

INTERMEDIATE CRYSTAL FIELDS (THE IRON GROUP)

19.1. Effect of the cubic crystal potential

WE have stated earlier that in the iron group, as contrasted with the rare-earth group, the crystal potential is as a rule much stronger than the spin-orbit coupling and that in a first step of the calculation the latter can be disregarded altogether. At this stage the distinction between Kramers and non-Kramers ions disappears, for the relevant quantum number is L rather than J and it is an integer for both types of ions.

A second difference from the rare-earth group arises from the important role played by the cubic crystal potential. In most compounds where resonance of iron-group elements has been observed, even if the local symmetry 'seen' by the paramagnetic ion is lower than cubic, the cubic part of the crystal potential is much larger than components of lower symmetry and it is very instructive for a first orientation to examine the behaviour of the various ions in a field of cubic symmetry.

An inspection of Table 19 shows that the ground terms in the iron group are S , D , F . The first is an orbital singlet unaffected by the crystal potential in the absence of spin-dependent forces. Table 3 shows that D terms are split into a doublet Γ_3 and a triplet Γ_5 , while F terms split into a singlet Γ_2 and two triplets Γ_4 and Γ_5 . The cubic potential energy may be written (eqn (16.13)) as $V_{\text{cubic}} = A_4 P_4$ (the sixth-order term gives a vanishing contribution for d -electrons) where P_4 is defined in (16.11). Within a (L, S) term, P_4 can be replaced by the equivalent operator $\beta A_4 \langle r^4 \rangle O_4(\mathbf{L})$, the values of $\beta = \langle L \| \beta \| L \rangle$ being given in Table 19 while $O_4 = O_4^0 + 5O_4^4$ is defined in Table 16. Using the matrix elements of the O_k^q operators given in Table 17 and the expansions of the wave-functions that span the various levels Γ_i , given in Table 4, the energy levels of the paramagnetic ions in the cubic field are easily computed. For D terms, with $L = 2$, we have

$$\begin{aligned} W(\Gamma_3) &= 72\beta A_4 \langle r^4 \rangle, \\ W(\Gamma_5) &= -48\beta A_4 \langle r^4 \rangle, \\ W(\Gamma_3) - W(\Gamma_5) &= 120\beta A_4 \langle r^4 \rangle, \end{aligned} \tag{19.1}$$

and for F terms, with $L = 3$, we have

$$\begin{aligned} W(\Gamma_2) &= -720\beta A_4 \langle r^4 \rangle, \\ W(\Gamma_5) &= -120\beta A_4 \langle r^4 \rangle, \\ W(\Gamma_4) &= 360\beta A_4 \langle r^4 \rangle, \end{aligned} \quad (19.2)$$

whence

$$\frac{W(\Gamma_2) - W(\Gamma_5)}{W(\Gamma_5) - W(\Gamma_4)} = \frac{5}{4}.$$

The triplet Γ_5 thus always lies between the singlet Γ_2 and the triplet Γ_4 and nearer to the latter by a factor $\frac{4}{5}$. With $B_4 = \beta A_4 \langle r^4 \rangle$, these results correspond to the splittings shown in Figs. 7.3–7.6.

If we assume that the point-charge model gives correctly at least the sign if not the magnitude of the cubic potential, we see from eqn (16.15) that A_4 is positive for octahedral coordination but negative for cubic or tetrahedral coordination, eqns (16.16), (16.17). Since, for a single d -electron, $\langle l \| \beta \| l \rangle = \frac{2}{5}$ is positive, (see Table 18), it follows from (19.1) that for such an electron in octahedral coordination the triplet Γ_5 is lower than the doublet Γ_3 by

$$120 \langle l \| \beta \| l \rangle A_4 \langle r^4 \rangle = \frac{80}{21} A_4 \langle r^4 \rangle.$$

In the point-charge model this becomes $\frac{5}{3}(e^2/R)(\langle r^4 \rangle/R^4)$. More generally from the signs of $\langle l \| \beta \| l \rangle$ in Table 18 and the formulae (19.1), (19.2), the nature of the ground multiplet within the iron group in octahedral coordination will be

$$\begin{pmatrix} d^1 & d^2 & d^3 & d^4 & d^5 & d^6 & d^7 & d^8 & d^9 \\ \Gamma_5 & \Gamma_4 & \Gamma_2 & \Gamma_3 & \Gamma_1 & \Gamma_5 & \Gamma_4 & \Gamma_2 & \Gamma_3. \end{pmatrix} \quad (19.3)$$

In cubic or tetrahedral coordination the ground multiplets will be

$$\Gamma_3 \quad \Gamma_2 \quad \Gamma_4 \quad \Gamma_5 \quad \Gamma_1 \quad \Gamma_3 \quad \Gamma_2 \quad \Gamma_4 \quad \Gamma_5. \quad (19.4)$$

The degeneracy and the spin of the ground level of an iron-group ion in a field of cubic symmetry can be predicted by a simple qualitative argument that makes it easy to memorize the important results (19.3), (19.4). Let us choose, for instance, octahedral coordination; assuming the validity of the point-charge approximation, let us consider for a single d -electron the two wave-functions $x^2 - y^2$ and xy which belong respectively to Γ_3 and Γ_5 and are obtained the one from the other by a $\pi/4$ rotation around the z -axis. The function xy vanishes along the x -axis and y -axis where four of the six negative charges surrounding the paramagnetic ion are situated. The electrostatic repulsion between

a d -electron and these charges will thus be smaller for the xy function than for the x^2-y^2 function (which has maxima along these axes) and the triplet Γ_5 will be lower than the doublet Γ_3 . The $3d$ wave-functions that span Γ_5 are usually called $d\varepsilon$ in the literature, while the two functions of Γ_3 are called $d\gamma$ (an alternative nomenclature is respectively t_{2g} and e_g).

With more than one d -electron, we obviously lower the energy of the ion by placing further electrons in the orbitals $d\varepsilon$ at lower energy.

On the other hand, because of Hund's rule we also reduce the energy of electrostatic repulsion between the electrons by giving to the total spin S the maximum possible value. When there is a conflict between the two rules, as will be the case for more than three d -electrons, we assume that Hund's rule should be the determining factor. This corresponds to the assumption of a crystal potential too weak to break the LS -coupling (we shall return to this question in Chapter 20 when discussing covalent bonding). The ground states are then as shown in Fig. 7.7. With one or two electrons in the $d\varepsilon$ shell, there are three possible arrangements with parallel spin, giving a triplet orbital ground state. However, three electrons with parallel spin give a half-filled $d\varepsilon$ shell, with only one possible arrangement; thus d^3 has a singlet orbital ground state. At d^4 one electron must enter the $d\gamma$ shell in order to have parallel spin, giving a twofold orbital degeneracy, while at d^5 both the $d\varepsilon$ and the $d\gamma$ shells are half-filled, giving an orbital singlet and the maximum spin $S = \frac{5}{2}$ for the half-filled d -shell. At d^6 the extra electron enters the $d\varepsilon$ shell with antiparallel spin, giving a lower total spin; as for d^1 , the antiparallel electron has three orbital possibilities, giving an orbital triplet ground state. Further electrons can only be added with anti-parallel spin, giving a progressive reduction in the value of S ; the orbital ground state of d^7 , like that of d^2 , is a triplet, while for d^8 , like d^3 , we have an orbital singlet, in this case because the $d\varepsilon$ shell is full and the $d\gamma$ shell half-full. Finally at d^9 we have just one hole in the $d\gamma$ shell, with a twofold orbital degeneracy; at d^{10} the whole shell is closed.

