

IONS IN A WEAK CRYSTAL FIELD (*f* ELECTRONS)

WE are now in a position to apply the mathematical techniques described in the previous chapters to the determination of the wave-functions and energy intervals of the low-lying levels of paramagnetic ions embedded in a crystal field. In this chapter we shall examine the weak-field case that applies to the $4f$ shell of the rare earths, delaying the intermediate field case applicable to the $3d$ shell of the iron group until Chapter 19.

18.1. Kramers ions in a weak crystal field

For experimental reasons the observability of paramagnetic resonance in an ion is dependent on the existence of at least two energy levels separated by a frequency gap $\Delta E/h$ which, using the technique of microwave spectrometers rather than infra-red spectrometers, rarely exceeds, say, five wave numbers (2 mm wavelength).

This condition singles out the so-called Kramers ions with an odd number of electrons which, in the absence of a magnetic field, will always possess at least a pair of degenerate levels. These levels, through the application of a magnetic field, can be separated by the desired amount. Kramers ions also have other features such as relatively long relaxation times and relatively narrow lines that make them particularly suitable for magnetic resonance work. Among them S -state ions, which are much less sensitive to the crystal field than any other ions, also occupy a special position.

If we exclude the cubic multiplet Γ_8 which requires a special treatment, the description of the resonance properties of all Kramers ions in the rare-earth group follows a uniform pattern. The ground multiplet (J, L, S) of the free ion will be split by the crystal field into $J + \frac{1}{2}$ doublets, and resonance, with a few exceptions, will in general be observed only between the two substates of the lowest doublet, split by the magnetic field. To calculate this splitting, that is the resonance frequency, we must know the wave-functions that span the ground level. This knowledge will enable us to calculate the magnetic 'tensor' $g_{p\alpha}$ and, for an ion with a nuclear spin, the hyperfine 'tensor' $a_{p\alpha}$ and the nuclear electric quadrupole coupling constant.

In the course of the determination of the wave-functions of the ground doublet the positions and the wave-functions of the excited doublets will also become known. These data are of interest, first because they can be confronted with the results of optical spectroscopy and susceptibility measurements, secondly because, for temperatures that are not too low, resonance can be observed between substates of some excited doublets as well, and thirdly because, as discussed in Chapter 10, down to the lowest temperatures obtainable, the relaxation properties of the ground doublet are determined by the positions and the nature of the excited levels.

The calculation proceeds in a series of steps:

(1) In first approximation one assumes that J is a good quantum number. From the assumed symmetry of the environment an expansion of the type (16.1) or (16.10) is written for the crystal potential, and the P_k^q are then replaced by the equivalent operators O_k^q . Secular equations are set up and solved for the wave-functions of the various doublets. In much paramagnetic work, the coefficients $A_k^q \langle r^k \rangle$ in the expansion (16.10) are largely unknown and are adjusted to give the best fit with the various experimental quantities listed above.

(2) The first-order approximation will often be inadequate and the crystal potential will drag in admixtures from excited multiplets. These can be handled mathematically by means of the off-diagonal matrix elements $(J+1 \parallel \alpha, \beta, \gamma \parallel J)$ listed in Table 20. It may sometimes (e.g. with one electron or one hole) be simpler to go back to the (L, S) representation.

(3) Further theoretical refinements can be introduced if warranted by the accuracy of the experimental data. For example, the spin-orbit coupling $\sum \zeta_i (\mathbf{l}_i \cdot \mathbf{s}_i)$ results in a small departure from LS -coupling, represented by an admixture into the ground state (J, L, S) of contributions from excited states (J, L', S') . Thus for the free ion we have a state of the form

$$(1 + \alpha'^2 + \alpha''^2 + \dots)^{-\frac{1}{2}} (|J, L, S\rangle + \alpha' |J, L', S'\rangle + \alpha'' |J, L'', S''\rangle + \dots). \quad (18.1)$$

Here all terms have the same value of J , and otherwise follow the selection rules $\Delta L = 0, \pm 1$; $\Delta S = 0, \pm 1$; but $\Delta L = \Delta S = 0$ is excluded because the ground term, which obeys Hund's rules, is unique.

For the magnetic moment $\mu = -\beta(L+2S)$ of the ion the matrix elements $\langle LS, \dots | \mu | L'S', \dots \rangle$ vanish unless $L = L'$ and $S = S'$, and

it therefore follows that changes in the magnetic moment due to the admixtures will be of order α^2 .

For the magnetic hyperfine operator (17.30), summed over all the electrons, the orbital term obeys the selection rule $\Delta L = 0$, $\Delta S = 0$ and therefore has no matrix elements linear in α . However the spin dipolar term, which obeys the rule $\Delta L = 0, \pm 1, \pm 2$; $\Delta S = 0, \pm 1$ may well have matrix elements between $|J, L, S\rangle$ and $|J, L', S'\rangle$ leading to a first-order correction due to intermediate coupling.

Fortunately for electron paramagnetic resonance experiments in solids, intermediate coupling plays a less important role in the ground (L, S) multiplet than in excited multiplets. Nevertheless, its effects are quite appreciable in the $5f$ group (see Chapter 6).

For ions with a large hyperfine structure or low-lying excited states or both, other second-order effects may be observable. Cross terms between the electron Zeeman coupling and the hyperfine coupling give a term, linear in the nuclear spin and in the applied field, which adds to the nuclear Zeeman coupling (we shall call it the pseudo-nuclear Zeeman coupling); and in second order the magnetic hyperfine coupling can give a pseudo-quadrupole interaction.

The pseudo-nuclear Zeeman coupling is given by the formula (where c.c. stands for the complex conjugate expression)

$$\sum_n' \frac{\langle O | -\boldsymbol{\mu} \cdot \mathbf{H} | n \rangle \langle n | -\gamma_n \hbar \mathbf{H}^e \cdot \mathbf{I} | O \rangle}{W_0 - W_n} + \text{c.c.}, \quad (18.2)$$

where $-\gamma_n \hbar \mathbf{H}^e \cdot \mathbf{I}$ is the operator for the magnetic hyperfine structure. $|O\rangle$ represents the ground doublet where the two substates are left unspecified. (18.2) can be written as

$$-\gamma_n \hbar \mathbf{H} \cdot \boldsymbol{\alpha} \cdot \mathbf{I} \quad (18.3)$$

where $\boldsymbol{\alpha}$ is a tensor with components

$$\alpha_{pq} = - \sum_n' \frac{\langle O | \mu_p | n \rangle \langle n | H_q^e | O \rangle + \langle O | H_q^e | n \rangle \langle n | \mu_p | O \rangle}{W_0 - W_n}. \quad (18.4)$$

The restricted summation in (18.4) is over all the excited doublets where the two Kramers-conjugate substates of each excited doublet give the same contribution. (18.4) can be written as the expectation value $\langle O | \mathcal{A}_{pq} | O \rangle$ in the ground doublet of the operator

$$\mathcal{A}_{pq} = - \left\{ \mu_p \left(\sum_n' \frac{|n\rangle \langle n|}{W_0 - W_n} \right) H_q^e + H_q^e \left(\sum_n' \frac{|n\rangle \langle n|}{W_0 - W_n} \right) \mu_p \right\}. \quad (18.5)$$

Here the Hermitian operator \mathcal{A}_{pq} is the symmetrized product of three operators: $\mu_p, C = \sum'_n \{|n\rangle\langle n|/(W_0 - W_n)\}, H_q^e$. The first and the last are time-odd, the middle one time-even. The symmetrized product \mathcal{A}_{pq} is time-even and therefore has the same expectation value for the two substates of the ground doublet $|O\rangle$. We can therefore treat α_{pq} as a constant. We shall see later that the situation is different if the ground state is a quadruplet Γ_8 .

If J is a good quantum number we may write $\mu/\beta = -\Lambda J$, $H^e/\beta = -2N J \langle r^{-3} \rangle$ and (18.4) becomes

$$\alpha_{pq} = -2\beta^2 \langle r^{-3} \rangle \Lambda N \sum'_n \frac{\langle O | J_p | n \rangle \langle n | J_q | O \rangle + \langle O | J_q | n \rangle \langle n | J_p | O \rangle}{W_0 - W_n}, \quad (18.6)$$

where for brevity we have written Λ for $(J \| \Lambda \| J)$ and N for $(J \| N \| J)$.

The relative importance of the pseudo-nuclear Zeeman coupling is given by the dimensionless expressions (18.4) or (18.6) for α_{pq} . Roughly speaking, its magnitude is of the order of a Zeeman electron energy βH^e divided by the splitting between two Kramers doublets, arising from the crystal field. Electronic hyperfine fields H^e of the order of a million gauss are not uncommon in the rare-earth group and βH^e can be as large as a 100 cm^{-1} , which is comparable to the crystal field splittings. In many cases the pseudo-nuclear Zeeman coupling will be as large or even larger than the direct nuclear Zeeman coupling. One may notice that the tensor α is not fundamentally different from the chemical shift tensor σ , well known in nuclear resonance. The difference in order of magnitude between α and σ is due to the proximity of excited levels in the rare-earth group (10 to 100 cm^{-1} as contrasted with, say, 10 eV or 10^5 cm^{-1} for an excited electronic state of a molecule). Also, compared with nuclear magnetic resonance measurements on light atoms we have a much larger value of $\langle r^{-3} \rangle$ due to the high atomic numbers Z in the rare-earth group.

