

THE THEORY OF Cr^{3+} PAIRS OF D_{3h} SYMMETRY

by

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To my Wife

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ABSTRACT

A novel approach to the problem of describing interacting magnetic ions has been put forward by Stevens. The work contained herein offers the first major test of the new formalism; applied specifically to binuclear systems in which magnetic Cr^{3+} ions occur in discrete pairs of D_{3h} symmetry.

Each interacting pair is regarded as a unit; wavefunctions suitable for describing the pair are constructed in determinantal form. The wavefunctions of D_{3h} symmetry are used to define the unperturbed Hamiltonian. An effective Hamiltonian is then used to obtain the energy levels in a restricted energy range. (The region of the 2T_1 levels of the single Cr^{3+} ion). A set of selection rules is derived.

With direct comparison with experimental results the success of theoretical predictions is estimated. Certain interval relations are obtained. There is no first order spin-orbit splitting. Through second order perturbation the maximum values of the spin-orbit coupling constant are found for three materials. The theoretical Zeeman splittings are stated.

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CHAPTER ONE

AN INTRODUCTION

1.1 EXCHANGE COUPLING

The phenomenon of exchange between magnetic ions in insulating crystals is an area of solid state physics that has sustained continued interest over many years. The reason for such active research is to explain the mechanism of exchange and thereby contribute to the understanding of magnetic ordering in solids - an essential part of modern magnetism. However, despite the abundance of information that has now been accumulated the present mathematical formulism for dealing with exchange interactions still has its limitations; these will be pointed out in due course. It is not intended that this account be a comprehensive review of all aspects of exchange coupling but rather a critical appraisal of the methods most currently employed in this field. It is hoped that the reader will gain an appreciation of the novelty of the work contained in this thesis and of the deficiencies in the current theories that the work herein sets out to rectify. An excellent review entitled 'Exchange Interactions in Magnetic Insulators' is given by Stevens [1] in which were laid down the foundations of the new formulism. Important discussions on exchange are also given by Anderson, Herring and Levy [2-5].

In the study of magnetic insulators it is customary when describing the low-lying energy levels to use a 'spin-Hamiltonian'. This is a method of approximation in which the Hamiltonian of the magnetic ion, with all of its states, is replaced by another Hamiltonian which accurately describes only the low-lying states. The principle involved is in finding an isomorphism between the subspace defined by the low-lying states and a

'fictitious spin' space defined by a set of orthogonal spin states. The eigenvalues of the latter are known.

To describe the pair interactions the magnetic ions are brought together with the assumption that their electronic wavefunctions are unchanged. This suggests using a spin Hamiltonian H_s :

$$H_s = \sum_i H_i + \sum_{i>j} H_{ij}$$

The terms H_i are quite well known and are the spin Hamiltonians for each ion in isolation, while the H_{ij} describe the interactions between ions taken in pairs. For H_{ij} , most often chosen is the Heisenberg-Dirac Hamiltonian, a cosine coupling between spins at sites i and j

$$H_{ij} = -J \underline{S}_i \cdot \underline{S}_j$$

The parameter J is expected to decrease rapidly as the ion separation increases (although it is often found that the next nearest neighbour exchange is greater than the nearest). This seems a valid approximation for many of the problems of magnetism in insulators, because the insulating property confines electrons with their spins to localised sites so that the orbital degrees of freedom are not needed to be included as part of the magnetic problem.

The suitability of the Heisenberg-Dirac Hamiltonian was proved by Dirac [6] for a particularly simple case; that of electrons each confined to a different orthogonal orbit. He showed that because of the antisymmetry principle the subspace of all states obtainable by placing one electron in each of N orbitals with arbitrary spin directions, and taking linear combinations, is isomorphic to an N -particle spin space. If ϕ_i, ϕ_j, \dots are mutually orthogonal functions at i, j, \dots there will be one electron in i , one in j , etc. All possible Slater determinants are then formed

$$\{\phi_i, \phi_j, \phi_k, \dots\}.$$

The matrix of the actual Hamiltonian within this manifold of antisymmetric, orthogonal many-electron states is set up and it is this matrix that Dirac showed to be identical with that of the operator

$$C - \frac{1}{2} \sum_{i>j} J(1 + \underline{S}_i \cdot \underline{S}_j)$$

where C is a constant and

$$J = \langle \phi_i \phi_j | e^2 / r_{ij} | \phi_j \phi_i \rangle.$$

This parameter J is determined by experiment and is positive for ferromagnetic interactions and negative for antiferromagnetic interactions. The discussion by Dirac shows how two apparently different operators can have identical matrix representations (within related manifolds of states) which hints at the possibility of spin Hamiltonians for more complicated systems. This also emphasises the fact that each spin Hamiltonian has to be defined separately for each problem.

The first formulation of J in terms of e^2/r_{ij} , which is correct for truly orthogonal orbits, is necessarily positive being the self energy of the charge distribution $\phi_i^* \phi_j$. This fact formed the basis of the Heisenberg theory of ferromagnetism [7] since the lowest state having all spins parallel is ferromagnetic. However in insulators, the only case in which the Heisenberg-Dirac Hamiltonian is correct, the interaction is almost universally antiferromagnetic. The reasons for the discrepancy are that the Dirac theory is confined to the states of a particular manifold, and being only a first order treatment the often more important second order perturbation effects are neglected. Among the second order effects is included the phenomenon of super-exchange, so called because of its long range, whereby electrons are

exchanged between magnetic ions via an intermediary closed-shell ion.

Also observations have been reported interpretable in terms of biquadratic exchange terms in the effective Hamiltonian, i.e. terms in $(\underline{S}_i \cdot \underline{S}_j)^2$.

In using this formulism there is yet another serious question to be considered, that of the orthogonality of the electronic wavefunctions. We have already said that to build up the solid free ions are brought together close enough for there to be interactions between them. The wavefunctions of course then overlap; which is in fact necessary if one is to obtain an antiferromagnetic sign for exchange [2], but overlap on the other hand, severely complicates the calculations as well as indicates that in some sense we are not working with the right set of functions. Besides overlap, the assumption that the free ion functions remain unchanged in the solid is surely invalid; there is every reason to believe that they become considerably modified [8].

So we have stated a spin Hamiltonian which is valid when describing pair interactions in specific cases, i.e. when the interacting ions are in states of a particular manifold, defined by putting each electron in a different orbital. The properties of ground state pairs have been reviewed by Owen and Harris [9] and it is fairly certain that the spin Hamiltonian description is applicable. However as a general theory of exchange the spin Hamiltonian description is too specific, indeed one of the major criticisms of this method is its lack of generality [10]. The need of a more general interaction was stressed by Van Vleck [11] who proposed the use of a variation of the Heisenberg-Dirac Hamiltonian, a phenomenological, orbital dependent exchange Hamiltonian:

$$H = J(\underline{s}_{ai} \cdot \underline{s}_{bj})$$

where \underline{s}_{ai} and \underline{s}_{bj} are the spins of the electrons occupying various one-electron orbitals on ions a and b in the pair. The operators in a spin

Hamiltonian are equivalent to those of the actual Hamiltonian (in a restricted range of states) and these reproduce the energy levels but not the eigenstates so it is difficult to give any physical meaning to the spin operators. So our main objective is to produce a formulism which is applicable in the general case and through which some physical meaning may be given to the mechanisms of exchange. By the general case is meant interactions between ions having no restrictions on the descriptions of the states so can mean states resulting from double electron occupancy of the orbitals. This will be particularly useful in the optical studies of pairs since the typical spin Hamiltonian fails to describe either the initial or the final states.

The proposed strategy for dealing with interactions between magnetic ions will now be briefly described: the problem begins with a general Hamiltonian H of the form:-

$$H = \sum_i p_i^2/2m - \sum_{i>j} Ze^2/r_i + \sum_{i>j} e^2/r_{ij} + \dots$$

and the solving of the Schroedinger equation containing this Hamiltonian. The equation is too complex to solve directly so approximation methods are needed. Perturbation theory will be used which necessitates the choosing of an unperturbed Hamiltonian H_0 . This presents no difficulty if the perturbation theory is to be taken to infinite order for then any deficiencies in H_0 should eventually be corrected. But if convergence in low order is required H_0 should be chosen to be a good approximation to H .

It has already been stated that the normal practice when describing interacting pairs of ions is to split up the Hamiltonian H into two parts

$$H = \sum_i H_i + \sum_{i>j} H_{ij}$$

where $\sum_i H_i$ is the sum of the individual parts and $\sum_{i>j} H_{ij}$ represents the interaction part. The unperturbed Hamiltonian H_0 is then taken to be the sum of the individual site operators $\sum_i H_i$ [9,12,13]. The difference $H - H_0$ is then regarded as a perturbation and it includes the interaction between ions. On experimental grounds this process appears to work but as a starting point for a proper theory the choice of H_0 must be rejected. The main objection is that the method distinguishes between electrons. We have H which is invariant with respect to interchanges of all electrons, and $\sum_i H_i$ which is invariant only with respect to interchanges of electrons on the same ion. Therefore electrons are distinguished even though exchange interactions primarily arise because electrons are indistinguishable. Also a substantial part of the crystal field potential at a site i is due to electrons at sites other than i . Since the electrons are not distinguished in H , H_0 has less symmetry and applying the perturbation $H - H_0$ increases the symmetry: an unusual feature for a perturbation theory to have. Considering the eigenstates of H , the perturbation development expresses them as linear combinations of those of H_0 . It seems unlikely that the higher symmetry of H can appear in the perturbed state unless the perturbation development is taken to infinite order. This method is unattractive in that the initial ideas are not suitable for a proper general theory, but the difficulties can be avoided by using an unperturbed Hamiltonian which has the same symmetries as H .

An unperturbed Hamiltonian H_0 needs to be found which is symmetric in electrons so that they are not distinguished and which is a good approximation to the actual Hamiltonian H . It is not clear how these requirements can be met by a straightforward modification of H , so H_0 is defined using as much of our knowledge concerning the system as possible. To make use of available perturbation techniques the

unperturbed Hamiltonian is chosen so that it has the states of interest as its eigenfunctions. The first step is to define a set of orthogonal many-electron wavefunctions which describe the pair states; the wavefunctions also being endowed with the correct symmetry. Then projection operators P_n for each state $|n\rangle$ will be defined by setting $P_n = |n\rangle\langle n|$. Any operator of the form $\sum \lambda_n P_n$ where λ_n are scalars have the states $|n\rangle$ as eigenstates and the λ_n as corresponding eigenvalues (which may be chosen as convenient). We have constructed our many-electron states to simulate the anticipated eigenstates of H , so it is supposed that their mean energies will approximate to the eigenvalues of H . Therefore, if λ_n is taken to equal the corresponding expectation value of H , $\langle n|H|n\rangle$, the corresponding unperturbed Hamiltonian H_0 becomes

$$\begin{aligned} H_0 &= \sum \langle n|H|n\rangle P_n \\ &= \sum |n\rangle\langle n|H|n\rangle\langle n|. \end{aligned}$$

The perturbation is $H - H_0$.

The manner in which H_0 is defined suggests it will have eigenstates that can be regarded as arranged into manifolds of degenerate or nearly degenerate states. This is obvious since the eigenvalues of H_0 are defined to coincide with the expectation values of H and the typical energy level diagram consists of groups of closely spaced levels separated by relatively large energy gaps. At a later stage an effective Hamiltonian will be introduced, this has the form of a perturbation expansion to infinite order and it gives the splitting of the manifolds under the perturbation $H - H_0$.

1.2 THE STUDY OF Cr^{3+} ION INTERACTIONS

Over the years much attention has been paid to the analysis of the absorption spectrum of ruby, a mineral consisting of corundum Al_2O_3 , doped with small concentrations of chromium. The spectrum of weakly doped samples of ruby can be understood in terms of a single $\text{Cr}^{3+}(\text{d}^3)$ ion residing in a field of octahedral symmetry [14]. However the absorption spectrum of dark ruby (typically 0.2 - 1% Cr) contains many additional sharp lines attributed to exchange coupled Cr^{3+} pairs [15,16]. The structure of corundum is such that each Cr^{3+} ion has at least four different near neighbour ion sites, but despite this complication several groups of workers have managed to assign most of the fine structure in the absorption spectrum to different Cr^{3+} pairs [17-20].

In a regular octahedron of neighbours the ground configuration of a single Cr^{3+} ion is expected to be t_{2g}^3 [21]. Now in order to apply the standard theory of exchange to Cr^{3+} ions the three electrons in the d-shell of Cr^{3+} are placed in the t_{2g} orbitals in such a way that there is precisely one electron in each orbital. A total of eight states can be formed by varying the possible spin orientations, these make up the terms $^4\text{A}_2$ and ^2E using the cubic axes, using the trigonal axes one finds the terms $^4\text{A}_2$, $^2\text{A}_1$ and $^2\text{A}_2$. With two Cr^{3+} ions sixty-four states can be formed and the pattern into which they are split should then be given by the Heisenberg-Dirac Hamiltonian. The lowest lying levels that have been assigned to pairs ($^4\text{A}_2 \times ^4\text{A}_2$) (when both ions are in the $^4\text{A}_2$ electronic ground state) are well accounted for by such a Hamiltonian when it includes the biquadratic term [17-20]. When applied to the excited pair states the correspondence between theory and experiment is poor [22]. Much better agreement with experiment is found using the Van Vleck phenomenological form of spin Hamiltonian which has been applied with some success to the ($^4\text{A}_2 \times ^2\text{E}$) excited pair states [23,24,25]. The analysis of

the (${}^4A_2 \times {}^2E$) state in the simplest case of first nearest neighbours, because of experimental difficulties, has still proved difficult [20,26].

Recently the family of crystals with the general formula $M_3Cr_2X_9$ ($M \equiv Cs, Rb, K$; $X \equiv Cl, Br$) has received attention because the crystal structures are such that the Cr^{3+} ions occur in crystallographically equivalent pairs, in an arrangement that is very similar to the first nearest neighbour pairs in heavily doped ruby. Such crystals are examples of so called binuclear systems and in the study of exchange interactions the advantages they possess over a doped system are many-fold. Suitable samples of ruby are formed by the doping of Cr^{3+} ions into the host Al_2O_3 in sufficient concentrations that pairs are formed by chance occupancy of the near neighbour sites. The absorption spectrum of the resulting sample may contain features that are due to single unpaired ions as well as lines due to several different pair types and higher order ion clusters. Consequently the interpretation of the spectral features is overly complicated. These problems are not encountered with a binuclear system because the Cr^{3+} ions occur in isolated, discrete pairs and therefore all lines in the spectrum can be expected to be due to pairs. Also the symmetry of the pair is high (D_{3h}) so the allowed optical transitions are severely limited; an important point in the interpretation of spectroscopic data. With these comments in mind it seems likely that the analysis of the spectrum of binuclear systems will prove much easier than the analysis of the corresponding spectrum of ruby.

Several papers have now appeared concerning the optical absorption spectra of binuclear systems: working with $Cs_3Cr_2Br_9$ Dubicki et al [27,28] have analysed the (${}^4A_2 \times {}^2E$) spectral region using a general spin Hamiltonian while Briat et al [29] have studied the same region of the spectrum of $Cs_3Cr_2Cl_9$. However, Briat et al [29] also tried to extend

the application of the theory to the (${}^4A_2 \times {}^2T_1$) excited states, apparently ignoring the limitations of the Dirac theory. Their interpretation of the data is now in conflict with the more recent analysis of Johnstone et al [30] given in terms of the new Stevens formalism [31]. In order to fit the experimental data to theory Briat et al [29] have found it necessary to invoke a large spin-orbit effect. Whereas using the new formalism [30] the gross features of the spectrum are understood without recourse to spin dependent effects, and only a small second order spin-orbit interaction is required to explain some details of the spectrum. It has been variously reported, see for instance [32], that the spin-orbit coupling parameter is reduced for ions in complexes, so it would appear that the spin-orbit effect required in [29] is anomalous and the theory in [31] more suitable for a description of the (${}^4A_2 \times {}^2T_1$) levels. Thus arises the first major test of the new formalism.

The aim of this thesis is to give a detailed study of the (${}^4A_2 \times {}^2T_1$) manifold of states of a pair of Cr^{3+} ions having overall symmetry D_{3h} ; the configuration found in binuclear systems. This study will then be applied to 'fitting the spectrum' of several different binuclear materials, for which much experimental data is now available [30,33]. The degree to which theory can explain the experimental findings will serve as a stringent test as to the generality of the new formalism. It should also be possible to give a physical interpretation to the mechanisms of exchange and to state which are the dominant factors.

1.3 Cr³⁺ PAIRS IN BINUCLEAR SYSTEMS

Each member of the family of crystals typified by the formula $M_3Cr_2X_9$ ($M \equiv Cs, Rb, K$ and $X \equiv Cl, Br$) is isostructural with $Cs_3Cr_2Cl_9$ whose structure has been reported by Wessel and Ijdo [34]. The structure of these compounds contains discrete $(Cr_2X_9)^{3-}$ units, with each Cr^{3+} ion in a trigonally distorted octahedron of X atoms having C_{3v} symmetry. Each Cr^{3+} ion is also a member of a pair with the two octahedra of X atoms joined by a shared triangular face. This shared face, perpendicular to the trigonal axis also forms a plane of reflection symmetry so that the overall symmetry of the pair is D_{3h} [$D_{3h} \equiv C_{3v} + \sigma_h C_{3v}$]. See Fig 1. The crystal c-axis runs parallel to the line joining the two Cr^{3+} ions, i.e. the trigonal axis (which will also be the axis of quantisation for the pair states).

To determine the term system of a complex ion such as $Cr^{3+}(d^3)$ the strong field method is employed because the crystal field is large compared with the interactions between the single d-electrons. The d-electrons in an octahedral crystal field are distributed between the threefold orbitally degenerate t_{2g} states and the doubly degenerate e_g states [35,36,37]. The single Cr^{3+} ion has three d-electrons and in a regular octahedron of neighbours the ground configuration is expected to be t_{2g}^3 [21], this configuration gives rise to the terms 4A_2 , 2T_1 , 2T_2 and 2E of which 4A_2 is lowest in energy. The term diagram for octahedral d^3 complexes due to Tanabe and Sugano [38] is shown in Fig 2, giving the term energies as functions of the parameters characterising the crystal field. A very similar term system would be expected for a pair of chromium ions provided one ion remains in the ground state. For instance, in the optical spectrum of the single Cr^{3+} ion a group of lines corresponding to the transition $^4A_2 \rightarrow ^2T_1$

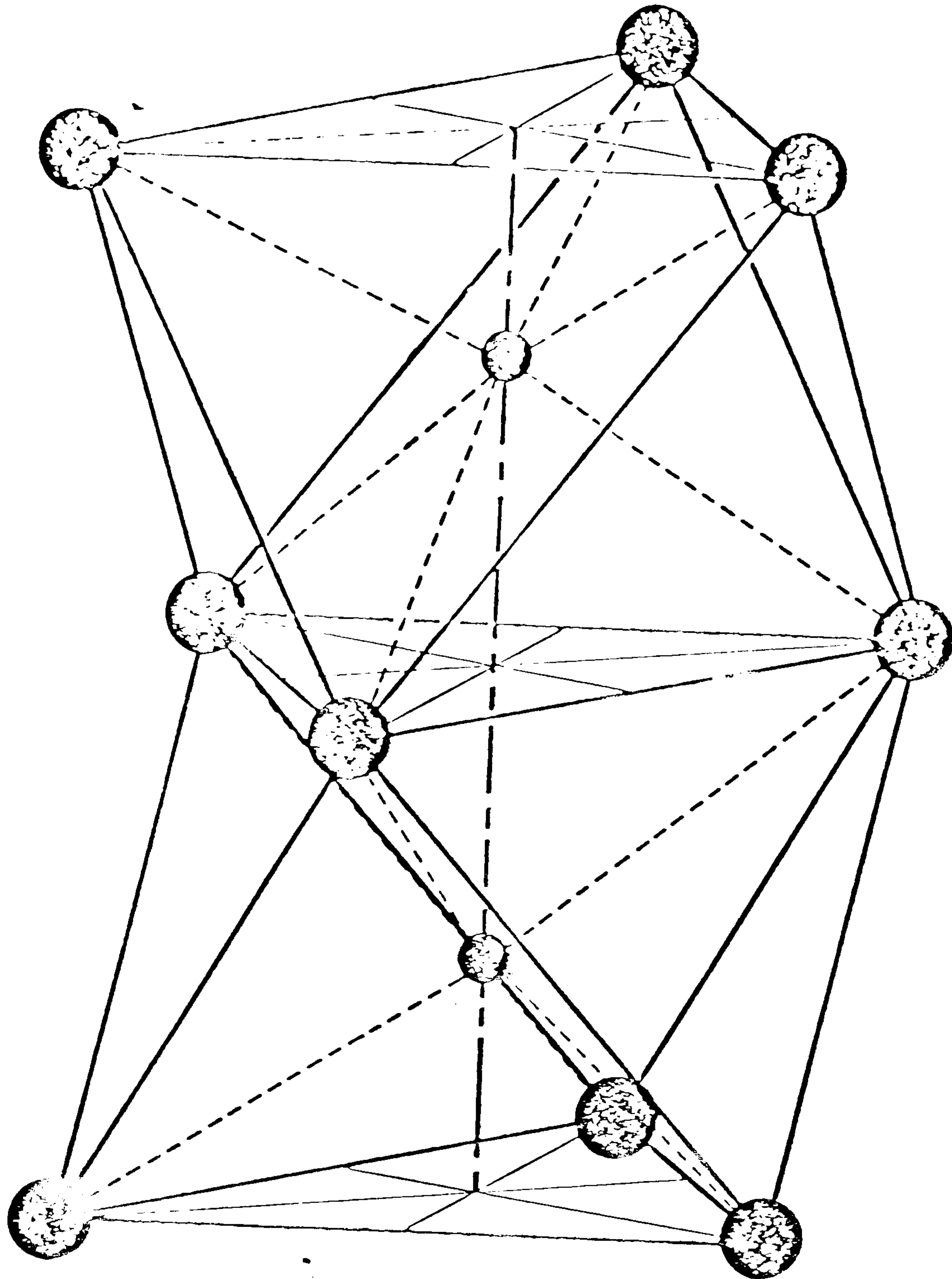


Fig 1: The $(Cr_2X_9)^{3-}$ anion unit [34].

is observed (a group of lines because terms in the Hamiltonian not yet considered may lift some of the degeneracies). For a pair of Cr^{3+} ions one would expect to observe in the same spectral region transitions corresponding to one of the ions in the pair being excited from 4A_2 to 2T_1 while the other remains in the ground state. The gross optical spectra of several binuclear systems are shown in Fig 3, and it is seen by comparison with Fig 2 that the pattern of the absorption bands closely resembles that of a single Cr^{3+} ion. Approximately, the values of D_q/B for the pair would vary from 1.7 for $Cs_3Cr_2Br_9$ to 2.0 for $K_3Cr_2Cl_9$.

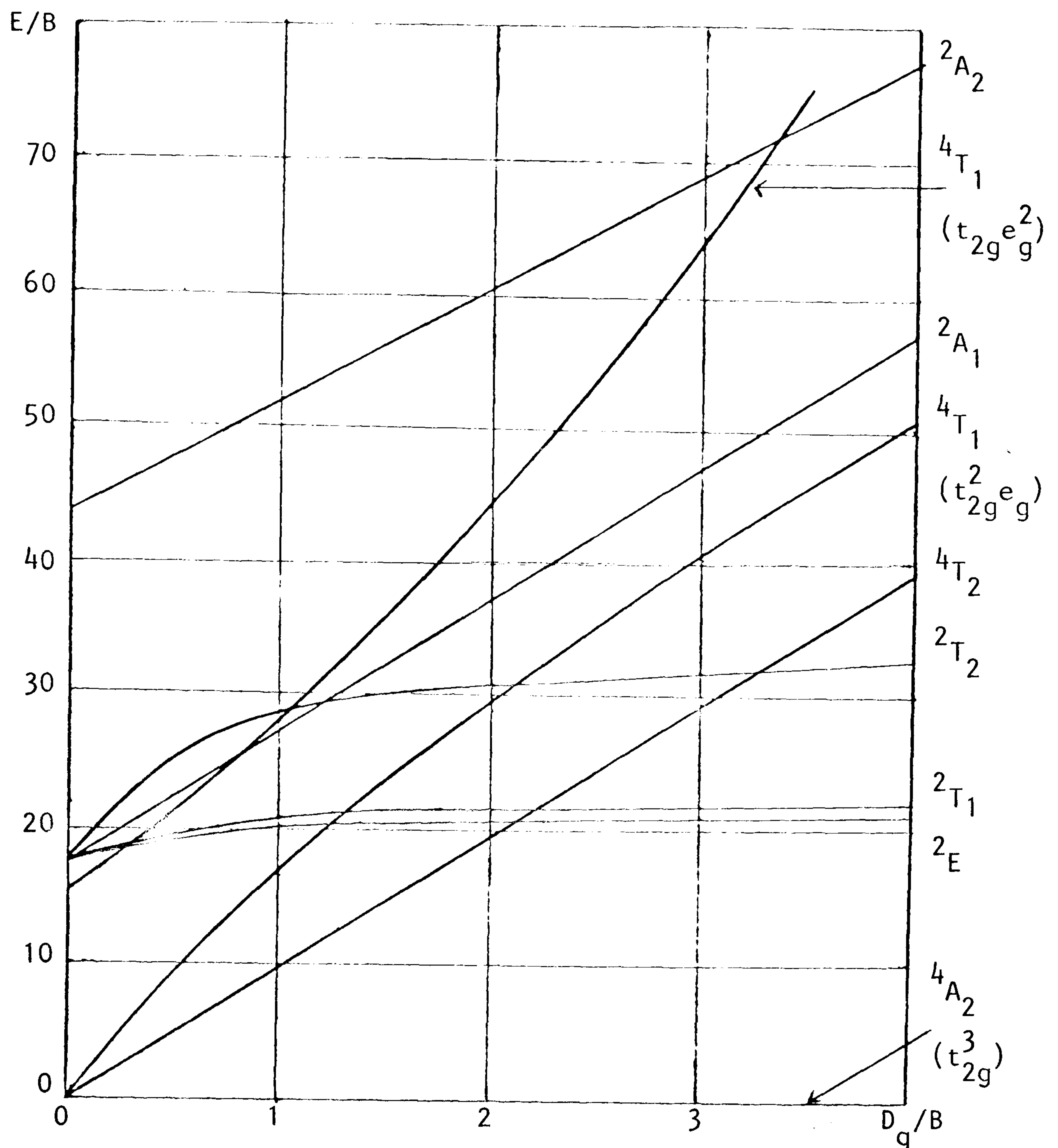


Fig 2: Term diagram for octahedral d^3 complexes ($C/B = 4$) [38].

However, the pair spectrum compared with the single ion spectrum contains additional structure because each ion of the pair is in a distorted octahedron of neighbours. Also exchange interactions take place between members of the pair and an additional type of degeneracy must be introduced because either member of the pair may be excited.

A comparison of the experimental bands Fig 3 with the theoretical bands Fig 2 allows an estimation of the Racah parameter B (and also C , since C has been set equal to $4B$ in the term diagram). These parameters which can be expressed in terms of Slater integrals are a measure of the

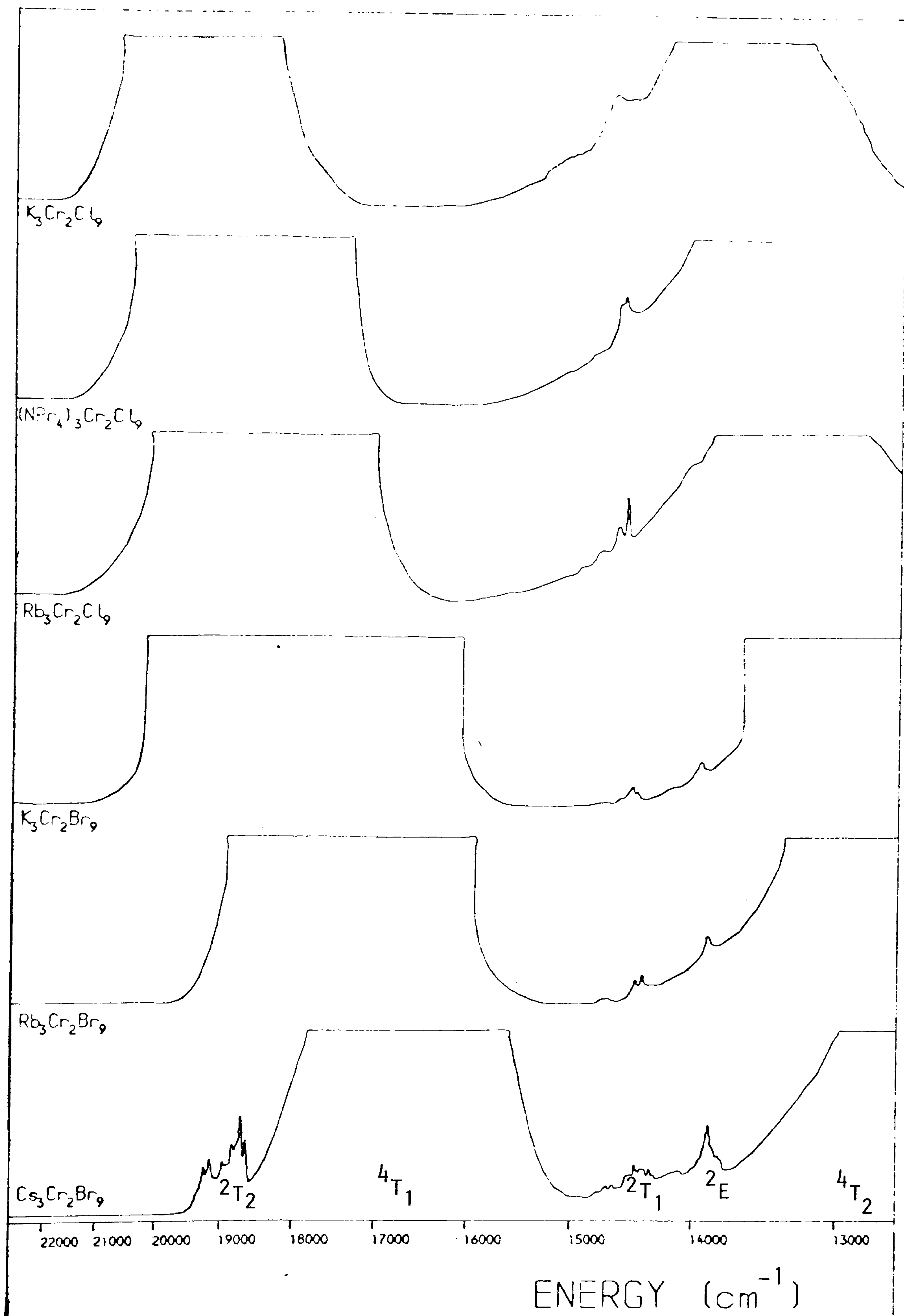


Fig 3: The gross optical spectra of several binuclear systems [33].

electron interaction. One finds that the optimum value of B for $\text{Cs}_3\text{Cr}_2\text{Br}_9$ is approximately 660 cm^{-1} , while for $\text{K}_3\text{Cr}_2\text{Cl}_9$ the best value of B is approximately 680 cm^{-1} . The free Cr^{3+} ion value for B is 918 cm^{-1} [38] so there is a reduction in the free ion B -value of about 29% for $\text{Cs}_3\text{Cr}_2\text{Br}_9$ and 26% for $\text{K}_3\text{Cr}_2\text{Cl}_9$. This reduction is to be expected since in complexes the charge cloud of the d -electrons is more spread out than in the free ion.

Each spectrum shown in Fig 3 is arranged into manifolds of states designated $(^4A_2 \times ^2T_2)$, $(^4A_2 \times ^4T_1)$, $(^4A_2 \times ^2T_1)$, $(^4A_2 \times ^2E)$ and $(^4A_2 \times ^4T_2)$. We shall be concentrating on the $(^4A_2 \times ^2T_1)$ group of levels so it will be necessary to work within the basis defined by the states of this manifold. The first object to be achieved therefore is the construction of a set of orthogonal wavefunctions which describe the $(^4A_2 \times ^2T_1)$ states and which transform irreducibly under D_{3h} symmetry. Later, the coupling between the $(^4A_2 \times ^2T_1)$ states and other excited states will be investigated so basis states for these manifolds need to be constructed also. (We note that the 4T_1 and 4T_2 terms arise from the $t_{2g}^2 e_g$ configuration).

Throughout this discussion it has been assumed that the one-electron orbitals are d -orbitals and that each Cr^{3+} ion lies in a regular octahedral environment; these assumptions lead to a notation that is quite inappropriate for the description of a pair in D_{3h} symmetry. The notation is retained however because it is readily understood in terms of conventional crystal field theory. Therefore, it must be remembered that each Cr^{3+} ion lies in a field of C_{3v} symmetry and in such a field the t_{2g} orbitals are reduced to $a_{1g} + e_g$ (this point will be incorporated into the definition of the one-electron orbitals). The many-electron terms are similarly reduced in the descent in symmetry from O_h to C_{3v} .

according to the following:

$$A_1 \rightarrow A_1$$

$$A_2 \rightarrow A_2$$

$$E \rightarrow E$$

$$T_1 \rightarrow A_2 + E$$

$$T_2 \rightarrow A_1 + E$$

CHAPTER TWO

STATES OF THE PAIR AND THE PERTURBATION THEORY

2.1 THE ONE-ELECTRON BASIS STATES

If one considers the problem of a complex containing a single Cr^{3+} ion one finds that the valence electrons are in d-orbitals modified by the presence of the crystal field. When the ion lies within a trigonally distorted octahedron of neighbours it is usual to work with linear combinations of the d-orbitals so that the trigonal axis becomes the axis of quantisation. This procedure cannot be followed in the case of a pair of interacting Cr^{3+} ions simply because the electrons can no longer be said to occupy d-orbitals; the orbitals occupied by the three electrons of one of the ions, due to the presence of the other ion are likely to be much less localised than d-orbitals. However, the symmetry properties of the pair one-electron orbitals are available and are used in their definition. Centred at one of the Cr^{3+} ion sites three one-electron states $|A\rangle$, $|B\rangle$ and $|C\rangle$ are defined having the following symmetry properties:

$$\begin{array}{ll} C_3^0 |A\rangle = |A\rangle & \sigma_V^0 |A\rangle = |A\rangle \\ C_3^0 |B\rangle = \omega |B\rangle & \sigma_V^0 |B\rangle = |C\rangle \\ C_3^0 |C\rangle = \omega^2 |C\rangle & \sigma_V^0 |C\rangle = |B\rangle \end{array}$$

where $\omega = \exp(2\pi i/3)$, C_3^0 denotes a rotation through $2\pi/3$ about the trigonal axis and σ_V^0 denotes reflection in a symmetry plane through the trigonal axis (the superscript o indicates that the operators act in one-electron configuration space). In spherical symmetry and taking the trigonal axis to be Oz, C_3^0 would be $\exp(-2\pi i l_z/3)$ and Ox and Oy would be axes such that σ_V^0 induces $x \rightarrow x$, $y \rightarrow -y$, $z \rightarrow z$. It is important

to notice that whereas $|B\rangle$ and $|C\rangle$ can be interchanged by symmetry operations there is no way in which $|A\rangle$ can be turned into either $|B\rangle$ or $|C\rangle$, which emphasises the point made at the end of Chapter One. The states $|A\rangle$, $|B\rangle$ and $|C\rangle$ correspond by virtue of their symmetry properties to the following combinations of d-orbitals, which in crystal field theory would be the t_{2g} (or $a_{1g} + e_g$) orbitals having the trigonal axis as the axis of quantisation:

$$|A\rangle \equiv d_0$$

$$|B\rangle \equiv \sqrt{\frac{2}{3}} d_2 - \sqrt{\frac{1}{3}} d_{-1}$$

$$|C\rangle \equiv \sqrt{\frac{2}{3}} d_{-2} + \sqrt{\frac{1}{3}} d_1$$

(the indices refer to the m_l values of the one-electron d-orbitals).

In a similar manner the crystal field analogues of the e_g orbitals $|D\rangle$ and $|E\rangle$ are introduced, defined by the symmetry properties:

$$C_3^0 |D\rangle = \omega |D\rangle$$

$$\sigma_V^0 |D\rangle = |E\rangle$$

$$C_3^0 |E\rangle = \omega^2 |E\rangle$$

$$\sigma_V^0 |E\rangle = |D\rangle.$$

and would have the form:

$$|D\rangle \equiv \sqrt{\frac{2}{3}} d_{-1} + \sqrt{\frac{1}{3}} d_2$$

$$|E\rangle \equiv -\sqrt{\frac{2}{3}} d_1 + \sqrt{\frac{1}{3}} d_{-2}$$

The correspondence between the orbitals $|A\rangle$, $|B\rangle$, $|C\rangle$, $|D\rangle$ and $|E\rangle$ and the d-orbitals is one of symmetry only; they can best be regarded as derived from a self-consistent model of a large molecule containing two Cr^{3+} ions. (The transformation properties of the one-electron orbitals are shown in Appendix II).

The pair has a reflection plane perpendicular to the trigonal axis and the reflection operator σ_h^0 relates the two ions. The one-electron

states at the other Cr^{3+} site $|a\rangle$, $|b\rangle$, $|c\rangle$, $|d\rangle$ and $|e\rangle$ are defined using this reflection operator σ_h^0 by:

$$|a\rangle = \sigma_h^0 |A\rangle$$

$$|b\rangle = \sigma_h^0 |B\rangle$$

$$|c\rangle = \sigma_h^0 |C\rangle$$

$$|d\rangle = \sigma_h^0 |D\rangle$$

$$|e\rangle = \sigma_h^0 |E\rangle$$

The question now arises concerning the orthogonality of the states at one site to those at the other site. Suppose that the states are not orthogonal and consider $|A\rangle + |a\rangle$ and $|A\rangle - |a\rangle$. These are certainly orthogonal because they behave differently under σ_h^0 but they may not be normalised. Therefore consider

$$|\phi_1\rangle = (1/N_1)\{|A\rangle + |a\rangle\} \quad \text{and} \quad |\phi_2\rangle = (1/N_2)\{|A\rangle - |a\rangle\}$$

where N_1 and N_2 are normalising constants. Then $(1/\sqrt{2})\{|\phi_1\rangle + |\phi_2\rangle\}$ and $(1/\sqrt{2})\{|\phi_1\rangle - |\phi_2\rangle\}$ are orthogonal and normalised and also approximate to $|A\rangle$ and $|a\rangle$. This shows that it is possible to define localised states for the two sites which are mutually orthogonal and have the desired symmetry properties so there is no loss of generality in assuming that the initial choices $|A\rangle$, $|B\rangle$, $|C\rangle$, ... etc are all mutually orthogonal.

2.2 THE SYMMETRY OPERATORS C_3 , σ_v , σ_h

Much use will be made of the symmetry operators C_3 , σ_v and σ_h and it will be necessary to apply them to one-electron orbital states, to one-electron spin states and to many-electron states. The notation must now be extended in anticipation of this. When applied to one-electron orbital states the superscript o will be added, as already indicated, when applied to one-electron spin states the superscript s will be added

and when applied to many-electron determinantal states which have both orbit and spin specified no superscript will be added.

The operators C_3^S , σ_V^S and σ_h^S which belong to the double group have yet to be defined. The components of \underline{s} are operators acting in a two dimensional space in which a possible basis is constituted by the two eigenvectors

$$|+\rangle = |\frac{1}{2}, \frac{1}{2}\rangle \quad |-\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle$$

of \underline{s}^2 and s_z . Using this basis it is a simple matter to write down the matrices representing the operators s_x , s_y and s_z .

The rotation operator in spin space is given by

$$R_U^S(\phi) = \exp(-i\phi s_U)$$

where the rotation is through an angle ϕ about some vector \underline{u} , and $s_U = \underline{u} \cdot \underline{s}$. Expanding the exponential and separately summing the terms even and odd in s_U with the aid of the relations

$$(s_U)^{2n} = (\frac{1}{2})^{2n} \quad (s_U)^{2n+1} = (\frac{1}{2}s_U)^{2n+1}$$

the simple expression is obtained

$$R_U^S(\phi) = \cos \frac{1}{2}\phi - 2is_U \sin \frac{1}{2}\phi.$$

This equation is now used in the definition of C_3^S , σ_V^S and σ_h^S . The operator C_3^S is a simple rotation of $2\pi/3$ about the z-axis so that

$$C_3^S \equiv R_Z^S(2\pi/3) = \frac{1}{2} - i\sqrt{3}s_z$$

hence

$$C_3^S |+\rangle = \frac{1}{2}(1 - i\sqrt{3}) |+\rangle = -\omega |+\rangle$$

and

$$C_3^S | -> = \frac{1}{2}(1 + i\sqrt{3}) | -> = -\omega^2 | ->.$$

Now σ_V^S is equivalent to an inversion followed by a rotation through π about the y-axis. This is defined with reference to the axes set up in section 2.1. Since the inversion has no effect in spin space

$$\sigma_V^S \equiv R_y^S(\pi) = -2is_y$$

and writing $s_y = \frac{1}{2}i(s_+ - s_-)$ we have

$$\sigma_V^S = s_- - s_+$$

so that

$$\sigma_V^S | +> = | -> \quad \text{and} \quad \sigma_V^S | -> = - | +>.$$

Finally σ_h^S is equivalent to an inversion followed by a rotation through π about the z-axis. Therefore

$$\sigma_h^S \equiv R_z^S(\pi) = -2is_z$$

and applying to $| +>$ and $| ->$ we have

$$\sigma_h^S | +> = -i | +> \quad \text{and} \quad \sigma_h^S | -> = i | ->.$$

Collecting all these results together

$$\begin{aligned} C_3^S | +> &= -\omega | +>, & \sigma_V^S | +> &= | ->, & \sigma_h^S | +> &= -i | +>, \\ C_3^S | -> &= -\omega^2 | ->, & \sigma_V^S | -> &= - | +>, & \sigma_h^S | -> &= i | ->. \end{aligned}$$

Supplementary to these results, due to the anticommutivity between s_+ , s_- and σ_h^S are

$$[s_-, \sigma_h^S]_+ = 0 \quad \text{and} \quad [s_+, \sigma_h^S]_+ = 0$$

and because the operators belong to the double group

$$\begin{aligned}
 (C_3^s)^5 s_- C_3^s &= \omega^2 s_-, & (C_3^s)^5 s_+ C_3^s &= \omega s_+, \\
 (\sigma_V^s)^3 s_- \sigma_V^s &= -s_+, & (\sigma_V^s)^3 s_+ \sigma_V^s &= -s_-, \\
 (\sigma_h^s)^2 &= -1, & (\sigma_V^s)^2 &= -1, & (C_V^s)^3 &= -1.
 \end{aligned}$$

2.3 MANY-ELECTRON BASIS STATES, t_{2g}^3 CONFIGURATION

Three electrons are placed in the t_{2g} orbitals $|A\rangle$, $|B\rangle$ and $|C\rangle$ and all possible antisymmetric products are constructed, taking into account the Pauli exclusion principle, i.e. all possible 3×3 Slater determinants are formed such as $(\overset{+}{A}, \overset{+}{B}, \bar{C})$ in which three electrons have been placed in the orbitals $|A\rangle$, $|B\rangle$ and $|C\rangle$ with $m_s = \frac{1}{2}$, $\frac{1}{2}$ and $-\frac{1}{2}$ respectively.

