

5 One-electron atoms: fine structure, hyperfine structure and interaction with external electric and magnetic fields

Our discussion of the energy levels and wave functions of one-electron atoms in Chapter 3 was based on the simple, non-relativistic Hamiltonian

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{(4\pi\epsilon_0)r} \quad [5.1]$$

where the first term represents the (non-relativistic) kinetic energy of the atom in the centre of mass system, and the second term is the electrostatic (Coulomb) interaction between the electron and the nucleus. Although the energy levels obtained in Chapter 3 from the Hamiltonian [5.1] are in good qualitative agreement with experiment, the very precise measurements carried out in atomic physics demonstrate the existence of several effects which cannot be derived from the Hamiltonian [5.1] and require the addition of correction terms to [5.1]. In this chapter we shall discuss several of these corrections and we shall also consider the problem of the interaction of one-electron atoms with external (static) electric and magnetic fields.

We begin by analysing the relativistic corrections to [5.1], which give rise to a splitting of the energy levels known as fine structure. Next, we discuss the effect of an external magnetic field (the Zeeman effect) or electric field (the Stark effect) on the spectra of one-electron atoms. We then describe a subtle effect called the Lamb shift, which displaces certain of the fine structure components and is therefore responsible for additional splittings of the energy levels. Finally, we consider various small corrections such as the hyperfine structure splitting and the volume effect, which take into account the fact that the nucleus is not simply a point charge, but has a finite size, and may possess an intrinsic angular momentum (spin), a magnetic dipole moment, an electric quadrupole moment, and so on.

5.1 FINE STRUCTURE OF HYDROGENIC ATOMS

The fine structure of the energy levels of hydrogenic atoms is due to relativistic effects. In order to analyse these effects we therefore need for the electron a basic wave equation which satisfies the requirements of special relativity as well as those of quantum mechanics. This is the Dirac equation, which is discussed briefly in Appendix 7, and which provides the correct relativistic wave equation for electrons.

The most rigorous way of obtaining the relativistic corrections to the Schrödinger (Bohr) energy levels of one-electron atoms is to solve the Dirac equation for an electron in the central field $V(r) = -Ze^2/(4\pi\epsilon_0)r$ of the nucleus which is assumed to be of infinite mass and at the origin of the coordinates. It turns out that the Dirac equation for a central field can be separated in spherical polar coordinates and that the resulting radial equations can be solved exactly for the Coulomb potential $V(r) = -Ze^2/(4\pi\epsilon_0)r$ [1]. However, these calculations are rather lengthy and since the relativistic corrections are very small (provided that Z is not too large), it is convenient to use perturbation theory, keeping terms up to order v^2/c^2 in the Dirac Hamiltonian. We shall therefore start from the Hamiltonian [A7.65] of Appendix 7 which we rewrite as

$$H = H_0 + H' \quad [5.2]$$

where

$$H_0 = \frac{p^2}{2m} - \frac{Ze^2}{(4\pi\epsilon_0)r} \quad [5.3]$$

is simply the Hamiltonian [5.1] with $\mu = m$ [2] and

$$H' = H'_1 + H'_2 + H'_3 \quad [5.4]$$

with

$$H'_1 = -\frac{p^4}{8m^3c^2} \quad [5.5]$$

$$H'_2 = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S} \quad [5.6]$$

and

$$H'_3 = \frac{\pi\hbar^2}{2m^2c^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \delta(\mathbf{r}) \quad [5.7]$$

The physical interpretation of the three terms which constitute H' is discussed in Appendix 7. We simply note here that H'_1 is a relativistic correction to the kinetic energy, H'_2 represents the spin-orbit interaction and H'_3 is the Darwin term.

Before we proceed to the evaluation of the energy shifts due to these three terms by using perturbation theory, we remark that the Schrödinger theory

[1] See for example Bethe and Salpeter (1957).

[2] For the sake of simplicity we shall ignore all reduced mass effects in discussing the fine structure calculations. It is of course straightforward to incorporate the reduced mass effect in H_0 and in the corresponding unperturbed energy levels E_n by replacing the electron mass m by its reduced mass μ . On the other hand, the reduced mass effects arising in H' cannot be obtained by just replacing m by μ in the results of the perturbation calculation. Fortunately, these latter reduced mass effects are very small since H' is already a correction to H_0 .

discussed in Chapter 3 does not include the spin of the electron. In order to calculate corrections involving the spin operator – such as those arising from H'_2 – we start from the ‘unperturbed’ equation

$$H_0\psi_{nlm_l m_s} = E_n\psi_{nlm_l m_s} \quad [5.8]$$

where E_n are the Schrödinger eigenvalues [3.29] (with $\mu = m$) and the zero order wave functions $\psi_{nlm_l m_s}$ are modified (two-component) Schrödinger wave functions (also referred to as Pauli wave functions or ‘spin-orbitals’) given by

$$\psi_{nlm_l m_s}(q) = \psi_{nlm_l}(\mathbf{r})\chi_{1/2, m_s} \quad [5.9]$$

where q denotes the space and spin coordinates collectively. The quantum number m_l which can take the values $-l, -l + 1, \dots, +l$ is the magnetic quantum number previously denoted by m [3], $\psi_{nlm_l}(\mathbf{r})$ is a one-electron Schrödinger wave function (see [3.48]) such that

$$H_0\psi_{nlm_l}(\mathbf{r}) = E_n\psi_{nlm_l}(\mathbf{r}) \quad [5.10]$$

and $\chi_{1/2, m_s}$ are the spin eigenfunctions for spin one-half ($s = 1/2$) introduced in Section 2.5, with $m_s = \pm 1/2$. We recall that $\chi_{1/2, m_s}$ is a two-component spinor and that the normalised spinors corresponding respectively to ‘spin up’ ($m_s = +1/2$) and ‘spin down’ ($m_s = -1/2$) are conveniently denoted by

$$\alpha \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \beta \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad [5.11]$$

Since H_0 does not act on the spin variable the two-component wave functions [5.9] are separable in space and spin variables. It is also worth noting that we now have *four* quantum numbers (n, l, m_l, m_s) to describe a one-electron atom, the effect of the spin on the ‘unperturbed’ solutions being to double the degeneracy, so that each Schrödinger energy level E_n is now $2n^2$ degenerate.

Energy shifts

We now calculate the energy corrections due to the three terms [5.5]–[5.7], using the Pauli wave functions as our zero-order wave functions.

$$1. H'_1 = -\frac{p^4}{8m^3c^2} \quad (\text{relativistic correction to the kinetic energy})$$

Since the unperturbed energy level E_n is $2n^2$ degenerate, we should use the degenerate perturbation theory discussed in Section 2.8. However, we first note that H'_1 does not act on the spin variable. Moreover, it commutes with the components of the orbital angular momentum (see Problem 2.12) so that the

[3] When no confusion is possible, we shall continue to write m instead of m_l for the magnetic quantum number associated with the operator L_z .

perturbation H'_1 is already 'diagonal' in l , m_l and m_s . The energy correction ΔE_1 due to H'_1 is therefore given in first-order perturbation theory by

$$\begin{aligned}\Delta E_1 &= \left\langle \psi_{nlm_l m_s} \left| -\frac{p^4}{8m^3 c^2} \right| \psi_{nlm_l m_s} \right\rangle \\ &= \left\langle \psi_{nlm_l} \left| -\frac{p^4}{8m^3 c^2} \right| \psi_{nlm_l} \right\rangle \\ &= -\frac{1}{2mc^2} \langle \psi_{nlm_l} | T^2 | \psi_{nlm_l} \rangle\end{aligned}\quad [5.12]$$

where $T = p^2/2m$ is the kinetic energy operator. From [5.3] we have

$$T = H_0 + \frac{Ze^2}{(4\pi\epsilon_0)r}\quad [5.13]$$

and therefore

$$\begin{aligned}\Delta E_1 &= -\frac{1}{2mc^2} \left\langle \psi_{nlm_l} \left| \left(H_0 + \frac{Ze^2}{(4\pi\epsilon_0)r} \right) \left(H_0 + \frac{Ze^2}{(4\pi\epsilon_0)r} \right) \right| \psi_{nlm_l} \right\rangle \\ &= -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle_{nlm_l} + \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle_{nlm_l} \right]\end{aligned}\quad [5.14]$$

where we have used [5.10]. From the results [3.30], [3.71] and [3.72] (with $\mu = m$) we finally obtain

$$\begin{aligned}\Delta E_1 &= -\frac{1}{2mc^2} \left\{ \left[\frac{mc^2(Z\alpha)^2}{2n^2} \right]^2 - 2 \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \frac{mc^2(Z\alpha)^2}{2n^2} \frac{Z}{a_0 n^2} \right. \\ &\quad \left. + \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{Z^2}{a_0^2 n^3 (l + 1/2)} \right\} \\ &= \frac{1}{2} mc^2 \frac{(Z\alpha)^2}{n^2} \frac{(Z\alpha)^2}{n^2} \left[\frac{3}{4} - \frac{n}{l + 1/2} \right] \\ &= -E_n \frac{(Z\alpha)^2}{n^2} \left[\frac{3}{4} - \frac{n}{l + 1/2} \right]\end{aligned}\quad [5.15]$$

$$2. H'_2 = \frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S} \quad (\text{spin-orbit term})$$

We shall first rewrite this term more simply as

$$H'_2 = \xi(r) \mathbf{L} \cdot \mathbf{S}\quad [5.16]$$

where we have introduced the quantity

$$\xi(r) = \frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr}\quad [5.17]$$

In our case $V(r) = -Ze^2/(4\pi\epsilon_0)r$, so that

$$\xi(r) = \frac{1}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \quad [5.18]$$

Since the operator \mathbf{L}^2 does not act on the radial variable r nor on the spin variable, and commutes with the components of \mathbf{L} , we see from [5.16] that \mathbf{L}^2 commutes with H'_2 . It follows that the perturbation H'_2 does not connect states with different values of the orbital angular momentum l . For a given value of n and l there are $2(2l + 1)$ degenerate eigenstates of H_0 (the factor of 2 arising from the two spin states), so that the calculation of the energy shift due to H'_2 requires the diagonalisation of $2(2l + 1) \times 2(2l + 1)$ submatrices.

This diagonalisation is greatly simplified by using for the zero-order wave functions a representation in which $\mathbf{L} \cdot \mathbf{S}$ is diagonal. It is clear that the functions ψ_{nlm,m_s} given by [5.9], which are simultaneous eigenfunctions of the operators H_0 , \mathbf{L}^2 , \mathbf{S}^2 , L_z and S_z are not adequate because $\mathbf{L} \cdot \mathbf{S}$ does not commute with L_z or S_z . However, we shall now show that satisfactory zero-order wave functions may be obtained by forming certain linear combinations of the functions ψ_{nlm,m_s} . To this end, we introduce the total angular momentum of the electron

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad [5.19]$$

and we note that

$$\mathbf{J}^2 = \mathbf{L}^2 + 2\mathbf{L} \cdot \mathbf{S} + \mathbf{S}^2 \quad [5.20]$$

so that

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) \quad [5.21]$$

Consider now wave functions ψ_{nljm_j} which are eigenstates of the operators H_0 , \mathbf{L}^2 , \mathbf{S}^2 , \mathbf{J}^2 and J_z , the corresponding eigenvalues being E_n , $l(l + 1)\hbar^2$, $s(s + 1)\hbar^2$, $j(j + 1)\hbar^2$ and $m_j\hbar$. In this particular case we have $s = 1/2$ and therefore (see Section 2.5)

$$\begin{aligned} j &= l \pm 1/2, & l &\neq 0 \\ j &= 1/2, & l &= 0 \end{aligned} \quad [5.22]$$

and

$$m_j = -j, -j + 1, \dots, +j \quad [5.23]$$

By using the methods of Section 2.5 and Appendix 4, we can form the functions ψ_{nljm_j} from linear combinations of the functions ψ_{nlm,m_s} [4]. Since $\mathbf{L} \cdot \mathbf{S}$ commutes with \mathbf{L}^2 , \mathbf{S}^2 , \mathbf{J}^2 and J_z it is apparent that the new zero-order wave functions ψ_{nljm_j} form a satisfactory basis set in which the operator $\mathbf{L} \cdot \mathbf{S}$ (and

