

# PART III

## THEORETICAL SURVEY

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### 11

#### THE ELECTRONIC ZEEMAN INTERACTION

##### 11.1. The interaction between electrons and a magnetic field

ELECTRONIC magnetic resonance occurs when an oscillating magnetic field induces transitions between two separated, discrete atomic levels. The most common case is one in which the levels are split through the application of a steady external magnetic field, but it sometimes happens that the two levels may be separated even in the absence of such a field. Nevertheless, it may still be convenient to apply to the system a magnetic field that will control within certain limits the spacing between the two levels.

An important problem, then, is to determine the position and the nature of the levels of an electronic system in the presence of an applied magnetic field  $\mathbf{H}_0$ . If  $\mathcal{H}_0$  is the Hamiltonian of the system in the absence of the field, it is known from electromagnetic theory that the effect of a uniform field  $\mathbf{H}_0$  is described by replacing in  $\mathcal{H}_0$  the momentum  $\mathbf{p}_i$  of each electron  $i$  of charge  $-e$  by the quantity

$$\mathbf{p}_i + (e/c)\mathbf{A}(\mathbf{r}_i),$$

where  $\mathbf{A}(\mathbf{r}_i) = \frac{1}{2}(\mathbf{H}_0 \wedge \mathbf{r}_i)$  is the value at the electron position  $\mathbf{r}_i$  of the vector potential from which the field  $\mathbf{H}_0$  is derived.

If the kinetic energy of the electrons has the correct relativistic form given by Dirac, the coupling of  $\mathbf{H}_0$  with both the orbital magnetic moment and the spin magnetic moment of the electrons is obtained directly. On the other hand, if the non-relativistic form of the kinetic energy

$$T = \frac{1}{2m} \sum_i \mathbf{p}_i^2$$

is being used, the spin magnetism does not appear and the orbital magnetism is obtained as follows: the substitution

$$\mathbf{p} \rightarrow \mathbf{p} + (e/c)\mathbf{A}$$

yields

$$T = \frac{1}{2m} \sum_i \left( \mathbf{p}_i + \frac{e}{c}\mathbf{A}(\mathbf{r}_i) \right)^2. \quad (11.1)$$

The extra terms containing the magnetic field can be written:

$$\mathcal{H}_m = \frac{e}{2mc} \mathbf{H}_0 \cdot \sum_i (\mathbf{r}_i \wedge \mathbf{p}_i) + \frac{e^2}{8mc^2} \sum_i (\mathbf{r}_i \wedge \mathbf{H}_0)^2. \quad (11.2)$$

If we now introduce the quantity

$$\sum_i (\mathbf{r}_i \wedge \mathbf{p}_i) = \hbar \mathbf{L}, \quad (11.3)$$

where  $\mathbf{L}$  is the orbital momentum of the system with respect to the origin of coordinates (the origin of the vectors  $\mathbf{r}_i$ ), and the Bohr magneton  $\beta = e\hbar/2mc$ , eqn (11.2) becomes

$$\mathcal{H}_m = \beta \mathbf{H}_0 \cdot \mathbf{L} + \frac{e^2}{8mc^2} \sum_i (\mathbf{r}_i \wedge \mathbf{H}_0)^2. \quad (11.4)$$

The first term in (11.4) represents the orbital magnetism. It shows that an electronic system with an orbital momentum  $\hbar \mathbf{L}$  possesses a magnetic moment  $\boldsymbol{\mu}_L = -\beta \mathbf{L}$ . The second term is the so-called diamagnetic term.

In the expression for the vector potential we did not specify the origin of the vectors  $\mathbf{r}_i$ . It is clear that the separation of (11.4) into a paramagnetic and a diamagnetic part depends on the choice of this origin. On the other hand, the principle of gauge invariance in electromagnetism tells us that this choice should not affect the result of the calculation of any physical quantity that can be observed experimentally. In this chapter, where we assume that the electrons responsible for the magnetic properties of the system are localized on a single atom, we shall choose as origin for the vector potential  $\mathbf{A}$  and the orbital momentum  $\mathbf{L}$ , the nucleus of this atom. It is then easily shown that for the values of the field  $\mathbf{H}_0$  that are currently used in laboratories the diamagnetic term is much smaller than the paramagnetic one.

