Chapter 5

Fine structure

In the previous four sets of notes we have been studying the **gross structure** of atoms. When we consider the gross structure, we include only the largest interaction terms in the Hamiltonian, namely, the electron kinetic energy, the electron-nuclear attraction, and the electron-electron repulsion.

It is now time to start considering the smaller interactions in the atom that arise from magnetic effects. In these notes we shall consider only those effects caused by *internal* magnetic fields, leaving the discussion of the effects produced by *external* fields to the next set. The internal fields within atoms cause **fine structure** in atomic spectra. We shall start by considering the fine structure of hydrogen and then move on to many-electron atoms. At the end of these notes we shall also look briefly at **hyperfine structure**, which is a similar, but smaller, effect due to the magnetic interactions between the electrons and the nucleus.

5.1 Orbital magnetic dipoles

The quantum numbers n and l were first introduced in the old quantum theory of Bohr and Sommerfeld. The **principal quantum number** n was introduced in the Bohr model as a fundamental postulate concerning the quantization of the angular momentum (see eqn 1.5), while the **orbital quantum number** l was introduced a few years later by Sommerfeld as a patch-up to account for the possibility that the atomic orbits might be elliptical rather than circular. In Lecture Notes 2, we saw how these two quantum numbers naturally re-appear in the full quantum mechanical treatment of the hydrogen atom. Then, in Section 4.1, we saw how they carry across to many-electron atoms.

Two key results that drop out of the quantum mechanical treatment of atoms are:

- The magnitude L of the orbital angular momentum of an electron is given by (see eqns 2.30 and 4.9):

$$L = \sqrt{l(l+1)}\hbar\,, \tag{5.1}$$

  where l can take integer values up to $(n-1)$.

- The component of the angular momentum along a particular axis (usually taken as the z axis) is quantized in units of $\hbar$ and its value is given by (see eqn 2.31):

$$L_z = m_l\hbar\,, \tag{5.2}$$

  where the magnetic quantum number m_l can take integer values from $-l$ to $+l$.

These two relationships give rise to the vector model of angular momentum illustrated in Fig. 2.1.

The orbital motion of the electron causes it to have a magnetic moment. Let us first consider an electron in a circular Bohr orbit, as illustrated in Fig. 5.1(a). The electron orbit is equivalent to a current loop, and we know from electromagnetism that current loops behave like magnets. The electron in the Bohr orbit is equivalent to a little magnet with a magnetic dipole moment μ given by:

$$\mu = i \times \text{Area} = -(e/T) \times (\pi r^2)\,, \tag{5.3}$$

where T is the period of the orbit. Now $T = 2\pi r/v$, and so we obtain

$$\mu = -\frac{ev}{2\pi r}\pi r^2 = -\frac{e}{2m_\mathrm{e}}m_\mathrm{e}vr = -\frac{e}{2m_\mathrm{e}}L, \tag{5.4}$$

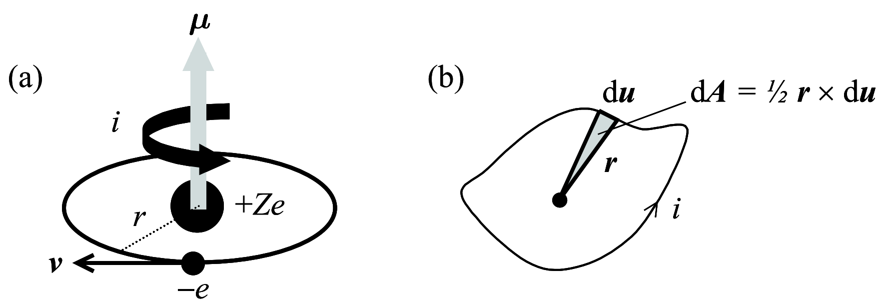

Figure 5.1: (a) The orbital motion of the electron around the nucleus in a circular Bohr orbit is equivalent to a current loop, which generates a magnetic dipole moment. (b) Magnetic dipole moment of an electron in a non-circular orbit.

where we have substituted L for the orbital angular momentum $m_{\mathrm{e}}vr$.

This relationship can easily be generalized to the case of electrons in non-circular orbits. Consider an electron at position vector $\boldsymbol{r}$ in a non-circular orbit with an origin O. The magnetic dipole moment is given by:

$$\boldsymbol{\mu} = \oint i\,\mathrm{d}\boldsymbol{A}\,, \tag{5.5}$$

where i is the current in the loop and $\mathrm{d}\boldsymbol{A}$ is the incremental area swept out by the electron as it performs its orbit. The incremental area $\mathrm{d}\boldsymbol{A}$ is related to the path element $\mathrm{d}\boldsymbol{u}$ by:

$$\mathrm{d}\boldsymbol{A} = \frac{1}{2}\boldsymbol{r}\times\mathrm{d}\boldsymbol{u}\,, \tag{5.6}$$

and so eqn 5.5 becomes:

$$\boldsymbol{\mu} = \frac{1}{2}\oint i\,\boldsymbol{r}\times\mathrm{d}\boldsymbol{u}\,. \tag{5.7}$$

We can write the current as $i = \mathrm{d}q/\mathrm{d}t$, where q is the charge, which implies:

$$\begin{aligned}\boldsymbol{\mu} &= \frac{1}{2}\oint \frac{\mathrm{d}q}{\mathrm{d}t}\boldsymbol{r}\times\mathrm{d}\boldsymbol{u}\,,\\ &= \frac{1}{2}\oint \mathrm{d}q\,\boldsymbol{r}\times\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}t}\,,\\ &= \frac{1}{2}\oint \mathrm{d}q\,\boldsymbol{r}\times\boldsymbol{v}\,,\\ &= \frac{1}{2m_{\mathrm{e}}}\oint \mathrm{d}q\,\boldsymbol{r}\times\boldsymbol{p}\,,\end{aligned} \tag{5.8}$$

where $\boldsymbol{v}$ is the velocity, and $\boldsymbol{p}$ is the momentum. The angular momentum is defined as usual by

$$\boldsymbol{L} = \boldsymbol{r}\times\boldsymbol{p} \tag{5.9}$$

and so we finally obtain:

$$\boldsymbol{\mu} = \frac{1}{2m_{\mathrm{e}}}\oint \boldsymbol{L}\mathrm{d}q = \frac{1}{2m_{\mathrm{e}}}\boldsymbol{L}\oint \mathrm{d}q = \frac{1}{2m_{\mathrm{e}}}\boldsymbol{L}(-e)\,, \tag{5.10}$$

as in eqn 5.4. Note that the result works because the angular momentum $\boldsymbol{L}$ is a constant of the motion, and so it can be taken out of the integral. From a classical perspective, $\boldsymbol{L}$ is constant because the force $\boldsymbol{F}$ is radial. We therefore have that:

$$\frac{\mathrm{d}\boldsymbol{L}}{\mathrm{d}t} = \boldsymbol{\Gamma} = \boldsymbol{r}\times\boldsymbol{F} = 0\,, \tag{5.11}$$

where $\boldsymbol{\Gamma}$ is the torque. This is why the angular momentum ends up being quantized with well-defined constant values when we consider the quantum mechanics of the atom.[1]

[1] Note that the requirement for the angular momentum to be constant is that the force should be radial. In many-electron atoms, this approximation is only valid in the central field limit. (See Section 4.1.) The inclusion of non-central forces via the residual electrostatic interaction would mean that the angular momentum states are not pure, but are slightly mixed with each other. This can explain why transitions that are apparently forbidden by selection rules can sometimes be observed, albeit with low transition probabilities. We shall not go further into this point in this course.