The total possible product functions are

$$\begin{array}{lll}
 & (\overset{+}{A}, \overset{+}{B}, \overset{+}{C}) & M_S = 3/2 \\
 & \left. \begin{array}{lll}
 (\overset{+}{A}, \overset{+}{B}, \bar{C}) & (\overset{+}{A}, \bar{B}, \overset{+}{C}) & (\bar{A}, \overset{+}{B}, \overset{+}{C}) \\
 (\overset{+}{A}, \bar{A}, \overset{+}{B}) & (\overset{+}{A}, \bar{A}, \overset{+}{C}) & (\overset{+}{A}, \overset{+}{B}, \bar{B}) \\
 (\overset{+}{B}, \bar{B}, \overset{+}{C}) & (\overset{+}{A}, \overset{+}{C}, \bar{C}) & (\overset{+}{B}, \overset{+}{C}, \bar{C})
 \end{array} \right\} & M_S = 1/2 \\
 & \left. \begin{array}{lll}
 (\overset{+}{A}, \bar{B}, \bar{C}) & (\bar{A}, \overset{+}{B}, \bar{C}) & (\bar{A}, \bar{B}, \overset{+}{C}) \\
 (\overset{+}{A}, \bar{A}, \bar{B}) & (\overset{+}{A}, \bar{A}, \bar{C}) & (\bar{A}, \overset{+}{B}, \bar{B}) \\
 (\overset{+}{B}, \bar{B}, \bar{C}) & (\bar{A}, \overset{+}{C}, \bar{C}) & (\bar{B}, \overset{+}{C}, \bar{C})
 \end{array} \right\} & M_S = -1/2 \\
 & (\bar{A}, \bar{B}, \bar{C}) & M_S = -3/2
 \end{array}$$

Some suitable linear combination of the antisymmetrised products must now be found to generate a set of symmetry adapted functions. Using the transformation properties of the one-electron orbitals under O_h symmetry the transformation properties of the quartet function $(\overset{+}{A}, \overset{+}{B}, \overset{+}{C})$ can be found. These properties are shown below:

| | E | C ₃ | C ₂ | C ₄ | C ₂ ' |
|---|---|---|---|--|--|
| (⁺ A, ⁺ B, ⁺ C) | (⁺ A, ⁺ B, ⁺ C) | (⁺ A, ⁺ B, ⁺ C) | (⁺ A, ⁺ B, ⁺ C) | -(⁺ A, ⁺ B, ⁺ C) | -(⁺ A, ⁺ B, ⁺ C) |
| χ | 1 | 1 | 1 | -1 | -1 |

Comparing with the character table of the O_h symmetry group (Appendix I) it is seen that (⁺A,⁺B,⁺C) transforms according to the irreducible representation A₂. Therefore the quartet term ⁴A₂ is present

$$|^4A_2, \frac{3}{2}\rangle = (\overset{+}{A}, \overset{+}{B}, \overset{+}{C})$$

and the remaining quartet terms are obtained using the s₋ operator

$$|^4A_2, \frac{1}{2}\rangle = \sqrt{\frac{1}{3}}[(\overset{+}{A}\overset{+}{B}\bar{C}) + (\overset{+}{A}\bar{B}\overset{+}{C}) + (\bar{A}\overset{+}{B}\overset{+}{C})]$$

$$|^4A_2, -\frac{1}{2}\rangle = \sqrt{\frac{1}{3}}[(\overset{+}{A}\bar{B}\bar{C}) + (\bar{A}\overset{+}{B}\bar{C}) + (\bar{A}\bar{B}\overset{+}{C})]$$

$$|^4A_2, -\frac{3}{2}\rangle = (\bar{A}\bar{B}\bar{C})$$

All other functions that can be constructed from the antisymmetric products which are also orthogonal to the quartet functions must be doublets. There are in total 16 doublet functions; those with M_S = $\frac{1}{2}$ are numbered |1> to |8>

$$|1\rangle = (1/\sqrt{6})[(\overset{+}{A}\overset{+}{B}\bar{C}) + (\overset{+}{A}\bar{B}\overset{+}{C}) - 2(\bar{A}\overset{+}{B}\overset{+}{C})]$$

$$|2\rangle = \sqrt{\frac{1}{2}}[(\overset{+}{A}\overset{+}{B}\bar{C}) - (\overset{+}{A}\bar{B}\overset{+}{C})]$$

$$|3\rangle = (\overset{+}{A}\bar{A}\bar{B})$$

$$|4\rangle = (\overset{+}{A}\bar{A}\overset{+}{C})$$

$$|5\rangle = (\overset{+}{A}\bar{B}\bar{B})$$

$$|6\rangle = (\overset{+}{B}\bar{B}\overset{+}{C})$$

$$|7\rangle = (\overset{+}{A}\bar{C}\bar{C})$$

$$|8\rangle = (\overset{+}{B}\bar{C}\bar{C}).$$

The transformation properties of these eight functions under O_h symmetry operators are collected in Appendix III. They form the basis for the reducible representation which contains the irreducible components

$$^2E + ^2T_1 + ^2T_2$$

The complete basis states are found to be

$$\begin{aligned}
 |a^2T_1, \frac{1}{2}\rangle &= (1/\sqrt{6}) [(\bar{A}^+\bar{B}^+\bar{C}) + (\bar{A}^+\bar{B}^+\bar{C}) - 2(\bar{A}^+\bar{B}^+\bar{C})] \\
 |a^2T_1, -\frac{1}{2}\rangle &= (1/\sqrt{6}) [2(\bar{A}^+\bar{B}^+\bar{C}) - (\bar{A}^+\bar{B}^+\bar{C}) - (\bar{A}^+\bar{B}^+\bar{C})] \\
 |b^2T_1, \frac{1}{2}\rangle &= (1/\sqrt{6}) [(\bar{A}^+\bar{A}^+\bar{B}) + (\bar{B}^+\bar{B}^+\bar{C}) - 2(\bar{A}^+\bar{C}^+\bar{C})] \\
 |b^2T_1, -\frac{1}{2}\rangle &= (1/\sqrt{6}) [(\bar{A}^+\bar{A}^+\bar{B}) + (\bar{B}^+\bar{B}^+\bar{C}) - 2(\bar{A}^+\bar{C}^+\bar{C})] \\
 |c^2T_1, \frac{1}{2}\rangle &= (1/\sqrt{6}) [-(\bar{A}^+\bar{A}^+\bar{C}) + 2(\bar{A}^+\bar{B}^+\bar{B}) - (\bar{B}^+\bar{C}^+\bar{C})] \\
 |c^2T_1, -\frac{1}{2}\rangle &= (1/\sqrt{6}) [-(\bar{A}^+\bar{A}^+\bar{C}) + 2(\bar{A}^+\bar{B}^+\bar{B}) - (\bar{B}^+\bar{C}^+\bar{C})] \\
 \\
 |a^2E, \frac{1}{2}\rangle &= \sqrt{\frac{1}{3}} [(\bar{A}^+\bar{A}^+\bar{B}) + (\bar{B}^+\bar{B}^+\bar{C}) + (\bar{A}^+\bar{C}^+\bar{C})] \\
 |a^2E, -\frac{1}{2}\rangle &= \sqrt{\frac{1}{3}} [(\bar{A}^+\bar{A}^+\bar{B}) + (\bar{B}^+\bar{B}^+\bar{C}) + (\bar{A}^+\bar{C}^+\bar{C})] \\
 |b^2E, \frac{1}{2}\rangle &= \sqrt{\frac{1}{3}} [(\bar{A}^+\bar{A}^+\bar{C}) + (\bar{A}^+\bar{B}^+\bar{B}) + (\bar{B}^+\bar{C}^+\bar{C})] \\
 |b^2E, -\frac{1}{2}\rangle &= \sqrt{\frac{1}{3}} [(\bar{A}^+\bar{A}^+\bar{C}) + (\bar{A}^+\bar{B}^+\bar{B}) + (\bar{B}^+\bar{C}^+\bar{C})] \\
 \\
 |a^2T_2, \frac{1}{2}\rangle &= \sqrt{\frac{1}{2}} [(\bar{A}^+\bar{B}^+\bar{C}) - (\bar{A}^+\bar{B}^+\bar{C})] \\
 |a^2T_2, -\frac{1}{2}\rangle &= \sqrt{\frac{1}{2}} [(\bar{A}^+\bar{B}^+\bar{C}) - (\bar{A}^+\bar{B}^+\bar{C})] \\
 |b^2T_2, \frac{1}{2}\rangle &= \sqrt{\frac{1}{2}} [(\bar{A}^+\bar{A}^+\bar{B}) - (\bar{B}^+\bar{B}^+\bar{C})] \\
 |b^2T_2, -\frac{1}{2}\rangle &= \sqrt{\frac{1}{2}} [(\bar{A}^+\bar{A}^+\bar{B}) - (\bar{B}^+\bar{B}^+\bar{C})] \\
 |c^2T_2, \frac{1}{2}\rangle &= \sqrt{\frac{1}{2}} [(\bar{A}^+\bar{A}^+\bar{C}) - (\bar{B}^+\bar{C}^+\bar{C})] \\
 |c^2T_2, -\frac{1}{2}\rangle &= \sqrt{\frac{1}{2}} [(\bar{A}^+\bar{A}^+\bar{C}) - (\bar{B}^+\bar{C}^+\bar{C})]
 \end{aligned}$$

2.4 MANY-ELECTRON BASIS STATES, $t_{2g}^2 e_g$ CONFIGURATION

Following exactly similar steps as in the t_{2g}^3 configuration we can write down the possible antisymmetrised product states for the $t_{2g}^2 e_g$ configuration; those with $M_S = 3/2$ are labelled ϕ_1 to ϕ_6 and are shown below:

$$\begin{aligned}
 \phi_1 &= (\bar{A}^+\bar{B}^+\bar{D}), & \phi_2 &= (\bar{A}^+\bar{B}^+\bar{E}) \\
 \phi_3 &= (\bar{A}^+\bar{C}^+\bar{D}), & \phi_4 &= (\bar{A}^+\bar{C}^+\bar{E}) \\
 \phi_5 &= (\bar{B}^+\bar{C}^+\bar{D}), & \phi_6 &= (\bar{B}^+\bar{C}^+\bar{E}).
 \end{aligned}$$

The transformation properties under the symmetry elements of the O_h group are collected in the following table:

| E | C_3 | C_2 | C_4 | C_2' |
|----------|-------------------|--|--|-----------|
| ϕ_1 | $\omega^2 \phi_1$ | $-\frac{1}{3}\phi_1 - \frac{2}{3}\phi_3 + \frac{2}{3}\phi_5$ | $(\frac{1}{3}+i\sqrt{\frac{1}{3}})\phi_2 - \frac{1}{3}\phi_4 + (\frac{1}{3}-i\sqrt{\frac{1}{3}})\phi_6$ | ϕ_4 |
| ϕ_2 | ϕ_2 | $-\frac{1}{3}\phi_2 - \frac{2}{3}\phi_4 + \frac{2}{3}\phi_6$ | $(\frac{1}{3}+i\sqrt{\frac{1}{3}})\phi_1 - \frac{1}{3}\phi_3 + (\frac{1}{3}-i\sqrt{\frac{1}{3}})\phi_5$ | ϕ_3 |
| ϕ_3 | ϕ_3 | $-\frac{2}{3}\phi_1 - \frac{1}{3}\phi_3 - \frac{2}{3}\phi_5$ | $-\frac{1}{3}\phi_2 + (\frac{1}{3}-i\sqrt{\frac{1}{3}})\phi_4 - (\frac{1}{3}+i\sqrt{\frac{1}{3}})\phi_6$ | ϕ_2 |
| ϕ_4 | $\omega \phi_4$ | $-\frac{2}{3}\phi_2 - \frac{1}{3}\phi_4 - \frac{2}{3}\phi_6$ | $-\frac{1}{3}\phi_1 + (\frac{1}{3}-i\sqrt{\frac{1}{3}})\phi_3 - (\frac{1}{3}+i\sqrt{\frac{1}{3}})\phi_5$ | ϕ_1 |
| ϕ_5 | $\omega \phi_5$ | $\frac{2}{3}\phi_1 - \frac{2}{3}\phi_3 - \frac{1}{3}\phi_5$ | $(\frac{1}{3}-i\sqrt{\frac{1}{3}})\phi_2 - (\frac{1}{3}+i\sqrt{\frac{1}{3}})\phi_4 + \frac{1}{3}\phi_6$ | $-\phi_6$ |
| ϕ_6 | $\omega^2 \phi_6$ | $\frac{2}{3}\phi_2 - \frac{2}{3}\phi_4 - \frac{1}{3}\phi_6$ | $(\frac{1}{3}-i\sqrt{\frac{1}{3}})\phi_1 - (\frac{1}{3}+i\sqrt{\frac{1}{3}})\phi_3 + \frac{1}{3}\phi_5$ | $-\phi_5$ |
| 6 | 0 | -2 | 0 | 0 |

Table 2.1: Transformation Properties of $(t_{2g}^2 e_g)$ Functions, with $M_S = 3/2$ under O_h .

These six functions span a space transforming according to a representation of the O_h group which contains the irreducible components T_1 and T_2 . It is a simple matter to find the correct linear combinations of the functions to reduce the representation into its component parts; the 4T_1 functions are found to be

$$\sqrt{\frac{1}{2}}(\phi_2 - \phi_3), \quad \sqrt{\frac{1}{2}}(\phi_1 + \phi_6), \quad \sqrt{\frac{1}{2}}(\phi_4 - \phi_5),$$

while the combination transforming as 4T_2 is

$$\sqrt{\frac{1}{2}}(\phi_2 + \phi_3), \quad \sqrt{\frac{1}{2}}(\phi_1 - \phi_6), \quad \sqrt{\frac{1}{2}}(\phi_4 + \phi_5).$$

Written in terms of determinantal states:

$$\begin{aligned} |a^4T, \frac{3}{2}\rangle &= \sqrt{\frac{1}{2}}[(\bar{A}\bar{B}\bar{E}) + (\bar{A}\bar{C}\bar{D})] \\ |a^4T, \frac{1}{2}\rangle &= (1/\sqrt{6})[(\bar{A}\bar{B}\bar{E}) + (\bar{A}\bar{B}\bar{E}) + (\bar{A}\bar{B}\bar{E}) + (\bar{A}\bar{C}\bar{D}) + (\bar{A}\bar{C}\bar{D}) + (\bar{A}\bar{C}\bar{D})] \\ |a^4T, -\frac{1}{2}\rangle &= (1/\sqrt{6})[(\bar{A}\bar{B}\bar{E}) + (\bar{A}\bar{B}\bar{E}) + (\bar{A}\bar{B}\bar{E}) + (\bar{A}\bar{C}\bar{D}) + (\bar{A}\bar{C}\bar{D}) + (\bar{A}\bar{C}\bar{D})] \\ |a^4T, -\frac{3}{2}\rangle &= \sqrt{\frac{1}{2}}[(\bar{A}\bar{B}\bar{E}) + (\bar{A}\bar{C}\bar{D})] \end{aligned}$$

$$|b^4T, \frac{3}{2}\rangle = \sqrt{\frac{1}{2}}[(\bar{A}\bar{B}\bar{D}) \pm (\bar{B}\bar{C}\bar{E})]$$

$$|b^4T, \frac{1}{2}\rangle = (1/\sqrt{6})[(\bar{A}\bar{B}\bar{D}) + (\bar{A}\bar{B}\bar{D}) + (\bar{A}\bar{B}\bar{D}) \pm (\bar{B}\bar{C}\bar{E}) \pm (\bar{B}\bar{C}\bar{E}) \pm (\bar{B}\bar{C}\bar{E})]$$

$$|b^4T, -\frac{1}{2}\rangle = (1/\sqrt{6})[(\bar{A}\bar{B}\bar{D}) + (\bar{A}\bar{B}\bar{D}) + (\bar{A}\bar{B}\bar{D}) \pm (\bar{B}\bar{C}\bar{E}) \pm (\bar{B}\bar{C}\bar{E}) \pm (\bar{B}\bar{C}\bar{E})]$$

$$|b^4T, -\frac{3}{2}\rangle = \sqrt{\frac{1}{2}}[(\bar{A}\bar{B}\bar{D}) \pm (\bar{B}\bar{C}\bar{E})]$$

$$|c^4T, \frac{3}{2}\rangle = \sqrt{\frac{1}{2}}[(\bar{A}\bar{C}\bar{E}) \mp (\bar{B}\bar{C}\bar{D})]$$

$$|c^4T, \frac{1}{2}\rangle = (1/\sqrt{6})[(\bar{A}\bar{C}\bar{E}) + (\bar{A}\bar{C}\bar{E}) + (\bar{A}\bar{C}\bar{E}) \mp (\bar{B}\bar{C}\bar{D}) \mp (\bar{B}\bar{C}\bar{D}) \mp (\bar{B}\bar{C}\bar{D})]$$

$$|c^4T, -\frac{1}{2}\rangle = (1/\sqrt{6})[(\bar{A}\bar{C}\bar{E}) + (\bar{A}\bar{C}\bar{E}) + (\bar{A}\bar{C}\bar{E}) \mp (\bar{B}\bar{C}\bar{D}) \mp (\bar{B}\bar{C}\bar{D}) \mp (\bar{B}\bar{C}\bar{D})]$$

$$|c^4T, -\frac{3}{2}\rangle = \sqrt{\frac{1}{2}}[(\bar{A}\bar{C}\bar{E}) \mp (\bar{B}\bar{C}\bar{D})]$$

The symmetry species has not been specified but in the signs \pm and \mp the first sign refers to 4T_1 and the second to 4T_2 . Altogether there are 36 doublet functions belonging to this configuration; those with $M_S = \frac{1}{2}$ are written in full in Appendix IV together with their transformation table under O_h symmetry.

2.5 (${}^4A_2 \times {}^2T_1$) MANIFOLD BASIS STATES (U, V, W)

From the basis states of the individual Cr^{3+} ions in the pair it is possible to form the basis states of the pair. At present we are interested in the states of the (${}^4A_2 \times {}^2T_1$) manifold; there are 48 such states having total spin values of either 1 or 2.

Consider a general pair state with one ion described by the function $|a^2T_1, \frac{1}{2}\rangle$ and the other by $|{}^4A_2, \frac{3}{2}\rangle$. The pair state in this situation will be written

$$|a^2T_1, \frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle.$$

In this particular example the total spin $S = 2$ and $M_S = 2$. The S and M_S values will be used in classifying the pair states. There are three components of 2T_1 defined in section 2.3 and to distinguish between these

the pair states shall carry the labels U, V and W for one of the ions being in a^2T_1 , b^2T_1 or c^2T_1 respectively. The above state is therefore written

$$|U, S=2, M_S=2\rangle = |a^2T_1, \frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle$$

and in terms of determinantal functions

$$|U, 2, 2\rangle = (1/\sqrt{6}) [\{ (\overset{++}{A}\overset{+-}{B}\overset{-}{C}) + (\overset{+-}{A}\overset{++}{B}\overset{-}{C}) - 2(\overset{-}{A}\overset{++}{B}\overset{++}{C}) \} \{ (\overset{++}{a}\overset{++}{b}\overset{++}{c}) \}]$$

The pair state appears to be written in terms of products of determinants, for instance $(\overset{++}{A}\overset{+-}{B}\overset{-}{C}) \times (\overset{++}{a}\overset{++}{b}\overset{++}{c})$. Each product is antisymmetric with respect to interchanges of electrons in the first ion orbitals and to interchanges of electrons in the second ion orbitals but not with respect to interchanges of electrons between ions. Any physically important states must be antisymmetric with respect to electron interchanges so any discussion of the properties of the Hamiltonian using basic states that are not symmetric would be invalid. The product of the determinants $(\overset{++}{A}\overset{+-}{B}\overset{-}{C}) \times (\overset{++}{a}\overset{++}{b}\overset{++}{c})$ becomes antisymmetric with respect to interchanges of all pairs of electrons if it is replaced by $(\overset{++}{A}\overset{+-}{B}\overset{-}{C}\overset{++}{a}\overset{++}{b}\overset{++}{c})$. In this way the product $(\overset{++}{A}\overset{+-}{B}\overset{-}{C}) \times (\overset{++}{a}\overset{++}{b}\overset{++}{c})$ is taken to mean a 6 x 6 Slater determinant formed from the two 3 x 3 determinants, being then appropriate to a six electron system.

Application of the spin lowering operator S_- on the pair state $|U, 2, 2\rangle$, already defined, enables those states with lower M_S values to be found. Thus we have:

$$\begin{aligned} |U, 2, 2\rangle &= |a^2T_1, \frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle \\ |U, 2, 1\rangle &= \frac{1}{2} |a^2T_1, -\frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle + \frac{1}{2}\sqrt{3} |a^2T_1, \frac{1}{2}; {}^4A_2, \frac{1}{2}\rangle \\ |U, 2, 0\rangle &= \sqrt{\frac{1}{2}} |a^2T_1, -\frac{1}{2}; {}^4A_2, \frac{1}{2}\rangle + \sqrt{\frac{1}{2}} |a^2T_1, \frac{1}{2}; {}^4A_2, -\frac{1}{2}\rangle \\ |U, 2, -1\rangle &= \frac{1}{2}\sqrt{3} |a^2T_1, -\frac{1}{2}; {}^4A_2, -\frac{1}{2}\rangle + \frac{1}{2} |a^2T_1, \frac{1}{2}; {}^4A_2, -\frac{3}{2}\rangle \\ |U, 2, -2\rangle &= |a^2T_1, -\frac{1}{2}; {}^4A_2, -\frac{3}{2}\rangle \end{aligned}$$

The state $|U,1,1\rangle$ is found by virtue of its orthogonality to $|U,2,1\rangle$ and because it is normalised.

$$\begin{aligned} |U,1,1\rangle &= \frac{1}{2}\sqrt{3}|a^2T_1, -\frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle - \frac{1}{2}|a^2T_1, \frac{1}{2}; {}^4A_2, \frac{1}{2}\rangle \\ |U,1,0\rangle &= \sqrt{\frac{1}{2}}|a^2T_1, -\frac{1}{2}; {}^4A_2, -\frac{1}{2}\rangle - \sqrt{\frac{1}{2}}|a^2T_1, \frac{1}{2}; {}^4A_2, -\frac{1}{2}\rangle \\ |U,1,-1\rangle &= \frac{1}{2}|a^2T_1, -\frac{1}{2}; {}^4A_2, -\frac{3}{2}\rangle - \frac{1}{2}\sqrt{3}|a^2T_1, \frac{1}{2}; {}^4A_2, -\frac{3}{2}\rangle \end{aligned}$$

The V and W states are easily obtained from the U states by the substitution of $|b^2T_1\rangle$ and $|c^2T_1\rangle$ respectively for $|a^2T_1\rangle$.

However the U, V and W do not behave irreducibly under σ_h so new states are defined thus

$$\begin{aligned} |U',1,1\rangle &= \sqrt{\frac{1}{2}}(1 + \sigma_h)|U,1,1\rangle \\ |U'',1,1\rangle &= \sqrt{\frac{1}{2}}(1 - \sigma_h)|U,1,1\rangle \end{aligned}$$

and similarly for $|V,1,1\rangle$, $|W,1,1\rangle$, $|U,2,2\rangle$, $|V,2,2\rangle$ and $|W,2,2\rangle$. The prime and double prime notation is consistent with the standard notation that prime states are invariant under σ_h whereas double prime states reverse.

The spin lowering operator has a somewhat unexpected effect when applied to the prime and double prime states, because of the anticommutivity between S_- and σ_h . For instance

$$\begin{aligned} S_-|U',1,1\rangle &= S_- \sqrt{\frac{1}{2}}(1 + \sigma_h)|U,1,1\rangle \\ &= \sqrt{\frac{1}{2}}(1 - \sigma_h)S_-|U,1,1\rangle \\ &= \sqrt{\frac{1}{2}}(1 - \sigma_h)\sqrt{2}|U,1,0\rangle \\ &= \sqrt{2}|U'',1,0\rangle \end{aligned}$$

i.e. the spin lowering operator applied to a prime state has produced a double prime state.

2.6 U, V AND W IN TERMS OF SINGLE ION BASIS STATES

The manipulation of the pair states is facilitated when they are expressed in terms of the single ion basis states (as opposed to writing them as determinantal states). We have that

$$|U, 2, 2\rangle = |a^2T_1, \frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle$$

and we shall use the convention that when describing a pair state in terms of single ion states the first term in the pair ket always refers to the ion whose electronic states are described by the orbitals $|A\rangle$, $|B\rangle$, $|C\rangle$ etc, and the second term in the pair ket always refers to the ion with states described in terms of $|a\rangle$, $|b\rangle$, $|c\rangle$, $|d\rangle$ and $|e\rangle$.

To write a prime or double prime state in terms of the single ion kets $|{}^2T_1\rangle$ and $|{}^4A_2\rangle$ the effects of the operator σ_h on them must first be computed (see sections 2.2, 2.3). Now

$$\begin{aligned}\sigma_h |U, 2, 2\rangle &= \sigma_h |a^2T_1, \frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle \\ &= |-i(a^2T_1, \frac{1}{2}):i({}^4A_2, \frac{3}{2})\rangle \\ &= |a^2T_1, \frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle\end{aligned}$$

but it must be remembered that in this case the first of the terms refers to the ion with states described by $|a\rangle$, $|b\rangle$, $|c\rangle$ etc. By the convention that has been adopted the order of the terms must be reversed giving the result

$$\sigma_h |U, 2, 2\rangle = -|{}^4A_2, \frac{3}{2}; a^2T_1, \frac{1}{2}\rangle$$

the prime and double prime states are then given by

$$|U', 2, 2\rangle = \sqrt{\frac{1}{2}}[|a^2T_1, \frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle - |{}^4A_2, \frac{3}{2}; a^2T_1, \frac{1}{2}\rangle]$$

$$|U'', 2, 2\rangle = \sqrt{\frac{1}{2}}[|a^2T_1, \frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle + |{}^4A_2, \frac{3}{2}; a^2T_1, \frac{1}{2}\rangle]$$

The lower M_S valued states are obtained by applying the spin lowering operator, remembering that application of S_- on a prime state produces a double prime state and vice versa.

The pair states can now be written in full; the following are a generalised form being applicable to any of the U, V or W by the insertion of the correct component of 2T_1 for the T specified. The \pm and \mp signs refer to the prime and double prime states with the first sign always referring to the prime state.

$$|2,2\rangle = \sqrt{\frac{1}{2}}[|T, \frac{1}{2}:A, \frac{3}{2}\rangle \mp |A, \frac{3}{2}:T, \frac{1}{2}\rangle]$$

$$|2,1\rangle = \frac{1}{2}\sqrt{\frac{1}{2}}[|T, -\frac{1}{2}:A, \frac{3}{2}\rangle + \sqrt{3}|T, \frac{1}{2}:A, \frac{1}{2}\rangle \pm \sqrt{3}|A, \frac{1}{2}:T, \frac{1}{2}\rangle \pm |A, \frac{3}{2}:T, -\frac{1}{2}\rangle]$$

$$|2,0\rangle = \frac{1}{2}[|T, -\frac{1}{2}:A, \frac{1}{2}\rangle + |T, \frac{1}{2}:A, -\frac{1}{2}\rangle \mp |A, -\frac{1}{2}:T, \frac{1}{2}\rangle \mp |A, \frac{1}{2}:T, -\frac{1}{2}\rangle]$$

$$|2,-1\rangle = \frac{1}{2}\sqrt{\frac{1}{2}}[\sqrt{3}|T, -\frac{1}{2}:A, -\frac{1}{2}\rangle + |T, \frac{1}{2}:A, -\frac{3}{2}\rangle \pm |A, -\frac{3}{2}:T, \frac{1}{2}\rangle \pm \sqrt{3}|A, -\frac{1}{2}:T, -\frac{1}{2}\rangle]$$

$$|2,-2\rangle = \sqrt{\frac{1}{2}}[|T, -\frac{1}{2}:A, -\frac{3}{2}\rangle \mp |A, -\frac{3}{2}:T, -\frac{1}{2}\rangle]$$

$$|1,1\rangle = \frac{1}{2}\sqrt{\frac{1}{2}}[\sqrt{3}|T, -\frac{1}{2}:A, \frac{3}{2}\rangle - |T, \frac{1}{2}:A, \frac{1}{2}\rangle \mp |A, \frac{1}{2}:T, \frac{1}{2}\rangle \pm \sqrt{3}|A, \frac{3}{2}:T, -\frac{1}{2}\rangle]$$

$$|1,0\rangle = \frac{1}{2}[|T, -\frac{1}{2}:A, \frac{1}{2}\rangle - |T, \frac{1}{2}:A, -\frac{1}{2}\rangle \pm |A, -\frac{1}{2}:T, \frac{1}{2}\rangle \mp |A, \frac{1}{2}:T, -\frac{1}{2}\rangle]$$

$$|1,-1\rangle = \frac{1}{2}\sqrt{\frac{1}{2}}[|T, -\frac{1}{2}:A, -\frac{1}{2}\rangle - \sqrt{3}|T, \frac{1}{2}:A, -\frac{3}{2}\rangle \mp \sqrt{3}|A, -\frac{3}{2}:T, \frac{1}{2}\rangle \pm |A, -\frac{1}{2}:T, -\frac{1}{2}\rangle]$$

2.7 U, V AND W (IN D_{3h} SYMMETRY)

The 48 basis states of the $({}^4A_2 \times {}^2T_1)$ manifold must now be operated on by the symmetry operators of the D_{3h} group and hence their transformation properties within this symmetry group deduced, with the express purpose of ascertaining the correct linear combinations of the basis states which transform according to the irreducible representations of the D_{3h} group. The elements of the D_{3h} group are E, σ_h , C_3 , S_3 , C'_2 and σ_v . Now σ_h commutes with C_3 and σ_v so that C_3 and σ_v have the same effect on both primed and double primed states. Also $S_3 = \sigma_h C_3$ and $C'_2 = \sigma_h \sigma_v$ so that acting on primed states $S_3 \equiv C_3$ and $C'_2 \equiv \sigma_v$ and acting

on double primed states $S_3 \equiv -C_3$ and $C'_2 \equiv -\sigma_v$.

The transformation properties of the unprimed states are shown in the Appendix V and from them a transformation table of the states under the D_{3h} symmetry elements can be formed. Consider the table of the primed states with $S = 1$.

| | E, σ_h | C_3, S_3 | C'_2, σ_v |
|---------------------|---------------------|------------------------------|---------------------|
| $ U', 1, 1\rangle$ | $ U', 1, 1\rangle$ | $\omega^2 U', 1, 1\rangle$ | $ U', 1, -1\rangle$ |
| $ U', 1, 0\rangle$ | $ U', 1, 0\rangle$ | $ U', 1, 0\rangle$ | $- U', 1, 0\rangle$ |
| $ U', 1, -1\rangle$ | $ U', 1, -1\rangle$ | $\omega U', 1, -1\rangle$ | $ U', 1, 1\rangle$ |
| $ V', 1, 1\rangle$ | $ V', 1, 1\rangle$ | $ V', 1, 1\rangle$ | $ W', 1, -1\rangle$ |
| $ V', 1, 0\rangle$ | $ V', 1, 0\rangle$ | $\omega V', 1, 0\rangle$ | $ W', 1, 0\rangle$ |
| $ V', 1, -1\rangle$ | $ V', 1, -1\rangle$ | $\omega^2 V', 1, -1\rangle$ | $ W', 1, 1\rangle$ |
| $ W', 1, 1\rangle$ | $ W', 1, 1\rangle$ | $\omega W', 1, 1\rangle$ | $ V', 1, -1\rangle$ |
| $ W', 1, 0\rangle$ | $ W', 1, 0\rangle$ | $\omega^2 W', 1, 0\rangle$ | $ V', 1, 0\rangle$ |
| $ W', 1, -1\rangle$ | $ W', 1, -1\rangle$ | $ W', 1, -1\rangle$ | $ V', 1, 1\rangle$ |
| χ | 9 | 0 | -1 |

Table 2.2: Transformation properties of primed (U,V,W) with $S = 1$ under D_{3h}

Comparing with the character table of the D_{3h} group Appendix I(ii), these 9 functions form the basis for the reducible representation of the D_{3h} group containing the irreducible components

$$A'_1 + 2A''_2 + 3E'$$

It is easily found that:

$|U', 1, 1\rangle$ and $|U', 1, -1\rangle$ form the basis for the representation E'

| | | | | | | | |
|--|---|---|---|---|---|---|---------------|
| $ U', 1, 0\rangle$ | " | " | " | " | " | " | A'_2 |
| $\sqrt{\frac{1}{2}}[V', 1, 1\rangle \pm W', 1, -1\rangle]$ | " | " | " | " | " | " | $A'_1 + A'_2$ |
| $ V', 1, 0\rangle$ and $ W', 1, 0\rangle$ | " | " | " | " | " | " | E' |
| $ V', 1, -1\rangle$ and $ W', 1, 1\rangle$ | " | " | " | " | " | " | E' |

and from now on these are the basis states of the (${}^4A_2 \times {}^2T_1$) manifold;
these and the rest of the symmetry adapted basis states are displayed
below:

| Orbital Parent | $\sigma_h = +1$ | $\sigma_h = -1$ |
|----------------|---|---|
| ${}^3A'_1$ | $ U', 1, 0\rangle$ A'_2 | $ U'', 1, 1\rangle, U'', 1, -1\rangle$ E'' |
| ${}^3A''_2$ | $ U', 1, 1\rangle, U', 1, -1\rangle$ E' | $ U'', 1, 0\rangle$ A''_1 |
| ${}^3E''$ | $\sqrt{\frac{1}{2}}[V', 1, 1\rangle \pm W', 1, -1\rangle]$ $A'_1 + A'_2$ $ V', 1, -1\rangle, W', 1, 1\rangle$ E' | $ V'', 1, 0\rangle, W'', 1, 0\rangle$ E'' |
| ${}^3E'$ | $ V', 1, 0\rangle, W', 1, 0\rangle$ E' | $\sqrt{\frac{1}{2}}[V'', 1, 1\rangle \mp W'', 1, -1\rangle]$ $A''_1 + A''_2$ $ V'', 1, -1\rangle, W'', 1, 1\rangle$ |
| ${}^5A'_1$ | $ U', 2, 0\rangle$ A'_1 $ U', 2, 2\rangle, U', 2, -2\rangle$ E' | $ U'', 2, 1\rangle, U'', 2, -1\rangle$ E'' |
| ${}^5A''_2$ | $ U', 2, 1\rangle, U', 2, -1\rangle$ E' | $ U'', 2, 0\rangle$ A''_2 $ U'', 2, 2\rangle, U'', 2, -2\rangle$ E'' |
| ${}^5E''$ | $\sqrt{\frac{1}{2}}[V', 2, 1\rangle \mp W', 2, -1\rangle]$ $A'_1 + A'_2$ $ V', 2, -1\rangle, W', 2, 1\rangle$ E' | $ V'', 2, 2\rangle, W'', 2, -2\rangle$ E'' $ V'', 2, 0\rangle, W'', 2, 0\rangle$ E'' $\sqrt{\frac{1}{2}}[V'', 2, -2\rangle \pm W'', 2, 2\rangle]$ $A''_1 + A''_2$ |
| ${}^5E'$ | $ V', 2, 2\rangle, W', 2, -2\rangle$ E' $ V', 2, 0\rangle, W', 2, 0\rangle$ E' $\sqrt{\frac{1}{2}}[V', 2, -2\rangle \pm W', 2, 2\rangle]$ $A'_1 + A'_2$ | $\sqrt{\frac{1}{2}}[V'', 2, 1\rangle \pm W'', 2, -1\rangle]$ $A''_1 + A''_2$ $ V'', 2, -1\rangle, W'', 2, 1\rangle$ E'' |

Table 7.3: Irreducible Representations of D_{3h} formed by (U, V, W).

It may be noticed that the table contains a column headed 'orbital parent'. This column contains the irreducible representations of the orbital component of the pair states, and is obtained by operating on the U' , V' , W' etc states with the symmetry operators of D_{3h} which refer only to the orbital parts; C_3^0 , σ_V^0 and σ_h^0 . The effects of these operators are independent of the total spin S and excepting σ_h^0 , independent of the σ_h nature of the states. So one can write:

$$\begin{aligned} C_3^0|U\rangle &= |U\rangle, & C_3^0|V\rangle &= \omega|V\rangle, & C_3^0|W\rangle &= \omega^2|W\rangle \\ \sigma_V^0|U\rangle &= |U\rangle, & \sigma_V^0|V\rangle &= -|W\rangle, & \sigma_V^0|W\rangle &= -|V\rangle. \end{aligned}$$

Combining these results with the operator σ_h^0 (σ_h^0 operating on a state can only give +1 or -1) and referring to the D_{3h} character table Appendix I, one finds that the orbital parts of the U states transform as $A_1' + A_2''$ and the V and W states transform as $E' + E''$ under D_{3h} .

The operator σ_h^0 mixes states of different symmetries under σ_h , i.e. both primed and double primed states, for instance, orbitally the states $|U'', 1, \pm 1\rangle$ and $|U', 1, 0\rangle$ form the basis for ${}^3A_1'$ in D_{3h} . One also notices that for states with $M_S = 0$ the symmetries under both σ_h^0 and σ_h are the same so that given the orbital parent it is easy to write down all the members of that particular multiplet.

2.8 BASIS STATES OF THE (${}^4A_2 \times {}^2T_2$) AND (${}^4A_2 \times {}^2E$) MANIFOLDS

When deriving the basis states of the (${}^4A_2 \times {}^2T_1$) manifold it may be noticed that only properties concerning the total spin of the states was involved, through the use of S_- and σ_h . The form of the states (see sections 2.5 and 2.6) does not depend on the orbital transformation properties of the 2T_1 states. By virtue of the fact that 2T_2 and 2E are spin doublets we can say that the (${}^4A_2 \times {}^2T_2$) and (${}^4A_2 \times {}^2E$) manifold

basis states have exactly the form as the states already given in section 2.6. Thus to obtain the state of the (${}^4A_2 \times {}^2T_2$) manifold for instance, the required component of 2T_2 is merely substituted for 2T_1 in the U, V and W states, e.g. a prime state of the (${}^4A_2 \times {}^2T_2$) having $S = 2$ and $M_S = 2$ might be written:

$$|P', 2, 2\rangle = \sqrt{\frac{1}{2}} [|a^2T_2, \frac{1}{2}; {}^4A_2, \frac{3}{2}\rangle - |{}^4A_2, \frac{3}{2}; a^2T_2, \frac{1}{2}\rangle]$$

As in the case of (${}^4A_2 \times {}^2T_1$) both S and M_S are used in classifying the states. Now 2T_2 has three orbital components and 2E has two orbital components and these need to be distinguished. Analogous to the definition of U, V and W we shall use the letters P, Q and R to distinguish between the components a^2T_2 , b^2T_2 and c^2T_2 of the (${}^4A_2 \times {}^2T_2$) manifold and G and H for the a and b components of 2E . The symmetry properties of the unprimed P, Q and R and the unprimed G and H are given in Appendix V.

2.9 BASIS STATES OF THE (${}^4A_2 \times {}^4T_1$) AND (${}^4A_2 \times {}^4T_2$) MANIFOLDS

The states to be constructed are those describing the situation in which one ion remains in the ground state ${}^4A_2(t_{2g}^3)$ while the other is excited to either 4T_1 or 4T_2 , both of the $t_{2g}^2 e_g$ configuration. In both of these cases there are 96 states having possible total spin $S = 0, 1, 2, 3$.

Beginning with the pair state in which $S = 3$ and $M_S = 3$, all other states can be formed by the use of S_- and by implementing the conditions of orthonormality. The following will be derived for a general 4T state as the result is applicable to any component of either 4T_1 or 4T_2 . The operators $\sqrt{\frac{1}{2}}(1 \pm \sigma_h)$ have been applied and the prime and double prime pair states produced. Where \pm or \mp is present the first sign refers to the prime states, the second to the double prime states.

S = 3:

$$|3,3\rangle = \sqrt{\frac{1}{2}} [|^4T, \frac{3}{2}: A, \frac{3}{2}\rangle \pm |A, \frac{3}{2}: ^4T, \frac{3}{2}\rangle]$$

$$|3,2\rangle = \frac{1}{2} [|^4T, \frac{1}{2}: A, \frac{3}{2}\rangle + |^4T, \frac{3}{2}: A, \frac{1}{2}\rangle \mp |A, \frac{3}{2}: ^4T, \frac{1}{2}\rangle \mp |A, \frac{1}{2}: ^4T, \frac{3}{2}\rangle]$$

$$|3,1\rangle = (1/\sqrt{10}) [|^4T, -\frac{1}{2}: A, \frac{3}{2}\rangle + \sqrt{3} |^4T, \frac{1}{2}: A, \frac{1}{2}\rangle + |^4T, \frac{3}{2}: A, \frac{1}{2}\rangle \pm |A, \frac{3}{2}: ^4T, -\frac{1}{2}\rangle \\ \pm \sqrt{3} |A, \frac{1}{2}: ^4T, \frac{1}{2}\rangle \pm |A, -\frac{1}{2}: ^4T, \frac{3}{2}\rangle]$$

$$|3,0\rangle = \frac{1}{2} (1/\sqrt{10}) [|^4T, -\frac{3}{2}: A, \frac{3}{2}\rangle + 3 |^4T, -\frac{1}{2}: A, \frac{1}{2}\rangle + 3 |^4T, \frac{1}{2}: A, -\frac{1}{2}\rangle + |^4T, \frac{3}{2}: A, -\frac{3}{2}\rangle \\ \mp |A, \frac{3}{2}: ^4T, -\frac{3}{2}\rangle \mp 3 |A, \frac{1}{2}: ^4T, -\frac{1}{2}\rangle \mp 3 |A, -\frac{1}{2}: ^4T, \frac{1}{2}\rangle \mp |A, -\frac{3}{2}: ^4T, \frac{3}{2}\rangle]$$

$$|3,-1\rangle = (1/\sqrt{10}) [|^4T, -\frac{3}{2}: A, \frac{1}{2}\rangle + \sqrt{3} |^4T, -\frac{1}{2}: A, -\frac{1}{2}\rangle + |^4T, \frac{1}{2}: A, -\frac{3}{2}\rangle \pm |A, \frac{1}{2}: ^4T, -\frac{3}{2}\rangle \\ \pm \sqrt{3} |A, -\frac{1}{2}: ^4T, -\frac{1}{2}\rangle \pm |A, -\frac{3}{2}: ^4T, \frac{1}{2}\rangle]$$

$$|3,-2\rangle = \frac{1}{2} [|^4T, -\frac{3}{2}: A, -\frac{1}{2}\rangle + |^4T, -\frac{1}{2}: A, -\frac{3}{2}\rangle \mp |A, -\frac{1}{2}: ^4T, -\frac{3}{2}\rangle \mp |A, -\frac{3}{2}: ^4T, -\frac{1}{2}\rangle]$$

$$|3,-3\rangle = \sqrt{\frac{1}{2}} [|^4T, -\frac{3}{2}: A, -\frac{3}{2}\rangle \pm |A, -\frac{3}{2}: ^4T, -\frac{3}{2}\rangle]$$

S = 2:

$$|2,2\rangle = \frac{1}{2} [|^4T, \frac{1}{2}: A, \frac{3}{2}\rangle - |^4T, \frac{3}{2}: A, \frac{1}{2}\rangle \mp |A, \frac{3}{2}: ^4T, \frac{1}{2}\rangle \pm |A, \frac{1}{2}: ^4T, \frac{3}{2}\rangle]$$

$$|2,1\rangle = \frac{1}{2} [|^4T, -\frac{1}{2}: A, \frac{3}{2}\rangle - |^4T, \frac{3}{2}: A, -\frac{1}{2}\rangle \pm |A, \frac{3}{2}: ^4T, -\frac{1}{2}\rangle \mp |A, -\frac{1}{2}: ^4T, \frac{3}{2}\rangle]$$

$$|2,0\rangle = \frac{1}{2} \sqrt{\frac{1}{2}} [|^4T, -\frac{3}{2}: A, \frac{3}{2}\rangle + |^4T, -\frac{1}{2}: A, \frac{1}{2}\rangle - |^4T, \frac{1}{2}: A, -\frac{1}{2}\rangle - |^4T, \frac{3}{2}: A, -\frac{3}{2}\rangle \\ \mp |A, \frac{3}{2}: ^4T, -\frac{3}{2}\rangle \mp |A, \frac{1}{2}: ^4T, -\frac{1}{2}\rangle \pm |A, -\frac{1}{2}: ^4T, \frac{1}{2}\rangle \pm |A, -\frac{3}{2}: ^4T, \frac{3}{2}\rangle]$$

$$|2,-1\rangle = \frac{1}{2} [|^4T, -\frac{3}{2}: A, \frac{1}{2}\rangle - |^4T, \frac{1}{2}: A, -\frac{3}{2}\rangle \pm |A, \frac{1}{2}: ^4T, -\frac{3}{2}\rangle \mp |A, -\frac{3}{2}: ^4T, \frac{1}{2}\rangle]$$

$$|2,-2\rangle = \frac{1}{2} [|^4T, -\frac{3}{2}: A, -\frac{1}{2}\rangle - |^4T, -\frac{1}{2}: A, -\frac{3}{2}\rangle \mp |A, -\frac{1}{2}: ^4T, -\frac{3}{2}\rangle \pm |A, -\frac{3}{2}: ^4T, -\frac{1}{2}\rangle]$$

S = 1

$$|1,1\rangle = \frac{1}{2} (1/\sqrt{5}) [\sqrt{3} |^4T, -\frac{1}{2}: A, \frac{3}{2}\rangle - 2 |^4T, \frac{1}{2}: A, \frac{1}{2}\rangle + \sqrt{3} |^4T, \frac{3}{2}: A, -\frac{1}{2}\rangle \\ \pm \sqrt{3} |A, \frac{3}{2}: ^4T, -\frac{1}{2}\rangle \mp 2 |A, \frac{1}{2}: ^4T, \frac{1}{2}\rangle \pm \sqrt{3} |A, -\frac{1}{2}: ^4T, \frac{3}{2}\rangle]$$

$$|1,0\rangle = \frac{1}{2} (1/\sqrt{10}) [3 |^4T, -\frac{3}{2}: A, \frac{3}{2}\rangle - |^4T, -\frac{1}{2}: A, \frac{1}{2}\rangle - |^4T, \frac{1}{2}: A, -\frac{1}{2}\rangle + 3 |^4T, \frac{3}{2}: A, -\frac{3}{2}\rangle \\ \mp 3 |A, \frac{3}{2}: ^4T, -\frac{3}{2}\rangle \pm |A, \frac{1}{2}: ^4T, -\frac{1}{2}\rangle \pm |A, -\frac{1}{2}: ^4T, \frac{1}{2}\rangle \mp 3 |A, -\frac{3}{2}: ^4T, \frac{3}{2}\rangle]$$

$$|1,-1\rangle = \frac{1}{2} (1/\sqrt{5}) [\sqrt{3} |^4T, -\frac{3}{2}: A, \frac{1}{2}\rangle - 2 |^4T, -\frac{1}{2}: A, -\frac{1}{2}\rangle + \sqrt{3} |^4T, \frac{1}{2}: A, -\frac{3}{2}\rangle \\ \pm \sqrt{3} |A, \frac{1}{2}: ^4T, -\frac{3}{2}\rangle \mp 2 |A, -\frac{1}{2}: ^4T, -\frac{1}{2}\rangle \pm \sqrt{3} |A, -\frac{3}{2}: ^4T, \frac{1}{2}\rangle]$$

S = 0

$$|0,0\rangle = \frac{1}{2} \sqrt{\frac{1}{2}} [|^4T, -\frac{3}{2}: A, \frac{3}{2}\rangle - |^4T, -\frac{1}{2}: A, \frac{1}{2}\rangle + |^4T, \frac{1}{2}: A, -\frac{1}{2}\rangle - |^4T, \frac{3}{2}: A, -\frac{3}{2}\rangle \\ \mp |A, \frac{3}{2}: ^4T, -\frac{3}{2}\rangle \pm |A, \frac{1}{2}: ^4T, -\frac{1}{2}\rangle \mp |A, -\frac{1}{2}: ^4T, \frac{1}{2}\rangle \pm |A, -\frac{3}{2}: ^4T, \frac{3}{2}\rangle]$$

As in the procedure previously followed, the orbital components of ~~these pair states~~ are distinguished by the use of letters. The states

of the (${}^4A_2 \times {}^4T_1$) manifold are labelled α , β and γ for the a,b and c components of 4T_1 respectively, and the (${}^4A_2 \times {}^4T_2$) states are labelled η , ζ and ξ corresponding to a^4T_2 , b^4T_2 and c^4T_2 respectively. The symmetry properties of the unprimed α , β , γ and η , ζ , ξ are shown in Appendix VI.

For easy reference, the labels used to distinguish the states in the various manifolds are collected together in the following table:

| Manifold | Pair State Label |
|------------------------------|-------------------------------|
| (${}^4A_2 \times {}^2T_1$) | U, V, W |
| (${}^4A_2 \times {}^2T_2$) | P, Q, R |
| (${}^4A_2 \times {}^2E$) | G, H |
| (${}^4A_2 \times {}^4T_1$) | α , β , γ |
| (${}^4A_2 \times {}^4T_2$) | η , ζ , ξ |

Table 2.4: Pair State Labels

2.10 THE PERTURBATION THEORY

In order to discuss the many-electron Hamiltonian H which is to contain all the usual terms, kinetic energy of the electrons, electron-nucleus interactions, Coulomb repulsion between electrons, spin-orbit interactions and so on, perturbation theory will be used. Since the full Hamiltonian is invariant under all interchanges of electrons and under the space group operations, the unperturbed Hamiltonian H_0 having the same properties must be invariant under all interchanges of electrons and must also possess D_{3h} symmetry.

A set of orthogonal functions has been found and defined so that they correspond to the expected states of a Cr^{3+} pair of D_{3h} symmetry. H_0 will be defined shortly so that it has these functions as its

eigenfunctions. It is unlikely that these functions will also be eigenfunctions of the actual Hamiltonian H since they have not resulted from a detailed study of the Hamiltonian, but it is likely they will not be very different from the eigenfunctions of H , therefore $H-H_0$ can be treated as the perturbation.

For each many-electron state a projection operator is defined. Denoting a typical state by $|m\rangle$, its projection operator $P_m = |m\rangle\langle m|$. The operator

$$\sum_m \lambda_m P_m$$

has each state $|m\rangle$ as an eigenstate with eigenvalue λ_m . The parameters λ_m are now chosen to be the mean values of the actual Hamiltonian taken over the family of states to which that particular state belongs. For example, all the basis states of the $(^4A_2 \times ^2T_1)$ manifold would be given the same λ_m .

The unperturbed Hamiltonian is defined as

$$H_0 = \sum_M \bar{\epsilon}_M P_M$$

where P_M is the projection operator for all the states in a particular manifold (the M th manifold) and $\bar{\epsilon}_M$ is the mean value of H for this manifold. The P_M are invariant under all electron interchanges and transform amongst themselves under all the symmetry operations of D_{3h} , thus H_0 has the properties required of it, properties identical to those of H .

If one considers the $(^4A_2 \times ^2T_1)$ family, it will contain a number of closely spaced energy levels about some energy E . If a state U' (or V' , W' etc) is a good approximation to an eigenstate of H then the expectation value of H for that state should also be close to E . Therefore, the unperturbed Hamiltonian is chosen to have these

approximate states as its eigenfunctions which are arranged to be degenerate at an energy close to E , by taking the average of all the expectation values of H for that family of states.

The unperturbed Hamiltonian has a whole series of degenerate well-spaced levels. There is an elegant formulation of perturbation theory for such a system, an expansion to infinite order which gives an effective Hamiltonian H_{eff} , which can be used to obtain the energy level pattern into which any particular degenerate family splits under the perturbation $H-H_0$ [39]. The theory yields the expansion, up to second order:-

$$H_{\text{eff}} = P_M \left[H - \sum_{M' \neq M} \frac{H P_M' H}{\bar{\epsilon}_M' - \bar{\epsilon}_M} + \dots \right] P_M$$

$$H_{\text{eff}} = P_M H P_M - \sum_{M' \neq M} \frac{P_M H P_M' H P_M}{\bar{\epsilon}_M' - \bar{\epsilon}_M} + \dots$$

for the M th manifold. Inspection of H_{eff} shows that it operates wholly within the subspace defined by the basis states of the M th manifold. In the second order term it is seen that the operator H connects states of the M and M' th families; M will be chosen to correspond to the members of the $({}^4A_2 \times {}^2T_1)$ manifold, M' will then represent some other excited manifold. It was for this reason that the basis states other than those belonging to the $({}^4A_2 \times {}^2T_1)$ were constructed, although there will be instances when M will be chosen to represent manifolds other than the $({}^4A_2 \times {}^2T_1)$.

When we come to evaluate the matrix elements of H_{eff} within the $({}^4A_2 \times {}^2T_1)$ the basis states are U' , V' , W' etc and the manifold corresponds to a 48-fold degenerate level. So H_{eff} will have 48 eigenvalues which are to give the levels into which the 48-fold degeneracy of $({}^4A_2 \times {}^2T_1)$ is split by the perturbation $H-H_0$.

CHAPTER THREE

SELECTION RULES AND EXPERIMENTAL RESULTS

3.1 PREAMBLE

In later chapters we are to evaluate the matrix elements of H_{eff} within the basis of the (${}^4A_2 \times {}^2T_1$) manifold and at the same time compare the theoretical predictions with the observed spectra. It is therefore convenient to present at this stage the experimental results together with the selection rules used in the identification of the spectral lines.