The diamagnetic term can be written

$$\frac{1}{4} \beta H_0 \frac{e^2}{\hbar c} \sum_i \left\{ \frac{r_i^2}{e} \sin^2 \theta_i \right\} H_0, \quad (11.5)$$

where  $\theta_i$  is the angle between the vector  $\mathbf{r}_i$  and the applied field. In order of magnitude, if we assume that we can take  $\mathbf{L}$  to be of order unity, this term is smaller than the paramagnetic term by a factor of  $\sim \frac{1}{4} \frac{1}{137} (\langle r^2 \rangle / e) H_0$  where  $\langle r^2 \rangle$  is the mean square radius of the atom. For  $H_0 = 10^4$  e.m.u., and atomic dimensions of the order of 0.1 nm, the ratio of the diamagnetic to the paramagnetic term is of order  $10^{-6}$ . This is comparable with the ratio between the diamagnetic and the paramagnetic susceptibility measured at very low temperatures

when the electron magnetic moments are almost completely aligned in the applied field and  $\langle L \rangle$  can indeed be of order unity.

Another reason why we shall often be able to disregard the diamagnetic term is that it has the same expectation value for both levels  $|a\rangle$  and  $|b\rangle$  between which the resonance is observed and thus does not affect the resonance frequency.

In the foregoing non-relativistic treatment the spin magnetism must be introduced phenomenologically by assigning to the electron an intrinsic spin magnetic moment  $\mu_s = -g_s\beta\mathbf{s}$ , which has the same position as the electron charge. It is well known (and will be proved (in § 17.3)) that reduction of the Dirac equation to the non-relativistic form due to Pauli leads to a value of 2 for  $g_s$ . However, both accurate experiments and a more refined theory that takes into account the interaction of the electron with the fluctuations of the radiation field lead to a slightly different value of 2.0023 for  $g_s$ . We are thus led to describe the magnetic coupling of an atom (or an ion) with an applied field by means of a Hamiltonian

$$Z = \beta\mathbf{H}_0 \cdot (\mathbf{L} + g_s\mathbf{S}), \quad (11.6)$$

where  $\mathbf{S}$  is the total spin of the atom. In some experiments of very high accuracy a few small corrections, most of them of a relativistic nature, have to be applied to (11.6), but we shall disregard them with one or two possible exceptions. Frequently we shall even neglect the difference  $g_s - 2$ .

## 11.2. The Zeeman effect in a free atom (or ion)

Whatever the interactions between the electrons of a free atom or ion, in the absence of external fields the magnitude  $J$  of its total angular momentum  $\mathbf{J}$  is a good quantum number and each energy level corresponding to a given value of  $J$  will have a degeneracy of  $2J+1$ .

The behaviour of the energy levels of the atom, when a steady magnetic field is applied to it, will depend on whether the Zeeman coupling (11.6) is large or small compared to the spacings of the atomic energy levels between which it possesses non-vanishing matrix elements. For magnetic fields currently used in laboratories,  $Z$  will in general be much smaller than these spacings. If we neglect the effects of the Zeeman coupling between different  $J$  levels, we may calculate the splitting of any given  $J$  level by first-order perturbation theory, using only the matrix elements of  $Z$  inside the manifold of degeneracy  $(2J+1)$ .

A fundamental theorem of group theory, the Wigner-Eckart theorem, of which we shall have more to say in § 13.5, tells us that inside the manifold  $J$  all vector operators have the same matrix elements within a constant factor. Within the approximation of the first-order perturbation theory we shall then write

$$\mathbf{L} + g_s \mathbf{S} = g_J \mathbf{J} \quad (11.7)$$

$$Z = g_J \beta \mathbf{H}_0 \cdot \mathbf{J}, \quad (11.8)$$

where  $g_J$  is a constant, called the Landé factor. The manifold  $J$  is split by a magnetic field into  $2J+1$  equidistant levels each corresponding to a different value of  $J_z$ , where  $z$  is the direction of the applied field. As magnetic resonance transitions are allowed only between successive levels for which  $J_z$  differs by one unit there is a single resonance frequency,

$$\nu = g_J \beta H_0 / h. \quad (11.9)$$

Whereas the proof of (11.7) is very general, the actual calculation of  $g_J$  requires more detailed hypotheses.

### 11.3. LS-coupling and the Landé formula

In a non-relativistic theory the interactions inside an atom can be divided into two parts: one, a spin-dependent part and two, a spin-independent part.

Quite generally (with the possible exception of the heaviest atoms) spin-dependent forces are much weaker than purely orbital forces and can be neglected in a first approximation. The description of atomic states in the framework of this approximation is known as the Russell-Saunders or  $LS$ -method of coupling. In this description it is well known that the magnitude  $L$  of the total orbital momentum is a good quantum number (this is a result of rotational invariance in the free atom and will be discussed in Chapter 13 from the viewpoint of group theory).