The second-order term from the magnetic hyperfine structure can be written

$$\gamma_n^2 \hbar^2 \sum'_n \frac{\langle O | H^e \cdot \mathbf{I} | n \rangle \langle n | H^e \cdot \mathbf{I} | O \rangle}{W_0 - W_n} = \gamma_n^2 \hbar^2 \sum_{p,q} \langle O | H_p^e C H_q^e | O \rangle I_p I_q. \quad (18.7)$$

Some caution should be exercised here in using the concept of time-even operators, as pointed out in § 15.4: the operator $H_p^e C H_q^e$ with $p \neq q$ is *not* time-even, for its transform by time reversal, $\theta H_p^e C H_q^e \theta^{-1}$

is equal to itself, $H_p^e C H_q^e$, rather than to its Hermitian conjugate $(H_p^e C H_q^e)^+ = H_q^e C H_p^e$. Eqn (18.7) can be rewritten as

$$\frac{1}{2} \gamma_n^2 \hbar^2 \left\{ \frac{1}{2} \sum_{p,q} \langle O | H_p^e C H_q^e + H_q^e C H_p^e | O \rangle (I_p I_q + I_q I_p) + \right. \\ \left. + \frac{1}{2} \sum_{p,q} \langle O | H_p^e C H_q^e - H_q^e C H_p^e | O \rangle (I_p I_q - I_q I_p) \right\}. \quad (18.8)$$

Here $\frac{1}{2} \gamma_n^2 \hbar^2 (H_p^e C H_q^e + H_q^e C H_p^e)$ is a Hermitian time-even operator and therefore within the manifold of a Kramers doublet, a component b_{pq} of a symmetric tensor, which is a real number. On the other hand $\frac{1}{2} \gamma_n^2 \hbar^2 (H_p^e C H_q^e - H_q^e C H_p^e)$ is a time-odd anti-Hermitian operator, which within the same manifold can be written $i \sum_{\alpha} d_{\alpha}^{pq} \sigma_{\alpha}$ where $d_{\alpha}^{pq} = -d_{\alpha}^{qp}$ is real. The commutator $(I_p I_q - I_q I_p)$ can be written $i \sum_r \varepsilon_{pqr} I_r$, where ε_{pqr} is the usual antisymmetrization symbol and (18.8) can be rewritten

$$\sum_{p,q} b_{pq} (I_p I_q + I_q I_p) - \sum_{r,\alpha} u_{r\alpha} I_r \sigma_{\alpha}, \quad (18.9)$$

where $u_{r\alpha} = \sum_{p,q} \varepsilon_{pqr} d_{\alpha}^{pq}$, or

$$u_{1,\alpha} = d_{\alpha}^{23}, \quad u_{2,\alpha} = d_{\alpha}^{31}, \quad u_{3,\alpha} = d_{\alpha}^{12}.$$

The first term in (18.9) is the pseudo-quadrupole hyperfine interaction and the second a contribution that adds to the magnetic hyperfine interaction. Both are smaller than the first-order magnetic hyperfine interaction by a factor of the order $|\hbar \gamma_n H^e| / \Delta W$, a ratio of the order of 10^{-3} . The pseudo-quadrupole interaction may be a very much larger fraction of the true quadrupole interaction, but since an accurate theoretical estimate of the latter is very difficult one might well question the interest of calculating these terms. A point to remember in calculating the second term of (18.9) is that it makes the ratio of the hyperfine structure coefficients for two isotopes different from that of their γ_n . This effect may be a nuisance in so far as it interferes with the measurement of the hfs anomaly, due to the penetration of the electron inside the nucleus.

The experimental results for ions of the rare-earth group have been discussed in Chapter 5, together with theoretical interpretations that embody most of the features outlined above. The extra hyperfine terms given above are of course most important in Endor measurements, some specific examples being given in Chapter 4. (Further small terms are mentioned in § 5.10.) It is thus unnecessary to give here an extensive discussion of the application of the theory to Kramers ions. We may however remark that for such ions in crystal fields possessing an

axis of threefold or sixfold symmetry, there may not be an allowed resonance transition within the ground Kramers doublet. The selection rule $\Delta J_z = \pm 1$ requires that the wave-function for one member of the doublet must contain at least one value of $J_z = M$ that differs by one unit from one of the values in the conjugate wave-function for the other member of the doublet. This produces the following result.

If there is an axis of q -fold symmetry, the doublet wave-functions will be generally of the form

$$\begin{aligned} & a_M |J, M\rangle + a_{M\pm q} |J, M\pm q\rangle + a_{M\pm 2q} |J, M\pm 2q\rangle + \dots \\ & a'_M |J, -M\rangle + a'_{M\pm q} |J, -(M\pm q)\rangle + a'_{M\pm 2q} |J, -(M\pm 2q)\rangle + \dots \end{aligned} \quad (18.10)$$

For resonance to be observable we need $-(M\pm nq) = M\pm 1$, or

$$|nq| = 2M\pm 1 \quad (18.11)$$

where $n = 0, 1, 2, \dots$. For sixfold symmetry ($q = 6$) this means that resonance is observable in the doublets spanned by

$$M = \pm \frac{1}{2}; (\pm \frac{7}{2}, \mp \frac{5}{2}); (\pm \frac{13}{2}, \pm \frac{1}{2}, \mp \frac{1}{2})$$

but not in doublets spanned by

$$M = \pm \frac{3}{2}; (\pm \frac{9}{2}, \mp \frac{3}{2}); (\pm \frac{15}{2}, \pm \frac{3}{2}, \mp \frac{9}{2}).$$

For threefold symmetry the wave-functions are more complicated in that they contain all values of M differing by 3 instead of just by 6, but the doublets in which resonance is allowed are otherwise unaltered. For fourfold symmetry ($q = 4$) the position is different; all possible doublets are of the form

$$(\pm \frac{15}{2}, \pm \frac{7}{2}, \mp \frac{1}{2}, \mp \frac{9}{2})$$

or

$$(\pm \frac{13}{2}, \pm \frac{5}{2}, \mp \frac{3}{2}, \mp \frac{1}{2}),$$

where the higher values of M do not of course occur for lower values of J . Inspection shows that resonance will be allowed in all such doublets for values of $J \geq \frac{5}{2}$, the lowest half-integral value to occur for the ground state of a $4f$ or $5f$ ion. For twofold symmetry the rules are clearly the same (with the addition that resonance is also possible in either doublet of $J = \frac{3}{2}$). We see therefore that we should always expect a resonance in the ground state of a Kramers rare-earth ion in a substance such as CaWO_4 , even if the fourfold symmetry of the Ca^{2+} site is not reduced by local charge compensation when a trippositive

rare-earth ion replaces it. On the other hand resonance cannot be observed, for example, in the ground doublet $\pm \frac{3}{2}$ of $4f^{13}$, Yb^{3+} , $^2F_{7/2}$ in lanthanide ethylsulphate or trichloride, for which $q = 6$.

18.2. Rare-earth ions in cubic symmetry

Following a suggestion by Bleaney (1959a,b), that rare-earth Kramers ions in cubic environment should provide suitable maser materials if their ground states were the quadruplet Γ_8 , there have been many studies both theoretical and experimental of the properties of rare-earth ions in cubic surroundings. Trivalent rare-earth ions M can be introduced substitutionally to replace divalent positive ions in such cubic crystals as, say, CaO , CaF_2 , MgO . Charge compensation will then demand the presence of a negative charge in the neighbourhood of M^{3+} . If the compensating charge is, with respect to M , in a direction $\langle 100 \rangle$ the symmetry of the distorted crystal field 'seen' by M will be tetragonal; it will be trigonal for a direction $\langle 111 \rangle$; for any other relative orientation of the compensating charge the symmetry will be lower. The compensation may also be long range, the negative charge being sufficiently removed from M to leave it in a symmetry indistinguishable from cubic. It is this situation that we propose to examine in this section. Often the cubic resonance spectrum will be observed simultaneously with spectra of lower symmetry, coming from ions M , less fortunate in their charge-compensating environment.

It has also proved possible to create in these environments divalent states of rare-earth ions. If in their normal trivalent state these ions, such as holmium or thulium, have an even number of electrons they will now in the divalent state be Kramers ions. No charge compensation is needed in this case and the symmetry is cubic.

Theoretically the problem of a cubic crystal potential is attractive because for *f*-electrons this potential depends on two constants only as in eqn (16.13),

$$V = A_4 P_4 + A_6 P_6,$$

the polynomials P_4 and P_6 being defined in (16.11) and (16.12). The wave-functions of the various crystal levels and the ratios of the intervals between the different levels depend on a single constant, the ratio of the fourth to sixth order potential; this makes it possible to tabulate them for all the values of J occurring in the ions of the rare-earth group at least in the framework of first-order theory, where J is taken to be a good quantum number. Such tables (see Lea, Leask, and Wolf (1962)) are organized as follows.

For each value of J it is convenient for practical reasons to write the cubic potential as

$$\mathcal{H} = B_4 F(4) \frac{O_4}{F(4)} + B_6 F(6) \frac{O_6}{F(6)}. \quad (18.12)$$

Here O_4 and O_6 are the equivalent operators

$$O_4 = (O_4^0 + 5O_4^4); \quad O_6 = (O_6^0 - 21O_6^4), \quad (18.13)$$

where the O_k^q are defined and tabulated in Table 16 and

$$B_4 = \langle J \| \beta \| J \rangle \langle r^4 \rangle A_4; \quad B_6 = \langle J \| \gamma \| J \rangle \langle r^6 \rangle A_6.$$

The values of $\langle J \| \beta \| J \rangle$, $\langle J \| \gamma \| J \rangle$ are tabulated in Table 20. The quantities $F(4)$ and $F(6)$ are certain positive factors common to all the matrix elements of the O_k^q for a given k separated out to keep all the eigenvalues in the same numerical range. (In Lea, Leask and Wolf (1962) they are not always the same as the values of F given in the Tables 17.)

Two constants W and x are then defined by

$$B_4 F(4) = Wx; \quad B_6 F(6) = W(1 - |x|); \quad (18.14a)$$

or

$$\frac{B_4}{B_6} = \frac{x}{1 - |x|} \frac{F(6)}{F(4)}. \quad (18.14b)$$

With these definitions, $B_4/B_6 = 0$ for $x = 0$ and $\pm \infty$ for $x = \pm 1$ so that all possible ratios of B_4/B_6 are included in the range $-1 \leq x \leq 1$. The Hamiltonian is then rewritten as

$$\mathcal{H} = W \left\{ x \frac{O_4}{F(4)} + (1 - |x|) \frac{O_6}{F(6)} \right\}. \quad (18.15)$$

For each value of x all the matrix elements of the operator in the curly brackets are known and its eigenvalues and eigenstates are then found by numerical calculations and tabulated, W being the single energy parameter.

We know from Tables 3 and 7 the decomposition of each manifold J into the irreducible representations Γ_i of the cubic group. If the representation occurs only once, the kets that span it are determined from symmetry alone and are independent of x . Their expressions are given in a closed form in Tables 4 and 9 and the eigenvalues are linear functions of x . We shall call such representations 'isolated'.

From (18.14a, b) we see that the sign of W is that of B_6 and the sign of x

is determined by B_4/B_6 . Since the β and γ are tabulated, to know the signs of B_4 and B_6 it is necessary to know only those of A_4 and A_6 . If we accept the qualitative validity of the point-charge model the latter are given in the various coordinations by eqns (16.15)–(16.17).

Resonance in Γ_6 and Γ_7

The pattern of resonance is very similar to that observed for lower symmetry since Γ_6 and Γ_7 are Kramers doublets. The only difference is that the magnetic ‘tensor’ g and the hyperfine ‘tensor’ a are isotropic and the nuclear electric quadrupole interaction vanishes.