The bands in the optical absorption spectra of transition metal complexes arise almost without exception from the so called electric dipole transitions between the ground and excited terms. Other sorts of transitions e.g. magnetic quadrupole transitions, have in general an intensity far too low to be observable in the absorption spectrum. The intensity with which an electric dipole transition between two states $|\psi_N\rangle$ and $|\psi_M\rangle$ can take place is essentially determined by the transition moment P :

$$P = \langle \psi_N | D | \psi_M \rangle,$$

where D is the dipole vector which has the same symmetry behaviour as the position vector. (In fact the line intensity is given by $|P|^2$).

Since D is an operator in coordinate space it has no effect on the spin coordinates of the wavevectors involved so that in the absence of spin-orbit coupling we may write for P :

$$P = \langle \psi_N^S | \psi_M^S \rangle \langle \psi_N^O | D | \psi_M^O \rangle$$

where the superscript s refers to the spin parts and the superscript o refers to the space parts of the electronic statefunctions. As a consequence of the orthogonality of the spin functions the integral over spin functions can be non-zero only if the spin quantum number S for the original and final states are equal. That is, for vanishing spin-orbit coupling electric dipole transitions occur only between states of the same multiplicity. This fact is readily observed in the optical spectra shown in Fig 1.3 when one sees the intensity of the spin forbidden bands e.g. ${}^4A_2 \rightarrow {}^2T_1$ much less than the intensity of the normal chromium bands (${}^4A_2 \rightarrow {}^4T_1$ and 4T_2). Needless to say, the spin forbidden bands are observed in actuality because the spin-orbit interaction couples states whose total spins differ by 0 or ± 1 .

We have yet to consider the orbital components of the electronic wavefunctions $|\psi_N\rangle$ and $|\psi_M\rangle$. In order that a transition can occur between them then

$$\langle \psi_N^o | D | \psi_M^o \rangle \neq 0.$$

This integral can only have non-zero values when the integrand or portions of the integrand are invariant with respect to all operations of the symmetry group of D. In the present context one is working with a system of D_{3h} symmetry so one needs to establish the representation of D in this symmetry group. In practice absorption experiments are carried out with polarised light and it is possible to align the E-vector of the light either parallel or perpendicular to the C-axis of the crystal. In the first of these cases, known as π -polarisation, D is parallel to the C-axis and takes the form $\sum_i (z)_i$ which transforms according to the A_2'' irreducible representation of D_{3h} . In the second case when the E-vector is perpendicular to the C-axis, one has σ -polarisation and in D_{3h} symmetry D transforms according to the E'

representation.

If Γ_N and Γ_M are the irreducible representations of the wave-functions $|\psi_N\rangle$ and $|\psi_M\rangle$ in D_{3h} then the condition that the transition moment P be non-zero is that the product representation

$$\Gamma_N^* \times A_2'' \times \Gamma_M \supset A_1'$$

for π -polarisation and

$$\Gamma_N^* \times E' \times \Gamma_M \supset A_1'$$

for σ -polarisation, i.e. the product representation contains the identity representation A_1' of D_{3h} . (The superscript * denotes the complex conjugate.

Using the multiplication table for the D_{3h} group (Appendix I (iv)) it is a simple matter to write down the allowed electric dipole transitions and the polarisation of the light for each particular transition. The results are shown in the Table 3.1:

| | A_1' | A_2' | A_1'' | A_2'' | E' | E'' |
|---------|----------|----------|----------|----------|----------|----------|
| A_1' | - | - | - | π | σ | - |
| A_2' | - | - | π | - | σ | - |
| A_1'' | - | π | - | - | - | σ |
| A_2'' | π | - | - | - | - | σ |
| E' | σ | σ | - | - | σ | π |
| E'' | - | - | σ | σ | π | σ |

Table 3.1: Allowed Electric Dipole Transitions and their Polarisations (D_{3h}).

To use the table the representations Γ_N and Γ_M of D_{3h} have to be specified.

In the previous work on pairs two types of electric dipole mechanism have been introduced. The first of these is the single-ion electric dipole transition, so called because only one ion of the pair undergoes any transition. The single-ion mechanism has been ascribed to a double perturbation process in which the constrictions of the parity forbidden and spin forbidden transitions are both lifted. (The La Porte Rule forbidding d-d transitions would not be expected to hold in our treatment of the pair interactions since we do not expect electrons to be in pure d-orbitals). The second transition mechanism has been called exchange-induced and is represented by the transition moment:

$$P_{ex} = \sum_{i>j} P_{ij} (\underline{s}_{ai} \cdot \underline{s}_{bj})$$

[40] where P_{ij} contains the electric dipole moment between the ground state and some excited state.

The expressions single-ion and exchange-induced have no direct counterparts in the Stevens approach to the problem since here the pair is taken to be a unit but it is possible to show how the transitions should be viewed in the context of the present theory. We have said that the transition moment P has the form $\langle \psi_N | D | \psi_M \rangle$ and implicitly assumed was that $|\psi_N\rangle$ and $|\psi_M\rangle$ are eigenstates of H . But the effective Hamiltonian given in section 2.10 is used to obtain the eigenvalues of a certain group of states and not their eigenstates. This is not a problem though, since the same theory shows that instead of evaluating the matrix elements of D between the actual eigenstates, the matrix elements of a related operator \tilde{D} , can be taken between the eigenstates of the respective effective Hamiltonians. \tilde{D} is given by

$$\tilde{D} = P_N \left(1 + \sum_n' \frac{V P_n}{E_N - E_n} + \dots \right) D \left(1 + \sum_m' \frac{P_m V}{E_M - E_m} + \dots \right) P_M$$

where $P_N(P_M)$ is the project on operator for the family to which $|\psi_N\rangle$ ($|\psi_M\rangle$) belongs, $E_N(E_M)$ is the energy of the Nth(Mth) manifold and the primes on the summations mean that any terms with vanishing denominators are to be omitted [31]. As with H_{eff} , \tilde{D} can be decomposed into spin-independent and spin-dependent terms. The two-electron terms in \tilde{D} which are not specified at this stage can be divided into intraionic and interionic processes; it is the former that correspond to the single-ion electric dipole transition and the latter to the exchange-induced transitions.

The first term in \tilde{D} is $P_N D P_M$ so that

$$\langle \psi_N | \tilde{D} | \psi_M \rangle = \langle \psi_N | D | \psi_M \rangle$$

which is almost the transition moment we have been considering, the difference being that $|\psi_N\rangle$ and $|\psi_M\rangle$ are now the eigenstates of H_0 . If $|\psi_M\rangle$ are the excited states corresponding to the U' , V' , W' etc basis states of $({}^4A_2 \times {}^2T_1)$ manifold, $|\psi_N\rangle$ correspond to the ground pair states. In order to see if the product representation $\Gamma_N^* \times \Gamma_D \times \Gamma_M$ contains A'_1 it is necessary to construct the ground pair states and to deduce the irreducible representations of D_{3h} of each state. We shall not attempt to evaluate the matrix elements of further terms of \tilde{D} at the present because in order to do so it would be necessary to evaluate the matrix elements of V (spin-dependent and spin-independent operators) between the pair states. Such matrix elements will be calculated in the following two chapters.

3.2 BASIS STATES OF THE GROUND MANIFOLD (${}^4A_2 \times {}^4A_2$)

The many-electron basis states of one ion of the pair being in the 4A_2 ground state have already been calculated, Section 2.3. The pair states of the ground manifold will be defined in an exactly similar manner to those of the (${}^4A_2 \times {}^2T_1$) manifold, Section 2.5, although the ground states are of simpler form. For instance, there are no orbital components to be distinguished and neither is there any extra degeneracy due to σ_h . Therefore the ground term consists of 16 states which have spins $S_g = 0, 1, 2, 3$. The state which has $S_g = 3$ and $M_S = 3$ is written:

$$|3, 3\rangle = |{}^4A_2, {}^3: {}^4A_2, {}^3\rangle \equiv |{}^3: {}^3\rangle$$

and those of lower M_S are found by the use of S_- . The states of the (${}^4A_2 \times {}^4A_2$) manifold are:

$$|3, 3\rangle = |{}^3: {}^3\rangle$$

$$|3, 2\rangle = \sqrt{\frac{1}{2}} [|{}^{\frac{1}{2}}: {}^3\rangle + |{}^3: {}^{\frac{1}{2}}\rangle]$$

$$|3, 1\rangle = (1/\sqrt{5}) [|{}^{-\frac{1}{2}}: {}^3\rangle + \sqrt{3} |{}^{\frac{1}{2}}: {}^{\frac{1}{2}}\rangle + |{}^3: {}^{-\frac{1}{2}}\rangle]$$

$$|3, 0\rangle = \frac{1}{2}(1/\sqrt{5}) [|{}^{-\frac{3}{2}}: {}^3\rangle + 3 |{}^{-\frac{1}{2}}: {}^{\frac{1}{2}}\rangle + 3 |{}^{\frac{1}{2}}: {}^{-\frac{1}{2}}\rangle + |{}^3: {}^{-\frac{3}{2}}\rangle]$$

$$|3, -1\rangle = (1/\sqrt{5}) [|{}^{-\frac{3}{2}}: {}^{\frac{1}{2}}\rangle + \sqrt{3} |{}^{-\frac{1}{2}}: {}^{-\frac{1}{2}}\rangle + |{}^{\frac{1}{2}}: {}^{-\frac{3}{2}}\rangle]$$

$$|3, -2\rangle = \sqrt{\frac{1}{2}} [|{}^{-\frac{3}{2}}: {}^{-\frac{1}{2}}\rangle + |{}^{-\frac{1}{2}}: {}^{-\frac{3}{2}}\rangle]$$

$$|3, -3\rangle = |{}^{-\frac{3}{2}}: {}^{-\frac{3}{2}}\rangle$$

$$|2, 2\rangle = \sqrt{\frac{1}{2}} [|{}^{\frac{1}{2}}: {}^3\rangle - |{}^3: {}^{\frac{1}{2}}\rangle]$$

$$|2, 1\rangle = \sqrt{\frac{1}{2}} [|{}^{-\frac{1}{2}}: {}^3\rangle - |{}^3: {}^{-\frac{1}{2}}\rangle]$$

$$|2, 0\rangle = \frac{1}{2} [|{}^{-\frac{3}{2}}: {}^3\rangle + |{}^{-\frac{1}{2}}: {}^{\frac{1}{2}}\rangle - |{}^{\frac{1}{2}}: {}^{-\frac{1}{2}}\rangle - |{}^3: {}^{-\frac{3}{2}}\rangle]$$

$$|2, -1\rangle = \sqrt{\frac{1}{2}} [|{}^{-\frac{3}{2}}: {}^{\frac{1}{2}}\rangle - |{}^{\frac{1}{2}}: {}^{-\frac{3}{2}}\rangle]$$

$$|2, -2\rangle = \sqrt{\frac{1}{2}} [|{}^{-\frac{3}{2}}: {}^{-\frac{1}{2}}\rangle - |{}^{-\frac{1}{2}}: {}^{-\frac{3}{2}}\rangle]$$

$$|1, 1\rangle = (1/\sqrt{10}) [\sqrt{3} |{}^{-\frac{1}{2}}: {}^3\rangle - 2 |{}^{\frac{1}{2}}: {}^{\frac{1}{2}}\rangle + \sqrt{3} |{}^3: {}^{-\frac{1}{2}}\rangle]$$

$$|1, 0\rangle = \frac{1}{2}(1/\sqrt{5}) [3 |{}^{-\frac{3}{2}}: {}^3\rangle - |{}^{-\frac{1}{2}}: {}^{\frac{1}{2}}\rangle - |{}^{\frac{1}{2}}: {}^{-\frac{1}{2}}\rangle + 3 |{}^3: {}^{-\frac{3}{2}}\rangle]$$

$$|1, -1\rangle = (1/\sqrt{10}) [\sqrt{3} |-\frac{3}{2}, \frac{1}{2}\rangle - 2 |-\frac{1}{2}, -\frac{1}{2}\rangle + \sqrt{3} |\frac{1}{2}, -\frac{3}{2}\rangle]$$

$$|0, 0\rangle = \frac{1}{2} [|-\frac{3}{2}, \frac{3}{2}\rangle - |-\frac{1}{2}, \frac{1}{2}\rangle + |\frac{1}{2}, -\frac{1}{2}\rangle - |\frac{3}{2}, -\frac{3}{2}\rangle]$$

The transformation properties of these unprimed pair states are shown in Appendix V(iv).

The D_{3h} symmetry adapted basis states of the (${}^4A_2 \times {}^4A_2$) manifold are shown in Table 3.2:

| Orbital Parent | $\sigma_h = +1$ | $\sigma_h = -1$ |
|----------------|---|---|
| ${}^7A_2''$ | $ 3, 3\rangle, 3, -3\rangle \quad A_1' + A_2'$ $ 3, 1\rangle, 3, -1\rangle \quad E'$ | $ 3, 2\rangle, 3, -2\rangle \quad E''$ $ 3, 0\rangle \quad A_1''$ |
| ${}^5A_1'$ | $ 2, 2\rangle, 2, -2\rangle \quad E'$ $ 2, 0\rangle \quad A_1'$ | $ 2, 1\rangle, 2, -1\rangle \quad E''$ |
| ${}^3A_2''$ | $ 1, 1\rangle, 1, -1\rangle \quad E'$ | $ 1, 0\rangle \quad A_1''$ |
| ${}^1A_1'$ | $ 0, 0\rangle \quad A_1'$ | |

Table 3.2: Irreducible Representations of D_{3h} formed by (${}^4A_2 \times {}^4A_2$) Basis States

Having found the irreducible representations of D_{3h} formed by the (${}^4A_2 \times {}^4A_2$) basis states it is possible to say which electric dipole transitions are allowed between states of the ground manifold and states of some excited manifold. To do this we shall make use of Table 3.1.

At low enough temperatures only the $S_g = 0$ state of the (${}^4A_2 \times {}^4A_2$) ground manifold is appreciably populated. We are interested in identifying the lines of the (${}^4A_2 \times {}^2T_1$) spectral region so we can say by spin selection rules that there will only be transitions to the $S = 1$ levels. Now from Table 3.2 the $S_g = 0$ state transforms according to the

A_1' irreducible representation of D_{3h} . From Table 3.1 one sees that π -polarised light can induce transitions only to states transforming according to A_2'' , while in σ -polarisation states transforming as E' are accessible from the ground state. The irreducible representations of the (${}^4A_2 \times {}^2T_1$) basis states are given in Table 2.3, examination of this shows that only four levels are accessible from $S_g = 0$. One level in the π -polarisation [$|V'', 1, 1\rangle - |W'', 1, -1\rangle$] $A_2''({}^3E')$ and three in σ -polarisation ($|V', 1, 0\rangle, |W', 1, 0\rangle$) $E'({}^3E')$, ($|V', 1, -1\rangle, |W', 1, 1\rangle$) $E'({}^3E'')$ and ($|U', 1, 1\rangle, |U', 1, -1\rangle$) $E'({}^3A_2'')$, where the symbols in paranthesis indicate the orbital parent in each case. As the crystal temperature is raised additional lines are observed due to thermal population of higher spin states of the ground manifold and consequent transitions from them to both the $S = 1$ and $S = 2$ states of (${}^4A_2 \times {}^2T_1$). It is also remembered that spin-orbit coupling allows transitions only between states for which $\Delta M_S = 0, \pm 1$.

It is yet possible to find a more accurate set of selection rules. Experimentally it is usual to apply a magnetic field to the sample, thus lowering the symmetry and to observe the removal of the degeneracy of some of the levels (Zeeman effect). The set of selection rules in the new lower symmetry may differ from the set in the higher symmetry, with perhaps fewer allowed transitions. Since a lowering of symmetry cannot remove a transition the predicted allowed transitions in the lower symmetry must be more accurate.

3.3 SAMPLE IN A MAGNETIC FIELD

The application of a magnetic field parallel to the z-axis of the pair, i.e. along the crystal C-axis, lowers the symmetry from D_{3h} to C_{3h} [41]. The C_{3h} group differs from the D_{3h} group in that σ_v is no longer a symmetry element, and C_3 and C_3^2 become distinct symmetry elements; the character table for C_{3h} is shown in Appendix I(iii). In the descent in symmetry from D_{3h} to C_{3h} the many-electron terms are reduced according to the following:

$$\left. \begin{matrix} A'_1 \\ A'_2 \end{matrix} \right\} \rightarrow A' \quad \left. \begin{matrix} A''_1 \\ A''_2 \end{matrix} \right\} \rightarrow A'' \quad E' \rightarrow E'_+ + E'_- \quad E'' \rightarrow E''_+ + E''_-$$

By similar arguments the symmetry of the electric dipole vector is found in C_{3h} . For π -polarisation the electric dipole vector transforms according to A'' , while for σ -polarisation it transforms as $E'_+ + E'_-$. (thus in σ -polarisation two directions of polarisation can be distinguished, mutually at right angles to the Z-axis, they are labelled + and -). The product representations for the C_{3h} group can be found in Appendix I. By evaluating the product representations $\Gamma_N^* \times \Gamma_D \times \Gamma_M$, the allowed electric dipole transitions and their polarisations in C_{3h} can be found. The results are shown in Table 3.3:

| | A' | A'' | E'_- | E'_+ | E''_- | E''_+ |
|---------|------------|------------|------------|------------|------------|------------|
| A' | - | π | σ_+ | σ_- | - | - |
| A'' | π | - | - | - | σ_+ | σ_- |
| E'_- | σ_- | - | - | σ_+ | π | - |
| E'_+ | σ_+ | - | σ_- | - | - | π |
| E''_- | - | σ_- | π | - | - | σ_+ |
| E''_+ | - | σ_+ | - | π | σ_- | - |

Table 3.3: Allowed Electric Dipole Transitions and Polarisation
(C_{3h})

The next step is to evaluate the irreducible representations of the C_{3h} group formed by the basis states of both the ground manifold and the excited (${}^4A_2 \times {}^2T_1$) manifold. There are only one dimensional representations of C_{3h} so that in moving from D_{3h} each of the two dimensional representations are reduced (i.e. $E' \rightarrow E'_+ + E'_-$ and $E'' \rightarrow E''_+ + E''_-$). To determine which member of a doublet transforms as E_+ and which as E_- it is a matter of operating on each with the operator C_3 . For instance consider the pair of states $|U', 1, \pm 1\rangle$ transforming as E' under D_{3h} : $C_3|U', 1, 1\rangle = \omega^2|U', 1, 1\rangle$ and $C_3|U', 1, -1\rangle = \omega|U', 1, -1\rangle$ (Appendix V(i)) so that $|U', 1, 1\rangle$ transforms as E'_+ and $|U', 1, -1\rangle$ transforms as E'_- under C_{3h} .

One can see now why the selection rules obtained in the presence of the perturbing magnetic field are more accurate. To consider a specific example, Table 3.1 shows that in σ -polarisation from a ground state transforming according to the E' representation of D_{3h} transitions are allowed to all those states of (${}^4A_2 \times {}^2T_1$) also transforming as E' . From the $S_g = 1$ ground states $|1, \pm 1\rangle E'({}^3A_2'')$ we should expect to see (Table 2.3) transitions to the following ($|V', 1, -1\rangle, |W', 1, 1\rangle$) $E'({}^3E'')$, ($|V', 1, 0\rangle, |W', 1, 0\rangle$) $E'({}^3E')$ and ($|U', 1, \pm 1\rangle$) $E'({}^3A_2')$ of the $S = 1$ levels of (${}^4A_2 \times {}^2T_1$). However in C_{3h} symmetry one finds that of the symmetry allowed transitions are $|1, 1\rangle \rightarrow |U', 1, -1\rangle$ and $|1, -1\rangle \rightarrow |U', 1, 1\rangle$, which are both disqualified by the spin selection rules $\Delta M_S = 0, \pm 1$. There are many such examples to be found, of transitions forbidden in C_{3h} but allowed in D_{3h} .

When the magnetic field is applied perpendicularly to the z-axis the symmetry of the pair is reduced to C_2 or C_s depending on whether it is applied along the x-axis or the y-axis. For these cases no additional information can be found concerning the selection rules.

The complete set of possible transitions between the ground states

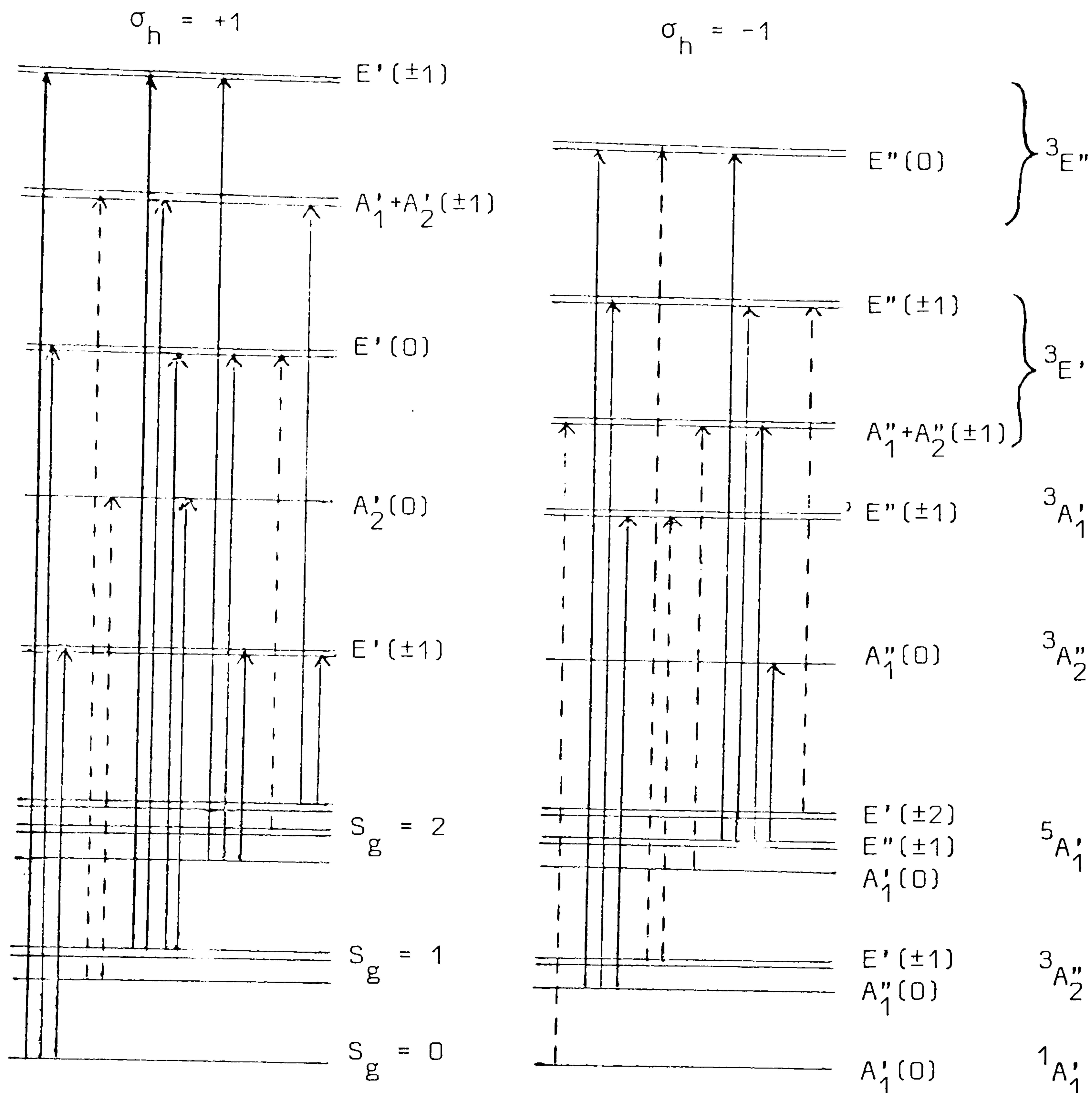


Fig 3.1: Energy level scheme to fit spectrum of transitions from $({}^4A_2 \times {}^4A_2)$ to the $S = 1$ levels of $({}^4A_2 \times {}^2T_1)$. [Full lines σ -polarisation, broken lines π -polarisation].

and the $({}^4A_2 \times {}^2T_1)$ excited states is shown schematically in Figs 3.1 and 3.2. Fig 3.1 is appropriate for transitions from the $S_g = 0, 1, 2$ states of the ground manifold to the $S = 1$ states of $({}^4A_2 \times {}^2T_1)$. Spin selection rules forbid transitions from the $S_g = 3$ level to the $S = 1$ states of $({}^4A_2 \times {}^2T_1)$. Allowed transitions to the $S = 2$ states of $({}^4A_2 \times {}^2T_1)$ are shown in Fig 3.2. The upper part of each energy level diagram is divided into two families depending on the transformation properties of the states under the reflection operator σ_h of the symmetry group D_{3h} . Each state is labelled by its irreducible representation and M_S value, and each set of

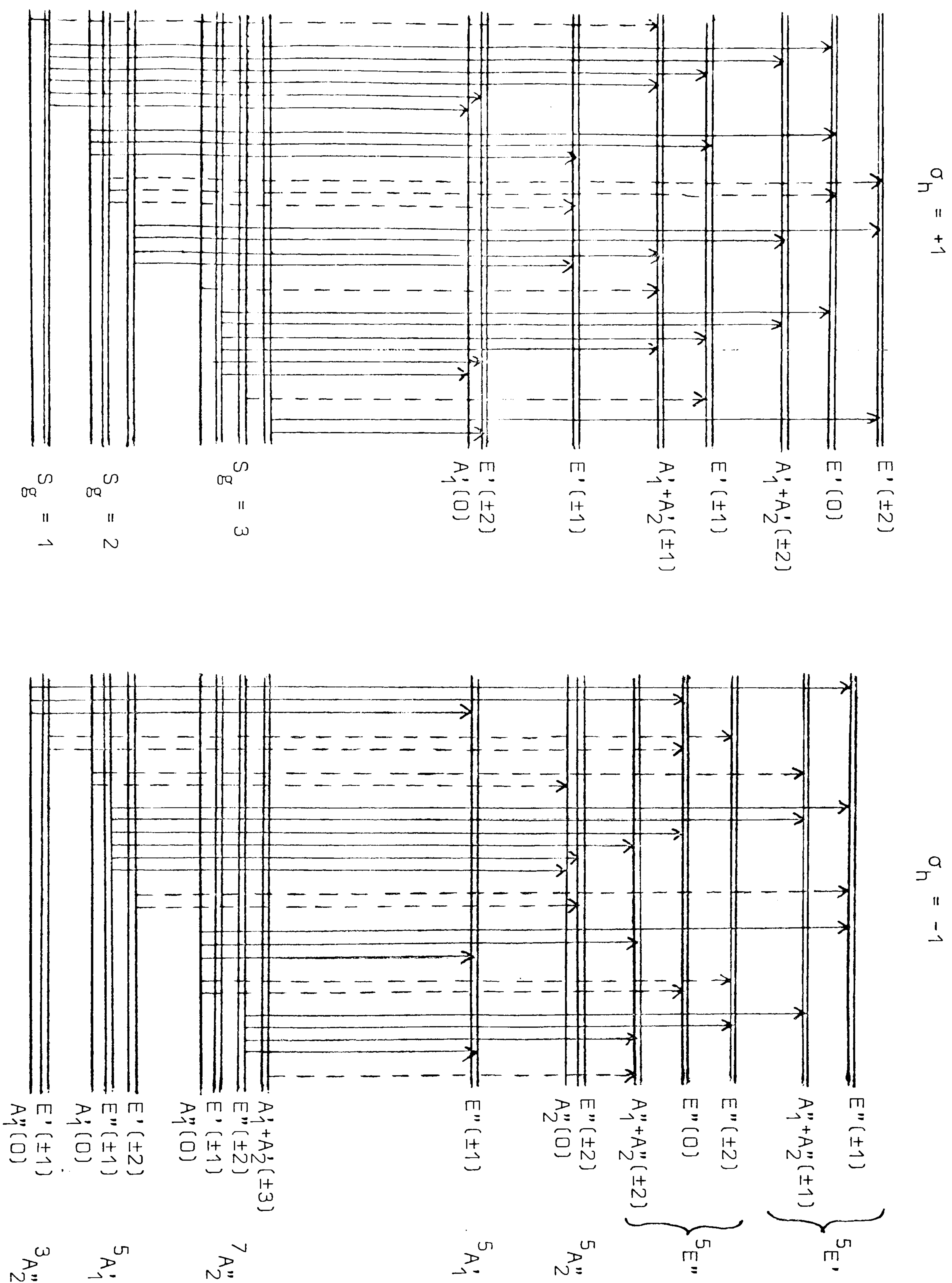


Fig 3.2: Allowed transitions from (${}^4A_2 \times {}^4A_2$) to the $S = 2$ levels of (${}^4A_2 \times {}^2T_1$). [Full lines σ -polarisation, broken lines π -polarisation].

states belonging to the same orbital parent is so labelled. The vertical lines show allowed transitions in π (dashed lines) and σ (full lines) polarisations.

3.4 EXPERIMENTAL RESULTS

The experimentally observed optical absorption spectra for many different binuclear materials are shown in Fig 1.3. Each spectrum contains two broad bands of high intensity and half-width $\sim 3000 \text{ cm}^{-1}$ and three groups of sharp lines of half-width $\sim 300 \text{ cm}^{-1}$. The low intensity of the sharp bands is understandable because the transitions are both parity forbidden and spin forbidden. Spin-orbit coupling is responsible for the appearance of such bands as was pointed out in Section 3.1. The question of the half-width of the absorption bands also deserves some discussion.

As explanation of the simultaneous appearance of broad indistinct bands and sharp bands or lines was first given by Tanabe and Sugano [38]. In the term diagram Fig 1.2, the slope of the Curve, giving the term energy as a function of the field strength is determined by the number of electrons in the electronic states t_{2g} and e_g . For an electronic transition between states of different slope, i.e. of different electronic configuration, the equilibrium distance metal ion-ligand is changed. One then observes a broad absorption band. The greater the difference between the slopes of the two states between which the transition takes place is, the greater the half-width of the band should be. Thus the transitions ${}^4A_2(t_{2g}^3) \rightarrow {}^4T_1$, ${}^4T_2(t_{2g}^2 e_g)$ lead to the broad bands of half-width $\sim 3000 \text{ cm}^{-1}$, while transitions such as ${}^4A_2 \rightarrow {}^2T_1$ both of the same configuration contain sharp distinct features.

In order to identify the sharp lines in the $({}^4A_2 \times {}^2T_1)$ region of the spectrum various investigative techniques are employed. High resolution

optical absorption experiments are carried out in the temperature range 1.3K to 70K for both π - and σ -polarisations. Also polarised high field Zeeman spectra are obtained for applied magnetic fields of up to 13T. For details of such experiments the reader is referred to the paper of Johnstone et al [30] and to the work of Dean [33]. These works together with [27] also contain the experimental results which will shortly be presented.

Firstly we need to give values to $\bar{\epsilon}_M$ of the unperturbed Hamiltonian defined in Section 2.10. Since $\bar{\epsilon}_M$ is the mean value of the actual Hamiltonian for the Mth manifold it must correspond to the energy of the centre of each absorption band in the spectra shown in Fig 1.3.

Next the results of the detailed analyses of the (${}^4A_2 \times {}^2T_1$) region of the spectra will be presented. It is found that the spectral features associated with the $S = 2$ levels of (${}^4A_2 \times {}^2T_1$) are generally broader and weaker than those of the $S = 1$ levels. To obtain transitions to the higher spin levels the temperature is increased in order to populate the higher energy states of the ground manifold. Individual transitions are not well resolved and some of the spectral features are attributed not to a single transition but to several transitions in a small energy range.

Finally the energies of the spin states in the (${}^4A_2 \times {}^4A_2$) ground manifold will be given, the $S_g = 0$ state being the zero of energy.

In comparison of theory and experiment the results that will be used are collected in the following tables:

| | $\text{Cs}_3\text{Cr}_2\text{Br}_9$ [33] | $\text{Rb}_3\text{Cr}_2\text{Br}_9$ [33] | $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ [27] |
|---------|--|--|--|
| 4T_2 | 12250 | 12900 | 13130 |
| 2E | 13900 | 13900 | 14090 |
| 2T_1 | 14400 | 14500 | 14680 |
| 4T_1 | 16650 | 17450 | 18090 |
| 2T_2 | 19000 | 19100 | 19300 |

Table 3.4: Average energy in cm^{-1} of the Absorption Bands for various Binuclear Materials. (The energy of 4T_1 and 4T_2 are $\pm 100 \text{ cm}^{-1}$, the rest are each $\pm 50 \text{ cm}^{-1}$).

| | $\text{Cs}_3\text{Cr}_2\text{Br}_9$ [33] | $\text{Rb}_3\text{Cr}_2\text{Br}_9$ [33] | $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ [30] |
|--|--|--|--|
| $^3A'_1$ | 409 | 439 | 554 |
| $^3A''_2$ | 374 | 398 | 514 |
| $^5A''_2$ | 342 | 343 | 448 |
| $^5A'_1$ | 204 | 193 | 327 |
| $^3E'' \left\{ \begin{array}{l} A'_1 + A'_2 (\pm 1) \\ E'' (0) \\ E' (\pm 1) \end{array} \right.$ | 456 458 447 | 462 469 471 | 600 600 609 |
| $^3E' \left\{ \begin{array}{l} A''_1 + A''_2 (\pm 1) \\ E' (0) \\ E'' (\pm 1) \end{array} \right.$ | 402 - - | 445 - - | 579 586 586 |
| $^5E''$ | 416 | - | - |
| $^5E'$ | 538 | 569 | - |

Table 3.5: Energy of the $(^4A_2x^2T_1)$ levels in cm^{-1} , normalised to 14000 cm^{-1} . (typical error $\pm 1 \text{ cm}^{-1}$). For the $S = 2$ orbital doublets no accurate values can be given.

| | $\text{Cs}_3\text{Cr}_2\text{Br}_9$ [33] | $\text{Rb}_3\text{Cr}_2\text{Br}_9$ [33] | $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ [30] |
|-----------|--|--|--|
| $S_g = 1$ | 6 | 12 | 12 |
| $S_g = 2$ | 18 | 34 | 38 |
| $S_g = 3$ | 31 | 65 | 77 |
| J | -4.9 ± 0.3 | -10.5 ± 0.5 | -13.5 |
| j | -0.21 ± 0.06 | -0.19 ± 0.08 | + 0.25 |

Table 3.6: Energy of the ($^4A_2 \times ^4A_2$) levels in cm^{-1} together with the estimated exchange parameters J and j (biquadratic exchange parameter).

CHAPTER FOUR

SPIN INDEPENDENT TERMS IN THE HAMILTONIAN

4.1 MATRIX ELEMENTS BETWEEN DETERMINANTAL FUNCTIONS

The following sections will be devoted to the evaluation, in some detail, of the matrix elements of H_{eff} between the basis states of the $(^4A_2 \times ^2T_1)$ manifold, i.e. U' , V' , W' , etc states. It is worth reviewing briefly here the method of evaluating matrix elements between determinantal functions as these will be used extensively throughout. The details of such methods can be found in many publications, e.g. [35,36,37].

The matrix elements that are to be evaluated have the form $\langle \Delta_k | H | \Delta_l \rangle$ where Δ_k and Δ_l are Slater determinants. The Hamiltonian H can be broken down into a summation of one-electron operators f and two-electron operators g (ignoring higher order electron operators). Thus:

$$H = \sum_i f_i + \sum_{i>j} g_{ij}$$

The calculation begins with a comparison of the spin-orbitals contained in Δ_k and Δ_l . The spin-orbitals within Δ_l are then permuted until their ordering is as coincident as possible with the ordering of the spin-orbitals in Δ_k , with each interchange of spin-orbitals changing the sign of Δ_l . There are then four cases to be differentiated:-

(i) When Δ_k and Δ_l differ in no spin-orbitals

$$\langle \Delta_k | H | \Delta_l \rangle = \sum_i \langle i | f | i \rangle + \sum_{i>j} [\langle ij | g | ij \rangle - \langle ij | g | ji \rangle]$$

(ii) When Δ_k and Δ_l differ in one spin-orbital

$$\langle \Delta_k | H | \Delta_l \rangle = \langle i | f | i' \rangle + \sum_{j \neq i} [\langle ij | g | i'j \rangle - \langle ij | g | ji' \rangle]$$

(iii) When Δ_k and Δ_l differ in two spin-orbitals

$$\langle \Delta_k | H | \Delta_l \rangle = \langle ij | g | i'j' \rangle - \langle ij | g | j'i' \rangle$$

(iv) When Δ_k and Δ_l differ in more than two spin-orbitals

$$\langle \Delta_k | H | \Delta_l \rangle = 0$$

Thus the matrix elements are reduced to integrals over spin-orbitals. An integral of the type $\langle ij | g | rs \rangle$ will vanish if the spin parts of orbitals i and r differ or if the spin parts of j and s differ. The spatial parts of the orbitals are assumed to be orthonormal.

If spin-orbit interaction and magnetic terms are disregarded the one-electron terms correspond to the electronic kinetic and Coulomb energies in the field of the nucleus. The two-electron operator may then be put into correspondence with the Coulomb interactions between electrons, viz

$$f_i = -Ze^2/r_i + eV(r_i)$$

$$g_{ij} = e^2/r_{ij}$$

In the case of an ion having electrons in well defined orbitals and f and g having the above form, it would be possible to evaluate the matrix elements specifically in terms of Slater F and G integrals. This is not possible when we use the states defined by the orbitals $|A\rangle$, $|B\rangle$, $|C\rangle$, etc since their actual form is not defined (it is only on the grounds of symmetry that they are compared with d-orbitals). It is possible to obtain an estimated value of the F and G integrals though, since we were able to find an approximate value for the Racah parameters in Section 1.3.

4.2 ONE-ELECTRON OPERATORS IN H_{eff}

If we consider only the one-electron terms f of the Hamiltonian H , representing the electron kinetic and Coulomb energies in the nuclear field, the effective Hamiltonian H_{eff} (Section 2.10) has the following form:

$$H_{\text{eff}} = P_M f P_M.$$

To evaluate the matrix elements of H_{eff} we shall use specifically the basis vectors $|U', 2, 2\rangle$ and $|U'', 2, 2\rangle$. Now each of these functions is composed of two parts $|U, 2, 2\rangle$ and $\sigma_h |U, 2, 2\rangle$. By inspection the two parts cannot be connected by one-electron operators, so it follows that the one-electron contributions to $|U', 2, 2\rangle$ are identical to the one-electron contributions to $|U'', 2, 2\rangle$. Specifically

$$\begin{aligned} \langle U', 2, 2 | H_{\text{eff}} | U', 2, 2 \rangle &= \langle U'', 2, 2 | H_{\text{eff}} | U'', 2, 2 \rangle \\ &= \frac{1}{2} [\langle U, 2, 2 | f | U, 2, 2 \rangle + \langle U, 2, 2 | \sigma_h f \sigma_h | U, 2, 2 \rangle] \end{aligned}$$

In Section 2.5 both $|U, 2, 2\rangle$ and $\sigma_h |U, 2, 2\rangle$ were found, they are in terms of Slater determinants:-

$$\begin{aligned} |U, 2, 2\rangle &= (1/\sqrt{6}) [(A\bar{B}C\bar{a}b\bar{c}) + (\bar{A}B\bar{C}a\bar{b}c) - 2(\bar{A}\bar{B}C\bar{a}b\bar{c})] \\ \sigma_h |U, 2, 2\rangle &= -(1/\sqrt{6}) [(A\bar{B}C\bar{a}b\bar{c}) + (\bar{A}B\bar{C}a\bar{b}c) - 2(\bar{A}\bar{B}C\bar{a}b\bar{c})] \end{aligned}$$

It is evident that $\langle U, 2, 2 | f | U, 2, 2 \rangle$ and $\langle U, 2, 2 | \sigma_h f \sigma_h | U, 2, 2 \rangle$ are identical and equal to

$$\langle A | f | A \rangle + \langle B | f | B \rangle + \langle C | f | C \rangle + \langle a | f | a \rangle + \langle b | f | b \rangle + \langle c | f | c \rangle.$$

If the corresponding expressions are derived for all the other basis states of the (${}^4A_2 \times {}^2T_1$) manifold it is found that they are all identical to that found above. This leads to the simple but significant

result if H_{eff} contained only one-electron operators there would be no splitting of the $\{^4A_2 \times ^2T_1\}$ manifold;

4.3 TWO-ELECTRON OPERATORS IN H_{eff}

We shall firstly consider the contribution to the energy of electrons in closed shells. With the two-electron operator representing the electrostatic interaction between electrons, the matrix elements of the first term in H_{eff} , $P_M g P_M$, will contain contributions of the type $\langle AF | e^2/r_{ij} | AF \rangle$, $\langle BF | e^2/r_{ij} | BF \rangle$, etc where F denotes a filled orbital. These can be regarded as describing the Coulomb energies in open shells due to the electrons in closed shells. For instance a filled orbital F has the following form

$$F = (\phi_1^+, \phi_1^-, \phi_2^+, \dots, \phi_N^+, \phi_N^-)$$

and a typical contribution to the energy of a $\{^4A_2 \times ^2T_1\}$ level would be

$$\begin{aligned} \langle \overset{+}{A}F | e^2/r_{ij} | \overset{+}{A}F \rangle &= \langle \overset{+}{A}, \phi_1^+, \phi_1^-, \dots, \phi_N^+, \phi_N^- | e^2/r_{ij} | \overset{+}{A}, \phi_1^+, \phi_1^-, \dots, \phi_N^+, \phi_N^- \rangle \\ &= \sum_{k=1}^N [2 \langle A\phi_k | e^2/r_{ij} | A\phi_k \rangle - \langle A\phi_k | e^2/r_{ij} | \phi_k A \rangle] \\ &\quad + \sum_i \langle \phi_i \phi_i | e^2/r_{ij} | \phi_i \phi_i \rangle \\ &\quad + 4 \sum_{i>j} \langle \phi_i \phi_j | e^2/r_{ij} | \phi_i \phi_j \rangle - 2 \sum_{i>j} \langle \phi_i \phi_j | e^2/r_{ij} | \phi_j \phi_i \rangle \end{aligned}$$

The contributions are then very similar to the one-electron terms and as with the one-electron terms do not produce any splittings.

The unperturbed Hamiltonian H_0 has been defined by considering the properties of a d-electron system bound in a complex but experiencing no electron interaction. We have already shown that one-electron terms in H_{eff} lead to no splitting of the degenerate levels defined by H_0 .

We now come to investigate the splittings induced in the (${}^4A_2 \times {}^2T_1$) manifold by the two-electron spin-independent operators g . The dominant two-electron term will come from the electrostatic energy of repulsion between electrons in the outer unfilled shells taken to first order. The effect of including the electron interaction is to split the degenerate pair states into a number of multiplets each of which is characterised by the same total spin angular momentum S . Since we are considering an operator that is spin-independent the states whose orbital parts transform according to the same irreducible representation will remain degenerate. This means that the states in the multiplets can further be characterised by the same orbital transformation properties. The 48 states will then split up according to the following schematic energy level pattern:

| | | | |
|-------|-------------|------------|----|
| _____ | ${}^5A'_1$ | degeneracy | 5 |
| _____ | ${}^5A''_2$ | " | 5 |
| _____ | ${}^5E'$ | " | 10 |
| _____ | ${}^5E''$ | " | 10 |
| _____ | ${}^3A'_1$ | " | 3 |
| _____ | ${}^3A''_2$ | " | 3 |
| _____ | ${}^3E'$ | " | 6 |
| _____ | ${}^3E''$ | " | 6 |

The states belonging to each multiplet can be obtained from Table 2.3.

4.4 FIRST ORDER PERTURBATION

The effective Hamiltonian has the form

$$H_{\text{eff}} = P_M g P_M$$

where M refers to the (${}^4A_2 \times {}^2T_1$) manifold and g is the two-electron operator corresponding to the Coulomb interaction between electrons e^2/r_{ij} . For brevity we shall refer to the Coulomb interaction as $1/r$.

In the last section we showed that the problem of evaluating all 48 x 48 matrix elements of H_{eff} in the (${}^4A_2 \times {}^2T_1$) manifold has a relatively simple solution. We have shown that only the diagonal elements are non-zero and among the diagonal elements there are only eight different values. Therefore to obtain the splitting of the manifold only eight matrix elements need be calculated.

In order to evaluate the energy of each multiplet we have to evaluate the matrix element of H_{eff} between any member state of that multiplet. To have some consistency in choosing the state with which to evaluate the multiplet energy only those states which have $M_S = 0$ will be used; we shall also find that this stipulation facilitates the calculations. It must be stressed that any multiplet contains both primed and double primed states so that the matrix element $\langle U', 1, 0 | H_{\text{eff}} | U', 1, 0 \rangle$ has the same value as $\langle U'', 1, \pm 1 | H_{\text{eff}} | U'', 1, \pm 1 \rangle$. We shall concentrate first of all on the orbital singlet states.

The U states can be found in Section 2.6, those with $M_S = 0$ are shown below:-

$$\left. \begin{array}{l} |U', 2, 0\rangle \\ |U'', 2, 0\rangle \end{array} \right\} = \frac{1}{2} \left[|T, -\frac{1}{2}; A, \frac{1}{2}\rangle + |T, \frac{1}{2}; A, -\frac{1}{2}\rangle \mp |A, -\frac{1}{2}; T, \frac{1}{2}\rangle \mp |A, \frac{1}{2}; T, -\frac{1}{2}\rangle \right]$$

$$\left. \begin{array}{l} |U', 1, 0\rangle \\ |U'', 1, 0\rangle \end{array} \right\} = \frac{1}{2} \left[|T, -\frac{1}{2}; A, \frac{1}{2}\rangle - |T, \frac{1}{2}; A, -\frac{1}{2}\rangle \pm |A, -\frac{1}{2}; T, \frac{1}{2}\rangle \mp |A, \frac{1}{2}; T, -\frac{1}{2}\rangle \right]$$

where the primed and double primed states are indicated by the \pm and \mp signs; the first sign always refers to the prime state. The following shorthand notation is now introduced:

$$|x_1\rangle = |T, -\frac{1}{2}; A, \frac{1}{2}\rangle$$

$$|x_2\rangle = |T, \frac{1}{2}; A, -\frac{1}{2}\rangle$$

$$|x_3\rangle = |A, -\frac{1}{2}; T, \frac{1}{2}\rangle$$

$$|x_4\rangle = |A, \frac{1}{2}; T, -\frac{1}{2}\rangle$$

whence the U states become

$$\left. \begin{array}{l} |U', 2, 0\rangle \\ |U'', 2, 0\rangle \end{array} \right\} = \frac{1}{2} [|x_1\rangle + |x_2\rangle \mp |x_3\rangle \mp |x_4\rangle]$$

$$\left. \begin{array}{l} |U', 1, 0\rangle \\ |U'', 1, 0\rangle \end{array} \right\} = \frac{1}{2} [|x_1\rangle - |x_2\rangle \pm |x_3\rangle \mp |x_4\rangle]$$

The matrix element of H_{eff} between the $S = 2$ states then becomes

$$\begin{aligned} \langle U', 2, 0 | H_{\text{eff}} | U', 2, 0 \rangle; \langle U'', 2, 0 | H_{\text{eff}} | U'', 2, 0 \rangle \\ = \frac{1}{4} [\langle x_1 | g | x_1 \rangle + \langle x_1 | g | x_2 \rangle \mp \langle x_1 | g | x_3 \rangle \mp \langle x_1 | g | x_4 \rangle \\ + \langle x_2 | g | x_1 \rangle + \langle x_2 | g | x_2 \rangle \mp \langle x_2 | g | x_3 \rangle \mp \langle x_2 | g | x_4 \rangle \\ \mp \langle x_3 | g | x_1 \rangle \mp \langle x_3 | g | x_2 \rangle + \langle x_3 | g | x_3 \rangle + \langle x_3 | g | x_4 \rangle \\ \mp \langle x_4 | g | x_1 \rangle \mp \langle x_4 | g | x_2 \rangle + \langle x_4 | g | x_3 \rangle + \langle x_4 | g | x_4 \rangle] \end{aligned}$$

Before continuing with the $S = 1$ states we shall prove the equality of many of the integrals containing the x-functions through the use of the symmetry operators σ_V^S and σ_h .