A second good quantum number is the total spin  $S$ . It is worth pointing out that, in contradistinction to  $L$ , the fact that  $S$  is a good quantum number has nothing to do with rotational invariance and stems simply from the fact that spin-dependent forces have been neglected. As Dirac (1930) has shown in his chapter on identical particles, the quantum number  $S$  is related to the type of symmetry of the electronic wave-function with respect to a permutation of the orbital coordinates of the various atomic electrons. Indeed one could (and did in the early days of quantum mechanics) classify atomic

energy levels, without mentioning the spin at all, by using the language of the theory of the permutation group. It is just the fact that the electronic wave-function is antisymmetric with respect to the permutation of *both* the orbital and the spin coordinates of two electrons that enables one to replace, at least partially, this complicated description by the introduction of the total spin  $S$  as a good quantum number.

In atomic spectroscopy an energy level specified by the values of  $L$  and  $S$  is called a term. In practice,  $L$  and  $S$  alone will often not be sufficient to specify a term and extra parameters have to be introduced. A given term  $(L, S)$  has a degeneracy  $(2L+1) \times (2S+1)$ . We consider now the effect on such a term of spin-dependent forces that will partially lift this degeneracy. Since the magnitude  $J$  of the total angular momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  is a good quantum number, the term  $(L, S)$  will be split into a number of submultiplets  $(J, L, S)$ , where each multiplet has still a degeneracy of order  $(2J+1)$  and where  $J$  ranges from  $L+S$  to  $|L-S|$ . The representation of each multiplet by  $(J, L, S)$  implies that, according to our assumptions, the spin-dependent forces that split the  $(L, S)$  term are small compared to the distance between two neighbouring terms  $(L, S)$  and  $(L', S')$ , and in a multiplet  $(J, L, S)$  the admixture of wave-functions originating in another term  $(L', S')$  is small.

We have made no assumptions so far about the nature of the spin-dependent forces and thus can tell nothing of the spacings between the various multiplets  $(J, L, S)$ . If these spacings are large compared to the Zeeman coupling  $Z$  we can compute the Landé factor  $g_J$  of formula (11.7) as follows. On multiplying each side of (11.7) by  $\mathbf{J}$  we have

$$\mathbf{L} \cdot \mathbf{J} + g_s \mathbf{S} \cdot \mathbf{J} = g_J J(J+1) \quad (11.10)$$

and from squaring the relations  $\mathbf{S} = \mathbf{J} - \mathbf{L}$  and  $\mathbf{L} = \mathbf{J} - \mathbf{S}$  we find

$$\left. \begin{aligned} 2\mathbf{L} \cdot \mathbf{J} &= L(L+1) + J(J+1) - S(S+1) \\ 2\mathbf{S} \cdot \mathbf{J} &= S(S+1) + J(J+1) - L(L+1) \end{aligned} \right\} \quad (11.11)$$

whence

$$g_J = \frac{1}{2J(J+1)} [(g_s+1)J(J+1) - (g_s-1)\{L(L+1) - S(S+1)\}]. \quad (11.12a)$$

In particular, if we make the approximation  $g_s = 2$ , eqn (11.12a) becomes

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (11.12b)$$

The formulae (11.12a) or (11.12b) become particularly simple if  $J$  has the maximum possible value  $J = L+S$ , for then the substate

$J_z = J$  is also the state  $L_z = L$ ,  $S_z = S$  and the  $z$  component of the vector equation (11.7) can be written as the scalar relation

$$L + g_s S = g_J J,$$

whence

$$g_J = \frac{L + g_s S}{J} = \frac{L + g_s S}{L + S}, \quad (11.13)$$

which could of course be obtained directly from (11.12a) by writing  $J = (L + S)$ .

It is worth emphasizing once more the extreme generality of the assumptions made so far. Equation (11.7) has simply implied that the Zeeman coupling  $Z$  is small compared to the spacings between the various levels of the free atom. The more detailed relations (11.12a) and (11.12b) are based on the further assumption that spin-dependent forces are small compared to orbital forces. The great simplicity of the Zeeman splitting in the free atom is related to the fact that the applied field  $\mathbf{H}_0$  is uniform and that its effects are not sensitive to the detailed structure of the wave-functions. To a lesser extent this holds for a paramagnetic ion embedded in a crystal potential and the main features of the Zeeman splitting in such an ion could be derived without introducing any further details about the electronic structure of the free atom. However this is unadvisable for the following reasons.

(a) While the foregoing simple assumptions of rotational symmetry of the atom and of relative weakness of the spin-dependent forces have demonstrated the existence of  $(L, S)$  levels, they have provided no indication of their number or of their relative positions. Far more detailed predictions for these levels can be obtained.

