

Magnetic and Hyperfine Interactions in Atoms, Ions and Crystals[©]

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Abstract. In these lectures I shall discuss the basic information needed to understand magnetic and hyperfine interactions in atoms, ions and crystals. We start with the nuclear shell model to gain an insight into nuclear groundstates and their interaction with magnetic fields. We then look at the multipole magnetic and electric moments of nuclei. Then follows some general remarks on electronic energy levels of atoms and ions. This will then lead into our main topic, magnetic and hyperfine interactions in atoms, ions and crystals.

... when he imagined his education was completed, it had in fact not commenced; and that, although he had been at a public school and a university, he in fact knew nothing. To be conscious that you are ignorant is a great step to knowledge.

Benjamin Disraeli, *Sybil or The Two Nations* (1844)

1. Introduction

The concept of quantum degeneracy and its controlled lifting by magnetic and electric fields is perhaps the most technologically important and practical development of the past century. It has led to the development of lasers, NMR imaging, modern telecommunications, the realization of Bose-Einstein condensation, and the potential realization of quantum computing. These applications have required a detailed understanding of the quantum theory of angular momentum in all its manifestations, starting with the angular momentum of nuclear states, the angular momentum of electronic states and of the coupling of angular momentum of nuclear with electronic states. In this course we first consider the rudiments of nuclear structure.

1.1. Basic Facts of Nuclei

We first establish some basic notations.

1.2. Nucleons

The basic building blocks of nuclei (here we ignore the quark substructure of the nucleons) are neutrons and protons. Both are spin $\frac{1}{2}$ particles with positive intrinsic parity, i.e. $J_p = \frac{1}{2}^+$. Following Heisenberg¹, the proton and neutron can be regarded as different charge states of the *nucleon*. The respective masses are (we will generally put $c = 1$)

$$M_p = 938.3MeV \quad M_n = 939.6MeV \quad (1-1)$$

In free space the neutron is unstable with a half-life of $t_{\frac{1}{2}} = 614.3s$ whereas the proton appears to be stable with $t_{\frac{1}{2}} > 10^{33}y$. Within the nucleus, as a consequence of the Pauli exclusion principle, the proton *and* the neutron are stable.

Remarkably, the proton *and* the neutron both possess magnetic moments.

$$\mu_p = 2.7928 \quad \mu_n = -1.9128 \quad (1-2)$$

where the units are the Bohr nuclear magneton defined as

$$\mu_{B_N} = \frac{eh}{2m_p} \quad (1-3)$$

An *isotope* of an element X having Z protons (Z is the *atomic number*) and N neutrons will be designated as

$${}^A_Z X$$

where

$$A = N + Z \quad (1-4)$$

with A being the *nucleon number*.

1.3. The Nuclear Force

The force between nucleons is, to a good approximation, charge independent and of a short range. Its origin is to be found in the quark model which we shall not explore here. The basic nuclear model we shall consider is the *nuclear shell model*. To a first approximation we can consider the nucleons as executing harmonic oscillations about the nuclear centre of mass and hence as nucleons in an isotropic 3-dimensional harmonic oscillator.

1.4. The isotropic harmonic oscillator

Recall that the energy eigenvalues of a 3-dimensional isotropic harmonic oscillator potential containing a single particle are given by

$$E_n = (n + \frac{3}{2})\hbar\omega \quad n = 0, 1, 2, \dots \quad (1-5)$$

corresponding to an infinite series of equally spaced levels. The n -th level has an orbital degeneracy of

$$\frac{(n+1)(n+2)}{2} \quad (1-6)$$

These are precisely the dimensions of the symmetric irreducible representations $\{n\}$ of the special unitary group $SU(3)$. The n -th level is associated with orbitals having the angular momentum quantum number ℓ such that

$$\ell = n, n-2, \dots, \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (1-7)$$

Given that the nucleons have *even* intrinsic parity the states associated with the n -th level are all of the *same* parity which is *even* or *odd* as n is *even* or *odd*. The nucleons have spin $\frac{1}{2}$ and hence each orbital ℓ has a spin-orbital degeneracy of $4\ell + 2$. NB. It is common in nuclear physics to prefix the orbital quantum number with the number of nodes in the single particle wavefunction. Thus the orbitals associated with n -level are in the sequence

$$1s; 1p; 2s, 1d; 2p, 1f; 3s, 2d, 1g; \dots \quad (1-8)$$

Since nucleons have spin $\frac{1}{2}$ they are *fermions* and hence must be associated with wavefunctions that are *totally antisymmetric*. This means that in building up many-nucleon states the Pauli exclusion principle must be followed. Many-nucleon states may be constructed by filling the spin-orbitals with neutrons and protons up to their maximum allowed occupancy. The building-up principle is very similar to that for periodic table for atoms except one fills neutron and proton orbitals separately to construct nuclei with given A, N, Z numbers.

1.5. Magic Nuclei Numbers

Nuclei in which the proton and neutron numbers Z, N belong to the *magic numbers*

$$\text{Nuclei Magic Numbers } 2, 8, 20, 28, 50, 82, 126 \quad (1-9)$$

tend to be exceptionally stable and evidently associated with the closure of shells. The magic numbers 2, 8, 20 correspond to the closure of the shells corresponding to the first, second and third levels of an isotropic 3-dimensional harmonic oscillator. But closure of the fourth level would give the fourth magic number as 40 rather than 28. This constituted a puzzle until M G Mayer introduced the spin-orbit interaction into the nuclear shell model. In her case the spin-orbit interaction has the *opposite sign* to the conventional spin-orbit interaction of electrons. This means, for example, that in the $1p$ shell the $1p_{3/2}$ level is *below* the $1p_{1/2}$ level whereas in atoms one has the opposite ordering. The effect of introducing the spin-orbit interaction is also to partially lift the single particle energy degeneracies so that, apart from the case of s -states each orbital ℓ becomes characterized by a total single particle angular momentum

$$j_{\pm} = \ell \pm s \quad (1-10)$$

Henceforth, let us use n as the *nodal* quantum number rather than as the harmonic oscillator level number so that a given spin-orbital is designated by the single particle quantum numbers $n\ell jm$. For a single nucleon moving in a nucleus we write the spin-orbit interaction as

$$V_{s.o} = \zeta(r)_{n\ell}(\mathbf{s} \cdot \ell) \quad (1-11)$$

where $\zeta(r)_{n\ell}$ is the *spin-orbit coupling constant* which is a *radial* function dependent on the nature of the nuclear field and upon the quantum numbers $n\ell$. For a single nucleon

$$(\mathbf{s} \cdot \ell) = \frac{1}{2}[j(j+1) - \ell(\ell+1) - \frac{3}{4}] \quad (1-12)$$

The energy separation between the two components of a spin-orbit split doublet characterized by the quantum numbers $n\ell$ becomes

$$\Delta E_{n\ell} = (\ell + \frac{1}{2})\zeta(r)_{n\ell} \quad (1-13)$$

Thus the level with j_+ is *lower* than the level with j_- . Furthermore, it is a practical observation that states with higher values of ℓ have larger doublet splittings.

Even with the introduction of the spin-orbit interaction the single nucleon degeneracy is only partially lifted. The degeneracy associated with the isotropic harmonic oscillators is partially lifted so that states of a given harmonic oscillator level are no longer degenerate with respect to ℓ while each set of states associated with a particular orbital angular momentum ℓ is split as a doublet of degenerate states labelled by the quantum numbers $n\ell jm$. The degeneracy with respect to the *total angular momentum projection quantum number* m remains and hence each level with total angular momentum j is $(2j+1)$ -fold degenerate. The spin-orbit splitting leads to subshells with a given j -level accommodating up to $2j+1$ protons or neutrons.

1.6. Nuclear Pairing Interactions

It is remarkable that nuclei having *even* numbers of protons *and* neutrons, so called *even-even* nuclei are always found to have zero nuclear angular momentum i.e. $I = 0$. NB. in nuclear physics the total angular momentum $J = L + S$ is nevertheless usually referred to as the *nuclear spin* and designated by the letter I . So called *odd-even* and *even-odd* nuclei always have *half-integer* nuclear spin while *odd-odd* nuclei always have *integer* nuclear spin. It would appear that *even* numbers of neutrons or protons *pair* to produce a lowest energy state that has nuclear spin $I = 0$. Indeed, Racah, showed that a strong short range nuclear force, such as a delta type force, leads to such a pairing. It is this feature that is the key to predicting the nuclear spin of the groundstates of nuclei. If there are an even number of protons or neutrons in a given orbital then those orbitals make no contribution to the nuclear spin of the groundstate. Furthermore, there is no nuclear spin contribution from closed shells.

1.6.1. Seniority and Pairing Interactions.

Racah introduced the concept of *seniority* in both atomic and nuclear physics (and indeed also in superconductivity where pairing is also important). Racah showed that for a strong pairing interaction such as occur in nuclei states of lowest seniority number v lie lowest. Thus in a configuration of identical nucleons, j^N , the integer, $[\frac{N-v}{2}]$, corresponds to the number of pairs of particles that are coupled to zero angular momentum where

$$v = \begin{cases} 0, 2, \dots, N & N \text{ even} \\ 1, 3, \dots, N & N \text{ odd} \end{cases} \quad (1-14)$$

This has the consequence that in a configuration j^N if N is *even* then the lowest state will have zero angular momentum whereas if N is *odd* the angular momentum of the lowest state will be $J = j$.

NB. In the case of atoms, where there is Coulomb repulsion between pairs of electrons, states of maximal seniority lie lowest and hence in some respects nuclear states are simpler than electronic states!

The angular momentum states J and seniority numbers for the identical particle configurations j^N are given for $j = \frac{1}{2}, \frac{3}{2}, \dots, \frac{7}{2}$ in Table 1. For $j = \frac{5}{2}, \frac{7}{2}$ we list just the states up to $N = j + \frac{1}{2}$.

1.7. Nuclear Spin of Nuclei Groundstates

In atomic physics interest is almost entirely restricted to atomic effects involving nuclei in their groundstates. A given isotope is characterized by the number of neutrons, N , and number of protons, Z . Starting with Fig. 1-1 giving the ordering of the $n\ell j$ quantum numbers for a single nucleon in an isotropic three-dimensional harmonic oscillator potential together with the spin-orbit interaction we can determine the nuclear spin of the groundstates of most nuclei. Let us now consider some examples.

Table 1-1. Angular momentum J and seniority numbers for some j^N configurations.

j^N	J	v	$\frac{N-v}{2}$
$(\frac{1}{2})^0$	0	0	0
$(\frac{1}{2})^1$	$\frac{1}{2}$	1	0
$(\frac{1}{2})^2$	0	0	1
$(\frac{3}{2})^0$	0	0	0
$(\frac{3}{2})^1$	$\frac{3}{2}$	1	0
$(\frac{3}{2})^2$	0	0	1
	2	2	0
$(\frac{3}{2})^3$	$\frac{3}{2}$	1	1
$(\frac{3}{2})^4$	0	0	2
$(\frac{5}{2})^0$	0	0	0
$(\frac{5}{2})^1$	$\frac{5}{2}$	1	0
$(\frac{5}{2})^2$	0	0	1
	2, 4	2	0
$(\frac{5}{2})^3$	$\frac{5}{2}$	1	1
	$\frac{3}{2}, \frac{9}{2}$	3	0
$(\frac{7}{2})^0$	0	0	0
$(\frac{7}{2})^1$	$\frac{7}{2}$	1	0
$(\frac{7}{2})^2$	0	0	1
	2, 4, 6	2	0
$(\frac{7}{2})^3$	$\frac{7}{2}$	1	1
	$\frac{3}{2}, \frac{5}{2}, \frac{9}{2}, \frac{11}{2}, \frac{15}{2}$	3	0
$(\frac{7}{2})^4$	0	0	2
	2, 4, 6	2	1
	2, 4, 5, 8	4	0

1.7.1. Nuclear Spin of H Isotopes.

Hydrogen has three well-known isotopes, hydrogen, 1_1H , deuterium, 2_1H , and tritium, 3_1H . Hydrogen involves a single proton which may be assigned to the $(1s_{\frac{1}{2}})_p^1$ configuration and hence 1_1H has a nuclear spin $I = \frac{1}{2}$. Deuterium has a single proton and neutron and hence the nuclear groundstate configuration is $(1s_{\frac{1}{2}})_p^1(1s_{\frac{1}{2}})_n^1$. The nuclear spin results from the coupling of two $\frac{1}{2}$ spins to produce $I = 0, 1$. Experiment shows that the groundstate has $I = 0$. Finally, tritium has a single proton and two

neutrons and hence the nuclear configuration $(1s_{\frac{1}{2}})_p^1(1s_{\frac{1}{2}})_n^2$. The two neutrons close the $1s_{\frac{1}{2}}$ shell and hence make no contribution to the nuclear spin and thus the nuclear spin of the tritium nucleus is $I = \frac{1}{2}$, the same as for hydrogen. Note that in each case the groundstate has *even* parity.

1.7.2. Nuclear Spin of He Isotopes.

The two principal isotopes of helium are ${}^4_2\text{He}$ and ${}^3_2\text{He}$. For the more abundant isotope, ${}^4_2\text{He}$, we have the nuclear configuration $(1s_{\frac{1}{2}})_p^2(1s_{\frac{1}{2}})_n^2$ and both shells are closed and hence the nuclear spin is $I = 0$ whereas for ${}^3_2\text{He}$ we have the nuclear configuration $(1s_{\frac{1}{2}})_p^2(1s_{\frac{1}{2}})_n^1$ and hence a nuclear spin of $I = \frac{1}{2}$.

1.7.3. Silicon Isotopes.

Silicon has three stable isotopes, $\{{}^{28}_{14}\text{Si}$ (92.23%), ${}^{29}_{14}\text{Si}$ (4.67%), ${}^{30}_{14}\text{Si}$ (3.10%)}. Two of the isotopes are *even-even* nuclei and hence both have nuclear spin and parity $I = 0^+$. All three isotopes have $Z = 14$ and hence the 14 protons occur in the proton configuration $(1s_{\frac{1}{2}}^2 1p_{\frac{3}{2}}^4 1p_{\frac{1}{2}}^2 1d_{\frac{5}{2}}^6)$. In practice we will normally omit all closed shells except for the highest and thus write the configuration as simply $(1d_{\frac{5}{2}}^6)_p$. Since the proton number is *even* it follows that the protons make no contribution to the nuclear spin. Fourteen of the neutrons go into the same type of configuration as the protons with the fifteenth neutron occupying the $(2s_{\frac{1}{2}})_n$ orbital. Thus the nuclear spin of ${}^{29}_{14}\text{Si}$ is $I = \frac{1}{2}^+$.

The above observations are of significance in considering the possibility of using silicon in quantum computing. Only the ${}^{29}_{14}\text{Si}$ nuclei will respond to an external magnetic field. Isotopically pure $\{{}^{28}_{14}\text{Si}$ with nuclear spin $I^p = 0^+$ gives no response to magnetic fields. Phosphorus has one stable isotope ${}^{31}_{15}\text{P}$ with one unpaired proton in the $2s_{\frac{1}{2}}$ shell and hence nuclear spin $I^p = \frac{1}{2}^+$. Noting these facts Kane (*Nature* **393**,133 (1998)) has proposed building a quantum computer using ${}^{28}_{14}\text{Si}$ doped with ${}^{31}_{15}\text{P}$. At the time of writing this is a very active field of research. To find out more go to google.com and search “quantum computing”+Kane.

1.7.4. Rubidium Isotopes.

Rubidium has two stable isotopes, ${}^{85}_{37}\text{Rb}$ (72.16%), ${}^{87}_{37}\text{Rb}$ (27.83%)[†]. The two nuclei are *odd-even* with the neutrons making no contribution to the nuclear spin. The first 28 protons go into filling closed shells leaving a further nine protons to be distributed among the $2p_{\frac{3}{2}}$ and $1f_{\frac{5}{2}}$ orbitals. Eight of the protons will pair to produce no contribution to the nuclear spin leaving one unpaired proton. Experimentally it is found that for ${}^{85}_{37}\text{Rb}$ the nuclear spin is $I^p = \frac{5}{2}^-$ while for ${}^{87}_{37}\text{Rb}$ $I^p = \frac{3}{2}^-$. These results

[†] Actually the isotope ${}^{87}_{37}\text{Rb}$ is slightly unstable with a half-life of $t_{\frac{1}{2}} = 4.75 \times 10^{10}y$.

show some of the limitations of the simple nuclear shell model, but as always, final appeal must be made to experiment. ‡

The rubidium isotopes play a key role in studies of *Bose-Einstein Condensation (BEC)*. Rubidium atoms behave as *bosons* since their nuclear spins are half-integer but the number of electrons is *odd* and hence the nett electron angular momentum J will necessarily be half-integer. The total angular momentum of the atom F comprises the vector addition of the nuclear spin I and electronic angular momentum J such that

$$\mathbf{F} = \mathbf{J} + \mathbf{I} \tag{1-15}$$

F is thus necessarily an integer and the rubidium atoms behave as *bosons*.

‡ For an excellent data base on properties of isotopes go to <http://ie.lbl.gov/education/isotopes.htm> or to <http://www.webelements.com/webelements/elements/text/periodic-table/isot.html>, the latter gives the Periodic Table and nuclear magnetic moments which we will need later.

Lecture 2

Pure mathematics is on the whole distinctly more useful than applied. For what is useful above all is technique, and mathematical technique is taught mainly through pure mathematics

G H Hardy

2. Notes on the Quantum Theory of Angular Momentum

Let us review some basic aspects of the quantum theory of angular momentum which we will need in later lectures. In making practical calculations we must ultimately be able to calculate matrix elements of interactions in suitable angular momenta bases. NB We shall normally put $\hbar = 1$.

2.1. The basic commutation relations

Consider the components, J_x , J_y and J_z of the angular momentum vector \mathbf{J} . Under commutation

$$[J_x, J_y] = iJ_z, \quad [J_y, J_z] = iJ_x, \quad [J_z, J_x] = iJ_y \quad (2-1)$$

States that are simultaneous eigenfunctions of \mathbf{J}^2 and J_z will be designated in Dirac's bra notation as $|JM\rangle$. We have the standard angular momentum operator relations

$$\mathbf{J}^2|JM\rangle = J(J+1)|JM\rangle \quad (2-2a)$$

$$J_z|JM\rangle = M|JM\rangle \quad (2-2b)$$

$$J_{\pm}|JM\rangle = [J(J+1) - M(M \pm 1)]^{\frac{1}{2}}|JM \pm 1\rangle \quad (2-2c)$$

where

$$J_{\pm} = J_x \pm iJ_y \quad (2-3)$$

are the usual angular momentum ladder operators.

Recall that for a given eigenvalue J there are $2J + 1$ values of the M quantum number

$$M = -J, J-1, \dots, J-1, J \quad (2-4)$$

and that

$$J_+|JJ\rangle = 0 \quad J_-|J-J\rangle = 0 \quad (2-5)$$

2.2. Coupling Angular Momentum

It is a common problem in the quantum theory of angular momentum to need to couple together two ket states, say $|j_1 m_1\rangle$, $|j_2 m_2\rangle$ to produce coupled states $|(j_1 j_2) JM\rangle$. Thus to have

$$|j_1 m_1\rangle |j_2 m_2\rangle = \sum_{J,M} \langle JM | m_1 m_2 \rangle |(j_1 j_2) JM\rangle \quad (2-6a)$$

or inversely to uncouple coupled states via

$$|(j_1 j_2) JM\rangle = \sum_{m_1, m_2} \langle m_1 m_2 | JM \rangle^* |j_1 m_1\rangle |j_2 m_2\rangle \quad (2-6b)$$

The *coupling coefficients* or *Clebsch-Gordan coefficients* $\langle j_1 m_1 j_2 m_2 | j_1 j_2 j m \rangle$ represent the elements of a unitary transformation that couples the uncoupled states $|j_1 m_1\rangle |j_2 m_2\rangle$ to produce the coupled states $|j_1 j_2 j m\rangle$. i.e.,

$$|j_1 j_2 j m\rangle = \sum_{m_1, m_2} \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m \rangle |j_1 m_1\rangle |j_2 m_2\rangle \quad (2-7)$$

Such transformations arise, for example in relating basis states in the $|SM_S LM_L\rangle$ scheme to the coupled basis states $|SLJM\rangle$ where $M = M_S + M_L$. Thus,

$$|SLJM\rangle = \sum_{M_S, M_L} \langle M_S M_L | SLJM \rangle |SM_S LM_L\rangle \quad (2-8)$$

Note that we shall often abbreviate the Clebsch-Gordan coefficient $\langle j_1 m_1 j_2 m_2 | j_1 j_2 j m \rangle$ to just $\langle m_1 m_2 | j_1 j_2 j m \rangle$.

2.3. An Example

Triply ionized thulium Tm^{3+} has as its groundstate the spectroscopic term $4f^{12} {}^3H_6$. That is it has the quantum numbers $S = 1$, $L = 5$, and $J = 6$. The state is $(2J + 1) = 13$ -fold degenerate with the degenerate states being distinguished by the quantum number M . These states could be described by the kets $|SLJM\rangle$ in so-called *Russell-Saunders* or *LS-coupling*. Alternatively the states could be described by the kets $|SM_S LM_L M\rangle$. These two sets of states correspond to two different bases that are linked by the Clebsch-Gordan coupling coefficients as in Eq(2-8). For maximal M we expect for the groundstate that

$$|(1, 5)66\rangle \equiv e^{i\phi} |(1, 1)(5, 5)6\rangle \quad (2-9)$$

where the left-hand ket is in the $|(SL)JM\rangle$ scheme and the right-hand in the $|(SM_S)(LM_L)M\rangle$ scheme and $e^{i\phi}$ is a phase factor which we will fix as unity.

The other states in the $SLJM$ scheme will be various linear combinations of those in the $SM_S LM_L M$ scheme. Let us determine some of these linear combinations. First note that

$$J_{\pm} = L_{\pm} + S_{\pm} \quad (2-10)$$

Let us apply the lowering ladder operator to both sides of Eq(2-9), noting Eq(2-2c),

$$J_-|(1, 5)66\rangle = \sqrt{6(6+1) - 6(6-1)}|(1, 5)65\rangle = \sqrt{12} |(1, 5)65\rangle \quad (2-11a)$$

$$\begin{aligned} (L_- + S_-)|(1, 1)(5, 5)6\rangle &= \sqrt{5(5+1) - 5(5-1)}|(1, 1)(5, 4)5\rangle \\ &+ \sqrt{1(1+1) - 1(1-0)}|(1, 0)(5, 5)5\rangle \\ &= \sqrt{10} |(1, 1)(5, 4)5\rangle + \sqrt{2} |(1, 0)(5, 5)5\rangle \end{aligned} \quad (2-11b)$$

Equating Eqs (2-11a) and (2-11b) gives

$$|(1, 5)65\rangle = \frac{1}{\sqrt{6}} \left[\sqrt{5} |(1, 1)(5, 4)5\rangle + |(1, 0)(5, 5)5\rangle \right] \quad (2-12)$$

2.4. Clebsch-Gordan Coefficients

Clebsch-Gordan coefficients may be expressed precisely as

$$\begin{aligned} \langle m_1 m_2 | j_1 j_2 j m \rangle &= \delta_{m_1+m_2, m} \sqrt{\frac{(2j+1)(j_1+j_2-j)! (j_1-m_1)! (j_2-m_2)! (j+m)! (j-m)!}{(j_1+j_2+j+1)! (j+j_1-j_2)! (j-j_1+j_2)! (j_1+m_1)! (j_2+m_2)!}} \\ &\times \sum_z (-1)^{j_1-m_1-z} \frac{(j_1+m_1+z)! (j+j_2-m_1-z)!}{z! (j-m-z)! (j_1-m_1-z)! (j_2-j+m_1+z)!} \end{aligned} \quad (2-13)$$

2.5. Exercises

2-1. Obtain the expansion for $|(1, 5)64\rangle$

2-2. Use Eq(13) to obtain the values of the Clebsch-Gordan coefficients to give an alternative derivation of Eq(2-12) via Eq(2-8).

2.6. The $3jm$ -Symbols

While Clebsch-Gordan coefficients possesses considerable symmetry a more symmetrical object was defined by Wigner and is now commonly known as the $3j$ -symbol or $3jm$ -symbol. The $3j$ -symbol is related to the Clebsch-Gordan coefficient by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3} \frac{\langle m_1 m_2 | j_1 j_2 j_3 - m_3 \rangle}{\sqrt{(2j_3+1)}} \quad (2-14)$$

The $3j$ -symbol is invariant with respect to an *even* permutation of its columns while for *odd* permutations of its columns is multiplied by a phase factor equal to the sum of the arguments in its top row. i.e.,

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} \quad (2-15)$$

Furthermore, changing the sign of all three lower arguments results also in multiplication by a phase factor equal to the sum of the arguments in its top row. i.e.,

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} \quad (2-16)$$

A $3j$ -symbol having all its m quantum numbers zero will be null unless $j_1 + j_2 + j_3$ is *even*. Likewise any $3j$ -symbol having two identical columns will vanish unless $j_1 + j_2 + j_3$ is *even*.

The unitarity property of the Clebsch-Gordan coefficients lead directly to the orthonormality conditions for the $3j$ -symbols

$$\sum_{j_3, m_3} (2j_3 + 1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m'_1 & m'_2 & m_3 \end{pmatrix} = \delta_{m_1, m'_1} \delta_{m_2, m'_2} \quad (2-17a)$$

$$\sum_{m_1, m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} = \frac{\delta_{j_3, j'_3} \delta_{m_3, m'_3}}{\sqrt{(2j_3 + 1)}} \quad (2-17b)$$

Extensive tables exist such as those of Rotenberg, Bivins, Metropolis and Wooten, "The $3 - j$ and $6 - j$ Symbols" Technology Press, Mass. (1959). I have a suite of Maple programmes for evaluating $3jm$ -symbols as well as $6j$ - and $9j$ -symbols.

2.7. The $6j$ -symbols

The $6j$ -symbol is defined by the relation

$$\begin{aligned} & \langle (j_1 j_2) j_{12}, j_3; jm | j_1, (j_2 j_3) j_{23}; jm \rangle = \\ & (-1)^{j_1 + j_2 + j_3 + j} \sqrt{(2j_{12} + 1)(2j_{23} + 1)} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix} \end{aligned} \quad (2-18)$$

The $6j$ -symbol may be evaluated by first expressing it as a sum over a triple product of $3j$ -symbols and then using the fact that the $6j$ -symbol is independent of m to produce a sum involving a single variable to finally yield

$$\begin{aligned} & \begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix} = \\ & \sqrt{\Delta(abc)\Delta(aef)\Delta(dbf)\Delta(dec)} \\ & \times \sum_z (-1)^z (z + 1)! \\ & \times [(z - a - b - c)!(z - a - e - f)!(z - d - b - f)!(z - d - e - c)! \\ & \times (a + b + d + e - z)!(b + c + e + f - z)!(a + c + d + f - z)!]^{-1} \end{aligned} \quad (2-19)$$

where

$$\Delta(abc) = [(a + b - c)!(a - b + c)!(b + c - 1)! / (a + b + c + 1)!]^{\frac{1}{2}} \quad (2-19')$$

etc. The $6j$ -symbol vanishes unless the four triangular conditions portrayed below are satisfied.

$$\begin{aligned} & \left\{ \begin{array}{ccc} & \circ & \\ \cdot\cdot & & \cdot\cdot \\ \circ & & \circ \end{array} \right\} \left\{ \begin{array}{ccccc} \circ & \dots & \circ & \dots & \circ \\ & & & & \\ & & & & \\ & & & & \\ & & & & \end{array} \right\} \\ & \left\{ \begin{array}{ccc} & & \circ \\ & \cdot\cdot & \\ \circ & \dots & \circ \end{array} \right\} \left\{ \begin{array}{ccc} \circ & & \\ & \cdot\cdot & \\ & & \circ \dots \circ \end{array} \right\} \end{aligned} \quad (2-20)$$

where for example $a + b \geq c \geq |a - b|$.

The $6j$ -symbol is invariant with respect to any interchange of columns and also with respect to the interchange of the upper and lower arguments of any two columns. The $6j$ -symbols satisfy the orthogonality condition

$$\sum_{j_{12}} (2j_{12} + 1)(2j_{23} + 1) \begin{Bmatrix} j_3 & j & j_{12} \\ j_1 & j_2 & j_{23} \end{Bmatrix} \begin{Bmatrix} j_3 & j & j_{12} \\ j_1 & j_2 & j'_{23} \end{Bmatrix} = \delta_{j_{23}, j'_{23}} \quad (2-21)$$

2.8. The $9j$ -symbol

The $6j$ -symbol arose in discussing the coupling of three angular momentum. Clearly more complex nj -symbols will arise for couplings involving more than three angular momentum. The $9j$ -symbol may be defined as

$$\begin{aligned} & \langle (j_1 j_2) j_{12}, (j_3 j_4) j_{34}; j | (j_1 j_3) j_{13}, (j_2 j_4) j_{24}; j \rangle \\ & = \sqrt{(2j_{12} + 1)(2j_{34} + 1)(2j_{13} + 1)(2j_{24} + 1)} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} \end{aligned} \quad (2-22)$$

The $9j$ -symbol may be expressed in terms of $6j$ -symbols as

$$\begin{aligned} & \begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix} \\ & = \sum_z (-1)^{2z} \begin{Bmatrix} a & d & g \\ h & i & z \end{Bmatrix} \begin{Bmatrix} b & e & h \\ d & z & f \end{Bmatrix} \begin{Bmatrix} c & f & i \\ z & a & b \end{Bmatrix} \end{aligned} \quad (2-23)$$

The $9j$ -symbol is left invariant with respect to any *even* permutation of its rows or columns or a transposition of rows and columns. Under an *odd* permutation of rows or columns the symbol is invariant but for a phase factor equal to the sum of its arguments. If one argument of the $9j$ -symbol is zero the symbol collapses to a single $6j$ -symbol *viz.*

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & 0 \end{Bmatrix} = \delta_{c,f} \delta_{g,h} \frac{(-1)^{b+d+f+g}}{\sqrt{(2c+1)(2g+1)}} \begin{Bmatrix} a & b & c \\ e & d & g \end{Bmatrix} \quad (2-24)$$

2.9. Tensor Operators

Our fundamental problem in these lectures will be to calculate matrix elements of relevant interactions. To do this we need to be able to express the interactions in terms of tensor operators as pioneered by Racah¹⁸⁻²¹ and outlined by Judd² and Edmonds¹⁷. The theory of tensor operators has a deep group theoretical basis which we shall not consider here^{2,22,23}. Here we follow Racah's original introduction of tensor

operators¹⁹. A *irreducible tensor operator* $\mathbf{T}(k)$, of rank k has $(2k + 1)$ components $T(kq)$ where $q = -k, -k + 1, \dots, k - 1, k$ which satisfy the commutation relations

$$[J_z, T(kq)] = qT(kq) \quad (2-25a)$$

$$[J_{\pm}, T(kq)] = \sqrt{k(k+1) - q(q \pm 1)}T(k, q \pm 1) \quad (2-25b)$$

Group theoretically this implies that the tensor operator components form a basis for the $(2k + 1)$ -dimensional irreducible representation $[k]$ of the rotation group in three dimensions, $SO(3)$. Furthermore they can be regarded as transforming like angular momentum states $|kq\rangle$. As a result we can use standard angular momentum coupling techniques to form coupled products of tensor operators. For a rank $k = 1$ tensor operator we have, in terms of the Cartesian tensor components (T_x, T_y, T_z)

$$T_{\pm 1}^{(1)} = \frac{\mp}{\sqrt{2}}(T_x \pm iT_y), \quad T_0^{(1)} = T_z \quad (2-26)$$

Thus \mathbf{J} is a tensor operator of rank $k = 1$ with components

$$J_0^{(1)} = J_z, \quad J_{\pm 1}^{(1)} = \pm \frac{J_{\mp}}{\sqrt{2}} \quad (2-27)$$

2.10. The Coulomb Interaction and Tensor Operators

The matrix elements of the N -particle repulsive Coulomb interaction

$$H_c = \sum_{i < j}^N \frac{e^2}{r_{ij}} \quad (2-28)$$

play an important role in atomic physics. The interaction between each pair of electrons may be expanded in terms of Legendre polynomials of the cosine of the angle ω_{ij} between the vectors from the nucleus to the two electrons as

$$\frac{e^2}{r_{ij}} = e^2 \sum_k \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos \omega_{ij}) \quad (2-29)$$

where $r_{<}$ indicates the distance from the nucleus of the nearer electron and $r_{>}$ the distance from the nucleus to the further away electron. Using the spherical harmonic addition theorem²⁴

$$\begin{aligned} P_k(\cos \omega_{ij}) &= \frac{4\pi}{2k+1} \sum_q Y_{kq}^*(\theta_i, \phi_i) Y_{kq}(\theta_j, \phi_j) \\ &= \sum_q (-1)^q (C_{-q}^{(k)})_i (C_q^{(k)})_j \\ &= (\mathbf{C}_i^{(k)} \cdot \mathbf{C}_j^{(k)}) \end{aligned} \quad (2-30)$$

where the $C_q^{(k)}$ are defined in terms of the usual spherical harmonics, Y_{kq} as

$$C_q^{(k)} = \left(\frac{4\pi}{2k+1} \right) Y_{kq} \quad (2-31)$$

The $C_q^{(k)}$ are the components of a rank k tensor operator $\mathbf{C}^{(k)}$.

2.11. The Wigner-Eckart Theorem for $SO(3)$

The key for calculating the matrix elements of tensor operators acting between angular momentum states comes from the Wigner-Eckart theorem as applied to $SO(3)$. Here we will simply state the theorem. Detailed derivations can be found elsewhere^{2,17,22,23}. The m -dependence of the matrix elements of the tensor operator component $T_q^{(k)}$ in the jm scheme is given by

$$\langle \alpha jm | T_q^{(k)} | \alpha' j' m' \rangle = (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \langle \alpha j || T^{(k)} || \alpha' j' \rangle \quad (2-32)$$

The important point to note is that the entire dependence of the matrix element on the m projection quantum numbers is encased in a phase factor and a $3jm$ -symbol. The quantity $\langle \alpha j || T^{(k)} || \alpha' j' \rangle$ is a *reduced matrix element* which is independent of the m quantum numbers. The numbers α and α' stand for any other descriptors required to complete the description of the states.

Note that the $3jm$ -symbol will vanish and hence render the matrix element null unless

$$j + j' \geq k \geq |j - j'| \quad \text{and} \quad m - m' = q \quad (2-33)$$

2.12. Examples of Reduced Matrix Elements

Some reduced matrix elements may be readily determined. Consider the reduced matrix element $\langle \alpha j || J^{(1)} || \alpha' j' \rangle$. We first note that

$$\langle \alpha jm | J_z | \alpha' j' m' \rangle = m \delta(\alpha, \alpha') \delta(j, j') \delta(m, m') \quad (2-34)$$

Choosing $m = m' = \frac{1}{2}$ and $q = 0$ we have from Eq(2-32)

$$\langle \alpha j \frac{1}{2} | J_0^{(1)} | \alpha' j' \frac{1}{2} \rangle = \frac{1}{2} \delta(\alpha, \alpha') \delta(j, j') = (-1)^{j-\frac{1}{2}} \begin{pmatrix} j & 1 & j \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \langle \alpha j || J^{(1)} || \alpha j \rangle \quad (2-35)$$

The $3jm$ -symbol may be expressed explicitly in terms of its arguments^{2,17} and the result

$$\langle \alpha j || J^{(1)} || \alpha j \rangle = \delta(\alpha, \alpha') \delta(j, j') \sqrt{j(j+1)(2j+1)} \quad (2-36)$$

obtained. In an exactly similar way

$$\langle \alpha L || L^{(1)} || \alpha' L' \rangle = \delta(\alpha, \alpha') \delta(L, L') \sqrt{L(L+1)(2L+1)} \quad (2-37a)$$

and

$$\langle \alpha S || S^{(1)} || \alpha' S' \rangle = \delta(\alpha, \alpha') \sqrt{S(S+1)(2S+1)} \quad (2-37b)$$

With somewhat greater difficulty²

$$\langle \alpha \ell || C^{(k)} || \alpha' \ell' \rangle = \delta(\alpha, \alpha') (-1)^\ell \sqrt{(2\ell+1)(2\ell'+1)} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \quad (2-37c)$$

2.13. Coupled Tensor Operators

We have noted the close connection between the transformation properties of tensor operators and angular momentum states. Consider two tensor operators $\mathbf{T}^{(k_1)}$ and $\mathbf{U}^{(k_2)}$. We can define a coupled tensor operator $\mathbf{X}^{(k_1 k_2; K)}$ via

$$\mathbf{X}_Q^{k_1 k_2; K} = \sum_{q_1, q_2} T_{q_1}^{(k_1)} U_{q_2}^{(k_2)} \langle k_1 q_1 k_2 q_2 | k_1 k_2; K Q \rangle \quad (2-38)$$

Explicit evaluation of the Clebsch-Gordan coefficient for the case of $K = 0$ leads to

$$[\mathbf{T}^{(k)} \mathbf{U}^{(k)}]_0^0 = \frac{(-1)^k}{\sqrt{(2k+1)}} \sum_q (-1)^{-q} T_q^{(k)} U_{-q}^{(k)} \quad (2-39)$$

The scalar product of two tensor operators is defined as

$$(\mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)}) = \sum_q (-1)^q T_q^{(k)} U_{-q}^{(k)} \quad (2-40)$$

It follows from Eqs.(2-39) and (2-40) that

$$[\mathbf{T}^{(k)} \mathbf{U}^{(k)}]_0^0 = \frac{(-1)^k}{\sqrt{(2k+1)}} (\mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)}) \quad (2-41)$$

2.14. Matrix Elements of Tensor Operators

Henceforth we shall often write simply $\mathbf{X}^{(K)}$ rather than $\mathbf{X}^{(k_1 k_2; K)}$ for a coupled tensor operator. It follows immediately from the Wigner-Eckart theorem that

$$\begin{aligned} & \langle \alpha j_1 j_2 J M | X_Q^{(K)} | \alpha' j_1' j_2' J' M' \rangle \\ &= (-1)^{J-M} \begin{pmatrix} J & K & J' \\ -M & Q & M \end{pmatrix} \langle \alpha j_1 j_2 J || X^{(K)} || \alpha' j_1' j_2' J' \rangle \end{aligned} \quad (2-42)$$

Our problem is now to evaluate the reduced matrix element in Eq.(2-42). Basically this is done by an uncoupling of the bra and ket states and of the tensor operator followed by appropriate recouplings and summations. For the details I refer you to the books of Judd² and of Edmonds¹⁷.

If $\mathbf{T}^{(k)}$ and $\mathbf{U}^{(k)}$ act separately on parts 1 and 2 of a system such as in spin and orbit spaces or on different particles, or sets of particles, then we obtain the result

$$\begin{aligned} \langle \alpha j_1 j_2 J || X^{(K)} || \alpha' j_1' j_2' J' \rangle &= \sum_{\alpha''} \langle \alpha j_1 || T^{(k_1)} || \alpha'' j_1' \rangle \langle \alpha'' j_2 || U^{(k_2)} || \alpha' j_2' \rangle \\ &\quad \times \sqrt{(2J+1)(2K+1)(2J'+1)} \begin{Bmatrix} j_1 & j_1' & k_1 \\ j_2 & j_2' & k_2 \\ J & J' & K \end{Bmatrix} \end{aligned} \quad (2-43)$$

We can specialize the above result for $K = 0$ to obtain the scalar product as

$$\begin{aligned} & \langle \alpha j_1 j_2 J M | (\mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)}) | \alpha' j'_1 j'_2 J' M' \rangle \\ &= \delta_{J,J'} \delta_{M,M'} (-1)^{j'_1 + j_2 + J} \begin{Bmatrix} j'_1 & j'_2 & J \\ j_2 & j_1 & k \end{Bmatrix} \\ & \times \sum_{\alpha''} \langle \alpha j_1 \| T^{(k)} \| \alpha'' j'_1 \rangle \langle \alpha'' j_2 \| U^{(k)} \| \alpha' j'_2 \rangle \end{aligned} \quad (2-44)$$

The action of an operator $\mathbf{T}^{(k)}$ acting on part 1 of a system can be found by putting $k_2 = 0$ in Eq.(2-43) to yield

$$\begin{aligned} \langle \alpha j_1 j_2 J \| T^{(k)} \| \alpha' j'_1 j'_2 J' \rangle &= \delta_{j_2, j'_2} (-1)^{j_1 + j_2 + J' + k} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & k & J' \\ j'_1 & j_2 & j_1 \end{Bmatrix} \\ & \times \langle \alpha j_1 \| T^{(k)} \| \alpha' j'_1 \rangle \end{aligned} \quad (2-45)$$

while the action on part 2 is found by putting $k_1 = 0$ in Eq.(2-43) to yield

$$\begin{aligned} \langle \alpha j_1 j_2 J \| U^{(k)} \| \alpha' j'_1 j'_2 J' \rangle &= \delta_{j_1, j'_1} (-1)^{j_1 + j'_2 + J + k} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & k & J' \\ j'_2 & j_1 & j_2 \end{Bmatrix} \\ & \times \langle \alpha j_2 \| U^{(k)} \| \alpha' j'_2 \rangle \end{aligned} \quad (2-46)$$

A weaker result applicable to both cases where the operators act either on different parts of a system or indeed the same system may be derived to give

$$\begin{aligned} \langle \alpha J \| X^{(K)} \| \alpha' J' \rangle &= (-1)^{J+K+J'} \sqrt{(2K+1)} \sum_{\alpha'', J''} \begin{Bmatrix} k_2 & K & k_1 \\ J & J'' & J' \end{Bmatrix} \\ & \times \langle \alpha J \| T^{(k_1)} \| \alpha'' J'' \rangle \langle \alpha'' J'' \| U^{(k_2)} \| \alpha' J' \rangle \end{aligned} \quad (2-47)$$

The results given by Eqs. (2-42) to (2-47) form the basis for all subsequent applications of the theory of tensor operators.

2.15. Some Special $3nj$ -symbols

For subsequent work it is useful to collect together a number of special cases of $3nj$ -symbols. A much fuller set can be found in Edmonds¹⁷. Beware, elsewhere some of the tabulations are erroneous!

$$\begin{pmatrix} j & j & 0 \\ m & -m & 0 \end{pmatrix} = \frac{(-1)^{j-m}}{\sqrt{2j+1}} \quad (2-48a)$$

$$\begin{pmatrix} j & k & j \\ -j & 0 & j \end{pmatrix} = \frac{(2j)!}{\sqrt{(2j-k)!(2j+k+1)!}} \quad (2-48b)$$

$$\begin{pmatrix} j & 1 & j \\ -m & 0 & m \end{pmatrix} = (-1)^{j-m} \frac{m}{\sqrt{j(2j+1)(j+1)}} \quad (2-48c)$$

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_2 & j_1 & 1 \end{matrix} \right\} = (-1)^{j_1+j_2+j_3+1} \frac{[-j_1(j_1+1) + j_2(j_2+1) + j_3(j_3+1)]}{\sqrt{4j_1(j_1+1)(2j_1+1)j_2(j_2+1)(2j_2+1)}} \quad (2-49a)$$

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_2-1 & j_1 & 1 \end{matrix} \right\} = (-1)^{j_1+j_2+j_3} \times \sqrt{\frac{2(j_1+j_2+j_3+1)(j_1+j_2-j_3)(j_2+j_3-j_1)(j_1-j_2+j_3+1)}{2j_1(2j_1+1)(2j_1+2)(2j_2-1)2j_2(2j_2+1)}} \quad (2-49b)$$

Let us now turn to some practical applications of the preceding formalism.

2.16. The Zeeman effect - Weak field case

Consider a magnetic field B_z directed along the z -axis and a set of states $|\alpha SLJM\rangle$ associated with a spectroscopic term ${}^{2S+1}L$. The presence of the magnetic field adds to the Hamiltonian a term

$$H_{mag} = -B_z\mu_z = B_z\mu_0[L_z + g_s S_z] \quad (2-50)$$

where $g_s \cong 2.0023$. In terms of tensor operators we need to evaluate the matrix elements of the operator $L_0^{(1)} + g_s S_0^{(1)}$. Consider first the diagonal matrix elements

$$\langle \alpha SLJM | L_0^{(1)} + g_s S_0^{(1)} | \alpha SLJM \rangle$$

Application of the Wigner-Eckart theorem gives

$$\begin{aligned} & \langle \alpha SLJM | L_0^{(1)} + g_s S_0^{(1)} | \alpha SLJM \rangle \\ &= (-1)^{J-M} \begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix} \langle \alpha SLJ || L^{(1)} + g_s S^{(1)} || \alpha SLJ \rangle \\ &= \frac{M}{\sqrt{J(J+1)(2J+1)}} \langle \alpha SLJ || L^{(1)} + g_s S^{(1)} || \alpha SLJ \rangle \end{aligned} \quad (2-51)$$

Use of Eq.(2-45) gives

$$\begin{aligned} & \langle \alpha SLJ || g_s S^{(1)} || \alpha SLJ \rangle \\ &= g_s (-1)^{S+L+J+1} (2J+1) \left\{ \begin{matrix} J & 1 & J \\ S & L & S \end{matrix} \right\} \langle \alpha S || S^{(1)} || \alpha S \rangle \end{aligned} \quad (2-52a)$$

Use of Eq.(2-46) gives

$$\begin{aligned} & \langle \alpha SLJ || L^{(1)} || \alpha SLJ \rangle \\ &= (-1)^{S+L+J+1} (2J+1) \left\{ \begin{matrix} J & 1 & J \\ L & S & L \end{matrix} \right\} \langle \alpha L || L^{(1)} || \alpha L \rangle \end{aligned} \quad (2-52b)$$

The reduced matrix elements follow from Eq.(2-37a,b) and the $6j$ -symbols may be evaluated explicitly. Combining terms we finally obtain

$$\langle \alpha SLJM | H_{mag} | \alpha SLJM \rangle = B_z \mu_0 M g(SLJ) \quad (2-53)$$

where

$$g(SLJ) = 1 + (g_s - 1) \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (2-54)$$

is the so-called Lande g -factor. Eq.(2-53) shows that for a weak magnetic field with states of different J well separated the magnetic field will produce splittings linearly dependent on the M quantum number. This is the so-called weak field Zeeman effect. For a $J = \frac{1}{2}$ level we obtain the pattern

$$\begin{array}{rcc}
 & & M_J \\
 & & \frac{1}{2} \\
 & \cdots & \uparrow \\
 J = \frac{1}{2} & \text{-----} & g\mu_0 B_z \\
 & \cdots & \downarrow \\
 & & -\frac{1}{2}
 \end{array}$$

Note that we have not only determined the number of sublevels (two) but also the *magnitude* of splitting. For a $J = 1$ level we obtain the pattern

$$\begin{array}{rcc}
 & & M_J \\
 & & 1 \\
 & \cdots & \uparrow \\
 J = 1 & \text{-----} & 0 \\
 & \cdots & \downarrow \\
 & & -1
 \end{array}$$

In this case we obtain three sublevels. In general we obtain $(2J+1)$ sublevels. For a system having an *odd* number of electrons we obtain an *even* number of sublevels while for an *even* number of electrons we obtain an *odd* number of sublevels.

2.17. Off-diagonal matrix elements and the Zeeman effect

For a magnetic field in the z -direction the M -quantum number remains a good quantum number. This is because we have preserved SO_2 symmetry. However, H_{mag} does not preserve SO_3 symmetry - we have chosen a particular direction in 3-space. The total angular momentum J is no longer a good quantum number. There exist matrix elements of H_{mag} coupling states with $\Delta J = \pm 1$. We first note that $J_z = L_z + S_z$ and hence $L_z + g_s S_z = J_z + (g_s - 1)S_z$. But the matrix elements of J_z are diagonal in J and hence to calculate the off-diagonal matrix elements we need only calculate the off-diagonal matrix element of S_z as follows:

$$\begin{aligned}
 & \langle \alpha SLJM | S_0^{(1)} | \alpha SLJ+1M \rangle \\
 & = (-1)^{J-M} \begin{pmatrix} J & 1 & J+1 \\ -M & 0 & M \end{pmatrix} \langle \alpha SLJ || S^{(1)} || \alpha SLJ+1 \rangle \quad (2-55)
 \end{aligned}$$

Explicit evaluation of the $3j$ -symbol gives

$$(-1)^{J-M} \begin{pmatrix} J & 1 & J+1 \\ -M & 0 & M \end{pmatrix} = -\sqrt{\frac{(J+M+1)(J-M+1)}{(2J+1)(J+1)(2J+3)}} \quad (2-56)$$

Evaluation of the reduced matrix element in Eq.(2-55) using Eq.(2-37b) gives

$$\begin{aligned}
& \langle \alpha SLJ \| S^{(1)} \| \alpha SLJ + 1 \rangle \\
&= (-1)^{S+L+J} \sqrt{(2J+1)(2J+3)} \left\{ \begin{matrix} J & 1 & J+1 \\ S & L & S \end{matrix} \right\} \langle S \| S^{(1)} \| S \rangle \\
&= -\sqrt{\frac{(S+L+J+2)(S+J+1-L)(J+1+L-S)(S-J+L)}{4(J+1)}} \quad (2-57)
\end{aligned}$$

Combining Eqs. (2-56) and (2-57) in Eq.(2-55) finally yields

$$\begin{aligned}
& \langle \alpha SLJM | H_{mag} | \alpha SLJ + 1M \rangle \\
&= B_z \mu_0 (g_s - 1) \sqrt{(J+1)^2 - M^2} \\
&\times \sqrt{\frac{(S+L+J+2)(S+J+1-L)(J+1+L-S)(S-J+L)}{4(J+1)^2(2J+1)(2J+3)}} \quad (2-58)
\end{aligned}$$

2.18. Calculation for a 3P Term

A 3P term has $S = 1$ and $L = 1$ from which we deduce that we can have $J = 0, 1$ and 2 . In a free atom we expect the spin-orbit coupling to give rise to the three spectroscopic levels:

$${}^3P_2 \quad {}^3P_1 \quad {}^3P_0$$

For simplicity we will assume $g_s = 2$. From Eq.(2-54) we find

$$g({}^3P_2) = \frac{3}{2} \quad g({}^3P_1) = \frac{3}{2}$$

(Recall the diagonal matrix element for a state with $M_J = 0$.) The off-diagonal matrix elements follow from Eq. (2-58) and we can obtain separate matrices, one for each value of M_J . The matrices for M_J and $-M_J$ differ only in the sign of the diagonal elements which is just the sign of M_J . In units of $\mu_0 B_z$ we obtain the following matrices:

$$M_J = \pm 2 \quad \langle {}^3P_2 \pm 2 | \begin{pmatrix} |{}^3P_2 \pm 2\rangle \\ \pm 3 \end{pmatrix} \quad (2-59a)$$

$$M_J = \pm 1 \quad \langle {}^3P_2 \pm 1 | \begin{pmatrix} |{}^3P_2 \pm 1\rangle & |{}^3P_1 \pm 1\rangle \\ \pm \frac{3}{2} & \frac{1}{2} \\ \frac{1}{2} & \pm \frac{3}{2} \end{pmatrix} \quad (2-59b)$$

$$M_J = 0 \quad \langle {}^3P_2 0 | \begin{pmatrix} |{}^3P_2 0\rangle & |{}^3P_1 0\rangle & |{}^3P_0 0\rangle \\ \frac{3}{2} & \frac{1}{2} & 0 \\ \frac{\sqrt{3}}{3} & 0 & \frac{\sqrt{6}}{3} \\ 0 & \frac{\sqrt{6}}{3} & 0 \end{pmatrix} \quad (2-59c)$$

The effect of the off-diagonal matrix elements is to mix states of different J and to lead to level shifts non-linear in M_J .

2.19. Strong Magnetic Fields and the Paschen-Back Effect

If the external magnetic field is strong and the energy separation of the different J states small then there will be strong J -mixing. So far we have considered states in an $|SLJM\rangle$ basis. The calculation of energy levels requires that we add to the above matrices the other terms in the Hamiltonian such as the Coulomb and spin-orbit interactions. In the event of a very strong magnetic field we may consider states in a $|SLM_S M_L\rangle$ basis. In that case we have the matrix elements

$$\begin{aligned} & \langle \alpha SLM_S M_L | H_{mag} | \alpha SLM_S M_L \rangle \\ &= \mu_0 B_z \langle \alpha SLM_S M_L | L_0^{(1)} + g_s S_0^{(1)} | \alpha SLM_S M_L \rangle \\ &= \mu_0 B_z [M_L + g_s M_S] \end{aligned} \quad (2-60)$$

where $M_J = M_S + M_L$. For the states $|^3P M_S M_L\rangle$, taking $g_s = 2$ we have, again in units of $\mu_0 B_z$:

$$M_J = \pm 2 \quad \langle ^3P \pm 1 \pm 1 | \begin{pmatrix} |^3P \pm 1 \pm 1\rangle \\ 3 \end{pmatrix} \quad (2-61a)$$

$$M_J = \pm 1 \quad \begin{matrix} \langle ^3P10 | \\ \langle ^3P01 | \end{matrix} \begin{pmatrix} |^3P10\rangle & |^3P01\rangle \\ 2 & 0 \\ 0 & 1 \end{pmatrix} \quad (2-61b)$$

$$M_J = 0 \quad \begin{matrix} \langle ^3P1-1 | \\ \langle ^3P-11 | \\ \langle ^3P00 | \end{matrix} \begin{pmatrix} |^3P1-1\rangle & |^3P-11\rangle & |^3P00\rangle \\ 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2-61c)$$

We note, as expected these matrices are diagonal. Their eigenvalues are precisely the eigenvalues that would be obtained if the matrices in Eq.(59) were diagonalised. This gives a method of checking Zeeman matrices calculated in the $|SLJM\rangle$ basis. Upon diagonalisation we must obtain the corresponding values found in the $|SLM_S M_L\rangle$ basis.

Lecture 3

He is rather a good mathematician, but he will never be as good as Schottky.

G Frobenius, in a letter recommending the appointment of David Hilbert at Gottingen

3. Introduction

We now try to use the ideas introduced in the previous lecture to the calculation of interactions in some one- and two-electron systems. Firstly, we consider the Coulomb repulsion in two-electron systems, secondly the spin-orbit interaction in one- and two-electron systems and thirdly, intermediate coupling and its effect on the Lande g -factors.

3.1. States of Two-electron Systems

Before starting to calculate matrix elements we need to choose a suitable angular momentum basis. The Coulomb repulsion operator for an N -electron system,

$$H_c = e^2 \sum_{i < j} \frac{1}{r_{ij}}, \quad (3-1)$$

commutes with the angular momentum operators

$$\mathbf{S} = \sum_{i=1}^N \mathbf{s}_i \quad \text{and} \quad \mathbf{L} = \sum_{i=1}^N \mathbf{l}_i \quad (3-2)$$

with the consequence that the matrix elements of H_c are diagonal in the $SLJM$ and SM_SLM_L schemes and independent of the M quantum numbers.

For a two-electron system say $n\ell n'\ell'$ the total orbital quantum number L takes on the range of values,

$$L = \ell + \ell', \ell + \ell' - 1, \dots, |\ell - \ell'|, \quad (3-3)$$

while the total spin S has just the two values,

$$S = 1, 0. \quad (3-4)$$

Thus we obtain triplet ($S = 1$) and singlet ($S = 0$) spin states. For the special case of *equivalent electrons* where $n = n'$ and $\ell = \ell'$ we must apply the Pauli Exclusion Principle which in this case amounts to excluding all values of S, L except those where $L + S$ is *even*. Thus for the $4f^2$ configuration we have the spectroscopic terms

$${}^3(PFH) + {}^1(SDGI) \quad (3-5)$$

whereas for the $4f5f$ configuration the terms are

$${}^{3,1}(SPDFGHI) \quad (3-6)$$

and in the $4f5d$ configuration

$${}^{3,1}(PDFGH) \quad (3-7)$$

Recall that spectroscopists use the somewhat bizarre, but historical letter notation for orbital angular momentum integers, L ,

$$L = \begin{array}{cccccccccc} 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & \dots \\ S & P & D & F & G & H & I & K & \dots \end{array}$$

with the orbital angular momentum of single electrons being represented by the corresponding lower case letters. In some cases we will suppress the principal quantum number n . Thus f^2 will stand for a generic configuration involving a pair of f orbitals having the same principal quantum number whereas ff' denotes a pair of f orbitals having different principal quantum numbers.

3.2. The Central Field Approximation

For N electrons moving about a point nucleus of charge Ze we have the approximate non-relativistic Hamiltonian

$$H = \sum_{i=1}^N \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i<j}^N \frac{e^2}{r_{ij}} \quad (3-8)$$

In terms of the central field approximation we may consider each electron to be moving independently in the field of the nuclear charge and a spherically averaged potential fields due to each of the other electrons. Hence each electron may be said to move in a spherically symmetric potential $-U(r_i)/e$. The Hamiltonian for the central field, H_{cf} , becomes

$$H_{cf} = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + U(r_i) \right]. \quad (3-9)$$

The difference, $H - H_{cf}$ may now be treated as a perturbation potential

$$H - H_{cf} = V = \sum_{i=1}^N \left[-\frac{Ze^2}{r_i} - U(r_i) \right] + \sum_{i<j}^N \frac{e^2}{r_{ij}} \quad (3-10)$$

Schrödinger's equation for the central field becomes

$$\sum_{i=1}^N \left[\frac{p_i^2}{2m} + U(r_i) \right] \Psi = E_{cf} \Psi \quad (3-11)$$

and can be separated by choosing a solution such that

$$\Psi = \prod_{i=1}^N \varphi_i(a^i) \quad \text{and} \quad E_{cf} = \sum_{i=1}^N E_i \quad (3-12)$$

Each electron moving in the central field, $U(r_i)$ will then satisfy equations of the type

$$\left[\frac{p^2}{2m} + U(r) \right] \varphi(a^i) = E(a^i) \varphi(a^i) \quad (3-13)$$

where (a^i) represents a set of one-electron quantum numbers $(nsm_s\ell m_\ell)$ which specify the state of the electron in the central field. A further separation of variables can be made by introducing polar coordinates (θ, ϕ, r) and separating the one-electron eigenfunctions into their *angular* and *radial* parts to give for bound states

$$\varphi(a^i) = r^{-1} R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi) \quad (3-14)$$

Let us introduce a spin coordinate, σ , which may equal $\pm\frac{1}{2}$, and a spin function $\delta(m_s, \sigma)$ satisfying the orthonormality relation

$$\sum_{\sigma} \delta(m_s, \sigma) \delta(m'_s, \sigma) = \delta(m_s, m'_s) \quad (3-15)$$

so that (3-14) becomes

$$\varphi(n\ell m_\ell m_s) = \delta(m_s, \sigma) r^{-1} R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi) \quad (3-16)$$

and

$$\Psi = \prod_{i=1}^N \varphi(\alpha^i) \quad (3-17)$$

where now α^i represents the quantum number quartet $(n\ell m_\ell m_s)$ associated with the i -th electron.

Taking into account the Pauli exclusion principle we must construct totally antisymmetric wavefunctions to give

$$\Psi = \frac{1}{\sqrt{N!}} \sum_p (-1)^p P \varphi_1(\alpha^1) \varphi_2(\alpha^2) \dots \varphi_N(\alpha^N) \quad (3-18)$$

where P represents a permutation of the *spin* and *spatial* coordinates of a pair of electrons and p is the *parity* of the permutation with the summation extending over all $N!$ permutations of the N -electron coordinates. In determinantal form (3-18) becomes

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\alpha^1) & \varphi_2(\alpha^1) & \dots & \varphi_N(\alpha^1) \\ \varphi_1(\alpha^2) & \varphi_2(\alpha^2) & \dots & \varphi_N(\alpha^2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(\alpha^N) & \varphi_2(\alpha^N) & \dots & \varphi_N(\alpha^N) \end{vmatrix} \quad (3-19)$$

3.3. Two-Electron Antisymmetrized States in LS -Coupling

Starting with Eq(3-19) for $N = 2$ we may write the antisymmetrized eigenfunction for two electrons whose angular momentum are LS -coupled as the bra vector

$$\langle n_a \ell_a, n_b \ell_b; SL | = \frac{1}{\sqrt{2}} (\langle n_{a1} \ell_{a1}, n_{b2} \ell_{b2}; SL | - \langle n_{a2} \ell_{a2}, n_{b1} \ell_{b1}; SL |) \quad (3-20)$$

where the indices 1 and 2 refer to the coordinates of the first and second electron respectively and for brevity we have suppressed the spin angular momenta. The second eigenstate in (3-20) differs from that of the first by an *odd* permutation of the electron coordinates relative to the quantum numbers. We can recouple the angular momenta of the second eigenstate to produce

$$\langle n_a \ell_a, n_b \ell_b; SL | = \frac{1}{\sqrt{2}} (\langle n_{a1} \ell_{a1}, n_{b2} \ell_{b2}; SL | - (-1)^{s_a + s_b + \ell_a + \ell_b + S + L} \langle n_{b1} \ell_{b1}, n_{a2} \ell_{a2}; SL |) \quad (3-21)$$

If $n_a \ell_a = n_b \ell_b = n \ell$ the antisymmetric bra vector may be taken as

$$\langle n \ell, n \ell; SL | = \langle (n \ell)^2; SL | \quad S + L \quad \text{even} \quad (3-22)$$

Likewise for the antisymmetrized ket vector of another two-electron configuration we may write the analogue of (3-21) as

$$|n_c \ell_c, n_d \ell_d; SL\rangle = \frac{1}{\sqrt{2}} (|n_{c1} \ell_{c1}, n_{d2} \ell_{d2}; SL\rangle - (-1)^{s_c + s_d + \ell_c + \ell_d + S + L} |n_{d1} \ell_{d1}, n_{c2} \ell_{c2}; SL\rangle) \quad (3-23)$$

and of (3-22) as

$$|n \ell, n \ell; SL\rangle = |(n \ell)^2; SL\rangle \quad S + L \quad \text{even} \quad (3-24)$$

3.4. Two-Electron Coulomb Matrix Elements

For a two-electron system we have from (3-21) and (3-23)

$$\begin{aligned} & \langle n_a \ell_a, n_b \ell_b; SL | e^2 / r_{12} | n_c \ell_c, n_d \ell_d; SL \rangle \\ &= \frac{1}{2} [\langle n_a \ell_a, n_b \ell_b; SL | e^2 / r_{12} | n_c \ell_c, n_d \ell_d; SL \rangle + \langle n_a \ell_a, n_b \ell_b; SL | e^2 / r_{12} | n_d \ell_c, n_c \ell_c; SL \rangle \\ &+ (-1)^{\ell_a + \ell_b + S + L} (\langle n_a \ell_a, n_b \ell_b; SL | e^2 / r_{12} | n_d \ell_c, n_c \ell_c; SL \rangle + \langle n_b \ell_b, n_a \ell_a; SL | e^2 / r_{12} | n_c \ell_c, n_d \ell_d; SL \rangle)] \end{aligned} \quad (3-25)$$

Owing to the symmetry of e^2 / r_{12} (3-25) simplifies to

$$\begin{aligned} & \langle n_a \ell_a, n_b \ell_b; SL | e^2 / r_{12} | n_c \ell_c, n_d \ell_d; SL \rangle \\ &= \langle n_a \ell_a, n_b \ell_b; SL | e^2 / r_{12} | n_c \ell_c, n_d \ell_d; SL \rangle + (-1)^{\ell_a + \ell_b + S + L} \langle n_a \ell_a, n_b \ell_b; SL | e^2 / r_{12} | n_d \ell_c, n_c \ell_c; SL \rangle \end{aligned} \quad (3-26)$$

We can now write (3-26) in tensorial form as

$$\begin{aligned} & \langle n_a \ell_a, n_b \ell_b; SL | e^2 / r_{12} | n_c \ell_c, n_d \ell_d; SL \rangle \\ &= e^2 \sum_k \left[\langle n_a \ell_a, n_b \ell_b; SL \left| \frac{r_{<}^k}{r_{>}^{k+1}} (C_1^{(k)} \cdot C_2^{(k)}) \right| n_c \ell_c, n_d \ell_d; SL \rangle \right. \\ & \left. + (-1)^{\ell_a + \ell_b + S + L} \langle n_a \ell_a, n_b \ell_b; SL \left| \frac{r_{<}^k}{r_{>}^{k+1}} (C_1^{(k)} \cdot C_2^{(k)}) \right| n_d \ell_d, n_c \ell_c; SL \rangle \right] \end{aligned} \quad (3-27)$$

$$= \sum_k [f_k(\ell_a, \ell_b; \ell_c, \ell_d) R^k(n_a \ell_a, n_b \ell_b; n_c \ell_c, n_d \ell_d) + g_k(\ell_a, \ell_b; \ell_d, \ell_c) R^k(n_a \ell_a, n_b \ell_b; n_c \ell_c, n_d \ell_d)] \quad (3-28)$$

where f_k and g_k represent the *angular* parts of the matrix elements and the R^k 's the *Slater radial integrals*. The angular factors can be evaluated by application of (2-44),

$$\begin{aligned} & \langle \alpha j_1 j_2 J M | (\mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)}) | \alpha' j'_1 j'_2 J' M' \rangle \\ &= \delta_{J, J'} \delta_{M, M'} (-1)^{j'_1 + j_2 + J} \begin{Bmatrix} j'_1 & j'_2 & J \\ j_2 & j_1 & k \end{Bmatrix} \\ & \times \sum_{\alpha''} \langle \alpha j_1 || T^{(k)} || \alpha'' j'_1 \rangle \langle \alpha'' j_2 || U^{(k)} || \alpha' j'_2 \rangle \end{aligned} \quad (2-44)$$

to give

$$f_k(\ell_a, \ell_b; \ell_c, \ell_d) = (-1)^{\ell_a + \ell_b + L} \langle \ell_a || C_1^{(k)} || \ell_c \rangle \langle \ell_b || C_2^{(k)} || \ell_d \rangle \begin{Bmatrix} \ell_a & \ell_c & k \\ \ell_d & \ell_b & L \end{Bmatrix} \quad (3-29a)$$

and

$$g_k(\ell_a, \ell_b; \ell_d, \ell_c) = (-1)^S \langle \ell_a || C_1^{(k)} || \ell_d \rangle \langle \ell_b || C_2^{(k)} || \ell_c \rangle \begin{Bmatrix} \ell_a & \ell_d & k \\ \ell_c & \ell_b & L \end{Bmatrix} \quad (3-29b)$$

with the reduced matrix elements being given by (2-37c),

$$\langle \alpha \ell || C^{(k)} || \alpha' \ell' \rangle = \delta(\alpha, \alpha') (-1)^\ell \sqrt{(2\ell + 1)(2\ell' + 1)} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \quad (2-37c)$$

The Slater radial integrals are defined by

$$R^k(n_a \ell_a, n_b \ell_b; n_c \ell_c, n_d \ell_d) = e^2 \int_0^\infty \int_0^\infty \frac{r_{<}^k}{r_{>}^{k+1}} R_{n_a \ell_a}(r_1) R_{n_b \ell_b}(r_2) R_{n_c \ell_c}(r_1) R_{n_d \ell_d}(r_2) dr_1 dr_2 \quad (3-30)$$

When $n_a \ell_a = n_c \ell_c$ and $n_b \ell_b = n_d \ell_d$ (3-28) simplifies to

$$\begin{aligned} & \langle n_a \ell_a, n_b \ell_b; SL | e^2 / r_{12} | n_a \ell_a, n_b \ell_b; SL \rangle \\ &= \sum_k [f_k(\ell_a, \ell_b) F^{(k)}(n_a \ell_a, n_b \ell_b) + g_k(\ell_a, \ell_b) G^k(n_a \ell_a, n_b \ell_b)] \end{aligned} \quad (3-31)$$

whereas

$$F^{(k)}(n_a \ell_a, n_b \ell_b) = R^k(n_a \ell_a, n_b \ell_b; n_a \ell_a, n_b \ell_b) \quad (3-32a)$$

and

$$G^{(k)}(n_a \ell_a, n_b \ell_b) = R^k(n_a \ell_a, n_b \ell_b; n_b \ell_b, n_a \ell_a) \quad (3-32b)$$

The $F^{(k)}$'s are known as *direct integrals* and are necessarily *positive* and *decreasing* functions of k while the $G^{(k)}$'s are known as *exchange integrals* and are *positive* and $G^{(k)}/(2k+1)$ is necessarily a *decreasing function* of k .