We have assumed above octahedral symmetry, which gives the $d\varepsilon$ orbitals a lower energy than the $d\gamma$ orbitals. In cubic (tetrahedral) symmetry we can proceed similarly, but the $d\gamma$ shell now lies below the $d\varepsilon$ shell in energy. It is readily seen that the required results are simply equivalent to working backwards in Fig. 7.7, interchanging the configurations d^n and d^{10-n} , or just by considering the 'holes' rather than the electrons.

The results for the orbital ground state are summed up in Table 7.2.

This gives a useful classification in preparation for the deduction of the appropriate spin Hamiltonian to describe the magnetic resonance behaviour. In fact the singlet and doublet ground states can often be treated together, for the following reason. As we have seen in § 14.2, the doublet Γ_3 is 'non-magnetic', and within its manifold there are no non-vanishing matrix elements of the spin-orbit coupling $\lambda(\mathbf{L} \cdot \mathbf{S})$. If a crystal field of lower symmetry is superimposed on the cubic field, the doublet Γ_3 splits into two orbitals $|O\rangle$ and $|O'\rangle$ (except in the case of a trigonal field which does *not* split Γ_3 and requires a special treatment). Since $\lambda(\mathbf{L} \cdot \mathbf{S})$ does not couple the ground state $|O\rangle$ to $|O'\rangle$ but only to states $|n\rangle$ lying above $|O\rangle$ by energies of the order of the cubic splitting, which is much larger than $|\lambda|$, it will prove possible to use the same perturbation methods for treating the spin-orbit coupling for the doublet states as for the singlet orbital ground states. (See however § 21.3).

For simplicity we shall call these ions with singlet or doublet ground orbital states 'ions of Type *A*', while those with triplet orbital ground states will be called 'ions of Type *B*'.

19.2. 'Singlet' orbital ground states (ions of type *A*)

In this section we are concerned with ions that have an orbital ground singlet state well-separated from all excited states. By this we mean that any excited states $|n\rangle$ that have matrix elements through the spin-orbit coupling with the ground state $|O\rangle$, lie at energies W_n such that $W_n - W_0 \gg |\lambda|$. We have written 'singlet' in inverted commas in the title of this section to signify that, when appropriate, split Γ_3 doublet states are also included, as discussed in the preceding paragraph. Our aim is to discover how the ground manifold, which has no orbital degeneracy left but which still possesses a spin degeneracy of $(2S+1)$, is split by the interactions we have not so far included. These interactions are as follows.

Spin-orbit coupling:

$$W_{LS} = W'_{LS} = \lambda(\mathbf{L} \cdot \mathbf{S}). \quad (19.5)$$

Spin-spin interaction (see eqn (16.43)):

$$W_{SS} = W'_{SS} = -\rho \sum_{p,q} \left\{ \frac{L_p L_q + L_q L_p}{2} - \frac{1}{3} L(L+1) \delta_{pq} \right\} S_p S_q. \quad (19.6)$$

Zeeman interaction:

$$Z = Z' + Z'' = \beta g_s (\mathbf{H} \cdot \mathbf{S}) + \beta (\mathbf{H} \cdot \mathbf{L}). \quad (19.7)$$

Magnetic hyperfine structure (see eqn (17.61)):

$$W_\mu = W'_\mu + W''_\mu,$$

where

$$W'_\mu = \mathcal{P}[\{\xi L(L+1) - \kappa\}(\mathbf{S} \cdot \mathbf{I}) - \frac{3}{2}\xi(\mathbf{L} \cdot \mathbf{S})(\mathbf{L} \cdot \mathbf{I}) - \frac{3}{2}\xi(\mathbf{L} \cdot \mathbf{I})(\mathbf{L} \cdot \mathbf{S})], \quad (19.8)$$

$$W''_\mu = \mathcal{P}(\mathbf{L} \cdot \mathbf{I}), \quad (19.9)$$

$$\mathcal{P} = 2\beta\gamma_n\hbar\langle r^{-3} \rangle. \quad (19.10)$$

Quadrupole hyperfine structure (eqn (17.24)):

$$W_q = W'_q = \sum_{p,q} q' \{ \frac{1}{2}(L_p L_q + L_q L_p) - \frac{1}{3}\delta_{pq} L(L+1) \} \{ \frac{1}{2}(I_p I_q + I_q I_p) - \frac{1}{3}\delta_{pq} I(I+1) \}, \quad (19.11)$$

where

$$q' = \frac{-3e^2Q}{2I(2I-1)} \langle r^{-3} \rangle \langle L \parallel \alpha \parallel L \rangle. \quad (19.12)$$

Nuclear Zeeman interaction:

$$Z_n = Z'_n = -\gamma_n\hbar(\mathbf{H} \cdot \mathbf{I}). \quad (19.13)$$

We have put a single prime on the interactions that are even with respect to components of the orbital momentum \mathbf{L} and have non-vanishing expectation values in the ground manifold, and a double prime on those that are linear with respect to components of \mathbf{L} and whose expectation value, according to Van Vleck's theorem, vanishes in the ground state. Thus in first-order perturbation theory, only the single primed interactions contribute to the splitting of the ground manifold.

The states spanning this manifold can be written $|O\rangle|i\rangle$ where $|O\rangle$ represents the non-degenerate orbital wave-function, and $|i\rangle$ specifies the various $(2S+1)$ spin-substates.

In taking the expectation values of the single primed interactions it is convenient to perform the integration over the orbital variables only, leaving out the spin-dependent parts in the operator form. We obtain thus a first contribution to what is called the spin-Hamiltonian

$$-\rho l_{pq} S_p S_q + g_s \beta \mathbf{H} \cdot \mathbf{S} - \mathcal{P}(\kappa \delta_{pq} + 3\xi l_{pq}) S_p I_q + q' l_{pq} I_p I_q - \gamma_n \hbar \mathbf{H} \cdot \mathbf{I}, \quad (19.14)$$

where

$$l_{pq} = \frac{1}{2} \langle O | L_p L_q + L_q L_p | O \rangle - \frac{1}{3} L(L+1) \delta_{pq}. \quad (19.15)$$

It would, however, be grossly incorrect to content ourselves with first-order perturbation theory because the spin-orbit coupling is very

much greater than the other interactions listed in (19.6)–(19.13), and second-order contributions involving the spin-orbit coupling, either quadratically or as cross terms with other interactions, may well be comparable to the first-order terms in (19.14). We can use for the excited levels of the bound ion, which are eigenstates of the crystal potential V , the same description as for the ground manifold: $|n\rangle|j\rangle$ where $|n\rangle$ represents an orbital state with an eigenvalue W_n and $|j\rangle$ the spin substates. If we remain inside the term (L, S) of the free ion (which is a necessary condition for eqns (19.5)–(19.12) for the various interactions to be valid), there are as many spin substates, $(2S+1)$, as for the ground level. In second-order perturbation theory the relevant operator is

$$C = \sum_{\substack{n \neq 0 \\ j}} \frac{|n\rangle|j\rangle\langle j|\langle n|}{W_0 - W_n}, \quad (19.16)$$

or, since $\sum_j |j\rangle\langle j| = 1$, we can write

$$C = - \sum_{n \neq 0} \frac{|n\rangle\langle n|}{W_n - W_0} \quad (19.17)$$

which is a purely orbital operator that is clearly time-even.