Firstly we can say that the electrostatic repulsion between electrons is not dependent on the orientation of electron spin on each ion, provided the M_S value for the pair remains (in this case) zero. The application of σ_V^S will show this. The effect of σ_V^S is to reverse the sign of the M_S value of each ion. Thus

$$\begin{aligned}\sigma_v^s |x_1\rangle &= |-T, \frac{1}{2} : A, -\frac{1}{2}\rangle = -|x_2\rangle \\ \sigma_v^s |x_2\rangle &= |T, -\frac{1}{2} : -A, \frac{1}{2}\rangle = -|x_1\rangle \\ \sigma_v^s |x_3\rangle &= |-A, \frac{1}{2} : T, -\frac{1}{2}\rangle = -|x_4\rangle \\ \sigma_v^s |x_4\rangle &= |A, -\frac{1}{2} : -T, \frac{1}{2}\rangle = -|x_3\rangle\end{aligned}$$

showing the equality of the following integrals

$$\begin{aligned}\langle x_1 | g | x_1 \rangle &= \langle x_2 | g | x_2 \rangle & \langle x_3 | g | x_1 \rangle &= \langle x_4 | g | x_2 \rangle \\ \langle x_1 | g | x_2 \rangle &= \langle x_2 | g | x_1 \rangle & \langle x_3 | g | x_2 \rangle &= \langle x_4 | g | x_1 \rangle \\ \langle x_1 | g | x_3 \rangle &= \langle x_2 | g | x_4 \rangle & \langle x_3 | g | x_3 \rangle &= \langle x_4 | g | x_4 \rangle \\ \langle x_1 | g | x_4 \rangle &= \langle x_2 | g | x_3 \rangle & \langle x_3 | g | x_4 \rangle &= \langle x_4 | g | x_3 \rangle\end{aligned}$$

The Coulomb interaction energy is obtained with no distinction between the ions being made. The application of σ_h shows the equality of the integrals in which the excited ion and the ground state ion are interchanged. Thus we have that

$$\begin{aligned}\sigma_h |x_1\rangle &= -|-iA, \frac{1}{2} : iT, -\frac{1}{2}\rangle = -|x_4\rangle \\ \sigma_h |x_2\rangle &= -|iA, -\frac{1}{2} : -iT, \frac{1}{2}\rangle = -|x_3\rangle \\ \sigma_h |x_3\rangle &= -|-iT, \frac{1}{2} : iA, -\frac{1}{2}\rangle = -|x_2\rangle \\ \sigma_h |x_4\rangle &= -|iT, -\frac{1}{2} : -iA, \frac{1}{2}\rangle = -|x_1\rangle\end{aligned}$$

from which we deduce

$$\begin{aligned}\langle x_1 | g | x_1 \rangle &= \langle x_4 | g | x_4 \rangle & \langle x_3 | g | x_1 \rangle &= \langle x_2 | g | x_4 \rangle \\ \langle x_1 | g | x_2 \rangle &= \langle x_4 | g | x_3 \rangle & \langle x_3 | g | x_2 \rangle &= \langle x_2 | g | x_3 \rangle \\ \langle x_1 | g | x_3 \rangle &= \langle x_4 | g | x_2 \rangle & \langle x_3 | g | x_3 \rangle &= \langle x_2 | g | x_2 \rangle \\ \langle x_1 | g | x_4 \rangle &= \langle x_4 | g | x_1 \rangle & \langle x_3 | g | x_4 \rangle &= \langle x_2 | g | x_1 \rangle\end{aligned}$$

If we combine both sets of results we find that the matrix elements of H_{eff} between the U states are considerably simplified. They are reduced to the following:

$$\begin{aligned}
 & \langle U', 2, 0 | H_{\text{eff}} | U', 2, 0 \rangle; \langle U'', 2, 0 | H_{\text{eff}} | U'', 2, 0 \rangle \\
 & = \langle x_1 | g | x_1 \rangle + \langle x_1 | g | x_2 \rangle + \langle x_1 | g | x_3 \rangle + \langle x_1 | g | x_4 \rangle \\
 & \langle U', 1, 0 | H_{\text{eff}} | U', 1, 0 \rangle; \langle U'', 1, 0 | H_{\text{eff}} | U'', 1, 0 \rangle \\
 & = \langle x_1 | g | x_1 \rangle - \langle x_1 | g | x_2 \rangle \pm \langle x_1 | g | x_3 \rangle + \langle x_1 | g | x_4 \rangle
 \end{aligned}$$

We have yet to consider the orbital doublet states V and W. If the same process is carried out using the V or W states with $M_S = 0$ one finds exactly the same result as for the U states. This is not surprising since both V and W have the same transformation properties under σ_V^S and σ_h as the U states. When we come to make a detailed examination of the matrix elements however, the component of 2T_1 will have to be specified.

4.5 DETAILED EXAMINATION OF THE MATRIX ELEMENTS

The determination of the expectation value of H_{eff} between the U states as basis functions, when H contains only the two-electron operator g, requires the evaluation of just four integrals: $\langle x_1 | g | x_1 \rangle, \langle x_1 | g | x_2 \rangle, \langle x_1 | g | x_3 \rangle$ and $\langle x_1 | g | x_4 \rangle$. A similar set of integrals is required to evaluate the matrix elements of H_{eff} between the V (or W) basis states. One can prove that the matrix elements between the V states are identical to those between the W states by the use of σ_V .

To calculate the integrals we must first write the x-functions in terms of Slater determinants and then we will be able to use the rules laid down in Section 4.1. From Section 2.3:

$$\begin{aligned}
 |x_1\rangle &= |T, -\frac{1}{2}; A, \frac{1}{2}\rangle \\
 &= (1/\sqrt{6})\{2(\bar{A}\bar{B}\bar{C}) - (\bar{A}\bar{B}\bar{C}) - (\bar{A}\bar{B}\bar{C})\} \times (1/\sqrt{3})\{(\bar{a}\bar{b}\bar{c}) + (\bar{a}\bar{b}\bar{c}) + (\bar{a}\bar{b}\bar{c})\} \\
 &= \frac{1}{3}\sqrt{2}\left[2(\bar{A}\bar{B}\bar{C}\bar{a}\bar{b}\bar{c}) + 2(\bar{A}\bar{B}\bar{C}\bar{a}\bar{b}\bar{c}) + 2(\bar{A}\bar{B}\bar{C}\bar{a}\bar{b}\bar{c}) - (\bar{A}\bar{B}\bar{C}\bar{a}\bar{b}\bar{c}) - (\bar{A}\bar{B}\bar{C}\bar{a}\bar{b}\bar{c}) \right. \\
 &\quad \left. - (\bar{A}\bar{B}\bar{C}\bar{a}\bar{b}\bar{c}) - (\bar{A}\bar{B}\bar{C}\bar{a}\bar{b}\bar{c}) - (\bar{A}\bar{B}\bar{C}\bar{a}\bar{b}\bar{c}) - (\bar{A}\bar{B}\bar{C}\bar{a}\bar{b}\bar{c})\right]
 \end{aligned}$$

$$\begin{aligned}
 |x_2\rangle &= |T, \frac{1}{2}:A, -\frac{1}{2}\rangle \\
 &= \frac{1}{3}\sqrt{\frac{1}{2}}[(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})+(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})+(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})+(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})+(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c}) \\
 &\quad +(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})-2(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})-2(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})-2(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})]
 \end{aligned}$$

$$\begin{aligned}
 |x_4\rangle &= |A, \frac{1}{2}:T, -\frac{1}{2}\rangle \\
 &= \frac{1}{3}\sqrt{\frac{1}{2}}[2(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})-(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})-(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})+2(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})-(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c}) \\
 &\quad -(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})+2(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})-(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})-(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c})]
 \end{aligned}$$

$$\begin{aligned}
 |x_3\rangle &= |A, -\frac{1}{2}:T, \frac{1}{2}\rangle \\
 &= \frac{1}{3}\sqrt{\frac{1}{2}}[(\overset{+}{A}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{c})+(\overset{+}{A}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{c})-2(\overset{+}{A}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{c})+(\overset{+}{A}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{c})+(\overset{+}{A}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{c}) \\
 &\quad -2(\overset{+}{A}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{c})+(\overset{+}{A}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{c})+(\overset{+}{A}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{c})-2(\overset{+}{A}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{c})]
 \end{aligned}$$

The integrals over determinantal functions are evaluated in terms of integrals over spin-orbitals; particular matrix elements occur so frequently that it is convenient to use the notation (following Condon and Shortley [35, Chap 6]).

$$J(ij) = \langle ij | 1/r | ij \rangle$$

$$K(ij) = \langle ij | 1/r | ji \rangle$$

where i and j are spin-orbitals.

The four integrals, now in terms of spin-orbitals are

$$\begin{aligned}
 (i) \quad &\langle T, -\frac{1}{2}:A, \frac{1}{2} | 1/r | T, -\frac{1}{2}:A, \frac{1}{2} \rangle \\
 &= (1/18) [18J(AB)+18J(AC)+18J(Aa)+18J(Ab)+18J(Ac) \\
 &\quad +18J(BC)+18J(Ba)+18J(Bb)+18J(Bc)+18J(Ca)+18J(Cb)+18J(Cc) \\
 &\quad +18J(ab)+18J(ac)+18J(bc) \\
 &\quad +9K(AB)+9K(AC)-10K(Aa)-10K(Ab)-10K(Ac) \\
 &\quad -18K(BC)-7K(Ba)-7K(Bb)-7K(Bc)-7K(Ca)-7K(Cb)-7K(Cc) \\
 &\quad -18K(ab)-18K(ac)-18K(bc)] \\
 &= (1/18) [72J(AB)+36J(BC)+18J(Aa)+72J(Ab)+36J(Bb)+36J(Bc) \\
 &\quad -18K(AB)-36K(BC)-10K(Aa)-34K(Ab)-14K(Bb)-14K(Bc)]
 \end{aligned}$$

This last line has been obtained by examining the equality of the integrals over spin-orbitals using the operators σ_v and σ_h . For instance by σ_v one can prove that $J(AB) = J(AC)$ and by σ_h that $J(AB) = J(ab)$ and $J(Ab) = J(Ba) = J(Ca) = J(Ac)$.

$$\begin{aligned} \text{(ii)} \quad & \langle T, -\frac{1}{2}:A, \frac{1}{2} | 1/r | T, \frac{1}{2}:A, -\frac{1}{2} \rangle \\ &= (1/18) [4K(Aa) + 4K(Ab) + 4K(Ac) - 8K(Ba) - 8K(Bb) - 8K(Bc) \\ &\quad - 8K(Ca) - 8K(Cb) - 8K(Cc)] \\ &= (1/18) [4K(Aa) - 8K(Ab) - 16K(Bb) - 16K(Bc)] \end{aligned}$$

$$\begin{aligned} \text{(iii)} \quad & \langle T, -\frac{1}{2}:A, \frac{1}{2} | 1/r | A, -\frac{1}{2}:T, \frac{1}{2} \rangle \\ &= (1/18) [-8K(Aa) + 4K(Ab) + 4K(Ac) + 4K(Ba) - 2K(Bb) - 2K(Bc) \\ &\quad + 4K(Ca) - 2K(Cb) - 2K(Cc)] \\ &= (1/18) [-8K(Aa) + 16K(Ab) - 4K(Bb) - 4K(Bc)] \end{aligned}$$

$$\begin{aligned} \text{(iv)} \quad & \langle T, -\frac{1}{2}:A, \frac{1}{2} | 1/r | A, \frac{1}{2}:T, -\frac{1}{2} \rangle \\ &= (1/18) [-4K(Aa) + 2K(Ab) + 2K(Ac) + 2K(Ba) - K(Bb) - K(Bc) \\ &\quad + 2K(Ca) - K(Cb) - K(Cc)] \\ &= (1/18) [-4K(Aa) + 8K(Ab) - 2K(Bb) - 2K(Bc)] \end{aligned}$$

Examining the results of these calculations the first thing to notice is that

$$\langle T, -\frac{1}{2}:A, \frac{1}{2} | 1/r | A, -\frac{1}{2}:T, \frac{1}{2} \rangle = 2 \langle T, -\frac{1}{2}:A, \frac{1}{2} | 1/r | A, \frac{1}{2}:T, -\frac{1}{2} \rangle,$$

which is in our shorthand notation

$$\langle x_1 | g | x_3 \rangle = 2 \langle x_1 | g | x_4 \rangle.$$

Therefore $\langle U', 2, 0 | H_{\text{eff}} | U', 2, 0 \rangle; \langle U'', 2, 0 | H_{\text{eff}} | U'', 2, 0 \rangle$

$$= \langle x_1 | g | x_1 \rangle + \langle x_1 | g | x_2 \rangle \mp 3 \langle x_1 | g | x_4 \rangle$$

and $\langle U', 1, 0 | H_{\text{eff}} | U', 1, 0 \rangle; \langle U'', 1, 0 | H_{\text{eff}} | U'', 1, 0 \rangle$

$$= \langle x_1 | g | x_1 \rangle - \langle x_1 | g | x_2 \rangle \pm \langle x_1 | g | x_4 \rangle$$

We are thus lead to the very useful result that

$$\frac{\langle U', 2, 0 | H_{\text{eff}} | U', 2, 0 \rangle - \langle U'', 2, 0 | H_{\text{eff}} | U'', 2, 0 \rangle}{\langle U', 1, 0 | H_{\text{eff}} | U', 1, 0 \rangle - \langle U'', 1, 0 | H_{\text{eff}} | U'', 1, 0 \rangle} = -3$$

The ratio of the splitting between primed and double primed U states with $S = 2$ to the splitting between the primed and double primed U states with $S = 1$ is 3:-1. This result may be compared with experiment; the ratio for $\text{Cs}_3\text{Cr}_2\text{Br}_9$ is approximately 3.9:-1, that for $\text{Rb}_3\text{Cr}_2\text{Br}_9$ is $\sim 3.6:-1$ and for $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ the ratio is $\sim 4.0:-1$. It is not surprising to find experimental departures from the predicted ratio since no effects higher in order than two-electron spin independent terms are considered.

Another point of interest is that the integrals over spin-orbitals can be divided into two distinct classes, depending on whether they describe electronic interactions that are intraionic or interionic in nature. For example $J(AB) = \langle AB | 1/r | AB \rangle$ and $K(bc) = \langle bc | 1/r | cb \rangle$ are intraionic matrix elements, while $J(Aa) = \langle Aa | 1/r | Aa \rangle$ is an example of an interionic matrix element. With this in mind it is seen that the splittings within the U family are due entirely to the interionic terms, and further are due to the interionic exchange terms. The intraionic terms and the interionic Coulomb terms are found only in the $\langle x_1 | g | x_1 \rangle$ integral which is common to all the matrix elements of H_{eff} between the U states.

To find the energy of the remaining four multiplets we must evaluate the expectation value of H_{eff} between either the V or W states. The expression containing the x-functions derived in Section 4.4 is applicable in this instance if the b or c component of 2T_1 is used. The x-functions applicable to the V states are:

$$\begin{aligned}
 |x_1\rangle &= |bT, -\frac{1}{2}; A, \frac{1}{2}\rangle \\
 &= (1/\sqrt{6}) \{ (\overset{+}{A}\overset{-}{A}\overset{-}{B}) + (\overset{+}{B}\overset{-}{B}\overset{-}{C}) - 2(\overset{-}{A}\overset{+}{C}\overset{-}{C}) \} \times (1/\sqrt{3}) \{ (\overset{+}{a}\overset{-}{b}\overset{-}{c}) + (\overset{+}{a}\overset{-}{c}\overset{+}{b}) + (\overset{-}{a}\overset{+}{b}\overset{+}{c}) \} \\
 &= \frac{1}{3}\sqrt{\frac{1}{2}} [(\overset{+}{A}\overset{-}{A}\overset{-}{B}\overset{+}{a}\overset{-}{b}\overset{-}{c}) + (\overset{+}{A}\overset{-}{A}\overset{-}{B}\overset{+}{a}\overset{-}{c}\overset{+}{b}) + (\overset{+}{A}\overset{-}{A}\overset{-}{B}\overset{+}{a}\overset{+}{b}\overset{-}{c}) + (\overset{+}{B}\overset{-}{B}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c}) + (\overset{+}{B}\overset{-}{B}\overset{-}{C}\overset{+}{a}\overset{-}{c}\overset{+}{b}) \\
 &\quad + (\overset{+}{B}\overset{-}{B}\overset{-}{C}\overset{+}{a}\overset{+}{b}\overset{-}{c}) - 2(\overset{-}{A}\overset{+}{C}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c}) - 2(\overset{-}{A}\overset{+}{C}\overset{-}{C}\overset{+}{a}\overset{-}{c}\overset{+}{b}) - 2(\overset{-}{A}\overset{+}{C}\overset{-}{C}\overset{+}{a}\overset{+}{b}\overset{-}{c})]
 \end{aligned}$$

$$\begin{aligned}
 |x_2\rangle &= |bT, \frac{1}{2}; A, -\frac{1}{2}\rangle \\
 &= \frac{1}{3}\sqrt{\frac{1}{2}} [(\overset{+}{A}\overset{-}{A}\overset{+}{B}\overset{+}{a}\overset{-}{b}\overset{-}{c}) + (\overset{+}{A}\overset{-}{A}\overset{+}{B}\overset{+}{a}\overset{-}{c}\overset{+}{b}) + (\overset{+}{A}\overset{-}{A}\overset{+}{B}\overset{+}{a}\overset{+}{b}\overset{-}{c}) + (\overset{+}{B}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c}) + (\overset{+}{B}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{-}{c}\overset{+}{b}) \\
 &\quad + (\overset{+}{B}\overset{-}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{-}{c}) - 2(\overset{+}{A}\overset{+}{C}\overset{-}{C}\overset{+}{a}\overset{-}{b}\overset{-}{c}) - 2(\overset{+}{A}\overset{+}{C}\overset{-}{C}\overset{+}{a}\overset{-}{c}\overset{+}{b}) - 2(\overset{+}{A}\overset{+}{C}\overset{-}{C}\overset{+}{a}\overset{+}{b}\overset{-}{c})]
 \end{aligned}$$

$$\begin{aligned}
 |x_4\rangle &= |A, \frac{1}{2}; bT, -\frac{1}{2}\rangle \\
 &= \frac{1}{3}\sqrt{\frac{1}{2}} [(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{+}{a}\overset{-}{b}) + (\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{+}{b}\overset{-}{b}) - 2(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{+}{c}\overset{-}{c}) + (\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{+}{a}\overset{+}{b}) + (\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{+}{b}\overset{+}{b}) \\
 &\quad - 2(\overset{+}{A}\overset{+}{B}\overset{-}{C}\overset{+}{a}\overset{+}{c}\overset{-}{c}) + (\overset{-}{A}\overset{+}{B}\overset{+}{C}\overset{+}{a}\overset{+}{a}\overset{-}{b}) + (\overset{-}{A}\overset{+}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{-}{b}) - 2(\overset{-}{A}\overset{+}{B}\overset{+}{C}\overset{+}{a}\overset{+}{c}\overset{-}{c})]
 \end{aligned}$$

$$\begin{aligned}
 |x_3\rangle &= |A, -\frac{1}{2}; bT, \frac{1}{2}\rangle \\
 &= \frac{1}{3}\sqrt{\frac{1}{2}} [(\overset{+}{A}\overset{-}{B}\overset{-}{C}\overset{+}{a}\overset{+}{a}\overset{+}{b}) + (\overset{+}{A}\overset{-}{B}\overset{-}{C}\overset{+}{a}\overset{+}{b}\overset{+}{b}) - 2(\overset{+}{A}\overset{-}{B}\overset{-}{C}\overset{+}{a}\overset{+}{c}\overset{-}{c}) + (\overset{-}{A}\overset{+}{B}\overset{+}{C}\overset{+}{a}\overset{+}{a}\overset{+}{b}) + (\overset{-}{A}\overset{+}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{b}) \\
 &\quad - 2(\overset{-}{A}\overset{+}{B}\overset{+}{C}\overset{+}{a}\overset{+}{c}\overset{-}{c}) + (\overset{-}{A}\overset{+}{B}\overset{+}{C}\overset{+}{a}\overset{+}{a}\overset{+}{b}) + (\overset{-}{A}\overset{+}{B}\overset{+}{C}\overset{+}{a}\overset{+}{b}\overset{+}{b}) - 2(\overset{-}{A}\overset{+}{B}\overset{+}{C}\overset{+}{a}\overset{+}{c}\overset{-}{c})]
 \end{aligned}$$

The required integrals over these determinantal functions, using the rules given in Section 4.1 are:

$$\begin{aligned}
 (i) \langle bT, -\frac{1}{2}; A, \frac{1}{2} | 1/r | bT, -\frac{1}{2}; A, \frac{1}{2} \rangle \\
 &= (1/18) [3J(AA) + 6J(AB) + 24J(AC) + 18J(Aa) + 18J(Ab) + 18J(Ac) \\
 &\quad + 3J(BB) + 6J(BC) + 9J(Ba) + 9J(Bb) + 9J(Bc) \\
 &\quad + 12J(CC) + 27J(Ca) + 27J(Cb) + 27J(Cc) \\
 &\quad + 18J(ab) + 18J(ac) + 18J(bc) \\
 &\quad - 3K(AB) - 12K(AC) - 7K(Aa) - 7K(Ab) - 7K(Ac) \\
 &\quad - 3K(BC) - 4K(Ba) - 4K(Bb) - 4K(Bc) - 13K(Ca) - 13K(Cb) - 13K(Cc) \\
 &\quad - 18K(ab) - 18K(ac) - 18K(bc) - 6\langle AA | 1/r | BC \rangle + 12\langle AB | 1/r | CC \rangle \\
 &\quad + 12\langle BB | 1/r | AC \rangle] \\
 &= (1/18) [3J(AA) + 66J(AB) + 18J(Aa) + 72J(Ab) \\
 &\quad + 15J(BB) + 24J(BC) + 36J(Bb) + 36J(Bc)
 \end{aligned}$$

$$\begin{aligned} & -51K(AB) - 7K(Aa) - 31K(Ab) - 21K(BC) - 17K(Bb) - 17K(Bc) \\ & -6\langle AA|1/r|BC\rangle + 24\langle AB|1/r|CC\rangle \end{aligned}$$

$$(ii) \langle bT, -\frac{1}{2}: A, \frac{1}{2} | 1/r | bT, \frac{1}{2}: A, -\frac{1}{2} \rangle$$

$$\begin{aligned} & = (1/18) [-8K(Aa) - 8K(Ab) - 8K(AC) - 2K(Ba) - 2K(Bb) - 2K(Bc) \\ & \quad - 2K(Ca) - 2K(Cb) - 2K(Cc)] \\ & = (1/18) [-8K(Aa) - 20K(AB) - 4K(Bb) - 4K(Bc)] \end{aligned}$$

$$(iii) \langle bT, -\frac{1}{2}: A, \frac{1}{2} | 1/r | A, -\frac{1}{2}: bT, \frac{1}{2} \rangle = 2\langle bT, -\frac{1}{2}: A, \frac{1}{2} | 1/r | A, \frac{1}{2}: bT, -\frac{1}{2} \rangle$$

$$\begin{aligned} & = (1/18) [-2\langle Ac|1/r|aC\rangle - 2\langle Aa|1/r|bC\rangle + 4\langle Ab|1/r|cC\rangle \\ & \quad - 2\langle Bc|1/r|aA\rangle - 2\langle Ba|1/r|bA\rangle + 4\langle Bb|1/r|cA\rangle \\ & \quad + 4\langle Cc|1/r|aB\rangle + 4\langle Ca|1/r|bB\rangle - 8\langle Cb|1/r|cB\rangle] \\ & = (1/18) [-4\langle Ac|1/r|aC\rangle - 8\langle Cb|1/r|cB\rangle - 4\langle Aa|1/r|bC\rangle + 16\langle Ab|1/r|cC\rangle] \end{aligned}$$

Once again one finds that

$$\langle x_1 | g | x_3 \rangle = 2\langle x_1 | g | x_4 \rangle$$

which when substituted in the expression derived in Section 4.4 gives the result that

$$\frac{\langle V', 2, 0 | H_{eff} | V', 2, 0 \rangle - \langle V'', 2, 0 | H_{eff} | V'', 2, 0 \rangle}{\langle V', 1, 0 | H_{eff} | V', 1, 0 \rangle - \langle V'', 1, 0 | H_{eff} | V'', 1, 0 \rangle} = -3$$

with the V and W states remaining degenerate.

One notices that the intraionic terms leave the (V,W) family degenerate; it is the interionic exchange terms that are responsible for any splittings. The indications from experiment are that the above ratio for the V or W states are similar to those reported in the case of the U family splittings; for $Cs_3Cr_2Br_9$ the ratio is $\sim 3.0:-1$.

An interesting approximation at this stage would be to allow no interaction to take place between the ions of a pair. Then each interionic term would be zero and only non-zero terms would be those of

intraionic nature in $\langle x_1 | g | x_1 \rangle$. The intraionic terms could then be determined in terms of Slater F-integrals, for instance

$$\begin{aligned} J(AA) &\equiv \langle d_o d_o | 1/r | d_o d_o \rangle \\ &= F_o + 4F_2 + 36F_4. \end{aligned}$$

The evaluation of the intraionic matrix elements has been carried out using the methods outlined in [35, Chap 6] and the results can be found in Appendix VII. The substitution of these values into $\langle x_1 | g | x_1 \rangle$ for both the U and the (V,W) states gives the same result

$$6F_o - 21F_2 - 84F_4.$$

A comparison with the single ion term energies of

$$\begin{aligned} {}^4A_2: & 3F_o - 15F_2 - 72F_4 \\ {}^2T_1: & 3F_o - 6F_2 - 12F_4 \end{aligned}$$

[37, Chap 10.d] shows that the energy of the pair system is simply the sum of the energy of two single ions, one in the ground term, the other in the 2T_1 term as one would expect. It is easy to see that the excited manifold lies above the $({}^4A_2 \times {}^4A_2)$ ground manifold by an amount equal to $9F_2 + 60F_4$.

In Section 1.3 an approximation to the Racah parameter B was given by comparing the pair spectra with the term diagram Fig 1.2 (for which the third Racah parameter C = 4B). For $\text{Cs}_3\text{Cr}_2\text{Br}_9$ $B \sim 660 \text{ cm}^{-1}$ giving $F_2 \sim 1040 \text{ cm}^{-1}$ and $F_4 \sim 76 \text{ cm}^{-1}$, leading to an energy of $\sim 13,920 \text{ cm}^{-1}$ for the $({}^4A_2 \times {}^2T_1)$ manifold. Table 3.4 gives the energy to be $14,400 \text{ cm}^{-1}$ so even in this crude approximation the agreement is fairly good.

The next approximation we shall make is to let each interionic term have a finite value. We shall make no distinction between the electronic orbitals so that all the interionic Coulomb terms are equal with the value J and all the interionic exchange terms are equal with the

value K. We can no longer write the intraionic terms in terms of F-integrals and we now expect them to contribute different energies to the U states than to the (V,W) states, say E and E' respectively.

Otherwise one finds that the expectation value of H_{eff} between U states and the expectation value of H_{eff} between the V (or W) states are equal.

In x-notation for the U states we have:

$$\langle x_1 | g | x_1 \rangle = E + 9J - 4K$$

$$\langle x_1 | g | x_2 \rangle = -2K$$

$$\langle x_1 | g | x_4 \rangle = 0$$

The Coulomb term J in this case corresponds to the electrostatic interaction between electrons on different ions; one would expect nine such interactions as there are three valence electrons on each ion.

Hence we find that in this approximation the (${}^4A_2 \times {}^2T_1$) manifold is split into two groups of states. The states belonging to each group have a different total spin, either $S = 1$ or $S = 2$, and there is no dependence on the σ_h nature of the states. We also find that the matrix elements of H_{eff} between the $S = 2$ U states have the value

$$E + 9J - 6K,$$

and the matrix elements of H_{eff} between the $S+1$ U states have the value

$$E + 9J - 2K.$$

Since K is necessarily positive the $S = 2$ states must lie lower in energy than the $S = 1$ states. This suggests a ferromagnetic interaction since the lowest energy of the system occurs when the spins on the ions are parallel. A look at Table 3.5 will show that for each material the ordering of the orbital singlet states complies with this prediction. However the ordering of the orbital doublets is reversed; the $S = 1$

states lie lower than the $S = 2$ states. This contradiction of theory by experiment must be expected in a first order treatment, as was pointed out in Section 1.1. The higher order two-electron terms must also be taken into account. The terms of higher order are expected to be of similar form to those of first order and are to be regarded as renormalising the coefficients of first order.

The splitting between the σ_h families of states can only be brought about by lifting the constraints of this approximation, by admitting the differences that are to be found between the interionic terms. This shows the importance of the orbital components of the states in the evaluation of the expectation values of H_{eff} between the basis states of the $(^4A_2 \times ^2T_1)$. The successive stages of approximation are shown diagrammatically in Fig 4.1.

4.6 APPLICATION TO THE GROUND MANIFOLD

We shall now evaluate the matrix elements of H_{eff} between the basis states of the $(^4A_2 \times ^4A_2)$ ground manifold, using $H_{\text{eff}} = P_M g P_M$ where M in this case represents the states of the ground manifold. The degenerate pair states will be split into multiplets, four in number, each characterised by the total spin $S_g = 0, 1, 2$ or 3 . Following the same procedure as in Section 4.4 we begin with the pair wave functions - which can be found in Section 3.2. The states with $M_S = 0$ are:

$$|3,0\rangle = \frac{1}{2}(1/\sqrt{5}) [|- \frac{3}{2} : \frac{3}{2} \rangle + 3| - \frac{1}{2} : \frac{1}{2} \rangle + 3| \frac{1}{2} : - \frac{1}{2} \rangle + | \frac{3}{2} : - \frac{3}{2} \rangle]$$

$$|2,0\rangle = \frac{1}{2} [|- \frac{3}{2} : \frac{3}{2} \rangle + | - \frac{1}{2} : \frac{1}{2} \rangle - | \frac{1}{2} : - \frac{1}{2} \rangle - | \frac{3}{2} : - \frac{3}{2} \rangle]$$

$$|1,0\rangle = \frac{1}{2}(1/\sqrt{5}) [3| - \frac{3}{2} : \frac{3}{2} \rangle - | - \frac{1}{2} : \frac{1}{2} \rangle - | \frac{1}{2} : - \frac{1}{2} \rangle + 3| \frac{3}{2} : - \frac{3}{2} \rangle]$$

$$|0,0\rangle = \frac{1}{2} [|- \frac{3}{2} : \frac{3}{2} \rangle - | - \frac{1}{2} : \frac{1}{2} \rangle + | \frac{1}{2} : - \frac{1}{2} \rangle - | \frac{3}{2} : - \frac{3}{2} \rangle]$$

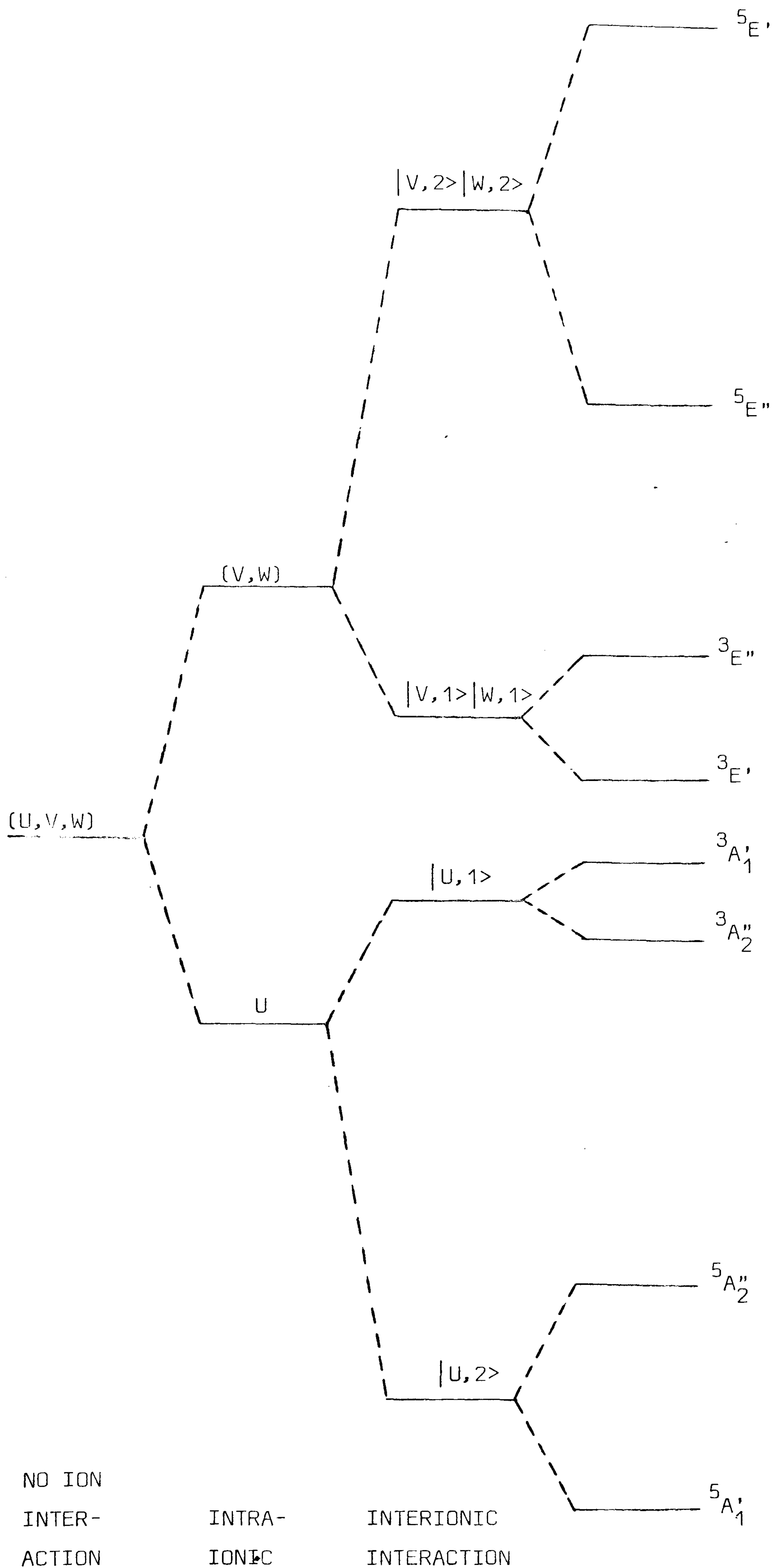


Fig 4.1: The $(^4A_2 \times ^2T_1)$ States.

Between these states we now examine the expectation values of H_{eff} , as in Section 4.4 the equality of many integrals is found by the use of the symmetry operators σ_v and σ_h . The final result is shown below:

$$\langle 3,0 | H_{\text{eff}} | 3,0 \rangle = (1/10) \left[\langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{3}{2}:\frac{3}{2} \rangle + 6 \langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle + 9 \langle -\frac{1}{2}:\frac{1}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle + 9 \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle \right]$$

$$\langle 2,0 | H_{\text{eff}} | 2,0 \rangle = \frac{1}{2} \left[\langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{3}{2}:\frac{3}{2} \rangle + 2 \langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle + \langle -\frac{1}{2}:\frac{1}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle - \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle \right]$$

$$\langle 1,0 | H_{\text{eff}} | 1,0 \rangle = (1/10) \left[9 \langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{3}{2}:\frac{3}{2} \rangle - 6 \langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle + \langle -\frac{1}{2}:\frac{1}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle + \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle \right]$$

$$\langle 0,0 | H_{\text{eff}} | 0,0 \rangle = \frac{1}{2} \left[\langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{3}{2}:\frac{3}{2} \rangle - 2 \langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle + \langle -\frac{1}{2}:\frac{1}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle - \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle \right]$$

To consider these matrix elements in detail each pair state must be written in determinantal form by using the single ion states of Section 2.3. Through the rules laid down in Section 4.1 we arrive at the following:

$$\begin{aligned} \langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{3}{2}:\frac{3}{2} \rangle &= \langle \bar{A}\bar{B}\bar{C}a^+b^+c^+ | 1/r | \bar{A}\bar{B}\bar{C}a^+b^+c^+ \rangle \\ &= 4J(AB) + 2J(BC) + J(Aa) + 4J(Bb) + 2J(Bc) - 4K(AB) - 2K(BC) \\ \langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle &= \frac{1}{3} [-K(Aa) - 4K(Ab) - 2K(Bb) - 2K(Bc)] \\ \langle -\frac{1}{2}:\frac{1}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle &= 4J(AB) + 2J(BC) + J(Aa) + 4J(Ab) + 2J(Bb) + 2J(Bc) - 4K(AB) - 2K(BC) \\ &\quad + (4/9) [-K(Aa) - 4K(Ab) - 2K(Bb) - 2K(Bc)] \\ \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle &= (4/9) [-K(Aa) - 4K(Ab) - 2K(Bb) - 2K(Bc)] \end{aligned}$$

One notices that there are some similarities in the form of these results, specifically one notices the following equalities:

$$\begin{aligned} \langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{3}{2}:\frac{3}{2} \rangle &= \langle -\frac{1}{2}:\frac{1}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle - \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle \\ \langle -\frac{3}{2}:\frac{3}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle &= \frac{3}{4} \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle \end{aligned}$$

On substitution into the matrix elements of H_{eff} between the pair states

$$\langle 3,0 | H_{\text{eff}} | 3,0 \rangle = \langle -\frac{1}{2}:\frac{1}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle + 5(\frac{1}{4}) \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle$$

$$\langle 2,0 | H_{\text{eff}} | 2,0 \rangle = \langle -\frac{1}{2}:\frac{1}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle - \frac{1}{4} \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle$$

$$\langle 1,0 | H_{\text{eff}} | 1,0 \rangle = \langle -\frac{1}{2}:\frac{1}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle - 5(\frac{1}{4}) \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle$$

$$\langle 0,0 | H_{\text{eff}} | 0,0 \rangle = \langle -\frac{1}{2}:\frac{1}{2} | g | -\frac{1}{2}:\frac{1}{2} \rangle - 7(\frac{1}{4}) \langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle$$

Relative to the $S_g = 0$ level the theory predicts that the $S_g = 1, 2$ and 3 multiplets lie at $\frac{1}{2}, \frac{3}{2}$ and 3 respectively, in units of $\langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle$. How does this compare with the spin Hamiltonian description? The spin Hamiltonian has the form

$$\begin{aligned} H_s &= -J \underline{S}_1 \cdot \underline{S}_2 \\ &= -J [S_{1z} S_{2z} + \frac{1}{2}(S_{1+} S_{2-} + S_{1-} S_{2+})] \end{aligned}$$

J is the exchange parameter. It is a simple matter to calculate the matrix elements of H_s between our basis states. One finds the following:

$$\langle 3,0 | H_s | 3,0 \rangle = -9J/4,$$

$$\langle 2,0 | H_s | 2,0 \rangle = 3J/4,$$

$$\langle 1,0 | H_s | 1,0 \rangle = 11J/4,$$

$$\langle 0,0 | H_s | 0,0 \rangle = 15J/4.$$

The energies of the $S_g = 1, 2$ and 3 multiplets in terms of J relative to the $S_g = 0$ are $J, 3J$ and $6J$ respectively. The splitting ratios are exactly as predicted using the Stevens approach.

The two methods have something else in common. They both predict a ferromagnetic interaction between the ions so the states with the highest spin should be lowest in energy. (The integral $\langle -\frac{1}{2}:\frac{1}{2} | g | \frac{1}{2}:-\frac{1}{2} \rangle$ is a negative number). In actuality the $S_g = 0$ level is observed to be lowest in energy (see Table 3.6); the interaction between ions is antiferromagnetic so that parameters describing the splitting are of the wrong sign. In Section 1.1 we anticipated this result and put the discrepancy of sign down to the limitations of the Dirac Hamiltonian. The same problems are also encountered in the Stevens approach; the

result quoted above is a product of the first term in an infinite series of terms. If we were to evaluate all of the higher order two-electron terms in the series, each would give a splitting of the same ratio as in first order but of a different magnitude. Some of the higher order terms may be of greater magnitude than first order and also of opposite sign. Thus it is possible for an antiferromagnetic interaction to be predicted by the theory.

We shall proceed no further with the spin independent operators: no further splittings will result from any of the higher order terms. The results of second order perturbation theory using general one- and two-electron operators are deduced by the methods of second quantisation and are described in the review by Stevens [1, Chap 5].

CHAPTER FIVE

SPIN DEPENDENT TERMS IN THE HAMILTONIAN

5.1 THE SPIN-ORBIT INTERACTION

In the discussion of the absorption spectra of the binuclear systems we have arrived at a series of multiplets, each characterised by the orbital transformation properties of the states, for the (${}^4A_2 \times {}^2T_1$) manifold. To treat the fine details of the spectra more accurately the so called spin-orbit interaction must be considered. The spin dependent interactions are small but their effects may be observed experimentally; Table 3.5 shows that the ${}^3E''$ multiplet is split into three unequally spaced doublets with separations of up to $\sim 10 \text{ cm}^{-1}$. It is hoped that the inclusion of the spin-orbit coupling into the Hamiltonian will provide some explanation of these features.

The interaction of the spins of a system of d-electrons with their own orbital motions in a central field of force may be written [35,36,37].

$$H_{SO} = \zeta_d \sum_i \underline{l}_i \cdot \underline{s}_i$$

where ζ_d is a characteristic of the radial part of the d-orbitals and of the central field, \underline{l} and \underline{s} are the orbital angular momentum and spin operators. The spin-orbit interactions written in the above form are only valid when the field in which the electron moves has spherical symmetry. This is, of course, not so in the present case and as it is not possible to give a complete relativistic treatment to a many-electron system the spin dependent part of the Hamiltonian must be approximated. However, we may use the above interaction if ζ_d is considered to be an

adjustable parameter and into which we may incorporate any deviations from the central field model. In the pair system, to emphasise the axial symmetry we can include two such parameters and write the spin-orbit interaction as:

$$H_{SO} = \sum_i \left[k_z u_z s_z + \frac{1}{2} k_{\pm} (u_+ s_- + u_- s_+) \right]_i$$

The two adjustable parameters are k_z and k_{\pm} . The operators u_z , u_+ and u_- are 'orbital' operators, i.e. operators acting on functions of spatial coordinates, analogous to l_z , l_+ and l_- of the single ion.

The matrix elements of u_z , u_+ and u_- between the electronic orbitals $|A\rangle$, $|B\rangle$, $|C\rangle$, $|D\rangle$, $|E\rangle$ are deduced by symmetry arguments, using the following relations:

$$\begin{aligned} (C_3^0)^2 u_z C_3^0 &= u_z & \sigma_V^0 u_z \sigma_V^0 &= -u_z \\ (C_3^0)^2 u_+ C_3^0 &= \omega u_+ & \sigma_V^0 u_+ \sigma_V^0 &= -u_- \\ (C_3^0)^2 u_- C_3^0 &= \omega^2 u_- & \sigma_V^0 u_- \sigma_V^0 &= -u_+ \end{aligned}$$

and the symmetry properties of the orbitals, given in Section 2.1.

The equality of the matrix elements may be found as in the examples:

$$\begin{aligned} \langle A | u_+ | B \rangle &= \langle A | \sigma_V^0 (\sigma_V^0 u_+ \sigma_V^0) \sigma_V^0 | B \rangle \\ &= \langle A | \sigma_V^0 u_+ \sigma_V^0 | C \rangle \\ &= -\langle A | u_- | C \rangle = \lambda, \text{ say} \end{aligned}$$

and

$$\begin{aligned} \langle A | u_z | B \rangle &= \langle A | C_3^0 ((C_3^0)^2 u_z C_3^0) (C_3^0)^2 | B \rangle \\ &= \omega^2 \langle A | (C_3^0)^2 u_z C_3^0 | B \rangle \\ &= \omega^2 \langle A | u_z | B \rangle \quad \text{i.e. } \langle A | u_z | B \rangle = 0 \end{aligned}$$

Applying these arguments to all the possible matrix elements between the one-electron basis states of one ion of the pair the following matrices are obtained:

$$u_z = \left[\begin{array}{ccc|cc} 0 & 0 & 0 & 0 & 0 \\ 0 & \theta & 0 & \psi & 0 \\ 0 & 0 & -\theta & 0 & - \\ \hline 0 & \psi & 0 & \phi & 0 \\ 0 & 0 & -\psi & 0 & -\phi \end{array} \right]$$

$$u_+ = \left[\begin{array}{ccc|cc} 0 & \lambda & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & \nu \\ -\lambda & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & -\nu & 0 & 0 \\ -\mu & 0 & 0 & 0 & 0 \end{array} \right]$$

$$u_- = \left[\begin{array}{ccc|cc} 0 & 0 & -\lambda & 0 & -\mu \\ \lambda & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\nu & 0 \\ \hline \mu & 0 & 0 & 0 & 0 \\ 0 & \nu & 0 & 0 & 0 \end{array} \right]$$

where θ , ϕ and ψ and λ , μ and ν are constants.

The matrices are divided up to emphasise the fact that the orbitals are basis states of the two representations t_{2g} and e_g , and to show the way in which the two representations are connected by the operators u_z , u_+ and u_- . For instance, to generate states of the $t_{2g}^2 e_g$ configuration by the action of the orbital operators on the t_{2g}^3 configuration states then the portion of the matrix connecting the two sub-spaces must be used.

From the matrices of u_z , u_+ and u_- we can write down the effect that these operators have on the one-electron basis states:

$$\begin{aligned}
 u_z|A\rangle &= 0 & u_+|A\rangle &= -\lambda|C\rangle - \mu|E\rangle & u_-|A\rangle &= \lambda|B\rangle + \mu|D\rangle \\
 u_z|B\rangle &= \theta|B\rangle + \psi|D\rangle & u_+|B\rangle &= \lambda|A\rangle & u_-|B\rangle &= \nu|E\rangle \\
 u_z|C\rangle &= -\theta|C\rangle - \psi|E\rangle & u_+|C\rangle &= -\nu|D\rangle & u_-|C\rangle &= -\lambda|A\rangle \\
 u_z|D\rangle &= \psi|B\rangle + \phi|D\rangle & u_+|D\rangle &= \mu|A\rangle & u_-|D\rangle &= -\nu|C\rangle \\
 u_z|E\rangle &= -\psi|C\rangle - \phi|E\rangle & u_+|E\rangle &= \nu|B\rangle & u_-|E\rangle &= -\mu|A\rangle
 \end{aligned}$$

Now if a similar set of operations are carried out using the angular momentum operators l_z , l_+ and l_- and the crystal field analogues of our $|A\rangle$, $|B\rangle$, ... etc given in Section 2.1, we obtain a set of relations identical to those above if the constants have the following values: $\theta = 1$, $\phi = 0$, $\psi = \sqrt{2}$ and $\lambda = -\sqrt{2}$, $\mu = 2$ and $\nu = -2$. This result is not surprising because to arrive at the relations using u_z , u_+ and u_- we have considered properties of symmetry only, and the symmetry properties of u_z , u_+ and u_- are defined to be identical to those of l_z , l_+ and l_- . We can now define the magnitudes of u_z , u_+ and u_- operating on our one-electron orbitals to be the same as the magnitudes of l_z , l_+ and l_- operating on the crystal field analogues. The scaling factors which allow this are incorporated in the factors k_z and k_{\pm} .

