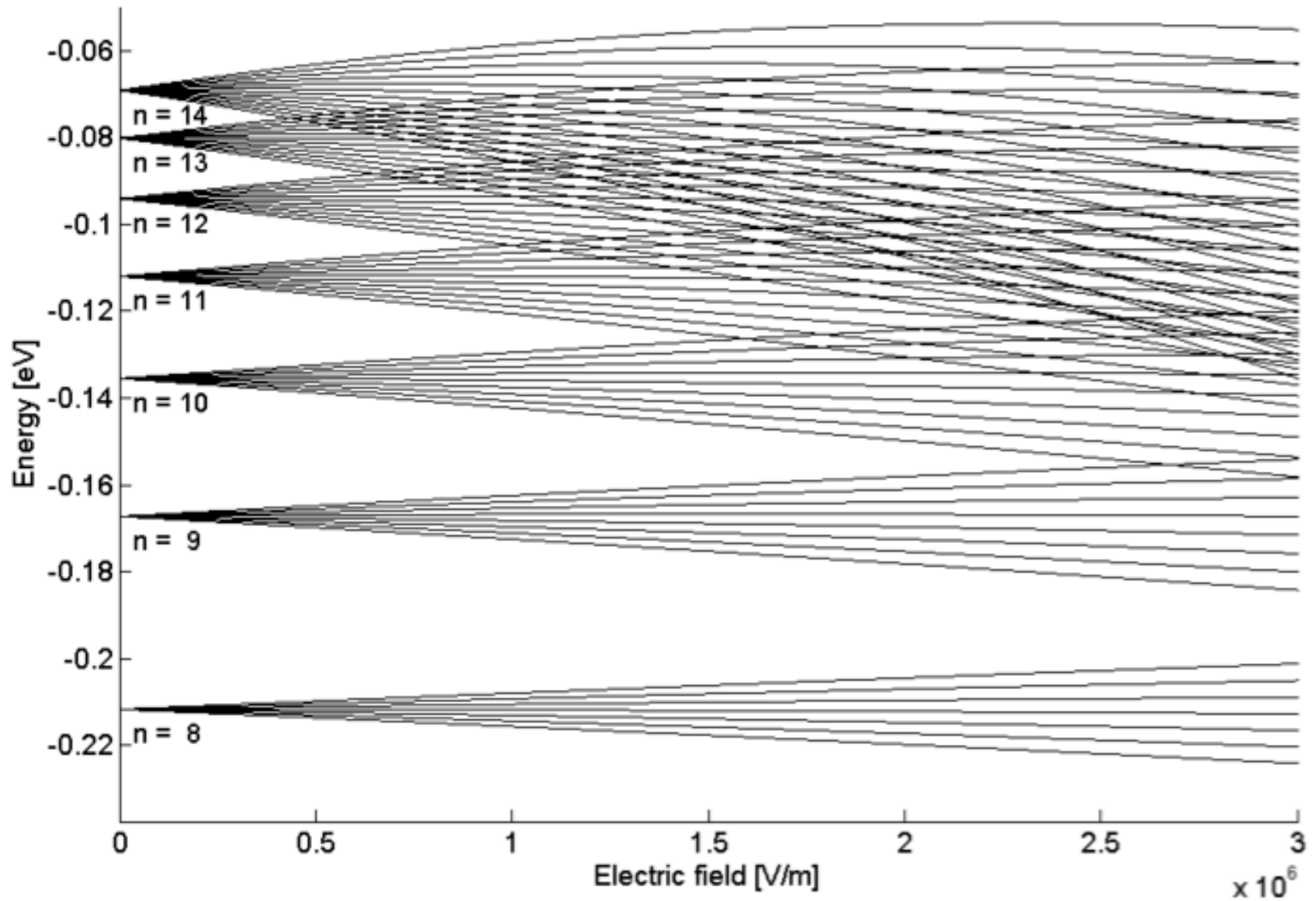


# **The Stark Shift**



# Stark effect in hydrogen



## 6 Interaction of one-electron atoms with external electric and magnetic fields

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In Chapter 4 we studied the interaction of hydrogenic atoms with electromagnetic radiation. In this chapter we shall study the effects of external static electric and magnetic fields on one-electron atoms. We shall start in Section 6.1 by considering the effect of a static electric field, called the *Stark effect*. In Section 6.2, we shall discuss the influence of a static magnetic field, known as the *Zeeman effect*.

### 6.1 The Stark effect

The effect of static electric fields on the spectrum of hydrogen and other atoms was studied by J. Stark and also by A. Lo Surdo in 1913. The splitting of spectral lines observed is known as the Stark effect. We shall assume that the external electric field is uniform over a region of atomic dimensions and we shall take it to be directed along the  $Z$  axis. We also suppose that the electric field strength  $\mathcal{E}$  is large enough for fine structure effects to be unimportant [1]. Neglecting reduced mass effects, the Hamiltonian of the unperturbed hydrogenic atom is given by

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} \quad (6.1)$$

The perturbation due to the external electric field is

$$H' = e\mathcal{E}z \quad (6.2)$$

where we recall that  $-e$  is the charge of the electron. Since  $H'$  does not depend on the electron spin we shall use for the zero-order wave functions the Schrödinger hydrogenic wave functions  $\psi_{nlm}(\mathbf{r})$  given by (3.53).

#### Linear Stark effect

Since the ground state (100) is non-degenerate, we see from (2.308) and (6.2) that the first-order correction to its energy is given by

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[1] This is a correct assumption for electric field strengths usually encountered, which are of the order of  $10^7 \text{ V m}^{-1}$ . On the other hand, the treatment given here must be modified for electric field strengths  $\mathcal{E} < 10^5 \text{ V m}^{-1}$ , since in this case the Stark splittings are of the same order of magnitude as the fine structure splittings studied in Section 5.1.

$$\begin{aligned}
 E_{100}^{(1)} &= e\mathcal{E}\langle\psi_{100}|z|\psi_{100}\rangle \\
 &= e\mathcal{E}\int|\psi_{100}(\mathbf{r})|^2z\,d\mathbf{r}
 \end{aligned}
 \tag{6.3}$$

In Section 3.3 we showed that the hydrogenic wave functions  $\psi_{nlm}(\mathbf{r})$  have a *definite* parity (even when the orbital quantum number  $l$  is even, odd when  $l$  is odd). On the other hand the perturbation (6.2) is an *odd* operator under the parity operation since it changes sign when the coordinates are reflected through the origin. Thus we have

$$\langle\psi_{nlm}|z|\psi_{nlm}\rangle = 0 \tag{6.4}$$

since the matrix element  $\langle\psi_{nlm}|z|\psi_{nlm}\rangle$  involves the product of the *even* function  $|\psi_{nlm}(\mathbf{r})|^2$  times the odd function  $z$  under the parity operation. In particular, we see from (6.3) and (6.4) that  $E_{100}^{(1)} = 0$ , so that for the ground state there is no energy shift that is linear in the electric field  $\mathcal{E}$ . Remembering that a classical system having an electric dipole moment  $\mathbf{D}$  will experience in an electric field  $\mathcal{E}$  an energy shift of magnitude  $-\mathbf{D}\cdot\mathcal{E}$ , and noting that  $-ez$  is the  $z$  component of the electric dipole moment operator in our case, we see that one-electron atoms in the ground state cannot possess a permanent electric dipole moment (energy change proportional to  $\mathcal{E}$ ).

Let us now examine the Stark effect on the first excited level ( $n = 2$ ) of one-electron atoms. Since we assume that  $\mathcal{E}$  is large enough for fine structure effects to be neglected we may consider the unperturbed system in the  $n = 2$  level to be fourfold degenerate, the four eigenfunctions

$$\psi_{200}, \quad \psi_{210}, \quad \psi_{211}, \quad \psi_{21-1} \tag{6.5}$$

corresponding to the same unperturbed energy  $E_{n=2} = -mc^2(Z\alpha)^2/8$  (see (3.30)). In principle we should therefore solve a homogeneous system (2.328) of four equations. However, we have already shown in our discussion of selection rules for electric dipole transitions (see Section 4.5) that matrix elements of the form  $\langle nlm|z|n'l'm'\rangle$  vanish unless  $m = m'$  and  $l = l' \pm 1$ . Thus the only non-vanishing matrix elements of the perturbation (6.2) are those connecting the  $2s$  ( $200$ ) and  $2p_0$  ( $210$ ) states, and the linear homogeneous equations (2.328) reduce to a set of two equations which we write in matrix form as

$$\begin{pmatrix} -E^{(1)} & H'_{12} \\ H'_{21} & -E^{(1)} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{6.6}$$

with

$$H'_{12} = H'_{21} = e\mathcal{E}\int\psi_{210}(\mathbf{r})z\psi_{200}(\mathbf{r})\,d\mathbf{r} \tag{6.7}$$

and we have used the fact that  $H'_{12}$  is real.

The reduction of the original homogeneous system of four equations to the two equations (6.6) may also be obtained easily by noting that (i) the operator  $H'$  commutes with  $L_z$ , the  $z$  component of the angular momentum, so that  $H'$  only connects states with the same value of the quantum number  $m$ , and (ii)  $H'$  is odd under the parity operation.

The matrix element  $H'_{12}$  can be evaluated by using the hydrogenic wave functions given in Table 3.1 of Chapter 3. Since  $z = r \cos \theta$ , we have

$$\begin{aligned} H'_{12} &= e \mathcal{E} \frac{Z^3}{16\pi a_0^3} \int_0^\infty dr r^3 \left( \frac{Zr}{a_0} \right) \left( 1 - \frac{Zr}{2a_0} \right) \exp(-Zr/a_0) \int_0^\pi d\theta \sin \theta \cos^2 \theta \int_0^{2\pi} d\phi \\ &= e \mathcal{E} \frac{Z^3}{8a_0^3} \frac{2}{3} \int_0^\infty dr r^3 \left( \frac{Zr}{a_0} \right) \left( 1 - \frac{Zr}{2a_0} \right) \exp(-Zr/a_0) \\ &= -3e \mathcal{E} a_0/Z \end{aligned} \quad (6.8)$$

Thus the two roots of the determinantal equation

$$\begin{vmatrix} -E^{(1)} & H'_{12} \\ H'_{12} & -E^{(1)} \end{vmatrix} = 0 \quad (6.9)$$

are given by

$$E^{(1)} = \pm |H'_{12}| = \pm 3e \mathcal{E} a_0/Z \quad (6.10)$$

Upon returning to (6.6) we see that for the lower root  $E_1^{(1)} = -3e\mathcal{E}a_0/Z$  one has  $c_1 = c_2$ . The corresponding normalised eigenstate  $\psi_1$  is given by

$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_{200} + \psi_{210}) \quad (6.11a)$$

The second root  $E_2^{(1)} = +3e\mathcal{E}a_0/Z$  yields  $c_1 = -c_2$  and a normalised eigenstate

$$\psi_2 = \frac{1}{\sqrt{2}} (\psi_{200} - \psi_{210}) \quad (6.11b)$$

It should be emphasised that the states (6.11) are neither eigenstates of the parity operator, nor of  $\mathbf{L}^2$ , so that neither parity nor  $l$  is a 'good' quantum number in this case. On the other hand,  $m$  is a good quantum number because  $H'$  commutes with  $L_z$  (that is, the system is invariant under rotation about the  $Z$  axis). We also remark that the wave number shifts  $\delta\tilde{\nu}$  corresponding to the energy corrections  $E^{(1)}$  are given by

$$\delta\tilde{\nu} = \pm \frac{3ea_0}{hc} \frac{\mathcal{E}}{Z} = \pm 12.8 \left( \frac{\mathcal{E}}{Z} \right) 10^{-7} \text{ cm}^{-1} \quad (6.12)$$

so that rather strong fields (of the order of  $10^7 \text{ V m}^{-1}$  in Stark's experiments) are required to demonstrate the effect.

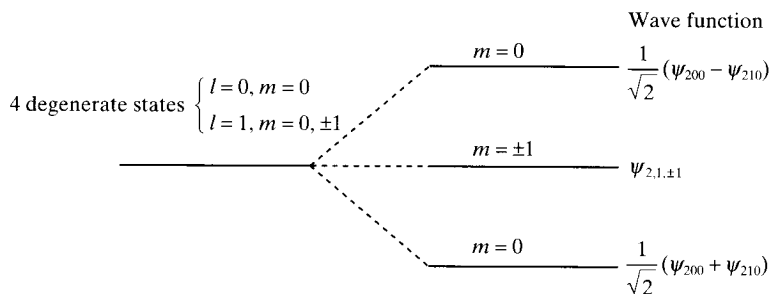


Figure 6.1 Splitting of the degenerate  $n = 2$  level of a one-electron atom due to the linear Stark effect.

The splitting of the degenerate  $n = 2$  level of a one-electron atom due to the linear Stark effect is illustrated in Fig. 6.1. The degeneracy is partly removed by the perturbation, the energies of the  $2p_{\pm 1}$  (that is,  $211$  and  $21-1$ ) states remaining unaltered. Thus the level  $n = 2$  splits in a symmetrical way into *three* sublevels, one of which (corresponding to  $m = \pm 1$ ) is twofold degenerate.

At this point it is worth recalling that a classical system having an electric dipole moment  $\mathbf{D}$  will experience in an electric field  $\mathcal{E}$  an energy shift  $-\mathbf{D} \cdot \mathcal{E}$ . This suggests that the hydrogen atom in the *degenerate* unperturbed states  $n = 2$  behaves as though it has a *permanent electric dipole moment* (independently of the value of  $\mathcal{E}$ ), of magnitude  $3ea_0$ , which can be orientated in three different ways (that is, gives rise to spatial quantisation) in the presence of the electric field: one state ( $\psi_1$ ) parallel to  $\mathcal{E}$ , one state ( $\psi_2$ ) antiparallel to  $\mathcal{E}$ , and two states with no component along the electric field.

On the other hand, we found above that for the hydrogen ground state, which is *non-degenerate* and hence is an eigenstate of the *parity* operator, there is no energy shift linear in the electric field strength, and hence no permanent electric dipole moment. This conclusion may readily be generalised. Indeed, apart from tiny effects which we shall not consider here [2] all the systems studied in this book may be described by Hamiltonians which are unaffected by the parity operation (that is, the reflection of the coordinates of all the particles through the origin) and therefore any *non-degenerate* state of such systems has a definite parity (even or odd). Now for a system containing  $N$  particles of charges  $e_i$  ( $i = 1, 2, \dots, N$ ) and coordinates  $\mathbf{r}_i$ , the electric dipole moment operator

$$\mathbf{D} = \sum_{i=1}^N e_i \mathbf{r}_i \quad (6.13)$$

is odd under the parity operation, so that its expectation value in a state of given parity is zero. As a result, *systems in non-degenerate states cannot have permanent*

[2] Parity non-conserving effects occur in the so-called *weak interactions*, which are responsible for weak decay processes of (elementary) particles, such as those observed in beta decay.