For ‘isolated’ Γ_6 or Γ_7 doublets the values of $g' = g/\Lambda$ are independent of x ; they are given in Table 22.

A number of experimental results are given in Tables 5.14 and 5.15. They are close to the simple theoretical values given in Table 22, but comparison with the free ions shows that even when intermediate coupling is taken into account there are small discrepancies that are presumably to be attributed to a certain amount of covalent bonding, or to effects of the zero-point vibrations of the lattice (see § 5.8), or to both.

18.3. The quadruplet Γ_8

We have been faced several times with the problem of finding the matrix elements of a vector operator such as say the magnetic moment μ or the electronic hyperfine field H_e , within a certain manifold. We saw in particular that thanks to the Wigner–Eckart theorem, a vector V could be replaced within a manifold J by aJ where a was a constant depending on the vector V . Similarly in cubic symmetry within a manifold Γ_4 or Γ_5 a vector could be taken proportional to a fictitious angular momentum \tilde{I} defined by eqn (14.5). We have emphasized the point that this representation was possible because the reduction of the direct products $\mathscr{D}^J \times \mathscr{D}^J$ in the rotation group, or of $\Gamma_4 \times \Gamma_4$ and $\Gamma_5 \times \Gamma_5$ in the cubic group, contained only once the representation of the group spanned by the components of a vector, namely \mathscr{D}^1 for the rotation group and Γ_4 for the cubic group.

On the other hand, we have shown in § 15.6 that within a Kramers doublet we could represent a time-odd vector V as $V = T \cdot s$, where $s = \sigma/2$ was a fictitious spin and T a so-called ‘tensor’. This result had *nothing* to do with spatial symmetry but resulted solely from invariance with respect to time reversal.

We require now to find the matrix elements of a vector within a

quadruplet Γ_8 . This quadruplet is spanned by four kets $|\tilde{m}\rangle$ which we have represented in § 14.4 as $|\pm\frac{3}{2}\rangle$ and $|\pm\frac{1}{2}\rangle$, meaning thereby that under the rotations of the cubic group they transform in the same way as the eigenstates $|J, m\rangle = |\frac{3}{2}, \pm\frac{3}{2}\rangle$ and $|\frac{3}{2}, \pm\frac{1}{2}\rangle$ of an angular momentum $J = \frac{3}{2}$. When the quadruplet Γ_8 results from the reduction of a given representation \mathcal{D}^J , the states $|\tilde{m}\rangle$ can be expanded as a linear combination $\sum_{J,m} C_{J,m} |J, m\rangle$ as shown in Table 9, but an arbitrary Γ_8 can naturally be spanned by kets with arbitrary values of J .

We can define in the manifold Γ_8 three operators $\tilde{S}_x, \tilde{S}_y, \tilde{S}_z$, components of a fictitious spin $\tilde{S} = \frac{3}{2}$, by the condition that they have the same matrix elements in the basis $|\tilde{m}\rangle$ as the components $\mathcal{J}_x, \mathcal{J}_y, \mathcal{J}_z$ of an angular momentum $\mathcal{J} = \frac{3}{2}$ have with respect to the states $|\frac{3}{2}, m\rangle$. $\tilde{S}_x, \tilde{S}_y, \tilde{S}_z$ have naturally the usual commutation relations $[\tilde{S}_x, \tilde{S}_y] = i\tilde{S}_z$, etc.

We see from Table 8 that the reduction of the direct product $\Gamma_8^* \times \Gamma_8$ (which is equivalent to that of $\Gamma_8 \times \Gamma_8$, since all the characters of Γ_8 are real) contains Γ_4 *twice*. It is not too difficult to show by an adaptation of the proof of the Wigner-Eckart theorem that the matrix elements of a vector within a manifold Γ_8 can be specified by two constants. The detailed argument can be found, for instance, in Koster and Statz (1959). We also see from Table 8 that it is the symmetrical direct product $[\Gamma_8 \times \Gamma_8]_s$ which contains Γ_4 twice, and therefore according to the rules given in § 15.9 only time-odd vectors have non-vanishing matrix elements inside the manifold Γ_8 .

This result and also the form of the operator equivalent to a vector V within Γ_8 can be obtained by an elementary method (Ayant, Beloritzky, and Rosset 1962). In the representation $|\tilde{m}\rangle$ the component V_z has no off-diagonal matrix elements $\langle \tilde{m} | V_z | \tilde{m}' \rangle$, since a rotation of $\pi/2$ around the z -axis, which must leave V_z invariant, multiplies such matrix elements by $e^{i\pi(\tilde{m}-\tilde{m}')}$. A rotation by π around the axis Oy changes $\langle \tilde{m} | V_z | \tilde{m}' \rangle$ into

$$\begin{aligned} \langle \tilde{m} | e^{-i\pi\tilde{S}_y} V_z e^{i\pi\tilde{S}_y} | \tilde{m}' \rangle &= -\langle \tilde{m} | V_z | \tilde{m}' \rangle \\ &= (-1)^{2(j-\tilde{m})} \langle -\tilde{m} | V_z | -\tilde{m}' \rangle = \langle -\tilde{m} | V_z | -\tilde{m}' \rangle. \end{aligned}$$

Hence we see that the non-vanishing matrix elements of V_z are of the form

$$\begin{aligned} \langle \frac{3}{2} | V_z | \frac{3}{2} \rangle &= -\langle -\frac{3}{2} | V_z | -\frac{3}{2} \rangle = P, \\ \langle \frac{1}{2} | V_z | \frac{1}{2} \rangle &= -\langle -\frac{1}{2} | V_z | -\frac{1}{2} \rangle = Q. \end{aligned} \tag{18.16}$$

As a consequence, V_z can be written as

$$V_z = a\tilde{S}_z + b\tilde{S}_z^3 \quad (18.17)$$

with

$$P = \frac{3a}{2} + \frac{27b}{8}, \quad Q = \frac{a}{2} + \frac{b}{8}; \quad (18.18)$$

or

$$a = -\frac{P}{12} + \frac{9Q}{4}, \quad b = \frac{P}{3} - Q.$$

It is obvious from the nature of cubic symmetry that we must also have

$$\begin{aligned} V_x &= a\tilde{S}_x + b\tilde{S}_x^3, \\ V_y &= a\tilde{S}_y + b\tilde{S}_y^3. \end{aligned} \quad (18.19)$$

It may be more convenient to use instead of (18.17) the form

$$V_z = a'\tilde{S}_z + b\{\tilde{S}_z^3 - \frac{3}{5}\tilde{S}(\tilde{S}+1)\tilde{S}_z + \frac{1}{5}\tilde{S}_z^5\} \quad (18.20)$$

with $a' = a + \frac{1}{5}b\{3\tilde{S}(\tilde{S}+1) - 1\}$. This has the advantage that the curly bracket in (18.20) is the operator O_3^0 which vanishes for $\tilde{S} < \frac{3}{2}$. Using (18.20) we can write the Zeeman and magnetic hyperfine Hamiltonians in the form

$$\begin{aligned} g\beta\tilde{\mathbf{S}} \cdot \mathbf{H} + A\tilde{\mathbf{S}} \cdot \mathbf{I} - g_n\beta_n\mathbf{H} \cdot \mathbf{I} + \\ + u\beta[\tilde{S}_x^3H_x + \tilde{S}_y^3H_y + \tilde{S}_z^3H_z - \frac{1}{5}(\tilde{\mathbf{S}} \cdot \mathbf{H})\{3\tilde{S}(\tilde{S}+1) - 1\}] + \\ + U[\tilde{S}_x^3I_x + \tilde{S}_y^3I_y + \tilde{S}_z^3I_z - \frac{1}{5}(\tilde{\mathbf{S}} \cdot \mathbf{I})\{3\tilde{S}(\tilde{S}+1) - 1\}]. \end{aligned} \quad (18.21)$$

Diagonalization of the spin Hamiltonian for Γ_8 quadruplet

Complete diagonalization of the spin Hamiltonian (18.21) is obviously rather complicated and we shall confine our treatment to two special cases: (A) the remaining terms are all small compared with the first term $g\beta(\tilde{\mathbf{S}} \cdot \mathbf{H})$, which we therefore diagonalize first and then treat the remaining terms by first-order perturbation theory; (B) the nuclear spin is zero, and the complete electronic Zeeman interaction is diagonalized exactly for an arbitrary direction of \mathbf{H} . In the former of these two cases we are assuming that the terms of third degree involving the parameter U are also small compared with $A(\tilde{\mathbf{S}} \cdot \mathbf{I})$; this situation is likely to occur in the $3d$ group rather than the $4f$ group, except for the half-filled shell $4f^7$, 8S , where small terms of the third and even higher degree may be required (see § 5.9).

(A) *Perturbation treatment*

Suppose that the external field \mathbf{H} is directed along an axis OZ whose direction cosines are (n_1, n_2, n_3) with respect to the fourfold axes

(x, y, z) of the cube. Since g is isotropic the first term in (18.21) is diagonalized simply by changing to a coordinate system (X, Y, Z) of which OZ is the Z -axis. We introduce the component

$$\tilde{S}_Z = n_1\tilde{S}_x + n_2\tilde{S}_y + n_3\tilde{S}_z \quad (18.22)$$

and two other components \tilde{S}_X, \tilde{S}_Y along two orthogonal axes that we need not specify. We can write

$$\tilde{S}_x = n_1\tilde{S}_Z + \alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y \quad (18.23)$$

together with two similar equations for \tilde{S}_y, \tilde{S}_z .