[4] Specifically, if we use the Dirac notation so that the ket $|nlsm,m_s\rangle$ corresponds to the wave function ψ_{nlm,m_s} and the ket $|nlsjm_j\rangle$ to the wave function ψ_{nljm_j} (with $s = 1/2$), we have

$$|nlsjm_j\rangle = \sum_{m_l, m_s} \langle lsm_l, m_s | jm_j \rangle |nlsm_l, m_s\rangle$$

The Clebsch–Gordan coefficients $\langle lsm_l, m_s | jm_j \rangle$ are not needed in the present calculation since we are only interested in expectation values.

hence the perturbation H'_2 is diagonal. Using [5.16] and [5.21], we see that for $l \neq 0$ the energy shift due to the term H'_2 is given by

$$\begin{aligned}\Delta E_2 &= \left\langle \psi_{nljm_j} \left| \frac{1}{2} \xi(r) [\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2] \right| \psi_{nljm_j} \right\rangle \\ &= \frac{\hbar^2}{2} \langle \xi(r) \rangle \left[j(j+1) - l(l+1) - \frac{3}{4} \right]\end{aligned}\quad [5.24]$$

where $\langle \xi(r) \rangle$ denotes the average value of $\xi(r)$ in the state ψ_{nljm_j} . From [5.17] and [3.73], we have

$$\begin{aligned}\langle \xi(r) \rangle &= \frac{1}{2m^2c^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r^3} \right\rangle \\ &= \frac{1}{2m^2c^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \frac{Z^3}{a_0^3 n^3 l(l+1/2)(l+1)}\end{aligned}\quad [5.25]$$

Thus, for $l \neq 0$, we obtain from [5.24] and [5.25]

$$\begin{aligned}\Delta E_2 &= \frac{mc^2(Z\alpha)^4}{4n^3l(l+1/2)(l+1)} \times \begin{cases} l & \text{for } j = l + 1/2 \\ -l - 1 & \text{for } j = l - 1/2 \end{cases} \\ &= -E_n \frac{(Z\alpha)^2}{2nl(l+1/2)(l+1)} \times \begin{cases} l & \text{for } j = l + 1/2 \\ -l - 1 & \text{for } j = l - 1/2 \end{cases}\end{aligned}\quad [5.26]$$

For $l = 0$ the spin-orbit interaction [5.16] vanishes and therefore $\Delta E_2 = 0$ in that case.

$$3. H'_3 = \frac{\pi\hbar^2}{2m^2c^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \delta(\mathbf{r}) \quad (\text{Darwin term})$$

This term does not act on the spin variable, is diagonal in l , m_l and m_s and applies only to the case $l = 0$. Calling ΔE_3 the corresponding energy correction and using the result [3.60], we have

$$\begin{aligned}\Delta E_3 &= \frac{\pi\hbar^2}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \langle \psi_{n00} | \delta(\mathbf{r}) | \psi_{n00} \rangle \\ &= \frac{\pi\hbar^2}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} |\psi_{n00}(0)|^2 \\ &= \frac{1}{2} mc^2 \frac{(Z\alpha)^2}{n^2} \frac{(Z\alpha)^2}{n} \\ &= -E_n \frac{(Z\alpha)^2}{n}, \quad l = 0\end{aligned}\quad [5.27]$$

We may now combine the effects of H'_1 , H'_2 and H'_3 to obtain the total energy shift $\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3$ due to relativistic corrections. From [5.15],

[5.26] and [5.27] we have for all l

$$\begin{aligned}\Delta E_{nj} &= -\frac{1}{2} mc^2 \frac{(Z\alpha)^2}{n^2} \frac{(Z\alpha)^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \\ &= E_n \frac{(Z\alpha)^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right)\end{aligned}\quad [5.28]$$

where the subscripts nj indicate that the correction depends on both the principal quantum number n and the total angular momentum quantum number j , with $j = 1/2, 3/2, \dots, n - 1/2$. To each value of j correspond two possible values of l given by $l = j \pm 1/2$, except for $j = n - 1/2$ where one can only have $l = j - 1/2 = n - 1$.

Adding the relativistic correction ΔE_{nj} to the non-relativistic energies E_n , we find that the energy levels of one-electron atoms are now given by

$$E_{nj} = E_n \left[1 + \frac{(Z\alpha)^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \right] \quad [5.29]$$

so that the binding energy $|E_{nj}|$ of the electron is slightly increased with respect to the non-relativistic value $|E_n|$, the absolute value $|\Delta E_{nj}|$ of the energy shift becoming smaller as n or j increases, and larger as Z increases. The formula [5.29] is easily shown to agree through order $(Z\alpha)^2$ with the result

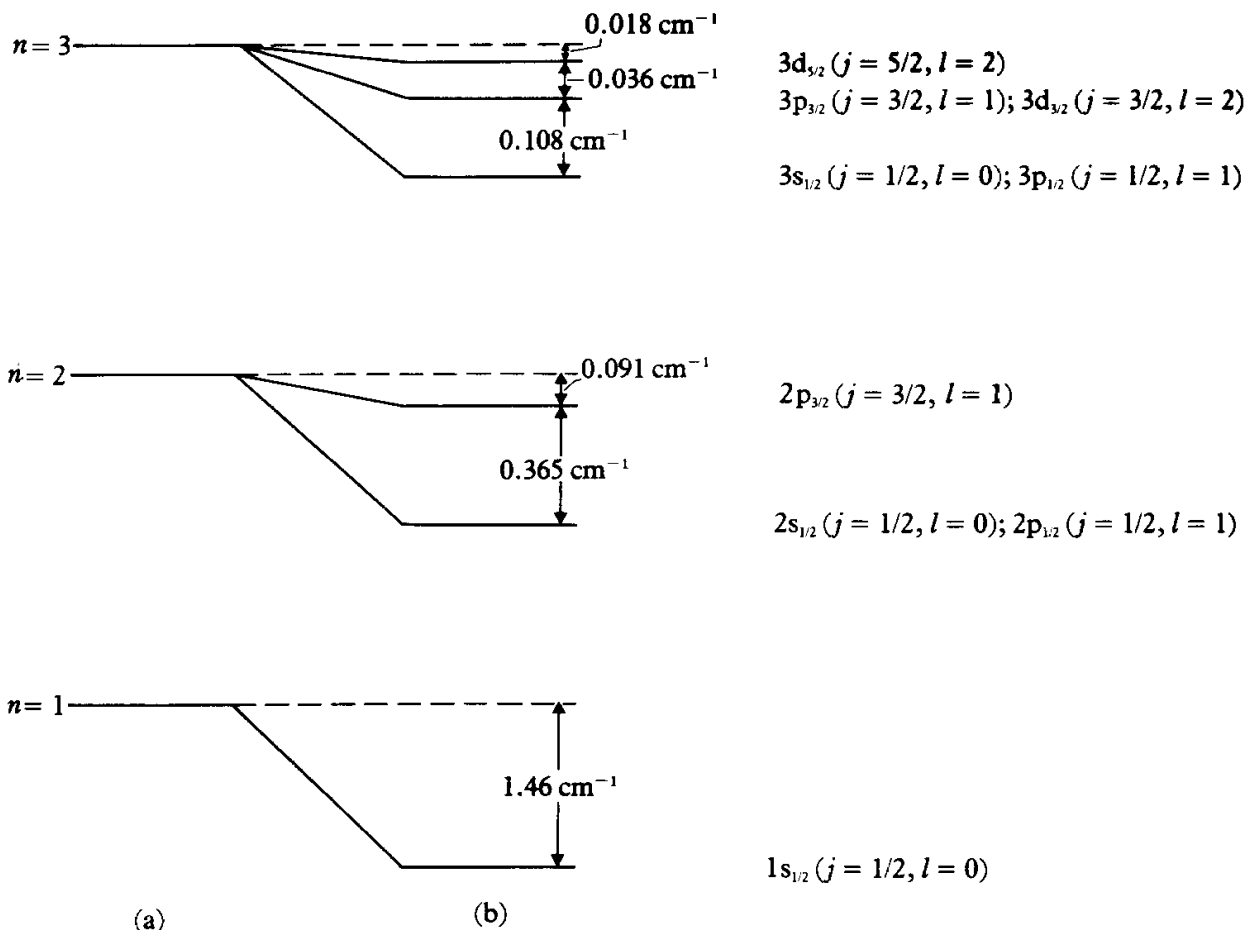
$$E_{nj}^{\text{exact}} = mc^2 \left\{ \left[1 + \frac{Z\alpha}{n-j-1/2 + [(j+1/2)^2 - Z^2\alpha^2]^{1/2}} \right]^2 - 1 \right\}^{-1/2} \quad [5.30]$$

obtained by solving the Dir. equation for the potential $V(r) = -Ze^2/(4\pi\epsilon_0)r$ [1]

Fine structure splitting

Starting from non-relativistic energy levels E_n which are $2n^2$ times degenerate (the factor of two arising from the spin) we see that in the Dirac theory this degeneracy is partly removed. In fact, a non-relativistic energy level E_n depending only on the principal quantum number n splits into n different levels in the Dirac theory, one for each value $j = 1/2, 3/2, \dots, n - 1/2$ of the total angular momentum quantum number j . This splitting is called *fine structure splitting*, and the n levels $j = 1/2, 3/2, \dots, n - 1/2$ are said to form a *fine structure multiplet*. We note that the dimensionless constant $\alpha \approx 1/137$ controls the scale of the splitting, and it is for this reason that it has been called the *fine structure constant*.

The fine structure splitting of the energy levels corresponding to $n = 1, 2, 3$ is illustrated in Fig. 5.1. We have used in that figure the spectroscopic notation

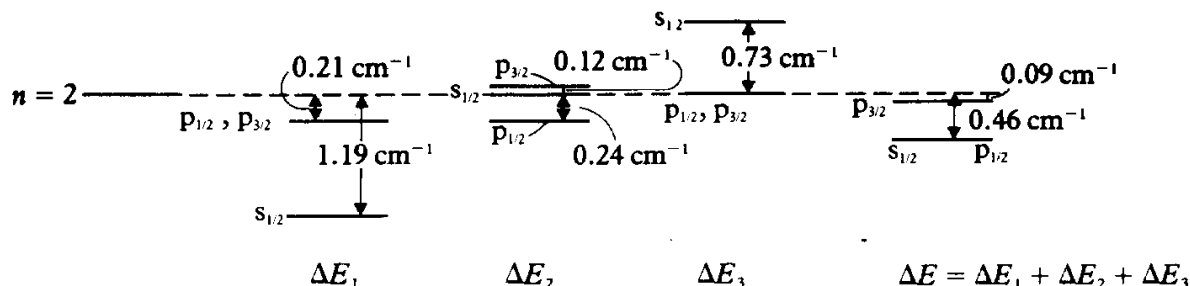


5.1 Fine structure of the hydrogen atom. The non-relativistic levels are shown on the left in column (a) and the split levels on the right in column (b), for $n = 1, 2$ and 3 . For clarity, the scale in each diagram is different.

nl_j (with the usual association of the letters s, p, d, . . . with the values $l = 0, 1, 2, \dots$ and an additional subscript for the value of j) to distinguish the various spectral terms corresponding to the Dirac theory [5].

It is important to emphasise that in Dirac's theory two states having the same value of the quantum number n and j but with values of l such that $l = j \pm 1/2$ have the same energy. The *parity* of the solutions is still given by $(-)^l$. Thus to each value of j correspond two series of $(2j + 1)$ solutions of opposite parity, except for $j = n - 1/2$ where there is only one series of solutions of parity $(-)^{n-1}$. It is also worth remarking that although the three separate contributions ΔE_1 , ΔE_2 and ΔE_3 depend on l (see [5.15], [5.26] and [5.27]), the total energy shift ΔE_{nj} (given by [5.28]) does not! This is illustrated in Fig. 5.2, where we show the splitting of the $n = 2$ levels of atomic hydrogen due to each of the three terms H'_1 , H'_2 and H'_3 , as well as the resulting degeneracy of the $2s_{1/2}$ and $2p_{1/2}$ levels. We shall see in Section 5.4 that this degeneracy of the levels with $l = j \pm 1/2$ is actually removed by small quantum electrodynamics effects,

[5] A similar notation with capital letters, such as $1S_{1/2}$, $2S_{1/2}$, $2P_{1/2}$, $2P_{3/2}$, etc., is also frequently used. We shall reserve capital letters for atomic systems with more than one electron.