Equation 5.4 shows us that the orbital angular momentum is directly related to the atomic dipole moment. The quantity $e/2m_\mathrm{e}$ that appears is called the **gyromagnetic ratio**. It specifies the proportionality constant between the angular momentum of an electron and its magnetic moment. It is apparent from eqn 5.1 that $|L| \sim \hbar$, and hence that the magnitude of atomic magnetic dipoles is given by:

$$|\mu| \sim \frac{e}{2m_\mathrm{e}}\hbar = \mu_\mathrm{B}\,, \tag{5.12}$$

where μ_B is the **Bohr magneton** defined by:

$$\mu_\mathrm{B} = \frac{e\hbar}{2m_\mathrm{e}} = 9.27 \times 10^{-24}\,\mathrm{JT}^{-1}. \tag{5.13}$$

5.2 Spin magnetism

In the Stern-Gerlach experiment, a beam of atoms is deflected by a non-uniform magnetic field. (See Fig. 1.4). The force on a magnetic dipole in a non-uniform magnetic field is given by:[2]

$$F_z = \mu_z \frac{\mathrm{d}B}{\mathrm{d}z}\,, \tag{5.14}$$

where $\mathrm{d}B/\mathrm{d}z$ is the field gradient, which is assumed to point along the z direction. The original Stern-Gerlach experiments was performed on silver atoms, which have a ground-state electronic configuration of[Kr] $4\mathrm{d}^{10}$ $5\mathrm{s}^1$. Filled shells have no net angular momentum, because there are as many positive m_l states occupied as negative ones. Furthermore, electrons in s-shells have $l = 0$ and therefore $\boldsymbol{L} = 0$. The total orbital angular momentum (and hence orbital magnetic dipole moment) of the atom is therefore zero, and we would therefore expect no deflection. However, the experiment showed that the atoms were deflected either up or down, as indicated in Fig.1.4.

In order to explain the up/down deflection of the atoms with $\boldsymbol{L} = 0$, we have to assume that each electron possesses an additional type of magnetic dipole moment. This magnetic dipole is attributed to an additional type of angular momentum called **spin**. In analogy with orbital angular momentum, spin angular momentum is described by two quantum numbers s and m_s, where m_s runs in integer steps from $-s$ to $+s$. The magnitude of the spin angular momentum is given by

$$|\boldsymbol{s}| = \sqrt{s(s+1)}\hbar\,, \tag{5.15}$$

and the component along the z axis is given by

$$s_z = m_s\hbar\,. \tag{5.16}$$

The up-down deflection of single-electron atoms with $\boldsymbol{L} = 0$ is consistent with the following values for s and m_s:

$$\begin{aligned} s &= \tfrac{1}{2}\,, \\ m_s &= \pm\tfrac{1}{2}\,. \end{aligned}$$

The deflections measured in the Stern-Gerlach experiment enabled the magnitude of the magnetic moment due to the spin angular momentum to be determined. The component along the z axis was found to obey:

$$\mu_z = -g_\mathrm{s}\mu_\mathrm{B} m_s\,, \tag{5.17}$$

where g_s is the **g-value** of the electron. The experimental value of g_s was found to be close to 2. The Dirac equation predicts that g_s should be exactly equal to 2, and more recent calculations based on quantum electrodynamics (QED) give a value of 2.0023192, which agrees very accurately with the most precise experimental data.

In the next section we shall start to discuss the interactions between the orbital motion and the spin of the electrons. We shall see that this causes fine structure in atomic spectra, which can only be explained by postulating that electrons possess spin. Before doing so, it is useful to list a few other pieces of experimental evidence that indicate that electrons possess spin.

[2]Note that we need a *non-uniform* magnetic field to deflect a magnetic dipole. A *uniform* magnetic field merely exerts a torque, not a force. We can understand this by analogy with electrostatics. Electric monopoles (i.e. free charges) can be moved by applying electric fields, but an electric dipole experiences no net force in a uniform electric field because the forces on the positive and negative charges cancel. If we wish to apply a force to an electric dipole, we therefore need to apply a non-uniform electric field, so that the forces on the two charges are different. Magnetic monopoles do not exist (as far as we know), and so all atomic magnets are dipoles. Hence we must apply a non-uniform magnetic field to exert a magnetic force on an atom.

- The periodic table of elements, which is the foundation of the whole subject of chemistry, cannot be explained unless we assume that the electrons possess spin.
- If we ignore spin, we expect to observe the normal Zeeman effect when an atom is placed in an external magnetic field. However, most atoms display the *anomalous* Zeeman effect, which is a consequence of spin. See Lecture Notes 6.
- We can measure the gyromagnetic ratio directly by a number of methods. In 1915, Einstein and de Haas measured the gyromagnetic ratio of iron and came up with a value twice as large as expected. They rejected this result, assigning it to experimental errors. However, we now know that the magnetism in iron is caused by the spin rather the orbital angular momentum, and so the experimental value of twice $e/2m_{\mathrm{e}}$ was correct due to the electron g-factor. This is a salutary lesson from the history that even great physicists like Einstein and de Haas can get their error analysis wrong!

5.3 Spin-orbit coupling

We have seen in the previous two sections that electrons in atoms possess both orbital and spin angular momentum. Both types of angular momentum produce magnetic dipoles, and this leads to a new magnetic interaction term in the Hamiltonian of the atom. This magnetic interaction between the orbital and spin angular momentum is called **spin-orbit coupling**.

Sophisticated theories of spin-orbit coupling (e.g. those based on the Dirac equation) indicate that it is actually a relativistic effect. At this stage it is more useful to consider the spin-orbit coupling in a more intuitive way as the interaction between the magnetic field due to the orbital motion of the electron and the magnetic moment due to its spin. This is the approach that we shall adopt here. We shall start by giving a simple order of magnitude estimate based on the semi-classical Bohr model, and then take a more general approach that works for the fully quantum mechanical picture.