Using the same procedure as for the first-order terms, namely, performing the integration over orbital variables only, we find that the double-primed operators bring in second order the following contributions to the splitting of the ground state:

$$\langle O | \lambda(\mathbf{L} \cdot \mathbf{S}) C \lambda(\mathbf{L} \cdot \mathbf{S}) | O \rangle = -\lambda^2 \sum_{p,q} \Lambda_{pq} S_p S_q, \quad (19.18)$$

where

$$\Lambda_{pq} = \sum_n \frac{\langle O | L_p | n \rangle \langle n | L_q | O \rangle}{W_n - W_0} \quad (19.19)$$

for the term quadratic in the spin-orbit coupling. From the definition (19.19), we see immediately that

$$\Lambda_{pq} = \Lambda_{qp}^*. \quad (19.20)$$

Actually it can be shown from time-reversal symmetry that Λ_{pq} is symmetrical, i.e. $\Lambda_{pq} = \Lambda_{qp}$ and is therefore real. For, since the state $|O\rangle$ is a non-degenerate eigenstate of the crystal field Hamiltonian, it must coincide within a phase factor with its time-reversed state $\theta|O\rangle$ and hence

$$\begin{aligned} -\Lambda_{pq} &= \langle O | L_p C L_q | O \rangle = \langle O, L_p C L_q O \rangle = \langle \theta L_p C L_q O, \theta O \rangle \\ &= \langle \theta L_p C L_q \theta^{-1} \theta O, \theta O \rangle = \langle L_p C L_q \theta O, \theta O \rangle = \langle \theta O, (L_p C L_q)^\dagger \theta O \rangle \\ &= \langle \theta O, L_q C L_p \theta O \rangle = \langle O | L_q C L_p | O \rangle = -\Lambda_{qp}. \end{aligned} \quad (19.21)$$

The cross term between $\lambda(\mathbf{L} \cdot \mathbf{S})$ and $Z'' = \beta(\mathbf{L} \cdot \mathbf{H})$ gives

$$\lambda\beta\langle O | (\mathbf{L} \cdot \mathbf{S})C(\mathbf{L} \cdot \mathbf{H}) + (\mathbf{L} \cdot \mathbf{H})C(\mathbf{L} \cdot \mathbf{S}) | O \rangle = -2\beta\lambda \sum_{p,q} \Lambda_{pq} H_p S_q \quad (19.22)$$

where Λ_{pq} is defined in (19.19).

The cross term between $\lambda(\mathbf{L} \cdot \mathbf{S})$ and W''_μ gives similarly:

$$-\lambda\mathcal{P}\langle O | (\mathbf{L} \cdot \mathbf{S})C(\mathbf{L} \cdot \mathbf{I}) + (\mathbf{L} \cdot \mathbf{I})C(\mathbf{L} \cdot \mathbf{S}) | O \rangle = -2\lambda\mathcal{P} \sum_{p,q} \Lambda_{pq} S_p I_q. \quad (19.23)$$

We may also consider cross terms between $\lambda(\mathbf{L} \cdot \mathbf{S})$ and single primed terms of (19.6)–(19.13). First, the spin Zeeman interaction

$$Z' = \beta g_s (\mathbf{H} \cdot \mathbf{S})$$

has no off-diagonal matrix elements between $|O\rangle$ and $|n\rangle$ and there is thus no second-order contribution from that term. There is, however, a cross term with the spin-spin interaction which is

$$\begin{aligned} -\rho\lambda\langle O | (\mathbf{L} \cdot \mathbf{S})C\left(\frac{L_p L_q + L_q L_p}{2}\right) S_p S_q + \left(\frac{L_p L_q + L_q L_p}{2}\right) S_p S_q C(\mathbf{L} \cdot \mathbf{S}) | O \rangle \\ = \frac{\rho\lambda}{2} \sum_{p,q,r} (\Lambda_{r,pq} S_r S_p S_q + \Lambda_{pq,r} S_p S_q S_r), \end{aligned} \quad (19.24)$$

where

$$\begin{aligned} \Lambda_{r,pq} &= \sum_n' \frac{\langle O | L_r | n \rangle \langle n | L_p L_q + L_q L_p | O \rangle}{W_n - W_0}, \\ \Lambda_{pq,r} &= \sum_n' \frac{\langle O | L_p L_q + L_q L_p | n \rangle \langle n | L_r | O \rangle}{W_n - W_0}. \end{aligned} \quad (19.25)$$

A time-reversal argument very similar to that used to demonstrate the symmetry of Λ_{pq} shows that $\Lambda_{r,pq} = -\Lambda_{pq,r}$. Since from Hermitian properties $\Lambda_{r,pq} = \Lambda_{pq,r}^*$, it follows that $\Lambda_{r,pq}$ is purely imaginary. Eqn (19.24) can then be rewritten

$$\frac{\lambda\rho}{2} \sum_{pq,r} \Lambda_{r,pq} [S_r, S_p S_q] \quad (19.26)$$

or, using the commutation relations $[S_r, S_p] = i \sum_j \varepsilon_{rpj} S_j$, as

$$+\lambda\rho(\Lambda'_{pq} + \Lambda'_{qp}) S_p S_q, \quad (19.27)$$

where

$$\begin{aligned} \Lambda'_{pq} &= -\frac{i}{2} \sum_{t,r} \varepsilon_{ptr} \Lambda_{r,qt} \\ &= -\frac{i}{2} \sum_{t,r} \varepsilon_{ptr} \sum_n' \frac{\langle O | L_r | n \rangle \langle n | L_q L_t + L_t L_q | O \rangle}{W_n - W_0}. \end{aligned} \quad (19.28)$$

From the symmetry of the $\Lambda_{r,qt}$ it follows that the coefficient Λ'_{pq} is real but not necessarily symmetrical. In practice (19.27) is smaller than the first-order effect of spin-spin interaction $-\rho l_{pq} S_p S_q$ given in (19.14) and indistinguishable from it.

The cross term between $\lambda(\mathbf{L} \cdot \mathbf{S})$ and W'_μ will give similarly:

$$3\xi\lambda\mathcal{P}\Lambda'_{pq}S_pI_q. \quad (19.29)$$

Finally, to be consistent we should add but will not write out the small cross term between $\lambda(\mathbf{L} \cdot \mathbf{S})$ and the quadrupole interaction W'_q .