Hence one defines the orbital operators by:

$$\begin{aligned}
 u_z|A\rangle &= 0 & u_+|A\rangle &= \sqrt{2}|C\rangle - 2|E\rangle & u_-|A\rangle &= -\sqrt{2}|B\rangle + 2|D\rangle \\
 u_z|B\rangle &= |B\rangle + \sqrt{2}|D\rangle & u_+|B\rangle &= -\sqrt{2}|A\rangle & u_-|B\rangle &= -2|E\rangle \\
 u_z|C\rangle &= -|C\rangle - \sqrt{2}|E\rangle & u_+|C\rangle &= 2|D\rangle & u_-|C\rangle &= \sqrt{2}|A\rangle \\
 u_z|D\rangle &= \sqrt{2}|B\rangle & u_+|D\rangle &= 2|A\rangle & u_-|D\rangle &= 2|C\rangle \\
 u_z|E\rangle &= -\sqrt{2}|C\rangle & u_+|E\rangle &= -2|B\rangle & u_-|E\rangle &= -2|A\rangle
 \end{aligned}$$

Acting on the second ion orbitals, the effects of the operators are found with the help of σ_h , $\sigma_h u_z = u_z$, $\sigma_h u_{\pm} = -u_{\pm}$, so that:

$$\begin{aligned}
 u_z |a\rangle &= 0 & u_+ |a\rangle &= -\sqrt{2}|c\rangle + 2|e\rangle & u_- |a\rangle &= \sqrt{2}|b\rangle - 2|d\rangle \\
 u_z |b\rangle &= |b\rangle + \sqrt{2}|d\rangle & u_+ |b\rangle &= \sqrt{2}|a\rangle & u_- |b\rangle &= 2|e\rangle \\
 u_z |c\rangle &= -|c\rangle - \sqrt{2}|e\rangle & u_+ |c\rangle &= -2|d\rangle & u_- |c\rangle &= -\sqrt{2}|a\rangle \\
 u_z |d\rangle &= \sqrt{2}|b\rangle & u_+ |d\rangle &= -2|a\rangle & u_- |d\rangle &= -2|c\rangle \\
 u_z |e\rangle &= -\sqrt{2}|c\rangle & u_+ |e\rangle &= 2|b\rangle & u_- |e\rangle &= 2|a\rangle
 \end{aligned}$$

5.2 FIRST ORDER PERTURBATION

We now have to evaluate all the matrix elements of H_{eff} , which are linear in spin operators between the basis states of the (${}^4A_2 \times {}^2T_1$) manifold. The effective Hamiltonian in this case is

$$H_{\text{eff}} = P_M H_{SO} P_M$$

so we must first operate on all the U, V and W states with the spin-orbit operator H_{SO} . The U, V and W states are made up of pair functions such as $|{}^2T_1, \frac{1}{2}; {}^4A_2, \frac{1}{2}\rangle$ - we can operate in turn on each of the component single ion terms with $u_z s_z$, $u_+ s_-$ and $u_- s_+$. Since in first order H_{eff} is operative within the subspace defined by the U, V and W states, we need only consider the u_z , u_+ and u_- within the subspace defined by the t_{2g} orbitals. For instance, with reference to Sections 2.3 and 5.1 we have

$$\begin{aligned}
 u_z s_z |{}^4A_2, \frac{1}{2}\rangle &= \sqrt{3} u_z s_z [(\bar{A}\bar{B}\bar{C}) + (\bar{A}\bar{B}\bar{C}) + (\bar{A}\bar{B}\bar{C})] \\
 &= \sqrt{3} [\frac{1}{2}(\bar{A}\bar{B}\bar{C}) + \frac{1}{2}(\bar{A}\bar{B}\bar{C}) - \frac{1}{2}(\bar{A}\bar{B}\bar{C}) - \frac{1}{2}(\bar{A}\bar{B}\bar{C}) + \frac{1}{2}(\bar{A}\bar{B}\bar{C}) - \frac{1}{2}(\bar{A}\bar{B}\bar{C})] \\
 &= \sqrt{3} [(\bar{A}\bar{B}\bar{C}) - (\bar{A}\bar{B}\bar{C})] \\
 &= \sqrt{3} |{}^2T_2, \frac{1}{2}\rangle
 \end{aligned}$$

It must be remembered that when using $u_+ s_-$ and $u_- s_+$ we must distinguish between the states of the first and second ions. If we operate on each of the single ion terms 4A_2 and 2T_1 with $u_z s_z$, $u_+ s_-$ and $u_- s_+$ we find

that in each case we generate states only of the 2T_2 term, the results are shown in Table 5.1:

| | $u_z s_z$ | $u_+ s_-$ | $u_- s_+$ |
|------------------------------|--|---|--|
| $ A, \frac{3}{2}\rangle$ | 0 | $\mp 2 cT_2, \frac{1}{2}\rangle$ | 0 |
| $ A, \frac{1}{2}\rangle$ | $\sqrt{\frac{2}{3}} aT_2, \frac{1}{2}\rangle$ | $\mp 2\sqrt{\frac{1}{3}} cT_2, -\frac{1}{2}\rangle$ | 0 |
| $ A, -\frac{1}{2}\rangle$ | $\sqrt{\frac{2}{3}} aT_2, -\frac{1}{2}\rangle$ | 0 | $\pm 2\sqrt{\frac{1}{3}} bT_2, \frac{1}{2}\rangle$ |
| $ A, -\frac{3}{2}\rangle$ | 0 | 0 | $\pm 2 bT_2, -\frac{1}{2}\rangle$ |
| $ aT_1, \frac{1}{2}\rangle$ | $\sqrt{\frac{1}{3}} aT_2, \frac{1}{2}\rangle$ | $\mp \sqrt{\frac{2}{3}} cT_2, -\frac{1}{2}\rangle$ | 0 |
| $ aT_1, -\frac{1}{2}\rangle$ | $-\sqrt{\frac{1}{3}} aT_2, -\frac{1}{2}\rangle$ | 0 | $\mp \sqrt{\frac{2}{3}} bT_2, \frac{1}{2}\rangle$ |
| $ bT_1, \frac{1}{2}\rangle$ | $\frac{1}{2}\sqrt{\frac{1}{3}} bT_2, \frac{1}{2}\rangle$ | $\pm \sqrt{\frac{2}{3}} aT_2, -\frac{1}{2}\rangle$ | 0 |
| $ bT_1, -\frac{1}{2}\rangle$ | $-\frac{1}{2}\sqrt{\frac{1}{3}} bT_2, -\frac{1}{2}\rangle$ | 0 | $\mp 2\sqrt{\frac{2}{3}} cT_2, \frac{1}{2}\rangle$ |
| $ cT_1, \frac{1}{2}\rangle$ | $\frac{1}{2}\sqrt{\frac{1}{3}} cT_2, \frac{1}{2}\rangle$ | $\mp 2\sqrt{\frac{2}{3}} bT_2, -\frac{1}{2}\rangle$ | 0 |
| $ cT_1, -\frac{1}{2}\rangle$ | $-\frac{1}{2}\sqrt{\frac{1}{3}} cT_2, -\frac{1}{2}\rangle$ | 0 | $\pm \sqrt{\frac{2}{3}} aT_2, \frac{1}{2}\rangle$ |

Table 5.1: $u_z s_z$, $u_+ s_-$, $u_- s_+$ on single ion states 4A_2 and 2T_1 . The \pm and \mp signs refer to the first and second ions in the pair functions.

We can apply these results to one of the basic pair states, e.g.

$$u_z s_z |aT_1, \frac{1}{2}; A, \frac{1}{2}\rangle = \sqrt{\frac{1}{3}}|aT_2, \frac{1}{2}; A, \frac{1}{2}\rangle + \sqrt{\frac{2}{3}}|aT_1, \frac{1}{2}; aT_2, \frac{1}{2}\rangle$$

$$u_+ s_- |aT_1, \frac{1}{2}; A, \frac{1}{2}\rangle = -\sqrt{\frac{2}{3}}|cT_2, -\frac{1}{2}; A, \frac{1}{2}\rangle + 2\sqrt{\frac{1}{3}}|aT_1, \frac{1}{2}; cT_2, -\frac{1}{2}\rangle$$

It is obvious from these results that if we operate on the states of the $({}^4A_2 \times {}^2T_1)$ manifold with H_{SO} only states of the $({}^4A_2 \times {}^2T_2)$ and $({}^2T_1 \times {}^2T_2)$ manifolds can possibly be generated. In conclusion it may be stated that in first-order perturbation theory there is no splitting of the $({}^4A_2 \times {}^2T_1)$ manifold due to spin-orbit coupling.

5.3 SECOND ORDER PERTURBATION

The contribution to the energy from the spin-orbit interaction taken to second order is given by the effective Hamiltonian

$$H_{\text{eff}} = - \sum_{M' \neq M} \frac{P_M H_{\text{SO}} P_{M'} H_{\text{SO}} P_M}{\bar{\epsilon}_{M'} - \bar{\epsilon}_M}$$

We shall consider H_{eff} as an operator acting from the left on the U, V and W states. Taking as an example $|V', 1, 1\rangle$, the operation by P_M leaves $|V', 1, 1\rangle$ unaltered (by definition). Then we have $H_{\text{SO}}|V', 1, 1\rangle$ which becomes a superposition of a number of states. In the last section we saw that the states of $(^4A_2 \times ^2T_1)$ are connected via the spin-orbit interaction to the states of the $(^4A_2 \times ^2T_2)$. To find the combinations of the P, Q and R states of $(^4A_2 \times ^2T_2)$ that are produced we must apply the results shown in Table 5.1 to $|V', 1, 1\rangle$ as given in Section 2.6. The resulting states must then be compared to those of P, Q and R given in Section 2.8, e.g.

$$\begin{aligned} u_{s_+} |V', 1, 1\rangle &= \frac{1}{2}\sqrt{\frac{1}{2}} u_{s_+} [\sqrt{3} |bT_1, -\frac{1}{2}; A, \frac{3}{2}\rangle - |bT_1, \frac{1}{2}; A, \frac{1}{2}\rangle - |A, \frac{1}{2}; bT_1, \frac{1}{2}\rangle \\ &\quad + \sqrt{3} |A, \frac{3}{2}; bT_1, -\frac{1}{2}\rangle] \\ &= \frac{1}{2}\sqrt{\frac{1}{2}} [\sqrt{3} \cdot -2\sqrt{\frac{2}{3}} |cT_2, \frac{1}{2}; A, \frac{3}{2}\rangle + 3 \cdot 2\sqrt{\frac{2}{3}} |A, \frac{3}{2}; cT_2, \frac{1}{2}\rangle] \\ &= - [|cT_2, \frac{1}{2}; A, \frac{3}{2}\rangle - |A, \frac{3}{2}; cT_2, \frac{1}{2}\rangle] \\ &= -\sqrt{2} |R', 2, 2\rangle \end{aligned}$$

The complete set of results for u_{s_z} , u_{s_-} and u_{s_+} acting on the unprimed U, V and W are shown in Appendix VIII(i).

The spin-orbit interaction however, connects the (U,V,W) to many other states besides P, Q and R. If we extend the range of application of the orbital operators used in Section 5.2 we can promote electrons to the e_g orbitals $|D\rangle$ and $|E\rangle$. And from states of the t_{2g}^3 configuration produce states of the $t_{2g}^2 e_g$ configuration. Now when we operate on the

2T_1 single ion states of Section 2.3 with the $u_z s_z$, $u_+ s_-$ and $u_- s_+$ (Section 5.1) we will produce a superposition of the $t_{2g}^2 e_g$ states; these are found in Section 2.4 and Appendix IV, of these we retain only the 4T_1 and 4T_2 . The results are shown in Table 5.2:

| | |
|-----------|--|
| $u_z s_z$ | $ a^2T_1, \pm\frac{1}{2}\rangle = \frac{1}{3}\sqrt{2} a^4T_2, \pm\frac{1}{2}\rangle$ $ b^2T_1, \pm\frac{1}{2}\rangle = -\sqrt{\frac{1}{2}} c^4T_1, \pm\frac{1}{2}\rangle - \frac{1}{3}\sqrt{\frac{1}{2}} c^4T_2, \pm\frac{1}{2}\rangle$ $ c^2T_1, \pm\frac{1}{2}\rangle = -\sqrt{\frac{1}{2}} b^4T_1, \pm\frac{1}{2}\rangle - \frac{1}{3}\sqrt{\frac{1}{2}} b^4T_2, \pm\frac{1}{2}\rangle$ |
| $u_+ s_-$ | $ a^2T_1, \frac{1}{2}\rangle = \mp b^4T_1, -\frac{1}{2}\rangle \pm \frac{1}{3} b^4T_2, -\frac{1}{2}\rangle$ $ a^2T_1, -\frac{1}{2}\rangle = \mp\sqrt{3} b^4T_1, -\frac{3}{2}\rangle \pm \sqrt{\frac{1}{3}} b^4T_2, -\frac{3}{2}\rangle$ $ b^2T_1, \frac{1}{2}\rangle = \mp a^4T_1, -\frac{1}{2}\rangle \pm \sqrt{\frac{1}{3}} a^4T_2, -\frac{1}{2}\rangle$ $ b^2T_1, -\frac{1}{2}\rangle = \mp\sqrt{3} a^4T_1, -\frac{3}{2}\rangle \pm \sqrt{\frac{1}{3}} a^4T_2, -\frac{3}{2}\rangle$ $ c^2T_1, \frac{1}{2}\rangle = \pm\frac{2}{3} c^4T_2, -\frac{1}{2}\rangle$ $ c^2T_1, -\frac{1}{2}\rangle = \pm 2\sqrt{\frac{1}{3}} c^4T_2, -\frac{3}{2}\rangle$ |
| $u_- s_+$ | $ a^2T_1, \frac{1}{2}\rangle = \pm\sqrt{3} c^4T_1, \frac{3}{2}\rangle \mp \sqrt{\frac{1}{3}} c^4T_2, \frac{3}{2}\rangle$ $ a^2T_1, -\frac{1}{2}\rangle = \pm c^4T_1, \frac{1}{2}\rangle \mp \frac{1}{3} c^4T_2, \frac{1}{2}\rangle$ $ b^2T_1, \frac{1}{2}\rangle = \mp 2\sqrt{\frac{1}{3}} b^4T_2, \frac{3}{2}\rangle$ $ b^2T_1, -\frac{1}{2}\rangle = \mp\frac{2}{3} b^4T_2, \frac{1}{2}\rangle$ $ c^2T_1, \frac{1}{2}\rangle = \mp\sqrt{3} a^4T_1, \frac{3}{2}\rangle \mp \sqrt{\frac{1}{3}} a^4T_2, \frac{3}{2}\rangle$ $ c^2T_1, -\frac{1}{2}\rangle = \mp a^4T_1, \frac{1}{2}\rangle \mp \frac{1}{3} a^4T_2, \frac{1}{2}\rangle$ |

Table 5.2: Combinations of 4T_1 and 4T_2 single ion states produced by spin-orbit operators acting on 2T_1 . For $u_+ s_-$ and $u_- s_+$ the \pm and \mp refer to first and second ions in pair functions.

Therefore the U, V and W are, via the spin-orbit interaction, coupled to the α , β and γ of ($^4A_2 \times ^4T_1$) and to the η , ζ and ξ of ($^4A_2 \times ^4T_2$). The linear combinations of these states that are generated by the application of the spin-orbit operators on the U, V and W unprimed

states can be found in Appendix VIII(i). They are obtained by applying the results of Table 5.2 to the states given in Section 2.6 and comparing the resulting states with those given in Section 2.9.

Thus $H_{SO}|V',1,1\rangle$ is a superposition of states belonging to the manifolds $(^4A_2 \times ^2T_2)$, $(^4A_2 \times ^4T_1)$ and $(^4A_2 \times ^4T_2)$. The next term in H_{eff} is $P_{M'}$, this picks out the states of each manifold in turn and M' adds in the correct energy denominator. For example, for M' corresponding to the $(^4A_2 \times ^2T_2)$ manifold and if we let

$$\Delta = \bar{\epsilon}(^2T_2) - \bar{\epsilon}(^2T_1)$$

then from Appendix VIII(i):

$$\frac{P_{M'} H_{SO}}{\bar{\epsilon}_{M'} - \bar{\epsilon}_M} |V',1,1\rangle = (1/\Delta) \left[-\frac{1}{2}k_z |Q',2,1\rangle - \frac{1}{2}k_z \sqrt{3} |Q',1,1\rangle - \frac{1}{2}k_{\pm} \sqrt{3} |P',2,0\rangle \right. \\ \left. - \frac{1}{2}k_{\pm} \sqrt{3} |P',1,0\rangle - k_{\pm} \sqrt{2} |R',2,2\rangle \right]$$

The second H_{SO} turns these states into another superposition of states but the next operator is P_M so only those belonging to the $(^4A_2 \times ^2T_1)$ need be retained. The linear combinations of U, V and W that are produced by the operation of $u_z s_z$, $u_+ s_-$ and $u_- s_+$ on (P,Q,R), (α, β, γ) and (η, ζ, ξ) are given in the Appendices VIII(ii), (iii) and (iv).

We shall now concentrate on the $^3E''$ multiplet and attempt to give some explanation to the pattern of energy levels found experimentally (Table 3.5). The component states of this multiplet are $\frac{1}{\sqrt{2}}[|V',1,1\rangle \pm |W',1,-1\rangle]$, (these two states shall from now on be known as $|A'_1(^3E'')\rangle$ and $|A'_2(^3E'')\rangle$), $|V'',1,0\rangle$ and $|W'',1,0\rangle$ (E'') and $|V',1,-1\rangle$ and $|W',1,1\rangle$ (E') and upon these states we shall now operate with H_{eff} . Continuing with the example of $H_{eff}|V',1,1\rangle$, with the use of Appendix VIII(ii) [$M' \equiv (^4A_2 \times ^2T_2)$], we can write down the non-zero matrix elements of H_{eff} :

$$\begin{aligned} \langle V', 1, 1 | H_{\text{eff}} | V', 1, 1 \rangle &= -(1/\Delta) \left[-\frac{1}{4}k_z(-\frac{1}{4}k_z) - \frac{1}{4}k_z\sqrt{\frac{1}{3}}(-\frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}) - \frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}(-\frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}) \right. \\ &\quad \left. - \frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}(-\frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}) - k_{\pm}\sqrt{\frac{1}{2}}(-k_{\pm}\sqrt{\frac{1}{2}}) \right] \\ &= -(1/24\Delta) [2k_z^2 + 13k_{\pm}^2] \end{aligned}$$

$$\begin{aligned} \langle V', 2, 1 | H_{\text{eff}} | V', 1, 1 \rangle &= -(1/\Delta) \left[-\frac{1}{4}k_z(\frac{1}{4}k_z\sqrt{\frac{1}{3}}) - \frac{1}{4}k_z\sqrt{\frac{1}{3}}(-\frac{1}{4}k_z) - \frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}(\frac{1}{4}k_{\pm}) \right. \\ &\quad \left. - \frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}(\frac{1}{4}k_{\pm}) - k_{\pm}\sqrt{\frac{1}{2}}(-k_{\pm}/\sqrt{6}) \right] \\ &= -\sqrt{3}(k_{\pm}^2/8\Delta) \end{aligned}$$

$$\begin{aligned} \langle U', 1, 0 | H_{\text{eff}} | V', 1, 1 \rangle &= -(1/\Delta) \left[-\frac{1}{4}k_z(-\frac{1}{4}k_{\pm}) - \frac{1}{4}k_z\sqrt{\frac{1}{3}}(\frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}) - \frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}(-k_z\sqrt{\frac{1}{3}}) \right. \\ &\quad \left. - \frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}(0) - k_{\pm}\sqrt{\frac{1}{2}}(0) \right] \\ &= -k_z k_{\pm}/8\Delta \end{aligned}$$

$$\begin{aligned} \langle U', 2, 0 | H_{\text{eff}} | V', 1, 1 \rangle &= -(1/\Delta) \left[-\frac{1}{4}k_z(-\frac{1}{4}k_{\pm}) - \frac{1}{4}k_z\sqrt{\frac{1}{3}}(\frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}) - \frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}(0) \right. \\ &\quad \left. - \frac{1}{4}k_{\pm}\sqrt{\frac{1}{3}}(-k_z\sqrt{\frac{1}{3}}) - k_{\pm}\sqrt{\frac{1}{2}}(0) \right] \\ &= -k_z k_{\pm}/8\Delta \end{aligned}$$

In a similar manner we can find all the non-zero matrix elements of H_{eff} containing the states of the ${}^3E''$ multiplet. Now $|V', 1, 1\rangle$ is not a basis state of the ${}^3E''$ multiplet, we have to use $|A'_1({}^3E'')\rangle$ and $|A'_2({}^3E'')\rangle$; this is a simple task if we evaluate the matrix elements containing $|W', 1, -1\rangle$, in the above manner, first.

We now allow M' to represent the remaining manifolds to which the ${}^3E''$ states are coupled, namely $({}^4A_2 \times {}^4T_1)$ and $({}^4A_2 \times {}^4T_2)$. In each case we have to specify the energy denominator so we define

$$\begin{aligned} \Delta_1 &= \bar{\epsilon}({}^4T_1) - \bar{\epsilon}({}^2T_1) \\ \Delta_2 &= \bar{\epsilon}({}^4T_2) - \bar{\epsilon}({}^2T_1) \end{aligned}$$

We are now in a position to state the non-zero matrix elements of H_{eff} between all the basis states of the $({}^4A_2 \times {}^2T_1)$ manifold and the states of the ${}^3E''$ multiplet. As in the explicit example for $|V', 1, 1\rangle$ when M' represents the $({}^4A_2 \times {}^2T_2)$ manifold we shall find that the off-

diagonal elements connect the $^3E''$ multiplet states with those of $^5E''$, $^3A_1'$ and $^5A_1'$ only. But first of all the diagonal elements are

$$\left. \begin{aligned} \langle A_1'(^3E'') | H_{\text{eff}} | A_1'(^3E'') \rangle \\ \langle A_2'(^3E'') | H_{\text{eff}} | A_2'(^3E'') \rangle \end{aligned} \right\} = -(k_{\pm}^2/72) [(39/\Delta) + (45/\Delta_1) + (17/\Delta_2)]$$

$$\left. \begin{aligned} \langle V'', 1, 0 | H_{\text{eff}} | V'', 1, 0 \rangle \\ \langle W'', 1, 0 | H_{\text{eff}} | W'', 1, 0 \rangle \end{aligned} \right\} = -(k_{\pm}^2/72) [(30/\Delta) + (36/\Delta_1) + (20/\Delta_2)]$$

$$\left. \begin{aligned} \langle V', 1, -1 | H_{\text{eff}} | V', 1, -1 \rangle \\ \langle W', 1, 1 | H_{\text{eff}} | W', 1, 1 \rangle \end{aligned} \right\} = -(k_{\pm}^2/72) [(21/\Delta) + (27/\Delta_1) + (23/\Delta_2)]$$

To each of these we must add the common term

$$-(k_z^2/36) [(3/\Delta) + (18/\Delta_1) + (21/\Delta_2)]$$

Thus there is a common term in k_z^2 which adds the same energy to each member of the multiplet, shifting in energy the multiplet as a whole. The multiplet is then split by the terms in k_{\pm}^2 into three equally spaced doublets. In order to fit the unequal splittings found by experiment to the theory the off-diagonal matrix elements must be taken into account and the matrix diagonalised.

The matrix elements connecting the $^3E''$ and $^5E''$ multiplets are:

$$\left. \begin{aligned} \langle A_1'(^5E'') | H_{\text{eff}} | A_1'(^3E'') \rangle \\ \langle A_2'(^5E'') | H_{\text{eff}} | A_2'(^3E'') \rangle \end{aligned} \right\} = -\sqrt{3}(k_{\pm}^2/24) [(3/\Delta) + (3/\Delta_1) - (1/\Delta_2)]$$

$$\left. \begin{aligned} \langle V'', 2, 0 | H_{\text{eff}} | V'', 1, 0 \rangle \\ \langle W'', 2, 0 | H_{\text{eff}} | W'', 1, 0 \rangle \end{aligned} \right\} = -(k_{\pm}^2/12) [(3/\Delta) + (3/\Delta_1) - (1/\Delta_2)]$$

$$\left. \begin{aligned} \langle V', 2, -1 | H_{\text{eff}} | V', 1, -1 \rangle \\ \langle W', 2, 1 | H_{\text{eff}} | W', 1, 1 \rangle \end{aligned} \right\} = -\sqrt{3}(k_{\pm}^2/24) [(3/\Delta) + (3/\Delta_1) - (1/\Delta_2)]$$

The off-diagonal elements connecting the ${}^3E''$ states with those of the ${}^3A_1'$ and ${}^5A_1'$ are:

$$\langle U', 1, 0 | H_{\text{eff}} | A_2' ({}^3E'') \rangle = -\sqrt{2}(k_z k_{\pm}/24) [(3/\Delta) + (3/\Delta_1) - (1/\Delta_2)]$$

$$\left. \begin{array}{l} \langle U'', 1, -1 | H_{\text{eff}} | V'', 1, 0 \rangle \\ \langle U'', 1, 1 | H_{\text{eff}} | W'', 1, 0 \rangle \end{array} \right\} = -(k_z k_{\pm}/24) [(3/\Delta) + (3/\Delta_1) - (1/\Delta_2)]$$

$$\langle U', 2, 0 | H_{\text{eff}} | A_1' ({}^3E'') \rangle = -\sqrt{2}(k_z k_{\pm}/24) [(3/\Delta) + (3/\Delta_1) - (1/\Delta_2)]$$

$$\left. \begin{array}{l} \langle U'', 2, -1 | H_{\text{eff}} | V'', 1, 0 \rangle \\ \langle U'', 2, 1 | H_{\text{eff}} | W'', 1, 0 \rangle \end{array} \right\} = -\sqrt{3}(k_z k_{\pm}/24) [(3/\Delta) + (3/\Delta_1) - (1/\Delta_2)]$$

$$\left. \begin{array}{l} \langle U', 2, -2 | H_{\text{eff}} | V', 1, -1 \rangle \\ \langle U', 2, 2 | H_{\text{eff}} | W', 1, 1 \rangle \end{array} \right\} = -\sqrt{6}(k_z k_{\pm}/24) [(3/\Delta) + (3/\Delta_1) - (1/\Delta_2)]$$

The contribution to the energy that is given by an off-diagonal element such as $\langle U'', 2, -1 | H_{\text{eff}} | V'', 1, 0 \rangle$ is obtained by adding to the diagonal element the term

$$- \frac{|\langle U'', 2, -1 | H_{\text{eff}} | V'', 1, 0 \rangle|^2}{E - \lambda}$$

where E is the energy of the ${}^5A_1'$ multiplet (in this case) and λ is the energy of the (E'') level of the ${}^3E''$ multiplet. We can already say the A_1' and A_2' will be split by spin-orbit coupling, since $|A_2' ({}^3E'') \rangle$ is coupled to $|U', 1, 0 \rangle$ and $|A_1' ({}^3E'') \rangle$ is coupled to $|U', 2, 0 \rangle$.

The spin-orbit operators shown in Appendix VIII act on unprimed pair states, the results shown are identical for primed and double primed states. Therefore the matrix elements found for the ${}^3E''$ multiplet states will be identical to those of the ${}^3E'$ multiplet, every prime is replaced by a double prime and vice versa. The contributions to the energy by the off-diagonal elements will be different in the two cases though as the value of $E - \lambda$ is not constant

5.4 COMPARISON WITH EXPERIMENT

We shall now compare the theoretical results given above to the experimental results using the data found in Table 3.4 and 3.5. We shall concentrate for the moment on the specific example of $\text{Cs}_3\text{Cr}_2\text{Br}_9$.

From Table 3.4 we obtain the values of Δ , Δ_1 and Δ_2 :

$$\Delta = 4600 \pm 100; \quad \Delta_1 = 2250 \pm 150; \quad \Delta_2 = -2150 \pm 150$$

With these values the diagonal matrix elements become

$$\begin{aligned} \langle A_1'(^3E'') | H_{\text{eff}} | A_1'(^3E'') \rangle &= -(2.857 \pm 0.278) \times 10^{-4} k_{\pm}^2 \\ \langle V'', 1, 0 | H_{\text{eff}} | V'', 1, 0 \rangle &= -(1.836 \pm 0.258) \times 10^{-4} k_{\pm}^2 \\ \langle V', 1, -1 | H_{\text{eff}} | V', 1, -1 \rangle &= -(0.815 \pm 0.228) \times 10^{-4} k_{\pm}^2 \end{aligned}$$

The off-diagonal elements each contain a common factor which we will call F:

$$F = (1/24) \left| (3/\Delta) + (3/\Delta_1) - (1/\Delta_2) \right|$$

The off-diagonal elements contain among them the following values:

$$\begin{aligned} F &= (1.021 \pm 0.055) \times 10^{-4} \\ 2F &= (2.042 \pm 0.110) \times 10^{-4} \\ F\sqrt{2} &= (1.443 \pm 0.078) \times 10^{-4} \\ F\sqrt{3} &= (1.768 \pm 0.095) \times 10^{-4} \\ F\sqrt{6} &= (2.500 \pm 0.135) \times 10^{-4} \end{aligned}$$

To incorporate the off-diagonal elements we have to determine the energy separations of the $^5E''$, $^3A_1'$ and $^5A_1'$ multiplets from the levels in the $^3E''$ multiplet (split by spin-orbit coupling). For instance the energy of the centre of the $^5A_1'$ multiplet is given in Table 3.5 as 14204 ± 1 and the energy of the doublet designated $E''(^3E'')$ is given as 14458 ± 1 . Therefore the contribution to the energy of the E'' doublet

by $\langle U'', 2, -1 | H_{\text{eff}} | V'', 1, 0 \rangle$ is

$$-\frac{|\langle U'', 2, -1 | H_{\text{eff}} | V'', 1, 0 \rangle|^2}{E - \lambda} = -\frac{(1.768 \pm 0.095)^2 \times 10^{-8} k^4}{(14204 - 14458 \pm 2)}$$

$$= +(1.231 \pm 0.094) \times 10^{-10} k^4$$

At this stage it will be convenient to drop the subscripts from the spin-orbit coupling parameters, we expect that k_z and k_{\pm} are unequal but we also expect their difference to be too small to make any contribution to a general test of the Stevens theory.

When we evaluated the off-diagonal elements we were able to predict that the $A'_1 + A'_2$ (${}^3E''$) doublet should be split; a look at Table 3.5 however will show that experimentally the two states are degenerate. This means that the splitting must be very small and not more than 1 cm^{-1} . Following the above procedure we arrive at the following relations concerning the energies $E(A'_1)$ and $E(A'_2)$ of the two levels:

$$E(A'_1) \equiv E + (0.826 \pm 0.066) \times 10^{-10} k^4$$

$$E(A'_2) \equiv E + (4.434 \pm 0.386) \times 10^{-10} k^4$$

where E is the sum of all terms common to both. If $|E(A'_1) - E(A'_2)| < 1$ then

$$(3.608 \pm 0.452) \times 10^{-10} k^4 < 1$$

$$k^4 < (27.72 \pm 3.48) \times 10^8$$

$$k < (229.5 \pm 7.2)$$

$$\text{i.e. } k < 236.7$$

(if we include the positive error).

This is just the sort of value we expect for k ; it represents a reduction of at least 14% over the free ion spin-orbit coupling parameter for Cr^{3+} of 275 cm^{-1} . In Section 1.3 we pointed out that for $\text{Cs}_3\text{Cr}_2\text{Br}_9$

the Racah parameter B is reduced by approximately 29% of its free ion value; we might expect a similar reduction for k . Is this value of k compatible with that required to explain the overall pattern of levels found in the ${}^3E''$ multiplet?

Before attempting to answer this question we note that the contributions made by the off-diagonal elements are very sensitive to changes in the magnitude of the energy denominators. The differences in the energies of the A_1' and A_2' pair are due solely to the off-diagonal elements $\langle U', 1, 0 | H_{\text{eff}} | A_2'({}^3E'') \rangle$ and $\langle U', 2, 0 | H_{\text{eff}} | A_1'({}^3E'') \rangle$. The experimental determination of the energies of the levels concerned $(A_1' + A_2')({}^3E'')$, $A_2'({}^3A_1')$ and $A_1'({}^5A_1')$ is accurate ($\pm 1 \text{ cm}^{-1}$); this leads to a reliable value for the energy denominators and hence the value of k is a reliable indication as to the magnitude of the spin-orbit coupling constant in the pair system $\text{Cs}_3\text{Cr}_2\text{Br}_9$. In order to predict the energy of each level in the ${}^3E''$ multiplet we have to consider the coupling of the ${}^3E''$ states with those of the ${}^5E''$ multiplet; the centre of this group of states has an energy $(14416 \pm 1) \text{ cm}^{-1}$. It is possible to make a guess as to the possible positions of the energy levels within the band but this is totally unsatisfactory. For instance if we assume that the relevant ${}^5E''$ levels all lie at 14416 ± 1 we arrive at a value for k of $(427.9 \pm 62.7) \text{ cm}^{-1}$. Then if we make a small adjustment and assume that $E''(0)({}^5E'')$ moves to 14418 ± 1 , $(A_1' + A_2')({}^5E'')$ remains at 14416 ± 1 and $E'({}^5E'')$ lies at 14407 ± 1 (chosen quite arbitrarily) we find the value of k has changed considerably to become $(372.7 \pm 27.8) \text{ cm}^{-1}$. Therefore until positive identification of the lines in the ${}^5E''$ band is made the question posed above cannot be answered.

The matrix elements that have been evaluated for the $A_1' + A_2'({}^3E'')$ pair are equally applicable to the $A_1'' + A_2''$ pair of $({}^3E')$. The difference in energy between the two levels $|E(A_1'') - E(A_2'')|$ is given by

$$\frac{|\langle U'', 1, 0 | H_{\text{eff}} | A_1''(^3E') \rangle|^2}{E(^3A_2'') - \lambda} - \frac{|\langle U'', 2, 0 | H_{\text{eff}} | A_2''(^3E') \rangle|^2}{E(^5A_2'') - \lambda}$$

where both matrix elements have the value $(F\sqrt{2})k^2$, (from Section 5.3) and from Table 3.5 $E(^3A_2'') = 14374 \pm 1$, $E(^5A_2'') = 14342 \pm 1$ and $\lambda = 14402 \pm 1$. No splitting is detected between A_1'' and A_2'' so the difference in their energy is at most 1 cm^{-1} . Therefore:

$$\begin{aligned} (3.966 \pm 1.062) \times 10^{-10} k^4 &< 1 \\ k^4 &< (25.21 \pm 6.75) \times 10^8 \\ k &< (224.1 \pm 15.0) \\ \text{i.e. } k &< 239.1 \end{aligned}$$

Thus we set another upper limit on the value of k . This value is larger than that found earlier so we quote the upper limit on the spin-orbit coupling parameter for $\text{Cs}_3\text{Cr}_2\text{Br}_9$ as being 236.7 cm^{-1} .

In a similar fashion, by the use of Section 5.3 and Tables 3.4 and 3.5 we can find the maximum value of k for the materials $\text{Rb}_3\text{Cr}_2\text{Br}_9$ and $\text{Cs}_3\text{Cr}_2\text{Cl}_9$. All the results are collected in Table 5.3:

| $\text{Cs}_3\text{Cr}_2\text{Br}_9$ | $\text{Rb}_3\text{Cr}_2\text{Br}_9$ | $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ |
|-------------------------------------|-------------------------------------|-------------------------------------|
| 236.7 cm^{-1} | 214.0 cm^{-1} | 248.3 cm^{-1} |

Table 5.3: Maximum spin-orbit coupling constants for various binuclear materials.

The Stevens theory has scored a limited success by predicting a value of spin-orbit coupling constant similar to the value anticipated. The further predictions of the pattern of energy levels are not possible due to insufficient data. However all the required theoretical tools necessary for such predictions are presented here awaiting further

experimental results.

5.5 THE ZEEMAN EFFECT

The effect of external magnetic fields on the energy states of the ion pair will now be investigated. If an atomic ion is subjected to a magnetic field then the atomic electrons by virtue of their magnetic orbital and spin moments can interact with the field. In a magnetic field \underline{B} the term H_Z giving the magnetic energy

$$H_Z = \sum_i \beta [\underline{B} \cdot (\underline{L} + 2\underline{S})]_i$$

must be added to the Hamiltonian. Here β is the Bohr magneton.

We now have to modify H_Z so that it is applicable to the pair system. The spin magnetic moment is insensitive to the influences of the environment of the metal ion but the orbital moment is not. With the same considerations that were given to defining the spin-orbit operation in Section 5.1 we shall describe the coupling of the orbital moments to the external field by

$$\sum_i \beta [g_3 B_z u_z + \frac{1}{2} g_1 (B_+ u_- + B_- u_+)]_i$$

where g_1 and g_3 are the orbital g-factors (for a free ion, $g_1 = g_3 = 1$). The 'orbital' operators u_z , u_+ and u_- were defined in Section 5.1. The coupling of the spin moments has the form

$$2\beta \underline{B} \cdot \underline{S}$$

The Zeeman Hamiltonian H_Z is the sum of these two terms.

Experimentally one studies the effect of the magnetic field with the field either parallel or perpendicular to the major axis of the crystal, the z-axis; we may split H_Z into two parts $H_Z^{(z)}$ and $H_Z^{(\pm)}$. We make the further approximation replacing B_+ and B_- by B_{\pm} and write:

$$H_Z^{(z)} = \sum_i \beta B_z (g_z u_z + 2s_z)_i$$

$$H_Z^{(\pm)} = \sum_i \beta B_{\pm} \left[\frac{1}{2} g_{\pm} (u_+ + u_-) + (s_+ + s_-) \right]_i$$

The separations within a given multiplet due to a field along the z-axis may be expressed in the form $g_z \beta B_z$. For the field perpendicular to z-axis the splittings can be expressed in the form $g_{\pm} \beta B_{\pm}$. Now g_z and g_{\pm} are spectroscopic splitting factors, whose values are determined experimentally.

The 'orbital' operators u_z , u_+ and u_- and their operations on the electronic orbitals have already been discussed in Section 5.1. We have yet to define their action when operating on the (U,V,W) pair states; these can be found in Table 5.4. The results given are for

| | u_z | u_+ | u_- |
|--------------|---------------|------------------------|------------------------|
| $ U'\rangle$ | 0 | $\sqrt{2} W''\rangle$ | $-\sqrt{2} V''\rangle$ |
| $ V'\rangle$ | $- V'\rangle$ | $-\sqrt{2} U''\rangle$ | 0 |
| $ W'\rangle$ | $ W'\rangle$ | 0 | $\sqrt{2} U''\rangle$ |

Table 5.4: u_z , u_+ and u_- acting on the primed (U,V,W).

primed states, to obtain the corresponding results for double primed states each prime is replaced by a double prime and vice versa. Only those states belonging to (${}^4A_2 \times {}^2T_1$) are retained in Table 5.4.

The spin operators S_z , S_+ and S_- have their usual effect on spin states; we remember also that S_{\pm} changes the σ_h nature of the state upon which it operates (see Section 2.5).

5.6 MAGNETIC FIELD PARALLEL TO CRYSTAL AXIS

The effective Hamiltonian is to first order

$$H_{\text{eff}} = P_M H_Z^{(z)} P_M$$

where M represents the states of the (${}^4A_2 \times {}^2T_1$) manifold and

$$H_Z^{(z)} = \sum_i \beta B_Z (g_3 u_z + 2s_z)_i$$

Firstly considering the orbital singlets, we find that all the off-diagonal elements are zero. The diagonal terms have for the general U state the value:

$$\langle U, S, M_S | H_Z^{(z)} | U, S, M_S \rangle = 2M_S \beta B_Z$$

Thus we predict that in first order the U states should show a spin only g value.

For the orbital doublets one also finds that the only non-zero matrix elements are the diagonal elements; these have the values:

$$\begin{aligned} \langle V, S, M_S | H_Z^{(z)} | V, S, M_S \rangle &= (-g_3 + 2M_S) \beta B_Z \\ \langle W, S, M_S | H_Z^{(z)} | W, S, M_S \rangle &= (g_3 + 2M_S) \beta B_Z \end{aligned}$$

If we apply these results to the $S = 1$ multiplets we see that the orbital and spin contributions are additive in the case of E (± 1), and for the A-states the orbital contribution subtracts from the spin contribution. The observed splitting factors should be very different from one another.

5.7 MAGNETIC FIELD PERPENDICULAR TO THE CRYSTAL AXIS

When the magnetic field is applied perpendicularly to the z axis we must use the following Hamiltonian

$$H_Z^{(\pm)} = \sum_i \beta B_{\pm} \left[\frac{1}{2} g_1 (u_+ + u_-) + (s_+ + s_-) \right]_i$$

in the first term of H_{eff} :

$$H_{\text{eff}} = P_M H_Z^{(\pm)} P_M$$

From Table 5.4 we see that the orbital operators mix states of the U and (V,W) families. However within any multiplet no states are coupled by the orbital operators, so we expect that the splitting factors observed in experiment should be primarily free-spin values.

Firstly we will consider the ${}^3A_2''$ multiplet. The non-zero matrix elements of H_{eff} between the states of this multiplet are:

$$\langle U'', 1, 0 | H_{\text{eff}} | U', 1, 1 \rangle = \sqrt{2} \beta B_{\pm}$$

$$\langle U', 1, 1 | H_{\text{eff}} | U'', 1, 0 \rangle = \sqrt{2} \beta B_{\pm}$$

$$\langle U', 1, -1 | H_{\text{eff}} | U'', 1, 0 \rangle = \sqrt{2} \beta B_{\pm}$$

$$\langle U'', 1, 0 | H_{\text{eff}} | U', 1, -1 \rangle = \sqrt{2} \beta B_{\pm}$$

Our U functions are no longer eigenstates of the Hamiltonian. It is a simple matter to diagonalise this matrix to obtain the new basis states of ${}^3A_2''$ when a magnetic field. (The symmetry is reduced to C_2 or C_s). On diagonalising the matrix we obtain three functions $|1\rangle$, $|2\rangle$ and $|3\rangle$.

$$|1\rangle = \frac{1}{\sqrt{2}} [|U', 1, 1\rangle - |U', 1, -1\rangle]$$

$$|2\rangle = \frac{1}{2} [|U', 1, 1\rangle + \sqrt{2} |U'', 1, 0\rangle + |U', 1, -1\rangle]$$

$$|3\rangle = \frac{1}{2} [|U', 1, 1\rangle - \sqrt{2} |U'', 1, 0\rangle + |U', 1, -1\rangle]$$

and now between these new functions we find the following matrix elements of H_{eff} :

$$\langle 1 | H_{\text{eff}} | 1 \rangle = 0$$

$$\langle 2 | H_{\text{eff}} | 2 \rangle = 2\beta B_{\pm}$$

$$\langle 3 | H_{\text{eff}} | 3 \rangle = -2\beta B_{\pm}$$

Similarly we may compute the non-zero matrix elements of H_{eff} within the basis formed by the orbital doublets, say ${}^3E''$, i.e. between the states $|A'_1 + A'_2\rangle = \frac{1}{2} [|V', 1, 1\rangle \pm |W', 1, -1\rangle]$, $|V'', 1, 0\rangle$, $|W'', 1, 0\rangle$, $|V', 1, -1\rangle$ and $|W', 1, 1\rangle$. If we diagonalise this matrix we find the following six functions:

$$|1'\rangle = \frac{1}{2}\sqrt{\frac{1}{2}} [\sqrt{2} |A'_1\rangle + \sqrt{2} |A'_2\rangle - 2 |V', 1, -1\rangle]$$

$$|2'\rangle = \frac{1}{2}\sqrt{\frac{1}{2}} [\sqrt{2} |A'_1\rangle - \sqrt{2} |A'_2\rangle - 2 |W', 1, 1\rangle]$$

$$|3'\rangle = \frac{1}{2}\sqrt{\frac{1}{2}} [\sqrt{2} |A'_1\rangle - \sqrt{2} |V'', 1, 0\rangle - \sqrt{2} |W'', 1, 0\rangle + |V', 1, -1\rangle + |W', 1, 1\rangle]$$

$$|4'\rangle = \frac{1}{2}\sqrt{\frac{1}{2}} [\sqrt{2} |A'_2\rangle - \sqrt{2} |V'', 1, 0\rangle + \sqrt{2} |W'', 1, 0\rangle + |V', 1, -1\rangle - |W', 1, 1\rangle]$$

$$|5'\rangle = \frac{1}{2}\sqrt{\frac{1}{2}} [\sqrt{2} |A'_1\rangle + \sqrt{2} |V'', 1, 0\rangle + \sqrt{2} |W'', 1, 0\rangle + |V', 1, -1\rangle + |W', 1, 1\rangle]$$

$$|6'\rangle = \frac{1}{2}\sqrt{\frac{1}{2}} [\sqrt{2} |A'_2\rangle + \sqrt{2} |V'', 1, 0\rangle - \sqrt{2} |W'', 1, 0\rangle + |V', 1, -1\rangle - |W', 1, 1\rangle]$$

And the expectation value of H_{eff} between these:

$$\langle 1' | H_{\text{eff}} | 1' \rangle = \langle 2' | H_{\text{eff}} | 2' \rangle = 0$$

$$\langle 3' | H_{\text{eff}} | 3' \rangle = \langle 4' | H_{\text{eff}} | 4' \rangle = -2\beta B_{\pm}$$

$$\langle 5' | H_{\text{eff}} | 5' \rangle = \langle 6' | H_{\text{eff}} | 6' \rangle = +2\beta B_{\pm}$$

We have ignored any differences in energy between the three doublets of this multiplet, differences that have come about because of spin-orbit coupling. Thus the new basis states and the predicted splittings are for large magnetic fields only.

We have diagonalised these matrices without consideration of the elements connecting the U and (V,W) families. That part of the larger

matrix (formed by using the states of ${}^3E''$ and ${}^3A_1'$ multiplets as basis states) connecting the two multiplets has the following form:

$$\begin{aligned} \langle U'', 1, 1 | H_{\text{eff}} | V', 1, 1 \rangle &= -X \\ \langle U'', 1, 1 | H_{\text{eff}} | W', 1, 1 \rangle &= X \\ \langle U', 1, 0 | H_{\text{eff}} | V'', 1, 0 \rangle &= -X \\ \langle U', 1, 0 | H_{\text{eff}} | W'', 1, 0 \rangle &= X \\ \langle U'', 1, -1 | H_{\text{eff}} | W', 1, -1 \rangle &= X \\ \langle U'', 1, -1 | H_{\text{eff}} | V', 1, -1 \rangle &= -X \end{aligned}$$

where $X = \sqrt{\frac{1}{2}} g_1 \beta B_{\pm}$. The amount of orbital contribution to the splitting factor is largely determined, in perpendicular field, by the energy separation of the two connected multiplets. The contribution being of the form $-\frac{1}{2}(g_1 \beta B_{\pm})^2 / (E - \lambda)$, $(E - \lambda)$ being the energy difference.

Nothing new is found when we consider the $S = 2$ states. The basis states of the $S = 2$ multiplets which lead to a diagonal matrix of H_{eff} are given in Appendix IX. All the considerations that were given to the $S = 1$ case apply, the spin-orbit splittings have been ignored and the matrix elements connecting different multiplets have also been ignored.

How do these theoretical predictions compare with the results of a Zeeman experiment? We shall briefly consider the observed splittings of the $E'(\pm 1)({}^3A_2'')$ doublet, in both parallel and perpendicular fields. The splitting factors for $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ are $g_z = 1.9 \pm 0.2$ and $g_{\pm} = 1.7 \pm 0.2$ [30] while for $\text{Cs}_3\text{Cr}_2\text{Br}_9$ we have $g_z = 1.42 \pm 0.08$ and $g_{\pm} = 1.39 \pm 0.08$ [33]. In the latter case the g -factors are obviously much reduced from the predicted spin only values. This indicates in the case of g_z a strong spin-orbit coupling between the U and the (V, W) states.