5.2 The contributions ΔE_1 , ΔE_2 , ΔE_3 to the splitting of the $n = 2$ level of hydrogen.

known as radiative corrections, which are responsible for additional energy shifts called Lamb shifts.

Another interesting point is that the three relativistic energy shifts ΔE_1 , ΔE_2 and ΔE_3 we have obtained above have the same order of magnitude, and must therefore be treated together. This is a special feature of hydrogenic atoms. For many-electron atoms (and in particular for alkali atoms) we shall see in Chapter 7 that it is the spin-orbit effect (due here to the term H'_2) which is mainly responsible for the fine structure splitting.

According to [5.28], for any Z and $n \neq 1$, the energy difference between the two extreme components of a fine structure multiplet (corresponding respectively to the values $j_1 = n - 1/2$ and $j_2 = 1/2$) is given by

$$\begin{aligned} \delta E(j_1 = n - 1/2, j_2 = 1/2) &= |E_n| (Z\alpha)^2 \frac{n-1}{n^2} \\ &= \frac{\alpha^2 Z^4 (n-1)}{2n^4} \text{ a.u., } n \neq 1 \quad [5.31] \end{aligned}$$

We may also use [5.28] to obtain for any Z , $n \neq 1$ and $l \neq 0$ the energy separation between two levels corresponding respectively to $j_1 = l + 1/2$ and $j_2 = l - 1/2$. The result is

$$\begin{aligned} \delta E(j_1 = l + 1/2, j_2 = l - 1/2) &= |E_n| \frac{(Z\alpha)^2}{nl(l+1)} \\ &= \frac{\alpha^2 Z^4}{2n^3 l(l+1)} \text{ a.u.} \quad [5.32] \end{aligned}$$

For example, in the case of atomic hydrogen the splitting of the levels $j = 3/2$ and $j = 1/2$ for $n = 2$ and $n = 3$ is, respectively, 0.365 cm^{-1} ($4.52 \times 10^{-5} \text{ eV}$) and 0.108 cm^{-1} ($1.34 \times 10^{-5} \text{ eV}$), while the splitting of the levels $j = 5/2$ and $j = 3/2$ for $n = 3$ is 0.036 cm^{-1} ($4.48 \times 10^{-6} \text{ eV}$) as shown in Fig. 5.1.

Fine structure of spectral lines

The set of *spectral lines* due to the transitions $nlj \rightarrow n'l'j'$ between the fine structure components of the levels nl and $n'l'$ is known as a *multiplet* of lines.

Since the electric dipole operator $\mathbf{D} = -e\mathbf{r}$ does not depend on the spin, the selection rule derived in Chapter 4 for the quantum number l (in the dipole approximation) remains

$$\Delta l = \pm 1 \quad [5.33]$$

from which it follows that the selection rule with respect to the quantum number j is

$$\Delta j = 0, \pm 1 \quad [5.34]$$

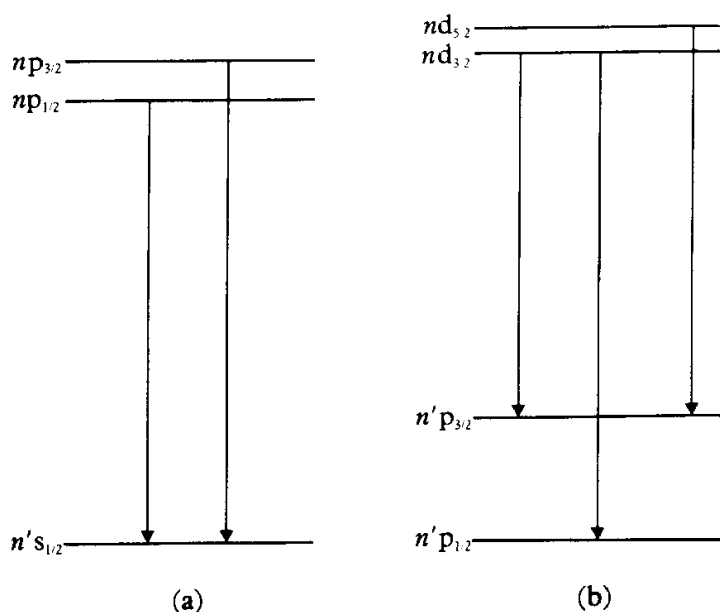
Using [5.33] and [5.34], it is a simple matter to establish the character of the fine structure splitting of the hydrogenic atom spectral lines. For example, we see from Fig. 5.3 that the multiplet $np-n's$ has two components. Thus each line of the Lyman series (lower state $n = 1$) is split by the fine structure into a pair of lines called a *doublet*, corresponding to the transitions

$$np_{1/2}-1s_{1/2}, \quad np_{3/2}-1s_{1/2}$$

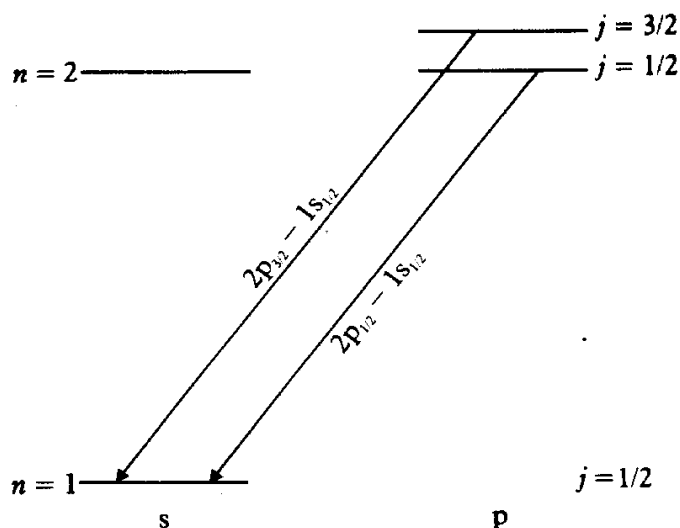
This is illustrated in Fig. 5.4 for the Lyman α line (upper state $n = 2$).

Referring to Fig. 5.3, we see that the multiplet $np-n's$ has two components, while the multiplet $nd-n'p$ has three components. Thus, in the case of the Balmer series (lower state $n = 2$) the following seven transitions are allowed:

$$\begin{aligned} np_{1/2}-2s_{1/2}, & \quad np_{3/2}-2s_{1/2} \\ ns_{1/2}-2p_{1/2}, & \quad ns_{1/2}-2p_{3/2} \\ nd_{3/2}-2p_{1/2}, & \quad nd_{3/2}-2p_{3/2}, \\ & \quad nd_{5/2}-2p_{3/2} \end{aligned}$$



5.3 Allowed transitions in (a) the multiplet $np-n's$ and (b) $nd-n'p$.



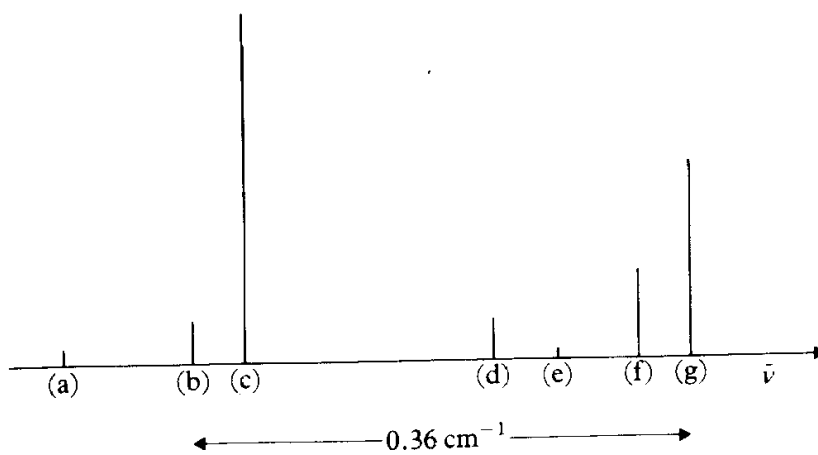
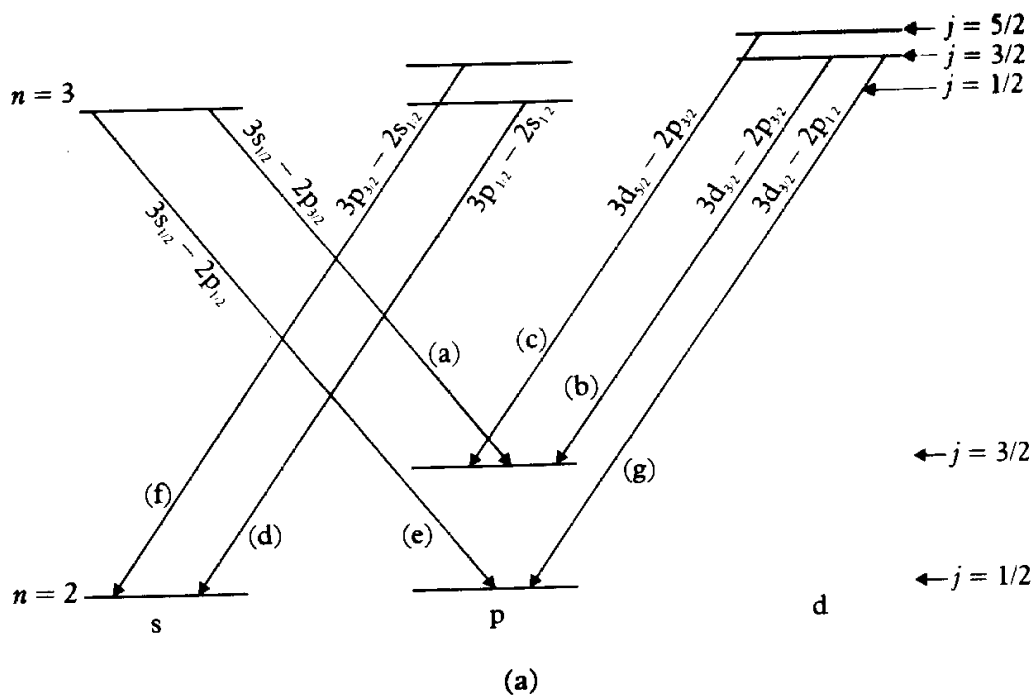
5.4 Allowed transitions between the $n = 2$ and $n = 1$ levels of atomic hydrogen giving rise to the Lyman alpha doublet (L_α).

However, since the levels $ns_{1/2}$ and $np_{1/2}$ coincide, as well as the levels $np_{3/2}$ and $nd_{3/2}$, each Balmer line only contains five distinct components. This is illustrated in Fig. 5.5 for the case of the fine structure of the H_α line, i.e. the red line of the Balmer series at 6563 \AA , corresponding to the transition between the upper state $n = 3$ and the lower state $n = 2$.

Because the energy differences [5.31] or [5.32] rapidly decrease with increasing n , the fine structure splitting of a spectral line corresponding to a transition between two levels of different n is mainly due to the fine structure of the *lower* level, with additional (finer) fine structure arising from the smaller splitting of the upper level. For example, each line of the Balmer series essentially consists of a *doublet*, or more precisely of *two groups* of closely spaced lines. The distance between these two groups is approximately given by the fine structure splitting of the lower ($n = 2$) level (i.e. about 0.365 cm^{-1}) and this distance is constant for all the lines of the series. Within each of the two groups the magnitude of the (small) residual splitting due to the fine structure of the upper level rapidly falls off as n increases, i.e. as one goes to higher lines of the series. Similarly, each line of the Paschen series (lower state $n = 3$) consists of *three groups* of closely spaced lines, etc. Finally, we remark that for hydrogenic ions the fine structure splitting is more important than for hydrogen since the energy shift ΔE_{nj} given by [5.28] is proportional to Z^4 .