To avoid large denominators appearing in explicit calculations Condon and Shortley²⁴ have redefined the radial $F^{(k)}$ and $G^{(k)}$ integrals in terms of reduced radial integrals F_k and G_k where

$$F_k = \frac{F^{(k)}}{D_k} \quad \text{and} \quad \frac{G^{(k)}}{D_k} \quad (3-33)$$

where the D_k 's are given in their tables 1⁶ and 2⁶.

3.5. Exercises

3-1. Show that the electrostatic interaction *between* the configurations $(n\ell)^2$ and $(n_a \ell_a, n_b \ell_b)$ is given by

$$\begin{aligned} \langle (n\ell)^2; SL | e^2/r_{12} | n_a \ell_a, n_b \ell_b; SL \rangle &= \sqrt{2} \sum_k \langle n\ell, n\ell; SL \left| \frac{r_{<}^k}{r_{>}^{k+1}} (C_1^{(k)} \cdot C_2^{(k)}) \right| n_a \ell_a, n_b \ell_b; SL \rangle \\ &= \sum_k f_k(\ell, \ell; \ell_a, \ell_b) R^k(n\ell, n\ell; n_a \ell_a, n_b \ell_b) \end{aligned} \quad (3-34)$$

where

$$f_k(\ell, \ell; \ell_a, \ell_b) = (-1)^{\ell+\ell_a+L} \sqrt{2} \langle \ell \| C^{(k)} \| \ell_a \rangle \langle \ell \| C^{(k)} \| \ell_b \rangle \begin{Bmatrix} \ell & \ell_a & k \\ \ell_b & \ell & L \end{Bmatrix} \quad (3-35)$$

3-2. Show that the electrostatic interaction *between* the configurations $(n\ell)^2$ and $(n'\ell')^2$ is given by

$$\langle (n\ell)^2; SL | e^2/r_{12} | (n'\ell')^2; SL \rangle = \sum_k f_k(\ell, \ell; \ell', \ell') R^k(n\ell, n\ell; n'\ell', n'\ell') \quad (3-36)$$

where

$$f_k(\ell, \ell; \ell', \ell') = (-1)^{\ell+\ell'+L} \langle \ell \| C^{(k)} \| \ell' \rangle^2 \begin{Bmatrix} \ell & \ell' & k \\ \ell' & \ell & L \end{Bmatrix} \quad (3-37)$$

and

$$R^k(n\ell, n\ell; n'\ell', n'\ell') = G^{(k)}(n\ell, n'\ell') \quad (3-38)$$

3.6. Coulomb Matrix Elements for the f^2 Electron Configuration

In the case of all the electrons being equivalent we have for the two-electron configuration $(n\ell)^2$

$$\langle (n\ell)^2; SL | e^2/r_{12} | (n\ell)^2; SL \rangle = \sum_k f_k(\ell, \ell) F^{(k)}(n\ell, n\ell) \quad (S+L) \text{ even} \quad (3-39)$$

with

$$f_k(\ell, \ell) = (-1)^L \langle \ell \| C^{(k)} \| \ell \rangle^2 \begin{Bmatrix} \ell & \ell & k \\ \ell & \ell & L \end{Bmatrix} \quad (3-40)$$

For the f^2 configuration we have $\ell = 3$ and the triangular conditions on the relevant $3jm-$ and $6j-$ symbols limit k to $k = 0, 2, 4, 6$. For the particular case of f^N configurations we also have

$$\begin{aligned} F_0 &= F^{(0)} \\ F_2 &= \frac{F^{(2)}}{225} \\ F_4 &= \frac{F^{(4)}}{1089} \\ F_6 &= \frac{25F^{(6)}}{184041} \end{aligned} \quad (3-41)$$

The following short MAPLE programme f2.map can evaluate (3-40)

```
read"njsym";
fk:=proc()
local result,L;
for L from 0 to 6 do;
result:=CLS(3,0,L)*F0+CLS(3,2,L)*225*F2+CLS(3,4,L)*1089*F4
+CLS(3,6,L)*184041/25*F6;
lprint('L =',L,result);
end do;
end;
```

which may be run in MAPLE as

```
> read"f2.map";
> fk();
'L =, 0, F0+60*F2+198*F4+1716*F6
'L =, 1, F0+45*F2+33*F4-1287*F6
'L =, 2, F0+19*F2-99*F4+715*F6
'L =, 3, F0-10*F2-33*F4-286*F6
'L =, 4, F0-30*F2+97*F4+78*F6
'L =, 5, F0-25*F2-51*F4-13*F6
'L =, 6, F0+25*F2+9*F4+F6
```

Let us write our Coulomb matrix elements in the form

$$E = \sum_{k=0}^6 f_k F^{(k)}(nf, nf) = \sum_{k=0}^6 f^k F_k(nf, nf) \quad (3-42a)$$

Racah²¹ has given a group-theoretical analysis of the Coulomb interaction for the f^N configurations rewriting the Coulomb matrix elements in the form

$$E = \sum_{k=0}^3 e_k E^k \quad (3-42b)$$

where

$$\begin{aligned} e_0 &= f^0 \\ e_1 &= \frac{9f^0}{7} + \frac{f^2}{42} + \frac{f^4}{77} + \frac{f^6}{462} \\ e_2 &= \frac{143f^2}{42} - \frac{130f^4}{77} + \frac{35f^6}{462} \\ e_3 &= \frac{11f^2}{42} + \frac{4f^4}{77} - \frac{7f^6}{462} \end{aligned} \quad (3-43)$$

and

$$\begin{aligned} E^0 &= F_0 - 10F_2 - 33F_4 - 286F_6 \\ E^1 &= \frac{70F_2 + 231F_4 + 2002F_6}{9} \\ E^2 &= \frac{F_2 - 3F_4 + 7F_6}{9} \\ E^3 &= \frac{5F_2 + 6F_4 - 91F_6}{3} \end{aligned} \quad (3-44)$$

Conversely, we have

$$\begin{aligned} F_0 &= \frac{7E^0 + 9E^1}{7} \\ F_2 &= \frac{E^1 + 143E^2 + 11E^3}{42} \\ F_4 &= \frac{E^1 - 130E^2 + 4E^3}{77} \\ F_6 &= \frac{E^1 + 35E^2 - 7E^3}{462} \end{aligned} \quad (3-45)$$

We can readily change the f2.map programme to

```

read"njsym";
fk:=proc()
local result,L,F0,F2,F4,F6;
F0:=(7*E0+9*E1)/7;
F2:=(E1+143*E2+11*E3)/42;
F4:=(E1-130*E2+4*E3)/77;
F6:=(E1+35*E2-7*E3)/462;
for L from 0 to 6 do;
result:=CLS(3,0,L)*F0+CLS(3,2,L)*225*F2+CLS(3,4,L)*1089*F4
+CLS(3,6,L)*184041/25*F6;
lprint('L =',L,result);
end do;
end;

```

which may be run to give the output:-

```

> fk();
'L =', 0, E0+9*E1
'L =', 1, E0+33*E3
'L =', 2, E0+2*E1+286*E2-11*E3
'L =', 3, E0
'L =', 4, E0+2*E1-260*E2-4*E3
'L =', 5, E0-9*E3
'L =', 6, E0+2*E1+70*E2+7*E3

```

Thus for the spectroscopic terms of the f^2 configuration we have for the triplet states

$$\begin{aligned}
 E(^3H) &= E^0 - 9E^3 \\
 E(^3F) &= E^0 \\
 E(^3P) &= E^0 + 33E^3
 \end{aligned}
 \tag{3-46a}$$

and for the singlets

$$\begin{aligned}
 E(^1G) &= E^0 + 2E^1 - 260E^2 - 4E^3 \\
 E(^1D) &= E^0 + 2E^1 + 286E^2 - 11E^3 \\
 E(^1I) &= E^0 + 2E^1 + 70E^2 + 7E^3 \\
 E(^1S) &= E^0 + 9E^1
 \end{aligned}
 \tag{3-46b}$$

Note that the relative Coulomb energies of the triplets depends only on the coefficient e_3 of E^3 . This is indeed the case for the states of maximum multiplicity in all f^N configurations.

3.7. The Spin-Orbit Interaction

The Coulomb interaction results in different SL terms having different energies but does not depend on the total angular momentum J of the electron states. The spin-orbit interaction, H_{s-o} , is a one-electron type operator of the form

$$H_{s-o} = \sum_{i=1}^N \xi(r_i) (\mathbf{s}_i \cdot \mathbf{l}_i) \quad (3-47)$$

where

$$\xi(r_i) = \frac{\hbar^2}{2m^2c^2r_i} \frac{dU(r_i)}{dr_i} \quad (3-48)$$

The spin-orbit interaction is diagonal in the one-electron orbital quantum number ℓ but *not* in the principal quantum number n . H_{s-o} commutes with \mathbf{J}^2 and J_z and is thus diagonal in J and independent of M_J . It does not commute with \mathbf{L}^2 or \mathbf{S}^2 and hence can couple states of different SL quantum numbers leading to a breakdown of LS -coupling.

The *spin-orbit coupling constant* ζ_{nl} is constant for the states of a given configuration and is defined as

$$\zeta_{nl} = \int_0^\infty R_{nl}^2 \xi(r) dr \quad (3-49)$$

For a single electron we have from (2-44)

$$\langle sljm | \zeta_{nl} (\mathbf{s} \cdot \mathbf{l}) | sljm \rangle = \zeta_{nl} (-1)^{j+l+s} \left\{ \begin{matrix} \ell & \ell & 1 \\ s & s & j \end{matrix} \right\} \langle sl || (\mathbf{s} \cdot \mathbf{l}) || sl \rangle \quad (3-50)$$

The reduced matrix element can be evaluated by noting that

$$\begin{aligned} \langle sl || (\mathbf{s} \cdot \mathbf{l}) || sl \rangle &= \langle s || s^{(1)} || s \rangle \langle \ell || l^{(1)} || \ell \rangle \\ &= \sqrt{s(s+1)(2s+1)\ell(\ell+1)(2\ell+1)} \end{aligned} \quad (3-51)$$

Explicit evaluation of the $6j$ -symbol in (3-50) combined with (3-51) leads to

$$\langle sljm | \zeta_{nl} (\mathbf{s} \cdot \mathbf{l}) | sljm \rangle = \zeta_{nl} \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{2} \quad (3-52)$$

Noting that $j = \ell \pm s$ leads to

$$\langle sljm | \zeta_{nl} (\mathbf{s} \cdot \mathbf{l}) | sljm \rangle = \begin{cases} \zeta_{nl} \frac{\ell}{2} & j = \ell + s \\ -\zeta_{nl} \frac{\ell+1}{2} & j = \ell - s \end{cases} \quad (3-53)$$

Thus for a single electron we obtain a doublet with the lowest j lowest and a splitting ΔE of

$$\Delta E = \zeta_{nl} \frac{2\ell+1}{2} \quad (3-54)$$

For a two-electron configuration $(n\ell)^2$ we can write, making use of (2-44),

$$\begin{aligned}
& \langle (n\ell)^2 SLJM | H_{s-o} | (n\ell)^2 S' L' JM \rangle \\
&= \langle (n\ell)^2 SLJM | \sum_{i=1}^2 \zeta_{n\ell}(\mathbf{s}_i^{(1)} \cdot \mathbf{l}_i^{(1)}) | (n\ell)^2 S' L' JM \rangle \\
&= (-1)^{S'+L+J} \left\{ \begin{matrix} S & S' & 1 \\ L' & L & J \end{matrix} \right\} \sum_{i=1}^2 \langle s_1 s_2 S || s_i^{(1)} || s_1 s_2 S' \rangle \langle \ell_1 \ell_2 L || l_i^{(1)} || \ell_1 \ell_2 L' \rangle \quad (3-55)
\end{aligned}$$

The reduced matrix elements may be evaluated by successive use of (2-45) and (2-46) followed by (2-37a,b) and remembering that for two equivalent electrons $S + L$ and $S' + L'$ must be *even* to finally yield

$$\begin{aligned}
& \langle (n\ell)^2 SLJM | H_{s-o} | (n\ell)^2 S' L' JM \rangle \\
&= (-1)^{S'+L+J+1} 2\zeta_{n\ell} \\
&\times \sqrt{s(s+1)(2s+1)\ell(\ell+1)(2\ell+1)(2S+1)(2S'+1)(2L+1)(2L'+1)} \\
&\times \left\{ \begin{matrix} S & S' & 1 \\ L' & L & J \end{matrix} \right\} \left\{ \begin{matrix} S & 1 & S' \\ s & s & s \end{matrix} \right\} \left\{ \begin{matrix} L & 1 & L' \\ \ell & \ell & \ell \end{matrix} \right\} \quad (3-56)
\end{aligned}$$

3.8. Exercises

- 3-3. Write out a full derivation of (3-54) starting with (3-50).
2. Give all the steps in deriving (3-56).

3.9. Spin-orbit Matrices for f^2

We can implement (3-56) for the f^2 configuration by writing the MAPLE programme `spinorbit.map` as

```

read"njsym";
so:= proc(S, L, Sp, Lp, J)
local result;
result := combine(simplify(6*sqrt(14)*(-1)^(Sp + L + J + 1)*
sqrt((2*S + 1)*(2*Sp + 1)*(2*L + 1)*(2*Lp + 1))*sixj(S, Sp, 1, Lp, L, J)*
sixj(S, Sp, 1, 1/2, 1/2, 1/2)*sixj(L, Lp, 1, 3, 3, 3)))
end proc

```

Thus to compute the matrix element $\langle f^{23} P_2 | H_{s-o} | f^{21} D_2 \rangle$ we have, after reading in `spinorbit.map`,

$$\begin{aligned}
& > \text{so}(1,1,0,2,2); \\
& \quad \quad \quad 3/2 \ 2^{1/2}
\end{aligned}$$

By repeatedly running the above programme we can construct the spin-orbit matrices for the f^2 configuration in terms of the spin-orbit coupling constant ζ_{nf}

to obtain

$$\begin{array}{c}
 J = 0 \quad \begin{array}{cc} {}^3P & {}^1S \end{array} \\
 \begin{array}{c} {}^3P \\ {}^1S \end{array} \begin{pmatrix} -1 & -2\sqrt{3} \\ -2\sqrt{3} & 0 \end{pmatrix}
 \end{array}
 \quad
 \begin{array}{c}
 J = 1 \quad \begin{array}{c} {}^3P \\ {}^3P \end{array} \\
 \begin{array}{c} {}^3P \\ {}^3P \end{array} \begin{pmatrix} -\frac{1}{2} \\ -\frac{1}{2} \end{pmatrix}
 \end{array}
 \quad
 \begin{array}{c}
 J = 2 \quad \begin{array}{ccc} {}^3P & {}^1D & {}^3F \end{array} \\
 \begin{array}{c} {}^3P \\ {}^1D \\ {}^3F \end{array} \begin{pmatrix} \frac{1}{2} & \frac{3}{2}\sqrt{2} & 0 \\ \frac{3}{2}\sqrt{2} & 0 & -\sqrt{6} \\ 0 & -\sqrt{6} & -2 \end{pmatrix}
 \end{array}
 \\
 \\
 \begin{array}{c}
 J = 3 \quad \begin{array}{c} {}^3F \\ {}^3F \end{array} \\
 \begin{array}{c} {}^3F \\ {}^3F \end{array} \begin{pmatrix} -\frac{1}{2} \\ -\frac{1}{2} \end{pmatrix}
 \end{array}
 \quad
 \begin{array}{c}
 J = 4 \quad \begin{array}{ccc} {}^3F & {}^1G & {}^3H \end{array} \\
 \begin{array}{c} {}^3F \\ {}^1G \\ {}^3H \end{array} \begin{pmatrix} \frac{3}{2} & \frac{\sqrt{33}}{3} & 0 \\ \frac{\sqrt{33}}{3} & 0 & -\frac{\sqrt{30}}{3} \\ 0 & -\frac{\sqrt{30}}{3} & -3 \end{pmatrix}
 \end{array}
 \quad
 \begin{array}{c}
 J = 5 \quad \begin{array}{c} {}^3H \\ {}^3H \end{array} \\
 \begin{array}{c} {}^3H \\ {}^3H \end{array} \begin{pmatrix} -\frac{1}{2} \\ -\frac{1}{2} \end{pmatrix}
 \end{array}
 \\
 \\
 \begin{array}{c}
 J = 6 \quad \begin{array}{cc} {}^3H & {}^1I \end{array} \\
 \begin{array}{c} {}^3H \\ {}^1I \end{array} \begin{pmatrix} \frac{5}{2} & \frac{\sqrt{6}}{2} \\ \frac{\sqrt{6}}{2} & 0 \end{pmatrix}
 \end{array}
 \end{array}$$

3.10. Exercise

3-5 If you diagonalise the above matrices you obtain just three distinct eigenvalues 3 (4), -4 (3), $-\frac{1}{2}$ (4) where the bracketed numbers are the number of times each eigenvalue occurs. Explain!

Hint:- You will need to think about (3-54) and jj -coupling.

3.11. Intermediate Coupling

To compute the combined effect of the Coulomb and spin-orbit interactions we need to construct the energy matrices for $H_c + H_{s-o}$ using the results of (107a,b) for the Coulomb matrix elements and the above spin-orbit matrices to give:-

$$\begin{array}{c}
 J = 0 \quad \begin{array}{cc} {}^3P & {}^1S \end{array} \\
 \begin{array}{c} {}^3P \\ {}^1S \end{array} \begin{pmatrix} E^0 + 33E^3 - \zeta & -2\sqrt{3}\zeta \\ -2\sqrt{3}\zeta & E^0 + 9E^1 \end{pmatrix}
 \end{array}
 \\
 \\
 \begin{array}{c}
 J = 1 \quad \begin{array}{c} {}^3P \\ {}^3P \end{array} \\
 \begin{array}{c} {}^3P \\ {}^3P \end{array} \begin{pmatrix} E^0 + 33E^3 - \frac{1}{2}\zeta \\ -\frac{1}{2}\zeta \end{pmatrix}
 \end{array}
 \\
 \\
 \begin{array}{c}
 J = 2 \quad \begin{array}{ccc} {}^3P & {}^1D & {}^3F \end{array} \\
 \begin{array}{c} {}^3P \\ {}^1D \\ {}^3F \end{array} \begin{pmatrix} E^0 + 33E^3 + \frac{1}{2}\zeta & \frac{3}{2}\sqrt{2}\zeta & 0 \\ \frac{3}{2}\sqrt{2}\zeta & E^0 - 2E^1 + 286E^2 - 11E^3 & -\sqrt{6}\zeta \\ 0 & -\sqrt{6}\zeta & E^0 - 2\zeta \end{pmatrix}
 \end{array}
 \end{array}$$

$$J = 3 \quad {}^3F \\ {}^3F \quad \left(E^0 - \frac{1}{2}\zeta \right)$$

$$J = 4 \quad {}^3F \quad {}^1G \quad {}^3H \\ {}^3F \quad \left(\begin{array}{ccc} E^0 + \frac{3}{2}\zeta & \frac{\sqrt{33}\zeta}{3} & 0 \\ \frac{\sqrt{33}\zeta}{3} & E^0 + 2E^1 - 260E^2 - 4E^3 & -\frac{\sqrt{30}\zeta}{3} \\ 0 & -\frac{\sqrt{30}\zeta}{3} & E^0 - 9E^3 - 3\zeta \end{array} \right)$$

$$J = 5 \quad {}^3H \\ {}^3H \quad \left(E^0 - 9E^3 - \frac{1}{2}\zeta \right)$$

$$J = 6 \quad {}^3H \quad {}^1I \\ {}^3H \quad \left(\begin{array}{cc} E^0 - 9E^3 + \frac{5}{2}\zeta & \frac{\sqrt{6}\zeta}{2} \\ \frac{\sqrt{6}\zeta}{2} & E^0 + 2E^1 + 70E^2 + 7E^3 \end{array} \right)$$

Let us choose the following values (in cm^{-1}) :=

$$E^0 = 6501, \quad E^1 = 4882, \quad E^2 = 21, \quad E^3 = 454, \quad \zeta = 737$$

and diagonalize the above matrices. We obtain the following eigenvalues and eigenvectors

$$\begin{array}{ll} -3 & -0.0282|{}^3F_4\rangle + 0.1523|{}^1G_4\rangle + 0.9879|{}^3H_4\rangle \\ 2057 & |{}^3H_5\rangle \\ 4209 & 0.9985|{}^3H_6\rangle - 0.0540|{}^1I_6\rangle \\ 4764 & .01321|{}^3P_2\rangle - 0.1444|{}^1D_2\rangle - 0.9894|{}^3F_2\rangle \\ 6132 & |{}^3F_3\rangle \\ 6799 & -0.8634|{}^3F_4\rangle + 0.4943|{}^1G_4\rangle - 0.1009|{}^3H_4\rangle \\ 10004 & 0.5037|{}^3F_4\rangle + 0.8558|{}^1G_4\rangle - 0.1175|{}^3H_4\rangle \\ 17040 & -0.3059|{}^3P_2\rangle + 0.9415|{}^1D_2\rangle - 0.1415|{}^3F_2\rangle \\ 20528 & 0.9964|{}^3P_0\rangle + 0.0850|{}^1S_0\rangle \\ 20962 & 0.0540|{}^3H_6\rangle + 0.9985|{}^1I_6\rangle \\ 21114 & |{}^3P_1\rangle \\ 22351 & 0.9520|{}^3P_2\rangle + 0.3046|{}^1D_2\rangle - 0.0317|{}^3F_2\rangle \\ 50656 & -0.0850|{}^3P_0\rangle + 0.9964|{}^1S_0\rangle \end{array}$$

The above energy levels are in reasonable agreement with experiment though the 1I_6 level is predicted significantly lower than observed. This observation led to the introduction of the effective operator $\alpha L(L+1)$ for the lanthanides²⁶. The explanation of the origin of that operator was to come later²⁷⁻²⁹.

3.12. Exercises

- 3-6. Calculate the correction to the groundstate Lande g -factor for Pr^{3+} due to intermediate coupling.
- 3-7. Likewise calculate the correction for the level at $10004cm^{-1}$.

Lecture 4

I find television very educating. Every time somebody turns on the set, I go into the other room and read a book

Groucho Marx

4. Introduction

In this lecture I would like to discuss several coupling schemes that will be relevant for subsequent discussions on hyperfine structure. The choice of a coupling scheme amounts to a choice of a particular basis in which to describe efficiently, and simply, the structure of a particular atomic configuration. Different coupling schemes are often appropriate to different regions of the periodic table. Thus for light elements where the Coulomb interactions dominant over the spin-orbit interaction the LS -coupling scheme (or Russell-Saunders coupling) is favoured. In such a scheme the Coulomb interactions are diagonal whereas the spin-orbit interactions can couple different LS terms. For heavy elements the spin-orbit interaction becomes comparable, or greater than, the Coulomb interaction and jj -coupling may be relevant. In other situations the relevant strengths of various interactions may favour other coupling schemes which we shall shortly explore.

4.1. Notes on jj -coupling

For a single electron, ℓ , the spin-orbit interaction follows from (3-53) and for $\ell = 3$ we have, in terms of ζ_{nf} , the two values

$$\begin{cases} \frac{3}{2} & j = \frac{7}{2} \\ -2 & j = \frac{5}{2} \end{cases} \quad (4-1)$$

The spin-orbit interaction commutes with \mathbf{j}^2 and j_z and hence is diagonal in any N -electron jj -coupled configuration j^N leading to, for $N = N_+ + N_-$ with $N_+ \leq j_+ + \frac{1}{2}$, $N_- \leq j_- + \frac{1}{2}$,

$$\langle j_+^{N_+} j_-^{N_-} JM | H_{s-o} | j_+^{N_+} j_-^{N_-} J' M' \rangle = \delta_{J,J'} \delta_{M,M'} \zeta_{n\ell} \left(N_+ \frac{\ell}{2} - N_- \frac{\ell+1}{2} \right) \quad (4-2)$$

For two f -electrons we have the three possible jj -coupled configurations

$$\frac{7}{2} \quad (+3), \quad \frac{5}{2} \quad (-4), \quad \frac{7}{2} \frac{5}{2} \quad \left(-\frac{1}{2}\right) \quad (4-3)$$

where we have encased the corresponding spin-orbit interaction matrix elements, in units of ζ_{nf} , in curved brackets $(,)$.

Any jj -coupling ket $|(s_1\ell_1)j_1(s_2\ell_2)j_2JM\rangle$ may be expanded as a linear combination of LS -coupled states $|(s_1s_2)S(\ell_1\ell_2)LJM\rangle$ by noting that

$$\begin{aligned} & |(s_1\ell_1)j_1(s_2\ell_2)j_2JM\rangle = \\ & p \times \sum_{S,L} \langle (s_1s_2)S(\ell_1\ell_2)LJ | (s_1\ell_1)j_1(s_2\ell_2)j_2J \rangle |(s_1s_2)S(\ell_1\ell_2)LJM\rangle \end{aligned} \quad (4-4)$$

where the recoupling coefficients are given by

$$\langle (s_1s_2)S(\ell_1\ell_2)LJ | (s_1\ell_1)j_1(s_2\ell_2)j_2J \rangle = \sqrt{[S, L, j_1, j_2]} \begin{Bmatrix} s_1 & s_2 & S \\ \ell_1 & \ell_2 & L \\ j_1 & j_2 & J \end{Bmatrix} \quad (4-5)$$

and

$$p = \begin{cases} 1 & \text{if } j_1 = j_2 \text{ and } \ell_1 = \ell_2 \\ \sqrt{2} & \text{otherwise} \end{cases} \quad (4-6)$$

(cf. the modification of (3-22) and (3-23) for jj -coupling). The expansion coefficients appearing on the rhs of (4-5) may be readily evaluated using the Maple programme below

```
read"njsym";
jjSL:=proc(j1,j2,S,L,J)
local result,p;
p:=1;
if (j1 <> j2) then p:=sqrt(2);
end if;
result:=simplify(p*sqrt((2*j1+1)*(2*j2+1)*(2*S+1)*(2*L+1))
*ninej(1/2,1/2,S,3,3,L,j1,j2,J));
end proc
```

leading to the transformation coefficients:-

$$\begin{array}{l} J = 0 \quad |^3P_0\rangle \quad |^1S_0\rangle \\ |(\frac{7}{2})_0^2\rangle \begin{pmatrix} -\frac{\sqrt{21}}{7} & \frac{2\sqrt{7}}{7} \\ \frac{2\sqrt{7}}{7} & \frac{\sqrt{21}}{7} \end{pmatrix} \end{array} \quad \begin{array}{l} J = 1 \quad |^3P_1\rangle \\ |(\frac{7}{2} \frac{5}{2})_1\rangle \begin{pmatrix} & \\ & 1 \end{pmatrix} \end{array} \quad \begin{array}{l} J = 2 \quad |^3P_2\rangle \quad |^1D_2\rangle \quad |^3F_2\rangle \\ |(\frac{7}{2})_2^2\rangle \begin{pmatrix} \frac{3\sqrt{2}}{7} & \frac{5}{7} & -\frac{\sqrt{6}}{7} \\ -\frac{2}{7} & \frac{3\sqrt{2}}{7} & \frac{3\sqrt{3}}{7} \\ \frac{3\sqrt{3}}{7} & -\frac{\sqrt{6}}{7} & \frac{4}{7} \end{pmatrix} \\ |(\frac{7}{2} \frac{5}{2})_2\rangle \end{array}$$

$$\begin{array}{l} J = 3 \quad |^3F_3\rangle \\ |(\frac{7}{2} \frac{5}{2})_3\rangle \begin{pmatrix} & & \\ & & 1 \end{pmatrix} \end{array} \quad \begin{array}{l} J = 4 \quad |^3F_4\rangle \quad |^1G_4\rangle \quad |^3H_4\rangle \\ |(\frac{7}{2})_4^2\rangle \begin{pmatrix} \frac{2\sqrt{66}}{21} & \frac{3\sqrt{2}}{7} & -\frac{\sqrt{15}}{21} \\ -\frac{2\sqrt{3}}{21} & \frac{\sqrt{11}}{7} & \frac{\sqrt{330}}{21} \\ \frac{\sqrt{165}}{21} & -\frac{2\sqrt{5}}{7} & \frac{4\sqrt{6}}{21} \end{pmatrix} \\ |(\frac{7}{2} \frac{5}{2})_4\rangle \end{array} \quad \begin{array}{l} J = 5 \quad |^3H_5\rangle \\ |(\frac{7}{2} \frac{5}{2})_5\rangle \begin{pmatrix} & & \\ & & 1 \end{pmatrix} \end{array}$$

$$\begin{array}{l}
J = 6 \quad |^3H_6\rangle \quad |^1I_6\rangle \\
|(\frac{7}{2})_6^2\rangle \quad \begin{pmatrix} \frac{\sqrt{42}}{7} & \frac{\sqrt{7}}{7} \\ \frac{\sqrt{7}}{7} & -\frac{\sqrt{42}}{7} \end{pmatrix} \\
|(\frac{7}{2}\frac{5}{2})_6\rangle
\end{array}$$

Suppose A_J is the $jj \rightarrow LS$ transformation matrix for a given J and B_J is a matrix corresponding to some interaction calculated in a LS -coupling basis, then the corresponding matrix C_J in the jj -coupling basis is given by the matrix multiplication

$$C_J = A_J \times B_J \times A_J^{-1} \quad (4-7)$$

For example, consider the spin-orbit matrix for the $J = 2$ states of f^2 that we found earlier,

$$\begin{array}{l}
J = 2 \quad ^3P \quad ^1D \quad ^3F \\
^3P \quad \begin{pmatrix} \frac{1}{2} & \frac{3}{2}\sqrt{2} & 0 \\ \frac{3}{2}\sqrt{2} & 0 & -\sqrt{6} \\ 0 & -\sqrt{6} & -2 \end{pmatrix} \\
^1D \quad \\
^3F
\end{array}$$

and the $jj \rightarrow LS$ transformation matrix A_2 for $J = 2$,

$$\begin{array}{l}
J = 2 \quad |^3P_2\rangle \quad |^1D_2\rangle \quad |^3F_2\rangle \\
\langle(\frac{7}{2})_2^2| \quad \begin{pmatrix} \frac{3\sqrt{2}}{7} & \frac{5}{7} & -\frac{\sqrt{6}}{7} \\ -\frac{2}{7} & \frac{3\sqrt{2}}{7} & \frac{3\sqrt{3}}{7} \\ \frac{3\sqrt{3}}{7} & -\frac{\sqrt{6}}{7} & \frac{4}{7} \end{pmatrix} \\
\langle(\frac{5}{2})_2^2| \\
\langle(\frac{7}{2}\frac{5}{2})_2|
\end{array}$$

The triple product given in (4-7) may be readily evaluated in Maple using the command “simplify(evalm(A&* C&* A^ (-1)))” to give

$$\begin{pmatrix} \frac{3\sqrt{2}}{7} & \frac{5}{7} & -\frac{\sqrt{6}}{7} \\ -\frac{2}{7} & \frac{3\sqrt{2}}{7} & \frac{3\sqrt{3}}{7} \\ \frac{3\sqrt{3}}{7} & -\frac{\sqrt{6}}{7} & \frac{4}{7} \end{pmatrix} \times \begin{pmatrix} \frac{1}{2} & \frac{3}{2}\sqrt{2} & 0 \\ \frac{3}{2}\sqrt{2} & 0 & -\sqrt{6} \\ 0 & -\sqrt{6} & -2 \end{pmatrix} \times \begin{pmatrix} \frac{3\sqrt{2}}{7} & -\frac{2}{7} & \frac{3\sqrt{3}}{7} \\ \frac{5}{7} & \frac{3\sqrt{2}}{7} & -\frac{\sqrt{6}}{7} \\ -\frac{\sqrt{6}}{7} & \frac{3\sqrt{3}}{7} & \frac{4}{7} \end{pmatrix} \\
= \begin{pmatrix} 3 & 0 & 0 \\ 0 & -4 & 0 \\ 0 & 0 & -\frac{1}{2} \end{pmatrix}$$

which is exactly the result we found earlier in diagonalising the $J = 2$ spin-orbit matrix.

It is perhaps interesting to consider the $J = 2$ energy matrix constructed in S3.11 as

$$\begin{array}{l}
J = 2 \quad ^3P \quad ^1D \quad ^3F \\
^3P \quad \begin{pmatrix} E^0 + 33E^3 + \frac{1}{2}\zeta & \frac{3}{2}\sqrt{2}\zeta & 0 \\ \frac{3}{2}\sqrt{2}\zeta & E^0 - 2E^1 + 286E^2 - 11E^3 & -\sqrt{6}\zeta \\ 0 & -\sqrt{6}\zeta & E^0 - 2\zeta \end{pmatrix} \\
^1D \quad \\
^3F
\end{array}$$

If we now repeat the transformation (4-7) we obtain the transformation of the energy matrix into the jj -coupling basis as

$$J = 2 \begin{pmatrix} |(\frac{7}{2})_2^2\rangle & |(\frac{5}{2})_2^2\rangle & |(\frac{7}{2}\frac{5}{2})_2\rangle \\ \langle(\frac{7}{2})_2^2| & \left(E^0 + \frac{1}{49}(-50E^1 + 7150E^2 + 319E^3) + 3\zeta \right) & \frac{3\sqrt{2}}{49}(-10E^1 + 1430E^2 - 121E^3) & \frac{2\sqrt{6}}{49}(5E^1 - 715E^2 + 176E^3) \\ \langle(\frac{5}{2})_2^2| & \frac{3\sqrt{2}}{49}(-10E^1 + 1430E^2 - 121E^3) & \left(E^0 + \frac{6}{49}(-6E^1 + 858E^2 - 11E^3) - 4\zeta \right) & \frac{12\sqrt{3}}{49}(E^1 + 143E^2 - 11E^3) \\ \langle(\frac{7}{2}\frac{5}{2})_2| & \frac{2\sqrt{6}}{49}(5E^1 - 715E^2 + 176E^3) & \frac{12\sqrt{3}}{49}(E^1 + 143E^2 - 11E^3) & \left(E^0 + \frac{3}{49}(-4E^1 + 572E^2 + 275E^3) - \frac{1}{2}\zeta \right) \end{pmatrix}$$

Notice that whereas in the LS -basis the energy matrix had the electrostatic interaction in diagonal form and the spin-orbit interaction had off-diagonal matrix elements in the jj -coupling basis we have the opposite situation.

4.2. J_1j -coupling

While most are familiar with the LS -coupling of Russell-Saunders and to a lesser extent jj -coupling there are other important coupling schemes that find significant applications in atomic physics. Here we consider the case of J_1j -coupling. This scheme is particularly relevant for electron configurations involving a core of the generic type ℓ^N to which an inequivalent electron orbital ℓ' is weakly coupled. In this case the core is coupled to form states characterised by a set of quantum numbers, say $S_1L_1J_1$. The spin and orbital angular momentum quantum numbers of the inequivalent electron ($s\ell'$) are coupled together to form states characterised by a total angular momentum j . Finally, the angular momenta J_1 and j are coupled together to form states of total angular momentum J . The manner in which the electrons of the core are coupled to form J_1 need not be restricted to LS -coupling, although for the purposes of making calculations in the J_1j -coupling scheme it is usually simplest to consider the states of the core in the LS -coupling basis.

For the purposes of labelling energy levels it is usual to give the designation of the core level and the quantum numbers J_1jJ . This coupling scheme may be considered as a direct consequence of the strong binding of the core electrons and the weak electrostatic interaction of the added electron with the core electrons. The separation of the levels of a given J_1j is a measure of the closeness of the physical coupling scheme to that of J_1jJ -coupling.

4.3. NdI and $NdII$ energy levels and J_1j -coupling

The low-lying energy levels of neutral neodymium, NdI , and singly ionised neodymium, $NdII$, provide a good illustration of J_1j -coupling[†]. The ground configurations are, $4f^46s^2$ and $4f^46s$, respectively. The ground term of the $4f^46s^2$ configuration is 5I with $J_1 = 4, \dots, 8$. The energies, in cm^{-1} , are given in Table 4-1.

[†] There is a comprehensive data base at http://physics.nist.gov/cgi-bin/AtData/main_asd which provides lists of atomic energy levels, transition probabilities etc.

Term	J_1	Level (cm^{-1})
5I	4	0.000
	5	1128.056
	6	2366.597
	7	3681.696
	8	5048.602

Table4-1. The energies of the ground term 5I of NdI($4f^46s^2$).

Term	J_1	Level (cm^{-1})
6I	$\frac{7}{2}$	0.000
	$\frac{9}{2}$	513.322
	$\frac{11}{2}$	1470.097
	$\frac{13}{2}$	2585.453
	$\frac{15}{2}$	3801.917
	$\frac{17}{2}$	5085.619
4I	$\frac{9}{2}$	1650.199
	$\frac{11}{2}$	3066.750
	$\frac{13}{2}$	4512.481
	$\frac{15}{2}$	5985.572

Table4-2. The energies of the ground terms, 6I and 4I of NdII($4f^46s$).

Inspection of Table4-2 has been arranged to display the levels as grouped into two separate LS -coupled multiplets which clearly overlap. An alternative would be to note the levels appearing in Table4-1 and to consider the weak coupling of a $6s$ electron to the $4f^4({}^5I_{J_1})$ core to give the arrangement given in Table4-3. This appears to give strong evidence that for these energy levels the description in terms of J_1j -coupling is closer to the physical situation than LS -coupling. To confirm this suspicion let us try to make an approximate, though realistic calculation. To do this we need to be able to calculate the relevant matrix elements of the electrostatic and spin-orbit interactions in a J_1j -coupling basis.*

In J_1j -coupling the treatment of the spin-orbit interaction is much simpler than in LS -coupling. Making the abbreviations

$$\psi_1 = \ell^N \alpha_1 S_1 L_1 \quad \text{and} \quad \psi_2 = \ell^N \alpha_2 S_2 L_2$$

* Many technical details of such calculations can be found in B R Judd, *Low-Lying Levels in Certain Actinide Atoms*, *Phys. Rev.***125**, 613 (1962)

${}^5I_{J_1}$	$J_1 s J$	level (<i>cm</i> -1)
5I_4	$4s\frac{7}{2}$	0.000
	$4s\frac{9}{2}$	513.322
5I_5	$5s\frac{11}{2}$	1470.097
	$5s\frac{9}{2}$	1650.199
5I_6	$6s\frac{13}{2}$	2585.453
	$6s\frac{11}{2}$	3066.750
5I_7	$7s\frac{15}{2}$	3801.917
	$7s\frac{13}{2}$	4512.481
5I_8	$8s\frac{17}{2}$	5085.619
	$8s\frac{15}{2}$	5985.572

Table4-3 The low-lying levels of NdII($4f^46s$) ordered in J_1j -coupling.

we can write the spin-orbit interaction matrix elements for the states of the configuration $\ell^N \ell'$ in J_1j -coupling as

$$\begin{aligned} & \langle \psi_1 J_1, s\ell', j; JM | H_{s-o} | \psi' J'_1, s\ell' j'; JM \rangle \\ &= \delta_{J_1, J'_1} \delta_{j, j'} \left[\delta_{\psi_1, \psi'_1} \zeta'_\ell \langle s\ell' j | (\mathbf{s} \cdot \mathbf{l}) | s\ell' j' \rangle + \zeta_\ell \langle \psi_1 J_1 | \sum_{i=1}^N ((\mathbf{s}_i \cdot \mathbf{l}_i)) | \psi' J'_1 \rangle \right] \end{aligned} \quad (4-8)$$

where

$$\langle s\ell' j | (\mathbf{s} \cdot \mathbf{l}) | s\ell' j \rangle = \frac{1}{2} [j(j+1) - \ell'(\ell'+1) - s(s+1)] \quad (4-9)$$

whereas for the second part of the right-hand-side of (4-8) the spin-orbit matrix elements are just those calculated for the ℓ^N core.

The treatment of the spin-orbit interaction in J_1j -coupling has the considerable advantage of being diagonal in J_1 and j . Thus the spin-orbit interaction is taken into account by simply adding the first term in the right-hand-side of (4-8) to the diagonal of the spin-orbit matrices calculated for the ℓ^N core.

In general the ease of calculating the spin-orbit matrix elements is offset by the difficulty of calculating the electrostatic matrix elements. Fortunately that is not a problem for the special case of the $\ell^N s$ configurations. Let us calculate the matrix elements for the electrostatic interaction between the core and the s -electron. For $J_1 = J'_1$ we obtain

$$\langle \psi_1 J_1 s; J | H_{el} | \psi'_1 J_1 s; J \rangle = \pm \delta_{\psi_1, \psi'_1} G^\ell(\ell, s) \frac{L_1(L_1+1) - S_1(S_1+1) - J_1(J_1+1)}{(2\ell+1)(2J+1)} \quad (4-10)$$

The plus sign is taken for $J = J_1 + \frac{1}{2}$ and the minus sign for $J = J_1 - \frac{1}{2}$. The off-diagonal matrix elements are given by

$$\begin{aligned} & \langle \psi_1 J \pm \frac{1}{2}, s; J | H_{el} | \psi' J \mp \frac{1}{2}, s; J \rangle \\ &= \frac{\delta_{\psi_1, \psi'_1} G^\ell(\ell, s)}{(2\ell + 1)(2J + 1)} \\ & \times \left[(S_1 + L_1 + J + \frac{3}{2})(S_1 + L_1 + \frac{1}{2} - J)(L_1 + J + \frac{1}{2} - S_1)(S_1 + J + \frac{1}{2} - L_1) \right]^{\frac{1}{2}} \end{aligned} \quad (4-11)$$

Explicit calculation for the case of NdII $4f^4(^5I_{J_1})6s; J$ we obtain the matrices

$$\begin{aligned} & J = \frac{7}{2} \quad |(^5I_4)s; \frac{7}{2}\rangle \\ & \langle (^5I_4)s; \frac{7}{2} | \left(\frac{2}{7}G^3(f, s) - \frac{7}{2}\zeta_f \right) \\ \\ & J = \frac{9}{2} \quad |(^5I_4)s; \frac{9}{2}\rangle \quad |(^5I_5)s; \frac{9}{2}\rangle \\ & \langle (^5I_4)s; \frac{9}{2} | \left(\frac{8}{35}G^3(f, s) - \frac{7}{2}\zeta_f \quad \frac{4\sqrt{7}}{35}G^3(f, s) \right) \\ & \langle (^5I_5)s; \frac{9}{2} | \left(\frac{4\sqrt{7}}{35}G^3(f, s) \quad \frac{-3}{35}G^3(f, s) - \frac{9}{4}\zeta_f \right) \\ \\ & J = \frac{11}{2} \quad |(^5I_5)s; \frac{11}{2}\rangle \quad |(^5I_6)s; \frac{11}{2}\rangle \\ & \langle (^5I_5)s; \frac{11}{2} | \left(\frac{1}{14}G^3(f, s) - \frac{9}{4}\zeta_f \quad \frac{5}{14}G^3(f, s) \right) \\ & \langle (^5I_6)s; \frac{11}{2} | \left(\frac{5}{14}G^3(f, s) \quad \frac{1}{14}G^3(f, s) - \frac{3}{4}\zeta_f \right) \\ \\ & J = \frac{13}{2} \quad |(^5I_6)s; \frac{13}{2}\rangle \quad |(^5I_7)s; \frac{13}{2}\rangle \\ & \langle (^5I_6)s; \frac{13}{2} | \left(\frac{-3}{49}G^3(f, s) - \frac{3}{4}\zeta_f \quad \frac{4\sqrt{15}}{49}G^3(f, s) \right) \\ & \langle (^5I_7)s; \frac{13}{2} | \left(\frac{4\sqrt{15}}{49}G^3(f, s) \quad \frac{10}{49}G^3(f, s) + \zeta_f \right) \\ \\ & J = \frac{15}{2} \quad |(^5I_7)s; \frac{15}{2}\rangle \quad |(^5I_8)s; \frac{15}{2}\rangle \\ & \langle (^5I_7)s; \frac{15}{2} | \left(\frac{-5}{28}G^3(f, s) + \zeta_f \quad \frac{\sqrt{187}}{56}G^3(f, s) \right) \\ & \langle (^5I_8)s; \frac{15}{2} | \left(\frac{\sqrt{187}}{56}G^3(f, s) \quad \frac{9}{28}G^3(f, s) + 3\zeta_f \right) \\ \\ & J = \frac{17}{2} \quad |(^5I_8)s; \frac{17}{2}\rangle \\ & \langle (^5I_8)s; \frac{17}{2} | \left(\frac{-2}{7}G^3(f, s) + 3\zeta_f \right) \end{aligned}$$

where we have included the spin-orbit interaction for the f^4 core. We can estimate the value of the spin-orbit coupling constant ζ_{4f} from the width of the 5I multiplet of NdI as $\sim 782cm^{-1}$. We can then adjust the value of $G^3(f, s)$ to optimise the separations of the pairs of levels for each value of J . Finally we add to the matrices a common term to match the ground state. The matrices may be readily set up as a Maple programme and the matrices diagonalised giving their eigenvalues and eigenvectors. We have made no attempt to include intermediate coupling in the f^4 core, configuration interaction etc. Nevertheless with our very simple calculation with

no sophisticated fitting procedure we obtain a reasonably satisfying result as shown in Table 4-4 using $G^3(f, s) = 1300\text{cm}^{-1}$, $\zeta_{4f} = 800\text{cm}^{-1}$ and a constant term of 3130cm^{-1}

J_1sJ	Expt.	Calc.	Eigenvector
$4s\frac{7}{2}$	0	29	$ (^5I_4)s; \frac{7}{2}\rangle$
$4s\frac{9}{2}$	513	496	$0.890 (^5I_4)s; \frac{9}{2}\rangle - 0.456 (^5I_5)s; \frac{9}{2}\rangle$
$5s\frac{11}{2}$	1470	1321	$0.948 (^5I_5)s; \frac{11}{2}\rangle - 0.317 (^5I_6)s; \frac{11}{2}\rangle$
$5s\frac{9}{2}$	1650	1464	$0.456 (^5I_4)s; \frac{9}{2}\rangle + 0.890 (^5I_4)s; \frac{9}{2}\rangle$
$6s\frac{13}{2}$	2585	2363	$0.970 (^5I_6)s; \frac{13}{2}\rangle - 0.243 (^5I_7)s; \frac{13}{2}\rangle$
$6s\frac{11}{2}$	3066	2785	$0.317 (^5I_5)s; \frac{11}{2}\rangle + 0.948 (^5I_6)s; \frac{11}{2}\rangle$
$7s\frac{15}{2}$	3802	3633	$0.990 (^5I_7)s; \frac{15}{2}\rangle - 0.139 (^5I_8)s; \frac{15}{2}\rangle$
$7s\frac{13}{2}$	4512	4106	$0.243 (^5I_6)s; \frac{13}{2}\rangle + 0.970 (^5I_7)s; \frac{13}{2}\rangle$
$8s\frac{17}{2}$	5086	5099	$ (^5I_8)s; \frac{17}{2}\rangle$
$8s\frac{15}{2}$	5985	5933	$0.139 (^5I_7)s; \frac{15}{2}\rangle + 0.990 (^5I_8)s; \frac{15}{2}\rangle$

Table4-4 Calculated and experimental low-lying energy levels of NdII.

4.4. J_1j -coupling in GdIII levels of $4f^7(^8S_7)6p$

A bra state $\langle(S_1L_1)J_1, (s\ell)j; J|$ may be expanded as a sum of LS -coupled states by writing

$$\begin{aligned} & \langle(S_1L_1)J_1, (s\ell)j; J| \\ &= \sum_{S,L} \langle(S_1L_1)J_1, (s\ell)j; J|(S_1s)S, (L_1\ell)L; J\rangle \langle(S_1s)S, (L_1\ell)L; J| \end{aligned} \quad (4-12)$$

The transformation coefficients follow from (2-22). Using this result we can transform matrix elements of an operator, H_o calculated in a LS -coupling basis into matrix elements appropriate to J_1j -coupling basis, in particular

$$\begin{aligned} & \langle\psi_1, J_1, (s\ell)j; J|H_o|\psi'_1, J'_1, (s\ell)j'; J'\rangle \\ &= ([J_1, J'_1, j, j']^{\frac{1}{2}} \sum_{S,L} ([S, L, S', L']^{\frac{1}{2}} \left\{ \begin{matrix} S_1 & s & S \\ L_1 & \ell & L \\ J_1 & j & J \end{matrix} \right\} \left\{ \begin{matrix} S'_1 & s & S' \\ L'_1 & \ell & L' \\ J'_1 & j' & J' \end{matrix} \right\} \\ & \times \langle\psi_1, s\ell; SLJ|H_o|\psi'_1, s\ell; S'L'J'\rangle \end{aligned} \quad (4-13)$$

In the particular case of the states of $4f^7(^8S_7)6p$ considerable simplification is possible leading to the J_1j -coupling result

$$\begin{aligned} & \langle f^7(^8S_7)6p_j; J|H_{el}|f^7(^8S_7)6p'_j; J\rangle \\ &= -56([j, j']^{\frac{1}{2}} \left\{ \begin{matrix} \frac{7}{2} & J & j' \\ \frac{1}{2} & j & 1 \\ 3 & \frac{7}{2} & \frac{1}{2} \end{matrix} \right\} \sum_k \binom{3}{0} \binom{k}{0} \binom{1}{0}^2 G^k(f, p) \end{aligned} \quad (4-14)$$

This formula may be further simplified and the electrostatic interactions expressed in terms of a single parameter, G , by defining

$$G(f, p) = 5G_2(f, p) + 4G_4(f, p) \quad (4-15)$$

where the Condon and Shortley denominator factors have been used,

$$175G_2(f, p) = G^2(f, p) \quad 189G_4(f, p) = G^4(f, p) \quad (4-16)$$

The relevant J_1j -coupled matrix elements may be evaluated using a simple Maple programme to yield

$$\begin{aligned} J = 5 & \quad |(\frac{7}{2}, \frac{3}{2})5\rangle \\ & \langle(\frac{7}{2}, \frac{3}{2})5| \left(F - 21G + \frac{\zeta_p}{2} \right) \\ \\ J = 4 & \quad |(\frac{7}{2}, \frac{3}{2})4\rangle \quad |(\frac{7}{2}, \frac{1}{2})4\rangle \\ & \langle(\frac{7}{2}, \frac{3}{2})4| \left(F - 11G + \frac{\zeta_p}{2} \quad -2\sqrt{35}G \right) \\ & \langle(\frac{7}{2}, \frac{1}{2})4| \left(-2\sqrt{35}G \quad F - 7G - \zeta_p \right) \\ \\ J = 3 & \quad |(\frac{7}{2}, \frac{3}{2})3\rangle \quad |(\frac{7}{2}, \frac{1}{2})3\rangle \\ & \langle(\frac{7}{2}, \frac{3}{2})3| \left(F - 3X + \frac{\zeta_p}{2} \quad -6\sqrt{(3)}G \right) \\ & \langle(\frac{7}{2}, \frac{1}{2})3| \left(-6\sqrt{(3)}G \quad F - 15G - \zeta_p \right) \\ \\ J = 2 & \quad |(\frac{7}{2}, \frac{3}{2})2\rangle \\ & \langle(\frac{7}{2}, \frac{3}{2})2| \left(F + 3G + \frac{\zeta_p}{2} \right) \end{aligned}$$

where we have added a constant term F to the diagonal of each matrix. The parameter G may be fixed by noting that independently of the coupling

$${}^7P_2 - {}^9P_5 = 24G$$

leading to the trial value of $G = 82cm^{-1}$. Then to fix the centre-of-gravity of the states we fix $F = 47424cm^{-1}$ and adjust the spin-orbit coupling constant ζ_p to give a best fit to the levels leading to $\zeta_p = 3050cm^{-1}$. Diagonalisation of the matrices yields the results shown in Table4-5.

$J_1 j J$	Expt.	Calc.	Eigenvector
$(\frac{7}{2}, \frac{1}{2})3$	43019	43022	$-0.1477 (\frac{7}{2}, \frac{3}{2})3\rangle - 0.9890 (\frac{7}{2}, \frac{1}{2})3\rangle$
$(\frac{7}{2}, \frac{1}{2})4$	43612	43593	$-0.2118 (\frac{7}{2}, \frac{3}{2})4\rangle - 0.9773 (\frac{7}{2}, \frac{1}{2})4\rangle$
$(\frac{7}{2}, \frac{3}{2})5$	47234	47234	$ (\frac{7}{2}, \frac{3}{2})5\rangle$
$(\frac{7}{2}, \frac{3}{2})4$	48339	48260	$-0.9773 (\frac{7}{2}, \frac{3}{2})4\rangle + 0.2118 (\frac{7}{2}, \frac{1}{2})4\rangle$
$(\frac{7}{2}, \frac{3}{2})3$	48860	48831	$-0.9890 (\frac{7}{2}, \frac{3}{2})3\rangle + 0.1477 (\frac{7}{2}, \frac{1}{2})3\rangle$
$(\frac{7}{2}, \frac{3}{2})2$	49195	49194	$ (\frac{7}{2}, \frac{3}{2})2\rangle$

Table 4-5 Calculated and experimental energy levels for $4f^7({}^8S_{\frac{7}{2}})6p$

Inspection of the eigenvectors shows clearly that in this case $J_1 j$ -coupling gives an excellent account of the complete set of states.

4.5. $J_1 \ell$ -coupling

The $J_1 \ell$ -coupling scheme has had considerable success in the interpretation of noble gas spectra and in lanthanides and actinides where configurations such as $f^N g$ arise. $J_1 \ell$ -coupling arises in $\ell^N \ell'$ configurations when the electrostatic interaction of the outer ℓ' electron with the $e\ell^N$ core is weak compared to the spin-orbit interaction of the external electron ℓ' . Here the orbital angular momentum ℓ' is first coupled to the total angular momentum J_1 of the core to give a resultant angular momentum K ; then K is coupled to the spin of the external electron ℓ' to yield the total angular momentum J .

For the angular momentum K to be a good quantum number it is necessary that *both* the electrostatic and spin-orbit interactions of the external electron ℓ' be very weak. In the absence of spin-dependent interactions with the outer electron, each level, classified according to its K -value, will be two-fold degenerate. The effect of weak spin-dependent interactions is to remove this two-fold degeneracy, giving rise to the appearance of pairs of levels.

A $J_1 \ell$ bra vector $\langle (S_1 L_1) J_1 \ell'; K s; J M |$ may be expanded as a sum of LS states by writing

$$\begin{aligned}
& \langle (S_1 L_1) J_1 \ell'; K s; J M | \\
&= \sum_{S, L} \langle (S_1 L_1) J_1 \ell'; K s; J M | \langle (S_1 s) S, (L_1 \ell') L; J M \rangle \langle (S_1 s) S, (L_1 \ell') L; J M | \\
&= \sum_{S, L} (-1)^{S_1 + L_1 + s + \ell' + S + L + 2K} ([J_1, S, L, K])^{\frac{1}{2}} \\
&\times \left\{ \begin{matrix} S_1 & L_1 & J_1 \\ \ell' & K & L \end{matrix} \right\} \left\{ \begin{matrix} S & L & J \\ K & s & S_1 \end{matrix} \right\} \langle (S_1 s) S, (L_1 \ell') L; J M | \quad (4-17)
\end{aligned}$$

The matrix elements for the electrostatic interaction of an electron $n' \ell'$ with a $n \ell^N$ core becomes

$$\begin{aligned}
& \langle \ell^N (S_1 L_1) J_1 \ell'; K s; J | H_{el} | \ell^N (S'_1 L'_1) J'_1 \ell'; K' s; J \rangle \\
& = \sum_k [\delta_{S_1, S'_1} \delta_{K, K'} f_k(J_1, J'_1, K) F^k(n\ell, n'\ell') + g_k(J_1, J'_1, K', K, J) G^k(n\ell, n'\ell')]
\end{aligned} \tag{4-18}$$

where

$$\begin{aligned}
f_k(J_1, J'_1, K) & = (-1)^{J_1+K+\ell'} \langle \ell \| C^{(k)} \| \ell \rangle \langle \ell' \| C^{(k)} \| \ell' \rangle \\
& \times \left\{ \begin{matrix} J_1 & J'_1 & k \\ \ell' & \ell' & K \end{matrix} \right\} \langle \ell^N S_1 L_1 J_1 \| U^{(k)} \| \ell^N S_1 L_1 J_1 \rangle
\end{aligned} \tag{4-19}$$

and

$$\begin{aligned}
g_k(J_1, J'_1, K', K, J) & = -N ([J_1, J'_1, S_1, S'_1, L_1, L'_1, K, K'])^{\frac{1}{2}} \langle \ell \| C^{(k)} \| \ell' \rangle^2 (-1)^{L_1+L'_1} \\
& \times \sum_{\bar{\psi}} (\psi \{ |\psi\rangle \} \langle \bar{\psi} | \psi' \rangle) \sum_t [t] \left\{ \begin{matrix} S_1 & L_1 & J_1 \\ \ell' & K & t \end{matrix} \right\} \left\{ \begin{matrix} S'_1 & L'_1 & J'_1 \\ \ell' & K' & t \end{matrix} \right\} \\
& \times \left\{ \begin{matrix} \bar{S} & s & S_1 \\ s & J & K \\ S'_1 & K' & t \end{matrix} \right\} \left\{ \begin{matrix} \bar{L} & \ell & L_1 \\ \ell & k & \ell' \\ L'_1 & \ell' & t \end{matrix} \right\}
\end{aligned} \tag{4-20}$$

The expression for the exchange interaction is rather formidable. Fortunately, where $J_1\ell$ -coupling is most appropriate the exchange interactions are negligible and frequently need not be calculated.

The matrix elements of the spin-orbit interaction within the ℓ^N core are just those computed in the absence of the added electron and are diagonal in J_1 . The corresponding matrix elements for the added electron $n'\ell'$ are

$$\begin{aligned}
& \langle \ell^N (S_1 L_1) J_1 \ell'; K s; J | H_{(s-1)} | \ell^N (S'_1 L'_1) J'_1 \ell'; K' s; J \rangle \\
& = (-1)^{K+K'+J_1+J+\ell'+s} \zeta_{n'\ell'} ([K, K', s, \ell'])^{\frac{1}{2}} [s(s+1)\ell'(\ell'+1)]^{\frac{1}{2}} \\
& \times \left\{ \begin{matrix} K & K' & 1 \\ s & s & J \end{matrix} \right\} \left\{ \begin{matrix} K & K' & 1 \\ \ell' & \ell' & J_1 \end{matrix} \right\}
\end{aligned} \tag{4-21}$$

Again, where $J_1\ell$ -coupling is valid these matrix elements will be negligible. In fact, for f^N configurations containing an outer electron with $\ell' \geq 3$ the spin-orbit interaction, to a very good approximation, maybe neglected and only the spin-dependent electrostatic interactions need be considered in calculating departures from $J_1\ell$ -coupling.

Since the direct electrostatic interaction leaves K as a good quantum number, we may calculate the energies of the two-fold degenerate levels characterised by different K values in *pure* $J_1\ell$ -coupling by simply adding the matrix elements of the direct electrostatic interaction between the added electron, $n'\ell'$ and the $n\ell^N$ core to the energy matrices of the $n\ell^N$ core. The direct interactions will normally be very weak

because of the external nature of the added electron and consequently if the terms in the $n\ell^N$ core are well separated we may, to a good approximation, neglect the matrix elements that couple the different terms. For g -electrons the direct interaction is nonnegligible only for the $F^2(n\ell, n'g)$ integral and as an added approximation we may neglect all other terms. Within this approximation we may write out explicitly the $6-j$ symbol of (4-19) to obtain the coefficients of $F^2(n\ell, n'\ell')$ as

$$\begin{aligned} f_2(J_1, K) &= \langle \ell \| C^{(2)} \| \ell \rangle \langle \ell' \| C^{(2)} \| \ell' \rangle \langle \ell^N S_1 L_1 J_1 \| U^{(2)} \| \ell^N S_1 L_1 J_1 \rangle \\ &\times (J_1(2J_1 - 1)(J_1 + 1)(2J_1 + 1)(2J_1 + 3)(2\ell' - 1)\ell'(\ell' + 1)(2\ell' + 1)(2\ell' + 3))^{-\frac{1}{2}} \\ &\times [3h(2h + 1) - 2J_1(J_1 + 1)\ell'(\ell' + 1)] \end{aligned} \quad (4-22)$$

where

$$h = \frac{K(K + 1) - J_1(J_1 + 1) - \ell'(\ell' + 1)}{2} \quad (4-23)$$

Thus for a particular term $\alpha_1 J_1$ of the $n\ell^N$ core the energies $E(\alpha_1 J_1 K)$ of the levels formed by adding an electron ℓ' in pure $J_1\ell$ -coupling will be given by

$$E(\alpha_1 J_1 K) = a_{J_1} h(2h + 1) + b_{J_1} \quad (4-24)$$

where b_{J_1} is a constant and a_{J_1} is the coefficient of the quantity $h(2h + 1)$ in (4-22). Notice that (4-24) is quadratic in h and hence for perfect $J_1\ell$ -coupling plotting $E(\alpha_1 J_1 K)$ against h will yield a parabola whose minima is at $h = -\frac{1}{4}$ regardless of the term being studied. The levels of different J_1 will lie on different parabolas.

$J_1\ell$ -coupling is well seen in the spectra of the noble gases and in rare earth spectra such as in the $4f5g$ configuration of doubly ionised cerium Ce III. We will now apply the results just developed to the analysis of $J_1\ell$ -coupling in Ce III. The energy levels of the $4f5g$ configuration are given in Table 4-6. Note the occurrence of close *pairs* of almost degenerate levels which is exactly what one expects in $J_1\ell$ -coupling. We give the mean energy for each pair. The $4f$ gives rise to two terms, ${}^2F_{\frac{5}{2}}$ and ${}^2F_{\frac{7}{2}}$ with, as expected, the $J_1 = \frac{5}{2}$ being of lower energy than the $J_1 = \frac{7}{2}$ due to the spin-orbit interaction given by (3-53) as $\frac{7}{2}\zeta_{4f}$. The angular momentum ℓ of the $5g$ electron is coupled to J_1 , in each case, to yield the various values of the quantum number K and we designate a particular $J_1\ell$ -coupling term by the quantum numbers $(J_1\ell K)$. Coupling the spin s of the added $5g$ electron then gives rise to the total angular momentum J given in the second column. In pure $J_1\ell$ -coupling the mean energy levels, $E(J_1 K)$, are given by (4-24), in terms of the parameters a_{J_1} and b_{J_1} . It follows from (4-22) that a_{J_1} is directly related to the radial integral $F^2(4f5g)$ and furthermore that, by explicit calculation, that

$$\frac{a_{\frac{5}{2}}}{a_{\frac{7}{2}}} = \frac{9}{5} \quad (4-25)$$

Term	J	Level	mean
$(\frac{5}{2}5g)\frac{9}{2}$	4	122905.69	122907.3
	5	122908.89	
$(\frac{5}{2}5g)\frac{11}{2}$	6	122919.83	122921.1
	5	122922.37	
$(\frac{5}{2}5g)\frac{7}{2}$	4	122932.21	122932.8
	3	122933.38	
$(\frac{5}{2}5g)\frac{5}{2}$	2	122976.30	122977.3
	3	122978.36	
$(\frac{5}{2}5g)\frac{13}{2}$	6	123010.29	123013.7
	7	123017.02	
$(\frac{5}{2}5g)\frac{3}{2}$	2	123028.39	123028.7
	1	123029.01	
$(\frac{7}{2}5g)\frac{11}{2}$	6	125155.89	125157.4
	5	125158.97	
$(\frac{7}{2}5g)\frac{9}{2}$	4	126164.86	125166.6
	5	125168.37	
$(\frac{7}{2}5g)\frac{13}{2}$	6	125181.54	125184.1
	7	125186.61	
$(\frac{7}{2}5g)\frac{7}{2}$	4	125193.91	125195.0
	3	125196.03	
$(\frac{7}{2}5g)\frac{5}{2}$	2	125230.90	125123.8
	3	125232.67	
$(\frac{7}{2}5g)\frac{3}{2}$	2	125268.40	125268.9
	1	125269.29	
$(\frac{7}{2}5g)\frac{15}{2}$	8	125270.97	125275.3
	7	125279.58	
$(\frac{7}{2}5g)\frac{1}{2}$	0	125295.21	125295.9
	1	125296.65	

Table 4-6 Experimental levels for the Ce III $4f5g$ configuration in $J_1\ell$ -coupling.

Using (4-24) we obtain the values of $E(J_1K)$ for the $4f5g$ $J_1\ell$ -coupling levels as shown in Table 4-7.