On our assumption that all the terms except $g\beta(\tilde{\mathbf{S}} \cdot \mathbf{H}) = g\beta\tilde{S}_ZH$ are small, first-order perturbation theory requires that we calculate the expectation values $\langle\tilde{S}_x^3\rangle, \langle\tilde{S}_y^3\rangle, \langle\tilde{S}_z^3\rangle$ in a state where $\tilde{S}_Z = M$. From (18.23), we get

$$\begin{aligned} \langle\tilde{S}_x^3\rangle = n_1^3\langle\tilde{S}_Z^3\rangle + n_1\langle(\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y)^2\tilde{S}_Z + \tilde{S}_Z(\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y)^2 + \\ + (\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y)\tilde{S}_Z(\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y)\rangle \end{aligned} \quad (18.24)$$

where we have omitted terms of odd powers in \tilde{S}_X and \tilde{S}_Y which clearly have a vanishing expectation value in the state $\tilde{S}_Z = M$. The first term of (18.24) is $n_1^3M^3$ and the second and the third have the same expectation value:

$$n_1 \frac{(\alpha_1^2 + \beta_1^2)}{2} \{\tilde{S}(\tilde{S}+1) - M^2\}M = n_1 \frac{(1-n_1^2)}{2} \{\tilde{S}(\tilde{S}+1) - M^2\}M. \quad (18.25)$$

The fourth term is more complicated:

$$\begin{aligned} n_1\langle(\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y)\tilde{S}_Z(\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y)\rangle \\ = n_1\langle\tilde{S}_Z(\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y)^2 + [\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y, \tilde{S}_Z](\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y)\rangle \\ = n_1 \frac{1-n_1^2}{2} \{\tilde{S}(\tilde{S}+1) - M^2\}M + n_1\langle[\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y, \tilde{S}_Z](\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y)\rangle. \end{aligned} \quad (18.26)$$

The last term of (18.26) can be written

$$\begin{aligned} n_1\langle(-i\alpha_1\tilde{S}_Y + i\beta_1\tilde{S}_X)(\alpha_1\tilde{S}_X + \beta_1\tilde{S}_Y)\rangle \\ = n_1\langle-i\alpha_1^2\tilde{S}_Y\tilde{S}_X + i\beta_1^2\tilde{S}_X\tilde{S}_Y + i\beta_1\alpha_1(\tilde{S}_X^2 - \tilde{S}_Y^2)\rangle \\ = n_1\left\langle i\left(\frac{\beta_1^2 + \alpha_1^2}{2}\right)[\tilde{S}_X, \tilde{S}_Y] + \right. \\ \left. + i\left(\frac{\beta_1^2 - \alpha_1^2}{2}\right)(\tilde{S}_X\tilde{S}_Y + \tilde{S}_Y\tilde{S}_X) + i\beta_1\alpha_1(\tilde{S}_X^2 - \tilde{S}_Y^2)\right\rangle \\ = n_1\left\langle -\left(\frac{\beta_1^2 + \alpha_1^2}{2}\right)\tilde{S}_Z + \frac{\beta_1^2 - \alpha_1^2}{4}(\tilde{S}_+^2 - \tilde{S}_-^2) + i\frac{\beta_1\alpha_1}{2}(\tilde{S}_+ - \tilde{S}_-) \right\rangle. \end{aligned} \quad (18.27)$$

On summing over the similar terms for $\langle \tilde{S}_y^3 \rangle$, $\langle \tilde{S}_z^3 \rangle$ we find that in the approximation in which we are working the eigenvalues of (18.21) are given by

$$W_{M,m} = g\beta HM + AMm - g_n\beta_n Hm + (u\beta H + Um) \times \\ \times \{M^3 - \frac{1}{6}(3S(S+1) - 1)M\} \{1 - 5(n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2)\}, \quad (18.28)$$

where the angular variation of the last term is just that of the quantity $p = 1 - 5(n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2) = \frac{5}{2}(n_1^4 + n_2^4 + n_3^4 - \frac{3}{2})$ (cf. § 3.4).

(B) *Exact diagonalization of the electronic Zeeman interaction*

This involves finding the eigenvalues of the Zeeman Hamiltonian $Z = -\boldsymbol{\mu} \cdot \mathbf{H}$ in the general case when the cubic terms are not small (Ayant, Beloritzky, and Rosset 1962).

In order to deal with dimensionless quantities we take for $V_z = -\mu_z/\beta$ the matrix form (18.16). Then, taking for $V_x = -\mu_x/\beta$, $V_y = -\mu_y/\beta$ the expressions (18.19), where a and b are related to P and Q by (18.18), and calculating from the known matrices for \tilde{S}_x and \tilde{S}_y those for \tilde{S}_x^3 and \tilde{S}_y^3 , we find the matrix expressions for V_x and V_y . In fact it is sufficient to give the non-vanishing matrix elements of $V_+ = V_x + iV_y$ that determine those of V_x and V_y :

$$\begin{aligned} (\frac{7}{2} | V_+ | \frac{1}{2}) &= (-\frac{1}{2} | V_+ | -\frac{3}{2}) = \frac{\sqrt{3}}{2}(P+Q), \\ (\frac{1}{2} | V_+ | -\frac{1}{2}) &= \frac{3P-Q}{2}, \quad (-\frac{3}{2} | V_+ | \frac{3}{2}) = \frac{P-3Q}{2}. \end{aligned} \quad (18.29)$$

For $P = 3Q$ the cubic coefficient b in (18.19) vanishes and the matrix elements (18.29) take their normal values for an ordinary multiplet $\mathcal{J} = \frac{3}{2}$. The secular equation for the eigenvalues $(W/\beta H) = y$ of $Z = -\boldsymbol{\mu} \cdot \mathbf{H}$ is obtained from (18.16) and (18.29). It is given by

$$y^4 - (P^2 + Q^2)y^2 + P^2Q^2 + \frac{3}{16}(P-3Q)(3P-Q)(P+Q)^2(n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2) = 0, \quad (18.30)$$

where n_1, n_2, n_3 are the cosines of the magnetic field with respect to the fourfold axes.

The absence of odd powers in (18.30) is a straightforward consequence of invariance with respect to time reversal. The energy levels are linear with H but they are neither equidistant nor independent of the direction of the field, unlike an ordinary quadruplet $S = \frac{3}{2}$. For an arbitrary orientation of the magnetic field with respect to the cubic axes, transitions can be induced between any of the four levels.

If **H** is along the *z*-axis the roots of (18.30) are $\pm P, \pm Q$, as follows immediately from (18.16). The selection rules and relative intensities obtained from (18.29) are, in this case, with the oscillatory field normal to *Oz*, as shown in Table 18.1.

TABLE 18.1

Transition	Energy	Relative intensity
$\frac{3}{2} \rightarrow -\frac{3}{2}$	$2P$	$(P-3Q)^2$
$\frac{1}{2} \rightarrow -\frac{1}{2}$	$2Q$	$(3P-Q)^2$
$\frac{3}{2} \rightarrow \frac{1}{2} = -\frac{1}{2} \rightarrow -\frac{3}{2}$	$P-Q$	$3(P+Q)^2$

The transitions $|\Delta\tilde{S}_z| = 2$ are forbidden for this particular orientation. It may be noted that if a rotating field H_1 is used, some of the transitions may require right-handed and others left-handed circular polarization (Bleaney 1959a,b).

It may be convenient, especially for a study of trigonal distortions of the cubic field to take as axis of quantization *OZ* a body diagonal (see below). Three new operators $\tilde{S}_X, \tilde{S}_Y, \tilde{S}_Z$ are defined through

$$\begin{aligned}\tilde{S}_Z &= \frac{\tilde{S}_x + \tilde{S}_y + \tilde{S}_z}{\sqrt{3}}, \\ \tilde{S}_Y &= \frac{\tilde{S}_x - \tilde{S}_y}{\sqrt{2}}, \\ \tilde{S}_X &= -\frac{\tilde{S}_x + \tilde{S}_y - 2\tilde{S}_z}{\sqrt{6}};\end{aligned}\tag{18.31}$$

$$\begin{aligned}\tilde{S}_z &= \frac{2\tilde{S}_X}{\sqrt{6}} + \frac{\tilde{S}_Z}{\sqrt{3}}, \\ \tilde{S}_y &= -\frac{\tilde{S}_X}{\sqrt{6}} - \frac{\tilde{S}_Y}{\sqrt{2}} + \frac{\tilde{S}_Z}{\sqrt{3}}, \\ \tilde{S}_x &= -\frac{\tilde{S}_X}{\sqrt{6}} + \frac{\tilde{S}_Y}{\sqrt{2}} + \frac{\tilde{S}_Z}{\sqrt{3}},\end{aligned}\tag{18.32}$$

together with operators V_X, V_Y, V_Z given by

$$\begin{aligned}V_Z &= a\tilde{S}_Z + \frac{b}{\sqrt{3}}(\tilde{S}_x^3 + \tilde{S}_y^3 + \tilde{S}_z^3), \\ V_Y &= a\tilde{S}_Y + \frac{b}{\sqrt{2}}(\tilde{S}_x^3 - \tilde{S}_y^3), \\ V_X &= a\tilde{S}_X - \frac{b}{\sqrt{6}}(\tilde{S}_x^3 + \tilde{S}_y^3 - 2\tilde{S}_z^3).\end{aligned}\tag{18.33}$$

In the representation where \tilde{S}_Z is diagonal and \tilde{S}_X and \tilde{S}_Y have the usual matrix form we find from (18.33) the non-vanishing matrix elements of V_X , V_Y , V_Z using (18.32):

$$\begin{aligned}\langle \tilde{\frac{3}{2}} | V_Z | \tilde{\frac{3}{2}} \rangle &= -\langle -\tilde{\frac{3}{2}} | V_Z | -\tilde{\frac{3}{2}} \rangle = \frac{5P+3Q}{6}, \\ \langle \tilde{\frac{1}{2}} | V_Z | \tilde{\frac{1}{2}} \rangle &= -\langle -\tilde{\frac{1}{2}} | V_Z | -\tilde{\frac{1}{2}} \rangle = \frac{P-Q}{2}, \\ \langle \tilde{\frac{3}{2}} | V_Z | -\tilde{\frac{3}{2}} \rangle &= \langle -\tilde{\frac{3}{2}} | V_Z | \tilde{\frac{3}{2}} \rangle = \frac{1}{\sqrt{2}} \left(\frac{P}{3} - Q \right).\end{aligned}\quad (18.34)$$

Apropos of the last term in (18.34) it is worth pointing out that when a body diagonal is chosen as axis of quantization OZ , a matrix element such as $\langle \tilde{\frac{3}{2}} | V_Z | -\tilde{\frac{3}{2}} \rangle$ need not vanish since it is left unchanged by a rotation $\pm 2\pi/3$ around OZ . Also,

$$\begin{aligned}\langle \tilde{\frac{3}{2}} | V_X + iV_Y | \tilde{\frac{1}{2}} \rangle &= \langle -\tilde{\frac{1}{2}} | V_X + iV_Y | -\tilde{\frac{3}{2}} \rangle = \frac{2P}{\sqrt{3}}, \\ \langle \tilde{\frac{1}{2}} | V_X + iV_Y | -\tilde{\frac{1}{2}} \rangle &= P+Q, \\ \langle -\tilde{\frac{1}{2}} | V_X + iV_Y | \tilde{\frac{3}{2}} \rangle &= -\langle -\tilde{\frac{3}{2}} | V_X + iV_Y | \tilde{\frac{1}{2}} \rangle = \frac{\sqrt{6}}{2} \left(\frac{P}{3} - Q \right).\end{aligned}\quad (18.35)$$

From (18.34) we find that when the field is along OZ , two of the eigenstates are $|\pm \tilde{\frac{3}{2}}\rangle$ and the other two a mixture of the states $|\pm \tilde{\frac{1}{2}}\rangle$. The eigenvalues are

$$\begin{aligned}y_{1,2} &= \pm \left(\frac{P-Q}{2} \right), \\ y_{3,4} &= \pm \frac{1}{2} \sqrt{\{3(P^2+Q^2)+2PQ\}}.\end{aligned}\quad (18.36)$$

Obviously (18.36) could have been obtained directly by solving the secular equation (18.30). It is clear from (18.35) that the transitions $\Delta M = 0, \pm 3$ between the levels y_3 and y_4 are forbidden for an oscillatory magnetic field perpendicular to the trigonal axis, and it can be shown that they are also forbidden for an oscillatory field along this axis.