*electric dipole moments.* Note, however, that if we have a positive ion  $A^+$  located at the position  $\mathbf{r}_1$  and a negative ion  $B^-$  at the position  $\mathbf{r}_2$ , the system ( $A^+ B^-$ ) does possess an electric dipole moment. This does not contradict the previous argument since the configuration for which  $A^+$  is at  $\mathbf{r}_2$  and  $B^-$  at  $\mathbf{r}_1$  has the same energy as the first arrangement and the system is necessarily degenerate. For the same reason, when atoms are bound together, the resulting molecules may possess permanent electric dipole moments [3].

Another remark concerns our use of degenerate perturbation theory for the treatment of the Stark effect on the  $n = 2$  level. As we know from our discussion in Chapter 5 there are small effects (fine structure, Lamb shift) which remove some of the degeneracies of this level, so that the situation will then correspond to a *near-degenerate* case. We shall not treat this problem in detail [4] but consider instead the simple model problem in which two unperturbed states  $\psi_1^{(0)}$  and  $\psi_2^{(0)}$  do not correspond exactly to the same unperturbed energy  $E^{(0)}$  ( $E_{n=2}$  in our case) but to energies given respectively by  $E_1^{(0)} = E^{(0)} - \varepsilon$  and  $E_2^{(0)} = E^{(0)} + \varepsilon$ , which differ by a small amount  $2\varepsilon$  (with  $\varepsilon > 0$ ). Instead of solving the equation (6.6), we must now solve the matrix equation

$$\begin{pmatrix} E^{(0)} - \varepsilon - E & H'_{12} \\ H'_{21} & E^{(0)} + \varepsilon - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad (6.14)$$

where  $H'_{12} = H'_{21}$  is given by (6.8). Thus we have

$$E = E^{(0)} \pm [(H'_{12})^2 + \varepsilon^2]^{1/2} \quad (6.15)$$

It is apparent from this result that for very weak fields (such that  $|H'_{12}| \ll \varepsilon$  and the Stark splitting is small with respect to fine structure effects), there is no linear Stark effect. On the other hand, for strong field strengths  $\mathcal{E}$  such that  $|H'_{12}| \gg \varepsilon$  we retrieve the results found above by using degenerate perturbation theory (linear Stark effect). In what follows we shall continue to assume that the field strength  $\mathcal{E}$  is large enough for the fine structure effects to be neglected.

The splitting of the  $n = 3$  level due to the linear Stark effect may be treated in a way similar to the  $n = 2$  case analysed above. It is found (Problem 6.1) that this level is split into *five* equally spaced levels, as shown in Fig. 6.2. Also displayed in Fig. 6.2 are the radiative transitions between the levels  $n = 2$  and  $n = 3$  (corresponding to the spectral line  $H_\alpha$ ) of atomic hydrogen in the presence of an electric field. The selection rules with respect to the magnetic quantum number  $m$  are the same as those we obtained in Chapter 4 without an external field. That is,

$$\Delta m = 0, \pm 1 \quad (6.16)$$

[3] The kind of degeneracy to which we have referred is often removed in an 'exact' calculation of molecular ground states. However, because the splittings involved are very small, in experiments an average is taken over the ground and neighbouring states, of different parities, resulting in an effective permanent electric dipole moment.

[4] A comprehensive treatment may be found in Bethe and Salpeter (1957).



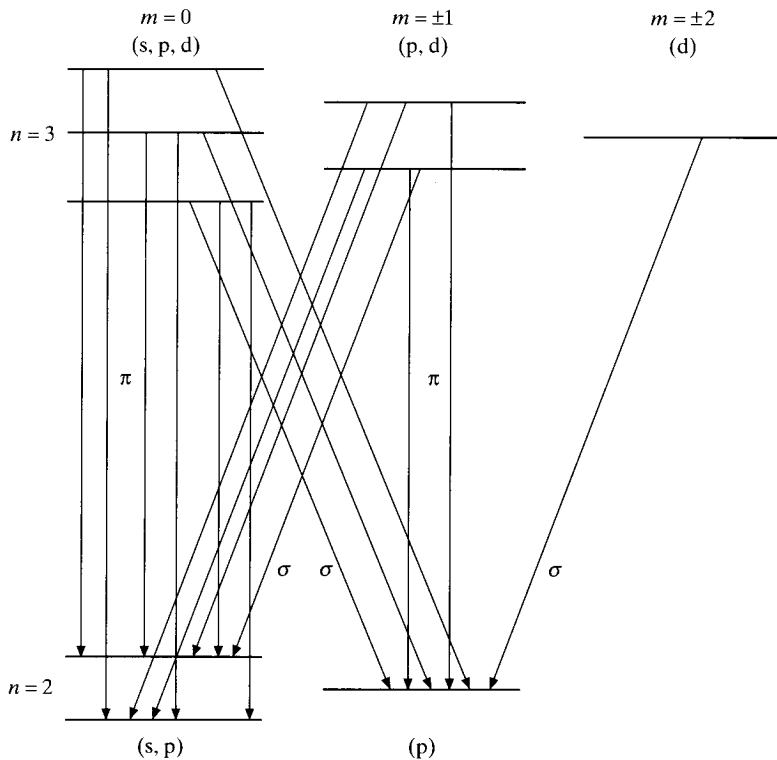


Figure 6.2 Splitting of the  $n=3$  and  $n=2$  levels of atomic hydrogen due to the linear Stark effect. The various possible transitions are shown; those with  $\Delta m=0$  correspond to  $\pi$  lines and those with  $\Delta m=\pm 1$  to  $\sigma$  lines.

The  $\Delta m=0$  transitions are said to correspond to  $\pi$  components, and the  $\Delta m=\pm 1$  to  $\sigma$  components.

On the other hand, since  $l$  is not a good quantum number in the presence of an external electric field, it is clear that the selection rules concerning  $l$  must be modified. In particular, because the operator  $H' = e\mathcal{E}z$  has a non-vanishing matrix element between the  $2s$  and  $2p_0$  states, these two states are 'mixed' by the perturbation  $H'$  with the result that the metastable  $2s$  state is 'contaminated' by the unstable  $2p$  state. Thus a radiative transition from the  $2s$  state to the  $1s$  state can be induced by an external electric field [5], so that the lifetime of the  $2s$  state is considerably shortened by comparison with its value ( $1/7$  s) in the absence of an electric field.

In order to examine in more detail this process, which is called 'quenching of the metastable  $2s$  states', let us assume that at the initial time  $t=0$  the hydrogen atom is in the  $2s$  ( $200$ ) state. We then apply a constant electric field of strength

[5] It is worth noting that this external electric field need not be a static field, as in the case studied here, but can also be a time-dependent (oscillating) field.

$\mathcal{E}$  directed along the  $Z$  axis, and use the results (6.10) and (6.11) to write the time-dependent wave function of the atom at  $t > 0$  as

$$\Psi(\mathbf{r}, t) = c_1 \psi_1(\mathbf{r}) \exp\left[-\frac{i}{\hbar}(E_{n=2} - \Delta E)t\right] + c_2 \psi_2(\mathbf{r}) \exp\left[-\frac{i}{\hbar}(E_{n=2} + \Delta E)t\right] \quad (6.17)$$

where  $E_{n=2} = -mc^2\alpha^2/8$  and  $\Delta E = |H'_{12}| = 3e\mathcal{E}a_0$  is the absolute value of the (first-order) energy shift. The coefficients  $c_1$  and  $c_2$  are easily found from the initial condition

$$\Psi(\mathbf{r}, t = 0) = \psi_{200}(r) \quad (6.18)$$

Using (6.11) and (6.18), we find that  $c_1 = c_2 = 2^{-1/2}$ , so that

$$\begin{aligned} \Psi(\mathbf{r}, t) &= \frac{1}{\sqrt{2}} \psi_1(\mathbf{r}) \exp\left[-\frac{i}{\hbar}(E_{n=2} - \Delta E)t\right] + \frac{1}{\sqrt{2}} \psi_2(\mathbf{r}) \exp\left[-\frac{i}{\hbar}(E_{n=2} + \Delta E)t\right] \\ &= \left[ \psi_{200}(r) \cos\left(\frac{\Delta E}{\hbar}t\right) + i\psi_{210}(\mathbf{r}) \sin\left(\frac{\Delta E}{\hbar}t\right) \right] \exp\left(-\frac{i}{\hbar}E_{n=2}t\right) \end{aligned} \quad (6.19)$$

Thus the atom oscillates between the 200 ( $2s$ ) and 210 ( $2p_0$ ) states, with a period

$$T = \frac{\pi\hbar}{\Delta E} \quad (6.20)$$

For example, in the case of an electric field of strength  $\mathcal{E} = 10^7 \text{ V m}^{-1}$ , we find from (6.20) that  $T \approx 1.3 \times 10^{-12} \text{ s}$  which is much shorter than the time  $\tau \approx 1.6 \times 10^{-9} \text{ s}$  corresponding to the radiative transition  $2p-1s$  (that is, the lifetime of the  $2p$  state in the absence of an external field). As a result, the average population of both states  $2s$  and  $2p_0$  is nearly equal during the entire decay time. This conclusion is easily seen to be true for initial conditions in which the atom is initially (at  $t = 0$ ) in an arbitrary superposition of the  $2s$  and  $2p_0$  states (Problem 6.2). Thus, in the presence of a strong electric field the radiative transitions  $2s-1s$  and  $2p-1s$  have the same transition probability per unit time, which is equal to  $1/(2\tau)$ . It is apparent from this discussion that in general, an external electric field will be able to induce  $n's-n_s$  radiative transitions.

### The linear Stark effect in parabolic coordinates

It is also possible to evaluate the linear Stark effect of hydrogenic atoms by using parabolic coordinates, and this treatment is actually simpler than the one using spherical polar coordinates for principal quantum numbers  $n \geq 3$ . As we saw in Section 3.5, the Schrödinger equation for one-electron atoms in the absence of external fields can be separated in parabolic coordinates. This separability is maintained in the presence of an external electric field. Indeed, using (3.90), the interaction (6.2) can be expressed in parabolic coordinates as

$$H' = \frac{1}{2} \mathcal{E}(\xi - \eta) \quad (6.21)$$

where we are using atomic units. The atomic unit of electric field strength is the strength of the Coulomb field experienced by an electron in the first Bohr orbit of atomic hydrogen (with infinite nuclear mass). That is,

$$\mathcal{E}_a = \frac{e}{(4\pi\epsilon_0)a_0^2} = 5.142\,21 \times 10^{11} \text{ V m}^{-1} \quad (6.22)$$

The electric field strengths considered in this section are such that  $\mathcal{E} \ll 1$  (in a.u.).

The Schrödinger equation for a hydrogenic atom in the presence of a static electric field reads (in a.u.)

$$\left( -\frac{1}{2} \nabla^2 - \frac{Z}{r} + H' \right) \psi = E\psi \quad (6.23)$$

and has separable solutions of the form (3.95). The angular function  $\Phi(\phi)$  is again given by (3.98), while the functions  $f(\xi)$  and  $g(\eta)$  satisfy the equations

$$\left[ \frac{d}{d\xi} \left( \xi \frac{d}{d\xi} \right) + \left( \frac{1}{2} E\xi - \frac{m^2}{4\xi} - \frac{1}{4} \mathcal{E}\xi^2 + v_1 \right) \right] f = 0 \quad (6.24a)$$

and

$$\left[ \frac{d}{d\eta} \left( \eta \frac{d}{d\eta} \right) + \left( \frac{1}{2} E\eta - \frac{m^2}{4\eta} + \frac{1}{4} \mathcal{E}\eta^2 + v_2 \right) \right] g = 0 \quad (6.24b)$$

where the separation constants  $v_1$  and  $v_2$  must fulfil the condition (see (3.99))

$$v_1 + v_2 = Z \quad (6.25)$$

Using the unperturbed hydrogenic wave functions in parabolic coordinates given in Section 3.5, and first-order perturbation theory, it is found [6] that the perturbed energies are (in a.u.)

$$E_{n_1 n_2} = -\frac{1}{2} \frac{Z^2}{n^2} + \frac{3}{2} \frac{\mathcal{E}}{Z} n (n_1 - n_2) \quad (6.26)$$

where  $n_1$  and  $n_2$  are the parabolic quantum numbers introduced in Section 3.5. The energies  $E_{n_1 n_2}$  are seen to depend on the principal quantum number  $n$  and on the difference  $n_1 - n_2$ . Although there is no explicit dependence in (6.26) on the magnetic quantum number  $m$ , there is an implicit dependence because of the relation (3.110). For a given value of  $n$ , the Stark component having the highest energy is obtained by setting  $n_1 = n - 1$  and  $n_2 = 0$ , which from (3.110) implies that

[6] See Bethe and Salpeter (1957).

$m = 0$ . The lowest Stark component corresponds to  $n_1 = 0$ ,  $n_2 = n - 1$ , which also implies that  $m = 0$ .

