability to labilize the trans position should have vacant π orbitals capable of accepting metal d electrons. The experimental evidence supports this interpretation in the majority of cases,[415,420] but an outstanding misfit is the hydride ion, which has a very large trans effect.[420]

The absorption spectra of Pt(IV) complexes follow the by now well-known pattern of a d^6 configuration.[377] As usual, they form diamagnetic complexes with a regular octahedral configuration. The crystal field bands are analogous to those of Co(III) and Rh(III) and are present as relatively weak shoulders in the spectra of the red complexes $PtCl_6^{=}$ and $PtBr_6^{=}$. The weakest bands, at 22,000 cm^{-1} and 19,000 cm^{-1}, respectively, are identified with the transition $^1A_{1g}(t_{2g})^6$ to either $^3T_{1g}(t_{2g})^5(e_g)$ or $^3T_{2g}(t_{2g})^5(e_g)$. The stronger bands, found at 28,400 cm^{-1} and 23,000 cm^{-1}, respectively, are then assigned to the transition $^1A_{1g}(t_{2g})^6 \rightarrow {}^1T_{1g}(t_{2g})^5(e_g)$. As is to be expected, the value of Dq for Pt(IV) complexes is at least twice as large[377] as the value found in the corresponding Co(III) compounds.

Platinum in the oxidation state six is found in the dark-red complex PtF_6. The electronic level scheme of d^4 in the intermediate coupling has been worked out by Moffitt et al.[400] As shown in their paper, it is possible to account for all four absorption peaks found in PtF_6 by using this coupling scheme. The infrared spectrum has been given by Claassen[402] together with a calculation of the force constants.

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