Comparison with experiment

A good example for which we can compare the foregoing theory with experiment is the spectrum of Er^{3+} , $4f^{11}$, $^4I_{15/2}$ in MgO . In a cubic field the $J = \frac{15}{2}$ manifold splits into five levels, of which three are Γ_8 quadruplets; resonance has been observed in the lowest of these, which is the ground state of the ion in MgO . Assuming a value of $\langle J \| \Lambda \| J \rangle = \frac{6}{5}$

(the simple Landé value) Descamps and Merle d'Aubigné (1964) found that the resonance results, both for H along a fourfold and along a threefold axis, corresponded to

$$P' = \langle \tilde{\frac{3}{2}} | J_z | \tilde{\frac{3}{2}} \rangle = 4.925,$$

$$Q' = \langle \tilde{\frac{1}{2}} | J_z | \tilde{\frac{1}{2}} \rangle = 1.925.$$

In the expansions

$$\begin{aligned} |\tilde{\frac{3}{2}}\rangle &= \sum_{M_J} C_{M_J} |J, M_J\rangle, \\ |\tilde{\frac{1}{2}}\rangle &= \sum_{M_J} C'_{M_J} |J, M_J\rangle, \end{aligned} \quad (18.37)$$

the C_{M_J} and C'_{M_J} , tabulated by Lea, Leask, and Wolf (1962), are functions of the parameter x defined in eqn (18.14). This parameter is overdetermined by the two relations,

$$\begin{aligned} P' &= \sum_{M_J} M_J |C_{M_J}(x)|^2, \\ Q' &= \sum_{M_J} M_J |C'_{M_J}(x)|^2, \end{aligned} \quad (18.38)$$

and, using the tables of Lea, Leask and Wolf (1962) slightly different values of x are obtained from the two eqns (18.38), respectively:

$$x = 0.765 \pm 0.005 \text{ from } P',$$

and

$$x = 0.715 \pm 0.005 \text{ from } Q'.$$

However a unique value of x can be obtained if in the relation $\mu = -\beta\Lambda\mathbf{J}$, Λ is given a value smaller than $\frac{6}{5}$ by a factor 0.983. Such a reduction could perhaps be caused by a spread of the wave-functions of the magnetic electrons on the neighbouring atoms, a phenomenon which as we shall see in the chapter on covalent bonding leads to a reduction of the orbital g -factor below its value of one. This reduction is similar to those found necessary in several Γ_6 , Γ_7 doublets, and in this case it leads to corrected values $P'' = 5.01$, $Q'' = 1.960$ which correspond to a unique value of $x = 0.72$.

A number of other results in reasonable if not perfect agreement with the theory of the Γ_8 quadruplet are mentioned in § 5.8. Here we merely note that if Γ_8 occurs only once in the decomposition of D^J , the values of P' , Q' are independent of x and can be calculated from eqns (18.37) and (18.38) using the values of C_{M_J} , C'_{M_J} given in Table 9, yielding the results:

$$\begin{aligned} J = \frac{5}{2}; P' &= -\frac{1}{6}, Q' = +\frac{1}{2}, \\ J = \frac{7}{2}; P' &= +\frac{1}{2}, Q' = -\frac{1}{6}. \end{aligned} \quad (18.39)$$

In general there are two possible ways of choosing which pair of states to call $|\pm\frac{3}{2}\rangle$ and which $|\pm\frac{1}{2}\rangle$. A natural choice, which has been followed above, is to denote by $|\tilde{M}\rangle$ that state which under a rotation through an angle $\omega = \pi/2$ or π about the Oz axis simply multiplies the state by $e^{-i\omega\tilde{M}}$. Then reference to Table 9 shows that in any Γ_8 quadruplet for J up to $\frac{7}{2}$ the $|J, M_J\rangle$ states always contain one pair in which $M_J = \pm\frac{1}{2}$ occurs, and on the above choice these become $|\tilde{M}\rangle = |\pm\frac{1}{2}\rangle$, while the companion pair contains $M_J = \pm\frac{3}{2}$, which similarly become $|\pm\frac{3}{2}\rangle$. The same result holds for higher values of J .

The effect of crystalline distortions on a Γ_8 quadruplet

There is an important qualitative difference between the transitions $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$, $+\frac{3}{2} \leftrightarrow -\frac{3}{2}$ on the one hand, and the transitions $+\frac{3}{2} \leftrightarrow +\frac{1}{2}$, $-\frac{1}{2} \leftrightarrow -\frac{3}{2}$ on the other: the former occur within two pairs of Kramers-conjugate states. It follows that in first order they are insensitive to small distortions of the crystal potential. Also, when higher-order Zeeman effects are considered, the change in resonant frequency involves terms proportional to H^3 . On the other hand, the frequencies of the transitions $+\frac{3}{2} \leftrightarrow +\frac{1}{2}$, $-\frac{1}{2} \leftrightarrow -\frac{3}{2}$ (and obviously also $\pm\frac{3}{2} \leftrightarrow \mp\frac{1}{2}$, if allowed) are affected by a crystalline distortion in first order, and by a higher-order Zeeman effect in second order. In large magnetic fields along a fourfold axis, for example, random crystalline distortions are likely to result in two relatively broad transitions of energy $(P-Q) \pm \alpha H^2$, while the transitions at $2P$ and $2Q$ (modified by terms in H^3) are much sharper.

For a *tetragonal* distortion, whose effect is small compared with the energy separation to other cubic levels, we may add a term $D\{\tilde{S}_z^2 - \frac{1}{3}\tilde{S}(\tilde{S}+1)\}$ to the Zeeman Hamiltonian $-(\boldsymbol{\mu} \cdot \mathbf{H})$, the components of $-\boldsymbol{\mu}/\beta$ being given by eqns (18.17), (18.19) or the matrix elements (18.16), (18.29).

For a *trigonal* distortion a similar term can be added, the OZ axis in this case being the threefold axis. The components of $-\boldsymbol{\mu}/\beta$ are then given by the matrix elements (18.34), (18.35).

If the effect of the distortion, expressed by the constant D , is much larger than the Zeeman energy, we can regard the quadruplet Γ_8 as split into two independent Kramers doublets, each of which has a g -tensor' (neglecting off-diagonal effects of the Zeeman interaction between the two doublets) given by the following formulae.

(a) *Tetragonal distortion*

The two doublets are clearly $|\pm\frac{\tilde{3}}{2}\rangle$ and $|\pm\frac{\tilde{1}}{2}\rangle$. For the former, it follows from the last matrix element in (18.29) that we must identify one pair of states as $|+\rangle = |-\frac{\tilde{3}}{2}\rangle$ and $|-\rangle = |+\frac{\tilde{3}}{2}\rangle$. Then, using also eqn (18.16), we have

$$\begin{aligned} g_{\parallel} &= 2\langle + | -\mu_z/\beta | + \rangle = -2P, \\ |g_{\perp}| &= 2|\langle - | -\mu_x/\beta | + \rangle| = \frac{1}{2}|(P-3Q)|; \end{aligned} \quad (18.40)$$

and

$$g^2 = (2P \cos \theta)^2 + \{\frac{1}{2}(P-3Q) \sin \theta\}^2, \quad (18.41)$$

where θ is the angle that **H** makes with the axis of tetragonal distortion. Here we note that g_{\perp} is not zero as it would be if our Γ_8 were an ordinary $D^{\frac{3}{2}}$ quadruplet, for which $(P-3Q) = 0$.

For the other doublet $|\pm\rangle = |\pm\frac{\tilde{1}}{2}\rangle$, we have

$$g_{\parallel} = 2Q, \quad |g_{\perp}| = \frac{1}{2}|(3P-Q)|; \quad (18.42)$$

and

$$g^2 = (2Q \cos \theta)^2 + \{\frac{1}{2}(3P-Q) \sin \theta\}^2. \quad (18.43)$$

(b) *Trigonal distortion*

For the doublet $|\pm\frac{\tilde{3}}{2}\rangle$ we may take $|+\frac{\tilde{3}}{2}\rangle$ and $|-\frac{\tilde{3}}{2}\rangle$ as basic states and we find from (18.34) that the 'tensor' $g_{q\alpha}$ defined in (15.31) has off-diagonal components

$$|g_{z1}| = \sqrt{(2)} \left| \frac{P}{3} - Q \right|, \quad g_{z2} = 0, \quad g_{z3} = \frac{5P+3Q}{3}, \quad (18.44)$$

whereas $g_{x\alpha} = g_{y\alpha} = 0$.

The tensor G_{pq} defined by (15.38) has one non-vanishing component

$$G_{ZZ} = g_{Z1}^2 + g_{Z2}^2 + g_{Z3}^2 = 3(P^2 + Q^2) + 2PQ, \quad (18.45)$$

and

$$g^2 = G_{ZZ} \cos^2 \theta = \{3(P^2 + Q^2) + 2PQ\} \cos^2 \theta. \quad (18.46)$$

No resonance is observable in principle in this doublet.