Another second-order term which, although very small is by no means unobservable because it competes with a first-order term also small, is the nuclear pseudo-Zeeman coupling defined by eqn (18.2). This is a cross term between the magnetic hyperfine structure W''_μ and the electronic Zeeman coupling $Z'' = \beta(\mathbf{L} \cdot \mathbf{H})$. The calculation is clearly identical to that which has given the second-order hyperfine terms (19.23), provided $\lambda(\mathbf{L} \cdot \mathbf{S})$ is replaced by $\beta(\mathbf{L} \cdot \mathbf{H})$, and yields

$$-2\mathcal{P}\beta\Lambda_{pq}H_pI_q = -\gamma_n\hbar(\mathbf{H} \cdot \boldsymbol{\alpha} \cdot \mathbf{I}), \quad (19.30)$$

with

$$\alpha_{pq} = 4\beta^2\langle r^{-3} \rangle \Lambda_{pq}. \quad (19.31)$$

Gathering together all the above terms, we obtain the so-called spin Hamiltonian

$$\begin{aligned} \mathcal{H}_S = & \{-\lambda^2\Lambda_{pq} - \rho l_{pq} + \lambda\rho(\Lambda'_{pq} + \Lambda'_{qp})\}S_pS_q + \\ & + \beta(g_s\delta_{pq} - 2\lambda\Lambda_{pq})H_pS_q - \mathcal{P}(\kappa\delta_{pq} + 3\xi l_{pq} + 2\lambda\Lambda_{pq} - 3\xi\lambda\Lambda'_{pq})S_pI_q + \\ & + q'l_{pq}I_pI_q - \gamma_n\hbar H_p(\delta_{pq} + \alpha_{pq})I_q, \end{aligned} \quad (19.32)$$

which we rewrite as

$$\begin{aligned} \mathcal{H}_S = & D_{pq}S_pS_q + \beta g_{pq}H_pS_q + A_{pq}S_pI_q + \\ & + P_{pq}I_pI_q - \gamma_n\hbar\{(\mathbf{H} \cdot \mathbf{I}) + (\mathbf{H} \cdot \boldsymbol{\alpha} \cdot \mathbf{I})\}. \end{aligned} \quad (19.33)$$

We have already met various spin-Hamiltonians in previous chapters; for instance in the description of Kramers doublets (eqn (15.36)) or of the cubic multiplet Γ_8 (eqn (18.21)). There are, however, important differences between those expressions and the spin-Hamiltonian (19.33). The former spin-Hamiltonians were written *a priori* as the most general expressions in operator form capable of describing the splitting of, say, a Kramers doublet or a Γ_8 quadruplet. On the contrary (19.33) does not claim such generality; it is an expression valid to the second order of perturbation theory only but to that order of accuracy explicit theoretical expressions are given for the various coefficients that appear

in it, which may at least in principle be compared with the numerical values extracted from the study of the resonance spectrum.

An even more important difference between the previous spin Hamiltonians and (19.33) resides in the fact that the former were constructed from components of fictitious spins that bear little relation to the actual spin of the ion. This was particularly striking in the description of non-Kramers ions in the rare-earth group where, as pointed out in § 18.5, different components of the fictitious spin had different time-reversal properties.

In contrast the spin S in (19.33) is almost exactly the real spin of the ion. We say almost exactly for the following reason: the coupling of states of the ground manifold $|O\rangle |i\rangle$ with excited states $|n\rangle |j\rangle$ changes the ground manifold into perturbed states

$$|Oi\rangle = T |O\rangle |i\rangle = (1 - \alpha_i) |O\rangle |i\rangle + \sum'_{n,j} \beta_{nj} |n\rangle |j\rangle, \quad (19.34)$$

where T is a unitary operator. The β_{nj} are of first order in the ratio $\lambda/(W_n - W_0)$ while α_i is of second order. A matrix element $\langle Oi | S_q | Oi' \rangle$ will thus differ from the usual spin matrix element $\langle i | S_q | i' \rangle$ by terms of the order of α_i and $\beta_{nj} \beta_{nj}^*$, that is in second order only.

It follows that to the same approximation the coefficients D_{pq} , g_{pq} , A_{pq} in (19.33) are indeed tensors (P_{pq} and α_{pq} are always tensors since \mathbf{I} and \mathbf{H} are always real vectors). The tensors g_{pq} and D_{pq} are always symmetrical but A_{pq} is not necessarily so because of the terms Λ'_{pq} . However for symmetry no lower than rhombic, that is if the environment possesses three orthogonal binary symmetry axes, the off-diagonal elements D_{pq} , g_{pq} , A_{pq} vanish and all tensors admit these symmetry axes as principal axes. We shall demonstrate it for Λ'_{pq} which is the least obvious. According to eqn (19.28)

$$\Lambda'_{12} = i \langle O | L_3 C L_2^2 - L_2 C \left(\frac{L_2 L_3 + L_3 L_2}{2} \right) | O \rangle = i \langle O | A | O \rangle. \quad (19.35)$$

Since $|O\rangle$ is a non-degenerate eigenstate of the system, a rotation by an angle π : $R = e^{-i\pi L_1}$ around the axis Ox_1 changes $|O\rangle$ into itself (within a phase factor) whereas it changes the sign of the operator inside the symbol $\langle O | \quad | O \rangle$. Hence

$$\begin{aligned} \Lambda'_{12} &= i \langle O | A | O \rangle = i \langle O | R^+ R A R^{-1} R | O \rangle = i \langle O | R A R^{-1} | O \rangle \\ &= -i \langle O | A | O \rangle = -\Lambda'_{12} = 0. \end{aligned} \quad (19.36)$$

For lower symmetry it is conceivable in principle to have, in the

magnetic hyperfine structure, terms of the form

$$(\Lambda'_{12} - \Lambda'_{21})(S_1 I_2 - S_2 I_1) = (\Lambda'_{12} - \Lambda'_{21})(S \wedge I)_3,$$

although no such terms appear to have been observed in practice. Experimentally at least, the tensors D , g , A , P , and α have so far always been found to have the same principal axes.

With respect to these axes the spin Hamiltonian (19.33) is usually rewritten as (see Chapter 3)

$$\begin{aligned} \mathcal{H}_S = & D\{S_z^2 - \frac{1}{3}S(S+1)\} + E(S_x^2 - S_y^2) + \beta(g_x H_z S_z + g_x H_x S_x + g_y H_y S_y) + \\ & + A_x S_z I_z + A_x S_x I_x + A_y S_y I_y + P_{\parallel} \left\{ I_z^2 - \frac{1}{3}I(I+1) + \frac{1}{3}\eta(I_x^2 - I_y^2) \right\} - \\ & - \gamma_n \hbar \{(1 + \alpha_x)H_x I_x + (1 + \alpha_y)H_y I_y + (1 + \alpha_z)H_z I_z\}. \quad (19.37) \end{aligned}$$

For tetragonal or trigonal symmetry

$$\begin{aligned} E &= 0, & g_x &= g_y = g_{\perp}, & g_z &= g_{\parallel}, \\ A_x &= A_y = A_{\perp}, & A_z &= A_{\parallel}, & \eta &= 0, \\ \alpha_x &= \alpha_y = \alpha_{\perp}, & \alpha_z &= \alpha_{\parallel}. \end{aligned} \quad (19.38)$$

We wish to emphasize once more that (19.33) is *not* the most general expression for the spin-Hamiltonian permitted by symmetry considerations. For instance in cubic symmetry in order to describe correctly the observed spectrum, terms of the form $S_x^4 + S_y^4 + S_z^4$ have to be added, and sometimes small Zeeman and hyperfine couplings involving S_x^3 , S_y^3 , S_z^3 as given in eqn (18.21). These terms can be obtained by methods similar to those used in deriving (19.33) by going to higher orders in perturbation theory.