5.3.1 Spin-orbit coupling in the Bohr model

The easiest way to understand the spin-orbit coupling is to consider the single electron of a hydrogen atom in a Bohr-like circular orbit around the nucleus, and then shift the origin to the electron, as indicated in Fig. 5.2. In this frame, the electron is stationary and the nucleus is moving in a circular orbit of radius r_n. The orbit of the nucleus is equivalent to a current loop, which produces a magnetic field at the origin. Now the magnetic field produced by a circular loop of radius r carrying a current i is given by:

$$B_z = \frac{\mu_0 i}{2r}\,, \tag{5.18}$$

where z is taken to be the direction perpendicular to the loop. As in Section 5.1, the current i is given by the charge Ze divided by the orbital period $T = 2\pi r/v$. On substituting for the velocity and radius in the Bohr model from eqns 1.15 and 1.16, we find:

$$B_z = \frac{\mu_0 Zev_n}{4\pi r_n^2} = \left(\frac{Z^4}{n^5}\right)\frac{\mu_0 \alpha ce}{4\pi a_0^2}\,, \tag{5.19}$$

where $\alpha = 1/137$ is the **fine structure constant** defined in eqn 1.18. For hydrogen with $Z = n = 1$, this gives $B_z \approx 12\,\text{Tesla}$, which is a large field.

The electron at the origin experiences this orbital field and we thus have a magnetic interaction energy of the form:

$$\Delta E_{\mathrm{so}} = -\boldsymbol{\mu}_{\mathrm{s}} \cdot \boldsymbol{B}_{\mathrm{orbital}}\,, \tag{5.20}$$

which, from eqn 5.17, becomes:

$$\Delta E_{\mathrm{so}} = g_{\mathrm{s}}\mu_{\mathrm{B}} m_s B_z = \pm\mu_{\mathrm{B}} B_z\,, \tag{5.21}$$

where we have used $g_{\mathrm{s}} = 2$ in the last equality. By substituting from eqn. 5.19 and making use of eqn 5.13, we find:

$$|\Delta E_{\mathrm{so}}| = \left(\frac{Z^4}{n^5}\right)\frac{\mu_0 \alpha c e^2 \hbar}{8\pi m_{\mathrm{e}} a_0^2} \equiv \alpha^2 \frac{Z^2}{n^3}|E_n|\,, \tag{5.22}$$

where E_n is the quantized energy given by eqn 1.10. For the $n = 1$ orbit of hydrogen, this gives:

$$|\Delta E_{\mathrm{so}}| = \alpha^2 R_H = 13.6\,\text{eV}/137^2 = 0.7\,\text{meV} \equiv 6\,\text{cm}^{-1}\,.$$

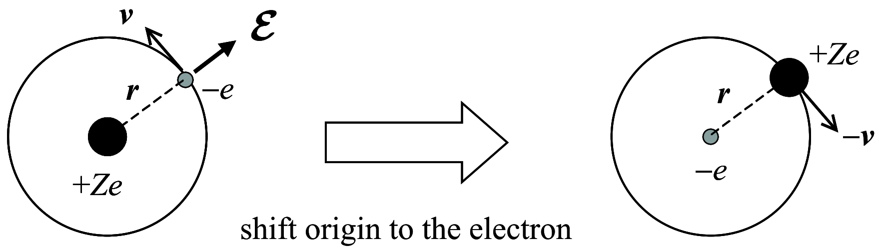

Figure 5.2: An electron moving with velocity $\boldsymbol{v}$ through the electric field $\boldsymbol{\mathcal{E}}$ of the nucleus experiences a magnetic field equal to $(\boldsymbol{\mathcal{E}}\times\boldsymbol{v})/c^2$. The magnetic field can be understood by shifting the origin to the electron and calculating the magnetic field due to the orbital motion of the nucleus around the electron. The velocity of the nucleus in this frame is equal to $-\boldsymbol{v}$.

This shows that the spin-orbit interaction is about 10^4 times smaller than the gross structure energy in hydrogen. Note that the relative size of the spin-orbit interaction grows as Z^2, so that spin-orbit effects are expected to become more important in heavier atoms, which is indeed the case. Note also that eqn 5.22 can be re-written using eqn 1.16 as

$$|\Delta E_{\text{so}}| = \left(\frac{v_n}{c}\right)^2 \frac{|E_n|}{n}\,, \tag{5.23}$$

which shows that the spin-orbit interaction energy is of the same magnitude as the relativistic corrections that would be expected for the Bohr model. This is hardly surprising, given that Dirac tells us that we should really think of spin-orbit coupling as a relativistic effect.

5.3.2 Spin-orbit coupling beyond the Bohr model

In this sub-section repeat the calculation of the spin-orbit interaction energy but without making use of the semi-classical results from the Bohr model. The electrons in an atom experience a magnetic field as they move through the electric field of the nucleus. If the electron velocity is $\boldsymbol{v}$, it will see the nucleus orbiting around it with a velocity of $-\boldsymbol{v}$, as shown in Fig. 5.2. The magnetic field generated at the electron can be calculated by the Biot-Savart law as shown by Fig. 5.3. This gives the magnetic field at the origin of a loop carrying a current i as:

$$\boldsymbol{B} = \frac{\mu_0}{4\pi}\oint_{\text{loop}} i\,\frac{\mathrm{d}\boldsymbol{u}\times\boldsymbol{r}}{r^3}\,, \tag{5.24}$$

where $\mathrm{d}\boldsymbol{u}$ is an orbital path element. For simplicity we consider the case of a circular orbit with constant r. In this case we have:

$$\oint i\,\mathrm{d}\boldsymbol{u} = \oint \frac{\mathrm{d}q}{\mathrm{d}t}\,\mathrm{d}\boldsymbol{u} = Ze\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}t} = Ze(-\boldsymbol{v})\,.$$

We thus obtain:

$$\boldsymbol{B} = -\frac{\mu_0}{4\pi}\frac{Ze}{r^3}\boldsymbol{v}\times\boldsymbol{r} = \frac{\mu_0}{4\pi}\frac{Ze}{r^3}\boldsymbol{r}\times\boldsymbol{v}\,. \tag{5.25}$$

For a Coulomb field the electric field $\boldsymbol{\mathcal{E}}$ is given by:

$$\boldsymbol{\mathcal{E}} = \frac{Ze}{4\pi\epsilon_0 r^2}\hat{\boldsymbol{r}} = \frac{Ze}{4\pi\epsilon_0 r^3}\boldsymbol{r}\,, \tag{5.26}$$

where the hat symbol on $\hat{\boldsymbol{r}}$ in the first equality indicates that it is a unit vector. On combining equations 5.25 and 5.26 we obtain:

$$\boldsymbol{B} = \mu_0\epsilon_0\,\boldsymbol{\mathcal{E}}\times\boldsymbol{v}\,. \tag{5.27}$$

We know from Maxwell's equations that $\mu_0\epsilon_0 = 1/c^2$, and so we can re-write this as:

$$\boldsymbol{B} = \frac{1}{c^2}\,\boldsymbol{\mathcal{E}}\times\boldsymbol{v}\,. \tag{5.28}$$

The same formula can also be derived for the more general case of non-circular orbits and non-Coulombic electric fields such as those found in multi-electron atoms.