### Quadratic Stark effect

We have shown above that for the ground state (100) of hydrogenic atoms there is no linear Stark effect. In order to investigate the effect of the perturbation (6.2) on that state we must therefore consider the second-order term of the perturbation series. Using (2.319) we see that in our case it reads

$$E_{100}^{(2)} = e^2 \mathcal{E}^2 \sum_{n \neq 1, l, m} \frac{|\langle \psi_{nlm} | z | \psi_{100} \rangle|^2}{E_1 - E_n} \quad (6.27)$$

where the sum implies a summation over the discrete set together with an integration over the continuous set of hydrogenic eigenfunctions. It is clear from (6.27) that the ground state energy will be *lowered* by the quadratic Stark effect, since the energy differences  $E_1 - E_n$  ( $n \geq 2$ ) are always negative. In fact, we may readily obtain a lower limit for  $E_{100}^{(2)}$  by replacing in (6.27) the energy differences  $E_1 - E_n$  by  $E_1 - E_2$ . That is,

$$\begin{aligned} E_{100}^{(2)} &= -e^2 \mathcal{E}^2 \sum_{n \neq 1, l, m} \frac{|\langle \psi_{nlm} | z | \psi_{100} \rangle|^2}{E_n - E_1} \\ &> -e^2 \mathcal{E}^2 \frac{1}{E_2 - E_1} \sum_{n \neq 1, l, m} |\langle \psi_{nlm} | z | \psi_{100} \rangle|^2 \end{aligned} \quad (6.28)$$

The summation on the right of (6.28) may now be performed as follows. We first note that because  $\langle \psi_{100} | z | \psi_{100} \rangle = 0$  we may write

$$\begin{aligned} \sum_{n \neq 1, l, m} |\langle \psi_{nlm} | z | \psi_{100} \rangle|^2 &= \sum_{n, l, m} |\langle \psi_{nlm} | z | \psi_{100} \rangle|^2 \\ &= \sum_{n, l, m} |\langle \psi_{100} | z | \psi_{nlm} \rangle \langle \psi_{nlm} | z | \psi_{100} \rangle| \end{aligned} \quad (6.29)$$

Using the completeness of the hydrogenic states, namely

$$\sum_{nlm} |\psi_{nlm}\rangle \langle \psi_{nlm}| = I \quad (6.30)$$

where  $I$  is the unit operator, we have

$$\begin{aligned} \sum_{n, l, m} \langle \psi_{100} | z | \psi_{nlm} \rangle \langle \psi_{nlm} | z | \psi_{100} \rangle &= \langle \psi_{100} | z^2 | \psi_{100} \rangle \\ &= \langle z^2 \rangle_{100} \end{aligned} \quad (6.31)$$

But

$$\langle z^2 \rangle_{100} = \langle x^2 \rangle_{100} = \langle y^2 \rangle_{100} = \frac{1}{3} \langle r^2 \rangle_{100} = \frac{a_0^2}{Z^2} \quad (6.32)$$

so that from (6.28)–(6.32) and (3.29) we have

$$E_{100}^{(2)} > -\frac{8}{3}(4\pi\epsilon_0)\frac{a_0^3}{Z^4}\mathcal{E}^2 \quad (6.33)$$

It is possible to obtain in a straightforward way another estimate for  $E_{100}^{(2)}$  (Problem 6.3):

$$E_{100}^{(2)} \simeq -2(4\pi\epsilon_0)\frac{a_0^3}{Z^4}\mathcal{E}^2 \quad (6.34)$$

The exact evaluation of the expression (6.27) can be carried out using parabolic coordinates. One finds (Bethe and Salpeter, 1957) that

$$\begin{aligned} E_{100}^{(2)} &= -2.25(4\pi\epsilon_0)\frac{a_0^3}{Z^4}\mathcal{E}^2 \\ &= -3.71 \times 10^{-41} \left( \frac{\mathcal{E}^2}{Z^4} \right) \text{J} \end{aligned} \quad (6.35)$$

It is worth noting that about one-third of the result (6.35) arises from the contribution of the continuum in the summation (6.27). We also remark that the quadratic Stark effect given by (6.35) is generally very small, being approximately  $0.02 \text{ cm}^{-1}$  for atomic hydrogen in the case of a field strength  $\mathcal{E} = 10^8 \text{ V m}^{-1}$ .

Upon differentiation of the expression (6.27) with respect to the electric field strength, we obtain for the magnitude of the dipole moment the result

$$D = -\frac{\partial E_{100}^{(2)}}{\partial \mathcal{E}} = \bar{\alpha}\mathcal{E} \quad (6.36)$$

where

$$\bar{\alpha} = 2e^2 \sum_{n \neq 1, l, m} \frac{|\langle \psi_{nlm} | z | \psi_{100} \rangle|^2}{E_n - E_1} \quad (6.37)$$

is the *static dipole polarisability* of the atom in the state (100). We note that because the matrix element  $\langle \psi_{nlm} | z | \psi_{100} \rangle$  vanishes unless  $m = 0$ , the sum over  $m$  reduces to one term. We see from (6.36) that  $D$  is proportional to  $\mathcal{E}$ , so that we have an *induced dipole moment*. We also note from (6.27) and (6.37) that

$$E_{100}^{(2)} = -\frac{1}{2}\bar{\alpha}\mathcal{E}^2 \quad (6.38)$$

and the result (6.35) implies that

$$\begin{aligned} \bar{\alpha} &= 4.50(4\pi\epsilon_0)\frac{a_0^3}{Z^4} \\ &= 7.42 \times 10^{-41} Z^{-4} \text{F m}^2 \\ &= 4.50 Z^{-4} \text{a.u.} \end{aligned} \quad (6.39)$$

### The quadratic Stark effect in parabolic coordinates

Starting from the equations (6.24), and using second-order perturbation theory, one obtains [6] for the perturbed energies (in a.u.)

$$E_{n_1 n_2 m} = -\frac{1}{2} \frac{Z^2}{n^2} + \frac{3}{2} \mathcal{E} \frac{n}{Z} (n_1 - n_2) - \frac{1}{16} \mathcal{E}^2 \left( \frac{n}{Z} \right)^4 [17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19] \quad (6.40)$$

As seen from this result, the quadratic Stark effects always leads to a lowering of the levels. We also note that the second-order shift removes the  $m$  degeneracy, and remains unaltered under the interchange of  $n_1$  and  $n_2$ .

The quadratic Stark effect is usually a small correction to the linear Stark effect. For example, in the case of the  $H_\alpha$  line, where the separation of the outermost components is about  $200 \text{ cm}^{-1}$  for a field strength of  $4 \times 10^7 \text{ V m}^{-1}$ , the corresponding (red) shift due to the quadratic Stark effect is only  $1 \text{ cm}^{-1}$ .

### Ionisation by a static electric field

So far we have used perturbation theory to study the energy shifts and the spectral lines of hydrogenic atoms in the presence of a static electric field. We shall now consider another effect due to the presence of an external electric field, namely the removal of the electron from the atom.

To see how this comes about, we first note that the total potential energy  $V$  of the electron is obtained by adding the potential energy  $e\mathcal{E}z$  arising from the external field (see (6.2)) to the Coulomb potential  $-Ze^2/(4\pi\epsilon_0 r)$  of the nucleus. Thus

$$V = -\frac{Ze^2}{(4\pi\epsilon_0)r} + e\mathcal{E}z \quad (6.41)$$

A schematic drawing of  $V$  is shown in Fig. 6.3 as a function of  $z$ , for  $x$  and  $y$  fixed. It is apparent that the nucleus is not the only place at which  $V$  has a minimum, since  $V$  can become even more negative if  $z$  is negative enough, that is at large enough distances of the atom in the direction of the anode. Thus the potential  $V$  has two minima, one at the nucleus and the other at the anode, separated by a potential barrier. The electron, which is initially in a bound state of the atom, has therefore a finite probability of 'escaping' from the atom by means of the *tunnel effect*, and being accelerated towards the anode, so that ionisation will occur.

This possibility of ionisation by the electric field was first pointed out by J. Oppenheimer in 1928. Experimentally it can be observed when the external electric field is very strong and (or) for levels with high principal quantum number  $n$ . It is then seen that the spectral lines are *weakened* because of the competition between the radiative transitions and the ionisation process. Moreover, in the presence of an external electric field the lifetime of the discrete levels is decreased because of the 'tunnel effect', so that the width of the spectral lines is increased. This is known as *Stark broadening*. In particular, the ground state itself is no

# Field Ionisation

### The quadratic Stark effect in parabolic coordinates

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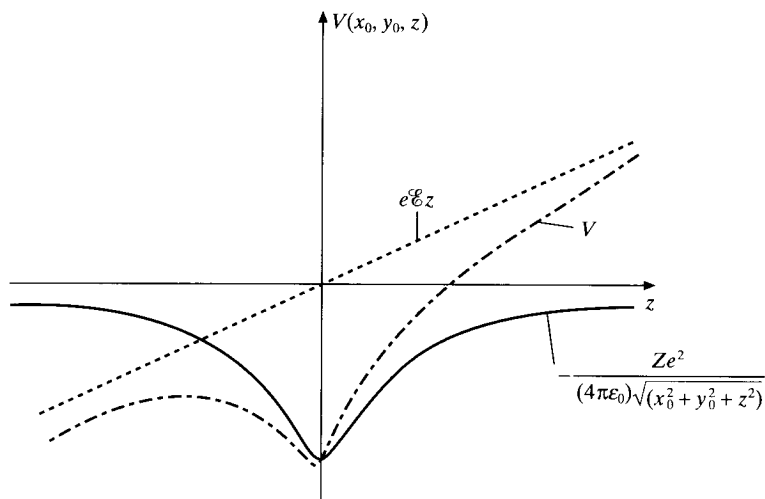


Figure 6.3 The potential  $V$  experienced by an electron interacting with a nucleus of charge  $Ze$ , in a uniform electric field of strength  $\mathcal{E}$ , as a function of  $z$ , for  $x = x_0$  and  $y = y_0$  fixed.

longer a stationary state, but becomes a metastable state when an external electric field is applied, and the perturbation series is found to be a semi-convergent (asymptotic) series. However, if the electric field is not too strong, the ground state is stable on a very large time scale, and the predictions of the first few terms of the perturbation series agree very well with experiment.

We shall now obtain an approximate expression for the rate of ionisation of a ground state hydrogen atom by a uniform electric field directed along the  $Z$  axis. It is convenient to use atomic units, and to perform the calculation in parabolic coordinates, starting from the equations (6.24). The field strengths that we shall consider are such that  $\mathcal{E} \ll 1$ .

By making in (6.24) the substitutions

$$f = \xi^{-1/2} F, \quad g = \eta^{-1/2} G \quad (6.42)$$

we obtain for  $F$  and  $G$  the pair of equations

$$-\frac{1}{2} \frac{d^2 F}{d\xi^2} + V_1(\xi) F = \frac{E}{4} F \quad (6.43a)$$

and

$$-\frac{1}{2} \frac{d^2 G}{d\eta^2} + V_2(\eta) G = \frac{E}{4} G \quad (6.43b)$$

where  $V_1$  and  $V_2$  are defined by

$$V_1(\xi) = \frac{m^2 - 1}{8\xi^2} - \frac{v_1}{2\xi} + \frac{\mathcal{E}\xi}{8} \quad (6.44a)$$

and

$$V_2(\eta) = \frac{m^2 - 1}{8\eta^2} - \frac{v_2}{2\eta} - \frac{\mathcal{E}\eta}{8} \quad (6.44b)$$

It is seen that the equations (6.43) have the form of two one-dimensional Schrödinger equations in which  $E/4$  plays the role of the energy, while  $V_1$  and  $V_2$  are potentials.

The unperturbed ground state wave function of atomic hydrogen, expressed in parabolic coordinates (see (3.119)) and in atomic units, namely

$$\psi_0 = \pi^{-1/2} \exp\left[-\frac{1}{2}(\xi + \eta)\right] \quad (6.45)$$

is a solution of the equations (6.43) when  $\mathcal{E} = 0$ . Since the magnetic quantum number for this state is  $m = 0$ , and because the perturbation (6.21) is independent of  $\phi$ , the perturbed ground state wave function, which will be denoted by  $\psi_0^p$ , must also be such that  $m = 0$ . It must therefore satisfy the equations (6.43) with  $\mathcal{E} > 0$ , in which the potentials  $V_1(\xi)$  and  $V_2(\eta)$  are calculated from (6.44) by setting  $m = 0$ .

Let us write the unperturbed ground state wave function (6.45) in the form

$$\psi_0 = \pi^{-1/2} (\xi\eta)^{-1/2} F_0(\xi) G_0(\eta) \quad (6.46)$$

The functions

$$F_0(\xi) = \xi^{1/2} \exp(-\xi/2) \quad (6.47a)$$

and

$$G_0(\eta) = \eta^{1/2} \exp(-\eta/2) \quad (6.47b)$$

satisfy the equations (6.43) with  $E = -1/2$ , where in (6.44)  $\mathcal{E} = 0$  and  $v_1 = v_2 = 1/2$ .

In Fig. 6.4, the potentials  $V_1$  and  $V_2$  are sketched for the cases  $\mathcal{E} = 0$  and  $\mathcal{E} > 0$ . When  $\mathcal{E} > 0$ , it is seen that  $V_1(\xi)$  has an infinite barrier as  $\xi \rightarrow +\infty$  and this prevents the wave function  $F(\xi)$  from penetrating into the region of large  $\xi$ . For  $\mathcal{E} \ll 1$ , the potential  $V_1(\xi)$  does not differ appreciably over the extent of the unperturbed function  $F_0(\xi)$  from its values when  $\mathcal{E} = 0$ . It follows that it is a good approximation to take

$$F(\xi) \approx F_0(\xi) \quad (6.48)$$

for all  $\xi$ , where  $F_0(\xi)$  is given by (6.47a). Since  $F_0(\xi)$  only satisfies (6.47a) if  $v_1 = 1/2$ , we must also take  $v_2 = 1/2$  because of the condition (6.25).

Referring to (6.44b), we see that if  $\mathcal{E} > 0$ ,  $V_2(\eta) \rightarrow -\infty$  as  $\eta \rightarrow +\infty$  so that for all non-zero values of  $\mathcal{E}$  the potential  $V_2(\eta)$  presents a *finite barrier* through which tunnelling is possible to reach large values of  $\eta$ . The region in which  $\xi$  is small but  $\eta$  is large corresponds in Cartesian coordinates to finite values of  $x$  and  $y$  while  $z \rightarrow -\infty$ . This is the region in which we must calculate the flux of electrons which have been ionised by the electric field. To find an approximate solution of (6.43b),

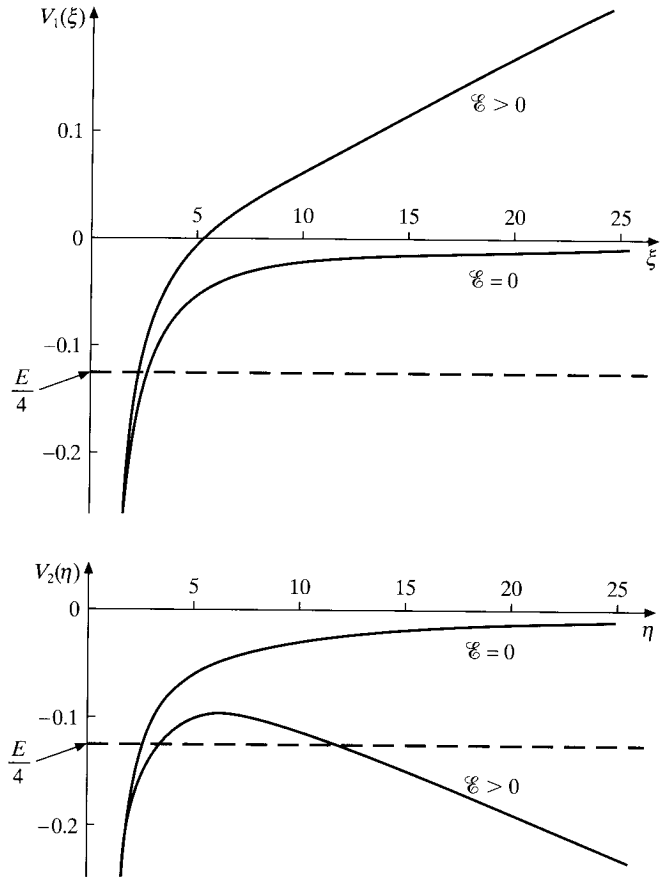


Figure 6.4 The form of the potentials  $V_1(\xi)$  and  $V_2(\eta)$  when  $m = 0$  for  $\xi = 0$  and  $\xi > 0$ .

we first choose a value  $\eta_0$  of  $\eta$ , such that  $\eta_0$  lies within the barrier presented by the potential  $V_2(\eta)$  and satisfies the conditions

$$\eta_0 \gg 1 \tag{6.49}$$

and

$$\xi \eta_0 \ll 1 \tag{6.50}$$

In view of the condition (6.50), the interaction  $-\xi\eta/8$  in (6.44b) can be neglected for  $\eta \leq \eta_0$  so that

$$G(\eta) \approx G_0(\eta), \quad \eta \leq \eta_0 \tag{6.51}$$

In the region  $\eta \geq \eta_0$ , the WKB approximation can be employed since the potential  $V_2(\eta)$  is smooth and slowly varying. Using (2.433),  $G(\eta)$  can be approximated as

$$G(\eta) \approx A|p(\eta)|^{-1/2} \exp \left[ i \int_{\eta_0}^{\eta} p(\eta') d\eta' \right], \quad \eta \geq \eta_0 \quad (6.52)$$

where  $p(\eta)$  is defined by (see (2.421))

$$\begin{aligned} p(\eta) &= \left\{ 2 \left[ \frac{E}{4} - V_2(\eta) \right] \right\}^{1/2} \\ &= \left[ -\frac{1}{4} + \frac{1}{4\eta^2} + \frac{1}{2\eta} + \frac{1}{4} \mathcal{E}\eta \right]^{1/2} \end{aligned} \quad (6.53)$$

since  $E = -1/2$ .