The doublet $|\pm\frac{\tilde{1}}{2}\rangle$ behaves quite normally and from (18.34), (18.35) we find

$$\begin{aligned} g_{\parallel} &= P - Q, \\ g_{\perp} &= P + Q, \end{aligned} \quad (18.47)$$

with

$$g^2 = (P-Q)^2 \cos^2 \theta + (P+Q)^2 \sin^2 \theta. \quad (18.48)$$

18.4. Representation of an irreducible tensor within the quadruplet Γ_8 -quadrupole coupling

To find how many constants are necessary to define an irreducible tensor T_2^a whose components provide a representation D^2 of the rotation group, we turn again to group theory. A matrix element such as $\langle \tilde{m} | T_2^a | \tilde{m}' \rangle$, where $|\tilde{m}\rangle$ and $|\tilde{m}'\rangle$ are the kets that span Γ_8 , transforms under the rotations of the cubic group like

$$\Gamma_8 \times D^2 \times \Gamma_8 = \Gamma_8 \times (\Gamma_3 + \Gamma_5) \times \Gamma_8.$$

The product $\Gamma_8 \times \Gamma_8$ contains Γ_3 once and Γ_5 twice. *A priori* three constants are thus necessary to define a tensor T_2 within a multiplet Γ_8 . However, as we saw in § 15.9, more detailed predictions can be made if the tensor T_2 has a definite time-reversal parity. This is the case for the quadrupole tensor which is time-even. Therefore according to the rules given in § 15.9 it is the antisymmetric product $[\Gamma_8 \times \Gamma_8]_A$ which must contain Γ_3 and Γ_5 , and we see in Table 8 that it contains each of them once. Two constants are thus necessary to specify the quadrupole moment tensor of the ion inside a multiplet Γ_8 .

We can obtain the same result by writing out the combinations of various products of the components $\tilde{S}_x, \tilde{S}_y, \tilde{S}_z$ of the fictitious spin $\frac{3}{2}$, which transform according to a given representation of the cubic group.

We have already seen that $\tilde{S}_x, \tilde{S}_y, \tilde{S}_z$ and $\tilde{S}_x^3, \tilde{S}_y^3, \tilde{S}_z^3$ each provide a representation of Γ_4 . $\tilde{S}_x^2 - \tilde{S}_y^2$ and $3\tilde{S}_z^2 - \tilde{S}(\tilde{S}+1)$ transform like Γ_3 and $(\tilde{S}_x\tilde{S}_y + \tilde{S}_y\tilde{S}_x)$, etc. like Γ_5 . A second representation of Γ_5 is provided by $\tilde{S}_z(\tilde{S}_x^2 - \tilde{S}_y^2) + (\tilde{S}_x^2 - \tilde{S}_y^2)\tilde{S}_z$, etc., but it is time-odd and cannot represent an electric quadrupole moment. It is contained in the symmetrical product $[\Gamma_8 \times \Gamma_8]_S$.

Within Γ_8 we have the following relations:

$$\begin{aligned} \sum_i \frac{3z_i^2 - r_i^2}{r_i^5} &= a\{3\tilde{S}_z^2 - \tilde{S}(\tilde{S}+1)\}, \\ \sum_i \frac{x_i y_i}{r_i^5} &= b(\tilde{S}_x\tilde{S}_y + \tilde{S}_y\tilde{S}_x). \end{aligned} \quad (18.49)$$

The quadrupole interaction within Γ_8 can thus be written (cf. § 17.1) as

$$\frac{-e^2 Q \langle r_q^{-3} \rangle}{I(2I-1)} \langle L \| \alpha \| L \rangle \left[\frac{m}{6} \sum_{q=1}^3 \{3I_q^2 - I(I+1)\} \{3\tilde{S}_q^2 - \tilde{S}(\tilde{S}+1)\} + \right. \\ \left. + \frac{3n}{4} \sum_{p \neq q} (I_p I_q + I_q I_p) (\tilde{S}_p \tilde{S}_q + \tilde{S}_q \tilde{S}_p) \right], \quad (18.50)$$

where m and n are two constants that depend on the particular manifold Γ_8 under consideration. They are equal if Γ_8 is an ordinary quadruplet, $J = \frac{3}{2}$.

If the multiplet Γ_8 results from the decomposition of a single J ,

$$m = \frac{\langle J \| \alpha \| J \rangle \langle \frac{3}{2} | 3J_z^2 - J(J+1) | \frac{3}{2} \rangle}{\langle L \| \alpha \| L \rangle 3} \quad (18.51)$$

and

$$n = \frac{\langle J \| \alpha \| J \rangle \langle \frac{3}{2} | J_z J_+ + J_+ J_z | \frac{1}{2} \rangle}{\langle L \| \alpha \| L \rangle 2\sqrt{3}}.$$

The constants m and n can be calculated from the expansions (18.37) of the kets $|\tilde{m}\rangle$ that span Γ_8 .

The pseudo-nuclear Zeeman coupling given in formula (18.4) will have the following general form quite different from that of a Kramers doublet:

$$\begin{aligned} \frac{Z_n^*}{-\beta_n g_n} = & p(\mathbf{H} \cdot \mathbf{I}) + q[H_x I_x \{3\tilde{S}_x^2 - \tilde{S}(\tilde{S}+1)\} + H_y I_y \{3\tilde{S}_y^2 - \tilde{S}(\tilde{S}+1)\} + \\ & + H_z I_z \{3\tilde{S}_z^2 - \tilde{S}(\tilde{S}+1)\}] + r\{(H_x I_y + H_y I_x)(\tilde{S}_x \tilde{S}_y + \tilde{S}_y \tilde{S}_x) + \\ & + (H_y I_z + H_z I_y)(\tilde{S}_y \tilde{S}_z + \tilde{S}_z \tilde{S}_y) + (H_z I_x + H_x I_z)(\tilde{S}_z \tilde{S}_x + \tilde{S}_x \tilde{S}_z)\}. \end{aligned} \quad (18.52)$$

18.5. Non-Kramers ions in the rare-earth group

These ions have been much less studied by resonance methods than the Kramers ions, for several reasons.

(a) There may be no degeneracy left even in the absence of an applied magnetic field and the distance between two neighbouring levels may be outside the range of microwave spectrometers. This requirement is all the more restrictive because, as we saw in Chapter 10, the relaxation times of non-Kramers ions are so short in many cases that only at helium temperatures can the resonance be observed at all. The two sublevels between which the resonance can be observed must then necessarily be the lowest or among the lowest of the bound ion, in order to have non-negligible populations.

(b) When the symmetry of the surroundings is such that there is still some degeneracy left in the absence of a magnetic field, this degeneracy can be lifted by slight local departures from the general symmetry due to crystal imperfections. This will result in an inhomogeneous broadening of the line.

We now consider briefly the main features of magnetic resonance for non-Kramers ions of the rare-earth group.

If the crystal potential had purely axial symmetry, a manifold J would be split into a singlet $J_z = 0$ together with J doublets $J_z = \pm M$. However in practice we find axes with 6-, 3-, 4-, or 2-fold symmetry.

(a) Sixfold symmetry effectively exists in the ethylsulphates and anhydrous trichlorides: with C_{3h} symmetry there are matrix elements $|\Delta M| = 6$, which couple together the states $M = \pm 3$, and also couple states $M = \pm 6$ with the state $M = 0$ and hence indirectly with one another. The behaviour of states $|\xi\rangle = \sum C_M |M\rangle$ with $M = 3p$ is thus different from those with $M = 3p \pm 1$.

(b) Threefold symmetry, typical of the double nitrates with nearly C_{3v} symmetry, gives additional matrix elements $|\Delta M| = 3$ which couple more states together but do not further lift the degeneracy found with sixfold symmetry.

(c) Fourfold symmetry, for which CaWO_4 is a typical host lattice, provided the full local symmetry at the Ca^{2+} site is not disturbed by charge compensation when a tripositive lanthanide ion is introduced, produces matrix elements $|\Delta M| = 4$. These couple together the states $M = \pm 2$, and hence indirectly those with $M = \pm 6$; also states $M = \pm 4$ (and hence indirectly $M = \pm 8$) are coupled to $M = 0$. Thus in this case states with even values of M behave differently from those with odd values of M .

(d) Twofold symmetry produces matrix elements $|\Delta M| = 2$, which couple all states of even M to one another, and all states of odd M to one another.

As an example of time-conjugate states that are not coupled with one another we may take the lowest doublet of Pr^{3+} , $4f^2$, 3H_4 in the double nitrate, for which the states given by eqn (5.67) are

$$\begin{aligned} |\xi_0\rangle &= \alpha | +4\rangle + \beta | +1\rangle + \gamma | -2\rangle, \\ |\bar{\xi}_0\rangle &= \alpha | -4\rangle - \beta | -1\rangle + \gamma | +2\rangle. \end{aligned} \quad (18.53)$$

The Zeeman Hamiltonian $Z = \Lambda\beta(\mathbf{J} \cdot \mathbf{H})$ has opposite expectation values in the two states $|\xi_0\rangle$ and $|\bar{\xi}_0\rangle$, separating them in energy by

$$2\langle \xi_0 | Z | \xi_0 \rangle = 2\Lambda\beta H_z(4\alpha^2 + \beta^2 - 2\gamma^2) = g_{\parallel}\beta H_z. \quad (18.54)$$

There are no off-diagonal elements between the two states (18.53), making it impossible to induce resonance transitions between them. This is a direct consequence of the discussion in § 15.4: for an even number of electrons, $\theta^2 = +1$, and a time-odd operator such as Z has opposite expectation values in two states conjugated by time reversal but with no matrix elements between them. Note that although

values of M differing by unity appear in $|\xi_0\rangle$ and $|\bar{\xi}_0\rangle$, the change in sign of the coefficient of the $|\pm 1\rangle$ states (which follows from the rules for the time-reversal operator given in § 15.5) makes the matrix element $\langle \bar{\xi}_0 | J_x | \xi_0 \rangle = 0$.