Intensities of fine structure lines

Since the radial integrals in [4.85] are the same for both the transitions $np_{3/2} - n's_{1/2}$ and $np_{1/2} - n's_{1/2}$, it is easy to obtain from the angular parts of those integrals (that is from angular momentum considerations) the ratio of the two transition probabilities, which is found to be equal to 2 (Problem 5.1). More generally, the ratios of the transition probabilities for the most important special



5.5 (a) Transitions contributing to the Balmer alpha (H_α) line between the $n = 3$ and $n = 2$ levels of atomic hydrogen.

(b) The relative intensities of the lines (a), (b)–(g). Note that (b) and (g) have the same upper level, so that the wave number difference between the lines is determined by the $2p_{1/2}$, $2p_{3/2}$ energy difference and is 0.36 cm^{-1} . In the same way, the wave number difference between lines (a) and (e) is also 0.36 cm^{-1} . We note that the lines (d) and (e) should coincide according to Dirac theory, as well as the lines (f) and (g).

cases are (Bethe and Salpeter, 1957)

$$\text{for sp transitions: } s_{1/2}-p_{3/2}:s_{1/2}-p_{1/2} = 2:1$$

$$\text{pd transitions: } p_{3/2}-d_{5/2}:p_{3/2}-d_{3/2}:p_{1/2}-d_{3/2} = 9:1:5$$

$$\text{df transitions: } d_{5/2}-f_{7/2}:d_{5/2}-f_{5/2}:d_{3/2}-f_{5/2} = 20:1:14$$

[5.35]

Under most circumstances the initial states are excited in proportion to their statistical weights, that is the $(2j + 1)$ degenerate levels corresponding to an initial state with a given value of j (but differing in $m_j = -j, -j + 1, \dots, +j$) are equally populated. In this case the ratios of line intensities are the same as those of the corresponding transition probabilities. The relative intensities of the fine structure components of the H_α line are shown in Fig. 5.5.

Comparison with experiment

The fine structure splitting of the spectral lines of atomic hydrogen and of hydrogenic ions (in particular He^+) has been the subject of many spectroscopic investigations. The experimental results are in good *semi-quantitative* agreement with the formula [5.28] obtained from the Dirac theory. Nevertheless, and in spite of the fact that precise optical measurements of fine structure are very difficult to perform, small deviations from the theoretical predictions of [5.28] were observed as early as 1934. In particular, detailed experimental studies of the H_α line of atomic hydrogen indicated that the energy separation of the $2s_{1/2}$ and $2p_{1/2}$ levels is not exactly zero, as predicted from the Dirac theory (see [5.28] or [5.30]) but is about 10 per cent of the fine structure splitting of the $n = 2$ levels. However, the Doppler broadening of the spectral lines prevented precise results being obtained from optical spectroscopy, and the situation remained ambiguous until the first measurements of Lamb and Retherford were published in 1947. Using new methods of microwave spectroscopy, Lamb and Retherford demonstrated in a decisive way the existence of an energy difference between the two levels $2s_{1/2}$ and $2p_{1/2}$. This 'Lamb shift', to which we have already alluded in the discussion following [5.30], will be considered in Section 5.4 after we have familiarised ourselves with the behaviour of hydrogenic atoms in external magnetic and electric fields.

5.2. 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 *constant* magnetic fields, which can be taken to be uniform over atomic dimensions. The vector potential \mathbf{A} can then be written as

$$\mathbf{A} = \frac{1}{2}(\mathbf{B} \times \mathbf{r}) \quad [5.36]$$

where \mathfrak{B} is the constant magnetic field, which satisfies the relation $\mathfrak{B} = \nabla \times \mathbf{A}$. If \mathfrak{B} is directed along the Z axis, the components of \mathbf{A} are $(-y\mathfrak{B}_z/2, +x\mathfrak{B}_z/2, 0)$.

The non-relativistic Schrödinger equation for a hydrogenic atom in the presence of a constant magnetic field is given by (see Appendix 6 and Section 4.1)

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} - \frac{i\hbar e}{m} \mathbf{A} \cdot \nabla + \frac{e^2}{2m} \mathbf{A}^2 \right] \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad [5.37]$$

where reduced mass effects have been neglected, \mathbf{A} is given by [5.36] and we have used the fact that $\nabla \cdot \mathbf{A} = 0$.

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

$$\begin{aligned} -\frac{i\hbar e}{m} \mathbf{A} \cdot \nabla &= -\frac{i\hbar e}{2m} (\mathfrak{B} \times \mathbf{r}) \cdot \nabla \\ &= -\frac{i\hbar e}{2m} \mathfrak{B} \cdot (\mathbf{r} \times \nabla) \\ &= \frac{e}{2m} \mathfrak{B} \cdot \mathbf{L} \end{aligned} \quad [5.38]$$

where

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = -i\hbar(\mathbf{r} \times \nabla) \quad [5.39]$$

is the orbital angular momentum of the electron. The quadratic term in \mathbf{A} appearing in [5.37] can be reduced as follows:

$$\begin{aligned} \frac{e^2}{2m} \mathbf{A}^2 &= \frac{e^2}{8m} (\mathfrak{B} \times \mathbf{r})^2 \\ &= \frac{e^2}{8m} [\mathfrak{B}^2 r^2 - (\mathfrak{B} \cdot \mathbf{r})^2] \end{aligned} \quad [5.40]$$

The relative magnitude of the two terms [5.38] and [5.40] can now be estimated. Assuming that the dimensions of the atomic system are of the order of a_0 , the Bohr radius of hydrogen, the quadratic term is of the order $e^2 a_0^2 \mathfrak{B}^2 / 8m$, while if we are dealing with states of low orbital angular momentum (say about \hbar) the linear term is approximately given by $e\hbar\mathfrak{B}/2m$. The ratio of the quadratic to the linear term is then

$$\frac{ea_0^2\mathfrak{B}}{4\hbar} \approx \mathfrak{B}10^{-6} \quad [5.41]$$

where \mathfrak{B} is expressed in Tesla (T). In the laboratory, the fields encountered do not exceed 10 T, so that for most purposes the quadratic term is negligible.

The linear term [5.38] corresponds to the interaction energy of a magnetic field \mathfrak{B} with a magnetic dipole moment \mathcal{M} , if \mathcal{M} is defined as the operator

$$\mathcal{M} = -\frac{e}{2m} \mathbf{L} = -\mu_B \mathbf{L}/\hbar \quad [5.42]$$

where

$$\mu_B = \frac{e\hbar}{2m} \quad [5.43]$$

is called the *Bohr magneton* and has the value 9.27408×10^{-24} joule/tesla or m^2A . The interaction energy [5.38] then takes the form

$$H'_1 = -\mathcal{M} \cdot \mathfrak{B} \quad [5.44]$$

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

$$\begin{aligned} H'_1 &= 2.13 \times 10^{-6} \mathfrak{B} \cdot \mathbf{L} \text{ a.u.} \\ &= 0.4669 \mathfrak{B} \cdot \mathbf{L}/\hbar \text{ cm}^{-1} \end{aligned} \quad [5.45]$$

where in both cases \mathfrak{B} is to be given in Tesla.

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

$$\mathcal{M}_s = -g_s \frac{e}{2m} \mathbf{S} \quad [5.46]$$

or

$$\mathcal{M}_s = -g_s \mu_B \mathbf{S}/\hbar \quad [5.47]$$

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 [6]. The spin magnetic moment \mathcal{M}_s gives rise to an additional interaction energy

$$H'_2 = -\mathcal{M}_s \cdot \mathfrak{B} = g_s \mu_B \mathfrak{B} \cdot \mathbf{S}/\hbar \quad [5.48]$$

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, the Darwin term and the quadratic (\mathbf{A}^2) term, is (with $g_s = 2$)

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} + \xi(r) \mathbf{L} \cdot \mathbf{S} + \frac{\mu_B}{\hbar} (\mathbf{L} + 2\mathbf{S}) \cdot \mathfrak{B} \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad [5.49]$$

[6] The corrections to the Dirac result $g_s = 2$ come from quantum electrodynamics, which yields a value $g_s = 2(1 + \alpha/2\pi + \dots)$ in excellent agreement with the experimental result $g_s = 2 \times 1.001\,159\,657$.

the eigenfunctions, written in Dirac notation, are of the form $|nlm_l m_s\rangle$, with $s = 1/2$ and $m_s = \pm 1/2$.

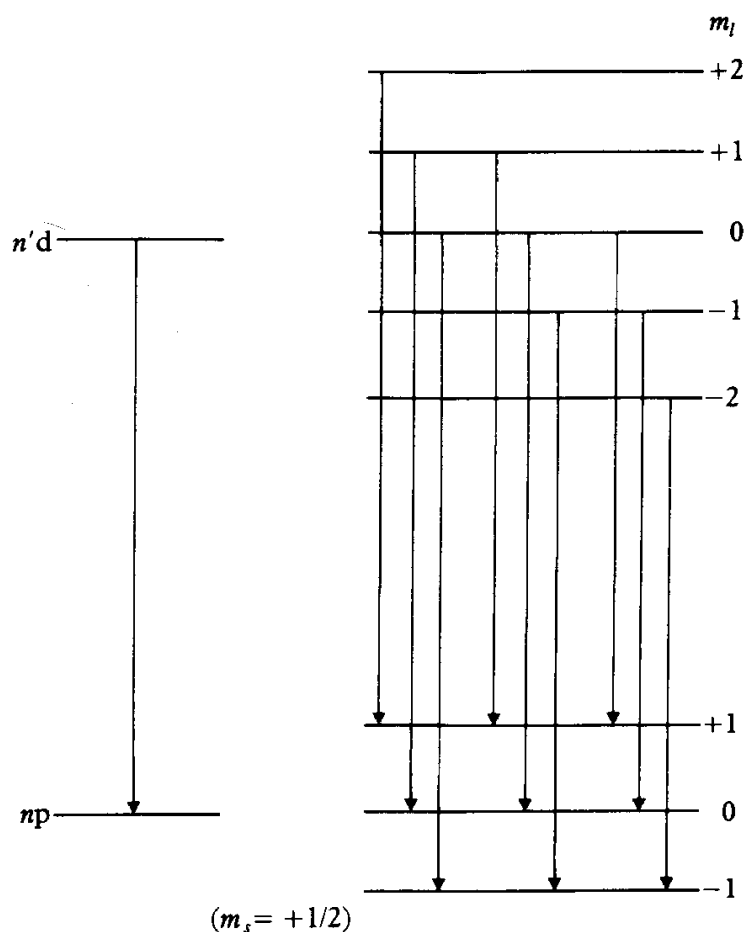
The selection rules for electric dipole transitions require $\Delta m_s = 0$ and $\Delta m_l = 0, \pm 1$. Thus the spectral line corresponding to a transition $n \rightarrow n'$ is split into *three* components. The line corresponding to $\Delta m_l = 0$ has the original frequency $\nu_{n'n}$ and is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

$$\nu_{n'n}^{\pm} = \nu_{n'n} \pm \nu_L \quad [5.52]$$

where

$$\nu_L = \frac{\mu_B \mathcal{B}_z}{h} \quad [5.53]$$

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. 5.7). Apart from the 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.



5.7 The normal Zeeman effect. In a strong magnetic field nine transitions are possible between the split levels consistent with $\Delta m_l = 0$ or ± 1 and $\Delta m_s = 0$. Of these, there are only three different frequencies and the lines form a Lorentz triplet. The frequencies of transitions associated with $m_s = -\frac{1}{2}$ are the same as those for $m_s = +\frac{1}{2}$.