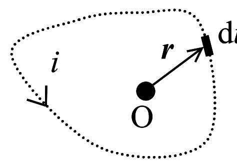

Figure 5.3: The magnetic field at the origin O due to a loop carrying a current i is calculated by the Biot-Savart law given in Eq. 5.24. The field points out of the paper.

The spin-orbit interaction energy is given by:

$$\Delta E_{\rm so} = -\boldsymbol{\mu}_{\rm s}\cdot\boldsymbol{B}_{\rm orbital}\,, \tag{5.29}$$

where $\boldsymbol{\mu}_{\rm s}$ is the magnetic moment due to spin, which is given by:

$$\boldsymbol{\mu}_{\rm s} = -g_{\rm s}\frac{|e|}{2m_{\rm e}}\boldsymbol{s} = -g_{\rm s}\frac{\mu_{\rm B}}{\hbar}\boldsymbol{s}\,. \tag{5.30}$$

On substituting Eqs. 5.28 and 5.30 into Eq. 5.29, we obtain:

$$\Delta E_{\rm so} = \frac{g_{\rm s}\mu_{\rm B}}{\hbar c^2}\boldsymbol{s}\cdot(\boldsymbol{\mathcal{E}}\times\boldsymbol{v})\,. \tag{5.31}$$

If we have a **central field** (ie the potential V is a function of r only), we can write:[3]

$$\boldsymbol{\mathcal{E}} = \frac{1}{e}\frac{\boldsymbol{r}}{r}\frac{{\rm d}V}{{\rm d}r}\,. \tag{5.32}$$

On making use of this, the spin-orbit energy becomes:

$$\Delta E_{\rm so} = \frac{g_{\rm s}\mu_{\rm B}}{\hbar c^2 e m_{\rm e}}\left(\frac{1}{r}\frac{{\rm d}V}{{\rm d}r}\right)\boldsymbol{s}\cdot(\boldsymbol{r}\times\boldsymbol{p})\,, \tag{5.33}$$

where we have substituted $\boldsymbol{v} = \boldsymbol{p}/m_{\rm e}$. On recalling that the angular momentum $\boldsymbol{l}$ is defined as $\boldsymbol{r}\times\boldsymbol{p}$, we find:

$$\Delta E_{\rm so} = \frac{g_{\rm s}\mu_{\rm B}}{\hbar c^2 e m_{\rm e}}\left(\frac{1}{r}\frac{{\rm d}V}{{\rm d}r}\right)\boldsymbol{s}\cdot\boldsymbol{l}\,. \tag{5.34}$$

This calculation of $\Delta E_{\rm so}$ does not take proper account of relativistic effects. In particular, we moved the origin from the nucleus to the electron, which is not really allowed because the electron is accelerating all the time and is therefore not an inertial frame. The translation to a rotating frame gives rise to an extra effect called the **Thomas precession** which reduces the energy by a factor of 2. (See Eisberg and Resnick, Appendix O.) On taking the Thomas precession into account, and recalling that $\mu_{\rm B} = e\hbar/2m_{\rm e}$, we obtain the final result:

$$\Delta E_{\rm so} = \frac{g_{\rm s}}{2}\frac{1}{2c^2m_{\rm e}^2}\left(\frac{1}{r}\frac{{\rm d}V}{{\rm d}r}\right)\boldsymbol{l}\cdot\boldsymbol{s}\,. \tag{5.35}$$

This is the same as the result derived from the Dirac equation, except that $g_{\rm s}$ is exactly equal to 2 in Dirac's theory. Equation 5.35 shows that the spin and orbital angular momenta are coupled together. If we have a simple Coulomb field and take $g_{\rm s} = 2$, we find

$$\Delta E_{\rm so} = \frac{Ze^2}{8\pi\epsilon_0 c^2 m_{\rm e}^2}\left(\frac{1}{r^3}\right)\boldsymbol{l}\cdot\boldsymbol{s}\,. \tag{5.36}$$

We can use this formula for hydrogenic atoms, while we can use the more general form given in Eq. 5.35 for more complicated multi-electron atoms where the potential will differ from the Coulombic $1/r$ dependence due to the repulsion between the electrons.

5.4 The total angular momentum

The orbital and spin angular momentum of the electron couple together through the spin-orbit interaction to form a resultant, as illustrated by Fig. 5.4(a).[4] The resultant angular momentum vector $\boldsymbol{j}$ is defined by:

$$\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}\,. \tag{5.37}$$

[3] It is easy to verify that this works for a Coulomb field where $V = -Ze^2/4\pi\epsilon_0 r$ and $\boldsymbol{\mathcal{E}}$ is given by eqn 5.26.

[4] Graphical representations of the type shown in Fig. 5.4 are called **vector models**. We shall encounter vector models again when we come to study the Zeeman effect in the next set of notes.

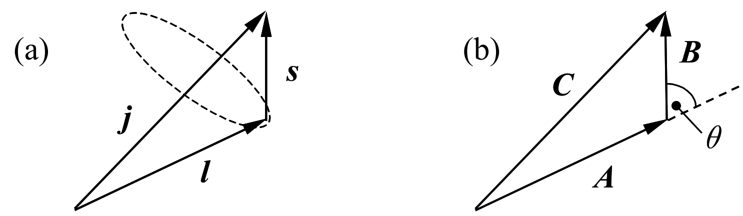

Figure 5.4: (a) Vector model of the atom. The spin-orbit interaction couples $\boldsymbol{l}$ and $\boldsymbol{s}$ together to form the resultant $\boldsymbol{j}$. The magnitudes of the vectors are given by: $|\boldsymbol{j}| = \sqrt{j(j+1)}\hbar$, $|\boldsymbol{l}| = \sqrt{l(l+1)}\hbar$, and $|\boldsymbol{s}| = \sqrt{s(s+1)}\hbar$. (b) Vector addition of two angular momentum vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ to form the resultant $\boldsymbol{C}$.