APPENDIX I

TABLES FOR SYMMETRY GROUPS

(i) CHARACTER TABLE OF THE O_h SYMMETRY GROUP

| O_h | E | $8C_3$ | $3C_2$ | $6C_4$ | $6C'_2$ |
|-------|---|--------|--------|--------|---------|
| A_1 | 1 | 1 | 1 | 1 | 1 |
| A_2 | 1 | 1 | 1 | -1 | -1 |
| E | 2 | -1 | 2 | 0 | 0 |
| T_1 | 3 | 0 | -1 | 1 | -1 |
| T_2 | 3 | 0 | -1 | -1 | 1 |

(ii) CHARACTER TABLE OF THE D_{3h} SYMMETRY GROUP

| D_{3h} | E | $2C_3$ | $3C_2$ | σ_h | $2S_3$ | $3\sigma_h$ |
|----------|---|--------|--------|------------|--------|-------------|
| A'_1 | 1 | 1 | 1 | 1 | 1 | 1 |
| A'_2 | 1 | 1 | -1 | 1 | 1 | -1 |
| A''_1 | 1 | 1 | 1 | -1 | -1 | -1 |
| A''_2 | 1 | 1 | -1 | -1 | -1 | 1 |
| E' | 2 | -1 | 0 | 2 | -1 | 0 |
| E'' | 2 | -1 | 0 | -2 | 1 | 0 |

(iii) CHARACTER TABLE OF THE C_{3h} SYMMETRY GROUP

| C_{3h} | E | C_3 | C_3^2 | σ_h | S_3 | $\sigma_h C_3^2$ |
|----------|---|------------|------------|------------|-------------|------------------|
| A' | 1 | 1 | 1 | 1 | 1 | 1 |
| A'' | 1 | 1 | 1 | -1 | -1 | -1 |
| E'_- | 1 | ω | ω^2 | 1 | ω | ω^2 |
| E'_+ | 1 | ω^2 | ω | 1 | ω^2 | ω |
| E''_- | 1 | ω | ω^2 | -1 | $-\omega$ | $-\omega^2$ |
| E''_+ | 1 | ω^2 | ω | -1 | $-\omega^2$ | $-\omega$ |

(iv) MULTIPLICATION TABLE FOR THE D_{3h} SYMMETRY GROUP

| | A'_1 | A'_2 | A''_1 | A''_2 | E' | E'' |
|---------|---------|---------|---------|---------|-----------------------|-----------------------|
| A'_1 | A'_1 | A'_2 | A''_1 | A''_2 | E' | E'' |
| A'_2 | A'_2 | A'_1 | A''_2 | A''_1 | E' | E'' |
| A''_1 | A''_1 | A''_2 | A'_1 | A'_2 | E'' | E' |
| A''_2 | A''_2 | A''_1 | A'_2 | A'_1 | E'' | E' |
| E' | E' | E' | E'' | E'' | $A'_1 + A'_2 + E'$ | $A''_1 + A''_2 + E''$ |
| E'' | E'' | E'' | E' | E' | $A''_1 + A''_2 + E''$ | $A'_1 + A'_2 + E'$ |

(v) MULTIPLICATION TABLE FOR THE C_{3h} SYMMETRY GROUP

| | A' | A'' | E' ₋ | E' ₊ | E'' ₋ | E'' ₊ |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| A' | A' | A'' | E' ₋ | E' ₊ | E'' ₋ | E'' ₊ |
| A'' | A'' | A' | E'' ₋ | E'' ₊ | E' ₋ | E' ₊ |
| E' ₋ | E' ₋ | E'' ₋ | E' ₊ | A' | E'' ₊ | A'' |
| E' ₊ | E' ₊ | E'' ₊ | A' | E' ₋ | A'' | E'' ₋ |
| E'' ₋ | E'' ₋ | E' ₋ | E'' ₊ | A'' | E' ₊ | A' |
| E'' ₊ | E'' ₊ | E' ₊ | A'' | E'' ₋ | A' | E' ₋ |

APPENDIX II

TRANSFORMATION PROPERTIES OF ONE-ELECTRON ORBITALS IN O_h SYMMETRY

The crystal field analogues of $|A\rangle$, $|B\rangle$, $|C\rangle$, $|D\rangle$ and $|E\rangle$ are:

$$|A\rangle \equiv d_0$$

$$|B\rangle \equiv -\sqrt{\frac{1}{3}}d_{-1} + \sqrt{\frac{2}{3}}d_2$$

$$|C\rangle \equiv \sqrt{\frac{1}{3}}d_1 + \sqrt{\frac{2}{3}}d_{-2}$$

$$|D\rangle \equiv \sqrt{\frac{2}{3}}d_{-1} + \sqrt{\frac{1}{3}}d_2$$

$$|E\rangle \equiv -\sqrt{\frac{2}{3}}d_1 + \sqrt{\frac{1}{3}}d_{-2}$$

and under O_h symmetry operators they transform as shown in the following table [37]

| E | $8C_3$ | $3C_2$ | $6C_4$ | $6C'_2$ |
|-------------|---------------------|---|---|-------------|
| $ A\rangle$ | $ A\rangle$ | $-\frac{1}{3} A\rangle + \frac{2}{3} B\rangle + \frac{2}{3} C\rangle$ | $-\frac{1}{3} A\rangle - (\frac{1}{3}-i\sqrt{\frac{1}{3}}) B\rangle - (\frac{1}{3}+i\sqrt{\frac{1}{3}}) C\rangle$ | $ A\rangle$ |
| $ B\rangle$ | $\omega B\rangle$ | $\frac{2}{3} A\rangle - \frac{1}{3} B\rangle + \frac{2}{3} C\rangle$ | $-(\frac{1}{3}+i\sqrt{\frac{1}{3}}) B\rangle - \frac{1}{3} C\rangle - (\frac{1}{3}-i\sqrt{\frac{1}{3}}) A\rangle$ | $ C\rangle$ |
| $ C\rangle$ | $\omega^2 C\rangle$ | $\frac{2}{3} A\rangle + \frac{2}{3} B\rangle - \frac{1}{3} C\rangle$ | $-\frac{1}{3} B\rangle - (\frac{1}{3}+i\sqrt{\frac{1}{3}}) A\rangle - (\frac{1}{3}-i\sqrt{\frac{1}{3}}) C\rangle$ | $ B\rangle$ |
| $ D\rangle$ | $\omega D\rangle$ | $ D\rangle$ | $ E\rangle$ | $ E\rangle$ |
| $ E\rangle$ | $\omega E\rangle$ | $ E\rangle$ | $ D\rangle$ | $ D\rangle$ |
| 5 | -1 | 1 | -1 | 1 |

APPENDIX III

TRANSFORMATION PROPERTIES OF t_{2g}^3 DOUBLET FUNCTIONS IN O_h SYMMETRY

In Section 2.3 the t_{2g}^3 doublet functions were introduced:

$$\begin{aligned} |1\rangle &= (1/\sqrt{6}) [(\bar{A}^+\bar{B}^-\bar{C}) + (\bar{A}^-\bar{B}^+\bar{C}) - 2(\bar{A}^+\bar{B}^+\bar{C})], & |2\rangle &= \sqrt{2} [(\bar{A}^+\bar{B}^-\bar{C}) - (\bar{A}^-\bar{B}^+\bar{C})], \\ |3\rangle &= (\bar{A}^+\bar{A}^+\bar{B}), & |4\rangle &= (\bar{A}^+\bar{A}^+\bar{C}), & |5\rangle &= (\bar{A}^+\bar{B}^+\bar{B}) \\ |6\rangle &= (\bar{B}^+\bar{B}^-\bar{C}), & |7\rangle &= (\bar{A}^+\bar{C}^-\bar{C}), & |8\rangle &= (\bar{B}^+\bar{C}^-\bar{C}); \end{aligned}$$

these have the following transformation properties:

| E | $8C_3$ | $3C_2$ | $6C'_2$ |
|-------------|---------------------|---|--------------|
| $ 1\rangle$ | $ 1\rangle$ | $-\frac{1}{3} 1\rangle - \frac{2}{3}(1/\sqrt{6}) [3\rangle - 4\rangle + 2 5\rangle + 6\rangle - 2 7\rangle - 8\rangle]$ | $- 1\rangle$ |
| $ 2\rangle$ | $ 2\rangle$ | $-\frac{1}{3} 2\rangle + \frac{2}{3}\sqrt{2} [3\rangle + 4\rangle - 6\rangle - 8\rangle]$ | $ 2\rangle$ |
| $ 3\rangle$ | $\omega 3\rangle$ | $-(1/9)\sqrt{6} 1\rangle + \frac{1}{3}\sqrt{2} 2\rangle$ $+(1/9) [3\rangle + 2 4\rangle + 2 5\rangle + 4 6\rangle + 4 7\rangle - 4 8\rangle]$ | $ 4\rangle$ |
| $ 4\rangle$ | $\omega^2 4\rangle$ | $(1/9)\sqrt{6} 1\rangle + \frac{1}{3}\sqrt{2} 2\rangle$ $+(1/9) [2 3\rangle + 4\rangle + 4 5\rangle - 4 6\rangle + 2 7\rangle + 4 8\rangle]$ | $ 3\rangle$ |
| $ 5\rangle$ | $\omega^2 5\rangle$ | $-(2/9)\sqrt{6} 1\rangle$ $+(1/9) [2 3\rangle + 4 4\rangle + 5\rangle + 2 6\rangle - 4 7\rangle + 4 8\rangle]$ | $ 7\rangle$ |
| $ 6\rangle$ | $\omega 6\rangle$ | $-(1/9)\sqrt{6} 1\rangle - \frac{1}{3}\sqrt{2} 2\rangle$ $+(1/9) [4 3\rangle - 4 4\rangle + 2 5\rangle + 6\rangle + 4 7\rangle + 2 8\rangle]$ | $ 8\rangle$ |
| $ 7\rangle$ | $\omega 7\rangle$ | $(2/9)\sqrt{6} 1\rangle$ $+(1/9) [4 3\rangle + 2 4\rangle - 4 5\rangle + 4 6\rangle + 7\rangle + 2 8\rangle]$ | $ 5\rangle$ |
| $ 8\rangle$ | $\omega^2 8\rangle$ | $(1/9)\sqrt{6} 1\rangle - \frac{1}{3}\sqrt{2} 2\rangle$ $+(1/9) [-4 3\rangle + 4 4\rangle + 4 5\rangle + 2 6\rangle + 2 7\rangle + 8\rangle]$ | $ 6\rangle$ |
| 8 | -1 | 0 | 0 |

The eight doublet functions of the t_{2g} configuration transform among themselves under C_4 of the O_h group in the following manner:

| | C_4 |
|-------------|--|
| $ 1\rangle$ | $\frac{1}{3} 1\rangle - (\frac{1}{3} - i\sqrt{\frac{1}{3}})(1/\sqrt{6})[3\rangle + 6\rangle - 2 7\rangle] - (\frac{1}{3} + i\sqrt{\frac{1}{3}})(1/\sqrt{6})[- 4\rangle + 2 5\rangle - 8\rangle]$ |
| $ 2\rangle$ | $-\frac{1}{3} 2\rangle - (\frac{1}{3} - i\sqrt{\frac{1}{3}})\sqrt{\frac{1}{2}}[3\rangle - 6\rangle] - (\frac{1}{3} + i\sqrt{\frac{1}{3}})\sqrt{\frac{1}{2}}[4\rangle - 8\rangle]$ |
| $ 3\rangle$ | $(\frac{1}{3} - i\sqrt{\frac{1}{3}})[-(1/\sqrt{6}) 1\rangle - \sqrt{\frac{1}{2}} 2\rangle] - \frac{1}{3}(\frac{1}{3} + i\sqrt{\frac{1}{3}})[3\rangle - 2 6\rangle + 7\rangle] + (1/9)[4\rangle + 4 5\rangle + 4 8\rangle]$ |
| $ 4\rangle$ | $(\frac{1}{3} + i\sqrt{\frac{1}{3}})[(1/\sqrt{6}) 1\rangle - \sqrt{\frac{1}{2}} 2\rangle] + (1/9)[3\rangle + 4 6\rangle + 4 7\rangle] - \frac{1}{3}(\frac{1}{3} - i\sqrt{\frac{1}{3}})[4\rangle + 5\rangle - 2 8\rangle]$ |
| $ 5\rangle$ | $-(\frac{1}{3} + i\sqrt{\frac{1}{3}}) \cdot \frac{1}{3}\sqrt{6} 1\rangle + (1/9)[4 3\rangle + 4 6\rangle + 7\rangle] - \frac{1}{3}(\frac{1}{3} - i\sqrt{\frac{1}{3}})[4\rangle - 2 5\rangle + 8\rangle]$ |
| $ 6\rangle$ | $(\frac{1}{3} - i\sqrt{\frac{1}{3}})[-(1/\sqrt{6}) 1\rangle + \sqrt{\frac{1}{2}} 2\rangle] + \frac{1}{3}(\frac{1}{3} + i\sqrt{\frac{1}{3}})[2 3\rangle - 6\rangle + 7\rangle]$ $+ (1/9)[4 4\rangle + 4 5\rangle + 8\rangle]$ |
| $ 7\rangle$ | $(\frac{1}{3} - i\sqrt{\frac{1}{3}}) \cdot \frac{1}{3}\sqrt{6} 1\rangle - \frac{1}{3}(\frac{1}{3} + i\sqrt{\frac{1}{3}})[3\rangle + 6\rangle - 2 7\rangle] + (1/9)[4 4\rangle + 5\rangle + 4 8\rangle]$ |
| $ 8\rangle$ | $(\frac{1}{3} + i\sqrt{\frac{1}{3}})[(1/\sqrt{6}) 1\rangle + \sqrt{\frac{1}{2}} 2\rangle] + (1/9)[4 3\rangle + 6\rangle + 4 7\rangle + \frac{1}{3}(\frac{1}{3} - i\sqrt{\frac{1}{3}})[2 4\rangle - 5\rangle - 8\rangle]$ |
| χ | 0 |

The functions $|1\rangle$ to $|8\rangle$ span the representation of O_h containing the irreducible components

$$E + T_1 + T_2$$

By the method of 'trial and error' one finds the combinations to span the irreducible representations. The component vectors of T_1 are

$$\begin{aligned} &|1\rangle \\ &(1/\sqrt{6})[|3\rangle + |6\rangle - 2|7\rangle] \\ &(1/\sqrt{6})[-|4\rangle + 2|5\rangle - |8\rangle] \end{aligned}$$

of T_2 are

$$\begin{aligned} &|2\rangle \\ &\sqrt{\frac{1}{2}}[|3\rangle - |6\rangle] \\ &\sqrt{\frac{1}{2}}[|4\rangle - |8\rangle] \end{aligned}$$

and those of E are

$$\sqrt{\frac{1}{3}}[|3\rangle + |6\rangle + |7\rangle]$$

$$\sqrt{\frac{1}{3}}[|4\rangle + |5\rangle + |8\rangle]$$

These are written as determinantal functions in Section 2.3.

APPENDIX IV

TRANSFORMATION PROPERTIES OF $t_{2g}^2 e_g$ DOUBLET FUNCTIONS IN O_h SYMMETRY

The eighteen $t_{2g}^2 e_g$ doublet functions with $M_S = \frac{1}{2}$, referred to in Section 2.4 are here labelled with the numbers 1 to 18 and have the following form:-

$$\begin{aligned}
 |1\rangle &= (1/\sqrt{6}) [-2(\overset{+}{A}\overset{+}{B}\overset{-}{D}) + (\overset{+}{A}\overset{-}{B}\overset{+}{D}) + (\overset{-}{A}\overset{+}{B}\overset{+}{D})] \\
 |2\rangle &= \sqrt{\frac{1}{2}} [(\overset{+}{A}\overset{-}{B}\overset{+}{D}) - (\overset{-}{A}\overset{+}{B}\overset{+}{D})] \\
 |3\rangle &= (1/\sqrt{6}) [-2(\overset{+}{A}\overset{+}{B}\overset{-}{E}) + (\overset{+}{A}\overset{-}{B}\overset{+}{E}) + (\overset{-}{A}\overset{+}{B}\overset{+}{E})] \\
 |4\rangle &= \sqrt{\frac{1}{2}} [(\overset{+}{A}\overset{-}{B}\overset{+}{E}) - (\overset{-}{A}\overset{+}{B}\overset{+}{E})] \\
 |5\rangle &= (1/\sqrt{6}) [-2(\overset{+}{A}\overset{+}{C}\overset{-}{D}) + (\overset{+}{A}\overset{-}{C}\overset{+}{D}) + (\overset{-}{A}\overset{+}{C}\overset{+}{D})] \\
 |6\rangle &= \sqrt{\frac{1}{2}} [(\overset{+}{A}\overset{-}{C}\overset{+}{D}) - (\overset{-}{A}\overset{+}{C}\overset{+}{D})] \\
 |7\rangle &= (1/\sqrt{6}) [-2(\overset{+}{A}\overset{+}{C}\overset{-}{E}) + (\overset{+}{A}\overset{-}{C}\overset{+}{E}) + (\overset{-}{A}\overset{+}{C}\overset{+}{E})] \\
 |8\rangle &= \sqrt{\frac{1}{2}} [(\overset{+}{A}\overset{-}{C}\overset{+}{E}) - (\overset{-}{A}\overset{+}{C}\overset{+}{E})] \\
 |9\rangle &= (1/\sqrt{6}) [-2(\overset{+}{B}\overset{+}{C}\overset{-}{D}) + (\overset{+}{B}\overset{-}{C}\overset{+}{D}) + (\overset{-}{B}\overset{+}{C}\overset{+}{D})] \\
 |10\rangle &= \sqrt{\frac{1}{2}} [(\overset{+}{B}\overset{-}{C}\overset{+}{D}) - (\overset{-}{B}\overset{+}{C}\overset{+}{D})] \\
 |11\rangle &= (1/\sqrt{6}) [-2(\overset{+}{B}\overset{+}{C}\overset{-}{E}) + (\overset{+}{B}\overset{-}{C}\overset{+}{E}) + (\overset{-}{B}\overset{+}{C}\overset{+}{E})] \\
 |12\rangle &= \sqrt{\frac{1}{2}} [(\overset{+}{B}\overset{-}{C}\overset{+}{E}) - (\overset{-}{B}\overset{+}{C}\overset{+}{E})] \\
 |13\rangle &= (\overset{+}{A}\overset{-}{A}\overset{+}{D}) \\
 |14\rangle &= (\overset{+}{A}\overset{-}{A}\overset{+}{E}) \\
 |15\rangle &= (\overset{+}{B}\overset{-}{B}\overset{+}{D}) \\
 |16\rangle &= (\overset{+}{B}\overset{-}{B}\overset{+}{E}) \\
 |17\rangle &= (\overset{+}{C}\overset{-}{C}\overset{+}{D}) \\
 |18\rangle &= (\overset{+}{C}\overset{-}{C}\overset{+}{E})
 \end{aligned}$$

Under the symmetry operators of O_h group they transform as shown in the following tables.

| E | $8C_3$ | $3C_2$ | $6C'_2$ |
|--------------|-----------------------|---|---------------|
| $ 1\rangle$ | $\omega^2 1\rangle$ | $\frac{1}{3} [- 1\rangle - 2 5\rangle + 2 9\rangle]$ | $ 7\rangle$ |
| $ 2\rangle$ | $\omega^2 2\rangle$ | $(1/9) [5 2\rangle + 2 6\rangle + 2 10\rangle - 2\sqrt{2} 13\rangle - 2\sqrt{2} 15\rangle + 4\sqrt{2} 17\rangle]$ | $ 8\rangle$ |
| $ 3\rangle$ | $ 3\rangle$ | $\frac{1}{3} [- 3\rangle - 2 7\rangle + 2 11\rangle]$ | $ 5\rangle$ |
| $ 4\rangle$ | $ 4\rangle$ | $(1/9) [5 4\rangle + 2 8\rangle + 2 12\rangle - 2\sqrt{2} 14\rangle - 2\sqrt{2} 16\rangle + 4\sqrt{2} 18\rangle]$ | $ 6\rangle$ |
| $ 5\rangle$ | $ 5\rangle$ | $\frac{1}{3} [-2 1\rangle - 5\rangle - 9\rangle]$ | $ 3\rangle$ |
| $ 6\rangle$ | $ 6\rangle$ | $(1/9) [2 2\rangle + 5 6\rangle + 2 10\rangle - 2\sqrt{2} 13\rangle + 4\sqrt{2} 15\rangle - 2\sqrt{2} 17\rangle]$ | $ 4\rangle$ |
| $ 7\rangle$ | $\omega 7\rangle$ | $\frac{1}{3} [-2 3\rangle - 7\rangle - 11\rangle]$ | $ 1\rangle$ |
| $ 8\rangle$ | $\omega 8\rangle$ | $(1/9) [2 4\rangle + 5 8\rangle + 2 12\rangle - 2\sqrt{2} 14\rangle + 4\sqrt{2} 16\rangle - 2\sqrt{2} 18\rangle]$ | $ 2\rangle$ |
| $ 9\rangle$ | $\omega 9\rangle$ | $\frac{1}{3} [2 1\rangle - 2 5\rangle - 9\rangle]$ | $- 11\rangle$ |
| $ 10\rangle$ | $\omega 10\rangle$ | $(1/9) [2 2\rangle + 2 6\rangle + 5 10\rangle + 4\sqrt{2} 13\rangle - 2\sqrt{2} 15\rangle - 2\sqrt{2} 17\rangle]$ | $ 12\rangle$ |
| $ 11\rangle$ | $\omega^2 11\rangle$ | $\frac{1}{3} [2 3\rangle - 2 7\rangle - 11\rangle]$ | $- 9\rangle$ |
| $ 12\rangle$ | $\omega^2 12\rangle$ | $(1/9) [2 4\rangle + 2 8\rangle + 5 12\rangle + 4\sqrt{2} 14\rangle - 2\sqrt{2} 16\rangle - 2\sqrt{2} 18\rangle]$ | $ 10\rangle$ |
| $ 13\rangle$ | $\omega 13\rangle$ | $(1/9) [-2\sqrt{2} 2\rangle - 2\sqrt{2} 6\rangle + 4\sqrt{2} 10\rangle + 13\rangle + 4 15\rangle + 4 17\rangle]$ | $ 14\rangle$ |
| $ 14\rangle$ | $\omega^2 14\rangle$ | $(1/9) [-2\sqrt{2} 4\rangle - 2\sqrt{2} 8\rangle + 4\sqrt{2} 12\rangle + 14\rangle + 4 16\rangle + 4 18\rangle]$ | $ 13\rangle$ |
| $ 15\rangle$ | $ 15\rangle$ | $(1/9) [-2\sqrt{2} 2\rangle + 4\sqrt{2} 6\rangle - 2\sqrt{2} 10\rangle + 4 13\rangle + 15\rangle + 4 17\rangle]$ | $ 18\rangle$ |
| $ 16\rangle$ | $\omega 16\rangle$ | $(1/9) [-2\sqrt{2} 4\rangle + 4\sqrt{2} 8\rangle - 2\sqrt{2} 12\rangle + 4 14\rangle + 16\rangle + 4 18\rangle]$ | $ 17\rangle$ |
| $ 17\rangle$ | $\omega^2 17\rangle$ | $(1/9) [4\sqrt{2} 2\rangle - 2\sqrt{2} 6\rangle - 2\sqrt{2} 10\rangle + 4 13\rangle + 4 15\rangle + 17\rangle]$ | $ 16\rangle$ |
| $ 18\rangle$ | $ 18\rangle$ | $(1/9) [4\sqrt{2} 4\rangle - 2\sqrt{2} 8\rangle - 2\sqrt{2} 12\rangle + 4 14\rangle + 4 16\rangle + 18\rangle]$ | $ 15\rangle$ |
| 18 | 0 | 2 | 0 |

| | C_4 |
|--------------|--|
| $ 1\rangle$ | $\frac{1}{3}[-2\omega^2 3\rangle - 7\rangle - 2\omega 11\rangle]$ |
| $ 2\rangle$ | $(1/9)[2\omega^2 4\rangle + 5 8\rangle + 2\omega 12\rangle - 2\sqrt{2}\omega 14\rangle + 4\sqrt{2} 16\rangle - 2\sqrt{2}\omega^2 18\rangle]$ |
| $ 3\rangle$ | $\frac{1}{3}[-2\omega^2 1\rangle - 5\rangle - 2\omega 9\rangle]$ |
| $ 4\rangle$ | $(1/9)[2\omega^2 2\rangle + 5 6\rangle + 2\omega 10\rangle - 2\sqrt{2}\omega 13\rangle + 4\sqrt{2} 15\rangle - 2\sqrt{2}\omega^2 17\rangle]$ |
| $ 5\rangle$ | $\frac{1}{3}[- 3\rangle - 2\omega 7\rangle + 2\omega^2 11\rangle]$ |
| $ 6\rangle$ | $(1/9)[5 4\rangle + 2\omega 8\rangle + 2\omega^2 12\rangle - 2\sqrt{2}\omega^2 14\rangle - 2\sqrt{2}\omega 16\rangle + 4\sqrt{2} 18\rangle]$ |
| $ 7\rangle$ | $\frac{1}{3}[- 1\rangle - 2\omega 5\rangle + 2\omega^2 9\rangle]$ |
| $ 8\rangle$ | $(1/9)[5 2\rangle + 2\omega 6\rangle + 2\omega^2 10\rangle - 2\sqrt{2}\omega^2 13\rangle - 2\sqrt{2}\omega 15\rangle + 4\sqrt{2} 17\rangle]$ |
| $ 9\rangle$ | $\frac{1}{3}[-2\omega 3\rangle + 2\omega^2 7\rangle + 11\rangle]$ |
| $ 10\rangle$ | $(1/9)[2\omega 4\rangle + 2\omega^2 8\rangle + 5 12\rangle + 4\sqrt{2} 14\rangle - 2\sqrt{2}\omega^2 16\rangle - 2\sqrt{2}\omega 18\rangle]$ |
| $ 11\rangle$ | $\frac{1}{3}[-2\omega 1\rangle + 2\omega^2 5\rangle + 9\rangle]$ |
| $ 12\rangle$ | $(1/9)[2\omega 2\rangle + 2\omega^2 6\rangle + 5 10\rangle + 4\sqrt{2} 13\rangle - 2\sqrt{2}\omega^2 15\rangle - 2\sqrt{2}\omega 17\rangle]$ |
| $ 13\rangle$ | $(1/9)[-2\sqrt{2}\omega 4\rangle - 2\sqrt{2}\omega^2 8\rangle + 4\sqrt{2} 12\rangle + 14\rangle + 4\omega^2 16\rangle + 4\omega 18\rangle]$ |
| $ 14\rangle$ | $(1/9)[-2\sqrt{2}\omega 2\rangle - 2\sqrt{2}\omega^2 6\rangle + 4\sqrt{2} 10\rangle + 13\rangle + 4\omega^2 15\rangle + 4\omega 17\rangle]$ |
| $ 15\rangle$ | $(1/9)[4\sqrt{2} 4\rangle - 2\sqrt{2}\omega 8\rangle - 2\sqrt{2}\omega^2 12\rangle + 4\omega^2 14\rangle + 4\omega 16\rangle + 18\rangle]$ |
| $ 16\rangle$ | $(1/9)[4\sqrt{2} 2\rangle - 2\sqrt{2}\omega 6\rangle - 2\sqrt{2}\omega^2 10\rangle + 4\omega^2 13\rangle + 4\omega 15\rangle + 17\rangle]$ |
| $ 17\rangle$ | $(1/9)[-2\sqrt{2}\omega^2 4\rangle + 4\sqrt{2} 8\rangle - 2\sqrt{2}\omega 12\rangle + 4\omega 14\rangle + 16\rangle + 4\omega^2 18\rangle]$ |
| $ 18\rangle$ | $(1/9)[-2\sqrt{2}\omega^2 2\rangle + 4\sqrt{2} 6\rangle - 2\sqrt{2}\omega 10\rangle + 4\omega 13\rangle + 15\rangle + 4\omega^2 17\rangle]$ |
| χ | 0 |

where $\omega = \exp(2\pi i/3)$. The eighteen functions form the basis for the representation of O_h containing the irreducible components:

$$A_1 + A_2 + 2E + 2T_1 + 2T_2$$

The functions $|1\rangle$, $|3\rangle$, $|5\rangle$, $|7\rangle$, $|9\rangle$ and $|11\rangle$ transform amongst themselves and form the basis for $T_1 + T_2$. The components of one of the T_1 are

$$\sqrt{\frac{1}{2}}[|1\rangle + |11\rangle]; \quad \sqrt{\frac{1}{2}}[|3\rangle - |5\rangle]; \quad \sqrt{\frac{1}{2}}[|7\rangle - |9\rangle].$$

and the components of one of the T_2 terms are found to be

$$\sqrt{\frac{1}{2}}[|1\rangle - |11\rangle]; \quad \sqrt{\frac{1}{2}}[|3\rangle + |5\rangle]; \quad \sqrt{\frac{1}{2}}[|7\rangle + |9\rangle].$$

The linear combinations of the eighteen functions that transform irreducibly under O_h shall be stated

$$|A_1\rangle = (1/\sqrt{6})[\sqrt{2}|4\rangle + \sqrt{2}|6\rangle + |15\rangle + |18\rangle]$$

$$|A_2\rangle = (1/\sqrt{6})[\sqrt{2}|4\rangle - \sqrt{2}|6\rangle - |15\rangle + |18\rangle]$$

$$|E(1)\rangle \begin{cases} = (1/\sqrt{6})[\sqrt{2}|2\rangle + \sqrt{2}|12\rangle + |14\rangle + |17\rangle] \\ = (1/\sqrt{6})[\sqrt{2}|8\rangle + \sqrt{2}|10\rangle + |13\rangle + |16\rangle] \end{cases}$$

$$|E(2)\rangle \begin{cases} = (1/\sqrt{6})[\sqrt{2}|2\rangle - \sqrt{2}|12\rangle - |14\rangle + |17\rangle] \\ = (1/\sqrt{6})[\sqrt{2}|8\rangle - \sqrt{2}|10\rangle - |13\rangle + |16\rangle] \end{cases}$$

$$|T_1(1)\rangle \begin{cases} = \sqrt{\frac{1}{2}}[|1\rangle + |11\rangle] \\ = \sqrt{\frac{1}{2}}[|3\rangle - |5\rangle] \\ = \sqrt{\frac{1}{2}}[|7\rangle - |9\rangle] \end{cases}$$

$$|T_1(2)\rangle \begin{cases} = (1/\sqrt{6})[|2\rangle - |12\rangle + \sqrt{2}|14\rangle - \sqrt{2}|17\rangle] \\ = (1/\sqrt{6})[|4\rangle - |6\rangle + \sqrt{2}|15\rangle - \sqrt{2}|18\rangle] \\ = (1/\sqrt{6})[|8\rangle - |10\rangle + \sqrt{2}|13\rangle - \sqrt{2}|16\rangle] \end{cases}$$

$$|T_2(1)\rangle \begin{cases} = \sqrt{\frac{1}{2}}[|1\rangle - |11\rangle] \\ = \sqrt{\frac{1}{2}}[|3\rangle + |5\rangle] \\ = \sqrt{\frac{1}{2}}[|7\rangle + |9\rangle] \end{cases}$$

$$|T_2(2)\rangle \begin{cases} = (1/\sqrt{6})[\sqrt{2}|2\rangle + \sqrt{2}|12\rangle - |14\rangle - |17\rangle] \\ = (1/\sqrt{6})[\sqrt{2}|8\rangle + \sqrt{2}|10\rangle - |13\rangle - |16\rangle] \\ = (1/\sqrt{6})[\sqrt{2}|4\rangle + \sqrt{2}|6\rangle - |15\rangle - |18\rangle] \end{cases}$$

In terms of determinantal states the doublet functions of the configuration $t_{2g}^2 e_g$ having $M_S = \frac{1}{2}$ are

$$|^2A_1, \frac{1}{2}\rangle = (1/\sqrt{6}) [(\bar{A}^+\bar{B}^+E^-) - (\bar{A}^+\bar{B}^+E^-) + (\bar{A}^+\bar{C}^+D^-) - (\bar{A}^+\bar{C}^+D^-) + (\bar{B}^+\bar{B}^+D^-) + (\bar{C}^+\bar{C}^+E^-)]$$

$$|^2A_2, \frac{1}{2}\rangle = (1/\sqrt{6}) [(\bar{A}^+\bar{B}^+E^-) - (\bar{A}^+\bar{B}^+E^-) - (\bar{A}^+\bar{C}^+D^-) + (\bar{A}^+\bar{C}^+D^-) - (\bar{B}^+\bar{B}^+D^-) + (\bar{C}^+\bar{C}^+E^-)]$$

$$|^2E(1), \frac{1}{2}\rangle = (1/\sqrt{6}) [(\bar{A}^+\bar{B}^+D^-) - (\bar{A}^+\bar{B}^+D^-) + (\bar{B}^+\bar{C}^+E^-) - (\bar{B}^+\bar{C}^+E^-) + (\bar{A}^+\bar{A}^+E^-) + (\bar{C}^+\bar{C}^+D^-)]$$

$$|^2E(1), \frac{1}{2}\rangle = (1/\sqrt{6}) [(\bar{A}^+\bar{C}^+E^-) - (\bar{A}^+\bar{C}^+E^-) + (\bar{B}^+\bar{C}^+D^-) - (\bar{B}^+\bar{C}^+D^-) + (\bar{A}^+\bar{A}^+D^-) + (\bar{B}^+\bar{B}^+E^-)]$$

$$|^2E(2), \frac{1}{2}\rangle = (1/\sqrt{6}) [(\bar{A}^+\bar{B}^+D^-) - (\bar{A}^+\bar{B}^+D^-) - (\bar{B}^+\bar{C}^+E^-) + (\bar{B}^+\bar{C}^+E^-) - (\bar{A}^+\bar{A}^+E^-) + (\bar{C}^+\bar{C}^+D^-)]$$

$$|^2E(2), \frac{1}{2}\rangle = (1/\sqrt{6}) [(\bar{A}^+\bar{C}^+E^-) - (\bar{A}^+\bar{C}^+E^-) - (\bar{B}^+\bar{C}^+D^-) + (\bar{B}^+\bar{C}^+D^-) - (\bar{A}^+\bar{A}^+D^-) + (\bar{B}^+\bar{B}^+E^-)]$$

$$|^2T_1(1), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [-2(\bar{A}^+\bar{B}^+D^-) + (\bar{A}^+\bar{B}^+D^-) + (\bar{A}^+\bar{B}^+D^-) - 2(\bar{B}^+\bar{C}^+E^-) + (\bar{B}^+\bar{C}^+E^-) + (\bar{B}^+\bar{C}^+E^-)]$$

$$|^2T_1(1), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [-2(\bar{A}^+\bar{B}^+E^-) + (\bar{A}^+\bar{B}^+E^-) + (\bar{A}^+\bar{B}^+E^-) + 2(\bar{A}^+\bar{C}^+D^-) - (\bar{A}^+\bar{C}^+D^-) - (\bar{A}^+\bar{C}^+D^-)]$$

$$|^2T_1(1), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [-2(\bar{A}^+\bar{C}^+E^-) + (\bar{A}^+\bar{C}^+E^-) + (\bar{A}^+\bar{C}^+E^-) + 2(\bar{B}^+\bar{C}^+D^-) - (\bar{B}^+\bar{C}^+D^-) - (\bar{B}^+\bar{C}^+D^-)]$$

$$|^2T_1(2), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [(\bar{A}^+\bar{B}^+D^-) - (\bar{A}^+\bar{B}^+D^-) - (\bar{B}^+\bar{C}^+E^-) + (\bar{B}^+\bar{C}^+E^-) + 2(\bar{A}^+\bar{A}^+E^-) - 2(\bar{C}^+\bar{C}^+D^-)]$$

$$|^2T_1(2), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [(\bar{A}^+\bar{B}^+E^-) - (\bar{A}^+\bar{B}^+E^-) - (\bar{A}^+\bar{C}^+D^-) + (\bar{A}^+\bar{C}^+D^-) + 2(\bar{B}^+\bar{B}^+D^-) - 2(\bar{C}^+\bar{C}^+E^-)]$$

$$|^2T_1(2), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [(\bar{A}^+\bar{C}^+E^-) - (\bar{A}^+\bar{C}^+E^-) - (\bar{B}^+\bar{C}^+D^-) + (\bar{B}^+\bar{C}^+D^-) + 2(\bar{A}^+\bar{A}^+D^-) - 2(\bar{B}^+\bar{B}^+E^-)]$$

$$|^2T_2(1), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [-2(\bar{A}^+\bar{B}^+D^-) + (\bar{A}^+\bar{B}^+D^-) + (\bar{A}^+\bar{B}^+D^-) + 2(\bar{B}^+\bar{C}^+E^-) - (\bar{B}^+\bar{C}^+E^-) - (\bar{B}^+\bar{C}^+E^-)]$$

$$|^2T_2(1), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [-2(\bar{A}^+\bar{B}^+E^-) + (\bar{A}^+\bar{B}^+E^-) + (\bar{A}^+\bar{B}^+E^-) - 2(\bar{A}^+\bar{C}^+D^-) + (\bar{A}^+\bar{C}^+D^-) + (\bar{A}^+\bar{C}^+D^-)]$$

$$|^2T_2(1), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [-2(\bar{A}^+\bar{C}^+E^-) + (\bar{A}^+\bar{C}^+E^-) + (\bar{A}^+\bar{C}^+E^-) - 2(\bar{B}^+\bar{C}^+D^-) + (\bar{B}^+\bar{C}^+D^-) + (\bar{B}^+\bar{C}^+D^-)]$$

$$|^2T_2(2), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [(\bar{A}^+\bar{B}^+D^-) - (\bar{A}^+\bar{B}^+D^-) + (\bar{B}^+\bar{C}^+E^-) - (\bar{B}^+\bar{C}^+E^-) - 2(\bar{A}^+\bar{A}^+E^-) - 2(\bar{C}^+\bar{C}^+D^-)]$$

$$|^2T_2(2), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [(\bar{A}^+\bar{B}^+E^-) - (\bar{A}^+\bar{B}^+E^-) + (\bar{A}^+\bar{C}^+D^-) - (\bar{A}^+\bar{C}^+D^-) - 2(\bar{B}^+\bar{B}^+D^-) - 2(\bar{C}^+\bar{C}^+E^-)]$$

$$|^2T_2(2), \frac{1}{2}\rangle = \frac{1}{2}\sqrt{3} [(\bar{A}^+\bar{C}^+E^-) - (\bar{A}^+\bar{C}^+E^-) + (\bar{B}^+\bar{C}^+D^-) - (\bar{B}^+\bar{C}^+D^-) - 2(\bar{A}^+\bar{A}^+D^-) - 2(\bar{B}^+\bar{B}^+E^-)]$$

APPENDIX V

SYMMETRY PROPERTIES OF THE UNPRIMED PAIR STATES, t_{2g}^3 CONFIGURATION

(Primed and double primed states have these properties also)

(i) $|U, S, M_S\rangle, |V, S, M_S\rangle, |W, S, M_S\rangle$ OF $(^4A_2 \times ^2T_1)$.

| | |
|--|---|
| $C_3 U, 2, 2\rangle = \omega U, 2, 2\rangle$ | $\sigma_V U, 2, 2\rangle = U, 2, -2\rangle$ |
| $C_3 U, 2, 1\rangle = \omega^2 U, 2, 1\rangle$ | $\sigma_V U, 2, 1\rangle = - U, 2, -1\rangle$ |
| $C_3 U, 2, 0\rangle = U, 2, 0\rangle$ | $\sigma_V U, 2, 0\rangle = U, 2, 0\rangle$ |
| $C_3 U, 2, -1\rangle = \omega U, 2, -1\rangle$ | $\sigma_V U, 2, -1\rangle = - U, 2, 1\rangle$ |
| $C_3 U, 2, -2\rangle = \omega^2 U, 2, -2\rangle$ | $\sigma_V U, 2, -2\rangle = U, 2, 2\rangle$ |
| $C_3 V, 2, 2\rangle = \omega^2 V, 2, 2\rangle$ | $\sigma_V V, 2, 2\rangle = W, 2, -2\rangle$ |
| $C_3 V, 2, 1\rangle = V, 2, 1\rangle$ | $\sigma_V V, 2, 1\rangle = - W, 2, -1\rangle$ |
| $C_3 V, 2, 0\rangle = \omega V, 2, 0\rangle$ | $\sigma_V V, 2, 0\rangle = W, 2, 0\rangle$ |
| $C_3 V, 2, -1\rangle = \omega^2 V, 2, -1\rangle$ | $\sigma_V V, 2, -1\rangle = - W, 2, 1\rangle$ |
| $C_3 V, 2, -2\rangle = V, 2, -2\rangle$ | $\sigma_V V, 2, -2\rangle = W, 2, 2\rangle$ |
| $C_3 W, 2, 2\rangle = W, 2, 2\rangle$ | $\sigma_V W, 2, 2\rangle = V, 2, -2\rangle$ |
| $C_3 W, 2, 1\rangle = \omega W, 2, 1\rangle$ | $\sigma_V W, 2, 1\rangle = - V, 2, -1\rangle$ |
| $C_3 W, 2, 0\rangle = \omega^2 W, 2, 0\rangle$ | $\sigma_V W, 2, 0\rangle = V, 2, 0\rangle$ |
| $C_3 W, 2, -1\rangle = W, 2, -1\rangle$ | $\sigma_V W, 2, -1\rangle = - V, 2, 1\rangle$ |
| $C_3 W, 2, -2\rangle = \omega W, 2, -2\rangle$ | $\sigma_V W, 2, -2\rangle = V, 2, 2\rangle$ |
| $C_3 U, 1, 1\rangle = \omega^2 U, 1, 1\rangle$ | $\sigma_V U, 1, 1\rangle = U, 1, -1\rangle$ |
| $C_3 U, 1, 0\rangle = U, 1, 0\rangle$ | $\sigma_V U, 1, 0\rangle = - U, 1, 0\rangle$ |
| $C_3 U, 1, -1\rangle = \omega U, 1, -1\rangle$ | $\sigma_V U, 1, -1\rangle = U, 1, 1\rangle$ |
| $C_3 V, 1, 1\rangle = V, 1, 1\rangle$ | $\sigma_V V, 1, 1\rangle = W, 1, -1\rangle$ |
| $C_3 V, 1, 0\rangle = \omega V, 1, 0\rangle$ | $\sigma_V V, 1, 0\rangle = - W, 1, 0\rangle$ |
| $C_3 V, 1, -1\rangle = \omega^2 V, 1, -1\rangle$ | $\sigma_V V, 1, -1\rangle = W, 1, 1\rangle$ |

$$\begin{aligned}
 C_3 |W, 1, 1\rangle &= \omega |W, 1, 1\rangle & \sigma_V |W, 1, 1\rangle &= |V, 1, -1\rangle \\
 C_3 |W, 1, 0\rangle &= \omega^2 |W, 1, 0\rangle & \sigma_V |W, 1, 0\rangle &= -|V, 1, 0\rangle \\
 C_3 |W, 1, -1\rangle &= |W, 1, -1\rangle & \sigma_V |W, 1, -1\rangle &= |V, 1, 1\rangle
 \end{aligned}$$

(ii) $|P, S, M_S\rangle, |Q, S, M_S\rangle, |R, S, M_S\rangle$ OF $(^4A_2 \times ^2T_2)$

$$\begin{aligned}
 C_3 |P, 2, 2\rangle &= \omega |P, 2, 2\rangle & \sigma_V |P, 2, 2\rangle &= -|P, 2, -2\rangle \\
 C_3 |P, 2, 1\rangle &= \omega^2 |P, 2, 1\rangle & \sigma_V |P, 2, 1\rangle &= |P, 2, -1\rangle \\
 C_3 |P, 2, 0\rangle &= |P, 2, 0\rangle & \sigma_V |P, 2, 0\rangle &= -|P, 2, 0\rangle \\
 C_3 |P, 2, -1\rangle &= \omega |P, 2, -1\rangle & \sigma_V |P, 2, -1\rangle &= |P, 2, 1\rangle \\
 C_3 |P, 2, -2\rangle &= \omega^2 |P, 2, -2\rangle & \sigma_V |P, 2, -2\rangle &= -|P, 2, 2\rangle \\
 \\
 C_3 |Q, 2, 2\rangle &= \omega^2 |Q, 2, 2\rangle & \sigma_V |Q, 2, 2\rangle &= -|R, 2, -2\rangle \\
 C_3 |Q, 2, 1\rangle &= |Q, 2, 1\rangle & \sigma_V |Q, 2, 1\rangle &= |R, 2, -1\rangle \\
 C_3 |Q, 2, 0\rangle &= \omega |Q, 2, 0\rangle & \sigma_V |Q, 2, 0\rangle &= -|R, 2, 0\rangle \\
 C_3 |Q, 2, -1\rangle &= \omega^2 |Q, 2, -1\rangle & \sigma_V |Q, 2, -1\rangle &= |R, 2, 1\rangle \\
 C_3 |Q, 2, -2\rangle &= |Q, 2, -2\rangle & \sigma_V |Q, 2, -2\rangle &= -|R, 2, 2\rangle \\
 \\
 C_3 |R, 2, 2\rangle &= |R, 2, 2\rangle & \sigma_V |R, 2, 2\rangle &= -|Q, 2, -2\rangle \\
 C_3 |R, 2, 1\rangle &= \omega |R, 2, 1\rangle & \sigma_V |R, 2, 1\rangle &= |Q, 2, -1\rangle \\
 C_3 |R, 2, 0\rangle &= \omega^2 |R, 2, 0\rangle & \sigma_V |R, 2, 0\rangle &= -|Q, 2, 0\rangle \\
 C_3 |R, 2, -1\rangle &= |R, 2, -1\rangle & \sigma_V |R, 2, -1\rangle &= |Q, 2, 1\rangle \\
 C_3 |R, 2, -2\rangle &= \omega |R, 2, -2\rangle & \sigma_V |R, 2, -2\rangle &= -|Q, 2, 2\rangle \\
 \\
 C_3 |P, 1, 1\rangle &= \omega^2 |P, 1, 1\rangle & \sigma_V |P, 1, 1\rangle &= -|P, 1, -1\rangle \\
 C_3 |P, 1, 0\rangle &= |P, 1, 0\rangle & \sigma_V |P, 1, 0\rangle &= |P, 1, 0\rangle \\
 C_3 |P, 1, -1\rangle &= \omega |P, 1, -1\rangle & \sigma_V |P, 1, -1\rangle &= -|P, 1, 1\rangle \\
 \\
 C_3 |Q, 1, 1\rangle &= |Q, 1, 1\rangle & \sigma_V |Q, 1, 1\rangle &= -|R, 1, -1\rangle \\
 C_3 |Q, 1, 0\rangle &= \omega |Q, 1, 0\rangle & \sigma_V |Q, 1, 0\rangle &= |R, 1, 0\rangle \\
 C_3 |Q, 1, -1\rangle &= \omega^2 |Q, 1, -1\rangle & \sigma_V |Q, 1, -1\rangle &= -|R, 1, 1\rangle
 \end{aligned}$$

$$C_3 |R, 1, 1\rangle = \omega |R, 1, 1\rangle$$

$$\sigma_V |R, 1, 1\rangle = -|Q, 1, -1\rangle$$

$$C_3 |R, 1, 0\rangle = \omega^2 |R, 1, 0\rangle$$

$$\sigma_V |R, 1, 0\rangle = |Q, 1, 0\rangle$$

$$C_3 |R, 1, -1\rangle = |R, 1, -1\rangle$$

$$\sigma_V |R, 1, -1\rangle = -|Q, 1, 1\rangle$$

(iii) $|G, S, M_S\rangle, |H, S, M_S\rangle$ of $(^4A_2 \times ^2E)$:

$$C_3 |G, 2, 2\rangle = \omega^2 |G, 2, 2\rangle$$

$$\sigma_V |G, 2, 2\rangle = -|H, 2, -2\rangle$$

$$C_3 |G, 2, 1\rangle = |G, 2, 1\rangle$$

$$\sigma_V |G, 2, 1\rangle = |H, 2, -1\rangle$$

$$C_3 |G, 2, 0\rangle = \omega |G, 2, 0\rangle$$

$$\sigma_V |G, 2, 0\rangle = -|H, 2, 0\rangle$$

$$C_3 |G, 2, -1\rangle = \omega^2 |G, 2, -1\rangle$$

$$\sigma_V |G, 2, -1\rangle = |H, 2, 1\rangle$$

$$C_3 |G, 2, -2\rangle = |G, 2, -2\rangle$$

$$\sigma_V |G, 2, -2\rangle = -|H, 2, 2\rangle$$

$$C_3 |H, 2, 2\rangle = |H, 2, 2\rangle$$

$$\sigma_V |H, 2, 2\rangle = -|G, 2, -2\rangle$$

$$C_3 |H, 2, 1\rangle = \omega |H, 2, 1\rangle$$

$$\sigma_V |H, 2, 1\rangle = |G, 2, -1\rangle$$

$$C_3 |H, 2, 0\rangle = \omega^2 |H, 2, 0\rangle$$

$$\sigma_V |H, 2, 0\rangle = -|G, 2, 0\rangle$$

$$C_3 |H, 2, -1\rangle = |H, 2, -1\rangle$$

$$\sigma_V |H, 2, -1\rangle = |G, 2, 1\rangle$$

$$C_3 |H, 2, -2\rangle = \omega |H, 2, -2\rangle$$

$$\sigma_V |H, 2, -2\rangle = -|G, 2, 2\rangle$$

$$C_3 |G, 1, 1\rangle = |G, 1, 1\rangle$$

$$\sigma_V |G, 1, 1\rangle = -|H, 1, -1\rangle$$

$$C_3 |G, 1, 0\rangle = \omega |G, 1, 0\rangle$$

$$\sigma_V |G, 1, 0\rangle = |H, 1, 0\rangle$$

$$C_3 |G, 1, -1\rangle = \omega^2 |G, 1, -1\rangle$$

$$\sigma_V |G, 1, -1\rangle = -|H, 1, 1\rangle$$

$$C_3 |H, 1, 1\rangle = \omega |H, 1, 1\rangle$$

$$\sigma_V |H, 1, 1\rangle = -|G, 1, -1\rangle$$

$$C_3 |H, 1, 0\rangle = \omega^2 |H, 1, 0\rangle$$

$$\sigma_V |H, 1, 0\rangle = |G, 1, 0\rangle$$

$$C_3 |H, 1, -1\rangle = |H, 1, -1\rangle$$

$$\sigma_V |H, 1, -1\rangle = -|G, 1, 1\rangle$$

(iv) UNPRIMED GROUND STATES (${}^4A_2 \times {}^4A_2$)

$$C_3|3,3\rangle = |3,3\rangle$$

$$\sigma_v|3,3\rangle = |3,-3\rangle$$

$$C_3|3,2\rangle = \omega|3,2\rangle$$

$$\sigma_v|3,2\rangle = -|3,-2\rangle$$

$$C_3|3,1\rangle = \omega^2|3,1\rangle$$

$$\sigma_v|3,1\rangle = |3,-1\rangle$$

$$C_3|3,0\rangle = |3,0\rangle$$

$$\sigma_v|3,0\rangle = -|3,0\rangle$$

$$C_3|3,-1\rangle = \omega|3,-1\rangle$$

$$\sigma_v|3,-1\rangle = |3,1\rangle$$

$$C_3|3,-2\rangle = \omega^2|3,-2\rangle$$

$$\sigma_v|3,-2\rangle = -|3,2\rangle$$

$$C_3|3,-3\rangle = |3,-3\rangle$$

$$\sigma_v|3,-3\rangle = |3,3\rangle$$

$$C_3|2,2\rangle = \omega|2,2\rangle$$

$$\sigma_v|2,2\rangle = |2,-2\rangle$$

$$C_3|2,1\rangle = \omega^2|2,1\rangle$$

$$\sigma_v|2,1\rangle = -|2,-1\rangle$$

$$C_3|2,0\rangle = |2,0\rangle$$

$$\sigma_v|2,0\rangle = |2,0\rangle$$

$$C_3|2,-1\rangle = \omega|2,-1\rangle$$

$$\sigma_v|2,-1\rangle = -|2,1\rangle$$

$$C_3|2,-2\rangle = \omega^2|2,-2\rangle$$

$$\sigma_v|2,-2\rangle = |2,2\rangle$$

$$C_3|1,1\rangle = \omega^2|1,1\rangle$$

$$\sigma_v|1,1\rangle = |1,-1\rangle$$

$$C_3|1,0\rangle = |1,0\rangle$$

$$\sigma_v|1,0\rangle = -|1,0\rangle$$

$$C_3|1,-1\rangle = \omega|1,-1\rangle$$

$$\sigma_v|1,-1\rangle = |1,1\rangle$$

$$C_3|0,0\rangle = |0,0\rangle$$

$$\sigma_v|0,0\rangle = |0,0\rangle$$

(v) IRREDUCIBLE REPRESENTATIONS OF D_{3h} FORMED BY (P,Q,R)

| ORBITAL PARENT | $\sigma_h = 1$ | $\sigma_h = -1$ |
|-------------------|---|---|
| ${}^5A'_2$ | $ P', 2, 2\rangle, P', 2, -2\rangle$ E' $ P', 2, 0\rangle$ A'_2 | $ P'', 2, 1\rangle, P'', 2, -1\rangle$ E'' |
| ${}^5A''_1$ | $ P', 2, 1\rangle, P', 2, -1\rangle$ E' | $ P'', 2, 2\rangle, P'', 2, -2\rangle$ E'' $ P'', 2, 0\rangle$ A''_1 |
| ${}^5E'$ | $ Q', 2, 2\rangle, R', 2, -2\rangle$ E' $ Q', 2, 0\rangle, R', 2, 0\rangle$ E' $[Q', 2, -2\rangle \mp R', 2, 2\rangle]$ $A'_1 + A'_2$ | $[Q'', 2, 1\rangle \mp R'', 2, -1\rangle]$ $A''_1 + A''_2$ $ Q'', 2, -1\rangle, R'', 2, 1\rangle$ E'' |
| ${}^5E''$ | $[Q', 2, 1\rangle \pm R', 2, -1\rangle]$ $A'_1 + A'_2$ $ Q', 2, -1\rangle, R', 2, 1\rangle$ E' | $ Q'', 2, 2\rangle, R'', 2, -2\rangle$ E'' $ Q'', 2, 0\rangle, R'', 2, 0\rangle$ E'' $[Q'', 2, -2\rangle \pm R'', 2, 2\rangle]$ $A''_1 + A''_2$ |
| ${}^3A''_1$ | $ P', 1, 1\rangle, P', 1, -1\rangle$ E' | $ P'', 1, 0\rangle$ A''_2 |
| ${}^3A'_2$ | $ P', 1, 0\rangle$ A'_1 | $ P'', 1, 1\rangle, P'', 1, -1\rangle$ E'' |
| ${}^3E''$ | $[Q', 1, 1\rangle \mp R', 1, -1\rangle]$ $A'_1 + A'_2$ $ Q', 1, -1\rangle, R', 1, 1\rangle$ E' | $ Q'', 1, 0\rangle, R'', 1, 0\rangle$ E'' |
| ${}^3E'$ | $ Q', 1, 0\rangle, R', 1, 0\rangle$ E' | $[Q'', 1, 1\rangle \pm R'', 1, -1\rangle]$ $A''_1 + A''_2$ $ Q'', 1, -1\rangle, R'', 1, 1\rangle$ E'' |

(vi) IRREDUCIBLE REPRESENTATIONS OF D_{3h} FORMED BY (G,H)

| ORBITAL PARENT | $\sigma_h = 1$ | $\sigma_h = -1$ |
|-------------------|---|---|
| ${}^5E'$ | $ G', 2, 2\rangle, H', 2, -2\rangle \quad E'$ $ G', 2, 0\rangle, H', 2, 0\rangle \quad E'$ $[G', 2, -2\rangle \mp H', 2, 2\rangle] \quad A'_1 + A'_2$ | $[G'', 2, 1\rangle \mp H'', 2, -1\rangle] \quad A''_1 + A''_2$ $ G'', 2, -1\rangle, H'', 2, 1\rangle \quad E''$ |
| ${}^5E''$ | $[G', 2, 1\rangle \pm H', 2, -1\rangle] \quad A'_1 + A'_2$ $ G', 2, -1\rangle, H', 2, 1\rangle \quad E'$ | $ G'', 2, 2\rangle, H'', 2, -2\rangle \quad E''$ $ G'', 2, 0\rangle, H'', 2, 0\rangle \quad E''$ $[G'', 2, -2\rangle \pm H'', 2, 2\rangle] \quad A''_1 + A''_2$ |
| ${}^3E''$ | $[G', 1, 1\rangle \mp H', 1, -1\rangle] \quad A'_1 + A'_2$ $ G', 1, -1\rangle, H', 1, 1\rangle \quad E'$ | $ G'', 1, 0\rangle, H'', 1, 0\rangle \quad E''$ |
| ${}^3E'$ | $ G', 1, 0\rangle, H', 1, 0\rangle \quad E'$ | $[G'', 1, 1\rangle \pm H'', 1, -1\rangle] \quad A''_1 + A''_2$ $ G'', 1, -1\rangle, H'', 1, 1\rangle \quad E''$ |

APPENDIX VI

SYMMETRY PROPERTIES OF THE UNPRIMED PAIR STATES, $t_{2g}^2 e_g$ CONFIGURATION

(Primed and double primed states have these properties also).