(b) Furthermore, in addition to the effects of a uniform magnetic field we shall have to consider those of the very inhomogeneous fields produced by the nuclear magnetic dipole and electric quadrupole moments that give rise to the hyperfine structure of the resonance lines; these are very sensitive to the details of the atomic wave-function.

#### 11.4. Self-consistent field configurations

The spin-independent part of the Hamiltonian of an atom can be written

$$\mathcal{H} = \frac{1}{2m} \sum_i p_i^2 - \sum_i \frac{Ze^2}{r_i} + \sum_{i < k} \frac{e^2}{r_{ik}} \quad (11.14)$$

(in which we have neglected small orbital magnetic interactions between electrons).



In practice, for free atoms, the trial functions are taken of the form

$$\varphi_i = P_{ni}(r) Y_l^{m_l}(\theta, \varphi) \chi_{m_s}(s),$$

where only the radial parts are unknown. The condition  $\delta\langle \mathcal{H} \rangle = 0$  leads to a set of integro-differential equations for the  $P_{ni}(r)$ , which are then solved numerically. The energy level that corresponds to a configuration is still highly degenerate since the quantum numbers  $m_l$  and  $m_s$  remain unspecified and can take all the values compatible with the exclusion principle.

Consider then two Slater determinants  $\Psi_{A'}$  and  $\Psi_{A''}$  belonging to a configuration  $A$  of energy  $W_A$ , and two other determinants  $\Psi_{B'}$  and  $\Psi_{B''}$  belonging to a different configuration  $B$  of energy  $W_B$ . If these Slater determinants were exact eigenfunctions of  $\mathcal{H}$  the following would hold:

$$\begin{aligned} (\Psi_{A'} | \mathcal{H} | \Psi_{A'}) &= (\Psi_{A''} | \mathcal{H} | \Psi_{A''}) = W_A, \\ (\Psi_{B'} | \mathcal{H} | \Psi_{B'}) &= (\Psi_{B''} | \mathcal{H} | \Psi_{B''}) = W_B, \\ (\Psi_{A'} | \mathcal{H} | \Psi_{B'}) &= (\Psi_{A''} | \mathcal{H} | \Psi_{B''}) = 0. \end{aligned} \quad (11.16)$$

In fact these equalities will be only approximate: the diagonal matrix elements  $(\Psi_{A'} | \mathcal{H} | \Psi_{A'})$  and  $(\Psi_{A''} | \mathcal{H} | \Psi_{A''})$  will be slightly different and will partially lift the degeneracy of configuration  $A$ . Off-diagonal matrix elements  $(\Psi_{A'} | \mathcal{H} | \Psi_{B'})$  will admix into each configuration wave-functions originating in another configuration, an effect known to the spectroscopists as configuration interaction. The usefulness of the self-consistent field approximation resides in the fact that off-diagonal matrix elements of  $\mathcal{H}$ , linking two different configurations  $A$  and  $B$ , are small compared to the energy difference  $W_A - W_B$  between these configurations. Configuration interaction can then be neglected and the 'correct' eigenfunctions  $\Phi_{A'}$  of  $\mathcal{H}$  are given by first-order perturbation theory as linear combinations of Slater determinants from a single configuration. The choice of the 'correct' linear combinations  $\Phi_A$  is greatly simplified through  $L$  and  $S$  being good quantum numbers. As is well known in spectroscopy, and as will appear in more detail later on in connection with a group-theoretical discussion, the determination of the 'correct' linear combination will involve solving a secular equation only if more than one term ( $L, S$ ) can be constructed from a given configuration. For instance, two distinct  ${}^3D$  terms can be constructed from the configuration  $d^3$ ; a quadratic secular equation must be solved in order to determine the structure of the wave-functions and the energies of the two  ${}^3D$  terms.



Thanks to a rule originally due to Hund, the ground state of an atom (which is with few exceptions, the one of widest interest in paramagnetic resonance) has a structure much simpler than that of the excited states. Hund's rule states that the ground state has the maximum possible total spin  $S$  and, among states of maximum  $S$ , the greatest orbital momentum  $L$ . For instance, in a configuration  $d^4$  the ground state will have  $S = 2$ ,  $L = 2$ ; in a configuration  $f^3$  the ground state is  $S = \frac{3}{2}$ ,  $L = 6$ , etc. For such a state, the magnetic substate  $L_z = L$ ,  $S_z = S$  is a single Slater determinant where all the electrons have the maximum values  $m_s$  and  $m_l$  compatible with the exclusion principle.