A spin Hamiltonian such as (19.33) (augmented if necessary by higher-order spin polynomials) is the meeting point between the theoretician who attempts to calculate the various coefficients in (19.33) from what is known or can be surmised about the crystal field and the wave-functions of the free ion, and the experimentalist who, using the methods of computation described in Chapter 3, extracts from the observed spectrum numerical values for the same coefficients.

19.3. Triplet orbital ground state (ions of type B)

We consider now those ions which in a cubic field have as their ground level an orbital triplet Γ_4 or Γ_5 .

Cubic symmetry

Assume first that the symmetry is exactly cubic. The degeneracy of the ground level is then $3(2S+1)$ including that due to spin. As we

pointed out earlier in § 14.2, within this manifold every orbital vector can be replaced by an equivalent vector operator $\alpha\tilde{\mathbf{l}}$, where $\tilde{\mathbf{l}}$ is a fictitious angular momentum of magnitude 1. In particular, the spin-orbit coupling can be written within this manifold as $\alpha\lambda(\tilde{\mathbf{l}} \cdot \mathbf{S})$, the values of α being tabulated in Table 4. If we neglect the admixtures into the ground manifold Γ_i , where i is 4 or 5, from excited orbital multiplets Γ_j , through spin-orbit coupling, we can couple $\tilde{\mathbf{l}}$ and \mathbf{S} according to the usual rules of angular momentum coupling and obtain $\tilde{\mathbf{J}}$ -multiplets where $\tilde{\mathbf{J}}$ is a fictitious total angular momentum that takes the values $S+1$, S , $|S-1|$. (The tilde emphasizes the fictitious character of $\tilde{\mathbf{J}}$.) In order to have a concrete example, we consider the ion Co^{2+} with a ground term 4F , split in an octahedral environment into a ground orbital triplet Γ_4 , an excited triplet Γ_5 , and an excited singlet Γ_2 . The spin-orbit coupling will lift the twelvefold degeneracy of the ground manifold into three pseudo- $\tilde{\mathbf{J}}$ multiplets $\tilde{\mathbf{J}} = \frac{1}{2}$, $\tilde{\mathbf{J}} = \frac{3}{2}$, $\tilde{\mathbf{J}} = \frac{5}{2}$ separated respectively by

$$\begin{aligned} W(\Gamma_4, \frac{5}{2}) - W(\Gamma_4, \frac{3}{2}) &= \frac{5}{2}\lambda\alpha, \\ W(\Gamma_4, \frac{3}{2}) - W(\Gamma_4, \frac{1}{2}) &= \frac{3}{2}\lambda\alpha. \end{aligned} \quad (19.39)$$

Since for Co^{2+} , which is in the second half of the $3d$ shell, λ is negative and α , from Table 4, is $-\frac{3}{2}$, the doublet $\tilde{\mathbf{J}} = \frac{1}{2}$ will be lowest. Its g -factor can be calculated by an adaptation of Landé's formula where the orbital gyromagnetic factor α or, more generally, \tilde{g}_l , is $-\frac{3}{2}$ rather than unity:

$$g(\Gamma_4, \tilde{\mathbf{J}}) = \frac{1}{\tilde{\mathbf{J}}(\tilde{\mathbf{J}}+1)}\{\tilde{g}_l(\tilde{\mathbf{l}} \cdot \tilde{\mathbf{J}}) + g_s(\mathbf{S} \cdot \tilde{\mathbf{J}})\} \quad (19.40)$$

which for $\tilde{\mathbf{J}} = \frac{1}{2}$ gives

$$\frac{5g_s - 2\tilde{g}_l}{3} \quad (19.40a)$$

or for $g_s = 2$, $\tilde{g}_l = -\frac{3}{2}$, $g_J = \frac{1}{3} = 4.33$, to be compared with experimental value obtained for Co^{2+} in MgO : $g = 4.28$. (Reasons for the slight discrepancy will be discussed in Chapters 20 and 21.)

If we tackle the same problem using orthodox group theory we find that the twelvefold degenerate ground manifold provides a representation $\Gamma_4 \times D^{\frac{3}{2}} = \Gamma_4 \times \Gamma_8$ of the cubic group which, according to Table 8, is split into:

$$\Gamma_6 + \Gamma_7 + 2\Gamma_8. \quad (19.41)$$

We recognize Γ_6 as being the level $\tilde{\mathbf{J}} = \frac{1}{2}$ and one of the representations Γ_8 as being $\tilde{\mathbf{J}} = \frac{3}{2}$. The other representation Γ_8 , and Γ_7 , originate in

the multiplet $\tilde{J} = \frac{5}{2}$ which in cubic symmetry, according to Table 7, contains the representations Γ_7 and Γ_8 . However, whereas the abstract group-theory gives us no indication about the distances between the four multiplets (19.41), our perturbation approach is much more explicit. In first approximation the distances between the various levels are given by (19.39), whereas the splitting of $\tilde{J} = \frac{5}{2}$ into Γ_7 and Γ_8 is very much smaller and due to a very much higher-order perturbation mechanism involving matrix elements of the spin-orbit coupling (for which now the correct form $\lambda(\mathbf{L} \cdot \mathbf{S})$ rather than the reduced form $\alpha\lambda(\tilde{\mathbf{L}} \cdot \mathbf{S})$ must be used) between the ground orbital triplet Γ_4 and the excited orbital multiplets Γ_2 and Γ_6 . Phenomenologically the splitting of $\tilde{J} = \frac{5}{2}$ into Γ_7 and Γ_8 can be described by an equivalent operator $(a/6)(\tilde{J}_x^4 + \tilde{J}_y^4 + \tilde{J}_z^4)$ added to the spin-Hamiltonian of $J = \frac{5}{2}$. The constant a would involve the spin-orbit constant λ in fourth order, or λ in second order and the spin-spin constant ρ in first order, or ρ in second order. Similarly the Zeeman and hyperfine structure would involve small terms in \tilde{J}_x^3 and \tilde{J}_x^5 for $\tilde{J} = \frac{5}{2}$ and terms \tilde{J}_x^3 for $\tilde{J} = \frac{3}{2}$ with coefficients that would again be polynomials in λ and ρ : (λ^4 , $\lambda^2\rho$, ρ^2 for the \tilde{J}_x^5 terms and λ^2 , ρ for the \tilde{J}_x^3 terms.)