The polarisation of the radiation in each of the emission lines has interesting properties. The transition rate for spontaneous emission of radiation described by a polarisation vector $\hat{\epsilon}$ is given by [4.70], namely

$$\begin{aligned} W_{ab}^s d\Omega &= \frac{1}{2\pi\hbar c^3} \left(\frac{e^2}{4\pi\epsilon_0} \right) \omega_{ba}^3 |\hat{\epsilon} \cdot \mathbf{r}_{ba}|^2 d\Omega \\ &= C(\omega_{ba}) |\hat{\epsilon} \cdot \mathbf{r}_{ba}|^2 d\Omega \end{aligned} \quad [5.54a]$$

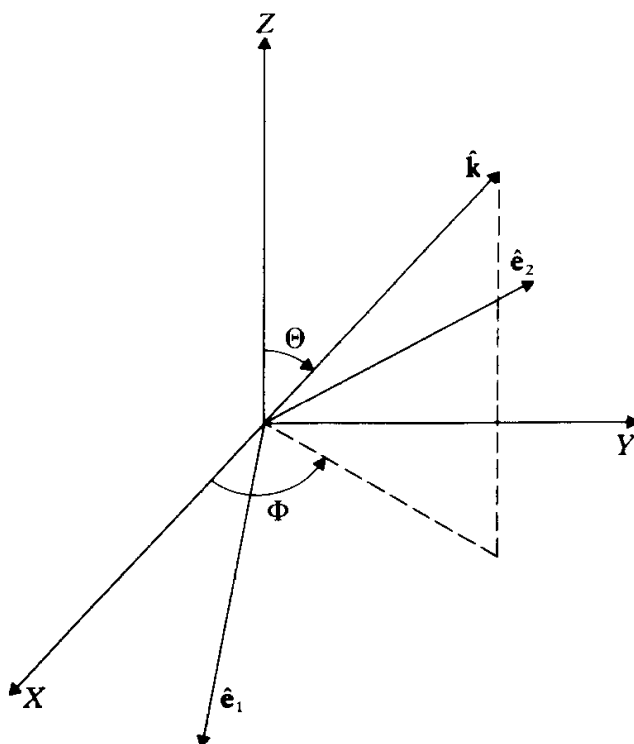
where we have set

$$C(\omega_{ba}) = \frac{1}{2\pi\hbar c^3} \left(\frac{e^2}{4\pi\epsilon_0} \right) \omega_{ba}^3 \quad [5.54b]$$

The vector $\hat{\epsilon}$ can be expressed in terms of two independent vectors $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$ as in [4.95], where $\hat{\epsilon}_1$, $\hat{\epsilon}_2$ and $\hat{\mathbf{k}}$ form a right-handed system of axes (see [4.96]). If we take (as can always be done) $\hat{\epsilon}_2$ to lie in the (X, Y) plane and if (Θ, Φ) are the polar angles of $\hat{\mathbf{k}}$ (see Fig. 5.8), we have

$$\begin{aligned} (\hat{\epsilon}_1)_x &= \cos \Theta \cos \Phi; & (\hat{\epsilon}_1)_y &= \cos \Theta \sin \Phi; & (\hat{\epsilon}_1)_z &= -\sin \Theta \\ (\hat{\epsilon}_2)_x &= -\sin \Phi; & (\hat{\epsilon}_2)_y &= \cos \Phi; & (\hat{\epsilon}_2)_z &= 0 \end{aligned} \quad [5.55]$$

Consider first the π 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



5.8 The unit vectors $\hat{\epsilon}_1$, $\hat{\epsilon}_2$ and $\hat{\mathbf{k}}$ form a right-handed set. The polar angles of $\hat{\mathbf{k}}$ are (Θ, Φ) and $\hat{\epsilon}_2$ lies in the XY plane, $\hat{\epsilon}_1$ pointing downwards.

polarisation \hat{e}_1 is then

$$W_{ab}^s d\Omega = C(\omega_{ba}) \sin^2 \Theta |z_{ba}|^2 d\Omega \quad [5.56]$$

and the rate is zero for emission of a photon with polarisation \hat{e}_2 . When the light is viewed longitudinally, so that \hat{k} is in the direction of the magnetic field (which is parallel to the Z axis), $\Theta = 0$ and the π line is absent. In transverse observation ($\Theta = \pi/2$), in a direction at right angles to the magnetic field, the π radiation is plane polarised with $\hat{\epsilon} = \hat{e}_1$ 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 [4.81]–[4.84])

$$\epsilon_{n'l'm'_l-1;nlm_l}^* = \frac{1}{\sqrt{2}} (\hat{\epsilon}_x + i\hat{\epsilon}_y) \frac{1}{\sqrt{2}} (x_{ba} - iy_{ba}) \quad [5.57]$$

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

$$W_{ab}^s(1) d\Omega = C(\omega_{ba}) \left| \frac{1}{\sqrt{2}} \cos \Theta e^{i\Phi} \right|^2 \left| \frac{1}{\sqrt{2}} (x_{ba} - iy_{ba}) \right|^2 d\Omega \quad [5.58]$$

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

$$W_{ab}^s(2) d\Omega = C(\omega_{ba}) \left| \frac{i}{\sqrt{2}} e^{i\Phi} \right|^2 \left| \frac{1}{\sqrt{2}} (x_{ba} - iy_{ba}) \right|^2 d\Omega \quad [5.59]$$

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 σ^+ line, is

$$W_{ab}^s(\sigma^+) d\Omega = C(\omega_{ba}) \frac{1}{2} (1 + \cos^2 \Theta) \left| \frac{1}{\sqrt{2}} (x_{ba} - iy_{ba}) \right|^2 d\Omega \quad [5.60]$$

In transverse observation $\Theta = \pi/2$ and the x and y components of \hat{e}_1 vanish. In this case the σ^+ line is plane polarised with $\hat{\epsilon} = \hat{e}_2$, where \hat{e}_2 lies in the (X, Y) plane. In contrast, in longitudinal observation along the direction of the magnetic field, we see from [4.102] that the radiation is left-hand circularly polarised, that is the emitted photon has helicity $+\hbar$.

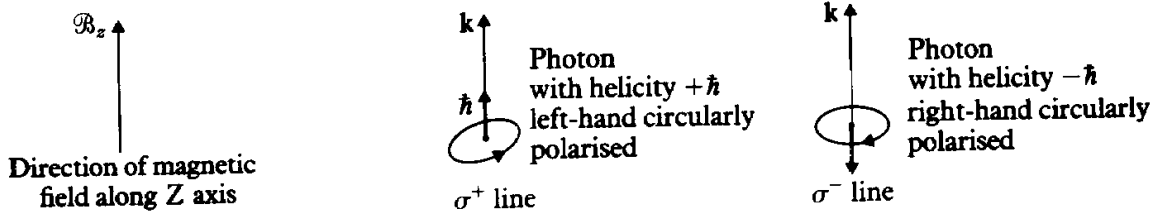
In the same way, the transition rate for the σ^- line corresponding to $\Delta m_l = m'_l - m_l = +1$ is given by

$$W_{ab}^s(\sigma^-) d\Omega = C(\omega_{ba}) \frac{1}{2} (1 + \cos^2 \Theta) \left| \frac{1}{\sqrt{2}} (x_{ba} + iy_{ba}) \right|^2 d\Omega \quad [5.61]$$

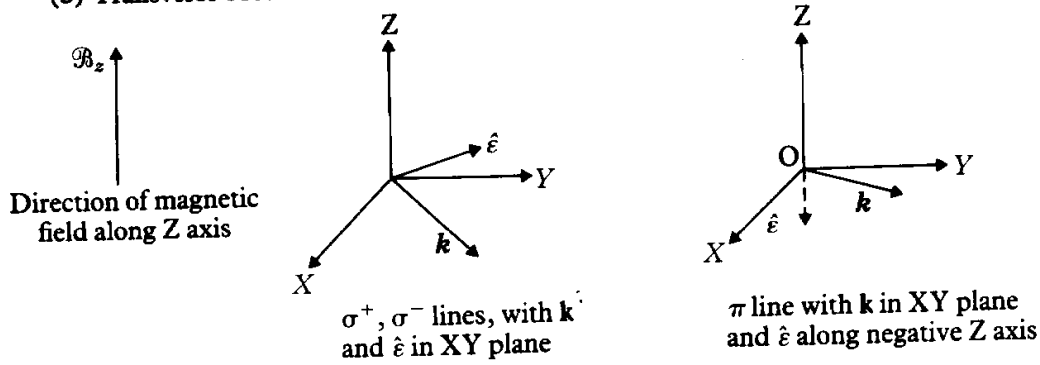
The σ^- line is right-hand circularly polarised when viewed along the direction of the magnetic field and is plane polarised in transverse observation.

The preceding discussion of the polarisations of the σ and π components is illustrated in Fig. 5.9. It is easily shown (Problem 5.3) that in the transverse direction the intensity of the π component is twice that of each σ component.

(a) Longitudinal observation (π line absent)



(b) Transverse observation



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

The Paschen-Back effect

At field strengths for which the spin-orbit interaction is appreciable, but still small compared with the term in \mathfrak{B} in [5.49], it can be treated in first order perturbation theory. We see that the perturbation is just $\xi(r)\mathbf{L} \cdot \mathbf{S}$, and its contribution to the total energy is therefore

$$\begin{aligned} \Delta E &= \int_0^\infty dr r^2 [R_{nl}(r)]^2 \xi(r) \left\langle l \frac{1}{2} m_l m_s \left| \mathbf{L} \cdot \mathbf{S} \right| l \frac{1}{2} m_l m_s \right\rangle \\ &= \lambda_{nl} m_l m_s, \quad l \neq 0 \end{aligned} \quad [5.62]$$

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

$$\begin{aligned} \lambda_{nl} &= \hbar^2 \int_0^\infty dr r^2 [R_{nl}(r)]^2 \xi(r) \\ &= -\frac{\alpha^2 Z^2}{n} E_n \frac{1}{l \left(l + \frac{1}{2} \right) (l + 1)}, \quad l \neq 0 \end{aligned} \quad [5.63]$$

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

$$\delta E = E_{n'} - E_n + \mu_B \mathfrak{B}_z (m'_l - m_l) + (\lambda_{n'l'} m'_l - \lambda_{nl} m_l) m_s \quad [5.64]$$

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, ± 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

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} + \xi(r)\mathbf{L} \cdot \mathbf{S} \quad [5.65]$$

The unperturbed wave functions are eigenfunctions of \mathbf{L}^2 , \mathbf{S}^2 , \mathbf{J}^2 and \mathcal{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)

$$\mathcal{Y}_{l_s}^{jm_j} = \sum_{m_l, m_s} \langle l m_l m_s | j m_j \rangle Y_{l m_l}(\theta, \phi) \chi_{s, m_s}, \quad [5.66]$$

where $\langle l m_l m_s | j m_j \rangle$ are Clebsch-Gordan coefficients and $s = 1/2$.

Taking the magnetic field \mathcal{B} to be along the Z axis, the perturbation is

$$\begin{aligned} H' &= \frac{\mu_B}{\hbar} (L_z + 2S_z) \mathcal{B}_z \\ &= \frac{\mu_B}{\hbar} (\mathcal{J}_z + S_z) \mathcal{B}_z \end{aligned} \quad [5.67]$$

The additional energy due to the magnetic interaction H' is thus

$$\Delta E = \mu_B \mathcal{B}_z m_j + \frac{\mu_B}{\hbar} \mathcal{B}_z \sum_{\text{spin}} \int d\Omega (\mathcal{Y}_{l, 1/2}^{jm_j})^* S_z \mathcal{Y}_{l, 1/2}^{jm_j} \quad [5.68]$$

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

Either of two methods can be used to evaluate the second term in [5.68].