The low energy of a state with maximum  $S$  corresponds to the fact that, being completely symmetrical with respect to spin variables, the wave-function is completely antisymmetrical with respect to space variables. This keeps the electrons apart and reduces the positive contribution to the energy arising from their electrostatic repulsion. Unfortunately no such simple interpretation can be given for the rule for maximum  $L$ .

### 11.5. Spin-orbit coupling

Among spin-dependent interactions the most important by far is the spin-orbit coupling; for each electron this can be written as  $\zeta(r)\mathbf{l} \cdot \mathbf{s}$ . A simple physical (and somewhat incorrect) model of this interaction obtains as follows: the electron moves with a velocity  $\mathbf{v} = \mathbf{p}/m$  in an electrostatic field  $\mathbf{E}$ , which is the gradient of an electrostatic central potential  $-V/e$ . The electron 'sees' a magnetic field

$$\mathbf{H} = -(\mathbf{v}/c) \wedge \mathbf{E} \quad (11.17)$$

where  $\mathbf{E}$  is related to the potential energy  $V$  by

$$\mathbf{E} = -\nabla\left(-\frac{V}{e}\right) = \frac{\mathbf{r}}{r} \frac{d}{dr}\left(\frac{V}{e}\right).$$

The magnetic coupling  $2\beta\mathbf{s} \cdot \mathbf{H}$  between the field (11.17) and the spin magnetic moment  $-2\beta\mathbf{s}$  of the electron can be written

$$-2\beta\mathbf{s} \cdot \left(\frac{\mathbf{p}}{mc} \wedge \frac{\mathbf{r}}{r}\right) \frac{d(V/e)}{dr} = \frac{\hbar^2}{m^2 c^2} \frac{1}{r} \frac{dV}{dr} (\mathbf{l} \cdot \mathbf{s}) \quad (11.18)$$

A correct calculation from Dirac's equation yields a result smaller by a factor 2 leading to

$$\zeta(r) = \frac{\hbar^2}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr}, \quad (11.19)$$

where  $\zeta(r)$  and  $V(r)$  have both the dimensions of an energy and  $(\hbar/mc)^2$ , the square of the Compton wavelength, the dimensions of an area.

The assumption of  $LS$ -coupling is that spin-orbit coupling is small compared to the energy difference between two neighbouring terms, and this makes it possible to neglect off-diagonal matrix elements of  $\sum_i \zeta(r_i) \mathbf{l}_i \cdot \mathbf{s}_i$  between two such terms. Inside each term the Wigner-Eckart theorem permits the replacement of  $\sum_i \zeta_i \mathbf{l}_i \cdot \mathbf{s}_i$  by a single scalar product  $\lambda \mathbf{L} \cdot \mathbf{S}$ . From this approximation it follows immediately that the energies of the various  $(J, L, S)$  multiplets originating from a given term  $(L, S)$  vary as  $(\lambda/2)\{J(J+1)\}$ , a result known as the Landé interval rule.

If, as happens in heavy atoms, the off-diagonal matrix elements of spin-orbit coupling between two different terms are not negligibly small,  $L$  and  $S$  are no longer good quantum numbers and both the Landé formula for the  $g$ -factor and the interval rule become more or less incorrect. This situation is called intermediate coupling. The extreme case of  $j$ - $j$  coupling, where the spin-orbit coupling is so strong that it is a better approximation to couple first  $\mathbf{l}$  and  $\mathbf{s}$  to a resultant  $\mathbf{j}$  for each electron and then to couple the various  $\mathbf{j}$  to a resultant  $\mathbf{J}$ , is never realized in practice.

Besides the spin-orbit coupling, by far the most important spin-dependent interaction, there are others much smaller, namely the spin-spin coupling between two electrons and the coupling of the spin of one electron with the orbit of another. These are discussed in some detail, together with the relation between  $\lambda$  and  $\zeta_i$  by Blume and Watson (1962, 1963) and Watson and Blume (1965).

### 11.6. Matrix elements between Slater determinants

We summarize here without proof (Condon and Shortley 1935) a few simple rules relating to the calculation of matrix elements. We assume that the wave-function is a single determinant of the form (11.15), which we shall write for brevity:

$$\Psi = (\varphi_1, \varphi_2, \dots, \varphi_n). \quad (11.20)$$

The extension to a linear combination of such determinants is straightforward.