The constant  $A$  in (6.52) is obtained from the relation (6.51) and is given by

$$A = [\eta_0 |p(\eta_0)|]^{1/2} \exp(-\eta_0/2) \quad (6.54)$$

Neglecting in (6.53) small terms in  $\eta^{-2}$  and  $\eta^{-1}$ ,  $p^2(\eta)$  is seen to have a zero at  $\eta = \eta_1$ , where

$$\eta_1 \approx \frac{1}{\mathcal{E}} \quad (6.55)$$

For  $\eta > \eta_1$ ,  $p^2(\eta) > 0$  and  $p(\eta)$  is real, while for  $\eta_0 \leq \eta \leq \eta_1$ ,  $p^2(\eta) < 0$  and  $p(\eta)$  is imaginary. Since  $G(\eta)$  must decrease from  $\eta_0$  to  $\eta_1$ , we must take  $p(\eta) = +i|p(\eta)|$  in this region.

To calculate the flux of outgoing electrons we require  $|G(\eta)|^2$  in the limit  $\eta \rightarrow +\infty$  and since  $p(\eta)$  is real for  $\eta > \eta_1$ , we have

$$\begin{aligned} |G(\eta)|^2 &= A^2 \frac{1}{|p(\eta)|} \exp \left[ -2 \int_{\eta_0}^{\eta_1} |p(\eta')| d\eta' \right] \\ &= \eta_0 \left| \frac{p(\eta_0)}{p(\eta)} \right| \exp \left[ -2 \int_{\eta_0}^{\eta_1} |p(\eta')| d\eta' - \eta_0 \right] \end{aligned} \quad (6.56)$$

In the factors multiplying the exponential, the approximations can be made that  $|p(\eta_0)| \approx 1/2$ . Moreover, for large  $\eta$  (such that  $\mathcal{E}\eta \gg 1$ )

$$|p(\eta)| \approx \frac{1}{2} (\mathcal{E}\eta - 1)^{1/2} \quad (6.57)$$

In the exponential,  $|p(\eta')|$  can be approximated by retaining in (6.53) the small term  $(2\eta')^{-1}$ , but neglecting the term in  $(4\eta'^2)^{-1}$ , so that, for  $\eta_0 \leq \eta' \leq \eta_1$ ,

$$\begin{aligned} |p(\eta')| &\approx \frac{1}{2} \left( 1 - \frac{2}{\eta'} - \mathcal{E}\eta' \right)^{1/2} \\ &\approx \frac{1}{2} (1 - \mathcal{E}\eta')^{1/2} - \frac{1}{2\eta'} (1 - \mathcal{E}\eta')^{-1/2} \end{aligned} \quad (6.58)$$

Evaluating the integral in the exponent of (6.56), using the approximation (6.58), noting that  $\mathcal{E}\eta_0 \ll 1$  and that  $\eta_1 \approx 1/\mathcal{E}$ , it is found that

$$\begin{aligned}
 -2 \int_{\eta_0}^{\eta_1} |p(\eta')| d\eta' &\simeq -\frac{2}{3\mathcal{E}}(1 - \mathcal{E}\eta_0)^{3/2} + \log \left[ \frac{1 + (1 - \mathcal{E}\eta_0)^{1/2}}{1 - (1 - \mathcal{E}\eta_0)^{1/2}} \right] \\
 &\simeq \eta_0 - \frac{2}{3\mathcal{E}} + \log \left( \frac{4}{\mathcal{E}\eta_0} \right)
 \end{aligned} \tag{6.59}$$

Thus, from (6.56) and (6.59), we have approximately, for large  $\eta$ ,

$$|G(\eta)|^2 \simeq \frac{4}{\mathcal{E}(\mathcal{E}\eta - 1)^{1/2}} \exp\left(-\frac{2}{3\mathcal{E}}\right) \tag{6.60}$$

For small  $\xi$  and large  $\eta$ , the perturbed ground state wave function  $\psi_0^p$  is

$$\psi_0^p = \pi^{-1/2}(\xi\eta)^{-1/2} F_0(\xi) G(\eta) \tag{6.61}$$

Hence, using (6.47a) and (6.60), we find that for small  $\xi$  and large  $\eta$

$$|\psi_0^p|^2 = \frac{1}{\pi} \frac{4}{\mathcal{E}\eta(\mathcal{E}\eta - 1)^{1/2}} \exp\left(-\frac{2}{3\mathcal{E}}\right) \exp(-\xi) \tag{6.62}$$

The ionisation rate  $W_{\text{ion}}$  is equal to the number of electrons passing through a plane perpendicular to the  $Z$  axis per unit time as  $z \rightarrow -\infty$ , so that

$$W_{\text{ion}} = \int_0^{2\pi} d\phi \int_0^\infty d\rho \rho |\psi_0^p|^2 v_z \tag{6.63}$$

where  $v_z$  is the  $z$  component of the electron velocity, and

$$\rho = (x^2 + y^2)^{1/2} = (\xi\eta)^{1/2} \tag{6.64}$$

A fixed value of  $-z$ , where  $|z|$  is large, corresponds to a fixed value of  $\eta$ , since the significant values of  $\xi$  are small. Thus we may set

$$d\rho = \frac{1}{2} \xi^{-1/2} \eta^{1/2} d\xi \tag{6.65}$$

and since  $\psi_0^p$  is independent of  $\phi$ , we have

$$W_{\text{ion}} = (2\pi) \frac{1}{2} \int_0^\infty \eta |\psi_0^p|^2 v_z d\xi \tag{6.66}$$

In the large  $|z|$  region the electron's motion is classical and using conservation of energy

$$E = \frac{1}{2} v_z^2 + \mathcal{E}z \tag{6.67}$$

so that with  $E = -1/2$ , and  $-z \approx \eta/2$ ,

$$\nu_z = (\mathcal{E}\eta - 1)^{1/2} \quad (6.68)$$

Making use of (6.62) and (6.68) in (6.66), it is found that

$$W_{\text{ion}} = \frac{4}{\mathcal{E}} \exp\left(-\frac{2}{3\mathcal{E}}\right) \quad (6.69)$$

and the lifetime of the hydrogen ground state in the electric field is (in a.u.)

$$\tau = \frac{1}{W_{\text{ion}}} = \frac{1}{4} \mathcal{E} \exp\left(\frac{2}{3\mathcal{E}}\right) \quad (6.70)$$

For small values of the electric field strength  $\mathcal{E}$  the lifetime of the ground state is extremely long and this state is essentially stable. For example, if  $\mathcal{E} = 10^{-2}$  a.u., then  $\tau = 2 \times 10^{26}$  a.u. As  $\mathcal{E}$  is increased, tunnelling through the barrier in the  $\eta$  coordinate becomes more probable and the lifetime diminishes exponentially. As can be seen from (6.44b) the height of the barrier presented by  $V_2(\eta)$  decreases as  $\mathcal{E}$  increases and a critical field strength can be defined at which the height of the barrier becomes less than the effective energy  $E/4$ . In this case ionisation can occur classically and the atom can no longer be considered to be in a quasi bound (resonant) state. For the ground state of hydrogen this critical field is about  $6 \times 10^{10} \text{ V m}^{-1}$ .

The critical field above which ionisation occurs classically decreases like  $n^{-4}$  for excited states and, for a hydrogen atom in a Rydberg state with  $n = 30$ , the critical field strength is about  $7 \times 10^4 \text{ V m}^{-1}$ . Experiments to detect the energies and properties of Rydberg atoms often make use of the sensitivity of these states to applied electric fields. For example, a beam of neutral atoms from an oven can be irradiated by a tunable laser and then passed through an electric field, the ions formed can be detected and the signal measured as a function of the laser frequency. When this frequency is the appropriate one to excite the atoms to a particular Rydberg level the ionic signal peaks, allowing the energy of the level to be determined.

A detailed account of the interaction of electric fields with Rydberg atoms can be found in the monograph by Gallagher (1994).

## 6.2 The Zeeman effect

In 1896, P. Zeeman observed that the spectral lines of atoms were split in the presence of an external magnetic field. In order to explain this effect, we shall discuss in this section the interaction of hydrogenic atoms with static magnetic fields, which can be taken to be uniform over atomic dimensions. The vector potential  $\mathbf{A}$  can then be written as

# **The Zeeman Effect**





# "Anomalous" Zeeman Effect

While the [Zeeman effect](#) in some atoms (e.g., [hydrogen](#)) showed the expected equally-spaced triplet, in other atoms the magnetic field split the lines into four, six, or even more lines and some triplets showed wider spacings than expected. These deviations were labeled the "anomalous Zeeman effect" and were very puzzling to early researchers. The explanation of these different patterns of splitting gave additional insight into the effects of [electron spin](#). With the inclusion of electron spin in the [total angular momentum](#), the other types of multiplets formed part of a consistent picture. So what has been historically called the "anomalous" Zeeman effect is really the normal Zeeman effect when electron spin is included.

## "Normal" Zeeman effect

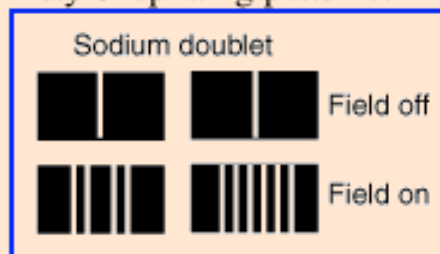
This type of splitting is observed with hydrogen and the zinc singlet.

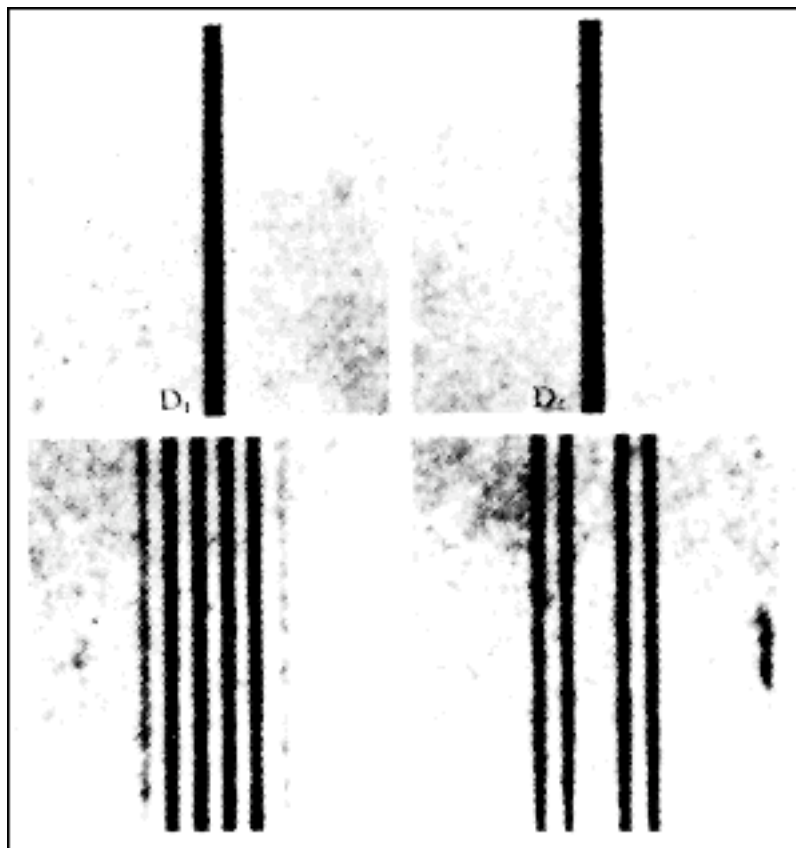


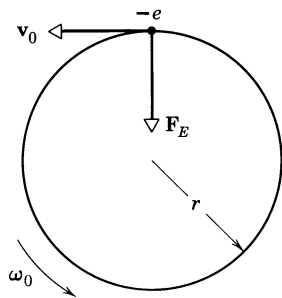
This type of splitting is observed for spin 0 states since the spin does not contribute to the angular momentum.

## "Anomalous" Zeeman effect

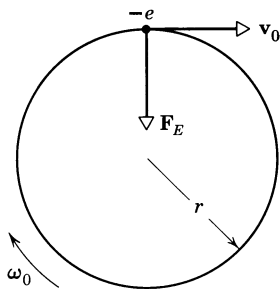
When electron spin is included, there is a greater variety of splitting patterns.