(i) $|\alpha, S, M_S\rangle, |\beta, S, M_S\rangle, |\gamma, S, M_S\rangle$ OF $(^4A_2 \times ^4T_1)$

$$C_3 |\alpha, 3, 3\rangle = |\alpha, 3, 3\rangle$$

$$\sigma_V |\alpha, 3, 3\rangle = |\alpha, 3, -3\rangle$$

$$C_3 |\alpha, 3, 2\rangle = \omega |\alpha, 3, 2\rangle$$

$$\sigma_V |\alpha, 3, 2\rangle = -|\alpha, 3, -2\rangle$$

$$C_3 |\alpha, 3, 1\rangle = \omega^2 |\alpha, 3, 1\rangle$$

$$\sigma_V |\alpha, 3, 1\rangle = |\alpha, 3, -1\rangle$$

$$C_3 |\alpha, 3, 0\rangle = |\alpha, 3, 0\rangle$$

$$\sigma_V |\alpha, 3, 0\rangle = -|\alpha, 3, 0\rangle$$

$$C_3 |\alpha, 3, -1\rangle = \omega |\alpha, 3, -1\rangle$$

$$\sigma_V |\alpha, 3, -1\rangle = |\alpha, 3, 1\rangle$$

$$C_3 |\alpha, 3, -2\rangle = \omega^2 |\alpha, 3, -2\rangle$$

$$\sigma_V |\alpha, 3, -2\rangle = -|\alpha, 3, 2\rangle$$

$$C_3 |\alpha, 3, -3\rangle = |\alpha, 3, -3\rangle$$

$$\sigma_V |\alpha, 3, -3\rangle = |\alpha, 3, 3\rangle$$

$$C_3 |\beta, 3, 3\rangle = \omega^2 |\beta, 3, 3\rangle$$

$$\sigma_V |\beta, 3, 3\rangle = -|\gamma, 3, -3\rangle$$

$$C_3 |\beta, 3, 2\rangle = |\beta, 3, 2\rangle$$

$$\sigma_V |\beta, 3, 2\rangle = |\gamma, 3, -2\rangle$$

$$C_3 |\beta, 3, 1\rangle = \omega |\beta, 3, 1\rangle$$

$$\sigma_V |\beta, 3, 1\rangle = -|\gamma, 3, -1\rangle$$

$$C_3 |\beta, 3, 0\rangle = \omega^2 |\beta, 3, 0\rangle$$

$$\sigma_V |\beta, 3, 0\rangle = |\gamma, 3, 0\rangle$$

$$C_3 |\beta, 3, -1\rangle = |\beta, 3, -1\rangle$$

$$\sigma_V |\beta, 3, -1\rangle = -|\gamma, 3, 1\rangle$$

$$C_3 |\beta, 3, -2\rangle = \omega |\beta, 3, -2\rangle$$

$$\sigma_V |\beta, 3, -2\rangle = |\gamma, 3, 2\rangle$$

$$C_3 |\beta, 3, -3\rangle = \omega^2 |\beta, 3, -3\rangle$$

$$\sigma_V |\beta, 3, -3\rangle = -|\gamma, 3, 3\rangle$$

$$C_3 |\gamma, 3, 3\rangle = \omega |\gamma, 3, 3\rangle$$

$$\sigma_V |\gamma, 3, 3\rangle = -|\beta, 3, -3\rangle$$

$$C_3 |\gamma, 3, 2\rangle = \omega^2 |\gamma, 3, 2\rangle$$

$$\sigma_V |\gamma, 3, 2\rangle = |\beta, 3, -2\rangle$$

$$C_3 |\gamma, 3, 1\rangle = |\gamma, 3, 1\rangle$$

$$\sigma_V |\gamma, 3, 1\rangle = -|\beta, 3, -1\rangle$$

$$C_3 |\gamma, 3, 0\rangle = \omega |\gamma, 3, 0\rangle$$

$$\sigma_V |\gamma, 3, 0\rangle = |\beta, 3, 0\rangle$$

$$C_3 |\gamma, 3, -1\rangle = \omega^2 |\gamma, 3, -1\rangle$$

$$\sigma_V |\gamma, 3, -1\rangle = -|\beta, 3, 1\rangle$$

$$C_3 |\gamma, 3, -2\rangle = |\gamma, 3, -2\rangle$$

$$\sigma_V |\gamma, 3, -2\rangle = |\beta, 3, 2\rangle$$

$$C_3 |\gamma, 3, -3\rangle = \omega |\gamma, 3, -3\rangle$$

$$\sigma_V |\gamma, 3, -3\rangle = -|\beta, 3, 3\rangle$$

$$C_3|\alpha, 2, 2\rangle = \omega|\alpha, 2, 2\rangle$$

$$C_3|\alpha, 2, 1\rangle = \omega^2|\alpha, 2, 1\rangle$$

$$C_3|\alpha, 2, 0\rangle = |\alpha, 2, 0\rangle$$

$$C_3|\alpha, 2, -1\rangle = \omega|\alpha, 2, -1\rangle$$

$$C_3|\alpha, 2, -2\rangle = \omega^2|\alpha, 2, -2\rangle$$

$$C_3|\beta, 2, 2\rangle = |\beta, 2, 2\rangle$$

$$C_3|\beta, 2, 1\rangle = \omega|\beta, 2, 1\rangle$$

$$C_3|\beta, 2, 0\rangle = \omega^2|\beta, 2, 0\rangle$$

$$C_3|\beta, 2, -1\rangle = |\beta, 2, -1\rangle$$

$$C_3|\beta, 2, -2\rangle = \omega|\beta, 2, -2\rangle$$

$$C_3|\gamma, 2, 2\rangle = \omega^2|\gamma, 2, 2\rangle$$

$$C_3|\gamma, 2, 1\rangle = |\gamma, 2, 1\rangle$$

$$C_3|\gamma, 2, 0\rangle = \omega|\gamma, 2, 0\rangle$$

$$C_3|\gamma, 2, -1\rangle = \omega^2|\gamma, 2, -1\rangle$$

$$C_3|\gamma, 2, -2\rangle = |\gamma, 2, -2\rangle$$

$$C_3|\alpha, 1, 1\rangle = \omega^2|\alpha, 1, 1\rangle$$

$$C_3|\alpha, 1, 0\rangle = |\alpha, 1, 0\rangle$$

$$C_3|\alpha, 1, -1\rangle = \omega|\alpha, 1, -1\rangle$$

$$C_3|\beta, 1, 1\rangle = \omega|\beta, 1, 1\rangle$$

$$C_3|\beta, 1, 0\rangle = \omega^2|\beta, 1, 0\rangle$$

$$C_3|\beta, 1, -1\rangle = |\beta, 1, -1\rangle$$

$$C_3|\gamma, 1, 1\rangle = |\gamma, 1, 1\rangle$$

$$C_3|\gamma, 1, 0\rangle = \omega|\gamma, 1, 0\rangle$$

$$C_3|\gamma, 1, -1\rangle = \omega^2|\gamma, 1, -1\rangle$$

$$C_3|\alpha, 0, 0\rangle = |\alpha, 0, 0\rangle$$

$$C_3|\beta, 0, 0\rangle = \omega^2|\beta, 0, 0\rangle$$

$$C_3|\gamma, 0, 0\rangle = \omega|\gamma, 0, 0\rangle$$

$$\sigma_v|\alpha, 2, 2\rangle = |\alpha, 2, -2\rangle$$

$$\sigma_v|\alpha, 2, 1\rangle = -|\alpha, 2, -1\rangle$$

$$\sigma_v|\alpha, 2, 0\rangle = |\alpha, 2, 0\rangle$$

$$\sigma_v|\alpha, 2, -1\rangle = -|\alpha, 2, 1\rangle$$

$$\sigma_v|\alpha, 2, -2\rangle = |\alpha, 2, 2\rangle$$

$$\sigma_v|\beta, 2, 2\rangle = -|\gamma, 2, -2\rangle$$

$$\sigma_v|\beta, 2, 1\rangle = |\gamma, 2, -1\rangle$$

$$\sigma_v|\beta, 2, 0\rangle = -|\gamma, 2, 0\rangle$$

$$\sigma_v|\beta, 2, -1\rangle = |\gamma, 2, 1\rangle$$

$$\sigma_v|\beta, 2, -2\rangle = -|\gamma, 2, 2\rangle$$

$$\sigma_v|\gamma, 2, 2\rangle = -|\beta, 2, -2\rangle$$

$$\sigma_v|\gamma, 2, 1\rangle = |\beta, 2, -1\rangle$$

$$\sigma_v|\gamma, 2, 0\rangle = -|\beta, 2, 0\rangle$$

$$\sigma_v|\gamma, 2, -1\rangle = |\beta, 2, 1\rangle$$

$$\sigma_v|\gamma, 2, -2\rangle = -|\beta, 2, 2\rangle$$

$$\sigma_v|\alpha, 1, 1\rangle = |\alpha, 1, -1\rangle$$

$$\sigma_v|\alpha, 1, 0\rangle = -|\alpha, 1, 0\rangle$$

$$\sigma_v|\alpha, 1, -1\rangle = |\alpha, 1, 1\rangle$$

$$\sigma_v|\beta, 1, 1\rangle = -|\gamma, 1, -1\rangle$$

$$\sigma_v|\beta, 1, 0\rangle = |\gamma, 1, 0\rangle$$

$$\sigma_v|\beta, 1, -1\rangle = -|\gamma, 1, 1\rangle$$

$$\sigma_v|\gamma, 1, 1\rangle = -|\beta, 1, -1\rangle$$

$$\sigma_v|\gamma, 1, 0\rangle = |\beta, 1, 0\rangle$$

$$\sigma_v|\gamma, 1, -1\rangle = -|\beta, 1, 1\rangle$$

$$\sigma_v|\alpha, 0, 0\rangle = |\alpha, 0, 0\rangle$$

$$\sigma_v|\beta, 0, 0\rangle = -|\gamma, 0, 0\rangle$$

$$\sigma_v|\gamma, 0, 0\rangle = -|\beta, 0, 0\rangle$$

(ii) $|\eta, S, M_S\rangle, |\zeta, S, M_S\rangle, |\xi, S, M_S\rangle$ OF $(^4A_2 \times ^4T_2)$

$$\begin{array}{ll} C_3 |\eta, 3, 3\rangle = |\eta, 3, 3\rangle & \sigma_V |\eta, 3, 3\rangle = -|\eta, 3, -3\rangle \\ C_3 |\eta, 3, 2\rangle = \omega |\eta, 3, 2\rangle & \sigma_V |\eta, 3, 2\rangle = |\eta, 3, -2\rangle \\ C_3 |\eta, 3, 1\rangle = \omega^2 |\eta, 3, 1\rangle & \sigma_V |\eta, 3, 1\rangle = -|\eta, 3, -1\rangle \\ C_3 |\eta, 3, 0\rangle = |\eta, 3, 0\rangle & \sigma_V |\eta, 3, 0\rangle = |\eta, 3, 0\rangle \\ C_3 |\eta, 3, -1\rangle = \omega |\eta, 3, -1\rangle & \sigma_V |\eta, 3, -1\rangle = -|\eta, 3, 1\rangle \\ C_3 |\eta, 3, -2\rangle = \omega^2 |\eta, 3, -2\rangle & \sigma_V |\eta, 3, -2\rangle = |\eta, 3, 2\rangle \\ C_3 |\eta, 3, -3\rangle = |\eta, 3, -3\rangle & \sigma_V |\eta, 3, -3\rangle = -|\eta, 3, 3\rangle \end{array}$$

$$\begin{array}{ll} C_3 |\zeta, 3, 3\rangle = \omega^2 |\zeta, 3, 3\rangle & \sigma_V |\zeta, 3, 3\rangle = -|\xi, 3, -3\rangle \\ C_3 |\zeta, 3, 2\rangle = |\zeta, 3, 2\rangle & \sigma_V |\zeta, 3, 2\rangle = |\xi, 3, -2\rangle \\ C_3 |\zeta, 3, 1\rangle = \omega |\zeta, 3, 1\rangle & \sigma_V |\zeta, 3, 1\rangle = -|\xi, 3, -1\rangle \\ C_3 |\zeta, 3, 0\rangle = \omega^2 |\zeta, 3, 0\rangle & \sigma_V |\zeta, 3, 0\rangle = |\xi, 3, 0\rangle \\ C_3 |\zeta, 3, -1\rangle = |\zeta, 3, -1\rangle & \sigma_V |\zeta, 3, -1\rangle = -|\xi, 3, 1\rangle \\ C_3 |\zeta, 3, -2\rangle = \omega |\zeta, 3, -2\rangle & \sigma_V |\zeta, 3, -2\rangle = |\xi, 3, 2\rangle \\ C_3 |\zeta, 3, -3\rangle = \omega^2 |\zeta, 3, -3\rangle & \sigma_V |\zeta, 3, -3\rangle = -|\xi, 3, 3\rangle \end{array}$$

$$\begin{array}{ll} C_3 |\xi, 3, 3\rangle = \omega |\xi, 3, 3\rangle & \sigma_V |\xi, 3, 3\rangle = -|\zeta, 3, -3\rangle \\ C_3 |\xi, 3, 2\rangle = \omega^2 |\xi, 3, 2\rangle & \sigma_V |\xi, 3, 2\rangle = |\zeta, 3, -2\rangle \\ C_3 |\xi, 3, 1\rangle = |\xi, 3, 1\rangle & \sigma_V |\xi, 3, 1\rangle = -|\zeta, 3, -1\rangle \\ C_3 |\xi, 3, 0\rangle = \omega |\xi, 3, 0\rangle & \sigma_V |\xi, 3, 0\rangle = |\zeta, 3, 0\rangle \\ C_3 |\xi, 3, -1\rangle = \omega^2 |\xi, 3, -1\rangle & \sigma_V |\xi, 3, -1\rangle = -|\zeta, 3, 1\rangle \\ C_3 |\xi, 3, -2\rangle = |\xi, 3, -2\rangle & \sigma_V |\xi, 3, -2\rangle = |\zeta, 3, 2\rangle \\ C_3 |\xi, 3, -3\rangle = \omega |\xi, 3, -3\rangle & \sigma_V |\xi, 3, -3\rangle = -|\zeta, 3, 3\rangle \end{array}$$

$$\begin{array}{ll} C_3 |\eta, 2, 2\rangle = \omega |\eta, 2, 2\rangle & \sigma_V |\eta, 2, 2\rangle = -|\eta, 2, -2\rangle \\ C_3 |\eta, 2, 1\rangle = \omega^2 |\eta, 2, 1\rangle & \sigma_V |\eta, 2, 1\rangle = |\eta, 2, -1\rangle \\ C_3 |\eta, 2, 0\rangle = |\eta, 2, 0\rangle & \sigma_V |\eta, 2, 0\rangle = -|\eta, 2, 0\rangle \\ C_3 |\eta, 2, -1\rangle = \omega |\eta, 2, -1\rangle & \sigma_V |\eta, 2, -1\rangle = |\eta, 2, 1\rangle \\ C_3 |\eta, 2, -2\rangle = \omega^2 |\eta, 2, -2\rangle & \sigma_V |\eta, 2, -2\rangle = -|\eta, 2, 2\rangle \end{array}$$

$$C_3|\zeta,2,2\rangle = |\zeta,2,2\rangle$$

$$C_3|\zeta,2,1\rangle = \omega|\zeta,2,1\rangle$$

$$C_3|\zeta,2,0\rangle = \omega^2|\zeta,2,0\rangle$$

$$C_3|\zeta,2,-1\rangle = |\zeta,2,-1\rangle$$

$$C_3|\zeta,2,-2\rangle = \omega|\zeta,2,-2\rangle$$

$$C_3|\xi,2,2\rangle = \omega^2|\xi,2,2\rangle$$

$$C_3|\xi,2,1\rangle = |\xi,2,1\rangle$$

$$C_3|\xi,2,0\rangle = \omega|\xi,2,0\rangle$$

$$C_3|\xi,2,-1\rangle = \omega^2|\xi,2,-1\rangle$$

$$C_3|\xi,2,-2\rangle = |\xi,2,-2\rangle$$

$$C_3|\eta,1,1\rangle = \omega^2|\eta,1,1\rangle$$

$$C_3|\eta,1,0\rangle = |\eta,1,0\rangle$$

$$C_3|\eta,1,-1\rangle = \omega|\eta,1,-1\rangle$$

$$C_3|\zeta,1,1\rangle = \omega|\zeta,1,1\rangle$$

$$C_3|\zeta,1,0\rangle = \omega^2|\zeta,1,0\rangle$$

$$C_3|\zeta,1,-1\rangle = |\zeta,1,-1\rangle$$

$$C_3|\xi,1,1\rangle = |\xi,1,1\rangle$$

$$C_3|\xi,1,0\rangle = \omega|\xi,1,0\rangle$$

$$C_3|\xi,1,-1\rangle = \omega^2|\xi,1,-1\rangle$$

$$C_3|\eta,0,0\rangle = |\eta,0,0\rangle$$

$$C_3|\zeta,0,0\rangle = \omega^2|\zeta,0,0\rangle$$

$$C_3|\xi,0,0\rangle = \omega|\xi,0,0\rangle$$

$$\sigma_V|\zeta,2,2\rangle = -|\xi,2,-2\rangle$$

$$\sigma_V|\zeta,2,1\rangle = |\xi,2,-1\rangle$$

$$\sigma_V|\zeta,2,0\rangle = -|\xi,2,0\rangle$$

$$\sigma_V|\zeta,2,-1\rangle = |\xi,2,1\rangle$$

$$\sigma_V|\zeta,2,-2\rangle = -|\xi,2,2\rangle$$

$$\sigma_V|\xi,2,2\rangle = -|\zeta,2,-2\rangle$$

$$\sigma_V|\xi,2,1\rangle = |\zeta,2,-1\rangle$$

$$\sigma_V|\xi,2,0\rangle = -|\zeta,2,0\rangle$$

$$\sigma_V|\xi,2,-1\rangle = |\zeta,2,1\rangle$$

$$\sigma_V|\xi,2,-2\rangle = -|\zeta,2,2\rangle$$

$$\sigma_V|\eta,1,1\rangle = -|\eta,1,-1\rangle$$

$$\sigma_V|\eta,1,0\rangle = |\eta,1,0\rangle$$

$$\sigma_V|\eta,1,-1\rangle = -|\eta,1,1\rangle$$

$$\sigma_V|\zeta,1,1\rangle = -|\xi,1,-1\rangle$$

$$\sigma_V|\zeta,1,0\rangle = |\xi,1,0\rangle$$

$$\sigma_V|\zeta,1,-1\rangle = -|\xi,1,1\rangle$$

$$\sigma_V|\xi,1,1\rangle = -|\zeta,1,-1\rangle$$

$$\sigma_V|\xi,1,0\rangle = |\zeta,1,0\rangle$$

$$\sigma_V|\xi,1,-1\rangle = -|\zeta,1,1\rangle$$

$$\sigma_V|\eta,0,0\rangle = -|\eta,0,0\rangle$$

$$\sigma_V|\zeta,0,0\rangle = -|\xi,0,0\rangle$$

$$\sigma_V|\xi,0,0\rangle = -|\zeta,0,0\rangle$$

(iii) IRREDUCIBLE REPRESENTATIONS FOR D_{3h} FORMED BY (α, β, γ)

| ORBITAL PARENT | $\sigma_h = 1$ | $\sigma_h = -1$ |
|------------------------|---|--|
| ${}^7A''_2$ | $[\alpha', 3, 3 \rangle \pm \alpha', 3, -3 \rangle$ $A'_1 + A'_2$ $ \alpha', 3, 1 \rangle, \alpha', 3, -1 \rangle$ E' | $ \alpha'', 3, 2 \rangle, \alpha'', 3, -2 \rangle$ E'' $ \alpha'', 3, 0 \rangle$ A''_1 |
| ${}^7A'_1$ | $ \alpha', 3, 2 \rangle, \alpha', 3, -2 \rangle$ E' $ \alpha', 3, 0 \rangle$ A'_2 | $[\alpha'', 3, 3 \rangle \mp \alpha'', 3, -3 \rangle$ $A''_1 + A''_2$ $ \alpha'', 3, 1 \rangle, \alpha'', 3, -1 \rangle$ E'' |
| ${}^7E''$ | $ \beta', 3, 3 \rangle, \gamma', 3, -3 \rangle$ E' $ \beta', 3, 1 \rangle, \gamma', 3, -1 \rangle$ E' $[\beta', 3, -1 \rangle \mp \gamma', 3, 1 \rangle$ $A'_1 + A'_2$ $ \beta', 3, -3 \rangle, \gamma', 3, 3 \rangle$ E' | $[\beta'', 3, 2 \rangle \mp \gamma'', 3, -2 \rangle$ $A''_1 + A''_2$ $ \beta'', 3, 0 \rangle, \gamma'', 3, 0 \rangle$ E'' $ \beta'', 3, -2 \rangle, \gamma'', 3, 2 \rangle$ E'' |
| ${}^7E'$ | $[\beta', 3, 2 \rangle \pm \gamma', 3, -2 \rangle$ $A'_1 + A'_2$ $ \beta', 3, 0 \rangle, \gamma', 3, 0 \rangle$ E' $ \beta', 3, -2 \rangle, \gamma', 3, 2 \rangle$ E' | $ \beta'', 3, 3 \rangle, \gamma'', 3, -3 \rangle$ E'' $ \beta'', 3, 1 \rangle, \gamma'', 3, -1 \rangle$ E'' $[\beta'', 3, -1 \rangle \pm \gamma'', 3, 1 \rangle$ $A''_1 + A''_2$ $ \beta'', 3, -3 \rangle, \gamma'', 3, 3 \rangle$ E'' |
| 5A_1 | $ \alpha', 2, 2 \rangle, \alpha', 2, -2 \rangle$ E' $ \alpha', 2, 0 \rangle$ A'_1 | $ \alpha'', 2, 1 \rangle, \alpha'', 2, -1 \rangle$ E'' |
| ${}^5A''_2$ | $ \alpha', 2, 1 \rangle, \alpha', 2, -1 \rangle$ E' | $ \alpha'', 2, 2 \rangle, \alpha'', 2, -2 \rangle$ E'' $ \alpha'', 2, 0 \rangle$ A''_2 |
| ${}^5E'$ | $[\beta', 2, 2 \rangle \mp \gamma', 2, -2 \rangle$ $A'_1 + A'_2$ $ \beta', 2, 0 \rangle, \gamma', 2, 0 \rangle$ E' $ \beta', 2, -2 \rangle, \gamma', 2, 2 \rangle$ E' | $ \beta'', 2, 1 \rangle, \gamma'', 2, -1 \rangle$ E'' $[\beta'', 2, -1 \rangle \mp \gamma'', 2, 1 \rangle$ $A''_1 + A''_2$ |
| ${}^5E''$ | $ \beta', 2, 1 \rangle, \gamma', 2, -1 \rangle$ E' $[\beta', 2, -1 \rangle \pm \gamma', 2, 1 \rangle$ $A'_1 + A'_2$ | $[\beta'', 2, 2 \rangle \pm \gamma'', 2, -2 \rangle$ $A''_1 + A''_2$ $ \beta'', 2, 0 \rangle, \gamma'', 2, 0 \rangle$ E'' $ \beta'', 2, -2 \rangle, \gamma'', 2, 2 \rangle$ E'' |
| ${}^3A'_2$ | $ \alpha', 1, 1 \rangle, \alpha', 1, -1 \rangle$ E' | $ \alpha'', 1, 0 \rangle$ A''_1 |
| ${}^3A'_1$ | $ \alpha', 1, 0 \rangle$ A'_2 | $ \alpha'', 1, 1 \rangle, \alpha'', 1, -1 \rangle$ E'' |
| ${}^3E''$ | $ \beta', 1, 1 \rangle, \gamma', 1, -1 \rangle$ E' $ \beta', 1, -1 \rangle \mp \gamma', 1, 1 \rangle$ $A'_1 + A'_2$ | $ \beta'', 1, 0 \rangle, \gamma'', 1, 0 \rangle$ E'' |
| ${}^3E'$ | $ \beta', 1, 0 \rangle, \gamma', 1, 0 \rangle$ E' | $ \beta'', 1, 1 \rangle, \gamma'', 1, -1 \rangle$ E'' $[\beta'', 1, -1 \rangle \pm \gamma'', 1, 1 \rangle$ $A''_1 + A''_2$ |
| ${}^1A'_1 + {}^1A''_2$ | $ \alpha', 0, 0 \rangle$ A'_1 | $ \alpha'', 0, 0 \rangle$ A''_2 |
| ${}^1E' + {}^1E''$ | $ \beta', 0, 0 \rangle, \gamma', 0, 0 \rangle$ E' | $ \beta'', 0, 0 \rangle, \gamma'', 0, 0 \rangle$ E'' |

(iv) IRREDUCIBLE REPRESENTATION OF D_{3h} FORMED BY (η, ζ, ξ)

| ORBITAL PARENT | $\sigma_h = 1$ | $\sigma_h = -1$ |
|------------------------|--|---|
| ${}^7A_1''$ | $[\eta', 3, 3\rangle \mp \eta', 3, -3\rangle]$ $A_1' + A_2'$ $ \eta', 3, 1\rangle, \eta', 3, -1\rangle$ E' | $ \eta'', 3, 2\rangle, \eta'', 3, -2\rangle$ E'' $ \eta'', 3, 0\rangle$ A_2'' |
| ${}^7A_2'$ | $ \eta', 3, 2\rangle, \eta', 3, -2\rangle$ E' $ \eta', 3, 0\rangle$ A_1' | $[\eta'', 3, 3\rangle \pm \eta'', 3, -3\rangle]$ $A_1'' + A_2''$ $ \eta'', 3, 1\rangle, \eta'', 3, -1\rangle$ E'' |
| ${}^7E''$ | $ \zeta', 3, 3\rangle, \xi', 3, -3\rangle$ E' $ \zeta', 3, 1\rangle, \xi', 3, -1\rangle$ E' $[\zeta', 3, -1\rangle \pm \xi', 3, 1\rangle]$ $A_1' + A_2'$ $ \zeta', 3, -3\rangle, \xi', 3, 3\rangle$ E' | $[\zeta'', 3, 2\rangle \pm \xi'', 3, -2\rangle]$ $A_1'' + A_2''$ $ \zeta'', 3, 0\rangle, \xi'', 3, 0\rangle$ E'' $ \zeta'', 3, -2\rangle, \xi'', 3, 2\rangle$ E'' |
| ${}^7E'$ | $[\zeta', 3, 2\rangle \mp \xi', 3, -2\rangle]$ $A_1' + A_2'$ $ \zeta', 3, 0\rangle, \xi', 3, 0\rangle$ E' $ \zeta', 3, -2\rangle, \xi', 3, 2\rangle$ E' | $ \zeta'', 3, 3\rangle, \xi'', 3, -3\rangle$ E'' $ \zeta'', 3, 1\rangle, \xi'', 3, -1\rangle$ E'' $[\zeta'', 3, -1\rangle \mp \xi'', 3, 1\rangle]$ $A_1'' + A_2''$ $ \zeta'', 3, -3\rangle, \xi'', 3, 3\rangle$ E'' |
| ${}^5A_2'$ | $ \eta', 2, 2\rangle, \eta', 2, -2\rangle$ E' $ \eta', 2, 0\rangle$ A_2' | $ \eta'', 2, 1\rangle, \eta'', 2, -1\rangle$ E'' |
| ${}^5A_1'$ | $ \eta', 2, 1\rangle, \eta', 2, -1\rangle$ E' | $ \eta'', 2, 2\rangle, \eta'', 2, -2\rangle$ E'' $ \eta'', 2, 0\rangle$ A_1'' |
| ${}^5E'$ | $[\zeta', 2, 2\rangle \pm \xi', 2, -2\rangle]$ $A_1' + A_2'$ $ \zeta', 2, 0\rangle, \xi', 2, 0\rangle$ E' $ \zeta', 2, -2\rangle, \xi', 2, 2\rangle$ E' | $ \zeta'', 2, 1\rangle, \xi'', 2, -1\rangle$ E'' $[\zeta'', 2, -1\rangle \pm \xi'', 2, 1\rangle]$ $A_1'' + A_2''$ |
| ${}^5E''$ | $ \zeta', 2, 1\rangle, \xi', 2, -1\rangle$ E' $[\zeta', 2, -1\rangle \mp \xi', 2, 1\rangle]$ $A_1' + A_2'$ | $[\zeta'', 2, 2\rangle \mp \xi'', 2, -2\rangle]$ $A_1'' + A_2''$ $ \zeta'', 2, 0\rangle, \xi'', 2, 0\rangle$ E'' $ \zeta'', 2, -2\rangle, \xi'', 2, 2\rangle$ E'' |
| ${}^3A_1''$ | $ \eta', 1, 1\rangle, \eta', 1, -1\rangle$ E' | $ \eta'', 1, 0\rangle$ A_2'' |
| ${}^3A_2'$ | $ \eta', 1, 0\rangle$ A_1' | $ \eta'', 1, 1\rangle, \eta'', 1, -1\rangle$ E'' |
| ${}^3E''$ | $ \zeta', 1, 1\rangle, \xi', 1, -1\rangle$ E' $[\zeta', 1, -1\rangle \pm \xi', 1, 1\rangle]$ $A_1' + A_2'$ | $ \zeta'', 1, 0\rangle, \xi'', 1, 0\rangle$ E'' |
| ${}^3E'$ | $ \zeta', 1, 0\rangle, \xi', 1, 0\rangle$ E' | $ \zeta'', 1, 1\rangle, \xi'', 1, -1\rangle$ E'' $[\zeta'', 1, -1\rangle \mp \xi'', 1, 1\rangle]$ $A_1'' + A_2''$ |
| ${}^1A_2' + {}^1A_1''$ | $ \eta', 0, 0\rangle$ A_2' | $ \eta'', 0, 0\rangle$ A_1'' |
| ${}^1E' + {}^1E''$ | $ \zeta', 0, 0\rangle, \xi', 0, 0\rangle$ E' | $ \zeta'', 0, 0\rangle, \xi'', 0, 0\rangle$ E'' |

APPENDIX VII

INTRAIONIC COULOMB AND EXCHANGE INTEGRALS

$$J(AA) = F_0 + 4F_2 + 36F_4$$

$$J(AB) = J(AC) = F_0 - 2F_2 - 4F_4$$

$$J(AD) = J(AE) = J(BD) = J(BE) = J(CD) = J(CE) = F_0 - 14F_4$$

$$J(BB) = J(BC) = J(CC) = F_0 + F_2 + 16F_4$$

$$J(DD) = J(DE) = J(EE) = F_0 + 21F_4$$

$$K(AB) = K(AC) = 3F_2 + 20F_4$$

$$K(AD) = K(AE) = K(BD) = K(BE) = K(CD) = K(CE) = 12F_2 + 25F_4$$

$$K(BC) = 6F_2 + 40F_4$$

$$K(DE) = 8F_2 + 30F_4$$

$$\langle AA | 1/r | BC \rangle = 3F_2 + 20F_4$$

$$\langle AB | 1/r | CC \rangle = \langle AC | 1/r | BB \rangle = 0$$

APPENDIX VIII

(i) SPIN-ORBIT OPERATORS ON (U,V,W) OF (${}^4A_2 \times {}^2T_1$)

| | $U \begin{smallmatrix} S \\ Z \end{smallmatrix}$ | $U \begin{smallmatrix} S \\ + - \end{smallmatrix}$ | $U \begin{smallmatrix} S \\ - + \end{smallmatrix}$ |
|---|--|--|---|
| $ U11\rangle$ $ U10\rangle$ $ U1-1\rangle$ | $-\frac{1}{2} P21\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} P11\rangle$ $-\sqrt{\frac{1}{3}} P20\rangle$ $-\frac{1}{2} P2-1\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} P1-1\rangle$ | $\frac{1}{2}\sqrt{\frac{1}{3}} R20\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} R10\rangle$ $\frac{1}{2} R2-1\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} R1-1\rangle$ $\sqrt{\frac{1}{2}} R2-2\rangle$ | $-\sqrt{\frac{1}{2}} Q22\rangle$ $-\frac{1}{2} Q21\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} Q11\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} Q20\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} Q10\rangle$ |
| $ V11\rangle$ $ V10\rangle$ $ V1-1\rangle$ | $-\frac{1}{4} Q21\rangle - \frac{1}{4}\sqrt{\frac{1}{3}} Q11\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} Q20\rangle$ $-\frac{1}{4} Q2-1\rangle + \frac{1}{4}\sqrt{\frac{1}{3}} Q1-1\rangle$ | $-\frac{1}{2}\sqrt{\frac{1}{3}} P20\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} P10\rangle$ $-\frac{1}{2} P2-1\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} P1-1\rangle$ $-\sqrt{\frac{1}{2}} P2-2\rangle$ | $-\sqrt{2} R22\rangle$ $- R21\rangle + \sqrt{\frac{1}{3}} R11\rangle$ $-\sqrt{\frac{1}{3}} R20\rangle + \sqrt{\frac{1}{3}} R10\rangle$ |
| $ W11\rangle$ $ W10\rangle$ $ W1-1\rangle$ | $-\frac{1}{4} R21\rangle - \frac{1}{4}\sqrt{\frac{1}{3}} R11\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} R20\rangle$ $-\frac{1}{4} R2-1\rangle + \frac{1}{4}\sqrt{\frac{1}{3}} R1-1\rangle$ | $\sqrt{\frac{1}{3}} Q20\rangle + \sqrt{\frac{1}{3}} Q10\rangle$ $ Q2-1\rangle + \sqrt{\frac{1}{3}} Q1-1\rangle$ $\sqrt{2} Q2-2\rangle$ | $\sqrt{\frac{1}{2}} P22\rangle$ $\frac{1}{2} P21\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} P11\rangle$ $\frac{1}{2}\sqrt{\frac{1}{3}} P20\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} P10\rangle$ |
| $ U22\rangle$ $ U21\rangle$ $ U20\rangle$ $ U2-1\rangle$ $ U2-2\rangle$ | $\sqrt{\frac{1}{3}} P22\rangle$ $\frac{1}{2}\sqrt{\frac{1}{3}} P21\rangle - \frac{1}{2} P11\rangle$ $-\sqrt{\frac{1}{3}} P10\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} P2-1\rangle - \frac{1}{2} P1-1\rangle$ $-\sqrt{\frac{1}{3}} P2-2\rangle$ | $-(1/\sqrt{6}) R21\rangle - \sqrt{\frac{1}{2}} R11\rangle$ $-\frac{1}{2} R20\rangle - \frac{1}{2} R10\rangle$ $-\frac{1}{2} R2-1\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} R1-1\rangle$ $-(1/\sqrt{6}) R2-2\rangle$ 0 | 0 $-(1/\sqrt{6}) Q22\rangle$ $-\frac{1}{2} Q21\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} Q11\rangle$ $-\frac{1}{2} Q20\rangle + \frac{1}{2} Q10\rangle$ $-(1/\sqrt{6}) Q2-1\rangle + \sqrt{\frac{1}{2}} Q1-1\rangle$ |
| $ V22\rangle$ $ V21\rangle$ $ V20\rangle$ $ V2-1\rangle$ $ V2-2\rangle$ | $\frac{1}{2}\sqrt{\frac{1}{3}} Q22\rangle$ $\frac{1}{4}\sqrt{\frac{1}{3}} Q21\rangle - \frac{1}{4} Q11\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} Q10\rangle$ $-\frac{1}{4}\sqrt{\frac{1}{3}} Q2-1\rangle - \frac{1}{4} Q1-1\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} Q2-2\rangle$ | $(1/\sqrt{6}) P21\rangle + \sqrt{\frac{1}{2}} P11\rangle$ $\frac{1}{2} P20\rangle + \frac{1}{2} P10\rangle$ $\frac{1}{2} P2-1\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} P1-1\rangle$ $(1/\sqrt{6}) P2-2\rangle$ 0 | 0 $-\sqrt{\frac{1}{3}} R22\rangle$ $- R21\rangle + \sqrt{\frac{1}{3}} R11\rangle$ $- R20\rangle + R10\rangle$ $-\sqrt{\frac{1}{3}} R2-1\rangle + \sqrt{2} R1-1\rangle$ |
| $ W22\rangle$ $ W21\rangle$ $ W20\rangle$ $ W2-1\rangle$ $ W2-2\rangle$ | $\frac{1}{2}\sqrt{\frac{1}{3}} R22\rangle$ $\frac{1}{4}\sqrt{\frac{1}{3}} R21\rangle - \frac{1}{4} R11\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} R10\rangle$ $-\frac{1}{4}\sqrt{\frac{1}{3}} R2-1\rangle - \frac{1}{4} R1-1\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} R2-2\rangle$ | $-\sqrt{\frac{1}{3}} Q21\rangle - \sqrt{2} Q11\rangle$ $- Q20\rangle - Q10\rangle$ $- Q2-1\rangle - \sqrt{\frac{1}{3}} Q1-1\rangle$ $-\sqrt{\frac{1}{3}} Q2-2\rangle$ 0 | 0 $(1/\sqrt{6}) P22\rangle$ $\frac{1}{2} P21\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} P11\rangle$ $\frac{1}{2} P20\rangle - \frac{1}{2} P10\rangle$ $(1/\sqrt{6}) P2-1\rangle - \sqrt{\frac{1}{2}} P1-1\rangle$ |

| | $U_{Z^S Z}$ |
|---|--|
| $ U11\rangle$ $ U10\rangle$ $ U1-1\rangle$ | $(1/6) [\sqrt{3} \eta21\rangle + \sqrt{5} \eta11\rangle]$ $(1/3) [\eta20\rangle - \eta00\rangle]$ $(1/6) [\sqrt{3} \eta2-1\rangle - \sqrt{5} \eta1-1\rangle]$ |
| $ V11\rangle$ $ V10\rangle$ $ V1-1\rangle$ | $-\frac{1}{4} [\sqrt{3} \gamma21\rangle + \sqrt{5} \gamma11\rangle] - (1/12) [\sqrt{3} \xi21\rangle + \sqrt{5} \xi11\rangle]$ $-\frac{1}{2} [\gamma20\rangle - \gamma00\rangle] - (1/6) [\xi20\rangle - \xi00\rangle]$ $-\frac{1}{4} [\sqrt{3} \gamma2-1\rangle - \sqrt{5} \gamma1-1\rangle] - (1/12) [\sqrt{3} \xi2-1\rangle - \sqrt{5} \xi1-1\rangle]$ |
| $ W11\rangle$ $ W10\rangle$ $ W1-1\rangle$ | $-\frac{1}{4} [\sqrt{3} \beta21\rangle + \sqrt{5} \beta11\rangle] - (1/12) [\sqrt{3} \zeta21\rangle + \sqrt{5} \zeta11\rangle]$ $-\frac{1}{2} [\beta20\rangle - \beta00\rangle] - (1/6) [\zeta20\rangle - \zeta00\rangle]$ $-\frac{1}{4} [\sqrt{3} \beta2-1\rangle - \sqrt{5} \beta1-1\rangle] - (1/12) [\sqrt{3} \zeta2-1\rangle - \sqrt{5} \zeta1-1\rangle]$ |
| $ U22\rangle$ $ U21\rangle$ $ U20\rangle$ $ U2-1\rangle$ $ U2-2\rangle$ | $\frac{1}{3} [\eta32\rangle + \eta22\rangle]$ $(1/6\sqrt{5}) [4\sqrt{2} \eta31\rangle + \sqrt{5} \eta21\rangle - \sqrt{3} \eta11\rangle]$ $(1/3\sqrt{5}) [3 \eta30\rangle - \eta10\rangle]$ $(1/6\sqrt{5}) [4\sqrt{2} \eta3-1\rangle - \sqrt{5} \eta2-1\rangle - \sqrt{3} \eta1-1\rangle]$ $\frac{1}{3} [\eta3-2\rangle - \eta2-2\rangle]$ |
| $ V22\rangle$ $ V21\rangle$ $ V20\rangle$ $ V2-1\rangle$ $ V2-2\rangle$ | $-\frac{1}{2} [\gamma32\rangle + \gamma22\rangle] - (1/6) [\xi32\rangle + \xi22\rangle]$ $-(1/4\sqrt{5}) [4\sqrt{2} \gamma31\rangle + \sqrt{5} \gamma21\rangle - \sqrt{3} \gamma11\rangle] - (1/12\sqrt{5}) [4\sqrt{2} \xi31\rangle + \sqrt{5} \xi21\rangle - \sqrt{3} \xi11\rangle]$ $-(1/2\sqrt{5}) [3 \gamma30\rangle - \gamma10\rangle] - (1/6\sqrt{5}) [3 \xi30\rangle - \xi10\rangle]$ $-(1/4\sqrt{5}) [4\sqrt{2} \gamma3-1\rangle - \sqrt{5} \gamma2-1\rangle - \sqrt{3} \gamma1-1\rangle] - (1/12\sqrt{5}) [4\sqrt{2} \xi3-1\rangle - \sqrt{5} \xi2-1\rangle - \sqrt{3} \xi1-1\rangle]$ $-\frac{1}{2} [\gamma3-2\rangle - \gamma2-2\rangle] - (1/6) [\xi3-2\rangle - \xi2-2\rangle]$ |
| $ W22\rangle$ $ W21\rangle$ $ W20\rangle$ $ W2-1\rangle$ $ W2-2\rangle$ | $-\frac{1}{2} [\beta32\rangle + \beta22\rangle] - (1/6) [\zeta32\rangle + \zeta22\rangle]$ $-(1/4\sqrt{5}) [4\sqrt{2} \beta31\rangle + \sqrt{5} \beta21\rangle - \sqrt{3} \beta11\rangle] - (1/12\sqrt{5}) [4\sqrt{2} \zeta31\rangle + \sqrt{5} \zeta21\rangle - \sqrt{3} \zeta11\rangle]$ $-(1/2\sqrt{5}) [3 \beta30\rangle - \beta10\rangle] - (1/6\sqrt{5}) [3 \zeta30\rangle - \zeta10\rangle]$ $-(1/4\sqrt{5}) [4\sqrt{2} \beta3-1\rangle - \sqrt{5} \beta2-1\rangle - \sqrt{3} \beta1-1\rangle] - (1/12\sqrt{5}) [4\sqrt{2} \zeta3-1\rangle - \sqrt{5} \zeta2-1\rangle - \sqrt{3} \zeta1-1\rangle]$ $-\frac{1}{2} [\beta3-2\rangle - \beta2-2\rangle] - (1/6) [\zeta3-2\rangle - \zeta2-1\rangle]$ |