A local distortion of crystal symmetry would result in a change $\Delta V(\mathbf{r})$ in the crystal potential seen by the ion. $\Delta V(\mathbf{r})$ is a time-even operator and, as shown in § 15.4, it will have the same expectation value in $|\xi_0\rangle$ and $|\bar{\xi}_0\rangle$, which displaces both levels by the same amount and will not affect the resonance frequency. However there is nothing to prevent $\Delta V(\mathbf{r})$ from having off-diagonal matrix elements between $|\xi_0\rangle$ and $|\bar{\xi}_0\rangle$ of the general form

$$\langle \xi_0 | \Delta V(\mathbf{r}) | \bar{\xi}_0 \rangle = \langle \bar{\xi}_0 | \Delta V(\mathbf{r}) | \xi_0 \rangle^* = \frac{\Delta_x + i\Delta_y}{2}.$$

Inside the doublet spanned by $|\xi_0\rangle$ and $|\bar{\xi}_0\rangle$ we may introduce a fictitious spin $\tilde{S} = \frac{1}{2}$ with

$$\begin{aligned} \langle \xi_0 | \tilde{S}_z | \xi_0 \rangle &= -\langle \bar{\xi}_0 | \tilde{S}_z | \bar{\xi}_0 \rangle = \frac{1}{2}, \\ \langle \xi_0 | \tilde{S}_x | \bar{\xi}_0 \rangle &= i\langle \xi_0 | \tilde{S}_y | \bar{\xi}_0 \rangle = \frac{1}{2}. \end{aligned} \quad (18.55)$$

The spin Hamiltonian for this doublet can then be written as

$$\mathcal{H} = g_{\parallel} \beta H_z \tilde{S}_z + \Delta_x \tilde{S}_x + \Delta_y \tilde{S}_y, \quad (18.56)$$

with

$$g_{\parallel} = 2\langle \xi_0 | \tilde{S}_z | \xi_0 \rangle = 2\langle J_{\parallel} | \Lambda | J_{\parallel} \rangle \langle \xi_0 | J_z | \xi_0 \rangle, \quad (18.57)$$

where the last expression for g_{\parallel} is appropriate to a rare-earth ion. The eigenvalues of (18.56) are given by

$$W = \pm \frac{1}{2}(\hbar\omega) = \pm \frac{1}{2}\{(g_{\parallel}\beta H_z)^2 + \Delta^2\}^{\frac{1}{2}} \quad (18.58)$$

where $\Delta^2 = \Delta_x^2 + \Delta_y^2$. The eigenstates are no longer just $|\xi_0\rangle$, $|\bar{\xi}_0\rangle$ but become

$$\begin{aligned} |\xi\rangle &= a|\xi_0\rangle + b|\bar{\xi}_0\rangle, \\ |\eta\rangle &= b^*|\xi_0\rangle - a^*|\bar{\xi}_0\rangle. \end{aligned} \quad (18.59)$$

These are no longer conjugate states under time reversal, and the operator \tilde{S}_z has matrix elements between them. This makes it possible for an oscillatory field, *parallel* to the z -axis and at the frequency corresponding to $(\hbar\omega)$, to induce transitions between them. The transition probability is given by the square of the matrix element, $|\mu_z\mu_z^*|$, whose value is given by

$$|\mu_z\mu_z^*| = \frac{1}{4}g_{\parallel}^2\beta^2\frac{\Delta^2}{(\hbar\omega)^2}. \quad (18.60)$$

If $\Delta^2 \ll (\hbar\omega)^2$, this will of course be considerably smaller than that of an ordinary allowed transition.

The existence of distortions represented by the terms in Δ_x , Δ_y is to be expected on the basis of the Jahn–Teller theorem, to be discussed in Chapter 21, which predicts that a state with electronic non-Kramers degeneracy may be unstable against small distortions of the surroundings, which would lower the symmetry of the crystal potential and lift the degeneracy. One may suppose that Δ_x and Δ_y vary from one site to another, independently of each other, and in a random way. If we assume a Gaussian distribution for Δ_x and Δ_y , Δ^2 will have an exponential distribution of the form

$$P(\Delta^2) d(\Delta^2) = \exp\left(-\frac{\Delta^2}{\Delta_0^2}\right) d\left(\frac{\Delta^2}{\Delta_0^2}\right) \quad (18.61)$$

where Δ_0^2 is the average value of Δ^2 .

Since the transition probability according to (18.60) is proportional to Δ^2 the resonance line will have an unusual shape which (assuming all other causes of broadening negligible) is given by

$$I(\Delta^2) d(\Delta^2) = \frac{\Delta^2}{\Delta_0^2} \exp\left(-\frac{\Delta^2}{\Delta_0^2}\right) d\left(\frac{\Delta^2}{\Delta_0^2}\right). \quad (18.62)$$

The resonance is usually observed by keeping the microwave frequency ($\omega/2\pi$) constant and sweeping the field, which we assume from now on to be parallel to the crystal axis: $H_z = H$. We define the symbols

$$H_0 = \frac{\hbar\omega}{g_{\parallel}\beta}, \quad h = H_0 - H, \quad (18.63)$$

in terms of which eqn (18.58) can be rewritten

$$(\hbar\omega)^2 = \Delta^2 + g_{\parallel}^2\beta^2(H_0 - h)^2,$$

giving

$$h \approx \frac{\Delta^2}{2g_{\parallel}^2\beta^2H_0}. \quad (18.64)$$

For values of $h \ll H_0$, we further introduce the symbol

$$h_0 = \frac{\Delta_0^2}{2g_{\parallel}^2\beta^2H_0}, \quad (18.65)$$

and the line shape obtained by sweeping the field will have the form

$$I(h) dh = \frac{h}{h_0} \exp\left(-\frac{h}{h_0}\right) d\left(\frac{h}{h_0}\right). \quad (18.66)$$

The line will have a cut-off for $h = 0$ which from (18.63) is at the high-field end, a maximum for $h = h_0$, or $H = H_0 - h_0$ and a rather long tail towards low fields. Increasing the microwave frequency should make the line narrower since h_0 is proportional to ω^{-1} , but also less intense since the transition probability varies as ω^{-2} . The existence of such a cut-off is independent of the particular form (18.61) assumed for the distribution $P(\Delta^2)$ and follows from (18.58) and (18.60). It permits a more accurate measurement of g_{\parallel} than would be expected from the overall line width.

If a hyperfine structure is present, it is necessarily of the form AI_zS_z and the only change is, for each hyperfine component, the replacement in (18.58) of $g_{\parallel}\beta H$ by $(g_{\parallel}\beta H + Am)$, where $m = I_z$. The hyperfine lines are identical and separated from each other by an interval A . If A is smaller than $g_{\parallel}\beta h_0$, they will overlap. A quadrupole term of the form $P_{\parallel}I_z^2$ will not affect the resonant frequencies since all transitions are of the type $\Delta m = 0$.

Para-electric transitions

It must be pointed out that the fictitious spin $\tilde{S} = \frac{1}{2}$ introduced above for non-Kramers doublets differs in an important respect from that discussed in § 15.6 for Kramers doublets. There the three components of \tilde{S} were time-odd operators, whereas here \tilde{S}_z is time-odd but \tilde{S}_x, \tilde{S}_y are necessarily time-even operators. This is a serious drawback in the spin $\tilde{S} = \frac{1}{2}$ formalism for a non-Kramers doublet, and Mueller (1968) has suggested alternative formalisms in which this drawback does not occur. A simple possibility is to take an $\tilde{S} = 1$ manifold in which the $\tilde{S}_z = 0$ state is suppressed, or removed by a term such as $D\tilde{S}_z^2$ away from the two $\tilde{S}_z = \pm 1$ states, which are left as a non-Kramers doublet, well isolated if $D \gg (\hbar\omega)$; (cf. § 3.14, where we led up to the subject of non-Kramers doublets by discussing the case of $S = 2$ with a splitting of the form $D\tilde{S}_z^2$).

An important point made independently by Williams (1967) and by Culvahouse, and Schinke and Foster (1967) is that for a non-Kramers ion at a site lacking in full inversion symmetry, there may be terms linear in an electric field for a non-Kramers doublet. For example, if the crystal field has odd parity for reflection in a plane normal to the x -axis, the system may have a permanent *electric* dipole along this axis whose interaction with an applied *electric* field may be represented (in the $\tilde{S} = \frac{1}{2}$ formalism) by a term of the form $g_x^{(E)}\beta\tilde{S}_xE_x$. In C_{3h} symmetry, where the only plane of even reflection symmetry is normal

to the z -axis, there will be an equivalent term for the y -axis, giving altogether

$$g_{\perp}^{(E)} \beta (\tilde{S}_x E_x + \tilde{S}_y E_y). \quad (18.67)$$

Thus if random crystal distortions are also present, the Hamiltonian becomes (with $\tilde{S} = \frac{1}{2}$)

$$\mathcal{H} = g_{\parallel} \beta H_z \tilde{S}_z + (\Delta_x + g_{\perp}^{(E)} \beta E_x) \tilde{S}_x + (\Delta_y + g_{\perp}^{(E)} \beta E_y) \tilde{S}_y, \quad (18.68)$$

which gives again eigenstates of the form (18.59), with suitably modified values of the coefficients a , b . The change in resonance frequency resulting from an applied static electric field follows from (18.58) if we replace Δ^2 by

$$\Delta'^2 = (\Delta_x + g_{\perp}^{(E)} \beta E_x)^2 + (\Delta_y + g_{\perp}^{(E)} \beta E_y)^2, \quad (18.69)$$

but with experimentally feasible values of the electric field it may not be easy to detect. More important is the fact that transitions between the two components of the doublet may be induced by a resonant microwave *electric* field *perpendicular* to the z -axis. The matrix elements for this and the transition rate are given by eqns (3.109)–(3.111); a significant feature is that the line shape is different (see Fig. 3.26). Transitions are now allowed for $\Delta_x = \Delta_y = 0$, because the perpendicular electric field has matrix elements between the states $|\xi_0\rangle$, $|\xi'_0\rangle$, in contrast with the magnetic field along the z -axis, for which matrix elements between the states exist only for $|\xi\rangle$, $|\eta\rangle$ and hence depend on the presence of a crystalline distortion. Experimental verification that the transitions in some praseodymium compounds are primarily due to the microwave electric field is discussed in § 3.14 (see particularly Fig. 3.27).

Non-Kramers doublets with 'allowed' magnetic transitions

It was shown in § 3.14 that for an ion with $S = 2$ and a large splitting of the form DS_z^2 , the $S_z = \pm 2$ states are slightly split if a term $E(S_x^2 - S_y^2) = V_2^2$ is present. The latter has matrix elements between the $S_z = 0$ state and the $S_z = \pm 2$ states, giving a splitting of the latter states, with an allowed transition between them when an oscillatory magnetic field at the resonance frequency is applied along the z -axis. This differs from the situation considered above because the V_2^2 term may have a unique value determined by the crystal potential in a perfect crystal instead of a range of values associated with crystal imperfections or Jahn–Teller distortions. The transition $+2 \leftrightarrow -2$ then has a sharp energy as far as the crystal potential is concerned,

giving a line of normal shape whose width is determined by other interactions such as spin-spin and spin-lattice relaxation.

A similar situation can arise for non-Kramers ions of the rare-earth group on sites of 2-, 3-, 4-, or 6-fold symmetry. Since it is easier to discuss a concrete example, we consider the case of Tb^{3+} , $4f^8$, 7F_6 in the ethylsulphate (Baker and Bleaney 1958), where the ground doublet is $|J_z\rangle = |\pm 6\rangle$ with a small admixture of the state $|J_z\rangle = |0\rangle$. The component μ_z of the magnetic moment parallel to the applied field does have matrix elements between the two states spanning the ground doublet even in the absence of local distortions of the crystal potential and the lines are relatively narrow. The experimental value $g_{\parallel} = 17.72$ is very nearly the value $12\Lambda = 18$ that one would expect for a doublet $|\pm 6\rangle$, but it is precisely the difference $g_{\parallel} - 18$, together with a splitting $\Delta = 0.387 \text{ cm}^{-1}$, that we have to explain.