In transition elements we shall specify a Slater determinant by the values of  $m_l$  and  $m_s$  for electrons outside closed shells. For instance, in the configuration  $d^3$ ,  $\Psi = (2^+, 1^-, 0^+)$  is a state where the quantum numbers of the three  $d$ -electrons are  $m_l = 2, m_s = \frac{1}{2}; m_l = 1, m_s = -\frac{1}{2};$

$m_l = 0$ ,  $m_s = +\frac{1}{2}$ . From well known properties of the determinants it follows that the interchange of two one-electron states leads to a change of sign of  $\Psi$ :

$$(\varphi_1, \varphi_2, \varphi_3) = -(\varphi_2, \varphi_1, \varphi_3). \quad (11.21)$$

*The diagonal matrix element*  $(\Psi | A | \Psi)$

The operators  $A$  that we shall deal with are either one-electron operators

$$A = \sum_i a(i), \quad (11.22)$$

such as the electrostatic coupling of an electron with the nucleus or with an external crystalline or magnetic field, etc., or two-electron operators (electrostatic repulsion, spin-spin interaction, etc. . . .) of the form

$$A = \sum_{i < j} a(i, j). \quad (11.23)$$

For a one-electron operator the following rule holds:

$$(\Psi | A | \Psi) = \sum_p (\varphi_p(1) | a(1) | \varphi_p(1)). \quad (11.24)$$

For a two-electron operator the rule is

$$(\Psi | A | \Psi) = \sum_{p < q} (\varphi_p(1)\varphi_q(2) | a(1, 2) | \varphi_p(1)\varphi_q(2)) - \sum_{p < q} (\varphi_p(1)\varphi_q(2) | a(1, 2) | \varphi_q(1)\varphi_p(2)). \quad (11.25)$$

The second term of (11.25) is the so-called exchange term. In particular, if the operator  $a(1, 2)$  is spin-independent the exchange term vanishes unless  $\varphi_p$  and  $\varphi_q$  correspond to the same spin orientation.

### *Off-diagonal matrix elements*

Consider two different Slater determinants

$$\Psi = (\varphi_1, \dots, \varphi_p), \quad \Psi' = (\varphi'_1, \dots, \varphi'_p).$$

The matrix elements  $(\Psi | A | \Psi')$  are then given by the following rules.

#### *(a) One-electron operators*

If  $\Psi$  and  $\Psi'$  differ by more than one one-electron state,  $(\Psi | A | \Psi') = 0$ . If they differ by a single individual state, which is  $\varphi$  in  $\Psi$  and  $\varphi'$  in  $\Psi'$ ,

$$(\Psi | A | \Psi') = \pm(\varphi | a | \varphi'). \quad (11.26)$$

The sign in (11.26) is that of the permutation that has to be performed among the states of  $\Psi'$  in order to bring  $\varphi'$  into the place corresponding

to that which  $\varphi$  has in  $\Psi$ , all other identical individual states appearing in the same order in both  $\Psi$  and  $\Psi'$ .

For instance,

$$\begin{aligned}(2^+, 1^-, 0^+ | A | 2^+, 0^+, -2^-) &= -(2^+, 1^-, 0^+ | A | 2^+, -2^-, 0^+) \\ &= -(1^- | a | -2^-).\end{aligned}$$

(b) *Two-electron operators*

If  $\Psi$  and  $\Psi'$  differ by more than two individual states,  $(\Psi | A | \Psi') = 0$ .

If  $\Psi$  and  $\Psi'$  differ by two individual states,  $\varphi$  and  $\chi$  for  $\Psi$  and  $\varphi'$ ,  $\chi'$  for  $\Psi'$

$$\begin{aligned}(\Psi | A | \Psi') &= \pm \{(\varphi(1)\chi(2) | a(1, 2) | \varphi'(1)\chi'(2)) - \\ &\quad - (\varphi(1)\chi(2) | a(1, 2) | \chi'(1)\varphi'(2))\}. \quad (11.27)\end{aligned}$$

The choice of sign is determined by the permutation on the states of  $\Psi'$  that will bring  $\varphi'$  in front of  $\varphi$  and  $\chi'$  in front of  $\chi$ .

If  $\Psi$  and  $\Psi'$  differ by a single state, namely  $\varphi$  and  $\varphi'$ ,

$$\begin{aligned}(\Psi | A | \Psi') &= \pm \sum_{\varphi_i \neq \varphi, \varphi'} \{(\varphi(1)\varphi_i(2) | a(1, 2) | \varphi'(1)\varphi_i(2)) - \\ &\quad - (\varphi(1)\varphi_i(2) | a(1, 2) | \varphi_i(1)\varphi'(2))\}. \quad (11.28)\end{aligned}$$

The choice of sign is determined as before.