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

$$\begin{aligned} \mathcal{Y}_{l, 1/2}^{l+1/2, m_j} &= \left(\frac{l + m_j + 1/2}{2l + 1} \right)^{1/2} Y_{l, m_j - 1/2}(\theta, \phi) \chi_{1/2, 1/2} \\ &\quad + \left(\frac{l - m_j + 1/2}{2l + 1} \right)^{1/2} Y_{l, m_j + 1/2}(\theta, \phi) \chi_{1/2, -1/2} \end{aligned} \quad [5.69a]$$

and

$$\begin{aligned} \mathcal{Y}_{l,1/2}^{l-1/2,m_j} = & - \left(\frac{l - m_j + 1/2}{2l + 1} \right)^{1/2} Y_{l,m_j-1/2}(\theta, \phi) \chi_{1/2,1/2} \\ & + \left(\frac{l + m_j + 1/2}{2l + 1} \right)^{1/2} Y_{l,m_j+1/2}(\theta, \phi) \chi_{1/2,-1/2} \end{aligned} \quad [5.69b]$$

from which one readily obtains

$$\sum_{\text{spin}} \int d\Omega (\mathcal{Y}_{l,1/2}^{l+1/2,m_j})^* \mathcal{S}_z \mathcal{Y}_{l,1/2}^{l+1/2,m_j} = \frac{m_j}{2l + 1} \hbar \quad [5.70a]$$

and

$$\sum_{\text{spin}} \int d\Omega (\mathcal{Y}_{l,1/2}^{l-1/2,m_j})^* \mathcal{S}_z \mathcal{Y}_{l,1/2}^{l-1/2,m_j} = -\frac{m_j}{2l + 1} \hbar \quad [5.70b]$$

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. Thus, if $V_u = \mathbf{V} \cdot \hat{\mathbf{u}}$ is the component of \mathbf{V} along the unit vector $\hat{\mathbf{u}}$ which defines the axis Ou , and if the unit vector $\hat{\mathbf{u}}'$ defines the axis Ou' obtained from Ou by performing the rotation \mathcal{R} , the transform of V_u under the rotation \mathcal{R} must be the component $V_{u'} = \mathbf{V} \cdot \hat{\mathbf{u}}'$ of \mathbf{V} along $\hat{\mathbf{u}}'$. It may be shown that the components V_x, V_y, V_z of a vector operator \mathbf{V} satisfy the commutation relations

$$\begin{aligned} [\mathcal{J}_x, V_x] &= 0, & [\mathcal{J}_y, V_x] &= -i\hbar V_z, & [\mathcal{J}_z, V_x] &= i\hbar V_y, \\ [\mathcal{J}_x, V_y] &= i\hbar V_z, & [\mathcal{J}_y, V_y] &= 0, & [\mathcal{J}_z, V_y] &= -i\hbar V_x, \\ [\mathcal{J}_x, V_z] &= -i\hbar V_y, & [\mathcal{J}_y, V_z] &= i\hbar V_x, & [\mathcal{J}_z, V_z] &= 0 \end{aligned} \quad [5.71]$$

The operators \mathbf{L}, \mathbf{S} and \mathbf{J} are examples of vector operators. Using [5.71] and the commutation relations for the components of \mathbf{J} , namely

$$[\mathcal{J}_x, \mathcal{J}_y] = i\hbar \mathcal{J}_z, \quad [\mathcal{J}_y, \mathcal{J}_z] = i\hbar \mathcal{J}_x, \quad [\mathcal{J}_z, \mathcal{J}_x] = i\hbar \mathcal{J}_y \quad [5.72]$$

it may be shown after some manipulation that a vector operator \mathbf{V} satisfies the equations

$$\mathbf{J} \times \mathbf{V} + \mathbf{V} \times \mathbf{J} = 2i\hbar \mathbf{V} \quad [5.73]$$

and

$$[\mathbf{J}^2, [\mathbf{J}^2, \mathbf{V}]] = 2\hbar^2(\mathbf{J}^2 \mathbf{V} + \mathbf{V} \mathbf{J}^2) - 4\hbar^2(\mathbf{V} \cdot \mathbf{J})\mathbf{J} \quad [5.74]$$

The matrix element of the left-hand side of the identity [5.74] with respect to states having the same value of j vanishes, so that

$$\langle l s j m_j | \mathbf{J}^2 \mathbf{V} + \mathbf{V} \mathbf{J}^2 | l s j m_j \rangle = 2 \langle l s j m_j | (\mathbf{V} \cdot \mathbf{J}) \mathbf{J} | l s j m_j \rangle \quad [5.75]$$

from which we have

$$j(j+1)\hbar^2\langle lsm_j|\mathbf{V}|lsm_j\rangle = \langle lsm_j|(\mathbf{V}\cdot\mathbf{J})|lsm_j\rangle \quad [5.76]$$

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

Setting $\mathbf{V} = \mathbf{S}$ in [5.76] and taking the z component, we have

$$\begin{aligned} j(j+1)\hbar^2\langle lsm_j|S_z|lsm_j\rangle &= \langle lsm_j|(\mathbf{S}\cdot\mathbf{J})\mathcal{J}_z|lsm_j\rangle \\ &= m_j\hbar\langle lsm_j|\mathbf{S}\cdot\mathbf{J}|lsm_j\rangle \end{aligned} \quad [5.77]$$

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

$$\langle lsm_j|S_z|lsm_j\rangle = m_j\hbar \left[\frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right] \quad [5.78]$$

which agrees with [5.70] when $s = 1/2$ and $j = l \pm 1/2$. The energy shift due to the magnetic field is seen from [5.68] and [5.70] (or [5.78]) to be proportional to $\mu_B\mathcal{B}_zm_j$ and may be written as

$$\Delta E_{m_j} = g\mu_B\mathcal{B}_zm_j \quad [5.79]$$

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

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad [5.80]$$

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

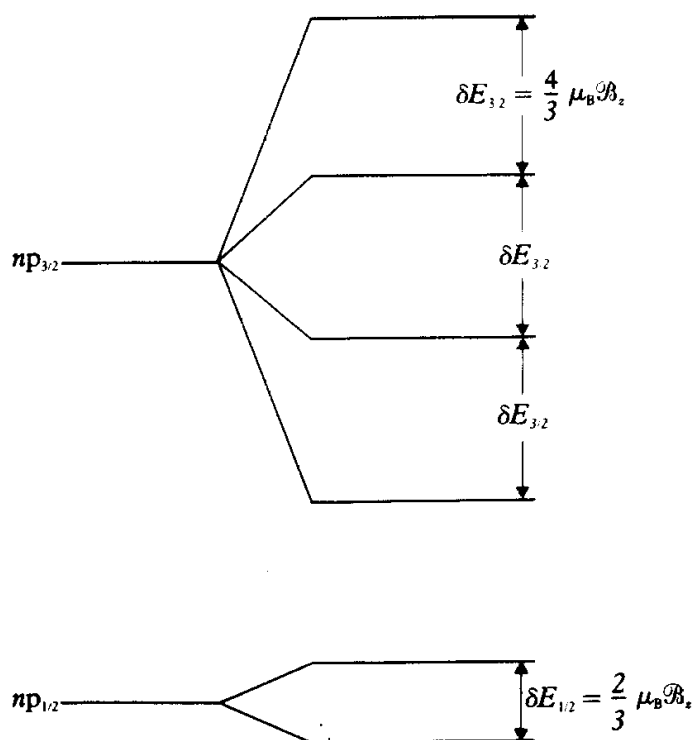
$$\begin{aligned} \Delta E_{m_j} &= \frac{2l+2}{2l+1} \mu_B\mathcal{B}_zm_j, & j &= l + 1/2 \\ &= \frac{2l}{2l+1} \mu_B\mathcal{B}_zm_j, & j &= l - 1/2 \end{aligned} \quad [5.81]$$

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

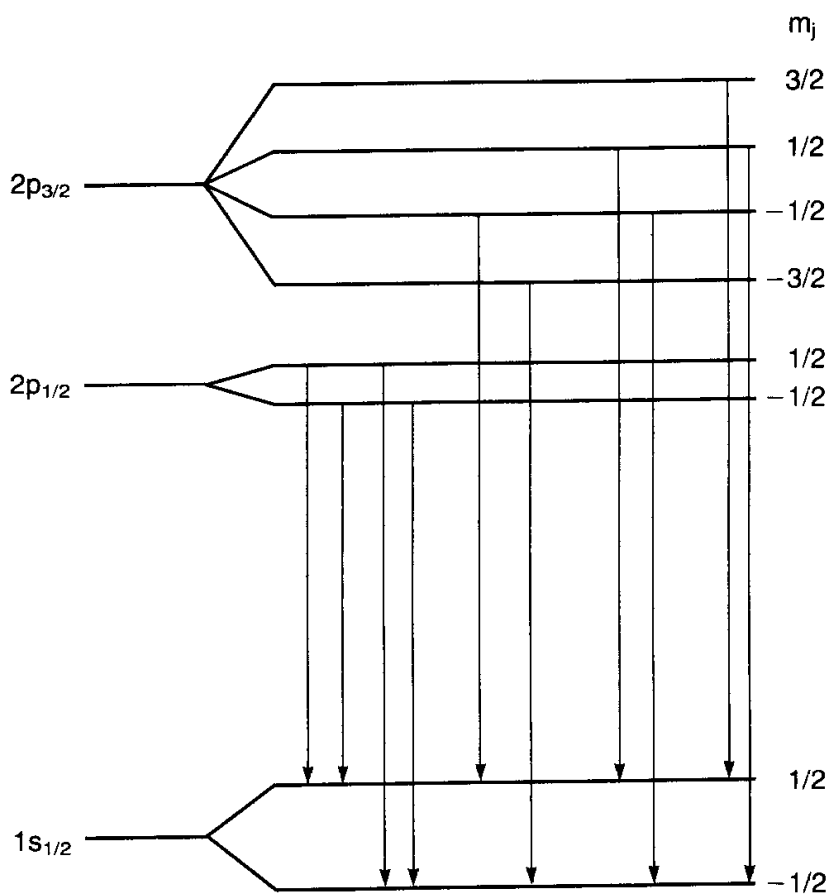
$$E_{n,j,m_j} = E_n + \Delta E_{n,j} + \Delta E_{m_j} \quad [5.82]$$

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 ΔE_{m_j} is the correction due to the (weak) magnetic field.

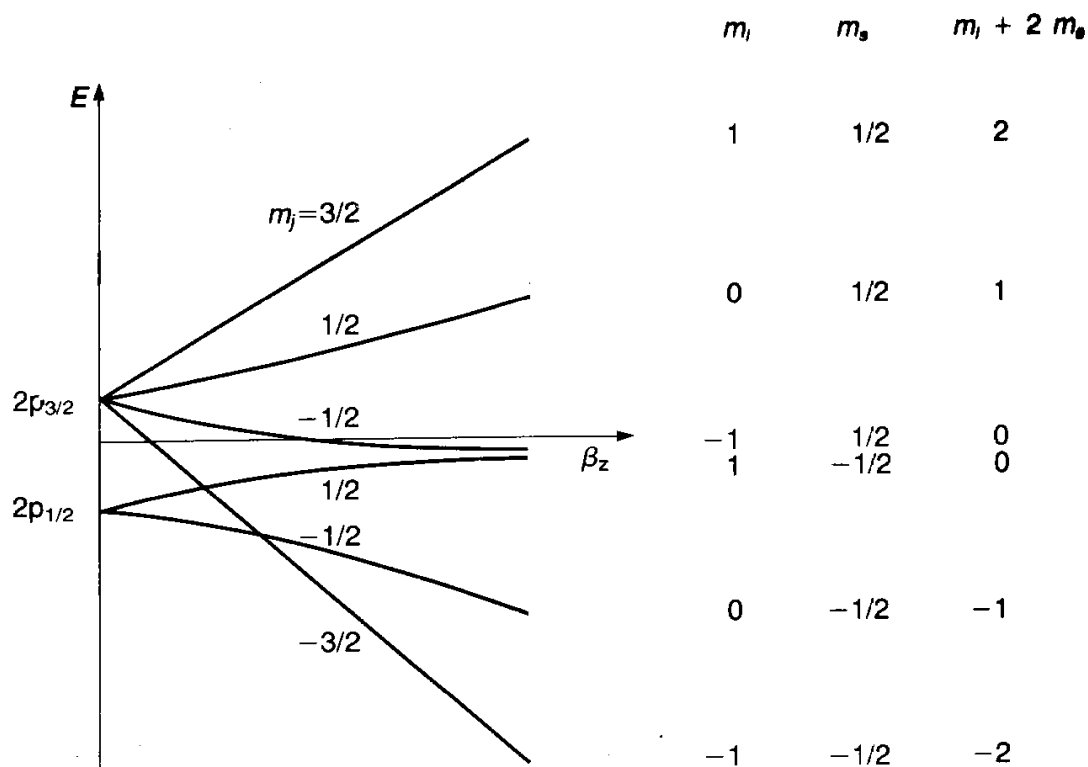
The splitting of levels, δE , corresponding to the ‘anomalous’ Zeeman effect discussed above is illustrated in Fig. 5.10. We remark that since the splitting of the levels is not the same for each multiplet, there will be more lines in this case than the three lines (Lorentz triplet) corresponding to the normal Zeeman effect. This is shown in Fig. 5.11, 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.