Term	h	$(E(J_1K))$
$(\frac{5}{2}5g)\frac{13}{2}$	10	$210a_{\frac{5}{2}} + b_{\frac{5}{2}}$
$(\frac{5}{2}5g)\frac{11}{2}$	$\frac{7}{2}$	$28a_{\frac{5}{2}} + b_{\frac{5}{2}}$
$(\frac{5}{2}5g)\frac{9}{2}$	-2	$6a_{\frac{5}{2}} + b_{\frac{5}{2}}$
$(\frac{5}{2}5g)\frac{7}{2}$	$-\frac{13}{2}$	$78a_{\frac{5}{2}} + b_{\frac{5}{2}}$
$(\frac{5}{2}5g)\frac{5}{2}$	-10	$190a_{\frac{5}{2}} + b_{\frac{5}{2}}$
$(\frac{5}{2}5g)\frac{3}{2}$	$-\frac{25}{2}$	$300a_{\frac{5}{2}} + b_{\frac{5}{2}}$
$(\frac{7}{2}5g)\frac{15}{2}$	14	$406a_{\frac{7}{2}} + b_{\frac{7}{2}}$
$(\frac{7}{2}5g)\frac{13}{2}$	$\frac{13}{2}$	$91a_{\frac{7}{2}} + b_{\frac{7}{2}}$
$(\frac{7}{2}5g)\frac{11}{2}$	0	$b_{\frac{7}{2}}$
$(\frac{7}{2}5g)\frac{9}{2}$	$-\frac{11}{2}$	$55a_{\frac{7}{2}} + b_{\frac{7}{2}}$
$(\frac{7}{2}5g)\frac{7}{2}$	-10	$190a_{\frac{7}{2}} + b_{\frac{7}{2}}$
$(\frac{7}{2}5g)\frac{5}{2}$	$-\frac{27}{2}$	$351a_{\frac{7}{2}} + b_{\frac{7}{2}}$
$(\frac{7}{2}5g)\frac{3}{2}$	-16	$496a_{\frac{7}{2}} + b_{\frac{7}{2}}$
$(\frac{7}{2}5g)\frac{1}{2}$	$-\frac{35}{2}$	$595a_{\frac{7}{2}} + b_{\frac{7}{2}}$

Table 4-7 Values of $E(J_1K)$ for the $4f5g$ $J_1\ell$ -coupling levels.

Noting that the position of the $(\frac{7}{2}5g)\frac{11}{2}$ level depends only upon $b_{\frac{7}{2}}$, that the separation of the two levels $(\frac{7}{2}5g)\frac{1}{2}$ and $(\frac{7}{2}5g)\frac{11}{2}$ is $595a_{7/2}$ and (4-25) leads to the parameter set (in cm^{-1})

$$a_{\frac{5}{2}} = 0.419, a_{\frac{7}{2}} = 0.233, b_{\frac{5}{2}} = 122903.8, b_{\frac{7}{2}} = 125157.4 \quad (4-26)$$

Using these values in Table 4-7 leads to the results displayed in Table 4-8.

Term	Experimental	Calculated
$(\frac{5}{2}5g)\frac{9}{2}$	122907.3	122906.3
$(\frac{5}{2}5g)\frac{11}{2}$	122921.1	122915.5
$(\frac{5}{2}5g)\frac{7}{2}$	122932.8	122936.5
$(\frac{5}{2}5g)\frac{5}{2}$	122977.3	122983.4
$(\frac{5}{2}5g)\frac{13}{2}$	123013.7	122991.8
$(\frac{5}{2}5g)\frac{3}{2}$	123028.7	123029.5
$(\frac{7}{2}5g)\frac{11}{2}$	125157.4	125157.4
$(\frac{7}{2}5g)\frac{9}{2}$	125166.6	125170.2
$(\frac{7}{2}5g)\frac{13}{2}$	125184.1	125178.6
$(\frac{7}{2}5g)\frac{7}{2}$	125195.0	125201.7
$(\frac{7}{2}5g)\frac{5}{2}$	125231.8	125239.2
$(\frac{7}{2}5g)\frac{3}{2}$	125268.9	125273.0
$(\frac{7}{2}5g)\frac{15}{2}$	125275.3	125252.0
$(\frac{7}{2}5g)\frac{1}{2}$	125296.0	125296.0

Table 4-8 Experimental and calculated $4f5g$ mean energy levels in $J_1\ell$ -coupling. Considering that we have totally ignored configuration interaction and have assumed pure $J_1\ell$ -coupling the agreement between experiment and theory is surprisingly good.

4.6. Exercises

4-1 Given that

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{\frac{1}{2}J} \left[\frac{(J-2j_1)!(J-2j_2)!(J-2j_3)!}{(\frac{1}{2}J-j_1)!(\frac{1}{2}J-j_2)!(\frac{1}{2}J-j_3)!} \right]^{\frac{1}{2}} \quad (4-28)$$

where $J = j_1 + j_2 + j_3$, show that

$$\begin{pmatrix} a & a & 2 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{a+1} \left[\frac{a(a+1)}{(2a+1)(2a-1)(2a+3)} \right]^{\frac{1}{2}} \quad (4-29)$$

and

$$\langle a \| C^{(2)} \| a \rangle = - \left[\frac{a(a+1)(2a+1)}{(2a+3)(2a-1)} \right]^{\frac{1}{2}} \quad (4-30)$$

4-2 Show that for $N = 1$ or $N = 4\ell + 1$ that

$$\langle s\ell j \| U^{(2)} \| s\ell j \rangle = \pm (-1)^{s+\ell+j} (2j+1) \begin{Bmatrix} 2 & j & j \\ \frac{1}{2} & \ell & \ell \end{Bmatrix} \quad (4-31)$$

where the sign is $+$ if $N = 1$ or $-$ if $N = 4\ell + 1$.

4-3 Use your results to put (4-22) into as simple a form as possible.

4-4 Use the NIST data base to obtain a list of the energy levels of neutral neon Ne I and make a list of configurations that could be best described in (a) LS -coupling, (b) J_1j -coupling and (c) $J_1\ell$ -coupling.

Lecture 5

Some people think that physics is over once the equation is found which governs some phenomena. To me this seems as foolish as somebody who says English is over once he has learned the words and the grammar and never goes on to read and understand Shakespeare. Physics is not the equation but the multitude of phenomena which result from it. To know the equation is not the end but the beginning and to deduce from it the physics is an unending quest.

(W. E. Thirring 1987)

5. Introduction

In this lecture we will first discuss the intermediate coupling corrections to the Lande g -factors and the g -sum rule. Then we will start to consider some of the properties of alkali atoms in magnetic fields leading up to an exploration of the combined effects of their fine structure, Zeeman effect and hyperfine structure. Later in the course, if time permits, we will return to higher-order corrections to the Lande g -factors.

5.1. Intermediate coupling and g -factors

The effect of diagonalizing the combined Coulomb and spin-orbit interaction energy matrices is to yield eigenstates that are independent of the M quantum number and for which the total electronic angular momentum J remains a good quantum number. A typical eigenstate will be of the form

$$|aJ\rangle = \sum_{\alpha,S,L} \langle \alpha SLJ | aJ \rangle | \alpha SLJ \rangle \quad (5-1)$$

where the $\langle \alpha SLJ | aJ \rangle$ are the eigenvector components. For example, we found for the groundstate of Pr^{3+} the linear combination

$$|a4\rangle = -0.0282|^3F_4\rangle + 0.1523|^1G_4\rangle + 0.9879|^3H_4\rangle \quad (5-2)$$

Recall that the diagonal matrix elements of the Zeeman Hamiltonian, H_{mag} for a state $|\alpha SLJM\rangle$ are given by

$$\langle \alpha SLJM | H_{mag} | \alpha SLJM \rangle = B_z \mu_0 M g(SLJ) \quad (2-53)$$

In intermediate coupling, we have from (5-1)

$$\begin{aligned} \langle aJM | H_{mag} | aJM \rangle &= \sum_{\alpha,S,L} \langle aJ | \alpha SLJ \rangle \langle \alpha SLJM | H_{mag} | \alpha SLJM \rangle \langle \alpha SLJ | aJ \rangle \\ &= B_z \mu_0 M \sum_{\alpha,S,L} \langle aJ | \alpha SLJ \rangle g(SLJ) \langle \alpha SLJ | aJ \rangle \end{aligned} \quad (5-3)$$

Thus, from (5-2) we have for the groundstate of Pr^{3+}

$$\begin{aligned} \langle a4M | H_{mag} | a4M \rangle &= B_z \mu_0 M \\ &\times [(-0.0282)^2 g(^3F_4) + (0.1523)^2 g(^1G_4) + (0.9879)^2 g(^3H_4)] \\ &= B_z \mu_0 M (0.8045) \end{aligned} \quad (5-4)$$

where

$$g({}^3F_4) = 1.2506 \quad g({}^1G_4) = 1.0000 \quad g({}^3H_4) = 0.79954 \quad (5-5)$$

Thus the effect of intermediate coupling has been to change from the pure 3H_4 g -factor of 0.7995 to the intermediate coupling corrected g -factor of 0.8045. Here the correction is rather small. As a second example consider the level calculated at $10,004\text{cm}^{-1}$ with the eigenstate

$$|b4\rangle = 0.5037|{}^3F_4\rangle + 0.8558|{}^1G_4\rangle - 0.1175|{}^3H_4\rangle \quad (5-6)$$

leading to an intermediate coupling corrected g -factor of 1.0607 compared with that of the pure 1G_4 g -factor of 1.0000. Finally, consider the third $J = 4$ eigenstate

$$|c4\rangle = -0.8634|{}^3F_4\rangle + 0.4943|{}^1G_4\rangle - 0.1009|{}^3H_4\rangle \quad (5-7)$$

where the intermediate coupling corrected g -factor is 1.1847 compared with that for a pure 3F_4 g -factor of 1.2506. Adding the three intermediate coupling corrected g -factors gives

$$\sum_{i=1}^3 g_i = 0.8045 + 1.0607 + 1.1847 = 3.0499$$

whereas the sum of the three LS g -factors gives

$$\sum_{i=1}^3 g_i = 0.7995 + 1.0000 + 1.2506 = 3.0501$$

The two values are the same to within the precision of the calculation. This is an example of the g -sum rule.

5.2. The g Sum Rule

Where the states differing in J are well separated and only the diagonal elements need be calculated, the intermediate coupling g -value becomes

$$g(\gamma J) = \sum_{\alpha SL} g(SLJ) \langle \alpha SLJ | \gamma J \rangle^2 \quad (5-8)$$

If we sum over the variable γ for a given J -value then

$$\sum_{\gamma} g(\gamma J) = \sum_{\alpha SL} g(SLJ) \quad (5-9)$$

since

$$\sum_{\alpha SL} \langle \alpha SLJ | \gamma J \rangle^2 = 1 \quad (5-10)$$

since the transformation is necessarily unitary for a complete set of states. Equation (5-9) is the statement of the g -sum rule. Note the important qualification for a complete set of states.

5.3. Fine Structure in Alkali Atoms

The alkali elements appear, along with hydrogen, in the first column of the Periodic table. The groundstate of the n -th alkali element is, apart from closed shells, $ns(^2S_{\frac{1}{2}})$.

The first excited multiplet is $np(^2P)$. There is no spin-orbit interaction associated with the groundstate whereas in the first excited multiplet the effect of the spin-orbit interaction is to split the 2P into two states $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ with the $^2P_{\frac{1}{2}}$ state lying below the $^2P_{\frac{3}{2}}$ as follows from Eq. (3-53).

Table 1. Energy levels of the lowest states of alkali atoms.

Element	State	Energy(cm^{-1})	ΔE	ζ_{np}
H	$1s\ ^2S_{\frac{1}{2}}^e$	0		
	$2p\ ^2P_{\frac{1}{2}}^o$	82258.9206		
	$2p\ ^2P_{\frac{3}{2}}^o$	82259.2865	0.3659	0.244
	$2s\ ^2S_{\frac{1}{2}}^e$	82258.9559		
Li	$2s\ ^2S_{\frac{1}{2}}^e$	0.0		
	$2p\ ^2P_{\frac{1}{2}}^o$	14903.66		
	$2p\ ^2P_{\frac{3}{2}}^o$	14904.00	0.34	0.226
Na	$3s\ ^2S_{\frac{1}{2}}^e$	0.000		
	$3p\ ^2P_{\frac{1}{2}}^o$	16956.172		
	$3p\ ^2P_{\frac{3}{2}}^o$	16973.368	17.20	11.47
K	$4s\ ^2S_{\frac{1}{2}}^e$	0.000		
	$4p\ ^2P_{\frac{1}{2}}^o$	12985.170		
	$4p\ ^2P_{\frac{3}{2}}^o$	13042.876	57.72	38.48
Rb	$5s\ ^2S_{\frac{1}{2}}^e$	0.000		
	$5p\ ^2P_{\frac{1}{2}}^o$	12578.96		
	$5p\ ^2P_{\frac{3}{2}}^o$	12816.56	237.60	158.38
Cs	$6s\ ^2S_{\frac{1}{2}}^e$	0.000		
	$6p\ ^2P_{\frac{1}{2}}^o$	11178.2		
	$6p\ ^2P_{\frac{3}{2}}^o$	11732.3	554.1	369.4

The splitting

$$\Delta E = E(^2P_{\frac{3}{2}}) - E(^2P_{\frac{1}{2}}) = \frac{3}{2}\zeta_{np} \quad (5-11)$$

is commonly referred to as the *fine structure* and is seen, for example, in the Sodium D lines which at sufficient spectroscopic resolution appear as the famous yellow Sodium D doublet. Knowing the value of the fine structure splitting we can deduce a value for the spin-orbit coupling constant ζ_{nl} as shown in Table I above.

5.4. Zeeman Effect in Alkali Atoms

The alkali atoms, particularly Rubidium (*Rb*), play an important role in Bose Einstein Condensation (BEC) and the interplay of the fine structure, Zeeman effect and hyperfine structure are of major significance. For the groundstate $ns(^2S_{\frac{1}{2}})$ the effect of an external magnetic field B_z is to lift the two-fold degeneracy to produce a doublet with a Zeeman splitting of

$$\Delta E = E(^2S_{\frac{1}{2}, \frac{1}{2}}) - E(^2S_{\frac{1}{2}, -\frac{1}{2}}) = g_s \mu_0 B_z \quad (5-12)$$

The behaviour of the $np(^2P)$ term is more complicated, especially if the magnetic field is sufficiently strong as to produce Zeeman splittings comparable with those of the fine structure. It is necessary then to include the off-diagonal Zeeman matrix elements introduced in Eq.(2-58) in addition to the diagonal matrix elements given by Eq. (2-53). The states with $M = \pm\frac{3}{2}$ there are no off-diagonal matrix elements and we have for the Hamiltonian

$$H = H_{s-o} + H_{mag} \quad (5-13)$$

$$\langle np \ ^2P_{\frac{3}{2}}^{\pm\frac{3}{2}} | H | np \ ^2P_{\frac{3}{2}}^{\pm\frac{3}{2}} \rangle = \frac{1}{2} \zeta_{np} \pm \frac{3}{2} g(^2P_{\frac{3}{2}}) \mu_0 B_z \quad (5-14)$$

whereas for the states with $M = \pm\frac{1}{2}$ we must consider the rank 2 matrices

$$\begin{array}{cc} |^2P_{\frac{1}{2}}^{\pm\frac{1}{2}}\rangle & |^2P_{\frac{3}{2}}^{\pm\frac{1}{2}}\rangle \\ \langle ^2P_{\frac{1}{2}}^{\pm\frac{1}{2}} | & \left(\begin{array}{cc} -\zeta_{np} \pm \frac{1}{2} g(^2P_{\frac{1}{2}}) \mu_0 B_z & 0.4714(g_s - 1) \mu_0 B_z \\ 0.4714(g_s - 1) \mu_0 B_z & \frac{1}{2} \zeta_{np} \pm \frac{3}{2} g(^2P_{\frac{3}{2}}) \mu_0 B_z \end{array} \right) \end{array} \quad (5-15)$$

where

$$g(^2P_{\frac{1}{2}}) = 0.6659 \quad \text{and} \quad g(^2P_{\frac{3}{2}}) = 1.3341 \quad (5-16)$$

Note that the groundstate exhibits a Zeeman splitting that is *linear* in the magnetic field B_z as do the states $np(^2P_{\frac{3}{2}}^{\pm\frac{3}{2}})$ whereas the states $np(^2P_{\frac{3}{2}}^{\pm\frac{1}{2}})$ and $np(^2P_{\frac{1}{2}}^{\pm\frac{1}{2}})$ will be mixed and the splittings of those states will no longer be linear in B_z . The amount of mixing will depend on the size of the fine structure splitting. However, the situation will change when we take into account the hyperfine splitting as we shall see shortly.

5.5. Introductory Remarks on Magnetic Hyperfine Structure

The nucleus possesses a total angular momentum \mathbf{I} , often referred to as *nuclear spin* and the electron system a total angular momentum \mathbf{J} with the total angular momentum of the atom \mathbf{F} being

$$\mathbf{F} = \mathbf{I} + \mathbf{J} \quad (1-15)$$

where the magnitude of \mathbf{F} is given by

$$F = I + J, I + J - 1, \dots, |I - J| \quad (5-17)$$

Thus the number of hyperfine sublevels arising from a level of a given J will be the minimum of $\{(2J + 1), (2I + 1)\}$. States of a given F will be $2F + 1$ -fold degenerate with respect to the quantum number M_F

$$M_F = F, F - 1, \dots, -F + 1, -F \quad (5-18)$$

This degeneracy may be lifted by an applied external magnetic field or partially or completely by external electric fields. Whether the electric field will completely lift the degeneracy depends on symmetry considerations. Of that more later.

5.6. Magnetic Hyperfine Structure in Hydrogen

In the case of the groundstate $1s(^2S_{1/2})$ of atomic hydrogen 1_1H the nuclear angular momentum is $I = \frac{1}{2}$ and the electronic angular momentum is $J = \frac{1}{2}$ and hence $F = 0, 1$ and thus we get two hyperfine sublevels, a singlet with $F = 0$ and a triplet with $F = 1$. Experimentally, the energy separation between the states is

$$\Delta E = E(F = 1) - E(F = 0) = 5.9 \times 10^{-6} eV \quad (5-19)$$

The frequency ν and wavelength λ associated with this transition are

$$\nu = 1420.4057517667(10) MHz \quad \text{and} \quad \lambda = 21.1 cm \quad (5-20)$$

This is the origin of the well-known 21cm line of radio astronomy associated with interstellar hydrogen. The transition is too slow to be seen in the laboratory by spontaneous emission but can be measured by stimulated emission to an extraordinary degree of accuracy. In the case of the interstellar medium the enormous amounts of hydrogen make the transition readily observable.

5.7. Magnetic Hyperfine Structure in $^{85}_{37}Rb$ and $^{87}_{37}Rb$

The rubidium isotopes, $^{85}_{37}Rb$ and $^{87}_{37}Rb$, have nuclear spins of $I = \frac{5}{2}$ and $I = \frac{3}{2}$ respectively. In both cases the electronic groundstate is $5s(^2S_{1/2})$ and hence $J = \frac{1}{2}$ and the two allowed values of F are

$$^{85}_{37}Rb \quad 5s(^2S_{1/2}) \quad F = 2, 3 \quad \quad ^{87}_{37}Rb \quad 5s(^2S_{1/2}) \quad F = 1, 2 \quad (5-21)$$

The first two excited electronic states of rubidium are the two fine structure levels $5p(^2P_{\frac{1}{2}})$ and $5p(^2P_{\frac{3}{2}})$, separated by 158.38cm^{-1} . The hyperfine sublevels will occur with the following values of the total angular momentum F

$${}^{85}_{37}\text{Rb} \quad 5p(^2P_{\frac{1}{2}}) \quad F = 2, 3 \quad 5p(^2P_{\frac{3}{2}}) \quad F = 1, 2, 3, 4 \quad (5-22a)$$

$${}^{87}_{37}\text{Rb} \quad 5p(^2P_{\frac{1}{2}}) \quad F = 1, 2 \quad 5p(^2P_{\frac{3}{2}}) \quad F = 0, 1, 2, 3 \quad (5-22b)$$

That gives a qualitative description of the magnetic hyperfine structure but tells us nothing about the ordering of the hyperfine sublevels of their separations.

5.8. Magnetic Hyperfine Structure

The nuclear magnetic-dipole moment vector μ_I for a nucleus may be written as

$$\mu_I = g_I \beta_N \mathbf{I} \quad (5-23)$$

where g_I is the nuclear g -factor and β_N is the nuclear magneton, which is defined as

$$\beta_N = \frac{e\hbar}{2M_p} = \frac{m_e \beta}{M_p} \quad (5-24)$$

where M_p is the proton mass, m_e the electron mass and β is the Bohr magneton. The magnetic-moment vector of the nucleus can be taken as proportional to its angular momentum I and written as

$$\mu_I = \frac{\mu_I \mathbf{I}}{I} \quad (5-25)$$

where μ_I is the *nuclear magnetic moment* expressed in units of nuclear magnetons.

Each electron i in an unfilled shell will produce a magnetic field B_i at the nucleus resulting in an interaction with the nuclear magnetic moment vector μ_I adding to the Hamiltonian a term

$$H_{hfs} = - \sum_{i=1}^N \mathbf{B}_i \cdot \mu_I \quad (5-26)$$

For an electron in an orbital with ($\ell \neq 0$) the magnetic field \mathbf{B} produced at the nucleus is³⁰⁻³²

$$\mathbf{B} = -2\beta \frac{[\mathbf{I} - \mathbf{s} + 3\mathbf{r}(\mathbf{s} \cdot \mathbf{r})/r^2]}{r^3} \quad (5-27)$$

For N electrons we obtain^{2,17,23}

$$H_{hfs} = 2\beta\beta_N g_I \sum_{i=1}^N \frac{\mathbf{N}_i \cdot \mathbf{I}}{r_i^3} \quad (5-28)$$

where

$$\mathbf{N}_i = \mathbf{l}_i - \mathbf{s}_i + \frac{3\mathbf{r}_i(\mathbf{s}_i \cdot \mathbf{r}_i)}{r_i^2} \quad (5-29)$$

\mathbf{N}_i may be put into tensor operator form to yield²

$$\mathbf{N}_i = \mathbf{l}_i - \sqrt{10}(\mathbf{s}\mathbf{C}^{(2)})_i^{(1)} \quad (5-30)$$

and finally

$$H_{hfs} = a_\ell \sum_{i=1}^N [\mathbf{l}_i - \sqrt{10}(\mathbf{s}\mathbf{C}^{(2)})_i^{(1)}] \cdot \mathbf{I} \quad (5-31)$$

with

$$a_\ell = 2\beta\beta_N g_I \langle r^{-3} \rangle = \frac{2\beta\beta_N \mu_I \langle r^{-3} \rangle}{I} \quad (5-32)$$

where $\langle r^{-3} \rangle$ is the expectation value of the inverse-cube radius of the electron orbital.

Note that the matrix elements of \mathbf{N}_i vanish for s -orbitals. However, for unpaired s -orbitals Fermi³³ showed that there is, what is now known as the *Fermi contact term*, such that

$$\mathbf{N}'_i = \mathbf{N}_i + \frac{8}{3}\pi|\Psi_s(0)|^2\mathbf{s}_i \quad (5-33)$$

where $\Psi_s(0)$ is the value at the nucleus of the normalized Schrödinger eigenfunction of the s -orbital. Thus for ($\ell \geq 1$) only the first term, \mathbf{N}_i , is non-zero while for ($\ell = 0$) only the second term is non-zero.

Matrix elements of H_{hfs} may be taken as diagonal in the nuclear spin I since states of different nuclear spin are usually separated by MeV compared with eV separations of electronic states. In the absence of external electric or magnetic fields the matrix elements are diagonal in F, M_F and independent of M_F . In such a situation it is convenient to work in a $JIFM_F$ scheme whereas if large external fields are present it is more realistic to work in a $JM_JIM_I M_F$ scheme. If the fine structure is small it may be necessary to consider matrix elements that are off-diagonal in J . In the case of intermediate coupling it may be necessary to consider matrix elements coupling different SL terms.

For simplicity let us first consider the matrix elements of H_{hfs} diagonal in J though not necessarily diagonal in other quantum numbers α, α' . We have, after recalling Eq. (2-44) and that \mathbf{I} is a rank $k = 1$ tensor operator

$$\begin{aligned} \langle \alpha JIFM | H_{hfs} | \alpha' JIFM \rangle &= (-1)^{J+I+F} a_\ell \begin{Bmatrix} J & J & 1 \\ I & I & F \end{Bmatrix} \langle I || I^{(1)} || I \rangle \\ &\times \langle \alpha J || \sum_{i=1}^N N_i^{(1)} || \alpha' J \rangle \end{aligned} \quad (5-34)$$

The $6j$ -symbol can be evaluated explicitly to yield

$$\begin{aligned} \langle \alpha JIFM | H_{hfs} | \alpha' JIFM \rangle &= \frac{1}{2} [F(F+1) - J(J+1) - I(I+1)] \\ &\times a_\ell \frac{\langle \alpha J || \sum_{i=1}^N N_i^{(1)} || \alpha' J \rangle}{\sqrt{J(J+1)(2J+1)}} \end{aligned} \quad (5-35a)$$

$$= \frac{1}{2} AK \quad (5-35b)$$

where

$$K = F(F + 1) - J(J + 1) - I(I + 1) \quad (5-35c)$$

and

$$A = a_\ell \frac{\langle \alpha J \| \sum_{i=1}^N N_i^{(1)} \| \alpha' J \rangle}{\sqrt{J(J + 1)(2J + 1)}} \quad (5-35d)$$

The *measured* value of A is known as the *magnetic hyperfine structure constant* and may be positive or negative. The quantity a_ℓ will be a constant for all the states of a given electron configuration. The second factor in A will be different for each of the states of the configuration and constant within the hyperfine splittings of a given level. If $A > 0$ then the lowest F -value lies lowest in energy whereas if $A < 0$ it lies highest. Knowing A from experiment it is possible to deduce a value for the nuclear magnetic moment if we can calculate $\langle r^{-3} \rangle$ and the angular part of (5-35d). Note that the reduced matrix element $\langle I \| I^{(1)} \| I \rangle$ will vanish unless $I > 0$.

5.9. Exercises

1. Show that

$$\begin{aligned} \frac{\langle SLJ \| L^{(1)} \| SLJ \rangle}{\sqrt{J(J + 1)(2J + 1)}} &= \frac{J(J + 1) + L(L + 1) - S(S + 1)}{2J(J + 1)} \\ &= 2 - g(SLJ) \end{aligned} \quad (5-36)$$

2. Show that

$$\langle \ell \| C^{(2)} \| \ell \rangle = -\sqrt{\frac{\ell(\ell + 1)(2\ell + 1)}{(2\ell - 1)(2\ell + 3)}} \quad (5-37)$$

3. Show that for a single electron in an orbital with ($\ell \geq 1$)

$$\begin{aligned} -\frac{\sqrt{10} \langle slj \| (s^{(1)} C^{(2)})^{(1)} \| slj \rangle}{\sqrt{j(j + 1)(2j + 1)}} &= (2j + 1) \sqrt{\frac{30s(s + 1)(2s + 1)\ell(\ell + 1)(2\ell + 1)}{j(j + 1)(2j + 1)(2\ell - 1)(2\ell + 3)}} \\ &\quad \times \begin{Bmatrix} s & s & 1 \\ \ell & \ell & 2 \\ j & j & 1 \end{Bmatrix} \end{aligned} \quad (5-38)$$

4. Show that

$$\begin{Bmatrix} \ell + \frac{1}{2} & \ell + \frac{1}{2} & 1 \\ \ell & \ell & 2 \\ \frac{1}{2} & \frac{1}{2} & 1 \end{Bmatrix} = -\frac{\sqrt{10\ell(2\ell - 1)}}{30(\ell + 1)(2\ell + 1)} \quad (5-39a)$$

and

$$\begin{Bmatrix} \ell - \frac{1}{2} & \ell - \frac{1}{2} & 1 \\ \ell & \ell & 2 \\ \frac{1}{2} & \frac{1}{2} & 1 \end{Bmatrix} = +\frac{\sqrt{10(2\ell + 3)(\ell + 1)}}{30\ell(2\ell + 1)} \quad (5-39b)$$

5. Show that for a single electron in an orbital with ($\ell \geq 1$) that

$$A = \begin{cases} a_\ell \frac{4\ell(\ell+1)}{(2\ell+1)(2\ell+3)} & j = \ell + \frac{1}{2} \\ a_\ell \frac{4\ell(\ell+1)}{(2\ell+1)(2\ell-1)} & j = \ell - \frac{1}{2} \end{cases} \quad (5-40)$$

6. Show that for a $J = \frac{1}{2}$ electronic level of an atom with a nuclear spin $I \geq \frac{1}{2}$ and magnetic hyperfine structure constant A a pair of sublevels is formed with an energy separation of

$$\Delta E = \frac{1}{2}(2I+1)A \quad (5-41)$$

Lecture 6

The road ahead can hardly help being strewn with many a mistake. The main point is to get those mistakes made and recognized as fast as possible!

John A Wheeler

6. Introduction

In this lecture we shall first consider the magnetic hyperfine structure in the JM_JIM_I scheme which will later be needed when we consider external magnetic or electric fields. The latter case will assume particular importance in considering ions in crystal fields. Afterwards we take up consideration of hyperfine structure associated with nuclear possessing electric quadrupole moments.

6.1. Experimental Data

An excellent compilation of data on the Sodium D lines and on Caesium D lines has been given by Steck³⁴. He has also given a similar database on the Rubidium 87 D lines³⁹. The collection includes an excellent set of references. From his Table 5 we have for $^{133}_{55}\text{Cs}$ the magnetic dipole hyperfine structure constants

$$A(6p^2P_{\frac{1}{2}}) = 291.920(19) \text{ MHz}$$

$$A(6p^2P_{\frac{3}{2}}) = 50.275(3) \text{ MHz}$$

and hence for their ratio

$$\frac{A(6p^2P_{\frac{1}{2}})}{A(6p^2P_{\frac{3}{2}})} = 5.8064$$

which may be compared with the ratio 5 coming from Eq. (5-40). Likewise one finds for $^{23}_{11}\text{Na}$ and $^{87}_{37}\text{Rb}$ the respective ratios

$$\frac{A(3p^2P_{\frac{1}{2}})}{A(3p^2P_{\frac{3}{2}})} = 5.005 \quad \text{and} \quad \frac{A(5p^2P_{\frac{1}{2}})}{A(5p^2P_{\frac{3}{2}})} = 4.82$$

6.2. Magnetic Hyperfine Structure in the JM_JIM_I Basis

In the $JIFM_F$ scheme we used the operator

$$H_{hfs} = a_\ell(\mathbf{N}^{(1)} \cdot \mathbf{I}^{(1)}) \tag{6-1}$$

Noting Eq. (2-40) we can write the scalar product in terms of tensor operator components to give

$$H_{hfs} = a_\ell \sum_{q=-1}^1 N_q^{(1)} I_{-q}^{(1)} \quad (6-2)$$

The matrix elements of H_{hfs} in the JM_JIM_I scheme then become

$$\begin{aligned} \langle \alpha SLJM_JIM_I | H_{hfs} | \alpha' S'L'JM'_JIM'_I \rangle &= a_\ell \sum_{q=-1}^1 (-1)^{J-M_J} \begin{pmatrix} J & 1 & J \\ -M_J & q & M'_J \end{pmatrix} \\ &\times (-1)^{I-M_I} \begin{pmatrix} I & 1 & I \\ -M_I & -q & M'_I \end{pmatrix} \langle \alpha SLJ || N^{(1)} || \alpha' S'L'J \rangle \langle I || I^{(1)} || I \rangle \end{aligned} \quad (6-3)$$

Explicit evaluation of the $3jm$ -symbols then allows us to write the diagonal matrix elements ($q = 0$) as

$$\langle \alpha SLJM_JIM_I | H_{hfs} | \alpha' S'L'JM_JIM_I \rangle = AM_JM_I \quad (6-4a)$$

and the off-diagonal matrix elements as

$$\begin{aligned} &\langle \alpha SLJM_JIM_I | H_{hfs} | \alpha' S'L'JM_J \pm 1IM_I \mp 1 \rangle \\ &= \frac{1}{2}A \sqrt{(J \mp M_J)(J \pm M_J + 1)(I \pm M_I)(I \mp M_I + 1)} \end{aligned} \quad (6-4b)$$

where A is the magnetic hyperfine structure constant defined in (5-35d).

6.3. Zeeman Effect in the $JIFM_F$ Basis

Let us consider a weak external magnetic field B_z acting on hyperfine levels in a $JIFM_F$ basis. The term in the Hamiltonian may be written in terms of the electron spin, orbital and nuclear g -factors as

$$H_{mag} = \mu_B B_z (L_0^{(1)} + g_s S_0^{(1)} + g_I I_0^{(1)}) \quad (6-5)$$

In general the nuclear Zeeman effect, given by the third term, is more than three orders of magnitude less than that of the electronic Zeeman effect and as such is often ignored. We shall retain it as it can lead to a direct method of determining nuclear magnetic moments. The diagonal matrix elements of H_{mag} may be determined using the tensor operator formalism developed in Eqs. (2-42) - (2-46) together with explicit forms for the relevant $3jm$ - and $6j$ -symbols. The Wigner-Eckart theorem (2-42) taken with (2-48c) gives

$$\begin{aligned} \langle \alpha JIFM_F | H_{mag} | \alpha' JIFM_F \rangle &= \mu_B B_z \frac{M_F}{\sqrt{F(F+1)(2F+1)}} \\ &\times [\langle \alpha JIF || (L^{(1)} + g_s S^{(1)}) || \alpha' JIF \rangle + \langle \alpha JIF || g_I I^{(1)} || \alpha' JIF \rangle] \end{aligned} \quad (6-6)$$

The first reduced matrix element can be developed using (2-45) and the second using (2-46) and the explicit form of the $6j$ -symbol to give

$$\begin{aligned} & \langle \alpha J I F M_F | H_{mag} | \alpha' J I F M_F \rangle \\ & = \mu_B B_z M_F \left[g_J \frac{[F(F+1) - I(I+1) + J(J+1)]}{2F(F+1)} + g_I \frac{[F(F+1) + I(I+1) - J(J+1)]}{2F(F+1)} \right] \end{aligned} \quad (6-7)$$

In the case of intermediate coupling the electronic Lande g -factor $g(J)$ may be replaced by its intermediate coupling corrected value. For experimental convenience Eq. (6-7) is often rewritten as

$$\langle \alpha J I F M_F | H_{mag} | \alpha' J I F M_F \rangle = \mu_B B_z M_F g_F \quad (6-8)$$

with

$$g_F = g_J \frac{[F(F+1) - I(I+1) + J(J+1)]}{2F(F+1)} + g_I \frac{[F(F+1) + I(I+1) - J(J+1)]}{2F(F+1)} \quad (6-9)$$

In the case of a weak magnetic field the energy shifts will be linear in the magnetic field B_z . For fields that produce splittings comparable with the hyperfine splittings, or greater it is necessary to consider matrix elements that are off-diagonal in F . In that case it is usually simplest to work in the $JM_JIM_I M_F$ scheme but let us first continue in the $JIFM_F$ scheme.

6.4. Off-Diagonal Zeeman Matrix Elements in the $JIFM_F$ Scheme

Let us assume that the fine structure splitting is sufficiently large that we can ignore J -mixing and just consider the matrix elements that couple states differing in F by one unit.

$$\begin{aligned} & \langle \alpha J I F M_F | H_{mag} | \alpha' J I F + 1 M_F \rangle \\ & = \mu_B B_z (-1)^{F-M_F} \begin{pmatrix} F & 1 & F+1 \\ -M_F & 0 & M_F \end{pmatrix} (-1)^{J+I+F+1} \sqrt{(2F+1)(2F+3)} \\ & \times \left[\left\{ \begin{matrix} F & 1 & F+1 \\ J & I & J \end{matrix} \right\} \langle \alpha J || (L^{(1)} + g_s S^{(1)}) || \alpha' J \rangle - \left\{ \begin{matrix} F & 1 & F+1 \\ I & J & I \end{matrix} \right\} \langle \alpha I || g_I I^{(1)} || \alpha' I \rangle \right] \end{aligned} \quad (6-10)$$

Explicit evaluation of the $3jm$ - and $6j$ -symbols using (2-56) and (2-49b) respectively leads to

$$\begin{aligned} & \langle \alpha J I F M_F | H_{mag} | \alpha' J I F + 1 M_F \rangle \\ & = \mu_B B_z (g_J - g_I) \sqrt{(F+1)^2 - M_F^2} \\ & \times \sqrt{\frac{(F+J+I+2)(F+J-I+1)(F-J+I+1)(I+J-F)}{4(F+1)^2(2F+1)(2F+3)}} \end{aligned} \quad (6-11)$$

6.5. Strong Zeeman Effect in the $JM_JIM_I M_F$ Basis

The Zeeman matrix elements in the $JM_JIM_I M_F$ basis are particularly simple. We shall assume that the fine structure is very much larger than the hyperfine structure, a good approximation for the heavier alkali atoms such as *Rb* and *Cs*. In that case we can ignore matrix elements that are non-diagonal in J and obtain

$$\langle \alpha JM_JIM_I M_F | H_{mag} | \alpha' JM_JIM_I M_F \rangle = \mu_B B_z (g_J M_J + g_I M_I) \quad \text{with } M_J + M_I = M_F \quad (6-12)$$

Note that M_F remains a conserved quantum number.

6.6. Example of a $J = \frac{1}{2}$ Electronic Level

The particular case of a $J = \frac{1}{2}$ electronic level is relatively simple and of great practical importance. Of considerable interest are the ground and first excited states of the alkali atoms^{34,35}. To construct a very specific example let us consider an atom with nuclear spin $I = \frac{7}{2}$ and $J = \frac{1}{2}$ as is indeed the case for the ground state of $^{133}_{55}\text{Cs}$. Ultimately we want to compare our calculations with known experimental data^{34,35}. Clearly, there are two hyperfine sublevels with

$$F = 3 \quad \text{with } M_F = \pm 3, \pm 2, \pm 1, 0 \quad (6-13a)$$

$$F = 4 \quad \text{with } M_F = \pm 4, \pm 3, \pm 2, \pm 1, 0 \quad (6-13b)$$

To simplify matters let us assume that the $J = \frac{1}{2}$ level has a Lande g -factor g_J and that the nuclear g -factor g_I is very small compared with g_J and can be ignored. The magnetic field matrix elements, in terms of $\mu_B B_z$ can be evaluated in the $JIFM_F$ scheme using (6-7) for the diagonal elements and (6-11) for the elements coupling the two F values. We find the matrices

$$M_F = \pm 4 \quad \begin{array}{c} | \frac{1}{2} \frac{7}{2} 4, \pm 4 \rangle \\ \langle \frac{1}{2} \frac{7}{2} 4, \pm 4 | \end{array} \left(\begin{array}{c} \pm \frac{g_J}{2} \end{array} \right)$$

$$M_F = \pm 3 \quad \begin{array}{cc} | \frac{1}{2} \frac{7}{2} 3, \pm 3 \rangle & | \frac{1}{2} \frac{7}{2} 4, \pm 3 \rangle \\ \langle \frac{1}{2} \frac{7}{2} 3, \pm 3 | & \left(\begin{array}{cc} \mp \frac{3g_J}{8} & \frac{\sqrt{7}g_J}{8} \\ \frac{\sqrt{7}g_J}{8} & \pm \frac{3g_J}{8} \end{array} \right) \end{array} \quad M_F = \pm 2 \quad \begin{array}{cc} | \frac{1}{2} \frac{7}{2} 3, \pm 2 \rangle & | \frac{1}{2} \frac{7}{2} 4, \pm 2 \rangle \\ \langle \frac{1}{2} \frac{7}{2} 3, \pm 2 | & \left(\begin{array}{cc} \mp \frac{g_J}{4} & \frac{g_J \sqrt{3}}{4} \\ \frac{g_J \sqrt{3}}{4} & \pm \frac{g_J}{4} \end{array} \right) \end{array}$$

$$M_F = \pm 1 \quad \begin{array}{cc} | \frac{1}{2} \frac{7}{2} 3, \pm 1 \rangle & | \frac{1}{2} \frac{7}{2} 4, \pm 1 \rangle \\ \langle \frac{1}{2} \frac{7}{2} 3, \pm 1 | & \left(\begin{array}{cc} -\frac{g_J}{8} & \frac{g_J \sqrt{15}}{8} \\ \frac{g_J \sqrt{15}}{8} & \frac{g_J}{8} \end{array} \right) \end{array} \quad M_F = 0 \quad \begin{array}{cc} | \frac{1}{2} \frac{7}{2} 3, 0 \rangle & | \frac{1}{2} \frac{7}{2} 4, 0 \rangle \\ \langle \frac{1}{2} \frac{7}{2} 3, 0 | & \left(\begin{array}{cc} 0 & \frac{g_J}{2} \\ \frac{g_J}{2} & 0 \end{array} \right) \end{array}$$

Diagonalisation of the above matrices yields just the two eigenvalues $\pm \frac{g_J}{2}$ each with a degeneracy of 5. This is exactly what would be expected if we had calculated in the $JM_JIM_I M_F$ scheme.

However, to complete the calculation we must include the magnetic hyperfine matrix elements calculated in the same basis. These follow from Eq.(5-35b) giving

$$\langle \frac{1}{2} \frac{7}{2} 4M_F | H_{hfs} | \frac{1}{2} \frac{7}{2} 4M_F \rangle = \frac{7}{4} A \quad (6-14a)$$

$$\langle \frac{1}{2} \frac{7}{2} 3M_F | H_{hfs} | \frac{1}{2} \frac{7}{2} 3M_F \rangle = -\frac{9}{4} A \quad (6-14b)$$

where A is the magnetic hyperfine structure constant. To calculate the Zeeman effect on the two hyperfine levels associated with a $J = \frac{1}{2}$ level we must combine the matrices of H_{mag} and H_{hfs} in consistent units and then diagonalize them. Experimentalists commonly express their measurements of hyperfine constants in terms of MHz since many of their measurements involve microwave techniques. Thus in the data tables³⁴ for caesium we find the Bohr magneton given as

$$\mu_B = h \cdot 1.399\ 624\ 624(56) MHz/G \quad (6-15)$$

which implies the magnetic field being measured in Gauss. The magnetic hyperfine structure constant A for the $6p\ ^2P_{\frac{1}{2}}$ state is given as

$$A_{6^2P_{\frac{1}{2}}} = h \cdot 291.920(19) MHz \quad (6-16)$$

6.7. The Secular Equation for $J = \frac{1}{2}$ levels

If $J = \frac{1}{2}$ then necessarily $F = I \pm \frac{1}{2}$. Let us put

$$k = \frac{\mu_b B_z g_J}{2I + 1} \quad (6-17)$$

Then for $M_F = \pm(I + \frac{1}{2})$ we have

$$\langle \frac{1}{2} II + \frac{1}{2}, \pm(I + \frac{1}{2}) | \left(\begin{array}{c} |\frac{1}{2} II + \frac{1}{2}, \pm(I + \frac{1}{2})\rangle \\ \frac{1}{2} IA \pm k(2I + 1) \end{array} \right) \quad (6-18)$$

For all other values of M_F we have the rank two matrices

$$\begin{array}{l} |M_F| \leq I - \frac{1}{2} \quad \left(\begin{array}{cc} |\frac{1}{2} II - \frac{1}{2}, M_F\rangle & |\frac{1}{2} II + \frac{1}{2}, M_F\rangle \\ \langle \frac{1}{2} II - \frac{1}{2}, M_F | \left(\begin{array}{cc} -\frac{1}{2}(I + 1)A - kM_F & k\sqrt{(I + \frac{1}{2})^2 - M_F^2} \\ k\sqrt{(I + \frac{1}{2})^2 - M_F^2} & \frac{1}{2}IA + kM_F \end{array} \right) \end{array} \right) \end{array} \quad (6-19)$$

Taking the determinant of (6-19)) we can evaluate the eigenvalues λ_{\pm} by solving the secular equation

$$\lambda^2 + \frac{1}{2}A\lambda - \frac{1}{4}[A^2I(I + 1) + 2kAM_F(2I + 1) + k^2(2I + 1)^2] \quad (6-20)$$

Solving for the roots of the quadratic equation gives

$$\lambda_{\pm} = -\frac{A}{4} \pm \frac{A}{4} \sqrt{1 + 4I(I+1) + \frac{8}{A} k M_F (2I+1) + \frac{k^2}{A^2} (2I+1)^2} \quad (6-21)$$

Putting

$$x = \frac{k}{A} \quad (6-22)$$

leads finally to

$$\lambda_{\pm} = \frac{1}{4} A \left(-1 \pm (2I+1) \sqrt{1 + \frac{8x}{2I+1} M_F + x^2} \right) \quad (6-23)$$

Eqs.(6-17) and (6-23) allow one to describe the behaviour of any $J = \frac{1}{2}$ level for any nuclear spin I having magnetic hyperfine structure in a magnetic field. Eq.(6-23) is related to the celebrated Breit-Rabi equation³⁶.

6.8. Example of $^{133}_{55}\text{Cs}$

In the case of $^{133}_{55}\text{Cs}$ we have $I = \frac{7}{2}$ and (6-23) becomes

$$\lambda_{\pm} = \frac{1}{4} A \left(-1 \pm 8 \sqrt{1 + x M_F + x^2} \right) \quad (6-24)$$

The case $x = 0$ corresponds to $B_z = 0$ and gives just the two hyperfine levels found in (6-14a,b). Given that the experimental value of A is positive we have the $F = 3$ state of $6p(^2P_{\frac{1}{2}})$ below that of $F = 4$ with a separation of $4A$. For small x i.e. $1 \gg x \gg x^2$ we have from (6-24)

$$\lambda_{\pm} = \lambda_{\pm} = \frac{1}{4} A \left(-1 \pm 8 \sqrt{1 + x M_F} \right) \quad (6-25)$$

Expanding the square root to first-order in x , noting (6-22) and (6-17) and that for $6p(^2P_{\frac{1}{2}})$ $g_J = \frac{2}{3}$ we find that the states with $F = 3$ and $F = 4$ splitting in a magnetic field $\overset{2}{B}_z$ as

$$E(F = 4) = \frac{9}{4} A + \frac{\mu_B}{12} B_z M_F \quad \text{MHz} \quad (6-26a)$$

$$E(F = 3) = -\frac{7}{4} A - \frac{\mu_B}{12} B_z M_F \quad \text{MHz} \quad (6-26b)$$

relative to the centre of gravity of the $6p(^2P_{\frac{1}{2}})$ state. Thus in a weak magnetic field the two hyperfine levels split into $2F + 1$ equi-spaced Zeeman sublevels. The separation of consecutive Zeeman sublevels being

$$\Delta E = \frac{\mu_B}{12} B_z = 0.1166 B_z \quad (6-27)$$

where in (6-26a,b) and (6-27) we have put $h = 1$ and B_z is in Gauss to give measurements of E and ΔE in MHz as is common in such experiments^{34,35}.

In the case of a very strong magnetic field and $g_J \gg g_I$, such that the Zeeman splittings are very much greater than the hyperfine splitting, the Zeeman levels will coalesce to give two levels corresponding to $M_J = \pm \frac{1}{2}$ each having a degeneracy of $2I + 1$.

6.9. The Clock Correction Equation

The groundstate of an alkali atom has $J = \frac{1}{2}$ and just the two hyperfine levels with $F = I \pm \frac{1}{2}$. These two hyperfine levels are separated by

$$\Delta E_{hfs} = \frac{1}{2}A(2I + 1) \quad (6-28)$$

It follows from (6-23) that there can be no first-order Zeeman shift for the Zeeman sublevels with $M_F = 0$ and (6-23) simplifies to

$$\lambda_{\pm} = \frac{A}{4} \left(-1 \pm (2I + 1)\sqrt{1 + x^2} \right) \quad M_F = 0 \quad (6-29)$$

The difference in the two levels with $M_F = 0$ becomes

$$\begin{aligned} \Delta\lambda &= \frac{1}{2}A(2I + 1)\sqrt{1 + x^2} \\ &\approx \frac{A}{4}(2I + 1)x^2 \\ &= \frac{k^2}{A}(2I + 1) \\ &= \frac{\mu_B^2 B_z^2 (g_J^2 - g_I^2)}{A(2I + 1)} \end{aligned} \quad (6-30)$$

where we have included, in this case, the nuclear g -factor, g_I . Using (6-28) we obtain the change $\Delta\omega$ in angular frequency ω for the clock transitions as

$$\Delta\omega = \frac{\mu_B^2 B_z^2 (g_J^2 - g_I^2)}{2\hbar\Delta E_{hfs}} \quad (6-31)$$

6.10. Electric Quadrupole Hyperfine Structure

Nuclei with $I \geq 1$ may exhibit deformation from spherical symmetry. The interaction between the charged nucleons and electrons may be written as

$$H_{EQ} = -e^2 \int_{\tau_e} \int_{\tau_n} \frac{\rho_e(r_e)\rho_n(r_n)d\tau_e d\tau_n}{|\mathbf{r}_e - \mathbf{r}_n|} \quad (6-32)$$

where $e\rho_e(r_e)$ and $e\rho_n(r_n)$ are the electron and nucleon charge densities and r_e and r_n are measured relative to the nuclear centre. Expanding the denominator of (6-32) in spherical harmonics (as in S2.10) gives

$$\frac{1}{|\mathbf{r}_e - \mathbf{r}_n|} = \sum_k \frac{r_n^k}{r_e^{k+1}} (\mathbf{C}^{(k)} \cdot \mathbf{C}^{(k)}) \quad (6-33)$$

Parity considerations allow us to drop all terms with *odd* k . The $k = 0$ term corresponds to a monopole, or single charge and may also be dropped. The $k = 2$ term corresponds to an electric quadrupole interaction. Higher electric multipole terms will

not be considered here. Thus for the electric-quadrupole interaction we will take the Hamiltonian term

$$H_{EQ} = -e^2 \int_{\tau_e} \int_{\tau_n} \rho_e(r_e) \rho_n(r_n) \frac{r_n^2}{r_e^3} (\mathbf{C}^{(2)} \cdot \mathbf{C}^{(2)}) d\tau_e d\tau_n \quad (6-34)$$

The matrix elements of H_{EQ} may be evaluated to give for the diagonal elements

$$\begin{aligned} \langle \alpha J I F | \mathbf{H}_{EQ} | \alpha' J I F \rangle &= -e^2 (-1)^{J+I+F} \begin{Bmatrix} J & J & 2 \\ I & I & F \end{Bmatrix} \langle \alpha J | r_e^{-3} C_e^{(2)} | \alpha' J \rangle \\ &\quad \langle I | r_n^2 C_n^{(2)} | I \rangle \end{aligned} \quad (6-35)$$

The nuclear quadrupole moment Q is commonly defined as the matrix element over the space of the nuclear coordinates evaluated when \mathbf{I} has its largest component in the z -direction, that is,

$$\begin{aligned} Q &= \langle I I | r_n^2 (3 \cos^2 \theta - \frac{1}{2}) | I I \rangle_{av} = 2 \langle I I | r_n^2 C_{n0}^{(2)} | I I \rangle \\ &= 2 \begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix} \langle I | r_n^2 C_n^{(2)} | I \rangle \end{aligned} \quad (6-36)$$

Evaluating the $3jm$ -symbol explicitly we obtain

$$Q = 2 \sqrt{\frac{I(2I-1)}{(I+1)(2I+1)(2I+3)}} \langle I | r_n^2 C_n^{(2)} | I \rangle \quad (6-37)$$

Inserting (6-37) into (6-35) and evaluating the $6j$ -symbol explicitly leads to

$$\begin{aligned} &\langle \alpha J I F | \mathbf{H}_{EQ} | \alpha' J I F \rangle \\ &= \frac{-e^2 Q \langle r^{-3} \rangle}{I(2I-1)} \langle \alpha J | C_e^{(2)} | \alpha' J \rangle \\ &\quad \times \frac{[\frac{3}{4}K(K+1) - I(I+1)J(J+1)]}{\sqrt{(2J-1)J(2J+1)(J+1)(2J+3)}} \\ &= b_\ell X_J \left[\frac{\frac{3}{4}K(K+1) - I(I+1)J(J+1)}{I(2I-1)J(2J-1)} \right] \end{aligned} \quad (6-38)$$

where

$$b_\ell = e^2 Q \langle r^{-3} \rangle \quad (6-39)$$

The *electric quadrupole hyperfine constant* B is usually defined as

$$B = b_\ell X_J \quad (6-40)$$

and K is defined as in (5-35c). X_J will be different for different electronic states while b_ℓ is a constant over the states of a given configuration. Specifically,

$$X_J = -\sqrt{\frac{J(2J-1)}{(J+1)(2J+1)(2J+3)}} \langle \alpha J | C_e^{(2)} | \alpha' J \rangle \quad (6-41)$$

Thus for nuclei with $I \geq 1$ we have

$$H_{hfs} = \frac{1}{2}AK + B \left[\frac{\frac{3}{4}K(K+1) - I(I+1)J(J+1)}{I(2I-1)J(2J-1)} \right] \quad (6-42)$$

In the JM_JIM_I scheme the matrix elements of the nuclear electric quadrupole interaction becomes

$$\begin{aligned} & \langle \alpha JM_JIM_I | H_{EQ} | \alpha' JM_J \pm q IM_I \mp q \rangle \\ &= (-1)^{J-M_J} \begin{pmatrix} J & 2 & J \\ -M_J & \mp q & M_J \pm q \end{pmatrix} (-1)^{I-M_I} \begin{pmatrix} I & 2 & I \\ -M_I & \pm q & M_I \mp q \end{pmatrix} \\ & \times \frac{B}{2} \sqrt{\frac{(2I+1)(I+1)(2I+3)(2J+1)(J+1)(2J+3)}{I(2I-1)J(2J-1)}} \end{aligned} \quad (6-41)$$

where q is limited to the values of 0, 1, 2. Note $M_F = M_J + M_I$ remains a good quantum number. The matrix elements that are diagonal in M_J and M_I may be found by explicit evaluation of the two $3jm$ -symbols to give

$$\begin{aligned} \langle \alpha JM_JIM_I | H_{EQ} | \alpha' JM_JIM_I \rangle &= \frac{B}{2} \left[\frac{3M_I^2 - I(I_1)}{IJ(2I-1)(2J-1)} \right] \\ & \times [3M_J^2 - J(J+1)] \end{aligned} \quad (6-42)$$

Thus, in the approximation that the off-diagonal matrix elements may be ignored we have in the JM_JIM_I scheme

$$\begin{aligned} \langle \alpha JM_JIM_I | H_{EQ} | \alpha' JM_JIM_I \rangle &= M_JM_IA \\ & + \frac{B}{2} \left[\frac{3M_I^2 - I(I_1)}{IJ(2I-1)(2J-1)} \right] [3M_J^2 - J(J+1)] \end{aligned} \quad (6-43)$$

Lecture 7

When the great innovation appears, it will almost certainly be in a muddled, incomplete and confusing form. To the discover himself it will be only half-understood; to everybody else it will be a mystery. For any speculation which does not at first glance look crazy, there is no hope. The reason why new concepts in any branch of science are hard to grasp is always the same; contemporary scientists try to picture the new concepts in terms of ideas which existed before
(Freeman J Dyson)

7. Introduction

In this lecture we will look at questions relating to intensities of electronic transitions, first in the absence of hyperfine structure and then with it. Our emphasis will be on relative intensities rather than absolute intensities. The latter are difficult to reliably compute and to measure. Two distinct types of transitions arise (1.) Parity *allowed* transitions that require a change of parity of the one-electron orbitals and parity *forbidden* transitions which occur when there is no change in the parity of the one-electron orbitals. Recall that the parity, \mathcal{P} , of the states of an electron configuration is

$$\mathcal{P} = (-1)^{\sum \ell} \quad (7-1)$$

where the summation is over all one-electron orbitals of the configuration. The parity is said to be *even* or *odd* as \mathcal{P} is *even* or *odd*. Closed shells are necessarily of even parity and may be omitted in the summation.

Electric dipole transitions occur between states of *opposite* parity and are commonly referred to as *allowed* transitions whereas magnetic dipole and electric quadrupole transitions only occur between states of the *same* parity and are referred to as *forbidden* transitions in the sense that they are forbidden as electric dipole transitions. In general the allowed transitions are orders of magnitude more intense than the forbidden transitions. We start by considering electric dipole transitions.

7.1. Electric Dipole Transitions in Atoms

In the absence of perturbing fields each energy level characterised by a total angular momentum J will be $2J+1$ -fold degenerate, each of the different states being characterised by a different value of M_J . A *spectral line* is defined as the radiation associated with all possible transitions between the states belonging to two levels. The radiation resulting from a transition between a particular pair of states will be called a *component* of the line.

Electric dipole transitions are induced by the electric dipole operator

$$P = -e \sum_i \mathbf{r}_i = -e \sum_i \sum_{q=-1}^{q=1} r_i C_q^{(1)} \quad (7-2)$$

where $q = -1, 0, 1$. The intensities of a given transition will be proportional to the absolute square of the matrix element of P coupling the two states. Applying the Wigner-Eckart theorem (2-32) we have

$$\langle \alpha J M_J | P | \alpha' J' M'_J \rangle = (-1)^{J-M_J} \begin{pmatrix} J & 1 & J' \\ -M_J & q & M'_J \end{pmatrix} \langle \alpha J || P || \alpha' J' \rangle \quad (7-3)$$

The triangular condition on the top row of the $3jm$ -symbol gives us the selection rule

$$\Delta J = 0, \pm 1 \quad (7-4a)$$

while the requirement that the arguments of the bottom row sum to zero gives the selection rule

$$\Delta M_J = 0, \pm 1 \quad \text{or} \quad M_J \rightarrow M_J - q \quad (7-4b)$$

If the light, absorbing or emitting, is polarised in the z direction then only $q = 0$ is active while if the light is right circularly polarised, σ_+ , $q = +1$ while if it is left circularly polarised, σ_- , $q = -1$. This, as we shall see later, assumes great importance in laser cooling down to nanoKelvin temperatures. Using laser beams left or right circularly polarised one can selectively induce transitions between different hyperfine levels which themselves have been split in a magnetic field, an important feature of magneto-optical traps and in Bose-Einstein-Condensation.

If the light is unpolarised and we observe from an initial state with M_J the complete set of transitions to the levels with M'_J then the intensity will involve

$$\sum_{M'_J, q} |\langle \alpha J M_J | P | \alpha' J' M'_J \rangle|^2 = |\langle \alpha J || P || \alpha' J' \rangle|^2 / (2J' + 1) \quad (7-5)$$

which follows from the orthogonality property of $3jm$ -symbols. The quantity

$$\mathcal{S}(\alpha J; \alpha' J') = |\langle \alpha J || P || \alpha' J' \rangle|^2 \quad (7-6)$$

is commonly referred to as the *line strength* of the transition. Often one is interested in first computing the *square root* of the line strength, $\mathcal{S}^{\frac{1}{2}}(\alpha J; \alpha' J')$, that being the relevant term to compute if one wishes to make corrections for intermediate coupling etc where preservation of phase information must be retained. After making the corrections the resultant square root of the line strength is squared.

7.2. Ratio of the line strengths for the D lines of alkali atoms

Expanding the state description for an alkali atom we have, noting (2-46),

$$\begin{aligned}
 & \langle s\ell j \| P \| s\ell' j' \rangle \\
 & = -e \langle r \rangle_{\ell\ell'} \langle s\ell j \| C^{(1)} \| s\ell' j' \rangle \\
 & = -e \langle r \rangle_{\ell\ell'} (-1)^{s+\ell'+j+1} \sqrt{(2j+1)(2j'+1)} \left\{ \begin{matrix} j & 1 & j' \\ \ell' & s & \ell \end{matrix} \right\} \langle \ell \| C^{(1)} \| \ell' \rangle
 \end{aligned} \tag{7-7}$$

Using this result in (7-6) we have for the ratio of the line strengths of the $D_2 : D_1$ transitions

$$\frac{\mathcal{S}(ns^2S_{\frac{1}{2}}; np^2P_{\frac{3}{2}})}{\mathcal{S}(ns^2S_{\frac{1}{2}}; np^2P_{\frac{1}{2}})} = 2 \tag{7-8}$$

which may be compared with the experimental value³⁷ of 1.9809(9) found for $^{133}_{55}\text{Cs}$.

7.3. Line Strengths for Many-Electron Atoms

In LS -coupling we can enlarge our state description and obtain the J -dependence of the line strengths as

$$\begin{aligned}
 & \mathcal{S}^{\frac{1}{2}}(\alpha SLJ; \alpha' S' L' J') \\
 & = (-1)^{J+L'+S+1} \sqrt{(2J+1)(2J'+1)} \left\{ \begin{matrix} J & 1 & J' \\ L' & S & L \end{matrix} \right\} \\
 & \times -e \langle \alpha SL \| \sum_i r_i C_i^{(1)} \| \alpha' S' L' \rangle
 \end{aligned} \tag{7-9}$$

The triangular conditions on the arguments of the $6j$ -symbol lead to the selection rules

$$\Delta J = 0, \pm 1 \quad (0 \not\leftrightarrow 0) \tag{7-10a}$$

$$\Delta L = 0, \pm 1 \quad (0 \not\leftrightarrow 0) \tag{7-10b}$$

$$\Delta S = 0 \tag{7-10c}$$

The J selection rule is, in the absence of hyperfine interactions and external fields, independent of the coupling scheme. Recall that the spin-orbit interaction may mix states of different S and L leading to a breakdown of (7-10b,c). In that case intermediate coupling must be considered.

To obtain the intermediate coupling corrected line strength we may write

$$\mathcal{S}^{\frac{1}{2}}(aJ; bJ') = \sum_{\alpha, \beta} (aJ | \alpha J) \mathcal{S}^{\frac{1}{2}}(\alpha J; \beta J') (\beta J' | bJ') \tag{7-11}$$

where $(aJ | \alpha J)$ represents the transformation matrix that transforms the states $|\alpha J\rangle$ into the state $|aJ\rangle$ of the actual coupling and analogously for $(\beta J' | bJ')$. For some detailed examples see¹.

7.4. Relative Line Strengths in LS -Coupling

It is sometimes useful to have explicit expressions for the relative line strengths in LS -coupling. These can be obtained from the square of (7-9) with explicit evaluation of the $6j$ -symbol to give

$$\mathcal{S}(\alpha SL, J; \alpha' SL, J) = \frac{(2J+1)[(S(S+1) - J(J+1) - L(L+1))]^2}{4J(J+1)} \mathcal{P} \quad (7-12a)$$

$$\mathcal{S}(\alpha SL, J; \alpha' SL, J+1) = \frac{(S+L+J+2)(L+J-S+1)(S-L+J+1)(S+L-J)}{4(J+1)} \mathcal{P} \quad (7-12b)$$

$$\mathcal{S}(\alpha SL, J; \alpha' SL, J-1) = \frac{(S+L+J+1)(L+J-S)(S-L+J)(S+L-J+1)}{4J} \mathcal{P} \quad (7-12c)$$

$$\mathcal{S}(\alpha SL, J; \alpha' SL+1, J) = \frac{(2J+1)(S+L+J+2)(L+J-S+1)(S-J+L+1)(S+J-L)}{4J(J+1)} \mathcal{P}' \quad (7-12d)$$

$$\mathcal{S}(\alpha SL, J; \alpha' SL-1, J) = \frac{(2J+1)(S+L+J+1)(L+J-S)(S-J+L)(S+J-L+1)}{4J(J+1)} \mathcal{P}'' \quad (7-12e)$$

$$\mathcal{S}(\alpha SL, J; \alpha' SL+1, J+1) = \frac{(S+L+J+2)(S+L+J+3)(L+J-S+1)(L+J-S+2)}{4(J+1)} \mathcal{P}' \quad (7-12f)$$

$$\mathcal{S}(\alpha SL, J; \alpha' SL-1, J+1) = \frac{(S+L-J-1)(S+L-J)(S-L+J+1)(S-L+J+2)}{4(J+1)} \mathcal{P}'' \quad (7-12g)$$

$$\mathcal{S}(\alpha SL, J; \alpha' SL+1, J-1) = \frac{(S-L+J-1)(S-L+J)(S+L-J+1)(S+L-J+2)}{4J} \mathcal{P}' \quad (7-12h)$$

where

$$\mathcal{P} = \frac{|\langle \alpha SL \| P \| \alpha' SL \rangle|^2}{L(L+1)(2L+1)}, \quad (7-13a)$$

$$\mathcal{P}' = \frac{|\langle \alpha SL \| P \| \alpha' SL+1 \rangle|^2}{(L+1)(2L+1)(2L+3)} \quad (7-13c)$$

and

$$\mathcal{P}'' = \frac{|\langle \alpha SL \| P \| \alpha' SL-1 \rangle|^2}{L(2L-1)(2L+1)} \quad (7-13c)$$

Thus we have from (7-12c,f) the line strength ratio

$$\frac{\mathcal{S}(\alpha SL, J; \alpha' SL+1, J+1)}{\mathcal{S}(\alpha SL, J; \alpha' SL+1, J)} = \frac{J(S+L+J+3)(L+J-S+2)}{(2J+1)(S-J+L+1)(S+J-L)} \quad (7-14)$$

which is, of course, consistent with (7-8).