$\boldsymbol{j}$ is described by the quantum numbers j and m_j according to the usual rules for quantum mechanical angular momenta, namely:

$$|\boldsymbol{j}| = \sqrt{j(j+1)}\hbar\,, \tag{5.38}$$

and

$$j_z = m_j\hbar\,, \tag{5.39}$$

where m_j takes values of $j, (j-1), \cdots, -j$.

We can find out the values that j can take by applying the rules for the addition of quantum mechanical angular momenta. Let us suppose that $\boldsymbol{C}$ is the resultant of two angular momentum vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ as shown in Fig. 5.4(b), so that:

$$\boldsymbol{C} = \boldsymbol{A} + \boldsymbol{B}\,. \tag{5.40}$$

We assume for the sake of simplicity that $|\boldsymbol{A}| > |\boldsymbol{B}|$. (The argument is unaffected if $|\boldsymbol{A}| < |\boldsymbol{B}|$.) We define θ as the angle between the two vectors, as shown in figure 5.4(b).

In *classical physics* the angle θ can take any value from $0°$ to $180°$. Therefore, $|\boldsymbol{C}|$ can take any value from $(|\boldsymbol{A}| + |\boldsymbol{B}|)$ to $(|\boldsymbol{A}| - |\boldsymbol{B}|)$. This is *not* the case in *quantum mechanics*, because the lengths of the angular momentum vectors must be quantized according to:

$$\begin{aligned} |\boldsymbol{A}| &= \sqrt{A(A+1)}\hbar \\ |\boldsymbol{B}| &= \sqrt{B(B+1)}\hbar \\ |\boldsymbol{C}| &= \sqrt{C(C+1)}\hbar \end{aligned} \tag{5.41}$$

where A, B and C are the quantum numbers. The rule is that:

$$C \text{ can take all values in integer steps from } (A+B) \text{ to } |A-B|\,. \tag{5.42}$$

This means that θ can only take specific values.

On applying this rule to the resultant $\boldsymbol{j}$ defined in Eq. 5.37, we are considering a single electron with orbital quantum number l and spin quantum number $s = 1/2$. We thus find that $j = (l+1/2)$ or $(l-1/2)$, except when $l = 0$, in which case we just have $j = 1/2$.

Here are some other examples of the application of the rule given in eqn 5.42:

- $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$, $L = 3$, $S = 1$:
  $L + S = 4$, $|L - S| = 2$, therefore $J = 4, 3, 2$.

- $\boldsymbol{L} = \boldsymbol{l}_1 + \boldsymbol{l}_2$, $l_1 = 2$, $l_2 = 0$:
  $l_1 + l_2 = 2$, $|l_1 - l_2| = 2$, therefore $L = 2$.

- $\boldsymbol{S} = \boldsymbol{s}_1 + \boldsymbol{s}_2$, $s_1 = 1/2$, $s_2 = 1/2$:
  $s_1 + s_2 = 1$, $|s_1 - s_2| = 0$, therefore $S = 1, 0$.

- $\boldsymbol{J} = \boldsymbol{j}_1 + \boldsymbol{j}_2$, $j_1 = 5/2$, $j_2 = 3/2$:
  $j_1 + j_2 = 4$, $|j_1 - j_2| = 1$, therefore $J = 4, 3, 2, 1$.

5.5 Evaluation of the spin-orbit energy for hydrogen

The magnitude of the spin-orbit energy can be calculated from eqn 5.35 as:

$$\Delta E_{\rm so} = \frac{1}{2c^2 m_{\rm e}^2} \left\langle \frac{1}{r}\frac{{\rm d}V}{{\rm d}r} \right\rangle \langle \boldsymbol{l} \cdot \boldsymbol{s} \rangle \,, \tag{5.43}$$

where we have taken $g_{\rm s} = 2$, and the $\langle \cdots \rangle$ notation indicates that we take expectation values:

$$\left\langle \frac{1}{r}\frac{{\rm d}V}{{\rm d}r} \right\rangle = \int\int\int \psi_{nlm}^* \left(\frac{1}{r}\frac{{\rm d}V}{{\rm d}r} \right) \psi_{nlm}\, r^2 \sin\theta \,{\rm d}r{\rm d}\theta{\rm d}\phi \,. \tag{5.44}$$

The function $({\rm d}V/{\rm d}r)/r$ depends only on r, and so we are left to calculate an integral over r only:

$$\left\langle \frac{1}{r}\frac{{\rm d}V}{{\rm d}r} \right\rangle = \int_0^\infty |R_{nl}(r)|^2 \left(\frac{1}{r}\frac{{\rm d}V}{{\rm d}r} \right) r^2 {\rm d}r \,, \tag{5.45}$$

where $R_{nl}(r)$ is the radial wave function. This integral can be evaluated exactly for the case of the Coulomb field in hydrogen where $({\rm d}V/{\rm d}r)/r \propto 1/r^3$, and the radial wave functions are known exactly. (See Table 2.2.) We then have, for $l \geq 1$:

$$\left\langle \frac{1}{r}\frac{{\rm d}V}{{\rm d}r} \right\rangle \propto \left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_0^3 n^3 l(l+\frac{1}{2})(l+1)} \,. \tag{5.46}$$

This shows that we can re-write eqn 5.43 in the form:

$$\Delta E_{\rm so} = C_{nl} \, \langle \boldsymbol{l} \cdot \boldsymbol{s} \rangle \,, \tag{5.47}$$

where C_{nl} is a constant that depends only on n and l.

We can evaluate $\langle \boldsymbol{l} \cdot \boldsymbol{s} \rangle$ by realizing from eqn 5.37 that we must have:

$$\boldsymbol{j}^2 = (\boldsymbol{l} + \boldsymbol{s})^2 = \boldsymbol{l}^2 + \boldsymbol{s}^2 + 2\boldsymbol{l} \cdot \boldsymbol{s} \,. \tag{5.48}$$

This implies that:

$$\langle \boldsymbol{l} \cdot \boldsymbol{s} \rangle = \left\langle \frac{1}{2}(\boldsymbol{j}^2 - \boldsymbol{l}^2 - \boldsymbol{s}^2) \right\rangle = \frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)] \,. \tag{5.49}$$

We therefore find:

$$\Delta E_{\rm so} = C'_{nl} \, [j(j+1) - l(l+1) - s(s+1)] \,, \tag{5.50}$$

where $C'_{nl} = C_{nl}\hbar^2/2$. On using eqn 5.46 we obtain the final result for states with $l \geq 1$:

$$\Delta E_{\rm so} = -\frac{\alpha^2 Z^2}{2n^2} E_n \frac{n}{l(l+\frac{1}{2})(l+1)} [j(j+1) - l(l+1) - s(s+1)] \,, \tag{5.51}$$

where $\alpha \approx 1/137$ is the **fine structure constant**, and $E_n = -R_{\rm H} Z^2/n^2$ is equal to the gross energy. For states with $l = 0$ it is apparent from eqn 5.43 that $\Delta E_{\rm so} = 0$.