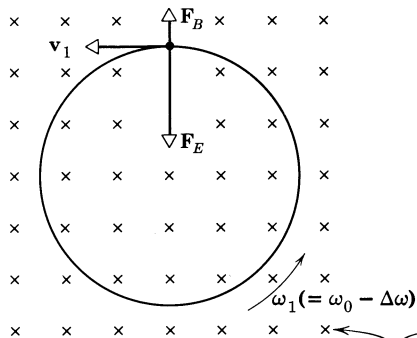




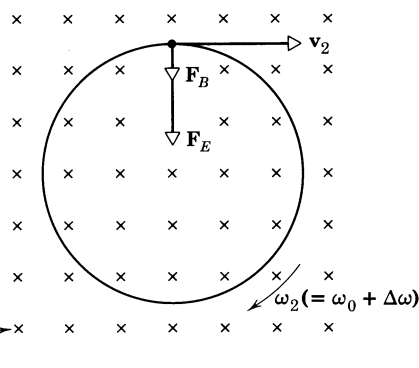
(a)



(b)

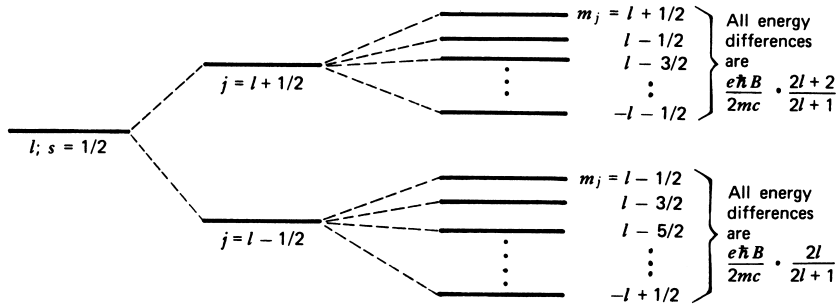
 $B = 0$ 

(c)

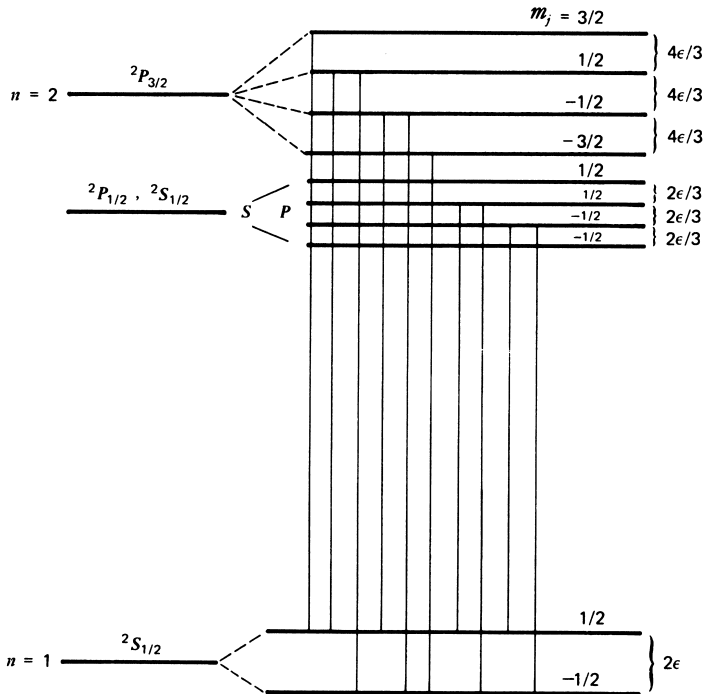


(d)

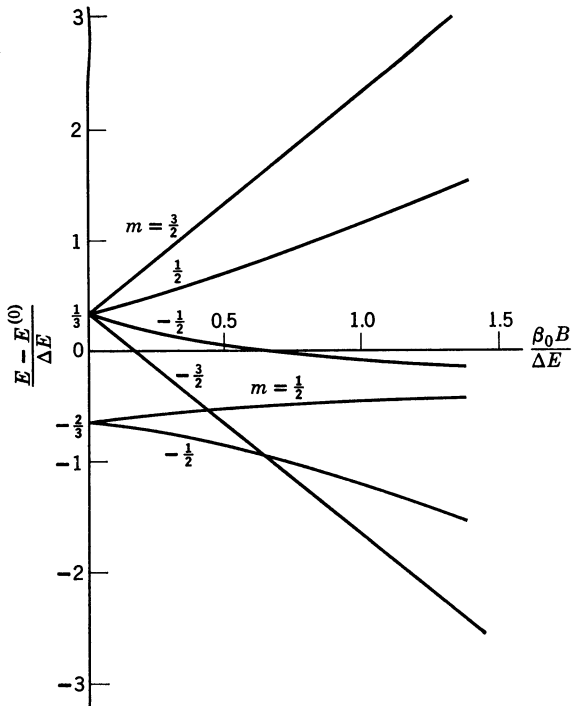
**Fig. 37-7** (a) An electron circulating in an atom. (b) An electron circulating in the opposite direction. (c) A magnetic field is introduced, *decreasing* the linear speed of the electron in (a), that is,  $v_1 < v_0$ . (d) The magnetic field *increases* the linear speed of the electron in (b), that is,  $v_2 > v_0$ .



**Figure 17-2.** General representation of anomalous Zeeman effect.



**Figure 17-3.** Zeeman effect in hydrogen,  $\epsilon$  represents the energy  $e\hbar B/2mc$ . The transitions for which  $l = 1$ ,  $\Delta m = 1, 0, -1$  are drawn in the figure. The location of the unperturbed states is given by Fig. 17-1.



**Figure 17.1.** Splitting of a  $2P$  energy level of hydrogen in a magnetic field  $\mathbf{B}$  (Zeeman effect).  $E^{(0)}$  is the unperturbed energy,  $\Delta E$  is the fine structure splitting.

so that with  $E = -1/2$ , and  $-z \approx \eta/2$ ,

$$v_z = (\mathcal{E}\eta - 1)^{1/2} \quad (6.68)$$

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In 1896, P. Zeeman observed that the spectral lines of atoms were split in the presence of an external magnetic field. In order to explain this effect, we shall discuss in this section the interaction of hydrogenic atoms with static magnetic fields, which can be taken to be uniform over atomic dimensions. The vector potential  $\mathbf{A}$  can then be written as

$$\mathbf{A} = \frac{1}{2}(\mathcal{B} \times \mathbf{r}) \quad (6.71)$$

where  $\mathcal{B}$  is a constant magnetic field, which satisfies the relation  $\mathcal{B} = \nabla \times \mathbf{A}$ .

The Hamiltonian of a hydrogenic atom in the presence of a constant magnetic field is given in the infinite nuclear mass approximation by (see Appendix 6)

$$\begin{aligned} H &= \frac{1}{2m}(\mathbf{p} + e\mathbf{A})^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} \\ &= -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} - \frac{i\hbar e}{m}\mathbf{A} \cdot \nabla + \frac{e^2}{2m}\mathbf{A}^2 \end{aligned} \quad (6.72)$$

where  $\mathbf{A}$  is given by (6.71) and we have used the fact that  $\nabla \cdot \mathbf{A} = 0$ . The corresponding time-independent Schrödinger equation reads

$$\left[ -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} - \frac{i\hbar e}{m}\mathbf{A} \cdot \nabla + \frac{e^2}{2m}\mathbf{A}^2 \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (6.73)$$

The linear term in  $\mathbf{A}$  becomes, in terms of  $\mathcal{B}$ ,

$$\begin{aligned} -\frac{i\hbar e}{m}\mathbf{A} \cdot \nabla &= -\frac{i\hbar e}{2m}(\mathcal{B} \times \mathbf{r}) \cdot \nabla \\ &= -\frac{i\hbar e}{2m}\mathcal{B} \cdot (\mathbf{r} \times \nabla) \\ &= \frac{e}{2m}\mathcal{B} \cdot \mathbf{L} \end{aligned} \quad (6.74)$$

where  $\mathbf{L} = -i\hbar(\mathbf{r} \times \nabla)$  is the orbital angular momentum operator of the electron.

The quadratic term in  $\mathbf{A}$  appearing in (6.73) can be written in the form

$$\begin{aligned} \frac{e^2}{2m}\mathbf{A}^2 &= \frac{e^2}{8m}(\mathcal{B} \times \mathbf{r})^2 \\ &= \frac{e^2}{8m}[\mathcal{B}^2 r^2 - (\mathcal{B} \cdot \mathbf{r})^2] \end{aligned} \quad (6.75)$$

The linear term (6.74) corresponds to the interaction energy of a magnetic field  $\mathcal{B}$  with the orbital magnetic dipole moment

$$\mathcal{M}_L = -\frac{e}{2m}\mathbf{L} = -\mu_B \mathbf{L}/\hbar \quad (6.76)$$

where

$$\mu_B = \frac{e\hbar}{2m} \quad (6.77)$$



is the *Bohr magneton* (see (1.110)) and has the value  $9.274\,01 \times 10^{-24} \text{ J T}^{-1}$  or  $\text{m}^2 \text{ A}$ . The interaction energy (6.74) then takes the form

$$H'_1 = -\mathcal{M}_L \cdot \mathfrak{B} \quad (6.78)$$

It is useful to express  $H'_1$  in various units. For example,

$$\begin{aligned} H'_1 &= 2.13 \times 10^{-6} \mathfrak{B} \cdot \mathbf{L} \text{ a.u.} \\ &= 0.4669 \mathfrak{B} \cdot \mathbf{L} / \hbar \text{ cm}^{-1} \end{aligned} \quad (6.79)$$

where in both cases the magnitude of  $\mathfrak{B}$  is to be given in tesla (T).

Until this point we have not taken into account the intrinsic magnetic moment of the electron, revealed by experiments of the Stern–Gerlach type (see Chapter 1). This intrinsic magnetic moment, due to the electron spin, is given by

$$\mathcal{M}_s = -g_s \frac{e}{2m} \mathbf{S} \quad (6.80)$$

or

$$\mathcal{M}_s = -g_s \mu_B \mathbf{S} / \hbar \quad (6.81)$$

where  $\mathbf{S}$  is the spin operator of the electron and  $g_s$  its spin *gyromagnetic ratio*. Dirac's relativistic theory predicts for  $g_s$  the value  $g_s = 2$  (see Appendix 7) which is in very good agreement with experiment [7]. The spin magnetic moment  $\mathcal{M}_s$  gives rise to an additional interaction energy, linear in the magnetic field,

$$H'_2 = -\mathcal{M}_s \cdot \mathfrak{B} = g_s \mu_B \mathfrak{B} \cdot \mathbf{S} / \hbar \quad (6.82)$$

The complete Schrödinger equation for a one-electron atom in a constant magnetic field, including the spin–orbit interaction, but neglecting the reduced mass effect, the relativistic kinetic energy correction and the Darwin term, is (with  $g_s = 2$ )

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} + \xi(r) \mathbf{L} \cdot \mathbf{S} + \frac{\mu_B}{\hbar} (\mathbf{L} + 2\mathbf{S}) \cdot \mathfrak{B} + \frac{e^2}{8m} (\mathfrak{B} \times \mathbf{r})^2 \right] \psi(q) = E\psi(q) \quad (6.83)$$

where  $\xi(r)$  is given by (5.18) and  $\psi(q)$  is now a Pauli 'spin-orbital' with two components (see (5.9)).

In what follows it will be convenient to take the magnetic field  $\mathfrak{B}$  to be directed along the  $Z$  axis. In this case, the equation (6.83) becomes

$$\begin{aligned} &\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} + \xi(r) \mathbf{L} \cdot \mathbf{S} + \frac{\mu_B}{\hbar} (L_z + 2S_z) \mathfrak{B} + \frac{e^2}{8m} \mathfrak{B}^2 r^2 \sin^2 \theta \right] \psi(q) \\ &= E\psi(q) \end{aligned} \quad (6.84)$$

where  $\theta$  is the angle between the vector  $\mathbf{r}$  and the  $Z$  axis.

[7] The corrections to the Dirac result  $g_s = 2$  come from quantum electrodynamics (see footnote [10] of Chapter 5).

The term linear in the magnetic field in equations (6.83) or (6.84), namely

$$\frac{\mu_B}{\hbar} (\mathbf{L} + 2\mathbf{S}) \cdot \mathcal{B} = \frac{\mu_B}{\hbar} (L_z + 2S_z) \mathcal{B} \quad (6.85)$$

is called the *paramagnetic term* because it gives rise to the alignment of magnetic moments in an external magnetic field, which leads to paramagnetism. The term quadratic in the magnetic field,

$$\frac{e^2}{8m} (\mathcal{B} \times \mathbf{r})^2 = \frac{e^2}{8m} \mathcal{B}^2 r^2 \sin^2 \theta \quad (6.86)$$

is called the *diamagnetic term*.

The relative magnitude of the linear (paramagnetic) and quadratic (diamagnetic) terms can be estimated as follows. For states of low angular momentum (say about  $\hbar$ ), we see by using (3.74) that the quadratic term is of the order  $e^2 a_0^2 n^4 \mathcal{B}^2 / (8mZ^2)$ . On the other hand, the order of magnitude of the linear term is  $\mu_B \mathcal{B} = e\hbar \mathcal{B} / (2m)$ . The ratio of the quadratic to the linear term is therefore given approximately by

$$\frac{ea_0^2 n^4 \mathcal{B}}{4\hbar Z^2} \approx \frac{n^4}{Z^2} \mathcal{B} 10^{-6} \quad (6.87)$$

where we recall that  $\mathcal{B}$  is expressed in tesla (T). In the laboratory, the fields do not usually exceed a few tens of tesla, so that the quadratic term can be safely neglected unless  $n$  is large. However, in some astrophysical situations, very large magnetic fields are believed to exist. For example, in neutron stars, field strengths at the surface may exceed  $10^8$  T and in such a case the quadratic term cannot be neglected.

The atomic unit of magnetic field strength is

$$\mathcal{B}_a = \frac{\hbar}{ea_0^2} = 2.35052 \times 10^5 \text{ T} \quad (6.88)$$

Using atomic units, the quantity (6.87) can be written as  $n^4 \mathcal{B} / (4Z^2)$ , and the quadratic term can be ignored if

$$\frac{n^4 \mathcal{B}}{Z^2} \ll 1 \quad (6.89)$$

### The linear Zeeman effect

Let us first consider the case for which the quadratic (diamagnetic) term can be neglected, so that the equation (6.84) reduces to

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} + \xi(r) \mathbf{L} \cdot \mathbf{S} + \frac{\mu_B}{\hbar} (L_z + 2S_z) \mathcal{B} \right] \psi(q) = E\psi(q) \quad (6.90)$$

The nature of the solution depends on whether the magnetic interaction is greater or less than the spin-orbit interaction. We shall first discuss the former case (strong magnetic fields) and then analyse the so-called ‘anomalous Zeeman effect’ which corresponds to weak fields.

### Strong fields

The fine structure splitting of the  $n = 2$  level of hydrogenic atoms is  $(0.365Z^4) \text{ cm}^{-1}$  and decreases for large  $n$  like  $n^{-3}$ . We see from (6.79) that the magnetic interaction energy will be greater than this for field strengths  $\mathcal{B} > Z^4$  tesla. By laboratory standards, these are very strong fields even for hydrogenic atoms with small  $Z$ , but such fields can occur in certain astrophysical situations, such as in some stars. In the strong field limit, we first solve the Schrödinger equation without the spin-orbit coupling, which can be subsequently treated as a perturbation. Thus we have

$$\left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} \right) \psi(q) = \left[ E - \frac{\mu_B \mathcal{B}}{\hbar} (L_z + 2S_z) \right] \psi(q) \quad (6.91)$$

The unperturbed hydrogenic spin-orbitals  $\psi_{nlm_l m_s}$ , defined by (5.9) are eigenfunctions of  $L_z$  and  $S_z$  and satisfy this equation if

$$E = E_n + \mu_B \mathcal{B} (m_l + 2m_s), \quad m_s = \pm 1/2 \quad (6.92)$$

The introduction of the magnetic field does not remove the degeneracy in  $l$ , but by providing a preferred direction in space, it removes partially the degeneracy in  $m_l$  and  $m_s$ , splitting each level with a given  $n$  into equally spaced terms. This is illustrated in Fig. 6.5 for the case of a p level ( $l = 1$ ). However, the energy of the states with  $m_l = +1$  and  $m_s = -1/2$  coincides with those with  $m_l = -1$  and  $m_s = +1/2$ . In the strong-field limit we are considering here (no spin-orbit coupling) the orbital and spin angular momenta are constants of the motion and the eigenfunctions, written in Dirac notation, are of the form  $|nlm_l m_s\rangle$ , with  $s = 1/2$  and  $m_s = \pm 1/2$ .