7.5. Relative Line Strengths for Hyperfine Levels

The treatment of the line strengths for electric dipole transitions between hyperfine levels, in the absence of external fields, parallels our earlier work on atomic transitions. Thus the relative line strengths for hyperfine levels can be derived from (7-12) to (7-14) by simply making the replacements

$$S \rightarrow I, \quad L \rightarrow J, \quad J \rightarrow F \quad (7-15)$$

and hence

$$\mathcal{S}(\alpha JI, F; \alpha' JI, F) = \frac{(2F+1)[(I(I+1) - F(F+1) - J(J+1))]^2}{4F(F+1)} \mathcal{P} \quad (7-16a)$$

$$\mathcal{S}(\alpha JI, F; \alpha' JI, F+1) = \frac{(I+J+F+2)(J+F-I+1)(I-J+F+1)(I+J-F)}{4(F+1)} \mathcal{P} \quad (7-16b)$$

$$\mathcal{S}(\alpha JI, F; \alpha' JI, F-1) = \frac{(I+J+F+1)(J+F-I)(I-J+F)(I+J-F+1)}{4F} \mathcal{P} \quad (7-16c)$$

$$\mathcal{S}(\alpha JI, F; \alpha' J+1I, F) = \frac{(2F+1)(I+J+F+2)(J+F-I+1)(I-F+J+1)(I+F-J)}{4F(F+1)} \mathcal{P}' \quad (7-16d)$$

$$\mathcal{S}(\alpha JI, F; \alpha' J-1I, F) = \frac{(2F+1)(I+J+F+1)(J+F-I)(I-F+J)(I+F-J+1)}{4F(F+1)} \mathcal{P}'' \quad (7-16e)$$

$$\mathcal{S}(\alpha JI, F; \alpha' J+1I, F+1) = \frac{(I+J+F+2)(I+J+F+3)(J+F-I+1)(J+F-I+2)}{4(F+1)} \mathcal{P}' \quad (7-16f)$$

$$\mathcal{S}(\alpha JI, F; \alpha' J-1I, F+1) = \frac{(I+J-F-1)(I+J-F)(I-J+F+1)(I-J+F+2)}{4(F+1)} \mathcal{P}'' \quad (7-16g)$$

$$\mathcal{S}(\alpha JI, F; \alpha' J+1I, F-1) = \frac{(I-J+F-1)(I-J+F)(I+J-F+1)(I+J-F+2)}{4F} \mathcal{P}' \quad (7-16h)$$

where

$$\mathcal{P} = \frac{|\langle \alpha JI || P || \alpha' JI \rangle|^2}{J(J+1)(2J+1)}, \quad (7-17a)$$

$$\mathcal{P}' = \frac{|\langle \alpha JI || P || \alpha' J+1I \rangle|^2}{(J+1)(2J+1)(2J+3)} \quad (7-17b)$$

and

$$\mathcal{P}'' = \frac{|\langle \alpha JI || P || \alpha' J-1I \rangle|^2}{J(2J-1)(2J+1)} \quad (7-17b)$$

Thus we have from (7-16b,d) the line strength ratio

$$\frac{\mathcal{S}(\alpha JI, F; \alpha' JI, F+1)}{\mathcal{S}(\alpha JI, F; \alpha' J+1I, F)} = \frac{F(I+J+F+3)(J+F-I+2)}{(2F+1)(I-F+J+1)(I+F-J)} \quad (7-18)$$

7.6. Relative line strengths for the D2 transitions of $^{87}_{37}\text{Rb}$

Recall that for $^{87}_{37}\text{Rb}$ the nuclear spin is $I = \frac{3}{2}$ and the groundstate is $5s \ ^2S_{\frac{1}{2}}$ and the spin-orbit interaction splits the first excited state into the two sublevels $5p \ ^2P_{\frac{1}{2}}$ and $5p \ ^2P_{\frac{3}{2}}$ with the $5p \ ^2P_{\frac{3}{2}}$ sublevel being highest. The D2 transitions are associated with transitions $5s \ ^2S_{\frac{1}{2}} \rightarrow 5p \ ^2P_{\frac{3}{2}}$. The magnetic hyperfine interaction results in the groundstate splitting into two sublevels with $F = 1$ and $F = 2$ respectively while for excited level $5p \ ^2P_{\frac{3}{2}}$ we obtain four sublevels with $F = 0, 1, 2, 3$. Here we are interested in the transition array $5s \ ^2S_{\frac{1}{2}} F \rightarrow 5p \ ^2P_{\frac{3}{2}} F'$ and their relative line strengths.

The relative line strengths may be calculated directly from (7-17b) together with (7-16d,f,h) and normalised to give the results below.

$$\begin{array}{cccc} & 0 & 1 & 2 & 3 \\ \begin{array}{l} 1 \\ 2 \end{array} & \left(\begin{array}{cccc} \frac{1}{6} & \frac{5}{12} & \frac{5}{12} & 0 \\ 0 & \frac{1}{20} & \frac{1}{4} & \frac{7}{20} \end{array} \right) \end{array}$$

7.7. Effective Operators and Perturbation Theory

The Stark effect involves the interaction of an atomic electric dipole moment, \mathbf{p} , with an external electric field, \mathbf{E} , which may be represented by the operator⁴⁰

$$H_E = -\mathbf{E} \cdot \mathbf{p} \quad (7-19)$$

For a H -atom there is a first-order Stark effect due to the degeneracy of states of opposite parity for a given principal quantum number n . For alkali atoms the degeneracy is lifted by the Coulomb field and there is no first-order energy shift of the states and one must go to second-order to obtain a Stark effect. Before proceeding to the quadratic Stark effect in atoms a few remarks about effective operators^{41,42} and perturbation theory.

Let us assume that the exact Hamiltonian H of the system can be split into two Hermitian operators, H_0 and V , i.e.,

$$H = H_0 + V \quad (7-20)$$

The spectral resolution of H_0 is assumed to be known explicitly. The eigenvalues $\lambda_A, \lambda_B, \dots$ associated with H_0 will normally possess degeneracy. We shall,

for convenience, refer to each eigenvalue as a “configuration”. For a particular configuration A we have the eigenvalue equation

$$H_0|A_i\rangle = \lambda_A|A_i\rangle \quad (7-21)$$

where i labels the g -degenerate eigenstates. It is assumed that a suitable orthonormal basis set can be constructed in terms of the zero-order eigenfunctions $|A_i\rangle$ such that

$$|A\alpha\rangle = \sum_{i=1}^g a_i|A_i\rangle \quad (7-22)$$

and

$$\langle A\alpha|A\alpha'\rangle = \delta(\alpha, \alpha') \quad (7-23)$$

The first-order correction to the eigenvalue λ_A due to the effect of the perturbation operator V acting on the unperturbed system is found by diagonalizing the $g \times g$ energy matrix formed by the matrix elements $\langle A\alpha|V|A\alpha'\rangle$. The diagonalization of this matrix will usually result in a lowering of the initial degeneracy.

The perturbing potential V will normally also couple the states of the configuration A to those of B, C, \dots . If one, or more, of these configurations is approximately degenerate with A then it is desirable to diagonalize the energy matrix for that set of configurations. If the perturbing configuration is well removed from A then their effect on the energy levels may be studied by perturbation theory. The *first-order* correction to the eigenfunction $|A\alpha'\rangle$ due to the perturbation by the states $|B\beta\rangle$ of the configuration B is given by

$$|A\alpha'\rangle_1 = \sum_{\beta} \frac{|B\beta\rangle\langle B\beta|V|A\alpha'\rangle}{\lambda_A - \lambda_B} \quad (7-24)$$

and the *second-order* correction to the energy matrix is given by the matrix elements

$$\langle A\alpha|V|A\alpha'\rangle = \sum_{\beta} \frac{\langle A\alpha|V|B\beta\rangle\langle B\beta|V|A\alpha'\rangle}{\lambda_A - \lambda_B} \quad (7-25)$$

where the summation is over all the states $|B\beta\rangle$ of the configuration B . Let us for the moment consider the object

$$\sum_{\beta} \langle A\alpha|V|B\beta\rangle\langle B\beta|V|A\alpha'\rangle \quad (7-26)$$

Recall the *closure theorem* that for a *complete* set of states

$$\sum_{B,\beta} |B\beta\rangle\langle B\beta| = 1 \quad (7-27)$$

Clearly we are not entitled to use (7-27) in (7-26) let alone in (7-25) since some of the intermediate states will include states of A and furthermore, in (7-25) the different

configurations occur at different energies. An alternative approach is to define the perturbing potential V in such a way that if the intermediate states belong to any configuration other than B a null result is obtained. It is then possible to use the closure theorem to obtain the result

$$\sum_{\beta} \langle A\alpha | V | B\beta \rangle \langle B\beta | V | A\alpha' \rangle = \langle A\alpha | V_{AB} V_{BA} | A\alpha' \rangle \quad (7-28)$$

The product operator, $V_{AB} V_{BA}$ now plays the role of an *effective operator* acting within the zero-order states $|A\alpha\rangle$ of the configuration of interest.

The problem is then to define suitable operators, $V_{AB} V_{BA}$ that have the desired properties. One obvious way would be to introduce annihilation and creation operators⁴³ or alternatively to use tensor operators that are essentially coupled products of annihilation and creation operators. We shall exploit the latter approach. To that end let us introduce tensor operators whose single particle operators are defined by the relation

$$\langle a || v^{(k)}(c, d) || b \rangle = \sqrt{2k+1} \delta(a, c) \delta(b, d) \quad (7-29)$$

where $|a\rangle$, $|b\rangle$, $|c\rangle$, $|d\rangle$ designate single particle states. For orbital operators we have the basic commutator relation

$$\begin{aligned} & [v^{(k_1)}(n\ell, n'\ell') v^{(k_2)}(n''\ell'', n'''\ell''')]_q^{(k)} \\ & - (-1)^{k_1+k_2-k} [v^{(k_2)}(n''\ell'', n'''\ell''') v^{(k_1)}(n\ell, n'\ell')]_q^{(k)} \\ & = \sqrt{(2k_1+1)(2k_2+1)} [\delta(n'\ell', n''\ell'') (-1)^{\ell+\ell''} \left\{ \begin{matrix} k_1 & k_2 & k \\ \ell''' & \ell & \ell' \end{matrix} \right\} v_q^{(k)}(n\ell, n''\ell'') \\ & + \delta(n\ell, n'''\ell''') (-1)^{\ell'+\ell''+k_1-k_2} \left\{ \begin{matrix} k_1 & k_2 & k \\ \ell'' & \ell' & \ell \end{matrix} \right\} v_q^{(k)}(n''\ell'', n'\ell')] \end{aligned} \quad (7-30)$$

Consider the case where in (7-25) the configuration A contains just one open shell ℓ^N of N equivalent particles and B differs by a single excitation into an empty shell. Then for one-particle spin-independent interactions a typical term in (7-25) (to within a multiplicative factor that includes radial integrals and the energy denominator and one particle reduced matrix elements of the tensor operators) would be

$$\sum_{\beta} \langle A\alpha | V_{q_1}^{(k_1)}(\ell\ell') | B\beta \rangle \langle B\beta | V_{q_2}^{(k_2)}(\ell'\ell) | A\alpha' \rangle \quad (7-31)$$

The summation over the states of B is accomplished by simply removing the intermediate states $|B\beta\rangle \langle B\beta|$ to give

$$\langle A\alpha | V_{q_1}^{(k_1)}(\ell\ell') V_{q_2}^{(k_2)}(\ell'\ell) | A\alpha' \rangle \quad (7-32)$$

The two operators may then be coupled together to yield

$$\sum_{k,q} \langle k_1 q_1 k_2 q_2 | k_1 k_2 k q \rangle \langle A\alpha | [V^{(k_1)}(\ell\ell') V^{(k_2)}(\ell'\ell)]_q^{(k)} | A\alpha' \rangle \quad (7-33)$$

The matrix element may now be simplified using the commutation result (7-30) and remembering that since $\langle A\alpha|$ and $|A\alpha'\rangle$ do not contain any particles in ℓ' orbitals the matrix elements of the operators $[V^{(k_2)}(\ell'\ell)V^{(k_1)}(\ell\ell')]_q^{(k)}$ and $V_q^{(k)}(\ell'\ell')$ vanish to give the final result

$$\begin{aligned} & \sum_{\beta} \langle A\alpha|V_{q_1}^{(k_1)}(\ell\ell')|B\beta\rangle \langle B\beta|V_{q_2}^{(k_2)}(\ell'\ell)|A\alpha'\rangle \\ &= \sum_{k,q} \langle k_1q_1k_2q_2|k_1k_2kq\rangle (-1)^{2\ell+k} \sqrt{(2k_1+1)(2k_2+1)} \begin{Bmatrix} k_1 & k_2 & k \\ \ell & \ell & \ell' \end{Bmatrix} \\ & \times \langle A\alpha|V_q^{(k)}|A\alpha'\rangle \end{aligned} \quad (7-34)$$

7.8. The Quadratic Stark Effect in Atoms

With the above outline of the relevant perturbation theory we can consider the quadratic Stark effect for atoms. For simplicity let us assume that the applied electric field is in the z -direction and that the electric dipole moment is as given earlier in (7-2). The perturbation term V_E is then

$$V_E = eE_z \sum_i r_i C_0^{(1)} \quad (7-35)$$

Let us assume that we are interested in a configuration $A = \ell^N$ that is perturbed by states from a configuration $B = \ell^{N-1}\ell'$ as considered below (7-30). For convenience, we introduce a constant, \mathcal{E} , which we shall define as

$$\mathcal{E} = \frac{1}{3} \frac{e^2 E_z^2}{\lambda_A - \lambda_B} \langle \ell|r|\ell'\rangle \langle \ell'|r|\ell\rangle \langle \ell||C^{(1)}||\ell'\rangle \langle \ell'||C^{(1)}||\ell\rangle \quad (7-36)$$

We note the parity selection rule $\Delta\ell = \pm 1$ is inherent in (7-36). Given the above definition the perturbation sum in (7-25) may be immediately found using (7-34) to give

$$\begin{aligned} & \mathcal{E} \sum_{\beta} \langle A\alpha|V_0^{(1)}(\ell\ell')|B\beta\rangle \langle B\beta|V_0^{(1)}(\ell'\ell)|A\alpha'\rangle \\ &= \mathcal{E} \sum_k \langle 10, 10|(1, 1)k0\rangle \langle A\alpha|V_0^{(k)}(\ell\ell)|A\alpha'\rangle (-1)^k 3 \begin{Bmatrix} 1 & 1 & k \\ \ell & \ell & \ell' \end{Bmatrix} \\ &= \mathcal{E} \sum_k \sqrt{2k+1} \begin{pmatrix} 1 & 1 & k \\ 0 & 0 & 0 \end{pmatrix} \langle A\alpha|V_0^{(k)}(\ell\ell)|A\alpha'\rangle (-1)^k 3 \begin{Bmatrix} 1 & 1 & k \\ \ell & \ell & \ell' \end{Bmatrix} \end{aligned} \quad (7-37)$$

The $3jm$ -symbol vanishes except for $k = 0, 2$ with

$$\begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} = -\frac{\sqrt{3}}{3} \quad \text{and} \quad \begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} = \frac{\sqrt{30}}{15} \quad (7-38)$$

The term with $k = 0$ is a complete scalar and has the effect of giving a uniform shift to all levels of the configuration A .

In the case of the $k = 2$ contribution let us put

$$\alpha_{\ell\ell'} = \mathcal{E} \begin{Bmatrix} \ell & \ell' & 1 \\ 1 & 2 & \ell \end{Bmatrix} \quad (7-39)$$

so that the $k = 2$ contribution becomes, after expanding the state description, and suppressing the constant $\alpha_{\ell\ell'}$

$$\begin{aligned} & \sqrt{6} \langle \alpha SLJIFM_F | V_0^{(2)}(\ell\ell) | \alpha' SL'J'IF'M_F \rangle \\ &= \sqrt{6} (-1)^{F-M_F} \begin{pmatrix} F & 2 & F' \\ -M_F & 0 & M_F \end{pmatrix} \langle \alpha SLJIF | V^{(2)}(\ell\ell) | \alpha' SL'J'IF' \rangle \\ &= (-1)^{F-M_F} \begin{pmatrix} F & 2 & F' \\ -M_F & 0 & M_F \end{pmatrix} (-1)^{J'+I+F} \sqrt{6(2F+1)(2F'+1)} \\ &\times \begin{Bmatrix} F & 2 & F' \\ J' & I & J \end{Bmatrix} \langle \alpha SLJ | V^{(2)}(\ell\ell) | \alpha' SL'J' \rangle \end{aligned} \quad (7-40)$$

For $N \geq 2$ the final reduced matrix element can be evaluated using Judd² Eq.(7-52) or the tables of Nielson and Koster⁴⁴. For a single electron outside of closed shells we have

$$\langle slj || V^{(2)}(\ell\ell) || slj' \rangle = (-1)^{s+\ell+j} \sqrt{5(2j+1)(2j'+1)} \begin{Bmatrix} 2 & j & j' \\ \frac{1}{2} & \ell & \ell \end{Bmatrix} \quad (7-41)$$

In particular

$$\langle {}^2P_{\frac{3}{2}} || V^{(2)}(p,p) || {}^2P_{\frac{3}{2}} \rangle = \frac{\sqrt{30}}{3} \quad (7-42)$$

Note that the $6j$ -symbol will vanish unless $\ell \geq 1$ and $j+j' \geq 2$. If the fine structure splittings are much greater than the hyperfine splittings then only the matrix elements diagonal in j need be considered. Note that the effect of an external electric field on the hyperfine levels is to, unlike the case of magnetic fields, only partially lift the degeneracy, states with $\pm M_F$ remain degenerate and hence, apart from states with $M_F = 0$, each sublevel is still two-fold degenerate.

7.9. Example of ${}^{133}_{55}\text{Cs}$

In the case of ${}^{133}_{55}\text{Cs}$ we will confine our attention to the $6p({}^2P_{\frac{3}{2}})$ hyperfine multiplet where, since the nuclear spin is $I = \frac{7}{2}$, the hyperfine levels have $F = 2, 3, 4, 5$. It follows from (7-39) that $\ell' = 0, 2$. Since the dependence on ℓ' is entirely contained in (7-39) let us just consider the matrix elements

$$\begin{aligned} & \sqrt{6} \langle {}^2P_{\frac{3}{2}} \frac{7}{2} F M_F | V_0^{(2)}(p,p) | {}^2P_{\frac{3}{2}} \frac{7}{2} F' M_F \rangle \\ &= (-1)^{M_F+1} 2 \sqrt{5(2F+1)(2F'+1)} \begin{pmatrix} F & 2 & F' \\ -M_F & 0 & M_F \end{pmatrix} \begin{Bmatrix} F & 2 & F' \\ \frac{3}{2} & \frac{7}{2} & \frac{3}{2} \end{Bmatrix} \end{aligned} \quad (7-43)$$

It is a simple matter to write a short MAPLE programme to evaluate the relevant matrix elements and to construct a matrix for each value of M_F . These matrices are given below. The states are designated by just $|FM_F\rangle$ since all other quantum numbers are fixed.

$$M_F = \pm 5 \quad |5 \pm 5\rangle \quad M_F = \pm 4 \quad |5 \pm 4\rangle \quad |4 \pm 4\rangle$$

$$\langle 5 \pm 5| \quad \begin{pmatrix} 1 \end{pmatrix} \quad \langle 5 \pm 4| \quad \begin{pmatrix} \frac{2}{5} & \mp \frac{\sqrt{21}}{5} \\ \mp \frac{\sqrt{21}}{5} & -\frac{2}{5} \end{pmatrix}$$

$$\langle 4 \pm 4|$$

$$M_F = \pm 3 \quad |5 \pm 3\rangle \quad |4 \pm 3\rangle \quad |3 \pm 3\rangle$$

$$\langle 5 \pm 3| \quad \begin{pmatrix} -\frac{1}{15} & \mp \frac{\sqrt{21}}{5} & \frac{\sqrt{35}}{15} \\ \mp \frac{\sqrt{21}}{5} & -\frac{1}{10} & \mp \frac{\sqrt{15}}{10} \\ \frac{\sqrt{35}}{15} & \mp \frac{\sqrt{15}}{10} & -\frac{5}{6} \end{pmatrix}$$

$$\langle 4 \pm 3|$$

$$\langle 3 \pm 3|$$

$$M_F = \pm 2 \quad |5 \pm 2\rangle \quad |4 \pm 2\rangle \quad |3 \pm 2\rangle \quad |2 \pm 2\rangle$$

$$\langle 5 \pm 2| \quad \begin{pmatrix} -\frac{2}{5} & \mp \frac{7}{10} & \frac{\sqrt{35}}{10} & 0 \\ \mp \frac{7}{10} & \frac{4}{35} & \mp \frac{2\sqrt{35}}{35} & \frac{5\sqrt{3}}{14} \\ \frac{\sqrt{35}}{10} & \mp \frac{2\sqrt{35}}{35} & 0 & \pm \frac{\sqrt{105}}{14} \\ 0 & \frac{5\sqrt{3}}{14} & \pm \frac{\sqrt{105}}{14} & \frac{2}{7} \end{pmatrix}$$

$$\langle 4 \pm 2|$$

$$\langle 3 \pm 2|$$

$$\langle 2 \pm 2|$$

$$M_F = \pm 1 \quad |5 \pm 1\rangle \quad |4 \pm 1\rangle \quad |3 \pm 1\rangle \quad |2 \pm 1\rangle$$

$$\langle 5 \pm 1| \quad \begin{pmatrix} -\frac{3}{5} & \mp \frac{\sqrt{14}}{10} & \frac{\sqrt{2}}{2} & 0 \\ \mp \frac{\sqrt{14}}{10} & \frac{17}{70} & \mp \frac{\sqrt{7}}{14} & \frac{5\sqrt{6}}{14} \\ \frac{\sqrt{2}}{2} & \mp \frac{\sqrt{7}}{14} & \frac{1}{2} & \pm \frac{\sqrt{42}}{14} \\ 0 & \frac{5\sqrt{6}}{14} & \pm \frac{\sqrt{42}}{14} & -\frac{1}{7} \end{pmatrix}$$

$$\langle 4 \pm 1|$$

$$\langle 3 \pm 1|$$

$$\langle 2 \pm 1|$$

$$M_F = 0 \quad |50\rangle \quad |40\rangle \quad |30\rangle \quad |20\rangle$$

$$\langle 50| \quad \begin{pmatrix} -\frac{2}{3} & 0 & \frac{\sqrt{5}}{3} & 0 \\ 0 & \frac{2}{7} & 0 & \frac{3\sqrt{5}}{7} \\ \frac{\sqrt{5}}{3} & 0 & \frac{2}{3} & 0 \\ 0 & \frac{3\sqrt{5}}{7} & 0 & -\frac{2}{7} \end{pmatrix}$$

$$\langle 40|$$

$$\langle 30|$$

$$\langle 20|$$

Diagonalization of the above matrices yields just two distinct eigenvalues $+1$ and -1 each with a degeneracy of 16. This is exactly what we would expect if we let the hyperfine structure constant approach zero. The Stark effect would lead to two levels, one for $m_j = \pm\frac{3}{2}$ and one for $m_j = \pm\frac{1}{2}$. The degeneracies associated with each $|m_j\rangle$ would be $2(2I+1)$. Indeed

$$\sqrt{6}\langle^2P_{\frac{3}{2}}m_j|V_0^{(2)}(p,p)|^2P_{\frac{3}{2}}m_j\rangle = (-1)^{|m_j|+\frac{1}{2}} \quad (7-44)$$

Lecture 8

It is never safe to affirm that the future of physical science has no marvels in store which may be even more astonishing than those of the past; but it seems probable that most of the grand underlying principles have now been firmly established and that further advances are to be sought chiefly in the rigorous application of these principles to all the phenomena which come under our notice ... An eminent physicist has remarked that the future truths of physical science are to be looked for in the sixth place of decimals. (A. A. Michelson University of Chicago Quarterly Calendar 10 (August 1894): 15)

8. Hyperfine Interactions and Laser Cooling

In this section I propose to give a largely qualitative picture of the practical application of hyperfine and magnetic interactions to laser cooling which is essential in areas of physics involving the cooling of materials to nanoKelvin temperatures such as is required in Bose-Einstein Condensation (BEC). For an excellent interactive website on laser cooling and BEC I strongly recommend a visit to:-

<http://www.colorado.edu/physics/PhysicsInitiative/Physics2000.03.99/bec/index.html>

Other sites of interest can be found at

<http://www.physicscentral.com/action/action-00-4.html>

<http://www.colorado.edu/physics/PhysicsInitiative/Physics2000/index.pl>

8.1. Motion and Temperature

Recall Boltzman's equipartition of energy - that molecules in thermal equilibrium have the same average energy, $\frac{1}{2}kT$ associated with each independent degree of freedom of their motion so that the average kinetic energy associated with three degrees of translation freedom is

$$\frac{1}{2}mv^2 = \frac{3}{2}kT \quad (8-1)$$

and hence can be taken as a definition of *kinetic temperature* with

$$T = \frac{mv^2}{3k} \quad (8-2)$$

Or for a given temperature T the average speed of a particle of mass m will be

$$v = \sqrt{\frac{3kT}{m}} \quad (8-3)$$

This suggests that if we can reduce the average speed of the particles we are equivalently lowering their temperature.

8.2. Some Basic Quantum Results

Let us recall some basic properties of photons and particles. For a photon we have the standard energy and momentum results

$$E = hf = \frac{hc}{\lambda} \quad (8-4)$$

$$p = \frac{h}{\lambda} \quad (8-5)$$

and for a non-relativistic particle of mass m travelling with a speed v we have for the de Broglie wavelength, λ_{dB} ,

$$\lambda_{dB} = \frac{h}{mv} \quad (8-6)$$

From (8-3) and (8-6) we can relate the de Broglie wavelength for an atom of mass m to temperature by writing

$$T = \frac{h^2}{3mk\lambda_{dB}^2} \quad (8-7)$$

In thermal physics it is common to define the *thermal de Broglie wavelength* as

$$\lambda_{th} = \frac{h}{\sqrt{2\pi mkT}} \quad (8-8)$$

Note that λ_{th} decreases as the square root of the temperature T . BEC arises when atoms are cooled to the temperature where λ_{th} is comparable with the interatomic spacing of the atoms and the atomic wave packets overlap to make a gas of indistinguishable particles with the result that a cloud of atoms all occupy the same quantum state. Note that for alkali atoms the BEC involves the alkali atoms as a very dilute vapour NOT a solid or liquid. Indeed typical densities are of the order of 10^{-5} of that of air. The vapour must consist of weakly interacting atoms otherwise liquifaction or solidification will occur before BEC can happen. Typical BEC's have dimensions $\sim 100\mu m$ which may be compared with the Bohr radius of a H -atom of $1a_0 = 0.0529nm$. Recall that for one atomic mass unit (amu)

$$1amu = 1.6605402 \times 10^{-27}kg$$

and specifically, in amu it is found that

$$^{23}Na \quad 22.989769$$

$$^{85}Rb \quad 84.911789$$

$$^{87}Rb \quad 86.909180$$

$$^{133}Cs \quad 132.905451$$

Furthermore,

$$h = 6.6260755 \times 10^{-34}Js \quad k = 1.380658 \times 10^{-23}JK^{-1}$$

To obtain BEC we clearly have to be able to cool the alkali vapour to orders of nanokelvin temperatures. To obtain sufficiently low temperatures for BEC to occur requires unconventional cooling techniques. Here we only sketch some of the broad features of these techniques.

It has been known since the mid-1920's that for BEC to occur the phase space density, ρ , defined as the number of particles per cubic thermal de Broglie wavelength, λ_{th} , must be of the order of unity, indeed it was early shown that if the atoms are bosons then BEC occurs when[‡] ρ reaches the critical value of 2.612. In most BEC experiments this requires temperatures between $500nK$ and $2\mu K$ with densities between 10^{14} and 10^{15} atoms per cm^3 .

8.3. Absorption and Emission of Photons

The absorption or emission of a photon will possibly occur between two states of energy E_1 and E_2 if the energy of the photon matches the energy difference $\Delta E = |E_1 - E_2|$ i.e.

$$\Delta E = \hbar\omega \quad (8-9)$$

where the wavelength λ is related to the angular frequency ω_0 in vacuum and to the wavenumber k_L by

$$\lambda = \frac{2\pi c}{\omega_0} \quad \text{and} \quad k_L = \frac{2\pi}{\lambda} \quad (8-10)$$

Note we say *possibly* as satisfaction of the energy criterion is not sufficient since in most cases certain selection rules must be satisfied.

If a resonant photon is absorbed or emitted by an atom the atoms velocity will be changed by a recoil velocity, v_r , given by

$$v_r = \frac{\hbar k_L}{m} \quad (8-11)$$

The recoil energy is related to the photon energy such that

$$\hbar\omega_r = \frac{\hbar^2 k_L^2}{2m} \quad (8-12)$$

This gives us the idea of how to use a laser to lower the velocity of a cloud of *Rb* vapour by using a laser tuned to a particular energy separation. Atoms approaching the laser beam will have their velocity reduced by absorption of photons while those travelling away from the beam will have their velocity increased. Of course things are more complicated. The photons of the incident light will be Doppler shifted due to the motion of the incident atoms. The Doppler shift of the incident light of frequency ω_0 due to the motion of the atom is

$$\Delta\omega_d = \frac{v_r}{c}\omega_0 \quad (8-13)$$

which, upon noting (8-12) and (8-10), becomes simply

$$\Delta\omega_d = 2\omega_r \quad (8-14)$$

[‡] For an early account of BEC see:- J E Mayer and M G Mayer, *Statistical Mechanics*, New York: J Wiley & Sons (1940) (p416)

8.4. Laser Cooling

To observe BEC and related phenomena it is necessary to cool the extremely low pressure vapour, commonly an alkali metal vapour such as $^{87}_{37}\text{Rb}$ to nanokelvin temperatures. This is accomplished using lasers, magnetic fields and sometimes electric fields. Usually a combination of methods are used, such as laser cooling, Doppler cooling, polarised gradient cooling and evaporative cooling. In laser cooling one usually chooses a specific atomic transition and uses three intersecting orthogonal pairs (mutually perpendicular) of counter-propagating laser beams of equal intensity and frequency tuned to just below the atomic transition frequency with the vapour trapped at the point of intersection of the beams. As noted earlier the absorption of photons slows down the atoms by transferring their momentum to the atoms against the direction of motion of the atom; spontaneous emission by the atom occurs in randomly oriented directions. Eventually, repetition of this process results in a slowing down of the atoms and hence a dramatic lowering of the temperature.

The Doppler effect plays a key role in laser cooling. Consider an atom travelling along the axis of a particular laser beam that has been tuned just below the resonance frequency of the atomic transition. If the atom is travelling towards the laser beam the atom will be Doppler shifted into resonance whereas if the atom is travelling in the opposite direction it will be Doppler shifted further away from the resonance frequency. As noted earlier the faster the atom is moving the greater the Doppler shift. If the atom is moving too fast towards the laser beam it will shift the atom beyond the resonance frequency. We now see the rationale for using counter-propagating laser beams of identical frequency and intensity. If the two beams are collinear then an atom moving in any direction along the beam axis has a greater absorption of photons travelling in the opposite direction. As a result the atom will experience, on average, a loss of momentum and hence a force that slows it down giving an effective cooling of the atom.

Thus it is as if the atom is being forced, in three dimensions, through a dense molasses like liquid and hence the picturesque terminology *optical molasses*. In this case the viscous medium is actually light. So, where does hyperfine structure and the Zeeman effect enter?

8.5. Magneto-Optical Traps

Two practical problems arise - containment of the vapour and tuning the laser frequency. The walls of any container will be “hot” so the vapour must be kept away from the walls. As to tuning the laser there are two possibilities. One is to adjust the frequency of the photons or change the frequency of the atomic transition. Recall that an alkali atom normally exhibits hyperfine structure. The $D2$ transitions, in the absence of hyperfine structure, correspond to the optical transitions $^2S_{\frac{1}{2}} \rightarrow ^2P_{\frac{3}{2}}$ (see S7.6) As a result of hyperfine interactions the $^2S_{\frac{1}{2}}$ groundstate splits into two hyperfine levels with $F = I \pm \frac{1}{2}$ and the $^2P_{\frac{3}{2}}$ level into up to four hyperfine levels,

in the case of ${}^{87}_{37}\text{Rb}$, with $F = 0, 1, 2, 3$. If we apply a weak external magnetic field we split each hyperfine level into $2F + 1$ Zeeman sublevels each characterised by a magnetic quantum number, M_F , where

$$M_F = F, F - 1, \dots, -F \quad (8-15)$$

The magnetic field shifts the energies of the hyperfine levels in proportion to the quantum number M_F and the strength of the magnetic field. Thus we can use a weak magnetic field to change the frequency of the atomic transitions rather than needing to change the frequency of the lasers. Furthermore, if we use circularly polarised laser beams, we can have σ_+ (right-circularly polarised) in one direction and σ_- (left-circularly polarised) in the opposite direction (Recall S7.1). The σ_+ light will only be absorbed if the value of M_F is *increased* by one unit while the σ_- light will only be absorbed if M_F is *decreased* by one unit.

As a concrete example let us assume that an atom is in its groundstate ${}^2S_{\frac{1}{2}}$ with say $F = 1$ and the lasers are tuned to just below the resonance frequency of the $F = 2$ hyperfine level of the excited ${}^2P_{\frac{3}{2}}$ level. The application of a weak magnetic field results in both levels splitting. The groundstate splits into three Zeeman sublevels with $M_F = \pm 1, 0$ with the $M_F = -1$ lowest in energy while the $F = 2$ excited level splits into five sublevels with $M_F = \pm 2, \pm 1, 0$. From S7.1, assuming circularly polarised light we from the $M_F = -1$ groundstate two allowed transitions $M_F = -1 \rightarrow M_F = -2$ for σ_- absorption and $M_F = -1 \rightarrow M_F = 0$ for σ_+ absorption. Let us now assume that the atom is moving along the z -axis away from $z = 0$ and that the $M_F = -2$ level is closer to the resonance frequency than is the $M_F = 0$ level. As a consequence there will be more absorption of the σ_- light than of the σ_+ light and hence the the effect of the net momentum imparted by the photons is to push the atom back towards $z = 0$. Adding a magnetic field that is zero at $z = 0$, the point of intersection of the polarised laser beams, and linearly increasing with distance z results in any atom not at the centre, ($z = 0$), having its resonance frequency Zeeman shifted towards the region of zero magnetic field. Such an arrangement confines the cooled atoms to the region of zero magnetic field and hence constitutes a *magneto-optical trap*. Such a trap can reduce the temperature of ${}^{87}_{37}\text{Rb}$ atoms to $\sim 240\mu\text{K}$. In practice one can cool to much lower temperatures using so-called polarised gradient cooling to get to $\sim 10\mu\text{K}$. To reach still lower temperatures requires further technology such as evaporative cooling where “hot” atoms are boiled off leaving “cold” atoms behind much as in the traditional cooling of a hot cup of coffee. Such techniques allow one to explore temperatures in the nanoKelvin range.

Lecture 9

He who can, does; he who cannot teaches

George Bernard Shaw *Man & Superman* (1903)

Those who can, do; those who can't, attend conferences

Daily Telegraph 6th August, (1979)

9. Ions in Crystals

So far we have considered isolated atoms and ions. Now we consider the additional effects that arise when an ion is confined in a crystalline environment. I will restrict attention to the particular cases of lanthanides and actinides and hence to principally ions containing electrons in the $4f$ - or $5f$ -shell. Here the spin-orbit interaction cannot be ignored and crystal field splittings are usually two orders of magnitude larger than hyperfine splittings. This means working in a $|\alpha SLJM_JIM_IM_F\rangle$ basis rather than a $|\alpha SLJIFM_F\rangle$ basis. Furthermore, a crystalline environment usually means describing the crystal fields surrounding the ions of interest in terms of finite point symmetry groups that are subgroups of the rotation group SO_3 , commonly extended to its covering group, SU_2 . In some cases the crystal field will be dominated by the symmetry of a point group G with a small departure from that symmetry to that described by a subgroup, $H \in G$. By way of examples we shall primarily concentrate on the ions Pr^{3+} and Ho^{3+} which will involve the electron configurations $4f^2$ and $4f^{10}$ respectively and whose hyperfine structure has been studied experimentally in some detail^{45–53}.

9.1. Crystal Field Splittings

For an ion in free space one has spherical symmetry and each energy level may be characterised by its total angular momentum \mathbf{J} (neglecting, at this moment, nuclear angular momentum) and each level will be $2J + 1$ -fold degenerate. This degeneracy will be at least partially lifted if the ion is placed in a crystal. The amount of degeneracy lifting depends on the value of \mathbf{J} and the symmetry surrounding the ion. The number of components into which a state of a given angular momentum \mathbf{J} splits in a symmetry field characterised by a site point group \mathcal{G} may be determined from a knowledge of the *branching rules* for the decomposition of the irreducible representation $[J]$ under the group-subgroup reduction $SU_2 \rightarrow \mathcal{G}$. This problem was first considered by Bethe⁵⁴ with later corrections by Opechowski⁵⁵. Detailed tables have been given by Koster *et al*⁵⁶. Here I restrict attention to simply giving results as required. Those of you unfamiliar with group theory will need to consult textbooks or my earlier lectures on symmetry. We now give some of the relevant data we shall

require for discussing the Pr^{3+} ion in a $CsCdBr_3$ crystalline environment followed by data for discussing the Ho^{3+} ion in $LiYF_4$ crystals.

9.2. Data on the Finite Groups $O \sim S_4$ and $C_{3v} \sim S_3$

The finite groups $O \sim S_4$ and $C_{3v} \sim S_3$ play a key role in understanding the Pr^{3+} ion in a $CsCdBr_3$ crystalline environment. The crystal field is predominantly octahedral with a small trigonal component (C_{3v}). Here we now collect together some data on the finite groups $O \sim S_4$ and $C_{3v} \sim S_3$. The natural stable isotope of Pr has a nuclear spin $I = \frac{5}{2}$ while the electronic angular momentum has integer values. As a result we want information on the double groups.

9.3. Table 9-1. The character table of the double Octahedral group O

$$\begin{array}{c}
 O \\
 \Gamma_1 \\
 \Gamma_2 \\
 \Gamma_3 \\
 \Gamma_4 \\
 \Gamma_5 \\
 \Gamma_6 \\
 \Gamma_7 \\
 \Gamma_8
 \end{array}
 \begin{array}{c}
 E \quad \bar{E} \quad 8C_3 \quad 8\bar{C}_3 \quad 3C_2, 3\bar{C}_2 \quad 6C'_2, 6\bar{C}'_2 \quad 6C_4 \quad 6\bar{C}_4 \\
 \left(\begin{array}{cccccccc}
 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 \\
 2 & 2 & -1 & -1 & 2 & 0 & 0 & 0 \\
 3 & 3 & 0 & 0 & -1 & -1 & 1 & 1 \\
 3 & 3 & 0 & 0 & -1 & 1 & -1 & -1 \\
 2 & -2 & 1 & -1 & 0 & 0 & \sqrt{2} & -\sqrt{2} \\
 2 & -2 & 1 & -1 & 0 & 0 & -\sqrt{2} & \sqrt{2} \\
 4 & -4 & -1 & 1 & 0 & 0 & 0 & 0
 \end{array} \right)
 \end{array}
 \quad (9-1)$$

9.4. Table 9-2. The character table of the double group C_{3v}

$$\begin{array}{c}
 C_{3v} \\
 \Gamma_1 \\
 \Gamma_2 \\
 \Gamma_3 \\
 \Gamma_4 \\
 \Gamma_5 \\
 \Gamma_6
 \end{array}
 \begin{array}{c}
 E \quad \bar{E} \quad 2C_3 \quad 2\bar{C}_3 \quad 3\sigma_v \quad 3\bar{\sigma}_v \\
 \left(\begin{array}{cccccc}
 1 & 1 & 1 & 1 & 1 & 1 \\
 1 & 1 & 1 & 1 & -1 & -1 \\
 2 & 2 & -1 & -1 & 0 & 0 \\
 1 & -1 & -1 & 1 & i & -i \\
 1 & -1 & -1 & 1 & -i & i \\
 2 & -2 & 1 & -1 & 0 & 0
 \end{array} \right)
 \end{array}
 \quad (9-2)$$

Note that the irreps Γ_4, Γ_5 form a complex pair (or doublet) sometimes designated as Y with Γ_6 designated as X (e.g. see B R Judd, *Proc. R. Soc.* **A241**, 122 (1957)).

9.5. Table 9-3. $SO(3) \rightarrow O$ branching rules

\mathcal{D}_J	J	O	
1	0	Γ_1	
3	1	Γ_4	
5	2	$\Gamma_3 + \Gamma_5$	
7	3	$\Gamma_2 + \Gamma_4 + \Gamma_5$	
9	4	$\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$	
11	5	$\Gamma_3 + 2\Gamma_4 + \Gamma_5$	
13	6	$\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5$	
2	1/2	Γ_6	
4	3/2	Γ_8	
6	5/2	$\Gamma_7 + \Gamma_8$	
8	7/2	$\Gamma_6 + \Gamma_7 + \Gamma_8$	
10	9/2	$\Gamma_6 + 2\Gamma_8$	
12	11/2	$\Gamma_6 + \Gamma_7 + 2\Gamma_8$	(9-3)

9.6. Table 9-4. $O \rightarrow C_{3v}$ branching rules

\mathcal{D}_Γ	O	C_{3v}	
1	Γ_1	Γ_1	
1	Γ_2	Γ_2	
2	Γ_3	Γ_3	
3	Γ_4	$\Gamma_2 + \Gamma_3$	
3	Γ_5	$\Gamma_1 + \Gamma_3$	
2	Γ_6	$\Gamma_4 + \Gamma_5$	(9-4)

9.7. Table 9-5. Kronecker products for the Octahedral group O

	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8
Γ_1	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8
Γ_2	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8
Γ_3	Γ_2	Γ_1	Γ_3	Γ_5	Γ_4	Γ_7	Γ_6	Γ_8
Γ_4	Γ_3	Γ_3	$\{\Gamma_1 + \Gamma_3\} + [\Gamma_2]$	$\Gamma_4 + \Gamma_5$	$\Gamma_4 + \Gamma_5$	Γ_7	Γ_6	Γ_8
Γ_5	Γ_4	Γ_5	$\Gamma_4 + \Gamma_5$	$\{\Gamma_1 + \Gamma_3 + \Gamma_4\} + [\Gamma_5]$	$\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5$	$\Gamma_6 + \Gamma_8$	$\Gamma_7 + \Gamma_8$	$\Gamma_6 + \Gamma_7 + 2\Gamma_8$
Γ_6	Γ_5	Γ_4	$\Gamma_4 + \Gamma_5$	$\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5$	$\{\Gamma_1 + \Gamma_3 + \Gamma_4\} + [\Gamma_5]$	$\Gamma_7 + \Gamma_8$	$\Gamma_6 + \Gamma_8$	$\Gamma_6 + \Gamma_7 + 2\Gamma_8$
Γ_7	Γ_6	Γ_7	Γ_7	$\Gamma_6 + \Gamma_8$	$\Gamma_7 + \Gamma_8$	$\{\Gamma_4\} + [\Gamma_1]$	$\Gamma_2 + \Gamma_5$	$\Gamma_3 + \Gamma_4 + \Gamma_5$
Γ_8	Γ_7	Γ_6	Γ_6	$\Gamma_7 + \Gamma_8$	$\Gamma_6 + \Gamma_8$	$\Gamma_2 + \Gamma_5$	$\{\Gamma_4\} + [\Gamma_1]$	$\Gamma_3 + \Gamma_4 + \Gamma_5$
Γ_8	Γ_8	Γ_8	Γ_8	$\Gamma_6 + \Gamma_7 + 2\Gamma_8$	$\Gamma_6 + \Gamma_7 + 2\Gamma_8$	$\Gamma_3 + \Gamma_4 + \Gamma_5$	$\Gamma_3 + \Gamma_4 + \Gamma_5$	$\{\Gamma_2 + 2\Gamma_4 + \Gamma_5\} + [\Gamma_1 + \Gamma_3 + \Gamma_5]$

(9-5)

9.8. Table 9-6. Kronecker products for the trigonal group C_{3v}

$$\begin{array}{c}
\Gamma_1 \quad \Gamma_2 \quad \Gamma_3 \quad \Gamma_4 \quad \Gamma_5 \quad \Gamma_6 \\
\Gamma_1 \left(\begin{array}{cccccc}
\Gamma_1 & \Gamma_2 & & \Gamma_3 & & \Gamma_4 & \Gamma_5 & & \Gamma_6 \\
\Gamma_2 & \Gamma_1 & & \Gamma_3 & & \Gamma_5 & \Gamma_4 & & \Gamma_6 \\
\Gamma_3 & \Gamma_3 & \Gamma_3 & \{\Gamma_1 + \Gamma_3\} + [\Gamma_2] & \Gamma_6 & \Gamma_6 & & \Gamma_4 + \Gamma_5 + \Gamma_6 & \\
\Gamma_4 & \Gamma_4 & \Gamma_5 & & \Gamma_6 & \Gamma_2 & \Gamma_1 & & \Gamma_3 \\
\Gamma_5 & \Gamma_5 & \Gamma_4 & & \Gamma_6 & \Gamma_1 & \Gamma_2 & & \Gamma_3 \\
\Gamma_6 & \Gamma_6 & \Gamma_6 & \Gamma_4 + \Gamma_5 + \Gamma_6 & \Gamma_3 & \Gamma_3 & & \{\Gamma_2 + \Gamma_3\} + [\Gamma_1] &
\end{array} \right) \quad (9-6)
\end{array}$$

In (9-5) and (9-6) the terms involved in the *symmetric* part of the Kronecker squares are enclosed in $\{, \}$ brackets and the antisymmetric terms in $[,]$ brackets.

9.9. Data on the Finite Groups for Ho^{3+} Ions in $LiYF_4$ Crystals

Ho^{3+} substitutes for the Y^{3+} in $LiYF_4$ at sites of tetragonal symmetry described by the point group S_4 , not to be confused with the symmetric group on four objects! Since the ionic radii of Ho^{3+} and Y^{3+} are almost the same there is little, if any, lattice distortion.

The group S_4 is a cyclic group isomorphic to C_4 , consisting of the identity, E , the rotation-reflection $S_4 = IC_4^{-1}$, a two-fold rotation C_2 and the inverse operator $S_4^{-1} = IC_4$. All rotations are taken about the z -axis. The character table is given below:-

	E	\bar{E}	S_4^{-1}	\bar{S}_4^{-1}	C_2	\bar{C}_2	S_4	\bar{S}_4
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1	1	-1	-1	1	1	-1	-1
Γ_3	1	1	i	i	-1	-1	$-i$	$-i$
Γ_4	1	1	$-i$	$-i$	-1	-1	i	i
Γ_5	1	-1	ω	$-\omega$	i	$-i$	$-\omega^3$	ω
Γ_6	1	-1	$-\omega^3$	ω^3	$-i$	i	ω	$-\omega^3$
Γ_7	1	-1	$-\omega$	ω	i	$-i$	ω^3	ω
Γ_8	1	-1	ω^3	$-\omega^3$	$-i$	i	$-\omega$	ω^3

9.10. Kronecker Products in S_4

The Kronecker products for S_4 may be easily established from the character table to yield the results given in Table 9-8 below:-

	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8
Γ_1	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8
Γ_2	Γ_2	Γ_1	Γ_4	Γ_3	Γ_7	Γ_8	Γ_5	Γ_6
Γ_3	Γ_3	Γ_4	Γ_2	Γ_1	Γ_8	Γ_5	Γ_6	Γ_7
Γ_4	Γ_4	Γ_3	Γ_1	Γ_2	Γ_6	Γ_7	Γ_8	Γ_5
Γ_5	Γ_5	Γ_7	Γ_8	Γ_6	Γ_3	Γ_1	Γ_4	Γ_2
Γ_6	Γ_6	Γ_8	Γ_5	Γ_7	Γ_1	Γ_4	Γ_2	Γ_3
Γ_7	Γ_7	Γ_5	Γ_6	Γ_8	Γ_4	Γ_2	Γ_3	Γ_1
Γ_8	Γ_8	Γ_6	Γ_7	Γ_5	Γ_2	Γ_3	Γ_1	Γ_4

Table 9-8. Kronecker Products for the Point Group S_4

9.11. The $O_3 \Rightarrow S_4$ Branching Rules

The degeneracies of the states of a given J in a crystal field of S_4 symmetry is determined by the $O_3 \Rightarrow S_4$ branching rules where O_3 is the *full* orthogonal group since the point group S_4 includes reflections and hence improper rotations. The irreducible representations of O_3 are labelled with a + or - superscript to distinguish those irreducible representations that are *even* under inversion (+) from those that are *odd* (-). Thus the results are given in the table below for integer and half-integer values of J . The decompositions of the D_j^- irreducible representations of O_3 may be obtained from those of D_j^+ by multiplication by Γ_2 . Note that since the spin irreducible representations of S_4 are all two-dimensional the for half-integer angular momentum the levels in a crystal with point group symmetry S_4 must necessarily remain two-fold degenerate. An external magnetic field is required to lift this residual Kramer's degeneracy.

In the case of Ho^{3+} in $LiYF_4$ the electronic angular momentum J is an integer and the Stark electric field degeneracies follow from the appropriate $O_3 \Rightarrow S_4$ branching rules. Adding the half-integer angular momentum of the Ho nucleus results in states of total angular momentum \mathbf{F} which is half-integer and hence the degeneracies are always two-fold. The hyperfine interaction will also change selection rules, as we shall see later.

D_J^+	S_4	D_J^-	S_4
D_0^+	Γ_1	D_0^-	Γ_2
D_1^+	$\Gamma_1 + \Gamma_3 + \Gamma_4$	D_1^-	$\Gamma_2 + \Gamma_3 + \Gamma_4$
D_2^+	$\Gamma_1 + 2\Gamma_2 + \Gamma_3 + \Gamma_4$	D_2^-	$2\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$
D_3^+	$\Gamma_1 + 2\Gamma_2 + 2\Gamma_3 + 2\Gamma_4$	D_3^-	$2\Gamma_1 + \Gamma_2 + 2\Gamma_3 + 2\Gamma_4$
D_4^+	$3\Gamma_1 + 2\Gamma_2 + 2\Gamma_3 + 2\Gamma_4$	D_4^-	$2\Gamma_1 + 3\Gamma_2 + 2\Gamma_3 + 2\Gamma_4$
D_5^+	$3\Gamma_1 + 2\Gamma_2 + 3\Gamma_3 + 3\Gamma_4$	D_5^-	$2\Gamma_1 + 3\Gamma_2 + 3\Gamma_3 + 3\Gamma_4$
D_6^+	$3\Gamma_1 + 4\Gamma_2 + 3\Gamma_3 + 3\Gamma_4$	D_6^-	$4\Gamma_1 + 3\Gamma_2 + 3\Gamma_3 + 3\Gamma_4$
D_7^+	$3\Gamma_1 + 4\Gamma_2 + 4\Gamma_3 + 4\Gamma_4$	D_7^-	$4\Gamma_1 + 3\Gamma_2 + 4\Gamma_3 + 4\Gamma_4$
D_8^+	$5\Gamma_1 + 4\Gamma_2 + 4\Gamma_3 + 4\Gamma_4$	D_8^-	$4\Gamma_1 + 5\Gamma_2 + 4\Gamma_3 + 4\Gamma_4$
$D_{1/2}^+$	$\Gamma_5 + \Gamma_6$	$D_{1/2}^-$	$\Gamma_7 + \Gamma_8$
$D_{3/2}^+$	$\Gamma_5 + \Gamma_6 + \Gamma_7 + \Gamma_8$	$D_{3/2}^-$	$\Gamma_5 + \Gamma_6 + \Gamma_7 + \Gamma_8$
$D_{5/2}^+$	$\Gamma_5 + \Gamma_6 + 2\Gamma_7 + 2\Gamma_8$	$D_{5/2}^-$	$2\Gamma_5 + 2\Gamma_6 + \Gamma_7 + \Gamma_8$
$D_{7/2}^+$	$2\Gamma_5 + 2\Gamma_6 + 2\Gamma_7 + 2\Gamma_8$	$D_{7/2}^-$	$2\Gamma_5 + 2\Gamma_6 + 2\Gamma_7 + 2\Gamma_8$
$D_{9/2}^+$	$3\Gamma_5 + 3\Gamma_6 + 2\Gamma_7 + 2\Gamma_8$	$D_{9/2}^-$	$2\Gamma_5 + 2\Gamma_6 + 3\Gamma_7 + 3\Gamma_8$
$D_{11/2}^+$	$3\Gamma_5 + 3\Gamma_6 + 3\Gamma_7 + 3\Gamma_8$	$D_{11/2}^-$	$3\Gamma_5 + 3\Gamma_6 + 3\Gamma_7 + 3\Gamma_8$
$D_{13/2}^+$	$3\Gamma_5 + 3\Gamma_6 + 4\Gamma_7 + 4\Gamma_8$	$D_{13/2}^-$	$4\Gamma_5 + 4\Gamma_6 + 3\Gamma_7 + 3\Gamma_8$
$D_{15/2}^+$	$4\Gamma_5 + 4\Gamma_6 + 4\Gamma_7 + 4\Gamma_8$	$D_{15/2}^-$	$4\Gamma_5 + 4\Gamma_6 + 4\Gamma_7 + 4\Gamma_8$
$D_{17/2}^+$	$5\Gamma_5 + 5\Gamma_6 + 4\Gamma_7 + 4\Gamma_8$	$D_{17/2}^-$	$4\Gamma_5 + 4\Gamma_6 + 5\Gamma_7 + 5\Gamma_8$
$D_{19/2}^+$	$5\Gamma_5 + 5\Gamma_6 + 5\Gamma_7 + 5\Gamma_8$	$D_{19/2}^-$	$5\Gamma_5 + 5\Gamma_6 + 5\Gamma_7 + 5\Gamma_8$
$D_{21/2}^+$	$5\Gamma_5 + 5\Gamma_6 + 6\Gamma_7 + 6\Gamma_8$	$D_{21/2}^-$	$6\Gamma_5 + 6\Gamma_6 + 5\Gamma_7 + 5\Gamma_8$
$D_{23/2}^+$	$6\Gamma_5 + 6\Gamma_6 + 6\Gamma_7 + 6\Gamma_8$	$D_{23/2}^-$	$6\Gamma_5 + 6\Gamma_6 + 6\Gamma_7 + 6\Gamma_8$

Table 9-9. Branching Rules for $O_3 \Rightarrow S_4$

9.12. The D_{2d} Symmetry

The point group D_{2d} contains S_4 as a subgroup and hence exists as an *approximate* symmetry for describing Ho^{3+} in $LiYF_4$ crystals. D_{2d} is isomorphic to the group D_4 and consists of the operations of D_2 and in addition has the operations S_4 and S_4^{-1} about one of the two-fold axes of rotation about the z -axis, as well as two reflections σ_d through perpendicular planes containing the axis of S_4 and which bisect the angles between the two rotations of D_2 about the axes x and y , $C_{2'}$. The character table, Kronecker products, and $O_3 \Rightarrow D_{2d}$ decompositions are given in Koster *etal*. We shall refer to these later.

9.13. The Crystal Field Expansion

While group theory tells us the *number* of levels into which a free ion level of angular momentum \mathbf{J} will split when the symmetry of the ion is reduced to that of some point group \mathcal{G} it tells us nothing about the *size* of the splittings. To that end

it is useful to consider a Hamiltonian \mathcal{H} that consists of a free ion part, \mathcal{H}_F , and a perturbing part, \mathcal{V}_c , such that

$$\mathcal{H} = \mathcal{H}_F + \mathcal{V}_c \quad (9-7)$$

The “free ion” part, \mathcal{H} , will include such terms as the Coulomb and spin-orbit interactions and possibly additional effective interactions to represent configuration interaction effects etc. The perturbing part, \mathcal{V}_c , represents terms that attempt to explicitly take into account the perturbation produced by the crystal. To a first approximation we will represent \mathcal{V}_c in terms of a linear combination of the tensor operators, $C_q^{(k)}$, introduced in S2.10 to give

$$\mathcal{V}_c = \sum_{k,q} B_q^k \sum_i (C_q^{(k)})_i \quad (9-8)$$

The quantities, B_q^k , are the coefficients of the linear combination, commonly called the *crystal field parameters*. The second summation is over all of the electrons of the ion of interest. Here we limit our attention to single particle type operators. The values of k and q are restricted by the symmetry of the point group and by the type of electron orbitals being considered. If the bra and ket states are of the same parity then k is necessarily *even* while for bra and ket states of opposite parity k will necessarily be *odd*. Furthermore, if the electron orbitals are ℓ and ℓ' then

$$\ell + \ell' \geq k \geq |\ell - \ell'| \quad (9-9)$$

Thus within a f^N configuration we would have

$$k = 0, 2, 4, 6 \quad \ell = \ell' = 3 \quad (9-10)$$

whereas the states of the f^N configuration would be coupled to the states of the opposite parity configurations, such as $f^{N-1}d$ or $f^{N-1}g$, by the *odd* values of k

$$k = \begin{cases} 1, 3, 5 & \ell = 3, \ell' = 2 \\ 1, 3, 5, 7 & \ell = 3, \ell' = 4 \end{cases} \quad (9-11)$$

These odd terms play a key role in the Judd-Ofelt theory^{57,58} of intensities for lanthanide and actinide ions in crystals.

Note that the term with $k = q = 0$ is spherically symmetric so leads to a uniform shift of all the levels of the configuration of interest. Further note that while the B_q^k will be real functions of the radial distance, the non-cylindrical terms (i.e. terms with $|q| > 0$) will not necessarily be real functions of the angular coordinates.

For f^N configurations the matrix elements of \mathcal{V}_c will be

$$\begin{aligned} & \langle f^N \alpha SLJM_J | \mathcal{V}_c | f^N \alpha' SL'J'M'_J \rangle \\ & = \sum_{k,q} B_q^k \langle f^N \alpha SLJM_J | U_q^{(k)} | f^N \alpha' SL'J'M'_J \rangle \langle f || C^{(k)} || f \rangle \end{aligned} \quad (9-12)$$

and from the Wigner-Eckart theorem

$$\begin{aligned} & \langle f^N \alpha SLJM_J | U_q^{(k)} | f^N \alpha' SL'J'M_J' \rangle \\ &= (-1)^{J-M_J} \begin{pmatrix} J & k & J' \\ -M_J & q & M_J' \end{pmatrix} \langle f^N \alpha SLJ || U^{(k)} || f^N \alpha' SL'J' \rangle \end{aligned} \quad (9-13)$$

where

$$\begin{aligned} & \langle f^N \alpha SLJ || U^{(k)} || f^N \alpha' SL'J' \rangle \\ &= (-1)^{S+L+J'+k} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & J' & k \\ L' & L & S \end{Bmatrix} \langle f^N \alpha SL || U^{(k)} || f^N \alpha' SL' \rangle \end{aligned} \quad (9-14)$$

The matrix elements of the doubly reduced matrix elements may be taken from the tables of Nielson and Koster⁴⁴ or from various computer programmes⁵⁹. Nielson and Koster list the matrix elements for the even values of k for the configurations ℓ^N ($\ell = p, d, f$) for $N \leq 2\ell + 1$. The corresponding matrix elements for $N > 2\ell + 1$ are obtained by multiplication by -1 of those for $\ell^{4\ell+2-N}$. Note that the matrix elements are diagonal in the spin S while the axial terms, $U_0^{(k)}$, will lead to a splitting of terms with different M_J and the non-axial terms, $U_q^{(k)}$, will mix states with $M_J - M_J' = q$. As a result J and M_J will cease to be good quantum numbers.

9.14. Point Group Symmetry Restrictions

The possible values of q are restricted by two requirements. The first being that $k \geq |q|$ and the second that the perturbing term, \mathcal{V}_c , be invariant with respect to all the symmetry operations of the relevant point group. The invariance with respect to the symmetry operations of the point group amounts to the requirement that the potential transform as the identity irreducible representation Γ_1 of the point group, \mathcal{G} . The number of independent expansion coefficients B_q^k for a given value of k is just the number of times Γ_1 occurs in the decomposition $O_3 \Rightarrow \mathcal{G}$ of the O_3 irreducible representation D_k^+ . In the case of the group, S_4 , we find from Table 9-9 that the identity irreducible representation Γ_1 occurs once for $k = 2$ and three times for $k = 4$ and $k = 6$. This may be compared with the higher symmetry group D_{2d} where Γ_1 occurs once for $k = 2$ and twice for each of $k = 4$ and $k = 6$. Thus in D_{2d} the crystal field expansion for the states of f^N configurations will be:-

$$D_{2d} : V = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_4^4 (C_{-4}^{(4)} + C_4^{(4)}) + B_0^6 C_0^{(6)} + B_4^6 (C_{-4}^{(6)} + C_4^{(6)}) \quad (9-15)$$

The potential is Hermitian with the expansion coefficients B_q^k all *real*.

The lower symmetry of the point group S_4 manifests itself in the need for an extra expansion coefficient for each of the non-axial terms. This can be realised by taking the non-axial terms as *complex* rather than real. Thus for S_4 the crystal field potential becomes:-

$$S_4 : V = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_{\pm 4}^4 C_{\pm 4}^{(4)} + B_0^6 C_0^{(6)} + B_{\pm 4}^6 C_{\pm 4}^{(6)} \quad (9-16)$$

where

$$B_{\pm q}^k = B_q^k \pm iA_q^k \quad (9-17)$$

with B_q^k and A_q^k are both real. Thus the S_4 crystal field is associated with seven independent crystal field parameters whereas D_{2d} has five independent parameters. This crystal field expansion is relevant for Ho^{3+} doped $LiYF_4$ crystals.

9.15. An Octahedral Crystal Field

In the case of Pr^{3+} doped $CsCdBr_3$ crystals To a first approximation, the Pr^{3+} ion sees a predominantly octahedral (O) crystal field which may be written as

$$V_{cryst} = B_4 \left[C_0^{(4)} - \frac{\sqrt{70}}{7} (C_3^{(4)} - C_{-3}^{(4)}) \right] + B_6 \left[C_0^{(6)} + \frac{\sqrt{210}}{24} (C_3^{(6)} - C_{-3}^{(6)}) + \frac{\sqrt{231}}{24} (C_6^{(6)} + C_{-6}^{(6)}) \right] \quad (9-18)$$

being the fourth and sixth order invariants associated with the integrity basis^{60,61} for $O \rightarrow \mathcal{T} \rightarrow C_3$. Note an *integrity basis* is the minimal set of independent invariants associated with a group \mathcal{G} such that all other invariants are polynomials of those of the minimal set. The success of parameterised crystal field calculations has more to do about getting the integrity basis right for the appropriate symmetry group than the success, or otherwise, of specific models of the crystal field.

Let us consider in some detail the behaviour of the $4f^2 \ ^3F_3$ level of Pr^{3+} in a pure octahedral field. This is the only $J = 3$ term for the $4f^2$ configuration so there is no intermediate coupling and the term can be treated as a pure LS -coupled term.

We first note that for the 3F_3 term of f^2 we have

$$\langle f^2 \ ^3F_3 || C^{(2)} || f^2 \ ^3F_3 \rangle = \frac{\sqrt{105}}{30} \quad (9-19a)$$

$$\langle f^2 \ ^3F_3 || C^{(4)} || f^2 \ ^3F_3 \rangle = -\frac{\sqrt{154}}{198} \quad (9-19b)$$

$$\langle f^2 \ ^3F_3 || C^{(6)} || f^2 \ ^3F_3 \rangle = -\frac{5\sqrt{3003}}{858} \quad (9-19c)$$

Furthermore,

$$\begin{aligned} & \langle f^2 \ ^3F_{3M} | C_q^{(k)} | f^2 \ ^3F_{3M'} \rangle \\ & = (-1)^{3-M} \begin{pmatrix} 3 & k & 3 \\ -M & q & M' \end{pmatrix} \langle f^2 \ ^3F_3 || C^{(k)} || f^2 \ ^3F_3 \rangle \end{aligned} \quad (9-20)$$

Let us construct the matrices for the operator

$$X_4 = 594 \left[C_0^{(4)} - \frac{\sqrt{70}}{7} (C_3^{(4)} - C_{-3}^{(4)}) \right] \quad (9-21)$$

where we have chosen the number 594 to yield simple matrix elements and consequently integer eigenvalues. Using (9-20) and (9-21) we obtain the matrices

$$\begin{array}{c} |^3F_{3,1}\rangle \quad |^3F_{3,-2}\rangle \\ \langle ^3F_{3,1}| \left(\begin{array}{cc} -1 & 2\sqrt{5} \\ 2\sqrt{5} & 7 \end{array} \right) \\ \langle ^3F_{3,-2}| \end{array} \quad (9-22a)$$

$$\begin{array}{c} |^3F_{3,-1}\rangle \quad |^3F_{3,2}\rangle \\ \langle ^3F_{3,-1}| \left(\begin{array}{cc} -1 & -2\sqrt{5} \\ -2\sqrt{5} & 7 \end{array} \right) \\ \langle ^3F_{3,2}| \end{array} \quad (9-22b)$$

$$\begin{array}{ccc} |^3F_{3,3}\rangle & |^3F_{3,0}\rangle & |^3F_{3,-3}\rangle \\ \langle ^3F_{3,3}| \left(\begin{array}{ccc} -3 & -3\sqrt{10} & 0 \\ -3\sqrt{10} & -6 & 3\sqrt{10} \\ 0 & 3\sqrt{10} & -3 \end{array} \right) \\ \langle ^3F_{3,0}| \\ \langle ^3F_{3,-3}| \end{array} \quad (9-22c)$$

Diagonalizing the matrices yields three distinct eigenvalues

$$-18(1) \quad -3(3) \quad 9(3) \quad (9-23)$$

with degeneracies encased in (,) brackets. The degeneracies are as expected for octahedral symmetry. The associated eigenvectors are:-

$$|(-18)\rangle = \frac{1}{3} \left[-\sqrt{2}|^3F_{3,3}\rangle - \sqrt{5}|^3F_{3,0}\rangle + \sqrt{2}|^3F_{3,-3}\rangle \right] \quad (9-24a)$$

$$|(-3)a\rangle = \frac{1}{\sqrt{2}} \left[|^3F_{3,3}\rangle + |^3F_{3,-3}\rangle \right] \quad (9-24b)$$

$$|(-3)b\rangle = \frac{1}{\sqrt{6}} \left[-\sqrt{5}|^3F_{3,1}\rangle + |^3F_{3,-2}\rangle \right] \quad (9-24c)$$

$$|(-3)c\rangle = \frac{1}{\sqrt{6}} \left[\sqrt{5}|^3F_{3,-1}\rangle + |^3F_{3,2}\rangle \right] \quad (9-24d)$$

$$|(9)a\rangle = \frac{1}{6} \left[-\sqrt{10}|^3F_{3,3}\rangle + 4|^3F_{3,0}\rangle + \sqrt{10}|^3F_{3,-3}\rangle \right] \quad (9-24e)$$

$$|(9)b\rangle = \frac{1}{\sqrt{6}} \left[|^3F_{3,1}\rangle + \sqrt{5}|^3F_{3,-2}\rangle \right] \quad (9-24f)$$

$$|(9)c\rangle = \frac{1}{\sqrt{6}} \left[|^3F_{3,-1}\rangle - \sqrt{5}|^3F_{3,2}\rangle \right] \quad (9-24g)$$

Let us repeat the above for the sixth-order operator

$$X_6 = 6864 \left[C_0^{(6)} + \frac{\sqrt{210}}{24} \left(C_3^{(6)} - C_{-3}^{(6)} \right) + \frac{\sqrt{231}}{24} \left(C_6^{(6)} + C_{-6}^{(6)} \right) \right] \quad (9-25)$$

This time we obtain the matrices

$$\begin{array}{c} |^3F_{3,1}\rangle \quad |^3F_{3,-2}\rangle \\ \langle ^3F_{3,1}| \left(\begin{array}{cc} -300 & 105\sqrt{5} \\ 105\sqrt{5} & 120 \end{array} \right) \\ \langle ^3F_{3,-2}| \end{array} \quad (9-26a)$$

$$\begin{array}{c} |^3F_{3,-1}\rangle \quad |^3F_{3,2}\rangle \\ \langle ^3F_{3,-1}| \left(\begin{array}{cc} -300 & -105\sqrt{5} \\ -105\sqrt{5} & 120 \end{array} \right) \\ \langle ^3F_{3,2}| \end{array} \quad (9-26b)$$

$$\begin{array}{c} |^3F_{3,3}\rangle \quad |^3F_{3,0}\rangle \quad |^3F_{3,-3}\rangle \\ \langle ^3F_{3,3}| \left(\begin{array}{ccc} -20 & 35\sqrt{10} & -385 \\ 35\sqrt{10} & 400 & -35\sqrt{10} \\ -385 & -35\sqrt{10} & -20 \end{array} \right) \\ \langle ^3F_{3,0}| \\ \langle ^3F_{3,-3}| \end{array} \quad (9-26c)$$

$$540(1), \quad 225(3), \quad -405(3) \quad (9-27)$$

Not surprisingly, the eigenvectors are the same as found in (9-24a-g), to within an overall phase, with the correlations (540 \rightarrow -18), (225 \rightarrow 9) and (-405 \rightarrow -3). We now give the matrices of the complete octahedral crystal field $V_{Oh} = X_4B^4 + X_6B^6$:-

$$\begin{array}{c} |^3F_{3,1}\rangle \quad |^3F_{3,-2}\rangle \\ \langle ^3F_{3,1}| \left(\begin{array}{cc} -B^4 - 300B^6 & \sqrt{5}(2B^4 + 105B^6) \\ \sqrt{5}(2B^4 + 105B^6) & 7B^4 + 120B^6 \end{array} \right) \\ \langle ^3F_{3,-2}| \end{array} \quad (9-28a)$$

$$\begin{array}{c} |^3F_{3,-1}\rangle \quad |^3F_{3,2}\rangle \\ \langle ^3F_{3,-1}| \left(\begin{array}{cc} -B^4 - 300B^6 & -\sqrt{5}(2B^4 + 105B^6) \\ -\sqrt{5}(2B^4 + 105B^6) & 7B^4 + 120B^6 \end{array} \right) \\ \langle ^3F_{3,2}| \end{array} \quad (9-28b)$$

$$\begin{array}{c} |^3F_{3,3}\rangle \quad |^3F_{3,0}\rangle \quad |^3F_{3,-3}\rangle \\ \langle ^3F_{3,3}| \left(\begin{array}{ccc} -3B^4 - 20B^6 & \sqrt{10}(-3B^4 + 35B^6) & -385B^6 \\ \sqrt{10}(-3B^4 + 35B^6) & -6B^4 + 400B^6 & \sqrt{10}(3B^4 - 35B^6) \\ -385B^6 & \sqrt{10}(3B^4 - 35B^6) & -3B^4 - 20B^6 \end{array} \right) \\ \langle ^3F_{3,0}| \\ \langle ^3F_{3,-3}| \end{array} \quad (9-28c)$$

The above matrices may be rewritten in terms of the octahedral states given in (9-24a-g) to give

$$\begin{array}{c} |(-3)a\rangle \quad |(-3)b\rangle \quad |(-3)c\rangle \\ \langle (-3)a| \left(\begin{array}{ccc} -3B^4 - 405B^6 & 0 & 0 \\ 0 & -3B^4 - 405B^6 & 0 \\ 0 & 0 & -3B^4 - 405B^6 \end{array} \right) \\ \langle (-3)b| \\ \langle (-3)c| \end{array} \quad (9-29a)$$

$$\begin{array}{c} |(\mathbf{9})a\rangle \quad |(\mathbf{9})b\rangle \quad |(\mathbf{9})c\rangle \\ \langle(\mathbf{9})a| \left(\begin{array}{ccc} 9B^4 + 225B^6 & 0 & 0 \\ 0 & 9B^4 + 225B^6 & 0 \\ 0 & 0 & 9B^4 + 225B^6 \end{array} \right) \\ \langle(\mathbf{9})b| \\ \langle(\mathbf{9})c| \end{array} \quad (9-29b)$$

$$\begin{array}{c} |(-18)\rangle \\ \langle(-18)| \left(-18B^4 + 540B^6 \right) \end{array} \quad (9-29c)$$

Not surprisingly, the matrices are diagonal in the octahedral basis.