Coming back to earth, that is to first-order perturbation theory, we are in a situation very similar to that prevailing in the rare-earth group. The main part of the magnetic hyperfine coupling will be of the form $A_J(\mathbf{I} \cdot \tilde{\mathbf{J}})$ where the constant A_J will be obtained by calculating in, say the state $|\tilde{J}, \tilde{J}_z = \tilde{J}\rangle$ the expectation value of the magnetic hyperfine structure as defined in eqn (17.61). Thus

$$A_J = \frac{\mathcal{P}}{\tilde{J}} \langle | L_z + \{\xi L(L+1) - \kappa\} S_z - \frac{3}{2}\xi \{L_z(\mathbf{L} \cdot \mathbf{S}) + (\mathbf{L} \cdot \mathbf{S})L_z\} | \rangle. \quad (19.42)$$

For instance, the state $\tilde{J} = \frac{5}{2}$, $\tilde{J}_z = \frac{5}{2}$ is the state $\tilde{l}_z = 1$, $S_z = \frac{3}{2}$. The state $\tilde{l}_z = 1$ of a multiplet Γ_4 originating in the reduction of an F -term is found from Table 4 to be: $|\tilde{1}\rangle = \sqrt{(\frac{5}{8})} | -3\rangle + \sqrt{(\frac{3}{8})} | 1\rangle$ where $| -3\rangle$ and $| 1\rangle$ refer to the value of L_z , the true orbital momentum. On replacing L by 3 in (19.42) and $| \rangle$ by $|\tilde{1}\rangle | \frac{3}{2}\rangle$ where $| \frac{3}{2}\rangle$ is an eigenstate of S_z , it is easily found that

$$A = \frac{2\mathcal{P}}{5} \left\{ \frac{-3\kappa}{2} - \frac{3}{2} - 9\xi \right\}. \quad (19.43)$$

The first term in (19.43) is the contact hyperfine interaction, the second the orbital hyperfine interaction and the third the dipolar hyperfine

interaction. For $l = 2$, $L = 3$, $S = \frac{3}{2}$, ξ , given by (17.46), has the value $\xi = -2/(9 \times 7 \times 5)$, so that

$$A_{\frac{3}{2}} = -\frac{3\mathcal{P}}{5} \left(1 + \kappa - \frac{4}{105} \right). \quad (19.44)$$

For $\tilde{J} = \frac{1}{2}$ the calculation is complicated by the fact that the state $\tilde{J} = \frac{1}{2}$, $\tilde{J}_z = \frac{1}{2}$ is

$$| \rangle = p |\tilde{1}\rangle |-\frac{1}{2}\rangle + q |\tilde{0}\rangle |\frac{1}{2}\rangle + r |-\tilde{1}\rangle |\frac{3}{2}\rangle,$$

where $p = 1/\sqrt{6}$, $q = -1/\sqrt{3}$, $r = 1/\sqrt{2}$ (cf. Table 7.18) are Clebsch-Gordan coefficients; $|\tilde{1}\rangle$, $|\tilde{0}\rangle$, $|-\tilde{1}\rangle$ the three fictitious \tilde{l}_z eigenstates given in Table 4; and $|-\frac{1}{2}\rangle$, $|\frac{1}{2}\rangle$, $|\frac{3}{2}\rangle$ eigenstates of S_z . The result is

$$A_{\frac{1}{2}} = \mathcal{P} \left(1 - \frac{5\kappa}{3} - \frac{5}{2}\xi \right) = \mathcal{P} \left(1 - \frac{5\kappa}{3} - \frac{1}{63} \right). \quad (19.45)$$

It will be seen that the dipolar hyperfine contribution, that is, the last term of (19.44) and (19.45) is very small, indicating that the distribution of spin magnetization is not far from spherical.

The nuclear electric quadrupole interaction will obviously vanish for the state $\tilde{J} = \frac{1}{2}$, since it is a Kramers doublet Γ_8 of cubic symmetry similar to those discussed in § 18.2. For higher values of \tilde{J} it can be derived as follows.

Within an orbital triplet state $l = 1$ we can use for the nuclear electric quadrupole Hamiltonian a form that is an obvious modification of eqn (17.24) in the light of the discussion preceding that equation (cf. also § 18.6):

$$\frac{-e^2 Q \langle r_q^{-3} \rangle}{I(2I-1)} \langle L \| \alpha \| L \rangle \left[\frac{m}{6} \sum_{x,y,z} \{ 3\tilde{l}_x^2 - \tilde{l}(\tilde{l}+1) \} \{ 3I_x^2 - I(I+1) \} + \right. \\ \left. + \frac{3n}{4} \sum_{x,y,z} (\tilde{l}_x \tilde{l}_y + \tilde{l}_y \tilde{l}_x) (I_x I_y + I_y I_x) \right], \quad (19.46)$$

in which the coefficients m , n are found from the equivalences

$$\begin{aligned} \{ 3L_z^2 - L(L+1) \} &= m \{ 3\tilde{l}_z^2 - \tilde{l}(\tilde{l}+1) \}, \\ (L_x L_y + L_y L_x) &= n (\tilde{l}_x \tilde{l}_y + \tilde{l}_y \tilde{l}_x). \end{aligned} \quad (19.47)$$

The values of m , n for $L = 2$ and $L = 3$ are given in Table 21.

Within a manifold (Γ_i, \tilde{J}) we can then replace the operators that occur in (19.46) in terms of \tilde{l} by similar operators in terms of \tilde{J} giving a

Hamiltonian of the form

$$\frac{-e^2 Q \langle r_q^{-3} \rangle}{I(2I-1)} \langle \tilde{J} \parallel \alpha \parallel \tilde{J} \rangle \left[\frac{n}{6} \sum_{x,y,z} \{3\tilde{J}_x^2 - \tilde{J}(\tilde{J}+1)\} \{3I_x^2 - I(I+1)\} + \right. \\ \left. + \frac{3n}{4} \sum_{x,y,z} (\tilde{J}_x \tilde{J}_y + \tilde{J}_y \tilde{J}_x)(I_x I_y + I_y I_x) \right], \quad (19.48)$$

where the value of the reduced matrix element $\langle \tilde{J} \parallel \alpha \parallel \tilde{J} \rangle$ is found from the relation

$$\frac{\langle \tilde{J} \parallel \alpha \parallel \tilde{J} \rangle}{\langle L \parallel \alpha \parallel L \rangle} = \frac{\langle \tilde{J}, \tilde{J}_z = \tilde{J} | 3\tilde{J}_z^2 - 2 | \tilde{J}, \tilde{J}_z = \tilde{J} \rangle}{\tilde{J}(2\tilde{J}-1)}. \quad (19.49)$$

The quadrupole interaction (19.48) has a form similar to that given by eqn (18.50) for a Γ_8 quartet, with \tilde{J} replacing \tilde{S} .