The fact that j takes values of $l+1/2$ and $l-1/2$ for $l \geq 1$ means that the spin-orbit interaction splits the two j states with the same value of l. We thus expect the electronic states of hydrogen with $l \geq 1$ to split into doublets. However, the actual fine structure of hydrogen is more complicated for two reasons:

1. States with the same n but different l are degenerate.

2. The spin-orbit interaction is small.

The first point is a general property of pure one-electron systems, and the second follows from the scaling of $\Delta E_{\rm so}/E_n$ with Z^2. A consequence of point 2 is that other relativistic effects that we have neglected up until now are of a similar magnitude to the spin-orbit coupling. In atoms with higher values of Z, the spin-orbit coupling is the dominant relativistic correction, and we can neglect the other effects.

The fine structure of the $n = 2$ level in hydrogen is illustrated in figure 5.5. The fully relativistic Dirac theory predicts that states with the same j are degenerate. The degeneracy of the two $j = 1/2$ states is ultimately lifted by a quantum electrodynamic (QED) effect called the Lamb shift. The complications of the fine structure of hydrogen due to other relativistic and QED effects means that hydrogen is not the paradigm for understanding spin-orbit effects. The alkali metals considered in Section 5.9 are in fact simpler to understand.

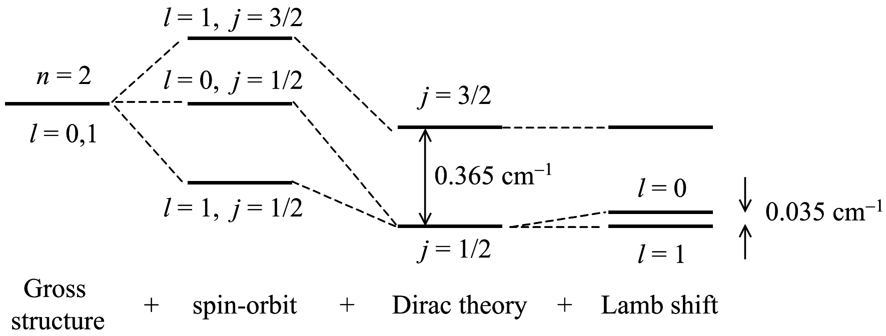

Figure 5.5: Fine structure in the $n = 2$ level of hydrogen.

5.6 Spin-orbit effects in multi-electron atoms

The Hamiltonian for an N-electron atom with the spin-orbit coupling included can be written in the form:

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2\,, \tag{5.52}$$

where:

$$\hat{H}_0 = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + V_{\text{central}}(r_i)\right)\,, \tag{5.53}$$

$$\hat{H}_1 = \sum_{i>j}^{N}\frac{e^2}{4\pi\epsilon_0|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{i=1}^{N}V_{\text{central}}(r_i)\,, \tag{5.54}$$

$$\hat{H}_2 = \sum_{i=1}^{N}\xi(r_i)\boldsymbol{l}_i\cdot\boldsymbol{s}_i\,. \tag{5.55}$$

As shown in Section 4.1, $\hat{H}_0$ is the central-field Hamiltonian and $\hat{H}_1$ is the residual electrostatic potential. $\hat{H}_2$ is the spin-orbit interaction summed over the electrons of the atom. (See eqn 5.35.)

In Chapter 4 we neglected both $\hat{H}_1$ and $\hat{H}_2$, and just concentrated on $\hat{H}_0$. This led to the conclusion that each electron occupies a state in a shell defined by the quantum numbers (n, l, m_l, m_s). The energy of these shells depends primarily on n and l. The reason why we neglected $\hat{H}_1$ is that the off-radial forces due to the electron-electron repulsion are smaller than the radial ones, while $\hat{H}_2$ was neglected because the spin-orbit effects are much smaller than the main terms in the Hamiltonian. It is now time to study what happens when these two terms are included. In doing so, there are two obvious limits:[5]

- **LS coupling**: $\hat{H}_1 \gg \hat{H}_2$. This mainly occurs in atoms of small and medium Z.
- **jj coupling**: $\hat{H}_2 \gg \hat{H}_1$. This limit occurs in some atoms with large Z.

We start by considering the more common LS-coupling limit, leaving jj-coupling until Section 5.11.

5.7 LS coupling

In the **LS-coupling** limit (alternatively called **Russell–Saunders coupling**), the residual electrostatic interaction is much stronger than the spin-orbit interaction. We therefore deal with the residual electrostatic interaction first and then apply the spin-orbit interaction as a perturbation. The LS coupling regime applies to most atoms of small and medium atomic number.

Let us first discuss some issues of notation. We shall need to distinguish between the quantum numbers that refer to the individual electrons within an atom and the state of the atom as a whole. The convention is:

- Lower case quantum numbers (j, l, s) refer to *individual electrons* within atoms.

[5]In some atoms with medium-large Z (e.g. germanium $Z = 32$) we are in the awkward situation where neither limit applies. We then have **intermediate coupling**, and the behaviour is quite complicated to describe.

- Upper case quantum numbers (J, L and S) refer to the angular momentum states of the *whole atom.*

For single electron atoms like hydrogen, there is no difference. However, in multi-electron atoms there is a real difference because we must distinguish between the angular momentum states of the individual electrons and the resultants which give the angular momentum states of the whole atom.

We can use this notation to determine the angular momentum states that the LS-coupling scheme produces. The residual electrostatic interaction has the effect of coupling the orbital and spin angular momenta of the individual electrons together, so that we find their resultants according to:

$$\boldsymbol{L} = \sum_i \boldsymbol{l}_i\,, \tag{5.56}$$

$$\boldsymbol{S} = \sum_i \boldsymbol{s}_i\,. \tag{5.57}$$

Filled shells of electrons have no net angular momentum, and so the summation only needs to be carried out over the valence electrons. In a many-electron atom, the rules for the addition of quantum mechanical angular momenta given in Section 5.4 usually allow several possible values of the quantum numbers L and S for a particular electronic configuration. Their energies will differ due to the residual electrostatic interaction. The atomic states defined by the values of L and S are called **terms**.