9.16. Identification of the Octahedral States for 3F_3

Inspection of Table 9-3 shows that in an octahedral field a state with $J = 3$ will split into three sublevels that belong to the $\Gamma_2, \Gamma_4, \Gamma_5$ irreducible representations of the octahedral group. The Γ_2 irreducible representation is one-dimensional while the Γ_4 and Γ_5 irreducible representations are both three-dimensional. This is consistent with our finding three distinct eigenvalues, one non-degenerate and two that were three-fold degenerate. Thus the eigenvector $|(-18)\rangle$ given in (9-24a) must be associated with the Γ_2 irreducible representation of the octahedral group. The correspondences for the other six eigenvectors must now be determined. This could be achieved by examining their behaviour under the symmetry operations of the octahedral group. It is instructive to adopt an alternative approach. Note that the angular momentum operator \mathbf{J} is a rank one tensor operator and transforms like a $J = 1$ state and from Table 9-3 its three components must span the Γ_4 irreducible representation. Furthermore, Table 9-5 gives the Kronecker product

$$\Gamma_2 \times \Gamma_4 = \Gamma_5 \quad (9-30)$$

This implies that the matrix elements of $\langle \Gamma_2 | J_z | \Gamma_4 \alpha \rangle$ must necessarily vanish. It is readily seen that that is indeed the case if Γ_2 is identified with the ket vector $|(-18)\rangle$ given by (9-24a) and the three ket vectors $|(-3)\alpha\rangle$ given by (9-24b,c,d) are taken as belonging to Γ_4 . Conversely, (9-30) is satisfied if the three ket vectors $|(\mathbf{9})\alpha\rangle$ are identified as three components of the Γ_5 irreducible representation.

9.17. Influence of the Trigonal C_{3v} Crystal Field

The crystal field is predominantly octahedral with a smaller trigonal component. The basic effect can be seen by introducing the operator

$$T = 120C_0^{(2)} \quad (9-31)$$

and considering the matrix elements

$$\begin{aligned} \langle(-18)\Gamma_2|T|(-18)\Gamma_2\rangle &= 0 \\ \langle(\mathbf{9})a\Gamma_4|T|(\mathbf{9})a\Gamma_4\rangle &= 2 \\ \langle(\mathbf{9})b\Gamma_4|T|(\mathbf{9})b\Gamma_4\rangle &= -1 = \langle(\mathbf{9})c\Gamma_4|T|(\mathbf{9})c\Gamma_4\rangle \\ \langle(-3)a\Gamma_5|T|(-3)a\Gamma_5\rangle &= 10 \\ \langle(-3)b\Gamma_5|T|(-3)b\Gamma_5\rangle &= -5 = \langle(-3)c\Gamma_5|T|(-3)c\Gamma_5\rangle \end{aligned} \quad (9-32)$$

The above results are consistent with the $O \rightarrow C_{3v}$ branching rules

$$\begin{aligned}\Gamma_2 &\rightarrow \Gamma_2 \\ \Gamma_4 &\rightarrow \Gamma_2 + \Gamma_3 \\ \Gamma_5 &\rightarrow \Gamma_1 + \Gamma_3\end{aligned}\tag{9-33}$$

i.e. the octahedral Γ_2 irrep remains non-degenerate while the Γ_4 and Γ_5 split into a singlet and a doublet. The trigonal splitting for the octahedral Γ_5 irrep is five times larger than for the Γ_4 irrep. Experimentally⁴⁶ one finds a ratio of the splittings to be of the order of four. The above result shows that one can often gain insight into the physics of a problem by relatively simple calculations. Frequently more insight is gained by such calculations than by very large calculations that often lead to an obscuring of simple things.

Lecture 10

Both liberty and equality are among the primary goals pursued by human beings through many centuries; but total liberty for wolves is death to lambs, total liberty of the powerful, the gifted, is not compatible with the rights to a decent existence of the weak and less gifted.

Isaiah Berlin, *On the Pursuit of the Ideal* (March 17, 1988).

10. Some Aspects of Crystal Field Theory and the Lanthanides and Actinides

Before returning to the subject of hyperfine interactions in crystals I need to make some further remarks on crystal field theory and on the Judd-Ofelt^{57,58} theory of intensities. Since the classical paper of Bethe⁵⁴, considerable attention has been given to the interpretation of the spectra of f -ions substituted into various crystal lattices. The simple theory⁶²⁻⁶⁶ based, initially, on the assumption that the substituted ion “sees” a purely electrostatic field with a point symmetry of the lattice site it occupies, met with considerable success. It allowed meaningful assignments to be made of most of the observed crystal field levels and, for the rare earths, the crystal field parameters usually reproduce the observed spectra to a standard deviation $\sim 10\text{cm}^{-1}$.

In this lecture I will first discuss selection rules that follow from the point group symmetry of the immersed ion, taking for specificity the point group S_4 introduced in S9.9. We deduce the relevant selection rules for electric dipole and magnetic dipole transitions in crystals with no reference to specific mechanisms. We note that hyperfine interactions can lead to a violation of these selection rules. We then consider the parameterisation of electric dipole transitions and then make connection with the Judd-Ofelt formulation.

10.1. Selection Rules for Ions in a Crystal Field of S_4 Point Symmetry

Electric dipole (E.d) transitions involve the matrix elements of z for polarisation parallel to the z -axis (π -polarisation) and for polarisation perpendicular to the z -axis (σ -polarisation) matrix elements of $x \pm iy$. For S_4 point symmetry z transforms as the Γ_2 representation and $x \pm iy$ as the (Γ_3, Γ_4) complex pair of representations. The E.d selection rules follow from inspection of the Kronecker product table 9-8 given in S9.10 to give for an *even* number of electrons

$$\begin{array}{ccccc}
 E.d & \Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 \\
 \Gamma_1 & \left(\begin{array}{cccc}
 - & \pi & \sigma & \sigma \\
 \pi & - & \sigma & \sigma \\
 \sigma & \sigma & - & \pi \\
 \sigma & \sigma & \pi & -
 \end{array} \right) & & & \\
 \Gamma_2 & & & & \\
 \Gamma_3 & & & & \\
 \Gamma_4 & & & &
 \end{array} \tag{10-1}$$

and for an *odd* number of electrons

$$\begin{array}{cccc}
 E.d & \Gamma_5 & \Gamma_6 & \Gamma_7 & \Gamma_8 \\
 \Gamma_5 & \left(\begin{array}{cccc} - & \sigma & \pi & \sigma \end{array} \right) \\
 \Gamma_6 & \left(\begin{array}{cccc} \sigma & - & \sigma & \pi \end{array} \right) \\
 \Gamma_7 & \left(\begin{array}{cccc} \pi & \sigma & - & \sigma \end{array} \right) \\
 \Gamma_8 & \left(\begin{array}{cccc} \sigma & \pi & \sigma & - \end{array} \right)
 \end{array} \tag{10-2}$$

For magnetic dipole transitions we need the matrix elements of J_z for σ -polarisation and $J_x \pm iJ_y$ for π -polarisation. For S_4 J_z transforms as Γ_1 and $J_x \pm iJ_y$ as the (Γ_3, Γ_4) complex pair of representations leading to the selection rules

$$\begin{array}{cccc}
 M.d & \Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 \\
 \Gamma_1 & \left(\begin{array}{cccc} \sigma & - & \pi & \pi \end{array} \right) \\
 \Gamma_2 & \left(\begin{array}{cccc} - & \sigma & \pi & \pi \end{array} \right) \\
 \Gamma_3 & \left(\begin{array}{cccc} \pi & \pi & \sigma & - \end{array} \right) \\
 \Gamma_4 & \left(\begin{array}{cccc} \pi & \pi & - & \sigma \end{array} \right)
 \end{array} \tag{10-3}$$

and for an *odd* number of electrons

$$\begin{array}{cccc}
 M.d & \Gamma_5 & \Gamma_6 & \Gamma_7 & \Gamma_8 \\
 \Gamma_5 & \left(\begin{array}{cccc} \sigma & \pi & - & \pi \end{array} \right) \\
 \Gamma_6 & \left(\begin{array}{cccc} \pi & \sigma & \pi & - \end{array} \right) \\
 \Gamma_7 & \left(\begin{array}{cccc} - & \pi & \sigma & \pi \end{array} \right) \\
 \Gamma_8 & \left(\begin{array}{cccc} \pi & - & \pi & \sigma \end{array} \right)
 \end{array} \tag{10-4}$$

Note that the crystal field can mix states of different J and L lifting the $\Delta J, \Delta L = 0, \pm 1$ restrictions of the free ion while the spin-orbit interaction can lead to a breakdown of the spin selection rule $\Delta S = 0$. Magnetic dipole transitions are allowed between states of the same parity. In the free ion in pure LS -coupling we have the magnetic dipole selection rules

$$\Delta S, \Delta L = 0, \quad \Delta J = 0, \pm 1 \tag{10-5}$$

Again these selection rules can be broken by spin-orbit and crystal field interactions. Nevertheless the group-theoretical selection rules (10-1)-(10-4) are rigorous. An exception can arise if hyperfine interactions exist and they mix close by crystal field levels.

Consider the trivalent ion, Ho^{3+} , having the electron configuration $4f^{10}$ and hence an *even* number of electrons and thus integer electronic angular momentum. However, the Ho nucleus is half-integer and hence the nett angular momentum is half-integer. As a result the crystal field levels, in the presence of the hyperfine interaction, will

involve the spin irreducible representations of S_4 and hence the selection rules will be given by (10-3) and (10-4) rather than (10-1) and (10-2). Taking into account the degeneracy of the pairs Γ_{56} and Γ_{78} we see that some of the transitions will occur in pure π - or σ - polarisation with the rest as $\sigma\pi$ -polarisation as shown below

$$\begin{array}{l} E.d \quad \Gamma_{56} \quad \Gamma_{78} \\ \Gamma_{56} \begin{pmatrix} \sigma & \sigma\pi \\ \sigma\pi & \sigma \end{pmatrix} \\ \Gamma_{78} \end{array} \quad (10-6)$$

and

$$\begin{array}{l} M.d \quad \Gamma_{56} \quad \Gamma_{78} \\ \Gamma_{56} \begin{pmatrix} \sigma\pi & \pi \\ \pi & \sigma\pi \end{pmatrix} \\ \Gamma_{78} \end{array} \quad (10-7)$$

which gives a way of sometimes distinguishing the different symmetries by polarisation measurements.

10.2. Crystal Field Quantum Numbers

The crystal field matrix elements must satisfy the selection rule

$$\Delta M_J = q \quad (10-8)$$

to be non-vanishing. Following Hellwege⁶⁸ we may conveniently introduce a set of crystal quantum numbers μ such that

$$M_J = \mu(\text{mod } q) \quad (10-9)$$

Thus for S_4 we have $q = 0, \pm 4$ leading to the crystal quantum numbers

$$\mu = \begin{cases} 0, \pm 1, 2 & J \text{ integer} \\ \pm \frac{1}{2}, \pm \frac{3}{2} & J \text{ half-integer} \end{cases} \quad (10-10)$$

Thus for $J = 8$ the following $|JM_J\rangle$ basis states will be coupled by the S_4 crystal field

$$\mu = 0 \quad |80\rangle, |8 \pm 4\rangle, |8 \mp 8\rangle \quad (10-11a)$$

$$\mu = \pm 1 \quad |8 \pm 1\rangle, |8 \mp 3\rangle, |8 \pm 5\rangle, |8 \mp 7\rangle \quad (10-11b)$$

$$\mu = 2 \quad |82\rangle, |8 - 2\rangle, |86\rangle, |8 - 6\rangle \quad (10-11c)$$

while for a hyperfine level with $F = \frac{15}{2}$, or an angular momentum level for an odd number of electrons with $J = \frac{15}{2}$, we would have the following basis states

$$\mu = \pm \frac{1}{2} \quad \left| \frac{15}{2} \pm \frac{1}{2} \right\rangle, \left| \frac{15}{2} \mp \frac{7}{2} \right\rangle, \left| \frac{15}{2} \pm \frac{9}{2} \right\rangle, \left| \frac{15}{2} \mp \frac{15}{2} \right\rangle \quad (10-12a)$$

$$\mu = \pm \frac{3}{2} \quad \left| \frac{15}{2} \pm \frac{3}{2} \right\rangle, \left| \frac{15}{2} \mp \frac{5}{2} \right\rangle, \left| \frac{15}{2} \pm \frac{11}{2} \right\rangle, \left| \frac{15}{2} \mp \frac{13}{2} \right\rangle \quad (10-12b)$$

The correlation between the crystal quantum numbers and the group representations of S_4 is readily seen to be

$$\mu = \begin{cases} 0 : \Gamma_1 \\ \pm 1 : \Gamma_{34} \\ 2 : \Gamma_2 \end{cases} \quad (10-13a)$$

$$\mu = \begin{cases} \pm \frac{1}{2} : \Gamma_{56} \\ \pm \frac{3}{2} : \Gamma_{78} \end{cases} \quad (10-13b)$$

where we have combined the complex pairs of irreducible representations of S_4 , emphasizing that they form doubly degenerate states in the crystal field. Note that in evaluating crystal field matrix elements the matrix elements vanish between states belonging to different crystal quantum numbers. Furthermore, it can be useful to introduce, for the symmetric and antisymmetric linear combinations relevant to the Γ_1 and Γ_2 irreducible representations

$$|JM_J\rangle_{\pm} = \frac{1}{\sqrt{2}}(|JM_J\rangle \pm |J - M_J\rangle) \quad (10-14)$$

We then have

$$\langle JM_J|V_{cryst}|JM'_J\rangle_{++} = \langle JM_J|V_{cryst}|JM'_J\rangle_{--}, \text{ real} \quad (10-15a)$$

$$\langle JM_J|V_{cryst}|JM'_J\rangle_{+-} = \langle JM_J|V_{cryst}|JM'_J\rangle_{-+}^*, \text{ imaginary} \quad (10-15b)$$

10.3. Intensities of Transitions and Effective operators for Ions in Crystals

In the preceding two sections we have developed the selection rules for electric dipole transitions for ions in crystals. These selection rules were developed independently of any specific mechanism. Thus in the case of S_4 point group symmetry we were considering the selection rules that would arise if we had constructed an effective operator having three components transforming as the irreducible representations, Γ_2 for the π -polarisation component and the (Γ_3, Γ_4) complex pair of representations for the two σ -polarisation components. This may be compared with our construction of an effective crystal field operator, V_{cryst} , where we constructed an operator involving linear combinations of the operators $C_q^{(k)}$ that transformed as the identity irreducible representation Γ_1 . In the latter case one was simply constructing an integrity basis and then endowing it with an interpretation based upon the parameterisation of the crystal field.

As pointed out by McLellan⁶⁹⁻⁷¹ the concept of an integrity basis can be generalised to polynomial bases for specific representations of a group \mathcal{G} . Thus one could construct an effective operator to represent the intensities of transitions by defining, once again, linear combinations of the operators $C_q^{(k)}$ but this time with the requirement that the linear combinations transform as the Γ_2, Γ_3 and Γ_4 irreducible representations of S_4 . These linear combinations would have associated parameters

depending upon the allowed values of (k, q) . If the operators are developed in terms of the $C_q^{(k)}$ operators acting within the f^N electron configuration then the rank k must be *even*. It would, however, be perfectly possible to develop operators with the appropriate transformation properties having *both* even and odd ranks if the unit tensor operators $U_q^{(k)}$ were used. Exclusion of the *odd* rank operators requires a physical argument such as that based upon the Judd-Ofelt^{57,58} perturbation approach where the odd rank operators approximately cancel in second-order (the degree of cancellation depends upon the choice of zero-order eigenfunctions) though not in third-order^{41,42}.

10.4. The Judd-Ofelt Theory of Intensities

The Judd-Ofelt^{57,58} theory of intensities forms a landmark in the theory of the spectroscopic properties of the lanthanides and actinides ions in crystals. Basically it represents a second-order perturbation formulation of forced electric dipole transitions almost exactly paralleling our effective operator treatment of the quadratic Stark effect in atoms outlined in S7.7 and S7.8. Here I give only the barest outline keeping largely to the notation developed in Lecture VII and to relevant papers^{41,42,57,58}. The second-order contribution to the electric dipole moment we write as

$$\begin{aligned} & \langle A\alpha | D_q^{(1)} | A\alpha' \rangle_1 \\ &= \sum_{\beta} \{ \langle A\alpha | V_{ed} | B\beta \rangle \langle B\beta | V_{cryst} | A\alpha' \rangle + \langle A\alpha | V_{cryst} | B\beta \rangle \langle B\beta | V_{ed} | A\alpha' \rangle \} / (\lambda_A - \lambda_B) \end{aligned} \quad (10-16)$$

where the configurations are of opposite parity, and we write^{41,42,57}

$$V_{cryst} = \sum_{t,p} A_{tp} D_p^{(t)} \quad (10-17)$$

with

$$D_p^{(t)} = \sum_j r^t C_p^{(t)}(\theta_j, \phi_j) \quad (10-18)$$

and, suppressing the factor of $-e$,

$$V_{ed} = D_q^{(1)} \quad (10-19)$$

Following Lecture VII we readily arrive at the result

$$\begin{aligned} & \langle A\alpha | D_q^{(1)} | A\alpha' \rangle_1 \\ &= \sum_{p,t,\lambda_{even}} T(\lambda, q, \rho) \langle A\alpha | U_{\rho}^{(\lambda)} | A\alpha' \rangle \\ &= \sum_{p,t,\lambda_{even}} (-1)^{p+q} (2\lambda + 1) A_{tp} \begin{pmatrix} 1 & \lambda & t \\ q & \rho & p \end{pmatrix} \Xi(t, \lambda) \langle A\alpha | U_{\rho}^{(\lambda)} | A\alpha' \rangle \end{aligned} \quad (10-20)$$

where

$$\begin{aligned} \Xi(t, \lambda) &= 2(2\ell + 1)(2\ell' + 1)(-1)^{\ell+\ell'} \begin{Bmatrix} 1 & \lambda & t \\ \ell & \ell' & \ell \end{Bmatrix} \begin{pmatrix} \ell & 1 & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & t & \ell \\ 0 & 0 & 0 \end{pmatrix} \\ &\times \langle n\ell|r|n'\ell'\rangle \langle n\ell|r^t|n'\ell'\rangle / (\lambda_{n\ell} - \lambda_{n'\ell'}) \end{aligned} \quad (10-21)$$

necessarily $\rho = -(p + q)$ and we have put $A \equiv n\ell^N$ and $B \equiv n\ell^{N-1}n'\ell'$.

The oscillator strength f_e of a transition at a wavenumber σ in a medium of refractive index η may be written as

$$f_e = \frac{8\pi^2 mc}{3he^2} \sigma \langle A | \mathcal{P}_\rho^{(1)} | B \rangle^2 \frac{(\eta^2 + 2)^2}{9} \quad (10-22)$$

$$= \sigma \sum_{\lambda, q, \rho} \mathcal{T}(\lambda, q, \rho) \langle A\alpha | U_\rho^{(\lambda)} | A\alpha' \rangle^2 \quad (10-23)$$

where

$$\mathcal{T}(\lambda, q, \rho) = \frac{8\pi^2 mc}{3he^2} \sigma \frac{(\eta^2 + 2)^2}{9} T(\lambda, q, \rho)^2 \quad (10-24)$$

Before continuing further with remarks on intensities I propose to give a simple example of a crystal field calculation of some of the levels of Pr^{3+} at a D_{3h} point group symmetry such as occurs, to a good approximation in the lanthanide trihalides.

10.5. A Simplified Crystal Field Calculation

The Pr^{3+} ion has $4f^2$ as its lowest energy electron configuration having the spectroscopic terms ${}^3PFH {}^1SDGI$. Hund's rules give the ground term as 3H_4 . Placed in a $LaCl_3$ single crystal the Pr^{3+} ion sees a nearest neighbour point symmetry environment of D_{3h} . (The 'exact' point group symmetry is C_{3h}). The crystal field levels may be labelled by the irreducible representations of the point group D_{3h} whose character table is given below.

$$\begin{array}{c} \Gamma_1 \\ \Gamma_2 \\ \Gamma_3 \\ \Gamma_4 \\ \Gamma_5 \\ \Gamma_6 \end{array} \begin{pmatrix} E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\ 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & 1 & 1 & -1 \\ 1 & 1 & -1 & -1 & -1 & 1 \\ 1 & 1 & 1 & -1 & -1 & -1 \\ 2 & -1 & 0 & 2 & -1 & 0 \\ 2 & -1 & 0 & -2 & 1 & 0 \end{pmatrix} \quad (10-25)$$

Table 10-1. Character table for the ordinary irreducible representations of D_{3h}

Under $SO_3 \rightarrow D_{3h}$ we have the branching rules

J	D_{3h} irreducible representations	
0	Γ_1	
1	$\Gamma_2 + \Gamma_6$	
2	$\Gamma_1 + \Gamma_5 + \Gamma_6$	
3	$\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5 + \Gamma_6$	
4	$\Gamma_1 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 + \Gamma_6$	
5	$\Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 + 2\Gamma_6$	
6	$2\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 + 2\Gamma_6$	(10-26)

Table 10-2 $SO_3 \rightarrow D_{3h}$ Branching Rules

The irreducible representations of D_{3h} form a wider class of labels than do the crystal quantum numbers. Levels with $\mu = 0$ may be divided according to whether they transform as Γ_1 or Γ_2 and those with $\mu = 3$ divided according to the irreducible representations Γ_3 or Γ_4 . The $\mu = \pm 1$ and $\mu = \pm 2$ levels span the two-dimensional Γ_5 and Γ_6 irreducible representations respectively. In the absence of magnetic fields the Γ_5 and Γ_6 levels will remain two-fold degenerate.

For a crystal field of D_{3h} symmetry the crystal field potential may be written as

$$V_{cryst} = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_0^{(6)} C_0^{(6)} + B_6^6 (C_6^{(6)} + C_{-6}^{(6)}) \quad (10-26)$$

The matrix elements of V_{cryst} for states of the $4f^2$ configuration follow, by now, standard tensor operator algebra using MAPLE. Here I will limit the calculations to just the triplets 3PFH and ignore departures from LS -coupling (explored earlier in Lecture III) and J -mixing. There is no splitting for the 3P_0 level which is a non-degenerate Γ_1 level. For the 3P_1 term we expect two levels, a non-degenerate Γ_2 and a two-fold degenerate Γ_6 level with crystal field energies of (we suppress the SL labels, just giving the $|JM_J\rangle$ numbers)

$$\langle 1, 0 | V_{cryst} | 1, 0 \rangle = +\frac{B_0^2}{5} \quad \text{and} \quad \langle 1, \pm 1 | V_{cryst} | 1, \pm 1 \rangle = -\frac{B_0^2}{10} \quad (10-27)$$

and thus a crystal field energy separation of

$$E(\Gamma_6) - E(\Gamma_2) = \frac{3B_0^2}{10} \quad (10-28)$$

Experimentally⁷² the separation is found to be 30.3cm^{-1} suggesting from Eq. (10-28) a value for B_0^2 of $\sim 103\text{cm}^{-1}$. Indeed on the basis of a least squares fit with the inclusion of intermediate coupling and J -mixing, Margolis⁷³, arrived at the parameter set

$$B_0^2 = 95\text{cm}^{-1}, \quad B_0^4 = -325\text{cm}^{-1}, \quad B_0^6 = -634\text{cm}^{-1}, \quad B_6^6 = 427\text{cm}^{-1} \quad (10-29)$$

For the 3P_2 level we expect from Table 10-1 a non-degenerate Γ_1 and two two-fold degenerate Γ_5, Γ_6 levels. Indeed we find the matrix elements

$$\langle 2, 0 | V_{cryst} | 2, 0 \rangle = -\frac{B_0^2}{5}, \quad \langle 2, \pm 1 | V_{cryst} | 2, \pm 1 \rangle = -\frac{B_0^2}{10}, \quad \langle 2, \pm 2 | V_{cryst} | 2, \pm 2 \rangle = \frac{B_0^2}{5} \quad (10-30)$$

Again the matrix elements involve just one parameter, B_0^2 , whereas the matrix elements for the 3F_2 term will involve B_0^4 as well as B_0^4 though the number of levels remains the same. Indeed we now find for the three levels

$$\langle 2, 0 | V_{cryst} | 2, 0 \rangle = -\frac{8B_0^2}{105} - \frac{2B_0^4}{63} \quad (10-31a)$$

$$\langle 2, \pm 1 | V_{cryst} | 2, \pm 1 \rangle = -\frac{4B_0^2}{105} + \frac{4B_0^4}{189} \quad (10-31b)$$

$$\langle 2, \pm 2 | V_{cryst} | 2, \pm 2 \rangle = \frac{8B_0^2}{105} - \frac{B_0^4}{189} \quad (10-31c)$$

In calculating the matrix elements for the 3F_3 term we take advantage, for the case of the $|3, \pm 3\rangle$ kets, of the symmetric and antisymmetric linear combinations $|3, 3\rangle_{\pm}$ defined in (10-24) with the symmetric combination belonging to Γ_4 and the antisymmetric to Γ_3 .

$$\langle 3, 0 | V_{cryst} | 3, 0 \rangle = -\frac{B_0^2}{15} - \frac{B_0^4}{99} + \frac{25B_0^6}{429} \quad (10-32a)$$

$$\langle 3, \pm 1 | V_{cryst} | 3, \pm 1 \rangle = -\frac{B_0^2}{20} - \frac{B_0^4}{594} - \frac{25B_0^6}{572} \quad (10-32b)$$

$$\langle 3, \pm 2 | V_{cryst} | 3, \pm 2 \rangle = \frac{7B_0^4}{594} + \frac{5B_0^6}{286} \quad (10-32c)$$

$$\pm \langle 3, 3 | V_{cryst} | 3, 3 \rangle_{\pm} = \frac{B_0^2}{12} - \frac{B_0^4}{198} - \frac{5B_0^6}{1716} \mp \frac{5\sqrt{231}B_0^6}{858} \quad (10-32d)$$

$$\pm \langle 3, 3 | V_{cryst} | 3, 3 \rangle_{\mp} = \mp \langle 3, 3 | V_{cryst} | 3, 3 \rangle_{\pm} = 0 \quad (10-32e)$$

Here we see that by starting with symmetrised states the rank 2 matrix formed by the $|3, \pm 3\rangle$ states has effectively been put in diagonal form.

As a final example we consider 3H_4 ground term.

$$\langle 4, 0 | V_{cryst} | 4, 0 \rangle = \frac{104B_0^2}{495} - \frac{12B_0^4}{121} - \frac{1360B_0^6}{14157} \quad (10-33a)$$

$$\langle 4, \pm 1 | V_{cryst} | 4, \pm 1 \rangle = \frac{442B_0^2}{2475} - \frac{6B_0^4}{121} + \frac{68B_0^6}{14157} \quad (10-33b)$$

$$\begin{array}{c} \mu = \pm 2 \\ \pm \langle 4, 2 | \\ \pm \langle 4, 4 | \end{array} \begin{array}{cc} |4, 2\rangle_{\pm} & |4, 4\rangle_{\pm} \\ \left(\begin{array}{cc} \frac{208B_0^2}{2475} + \frac{2B_0^4}{33} + \frac{136B_0^6}{1287} & \pm \frac{272\sqrt{33}B_0^6}{14157} \\ \pm \frac{272\sqrt{33}B_0^6}{14157} & -\frac{728B_0^2}{2475} - \frac{28B_0^4}{363} + \frac{272B_0^6}{14157} \end{array} \right) \end{array} \quad (10-33c)$$

$$\pm \langle 4, 3 | V_{cryst} | 4, 3 \rangle_{\pm} = -\frac{182B_0^2}{2475} + \frac{14B_0^4}{121} - \frac{1156B_0^6}{14157} \pm \frac{136\sqrt{231}B_0^6}{14157} \quad (10-33d)$$

Notice that (10-33c) corresponds to a pair of rank 2 matrices which have identical pairs of eigenvalues though differing eigenfunctions.

10.6. The MAPLE Programme

The preceding calculations were done by the simple MAPLE programme given below. Note that the crystal field parameters B_q^k are declared globally. If you do not specify them then you get the expressions given earlier. If you declare the values of the parameters then the output will be numerical.

Table 10-2. The MAPLE programme

```

print('This routine calculates the crystal field matrix elements for');
print('the triplet states of the f^2 configuration with D3h symmetry');
read'njsym";
fck:=proc(L,J,M1,M2,k,q)
local result;
result:=simplify(combine((((-1)^(J-M1))*threej(J,k,J,-M1,q,M2)*
(-2)*(2*L+1)*sixj(L,k,L,3,3,3)*ck(3,3,k)*((-1)^(1+L+J+k))*(2*J+1)*
sixj(J,k,J,L,1,L))));
end:
V:=proc(L,J,M1,M2)
local me;
global B20,B40,B60,B66;
me:=B20*fck(L,J,M1,M2,2,0)+B40*fck(L,J,M1,M2,4,0)
+B60*fck(L,J,M1,M2,6,0)
+B66*(fck(L,J,M1,M2,6,6)+fck(L,J,M1,M2,6,-6));
end:
print('Example to calculate the matrix element <3H43|V|3H43');
print('Enter V(5,4,3,3);');
V(5,4,3,3);

```

Using the Margolis parameter set, Eq.(10-29), in Eqs (10-33a-d) leads to the numerical results (in cm^{-1})

$$\langle 4, 0 | V_{cryst} | 4, 0 \rangle = 113 \quad (10-33a')$$

$$\langle 4, \pm 1 | V_{cryst} | 4, \pm 1 \rangle = 30 \quad (10-33b')$$

$$\begin{matrix} \mu = \pm 2 & |4, 2\rangle_{\pm} & |4, 4\rangle_{\pm} \\ \pm \langle 4, 2 | & \begin{pmatrix} -79 & \pm 47 \\ \pm 47 & -15 \end{pmatrix} & \\ \pm \langle 4, 4 | & & \end{matrix} \quad (10-33c')$$

$$\pm \langle 4, 3 | V_{cryst} | 4, 3 \rangle_{\pm} = 7 \pm 62 \quad (10-33d')$$

Diagonalisation of the matrix in Eq. (10-33c') yields the eigenvalues -55 and 69 . Adjusting the eigenvalues found in Eqs. (10-33a'-d') so that the lowest eigenvalue matches the lowest crystal field level for the ground state we have the comparison with the experimental data⁷⁴ given in (10-34) below.

D_{3h}	μ	E_{expt}	E_{calc}	
Γ_5	2	0	0	
Γ_3	3	49	33	
Γ_5	2	114	96	
Γ_6	1	134	130	
Γ_4	3	173	137	
Γ_1	0	217	199	(10-34)

The agreement between the experimental and calculated levels is reasonable considering the simplicity of our calculation where we have been more interested in illustrating principles rather than precision. Note that the order of the levels is correctly given.

10.7. Further Remarks on Integrity Bases

Crystal field calculations that involve parameterised fits of symmetrised sets of spherical harmonics are to a large extent model independent with a "good fit" being indicative of the correct symmetry. As noted earlier such calculations are what one expects if all the invariants of the appropriate integrity basis are used. In many respects the parameterised Judd-Ofelt theory of intensities can be regarded as essentially a generalised integrity basis. Thus for the point group D_{3h} one knows that the electric dipole selection rules arise from the knowledge that z belongs to the Γ_4 irrep and $x \pm iy$ to Γ_6 . We may attempt to construct an effective operator from the even rank unit tensor operators $U_q^{(k)}$ that mimic the selection rules. Two such operators would be

$$O(\Gamma_4) = T_3^4(U_3^{(4)} + U_{-3}^{(4)}) + T_3^6(U_3^{(6)} + U_{-3}^{(6)}) \quad (10-35a)$$

$$O(\Gamma_6) = T_2^2(U_2^{(2)} + U_{-2}^{(2)}) + T_2^4(U_2^{(4)} + U_{-2}^{(4)}) + T_4^4(U_4^{(4)} + U_{-4}^{(4)}) \\ + T_2^6(U_2^{(6)} + U_{-2}^{(6)}) + T_4^6(U_4^{(6)} + U_{-4}^{(6)}) \quad (10-34b)$$

The operator $O(\Gamma_4)$ would parameterise the π -polarised transitions and $O(\Gamma_6)$ the σ -polarised transitions. The first operator involving two parameters and the second five parameters.

Lecture 11

11. Introduction

We now return to the subject of hyperfine interactions in crystals. The earliest studies came from electron spin resonance studies. Later work by the groups of Hellwege in Darmstadt and Dieke at Johns Hopkins reported observations of hyperfine structure in optical absorption spectra of Pr^{3+} and Ho^{3+} ions in crystals. The substantive development came with the very high resolution studies by M Popova and her associates^{45,46,49-53} at Troitsk, near Moscow. In this lecture our primary aim will be to calculate the magnetic dipole hyperfine structure in the 3F_3 term of the $4f^2$ configuration of the Pr^{3+} ion in a $CsCdBr_3$ crystalline environment assuming that the Pr^{3+} ion is at a site of symmetry $SO(3) \rightarrow O_h \rightarrow C_{3v}$ symmetry. Our objective is to explain by example, and specific calculations, the principal features of the observed hyperfine structure. We do not aim for high precision but rather relatively simple descriptions of the broad features of the observed hyperfine structure. We shall ignore electric quadrupole contributions. Our attention will be almost entirely focussed on the 3F_3 level of the $4f^2$ electron configuration. Many of the calculations will be done by writing simple MAPLE programmes. Let us first recall some of the content of earlier lectures.

11.1. Coulomb Matrix Elements for the f^2 Electron Configuration

The f^2 configuration involves just seven ${}^{2S+1}L$ terms whose Coulomb energies in terms of the Slater F_k integrals are²

$$\begin{aligned}
 E({}^1S) &= F_0 + 60F_2 + 198F_4 + 1716F_6 \\
 E({}^3P) &= F_0 + 45F_2 + 33F_4 - 1287F_6 \\
 E({}^1D) &= F_0 + 19F_2 - 99F_4 + 715F_6 \\
 E({}^3F) &= F_0 - 10F_2 - 33F_4 - 286F_6 \\
 E({}^1G) &= F_0 - 30F_2 + 97F_4 + 78F_6 \\
 E({}^3H) &= F_0 - 25F_2 - 51F_4 - 13F_6 \\
 E({}^1I) &= F_0 + 25F_2 + 9F_4 + F_6
 \end{aligned} \tag{11-1}$$

11.2. Spin-orbit Interaction Matrices for the f^2 Electron Configuration

We give below the complete spin-orbit interaction matrices for all the ${}^{2S+1}L_J$ levels of the f^2 electron configuration. Notice that there is no spin-orbit coupling between the 3F_3 level and any other levels and hence there are no intermediate coupling corrections

to be made.

$$\begin{array}{ccc}
\begin{array}{cc}
{}^3P_0 & {}^1S_0 \\
{}^3P_0 \begin{pmatrix} -1 & -2\sqrt{3} \\ -2\sqrt{3} & 0 \end{pmatrix} & {}^1S_0 \begin{pmatrix} -1 & -2\sqrt{3} \\ -2\sqrt{3} & 0 \end{pmatrix}
\end{array} &
\begin{array}{c}
{}^3P_1 \\
{}^3P_1 \begin{pmatrix} -\frac{1}{2} \end{pmatrix}
\end{array} &
\begin{array}{ccc}
{}^3P_2 & {}^1D_2 & {}^3F_2 \\
{}^3P_2 \begin{pmatrix} \frac{1}{2} & \frac{3}{2}\sqrt{2} & 0 \\ \frac{3}{2}\sqrt{2} & 0 & -\sqrt{6} \\ 0 & -\sqrt{6} & -2 \end{pmatrix} & &
\end{array} \\
\begin{array}{c}
{}^3F_3 \\
{}^3F_3 \begin{pmatrix} -\frac{1}{2} \end{pmatrix}
\end{array} &
\begin{array}{ccc}
{}^3F_4 & {}^1G_4 & {}^3H_4 \\
{}^3F_4 \begin{pmatrix} \frac{3}{2} & \frac{\sqrt{33}}{3} & 0 \\ \frac{\sqrt{33}}{3} & 0 & -\frac{\sqrt{30}}{3} \\ 0 & -\frac{\sqrt{30}}{3} & -3 \end{pmatrix} & &
\end{array} &
\begin{array}{ccc}
{}^3H_5 & {}^3H_6 & {}^1I_6 \\
{}^3H_5 \begin{pmatrix} -\frac{1}{2} \end{pmatrix} & {}^3H_6 \begin{pmatrix} \frac{5}{2} & \frac{\sqrt{6}}{2} \\ \frac{\sqrt{6}}{2} & 0 \end{pmatrix} & {}^1I_6 \begin{pmatrix} \frac{5}{2} & \frac{\sqrt{6}}{2} \\ \frac{\sqrt{6}}{2} & 0 \end{pmatrix}
\end{array}
\end{array} \quad (11-2)$$

NB. The individual matrix elements are to be multiplied by the spin-orbit coupling constant ζ .

11.3. Matrix Elements of Magnetic Dipole Hyperfine Interactions

Let us recall some of our earlier results. Define

$$a_\ell = 2\mu_B^2(m_e/M_p)g_I\langle r^{-3} \rangle \quad (11-3)$$

where μ_B is the Bohr magneton, g_I the nuclear g factor and $\langle r^{-3} \rangle$ the average inverse-cube radius of the electron orbital ℓ . Further, let

$$\begin{aligned}
\mathbf{H}_m(i)^{(1)} &= a_\ell[\mathbf{l}_i^{(1)} - \sqrt{10}(\mathbf{s}^{(1)}\mathbf{x}\mathbf{C}^{(2)})_i^{(1)}] \\
&= a_\ell[\mathbf{l}_i - \sqrt{10}\mathbf{X}_i^{(1)}]
\end{aligned} \quad (11-4)$$

with

$$\mathbf{H}_m^{(1)} = \sum_{i=1}^n H_m(i)^{(1)} \quad (11-5)$$

where the sum is over a group of equivalent electrons in the configuration ℓ^n .

The interaction of a nuclear magnetic moment with the orbital and spin moments of n electrons can be written in the above tensor operator notation as

$$\mathcal{H}_m = a_\ell(\mathbf{H}^{(1)} \cdot \mathbf{I}^{(1)}) \quad (11-6)$$

In the *JIFM* scheme we have

$$\begin{aligned}
&\langle \alpha JIFM | a_\ell(\mathbf{H}^{(1)} \cdot \mathbf{I}^{(1)}) | \alpha' J'IF'M' \rangle \\
&= a_\ell(-1)^{J'+I+F} \delta_{F,F'} \delta_{M,M'} \begin{Bmatrix} J' & I & F \\ I & J & 1 \end{Bmatrix} \langle \alpha J || H^{(1)} || \alpha' J' \rangle \langle I || I^{(1)} || I \rangle
\end{aligned} \quad (11-7)$$

For matrix elements diagonal in J Eq.(11-7) simplifies to

$$\begin{aligned} & \langle \alpha JIFM | a_\ell (\mathbf{H}^{(1)} \cdot \mathbf{I}^{(1)}) | \alpha' JIFM \rangle \\ &= a_\ell \frac{K}{2\sqrt{J(J+1)}(2J+1)} \langle \alpha J || H^{(1)} || \alpha' J \rangle \end{aligned} \quad (11-8)$$

where

$$K = F(F+1) - J(J+1) - I(I+1) \quad (11-9)$$

While there is no difficulty in calculating matrix elements with J -mixing we shall leave that extension as an exercise. The calculation of the magnetic dipole hyperfine interaction involves two parts, an orbital part (\mathcal{L}) and a spin part (\mathcal{S}).

For the orbital part we have

$$\mathcal{L} = \frac{\langle \alpha SLJ || L^{(1)} || \alpha' S' L' J \rangle}{\sqrt{J(J+1)}(2J+1)} = \delta_{\alpha, \alpha'} \delta_{S, S'} \delta_{L, L'} (2-g) \quad (11-10)$$

where g is the usual Lande g -factor

$$2-g = \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} \quad (11-11)$$

This part may be corrected for intermediate coupling by simply replacing g by its intermediate coupling value.

For the spin part we have

$$\mathcal{S} = -\frac{\sqrt{10} \langle \alpha SLJ || \sum_{i=1}^n (\mathbf{s}^{(1)} \mathbf{C}^{(2)})_i^{(1)} || \alpha' S' L' J \rangle}{\sqrt{J(J+1)}(2J+1)} \quad (11-12)$$

which evaluates to

$$\begin{aligned} \mathcal{S} &= (-1)^{\ell+1} (2\ell+1) \begin{pmatrix} \ell & \ell & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} S & S' & 1 \\ L & L' & 2 \\ J & J & 1 \end{Bmatrix} \\ &\times \sqrt{\frac{30(2J+1)}{J(J+1)}} \langle \alpha SL || V^{(12)} || \alpha' S' L' \rangle \end{aligned} \quad (11-13)$$

where the last matrix element involves the double tensor operator $\mathbf{V}^{(12)}$ that acts in the spin and orbital spaces and whose one-electron reduced matrix elements satisfy

$$\langle \ell || v^{(12)} || \ell \rangle = \sqrt{\frac{3}{2}} \quad (11-14)$$

For the special case of a two-electron configuration ℓ^2 we have

$$\begin{aligned} \langle \alpha SL || V^{(12)} || \alpha' S' L' \rangle &= \sqrt{6(2S+1)(2S'+1)(2L+1)(2L'+1)} \\ &\times \begin{Bmatrix} S & 1 & S' \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & 2 & L' \\ \ell & \ell & \ell \end{Bmatrix} \end{aligned} \quad (11-15)$$

From Eqs.(11-10) and (11-12) we find for $f^2(^3F_3)$ the values

$$\mathcal{L} = \frac{11}{12} \quad \text{and} \quad \mathcal{S} = -\frac{1}{36} \quad (11-16)$$

The magnetic hyperfine structure constant, A , as normally defined, is given by

$$A = a_\ell[\mathcal{L} + \mathcal{S}] \quad (11-17)$$

and hence

$$A(^3F_3) = a_\ell \left[\frac{8}{9} \right] \quad (11-18)$$

We note that for the 3F_3 state there is no intermediate coupling correction.

11.4. Nuclear Magnetic Hyperfine Matrix Elements in the JJ_zII_z Scheme

In a crystal the splittings that arise from the internal electric fields are substantially greater than the hyperfine splittings so that it is more realistic to calculate the hyperfine matrix elements in the JJ_zII_z scheme where the diagonal matrix elements are given by

$$\langle \alpha SLJJ_zII_z | \mathbf{H}_m | \alpha' S'L'JJ_zII_z \rangle = J_z I_z A \quad (11-19)$$

and the off-diagonal matrix elements by

$$\begin{aligned} & \langle \alpha SLJJ_zII_z | \mathbf{H}_m | \alpha' S'L'JJ_z \pm 1II_z \mp 1 \rangle \\ & = \frac{1}{2} A \sqrt{(J \mp J_z)(J \pm J_z + 1)(I \pm I_z)(I \mp I_z + 1)} \end{aligned} \quad (11-20)$$

In order to obtain practical results one needs to obtain the crystal field states as linear combinations of the $|JJ_z\rangle$ kets. In the present case that involves first obtaining states symmetrised with respect to the octahedral point group as done in Lecture **IX**. We recall some of those results.

11.5. An Octahedral Crystal Field

To a first approximation, the Pr^{3+} ion sees a predominantly octahedral (O) crystal field which may be written as

$$\begin{aligned} V_{cryst} = & B_4 \left[C_0^{(4)} - \frac{\sqrt{70}}{7} (C_3^{(4)} - C_{-3}^{(4)}) \right] \\ & + B_6 \left[C_0^{(6)} + \frac{\sqrt{210}}{24} (C_3^{(6)} - C_{-3}^{(6)}) + \frac{\sqrt{231}}{24} (C_6^{(6)} + C_{-6}^{(6)}) \right] \end{aligned} \quad (11-21)$$

Following Lecture **IX**, we construct for the 3F_3 term the matrix elements of the operator

$$X_4 = 594 \left[C_0^{(4)} - \frac{\sqrt{70}}{7} (C_3^{(4)} - C_{-3}^{(4)}) \right] \quad (11-22)$$

where we chose the number 594 to yield simple matrix elements and consequently integer eigenvalues. The matrix elements were evaluated in a $|JJ_z\rangle$ basis and diagonalised so as to yield the octahedrally symmetrised states

$$|({}^3\Gamma_1)\rangle = \frac{1}{3} \left[-\sqrt{2}|{}^3F_{3,3}\rangle - \sqrt{5}|{}^3F_{3,0}\rangle + \sqrt{2}|{}^3F_{3,-3}\rangle \right] \quad (11-23a)$$

$$|({}^3\Gamma_4)a\rangle = \frac{1}{\sqrt{2}} \left[|{}^3F_{3,3}\rangle + |{}^3F_{3,-3}\rangle \right] \quad (11-23b)$$

$$|({}^3\Gamma_4)b\rangle = \frac{1}{\sqrt{6}} \left[-\sqrt{5}|{}^3F_{3,1}\rangle + |{}^3F_{3,-2}\rangle \right] \quad (11-23c)$$

$$|({}^3\Gamma_4)c\rangle = \frac{1}{\sqrt{6}} \left[\sqrt{5}|{}^3F_{3,-1}\rangle + |{}^3F_{3,2}\rangle \right] \quad (11-23d)$$

$$|({}^3\Gamma_5)a\rangle = \frac{1}{6} \left[-\sqrt{10}|{}^3F_{3,3}\rangle + 4|{}^3F_{3,0}\rangle + \sqrt{10}|{}^3F_{3,-3}\rangle \right] \quad (11-23e)$$

$$|({}^3\Gamma_5)b\rangle = \frac{1}{\sqrt{6}} \left[|{}^3F_{3,1}\rangle + \sqrt{5}|{}^3F_{3,-2}\rangle \right] \quad (11-23f)$$

$$|({}^3\Gamma_5)c\rangle = \frac{1}{\sqrt{6}} \left[|{}^3F_{3,-1}\rangle - \sqrt{5}|{}^3F_{3,2}\rangle \right] \quad (11-23g)$$

Introduction of the sixth-order invariant

$$X_6 = 6864 \left[C_0^{(6)} + \frac{\sqrt{210}}{24} (C_3^{(6)} - C_{-3}^{(6)}) + \frac{\sqrt{231}}{24} (C_6^{(6)} + C_{-6}^{(6)}) \right] \quad (11-24)$$

allowed us to write the complete octahedral crystal field as $V_{Oh} = X_4B^4 + X_6B^6$ and to obtain the crystal field matrices as

$$\begin{array}{cc} & |{}^3F_{3,1}\rangle & |{}^3F_{3,-2}\rangle \\ \langle {}^3F_{3,1}| & \left(\begin{array}{cc} -B^4 - 300B^6 & \sqrt{5}(2B^4 + 105B^6) \\ \sqrt{5}(2B^4 + 105B^6) & 7B^4 + 120B^6 \end{array} \right) & \\ \langle {}^3F_{3,-2}| & & \end{array} \quad (11-25a)$$

$$\begin{array}{cc} & |{}^3F_{3,-1}\rangle & |{}^3F_{3,2}\rangle \\ \langle {}^3F_{3,-1}| & \left(\begin{array}{cc} -B^4 - 300B^6 & -\sqrt{5}(2B^4 + 105B^6) \\ -\sqrt{5}(2B^4 + 105B^6) & 7B^4 + 120B^6 \end{array} \right) & \\ \langle {}^3F_{3,2}| & & \end{array} \quad (11-25b)$$

$$\begin{array}{ccc} & |{}^3F_{3,3}\rangle & |{}^3F_{3,0}\rangle & |{}^3F_{3,-3}\rangle \\ \langle {}^3F_{3,3}| & \left(\begin{array}{ccc} -3B^4 - 20B^6 & \sqrt{10}(-3B^4 + 35B^6) & -385B^6 \\ \sqrt{10}(-3B^4 + 35B^6) & -6B^4 + 400B^6 & \sqrt{10}(3B^4 - 35B^6) \\ -385B^6 & \sqrt{10}(3B^4 - 35B^6) & -3B^4 - 20B^6 \end{array} \right) & & \\ \langle {}^3F_{3,0}| & & & \\ \langle {}^3F_{3,-3}| & & & \end{array} \quad (11-25c)$$

which in terms of the octahedrally symmetrised states of (11-23a-g) gave the matrices

$$\begin{array}{ccc} & |({}^3\Gamma_4)a\rangle & |({}^3\Gamma_4)b\rangle & |({}^3\Gamma_4)c\rangle \\ \langle ({}^3\Gamma_4)a| & \left(\begin{array}{ccc} -3B^4 - 405B^6 & 0 & 0 \\ 0 & -3B^4 - 405B^6 & 0 \\ 0 & 0 & -3B^4 - 405B^6 \end{array} \right) & & \\ \langle ({}^3\Gamma_4)b| & & & \\ \langle ({}^3\Gamma_4)c| & & & \end{array} \quad (11-26a)$$

$$\begin{array}{c} |({}^3\Gamma_5)a\rangle \quad |({}^3\Gamma_5)b\rangle \quad |({}^3\Gamma_5)c\rangle \\ \langle({}^3\Gamma_5)a| \left(\begin{array}{ccc} 9B^4 + 225B^6 & 0 & 0 \\ 0 & 9B^4 + 225B^6 & 0 \\ 0 & 0 & 9B^4 + 225B^6 \end{array} \right) \\ \langle({}^3\Gamma_5)b| \\ \langle({}^3\Gamma_5)c| \end{array} \quad (11-26b)$$

$$\begin{array}{c} |({}^3\Gamma_1)\rangle \\ \langle({}^3\Gamma_1)| \left(-18B^4 + 540B^6 \right) \end{array} \quad (11-26c)$$

The matrices are, as expected, diagonal in the octahedral basis.

11.6. Calculation of Magnetic Dipole Hyperfine Matrix Elements

For a free ion 3F_3 term we would compute the magnetic dipole hyperfine matrix elements in a $|JIFM_F\rangle$ basis using the results of S6.3 to obtain the matrices

$$\begin{array}{c} M_F = \frac{11}{2} \quad |33\frac{5}{2}\frac{5}{2}\rangle \\ \langle 33\frac{5}{2}\frac{5}{2}| \left(\begin{array}{c} \frac{15}{2} \end{array} \right) \end{array} \quad (11-27a)$$

$$\begin{array}{c} M_F = \frac{9}{2} \quad |33\frac{5}{2}\frac{3}{2}\rangle \quad |32\frac{5}{2}\frac{5}{2}\rangle \\ \langle 33\frac{5}{2}\frac{3}{2}| \left(\begin{array}{cc} \frac{9}{2} & \frac{\sqrt{30}}{2} \\ \frac{\sqrt{30}}{2} & 5 \end{array} \right) \\ \langle 32, \frac{5}{2}\frac{5}{2}| \end{array} \quad (11-27b)$$

$$\begin{array}{c} M_F = \frac{7}{2} \quad |33\frac{5}{2}\frac{1}{2}\rangle \quad |32\frac{5}{2}\frac{3}{2}\rangle \quad |31\frac{5}{2}\frac{5}{2}\rangle \\ \langle 33\frac{5}{2}\frac{1}{2}| \left(\begin{array}{ccc} \frac{3}{2} & 2\sqrt{3} & 0 \\ 2\sqrt{3} & 3 & \frac{5}{2}\sqrt{2} \\ 0 & \frac{5}{2}\sqrt{2} & \frac{5}{2} \end{array} \right) \\ \langle 32\frac{5}{2}\frac{3}{2}| \\ \langle 31\frac{5}{2}\frac{5}{2}| \end{array} \quad (11-27c)$$

$$\begin{array}{c} M_F = \frac{5}{2} \quad |33\frac{5}{2} - \frac{1}{2}\rangle \quad |32\frac{5}{2}\frac{1}{2}\rangle \quad |31\frac{5}{2}\frac{3}{2}\rangle \quad |30\frac{5}{2}\frac{5}{2}\rangle \\ \langle 33\frac{5}{2} - \frac{1}{2}| \left(\begin{array}{cccc} -\frac{3}{2} & \frac{3}{2}\sqrt{6} & 0 & 0 \\ \frac{3}{2}\sqrt{6} & 1 & 2\sqrt{5} & 0 \\ 0 & 2\sqrt{5} & \frac{3}{2} & \sqrt{15} \\ 0 & 0 & \sqrt{15} & 0 \end{array} \right) \\ \langle 32\frac{5}{2}\frac{1}{2}| \\ \langle 31\frac{5}{2}\frac{3}{2}| \\ \langle 30, \frac{5}{2}\frac{5}{2}| \end{array} \quad (11-27d)$$

$$\begin{array}{c} M_F = \frac{3}{2} \quad |33\frac{5}{2} - \frac{3}{2}\rangle \quad |32\frac{5}{2} - \frac{1}{2}\rangle \quad |31\frac{5}{2}\frac{1}{2}\rangle \quad |30\frac{5}{2}\frac{3}{2}\rangle \quad |3 - 1\frac{5}{2}\frac{5}{2}\rangle \\ \langle 33\frac{5}{2} - \frac{3}{2}| \left(\begin{array}{ccccc} -\frac{9}{2} & 2\sqrt{3} & 0 & 0 & 0 \\ 2\sqrt{3} & -1 & \frac{3}{2}\sqrt{10} & 0 & 0 \\ 0 & \frac{3}{2}\sqrt{10} & \frac{1}{2} & 2\sqrt{6} & 0 \\ 0 & 0 & 2\sqrt{6} & 0 & \sqrt{15} \\ 0 & 0 & 0 & \sqrt{15} & -\frac{5}{2} \end{array} \right) \\ \langle 32\frac{5}{2} - \frac{1}{2}| \\ \langle 31\frac{5}{2}\frac{1}{2}| \\ \langle 30\frac{5}{2}\frac{3}{2}| \\ \langle 3 - 1\frac{5}{2}\frac{5}{2}| \end{array} \quad (11-27e)$$

$$\begin{array}{l}
M_F = \frac{1}{2} \quad |33\frac{5}{2} - \frac{5}{2}\rangle \quad |32\frac{5}{2} - \frac{3}{2}\rangle \quad |31\frac{5}{2} - \frac{1}{2}\rangle \quad |30\frac{5}{2}\frac{1}{2}\rangle \quad |3 - 1\frac{5}{2}\frac{3}{2}\rangle \quad |3 - 2\frac{5}{2}\frac{5}{2}\rangle \\
\langle 33\frac{5}{2} - \frac{5}{2}| \left(\begin{array}{cccccc}
-\frac{15}{2} & \frac{1}{2}\sqrt{30} & 0 & 0 & 0 & 0 \\
\frac{1}{2}\sqrt{30} & -3 & 2\sqrt{5} & 0 & 0 & 0 \\
0 & 2\sqrt{5} & -\frac{1}{2} & 3\sqrt{3} & 0 & 0 \\
0 & 0 & 3\sqrt{3} & 0 & 2\sqrt{6} & 0 \\
0 & 0 & 0 & 2\sqrt{6} & -\frac{3}{2} & \frac{5}{2}\sqrt{2} \\
0 & 0 & 0 & 0 & \frac{5}{2}\sqrt{2} & -5
\end{array} \right) \\
\langle 32\frac{5}{2} - \frac{3}{2}| \\
\langle 31\frac{5}{2} - \frac{1}{2}| \\
\langle 30\frac{5}{2}\frac{1}{2}| \\
\langle 3 - 1\frac{5}{2}\frac{3}{2}| \\
\langle 3 - 2\frac{5}{2}\frac{5}{2}|
\end{array} \quad (11-27f)$$

$$\begin{array}{l}
M_F = -\frac{1}{2} \quad |32\frac{5}{2} - \frac{5}{2}\rangle \quad |31\frac{5}{2} - \frac{3}{2}\rangle \quad |30\frac{5}{2} - \frac{1}{2}\rangle \quad |3 - 1\frac{5}{2}\frac{1}{2}\rangle \quad |3 - 2\frac{5}{2}\frac{3}{2}\rangle \quad |3 - 3\frac{5}{2}\frac{5}{2}\rangle \\
\langle 32\frac{5}{2} - \frac{5}{2}| \left(\begin{array}{cccccc}
-5 & \frac{5}{2}\sqrt{2} & 0 & 0 & 0 & 0 \\
\frac{5}{2}\sqrt{2} & -\frac{3}{2} & 2\sqrt{6} & 0 & 0 & 0 \\
0 & 2\sqrt{6} & 0 & 3\sqrt{3} & 0 & 0 \\
0 & 0 & 3\sqrt{3} & -\frac{1}{2} & 2\sqrt{5} & 0 \\
0 & 0 & 0 & 2\sqrt{5} & -3 & \frac{1}{2}\sqrt{30} \\
0 & 0 & 0 & 0 & \frac{1}{2}\sqrt{30} & -\frac{15}{2}
\end{array} \right) \\
\langle 31\frac{5}{2} - \frac{3}{2}| \\
\langle 30\frac{5}{2} - \frac{1}{2}| \\
\langle 3 - 1\frac{5}{2}\frac{1}{2}| \\
\langle 3 - 2\frac{5}{2}\frac{3}{2}| \\
\langle 3 - 3\frac{5}{2}\frac{5}{2}|
\end{array} \quad (11-27g)$$

$$\begin{array}{l}
M_F = -\frac{3}{2} \quad |31\frac{5}{2} - \frac{5}{2}\rangle \quad |30\frac{5}{2} - \frac{3}{2}\rangle \quad |3 - 1\frac{5}{2} - \frac{1}{2}\rangle \quad |3 - 2\frac{5}{2}\frac{1}{2}\rangle \quad |3 - 3\frac{5}{2}\frac{3}{2}\rangle \\
\langle 31\frac{5}{2} - \frac{5}{2}| \left(\begin{array}{ccccc}
-\frac{5}{2} & \sqrt{15} & 0 & 0 & 0 \\
\sqrt{15} & 0 & 2\sqrt{6} & 0 & 0 \\
0 & 2\sqrt{6} & \frac{1}{2} & \frac{3}{2}\sqrt{10} & 0 \\
0 & 0 & \frac{3}{2}\sqrt{10} & -1 & 2\sqrt{3} \\
0 & 0 & 0 & 2\sqrt{3} & -\frac{9}{2}
\end{array} \right) \\
\langle 30\frac{5}{2} - \frac{3}{2}| \\
\langle 3 - 1\frac{5}{2} - \frac{1}{2}| \\
\langle 3 - 2\frac{5}{2}\frac{1}{2}| \\
\langle 3 - 3\frac{5}{2}\frac{3}{2}|
\end{array} \quad (11-27h)$$

$$\begin{array}{l}
M_F = -\frac{5}{2} \quad |30\frac{5}{2} - \frac{5}{2}\rangle \quad |3 - 1\frac{5}{2} - \frac{3}{2}\rangle \quad |3 - 2\frac{5}{2} - \frac{1}{2}\rangle \quad |3 - 3\frac{5}{2}\frac{1}{2}\rangle \\
\langle 30\frac{5}{2} - \frac{5}{2}| \left(\begin{array}{cccc}
0 & \sqrt{15} & 0 & 0 \\
\sqrt{15} & \frac{3}{2} & 2\sqrt{5} & 0 \\
0 & 2\sqrt{5} & 1 & \frac{3}{2}\sqrt{6} \\
0 & 0 & \frac{3}{2}\sqrt{6} & -\frac{3}{2}
\end{array} \right) \\
\langle 3 - 1\frac{5}{2} - \frac{3}{2}| \\
\langle 3 - 2\frac{5}{2} - \frac{1}{2}| \\
\langle 3 - 3\frac{5}{2}\frac{1}{2}|
\end{array} \quad (11-27i)$$

$$\begin{array}{l}
M_F = -\frac{7}{2} \quad |3 - 1\frac{5}{2} - \frac{5}{2}\rangle \quad |3 - 2\frac{5}{2} - \frac{3}{2}\rangle \quad |3 - 3\frac{5}{2} - \frac{1}{2}\rangle \\
\langle 3 - 1\frac{5}{2} - \frac{5}{2}| \left(\begin{array}{ccc}
\frac{5}{2} & \frac{5}{2}\sqrt{2} & 0 \\
\frac{5}{2}\sqrt{2} & 3 & 2\sqrt{3} \\
0 & 2\sqrt{3} & \frac{3}{2}
\end{array} \right) \\
\langle 3 - 2\frac{5}{2} - \frac{3}{2}| \\
\langle 3 - 3\frac{5}{2} - \frac{1}{2}|
\end{array} \quad (11-27j)$$

$$\begin{aligned}
M_F = -\frac{9}{2} & \quad |3 - 2\frac{5}{2} - \frac{5}{2}\rangle \quad |3 - 3\frac{5}{2} - \frac{3}{2}\rangle \\
\langle 3 - 2\frac{5}{2} - \frac{5}{2}| & \left(\begin{array}{cc} 5 & \frac{1}{2}\sqrt{30} \\ \frac{1}{2}\sqrt{30} & \frac{9}{2} \end{array} \right) \\
\langle 3 - 3\frac{5}{2} - \frac{3}{2}| &
\end{aligned} \tag{11-27k}$$

$$\begin{aligned}
M_F = -\frac{11}{2} & \quad |3 - 3\frac{5}{2} - \frac{5}{2}\rangle \\
\langle 3 - 3\frac{5}{2} - \frac{5}{2}| & \left(\begin{array}{c} \frac{15}{2} \end{array} \right)
\end{aligned} \tag{11-27\ell}$$

The above matrices can be checked by diagonalisation. The resultant eigenvalues should be proportional to the value K defined in (11-9) where F has its maximal value of M_F . The eigenvalues for the above matrices are:

$$M_F = \frac{11}{2} \quad \frac{15}{2} \tag{11-28a}$$

$$M_F = \frac{9}{2} \quad \frac{15}{2}, \quad 2 \tag{11-28b}$$

$$M_F = \frac{7}{2} \quad \frac{15}{2}, \quad 2, \quad -\frac{5}{2} \tag{11-28c}$$

$$M_F = \frac{5}{2} \quad \frac{15}{2}, \quad 2, \quad -\frac{5}{2}, \quad -6 \tag{11-28d}$$

$$M_F = \frac{3}{2} \quad \frac{15}{2}, \quad 2, \quad -\frac{5}{2}, \quad -6, \quad -\frac{17}{2} \tag{11-28e}$$

$$M_F = \frac{1}{2} \quad \frac{15}{2}, \quad 2, \quad -\frac{5}{2}, \quad -6, \quad -\frac{17}{2}, \quad -10 \tag{11-28f}$$

$$M_F = -\frac{1}{2} \quad -\frac{17}{2}, \quad 2, \quad -\frac{5}{2}, \quad -10, \quad -6, \quad \frac{15}{2} \tag{11-28g}$$

$$M_F = -\frac{3}{2} \quad -\frac{17}{2}, \quad 2, \quad -\frac{5}{2}, \quad -6, \quad \frac{15}{2} \tag{11-28h}$$

$$M_F = -\frac{5}{2} \quad 2, \quad -\frac{5}{2}, \quad -6, \quad \frac{15}{2} \tag{11-28i}$$

$$M_F = -\frac{7}{2} \quad 2, \quad -\frac{5}{2}, \quad \frac{15}{2} \tag{11-28j}$$

$$M_F = -\frac{9}{2} \quad 2, \quad \frac{15}{2} \tag{11-28k}$$

$$M_F = -\frac{11}{2} \quad \frac{15}{2} \tag{11-28\ell}$$

The above values should correspond to those that would be obtained in a strong field basis.