Finally, we compute the pseudo-nuclear Zeeman effect, arising from the cross term between the electron Zeeman interaction $-(\boldsymbol{\mu} \cdot \mathbf{H})$ and the hyperfine interaction $-\gamma_n \hbar (\mathbf{I} \cdot \mathbf{H}_e)$. This is

$$Z_n^* = -\gamma_n \hbar \sum_{\tilde{J}' \neq \tilde{J}} \frac{\langle \Gamma_i, \tilde{J} | -\boldsymbol{\mu} \cdot \mathbf{H} | \Gamma_i, \tilde{J}' \rangle \langle \Gamma_i, \tilde{J}' | \mathbf{I} \cdot \mathbf{H}_e | \Gamma_i, \tilde{J} \rangle}{W(\Gamma_i, \tilde{J}) - W(\Gamma_i, \tilde{J}')} + \text{c.c.} \quad (19.50)$$

Here $|\Gamma_i, \tilde{J}\rangle$ is the ground \tilde{J} -multiplet and

$$W(\Gamma_i, \tilde{J}) - W(\Gamma_i, \tilde{J}') = \frac{\lambda \alpha}{2} \{ \tilde{J}(\tilde{J}+1) - \tilde{J}'(\tilde{J}'+1) \}. \quad (19.51)$$

The excited cubic levels Γ_j , with $j \neq i$ bring to (19.50) a much smaller contribution because of much larger energy denominators. For $\tilde{J} > \frac{1}{2}$ Z_n^* has the same form as that given in (18.52) for Γ_8 , \tilde{S} being replaced by \tilde{J} .

19.4. Departures from cubic symmetry

If we superimpose on the cubic field K another field T of lower symmetry the situation does not change markedly for the ions of type 'A' considered in § 19.2. However for ions of type 'B', the situation may become a good deal more complicated and the general predictions of the magnetic behaviour of the ion much less detailed. A tetragonal or trigonal field will split an orbital triplet Γ_4 or Γ_5 into a singlet and a doublet. A field of lower symmetry will split it into three orbital singlets.

(a) If the lowest level is a singlet and the distance to the nearest excited orbital level (doublet or singlet) is very much larger than the

spin-orbit coupling, that is if $T \gg \lambda$, we are back to the situation for which we have derived a spin Hamiltonian in § 19.2.

(b) If T is comparable to λ , and hence very much smaller than the cubic field K , we can in first approximation neglect admixtures from the higher cubic multiplets Γ_j . Inside the manifold of degeneracy $3(2S+1)$ we can represent the non-cubic field T by the equivalent operator $T = \sum_{i \leq j} \Delta_{ij}(\tilde{l}_i \tilde{l}_j + \tilde{l}_j \tilde{l}_i)$, which by a suitable rotation of coordinate axes can be brought to the form

$$T = \Delta_1 \tilde{l}_x^2 + \Delta_2 \tilde{l}_y^2 + \Delta_3 \tilde{l}_z^2 \quad (19.52)$$

with

$$\Delta_1 + \Delta_2 + \Delta_3 = 0$$

and the spin-orbit coupling is again represented by $\alpha\lambda(\tilde{\mathbf{l}} \cdot \mathbf{S})$.

The secular equation for the diagonalization of $T + \alpha\lambda(\tilde{\mathbf{l}} \cdot \mathbf{S})$ will factorize into equations of order no higher than cubic. Once the eigenstates are found as linear combinations of states $|\tilde{l}_z\rangle |S_z\rangle$, the expectation values of $Z = \beta \mathbf{H} \cdot (g_s \mathbf{S} + \alpha \tilde{\mathbf{l}})$ can be calculated immediately.

In particular, if T has tetragonal or trigonal symmetry around the z -axis, $\Delta_1 = \Delta_2 = -\Delta_3/2 = -\Delta/3$ and T can be written

$$T = \Delta(\tilde{l}_z^2 - \frac{2}{3}) \quad (19.53)$$

and $\tilde{J}_z = \tilde{l}_z + S_z$ is a good quantum number (while \tilde{J} is no longer so), which simplifies the classification of the eigenstates according to the values of \tilde{J}_z . However, for the calculation of the magnetic and quadrupole hyperfine structure as expectation values of the operators in eqn (17.61) one must use the expansions of the $|\tilde{l}_z\rangle$ as sums of states $|L_z\rangle$ given in Tables 4 or 5.

Finally, if the field T is not very much smaller than K it may bring into the lower orbital cubic multiplet Γ_i admixtures from excited cubic levels Γ_j . Thus for an F -term a tetragonal or a trigonal field will mix into the triplet Γ_4 , formed from an F -term, wave-functions from Γ_5 (see Figs. 7.5, 7.6). Using Table 4 it is easy to show that the three lower orbital eigenstates of $K + T$ will be of the form

$$\xi'_{+1} = p\xi_{+1} + q\eta_{-1}, \quad \xi'_0 = \xi_0, \quad \xi'_{-1} = p\xi_{-1} + q\eta_{+1}, \quad (19.54)$$

where ξ_m and η_m are the states $|\tilde{m}\rangle$ respectively for Γ_4 and Γ_5 for tetragonal symmetry; p and q depend on the field T and $p^2 + q^2 = 1$. Slightly different formulae are needed for trigonal symmetry, which also admixes Γ_2 into $|\Gamma_4, \tilde{0}\rangle$ (see Fig. 7.6). Similarly, it is worth noticing

that Γ_5 formed from a D -term is coupled to the doublet Γ_3 by a trigonal but not by a tetragonal field; see Figs. 7.3, 7.4. We can still define a fictitious momentum $\tilde{\mathbf{l}}$ by taking ξ'_{+1} , ξ'_0 , ξ'_{-1} of (19.54) as eigenstates of $\tilde{l}_z = 1, 0, -1$. Within the manifold of these states T keeps the form $\Delta(\tilde{l}_z^2 - \frac{2}{3})$ but the equivalence

$$\mathbf{L} = \alpha \tilde{\mathbf{l}} \quad (19.55)$$

with a single constant is replaced by

$$L_x = \alpha \tilde{l}_x, L_y = \alpha \tilde{l}_y, L_z = \alpha \tilde{l}_z. \quad (19.56)$$

In the new Hamiltonian for the $3(2S+1)$ manifold

$$\Delta(\tilde{l}_z^2 - \frac{2}{3}) + \lambda \{ \alpha \tilde{l}_z S_z + \alpha' (\tilde{l}_x S_x + \tilde{l}_y S_y) \}, \quad (19.57)$$

$\tilde{J}_z = \tilde{l}_z + S_z$ is still a good quantum number. The expectation value of

$$Z = \beta g_s (\mathbf{H} \cdot \mathbf{S}) + \beta \{ \alpha H_z \tilde{l}_z + \alpha' (H_x \tilde{l}_x + H_y \tilde{l}_y) \} \quad (19.58)$$

is calculated as before. For the evaluation of the expectation values of the hyperfine interaction, care should be taken to use for the states $|\tilde{1}\rangle$, $|\tilde{0}\rangle$, $|\tilde{-1}\rangle$ the correct expansion (either (19.54) or its equivalent for trigonal symmetry) and Tables 4 or 5.