In the absence of an applied field it is simplest to start from the states

$$\begin{aligned} |6^s\rangle &= \frac{1}{\sqrt{2}} \{|6\rangle + |-6\rangle\}, \\ |6^a\rangle &= \frac{1}{\sqrt{2}} \{|6\rangle - |-6\rangle\}. \end{aligned} \quad (18.70)$$

The term V_6^s of the crystal potential admixes into $|6^s\rangle$ a certain amplitude q of the higher state $|0\rangle$ and pushes it down by a certain amount Δ ; but $|6^a\rangle$ is not coupled to $|0\rangle$. In first-order perturbation theory

$$q = -\frac{c\sqrt{2}}{d}, \quad \Delta = \frac{2c^2}{d}, \quad (18.71)$$

where

$$c = \langle 0 | V_6^s | 6 \rangle, \quad d = \langle 0 | V | 0 \rangle - \langle 6 | V | 6 \rangle.$$

The use of perturbation theory is justified *a posteriori* by the fact that experimentally it turns out that $|c| \ll d$.

The basic states are then, with $p^2 + q^2 = 1$,

$$\begin{aligned} |\xi'\rangle &= p |6^s\rangle + q |0\rangle, \\ |\eta'\rangle &= |6^a\rangle. \end{aligned} \quad (18.72)$$

In the presence of a magnetic field it is convenient to replace $|\xi'\rangle$ and $|\eta'\rangle$ by the linear combinations

$$\begin{aligned} |\xi\rangle &= \frac{|\xi'\rangle + |\eta'\rangle}{\sqrt{2}} = \frac{1+p}{2} |6\rangle - \frac{1-p}{2} |-6\rangle + \frac{q}{\sqrt{2}} |0\rangle, \\ |\eta\rangle &= \frac{|\xi'\rangle - |\eta'\rangle}{\sqrt{2}} = -\frac{1-p}{2} |6\rangle + \frac{1+p}{2} |-6\rangle + \frac{q}{\sqrt{2}} |0\rangle. \end{aligned} \quad (18.73)$$

The Zeeman coupling $-\boldsymbol{\mu} \cdot \mathbf{H} = \Lambda\beta(\mathbf{J} \cdot \mathbf{H})$ has no matrix elements between $|\xi\rangle$ and $|\eta\rangle$ and opposite expectation values in either state:

$$\langle \xi | Z | \xi \rangle = -\langle \eta | Z | \eta \rangle = 6\Lambda\beta p H_z = 6\Lambda\beta(1-q^2)^{\frac{1}{2}} H_z. \quad (18.74)$$

With a fictitious spin $\tilde{S} = \frac{1}{2}$ the spin Hamiltonian becomes

$$\mathcal{H} = g_{\parallel} \beta H_z \tilde{S}_z + \Delta \tilde{S}_x, \quad (18.75)$$

where

$$g_{\parallel} = 12\Lambda(1-q^2)^{\frac{1}{2}} \approx 12\Lambda \left(1 - \frac{c^2}{d^2}\right); \quad \Delta = \frac{2c^2}{d}.$$

The experimental results for terbium in the ethylsulphate are discussed in § 5.6. It turns out that the major part of the difference between the measured value $g_{\parallel} = 17.72$ and the simple theoretical value of 18 is due to the influence of intermediate coupling, which leads to a value $\Lambda = 1.491$ rather than $\frac{3}{2}$. Also there are appreciable corrections to Δ through matrix elements of the crystal field with excited states such as $J = 5$.

18.6. Non-Kramers rare-earth ions in cubic surroundings

There are few experimental resonance results on non-Kramers rare-earth ions in cubic surroundings and we shall limit ourselves to a brief group theoretical discussion of the form to be expected for the spin Hamiltonian.

The ground level will belong to one of the five non-specific representations of the cubic groups Γ_1 to Γ_5 . Γ_1 and Γ_2 are non-degenerate singlet states and as shown in § 15.4 have no permanent moment. There is (in first order) no Zeeman or magnetic hyperfine energy in those states. The quadrupole interactions vanish also because the spatial symmetry is cubic; they would not vanish for a non-cubic singlet.

For the representations Γ_4 and Γ_5 , the direct products have the same decomposition:

$$\Gamma_4 \times \Gamma_4 = \Gamma_5 \times \Gamma_5 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5. \quad (18.76)$$

Since the representation Γ_4 appears only *once* on the right-hand side of (18.76) it follows that, as already explained at the beginning of § 18.3, all vectors \mathbf{V} have within either Γ_4 or Γ_5 the same representation, apart from a proportionality constant. Furthermore, as shown in § 15.9, Γ_4 is contained in $[\Gamma_4 \times \Gamma_4]_A$ and only time-odd vectors \mathbf{V} have non-vanishing matrix elements inside Γ_4 or Γ_5 . We can thus write the Zeeman coupling, as $g\beta(\mathbf{H} \cdot \tilde{\mathbf{S}})$, and the hyperfine coupling as $A(\mathbf{I} \cdot \tilde{\mathbf{S}})$, where $\tilde{\mathbf{S}}$ is a fictitious spin $\tilde{S} = 1$.

On the other hand, just as for Γ_8 , *two* constants are necessary to describe the nuclear quadrupole coupling. This coupling is represented by the same formula (18.50) as for Γ_8 ; the only change is that the fictitious spin is $\tilde{S} = 1$ rather than $\frac{3}{2}$. The formulae (18.51) giving m and n should be replaced by the following:

$$\begin{aligned} m &= \frac{\langle J \| \alpha \| J \rangle}{\langle L \| \alpha \| L \rangle} \langle \tilde{1} | 3J_z^2 - J(J+1) | \tilde{1} \rangle, \\ n &= \frac{\langle J \| \alpha \| J \rangle}{\langle L \| \alpha \| L \rangle} \frac{\langle \tilde{1} | J_z J_+ + J_+ J_z | \tilde{0} \rangle}{\sqrt{2}}. \end{aligned} \quad (18.77)$$

For instance in the Γ_8 triplet for $J = 3$, we find from the kets in Table 4 that

$$\begin{aligned} \langle \tilde{1} | 3J_z^2 - J(J+1) | \tilde{1} \rangle &= 0, \\ \frac{1}{\sqrt{2}} \langle \tilde{1} | J_z J_+ + J_+ J_z | \tilde{0} \rangle &= -\frac{1}{2}^{1/2}. \end{aligned}$$

The doublet Γ_3

This has some rather peculiar features. The direct product $\Gamma_3 \times \Gamma_3 = \Gamma_1 + \Gamma_2 + \Gamma_3$ and the matrix elements of any vector vanish within the manifold Γ_3 , which has neither Zeeman nor magnetic hyperfine energy. Since $\Gamma_3 \times \Gamma_3$ (more precisely $[\Gamma_3 \times \Gamma_3]_S$) does contain Γ_3 , this doublet does however have a non-vanishing quadrupole coupling.

The components $-e \sum_i (3z_i^2 - r_i^2)$ and $-e \sum_i (x_i^2 - y_i^2)$ of the electronic quadrupole moment, which transform according to Γ_3 , will have the same representation, apart from a proportionality factor, in *all* doublets Γ_3 and we can therefore without loss of generality choose for the states spanning Γ_3 the eigenstates of $J = 2$,

$$\begin{aligned} |a'\rangle &= \frac{|2, 2\rangle + |2, -2\rangle}{\sqrt{2}}, \\ |b'\rangle &= |2, 0\rangle; \end{aligned} \quad (18.78)$$

and use as components of the electronic quadrupole moment, $3J_z^2 - J(J+1)$ and $(J_x^2 - J_y^2)$.

The matrix representation of the quadrupole interaction which is proportional to (see eqn (17.21))

$$\frac{1}{3} \{3J_z^2 - J(J+1)\} \{3I_z^2 - I(I+1)\} + (J_x^2 - J_y^2)(I_x^2 - I_y^2) \quad (18.79)$$

becomes in the basis $|a'\rangle, |b'\rangle$

$$2 \begin{vmatrix} 3I_z^2 - I(I+1) & \sqrt{3}(I_x^2 - I_y^2) \\ \sqrt{3}(I_x^2 - I_y^2) & -\{3I_z^2 - I(I+1)\} \end{vmatrix} \quad (18.80)$$

which, by introducing a fictitious spin $\tilde{s} = \frac{1}{2}$ with

$$\langle a' | \tilde{s}_3 | a' \rangle = -\langle b' | \tilde{s}_3 | b' \rangle = \frac{1}{2},$$

corresponds to a spin Hamiltonian

$$\tilde{s}_3\{3I_z^2 - I(I+1)\} + \sqrt{3}\tilde{s}_1(I_x^2 - I_y^2). \quad (18.81)$$

We can always define two new states $|a\rangle$ and $|b\rangle$ through a unitary unimodular substitution of the basis states

$$\begin{aligned} |a'\rangle &= p|a\rangle + q|b\rangle, \\ |b'\rangle &= -q^*|a\rangle + p|b\rangle, \\ pp^* + qq^* &= 1. \end{aligned} \quad (18.82)$$

This is equivalent to a 'rotation' of the components of \tilde{s} (which has *nothing* to do with a spatial rotation of the coordinate axes). If we choose for the 'rotation'

$$\begin{aligned} \tilde{s}_1 &= \frac{-\tilde{s}_x + \tilde{s}_y}{\sqrt{2}}, \\ \tilde{s}_2 &= \frac{\tilde{s}_x + \tilde{s}_y + \tilde{s}_z}{\sqrt{3}}, \\ \tilde{s}_3 &= \frac{\tilde{s}_x + \tilde{s}_y - 2\tilde{s}_z}{\sqrt{6}}, \end{aligned} \quad (18.83)$$

where $\tilde{s}_x, \tilde{s}_y, \tilde{s}_z$ are the new components of the fictitious spin, the Hamiltonian (18.81) takes the symmetrical form

$$-\frac{2}{\sqrt{6}}[\tilde{s}_x\{3I_x^2 - I(I+1)\} + \tilde{s}_y\{3I_y^2 - I(I+1)\} + \tilde{s}_z\{3I_z^2 - I(I+1)\}]. \quad (18.84)$$

We have explained in § 13.2 how coefficients such as p and q of the unimodular transformation (18.82) are related to those of the three-dimensional 'rotation' (18.83).