11.7. Magnetic Hyperfine Matrix Elements in an Octahedral Field

It is instructive to compute the magnetic hyperfine matrix elements for an octahedral field starting with the symmetrized eigenfunctions given in (11-23a-g). Let us put

$$M_{\pm} = \sqrt{(\frac{5}{2} \pm M_I)(\frac{7}{2} \mp M_I)} \tag{11-29}$$

The matrix elements follow from use of (11-23a-g) with (11-19) and (11-20) to give

$$\langle (^3\Gamma_2)IM_I|H_m|(^3\Gamma_2)IM_I\rangle = 0 \tag{11-30a}$$

$$\langle (^3\Gamma_2)IM_I|H_m|(^3\Gamma_5)aIM_I\rangle = -2M_I$$

$$\begin{aligned}
\langle ({}^3\Gamma_2)IM_I|H_m|({}^3\Gamma_5)bIM_I - 1 \rangle &= \sqrt{2}M_+ \\
\langle ({}^3\Gamma_2)IM_I|H_m|({}^3\Gamma_5)cIM_I + 1 \rangle &= -\sqrt{2}M_-
\end{aligned} \tag{11-30b}$$

$$\begin{aligned}
\langle ({}^3\Gamma_2)IM_I|H_m|({}^3\Gamma_4)aIM_I \rangle &= 0 \\
\langle ({}^3\Gamma_2)IM_I|H_m|({}^3\Gamma_4)bIM_I \rangle &= 0 \\
\langle ({}^3\Gamma_2)IM_I|H_m|({}^3\Gamma_4)cIM_I \rangle &= 0
\end{aligned} \tag{11-30c}$$

$$\begin{aligned}
\langle ({}^3\Gamma_5)aIM_I|H_m|({}^3\Gamma_5)aIM_I \rangle &= 0 \\
\langle ({}^3\Gamma_5)bIM_I|H_m|({}^3\Gamma_5)bIM_I \rangle &= \frac{M_I}{2} \\
\langle ({}^3\Gamma_5)cIM_I|H_m|({}^3\Gamma_5)cIM_I \rangle &= -\frac{M_I}{2}
\end{aligned} \tag{11-30d}$$

$$\begin{aligned}
\langle ({}^3\Gamma_5)aIM_I|H_m|({}^3\Gamma_5)bIM_I - 1 \rangle &= \frac{\sqrt{2}}{4}M_+ \\
\langle ({}^3\Gamma_5)aIM_I|H_m|({}^3\Gamma_5)cIM_I + 1 \rangle &= \frac{\sqrt{2}}{4}M_- \\
\langle ({}^3\Gamma_5)bIM_I|H_m|({}^3\Gamma_5)cIM_I \rangle &= 0
\end{aligned} \tag{11-30e}$$

$$\begin{aligned}
\langle ({}^3\Gamma_5)aIM_I|H_m|({}^3\Gamma_4)aIM_I \rangle &= -\sqrt{5}M_I \\
\langle ({}^3\Gamma_5)aIM_I|H_m|({}^3\Gamma_4)bIM_I - 1 \rangle &= \frac{\sqrt{10}}{4}M_+ \\
\langle ({}^3\Gamma_5)aIM_I|H_m|({}^3\Gamma_4)cIM_I + 1 \rangle &= -\frac{\sqrt{10}}{4}M_- \\
\langle ({}^3\Gamma_5)bIM_I|H_m|({}^3\Gamma_4)aIM_I + 1 \rangle &= -\frac{\sqrt{10}}{4}M_- \\
\langle ({}^3\Gamma_5)bIM_I|H_m|({}^3\Gamma_4)bIM_I \rangle &= -\frac{\sqrt{5}}{2}M_I \\
\langle ({}^3\Gamma_5)bIM_I|H_m|({}^3\Gamma_4)cIM_I - 1 \rangle &= \frac{\sqrt{10}}{2}M_+ \\
\langle ({}^3\Gamma_5)cIM_I|H_m|({}^3\Gamma_4)aIM_I - 1 \rangle &= \frac{\sqrt{10}}{4}M_+ \\
\langle ({}^3\Gamma_5)cIM_I|H_m|({}^3\Gamma_4)bIM_I + 1 \rangle &= \frac{\sqrt{10}}{2}M_- \\
\langle ({}^3\Gamma_5)cIM_I|H_m|({}^3\Gamma_4)cIM_I \rangle &= -\frac{\sqrt{5}}{2}M_I
\end{aligned} \tag{11-30f}$$

$$\begin{aligned}
\langle ({}^3\Gamma_4)aIM_I|H_m|({}^3\Gamma_4)aIM_I \rangle &= 0 \\
\langle ({}^3\Gamma_4)bIM_I|H_m|({}^3\Gamma_4)bIM_I \rangle &= -\frac{3M_I}{2} \\
\langle ({}^3\Gamma_4)cIM_I|H_m|({}^3\Gamma_4)cIM_I \rangle &= +\frac{3M_I}{2}
\end{aligned}$$

$$\begin{aligned}
\langle ({}^3\Gamma_4)aIM_I|H_m|({}^3\Gamma_4)bIM_I - 1\rangle &= \frac{3\sqrt{2}}{4}M_+ \\
\langle ({}^3\Gamma_4)aIM_I|H_m|({}^3\Gamma_4)cIM_I + 1\rangle &= \frac{3\sqrt{2}}{4}M_- \\
\langle ({}^3\Gamma_4)bIM_I|H_m|({}^3\Gamma_4)cIM_I\rangle &= 0
\end{aligned} \tag{11-30g}$$

We note that under the octahedral group H_m transforms as Γ_4 .

We note from (11-30a), (11-30d) and (11-30g) that the Γ_2 state has no first-order magnetic hyperfine structure whereas the splitting for the Γ_4 states is three times larger than for the Γ_5 states.

11.8. Octahedral Magnetic Hyperfine Matrix Elements

Using (11-30a,d,e,g) we can readily calculate the matrix elements within each octahedral state to give the matrices and their respective eigenvalues and eigenvectors (in designating the eigenvectors we have suppressed the $I = \frac{5}{2}$) as

$$\begin{aligned}
({}^3\Gamma_5) \quad & \begin{array}{cc} |a_{\frac{5}{2}\frac{5}{2}}\rangle & |b_{\frac{5}{2}\frac{3}{2}}\rangle \end{array} \\
\langle a_{\frac{5}{2}\frac{5}{2}}| & \begin{pmatrix} 0 & \frac{\sqrt{10}}{4} \\ \frac{\sqrt{10}}{4} & \frac{3}{4} \end{pmatrix} \quad \left(-\frac{1}{2}, \quad \frac{5}{4}\right) \\
\langle b_{\frac{5}{2}\frac{3}{2}}| & \\
|-\frac{1}{2}\rangle_1^{(-3)} &= \frac{1}{\sqrt{7}}[\sqrt{2}|a_{\frac{5}{2}}\rangle - \sqrt{5}|b_{\frac{3}{2}}\rangle] \\
|\frac{5}{4}\rangle_1^{(-3)} &= \frac{1}{\sqrt{7}}[\sqrt{5}|a_{\frac{5}{2}}\rangle + \sqrt{2}|b_{\frac{3}{2}}\rangle]
\end{aligned} \tag{11-31a}$$

$$\begin{aligned}
({}^3\Gamma_5) \quad & \begin{array}{ccc} |a_{\frac{5}{2}\frac{3}{2}}\rangle & |b_{\frac{5}{2}\frac{1}{2}}\rangle & |c_{\frac{5}{2}\frac{5}{2}}\rangle \end{array} \\
\langle a_{\frac{5}{2}\frac{3}{2}}| & \begin{pmatrix} 0 & 1 & \frac{\sqrt{10}}{4} \\ 1 & \frac{1}{4} & 0 \\ \frac{\sqrt{10}}{4} & 0 & -\frac{5}{4} \end{pmatrix} \quad \left(-\frac{7}{4}, \quad -\frac{1}{2}, \quad \frac{5}{4}\right) \\
\langle b_{\frac{5}{2}\frac{1}{2}}| & \\
\langle c_{\frac{5}{2}\frac{5}{2}}| & \\
|-\frac{1}{2}\rangle_2^{(-3)} &= \frac{1}{\sqrt{35}}[3|a_{\frac{3}{2}}\rangle - 4|b_{\frac{1}{2}}\rangle + \sqrt{10}|c_{\frac{5}{2}}\rangle] \\
|\frac{5}{4}\rangle_2^{(-3)} &= \frac{1}{\sqrt{21}}[\sqrt{10}|a_{\frac{3}{2}}\rangle + \sqrt{10}|b_{\frac{1}{2}}\rangle + |c_{\frac{5}{2}}\rangle] \\
|-\frac{7}{4}\rangle_1^{(-3)} &= \frac{1}{\sqrt{15}}[-2|a_{\frac{3}{2}}\rangle + |b_{\frac{1}{2}}\rangle + \sqrt{10}|c_{\frac{5}{2}}\rangle]
\end{aligned} \tag{11-31b}$$

$$\begin{aligned}
({}^3\Gamma_5) \quad & \begin{array}{ccc} |a_{\frac{5}{2}\frac{1}{2}}\rangle & |b_{\frac{5}{2}-\frac{1}{2}}\rangle & |c_{\frac{5}{2}\frac{3}{2}}\rangle \end{array} \\
\langle a_{\frac{5}{2}\frac{1}{2}}| & \begin{pmatrix} 0 & \frac{3\sqrt{2}}{4} & 1 \\ \frac{3\sqrt{2}}{4} & -\frac{1}{4} & 0 \\ 1 & 0 & -\frac{3}{4} \end{pmatrix} \quad \left(-\frac{7}{4}, \quad -\frac{1}{2}, \quad \frac{5}{4}\right) \\
\langle b_{\frac{5}{2}-\frac{1}{2}}| & \\
\langle c_{\frac{5}{2}\frac{3}{2}}| &
\end{aligned}$$

$$\begin{aligned}
|-\frac{1}{2}\rangle_3^{(-3)} &= \frac{1}{\sqrt{35}}[|a\frac{1}{2}\rangle - 3\sqrt{2}|b-\frac{1}{2}\rangle + 4|c\frac{3}{2}\rangle] \\
|\frac{5}{4}\rangle_3^{(-3)} &= \frac{1}{\sqrt{7}}[2|a\frac{1}{2}\rangle + \sqrt{2}|b-\frac{1}{2}\rangle + |c\frac{3}{2}\rangle] \\
|-\frac{7}{4}\rangle_2^{(-3)} &= \frac{1}{\sqrt{5}}[-\sqrt{2}|a\frac{1}{2}\rangle + |b-\frac{1}{2}\rangle + \sqrt{2}|c\frac{3}{2}\rangle]
\end{aligned} \tag{11-31c}$$

$$\begin{aligned}
({}^3\Gamma_5) \quad & |a\frac{5}{2}-\frac{1}{2}\rangle \quad |b\frac{5}{2}-\frac{3}{2}\rangle \quad |c\frac{5}{2}\frac{1}{2}\rangle \\
\langle a\frac{5}{2}-\frac{1}{2}| & \begin{pmatrix} 0 & 1 & \frac{3\sqrt{2}}{4} \\ 1 & -\frac{3}{4} & 0 \\ \frac{3\sqrt{2}}{4} & 0 & -\frac{1}{4} \end{pmatrix} \quad \left(-\frac{7}{4}, \quad -\frac{1}{2}, \quad \frac{5}{4}\right) \\
\langle b\frac{5}{2}-\frac{3}{2}| & \\
\langle c\frac{5}{2}\frac{1}{2}| & \\
|-\frac{1}{2}\rangle_4^{(-3)} &= \frac{1}{\sqrt{35}}[|a-\frac{1}{2}\rangle + 4|b-\frac{3}{2}\rangle - 3\sqrt{2}|c\frac{1}{2}\rangle] \\
|\frac{5}{4}\rangle_4^{(-3)} &= \frac{1}{\sqrt{7}}[2|a-\frac{1}{2}\rangle + |b-\frac{3}{2}\rangle + \sqrt{2}|c\frac{1}{2}\rangle] \\
|-\frac{7}{4}\rangle_3^{(-3)} &= \frac{1}{\sqrt{5}}[-\sqrt{2}|a-\frac{1}{2}\rangle + \sqrt{2}|b-\frac{3}{2}\rangle + |c\frac{1}{2}\rangle]
\end{aligned} \tag{11-31d}$$

$$\begin{aligned}
({}^3\Gamma_5) \quad & |a\frac{5}{2}-\frac{3}{2}\rangle \quad |b\frac{5}{2}-\frac{5}{2}\rangle \quad |c\frac{5}{2}-\frac{1}{2}\rangle \\
\langle a\frac{5}{2}-\frac{3}{2}| & \begin{pmatrix} 0 & \frac{\sqrt{10}}{4} & 1 \\ \frac{\sqrt{10}}{4} & -\frac{5}{4} & 0 \\ 1 & 0 & \frac{1}{4} \end{pmatrix} \quad \left(-\frac{7}{4}, \quad -\frac{1}{2}, \quad \frac{5}{4}\right) \\
\langle b\frac{5}{2}-\frac{5}{2}| & \\
\langle c\frac{5}{2}-\frac{1}{2}| & \\
|-\frac{1}{2}\rangle_5^{(-3)} &= \frac{1}{\sqrt{35}}[-3|a-\frac{3}{2}\rangle - \sqrt{10}|b-\frac{5}{2}\rangle + 4|c-\frac{1}{2}\rangle] \\
|\frac{5}{4}\rangle_5^{(-3)} &= \frac{1}{\sqrt{21}}[\sqrt{10}|a-\frac{3}{2}\rangle + |b-\frac{5}{2}\rangle + \sqrt{10}|c-\frac{1}{2}\rangle] \\
|-\frac{7}{4}\rangle_4^{(-3)} &= \frac{1}{\sqrt{15}}[-2|a-\frac{3}{2}\rangle + \sqrt{10}|b-\frac{5}{2}\rangle + |c-\frac{1}{2}\rangle]
\end{aligned} \tag{11-31e}$$

$$\begin{aligned}
({}^3\Gamma_5) \quad & |a\frac{5}{2}-\frac{5}{2}\rangle \quad |c\frac{5}{2}-\frac{3}{2}\rangle \\
\langle a\frac{5}{2}-\frac{5}{2}| & \begin{pmatrix} 0 & \frac{\sqrt{10}}{4} \\ \frac{\sqrt{10}}{4} & \frac{3}{4} \end{pmatrix} \quad \left(-\frac{1}{2}, \quad \frac{5}{4}\right) \\
\langle c\frac{5}{2}-\frac{3}{2}| & \\
|-\frac{1}{2}\rangle_6^{(-3)} &= \frac{1}{\sqrt{7}}[-\sqrt{5}|a-\frac{5}{2}\rangle + \sqrt{2}|c-\frac{3}{2}\rangle] \\
|\frac{5}{4}\rangle_6^{(-3)} &= \frac{1}{\sqrt{7}}[\sqrt{2}|a-\frac{5}{2}\rangle + \sqrt{5}|c-\frac{3}{2}\rangle]
\end{aligned} \tag{11-31f}$$

$$\begin{aligned}
({}^3\Gamma_5) \quad & |b\frac{5}{2}\frac{5}{2}\rangle \\
\langle b\frac{5}{2}\frac{5}{2}| & \begin{pmatrix} \frac{5}{4} \end{pmatrix} \quad \left(\frac{5}{4}\right) \\
|\frac{5}{4}\rangle_7^{(-3)} &= |b\frac{5}{2}\rangle
\end{aligned} \tag{11-31g}$$

$$\begin{aligned}
& ({}^3\Gamma_5) \quad |c_{\frac{5}{2}}^{\frac{5}{2}} - \frac{5}{2}\rangle \\
\langle c_{\frac{5}{2}}^{\frac{5}{2}} - \frac{5}{2} | & \begin{pmatrix} & \frac{5}{4} \\ & \end{pmatrix} \quad ({}^{\frac{5}{4}}) \\
| \frac{5}{4} \rangle_8^{(-3)} & = |c - \frac{5}{2}\rangle
\end{aligned} \tag{11-31h}$$

$$\begin{aligned}
& ({}^3\Gamma_4) \quad |a_{\frac{5}{2}\frac{5}{2}}^{\frac{5}{2}}\rangle \quad |b_{\frac{5}{2}\frac{3}{2}}^{\frac{5}{2}}\rangle \\
\langle a_{\frac{5}{2}\frac{5}{2}}^{\frac{5}{2}} | & \begin{pmatrix} 0 & \frac{3\sqrt{10}}{4} \\ \frac{3\sqrt{10}}{4} & -\frac{9}{4} \end{pmatrix} \quad (-\frac{15}{4}, \quad \frac{3}{2}) \\
\langle b_{\frac{5}{2}\frac{3}{2}}^{\frac{5}{2}} | & \\
| \frac{3}{2} \rangle_1^{(9)} & = \frac{1}{\sqrt{7}}[\sqrt{5}|a_{\frac{5}{2}}^{\frac{5}{2}}\rangle + \sqrt{2}|b_{\frac{3}{2}}^{\frac{3}{2}}\rangle] \\
| -\frac{15}{4} \rangle_1^{(9)} & = \frac{1}{\sqrt{7}}[\sqrt{2}|a_{\frac{5}{2}}^{\frac{5}{2}}\rangle - \sqrt{5}|b_{\frac{3}{2}}^{\frac{3}{2}}\rangle]
\end{aligned} \tag{11-32a}$$

$$\begin{aligned}
& ({}^3\Gamma_4) \quad |a_{\frac{5}{2}\frac{3}{2}}^{\frac{5}{2}}\rangle \quad |b_{\frac{5}{2}\frac{1}{2}}^{\frac{5}{2}}\rangle \quad |c_{\frac{5}{2}\frac{5}{2}}^{\frac{5}{2}}\rangle \\
\langle a_{\frac{5}{2}\frac{3}{2}}^{\frac{5}{2}} | & \begin{pmatrix} 0 & 3 & \frac{3\sqrt{10}}{4} \\ 3 & -\frac{3}{4} & 0 \\ \frac{3\sqrt{10}}{4} & 0 & \frac{15}{4} \end{pmatrix} \quad (-\frac{15}{4}, \quad \frac{3}{2}, \quad \frac{21}{4}) \\
\langle b_{\frac{5}{2}\frac{1}{2}}^{\frac{5}{2}} | & \\
\langle c_{\frac{5}{2}\frac{5}{2}}^{\frac{5}{2}} | & \\
| \frac{3}{2} \rangle_2^{(9)} & = \frac{1}{\sqrt{35}}[3|a_{\frac{3}{2}}^{\frac{3}{2}}\rangle + 4|b_{\frac{1}{2}}^{\frac{1}{2}}\rangle - \sqrt{10}|c_{\frac{5}{2}}^{\frac{5}{2}}\rangle] \\
| -\frac{15}{4} \rangle_2^{(9)} & = \frac{1}{\sqrt{21}}[-\sqrt{10}|a_{\frac{3}{2}}^{\frac{3}{2}}\rangle + \sqrt{10}|b_{\frac{1}{2}}^{\frac{1}{2}}\rangle + |c_{\frac{5}{2}}^{\frac{5}{2}}\rangle] \\
| \frac{21}{4} \rangle_1^{(9)} & = \frac{1}{\sqrt{15}}[2|a_{\frac{3}{2}}^{\frac{3}{2}}\rangle + |b_{\frac{1}{2}}^{\frac{1}{2}}\rangle + \sqrt{10}|c_{\frac{5}{2}}^{\frac{5}{2}}\rangle]
\end{aligned} \tag{11-32b}$$

$$\begin{aligned}
& ({}^3\Gamma_4) \quad |a_{\frac{5}{2}\frac{1}{2}}^{\frac{5}{2}}\rangle \quad |b_{\frac{5}{2} - \frac{1}{2}}^{\frac{5}{2}}\rangle \quad |c_{\frac{5}{2}\frac{3}{2}}^{\frac{5}{2}}\rangle \\
\langle a_{\frac{5}{2}\frac{1}{2}}^{\frac{5}{2}} | & \begin{pmatrix} 0 & \frac{9\sqrt{2}}{4} & 3 \\ \frac{9\sqrt{2}}{4} & \frac{3}{4} & 0 \\ 3 & 0 & \frac{9}{4} \end{pmatrix} \quad (-\frac{15}{4}, \quad \frac{3}{2}, \quad \frac{21}{4}) \\
\langle b_{\frac{5}{2} - \frac{1}{2}}^{\frac{5}{2}} | & \\
\langle c_{\frac{5}{2}\frac{3}{2}}^{\frac{5}{2}} | & \\
| \frac{3}{2} \rangle_3^{(9)} & = \frac{1}{\sqrt{35}}[|a_{\frac{1}{2}}^{\frac{1}{2}}\rangle + 3\sqrt{2}|b - \frac{1}{2}\rangle - 4|c_{\frac{3}{2}}^{\frac{3}{2}}\rangle] \\
| -\frac{15}{4} \rangle_3^{(9)} & = \frac{1}{\sqrt{7}}[-2|a_{\frac{1}{2}}^{\frac{1}{2}}\rangle + \sqrt{2}|b - \frac{1}{2}\rangle + |c_{\frac{3}{2}}^{\frac{3}{2}}\rangle] \\
| \frac{21}{4} \rangle_2^{(9)} & = \frac{1}{\sqrt{5}}[\sqrt{2}|a_{\frac{1}{2}}^{\frac{1}{2}}\rangle + |b - \frac{1}{2}\rangle + \sqrt{2}|c_{\frac{3}{2}}^{\frac{3}{2}}\rangle]
\end{aligned} \tag{11-32c}$$

$$\begin{aligned}
& ({}^3\Gamma_4) \quad |a_{\frac{5}{2} - \frac{1}{2}}^{\frac{5}{2}}\rangle \quad |b_{\frac{5}{2} - \frac{3}{2}}^{\frac{5}{2}}\rangle \quad |c_{\frac{5}{2}\frac{1}{2}}^{\frac{5}{2}}\rangle \\
\langle a_{\frac{5}{2} - \frac{1}{2}}^{\frac{5}{2}} | & \begin{pmatrix} 0 & 3 & \frac{9\sqrt{2}}{4} \\ 3 & \frac{9}{4} & 0 \\ \frac{9\sqrt{2}}{4} & 0 & \frac{3}{4} \end{pmatrix} \quad (-\frac{15}{4}, \quad \frac{3}{2}, \quad \frac{21}{4}) \\
\langle b_{\frac{5}{2} - \frac{3}{2}}^{\frac{5}{2}} | & \\
\langle c_{\frac{5}{2}\frac{1}{2}}^{\frac{5}{2}} | &
\end{aligned}$$

$$\begin{aligned}
\left|\frac{3}{2}\right\rangle_4^{(9)} &= \frac{1}{\sqrt{35}}[|a - \frac{1}{2}\rangle - 4|b - \frac{3}{2}\rangle + 3\sqrt{2}|c\frac{1}{2}\rangle] \\
\left|-\frac{15}{4}\right\rangle_4^{(9)} &= \frac{1}{\sqrt{7}}[-2|a - \frac{1}{2}\rangle + |b - \frac{3}{2}\rangle + \sqrt{2}|c\frac{1}{2}\rangle] \\
\left|\frac{21}{4}\right\rangle_3^{(9)} &= \frac{1}{\sqrt{5}}[\sqrt{2}|a - \frac{1}{2}\rangle + \sqrt{2}|b - \frac{3}{2}\rangle + |c\frac{1}{2}\rangle]
\end{aligned} \tag{11-32d}$$

$$\begin{aligned}
({}^3\Gamma_4) \quad & \begin{matrix} |a\frac{5}{2} - \frac{3}{2}\rangle & |b\frac{5}{2} - \frac{5}{2}\rangle & |c\frac{5}{2} - \frac{1}{2}\rangle \\ \langle a\frac{5}{2} - \frac{3}{2}| & \left(\begin{matrix} 0 & \frac{3\sqrt{10}}{4} & 3 \\ \frac{3\sqrt{10}}{4} & \frac{15}{4} & 0 \\ 3 & 0 & -\frac{3}{4} \end{matrix} \right) & \left(-\frac{15}{4}, \quad \frac{3}{2}, \quad \frac{21}{4} \right) \\ \langle b\frac{5}{2} - \frac{5}{2}| & \\ \langle c\frac{5}{2} - \frac{1}{2}| & \end{matrix} \\
\left|\frac{3}{2}\right\rangle_5^{(9)} &= \frac{1}{\sqrt{35}}[3|a - \frac{3}{2}\rangle - \sqrt{10}|b - \frac{5}{2}\rangle + 4|c - \frac{1}{2}\rangle] \\
\left|-\frac{15}{4}\right\rangle_5^{(9)} &= \frac{1}{\sqrt{21}}[-\sqrt{10}|a - \frac{3}{2}\rangle + |b - \frac{5}{2}\rangle + \sqrt{10}|c - \frac{1}{2}\rangle] \\
\left|\frac{21}{4}\right\rangle_4^{(9)} &= \frac{1}{\sqrt{15}}[2|a - \frac{3}{2}\rangle + \sqrt{10}|b - \frac{5}{2}\rangle + |c - \frac{1}{2}\rangle]
\end{aligned} \tag{11-32e}$$

$$\begin{aligned}
({}^3\Gamma_4) \quad & \begin{matrix} |a\frac{5}{2} - \frac{5}{2}\rangle & |c\frac{5}{2} - \frac{3}{2}\rangle \\ \langle a\frac{5}{2} - \frac{5}{2}| & \left(\begin{matrix} 0 & \frac{3\sqrt{10}}{4} \\ \frac{3\sqrt{10}}{4} & -\frac{9}{4} \end{matrix} \right) & \left(-\frac{15}{4}, \quad \frac{3}{2} \right) \\ \langle c\frac{5}{2} - \frac{3}{2}| & \end{matrix} \\
\left|\frac{3}{2}\right\rangle_6^{(9)} &= \frac{1}{\sqrt{7}}[\sqrt{5}|a - \frac{5}{2}\rangle + \sqrt{2}|c - \frac{3}{2}\rangle] \\
\left|-\frac{15}{4}\right\rangle_6^{(9)} &= \frac{1}{\sqrt{7}}[\sqrt{2}|a - \frac{5}{2}\rangle - \sqrt{5}|c - \frac{3}{2}\rangle]
\end{aligned} \tag{11-32f}$$

$$\begin{aligned}
({}^3\Gamma_4) \quad & |b\frac{5}{2}\frac{5}{2}\rangle \\
\langle b\frac{5}{2}\frac{5}{2}| & \left(-\frac{15}{4} \right) \quad \left(-\frac{15}{4} \right) \\
\left|\frac{3}{2}\right\rangle_7^{(9)} &= |b\frac{5}{2}\rangle
\end{aligned} \tag{11-32g}$$

$$\begin{aligned}
({}^3\Gamma_4) \quad & |c\frac{5}{2} - \frac{5}{2}\rangle \\
\langle c\frac{5}{2} - \frac{5}{2}| & \left(-\frac{15}{4} \right) \quad \left(-\frac{15}{4} \right) \\
\left|\frac{3}{2}\right\rangle_8^{(9)} &= |c - \frac{5}{2}\rangle
\end{aligned} \tag{11-32h}$$

Note that the eigenvectors associated with each matrix form an orthonormal set but they are determined only to within an overall phase and hence caution must be

exercised in using them to calculate matrix elements involving eigenvectors associated with different orthonormal sets.

Further, note that the above eigenvalues are associated with considerable degeneracies, more than might at first be expected. In particular,

$$\langle {}^3\Gamma_2 \quad 6(0) \quad \rangle \quad (11-33a)$$

$$\langle {}^3\Gamma_4 \quad 6(\frac{3}{2}) \quad 8(-\frac{15}{4}) \quad 4(\frac{21}{4}) \quad \rangle \quad (11-33b)$$

$$\langle {}^3\Gamma_5 \quad 6(-\frac{1}{2}) \quad 8(\frac{5}{4}) \quad 4(-\frac{7}{4}) \quad \rangle \quad (11-33c)$$

Furthermore, there are just three distinct eigenvalues for the Γ_4 and Γ_5 irreps. Noting that

$$\Gamma_4 \times (\Gamma_7 + \Gamma_8) = 2\Gamma_6 + \Gamma_7 + 3\Gamma_8 \quad (11-34a)$$

$$\Gamma_5 \times (\Gamma_7 + \Gamma_8) = \Gamma_6 + 2\Gamma_7 + 3\Gamma_8 \quad (11-34b)$$

we might have expected two sets of six distinct eigenvalues arising from the Γ_4 and Γ_5 irreps. Nor does the eigenvalue spectrum involve equal spacings. Some of the extra degeneracy would be lifted if we included the magnetic hyperfine interaction between the states of the three irreps, ($\Gamma_2, \Gamma_4, \Gamma_5$) as seen by inspection of (11-31b) and 11-31f). However, a more important consideration is the influence of the trigonal C_{3v} crystal field.

11.9. Influence of the Trigonal C_{3v} Crystal Field

The crystal field is predominantly octahedral with a smaller trigonal component. The basic effect can be seen by introducing the operator

$$T = 120C_0^{(2)} \quad (11-35)$$

and considering the matrix elements

$$\begin{aligned} \langle \Gamma_2 | T | \Gamma_2 \rangle &= 0 \\ \langle ({}^3\Gamma_4)a | T | ({}^3\Gamma_4)a \rangle &= 2 \\ \langle ({}^3\Gamma_4)b | T | ({}^3\Gamma_4)b \rangle &= -1 = \langle ({}^3\Gamma_4)c | T | ({}^3\Gamma_4)c \rangle \\ \langle ({}^3\Gamma_5)a | T | ({}^3\Gamma_5)a \rangle &= 10 \\ \langle ({}^3\Gamma_5)b | T | ({}^3\Gamma_5)b \rangle &= -5 = \langle ({}^3\Gamma_5)c | T | ({}^3\Gamma_5)c \rangle \end{aligned} \quad (11-36)$$

The above results are consistent with the $O \rightarrow C_{3v}$ branching rules

$$\begin{aligned} \Gamma_2 &\rightarrow \Gamma_2 \\ \Gamma_4 &\rightarrow \Gamma_2 + \Gamma_3 \\ \Gamma_5 &\rightarrow \Gamma_1 + \Gamma_3 \end{aligned} \quad (11-37)$$

i.e. the octahedral Γ_2 irrep remains non-degenerate while the Γ_4 and Γ_5 split into a singlet and a doublet. The trigonal splitting octahedral Γ_5 irrep is five times larger than for the Γ_4 irrep. Inspection of the magnetic hyperfine matrices (11-31a-h) and (11-32a-h) shows that for both of the octahedral irreps Γ_4 and Γ_5 there is no coupling between the b and c components but there is coupling with the a components. If the trigonal crystal field interaction is significantly greater than that of the magnetic hyperfine interaction then the off-diagonal matrix elements of the magnetic hyperfine interaction may be ignored. Then only the diagonal magnetic hyperfine matrix elements in (11-31a-h) and (11-32a-h) need be considered. It is readily seen that the diagonal elements, and their degeneracies are

$${}^3\Gamma_4 \quad (0)6, \left(\frac{15}{4}\right)2, \left(\frac{9}{4}\right)2, \left(\frac{3}{4}\right)2, \left(-\frac{3}{4}\right)2, \left(-\frac{9}{4}\right)2, \\ \left(-\frac{15}{4}\right)2 \quad (11-38a)$$

$${}^3\Gamma_5 \quad (0)6, \left(\frac{5}{4}\right)2, \left(\frac{3}{4}\right)2, \left(\frac{1}{4}\right)2, \left(-\frac{1}{4}\right)2, \left(-\frac{3}{4}\right)2, \\ \left(-\frac{5}{4}\right)2 \quad (11-38b)$$

$$\Gamma_2 \quad (0)6 \quad (11-38c)$$

Recalling that under $SO(3) \rightarrow C_{3v}$

$$[5/2] \rightarrow 2(\Gamma_4 + \Gamma_5) + \Gamma_6 \quad (11-39)$$

and that for C_{3v}

$$\begin{aligned} \Gamma_1 \times 2(\Gamma_4 + \Gamma_5) + \Gamma_6 &= 2(\Gamma_4 + \Gamma_5) + \Gamma_6 \\ \Gamma_2 \times 2(\Gamma_4 + \Gamma_5) + \Gamma_6 &= 2(\Gamma_4 + \Gamma_5) + \Gamma_6 \\ \Gamma_3 \times 2(\Gamma_4 + \Gamma_5) + \Gamma_6 &= (\Gamma_4 + \Gamma_5) + 5\Gamma_6 \end{aligned} \quad (11-40)$$

it is not surprising that the eigenvalue spectrum involves, to first order, 6-fold eigenvalues that show no hyperfine splittings and two groups of six two-fold degenerate equi-spaced eigenvalues, each set being derived from the interaction of the nuclear magnetic moment with a Γ_3 C_{3v} crystal field level. The spacing, and total width of the six hyperfine levels derived from the Γ_3 C_{3v} irrep originating from the octahedral Γ_4 irrep is 3/2 times larger than that derived from the octahedral Γ_5 irrep in accord with observation. Departures from equi-spacing probably come from the consequences of off-diagonal hyperfine matrix elements rather than more exotic conjectured effects.

Lecture 12

"No one accustomed to mix with the higher classes of society will be at all inclined to dispute the advantages arising from a genteel appearance; it therefore becomes necessary that the means of acquiring this distinction should be clearly demonstrated. An attentive perusal of the following pages will conduce to this desired effect."

The Art of Tying the Cravat(1828) (From *the 85 ways to tie a tie*, thomas fink&yong mao *Fourth Estate* London (1999))

12. Relativistic Effects

In this lecture I intend to discuss the effects that arise in crystal field theory when one considers relativity. Relativistic crystal field theory¹⁰ started with attempts to calculate the electric quadrupole moment of the ground state $4f^7 6s^2 [^8S_{7/2}]$ of neutral europium in an atomic beam^{6,75}, a problem very analogous to the crystal field splitting of the ground state $4f^7 [^8S_{7/2}]$ of trivalent gadolinium^{10,76}. If we solve Dirac's equation for an electron $n\ell j$ in a central field we obtain two radial functions, F and G , that are associated with the small and large components of the Dirac wavefunction, respectively, and which depend on the total angular momentum j of the electron. Here we consider the simple case of a single electron in an f -orbital and then remark upon some of the consequences for such things as the Judd-Ofelt theory of intensities looking for effects that go beyond the standard non-relativistic theory.

12.1. Relativistic Crystal Field Theory

To give a specific example, assume a crystal field potential

$$V = A_2^0 r^2 C_0^{(2)} + A_4^0 r^4 C_0^{(4)} + A_6^0 r^6 C_0^{(6)} + A_6^6 r^6 (C_6^{(6)} + C_{-6}^{(6)}) \quad (12-1)$$

For a single f -electron we have the fourteen states

$$|\frac{7}{2} \pm \frac{1}{2}\rangle, |\frac{7}{2} \pm \frac{3}{4}\rangle, |\frac{7}{2} \pm \frac{5}{2}\rangle, |\frac{7}{2} \pm \frac{7}{2}\rangle, |\frac{5}{2} \pm \frac{1}{2}\rangle, |\frac{5}{2} \pm \frac{3}{4}\rangle, |\frac{5}{2} \pm \frac{5}{2}\rangle \quad (12-2)$$

Noting that²

$$\langle slj || C^{(k)} || slj' \rangle = \langle \ell || C^{(k)} || \ell \rangle (-1)^{s+\ell+j+k} \sqrt{(2j+1)(2j'+1)} \begin{Bmatrix} j & k & j' \\ \ell & s & \ell \end{Bmatrix} \quad (12-3)$$

leading to

$$\begin{aligned} & \langle sljm | r^k C_q^{(k)} | slj'm' \rangle \\ &= \langle \ell || C^{(k)} || \ell \rangle R_{jj'} (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \\ & \times (-1)^{s+\ell+j+k} \sqrt{(2j+1)(2j'+1)} \begin{Bmatrix} j & k & j' \\ \ell & s & \ell \end{Bmatrix} \end{aligned} \quad (12-4)$$

where each non-relativistic radial integral

$$R_{\ell\ell}^k = \int_0^\infty R_{n\ell}(r)r^k R_{n\ell} dr, \quad (12-5)$$

is now replaced three relativistic radial integrals $R_{jj'}^k$, such that

$$\begin{aligned} R_{++}^k &= \int_0^\infty r^k (F_+^2 + G_+^2) dr, \\ R_{+-}^k &= \int_0^\infty r^k (F_+ F_- + G_+ G_-) dr, \\ R_{--}^k &= \int_0^\infty r^k (F_-^2 + G_-^2) dr, \end{aligned} \quad (12-6)$$

with the + referring to $j = \ell + \frac{1}{2}$ and the - to $j = \ell - \frac{1}{2}$.

For fourteen states of a single f -electron we obtain the crystal field matrices

$$\begin{array}{ccc} \mu = \pm\frac{1}{2} & \left| \frac{7}{2} \pm \frac{1}{2} \right\rangle & \left| \frac{5}{2} \pm \frac{1}{2} \right\rangle \\ \left\langle \frac{7}{2} \pm \frac{1}{2} \right| & \left(\begin{array}{cc} \frac{5}{21} A_2^0 R_{++}^2 + \frac{9}{77} A_4^0 R_{++}^4 + \frac{25}{429} A_6^0 R_{++}^6 & \sqrt{3} (\pm \frac{2}{105} A_2^0 R_{+-}^2 \pm \frac{10}{231} A_4^0 R_{+-}^4 \\ & \pm \frac{50}{429} A_6^0 R_{+-}^6) \\ \sqrt{3} (\pm \frac{2}{105} A_2^0 R_{+-}^2 \pm \frac{10}{231} A_4^0 R_{+-}^4 & \frac{8}{35} A_2^0 R_{--}^2 + \frac{2}{21} A_4^0 R_{--}^4 \\ & \pm \frac{50}{429} A_6^0 R_{+-}^6) \end{array} \right) \end{array} \quad (12-7a)$$

$$\begin{array}{ccc} \mu = \pm\frac{3}{2} & \left| \frac{7}{2} \pm \frac{3}{2} \right\rangle & \left| \frac{5}{2} \pm \frac{3}{2} \right\rangle \\ \left\langle \frac{7}{2} \pm \frac{7}{2} \right| & \left(\begin{array}{cc} -\frac{1}{3} A_2^0 R_{++}^2 + \frac{1}{11} A_4^0 R_{++}^4 & \sqrt{10} (\pm \frac{1}{35} A_2^0 R_{+-}^2 \pm \frac{8}{231} A_4^0 R_{+-}^4 \\ & \mp \frac{5}{143} A_6^0 R_{+-}^6) \\ \sqrt{10} (\pm \frac{1}{35} A_2^0 R_{+-}^2 \pm \frac{8}{231} A_4^0 R_{+-}^4 \mp \frac{5}{143} A_6^0 R_{+-}^6) & \frac{2}{35} A_2^0 R_{--}^2 - \frac{1}{7} A_4^0 R_{--}^4 \end{array} \right) \end{array} \quad (12-7b)$$

$$\begin{array}{ccc} \mu = \pm\frac{5}{2} & \left| \frac{7}{2} \pm \frac{7}{2} \right\rangle & \left| \frac{7}{2} \mp \frac{5}{2} \right\rangle & \left| \frac{5}{2} \mp \frac{5}{2} \right\rangle \\ \left\langle \frac{7}{2} \pm \frac{7}{2} \right| & \left(\begin{array}{cc} -\frac{1}{3} A_2^0 R_{++}^2 + \frac{1}{11} A_4^0 R_{++}^4 - \frac{10\sqrt{33}}{429} A_6^0 R_{++}^6 & \mp \frac{10\sqrt{22}}{143} A_6^0 R_{++}^6 \\ & -\frac{5}{429} A_6^0 R_{++}^6 \\ \left\langle \frac{7}{2} \mp \frac{5}{2} \right| & \left(\begin{array}{cc} -\frac{10\sqrt{33}}{429} A_6^0 R_{++}^6 & \sqrt{6} (\mp \frac{1}{21} A_2^0 R_{+-}^2 \pm \frac{10}{231} A_4^0 R_{+-}^4 \\ & + \frac{25}{429} A_6^0 R_{+-}^6) \\ & \mp \frac{5}{429} A_6^0 R_{+-}^6) \\ \left\langle \frac{5}{2} \mp \frac{5}{2} \right| & \left(\begin{array}{cc} \mp \frac{10\sqrt{22}}{143} A_6^0 R_{+-}^6 & \sqrt{6} (\mp \frac{1}{21} A_2^0 R_{+-}^2 \pm \frac{10}{231} A_4^0 R_{+-}^4 \\ & - \frac{2}{7} A_2^0 R_{--}^2 + \frac{1}{21} A_4^0 R_{--}^4 \\ & \mp \frac{5}{429} A_6^0 R_{+-}^6) \end{array} \right) \end{array} \right) \end{array} \quad (12-7c)$$

If in the above matrices we were to make all the radial integrals $R_{jj'}^k$, of the same rank k equal we would obtain the standard non-relativistic crystal field matrices. The next problem is to extend the formulation to many-electron configurations. Two ways are open (1). Do the entire calculation in a jj -coupling basis; or (2). Follow Sandars and

Beck⁶ and continue to use the traditional LS -coupling basis by making the operator replacements

$$r^k \mathbf{C}^{(k)} \rightarrow \sum_{\kappa, \kappa'} b_k(\kappa \kappa') \mathbf{w}^{(\kappa \kappa')k}, \quad (12-8)$$

where the $\mathbf{w}^{(\kappa \kappa')k}$ are single-particle tensor operators² and the $b_k(\kappa \kappa')$ involve the relativistic radial integrals. One finds that

$$r^2 \mathbf{C}^{(2)} \rightarrow b_2(11) \mathbf{w}^{(11)2} + b_2(13) \mathbf{w}^{(13)2} + b_2(02) \mathbf{w}^{(02)2}, \quad (12-9a)$$

$$r^4 \mathbf{C}^{(4)} \rightarrow b_4(13) \mathbf{w}^{(13)4} + b_4(15) \mathbf{w}^{(15)4} + b_4(04) \mathbf{w}^{(04)4}, \quad (12-9b)$$

$$r^6 \mathbf{C}^{(6)} \rightarrow b_6(15) \mathbf{w}^{(15)6} + b_6(06) \mathbf{w}^{(06)6}, \quad (12-9c)$$

where

$$\begin{aligned} b_2(11) &= 4\sqrt{21} [-5R_{++}^2 + 3R_{+-}^2 + 2R_{--}^2] / 245 \\ b_2(13) &= 4\sqrt{7} [5R_{++}^2 + 4R_{+-}^2 - 9R_{--}^2] / 245 \\ b_2(02) &= -2\sqrt{42} [25R_{++}^2 + 6R_{+-}^2 + 18R_{--}^2] / 735 \end{aligned} \quad (12-10a)$$

$$\begin{aligned} b_4(13) &= 4\sqrt{21} [6R_{++}^4 - 5R_{+-}^4 - R_{--}^4] / 441 \\ b_4(15) &= 2\sqrt{2310} [-3R_{++}^4 - 8R_{+-}^4 + 11R_{--}^4] / 4851 \\ b_4(04) &= 2\sqrt{77} [18R_{++}^4 + 20R_{+-}^4 + 11R_{--}^4] / 1617 \end{aligned} \quad (12-10b)$$

$$\begin{aligned} b_6(15) &= 20\sqrt{77} [-R_{++}^6 + R_{+-}^6] / 1001 \\ b_6(06) &= -10\sqrt{462} [R_{++}^6 + 6R_{+-}^6] / 3003 \end{aligned} \quad (12-10c)$$

Not surprisingly, calculation with the replacement operators yields exactly the same results, for a single electron, as found in Eq.(12-7a-c). For states involving n equivalent electrons the $\mathbf{w}^{(\kappa \kappa')}$ are simply replaced by

$$\mathbf{W}^{(\kappa \kappa')} \rightarrow \sum_{i=1}^n \mathbf{w}^{(\kappa \kappa')} \quad (12-11)$$

and the matrix elements may be evaluated in the usual non-relativistic LS -coupling basis but with the associated radial integrals being taken from appropriate relativistic Dirac-Hartree-Fock wavefunctions. The important point to notice is that the replacement operators are *double tensor operators* that act in *both* the spin and orbital spaces whereas the non-relativistic crystal field operators act only in the orbital space. It is this property that leads to a second-order contribution to the ground state splitting for rare earth and actinide ions having a half-filled f -shell^{10,76,15}. Smentek *et al*¹⁵ have recently given detailed calculations of a relativistic crystal field for S -state f electron ions. Free ion non-relativistic calculations were performed using Froese-Fischer's MCHF programme while the relativistic radial integrals were evaluated using the GRASP² package. The inner s and p orbitals are contracted and hence the effective nuclear charge seen by the f -orbitals is *decreased* and the orbitals *expand*. Further numerical calculations need to be attempted.

12.2. Relativistic $f \longleftrightarrow f$ Transitions in Crystal Fields

Here we have products of the electric dipole and crystal field matrix elements coupling the f^N configuration to those of opposite parity. Again, whereas in the non-relativistic Judd-Ofelt theory transitions depend on the tensor operators $\mathbf{U}^{(k)}$ the relativistic treatment leads to double-tensor operators $\mathbf{W}^{(\kappa\kappa')k}$. In the Judd-Ofelt theory the single particle unit tensor operators $\mathbf{u}(n\ell, n'\ell')^{(k_{odd})}$ link a ground configuration orbital $n\ell$ to an orbital $n'\ell'$ in an excited configuration and closure results in single particle tensor operators $\mathbf{u}(n\ell, n\ell)^{(k_{even})}$. In the relativistic extension the double tensor operators $\mathbf{w}(n\ell, n'\ell')^{(\kappa\kappa')k}$ couple the orbitals and closure results in single particle double tensor operators $\mathbf{w}(n\ell, n\ell)^{(\kappa\kappa')k}$ where again k is *even* but κ' is *even* or *odd* as κ is 0 or 1 respectively. The effective operators obtained in the detailed analysis^{13,14} generalize the standard Judd-Ofelt effective operators, the latter becoming a limiting case of the former. Whereas in our discussion of relativistic crystal field theory we limited ourselves to action within the f -shell here the action takes place between configurations and the radial functions are more complex, involving f -orbitals and orbitals of opposite parity. It is not my intention to discuss in detail the technicalities of the calculations - these are covered in the recent literature^{13,14}

12.3. Concluding Remarks

In terms of the *angular* parts which reflect the symmetry properties of f -orbitals there is a remarkable, and understandable, similarity between crystal field theory and the theory of $f \longleftrightarrow f$ transitions. In the non-relativistic theory both involve, to second-order, the matrix elements of the unit tensor operators $\mathbf{U}^{(k)}$ with $k = 0, 2, 4, 6$ while in the extension to the relativistic theory both involve the replacement of the $\mathbf{U}^{(k)}$ operators by the double tensor operators $\mathbf{W}^{(\kappa\kappa')k}$. The fundamental difference comes in the radial integrals involved. It is only in relatively recent times that it has become possible to give serious consideration to detailed calculation of such integrals. Future work will undoubtedly be more directed to such calculations and to estimates of the significance of relativistic effects both for crystal field interactions and transition intensities. One expects these effects to become increasingly important as the calculations, and hopefully experiments, are made on the heavy actinides. It may well be that in the future studies will be directed towards calculations in the jj -coupling basis which is the natural basis to use when relativistic effects become significant.

12.4. Finis...

This is the end of this series. I have tried to introduce you to some aspects of the theory of hyperfine structure in atoms, ions and crystals. In many instances we have limited our attention to the barest details. While we could treat many topics in greater details I hope I have given enough for you to develop your own interests and to teach yourself. Learning to teach yourself is probably the greatest thing anyone can gain from a university education.

These lectures continue from Part I with particular emphasis on the detailed calculation of the properties of the low lying states of the Eu^{3+} ion both in free space and in crystal environments. Special attention is paid to the ground multiplet 7F of the $4f^6$ configuration and to the highly forbidden ${}^7F_0 \leftrightarrow {}^5D_0$ transitions that are relevant in the possible development of rare earth ion based quantum computers.

Real mathematical theorems will require the same stamina whether you measure the effort in months or years. You can forget the idea, if you ever had it, that all you require is a bit of natural genius and that then you can wait for inspiration to strike. There is simply no substitute for hard work and perserverance (Andrew Wiles 13 July 2001)

Lecture 13: Calculating Magnetic Interactions in f^n electron configurations

Synopsis

In this lecture we start with a brief discussion of units and then some remarks on the structure of f^n electron configurations turning then to the f^6 configuration as realized in neutral samarium, (SmI), and in triply ionized europium, ($EuIV$) or (Eu^{3+}). We then give a detailed account, and calculation, of the Zeeman effect with particular emphasis on the two lowest levels, 7F_0 and 7F_1 , of the f^6 configuration for both weak and strong magnetic fields in the presence of magnetic hyperfine interactions.

13. Introduction

These lectures follow on from those of Part I and familiarity with the previous lectures is assumed. References will be numbered following from those of Part I. Reference numbers ≤ 76 are from Part I. In Part II the emphasis is on practical calculation and it is essential that students work through the exercises and derive for themselves the various calculations. There is currently considerable interest in the possibility of realising quantum computers with rare earth ion doped crystals^{77,78}. The rare earth ion Eu^{3+} doped in crystals of Y_2SiO_5 is of particular interest⁷⁹. The precursor to this work goes back to the theory of nuclear magnetic resonance in Eu^{3+} developed in the late 1950's by R J Elliott⁸⁰ and studies of the anomalous quadrupole coupling in europium ethylsulphate⁸¹. The role of hyperfine and magnetic interactions in determining the very small splittings in the groundstate and the exceedingly low probabilities associated with the ${}^7F_0 \rightarrow {}^5D_0$ transition play a crucial role in the possibility of creating rare earth ion based quantum computers. These subjects will be treated in detail in this part of our course.

13.1. The Matter of Units

In order to do practical calculations that can be compared with experimental measurements we must give some consideration to units. The units appearing in experimental papers usually reflect the type of experimental equipment being used. Thus an optical spectroscopist might report wavelengths in Ångströms ($1\text{Å} = 10^{-8}\text{cm}$) or in nanometres ($1\text{nm} = 10^{-1}\text{Å} = 10^{-9}\text{cm}$) while a radioastronomer might report wavelengths in centimetres or metres. Or again an optical spectroscopist may choose to report “energies” of atomic levels in *wave numbers*, the reciprocal of wavelength using cm^{-1} with the electron spin resonance (ESR) spectroscopist using MHz ($1\text{MHz} = 10^6\text{Hz}$) or possibly GHz ($1\text{GHz} = 10^9\text{Hz}$). We may wish that all used a common system of units but things are different when one works in the real world rather than Utopia and we must be able to switch between units. In much of these lectures we will need to be able to switch between various units. In particular note that⁸²

$$\begin{aligned} 1\text{eV} &= 8.0655 \times 10^3 \text{cm}^{-1} = 2.418 \times 10^5 \text{MHz} = 1.602 \times 10^{-19} \text{J} \\ 1\text{cm}^{-1} &= 1.2398 \times 10^{-4} \text{eV} = 2.998 \times 10^4 \text{MHz} \\ 1\text{MHz} &= 4.136 \times 10^{-6} \text{eV} = 3.336 \times 10^{-5} \text{cm}^{-1} \end{aligned}$$

In much of our discussion of magnetic field effects we will give magnetic fields in the unit Tesla (T) and make use of the Bohr magneton $\mu_B = \frac{e\hbar}{2m_e}$. In that case we will frequently put

$$\mu_B = 0.46696 \text{cm}^{-1} \text{T}^{-1} \quad (13-1)$$

13.2. The f^n Electron Configurations

The lanthanides and actinides¹ are characterized by the systematic filling of the $4f^n$ and $5f^n$ shells respectively where $n = 0, 1, \dots, 14$. The enumeration of the states of the f^n configurations has been outlined by Judd² using the group schemes introduced by Racah²¹. There the states are labelled by the irreducible representations of the group chain

$$U_{14} \supset SU_2 \times SU_7 \supset SO_7 \supset G_2 \supset SO_3 \quad (13-2)$$

In *SmI* the lowest electron configuration is $4f^6 6s^2$ whereas in *EuIV* it is just $4f^6$. Since the $6s^2$ shell is closed the *SL* terms of the two configurations are identical. A complete listing of the group labelled terms is given in Table 13.1. It follows from Hund’s rules that the ground term is 7F and the ground state is 7F_0 .

Table 13.1 Group classification of the states of the f^6 electron configuration

SU_7	SO_7	G_2	$2S+1L$	
$\{1^6\}$	[100]	(10)	7F	
$\{21^4\}$	[210]	(21)	5DFGHKL	
		(20)	5DGI	
$\{2^21^2\}$	[111]	(11)	5PH	
		(20)	5DGI	
		(10)	5F	
		(00)	5S	
		(31)	3PDF_2GH_2I_2K_2LMNO	
	[221]	(30)	3PFGHIKM	
		(21)	3DFGHKL	
		(20)	3DGI	
		(11)	3PH	
		(10)	3F	
[211]	(30)	3PFGHIKM		
	(21)	3DFGHKL		
	(20)	3DGI		
	(11)	3PH		
	(10)	3F		
[110]	(11)	3PH		
	(10)	3F		
	$\{2^3\}$	[222]	(40)	1SDFG_2HI_2KL_2MNQ
			(30)	1PFGHIKM
			(20)	1DGI
(10)			1F	
(00)			1S	
[220]	(22)	1SDGHILN		
	(21)	1DFGHKL		
	(20)	1DGI		
[200]	(20)	1DGI		
[000]	(00)	1S		

13.3. The Low Lying Levels of $Sm I$ and $Eu IV$

The experimentally determined low lying energy levels of $Sm I$ and $Eu IV$ may be extracted from the NIST database⁸³. In Table 13.2 we give the levels of the 7F multiplet and the lowest 5D multiplet for the $4f^66s^2$ configuration in $Sm I$. Note we have omitted the $4f^65d6s$ levels that commence at $\sim 10800cm^{-1}$. The Lande g -factors were determined by atomic beam measurements⁸. Note we will usually list energy levels as cm^{-1} wavenumbers.

Table 13.2 The energy levels of the 7F multiplet and the lowest 5D multiplet of SmI

Configuration	Term	J Level	Lande-g
$4f^66s^2$	7F_0	0.00	
	7F_1	202.58	1.49839
	7F_2	811.92	1.49779
	7F_3	1489.55	1.49707
	7F_4	2273.09	1.49625
	7F_5	3125.46	1.49532
	7F_6	4020.66	1.49417
	5D_0
	5D_1	15914.55	...
	5D_2	17864.29	...
	5D_3	20195.76	...
	5D_4

Note that the positions of the 5D_0 and 5D_4 are, as yet, undetermined.

Table 13.3 Low lying terms of $EuIV$

Configuration	Term	J Level
$4f^6$	7F_0	0
	7F_1	[370]
	7F_2	[1040]
	7F_3	[1890]
	7F_4	[2860]
	7F_5	[3910]
	7F_6	[4940]
	5D_0	[17270]
	5D_1	[19030]
	5D_2	[21510]
	5D_3	[24390]
	5D_4	[27640]

The energy levels of the 7F multiplet and the lowest 5D multiplet of the $4f^6$ configuration of $Eu IV$ are listed in Table 13.3. Note that these data are *not* those of ionized Eu^{3+} but are levels deduced from experimental studies of trivalent europium in crystals and hence must be viewed as approximate and are indicated by enclosing the wavenumbers in square, [], brackets.

13.4. Calculation of the Free Ion Energy Levels of $Sm I$

Conway and Wybourne⁷ used the complete Coulomb and spin-orbit interaction matrices for the f^6 configuration to calculate the free ion energy levels of the 7F multiplet for $Sm I$. In some senses their calculation could be thought as rather crude

because they chose to fix the ratios of the Slater integrals F_4/F_2 and F_6/F_2 to those of a $4f$ hydrogenic eigenfunction, i.e.,

$$F_4/F_2 = 0.13805 \quad F_6/F_2 = 0.015108 \quad (13-3)$$

and then expressed the elements of the energy matrices in terms of the two integrals F_2 and ζ_{4f} . These two integrals were then treated as freely variable parameters to be determined from the experimental data. In spite of the apparent crudity of the calculation they found the mean error between the experimental and calculated energy levels was $< 0.2\text{cm}^{-1}$. Using the resultant eigenvectors they were able to calculate intermediate coupling corrected Lande g -values that, with the appropriate relativistic corrections⁵, agreed with the experiment values to within the fifth decimal place. A reanalysis of the experimental data using atomic beam measurements⁸ produced an even smaller discrepancy between the calculated and experimental values.

The atomic beam measurements were made on the two stable isotopes of samarium, ^{147}Sm and ^{149}Sm . Both isotopes have $I = \frac{7}{2}$. Before discussing the hyperfine structure in detail let us consider the Zeeman effect for the levels of the 7F multiplet in the two coupling schemes $JIFM_F$ and $JM_JIM_I M_F$ in sufficient detail to include interactions that do not preserve J or F as good quantum numbers.

13.5. The Zeeman Effect in $\text{Sm}I$ (ignoring nuclear spin effects)

We note from Table 13.2 that the groundstate of $\text{Sm} I$ is 7F_0 and the 7F_1 level occurs at 202.58cm^{-1} and we would like to include the coupling, in a magnetic field, of these two levels. The Zeeman part of the Hamiltonian may be written as (recall S6.3)

$$H_{mag} = \mu_B B_z (L_0^{(1)} + g_s S_0^{(1)} + g_I I_0^{(1)}) \quad (13-4)$$

For completeness we will often retain the nuclear Zeeman term, though realising that it is usually about three orders of magnitude less than the electronic term. As a first exercise let us ignore the hyperfine interaction and consider the behaviour of the two lowest 7F terms in a magnetic field B_z working in a $|JM\rangle$ basis. Thus we have four basis states

$$|{}^7F00\rangle, \quad |{}^7F10\rangle, \quad |{}^7F11\rangle, \quad |{}^7F1-1\rangle$$

The method of calculating the diagonal and off-diagonal Zeeman matrix elements was developed in S2.16. Thus from (2-53) we have

$$\langle \alpha SLJM | H_{mag} | \alpha SLJM \rangle = B_z \mu_B M g(SLJ) \quad (2-53)$$

and from (2-54) we have

$$g({}^7F_1) = \frac{1 + g_s}{2} \quad (13-5)$$

while for the required off-diagonal matrix element we make use of (2-58) to obtain

$$\langle {}^7F00 | H_{mag} | {}^7F10 \rangle = B_z \mu_B 2(g_s - 1) \quad (13-6)$$

We observe from Table 13.2 that the 7F_1 and 7F_0 levels in SmI are separated by $202.58cm^{-1}$. This splitting comes almost entirely from the spin-orbit interaction. Within the 7F multiplet the spin-orbit interaction matrix elements are given by²

$$\langle f^6 {}^7F_J | H_{s.o.} | f^6 {}^7F_J \rangle = \frac{\zeta_f}{12} [J(J+1) - L(L+1) - S(S+1)] \quad (13-7)$$

and since $S = L = 3$ we have

$$\Delta E = E({}^7F_1) - E({}^7F_0) = \frac{\zeta_f}{6} = 202.58cm^{-1} \quad (13-8)$$

and hence we deduce that $\zeta_f \sim 1215.5cm^{-1}$. Thus relative to the ground state the energy of the $|{}^7F1 \pm 1\rangle$ states is given by

$$E({}^7F1 \pm 1) = \frac{\zeta_f}{6} \pm \frac{1 + g_s}{2} \mu_B B_z \quad (13-9)$$

Hence the Zeeman splitting in this case is $\sim \pm 0.7cm^{-1}$ with the magnetic field in Tesla.

The $|{}^7F00\rangle$ and $|{}^7F10\rangle$ states are coupled by the magnetic field and hence a complete treatment would require diagonalization of the matrix

$$\begin{array}{cc} |{}^7F00\rangle & |{}^7F10\rangle \\ \langle {}^7F00| \left(\begin{array}{cc} 0 & 2(g_s - 1)\mu_B B_z \\ 2(g_s - 1)\mu_B B_z & \frac{\zeta_f}{6} \end{array} \right) & \end{array} \quad (13-10)$$

The eigenvalues follow from the secular equation

$$\lambda^2 - \frac{\zeta_f}{6}\lambda - 4(g_s - 1)^2 \mu_B^2 B_z^2 = 0 \quad (13-11)$$

to give

$$\lambda_{\pm} = \frac{\zeta_f}{12} \left[1 \pm \sqrt{1 + [24(g_s - 1) \frac{\mu_B B_z}{\zeta_f}]^2} \right] \quad (13-12)$$

The nett effect is for the ground state to be decreased in energy and the other level with $M = 0$ to be increased in energy i.e. the two levels mutually repel. Recalling from (13-1) that $\mu_B \sim 0.47cm^{-1}T^{-1}$, that in $Sm I$ $\zeta_{4f} \sim 1215cm^{-1}$ and that $(g_s - 1) \sim 1$ we have from (13-12)

$$\lambda_{\pm} \sim 101.3 \left[1 \pm \sqrt{1 + 8.5 \times 10^{-5} B_z^2} \right]$$

to give

$$\begin{aligned} \lambda_+ &\sim 202.6 + 4.25 \times 10^{-5} B_z^2 \text{ cm}^{-1} \\ \lambda_- &\sim -4.25 \times 10^{-5} B_z^2 \text{ cm}^{-1} \end{aligned}$$

In a typical Zeeman experiment $B_z \sim 1T$ and thus the Zeeman shift for the two $M = 0$ states is very small. The eigenvectors associated with the two levels will be of the form

$$|0\rangle = a|{}^7F00\rangle + b|{}^7F10\rangle \quad (13-13a)$$

$$|1\rangle = -b|{}^7F00\rangle + a|{}^7F10\rangle \quad (13-13b)$$

and as a consequence the groundstate will have a very small $J = 1$ character though the groundstate remains non-degenerate as expected.

13.6. Zeeman Effect in $Sm I$ including Nuclear Spin

If we include nuclear spin we need to work in either a $|JIFM_F\rangle$ basis or a $|JM_JIM_IM_F\rangle$ basis. Which basis to choose will depend on the relative strengths of the magnetic and hyperfine interactions. For a weak magnetic field the $|JIFM_F\rangle$ basis is usually simplest whereas for a strong magnetic field the $|JM_JIM_IM_F\rangle$ basis is often simpler. Let us start with the former basis.

As found earlier(S6.3-6.6), the diagonal matrix element may be expressed as

$$\langle \alpha JIFM_F | H_{mag} | \alpha' JIFM_F \rangle = \mu_B B_z M_F g_F \quad (13-14)$$

with

$$g_F = g_J \frac{[F(F+1) - I(I+1) + J(J+1)]}{2F(F+1)} + g_I \frac{[F(F+1) + I(I+1) - J(J+1)]}{2F(F+1)} \quad (13-15)$$

In the case of intermediate coupling one simply replaces g_J by its intermediate coupling value.

13.7. Exercises

(a) Show that

$$\langle \alpha SLJ || L^{(1)} + g_s S^{(1)} || \alpha SLJ \rangle = g(SLJ) \sqrt{J(J+1)(2J+1)} \quad (13-16)$$

(b) Show that

$$\frac{\langle \alpha SLJ || L^{(1)} + g_s S^{(1)} || \alpha SLJ + 1 \rangle}{\frac{1 - g_s}{2} \sqrt{\frac{(J+L+S+2)(J+L-S+1)(J-L+S+1)(S+L-J)}{J+1}}} \quad (13-17)$$

Note that in the above two exercises the matrix elements are diagonal in α , S and L . Note also the special 6-j symbols

$$\left\{ \begin{array}{ccc} a & b & c \\ 1 & c & b \end{array} \right\} = (-1)^s \frac{2[a(a+1) - b(b+1) - c(c+1)]}{\sqrt{2b(2b+1)(2b+2)2c(2c+1)(2c+2)}} \quad (13-18)$$

and

$$\left\{ \begin{array}{ccc} a & b & c \\ 1 & c-1 & b \end{array} \right\} = (-1)^s \sqrt{\frac{2(s+1)(s-2a)(s-2b)(s-2c+1)}{2b(2b+1)(2b+2)(2c-1)2c(2c+1)}} \quad (13-19)$$

where $s = a + b + c$ and in (13-16) $g(SLJ)$ is the Lande g -factor defined in (2-54).