For each atomic term, we can find the total angular momentum of the whole atom from:

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}\,. \tag{5.58}$$

The values of J, the quantum number corresponding to $\boldsymbol{J}$, are found according to the rules for the addition of quantum mechanical angular momenta given in Section 5.4. The **levels** of different J corresponding to the particular values of L and S will have different energies due to the spin-orbit interaction. The spin-orbit interaction is now of the form :

$$\Delta E_{\text{so}} \propto -\boldsymbol{\mu}_{\text{s}}^{\text{atom}} \cdot \boldsymbol{B}_{\text{orbital}}^{\text{atom}} \propto \boldsymbol{L} \cdot \boldsymbol{S}\,, \tag{5.59}$$

where the 'atom' superscript indicates that we take the resultant values for the whole atom. On following an analogous method to Section 5.5, we then find:

$$\Delta E_{SO} = C_{LS}\,[J(J+1) - L(L+1) - S(S+1)]\,. \tag{5.60}$$

This implies that levels with the same L and S but different J are separated by an energy which is proportional to J.

It is convenient to introduce a shorthand notation to label the energy levels that occur in the LS coupling regime. Each level is labelled by the quantum numbers J, L and S and is represented in the form:

$$^{2S+1}\mathrm{L}_J\,.$$

The factors $(2S + 1)$ and J appear as numbers, whereas L is a letter that follows the rule:

- S implies $L = 0$,
- P implies $L = 1$,
- D implies $L = 2$,
- F implies $L = 3$, etc.

Thus, for example, a $^2\mathrm{P}_{1/2}$ term is the energy level with quantum numbers $S = 1/2$, $L = 1$, and $J = 1/2$, while a $^3\mathrm{D}_3$ has $S = 1$, $L = 2$ and $J = 3$. The factor of $(2S+1)$ in the top left is called the **multiplicity**. It indicates the degeneracy of the level due to the spin: i.e. the number of M_S states available. If $S = 0$, the multiplicity is 1, and the terms are called **singlets**. If $S = 1/2$, the multiplicity is 2 and we have **doublet** terms. If $S = 1$ we have **triplet** terms, etc.

Figure 5.6 illustrates the main points that we have been considering in this section for the (3s,3p) electronic configuration of magnesium. The details of the energy levels should not concern us at this stage. The main point to realize is the general way the states split as the new interactions are turned on, and the terminology used to designate the states.

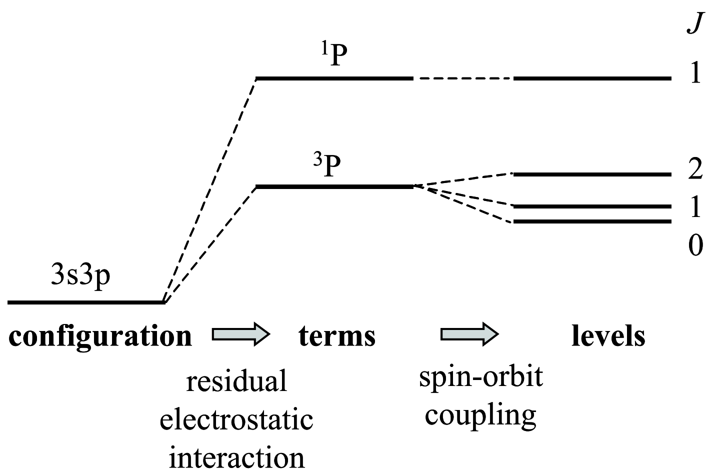

Figure 5.6: Splitting of the energy levels for the (3s,3p) configuration of magnesium in the LS coupling regime.

5.8 Electric dipole selection rules in the LS coupling limit

When considering electric-dipole transitions between the states of many-electron atoms that have LS-coupling, a single electron makes a jump from one atomic shell to a new one. The rules that apply to this electron are the same as the ones discussed in Section 3.4. However, we also have to think about the angular momentum state of the whole atom as specified by the quantum numbers (L, S, J). The rules that emerges are as follows:

1. The parity of the wave function must change.
2. $\Delta l = \pm 1$ for the electron that jumps between shells.
3. $\Delta L = 0, \pm 1$, but $L = 0 \to 0$ is forbidden.
4. $\Delta J = 0, \pm 1$, but $J = 0 \to 0$ is forbidden.
5. $\Delta S = 0$.

Rule 1 follows from the odd parity of the dipole operator. Rule 2 applies the single-electron rule to the individual electron that makes the jump in the transition, and rule 3 applies this rule to the whole atom.[6] Rules 4 follows from the fact that the total angular momentum must be conserved in the transition, allowing us to write:

$$\boldsymbol{J}^{\text{initial}} = \boldsymbol{J}^{\text{final}} + \boldsymbol{J}^{\text{photon}} . \tag{5.61}$$

The photon carries one unit of angular momentum, and so by applying the rules given in Section 5.4, we conclude that $\Delta J = -1,\ 0,$ or $+1$. However, the $\Delta J = 0$ rule cannot be applied to $J = 0 \to 0$ transitions because it is not possible to satisfy eqn 5.61 in these circumstances. Finally, rule 5 is a consequence of the fact that the photon does not interact with the spin.[7]

5.9 Spin-orbit coupling in alkali atoms

We can apply the result given in eqn 5.60 to the alkali metals, which are quasi one-electron atoms. With only one valence electron, the distinction between LS and jj coupling is irrelevant. If the one valence electron is in the nl shell, we just have $L = l$, $S = s = 1/2$ and $J = j$, where $j = l \pm 1/2$ for $l \geq 1$ and $j = 1/2$ for $l = 0$.

The simplest case to consider is when the electron is in an s-shell. We then have $L = 0$, $S = 1/2$ and $J = 1/2$, so that $\boldsymbol{L} \cdot \boldsymbol{S} = 0$. Hence the spin-orbit energy of the s-electron is zero.

[6] $\Delta L = 0$ transitions are obviously forbidden in one-electron atoms, because $L = l$ and l must change. However, in atoms with more than one valence electron, it is possible to get transitions between different configurations that satisfy rule 2, but have the same value of L: e.g. 3p4p $^3\mathrm{P}_1 \to$ 3p4s $^3\mathrm{P}_1$.

[7] $\Delta S \neq 0$ transitions can be weakly allowed when the spin-orbit coupling is strong, because the spin is then mixed with the orbital motion.

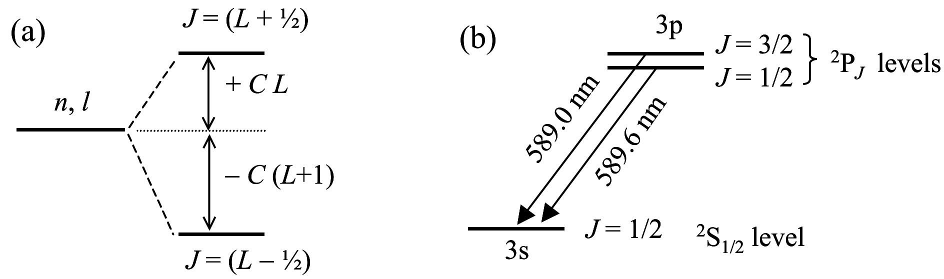

Figure 5.7: Spin-orbit interactions in alkali atoms. (a) The spin-orbit interaction splits the nl states into a doublet if $l \neq 0$. (b) Fine structure in the yellow sodium D lines.