| | $u_+ s_-$ |
|--|--|
| $ U_{11}\rangle$ $ U_{10}\rangle$ $ U_{1-1}\rangle$ | $-\frac{1}{2} [\beta_{20}\rangle + \sqrt{5} \beta_{10}\rangle + 2 \beta_{00}\rangle] + (1/6) [\zeta_{20}\rangle + \sqrt{5} \zeta_{10}\rangle + 2 \zeta_{00}\rangle]$ $-\frac{1}{2} [\sqrt{3} \beta_{2-1}\rangle + \sqrt{5} \beta_{1-1}\rangle] + (1/6) [\sqrt{3} \zeta_{2-1}\rangle + \sqrt{5} \zeta_{1-1}\rangle]$ $-\frac{1}{2}\sqrt{6}[\beta_{2-2}\rangle + (1/\sqrt{6}) \zeta_{2-2}\rangle]$ |
| $ V_{11}\rangle$ $ V_{10}\rangle$ $ V_{1-1}\rangle$ | $-\frac{1}{2} [\alpha_{20}\rangle + \sqrt{5} \alpha_{10}\rangle + 2 \alpha_{00}\rangle] + (1/6) [\eta_{20}\rangle + \sqrt{5} \eta_{10}\rangle + 2 \eta_{00}\rangle]$ $-\frac{1}{2} [\sqrt{3} \alpha_{2-1}\rangle + \sqrt{5} \alpha_{1-1}\rangle] + (1/6) [\sqrt{3} \eta_{2-1}\rangle + \sqrt{5} \eta_{1-1}\rangle]$ $-\frac{1}{2}\sqrt{6}[\alpha_{2-2}\rangle + (1/\sqrt{6}) \eta_{2-2}\rangle]$ |
| $ W_{11}\rangle$ $ W_{10}\rangle$ $ W_{1-1}\rangle$ | $\frac{1}{3} [\xi_{20}\rangle + \sqrt{5} \xi_{10}\rangle + 2 \xi_{00}\rangle]$ $\frac{1}{3} [\sqrt{3} \xi_{2-1}\rangle + \sqrt{5} \xi_{1-1}\rangle]$ $\frac{1}{3}\sqrt{6} \xi_{2-2}\rangle$ |
| $ U_{22}\rangle$ $ U_{21}\rangle$ $ U_{20}\rangle$ $ U_{2-1}\rangle$ $ U_{2-2}\rangle$ | $-(1/\sqrt{10}) [\sqrt{2} \beta_{31}\rangle + \sqrt{5} \beta_{21}\rangle + \sqrt{3} \beta_{11}\rangle] + (1/3\sqrt{10}) [\sqrt{2} \zeta_{31}\rangle + \sqrt{5} \zeta_{21}\rangle + \sqrt{3} \zeta_{11}\rangle]$ $-\sqrt{(3/20)} [2 \beta_{30}\rangle + \sqrt{5} \beta_{20}\rangle + \beta_{10}\rangle] + (1/\sqrt{60}) [2 \zeta_{30}\rangle + \sqrt{5} \zeta_{20}\rangle + \zeta_{10}\rangle]$ $-(1/2\sqrt{5}) [2\sqrt{6} \beta_{3-1}\rangle + \sqrt{15} \beta_{2-1}\rangle + \beta_{1-1}\rangle] + (1/6\sqrt{5}) [2\sqrt{6} \zeta_{3-1}\rangle + \sqrt{15} \zeta_{2-1}\rangle + \zeta_{1-1}\rangle]$ $-\frac{\sqrt{1}}{2} [2 \beta_{3-2}\rangle + \beta_{2-2}\rangle] + \frac{1}{3}\frac{\sqrt{1}}{2} [2 \zeta_{3-2}\rangle + \zeta_{2-2}\rangle]$ $-\sqrt{3} \beta_{3-3}\rangle + \sqrt{\frac{1}{3}} \zeta_{3-3}\rangle$ |
| $ V_{22}\rangle$ $ V_{21}\rangle$ $ V_{20}\rangle$ $ V_{2-1}\rangle$ $ V_{2-2}\rangle$ | $-(1/\sqrt{10}) [\sqrt{2} \alpha_{31}\rangle + \sqrt{5} \alpha_{21}\rangle + \sqrt{3} \alpha_{11}\rangle] + (1/3\sqrt{10}) [\sqrt{2} \eta_{31}\rangle + \sqrt{5} \eta_{21}\rangle + \sqrt{3} \eta_{11}\rangle]$ $-\sqrt{(3/20)} [2 \alpha_{30}\rangle + \sqrt{5} \alpha_{20}\rangle + \alpha_{10}\rangle] + (1/\sqrt{60}) [2 \eta_{30}\rangle + \sqrt{5} \eta_{20}\rangle + \eta_{10}\rangle]$ $-(1/2\sqrt{5}) [2\sqrt{6} \alpha_{3-1}\rangle + \sqrt{15} \alpha_{2-1}\rangle + \alpha_{1-1}\rangle] + (1/6\sqrt{5}) [2\sqrt{6} \eta_{3-1}\rangle + \sqrt{15} \eta_{2-1}\rangle + \eta_{1-1}\rangle]$ $-\frac{\sqrt{1}}{2} [2 \alpha_{3-2}\rangle + \alpha_{2-2}\rangle] + \frac{1}{3}\frac{\sqrt{1}}{2} [2 \eta_{3-2}\rangle + \eta_{2-2}\rangle]$ $-\sqrt{3} \alpha_{3-3}\rangle + \sqrt{\frac{1}{3}} \eta_{3-3}\rangle$ |
| $ W_{22}\rangle$ $ W_{21}\rangle$ $ W_{20}\rangle$ $ W_{2-1}\rangle$ $ W_{2-2}\rangle$ | $\frac{1}{3}\sqrt{(2/5)} [\sqrt{2} \xi_{31}\rangle + \sqrt{5} \xi_{21}\rangle + \sqrt{3} \xi_{11}\rangle]$ $(1/\sqrt{15}) [2 \xi_{30}\rangle + \sqrt{5} \xi_{20}\rangle + \xi_{10}\rangle]$ $(1/3\sqrt{5}) [2\sqrt{6} \xi_{3-1}\rangle + \sqrt{15} \xi_{2-1}\rangle + \xi_{1-1}\rangle]$ $\frac{1}{3}\sqrt{2} [2 \xi_{3-2}\rangle + \xi_{2-2}\rangle]$ $(2/\sqrt{3}) \xi_{3-3}\rangle$ |

| | u_{-s+} |
|---|--|
| $ U11\rangle$ $ U10\rangle$ $ U1-1\rangle$ | $\frac{1}{2}\sqrt{6} \gamma_{22}\rangle - (1/\sqrt{6}) \xi_{22}\rangle$ $\frac{1}{2}[\sqrt{3} \gamma_{21}\rangle - \sqrt{5} \gamma_{11}\rangle] - (1/6)[\sqrt{3} \xi_{21}\rangle - \sqrt{5} \xi_{11}\rangle]$ $\frac{1}{2}[\gamma_{20}\rangle - \sqrt{5} \gamma_{10}\rangle + 2 \gamma_{00}\rangle] - (1/6)[\xi_{20}\rangle - \sqrt{5} \xi_{10}\rangle + 2 \xi_{00}\rangle]$ |
| $ V11\rangle$ $ V10\rangle$ $ V1-1\rangle$ | $-\frac{1}{3}\sqrt{6} \zeta_{22}\rangle$ $-\frac{1}{3}[\sqrt{3} \zeta_{21}\rangle - \sqrt{5} \zeta_{11}\rangle]$ $-\frac{1}{3}[\zeta_{20}\rangle - \sqrt{5} \zeta_{10}\rangle + 2 \zeta_{00}\rangle]$ |
| $ W11\rangle$ $ W10\rangle$ $ W1-1\rangle$ | $-\frac{1}{2}\sqrt{6} \alpha_{22}\rangle - (1/\sqrt{6}) \eta_{22}\rangle$ $-\frac{1}{2}[\sqrt{3} \alpha_{21}\rangle - \sqrt{5} \alpha_{11}\rangle] - (1/6)[\sqrt{3} \eta_{21}\rangle - \sqrt{5} \eta_{11}\rangle]$ $-\frac{1}{2}[\alpha_{20}\rangle - \sqrt{5} \alpha_{10}\rangle + 2 \alpha_{00}\rangle] - (1/6)[\eta_{20}\rangle - \sqrt{5} \eta_{10}\rangle + 2 \eta_{00}\rangle]$ |
| $ U22\rangle$ $ U21\rangle$ $ U20\rangle$ $ U2-1\rangle$ $ U2-2\rangle$ | $\sqrt{3} \gamma_{33}\rangle - \sqrt{\frac{1}{3}} \xi_{33}\rangle$ $\sqrt{\frac{1}{2}}[2 \gamma_{32}\rangle - \gamma_{22}\rangle] - \frac{1}{3}\sqrt{\frac{1}{2}}[2 \xi_{32}\rangle - \xi_{22}\rangle]$ $(1/2\sqrt{5})[2\sqrt{6} \gamma_{31}\rangle - \sqrt{15} \gamma_{21}\rangle + \gamma_{11}\rangle] - (1/6\sqrt{5})[2\sqrt{6} \xi_{31}\rangle - \sqrt{15} \xi_{21}\rangle + \xi_{11}\rangle]$ $\sqrt{(3/20)}[2 \gamma_{30}\rangle - \sqrt{5} \gamma_{20}\rangle + \gamma_{10}\rangle] - (1/\sqrt{60})[2 \xi_{30}\rangle - \sqrt{5} \xi_{20}\rangle + \xi_{10}\rangle]$ $(1/\sqrt{10})[\sqrt{2} \gamma_{3-1}\rangle - \sqrt{5} \gamma_{2-1}\rangle + \sqrt{3} \gamma_{1-1}\rangle] - (1/3\sqrt{10})[\sqrt{2} \xi_{3-1}\rangle - \sqrt{5} \xi_{2-1}\rangle + \sqrt{3} \xi_{1-1}\rangle]$ |
| $ V22\rangle$ $ V21\rangle$ $ V20\rangle$ $ V2-1\rangle$ $ V2-2\rangle$ | $-(2/\sqrt{3}) \zeta_{33}\rangle$ $-\frac{1}{3}\sqrt{2}[2 \zeta_{32}\rangle - \zeta_{22}\rangle]$ $-(1/3\sqrt{5})[2\sqrt{6} \zeta_{31}\rangle - \sqrt{15} \zeta_{21}\rangle + \zeta_{11}\rangle]$ $-(1/\sqrt{15})[2 \zeta_{30}\rangle - \sqrt{5} \zeta_{20}\rangle + \zeta_{10}\rangle]$ $-\frac{1}{3}\sqrt{(2/5)}[\sqrt{2} \zeta_{3-1}\rangle - \sqrt{5} \zeta_{2-1}\rangle + \sqrt{3} \zeta_{1-1}\rangle]$ |
| $ W22\rangle$ $ W21\rangle$ $ W20\rangle$ $ W2-1\rangle$ $ W2-2\rangle$ | $-\sqrt{3} \alpha_{33}\rangle - \sqrt{\frac{1}{3}} \eta_{33}\rangle$ $-\sqrt{\frac{1}{2}}[2 \alpha_{32}\rangle - \alpha_{22}\rangle] - \frac{1}{3}\sqrt{\frac{1}{2}}[2 \eta_{32}\rangle - \eta_{22}\rangle]$ $-(1/2\sqrt{5})[2\sqrt{6} \alpha_{31}\rangle - \sqrt{15} \alpha_{21}\rangle + \alpha_{11}\rangle] - (1/6\sqrt{5})[2\sqrt{6} \eta_{31}\rangle - \sqrt{15} \eta_{21}\rangle + \eta_{11}\rangle]$ $-\sqrt{(3/20)}[2 \alpha_{30}\rangle - \sqrt{5} \alpha_{20}\rangle + \alpha_{10}\rangle] - (1/\sqrt{60})[2 \eta_{30}\rangle - \sqrt{5} \eta_{20}\rangle + \eta_{10}\rangle]$ $-(1/\sqrt{10})[\sqrt{2} \alpha_{3-1}\rangle - \sqrt{5} \alpha_{2-1}\rangle + \sqrt{3} \alpha_{1-1}\rangle] - (1/3\sqrt{10})[\sqrt{2} \eta_{3-1}\rangle - \sqrt{5} \eta_{2-1}\rangle + \sqrt{3} \eta_{1-1}\rangle]$ |

(ii) SPIN-ORBIT OPERATORS ON (P,Q,R) STATES OF (${}^4A_2 \times {}^2T_2$)

| | $U_Z S_Z$ | $U_+ S_-$ | $U_- S_+$ |
|--|---|---|--|
| $ P_{11}\rangle$ $ P_{10}\rangle$ $ P_{1-1}\rangle$ | $-\frac{1}{2} U_{21}\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} U_{11}\rangle$ $-\sqrt{\frac{1}{3}} U_{20}\rangle$ $-\frac{1}{2} U_{2-1}\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} U_{1-1}\rangle$ | $-\frac{1}{2}\sqrt{\frac{1}{3}} W_{20}\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} W_{10}\rangle$ $-\frac{1}{2} W_{2-1}\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} W_{1-1}\rangle$ $-\sqrt{\frac{1}{2}} W_{2-2}\rangle$ | $\sqrt{\frac{1}{2}} V_{22}\rangle$ $\frac{1}{2} V_{21}\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} V_{11}\rangle$ $\frac{1}{2}\sqrt{\frac{1}{3}} V_{20}\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} V_{10}\rangle$ |
| $ Q_{11}\rangle$ $ Q_{10}\rangle$ $ Q_{1-1}\rangle$ | $-\frac{1}{4} V_{21}\rangle - \frac{1}{4}\sqrt{\frac{1}{3}} V_{11}\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} V_{20}\rangle$ $-\frac{1}{4} V_{2-1}\rangle + \frac{1}{4}\sqrt{\frac{1}{3}} V_{1-1}\rangle$ | $\frac{1}{2}\sqrt{\frac{1}{3}} U_{20}\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} U_{10}\rangle$ $\frac{1}{2} U_{2-1}\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} U_{1-1}\rangle$ $\sqrt{\frac{1}{2}} U_{2-2}\rangle$ | $-\sqrt{2} W_{22}\rangle$ $- W_{21}\rangle + \sqrt{\frac{1}{3}} W_{11}\rangle$ $-\sqrt{\frac{1}{3}} W_{20}\rangle + \sqrt{\frac{1}{3}} W_{10}\rangle$ |
| $ R_{11}\rangle$ $ R_{10}\rangle$ $ R_{1-1}\rangle$ | $-\frac{1}{4} W_{21}\rangle - \frac{1}{4}\sqrt{\frac{1}{3}} W_{11}\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} W_{20}\rangle$ $-\frac{1}{4} W_{2-1}\rangle + \frac{1}{4}\sqrt{\frac{1}{3}} W_{1-1}\rangle$ | $\sqrt{\frac{1}{3}} V_{20}\rangle + \sqrt{\frac{1}{3}} V_{10}\rangle$ $ V_{2-1}\rangle + \sqrt{\frac{1}{3}} V_{1-1}\rangle$ $\sqrt{2} V_{2-2}\rangle$ | $-\sqrt{\frac{1}{2}} U_{22}\rangle$ $-\frac{1}{2} U_{21}\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} U_{11}\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} U_{20}\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} U_{10}\rangle$ |
| $ P_{22}\rangle$ $ P_{21}\rangle$ $ P_{20}\rangle$ $ P_{2-1}\rangle$ $ P_{2-2}\rangle$ | $\sqrt{\frac{1}{3}} U_{22}\rangle$ $\frac{1}{2}\sqrt{\frac{1}{3}} U_{21}\rangle - \frac{1}{2} U_{11}\rangle$ $-\sqrt{\frac{1}{3}} U_{10}\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} U_{2-1}\rangle - \frac{1}{2} U_{1-1}\rangle$ $-\sqrt{\frac{1}{3}} U_{2-2}\rangle$ | $(1/\sqrt{6}) W_{21}\rangle + \sqrt{\frac{1}{2}} W_{11}\rangle$ $\frac{1}{2} W_{20}\rangle + \frac{1}{2} W_{10}\rangle$ $\frac{1}{2} W_{2-1}\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} W_{1-1}\rangle$ $(1/\sqrt{6}) W_{2-2}\rangle$ 0 | 0 $(1/\sqrt{6}) V_{22}\rangle$ $\frac{1}{2} V_{21}\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} V_{11}\rangle$ $\frac{1}{2} V_{20}\rangle - \frac{1}{2} V_{10}\rangle$ $(1/\sqrt{6}) V_{2-1}\rangle - \sqrt{\frac{1}{2}} V_{1-1}\rangle$ |
| $ Q_{22}\rangle$ $ Q_{21}\rangle$ $ Q_{20}\rangle$ $ Q_{2-1}\rangle$ $ Q_{2-2}\rangle$ | $\frac{1}{2}\sqrt{\frac{1}{3}} V_{22}\rangle$ $\frac{1}{4}\sqrt{\frac{1}{3}} V_{21}\rangle - \frac{1}{4} V_{11}\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} V_{10}\rangle$ $-\frac{1}{4}\sqrt{\frac{1}{3}} V_{2-1}\rangle - \frac{1}{4} V_{1-1}\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} V_{2-2}\rangle$ | $-(1/\sqrt{6}) U_{21}\rangle - \sqrt{\frac{1}{2}} U_{11}\rangle$ $-\frac{1}{2} U_{20}\rangle - \frac{1}{2} U_{10}\rangle$ $-\frac{1}{2} U_{2-1}\rangle - \frac{1}{2}\sqrt{\frac{1}{3}} U_{1-1}\rangle$ $-(1/\sqrt{6}) U_{2-2}\rangle$ 0 | 0 $-\sqrt{\frac{1}{3}} W_{22}\rangle$ $- W_{21}\rangle + \sqrt{\frac{1}{3}} W_{11}\rangle$ $- W_{20}\rangle + W_{10}\rangle$ $-\sqrt{\frac{1}{3}} W_{2-1}\rangle + \sqrt{2} W_{1-1}\rangle$ |
| $ R_{22}\rangle$ $ R_{21}\rangle$ $ R_{20}\rangle$ $ R_{2-1}\rangle$ $ R_{2-2}\rangle$ | $\frac{1}{2}\sqrt{\frac{1}{3}} W_{22}\rangle$ $\frac{1}{4}\sqrt{\frac{1}{3}} W_{21}\rangle - \frac{1}{4} W_{11}\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} W_{10}\rangle$ $-\frac{1}{4}\sqrt{\frac{1}{3}} W_{2-1}\rangle - \frac{1}{4} W_{1-1}\rangle$ $-\frac{1}{2}\sqrt{\frac{1}{3}} W_{2-2}\rangle$ | $-\sqrt{\frac{1}{3}} V_{21}\rangle - \sqrt{2} V_{11}\rangle$ $- V_{20}\rangle - V_{10}\rangle$ $- V_{2-1}\rangle - \sqrt{\frac{1}{3}} V_{1-1}\rangle$ $-\sqrt{\frac{1}{3}} V_{2-2}\rangle$ 0 | 0 $-(1/\sqrt{6}) U_{22}\rangle$ $-\frac{1}{2} U_{21}\rangle + \frac{1}{2}\sqrt{\frac{1}{3}} U_{11}\rangle$ $-\frac{1}{2} U_{20}\rangle + \frac{1}{2} U_{10}\rangle$ $-(1/\sqrt{6}) U_{2-1}\rangle + \sqrt{\frac{1}{2}} U_{1-1}\rangle$ |

(iii) SPIN-ORBIT OPERATORS ON (α, β, γ) STATES OF $({}^4A_2 \times {}^4T_1)$

| | U_{+S_-} | U_{-S_+} |
|------------------------|---|---|
| $ \alpha_{33}\rangle$ | $-\sqrt{3} W_{22}\rangle$ | 0 |
| $ \alpha_{32}\rangle$ | $-\sqrt{2} W_{21}\rangle$ | 0 |
| $ \alpha_{31}\rangle$ | $-\sqrt{(6/5)} W_{20}\rangle$ | $-(1/\sqrt{5}) V_{22}\rangle$ |
| $ \alpha_{30}\rangle$ | $-\sqrt{(3/5)} W_{2-1}\rangle$ | $-\sqrt{(3/5)} V_{21}\rangle$ |
| $ \alpha_{3-1}\rangle$ | $-(1/\sqrt{5}) W_{2-2}\rangle$ | $-\sqrt{(6/5)} V_{20}\rangle$ |
| $ \alpha_{3-2}\rangle$ | 0 | $-\sqrt{2} V_{2-1}\rangle$ |
| $ \alpha_{3-3}\rangle$ | 0 | $-\sqrt{3} V_{2-2}\rangle$ |
| $ \alpha_{22}\rangle$ | $\sqrt{\frac{1}{2}} W_{21}\rangle - \frac{1}{2}\sqrt{6} W_{11}\rangle$ | 0 |
| $ \alpha_{21}\rangle$ | $\frac{1}{2}\sqrt{3} W_{20}\rangle - \frac{1}{2}\sqrt{3} W_{10}\rangle$ | $-\sqrt{\frac{1}{2}} V_{22}\rangle$ |
| $ \alpha_{20}\rangle$ | $\frac{1}{2}\sqrt{3} W_{2-1}\rangle - \frac{1}{2} W_{1-1}\rangle$ | $-\frac{1}{2}\sqrt{3} V_{21}\rangle - \frac{1}{2} V_{11}\rangle$ |
| $ \alpha_{2-1}\rangle$ | $\sqrt{\frac{1}{2}} W_{2-2}\rangle$ | $-\frac{1}{2}\sqrt{3} V_{20}\rangle - \frac{1}{2}\sqrt{3} V_{10}\rangle$ |
| $ \alpha_{2-2}\rangle$ | 0 | $-\sqrt{\frac{1}{2}} V_{2-1}\rangle - \frac{1}{2}\sqrt{6} V_{1-1}\rangle$ |
| $ \alpha_{11}\rangle$ | $-\frac{1}{2}(1/\sqrt{5})[W_{20}\rangle - 5 W_{10}\rangle]$ | $-\sqrt{(3/10)} V_{22}\rangle$ |
| $ \alpha_{10}\rangle$ | $-\frac{1}{2}(1/\sqrt{5})[\sqrt{3} W_{2-1}\rangle - 5 W_{1-1}\rangle]$ | $-\frac{1}{2}(1/\sqrt{5})[\sqrt{3} V_{21}\rangle + 5 V_{11}\rangle]$ |
| $ \alpha_{1-1}\rangle$ | $-\sqrt{(3/10)} W_{2-2}\rangle$ | $-\frac{1}{2}(1/\sqrt{5})[V_{20}\rangle + 5 V_{10}\rangle]$ |
| $ \alpha_{00}\rangle$ | $- W_{1-1}\rangle$ | $- V_{11}\rangle$ |

U_{ZS_Z} on all α states give zero

| | $u_z s_z$ | $u_- s_+$ |
|-----------------------|--|---|
| $ \beta_{33}\rangle$ | 0 | 0 |
| $ \beta_{32}\rangle$ | $-\frac{1}{2} W_{22}\rangle$ | 0 |
| $ \beta_{31}\rangle$ | $-\sqrt{(2/5)} W_{21}\rangle$ | $-(1/\sqrt{5}) U_{22}\rangle$ |
| $ \beta_{30}\rangle$ | $-(3/2\sqrt{5}) W_{20}\rangle$ | $-\sqrt{(3/5)} U_{21}\rangle$ |
| $ \beta_{3-1}\rangle$ | $-\sqrt{(2/5)} W_{2-1}\rangle$ | $-\sqrt{(6/5)} U_{20}\rangle$ |
| $ \beta_{3-2}\rangle$ | $-\frac{1}{2} W_{2-2}\rangle$ | $-\sqrt{2} U_{2-1}\rangle$ |
| $ \beta_{3-3}\rangle$ | 0 | $-\sqrt{3} U_{2-2}\rangle$ |
| $ \beta_{22}\rangle$ | $-\frac{1}{2} W_{22}\rangle$ | 0 |
| $ \beta_{21}\rangle$ | $-\frac{1}{4} W_{21}\rangle - \frac{1}{4}\sqrt{3} W_{11}\rangle$ | $-\sqrt{\frac{1}{2}} U_{22}\rangle$ |
| $ \beta_{20}\rangle$ | $-\frac{1}{2} W_{10}\rangle$ | $-\frac{1}{2}\sqrt{3} U_{21}\rangle - \frac{1}{2} U_{11}\rangle$ |
| $ \beta_{2-1}\rangle$ | $\frac{1}{4} W_{2-1}\rangle - \frac{1}{4}\sqrt{3} W_{1-1}\rangle$ | $-\frac{1}{2}\sqrt{3} U_{20}\rangle - \frac{1}{2}\sqrt{3} U_{10}\rangle$ |
| $ \beta_{2-2}\rangle$ | $\frac{1}{2} W_{2-2}\rangle$ | $-\sqrt{\frac{1}{2}} U_{2-1}\rangle - \frac{1}{2}\sqrt{6} U_{1-1}\rangle$ |
| $ \beta_{11}\rangle$ | $\frac{1}{4}(1/\sqrt{5}) [\sqrt{3} W_{21}\rangle - 5 W_{11}\rangle]$ | $-\sqrt{(3/10)} U_{22}\rangle$ |
| $ \beta_{10}\rangle$ | $\frac{1}{2}(1/\sqrt{5}) W_{20}\rangle$ | $-\frac{1}{2}(1/\sqrt{5}) [\sqrt{3} U_{21}\rangle + 5 U_{11}\rangle]$ |
| $ \beta_{1-1}\rangle$ | $\frac{1}{4}(1/\sqrt{5}) [\sqrt{3} W_{2-1}\rangle + 5 W_{1-1}\rangle]$ | $-\frac{1}{2}(1/\sqrt{5}) [U_{20}\rangle + 5 U_{10}\rangle]$ |
| $ \beta_{00}\rangle$ | $\frac{1}{2} W_{10}\rangle$ | $- U_{11}\rangle$ |

$u_+ s_-$ on all β states give zero.

| | $U_Z S_Z$ | $U_+ S_-$ |
|------------------------|--|--|
| $ \gamma_{33}\rangle$ | 0 | $\sqrt{3} U_{22}\rangle$ |
| $ \gamma_{32}\rangle$ | $-\frac{1}{2} V_{22}\rangle$ | $\sqrt{2} U_{21}\rangle$ |
| $ \gamma_{31}\rangle$ | $-\sqrt{(2/5)} V_{21}\rangle$ | $\sqrt{(6/5)} U_{20}\rangle$ |
| $ \gamma_{30}\rangle$ | $-(3/2\sqrt{5}) V_{20}\rangle$ | $\sqrt{(3/5)} U_{2-1}\rangle$ |
| $ \gamma_{3-1}\rangle$ | $-\sqrt{(2/5)} V_{2-1}\rangle$ | $(1/\sqrt{5}) U_{2-2}\rangle$ |
| $ \gamma_{3-2}\rangle$ | $-\frac{1}{2} V_{2-2}\rangle$ | 0 |
| $ \gamma_{3-3}\rangle$ | 0 | 0 |
| $ \gamma_{22}\rangle$ | $-\frac{1}{2} V_{22}\rangle$ | $-\sqrt{\frac{1}{2}} U_{21}\rangle + \frac{1}{2}\sqrt{6} U_{11}\rangle$ |
| $ \gamma_{21}\rangle$ | $-\frac{1}{4} V_{21}\rangle - \frac{1}{4}\sqrt{3} V_{11}\rangle$ | $-\frac{1}{2}\sqrt{3} U_{20}\rangle + \frac{1}{2}\sqrt{3} U_{10}\rangle$ |
| $ \gamma_{20}\rangle$ | $-\frac{1}{2} V_{10}\rangle$ | $-\frac{1}{2}\sqrt{3} U_{2-1}\rangle + \frac{1}{2} U_{1-1}\rangle$ |
| $ \gamma_{2-1}\rangle$ | $\frac{1}{4} V_{2-1}\rangle - \frac{1}{4}\sqrt{3} V_{1-1}\rangle$ | $-\sqrt{\frac{1}{2}} U_{2-2}\rangle$ |
| $ \gamma_{2-2}\rangle$ | $\frac{1}{2} V_{2-2}\rangle$ | 0 |
| $ \gamma_{11}\rangle$ | $\frac{1}{4}(1/\sqrt{5}) [\sqrt{3} V_{21}\rangle - 5 V_{11}\rangle]$ | $\frac{1}{2}(1/\sqrt{5}) [U_{20}\rangle - 5 U_{10}\rangle]$ |
| $ \gamma_{10}\rangle$ | $\frac{1}{2}(1/\sqrt{5}) V_{20}\rangle$ | $\frac{1}{2}(1/\sqrt{5}) [\sqrt{3} U_{2-1}\rangle - 5 U_{1-1}\rangle]$ |
| $ \gamma_{1-1}\rangle$ | $\frac{1}{4}(1/\sqrt{5}) [\sqrt{3} V_{2-1}\rangle + 5 V_{1-1}\rangle]$ | $\sqrt{(3/10)} U_{2-2}\rangle$ |
| $ \gamma_{00}\rangle$ | $\frac{1}{2} V_{10}\rangle$ | $ U_{1-1}\rangle$ |

$U_- S_+$ on all γ states give zero.

(iv) SPIN-ORBIT OPERATORS ON (η, ζ, ξ) STATES OF $({}^4A_2 \times {}^4T_2)$

| | u_{s_z} | u_{s_-} | u_{s_+} |
|----------------------|--|---|---|
| $ \eta_{33}\rangle$ | 0 | $-\sqrt{3} w_{22}\rangle$ | 0 |
| $ \eta_{32}\rangle$ | $ u_{22}\rangle$ | $-\sqrt{2} w_{21}\rangle$ | 0 |
| $ \eta_{31}\rangle$ | $\sqrt{(8/5)} u_{21}\rangle$ | $-\sqrt{(6/5)} w_{20}\rangle$ | $(1/\sqrt{5}) v_{22}\rangle$ |
| $ \eta_{30}\rangle$ | $(3/\sqrt{5}) u_{20}\rangle$ | $-\sqrt{(3/5)} w_{2-1}\rangle$ | $\sqrt{(3/5)} v_{21}\rangle$ |
| $ \eta_{3-1}\rangle$ | $\sqrt{(8/5)} u_{2-1}\rangle$ | $-(1/\sqrt{5}) w_{2-2}\rangle$ | $\sqrt{(6/5)} v_{20}\rangle$ |
| $ \eta_{3-2}\rangle$ | $ u_{2-2}\rangle$ | 0 | $\sqrt{2} v_{2-1}\rangle$ |
| $ \eta_{3-3}\rangle$ | 0 | 0 | $\sqrt{3} v_{2-2}\rangle$ |
| $ \eta_{22}\rangle$ | $ u_{22}\rangle$ | $\sqrt{1/2} w_{21}\rangle - \frac{1}{2}\sqrt{6} w_{11}\rangle$ | 0 |
| $ \eta_{21}\rangle$ | $\frac{1}{2} u_{21}\rangle + \frac{1}{2}\sqrt{3} u_{11}\rangle$ | $\frac{1}{2}\sqrt{3} w_{20}\rangle - \frac{1}{2}\sqrt{3} w_{10}\rangle$ | $\sqrt{1/2} v_{22}\rangle$ |
| $ \eta_{20}\rangle$ | $ u_{10}\rangle$ | $\frac{1}{2}\sqrt{3} w_{2-1}\rangle - \frac{1}{2} w_{1-1}\rangle$ | $\frac{1}{2}\sqrt{3} v_{21}\rangle + \frac{1}{2} v_{11}\rangle$ |
| $ \eta_{2-1}\rangle$ | $-\frac{1}{2} u_{2-1}\rangle + \frac{1}{2}\sqrt{3} u_{1-1}\rangle$ | $\sqrt{1/2} w_{2-2}\rangle$ | $\frac{1}{2}\sqrt{3} v_{20}\rangle + \frac{1}{2}\sqrt{3} v_{10}\rangle$ |
| $ \eta_{2-2}\rangle$ | $- u_{2-2}\rangle$ | 0 | $\sqrt{1/2} v_{2-1}\rangle + \frac{1}{2}\sqrt{6} v_{1-1}\rangle$ |
| $ \eta_{11}\rangle$ | $-\frac{1}{2}(1/\sqrt{5})[\sqrt{3} u_{21}\rangle - 5 u_{11}\rangle]$ | $-\frac{1}{2}(1/\sqrt{5})[w_{20}\rangle - 5 w_{10}\rangle]$ | $\sqrt{(3/10)} v_{22}\rangle$ |
| $ \eta_{10}\rangle$ | $-(1/\sqrt{5}) u_{20}\rangle$ | $-\frac{1}{2}(1/\sqrt{5})[\sqrt{3} w_{2-1}\rangle - 5 w_{1-1}\rangle]$ | $\frac{1}{2}(1/\sqrt{5})[\sqrt{3} v_{21}\rangle + 5 v_{11}\rangle]$ |
| $ \eta_{1-1}\rangle$ | $-\frac{1}{2}(1/\sqrt{5})[\sqrt{3} u_{2-1}\rangle + 5 u_{1-1}\rangle]$ | $-\sqrt{(3/10)} w_{2-2}\rangle$ | $\frac{1}{2}(1/\sqrt{5})[v_{20}\rangle + 5 v_{10}\rangle]$ |
| $ \eta_{00}\rangle$ | $- u_{10}\rangle$ | $- w_{1-1}\rangle$ | $ v_{11}\rangle$ |

All coefficients must be multiplied by $\frac{1}{2}$.

| | $u_{z,z}$ | $u_{+,-}$ | $u_{-,+}$ |
|-----------------------|---|--|---|
| $ \zeta_{33}\rangle$ | 0 | $-2\sqrt{3} V_{22}\rangle$ | 0 |
| $ \zeta_{32}\rangle$ | $-\frac{1}{2} W_{22}\rangle$ | $-2\sqrt{2} V_{21}\rangle$ | 0 |
| $ \zeta_{31}\rangle$ | $-\sqrt{(2/5)} W_{21}\rangle$ | $-2\sqrt{(6/5)} V_{20}\rangle$ | $(1/\sqrt{5}) U_{22}\rangle$ |
| $ \zeta_{30}\rangle$ | $-(3/2\sqrt{5}) W_{20}\rangle$ | $-2\sqrt{(3/5)} V_{2-1}\rangle$ | $\sqrt{(3/5)} U_{21}\rangle$ |
| $ \zeta_{3-1}\rangle$ | $-\sqrt{(2/5)} W_{2-1}\rangle$ | $-2(1/\sqrt{5}) V_{2-2}\rangle$ | $\sqrt{(6/5)} U_{20}\rangle$ |
| $ \zeta_{3-2}\rangle$ | $-\frac{1}{2} W_{2-2}\rangle$ | 0 | $\sqrt{2} U_{2-1}\rangle$ |
| $ \zeta_{3-3}\rangle$ | 0 | 0 | $\sqrt{3} U_{2-2}\rangle$ |
| $ \zeta_{22}\rangle$ | $-\frac{1}{2} W_{22}\rangle$ | $\sqrt{2} V_{21}\rangle - \sqrt{6} V_{11}\rangle$ | 0 |
| $ \zeta_{21}\rangle$ | $-\frac{1}{4} W_{21}\rangle - \frac{1}{4}\sqrt{3} W_{11}\rangle$ | $\sqrt{3} V_{20}\rangle - \sqrt{3} V_{10}\rangle$ | $\sqrt{\frac{1}{2}} U_{22}\rangle$ |
| $ \zeta_{20}\rangle$ | $-\frac{1}{2} W_{10}\rangle$ | $\sqrt{3} V_{2-1}\rangle - V_{1-1}\rangle$ | $\frac{1}{2}\sqrt{3} U_{21}\rangle + \frac{1}{2} U_{11}\rangle$ |
| $ \zeta_{2-1}\rangle$ | $\frac{1}{4} W_{2-1}\rangle - \frac{1}{4}\sqrt{3} W_{1-1}\rangle$ | $\sqrt{2} V_{2-2}\rangle$ | $\frac{1}{2}\sqrt{3} U_{20}\rangle + \frac{1}{2}\sqrt{3} U_{10}\rangle$ |
| $ \zeta_{2-2}\rangle$ | $\frac{1}{2} W_{2-2}\rangle$ | 0 | $\sqrt{\frac{1}{2}} U_{2-1}\rangle + \frac{1}{2}\sqrt{6} U_{1-1}\rangle$ |
| $ \zeta_{11}\rangle$ | $\frac{1}{4}\sqrt{(3/5)} W_{21}\rangle - \frac{1}{4}\sqrt{5} W_{11}\rangle$ | $-(1/\sqrt{5}) V_{20}\rangle + \sqrt{5} V_{10}\rangle$ | $\sqrt{(3/10)} U_{22}\rangle$ |
| $ \zeta_{10}\rangle$ | $\frac{1}{2}(1/\sqrt{5}) W_{20}\rangle$ | $-\sqrt{(3/5)} V_{2-1}\rangle + \sqrt{5} V_{1-1}\rangle$ | $\frac{1}{2}\sqrt{(3/5)} U_{21}\rangle + \frac{1}{2}\sqrt{5} U_{11}\rangle$ |
| $ \zeta_{1-1}\rangle$ | $\frac{1}{4}\sqrt{(3/5)} W_{2-1}\rangle + \frac{1}{4}\sqrt{5} W_{1-1}\rangle$ | $-\sqrt{(6/5)} V_{2-2}\rangle$ | $\frac{1}{2}\sqrt{(1/5)} U_{20}\rangle + \frac{1}{2}\sqrt{5} U_{10}\rangle$ |
| $ \zeta_{00}\rangle$ | $\frac{1}{2} W_{10}\rangle$ | $-2 V_{1-1}\rangle$ | $ U_{11}\rangle$ |

All coefficients must be multiplied by $\frac{1}{3}$.

| | $u_{z s_z}$ | $u_{+ s_-}$ | $u_{- s_+}$ |
|---------------------|---|--|---|
| $ \xi_{33}\rangle$ | 0 | $-\sqrt{3} u_{22}\rangle$ | 0 |
| $ \xi_{32}\rangle$ | $-\frac{1}{2} v_{22}\rangle$ | $-\sqrt{2} u_{21}\rangle$ | 0 |
| $ \xi_{31}\rangle$ | $-\sqrt{(2/5)} v_{21}\rangle$ | $-\sqrt{(6/5)} u_{20}\rangle$ | $2(1/\sqrt{5}) w_{22}\rangle$ |
| $ \xi_{30}\rangle$ | $-(3/2\sqrt{5}) v_{20}\rangle$ | $-\sqrt{(3/5)} u_{2-1}\rangle$ | $2\sqrt{(3/5)} w_{21}\rangle$ |
| $ \xi_{3-1}\rangle$ | $-\sqrt{(2/5)} v_{2-1}\rangle$ | $-(1/\sqrt{5}) u_{2-2}\rangle$ | $2\sqrt{(6/5)} w_{20}\rangle$ |
| $ \xi_{3-2}\rangle$ | $-\frac{1}{2} v_{2-2}\rangle$ | 0 | $2\sqrt{2} w_{2-1}\rangle$ |
| $ \xi_{3-3}\rangle$ | 0 | 0 | $2\sqrt{3} w_{2-2}\rangle$ |
| $ \xi_{22}\rangle$ | $-\frac{1}{2} v_{22}\rangle$ | $\sqrt{\frac{1}{2}} u_{21}\rangle - \frac{1}{2}\sqrt{6} u_{11}\rangle$ | 0 |
| $ \xi_{21}\rangle$ | $-\frac{1}{4} v_{21}\rangle - \frac{1}{4}\sqrt{3} v_{11}\rangle$ | $\frac{1}{2}\sqrt{3} u_{20}\rangle - \frac{1}{2}\sqrt{3} u_{10}\rangle$ | $\sqrt{2} w_{22}\rangle$ |
| $ \xi_{20}\rangle$ | $-\frac{1}{2} v_{10}\rangle$ | $\frac{1}{2}\sqrt{3} u_{2-1}\rangle - \frac{1}{2} u_{1-1}\rangle$ | $\sqrt{3} w_{21}\rangle + w_{11}\rangle$ |
| $ \xi_{2-1}\rangle$ | $\frac{1}{4} v_{2-1}\rangle - \frac{1}{4}\sqrt{3} v_{1-1}\rangle$ | $\sqrt{\frac{1}{2}} u_{2-2}\rangle$ | $\sqrt{3} w_{20}\rangle + \sqrt{3} w_{10}\rangle$ |
| $ \xi_{2-2}\rangle$ | $\frac{1}{2} v_{2-2}\rangle$ | 0 | $\sqrt{2} w_{2-2}\rangle + \sqrt{6} w_{1-1}\rangle$ |
| $ \xi_{11}\rangle$ | $\frac{1}{4}\sqrt{(3/5)} v_{21}\rangle - \frac{1}{4}\sqrt{5} v_{11}\rangle$ | $-\frac{1}{2}(1/\sqrt{5}) u_{20}\rangle + \frac{1}{2}\sqrt{5} u_{10}\rangle$ | $\sqrt{(6/5)} w_{22}\rangle$ |
| $ \xi_{10}\rangle$ | $\frac{1}{2}(1/\sqrt{5}) v_{20}\rangle$ | $-\frac{1}{2}\sqrt{(3/5)} u_{2-1}\rangle + \frac{1}{2}\sqrt{5} u_{1-1}\rangle$ | $\sqrt{(3/5)} w_{21}\rangle + \sqrt{5} w_{11}\rangle$ |
| $ \xi_{1-1}\rangle$ | $\frac{1}{4}\sqrt{(3/5)} v_{2-1}\rangle + \frac{1}{4}\sqrt{5} v_{1-1}\rangle$ | $-\sqrt{(3/10)} u_{2-2}\rangle$ | $(1/\sqrt{5}) w_{20}\rangle + \sqrt{5} w_{10}\rangle$ |
| $ \xi_{00}\rangle$ | $\frac{1}{2} v_{10}\rangle$ | $- u_{1-1}\rangle$ | $2 w_{11}\rangle$ |

All coefficients must be multiplied by $\frac{1}{3}$.

APPENDIX IX

BASIS STATES FOR THE $^5A_1'$ MULTIPLY IN PERPENDICULAR MAGNETIC FIELD

$$\begin{aligned}
 |1\rangle &= \frac{1}{4} [|U', 2, 2\rangle + 2|U'', 2, 1\rangle + \sqrt{6}|U', 2, 0\rangle + 2|U'', 2, -1\rangle + |U', 2, -2\rangle] & g &= 2 \\
 |2\rangle &= \frac{1}{2} [|U', 2, 2\rangle + |U'', 2, 1\rangle - |U'', 2, -1\rangle - |U', 2, -2\rangle] & g &= 1 \\
 |3\rangle &= \frac{1}{2} (3\sqrt{3}) [\sqrt{6}|U', 2, 2\rangle - 2|U', 2, 0\rangle + \sqrt{6}|U', 2, -2\rangle] & g &= 0 \\
 |4\rangle &= \frac{1}{2} [|U', 2, 2\rangle - |U'', 2, 1\rangle + |U'', 2, -1\rangle - |U', 2, -2\rangle] & g &= -1 \\
 |5\rangle &= \frac{1}{4} [|U', 2, 2\rangle - 2|U'', 2, 1\rangle + \sqrt{6}|U', 2, 0\rangle - 2|U'', 2, -1\rangle + |U', 2, -2\rangle] & g &= -2
 \end{aligned}$$

BASIS STATES FOR THE $^5E'$ MULTIPLY

With $|A_1' + A_2'\rangle = \frac{1}{\sqrt{2}} [|V', 2, -2\rangle \pm |W', 2, 2\rangle]$ and $|A_1'' + A_2''\rangle = \frac{1}{\sqrt{2}} [|V'', 2, 1\rangle \pm |W'', 2, -1\rangle]$

$$\begin{aligned}
 |1'\rangle &= \frac{1}{4} \frac{1}{\sqrt{2}} [\sqrt{2}|V', 2, 2\rangle + 2|A_2''\rangle + 2|A_1''\rangle + 2\sqrt{3}|V', 2, 0\rangle + 2\sqrt{2}|V'', 2, -1\rangle + |A_1'\rangle + |A_2'\rangle] & g &= 4 \\
 |2'\rangle &= \frac{1}{4} \frac{1}{\sqrt{2}} [\sqrt{2}|W', 2, -2\rangle + 2|A_2''\rangle - 2|A_1''\rangle + 2\sqrt{3}|W', 2, 0\rangle + 2\sqrt{2}|W'', 2, 1\rangle + |A_1'\rangle - |A_2'\rangle] & g &= 4 \\
 |3'\rangle &= \frac{1}{4} [-2|V', 2, 2\rangle - \sqrt{2}|A_2''\rangle - \sqrt{2}|A_1''\rangle + 2|V'', 2, -1\rangle + \sqrt{2}|A_1'\rangle + \sqrt{2}|A_2'\rangle] & g &= 2 \\
 |4'\rangle &= \frac{1}{4} [-2|W', 2, -2\rangle - \sqrt{2}|A_2''\rangle + \sqrt{2}|A_1''\rangle + 2|W'', 2, 1\rangle + \sqrt{2}|A_1'\rangle - \sqrt{2}|A_2'\rangle] & g &= 2 \\
 |5'\rangle &= \frac{1}{4} [-\sqrt{3}|V', 2, 2\rangle - \sqrt{3}|W', 2, -2\rangle + \sqrt{2}|V', 2, 0\rangle + \sqrt{2}|W', 2, 0\rangle - \sqrt{6}|A_1'\rangle] & g &= 0 \\
 |6'\rangle &= \frac{1}{4} [-\sqrt{3}|V', 2, 2\rangle + \sqrt{3}|W', 2, -2\rangle + \sqrt{2}|V', 2, 0\rangle - \sqrt{2}|W', 2, 0\rangle - \sqrt{6}|A_2'\rangle] & g &= 0 \\
 |7'\rangle &= \frac{1}{4} [-2|V', 2, 2\rangle + \sqrt{2}|A_2''\rangle + \sqrt{2}|A_1''\rangle - 2|V'', 2, -1\rangle + \sqrt{2}|A_1'\rangle + \sqrt{2}|A_2'\rangle] & g &= -2 \\
 |8'\rangle &= \frac{1}{4} [-2|W', 2, -2\rangle + \sqrt{2}|A_2''\rangle - \sqrt{2}|A_1''\rangle - 2|W'', 2, 1\rangle + \sqrt{2}|A_1'\rangle - \sqrt{2}|A_2'\rangle] & g &= -2 \\
 |9'\rangle &= \frac{1}{4} \frac{1}{\sqrt{2}} [\sqrt{2}|V', 2, 2\rangle - 2|A_2''\rangle - 2|A_1''\rangle + 2\sqrt{3}|V', 2, 0\rangle - 2\sqrt{2}|V'', 2, -1\rangle + |A_1'\rangle + |A_2'\rangle] & g &= -4 \\
 |10'\rangle &= \frac{1}{4} \frac{1}{\sqrt{2}} [\sqrt{2}|W', 2, -2\rangle - 2|A_2''\rangle + 2|A_1''\rangle + 2\sqrt{3}|W', 2, 0\rangle - 2\sqrt{2}|W'', 2, 1\rangle + |A_1'\rangle + |A_2'\rangle] & g &= -4
 \end{aligned}$$

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