(c) Show that

$$\begin{aligned}
& \langle \alpha JIFM_F | H_{mag} | \alpha JIF + 1M_F \rangle \\
&= \mu_B B_z (g_J - g_I) \sqrt{(F+1)^2 - M_F^2} \\
&\times \sqrt{\frac{(F+J+I+2)(F+J-I+1)(F-J+I+1)(I+J-F)}{4(F+1)^2(2F+1)(2F+3)}}
\end{aligned} \tag{13-20}$$

(d) Show that

$$\begin{aligned}
& \langle \alpha SLJIFM_F | H_{mag} | \alpha SLJ + 1IFM_F \rangle \\
&= \mu_B B_z \frac{M_F(1-g_s)}{4F(F+1)(J+1)} \\
&\times \sqrt{\frac{(F+I+J+2)(F+J-I+1)(J+I-F+1)(I+F-J)}{(2J+1)(2J+3)}} \\
&\times \sqrt{(J+L+S+2)(J+L-S+1)(J-L+S+1)(S+L-J)}
\end{aligned} \tag{13-21}$$

(e) Show that

$$\begin{aligned}
& \langle \alpha SLJIFM_F | H_{mag} | \alpha SLJ + 1IF + 1M_F \rangle \\
&= \mu_B B_z \frac{(g_s - 1)}{4(F+1)(J+1)} \sqrt{\frac{(F+1)^2 - M_F^2}{(2F+1)(2F+3)(2J+1)(2J+3)}} \\
&\times \sqrt{(F+J+I+2)(F+J+I+3)(F+J-I+1)(F+J-I+2)} \\
&\times \sqrt{(J+L+S+2)(J+L-S+1)(J-L+S+1)(S+L-J)}
\end{aligned} \tag{13-22}$$

In this exercise you will need to note that

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b-1 \end{matrix} \right\} = (-1)^s \sqrt{\frac{s(s+1)(s-2a-1)(s-2a)}{(2b-1)2b(2b+1)(2c-1)2c(2c+1)}} \tag{13-23}$$

(f) Show that

$$\begin{aligned}
& \langle \alpha SLJIFM_F | H_{mag} | \alpha SLJ + 1IF - 1M_F \rangle \\
&= \mu_B B_z \frac{(g_s - 1) \sqrt{F^2 - M_F^2}}{4F(J+1)} \\
&\times \sqrt{(I+F-J-1)(I+F-J)(I+J-F+1)(I+J-F+2)} \\
&\times \frac{\sqrt{(J+L+S+2)(J+L-S+1)(J-L+S+1)(S+L-J)}}{(2J+1)(2J+3)(2F-1)(2F+1)}
\end{aligned} \tag{13-24}$$

13.8. Some MAPLE Zeeman Effect Programmes

The results of the above exercises can easily be written as simple MAPLE programmes and the matrix elements for H_{mag} evaluated in the $|JIFM_F\rangle$ scheme.

```
#Diagonal Zeeman Effect (13-14)#
gf:=proc(J,i,F,M)
local result;
result:=simplify(M*gi*((F*(F+1)-i*(i+1)+J*(J+1))/(2*F*(F+1)))
+ M*gi*((F*(F+1)+i*(i+1)-J*(J+1))/(2*F*(F+1))));
end;
```

```
#Off-diagonal in F (13-20)#
gof:=proc(J,i,F,M)
local result;
result:=simplify((gj-gi)*sqrt((F+1)^2 - M^2)*sqrt(((F+J+i+2)
*(F+J-i+1)*(F-J+i+1)*(i+J-F))/(4*(F+1)^2*(2*F+1)*(2*F+3))));
end;
```

```
#Off-diagonal in J (13-21)#
goj:=proc(J,i,F,M,S,L)
local result;
result:=simplify(((M*(1-gs))/(4*F*(F+1)*(J+1)))
*sqrt((F+i+J+2)*(F+J-i+1)*(J+i-F+1)*(i+F-J)*(J+L+S+2)
*(J+L-S+1)*(J-L+S+1)*(S+L-J))/sqrt((2*J+1)*(2*J+3)));
end;
```

```
#Off-diagonal in J and F (13-22)#
gojf:=proc(J,i,F,M,S,L)
local result;
result:=simplify(((gs-1)/(4*(F+1)*(J+1)))
*sqrt((F+M+1)*(F-M+1))
*sqrt((F+J+i+2)*(F+J+i+3)*(F+J-i+1)*(F+J-i+2))
*sqrt((J+L+S+2)*(J+L-S+1)*(J-L+S+1)*(S+L-J))/sqrt((2*F+1)
*(2*F+3)*(2*J+1)*(2*J+3)));
end;
```

```

#Off-diagonal in J and F → F-1 (13-24)#
gojfd:=proc(J,i,F,M,S,L)
local result;
result:=simplify((((gs-1)*sqrt(F^2-M^2))/(4*F*(J+1)))*
sqrt((i+F-J-1)*(i+F-J)*(i+J-F+1)
*(i+J-F+2)*(J+L+S+2)*(J+L-S+1)*(J-L+S+1)*(S+L-J)))
/(sqrt((2*J+1)*(2*J+3)*(2*F-1)
*(2*F+1)))));
end;

```

The above MAPLE programmes make the calculation of the Zeeman matrices a trivial process. In the case of a nuclear spin of $I = \frac{7}{2}$ we obtain the typical magnetic interaction matrices (in terms of the magnetic field B_z). I list the matrices for the positive values of M_F leaving it as an exercise for you to state what changes must be made to obtain the matrices for the negative values of M_F .

13.9. Magnetic Interaction Matrices

$$M_F = \frac{9}{2} \quad \left| \left(1, \frac{7}{2}\right) \frac{9}{2}, \frac{9}{2} \right\rangle$$

$$\left\langle \left(1, \frac{7}{2}\right) \frac{9}{2}, \frac{9}{2} \right| \left(g_J + \frac{7}{2}g_I \right) \quad (13-25a)$$

$$M_F = \frac{7}{2} \quad \left| \left(0, \frac{7}{2}\right) \frac{7}{2}, \frac{7}{2} \right\rangle \quad \left| \left(1, \frac{7}{2}\right) \frac{7}{2}, \frac{7}{2} \right\rangle \quad \left| \left(1, \frac{7}{2}\right) \frac{9}{2}, \frac{7}{2} \right\rangle$$

$$\left\langle \left(0, \frac{7}{2}\right) \frac{7}{2}, \frac{7}{2} \right| \left(\begin{array}{ccc} \frac{7}{2}g_I & 2(1-g_s)\frac{\sqrt{7}}{3} & 2(g_s-1)\frac{\sqrt{2}}{3} \\ 2(1-g_s)\frac{\sqrt{7}}{3} & \frac{2}{9}g_J + \frac{59}{18}g_I & \frac{\sqrt{14}}{9}(g_J-g_I) \\ 2(g_s-1)\frac{\sqrt{2}}{3} & \frac{\sqrt{14}}{9}(g_J-g_I) & \frac{7}{9}g_J + \frac{49}{18}g_I \end{array} \right) \quad (13-25b)$$

$$M_F = \frac{5}{2} \quad \left| \left(0, \frac{7}{2}\right) \frac{7}{2}, \frac{5}{2} \right\rangle \quad \left| \left(1, \frac{7}{2}\right) \frac{9}{2}, \frac{5}{2} \right\rangle \quad \left| \left(1, \frac{7}{2}\right) \frac{7}{2}, \frac{5}{2} \right\rangle \quad \left| \left(1, \frac{7}{2}\right) \frac{5}{2}, \frac{5}{2} \right\rangle$$

$$\left\langle \left(0, \frac{7}{2}\right) \frac{7}{2}, \frac{5}{2} \right| \left(\begin{array}{cccc} \frac{5}{2}g_I & \frac{\sqrt{14}}{3}(g_s-1) & -\frac{10\sqrt{7}}{21}(g_s-1) & \frac{\sqrt{42}}{7}(g_s-1) \\ \frac{\sqrt{14}}{3}(g_s-1) & \frac{5}{9}g_J + \frac{35}{18}g_I & \frac{7\sqrt{2}}{18}(g_J-g_I) & 0 \\ -\frac{10\sqrt{7}}{21}(g_s-1) & \frac{7\sqrt{2}}{18}(g_J-g_I) & \frac{10}{63}g_J + \frac{295}{126}g_I & \frac{3\sqrt{6}}{14}(g_J-g_I) \\ \frac{\sqrt{42}}{7}(g_s-1) & 0 & \frac{3\sqrt{6}}{14}(g_J-g_I) & -\frac{5}{7}g_J + \frac{45}{14}g_I \end{array} \right) \quad (13-25c)$$

$$M_F = \frac{3}{2} \quad \left| \left(0, \frac{7}{2}\right) \frac{7}{2}, \frac{3}{2} \right\rangle \quad \left| \left(1, \frac{7}{2}\right) \frac{9}{2}, \frac{3}{2} \right\rangle \quad \left| \left(1, \frac{7}{2}\right) \frac{7}{2}, \frac{3}{2} \right\rangle \quad \left| \left(1, \frac{7}{2}\right) \frac{5}{2}, \frac{3}{2} \right\rangle$$

$$\left\langle \left(0, \frac{7}{2}\right) \frac{7}{2}, \frac{3}{2} \right| \left(\begin{array}{cccc} \frac{3}{2}g_I & \sqrt{2}(g_s-1) & -\frac{2\sqrt{7}}{7}(g_s-1) & \frac{\sqrt{70}}{7}(g_s-1) \\ \sqrt{2}(g_s-1) & \frac{1}{6}(2g_J+7g_I) & \frac{\sqrt{14}}{6}(g_J-g_I) & 0 \\ -\frac{2\sqrt{7}}{7}(g_s-1) & \frac{\sqrt{14}}{6}(g_J-g_I) & \frac{1}{42}(4g_J+59g_I) & \frac{3\sqrt{10}}{14}(g_J-g_I) \\ \frac{\sqrt{70}}{7}(g_s-1) & 0 & \frac{3\sqrt{10}}{14}(g_J-g_I) & \frac{3}{14}(-2g_J+9g_I) \end{array} \right) \quad (13-25d)$$

$$\begin{array}{l}
M_F = \frac{1}{2} \\
\langle (0, \frac{7}{2}, \frac{7}{2}, \frac{1}{2}) | \\
\langle (1, \frac{7}{2}, \frac{9}{2}, \frac{1}{2}) | \\
\langle (1, \frac{7}{2}, \frac{7}{2}, \frac{1}{2}) | \\
\langle (1, \frac{7}{2}, \frac{5}{2}, \frac{1}{2}) |
\end{array}
\begin{array}{cccc}
|(0, \frac{7}{2}, \frac{7}{2}, \frac{1}{2})\rangle & |(1, \frac{7}{2}, \frac{9}{2}, \frac{1}{2})\rangle & |(1, \frac{7}{2}, \frac{7}{2}, \frac{1}{2})\rangle & |(1, \frac{7}{2}, \frac{5}{2}, \frac{1}{2})\rangle \\
\frac{1}{2}g_I & \frac{2\sqrt{5}}{3}(g_s - 1) & -\frac{2\sqrt{7}}{21}(g_s - 1) & \frac{2\sqrt{21}}{7}(g_s - 1) \\
\frac{2\sqrt{5}}{3}(g_s - 1) & g_J + \frac{7}{18}g_I & \frac{\sqrt{35}}{9}(g_J - g_I) & 0 \\
-\frac{2\sqrt{7}}{21}(g_s - 1) & \frac{\sqrt{35}}{9}(g_J - g_I) & \frac{1}{126}(4g_J + 59g_I) & \frac{3\sqrt{3}}{7}(g_J - g_I) \\
\frac{2\sqrt{21}}{7}(g_s - 1) & 0 & \frac{3\sqrt{3}}{7}(g_J - g_I) & \frac{1}{14}(-4g_J + 9g_I)
\end{array}
\right) \quad (13-25e)$$

Note that in the absence of nuclear spin the ground state (7F_0) is non-degenerate but with the occurrence of a nuclear spin I the groundstate has a degeneracy of $2I + 1$ and this degeneracy can be lifted by an external magnetic field. Can the hyperfine interaction, at higher than first-order, lift the degeneracy or could an external electric field, perhaps in a crystal, lift the degeneracy, at least partially? What about relativistic effects? The objective of this course is to supply quantitative answers to these questions.

13.10. Zeeman Matrices in a $|JM_JIM_I M_F\rangle$ Basis

We could also calculate the Zeeman matrix elements in a $|JM_JIM_I M_F\rangle$ basis. As an exercise see if you can derive the following results:-

$$\begin{array}{l}
M_F = \frac{9}{2} \\
\langle 11, \frac{7}{2}, \frac{7}{2}, \frac{9}{2} | \\
\langle 11, \frac{7}{2}, \frac{7}{2}, \frac{9}{2} |
\end{array}
\begin{array}{c}
|11, \frac{7}{2}, \frac{7}{2}, \frac{9}{2}\rangle \\
\left(g_J + \frac{7}{2}g_I \right)
\end{array}
\quad (13-26a)$$

$$\begin{array}{l}
M_F = \frac{7}{2} \\
\langle 00, \frac{7}{2}, \frac{7}{2}, \frac{7}{2} | \\
\langle 10, \frac{7}{2}, \frac{7}{2}, \frac{7}{2} | \\
\langle 11, \frac{7}{2}, \frac{5}{2}, \frac{7}{2} |
\end{array}
\begin{array}{ccc}
|00, \frac{7}{2}, \frac{7}{2}, \frac{7}{2}\rangle & |10, \frac{7}{2}, \frac{7}{2}, \frac{7}{2}\rangle & |11, \frac{7}{2}, \frac{5}{2}, \frac{7}{2}\rangle \\
\left(\begin{array}{ccc}
\frac{7}{2}g_I & 2(g_s - 1) & 0 \\
2(g_s - 1) & \frac{7}{2}g_I & 0 \\
0 & 0 & g_J + \frac{5}{2}g_I
\end{array} \right)
\end{array}
\quad (13-26b)$$

$$\begin{array}{l}
M_F = \frac{5}{2} \\
\langle 00, \frac{7}{2}, \frac{5}{2}, \frac{5}{2} | \\
\langle 10, \frac{7}{2}, \frac{5}{2}, \frac{5}{2} | \\
\langle 11, \frac{7}{2}, \frac{3}{2}, \frac{5}{2} | \\
\langle 1 - 1, \frac{7}{2}, \frac{7}{2}, \frac{5}{2} |
\end{array}
\begin{array}{cccc}
|00, \frac{7}{2}, \frac{5}{2}, \frac{5}{2}\rangle & |10, \frac{7}{2}, \frac{5}{2}, \frac{5}{2}\rangle & |11, \frac{7}{2}, \frac{3}{2}, \frac{5}{2}\rangle & |1 - 1, \frac{7}{2}, \frac{7}{2}, \frac{5}{2}\rangle \\
\left(\begin{array}{cccc}
\frac{5}{2}g_I & 2(g_s - 1) & 0 & 0 \\
2(g_s - 1) & \frac{5}{2}g_I & 0 & 0 \\
0 & 0 & g_J + \frac{3}{2}g_I & 0 \\
0 & 0 & 0 & -g_J + \frac{7}{2}g_I
\end{array} \right)
\end{array}
\quad (13-26c)$$

$$\begin{array}{l}
M_F = \frac{3}{2} \\
\langle 00, \frac{7}{2}, \frac{3}{2}, \frac{3}{2} | \\
\langle 10, \frac{7}{2}, \frac{3}{2}, \frac{3}{2} | \\
\langle 11, \frac{7}{2}, \frac{1}{2}, \frac{3}{2} | \\
\langle 1 - 1, \frac{7}{2}, \frac{5}{2}, \frac{3}{2} |
\end{array}
\begin{array}{cccc}
|00, \frac{7}{2}, \frac{3}{2}, \frac{3}{2}\rangle & |10, \frac{7}{2}, \frac{3}{2}, \frac{3}{2}\rangle & |11, \frac{7}{2}, \frac{1}{2}, \frac{3}{2}\rangle & |1 - 1, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}\rangle \\
\left(\begin{array}{cccc}
\frac{3}{2}g_I & 2(g_s - 1) & 0 & 0 \\
2(g_s - 1) & \frac{3}{2}g_I & 0 & 0 \\
0 & 0 & g_J - \frac{1}{2}g_I & 0 \\
0 & 0 & 0 & -g_J + \frac{3}{2}g_I
\end{array} \right)
\end{array}
\quad (13-26d)$$

$$\begin{array}{l}
M_F = \frac{1}{2} \\
\langle 00, \frac{7}{2}\frac{1}{2}; \frac{1}{2} | \\
\langle 10, \frac{7}{2}\frac{1}{2}; \frac{1}{2} | \\
\langle 11\frac{7}{2} - \frac{1}{2}; \frac{1}{2} | \\
\langle 1 - 1, \frac{7}{2}\frac{3}{2}; \frac{1}{2} |
\end{array}
\begin{array}{cccc}
|00, \frac{7}{2}\frac{1}{2}; \frac{1}{2}\rangle & |10, \frac{7}{2}\frac{1}{2}; \frac{1}{2}\rangle & |11\frac{7}{2} - \frac{1}{2}; \frac{1}{2}\rangle & |1 - 1, \frac{7}{2}\frac{3}{2}; \frac{1}{2}\rangle \\
\left(\begin{array}{cccc}
\frac{1}{2}g_I & 2(g_s - 1) & 0 & 0 \\
2(g_s - 1) & \frac{1}{2}g_I & 0 & 0 \\
0 & 0 & g_J - \frac{1}{2}g_I & 0 \\
0 & 0 & 0 & -g_J + \frac{3}{2}g_I
\end{array} \right)
\end{array}
\quad (13-26e)$$

Check that the traces of the matrices of the two sets (13-25) and (13-26) are in one-to-one correspondence. Are the respective sets of eigenvalues the same in spite of the different bases?

This concludes our introduction to the Zeeman effect and its application to the free atom Sm . In the next lecture we examine the hyperfine interaction for the free atom.

Lecture 14: Calculating Magnetic Hyperfine Interactions for a free Atom or Ion

The present generation has no right to complain of the great discoveries already made, as if they left no room for further enterprise. They have only given Science a wider boundary, and we have not only to reduce to order the regions that have been conquered, but to keep up constant operations on the frontier, on a continually increasing scale. J C Maxwell, Inaugural Lecture

14. Introduction

In the previous lecture we examined the effect of an external magnetic field on the 7F_0 and 7F_1 levels of the $4f^6$ configuration. In this lecture we consider, in some detail, the role of the magnetic hyperfine interaction on these two levels for atoms and free ions and in particular the two stable isotopes, ${}^{147}\text{Sm}$, ${}^{149}\text{Sm}$. Each of these isotopes have nuclear spin $I = \frac{7}{2}$.

14.1. Magnetic Hyperfine Matrix Elements in JM_JIM_I Coupling

Recall (5-31) we have for the magnetic hyperfine interaction, H_{hfs} , for an electron configuration ℓ^n

$$H_{hfs} = a_\ell \sum_{i=1}^n [\mathbf{l}_i - \sqrt{10}(\mathbf{s}\mathbf{C}^{(2)})_i^{(1)}] \cdot \mathbf{I} \quad (14-26)$$

with

$$a_\ell = 2\beta\beta_N g_I \langle r^{-3} \rangle = \frac{2\beta\beta_N \mu_I \langle r^{-3} \rangle}{I} \quad (14-27)$$

where $\langle r^{-3} \rangle$ is the expectation value of the inverse-cube radius of the electron orbital. Noting (14-26), define

$$\mathbf{N}^{(1)} = \sum_{i=1}^n \mathbf{N}_i^{(1)} = \sum_{i=1}^n \left(\mathbf{l}_i - \sqrt{10}(\mathbf{s}\mathbf{C}^{(2)})_i^{(1)} \right) \quad (14-28)$$

Let us consider the scalar tensor product

$$\mathbf{N}^{(1)} \cdot \mathbf{I}^{(1)} = N_0^{(1)} I_0^{(1)} - \left(N_1^{(1)} I_{-1}^{(1)} + N_{-1}^{(1)} I_1^{(1)} \right) \quad (14-29)$$

and the evaluation of the matrix elements in JM_JIM_I coupling. Since the tensors are of rank 1 the matrix elements will be null unless $J' = J$ or $J' = J \pm 1$. Recalling the Wigner-Eckart theorem we may evaluate (14-29) as

$$\begin{aligned} & \langle \alpha JM_J IM_I M_F | \mathbf{N}^{(1)} \cdot \mathbf{I}^{(1)} | \alpha' J' M'_J I M'_I M'_F \rangle \\ &= \delta_{M_F, M'_F} \sum_{q=-1}^1 (-1)^q \langle \alpha JM_J IM_I M_F | \mathbf{N}_q^{(1)} I_{-q}^{(1)} | \alpha' J' M'_J I M'_I M'_F \rangle \\ &= \delta_{M_F, M'_F} \sum_{q=-1}^1 (-1)^q (-1)^{J-M_J} \begin{pmatrix} J & 1 & J' \\ -M_J & q & M_J - q \end{pmatrix} \langle \alpha J || N^{(1)} || \alpha' J' \rangle \\ &\times (-1)^{I-M_I} \begin{pmatrix} I & 1 & I \\ -M_I & -q & M_I + q \end{pmatrix} \langle I || I^{(1)} || I \rangle \end{aligned} \quad (14-30)$$

where we choose to consider only matrix elements diagonal in the nuclear spin I . The last reduced matrix element in (14-30) is simply

$$\langle I || I^{(1)} || I \rangle = \sqrt{I(I+1)(2I+1)} \quad (14-31)$$

We now use (14-30) to obtain expressions for the various particular matrix elements.

Let us start with the matrix elements that are diagonal in all the quantum numbers other than, possibly, α, α' . To that end we use (2-48c) to expand the two $3-j$ symbols to obtain

$$\langle \alpha J M_J I M_I M_F | \mathbf{N}^{(1)} \cdot \mathbf{I}^{(1)} | \alpha' J M_J I M_I M_F \rangle = M_I M_J \frac{\langle \alpha J || N^{(1)} || \alpha' J \rangle}{\sqrt{J(J+1)(2J+1)}} \quad (14-31a)$$

The matrix elements diagonal in the M quantum numbers but with $J' = J + 1$ become, after noting (2-56)

$$\begin{aligned} \langle \alpha J M_J I M_I M_F | \mathbf{N}^{(1)} \cdot \mathbf{I}^{(1)} | \alpha' J + 1 M_J I M_I M_F \rangle &= -M_I \sqrt{\frac{(J + M_J + 1)(J - M_J + 1)}{(J + 1)(2J + 1)(2J + 3)}} \\ &\times \langle \alpha J || N^{(1)} || \alpha' J + 1 \rangle \end{aligned} \quad (14-31b)$$

Next consider the matrix elements while diagonal in J and M_F are off-diagonal in the quantum numbers, M_J, M_I . These matrix elements will have $q = \pm 1$ whereas the previous all involved $q = 0$. Evaluating the $3j$ -symbols leads to the expressions

$$\begin{aligned} \langle \alpha J M_J I M_I M_F | \mathbf{N}^{(1)} \cdot \mathbf{I}^{(1)} | \alpha' J M_J \pm 1 M_I \mp 1 M_F \rangle &= \\ \mp \frac{1}{2} \sqrt{\frac{(J \mp M_J)(J \pm M_J + 1)}{J(J+1)(2J+1)}} \sqrt{(I \pm M_I)(I \mp M_I + 1)} &\langle \alpha J || N^{(1)} || \alpha' J \rangle \end{aligned} \quad (14-31c)$$

and the matrix elements with $J' = J + 1$ become

$$\begin{aligned} \langle \alpha J M_J I M_I M_F | \mathbf{N}^{(1)} \cdot \mathbf{I}^{(1)} | \alpha' J + 1 M_J \pm 1 M_I \mp 1 M_F \rangle &= \\ \pm \frac{1}{2} \sqrt{\frac{(J \pm M_J + 1)(J \pm M_J + 2)(I \mp M_I + 1)(I \pm M_I)}{(J + 1)(2J + 1)(2j + 3)}} &\langle \alpha J || N^{(1)} || \alpha' J + 1 \rangle \end{aligned} \quad (14-31d)$$

In the above we have made use of the special $3j$ -symbols

$$\begin{pmatrix} J & J & 1 \\ M & -M - 1 & 1 \end{pmatrix} = (-1)^{J-M} \sqrt{\frac{(J-M)(J-M+1)}{2J(J+1)(2J+1)}} \quad (14-32a)$$

and

$$\begin{pmatrix} J + 1 & J & 1 \\ M & -M - 1 & 1 \end{pmatrix} = (-1)^{J-M-1} \sqrt{\frac{(J-M)(J-M+1)}{2(2J+1)(J+1)(2J+3)}} \quad (14-32b)$$

To complete the calculation we need to evaluate the reduced matrix elements $\langle \alpha J \| N^{(1)} \| \alpha' J' \rangle$. Noting (14-26) this amounts to evaluating the two reduced matrix elements, after enlarging the state description,

$$\langle \alpha SLJ \| L^{(1)} \| \alpha' S' L' J' \rangle \quad (14-33a)$$

and

$$- \sqrt{10} \langle \alpha SLJ \| \sum_i (s^{(1)} C^{(2)})_i^{(1)} \| \alpha' S' L' J' \rangle \quad (14-33b)$$

The first matrix element (14-33a) may be evaluated using (2-46) and then explicitly evaluating the $6j$ -symbol to give for the two cases

$$\begin{aligned} \langle \alpha SLJ \| L^{(1)} \| \alpha' S' L' J \rangle = \\ \delta_{\alpha, \alpha'} \delta_{S, S'} \delta_{L, L'} \frac{1}{2} [J(J+1) + L(L+1) - S(S+1)] \sqrt{\frac{2J+1}{J(J+1)}} \end{aligned} \quad (14-34a)$$

and

$$\begin{aligned} \langle \alpha SLJ \| L^{(1)} \| \alpha' S' L' J + 1 \rangle = \\ \delta_{\alpha, \alpha'} \delta_{S, S'} \delta_{L, L'} \frac{1}{2} \sqrt{\frac{(S+L+J+2)(J+L-S+1)(J-L+S+1)(S+L-J)}{(J+1)}} \end{aligned} \quad (14-34b)$$

The second matrix element (14-33b) can be evaluated using (2-43) to give

$$\begin{aligned} \langle \alpha SLJ \| -\sqrt{10} \sum_i (s^{(1)} C^{(2)})_i^{(1)} \| \alpha' S' L' J \rangle = \\ - \sqrt{2(2J+1)(2J'+1)} \begin{Bmatrix} S & S' & 1 \\ L & L' & 2 \\ J & J' & 1 \end{Bmatrix} \langle s \| s^{(1)} \| s \rangle \langle \ell \| C^{(2)} \| \ell \rangle \langle \alpha SL \| W^{(12)} \| \alpha' S' L' \rangle \end{aligned} \quad (14-35)$$

where we have introduced the double tensor operators $\mathbf{W}^{(\kappa, k)}$ whose one electron reduced matrix elements satisfy

$$\langle s \ell \| w^{(\kappa, k)} \| s' \ell' \rangle = \delta_{s, s'} \delta_{\ell, \ell'} \sqrt{(2\kappa+1)(2k+1)} \quad (14-36)$$

Their properties are discussed in detail in Chapter 6 of Judd's book². For the $f^6 \ ^7F$ multiplet Judd (page 218) gives

$$\langle \ ^7F \| W^{(12)} \| \ ^7F \rangle = -\sqrt{\frac{70}{3}} \quad (14-37)$$

With the above results established it is not difficult to deduce that

$$\langle f^6 \ ^7F_1 \| N^{(1)} \| f^6 \ ^7F_1 \rangle = \sqrt{\frac{2}{3}} \quad (14-38a)$$

$$\langle f^6 \ ^7F_0 \| N^{(1)} \| f^6 \ ^7F_0 \rangle = 0 \quad (14-38b)$$

$$\langle f^6 \ ^7F_0 \| N^{(1)} \| f^6 \ ^7F_1 \rangle = \frac{5\sqrt{3}}{3} \quad (14-38c)$$

14.2. Magnetic Hyperfine Matrix Elements for the 7F $J = 0, 1$ Levels

We are now in a position to be able to calculate the magnetic hyperfine matrix elements for the 7F $J = 0, 1$ levels in the $|JM_JIM_I M_F\rangle$ basis in a similar manner as was done for the Zeeman effect in the previous lecture to obtain the matrices as

$$M_F = \frac{9}{2} \quad |11, \frac{7}{2}, \frac{9}{2}\rangle \\ \langle 11, \frac{7}{2}, \frac{9}{2} | \left(\begin{array}{c} \frac{7}{6} \end{array} \right) \quad (14-39a)$$

$$M_F = \frac{7}{2} \quad |00, \frac{7}{2}, \frac{7}{2}\rangle \quad |10, \frac{7}{2}, \frac{7}{2}\rangle \quad |11, \frac{7}{2}, \frac{7}{2}\rangle \\ \langle 00, \frac{7}{2}, \frac{7}{2} | \left(\begin{array}{ccc} 0 & -\frac{35}{6} & \frac{5\sqrt{14}}{6} \\ -\frac{35}{6} & 0 & -\frac{\sqrt{14}}{6} \\ \frac{5\sqrt{14}}{6} & -\frac{\sqrt{14}}{6} & \frac{5}{6} \end{array} \right) \quad (14-39b)$$

$$M_F = \frac{5}{2} \quad |00, \frac{7}{2}, \frac{5}{2}\rangle \quad |10, \frac{7}{2}, \frac{5}{2}\rangle \quad |11, \frac{7}{2}, \frac{5}{2}\rangle \quad |1-1, \frac{7}{2}, \frac{5}{2}\rangle \\ \langle 00, \frac{7}{2}, \frac{5}{2} | \left(\begin{array}{cccc} 0 & -\frac{25}{6} & \frac{5\sqrt{6}}{3} & -\frac{5\sqrt{14}}{6} \\ -\frac{25}{6} & 0 & \frac{\sqrt{6}}{3} & \frac{\sqrt{14}}{6} \\ \frac{5\sqrt{6}}{3} & \frac{\sqrt{6}}{3} & \frac{1}{2} & 0 \\ -\frac{5\sqrt{14}}{6} & \frac{\sqrt{14}}{6} & 0 & -\frac{7}{6} \end{array} \right) \quad (14-39c)$$

$$M_F = \frac{3}{2} \quad |00, \frac{7}{2}, \frac{3}{2}\rangle \quad |10, \frac{7}{2}, \frac{3}{2}\rangle \quad |11, \frac{7}{2}, \frac{3}{2}\rangle \quad |1-1, \frac{7}{2}, \frac{3}{2}\rangle \\ \langle 00, \frac{7}{2}, \frac{3}{2} | \left(\begin{array}{cccc} 0 & -\frac{5}{2} & \frac{5\sqrt{30}}{6} & -\frac{5\sqrt{6}}{3} \\ -\frac{5}{2} & 0 & -\frac{\sqrt{30}}{6} & \frac{\sqrt{6}}{3} \\ \frac{5\sqrt{30}}{6} & -\frac{\sqrt{30}}{6} & \frac{1}{6} & 0 \\ -\frac{5\sqrt{6}}{3} & \frac{\sqrt{6}}{3} & 0 & -\frac{5}{6} \end{array} \right) \quad (14-39d)$$

$$M_F = \frac{1}{2} \quad |00, \frac{7}{2}, \frac{1}{2}\rangle \quad |10, \frac{7}{2}, \frac{1}{2}\rangle \quad |11, \frac{7}{2}, \frac{1}{2}\rangle \quad |1-1, \frac{7}{2}, \frac{1}{2}\rangle \\ \langle 00, \frac{7}{2}, \frac{1}{2} | \left(\begin{array}{cccc} 0 & -\frac{5}{6} & \frac{10\sqrt{2}}{3} & -\frac{5\sqrt{30}}{6} \\ -\frac{5}{6} & 0 & -\frac{2\sqrt{2}}{3} & \frac{\sqrt{30}}{6} \\ \frac{10\sqrt{2}}{3} & -\frac{2\sqrt{2}}{3} & -\frac{1}{6} & 0 \\ -\frac{5\sqrt{30}}{6} & \frac{\sqrt{30}}{6} & 0 & -\frac{1}{2} \end{array} \right) \quad (14-39e)$$

For numerical work the matrix elements must be multiplied by a_ℓ as defined in (14-27). Note that there is no first-order hyperfine splitting for the 7F_0 groundstate. This is not surprising the matrix elements of any non-scalar interaction must vanish between states with $J = 0$. However, is some splitting possible by second-order interaction via

the 7F_1 level. We need to determine how big such a splitting could be. Would it be measurable?

The second-order perturbation on the 7F_0 level by magnetic hyperfine interaction with the 7F_1 level is approximately given by

$$E({}^7F00\frac{7}{2}M_I; M_F) = -\frac{1}{\Delta} \sum_{M_J, M'_I} (a_\ell \langle {}^7F00\frac{7}{2}M_I; M_F | H_{hfs} | {}^7F1M_J\frac{7}{2}M'_I; M_F \rangle)^2 \quad (14-40)$$

where $\Delta = E({}^7F_1) - E({}^7F_0)$. The summation in (14-40) proceeds by summing the squares of the matrix elements for the first row of each of the matrices for each value of M_F . However, each summation results in the number

$$a_\ell^2 \frac{175}{4} \quad (14-41)$$

and hence the shift is the *same* for all the values of M_F and thus this mechanism cannot lift the groundstate degeneracy!

Experimentally⁸, it is found for ${}^{147}\text{Sm } I$ that $a_\ell \sim -140\text{MHz}$ allowing us to estimate the size of the shift of the groundstate of this atom. Using (14-41), $\Delta \sim 202\text{cm}^{-1}$ in (14-40) yields

$$\begin{aligned} E({}^7F00\frac{7}{2}M_I; M_F) &\sim - \left(140 \times \frac{175}{4} \right)^2 \times (202 \times 2.998 \times 10^4)^{-1} \\ &= -6.3\text{MHz} = -2 \times 10^{-5}\text{cm}^{-1} \end{aligned} \quad (14-42)$$

14.3. Combined Magnetic + Hyperfine fields in $\text{Sm } I$

Let us now consider the combined action of an external magnetic field B_z and the magnetic hyperfine interaction on the 7F_0 groundstate of $\text{Sm } I$. We have seen that neither, by itself, can produce a splitting at second-order. In second-order we need to evaluate the cross terms

$$\begin{aligned} E({}^7F00\frac{7}{2}M_I; M_F) &= -\delta_{M_I, M_F} \frac{2a_\ell \mu_B B_z}{\Delta} \\ &\times \langle {}^7F00\frac{7}{2}M_I; M_F | \mathbf{N}^{(1)} \cdot \mathbf{I}^{(1)} | {}^7F10M_I M_F \rangle \\ &\times \langle {}^7F10M_I M_F | L + g_s S | {}^7F00\frac{7}{2}M_I; M_F \rangle \end{aligned} \quad (14-43)$$

The first matrix element follows from specialisation of (14-31b) to give

$$\langle {}^7F00\frac{7}{2}M_I; M_F | \mathbf{N}^{(1)} \cdot \mathbf{I}^{(1)} | {}^7F10M_I M_F \rangle = -\frac{5}{3} M_F \quad (14-44)$$

and the second from (13-6)

$$\langle {}^7F10M_I M_F | L + g_s S | {}^7F00\frac{7}{2}M_I; M_F \rangle = 2(g_s - 1) \mu_B B_z \quad (14-45)$$

and hence (14-43) evaluates as

$$E({}^7F00\frac{7}{2}M_I; M_F) = \frac{\delta_{M_I, M_F}}{\Delta} M_F 2a_\ell \mu_B B_z \frac{5}{3} 2(g_s - 1) \quad (14-46)$$

Here we notice that the perturbation is directly proportional to the M_F quantum number and to the applied magnetic field and thus the combined effect is to produce a small hyperfine splitting of the groundstate - how small? Assuming an external field of $1T$ we find from (14-46) that

$$E(^7F00\frac{7}{2}M_I; M_F) \sim 2.2M_F MHz \sim 7 \times 10^{-5} M_F cm^{-1} \quad (14-47)$$

14.4. Exercises

14-1 Give a physical interpretation of the result found in (14-41).

14-2 Explain why if you diagonalise the matrices (14-39a-e), with the elements off-diagonal in J put to zero you get just 4 distinct eigenvalues $(0, -\frac{1}{3}, -\frac{3}{2}, \frac{7}{6})$.

Lecture 15: Electric Quadrupole Hyperfine Structure

Never having experienced the classical education as fragmentarily delivered by the English public and grammar schools, nor a university grounding in Newtonian science, Faraday had no preconceptions, and was thus uniquely receptive when he first encountered science in London. James Hamilton, *Faraday, the life* London: HarperCollins (2002)

15. Introduction

In this lecture we explore the role of electric quadrupole hyperfine interactions in the $4f^{67}F$ multiplet of the trivalent europium ion Eu^{3+} ion. Recall europium has two stable isotopes ^{151}Eu and ^{153}Eu each having a nuclear spin of $I = \frac{5}{2}$ and hence each possess both a nuclear magnetic moment and an electric quadrupole moment. Throughout we will be drawing on Chapters 2 and 6 of Part I.

15.1. The Electric Quadrupole Interaction Matrix Elements in the $|JIFM_F\rangle$ Basis

Noting S6.10 and (2-44) we have

$$\begin{aligned} & \langle \alpha JIFM_F | H_{EQ} | \alpha' J'IFM_F \rangle \\ &= -e^2 (-1)^{J'+I+F} \begin{Bmatrix} J' & I & F \\ I & J & 2 \end{Bmatrix} \langle \alpha J || r_e^{-3} C_e^{(2)} || \alpha' J' \rangle \langle I || r_n^2 C_n^{(2)} || I \rangle \end{aligned} \quad (15-1)$$

Note from (6-37) we can write

$$Q = \sqrt{\frac{4I(2I-1)}{(I+1)(2I+1)(2I+3)}} \langle I || r_n^2 C_n^{(2)} || I \rangle \quad (15-2)$$

allowing us to rewrite (15-1) as

$$\begin{aligned} & \langle \alpha JIFM_F | H_{EQ} | \alpha' J'IFM_F \rangle \\ &= -b_\ell (-1)^{J'+I+F} \begin{Bmatrix} J' & I & F \\ I & J & 2 \end{Bmatrix} \sqrt{\frac{(I+1)(2I+1)(2I+3)}{4I(2I-1)}} \langle \ell || C^{(2)} || \ell \rangle \\ &\times \langle \alpha J || U^{(2)} || \alpha' J' \rangle \end{aligned} \quad (15-3)$$

Expanding the description of the last reduced matrix element in (15-3) we have

$$\begin{aligned} & \langle \alpha SLJ || U^{(2)} || \alpha' S'L'J' \rangle \\ &= \delta_{S,S'} (-1)^{S+L'+J} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & 2 & J' \\ L' & S & L \end{Bmatrix} \\ &\times \langle \alpha SL || U^{(2)} || \alpha' S'L' \rangle \end{aligned} \quad (15-4)$$

where for a single electron we define the unit tensor operator $\mathbf{u}^{(k)}$ by

$$\langle \ell || \mathbf{u}^{(k)} || \ell' \rangle = \delta_{\ell,\ell'} \quad (15-5)$$

The reduced matrix elements of $U^{(2)}$ have been tabulated by Nielson and Koster⁴⁴. In particular

$$\langle f^6 \ ^7F \| U^{(2)} \| f^6 \ ^7F \rangle = -1 \quad (15-6)$$

It follows from (15-4) that

$$\begin{array}{l} U^{(2)} \quad |^7F_0\rangle \quad |^7F_1\rangle \quad |^7F_2\rangle \\ \langle ^7F_0| \left(\begin{array}{ccc} 0 & 0 & -\frac{\sqrt{7}}{7} \\ 0 & \frac{3\sqrt{14}}{28} & -\frac{\sqrt{42}}{28} \\ -\frac{\sqrt{7}}{7} & \frac{\sqrt{42}}{28} & \frac{11\sqrt{6}}{84} \end{array} \right) \\ \langle ^7F_1| \\ \langle ^7F_2| \end{array} \quad (15-7)$$

15.2. Electric Quadrupole Interaction for $^{151}\text{Eu}(4f^6 \ ^7F_0)$

Let us use the preceding results to estimate the extent to which the ground state of $^{151}\text{Eu}^{3+}$ is perturbed by electric quadrupole interaction with the 7F_2 state at $\sim 1040\text{cm}^{-1}$ above the ground state. Thus from (15-3), (15-7) and noting that

$$\langle 3 \| C^{(2)} \| 3 \rangle = -\frac{2\sqrt{105}}{15} \quad (15-8)$$

we have

$$\begin{aligned} & \langle (0\frac{5}{2})\frac{5}{2} | H_{EQ} | (2\frac{5}{2})\frac{5}{2} \rangle \\ &= -b_{4f}(-1)^{2+\frac{5}{2}+\frac{5}{2}} \left\{ \begin{array}{ccc} 2 & \frac{5}{2} & \frac{5}{2} \\ \frac{5}{2} & 0 & 2 \end{array} \right\} \sqrt{\frac{\frac{7}{2} \cdot 6 \cdot 8}{4 \cdot \frac{5}{2} \cdot 4}} \cdot \frac{2\sqrt{105}}{15} \cdot \frac{\sqrt{7}}{7} \\ &= -\frac{\sqrt{210}}{75} b_{4f} \end{aligned} \quad (15-9)$$

15.3. Electric Quadrupole Interaction in the $|JM_JIM_I\rangle$ Basis

Within a crystal field the $|JM_JIM_I\rangle$ basis is most appropriate. To that end we need to extend the results of S6.10 to compute matrix elements off-diagonal in J . We have

$$\begin{aligned} & \langle \alpha JM_JIM_I M_F | H_{EQ} | \alpha' J' M_J \pm q \ IM_I \mp q M'_F \rangle \\ &= -e^2 \delta_{M_F, M'_F} (-1)^{J-M_J} \begin{pmatrix} J & 2 & J' \\ -M_J & \mp q & M_J \pm q \end{pmatrix} (-1)^{I-M_I} \begin{pmatrix} I & 2 & I \\ -M_I & \pm q & M_I \mp q \end{pmatrix} \\ & \times \langle \alpha J \| r_e^{-3} C_e^2 \| \alpha' J' \rangle \langle I \| r_n^2 C_n^{(2)} \| I \rangle \end{aligned} \quad (15-10)$$

Noting (15-2) and (15-4) we have

$$\begin{aligned} & \langle \alpha SLJM_JIM_I M_F | H_{EQ} | \alpha' SL'J'M_J \pm q \ IM_I \mp q M'_F \rangle \\ &= \delta_{M_F, M'_F} (-1)^{J-M_J} \begin{pmatrix} J & 2 & J' \\ -M_J & \mp q & M_J \pm q \end{pmatrix} (-1)^{I-M_I} \begin{pmatrix} I & 2 & I \\ -M_I & \pm q & M_I \mp q \end{pmatrix} \\ & \times -e^2 \langle r_e^{-3} \rangle Q \sqrt{\frac{(I+1)(2I+1)(2I+3)}{4I(2I-1)}} \langle \ell \| C^{(2)} \| \ell \rangle \\ & \times (-1)^{S+L'+J} \sqrt{(2J+1)(2J'+1)} \left\{ \begin{array}{ccc} J & 2 & J' \\ L' & S & L \end{array} \right\} \langle \alpha SL \| U^{(2)} \| \alpha' S'L' \rangle \end{aligned} \quad (15-11)$$

15.4. Electric Quadrupole Coupling between 7F_0 and 7F_2 in Eu^{3+}

Let us use the above results to compute the matrix elements

$$E(M_I) = \langle 4f^6 {}^7F_0 M_J = 0 \frac{5}{2} M_I | H_{EQ} | 4f^6 {}^7F_2 M_J = 0 \frac{5}{2} M_I \rangle \quad (15-12)$$

Using

$$\begin{pmatrix} 2 & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{\sqrt{5}} \quad (15-13)$$

and

$$(-1)^{\frac{5}{2}-M_I} \begin{pmatrix} \frac{5}{2} & 2 & \frac{5}{2} \\ -M_I & 0 & M_I \end{pmatrix} = \frac{12M_I^2 - 35}{16\sqrt{105}} \quad (15-14)$$

together with (15-7) and (15-8) in (15-11) leads to

$$E(M_I) = -e^2 Q \langle r_e^{-3} \rangle \frac{\sqrt{3}}{600} [12M_I^2 - 35] \quad (15-15)$$

from which we can deduce that were a second-order perturbation responsible for the ground state hyperfine splitting, say by crystal field mixing, the electric quadrupole hyperfine splittings will be proportional to M_I^2 and states with $\pm M_I$ will be two-fold degenerate. We have from (15-15) the ratio

$$\Delta_{calc} = \frac{E(\pm\frac{5}{2}) - E(\pm\frac{3}{2})}{E(\pm\frac{3}{2}) - E(\pm\frac{1}{2})} = 2 \quad (15-16)$$

which may be compared with the experimental ratios in $YAlO_3 : Eu^{3+}$ of⁸⁴

$$\Delta_{expt}({}^{151}Eu) = \frac{45.99}{23.03} = 1.997 \quad (15-17a)$$

and

$$\Delta_{expt}({}^{153}Eu) = \frac{119.20}{59.65} = 1.998 \quad (15-17b)$$

15.5. A Derivation

The above results are encouraging but we still have to consider the *sign* of the splitting so as to determine the *ordering* of the three hyperfine levels and finally the *magnitude* of the splittings. We also want to make sure that our results are consistent. To that end we attempt an alternative derivation based upon an expression for the electric quadrupole hyperfine interaction due to Abragam and Pryce⁸⁵ who give the interaction as

$$H_{EQ} = \frac{e^2 Q}{2I(2I-1)} \sum_i \left\{ \frac{I(I+1)}{r_i^3} - \frac{3(\mathbf{r} \cdot \mathbf{I})^2}{r_i^5} \right\} \quad (15-18)$$

where the summation is over all electrons outside of closed shells. Our task is to first express the operator enclosed in curly brackets in terms of tensor operators. We start with the second term.

$$(\mathbf{r} \cdot \mathbf{I}) = r(\mathbf{C}^{(1)} \cdot \mathbf{I}^{(1)}) = -\sqrt{3}r(\mathbf{C}^{(1)}\mathbf{I}^{(1)})_0^{(0)} \quad (15-19)$$

Next

$$\begin{aligned} (\mathbf{r} \cdot \mathbf{I})^2 &= 3r^2(\mathbf{C}^{(1)}\mathbf{I}^{(1)})_0^{(0)}(\mathbf{C}^{(1)}\mathbf{I}^{(1)})_0^{(0)} \\ &= 3r^2((\mathbf{C}^{(1)}\mathbf{I}^{(1)})_0^{(0)}(\mathbf{C}^{(1)}\mathbf{I}^{(1)})_0^{(0)})_0^{(0)} \\ &= 3r^2 \sum_k \langle (11)0(11)0; 0 | (11)k(11)k; 0 \rangle ((\mathbf{C}^{(1)}\mathbf{C}^{(1)})^{(k)}(\mathbf{I}^{(1)}\mathbf{I}^{(1)})^{(k)})_0^{(0)} \\ &= 3r^2 \sum_k (2k+1) \begin{Bmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ k & k & 0 \end{Bmatrix} ((\mathbf{C}^{(1)}\mathbf{C}^{(1)})^{(k)}(\mathbf{I}^{(1)}\mathbf{I}^{(1)})^{(k)})_0^{(0)} \end{aligned} \quad (15-20)$$

The $9j$ -symbol vanishes unless $k = 0, 1, 2$. Furthermore

$$(\mathbf{C}^{(1)}\mathbf{C}^{(1)})_0^{(0)} = -\frac{1}{\sqrt{3}} \quad (15-21a)$$

$$(\mathbf{C}^{(1)}\mathbf{C}^{(1)})_0^{(1)} = 0 \quad (15-21b)$$

$$(\mathbf{C}^{(1)}\mathbf{C}^{(1)})_0^{(2)} = \sqrt{\frac{2}{3}}\mathbf{C}^{(2)} \quad (15-21c)$$

Consider the $k = 0$ term in (15-20). Evaluating the $9j$ -symbol and using (15-21a) leads to

$$3r^2 \cdot \frac{1}{3} \cdot -\frac{1}{\sqrt{3}}(\mathbf{I}^{(1)}\mathbf{I}^{(1)})_0^{(0)} = -\frac{r^2}{\sqrt{3}}(\mathbf{I}^{(1)}\mathbf{I}^{(1)})_0^{(0)} \quad (15-22)$$

Then

$$\begin{aligned} &\langle IM_I | (\mathbf{I}^{(1)}\mathbf{I}^{(1)})_0^{(0)} | IM_I \rangle \\ &= (-1)^{I-M_I} \begin{pmatrix} I & 0 & I \\ -M_I & 0 & M_I \end{pmatrix} \langle I || (\mathbf{I}^{(1)}\mathbf{I}^{(1)})_0^{(0)} || I \rangle \\ &= \frac{(-1)^{2I}}{\sqrt{2I+1}} \begin{Bmatrix} 1 & 0 & 1 \\ I & I & I \end{Bmatrix} \langle I || I^{(1)} || I \rangle^2 \\ &= -\frac{1}{\sqrt{3}(2I+1)} I(I+1)(2I+1) \\ &= -\frac{I(I+1)}{\sqrt{3}} \end{aligned} \quad (15-23)$$

Noting (15-22) we see that the $k = 0$ term exactly cancels the first term in (15-18). Thus only the $k = 2$ term need be considered. We first note that

$$\begin{aligned}
& \langle I || (I^{(1)} I^{(1)})^{(2)} || I \rangle \\
&= \sqrt{5} (-1)^{2I} \begin{Bmatrix} I & 1 & I \\ 2 & I & 1 \end{Bmatrix} \langle I || I^{(1)} || I \rangle^2 \\
&= \sqrt{5} (-1)^{2I} \begin{Bmatrix} I & I & 2 \\ 1 & 1 & I \end{Bmatrix} I(I+1)(2I+1) \\
&= \sqrt{\frac{I(I+1)(2I+1)(2I+3)(2I-1)}{6}} \quad (15-24)
\end{aligned}$$

and from the Wigner-Eckart theorem

$$\begin{aligned}
& \langle IM_I | (I^{(1)} I^{(1)})_0^{(2)} | IM_I \rangle \\
&= (-1)^{I-M_I} \begin{pmatrix} I & 2 & I \\ -M_I & 0 & M_I \end{pmatrix} \langle I || (I^{(1)} I^{(1)})^{(2)} || I \rangle \quad (15-25)
\end{aligned}$$

Evaluating the $3j$ -symbol and using (15-24) we obtain

$$\langle IM_I | (I^{(1)} I^{(1)})_0^{(2)} | IM_I \rangle = \frac{3M_I^2 - I(I+1)}{\sqrt{6}} \quad (15-26)$$

Evaluation of the $9j$ -symbol and use of (15-21b) results in the $k = 2$ portion of (15-20) becoming

$$r^2 \frac{\sqrt{6}}{3} \sum_q (-1)^q C_q^{(2)} (I^{(1)} I^{(1)})_{-q}^{(2)} \quad (15-27)$$

and hence

$$\left\{ \frac{I(I+1)}{r_i^3} - \frac{3(\mathbf{r} \cdot \mathbf{I})^2}{r_i^5} \right\} = -\langle r_e^{-3} \rangle_i \sqrt{6} \sum_q (-1)^q C_q^{(2)} (I^{(1)} I^{(1)})_{-q}^{(2)} \quad (15-28)$$

Returning this result to (15-18) leads to

$$\begin{aligned}
& \langle {}^7F00IM_I | H_{EQ} | {}^7F20IM_I \rangle \\
&= -\frac{e^2 Q \langle r_e^{-3} \rangle}{2I(2I-1)} \sqrt{6} \langle {}^7F00 | C_0^{(2)} | {}^7F20 \rangle \langle IM_I | (I^{(1)} I^{(1)})_0^{(2)} | IM_I \rangle \quad (15-29)
\end{aligned}$$

Noting that

$$\langle {}^7F00 | C_0^{(2)} | {}^7F20 \rangle = \frac{2\sqrt{3}}{15} \quad (15-30)$$

and (15-26) we obtain (15-29), with $I = \frac{5}{2}$, as

$$\langle {}^7F00 \frac{5}{2} M_I | H_{EQ} | {}^7F20 \frac{5}{2} M_I \rangle = -e^2 Q \langle r_e^{-3} \rangle \frac{\sqrt{3}}{600} [12M_I^2 - 35] \quad (15-31)$$

in agreement with (15-15).

15.6. Crystal Field J -mixing in the 7F Multiplet

Ultimately our concern is with Eu^{3+} ions in a crystal field, V_{cryst} . In the usual crystal field expansion one has typically

$$V_{cryst} = \sum_{k,q} B_q^k C_q^{(k)} \quad (15-32)$$

A typical matrix element of the tensor operator, $C_q^{(k)}$, will be of the form

$$\begin{aligned} & \langle \alpha SLJM | C_q^{(k)} | \alpha' SL'J'M' \rangle \\ & = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \\ & \times (-1)^{S+L'+J+k} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & k & J' \\ L' & S & L \end{Bmatrix} \\ & \times \langle \alpha SL || C^{(k)} || \alpha' SL' \rangle \end{aligned} \quad (15-33)$$

Inspection of the above leads to the selection rules that must be satisfied if the matrix element is not to vanish

$$\Delta S = 0, \quad \Delta L \leq k, \quad \Delta J \leq k, \quad M' = M - q \quad (15-34)$$

In the preceding section we saw that the electric quadrupole hyperfine interaction can couple the $M_J = 0$ states of the 7F_0 level to that of the 7F_2 level. Clearly any crystal field having an axial quadrupole term such as $B_0^2 C_0^{(2)}$ can likewise mix those two levels. Thus we can anticipate a second-order splitting mechanism of the form

$$- 2 \frac{\langle {}^7F00IM_I | B_0^2 C_0^{(2)} | {}^7F20IM_I \rangle \langle {}^7F20IM_I | H_{EQ} | {}^7F00IM_I \rangle}{E({}^7F_2) - E({}^7F_0)} \quad (15-35)$$

That will be the subject of the next lecture.

Lecture 16: Electric Quadrupole Hyperfine structure in Crystals

Symmetry, as wide or as narrow as you may define its meaning, is one idea by which man through the ages has tried to comprehend and create order, beauty, and perfection. Hermann Weyl, *Symmetry* Princeton: Princeton University Press (1952)

16. Introduction

In this lecture I want to focus on the evaluation of the *sign* and *magnitude* of the groundstate hyperfine splitting of Eu^{3+} in a crystalline environment.

16.1. Derivation of Elliott's Second-order Electric Quadrupole Splitting Result

Initially let us consider a purely axial crystal field. Since we will consider an interaction between the 7F_0 and 7F_2 levels the crystal field could be represented, as traditionally⁸⁰, as

$$V_{cryst} = A_2^0 \sum_i (3z_i^2 - r_i^2) \quad (16-1)$$

where the summation is over all electrons in unclosed shells and A_2^0 is a parameter that reflects the structure of the crystal. Eq. (16-1) can be rewritten in tensor operator form as

$$V_{cryst} = 2A_2^0 \langle r^2 \rangle \sum_i C_{i0}^{(2)} \quad (16-2)$$

Let us now consider the splitting mechanism alluded to in (15-35) with a minor change of notation,

$$E(I, M_I) = -4A_2^0 \langle r^2 \rangle \frac{\langle {}^7F00IM_I | \sum_i C_{i0}^{(2)} | {}^7F20IM_I \rangle \langle {}^7F20IM_I | H_{EQ} | {}^7F00IM_I \rangle}{E({}^7F_2) - E({}^7F_0)} \quad (16-3)$$

The operator in the first matrix element acts only in the space of the electrons and is thus independent of, and diagonal in, the IM_I nuclear quantum numbers. This matrix element was evaluated in (15-30) while the second matrix element was evaluated in (15-29) as

$$\langle {}^7F20IM_I | H_{EQ} | {}^7F00IM_I \rangle = -e^2 Q \langle r_e^{-3} \rangle \frac{\sqrt{3} [3M_I^2 - I(I+1)]}{15 I(2I-1)} \quad (16-4)$$

to yield (16-3) as

$$E(I, M_I) = \frac{8}{75} \frac{e^2 Q A_2^0 \langle r^2 \rangle \langle r_e^{-3} \rangle [3M_I^2 - I(I+1)]}{\Delta_2 I(2I-1)} \quad (16-5)$$

which is identical with (11) of Elliott⁸⁰ where

$$\Delta_2 = E({}^7F_2) - E({}^7F_0) \quad (16-6)$$

For the stable europium isotopes $I = \frac{5}{2}$ and (16-5) becomes

$$E(\frac{5}{2}, M_I) = \frac{4}{375} \frac{e^2 Q A_2^0 \langle r^2 \rangle \langle r_e^{-3} \rangle}{\Delta_2} [3M_I^2 - \frac{35}{4}] \quad (16-7)$$

which again agrees with Elliott's result⁸⁰ *but* has the opposite sign to the observed splittings so cannot, by itself, explain the ground state hyperfine structure. This situation is reminiscent of similar problems in explaining the crystal field splitting⁸⁶ of the $|4f^7 \ ^8S_{7/2} \rangle$ groundstate of Gd^{3+} .

16.2. Explicit Calculation of the Elliott Term

Elliott⁸⁰ has expressed (16-5) in the form

$$E(I, M_I) = P[M_I^2 - \frac{1}{3}I(I+1)] \quad (16-8)$$

with

$$P = \frac{8}{25} e^2 Q A_2^0 \langle r^2 \rangle \frac{\langle r_e^{-3} \rangle}{I(2I-1)\Delta_2} \quad (16-9)$$

To obtain a numerical value for P we need estimates of the various quantities appearing in (16-9). Elliott did this for Eu^{3+} in europium ethylsulphate crystals, we will follow his calculation. A value for A_2^0 can be obtained, to a reasonable approximation, by noting that experimentally the two 7F_1 sublevels, $M_J = \pm 1$ and $M_J = 0$ are separated by $42cm^{-1}$. This splitting can be calculated, neglecting possible J -mixing, using (16-2) and (15-33) and noting (15-7). Thus

$$\begin{aligned} & \langle {}^7F_1 1 | C_0^{(2)} | {}^7F_1 1 \rangle \\ &= (-1)^{1-1} \begin{pmatrix} 1 & 2 & 1 \\ -1 & 0 & 1 \end{pmatrix} \langle 3 || C^{(2)} || 3 \rangle \langle {}^7F_1 || U^{(2)} || {}^7F_1 \rangle \\ &= 1 \times \frac{\sqrt{30}}{30} \times -\frac{2\sqrt{105}}{15} \times \frac{3\sqrt{14}}{28} \\ &= -\frac{1}{10} \end{aligned} \quad (16-10a)$$

$$\begin{aligned} & \langle {}^7F_1 0 | C_0^{(2)} | {}^7F_1 0 \rangle \\ &= (-1)^{1-0} \begin{pmatrix} 1 & 2 & 1 \\ 0 & 0 & 0 \end{pmatrix} \langle 3 || C^{(2)} || 3 \rangle \langle {}^7F_1 || U^{(2)} || {}^7F_1 \rangle \\ &= -1 \times \frac{\sqrt{30}}{15} \times -\frac{2\sqrt{105}}{15} \times \frac{3\sqrt{14}}{28} \\ &= +\frac{1}{5} \end{aligned} \quad (16-10b)$$

and hence

$$\langle {}^7F_1 0 | V_{cryst} | {}^7F_1 0 \rangle - \langle {}^7F_1 \pm 1 | V_{cryst} | {}^7F_1 \pm 1 \rangle = \frac{3}{5} A_2^0 \langle r^2 \rangle \quad (16-11)$$

From which we deduce

$$A_2^0 \langle r^2 \rangle = 70 \text{cm}^{-1} \quad (16-12)$$

Experimentally the energy separation of the 7F_0 and 7F_2 levels is

$$\Delta_2 = 1015 \text{cm}^{-1} \quad (16-13)$$

Bleaney⁸⁷ had deduced a value of

$$\langle r_e^{-3} \rangle = 57 \text{\AA}^{-3} = 57 \times 10^{-24} \text{cm}^{-3} \quad (16-14)$$

Furthermore,

$$e^2 = R a_0 \quad (16-15)$$

where R is the Rydberg constant and a_0 is the Bohr radius. Following tradition the electric quadrupole moment Q is expressed in *barns* with

$$1 \text{barn} = 10^{-24} \text{cm}^2 \quad (16-16)$$

To obtain P in cm^{-1} we take

$$R = 109736 \text{cm}^{-1} \quad \text{and} \quad a_0 = 0.5292 \times 10^{-8} \text{cm} \quad (16-17)$$

Taking the above values together with $I = \frac{5}{2}$ and Q in barns we obtain from (16-9) Elliott's estimate of

$$\begin{aligned} P &= +Q \times \frac{4}{125} \times \frac{e^2 A_2^0 \langle r^2 \rangle}{\Delta_2} \times \langle r_e^{-3} \rangle \\ &= +Q \times \frac{4 \times 2 \times 109736 \times 0.5292 \times 10^{-8} \times 70 \times 57}{125 \times 1015} \\ &= +1.46Q \times 10^{-4} \text{cm}^{-1} \\ &= +4.38Q \text{ MHz} \end{aligned} \quad (16-18)$$

Elliott's estimate for P could be brought up-to-date using modern values but the change is relatively small. Before exploring the subject further let us consider the impact of spin-orbit interaction of the 5D_0 state with the ground state 7F_0 . To that end we must first consider the Coulomb interaction among the three 5D states of $4f^6$ to determine the linear combination of the three 5D states corresponding to the lowest 5D term.

16.3. The Lowest $4f^6$ 5D Term

The detailed calculation can be found in Judd² S8-7. The three 5D states are labelled as

$$|(210)(20){}^5D\rangle, |(210)21){}^5D\rangle, |(111)(20){}^5D\rangle \quad (16-19)$$

The Coulomb matrix evaluates as

$$\begin{pmatrix} 15E^0 + 6E^1 + \frac{858}{7}E^2 + 11E^3 & \frac{468\sqrt{33}}{7}E^2 & \frac{22\sqrt{14}}{7}E^3 \\ \frac{468\sqrt{33}}{7}E^2 & 15E^0 + 6E^1 - \frac{1131}{7}E^2 + 18E^3 & \frac{12\sqrt{462}}{7}E^3 \\ \frac{22\sqrt{14}}{7}E^3 & \frac{12\sqrt{462}}{7}E^3 & 15E^0 + 9E^1 - 11E^3 \end{pmatrix} \quad (16-20)$$

Judd chose to diagonalise the matrix (16-20) using $4f$ -hydrogenic eigenfunction ratios for the Slater integrals and obtained the eigenfunction for the lowest 5D term as

$$|{}^5D\rangle = -0.196|(210)(20){}^5D\rangle + 0.770|(210)21){}^5D\rangle - 0.607|(111)(20){}^5D\rangle \quad (16-21)$$

16.4. Spin-orbit Interaction Between 7F_0 and the Lowest 5D_0

To calculate the spin-orbit interaction we first note that

$$\begin{aligned} & \langle \ell^n \alpha SLJM | \sum_{i=1}^n (\mathbf{s} \cdot \boldsymbol{\ell}) | \ell^n \alpha' S' L' J' M' \rangle \\ &= \delta_{J,J'} \delta_{M,M'} (-1)^{S'+L+J} \frac{\sqrt{\ell(\ell+1)(2\ell+1)}}{6} \begin{Bmatrix} S & S' & 1 \\ L' & L & J \end{Bmatrix} \\ & \times \langle \ell^n \alpha SL || W^{(11)} || \ell^n \alpha' S' L' \rangle \end{aligned} \quad (16-22)$$

Judd² p203 gives a table of some of the relevant spin-orbit matrix elements. In particular he tabulates the $\langle {}^7F_1 | H_{so} | {}^5D_1 \rangle$ matrix elements. We however want the corresponding matrix elements for $J = 0$. We can obtain these by noting from (16-22) that

$$\frac{\langle {}^7F_0 | H_{so} | {}^5D_0 \rangle}{\langle {}^7F_1 | H_{so} | {}^5D_1 \rangle} = \frac{3\sqrt{2}}{4} \quad (16-23)$$

and hence

$$\langle {}^7F_0 | \begin{pmatrix} |(210)(20){}^5D\rangle & |(210)21){}^5D\rangle & |(111)(20){}^5D\rangle \\ -\frac{\sqrt{42}}{7} \zeta_{4f} & -\frac{\sqrt{154}}{7} \zeta_{4f} & 2\sqrt{3} \zeta_{4f} \end{pmatrix} \quad (16-24)$$

Making use of (16-21) and (16-24) then leads, for the lowest 5D_0 level, to

$$\begin{aligned} & \langle {}^7F_0 | H_{so} | {}^5D_0 \rangle \\ &= (-0.196 \times -\frac{\sqrt{42}}{7} + 0.770 \times -\frac{\sqrt{154}}{7} - 0.607 \times 2\sqrt{3}) \zeta_{4f} \\ &= -3.3 \zeta_{4f} \end{aligned} \quad (16-25)$$

Let us suppose that the 5D_0 is above the 7F_0 level by an amount E and try to estimate the amount of $|{}^5D_0\rangle$ character that gets mixed into the $|{}^7F_0\rangle$ ground state by spin-orbit interaction. Using the previous results we have the energy matrix

$$\begin{pmatrix} |{}^7F_0\rangle & |{}^5D_0\rangle \\ \langle {}^7F_0 | \begin{pmatrix} 0 & -3.3 \zeta_{4f} \\ -3.3 \zeta_{4f} & E \end{pmatrix} & \end{pmatrix} \quad (16-26)$$

to consider.

16.5. Note on rank two matrices

Consider a rank two matrix of the form

$$\begin{array}{c} |\alpha\rangle \quad |\beta\rangle \\ \langle\alpha| \left(\begin{array}{cc} 0 & a \\ a & E \end{array} \right) \\ \langle\beta| \end{array} \quad (16-27)$$

The two eigenvalues λ_{\pm} may be found from the requirement that

$$\begin{vmatrix} -\lambda & a \\ a & E - \lambda \end{vmatrix} = 0 \quad (16-28)$$

leading to the secular equation

$$\lambda^2 - E\lambda - a^2 = 0 \quad (16-29)$$

with

$$\begin{aligned} \lambda_{\pm} &= \frac{1}{2} \left[E \pm \sqrt{E^2 + 4a^2} \right] \\ &= \frac{1}{2} E \left[1 \pm \sqrt{1 + \frac{4a^2}{E^2}} \right] \end{aligned} \quad (16-30)$$

If $E \gg a$ then we can approximate the square root to get the two eigenvalues as

$$\lambda_+ = E + \frac{a^2}{E} \quad \text{and} \quad \lambda_- = -\frac{a^2}{E} \quad (16-31)$$

The corresponding eigenvectors will be

$$|\lambda_+\rangle = x|\alpha\rangle + y|\beta\rangle \quad \text{and} \quad |\lambda_-\rangle = y|\alpha\rangle - x|\beta\rangle \quad (16-32)$$

with

$$xx^* + yy^* = 1 \quad (16-33)$$

. We may choose x, y to be real. The components (x, y) may be determined from the requirement that

$$\begin{pmatrix} 0 & a \\ a & E \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \lambda_{\pm} \begin{pmatrix} x \\ y \end{pmatrix} \quad (16-34)$$

leading to

$$y = \lambda_{\pm} \frac{x}{a} \quad (16-35)$$

Noting (16-33) we may write

$$x = e^{i\theta} \frac{a}{\sqrt{a^2 + \lambda_{\pm}^2}} \quad (16-36)$$

Fixing the phase angle θ so that $e^{i\theta} = +1$ leads to the two eigenvectors

$$|\lambda_{-}\rangle = \frac{1}{\sqrt{E^2 + a^2}} (E|\alpha\rangle - a|\beta\rangle) \quad (16-37a)$$

$$|\lambda_{+}\rangle = \frac{1}{\sqrt{E^2 + a^2}} (a|\alpha\rangle + E|\beta\rangle) \quad (16-37b)$$

Returning to (16-26) and choosing $E = 18,000\text{cm}^{-1}$ and $\zeta_{4f} = 1015\text{cm}^{-1}$ we obtain from (16-32)

$$E(^7F_0) = -623\text{cm}^{-1} \quad \text{and} \quad E(^5D_0) = +18,623\text{cm}^{-1} \quad (16-38)$$

and from (16-37a,b) the eigenvectors

$$|E(^7F_0)\rangle = 0.983|^7F_0\rangle + 0.183|^5D_0\rangle \quad (16-39a)$$

$$|E(^5D_0)\rangle = -0.183|^7F_0\rangle + 0.983|^5D_0\rangle \quad (16-39b)$$

The preceding calculation should be regarded as an illustrative example and certainly not as an optimised calculation. The main conclusion to be drawn is that the mixing of the 7F_0 and 5D_0 states via the spin-orbit interaction is relatively small and will certainly not remedy the Elliott mechanism. That we take up in the next lecture.