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



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



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

As the magnitude of the magnetic field \mathcal{B}_z increases from the weak field to the strong field limit, the energy changes smoothly. This is depicted in Fig. 5.12 for the 2p states of atomic hydrogen.

5.3 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 has become known as the *Stark effect*. We shall assume that the external electric field is constant over a region of atomic dimensions and is 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 [7]. The Hamiltonian H_0 for the unperturbed hydrogenic atom, given by [5.3] (we neglect reduced mass effects) is therefore modified by the addition of the perturbation

$$H' = e \mathcal{E} z \quad [5.83]$$

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

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

Schrödinger hydrogenic wave functions $\psi_{nlm}(\mathbf{r})$ where we have set $m \equiv m_l$ [3] in order to simplify the notation.

Linear Stark effect

Since the ground state (100) is non-degenerate, we see from [2.308] and [5.83] that the first-order correction to its energy is given by

$$\begin{aligned} E_{100}^{(1)} &= e \mathcal{E} \langle \psi_{100} | z | \psi_{100} \rangle \\ &= e \mathcal{E} \int |\psi_{100}(\mathbf{r})|^2 z \, d\mathbf{r} \end{aligned} \quad [5.84]$$

Now our discussion at the end of Section 3.3 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 [5.83] is an *odd* operator under the parity operation since it changes sign when the coordinates are reflected through the origin. Thus we have

$$\langle \psi_{nlm} | z | \psi_{nlm} \rangle = 0 \quad [5.85]$$

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 [5.84] and [5.85] 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 atomic hydrogen 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 the hydrogen atom. 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

$$\psi_{200}, \quad \psi_{210}, \quad \psi_{211}, \quad \psi_{21-1} \quad [5.86]$$

corresponding to the same unperturbed energy $E_{n=2} = -mc^2\alpha^2/8$ (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 [5.83] 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

$$\begin{pmatrix} -E^{(1)} & H'_{12} \\ H'_{21} & -E^{(1)} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad [5.87]$$

with

$$H'_{12} = H'_{21} = e \mathcal{E} \int \psi_{210}(\mathbf{r}) z \psi_{200}(\mathbf{r}) d\mathbf{r} \quad [5.88]$$

The reduction of the original homogeneous system of four equations to the two equations [5.87] 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

$$\begin{aligned} H'_{12} &= e \mathcal{E} \frac{Z^3}{16\pi a_0^3} \int_0^\infty dr r^3 \left(\frac{Zr}{a_0}\right) \left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/a_0} \int_0^\pi d\theta \sin \theta \cos^2 \theta \int_0^{2\pi} d\phi \\ &= e \mathcal{E} \frac{Z^3}{8a_0^3} \frac{2}{3} \int_0^\infty dr r^3 \left(\frac{Zr}{a_0}\right) \left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/a_0} \\ &= -3e \mathcal{E} a_0/Z \end{aligned} \quad [5.89]$$

and $H'_{21} = H'_{12}$ since H'_{12} is real. Thus the two roots of the determinantal equation

$$\begin{vmatrix} -E^{(1)} & H'_{12} \\ H'_{12} & -E^{(1)} \end{vmatrix} = 0 \quad [5.90]$$

are given by

$$E^{(1)} = \pm |H'_{12}| = \pm 3e \mathcal{E} a_0/Z \quad [5.91]$$

Upon returning to [5.87] 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 ψ_1 is given by

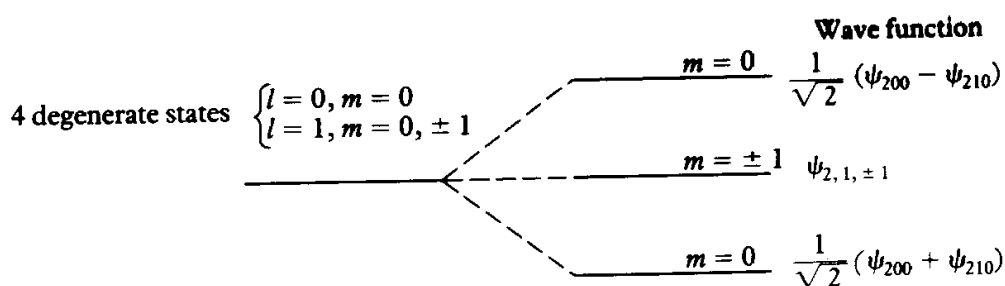
$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_{200} + \psi_{210}) \quad [5.92a]$$

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

$$\psi_2 = \frac{1}{\sqrt{2}} (\psi_{200} - \psi_{210}) \quad [5.92b]$$

It should be emphasised that the states [5.92] are neither eigenstates of the parity operator, nor of 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 $\delta\bar{\nu}$ corresponding to the energy correction $E^{(1)}$ are given by

$$\delta\bar{\nu} = \pm \frac{3ea_0}{hc} \frac{\mathcal{E}}{Z} = \pm 12.8 \left(\frac{\mathcal{E}}{Z}\right) 10^{-7} \text{ cm}^{-1} \quad [5.93]$$



5.13 Splitting of the degenerate $n = 2$ levels of atomic hydrogen due to the linear Stark effect.

so that rather strong fields (of the order of 10^7 V/m in Stark's experiments) are required to demonstrate the effect.

The splitting of the degenerate $n = 2$ levels of atomic hydrogen due to the linear Stark effect is illustrated in Fig. 5.13. The degeneracy is partly removed by the perturbation, the energies of the $2p_{\pm 1}$ (i.e. 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 again 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 field: one state (ψ_1) parallel to the field \mathcal{E} , one state (ψ_2) antiparallel to \mathcal{E} , and two states with no component along the 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 [8] 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

$$\mathbf{D} = \sum_{i=1}^N e_i \mathbf{r}_i \quad [5.94]$$

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 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^-)

[8] 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.

does possess an electric dipole moment. This does not contradict the previous argument since the configuration for which A^+ is at r_2 and B^- at 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 [9].

Another remark concerns our use of degenerate perturbation theory for the treatment of the Stark effect on the $n = 2$ levels. As we know from our discussion in Section 5.1 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 [10] 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 2ε . Instead of solving an equation of the type [5.87] we must now solve the matrix equation

$$\begin{pmatrix} E^{(0)} - \varepsilon - E & H'_{12} \\ H'_{21} & E^{(0)} + \varepsilon - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad [5.95]$$

where $H'_{12} = H'_{21}$ is given by [5.88]. Thus we have

$$E = E^{(0)} \pm [(H'_{12})^2 + \varepsilon^2]^{1/2} \quad [5.96]$$

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 5.4) that this level is split into *five* equally spaced levels, as shown in Fig. 5.14.

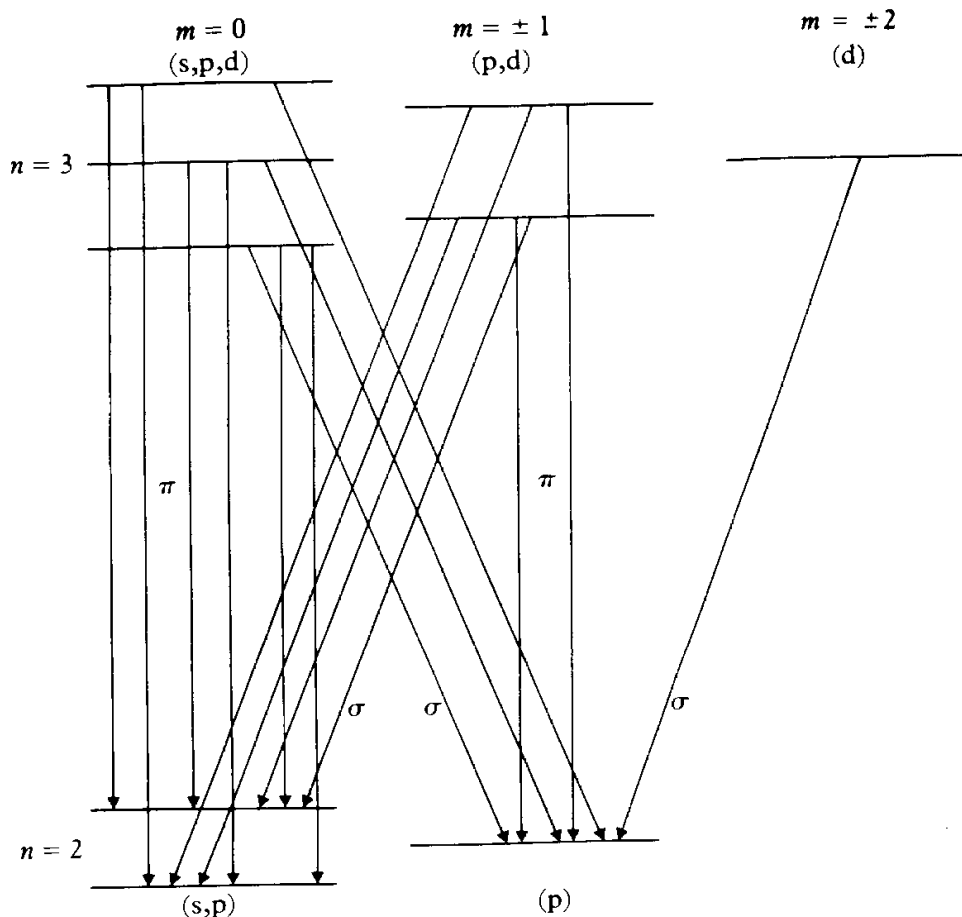
Also displayed in Fig. 5.14 are the radiative transitions between the levels $n = 2$ and $n = 3$ (corresponding to the spectral line H_α) of atomic hydrogen in the presence of an electric field. The selection rules with respect to the magnetic quantum number m are the same as those we obtained in Chapter 4 without an external field. That is

$$\Delta m = 0, \pm 1 \quad [5.97]$$

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

[9] 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 any experiment an average is taken over the ground and neighbouring states, of different parities, resulting in an effective permanent electric dipole moment.

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



5.14 Splitting of the $n = 3$ and $n = 2$ levels of hydrogen due to the linear Stark effect. The various possible transitions are shown, those with $\Delta m = 0$ correspond to π lines and those with $\Delta m = \pm 1$ to σ lines.

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 [5.83] 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 [11], so that the lifetime of the $2s$ state is considerably shortened by comparison with its value ($1/7$ s) in the absence of electric field.

In order to examine in more detail this process, which is called ‘quenching of the metastable $2s$ state’, 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 \mathcal{E} directed along the Z axis, and use the results [5.91] and [5.92] to write the time-dependent wave function of the atom at $t > 0$ as

$$\Psi(\mathbf{r}, t) = c_1\psi_1(\mathbf{r})e^{-(i/\hbar)(E_{n=2}-\Delta E)t} + c_2\psi_2(\mathbf{r})e^{-(i/\hbar)(E_{n=2}+\Delta E)t} \quad [5.98]$$

[11] 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.

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

$$\Psi(\mathbf{r}, t = 0) = \psi_{200}(\mathbf{r}) \quad [5.99]$$

Using [5.92] and [5.99], we find that $c_1 = c_2 = 2^{-1/2}$, so that

$$\begin{aligned} \Psi(\mathbf{r}, t) &= \frac{1}{\sqrt{2}} \psi_1(\mathbf{r}) e^{-(i/\hbar)(E_{n-2}-\Delta E)t} + \frac{1}{\sqrt{2}} \psi_2(\mathbf{r}) e^{-(i/\hbar)(E_{n-2}+\Delta E)t} \\ &= \left[\psi_{200}(\mathbf{r}) \cos\left(\frac{\Delta E}{\hbar} t\right) + i\psi_{210}(\mathbf{r}) \sin\left(\frac{\Delta E}{\hbar} t\right) \right] e^{-(i/\hbar)E_{n-2}t} \quad [5.100] \end{aligned}$$

Thus the atom oscillates between the 200 (2s) and 210 (2p₀) states, with a period

$$T = \frac{\pi\hbar}{\Delta E} \quad [5.101]$$

For example, in the case of an electric field of strength $\mathcal{E} = 10^7$ V/m, we find from [5.101] that $T \approx 1.3 \times 10^{-12}$ s which is much shorter than the time $\tau \approx 1.6 \times 10^{-9}$ s corresponding to the radiative transition 2p–1s (i.e. the lifetime of the 2p state in the absence of external field). As a result, the average population of both states 2s and 2p₀ 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 2p₀ states (Problem 5.5). 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 $n's - ns$ radiative transitions.