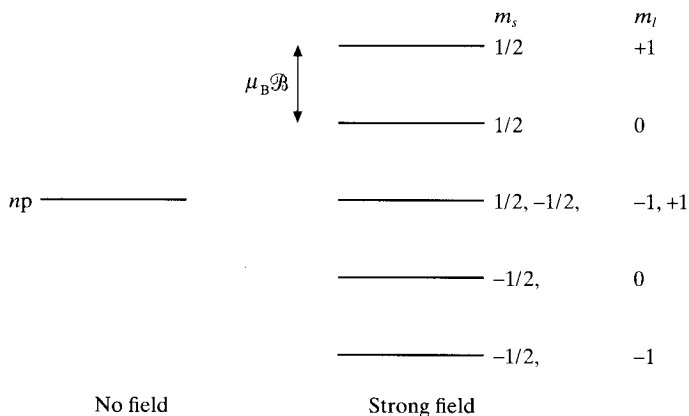


Figure 6.5 The splitting of a p level into five equally spaced levels by a strong magnetic field.

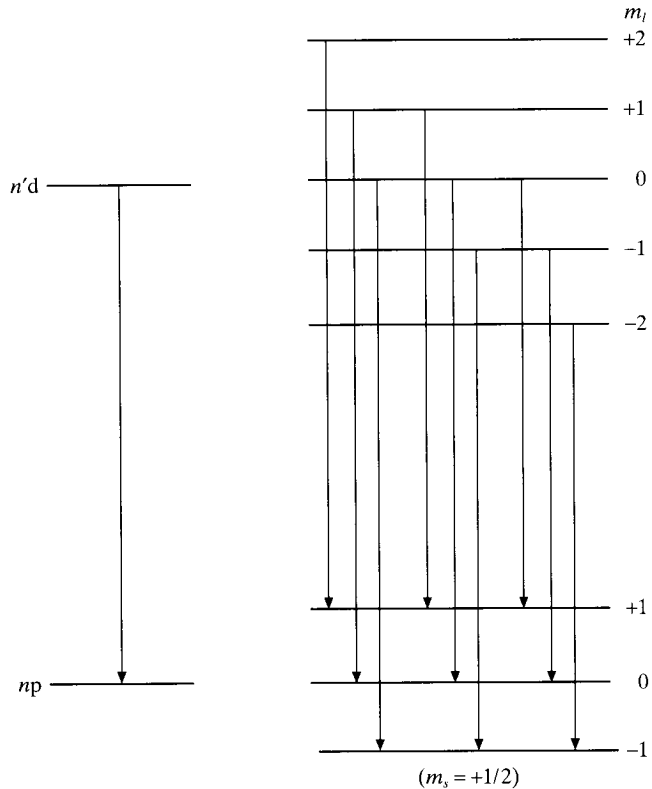
The selection rules for electric dipole transitions require that  $\Delta m_s = 0$  and  $\Delta m_l = 0, \pm 1$ . Thus the spectral line corresponding to a transition  $n \rightarrow n'$  is split into *three* components. The line corresponding to  $\Delta m_l = 0$  has the original frequency  $\nu_{n'n}$  and is called the  $\pi$  line, while the two lines with  $\Delta m_l = \pm 1$  are called  $\sigma$  lines and correspond to frequencies

$$\nu_{n'n}^{\pm} = \nu_{n'n} \pm \nu_L \quad (6.93)$$

where

$$\nu_L = \frac{\mu_B \mathcal{B}}{h} \quad (6.94)$$

is known as the *Larmor frequency*. This splitting is called the *normal Zeeman effect* and the three lines are said to form a *Lorentz triplet* (see Fig. 6.6). Apart from the



*Figure 6.6* Illustration of the normal Zeeman effect for the transition  $n'd \rightarrow np$ , with  $m_s = +1/2$ . In a strong magnetic field nine transitions are possible between the split levels consistent with  $\Delta m_l = 0, \pm 1$  and  $\Delta m_s = 0$ . Of these, there are only three different frequencies corresponding to the  $\pi$  line ( $\Delta m_l = 0$ ) and the two  $\sigma$  lines ( $\Delta m_l = \pm 1$ ), which form a Lorentz triplet. The frequencies of the transitions associated with  $m_s = -1/2$  are the same as those for  $m_s = +1/2$ .

case of very strong fields, Lorentz triplets can be observed in many-electron systems for which the total spin is zero, as in this case the spin-orbit coupling vanishes.

The polarisation of the radiation in each of the emission lines has interesting properties. The transition rate for spontaneous emission of radiation having a polarisation vector  $\hat{\mathbf{e}}$  is given in the dipole approximation by (4.79), namely

$$\begin{aligned} W_{ab}^{s,D} d\Omega &= \frac{1}{2\pi\hbar c^3} \left( \frac{e^2}{4\pi\epsilon_0} \right) \omega_{ba}^3 |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 d\Omega \\ &= C(\omega_{ba}) |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 d\Omega \end{aligned} \quad (6.95a)$$

where we have set

$$C(\omega_{ba}) = \frac{1}{2\pi\hbar c^3} \left( \frac{e^2}{4\pi\epsilon_0} \right) \omega_{ba}^3 \quad (6.95b)$$

The vector  $\hat{\mathbf{e}}$  can be expressed in terms of two independent vectors  $\hat{\mathbf{e}}_1$  and  $\hat{\mathbf{e}}_2$  as in (4.123), where  $\hat{\mathbf{e}}_1$ ,  $\hat{\mathbf{e}}_2$  and  $\hat{\mathbf{k}}$  form a right-handed system of axes (see (4.124)). If we take (as can always be done)  $\hat{\mathbf{e}}_2$  to lie in the  $(X, Y)$  plane and if  $(\Theta, \Phi)$  are the polar angles of  $\hat{\mathbf{k}}$  (see Fig. 6.7), we have

$$\begin{aligned} (\hat{e}_1)_x &= \cos \Theta \cos \Phi; & (\hat{e}_1)_y &= \cos \Theta \sin \Phi; & (\hat{e}_1)_z &= -\sin \Theta; \\ (\hat{e}_2)_x &= -\sin \Phi; & (\hat{e}_2)_y &= \cos \Phi; & (\hat{e}_2)_z &= 0 \end{aligned} \quad (6.96)$$

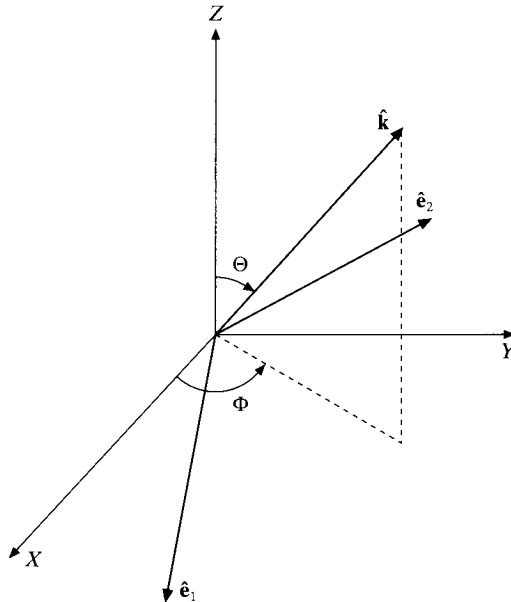


Figure 6.7 The unit vectors  $\hat{\mathbf{e}}_1$ ,  $\hat{\mathbf{e}}_2$  and  $\hat{\mathbf{k}}$  form a right-handed set. The polar angles of  $\hat{\mathbf{k}}$  are  $(\Theta, \Phi)$  and  $\hat{\mathbf{e}}_2$  lies in the  $XY$  plane,  $\hat{\mathbf{e}}_1$  pointing downwards.

Consider first the  $\pi$  line, with  $\Delta m_l = 0$ . From the discussion given in Section 4.5 we see that in this case  $x_{ba} = y_{ba} = 0$  and we are only concerned with  $z_{ba}$ . The transition rate for emission in the solid angle  $d\Omega$  of a photon with polarisation  $\hat{\mathbf{e}}_1$  is then

$$W_{ab}^{s,D} d\Omega = C(\omega_{ba}) \sin^2\Theta |z_{ba}|^2 d\Omega \quad (6.97)$$

and the rate is zero for emission of a photon with polarisation  $\hat{\mathbf{e}}_2$ . When the light is viewed longitudinally, so that  $\hat{\mathbf{k}}$  is in the direction of the magnetic field (which is parallel to the  $Z$  axis),  $\Theta = 0$  and the  $\pi$  line is absent. In transverse observation ( $\Theta = \pi/2$ ), in a direction at right angles to the magnetic field, the  $\pi$  radiation is plane-polarised with  $\hat{\mathbf{e}} = \hat{\mathbf{e}}_1$  in the direction of the negative  $Z$  axis.

Let us now consider the case in which  $\Delta m_l = m'_l - m_l = -1$  which corresponds to the amplitude (see (4.110)–(4.112))

$$\mathcal{E}_{-1}^* I_{n'l'm'_l-1, nlm_l}^{-1} = \frac{1}{\sqrt{2}} (\hat{\mathbf{e}}_x + i\hat{\mathbf{e}}_y) \frac{1}{\sqrt{2}} (x_{ba} - iy_{ba}) \quad (6.98)$$

The transition rate for emission of a photon with polarisation  $\hat{\mathbf{e}} = \hat{\mathbf{e}}_1$  is then

$$W_{ab}^{s,D}(1) d\Omega = C(\omega_{ba}) \left| \frac{1}{\sqrt{2}} \cos\Theta e^{i\Phi} \right|^2 \left| \frac{1}{\sqrt{2}} (x_{ba} - iy_{ba}) \right|^2 d\Omega \quad (6.99)$$

and that for polarisation  $\hat{\mathbf{e}} = \hat{\mathbf{e}}_2$  is

$$W_{ab}^{s,D}(2) d\Omega = C(\omega_{ba}) \left| \frac{i}{\sqrt{2}} e^{i\Phi} \right|^2 \left| \frac{1}{\sqrt{2}} (x_{ba} - iy_{ba}) \right|^2 d\Omega \quad (6.100)$$

Summing over both independent polarisation directions, the transition rate for the line corresponding to  $\Delta m_l = m'_l - m_l = -1$ , which is known as the  $\sigma^-$  line, is

$$W_{ab}^{s,D}(\sigma^-) d\Omega = C(\omega_{ba}) \frac{1}{2} (1 + \cos^2\Theta) \left| \frac{1}{\sqrt{2}} (x_{ba} - iy_{ba}) \right|^2 d\Omega \quad (6.101)$$

In transverse observation  $\Theta = \pi/2$  and the  $x$  and  $y$  components of  $\hat{\mathbf{e}}_1$  vanish. In this case the  $\sigma^-$  line is plane-polarised with  $\hat{\mathbf{e}} = \hat{\mathbf{e}}_2$ , where  $\hat{\mathbf{e}}_2$  lies in the  $(X, Y)$  plane. In contrast, in longitudinal observation along the direction of the magnetic field, we see from (4.131) that the radiation is left-hand circularly polarised, that is the emitted photon has helicity  $+\hbar$ .

In the same way, the transition rate for the  $\sigma^+$  line corresponding to  $\Delta m_l = m'_l - m_l = +1$  is given by

$$W_{ab}^{s,D}(\sigma^+) d\Omega = C(\omega_{ba}) \frac{1}{2} (1 + \cos^2\Theta) \left| -\frac{1}{\sqrt{2}} (x_{ba} + iy_{ba}) \right|^2 d\Omega \quad (6.102)$$

The  $\sigma^+$  line is right-hand circularly polarised when viewed along the direction of the magnetic field and is plane-polarised in transverse observation.

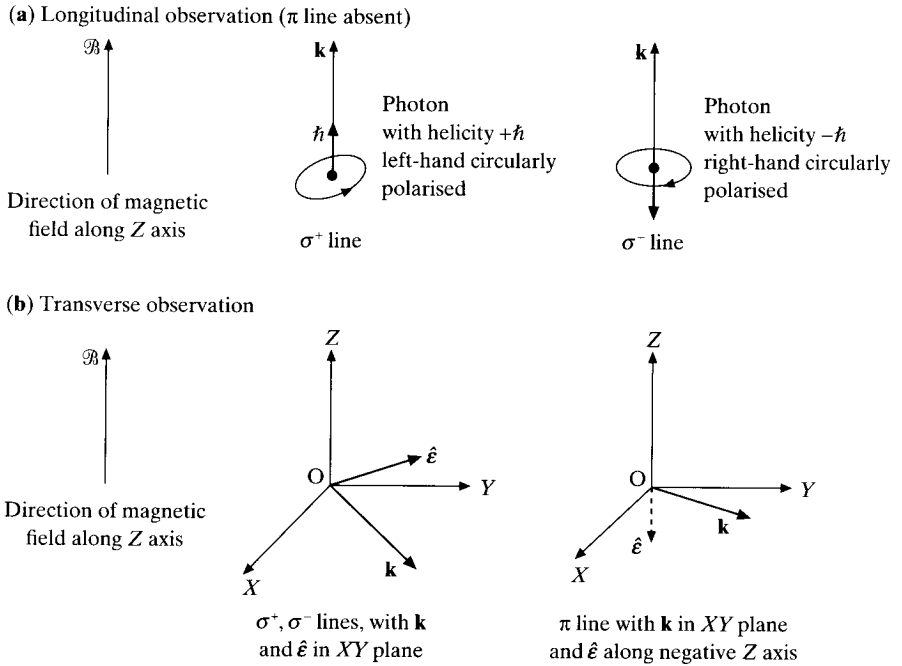


Figure 6.8 Polarisation of photons emitted in the direction of a magnetic field, or at right angles to a magnetic field.

The preceding discussion of the polarisations of the  $\sigma$  and  $\pi$  components is illustrated in Fig. 6.8. It is easily shown (Problem 6.4) that in the transverse direction the intensity of the  $\pi$  component is twice that of each  $\sigma$  component.