Lecture 17 :The JLS Anomalous Quadrupole Coupling Mechanism in Crystals*What an imperfect world it would be if every symmetry was perfect***17. Introduction**

In this lecture we outline the early attempt of Judd, Lovejoy and Shirley's attempt⁸¹ to reconcile the discrepancy between Elliott's mechanism⁸⁰ for the groundstate of europium ethylsulphate and the experimental observation that the splitting had about twice the predicted magnitude and the opposite sign.

17.1. The Experimental Results

Judd *et al* fitted their experimental data to a predominantly quadrupolar Hamiltonian

$$\mathcal{H} = P \left[M_I^2 - \frac{1}{3}I(I+1) \right] \quad (17-1)$$

reporting⁸¹ for the two $I = 3$ isotopes Eu^{152} and Eu^{154}

$$P_{152} = -(6.7 \pm 0.5) \times 10^{-4} \text{ cm}^{-1} \quad (17-2a)$$

$$P_{154} = -(8.3 \pm 0.7) \times 10^{-4} \text{ cm}^{-1} \quad (17-2b)$$

These results are clearly of opposite sign to that predicted by Elliott. The breakdown of Russell-Saunders coupling, considered in the previous lecture, is at least two orders of magnitude too small to account for the negative sign of P .

17.2. Configuration Interaction Mechanisms

Given the failure to explain the observed quadrupole splittings in terms of interactions confined to the states of the $4f^6$ configuration it is natural to investigate the possibility of explaining the discrepancy by including the interactions with other electron configurations. In the following we shall, in the main, use the notations of Judd *et al* writing the Coulombic interelectronic interaction as

$$V_A = \sum_{i>j} \frac{e^2}{r_{ij}} \quad (17-3)$$

Judd *et al* note that since the crystal field parameters are deduced from experiment rather than by explicit calculation they already accommodate the contributions from mechanisms such as

$$\begin{aligned} &\langle 4f^6 5s^2 {}^7F_0 | V_A | 4f^6 5s 5d {}^7F_0 \rangle \langle 4f^6 5s 5d {}^7F_0 | V_{cryst} | 4f^6 5s^2 {}^7F_2 \rangle \langle 4f^6 5s^2 {}^7F_2 | V_{EQ} | 4f^6 5s^2 {}^7F_0 \rangle \\ &\times [\Delta_1 \Delta_2]^{-1} \end{aligned} \quad (17-4)$$

where

$$\Delta_1 = E(4f^6 5s 5d \ ^7F_0) - E(4f^6 5s^2 \ ^7F_0) \quad (17-5a)$$

$$\Delta_2 = E(4f^6 5s^2 \ ^7F_2) - E(4f^6 5s^2 \ ^7F_0) \quad (17-5b)$$

While the first pair of matrix elements in the mechanism

$$\begin{aligned} & \langle 4f^6 5s^2 \ ^7F_0 | V_A | 4f^6 5s 5d \ ^7F_0 \rangle \langle 4f^6 5s 5d \ ^7F_0 | V_{EQ} | 4f^6 5s^2 \ ^7F_2 \rangle \\ & \times \langle 4f^6 5s^2 \ ^7F_2 | V_{cryst} | 4f^6 5s^2 \ ^7F_0 \rangle [\Delta_1 \Delta_2]^{-1} \end{aligned} \quad (17-6)$$

along with the energy denominator Δ_1 amount to a shielding correction to the matrix element

$$\langle 4f^6 \ ^7F_0 | V_{EQ} | 4f^6 \ ^7F_2 \rangle \quad (17-7)$$

Judd *et al* note that such a mechanism cannot account for the required change of sign.

Judd *et al* suggest that the most likely configuration interaction mechanism must be of the form

$$- 2 \frac{\langle 4f^6 \ ^7F_0 | V_{cryst} | T \ ^7L_2 \rangle \langle T \ ^7L_2 | V_{EQ} | 4f^6 \ ^7F_0 \rangle}{E(T)} \quad (17-8)$$

where T denotes an excited electron configuration of *even* parity at an energy $E(T)$ above the groundstate. Of course, several configurations T may contribute. Attention is focussed upon the ratio

$$R = \frac{\langle 4f^6 \ ^7F_0 | V_{cryst} | T \ ^7L_2 \rangle \langle T \ ^7L_2 | V_{EQ} | 4f^6 \ ^7F_0 \rangle \times \Delta_2}{\langle 4f^6 \ ^7F_0 | V_{cryst} | 4f^6 \ ^7F_2 \rangle \langle 4f^6 \ ^7F_2 | V_{EQ} | 4f^6 \ ^7F_0 \rangle \times E(T)} \quad (17-9)$$

The operators, V_{cryst} and V_{EQ} , are single particle operators and hence at second-order we can restrict the excited configurations T to those involving the excitation of a single electron. Let us suppose a single electron $n\ell$ is excited into an orbital $n'\ell'$. Cancelling out the common angular dependencies of the matrix elements in R leaves the ratio as

$$R = A \frac{\langle n\ell | r^2 | n'\ell' \rangle \langle n'\ell' | r^{-3} | n\ell \rangle \times \Delta_2}{\langle 4f | r^2 | 4f \rangle \langle 4f | r^{-3} | 4f \rangle \times E(T)} \quad (17-10)$$

where A contains residual angular factors that do not cancel and vanishes if the triad $(\ell, \ell', 2)$ does not satisfy the usual triangular condition.

17.3. The Angular Factor A

Let us consider the angular factor contained in (17-10). First we note that the nuclear factors appearing in R as defined in (17-9) necessarily cancel and hence for an axial field

$$A = \frac{\langle 4f^6 \ ^7F_0 || C_e^{(2)} || T \ ^7L_2 \rangle \langle T \ ^7L_2 || C_e^{(2)} || 4f^6 \ ^7F_0 \rangle}{\langle 4f^6 \ ^7F_0 || C_e^{(2)} || 4f^6 \ ^7F_2 \rangle \langle 4f^6 \ ^7F_2 || C_e^{(2)} || 4f^6 \ ^7F_0 \rangle} \quad (17-11)$$

Note that the tensor operators $C_e^{(k)}$ are orbital operators and hence are diagonal in all spin quantum numbers. JLS considered the case where the electron configuration T involves the excitation of a single electron from a closed shell, $n\ell^{4\ell+2}$, to $n\ell^{4\ell+1}n'\ell'$. Thus the full description of a typical initial state in (17-11) would be of the form

$$|4f^6 \ ^7F(n\ell^{4\ell+2})^1S; \ ^7F_00\rangle \quad (17-12a)$$

and a typical excited state of the form

$$|4f^6 \ ^7F(n\ell^{4\ell+1}n'\ell')^1D; \ ^7L_20\rangle \quad (17-12b)$$

with L restricted to

$$F \times D = P + D + F + G + H, \quad \text{i.e. } L = 1, \dots, 5 \quad (17-13)$$

Recall that $C_e^{(2)}$ is a single particle operator so that the bra and ket vectors of a given matrix element can differ in, at most, a single particle state.

The dependence of the matrix elements in (17-11) upon the total angular momentum quantum numbers JM_J is such as to cancel between the numerator and denominator and hence we can rewrite A as

$$A = \frac{\left| \langle 4f^6 F(\dots)S; F \| C_e^{(2)} \| 4f^6 F(\dots)^*D; L \rangle \right|^2}{\left| \langle 4f^6 F(\dots)S; F \| C_e^{(2)} \| 4f^6 F(\dots)S; F \rangle \right|^2} \quad (17-14)$$

where for brevity we have indicated the closed shell as (\dots) and $(\dots)^*$ the single particle excitation.

Exercise 17-1 Verify that (17-14) follows from (17-11).

Exercise 17-2 Show that

$$\begin{aligned} & \left| \langle 4f^6 F(\dots)S; F \| C_e^{(2)} \| 4f^6 F(\dots)S; F \rangle \right|^2 \\ &= \left| \langle 3 \| C^{(2)} \| 3 \rangle \langle 4f^6 \ ^7F \| U^{(2)} \| 4f^6 \ ^7F \rangle \right|^2 \\ &= \langle 3 \| C^{(2)} \| 3 \rangle^2 \\ &= \frac{28}{15} \end{aligned} \quad (17-15)$$

Now to compute the numerator of (17-14). The action of $C_e^{(2)}$ is such that

$$\begin{aligned} & \langle F(\dots)S; F \| C_e^{(2)} \| F(\dots)^*D; L \rangle \\ &= (-1)^{3+2+3+2} \sqrt{7(2L+1)} \begin{Bmatrix} 3 & 2 & L \\ 2 & 3 & 0 \end{Bmatrix} \langle (n\ell^{4\ell+2})S \| C_e^{(2)} \| (n\ell^{4\ell+1}n'\ell')D \rangle \\ &= -(-1)^L \sqrt{\frac{2L+1}{5}} \langle \ell \| C_e^{(2)} \| \ell' \rangle \langle (n\ell^{4\ell+2})S \| U_{\ell\ell'}^{(2)} \| (n\ell^{4\ell+1}n'\ell')D \rangle \end{aligned} \quad (17-16)$$

where

$$\langle n\ell \| u_{\ell\ell'} \| n'\ell' \rangle = 1 \quad (17-17)$$

leading to

$$\langle (n\ell^{4\ell+2})S \| U_{\ell\ell'}^{(2)} \| (n\ell^{4\ell+1}n'\ell')D \rangle = \frac{1}{\sqrt{(2\ell+1)}} \quad (17-18)$$

and hence (17-16) becomes

$$= -(-1)^L \sqrt{\frac{2L+1}{5(2\ell+1)}} \langle \ell \| C^{(2)} \| \ell' \rangle \quad (17-19)$$

JLS consider the case of a $5p \rightarrow 6p$ excitation for the closed shell $5p^6$ and putting $\ell = 1$ in (17-19) and then returning, with (17-15), to (17-14) we obtain

$$A = \frac{3}{70}(2L+1) \quad (17-19)$$

To compute the total contribution from each value L we should replace A by its sum over L to get

$$A = \frac{3}{70}[3 + 5 + 7 + 9 + 11] = \frac{3}{2} \quad (17-20)$$

in agreement with JLS. Thus for a $5p \rightarrow 6p$ excitation we obtain the ratio R as

$$R = \frac{3}{2} \frac{\langle 5p|r^2|6p \rangle \langle 6p|r^{-3}|5p \rangle \times \Delta_2}{\langle 4f|r^2|4f \rangle \langle 4f|r^{-3}|4f \rangle \times E(T)} \quad (17-21)$$

where we assume that the energy spread of the excited states with respect to L is small compared to $E(T)$. JLS compute the relevant quantities in (17-21) and find a negative value for $\langle 5p|r^2|6p \rangle$ leading to a negative value for R . One could, of course, extend the calculation of R to include other single-particle excitations and use more sophisticated methods to calculate the radial integrals than were available at the time of the JLS estimate.

Lecture 18: Hyperfine Induced Transitions

His advisor, Harold Davenport, was an eminent number theorist. "He gave me a very difficult problem - proving a conjecture that said every integer can be written as the sum of thirty seven numbers, each raised to the fifth power. When I told him that I had solved it, he didn't believe me." But the proof was correct. Charles Seife, Interview with John Horton Conway⁸⁸

18. Introduction

In this lecture I discuss the subject of hyperfine induced transitions. This might seem out of place in a series of lectures largely concerned with hyperfine interactions in lanthanides in crystalline environments. I had suggested¹⁶ in 1962 that under certain circumstances highly forbidden transitions might become allowed in a crystalline environment by a nuclear magnetic moment mixing nearby crystal field levels, particularly in the case of holmium salts. Baker and Bleaney⁸⁹ had reported an apparent violation of selection rules in their paramagnetic resonance studies and suggested a mechanism based on the Jahn-Teller effect. It was only in the late 1980's that high resolution optical studies of hyperfine structure by Popova and her associates⁴⁹ revealed that indeed the interaction of nuclear magnetic dipole and electric quadrupole moments with $4f$ -electrons lead to the observation of the "forbidden transitions". Remarkably, the possibility of hyperfine induced transitions started with the spectroscopic observation of gaseous nebulae. In this lecture we first define what is meant by *forbidden transitions* and after a brief sketch of the early history of hyperfine induced transitions we outline the calculation of such processes in atoms and ions focussing particularly upon the recently observed highly forbidden transition⁹⁰ $(2s2p) {}^3P_0^o \rightarrow (2s^2) {}^1S_0^e$ in $N IV$.

18.1. Forbidden Transitions

In atomic spectroscopy all transitions that violate the rigorous selection rules for electric dipole radiation in free atoms are termed *forbidden transitions*⁹¹

Table 18-1 Selection rules for atomic spectra⁹¹

Electric Dipole	Magnetic Dipole	Electric Quadrupole
$\Delta J = 0, \pm 1$	$\Delta J = 0, \pm 1$	$\Delta J = 0, \pm 1, \pm 2$
$0 \not\leftrightarrow 0$	$0 \not\leftrightarrow 0$	$0 \not\leftrightarrow 0, 1$ or $\frac{1}{2} \not\leftrightarrow \frac{1}{2}$
$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1, \pm 2$
parity change	no parity change	no parity change
$\Delta \ell = \pm 1$	$\Delta \ell = 0$	$\Delta \ell = 0, \pm 2$
	$\Delta n = 0$	
$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
$\Delta L = 0, \pm 1$	$\Delta L = 0$	$\Delta L = 0, \pm 1, \pm 2$
$0 \not\leftrightarrow 0$	$0 \not\leftrightarrow 0$	$0 \not\leftrightarrow 0, 1$

The earliest observation of electric quadrupole transitions were in the ${}^2D \langle - \rangle {}^2S$ transitions of potassium by Datta⁹² in 1922 followed by Lord Rayleigh's observations on *Hg* spectra⁹³ in 1927. Babcock⁹⁴ observed in Aurora Borealis a green line at 5577.3Å which was later attributed to the forbidden *O I* line resulting from the transition $(2p^4) {}^1S_0^e \rightarrow (2p^4) {}^1D_2^e$. This line I found was readily observed in Aurora Australis using a pocket spectroscope. Bowen⁹⁵ found in 1928 that many of the strong spectral lines found in gaseous nebulae were attributable to forbidden transitions in *O II*, *O III* and *N II*. In a sense gaseous nebulae form an extraterrestrial atomic spectroscopy laboratory because they constitute physical conditions appropriate to the observation of strongly forbidden transitions that would be impossible to realise on earth. The very low densities but very large volume of gaseous nebulae reduce the possibilities of collisional de-excitation. The calculation of the transition probabilities of magnetic dipole and electric quadrupole transitions has been reviewed by Garstang⁹¹ who was largely responsible for introducing the Racah methods to the subject (See references therein).

18.2. Note on the early history of hyperfine induced transitions

In 1930 Huff and Houston⁹⁶ appended to their paper the following:-

Note add August 15: Dr. Bowen has called our attention to the fact that the line $\lambda 2270$ in *Hg* is probably due to the coupling of the nuclear spin with the electronic angular momentum. An estimate based on the relative separation of the multiplets and the hyperfine structure gives the right order of magnitude for the intensity. The statements made above with respect to *J* really refer strictly to the total angular momentum.

That note appears to be the first time that the possibility of hyperfine induced transitions was considered. Much of the early history is covered in an important article by Garstang⁹⁷ who also outlines details of the calculation of line intensities for hyperfine induced transitions. Here I propose to illustrate some of the methodology in the particular case of the highly forbidden transition $(2s2p) {}^3P_0^o \rightarrow (2s^2) {}^1S_0^e$ in *N IV* alluded to previously.

18.3. Low Lying Energy Levels of *N IV*

The lowest energy levels of triply ionised nitrogen are associated with the $(2s^2)$ and $(2s2p)$ electron configurations which are of opposite parity. Their energy levels are given in cm^{-1} in Table 18-2. The transition $(2s2p) {}^3P_0^o \rightarrow (2s^2) {}^1S_0^e$ occurs at 1487Å and is thus expected to occur in the vacuum ultraviolet and to be extraordinarily weak. It violates the $\Delta J = 0 \ 0 \not\leftrightarrow 0$ selection rule as well as the spin selection rule $\Delta S = 0$. To overcome the spin selection rule one might consider the effect of spin-orbit mixing but there is only one $J = 0$ state in $(2s2p)$ while to overcome the *J* selection rule it would require an interaction that couples different *J* values. This would suggest that a combination of nuclear magnetic hyperfine interactions and spin-orbit interaction

might be required. To that end we shall first consider the calculation of the energy levels of the $(2s2p)$ and $(2s^2)$ electron configurations in $N IV$.

Table 18-2 The $2s^2$ and $2s2p$ energy levels of $N IV$

Configuration	Term	J	Level
$2s^2$	$^1S^e$	0	0.0
$2s2p$	$^3P^o$	0	67209.2
		1	67272.3
		2	67416.3
$2s2p$	$^1P^o$	1	130693.9

18.4. The Electron Configurations $(2s2p)$ and $(2s^2)$ in $N IV$ Ions

The Coulomb matrix elements for the two terms, 3P and 1P of the $(2s2p)$ configuration may be calculated by standard tensor operator methods to give

$$E(^3P) = F_0(2s, 2p) - G_1(2s, 2p) \quad (18-1a)$$

$$E(^1P) = F_0(2s, 2p) + G_1(2s, 2p) \quad (18-1b)$$

The spin-orbit interaction matrices may likewise be computed in terms of the spin-orbit coupling constant, ζ_{2p} , to give

$$\begin{array}{ccc} J = 2 & |^3P_2\rangle & J = 1 & |^3P_1\rangle & |^1P_1\rangle & J = 0 & |^3P_0\rangle \\ \langle ^3P_2| & \left(\begin{array}{c} \frac{1}{2} \end{array} \right) & \langle ^3P_1| & \left(\begin{array}{cc} -\frac{3}{2} & \frac{\sqrt{2}}{2} \\ \frac{\sqrt{2}}{2} & 0 \end{array} \right) & & \langle ^3P_0| & \left(\begin{array}{c} -1 \end{array} \right) \end{array} \quad (18-2)$$

We can estimate the size of the spin-orbit coupling constant by noting (18-1a) and (18-2) to give, in cm^{-1} ,

$$E(^3P_2) - E(^3P_0) = \frac{3}{2}\zeta_{2p} = 67416.3 - 67209.2 = 207.1 \quad (18-3)$$

and hence

$$\zeta_{2p} = 138.1cm^{-1} \quad (18-4)$$

We can now estimate the Coulomb integral, $G_1(2s, 2p)$, by noting that

$$E(^1P_1) - E(^3P_1) \sim 2G_1(2s, 2p) + \frac{1}{2}\zeta_{2p} = 63421.6 \quad (18-4)$$

and hence

$$G_1(2s, 2p) = 36726cm^{-1} \quad (18-5)$$

Returning to (18-1a) we are led to the estimated value of

$$F_0(2s, 2p) = 104073cm^{-1} \quad (18-6)$$

We are now in a position to estimate the spin-orbit mixing between the 3P_1 and 1P_1 states of the $(2s2p)$. We have the energy matrix for the two $J = 1$ states as

$$\begin{array}{c} J = 1 \\ \langle ^3P_1 | \\ \langle ^1P_1 | \end{array} \begin{array}{cc} | ^3P_1 \rangle & | ^1P_1 \rangle \\ \left(\begin{array}{cc} F_0(2s, 2p) - G_1(2s, 2p) - \frac{1}{2}\zeta_{2p} & \frac{\sqrt{2}}{2}\zeta_{2p} \\ \frac{\sqrt{2}}{2}\zeta_{2p} & F_0(2s, 2p) + G_1(2s, 2p) \end{array} \right) \end{array} \quad (18-7)$$

Putting in the numerical values for the integrals and diagonalizing the matrix to obtain the eigenvalues and eigenvectors leads to

$$E(^3P_1) = 67278cm^{-1} \quad (18-8a)$$

$$|E(^3P_1)\rangle = .9999988|^3P_1\rangle - .00154214|^1P_1\rangle \quad (18-8b)$$

$$E(^1P_1) = 130600cm^{-1} \quad (18-9a)$$

$$|E(^1P_1)\rangle = .00154214|^3P_1\rangle + .9999988|^1P_1\rangle \quad (18-9b)$$

There is thus a very small amount of spin-mixing of the two $J = 1$ states that could lead to a very small breakdown of the spin selection rule. However, that, by itself, cannot explain the observed transition unless there is also some J -mixing - for that we need to consider the role of the nucleus. Note that the small spin admixture in (18-8b) is to a very good approximation

$$- \left(\frac{\sqrt{2}}{2}\zeta_{2p} \right) / (2G_1(2s, 2p) + \frac{1}{2}\zeta_{2p}) \quad (18-10)$$

18.5. Nuclear Properties of the Stable Isotopes of Nitrogen

We can obtain information on the nuclear properties of the stable isotopes of nitrogen from the WEB⁹⁸ where we find the following data

Table 18-3 Nuclear properties of the stable isotopes of nitrogen

Isotope	Atomic mass	Abundance	Nuclear spin(I)	Magnetic moment
^{14}N	14.003074002	99.632	1	0.4037607
^{15}N	15.00010897	0.368	$\frac{1}{2}$	-0.2831892

We note that indeed both isotopes of nitrogen have nuclear magnetic moments. It is significant that while the 1487\AA spectral line occurs in triply ionized nitrogen there is no analogous spectral line seen in ^{12}C which has no nuclear spin and hence no nuclear magnetic moment.

18.6. Nuclear Magnetic Dipole Hyperfine Matrix Elements in (2s2p)

The calculation of the matrix elements of the magnetic dipole hyperfine matrix elements among the various states of the (2s2p) electron configuration is a fairly straightforward, though somewhat tedious, tensor operator task. One is essentially calculating the matrix elements of the scalar product ($\mathbf{N}^{(1)} \cdot \mathbf{I}^{(1)}$) where

$$N^{(1)} = \sum_i \left[\ell_i^{(1)} - \sqrt{10}(s^{(1)}C^{(2)})_i^{(1)} + (8\pi/3)\delta(r_i)s_i^{(1)} \right] \quad (18-11)$$

where the last term in (18-11) is the Fermi contact term that arises when s - orbitals are involved. Basically the matrix elements will involve the hyperfine constants a_p and a_s . Using the results of Chapter Two it is left as exercise to derive the relevant formulae for the matrix elements. Below we give the results for $I = \frac{1}{2}$ and $I = 1$ which covers the nuclear spins of the stable isotopes of nitrogen. The results are given for LS-basis states.

For $I = \frac{1}{2}$ we obtain

$$F = \frac{5}{2} \quad |^3P_2\rangle \\ \langle ^3P_2 | \left(\frac{1}{20}(8a_p + 5a_s) \right) \quad (18-12a)$$

$$F = \frac{3}{2} \quad |^3P_2\rangle \quad |^3P_1\rangle \quad |^1P_1\rangle \\ \langle ^3P_2 | \left(\begin{array}{ccc} -\frac{3}{40}(8a_p + 5a_s) & \frac{\sqrt{5}}{40}(6a_p - 5a_s) & \frac{\sqrt{10}}{40}(a_p - 5a_s) \\ \frac{\sqrt{5}}{40}(6a_p - 5a_s) & \frac{1}{8}(4a_p + a_s) & -\frac{\sqrt{2}}{8}(a_p + a_s) \\ \frac{\sqrt{10}}{40}(a_p - 5a_s) & -\frac{\sqrt{2}}{8}(a_p + a_s) & \frac{1}{2}a_p \end{array} \right) \quad (18-12b)$$

$$F = \frac{1}{2} \quad |^3P_1\rangle \quad |^3P_0\rangle \quad |^1P_1\rangle \\ \langle ^3P_1 | \left(\begin{array}{ccc} -\frac{1}{4}(4a_p + a_s) & \frac{\sqrt{2}}{4}(3a_p - a_s) & \frac{\sqrt{2}}{4}(3a_p + a_s) \\ \frac{\sqrt{2}}{4}(3a_p - a_s) & 0 & -\frac{1}{4}(2a_p - a_s) \\ \frac{\sqrt{2}}{4}(3a_p - a_s) & -\frac{1}{4}(2a_p - a_s) & -a_p \end{array} \right) \quad (18-12c)$$

and for $I = 1$ we obtain

$$F = 3 \quad |^3P_2\rangle \\ \langle ^3P_2 | \left(\frac{1}{10}(8a_p + 5a_s) \right) \quad (18-13a)$$

$$F = 2 \quad |^3P_2\rangle \quad |^3P_1\rangle \quad |^1P_1\rangle \\ \langle ^3P_2 | \left(\begin{array}{ccc} -\frac{1}{20}(8a_p + 5a_s) & \frac{\sqrt{3}}{20}(6a_p - 5a_s) & \frac{\sqrt{6}}{20}(a_p - 5a_s) \\ \frac{\sqrt{3}}{20}(6a_p - 5a_s) & \frac{1}{4}(4a_p + a_s) & -\frac{\sqrt{2}}{4}(a_p + a_s) \\ \frac{\sqrt{6}}{20}(a_p - 5a_s) & -\frac{\sqrt{2}}{4}(a_p + a_s) & a_p \end{array} \right) \quad (18-13b)$$

$$\begin{array}{l}
F = 1 \quad |^3P_2\rangle \quad |^3P_1\rangle \quad |^1P_1\rangle \quad |^3P_0\rangle \\
\langle ^3P_2| \left(\begin{array}{cccc}
-\frac{3}{20}(8a_p + 5a_s) & \frac{\sqrt{15}}{60}(6a_p - 5a_s) & \frac{\sqrt{30}}{60}(a_p - 5a_s) & 0 \\
\frac{\sqrt{15}}{60}(6a_p - 5a_s) & -\frac{1}{4}(4a_p + a_s) & \frac{\sqrt{2}}{4}(a_p + a_s) & \frac{\sqrt{3}}{3}(3a_p - a_s) \\
\frac{\sqrt{30}}{60}(a_p - 5a_s) & \frac{\sqrt{2}}{4}(a_p + a_s) & -a_p & -\frac{\sqrt{6}}{6}(2a_p - a_s) \\
0 & \frac{\sqrt{3}}{3}(3a_p - a_s) & -\frac{\sqrt{6}}{6}(2a_p - a_s) & 0
\end{array} \right) \\
\langle ^3P_1| \\
\langle ^1P_1| \\
\langle ^3P_0|
\end{array} \quad (18-13c)$$

$$\begin{array}{l}
F = 0 \quad |^3P_1\rangle \quad |^1P_1\rangle \\
\langle ^3P_1| \left(\begin{array}{cc}
-\frac{1}{2}(4a_p + a_s) & \frac{\sqrt{2}}{2}(a_p + a_s) \\
\frac{\sqrt{2}}{2}(a_p + a_s) & -2a_p
\end{array} \right) \\
\langle ^1P_1|
\end{array} \quad (18-13d)$$

In the above results we omit in the bra and ket vectors the quantum numbers I, F which may be readily inferred.

It is not difficult to derive the corresponding results for a jj -coupling basis for $I = 1$ which we give below. Note again the quantum numbers I, F have been omitted as well as the principal quantum numbers, those of the fixed $2s\frac{1}{2}$ state.

$$\begin{array}{l}
F = 3 \quad |p_{\frac{3}{2}}, 2\rangle \\
\langle p_{\frac{3}{2}}, 2| \left(\frac{1}{10}(8a_p + 5a_s) \right)
\end{array} \quad (18-14a)$$

$$\begin{array}{l}
F = 2 \quad |p_{\frac{3}{2}}, 2\rangle \quad |p_{\frac{3}{2}}, 1\rangle \quad |p_{\frac{1}{2}}, 1\rangle \\
\langle p_{\frac{3}{2}}, 2| \left(\begin{array}{ccc}
-\frac{1}{20}(8a_p + 5a_s) & \frac{1}{20}(8a_p - 15a_s) & \frac{\sqrt{2}}{4}a_p \\
\frac{1}{20}(8a_p - 15a_s) & \frac{1}{12}(8a_p - 3a_s) & -\frac{\sqrt{2}}{12}a_p \\
\frac{\sqrt{2}}{4}a_p & -\frac{\sqrt{2}}{12}a_p & \frac{1}{6}(8a_p + 3a_s)
\end{array} \right) \\
\langle p_{\frac{3}{2}}, 1| \\
\langle p_{\frac{1}{2}}, 1|
\end{array} \quad (18-14b)$$

$$\begin{array}{l}
F = 1 \quad |p_{\frac{3}{2}}, 2\rangle \quad |p_{\frac{3}{2}}, 1\rangle \quad |p_{\frac{1}{2}}, 1\rangle \quad |p_{\frac{1}{2}}, 0\rangle \\
\langle p_{\frac{3}{2}}, 2| \left(\begin{array}{cccc}
-\frac{3}{20}(8a_p + 5a_s) & \frac{\sqrt{5}}{60}(8a_p - 15a_s) & \frac{\sqrt{10}}{12}a_p & 0 \\
\frac{\sqrt{5}}{60}(8a_p - 15a_s) & -\frac{1}{12}(8a_p - 3a_s) & \frac{\sqrt{2}}{12}a_p & \frac{1}{3}a_p \\
\frac{\sqrt{10}}{12}a_p & \frac{\sqrt{2}}{12}a_p & -\frac{1}{6}(8a_p + 3a_s) & \frac{\sqrt{2}}{6}(8a_p - 3a_s) \\
0 & \frac{1}{3}a_p & \frac{\sqrt{2}}{6}(8a_p - 3a_s) & 0
\end{array} \right) \\
\langle p_{\frac{3}{2}}, 1| \\
\langle p_{\frac{1}{2}}, 1| \\
\langle p_{\frac{1}{2}}, 0|
\end{array} \quad (18-14c)$$

$$\begin{array}{l}
F = 0 \quad \begin{array}{cc} |p_{\frac{3}{2}}, 1\rangle & |p_{\frac{1}{2}}, 1\rangle \\
\langle p_{\frac{3}{2}}, 1| \left(\begin{array}{cc} -\frac{1}{12}(8a_p - 3a_s) & \frac{\sqrt{2}}{12}a_p \\
\frac{\sqrt{2}}{12}a_p & \frac{1}{6}(8a_p + 3a_s) \end{array} \right) & \end{array}
\end{array} \quad (18-14d)$$

18.7. The MAPLE Procedures used to Calculate the Hyperfine Matrix Elements

The preceding hyperfine matrix elements were calculated using MAPLE. The procedure “njsym” is a collection of MAPLE routines for calculating the various $3njs$ symbols. Note that the nuclear spin is designated by the lower case “i” since MAPLE reserves “I” for $\sqrt{-1}$. To run the programme you will need to have in your MAPLE directory the two files njsym and hsp.map. Once MAPLE is running you need to issue the command <read”hsp.map”>. To compute the matrix element $\langle (2s2p)^3P1, I = 1, F = 1 | H_{hfs} | (2s2p)^3P0, I = 1, F = 1 \rangle$ you issue the command <hsp(1,1,1,0,1,1)> and MAPLE should respond with

$$3^{\frac{1}{2}}a_p - 1/3 \ 3^{\frac{1}{2}}a_s$$

We list below the actual MAPLE procedures.

```

# These procedures compute the matrix elements of the magnetic and contact#
# hyperfine interactions in the sp electron configuration in the LS basis #
# (hsp) or in the jj basis (hjj)#
read”njsym”;
hss:=proc(S1,J1,S2,J2,i,F)
local result,X,Y,Z,as;
X:=(-1)^(S2)*sqrt(6*(2*S1+1)*(2*S2+1))*sixj(S1,1,S2,1/2,1/2,1/2)/2;
Y:=(-1)^(S1+J2)*sqrt((2*J1+1)*(2*J2+1))*sixj(J1,1,J2,S2,1,S1)*X;
Z:=(-1)^(J2+i+F)*sqrt(i*(i+1)*(2*i+1))*sixj(J2,i,F,i,J1,1)*Y*as;
result:=combine(simplify(Z));
end:

hsp1:=proc(S1,J1,S2,J2,i,F)
local result,X,Y,Z,ap;
X:=(-1)^(J2+i+F)*sixj(J2,i,F,i,J1,1)*sqrt(i*(i+1)*(2*i+1));
Y:=0;
if (S1=S2) then
Y:=(-1)^(S1+J1)*sqrt(6*(2*J1+1)*(2*J2+1))*sixj(J1,1,J2,1,S1,1);
end if;
Z:=(-1)^(S1+1)*3*sqrt(5*(2*J1+1)*(2*J2+1)*(2*S1+1)*(2*S2+1))*ck(1,1,2)
*sixj(S1,1,S2,1/2,1/2,1/2)*ninej(S1,S2,1,1,1,2,J1,J2,1);
result:=combine(simplify(X*(Y+Z)))*ap;
end:

```

```

hjp:=proc(j1,J1,j2,J2,i,F)
local result,X,Y,Z,ap;
X:=sqrt(6*(2*j1+1)*(2*j2+1))*((-1)^(j1+(1/2))*sixj(j1,1,j2,1,1/2,1)
+3*ninej(1/2,1/2,1,1,1,2,j1,j2,1));
Y:=(-1)^(j2+J1+(3/2))*sqrt((2*J1+1)*(2*J2+1))*sixj(J1,1,J2,j2,1/2,j1)*X;
Z:=(-1)^(J2+i+F)*sqrt(i*(i+1)*(2*i+1))*sixj(J2,i,F,i,J1,1)*Y*ap;
result:=combine(simplify(Z));
end:

hjs:=proc(j1,J1,j2,J2,i,F)
local result,X,Y,Z,as;
if (j1<=j2) then result:=0;
else
result:=combine(simplify((-1)^(i+F+j1+(3/2))*sqrt(i*(i+1)*(2*i+1)*(2*J1+1)
*(2*J2+1)*6)*sixj(J2,i,F,i,J1,1)*sixj(J1,1,J2,1/2,j1,1/2)/2)*as);
end if;
end:

hsp:=proc(S1,J1,S2,J2,i,F)
local result;
result:=hsp1(S1,J1,S2,J2,i,F)+hss(S1,J1,S2,J2,i,F);
end:

hjj:=proc(j1,J1,j2,J2,i,F)
local result;
result:=hjp(j1,J1,j2,J2,i,F)+hjs(j1,J1,j2,J2,i,F);
end:

```

By careful inspection of the above procedures you should be able to reconstruct the tensor operator formulae used in the calculations.

Having established the forgoing results the next step would be to explore the mechanisms contributing to the observation of the highly forbidden transition observed in triply ionised nitrogen.

Lecture 19 : Magnetic Dipole Transitions in Crystals

Six hours a-day the young students were employed in this labour; and the professor shewed me several volumes in large folio already collected, of broken sentences, which he intended to piece together; and out of those rich materials to give the world a compleat body of all the arts and sciences;Jonathan Swift Gulliver's Travels (1726)

19. Introduction

Here I return to the question of the role of magnetic dipole transitions in crystals. Much attention is given, and rightly so, to forced electric dipole transitions in crystals so much so that the possibility of magnetic dipole transitions is often overlooked. In the following we outline the principal features of magnetic dipole transitions and those characteristics that distinguish them from electric dipole transitions.

19.1. Magnetic Dipole Transitions in Atoms and Ions

We already noted in Table 18-1 the selection rules for magnetic dipole transitions in free atoms or ions. They involve transitions between states of the *same* parity within a given electron configuration, and in the absence of spin-orbit coupling, with the same *LS* multiplet. The basic theory was worked out by Pasternack⁹⁹ and Shortley¹⁰⁰. The magnetic dipole moment is given by

$$\mu = -\frac{e}{2mc}(\mathbf{L} + g_s\mathbf{S}) \quad (19-1)$$

We note that the selection rules are essentially the same as in the Zeeman effect.

19.2. Polarisation of Light and Transitions

Polarisation of light gives an important experimental tool for distinguishing between electric dipole and magnetic dipole transitions. In electric dipole transitions it is the electric vector of the light that is active whereas in magnetic dipole transitions the magnetic vector is active. Recall that in light the directions of the electric vector, magnetic vector and direction of propagation are mutually perpendicular to one another. Consider a uniaxial crystal; the light path *parallel* to the crystallographic axis will be termed the "*axial*" spectrum while for a light path *perpendicular* to the axis will be termed the "*transverse*" spectrum. The *transverse* spectrum is split into π or σ spectra depending on whether the axis of polarisation is such that the direction of the electric vector is parallel to or perpendicular to the crystal axis. If a line in the axial spectrum and σ spectra coincide the transition is electric dipole while if the axial and π spectra coincide the transition is either magnetic dipole or electric quadrupole. Electric quadrupole transitions are usually a couple of orders of magnitude weaker than magnetic dipole transitions and will henceforth be ignored. Practically, in the absorption of light in a uniaxial crystal the incident light may be polarised so that

the axial or transverse spectra are observed and conversely in fluorescence the axial and transverse spectra are determined by examining the polarisation of the emitted radiation.

19.3. Selection Rules for Transitions in Crystals

In many cases a given transition between a pair of crystal field levels of an ion located at a site whose symmetry is characterised by a particular crystallographic point group G may be determined to be of electric dipole or magnetic dipole origin by determining the polarisation state of the photons emitted or absorbed by the transition. In the case of electric dipole transitions the transformation of the components (x, y, z) with respect to the operations of the group G lead directly to the symmetry selection rules whereas for magnetic dipole transitions one needs the transformation of the rotation components (R_x, R_y, R_z) or equivalently those of (L_x, L_y, L_z) . If components (x, y, z) transform according to different representations of G than those of (L_x, L_y, L_z) then the electric dipole transitions may be unequivocally distinguished from those of magnetic dipole transitions by experimentally determining the polarisation of the transitions.

19.4. The Example of D_{3h} Symmetry

The point symmetry group D_{3h} is associated with a wide range of uniaxial crystals such as is found in the lanthanide trichlorides and ethylsulphates. The group character table is given below⁵⁶ with the spin (or projective) representations being separated from the ordinary irreducible representations by an empty line. The ordinary irreducible representations ($\Gamma_i, i = 1, \dots, 6$) are associated with an *even* number of electrons and the spin irreducible representations ($\Gamma_i, i = 7, \dots, 9$) with an *odd* number of electrons.

Γ_i	E	\bar{E}	σ_h	$\bar{\sigma}_h$	$2C_3$	$2\bar{C}_3$	$2S_3$	$2\bar{S}_3$	$3C'_2$	$3\bar{C}'_2$	$3\sigma_v$	$3\bar{\sigma}_v$
Γ_1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	1	1	1	-1	-1	-1	-1
Γ_3	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1
Γ_4	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1
Γ_5	2	2	-2	-2	-1	-1	1	1	0	0	0	0
Γ_6	2	2	2	2	-1	-1	-1	-1	0	0	0	0
Γ_7	2	-2	0	0	1	-1	$\sqrt{3}$	$-\sqrt{3}$	0	0	0	0
Γ_8	2	-2	0	0	1	-1	$-\sqrt{3}$	$\sqrt{3}$	0	0	0	0
Γ_9	2	-2	0	0	-2	-2	0	0	0	0	0	0

Table 19-1 The characters of D_{3h}

For electric dipole transitions z transforms as the Γ_4 representation with (x, y) spanning the Γ_6 representation. For magnetic dipole transitions L_z transforms as the Γ_2 representation with (L_x, L_y) spanning the Γ_5 representation. Since the irreducible

representations of D_{3h} are all real we may succinctly write the magnetic dipole (md) and electric dipole (ed) selection rules as

$$\Gamma_i \times \Gamma_j \supset \begin{cases} \Gamma_2 & \sigma \text{ md} \\ \Gamma_5 & \pi \text{ md} \\ \Gamma_4 & \pi \text{ ed} \\ \Gamma_6 & \sigma \text{ ed} \end{cases} \quad (19-1)$$

The Kronecker products $\Gamma_i \times \Gamma_j$ for the ordinary irreducible representations may be readily evaluated⁵⁶ to give

$$\begin{array}{c} \Gamma_1 \\ \Gamma_2 \\ \Gamma_3 \\ \Gamma_4 \\ \Gamma_5 \\ \Gamma_6 \end{array} \begin{array}{c} \Gamma_1 \quad \Gamma_2 \quad \Gamma_3 \quad \Gamma_4 \quad \Gamma_5 \quad \Gamma_6 \\ \left(\begin{array}{cccccc} \Gamma_1 & \Gamma_2 & \Gamma_3 & \Gamma_4 & \Gamma_5 & \Gamma_6 \\ \Gamma_2 & \Gamma_1 & \Gamma_4 & \Gamma_3 & \Gamma_5 & \Gamma_6 \\ \Gamma_3 & \Gamma_4 & \Gamma_1 & \Gamma_3 & \Gamma_6 & \Gamma_5 \\ \Gamma_4 & \Gamma_3 & \Gamma_2 & \Gamma_1 & \Gamma_5 & \Gamma_6 \\ \Gamma_5 & \Gamma_5 & \Gamma_6 & \Gamma_6 & \Gamma_1 + \Gamma_2 + \Gamma_6 & \Gamma_3 + \Gamma_4 + \Gamma_5 \\ \Gamma_6 & \Gamma_6 & \Gamma_5 & \Gamma_5 & \Gamma_3 + \Gamma_4 + \Gamma_5 & \Gamma_1 + \Gamma_2 + \Gamma_6 \end{array} \right) \end{array} \quad (19-2)$$

and for the spin irreducible representations

$$\begin{array}{c} \Gamma_7 \\ \Gamma_8 \\ \Gamma_9 \end{array} \begin{array}{c} \Gamma_7 \quad \Gamma_8 \quad \Gamma_9 \\ \left(\begin{array}{ccc} \Gamma_1 + \Gamma_2 + \Gamma_5 & \Gamma_3 + \Gamma_4 + \Gamma_6 & \Gamma_5 + \Gamma_6 \\ \Gamma_3 + \Gamma_4 + \Gamma_6 & \Gamma_1 + \Gamma_2 + \Gamma_5 & \Gamma_5 + \Gamma_6 \\ \Gamma_5 + \Gamma_6 & \Gamma_5 + \Gamma_6 & \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 \end{array} \right) \end{array} \quad (19-3)$$

Noting (19-1) and (19-2) it is a simple matter to deduce that for an *even* number of electrons the D_{3h} symmetry electric dipole selection rules are

$$\begin{array}{c} \Gamma_1 \\ \Gamma_2 \\ \Gamma_3 \\ \Gamma_4 \\ \Gamma_5 \\ \Gamma_6 \end{array} \begin{array}{c} \Gamma_1 \quad \Gamma_2 \quad \Gamma_3 \quad \Gamma_4 \quad \Gamma_5 \quad \Gamma_6 \\ \left(\begin{array}{cccccc} - & - & - & \pi & - & \sigma \\ - & - & \pi & - & - & \sigma \\ - & \pi & - & - & \sigma & - \\ \pi & - & - & - & \sigma & - \\ - & - & \sigma & \sigma & \sigma & \pi \\ \sigma & \sigma & - & - & \pi & \sigma \end{array} \right) \end{array} \quad (19-4)$$

and for an *odd* number of electrons

$$\begin{array}{c} \Gamma_7 \\ \Gamma_8 \\ \Gamma_9 \end{array} \begin{array}{c} \Gamma_7 \quad \Gamma_8 \quad \Gamma_9 \\ \left(\begin{array}{ccc} - & \sigma\pi & \sigma \\ \sigma\pi & - & \sigma \\ - & \sigma & \pi \end{array} \right) \end{array} \quad (19-5)$$

Note the appearance of $\sigma\pi$ transitions - these effectively correspond to elliptical polarisation.

In an exactly similar manner we can deduce the corresponding selection rules for magnetic dipole transitions for an *even* number of electrons in D_{3h} symmetry as

$$\begin{array}{c} \Gamma_1 \quad \Gamma_2 \quad \Gamma_3 \quad \Gamma_4 \quad \Gamma_5 \quad \Gamma_6 \\ \Gamma_1 \left(\begin{array}{cccccc} - & \sigma & - & - & \pi & - \\ \sigma & - & - & - & \pi & - \\ - & - & - & \sigma & - & \pi \\ - & - & \sigma & - & \pi & - \\ \pi & \pi & - & \pi & \sigma & - \\ - & - & \pi & - & - & \sigma \end{array} \right) \end{array} \quad (19-6)$$

and for an *odd* number of electrons

$$\begin{array}{c} \Gamma_7 \quad \Gamma_8 \quad \Gamma_9 \\ \Gamma_7 \left(\begin{array}{ccc} \sigma & - & \pi \\ - & \sigma & \pi \\ \pi & \pi & \sigma \end{array} \right) \end{array} \quad (19-7)$$

Comparison of the selection rules for electric dipole transitions with those for magnetic dipole transitions show significant differences and allow us to often distinction, experimentally, between the two types of transitions.

19.5. Exercises

$$\begin{array}{c} E \quad \bar{E} \quad 2C_3 \quad 2\bar{C}_3 \quad 3\sigma_v \quad 3\bar{\sigma} \\ \Gamma_1 \left(\begin{array}{cccccc} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & -1 & -1 \\ 2 & 2 & -1 & -1 & 0 & 0 \\ 2 & -2 & 1 & -1 & 0 & 0 \\ 1 & -1 & -1 & 1 & i & -i \\ 1 & -1 & -1 & 1 & -i & i \end{array} \right) \end{array} \quad (19-8)$$

Table 19.2 The characters table of the point group C_{3v}

Ex 19.1 Use the character table for the point group C_{3v} to construct two tables of Kronecker products, one for the ordinary irreducible representations and one for the spin irreducible representations of C_{3v} .

Ex 19.2 Given that z transforms as Γ_1 , and (x, y) as Γ_3 deduce the selection rules for electric dipole transitions for even and odd numbers of electrons for C_{3v} symmetry.

Ex 19.3 Given that L_z transforms as Γ_2 and (L_x, L_y) as Γ_3 deduce the selection rules for magnetic dipole transitions for even and odd numbers of electrons for C_{3v} symmetry.

19.6. Oscillator Strengths of Magnetic Dipole Transitions

The oscillator strength, f_σ , of a magnetic dipole transition may be written as^{101,102}

$$\begin{aligned} f_\sigma &= \frac{8\pi^2 mc}{3he^2} \sigma \left| \frac{-e}{2mc} \langle \alpha SLJM_J | (\mathbf{L} + g_s \mathbf{S})_\rho^{(1)} | \alpha SLJ'M'_J \rangle \right|^2 \eta \\ &= 4.028 \times 10^{-11} \sigma \left| \langle \alpha SLJM_J | (\mathbf{L} + g_s \mathbf{S})_\rho^{(1)} | \alpha SLJ'M'_J \rangle \right|^2 \eta \end{aligned} \quad (19-9)$$

where σ is in units of cm^{-1} and η is the refractive index of the medium. Using the Wigner-Eckart theorem, the matrix elements of $(\mathbf{L} + g_s \mathbf{S})_\rho^{(1)}$ are given by

$$\begin{aligned} \langle \alpha SLJM_J | (\mathbf{L} + g_s \mathbf{S})_\rho^{(1)} | \alpha SLJ'M'_J \rangle &= (-1)^{J-M_J} \begin{pmatrix} J & 1 & J' \\ -M_J & \rho & M'_J \end{pmatrix} \\ &\times \langle \alpha SLJ || (L + g_s S)^{(1)} || \alpha SLJ' \rangle \end{aligned} \quad (19-10)$$

where $\rho = 0$ gives the z component of the magnetic vector and will correspond to the absorption or emission of σ -polarised light and $\rho = \pm 1$ gives the $x \pm iy$ components corresponding to π -polarised light. The calculation of the matrix elements in (19-10) is exactly similar to that for the Zeeman effect discussed in S2.

19.7. The Oscillator Strengths for the ${}^7F_{00} \leftrightarrow {}^7F_{1M}$ Transitions

Magnetic dipole transitions are well-known in trivalent Europium and divalent Samarium. In both cases the ground multiplet is $4f^6 {}^7F$. In the free ion the spin-orbit interaction results in seven levels 7F_J with $J = 0, 1, \dots, 6$. The groundstate has $J = 0$ and in the absence of hyperfine interactions is non-degenerate. The first excited level is 7F_1 . In a crystal with D_{3h} point symmetry the 7F_1 level splits into two sub-levels. In terms of the crystal quantum numbers introduced in S10.2 the sublevels may be labelled as $\mu = 0$ and $\mu = \pm 1$ or in terms of D_{3h} group labels as Γ_2 and Γ_5 with the latter being two-fold degenerate. The groundstate corresponds to a Γ_1 level. Absorption from the groundstate to the two sub-levels involves two distinct transitions, $\Gamma_1 \rightarrow \Gamma_2$ and $\Gamma_1 \rightarrow \Gamma_5$. Inspection of (19-4) shows that these two transitions are electric dipole forbidden whereas inspection of (19-6) shows that both transitions are magnetic dipole allowed with the $\Gamma_1 \rightarrow \Gamma_2$ transition being σ -polarised and the $\Gamma_1 \rightarrow \Gamma_5$ transition being π -polarised.

To calculate the oscillator strengths of these transitions we first note that

$$\langle {}^7F_0 || (L + g_s S)^{(1)} || {}^7F_1 \rangle = -2\sqrt{3}(g_s - 1) \quad (19-11)$$

Evaluation of the $3j$ -symbol in (19-10) then yields

$$\langle {}^7F_{00} | (L + g_s S)_0^{(1)} | {}^7F_{10} \rangle = -2(g_s - 1) \quad (19-12a)$$

$$\langle {}^7F_{00} | (L + g_s S)_{\pm 1}^{(1)} | {}^7F_{10 \mp 1} \rangle = 2(g_s - 1) \quad (19-12b)$$

The two matrix elements are, to within a sign, equal. To a good approximation we can take $g_s = 2$ and hence the squares of both matrix elements become the integer 4.

Using these values in (19-9), and remembering that the Γ_5 is two-fold degenerate we find for the two transitions the oscillator strengths as

$$f(\Gamma_1 \rightarrow \Gamma_2) = 1.6 \times 10^{-10} \sigma \eta \quad (19-13a)$$

$$f(\Gamma_1 \rightarrow \Gamma_5) = 3.2 \times 10^{-10} \sigma \eta \quad (19-13b)$$

The ratio of the two oscillator strengths is 1 : 2 and independent of σ . Thus we would expect this ratio to be the same for both Sm^{2+} and Eu^{3+} when in the same medium.

19.8. Intermediate Coupling and ${}^5D_1 \leftrightarrow {}^7F_0$ Transitions

The selection rules for magnetic dipole transitions, given in Table 18.2, are highly restrictive and at first sight seem to preclude the possibility of magnetic dipole transitions between states belonging to different multiplets, for example, ${}^5D_1 \leftrightarrow {}^7F_0$ transitions. Nevertheless polarisation studies show these transitions to be definitely of magnetic dipole origin. This possibility arises as a result of intermediate coupling via the spin-orbit interaction. Let us consider the case of Eu^{3+} in a $LaCl_3$ lattice where the Eu^{3+} is located at a site of D_{3h} symmetry. Ofelt¹⁰³ has diagonalised the complete Coulomb + Spin-orbit energy matrices for a set of parameters appropriate to this case and given the eigenfunctions for many levels. In particular he gives for the two levels being considered here the principal components of their eigenvectors as

$$|{}^7\mathcal{F}_0\rangle = 0.9680|{}^7F_0\rangle + 0.0016|{}^5D_0\rangle + 0.1659|{}^5D'_0\rangle - 0.1815|{}^5D''_0\rangle \quad (19-14a)$$

$$|{}^5\mathcal{D}_1\rangle = -0.2096|{}^7F_1\rangle - 0.2066|{}^5D_1\rangle + 0.7162|{}^5D'_1\rangle - 0.5561|{}^5D''_1\rangle \quad (19-14b)$$

For brevity let us write

$$H_{md} = (L + g_s S)^{(1)} \quad (19-15)$$

Using the eigenvectors we can write

$$\langle {}^7\mathcal{F}_0 || H_{md} || {}^5\mathcal{D}_1 \rangle = -0.2028 \langle {}^7F_0 || H_{md} || {}^7F_1 \rangle + 0.2201 \langle {}^5D_1 || H_{md} || {}^5D_1 \rangle \quad (19-16)$$

The reduced matrix elements evaluate as

$$\langle {}^7F_0 || H_{md} || {}^7F_1 \rangle = -2\sqrt{3} \quad (19-17a)$$

$$\langle {}^5D_1 || H_{md} || {}^5D_1 \rangle = -\sqrt{6} \quad (19-17b)$$

leading to the numerical value, again putting $g_s = 2$,

$$\langle {}^7\mathcal{F}_0 || H_{md} || {}^5\mathcal{D}_1 \rangle = 0.1634 \quad (19-18)$$

Use of (19-10), with evaluation of the $3j$ -symbols leads to the oscillator strengths of the two transitions as

$$f(\Gamma_1 \rightarrow \Gamma_2) = 3.58 \times 10^{-13} \sigma \eta \quad (19-19a)$$

$$f(\Gamma_1 \rightarrow \Gamma_5) = 7.17 \times 10^{-13} \sigma \eta \quad (19-19b)$$

At first sight the above oscillator strengths appear much smaller than those found in (19-13) however the factor σ is $\sim 300cm^{-1}$ in (19-13) but $\sim 19,000cm^{-1}$ in (19-19) leading to the two sets of oscillator strengths being comparable.

19.9. Oscillator Strengths for the ${}^5D_1 \leftrightarrow {}^7F_1$ Magnetic Dipole Transitions

Ofelt¹⁰³ gives the principal components of the eigenvector of the $|{}^7\mathcal{F}_1\rangle$ state as

$$|{}^7\mathcal{F}_1\rangle = 0.9742|{}^7F_1\rangle + 0.0052|{}^5D_1\rangle + 0.1472|{}^5D'_1\rangle - 0.1645|{}^5D''_1\rangle \quad (19-20)$$

Making use of the corresponding expansion for the $|{}^5\mathcal{D}_1\rangle$ state given in (19-14b) we obtain the reduced matrix element as

$$\langle{}^7\mathcal{F}_1||H_{md}||{}^5\mathcal{D}_1\rangle = -0.2042\langle{}^7F_1||H_{md}||{}^7F_1\rangle + 0.1959\langle{}^5D_1||H_{md}||{}^5D_1\rangle \quad (19-21)$$

In this case the two reduced matrix elements on the left-hand-side of (19-21) are both equal to

$$\langle{}^7F_1||H_{md}||{}^7F_1\rangle = \langle{}^5D_1||H_{md}||{}^5D_1\rangle = \frac{\sqrt{6}}{2}(g_s + 1) \quad (19-22)$$

As a result there is strong cancellation of the two terms in (19-21) and as noted by Judd¹⁰⁴ the ${}^5D_1 \leftrightarrow {}^7F_1$ are of electric dipole character rather than magnetic dipole.

19.10. J -Mixing and “Intensity Borrowing”

In the preceding sections we have seen how intermediate coupling, via the spin-orbit interaction can overcome the usual selection rules on the spin, S , and orbital, L , quantum numbers while still leaving J as a “good” quantum number. The presence of a crystal field can destroy J and M_J as “good” quantum numbers leading to J - and M -mixing. This can make possible some transitions which at first sight seem to be highly forbidden. A case in point would be the transition ${}^7F_0 \leftrightarrow {}^5D_0$. Evidence that such a transition can come from J -mixing via a crystal field comes from the observation that the groundstate of Eu^{3+} in crystals exhibits an electric quadrupole hyperfine splitting coming from the crystal field coupling via the axial crystal field term $B_0^2 C_0^{(2)}$. This results in the groundstate having a small admixture of $|{}^7F_0\rangle$ character. We can estimate the amount of mixing by calculating the matrix element

$$\begin{aligned} \langle{}^7F_0||C_0^{(2)}||{}^7F_0\rangle &= (-1)^{0-0} \begin{pmatrix} 0 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} \langle 3||C^{(2)}||3\rangle \langle{}^7F_0||U^{(2)}||{}^7F_2\rangle \\ &= -\frac{2}{15}\sqrt{21}\langle{}^7F_0||U^{(2)}||{}^7F_2\rangle \\ &= -\frac{2}{15}\sqrt{21}(-1)^{3+3+0+2}\sqrt{1 \times 5} \begin{Bmatrix} 3 & 2 & 3 \\ 2 & 3 & 0 \end{Bmatrix} \langle{}^7F||U^{(2)}||{}^7F\rangle \\ &= -\frac{2}{15}\sqrt{3}\langle{}^7F||U^{(2)}||{}^7F\rangle \\ &= +\frac{2}{15}\sqrt{3} \end{aligned} \quad (19-23)$$

where in the last step we have used

$$\langle{}^7F||U^{(2)}||{}^7F\rangle = -1 \quad (19-24)$$

Let

$$\Delta_{20} = E({}^7F20) - E({}^7F00) \quad (19-25)$$

Then recalling the S16.5 note on rank two matrices we can express the groundstate energy as

$$E({}^7\mathcal{F}00) \sim E({}^7F00) - \frac{4}{75} \frac{(B_0^2)^2}{\Delta_{20}} \quad (19-26)$$

and the corresponding groundstate eigenvector as

$$|{}^7\mathcal{F}00\rangle \sim \frac{1}{1 + \frac{\sqrt{3}B_0^2}{15\Delta_{20}}} \left(|{}^7F00\rangle - \frac{2\sqrt{3}}{15} \frac{B_0^2}{\Delta_{20}} |{}^7F20\rangle \right) \quad (19-27)$$

We can estimate the value of the crystal field parameter from the observed crystal field splitting of the 7F_1 level in D_{3h} symmetry. Calculating in a similar manner to (19-23) we readily find that

$$\langle {}^7F10 | B_0^2 C_0^{(2)} | {}^7F10 \rangle = +\frac{1}{5} B_0^2 \quad (19-28a)$$

$$\langle {}^7F1 \pm 1 | B_0^2 C_0^{(2)} | {}^7F1 \pm 1 \rangle = -\frac{1}{10} B_0^2 \quad (19-28b)$$

and hence the splitting, Δ_1 , of the 7F_1 level by such an axial field is approximately

$$\Delta_1 = \frac{3}{10} B_0^2 \quad (19-29)$$

In europium ethyl sulphate the observed splitting is $\sim 42\text{cm}^{-1}$ leading to

$$B_0^2 \sim 145\text{cm}^{-1} \quad (19-30)$$

leading to the numerical value

$$\langle {}^7\mathcal{F}00 | B_0^2 C_0^{(2)} | {}^7\mathcal{F}20 \rangle \approx 33.5\text{cm}^{-1} \quad (19-31)$$

Given that experimentally the 7F_1 level is about 1100cm^{-1} above the groundstate we can deduce that the groundstate is, to a first approximation,

$$|{}^7\mathcal{F}00\rangle = 0.9995 |{}^7F00\rangle - 0.03041 |{}^7F20\rangle \quad (19-32)$$

While the mixing coefficient is very small there is nevertheless some possibility, even at this level, of the nominally ${}^7F_0 \leftrightarrow {}^5D_0$ transition going by “borrowing intensity” from the electric dipole transition, allowed via the Judd-Ofelt mechanism. Clearly our calculation is overly simplistic. Ideally we should consider a complete crystal field J -mixing calculation that includes J -mixing in at least the 5D multiplet. The square of the coefficient of $|{}^7F20\rangle$ in (19-27) gives a direct measure of the “borrowing of intensity” from the ${}^7F_2 \leftrightarrow {}^5D_0$ transition. The whole subject of J -mixing as affects the ${}^7F_0 \leftrightarrow {}^5D_0$ transition has been extensively studied by Tanaka and Kushida and their associates^{105–112} both theoretically and experimentally.

We might ask “Are there other contributing mechanisms?” That will be the subject of the next lecture.

Lecture 20 : The Wybourne-Downer Mechanism

Although Wybourne suggested the possible importance of these linkages in 1968, neither Wybourne nor subsequent investigators ever introduced them into any quantitative intensity analysis^{113,114}

20. Introduction

So far we have looked at two distinct contributions to the line strength of a transition, the forced electric dipole as developed in the Judd-Ofelt theory (see S10) and the magnetic dipole as developed in the previous section. Thus the square root of the line strength of a generic transition could be written as the sum of two terms viz.,

$$\mathcal{S}^{\frac{1}{2}}(\alpha\Gamma_i \leftrightarrow \alpha'\Gamma_j) = \mathcal{S}^{\frac{1}{2}}(\alpha\Gamma_i \leftrightarrow \alpha'\Gamma_j)_{ed} + \mathcal{S}^{\frac{1}{2}}(\alpha\Gamma_i \leftrightarrow \alpha'\Gamma_j)_{md} \quad (20-1)$$

Recall the relevant quantity for the oscillator strength is the line strength, the square of (20-1) and hence interference terms may arise if both electric dipole *and* magnetic dipole terms are simultaneously involved. The situation becomes more complicated if one considers other possible contributions to the square root of the line strength. One such contribution is the so-called Wybourne-Downer mechanism^{41,42,113–115}

20.1. The Wybourne-Downer Mechanism

The term Wybourne-Downer mechanism appears to have been so-named by Tanaka and Kushida¹¹⁶ and arose in attempts to explain the origin of the observed ${}^5D_0 \leftrightarrow {}^7F_0$ transitions of Eu^{3+} and Sm^{2+} in low symmetry sites. I suggested^{41,42} that these transitions could arise as a result of two mechanisms that involve linked terms of the form (apart from appropriate energy denominators)

$$\begin{aligned} & \sum_{L,J,L',J'} \langle f^6 {}^7F_0 | V_c^{odd} | f^5 d {}^7L_J \rangle \langle f^5 d {}^7L_J | \sum_i (\mathbf{s} \cdot \mathbf{l})_i | f^5 d {}^7L'_{J'} \rangle \\ & \times \langle f^5 d {}^7L'_{J'} | \mathbf{er} | f^6 {}^5D_0 \rangle \end{aligned} \quad (20-2)$$

and

$$\begin{aligned} & \sum_{J,L,J'} \langle f^6 {}^7F_0 | V_c^{even} | f^6 {}^7F_J \rangle \langle f^6 {}^7F_J | V_c^{odd} | f^5 d {}^7LJ' \rangle \\ & \times \langle f^5 d {}^7L'_{J'} | \mathbf{er} | f^6 {}^7F_0 \rangle \langle f^6 {}^7F_0 | \sum_i (\mathbf{s} \cdot \mathbf{l})_i | f^6 {}^5D_0 \rangle \end{aligned} \quad (20-3)$$

The second mechanism “borrows” intensity principally from the $0 \leftrightarrow 2$ transitions and is essentially as discussed in S19.10. The first mechanism is the so-called Wybourne-Downer (WD) mechanism, suggested by Wybourne^{41,42} and initially developed by Downer and his associates^{113–115}. Note that in the above representation of the two mechanisms d -orbitals are indicated whereas in reality one must consider also g -orbitals and charge transfer states. The WD mechanism involves spin-orbit

interaction among states of the excited configuration and if there is a breakdown of LS -coupling in the excited configuration this will be reflected into the f^n configuration even if there is not a breakdown in the f^n configuration. Thus the WD mechanism can lead to a violation of the spin selection rule and in the J -selection rules. As a result *both* mechanisms can contribute to the strongly forbidden ${}^7F_0 \leftrightarrow {}^5D_0$ transition. Furthermore, interference between the two mechanisms can occur¹¹⁶. Recall that in computing line strengths one sums the square root of the line strength for each contribution and then squares the resultant sum.

The ${}^7F_0 \leftrightarrow {}^5D_0$ transition is commonly associated with Eu^{3+} and Sm^{2+} ions in crystals of low symmetry. These are the hosts that exhibit *hypersensitive* transitions.

20.2. Hypersensitive Transitions

Back in 1940 Freed *et al*¹¹⁷ noted that some transitions involving europium salts seem unusually sensitive to changes in their environment. These were considered in some detail by Jørgensen and Judd¹¹⁸. A noteworthy feature of hypersensitive transitions is that they involve a selection rule $\Delta J \leq 2$ and in the Judd-Ofelt theory of intensities seem to be associated with the parameter \mathcal{T}_2 and the matrix elements of the rank 2 tensor operator $\mathbf{U}^{(2)}$. We note that the Judd-Ofelt and Wybourne-Downer mechanisms both involve *odd* rank k crystal field interactions. Generally, k is limited to the values $k = 3, 5, 7$ ($k = 3, 5$ for d -orbitals, $k = 3, 5, 7$ for g -orbitals). Only in the low symmetry fields C_1, C_2, C_s, C_{2v} is it possible for $k = 1$ to arise. An odd rank $k = 1$ crystal field component can only contribute to the matrix elements of the tensor operator $\mathbf{U}^{(2)}$ and its associated Judd-Ofelt parameter \mathcal{T}_2 . Such hypersensitivity is well known for the ${}^7F_2 \leftrightarrow {}^5D_0$ and ${}^7F_0 \leftrightarrow {}^5D_2$ transitions in Eu^{3+} and Sm^{2+} ions in low symmetry sites as opposed to the corresponding transitions in higher symmetry sites. The enhancement of these transitions leads, by the “borrowing” and Wybourne-Downer mechanisms, to an enhancement of the ${}^7F_0 \leftrightarrow {}^5D_0$ transition.

20.3. Other Third-Order Contributions

We note that other third-order, and higher, are possible⁴². I have discussed these elsewhere^{41,42} and will not pursue them in detail here. These contributions involve effects such as Coulomb interactions between excited configurations. Some of the effects contribute angular factors identical to those of the Judd-Ofelt contribution and hence are already accommodated in the parameters of the Judd-Ofelt theory. Others introduce angular factors that go beyond the Judd-Ofelt theory. In some cases *odd* rank operators arise in addition to the usual *even* rank operators of the Judd-Ofelt formalism. In other cases double tensors arise with a spin rank and hence lead directly to a violation of the $\Delta = 0$ spin selection rule.

What never? Well hardly ever!

Gilbert and Sullivan “HMS Pinafore”

20.4. Relativistic Contributions

Relativistic effects, as noted in S12, also lead to further contributions that go beyond the Judd-Ofelt formalism. It is clear that the multitude of contributions make any meaningful parametric fitting to observed spectral intensities impossible. The problem of estimating the relative size of the various contributions is considerable. Many of the relevant radial integrals can be calculated *ab initio* using modern implementations of relativistic Hartree-Fock-Dirac theory. However, this has still not given a truly *ab initio* computation of the crystal field parameters. Furthermore, our knowledge of the *odd* crystal field parameters, essential in understanding intensities remains very limited. These are undoubtedly problems for the future.

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