To proceed further one must consider separately the cases of Kramers and non-Kramers ions.

(i) *Kramers ions*

For these, \tilde{J}_z is a good quantum number and there will be a certain number of Kramers doublets $|\tilde{J}_z| = m$. For instance for Co^{2+} , 4F there will be one doublet $|\tilde{J}_z| = \frac{5}{2}$, two doublets $|\tilde{J}_z| = \frac{3}{2}$ and three doublets $|\tilde{J}_z| = \frac{1}{2}$. The secular equation factors into three equations of the third, second, and first order. Resonance will be observable in the doublets $|\tilde{J}_z| = \frac{1}{2}$ only. A doublet $|\tilde{J}_z| = \frac{1}{2}$ happens to be the lowest in the case of Co^{2+} in tutton salts where the field T is approximately tetragonal and in the fluosilicate where it is trigonal. If we add to T a component of lower symmetry it will naturally not be able to lift the Kramers degeneracy, but as \tilde{J}_z ceases to be a good quantum number, the resonance may become observable in all doublets.

(ii) *Non-Kramers ions*

In tetragonal or trigonal symmetry there will be a singlet $\tilde{J}_z = 0$ and doublets $|\tilde{J}_z| = m$.

Higher-order perturbations may lift the degeneracy of some of the

doublets, and so will a field of lower symmetry in first order. No general prediction about the observability of resonance can be made.

19.5. The influence of excited terms

In the foregoing we have consistently assumed that the wave-function of the ground level of the bound ion was constructed from eigenstates of the ground term (L, S) of the free ion. We have used this assumption in several places: in the expressions (19.5)–(19.12) for the spin-orbit coupling, spin-spin coupling, and hyperfine structure couplings, in the expansion given in Tables 4 or 5 for the kets spanning the various multiplets Γ_i , etc. . . . This procedure rests on the assumption that off-diagonal matrix elements of the crystal potential between the ground term (L, S) of the free ion and excited terms (L', S) are small compared to the energy differences $W(L, S) - W(L', S)$. We shall defer to a later chapter the study of situations where this assumption is completely unwarranted, as in covalent complexes, and describe briefly the changes introduced in our description of the paramagnetic ion by relatively small admixtures from excited terms brought by the crystal potential (admixtures caused by the spin-orbit coupling are very much smaller and will be disregarded).

Let us consider first the case of ions of type B and to be specific the example of Co^{2+} , $3d^7$, where to the cubic multiplet Γ_4 of the ground term 4F the cubic field admixes the excited term 4P , the amplitude of the admixture being of the order of $\tau \approx 0.2$. The lifting of the twelve-fold degeneracy of the ground manifold can still be described for tetragonal or trigonal symmetry by a reduced equivalent Hamiltonian of the same form as (19.57)

$$\Delta(\tilde{l}_z^2 - \frac{2}{3}) + \lambda\{\alpha\tilde{l}_zS_z + \alpha'(\tilde{l}_xS_x + \tilde{l}_yS_y)\},$$

but the eigenstates $|\tilde{1}\rangle$, $|\tilde{0}\rangle$, $|\tilde{-1}\rangle$ of \tilde{l}_z will involve admixtures from states belonging to the 4P level.

To obtain the constants $\lambda\alpha$, $\lambda\alpha'$ of the spin-orbit coupling in (19.57) it is necessary in principle to start from the general expression $\sum_i \zeta(\mathbf{l}_i \cdot \mathbf{S}_i)$ for the spin-orbit coupling. However, because of the selection rule $|\Delta L| = 0, 1$, the operator $\sum_i \zeta(\mathbf{l}_i \cdot \mathbf{S}_i)$ has no matrix elements between the terms 4F and 4P and the representation of the spin-orbit coupling by $\lambda({}^4F)(\mathbf{L} \cdot \mathbf{S})$ leads to an error only of the order of τ^2 . Similarly, for the Zeeman coupling $\beta\mathbf{H} \cdot (g_s\mathbf{S} + \mathbf{L})$, which has no cross terms between

4P and 4F , the admixture from the excited term 4P changes its expectation value by a quantity of order τ^2 .

For instance, for Co^{2+} in octahedral environment, for the lower triplet Γ_4 , the admixture of 4P changes \tilde{g}_i from $-\frac{3}{2}$ into $-\frac{3}{2} + 5\tau^2/2$, causing according to (19.40a) a change δg of $-5\tau^2/3$. To explain the discrepancy -0.05 from the observed value it is sufficient to take $\tau^2 = 0.03$, or $|\tau| = 0.17$ which is of the right order of magnitude.

It is in the calculation of hyperfine structure that the changes are most important. The expressions (19.8)–(19.11) for the hyperfine structure can be used for diagonal terms $\langle LS | \quad | LS \rangle$; for instance, for Co^{2+} , this yields

$$(1 - \tau^2) \langle 3, \frac{3}{2} | W_n | 3, \frac{3}{2} \rangle + \tau^2 \langle 1, \frac{3}{2} | W_n | 1, \frac{3}{2} \rangle, \quad (19.59)$$

the first term being the contribution of the 4F and the second of the 4P term. The constant ξ in (19.8) has a different value for the terms 4F and 4P and for the latter *cannot* be computed by eqn (17.46) since 4P is a term that does not obey Hund's rule. Off-diagonal terms $\langle LS | W_n | L'S \rangle$ or, for Co^{2+} , $\langle {}^4F | W_n | {}^4P \rangle$ must be computed using for the hyperfine interactions the more general expressions (17.12) for the quadrupole interaction, and (17.30) or (17.42) for the magnetic interaction, summed over all the electrons. The actual calculations although straightforward are too lengthy to be outlined in a general survey.

Passing on to ions of type A for which the spin Hamiltonian (19.33) has been derived by a perturbation method, the following remarks can be made. The assumption that the ground state has no orbital degeneracy and that it is an eigenstate of S (but not necessarily of L) is sufficient for the derivation of a spin Hamiltonian of the form (19.33). The only other important assumption is that of the smallness of the spin-orbit coupling relative to the crystal field, that permits the treatment of the operator C in (19.16) as a purely orbital operator.

The assumption that the ground state and the excited states are eigenstates of L and, for the excited states, the assumption that they are eigenstates of the same value of S as the ground state, are not essential. On using for the various interactions, the more general expressions $\zeta \sum (\mathbf{l}_i \cdot \mathbf{s}_i)$ for the spin-orbit coupling, (17.12), (17.30) for the hyperfine interaction, and (16.42) for the spin-spin interaction, we end up in the ground state with an operator expression linear or quadratic with respect to the components of the spins of the individual electrons, which by the Wigner-Eckart theorem can be cast into the form (19.33). The various symmetry properties of the coefficients of

(19.33) based on time-reversal and spatial symmetry will be valid as well. On the other hand, the various analytical expressions (19.32) giving the coefficients of (19.33) will no longer be valid.

The main advantage of these expressions is their relative simplicity. For the more complicated situations where L is not a good quantum number general formulae become unwieldy and each special case is best dealt with separately.