The simplicity of the formulae (11.24)–(11.28) rests entirely on the assumption that the one-electron wave-functions  $\varphi_i$  are orthogonal to each other. This is always the case if one-electron Hartree–Fock wave-functions of a single atom are used. On the other hand, if we allow the magnetic electrons to be spread over several atoms, as will be the case when we shall consider the effects of covalent bonding, one-electron orbitals belonging to different atoms are no longer mutually orthogonal and the calculation of matrix elements of the energy becomes far more complicated.

## 11.7. Introduction of the crystal field

In the years from 1929 onwards it was suggested by a number of authors that the paramagnetic properties of an ion should be greatly affected by its electrostatic interactions with its surroundings. These interactions, at least in a first approximation, could be described by introducing an electrostatic potential in the region occupied by the electrons of the paramagnetic ion, produced by the neighbouring atoms or ions. Van Vleck (1932) and Bethe (1929) put this description on a quantitative basis, developing what is known as the crystal field theory, of paramount importance for our understanding of magnetism in

general and more specifically of the results of paramagnetic resonance experiments. The first success of crystal field theory was the explanation of the 'quenching' of the orbital momentum in the iron group. It had been found that experimental values of the susceptibilities of a good many salts of the iron group could be made to agree with the theoretical formulae if in the latter the orbital contribution to the magnetic moment were equated to zero; that is, if  $\Psi$  is the wave-function of the ion, one had to assume that

$$\langle \Psi | L_x | \Psi \rangle \equiv \langle L_x \rangle = 0 = \langle L_y \rangle = \langle L_z \rangle. \quad (11.29)$$

Van Vleck has shown that the absence of orbital degeneracy is a sufficient condition for this quenching of the orbital momentum, his proof being as follows. Let  $\Psi$  be an eigenstate of the system, assumed non-degenerate. If spin-dependent forces can be neglected, the Hamiltonian  $\mathcal{H}$ , the sum of the kinetic and potential energy of the electrons, is a real operator. We can then assume that  $\Psi$  is real; for, if it were complex, of the form  $\Psi_1 + i\Psi_2$ ,  $\mathcal{H}$  being real,  $\Psi_1$  and  $\Psi_2$  would be separately eigenfunctions of  $\mathcal{H}$  with the same energy and the level would be degenerate, in contradiction with the initial assumption. However the angular momentum operator equivalent to (11.3) is

$$\mathbf{L} = \frac{1}{i}(\mathbf{r} \wedge \nabla), \quad (11.30)$$

which is purely imaginary, so that the expectation value of any of its components taken over a real wave-function is imaginary. On the other hand, since  $\mathbf{L}$  is Hermitian, this expectation value must be real. It must therefore vanish.

We shall present in § 15.4 a more general proof of the foregoing statement. Here we note that the quenching of the orbital momentum is a prime instance of the influence of the surroundings on the magnetic properties of an ion and more specifically of the close connection between magnetism and degeneracy. The rotational symmetry enjoyed by a free ion corresponds to a degeneracy that, in surroundings of the lower symmetry encountered in a crystal, may be lifted partially or even totally, leading to a change of the magnetic properties of the ion.

In order to estimate the effects of the crystal potential, the most important question is its magnitude relative to the energy spacings encountered in the free ion. These spacings can be classified according to their order of magnitude into three different categories:

- (a) the energy separation  $C$  between two neighbouring configurations, of the order of the excitation energy of an individual electron;
- (b) the separation  $T$  between two terms originating in the same configuration; as stated above the usefulness of the central field approximation resides in the condition  $T \ll C$ ;
- (c) spin-orbit coupling energies  $\lambda$ , which are smaller than  $T$  in  $LS$ -coupling, comparable to it in intermediate coupling and larger in  $j$ - $j$  coupling.

In the following we shall always assume  $\lambda \leq T$  and often  $\lambda \ll T$ .

We now compare the magnitude  $V$  of the crystal potential with the energy spacings of the free ion. Three extreme situations can be used as starting points for a quantitative description of the properties of an ion embedded in a crystal field, all of which are actually encountered in transition elements.

### (1) *Weak field case*

The crystal field energy is smaller than the distance between two spin-orbit multiplets  $(J, L, S)$  and  $(J', L, S)$ . It lifts partially or wholly the degeneracy  $2J+1$  of each multiplet, which at least in a first approximation can be studied by neglecting the admixture from neighbouring multiplets so that  $J$  is approximately a good quantum number.

The weak field case is a good approximation for the rare-earth group where the spin-orbit coupling is larger and the crystal fields as a rule are smaller than in the iron group.