### The Paschen-Back effect

At field strengths for which the spin-orbit interaction is appreciable, but still small compared with the term in  $\mathcal{B}$  in (6.90), it can be treated in first-order perturbation theory. The perturbation is  $\xi(r)\mathbf{L}\cdot\mathbf{S}$ , and it can be verified (Problem 6.5) that it does not connect the degenerate states with  $m_l = +1, m_s = -1/2$  and  $m_l = -1, m_s = +1/2$ . As a consequence, first-order non-degenerate perturbation theory can be used, and the contribution of the spin-orbit interaction  $\xi(r)\mathbf{L}\cdot\mathbf{S}$  to the total energy is

$$\begin{aligned} \Delta E &= \int_0^\infty dr r^2 [R_{nl}(r)]^2 \xi(r) \left\langle l \frac{1}{2} m_l m_s \left| \mathbf{L}\cdot\mathbf{S} \right| l \frac{1}{2} m_l m_s \right\rangle \\ &= \lambda_{nl} m_l m_s, \quad l \neq 0 \end{aligned} \tag{6.103}$$

while  $\Delta E = 0$  for s states ( $l = 0$ ). The quantity  $\lambda_{nl}$  is given by

$$\lambda_{nl} = \hbar^2 \int_0^\infty dr r^2 [R_{nl}(r)]^2 \xi(r) = -\frac{\alpha^2 Z^2}{n} E_n \frac{1}{l(l + \frac{1}{2})(l + 1)}, \quad l \neq 0 \tag{6.104}$$

The degeneracy in  $l$  is removed, as we expect. The energy difference between levels  $(nlm_l m_s)$  and  $(n'l'm'_l m'_s)$  with  $m_s = m'_s$  is

$$\delta E = E'_n - E_n + \mu_B \mathcal{B}(m'_l - m_l) + (\lambda_{n'l'} m'_l - \lambda_{nl} m_l) m_s \tag{6.105}$$

This expression gives the frequencies  $\delta E/h$  of the observed lines, with  $\Delta m_l = m'_l - m_l$  restricted to the values  $0, \pm 1$ . The observed splitting in this case is known as the *Paschen–Back effect*.

**Weak fields: the anomalous Zeeman effect**

For historical reasons the case of a weak magnetic field is known as the *anomalous Zeeman effect*, although in fact this effect is the one most commonly encountered. In the early days of spectroscopy, before the electron spin was discovered, the normal Zeeman effect was predicted, on classical grounds, but the observations did not conform to the predictions and were said to be ‘anomalous’. The explanation was finally given in terms of quantum mechanics and the electron spin.

When the interaction caused by the external magnetic field is small compared with the spin–orbit term, the unperturbed Hamiltonian can be taken to be

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} + \xi(r) \mathbf{L} \cdot \mathbf{S} \tag{6.106}$$

The unperturbed wave functions are eigenfunctions of  $\mathbf{L}^2, \mathbf{S}^2, \mathbf{J}^2$  and  $J_z$ , but not of  $L_z$  and  $S_z$ . They are therefore products of radial functions times the ‘generalised spherical harmonics’ (see Appendix 4)

$$\mathcal{Y}_{ls}^{jm_l} = \sum_{m_l m_s} \langle lsm_l m_s | jm_l \rangle Y_{lm_l}(\theta, \phi) \chi_{s, m_s} \tag{6.107}$$

where  $\langle lsm_l m_s | jm_l \rangle$  are Clebsch–Gordan coefficients and  $s = 1/2$ . The perturbation is

$$\begin{aligned} H' &= \frac{\mu_B}{\hbar} (L_z + 2S_z) \mathcal{B} \\ &= \frac{\mu_B}{\hbar} (J_z + S_z) \mathcal{B} \end{aligned} \tag{6.108}$$

The additional energy due to this perturbation is

$$\Delta E = \mu_B \mathcal{B} m_j + \frac{\mu_B}{\hbar} \mathcal{B} \int d\Omega (\mathcal{Y}_{l,1/2}^{jm_l})^* S_z \mathcal{Y}_{l,1/2}^{jm_l} \tag{6.109}$$

where we have made use of the fact that  $\mathcal{Y}_{l,1/2}^{jm_l}$  is a normalised eigenfunction of  $J_z$  belonging to the eigenvalue  $m_j \hbar$ .



Either of two methods can be used to evaluate the second term in (6.109).

1. The most straightforward procedure is to use the explicit expressions for the Clebsch–Gordan coefficients  $\langle l1/2m_jm_s | jm_j \rangle$  given in Appendix 4. Setting  $j = l \pm 1/2$ , we have

$$\begin{aligned} \mathcal{Y}_{l,1/2}^{l+1/2,m_j} &= \left( \frac{l+m_j+1/2}{2l+1} \right)^{1/2} Y_{l,m_j-1/2}(\theta, \phi) \chi_{1/2,1/2} \\ &\quad + \left( \frac{l-m_j+1/2}{2l+1} \right)^{1/2} Y_{l,m_j+1/2}(\theta, \phi) \chi_{1/2,-1/2} \end{aligned} \quad (6.110a)$$

and

$$\begin{aligned} \mathcal{Y}_{l,1/2}^{l-1/2,m_j} &= - \left( \frac{l-m_j+1/2}{2l+1} \right)^{1/2} Y_{l,m_j-1/2}(\theta, \phi) \chi_{1/2,1/2} \\ &\quad + \left( \frac{l+m_j+1/2}{2l+1} \right)^{1/2} Y_{l,m_j+1/2}(\theta, \phi) \chi_{1/2,-1/2} \end{aligned} \quad (6.110b)$$

from which one readily obtains

$$\int d\Omega (\mathcal{Y}_{l,1/2}^{l+1/2,m_j})^* S_z \mathcal{Y}_{l,1/2}^{l+1/2,m_j} = \frac{m_j}{2l+1} \hbar \quad (6.111a)$$

and

$$\int d\Omega (\mathcal{Y}_{l,1/2}^{l-1/2,m_j})^* S_z \mathcal{Y}_{l,1/2}^{l-1/2,m_j} = - \frac{m_j}{2l+1} \hbar \quad (6.111b)$$

2. The same result can be obtained by operator methods. A *vector operator*  $\mathbf{V}$  has three components ( $V_x, V_y, V_z$ ) along three orthogonal axes, where  $V_x, V_y$  and  $V_z$  are operators which transform under rotations like the components of a vector (see Appendix 4). In particular, a vector operator  $\mathbf{V}$  satisfies the identity (A4.47). The matrix element of the left-hand side of this identity with respect to states having the same value of  $j$  vanishes, so that

$$\langle lsm_j | \mathbf{J}^2 \mathbf{V} + \mathbf{V} \mathbf{J}^2 | lsm_j \rangle = 2 \langle lsm_j | (\mathbf{V} \cdot \mathbf{J}) \mathbf{J} | lsm_j \rangle \quad (6.112)$$

from which we have

$$j(j+1) \hbar^2 \langle lsm_j | \mathbf{V} | lsm_j \rangle = \langle lsm_j | (\mathbf{V} \cdot \mathbf{J}) \mathbf{J} | lsm_j \rangle \quad (6.113)$$

This relationship can also be obtained by using the Wigner–Eckart theorem discussed in Appendix 4.

Setting  $\mathbf{V} = \mathbf{S}$  in (6.113) and taking the  $z$  component, we have

$$\begin{aligned} j(j+1) \hbar^2 \langle lsm_j | S_z | lsm_j \rangle &= \langle lsm_j | (\mathbf{S} \cdot \mathbf{J}) J_z | lsm_j \rangle \\ &= m_j \hbar \langle lsm_j | \mathbf{S} \cdot \mathbf{J} | lsm_j \rangle \end{aligned} \quad (6.114)$$

Since  $\mathbf{S} \cdot \mathbf{J} = (\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2)/2$ , the matrix element of  $S_z$  is

$$\langle l s j m_j | S_z | l s j m_j \rangle = m_j \hbar \left[ \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right] \quad (6.115)$$

which agrees with (6.111) when  $s = 1/2$  and  $j = l \pm 1/2$ .

The energy shift due to the magnetic field is seen from (6.109) and (6.111) (or (6.115)) to be proportional to  $\mu_B \mathcal{B} m_j$  and may be written as

$$\Delta E_{m_j} = g \mu_B \mathcal{B} m_j \quad (6.116)$$

where  $g$  is called the *Landé g factor* and is given by

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad (6.117)$$

The result (6.116) shows that, within a multiplet, the magnetic moment operator  $\mathcal{M}$  of an atom is related to the total angular momentum operator  $\mathbf{J}$  by

$$\mathcal{M} = -g \mu_B \mathbf{J} / \hbar \quad (6.118)$$

in conformity with (1.126).

Since in our case  $s = 1/2$  we have

$$\Delta E_{m_j} = \frac{2l+2}{2l+1} \mu_B \mathcal{B} m_j, \quad j = l + 1/2 \quad (6.119a)$$

$$= \frac{2l}{2l+1} \mu_B \mathcal{B} m_j, \quad j = l - 1/2 \quad (6.119b)$$

The total energy of the level with quantum numbers  $n, j, m_j$  of a hydrogenic atom in a constant magnetic field is therefore

$$E_{n,j,m_j} = E_n + \Delta E_{n,j} + \Delta E_{m_j} \quad (6.120)$$

where  $E_n$  is the non-relativistic energy (3.29) (with  $\mu = m$ ),  $\Delta E_{n,j}$  is the fine structure correction (5.28) and  $\Delta E_{m_j}$  is the correction due to the (weak) magnetic field.

The splitting of levels,  $\delta E$ , corresponding to the ‘anomalous’ Zeeman effect discussed above is illustrated in Fig. 6.9. We remark that since the splitting of the levels is not the same for each multiplet, there will be more lines in this case than the three lines (Lorentz triplet) corresponding to the normal Zeeman effect. This is shown in Fig. 6.10, where we display the allowed transitions (corresponding to  $\Delta l = \pm 1$  and  $\Delta m_j = 0, \pm 1$ ) between the  $n = 2$  and  $n = 1$  levels of atomic hydrogen occurring in the presence of a weak magnetic field.

As the magnitude of the magnetic field  $\mathcal{B}$  increases from the weak field to the strong field limit, the energy changes smoothly. This is depicted in Fig. 6.11 for the 2p states of atomic hydrogen.

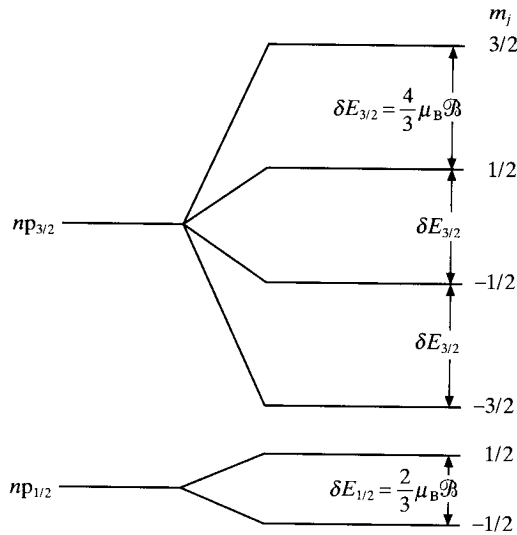


Figure 6.9 Splitting of  $np_{3/2}$  and  $np_{1/2}$  levels of atomic hydrogen in a weak magnetic field.

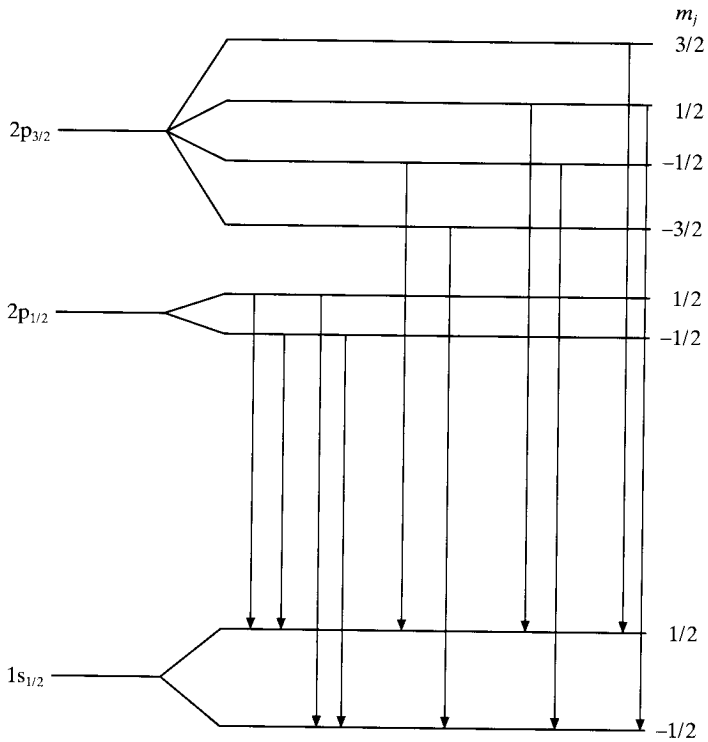


Figure 6.10 In electric dipole transitions between the  $n = 2$  and  $n = 1$  levels of atomic hydrogen, in a weak magnetic field, four lines result from the  $2p_{1/2} \rightarrow 1s_{1/2}$  transitions and six lines from the  $2p_{3/2} \rightarrow 1s_{1/2}$  transitions.

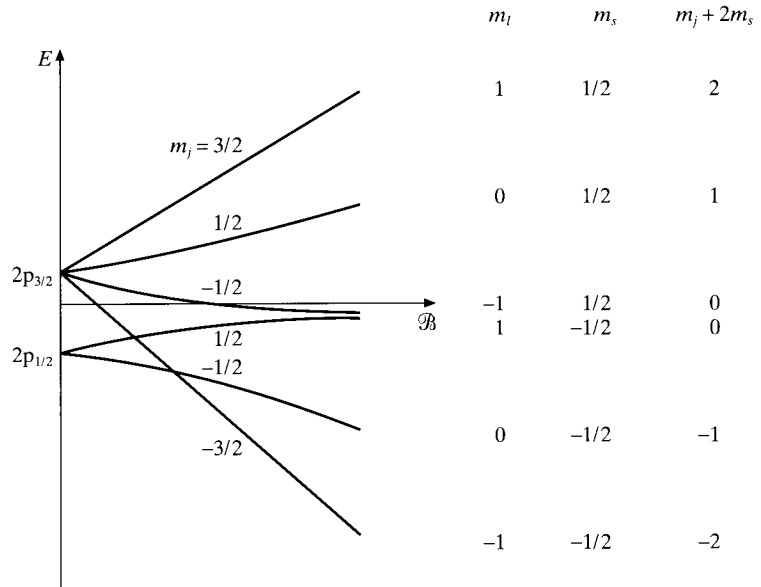


Figure 6.11 The energy of the levels of a hydrogen atom in a magnetic field are a smooth function of  $\mathcal{B}$ . For small  $\mathcal{B}$ , the splitting is uneven (the anomalous Zeeman effect), but for large  $\mathcal{B}$ , the splitting is even and only three lines are seen (the Lorentz triplet). A schematic diagram is shown for the  $2p$  levels.