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 [5.83] 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

$$E_{100}^{(2)} = e^2 \mathcal{E}^2 \sum_{\substack{n \neq 1 \\ l, m}} \frac{|\langle \psi_{nlm} | z | \psi_{100} \rangle|^2}{E_1 - E_n} \quad [5.102]$$

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 [5.102] 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 [5.102] the energy

differences $E_1 - E_n$ by $E_1 - E_2$. That is,

$$E_{100}^{(2)} = -e^2 \mathcal{E}^2 \sum_{\substack{n \neq 1 \\ l, m}} \frac{|\langle \psi_{nlm} | z | \psi_{100} \rangle|^2}{E_n - E_1} > -e^2 \mathcal{E}^2 \frac{1}{E_2 - E_1} \sum_{\substack{n \neq 1 \\ l, m}} |\langle \psi_{nlm} | z | \psi_{100} \rangle|^2 \quad [5.103]$$

The summation on the right of [5.103] may now be performed as follows. We first note that because $\langle \psi_{100} | z | \psi_{100} \rangle = 0$ we may write

$$\sum_{\substack{n \neq 1 \\ l, m}} |\langle \psi_{nlm} | z | \psi_{100} \rangle|^2 = \sum_{n, l, m} |\langle \psi_{nlm} | z | \psi_{100} \rangle|^2 = \sum_{n, l, m} \langle \psi_{100} | z | \psi_{nlm} \rangle \langle \psi_{nlm} | z | \psi_{100} \rangle \quad [5.104]$$

Using the completeness of the hydrogenic states, namely

$$\sum_{nlm} |\psi_{nlm}\rangle \langle \psi_{nlm}| = 1 \quad [5.105]$$

we have

$$\sum_{n, l, m} \langle \psi_{100} | z | \psi_{nlm} \rangle \langle \psi_{nlm} | z | \psi_{100} \rangle = \langle \psi_{100} | z^2 | \psi_{100} \rangle = \langle z^2 \rangle_{100} \quad [5.106]$$

But

$$\langle z^2 \rangle_{100} = \langle x^2 \rangle_{100} = \langle y^2 \rangle_{100} = \frac{1}{3} \langle r^2 \rangle_{100} = \frac{a_0^2}{Z^2} \quad [5.107]$$

so that from [5.103]–[5.107] and [3.29] we have

$$E_{100}^{(2)} > -\frac{8}{3} (4\pi\epsilon_0) \frac{a_0^3}{Z^4} \mathcal{E}^2 \quad [5.108]$$

It is possible to obtain in a straightforward way another estimate for $E_{100}^{(2)}$ (Problem 5.6):

$$E_{100}^{(2)} \approx -2(4\pi\epsilon_0) \frac{a_0^3}{Z^4} \mathcal{E}^2 \quad [5.109]$$

The exact evaluation of the expression [5.102] is more tedious and we shall not discuss it in detail here. One finds (Bethe and Salpeter, 1957) that

$$E_{100}^{(2)} = -2.25(4\pi\epsilon_0) \frac{a_0^3}{Z^4} \mathcal{E}^2 = -3.71 \times 10^{-41} \left(\frac{\mathcal{E}^2}{Z^4} \right) \text{joule} \quad [5.110]$$

It is worth noting that about one-third of the result [5.110] arises from the contribution of the continuum in the summation [5.102]. We also remark that the quadratic Stark effect given by [5.110] is generally very small, being approximately 0.02 cm^{-1} for atomic hydrogen in the case of a field strength $\mathcal{E} = 10^8 \text{ volt/metre}$.

Upon differentiation of the expression [5.102] with respect to the electric field strength, we obtain for the magnitude of the dipole moment the result

$$D = -\frac{\partial E_{100}^{(2)}}{\partial \mathcal{E}} = \bar{\alpha} \mathcal{E} \quad [5.111]$$

where

$$\bar{\alpha} \doteq 2e^2 \sum_{\substack{n \neq 1 \\ l, m}} \frac{|\langle \psi_{nlm} | z | \psi_{100} \rangle|^2}{E_n - E_1} \quad [5.112]$$

is called the *dipole polarisability* of the atom in the state (100). We see from [5.111] that D is proportional to \mathcal{E} , so that we have an *induced dipole moment*. We also note from [5.102] and [5.112] that

$$E_{100}^{(2)} = -\frac{1}{2} \bar{\alpha} \mathcal{E}^2 \quad [5.113]$$

and the result [5.110] shows that

$$\begin{aligned} \bar{\alpha} &= 4.50(4\pi\epsilon_0) \frac{a_0^3}{Z^4} \\ &= 7.42 \times 10^{-41} Z^{-4} \text{ F m}^2 \end{aligned} \quad [5.114]$$

The foregoing discussion of the quadratic Stark effect has been limited to the ground state of hydrogenic atoms, for which it is the first non-vanishing term of the perturbation series. Similar calculations may be carried out for excited states, where the quadratic Stark effect is a correction to the linear Stark effect studied above. This correction is in general quite small. For example, in the case of the H_α line, where the separation of the outermost components is about 200 cm^{-1} for a field strength of $4 \times 10^7 \text{ volt/metre}$, the corresponding (red) shift due to the quadratic Stark effect is only 1 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.

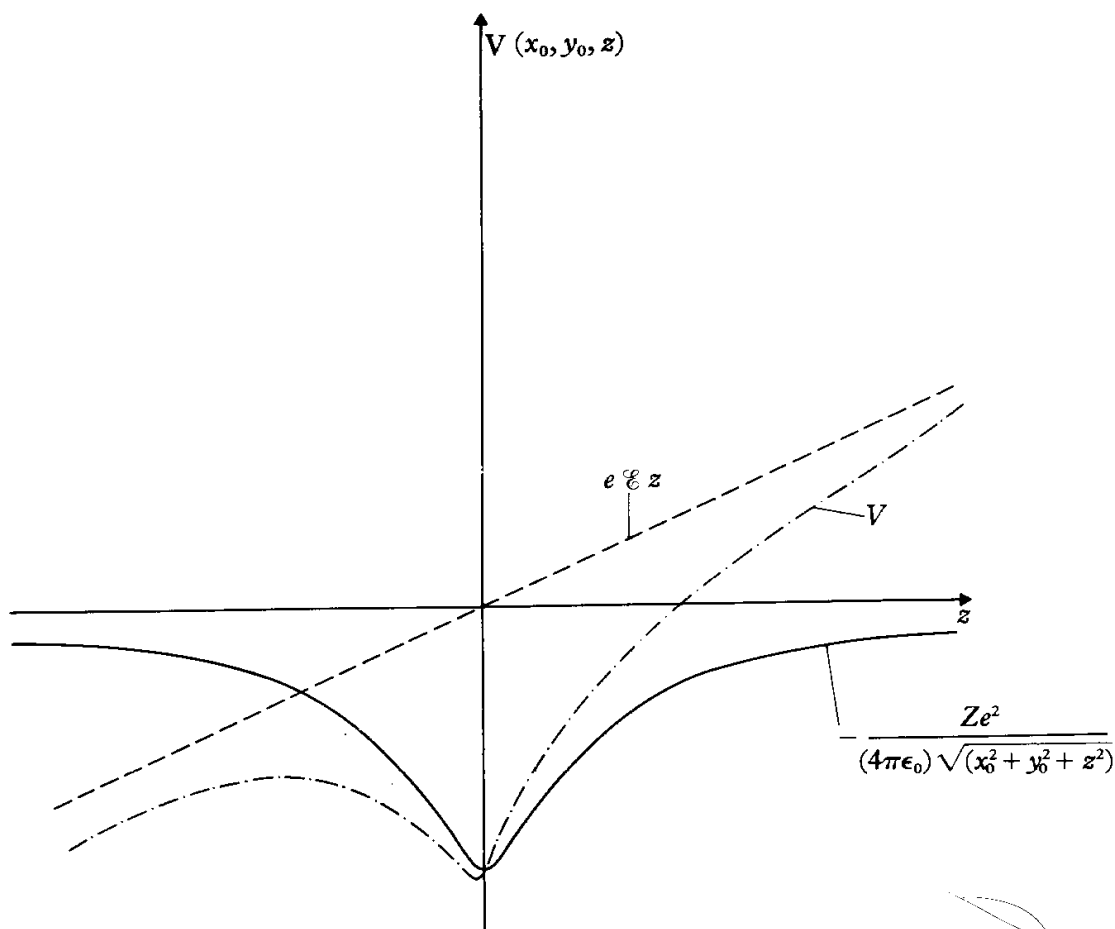
To see how this comes about, we first note that the total potential energy V of the electron is obtained by adding the potential energy $e \mathcal{E} z$ arising from the external field (see [5.83]) to the Coulomb potential $-Ze^2/(4\pi\epsilon_0)r$ of the nucleus,

Thus

$$V = -\frac{Ze^2}{(4\pi\epsilon_0)r} + e\mathcal{E}z \quad [5.115]$$

A schematic drawing of V is shown in Fig. 5.15 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 toward 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 such that the radius of the electron orbit is large. 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



5.15 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.

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 longer a stationary state, but becomes a metastable state when an external electric field is applied, and the perturbation series is found to diverge. 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.

5.4 THE LAMB SHIFT

We have seen in Section 5.1 that, according to the Dirac theory, energy levels of one-electron atoms with the same value of the quantum number j but different values of l should coincide. We also pointed out at the end of that section that in trying to resolve the fine structure of hydrogenic atoms by optical measurements, several investigators had reported small discrepancies between the observed spectra and the Dirac theory. In particular, W. V. Houston in 1937 and R. C. Williams in 1938 carried out experiments which were interpreted by S. Pasternack (1938) as showing that the $2s_{1/2}$ and $2p_{1/2}$ levels did not coincide, but that there existed a slight upward shift of the $2s_{1/2}$ level of about 0.03 cm^{-1} . However, the experimental attempts to obtain accurate information about the fine structure of atomic hydrogen (and in particular about the lines of the Balmer series) were frustrated by the broadening of the spectral lines due mainly to the Doppler effect. In fact other spectroscopists disagreed with the results of Houston and Williams, and found no discrepancy with the Dirac theory.

The question was settled in 1947 by W. E. Lamb and R. C. Retherford who performed a brilliant experiment which we shall now briefly describe. Instead of attempting to resolve the fine structure of hydrogen by investigating its optical spectrum, Lamb and Retherford used *microwave techniques* [12] to stimulate a direct *radio-frequency* transition between the $2s_{1/2}$ and $2p_{1/2}$ levels. As we noted in Section 4.5 there is no selection rule on the principal quantum number n for electric dipole transitions. In particular, these transitions can occur between levels having the *same* principal quantum number. This fact was pointed out as early as 1928 by Grotrian, who suggested that it should be possible with radio waves to induce such transitions among the excited states of the hydrogen atom. For example, in the case of the transition $2s_{1/2} - 2p_{3/2}$, the energy separation $\delta E = 4.52 \times 10^{-5} \text{ eV} = 0.365 \text{ cm}^{-1}$ which we obtained in [5.32] corresponds to a wavelength of 2.74 cm or a frequency of 10949 MHz. Because the frequencies of radio waves are much smaller than those corresponding to optical lines (such as the H_α line), the Doppler broadening, which is proportional to the frequency (see [4.145]) is considerably reduced in radio-frequency experiments, and could in fact be neglected in the experiment of Lamb and Retherford. Of course, since the frequencies of radio waves are small, the transition rates for spontaneous emission, which are proportional to ν^3 (see [4.71]) are very small.

[12] A detailed account of microwave spectroscopy may be found in Townes and Schawlow (1955).