It is sometimes stated that the crystal fields are small because the  $4f$  electrons of the rare-earth ions are shielded by the  $5s$  and  $5p$  electrons of external closed shells, but there is some doubt as to the reality of this shielding effect. Rather the result is due to the ligand ions being pushed further away by the extended  $5s$ ,  $5p$  orbitals.

### (2) *Intermediate case*

Here the multiplet structure disappears completely and  $J$  ceases to be a good quantum number, even approximately.

Since perturbation theory requires that the various terms of the Hamiltonian should be introduced in order of decreasing magnitude, one must consider first the effect of the crystal potential on an  $(L, S)$  term and only afterwards examine how spin-orbit coupling affects the wave-functions and the energy levels modified by the crystal potential. In first approximation the admixtures from neighbouring terms  $(L', S')$

may be neglected in the study of the splitting of a given term ( $L, S$ ) so that  $L$ , and to a better approximation  $S$ , remain good quantum numbers; in more refined calculations these admixtures have to be considered.

This is the situation for many salts of the iron group. It often happens that the crystal potential  $V$  can be split into terms of decreasing symmetry  $V_1, V_2$ , etc. of which only the first is much larger than  $\lambda$ , which is a complication. One may have to calculate first the effect of  $V_1$ , then apply to the resulting structure simultaneously  $V_2$  and the spin-orbit coupling as a perturbation, etc.

### (3) *Strong field case*

The crystal field energy is stronger than the electronic repulsion energy responsible for the  $LS$ - coupling.

The term structure is washed out and  $L$  itself ceases to be even an approximately good quantum number. The correct treatment is then to go back to the configuration to see how each one-electron orbit is modified by the crystal potential and how the degeneracy of individual electron levels is lifted. The various electrons are then placed in the new orbits and a new configuration of minimum energy is built up. We shall call it a 'crystal field configuration'. One can then switch on as a perturbation the electron-electron interaction; this will partially lift the degeneracy of the crystal field configuration, introducing new levels that we may call by analogy 'crystal field terms' with new good quantum numbers that replace the total orbital momentum  $L$ . The correct interpretation of these new quantum numbers will appear in the group-theoretical discussion to follow. This situation is encountered mainly in the  $4d$  and  $5d$  group (palladium and platinum groups) and also for certain complexes in the iron group. Actually we shall see that the so-called strong field case is generally associated with covalent bonding where the description of the magnetic behaviour of an ion in terms of wave-functions strictly localized on this ion becomes inadequate. Nevertheless, the main features of the magnetic properties of the ion can still be understood in the framework of the crystal field theory. This is due to the fact that many of these properties are already determined by the symmetry of the surroundings without any detailed assumptions about their interactions with the paramagnetic ion.

In order to obtain a detailed quantitative description of the magnetic properties of a paramagnetic ion, in principle the following information should be available:

(i) The wave-functions and the energy levels of the free ion must be known. Fortunately, very often the knowledge of the ground term ( $L, S$ ) is sufficient and, as mentioned earlier, this term being of maximum  $S$  and  $L$  has a simpler structure than that of excited states. If the crystal field is sufficiently weak, as in the case of the rare earths, it may be enough to know the ground spin-orbit multiplet ( $J, L, S$ ).

(ii) One must be able to calculate the crystal field acting on the ion. Even if the positions of all neighbouring nuclei are known accurately from X-ray analysis, this is a very difficult problem fraught with considerable uncertainty. We shall discuss it in some detail in Chapter 16.

(iii) The matrix elements of the crystal field between the various states of the free ion must be computed. This involves in particular the knowledge of the radial parts of the one-electron Hartree-Fock wave-function of the free ion. These are matrix elements of one particle operators, and the only ones that appear for weak and intermediate crystal fields. For strong fields one has also to compute matrix elements of the electron-electron repulsion, a two-particle operator.

(iv) With the matrix elements thus calculated, secular equations must be set up and solved. It is particularly important to extract any multiple roots that correspond to degenerate energy levels. Wave-functions for the paramagnetic ion, which are linear combinations of the wave-functions for the free ion, are also obtained.

(v) With these functions, expectation values and, if necessary, off-diagonal matrix elements are computed for the physical quantities of interest in paramagnetic resonance: components of the magnetic moment, electron spin-spin interaction, magnetic dipole and electric quadrupole hyperfine interaction, etc. The hyperfine structure is very sensitive to the details of the wave-functions and configuration interaction must often be taken into account in its evaluation.

This is a rather formidable programme and it is neither possible nor fortunately always necessary to determine quantitatively all the elements listed above.