### The quadratic Zeeman effect

As we have seen from the condition (6.89) the diamagnetic term proportional to  $\mathcal{B}^2$ , in the Schrödinger equation (6.84), can be neglected for the magnetic fields encountered in the laboratory, provided the principal quantum number  $n$  of the atom concerned is not too large. For Rydberg atoms for which  $n$  is large this is not the case and the diamagnetic term is significant for values of  $n$  greater than 10–20. The observed spectra of white dwarfs and neutron stars indicate that the surface magnetic fields can range from  $10^4$  to  $10^8$  T, or more, and for such fields the diamagnetic interaction cannot be ignored even for small principal quantum numbers.

For strong fields the spin–orbit interaction is small compared with the other terms in (6.84) and can be omitted. When this is done, the Schrödinger equation can be written as

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} + \frac{\mu_B}{\hbar} (L_z + 2S_z)\mathcal{B} + \frac{e^2}{8m} \mathcal{B}^2 r^2 \sin^2\theta \right] \psi(q) = E\psi(q) \quad (6.121)$$

Since  $L_z$  and  $S_z$  commute with  $H$ ,  $\psi$  can be taken to be a simultaneous eigenfunction of  $L_z$  and  $S_z$  with eigenvalues  $m_l\hbar$  and  $m_s\hbar$  respectively, in which case (6.121) can be written as

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} + \mu_B(m_l + 2m_s)\mathcal{B} + \frac{e^2}{8m} \mathcal{B}^2 r^2 \sin^2\theta \right] \psi(q) = E\psi(q) \quad (6.122)$$

Three cases need to be considered. In the first  $\mathcal{B}$  is so large that the Coulomb interaction can be neglected in comparison with the magnetic interaction, in the second the Coulomb and magnetic interactions are comparable, while in the third the diamagnetic term is sufficiently small to be treated as a perturbation.

### Ultra-strong magnetic fields

If the magnetic interaction is so strong that the Coulomb potential can be neglected in comparison, the Schrödinger equation (6.122) can be expressed as

$$\left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + (m_l + 2m_s)\hbar\omega_L + \frac{1}{2}m\omega_L^2(x^2 + y^2) \right] \psi(q) = E\psi(q) \quad (6.123)$$

where Cartesian coordinates have been used and  $\omega_L = \mu_B\mathcal{B}/\hbar = 2\pi\nu_L$  is the Larmor angular frequency. Equation (6.123) admits solutions of the form

$$\psi = \Phi_q(x, y) \exp(ikz) \begin{cases} \alpha & \text{for } m_s = \frac{1}{2} \\ \beta & \text{for } m_s = -\frac{1}{2} \end{cases} \quad (6.124)$$

where  $\Phi_q$  is the wave function for a two-dimensional harmonic oscillator. The eigenenergies of the Hamiltonian are correspondingly

$$E = \frac{\hbar^2 k^2}{2m} + \hbar\omega_L(m_l + 2m_s) + \hbar\omega_L(n_x + n_y + 1),$$

$$-\infty < k < \infty; \quad m_l = 0, \pm 1, \pm 2, \dots; \quad m_s = \pm \frac{1}{2};$$

$$n_x = 0, 1, 2, \dots; \quad n_y = 0, 1, 2, \dots \quad (6.125)$$

It is seen that the motion parallel to the  $Z$  axis is free, but the motion is bounded in the  $(X, Y)$  plane. Making use of the fact that the Hamiltonian can be written as a square (see Problem 6.6), it follows that the eigenvalues  $E$  are either positive or zero and that if  $n = n_x + n_y$ , then

$$n + m_l \geq 0 \quad (6.126)$$

The Hamiltonian for a two-dimensional harmonic oscillator is invariant under the parity operation  $x \rightarrow -x, y \rightarrow -y$  so that the eigenfunctions  $\Phi_q(x, y)$  are eigenstates of parity. The quantum number  $n$  is even for states of even parity and odd for those of odd parity. Using these facts it follows that  $n + m_l$  is even,

$$n + m_l = 2r, \quad r = 0, 1, 2, \dots \quad (6.127)$$

Using (6.126) and (6.127) the eigenvalues  $E$  can be written as

$$E = \frac{\hbar^2 k^2}{2m} + \hbar\omega_L(2r + 2m_s + 1)$$

$$-\infty < k < \infty; \quad r = 0, 1, 2, \dots; \quad m_s = \pm \frac{1}{2} \quad (6.128)$$

For given values of  $k$  and  $m_s$ , the discrete energy levels labelled by the quantum number  $r$  are called *Landau levels*.

### The intermediate region

We shall now consider the case in which both the Coulomb potential and the diamagnetic interaction are important. The ratio  $\gamma$  of the energy  $\hbar\omega_L$  to the ionisation potential of atomic hydrogen can be taken as a measure of the relative importance of the diamagnetic and Coulomb interactions. We have

$$\gamma = \frac{\hbar\omega_L}{I_p} = \frac{\mathcal{B}}{\mathcal{B}_a} \quad (6.129)$$

where  $\mathcal{B}_a = 2.35052 \times 10^5$  T is the atomic unit of magnetic field strength (see (6.88)). For small values of the principal quantum number  $n$  the size of  $\gamma$  indicates the relative importance of the diamagnetic and Coulomb interactions. As we have already seen, in the case of magnetic fields encountered in the laboratory, for which  $\gamma$  is of the order of  $10^{-5}$ , the influence of the diamagnetic interaction on low-lying atomic states is negligible. However, for Rydberg states with large  $n$ , the spacing of the energy levels is approximately  $2I_p/n^3$  and the diamagnetic effect will be significant for field strengths  $\mathcal{B} \gg \mathcal{B}_a/n^3$ . If  $\gamma n^3$  is much greater than unity the Coulomb interaction  $-Ze^2/(4\pi\epsilon_0 r)$  can be treated as a small perturbation of the Landau levels. The energy spectrum in the region in which the Coulomb and diamagnetic interactions are comparable ( $\gamma n^3 \approx 1$ ) is harder to calculate. One approach is to expand the wave function in a set of Landau states:

$$\psi(x, y, z) = \sum_{q=0}^{\infty} \Phi_q(x, y) F_q(z) \quad (6.130)$$

By inserting this expansion into the Schrödinger equation (6.121), and projecting successively with the functions  $\Phi_q$ , a set of coupled equations for the expansion coefficients  $F_q$  is obtained, which can be solved numerically.

Interest was first aroused in the region in which the Coulomb and magnetic interactions are comparable by the discovery by W.R.S. Garton and T.S. Tomkins in 1969 that the absorption spectrum of Rydberg atoms in a strong magnetic field displays regular oscillations, now known as *quasi-Landau* resonances. Their measurements of the photoabsorption spectrum of barium in magnetic fields of different strengths are shown in Fig. 6.12. It is seen that the level spacing increases

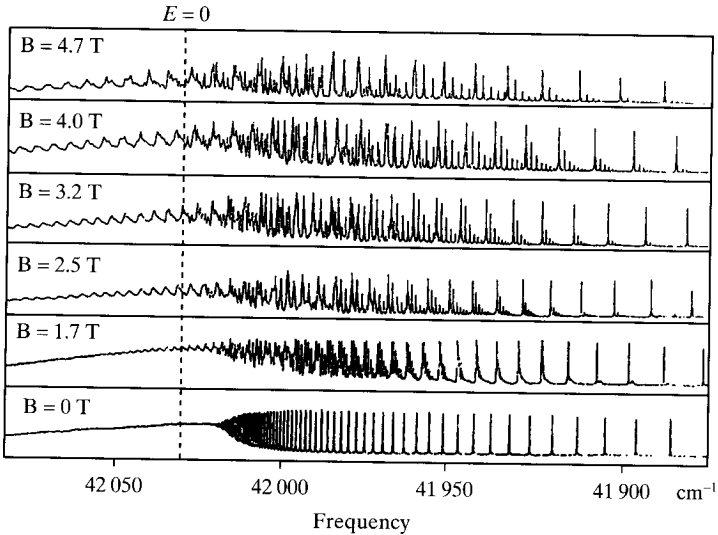


Figure 6.12 The photoabsorption spectrum of Rydberg Ba atoms for  $n > 30$ , for magnetic field strengths ranging from  $\mathcal{B} = 0$  to 4.7 T, as observed by Garton and Tomkins.

with increasing field strengths  $\mathcal{B}$ , and it is found to be approximately  $1.5\hbar\omega_L$  in the region below the ionisation threshold at  $E = 0$ . This spacing is 1.5 times as large as that of the Landau levels and was at first difficult to understand. However, A.R. Edmonds and A.F. Starace showed that the observed distribution of energy levels could be explained in terms of a simple semi-classical model. It was assumed that the energy levels near the ionisation threshold were associated with the motion in the  $(X, Y)$  plane and that the motion in the  $Z$  direction could be ignored. In the  $(X, Y)$  plane, with  $z$  set equal to zero, the potential energy can be expressed as

$$\begin{aligned}
 V(\rho) &= -\frac{Ze^2}{(4\pi\epsilon_0)\rho} + \frac{e^2}{8m}\mathcal{B}^2\rho^2 \\
 &= -\frac{Ze^2}{(4\pi\epsilon_0)\rho} + \frac{1}{2}m\omega_L^2\rho^2
 \end{aligned}
 \tag{6.131}$$

where  $\rho^2 = x^2 + y^2$  and the linear term in  $\mathcal{B}$  has been dropped. Moreover, since all neutral Rydberg atoms behave like Rydberg hydrogen atoms (see Section 3.6), one can set  $Z = 1$  in (6.131). By using the WKB approximation to obtain the energy levels in the one-dimensional well  $V(\rho)$ , Edmonds and Starace found that the spacing was indeed  $1.5\hbar\omega_L$ , as experiment indicated. Further research has shown that the structure of the energy spectrum of the quasi-Landau resonances is extremely complicated when  $\gamma n^3 \approx 1$ . This is of great interest since it is the region in which the corresponding classical motion becomes chaotic. The connection

between the distribution of quantum energy in systems with large quantum numbers and the onset of classical chaos has been the subject of many studies [8].

### Weak diamagnetic interaction

From (6.87) it is seen that the diamagnetic interaction is small compared with the linear magnetic term when  $\mathcal{B} \ll 10^6 Z^2/n^4$  (with  $\mathcal{B}$  in tesla)

$$H' = \frac{e^2}{8m} \mathcal{B}^2 r^2 \sin^2 \theta \quad (6.132)$$

can be treated as a small perturbation. The matrix element of  $H'$  with respect to unperturbed hydrogenic states,  $\langle n'l'm'_l | H' | nlm_l \rangle$ , is diagonal in  $m_l$ , but satisfies the condition  $|l' - l| = 0, 2$ . There is no restriction on  $n$ . In hydrogenic atoms all the states with the same  $n$  but different  $l$  are degenerate, so that degenerate perturbation theory must be used. All states with the same parity but different  $l$  are coupled and  $l$  is no longer a good quantum number; the states are said to be *l-mixed*.

Alkali atoms can be treated as quasi one-electron atoms in which the valence electron moves in a Coulomb potential modified at short distances. In such atoms the degeneracy in  $l$  is removed and first-order non-degenerate perturbation theory can be employed. The shift in energy due to the magnetic interaction is given to first order by

$$\Delta E = (m_l + 2m_s) \hbar \omega_L + \frac{1}{2} m \omega_L^2 \langle nlm_l | r^2 \sin^2 \theta | nlm_l \rangle \quad (6.133)$$

Since the matrix element  $\langle nlm_l | r^2 \sin^2 \theta | nlm_l \rangle$  behaves like  $n^4$  for large  $n$ , the region in which first-order perturbation theory is accurate is extremely limited.

### Problems

**6.1** Show that in the linear Stark effect the  $n = 3$  level of a hydrogen atom is split into five equally spaced components, and obtain an expression for the level separation (in  $\text{cm}^{-1}$ ) as a function of the electric field strength (in  $\text{V m}^{-1}$ ).

**6.2** Suppose that at time  $t = 0$  a hydrogen atom is in an arbitrary superposition of the  $2s$  and  $2p_0$  states. A constant electric field of strength  $10^7 \text{ V m}^{-1}$  is then applied along the  $Z$  axis. Show that during the lifetime of the  $2p_0$  state (due to radiative decay to the  $1s$  state), the average population of the  $2s$  level is nearly the same as that of the  $2p_0$  level.

**6.3** Show that the second-order correction to the energy in perturbation theory can be written as

$$E_k^{(2)} = \frac{(H'^2)_{kk}}{E_k^{(0)}} - \frac{(H'_{kk})^2}{E_k^{(0)}} + \sum_{m \neq k} \frac{E_m^{(0)} |H'_{mk}|^2}{E_k^{(0)} (E_k^{(0)} - E_m^{(0)})}$$

[8] See for example Blümel and Reinhardt (1997) or Friedrich (1998).



By neglecting the sum of the right-hand side, obtain the approximation (6.34) for the quadratic Stark effect.

**6.4** Show that in the limit of strong magnetic fields in transverse observation the intensity of the  $\pi$  Zeeman component is twice that of each  $\sigma$  component.

**6.5** Verify that the perturbation  $\xi(r)\mathbf{L}\cdot\mathbf{S}$  does not connect the degenerate states with  $m_l = +1, m_s = -1/2$  and  $m_l = -1, m_s = +1/2$ .

(Hint: Use the raising and lowering operators  $L_{\pm} = L_x \pm iL_y$ .)

**6.6** (a) Show that the Hamiltonian of a free electron in a uniform time-independent magnetic field  $\mathfrak{B} = \mathfrak{B}\hat{\mathbf{z}}$  is given by

$$H = H_{xy} + H_z$$

with

$$H_{xy} = \frac{1}{2m}(p_x^2 + p_y^2) + \frac{1}{2}m\omega_L^2(x^2 + y^2)$$

and

$$H_z = \frac{1}{2m}p_z^2 + \omega_L(L_z + 2S_z)$$

where  $\omega_L = (\mu_B/\hbar)\mathfrak{B} = 2\pi\nu_L$  is the Larmor angular frequency.

(b) Using the fact that  $H$  can be written as a square,  $H = (\mathbf{p} + e\mathbf{A})^2/(2m)$ , and that the Hamiltonian  $H_{xy}$  of the harmonic motion in the  $XY$  plane is invariant under the reflection  $x \rightarrow -x, y \rightarrow -y$ , show that the energy eigenvalues are given by

$$E = \frac{\hbar^2 k^2}{2m} + \hbar\omega_L(2r + 2m_s + 1)$$

where  $-\infty < k < +\infty, r = 0, 1, 2, \dots$  and  $m_s = \pm 1/2$ . For given  $k$  and  $m_s$ , the discrete energy levels labelled by the quantum number  $r$  are the *Landau levels* [see (6.128)].

(c) In neutron stars magnetic fields of the order of  $10^8$  T may occur. Find the energy separation between the adjacent Landau levels. What is the size of the region to which the motion in the  $XY$  plane is confined?