Now consider the case when the valence electron is in a shell with $l \neq 0$. We now have $L = l$ and $S = 1/2$, so that $\boldsymbol{L} \cdot \boldsymbol{S} \neq 0$. J has two possible values, namely $(L + 1/2)$ and $(L - 1/2)$. The spin-orbit energy of the $J = (L + 1/2)$ state is given by eqn 5.60 as:

$$\Delta E_{\text{so}} = C \left[(L + \frac{1}{2})(L + \frac{3}{2}) - L(L+1) - \frac{1}{2} \cdot \frac{3}{2} \right] = +CL\,,$$

whereas for the $J = (L - 1/2)$ level we have

$$\Delta E_{\text{so}} = C \left[(L - \frac{1}{2})(L + \frac{1}{2}) - L(L+1) - \frac{1}{2} \cdot \frac{3}{2} \right] = -C(L+1)\,.$$

Hence the term defined by the quantum numbers n and l is split by the spin-orbit coupling into two new states, as illustrated in figure 5.7(a). This gives rise to the appearance of doublets in the atomic spectra. The most well-known of these, namely the yellow sodium D-line doublet, is discussed below. The magnitude of the splitting is smaller than the gross energy by a factor $\sim \alpha^2 = 1/137^2$. (See Eq. 5.51.) This is why these effects are called "fine structure", and α is called the "fine structure constant".

Example: The sodium D lines

Sodium has 11 electrons, with one valence electron in the 3s shell outside filled 1s, 2s and 2p shells. It can therefore be treated as a one electron system, provided we remember that this is only an approximation. One immediate consequence is that the differing l states arising from the same n are not degenerate as they are in hydrogen. (See section 4.5.) The bright yellow D lines of sodium correspond to the 3p→3s transition.

It is well known that the D-lines actually consist of a doublet, as shown in Fig. 5.7(b). The doublet arises from the spin-orbit coupling. The ground state is a $^2\mathrm{S}_{1/2}$ level with zero spin-orbit splitting. The excited state is split into the two levels derived from the different J values for $L = 1$ and $S = 1/2$, namely the $^2\mathrm{P}_{3/2}$ and $^2\mathrm{P}_{1/2}$ levels. The two transitions in the doublet are therefore:

$$^2\mathrm{P}_{3/2} \rightarrow {}^2\mathrm{S}_{1/2}$$

and

$$^2\mathrm{P}_{1/2} \rightarrow {}^2\mathrm{S}_{1/2}\,.$$

The energy difference of $17\,\mathrm{cm}^{-1}$ between them arises from the spin-orbit splitting of the two J states of the $^2\mathrm{P}$ term.

Similar arguments can be applied to the other alkali elements. The spin–orbit energy splittings of their first excited states are tabulated in Table 5.1. Note that the splitting increases with Z, and that the splitting energy is roughly proportional to Z^2, as shown in Fig. 5.8. This is an example of the fact that spin–orbit interactions generally increase with the atomic number, so that the spin–orbit coupling is stronger in heavier elements.

5.10 Hund's rules

We have seen above that there are many terms in the energy spectrum of a multi-electron atom. Of these, one will have the lowest energy, and will form the **ground state**. All the others are excited states. Each

Element	Z	Ground state	1st excited state	Transition	ΔE (cm^{-1})
Lithium	3	[He] 2s	2p	2p →2s	0.33
Sodium	11	[Ne] 3s	3p	3p →3s	17
Potassium	19	[Ar] 4s	4p	4p →4s	58
Rubidium	37	[Kr] 5s	5p	5p →5s	238
Cesium	55	[Xe] 6s	6p	6p →6s	554

Table 5.1: Spin-orbit splitting ΔE of the D lines of the alkali elements. The energy splitting is equal to the difference of the energies of the $J = 3/2$ and $J = 1/2$ levels of the first excited state.

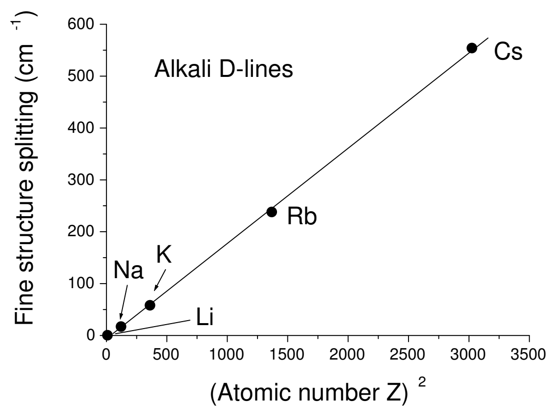

Figure 5.8: Spin-orbit splitting of the first excited state of the alkali atoms versus Z^2, as determined by the fine structure splitting of the D-lines. (See Table 5.1.)

atom has a *unique* ground state, which is determined by minimizing the energy of its valence electrons with the residual electrostatic and spin-orbit interactions included. In principle, this is a very complicated calculation. Fortunately, however, **Hund's rules** allow us to determine which level is the ground state without lengthy calculation. The rules are:

1. Maximize the quantum number $M_S = \sum m_s$ and set $S = |M_S|$.

2. Maximize $M_L = \sum m_l$ subject to rule 1, and set $L = |M_L|$.

3. $J = |L - S|$ if the shell is less than half full, otherwise $J = |L + S|$.

The first of these rules basically tells us that the electrons try to align themselves with their spins parallel. This is caused by the exchange interaction (see Chapter 7) and is the origin of ferromagnetism. Note that these rules *cannot* be used to find the energy ordering of excited states.

Let's have a look at carbon as an example. Carbon has an atomic number $Z = 6$ with two valence electrons in the outermost 2p shell. Each valence electron therefore has $l = 1$ and $s = 1/2$. Consider first the (2p,np) excited state configuration with one electron in the 2p shell and the other in the np shell, where $n \geq 3$. By the rules of addition of angular momenta, we can have L equal to 0, 1 or 2, and S equal to 0 or 1. This gives rise to three singlet terms

$$^1\mathrm{S}_0,\ \ ^1\mathrm{P}_1,\ \ ^1\mathrm{D}_2\,,$$

and seven triplets:

$$^3\mathrm{S}_1,\ \ ^3\mathrm{P}_0,\ \ ^3\mathrm{P}_1,\ \ ^3\mathrm{P}_2,\ \ ^3\mathrm{D}_1,\ \ ^3\mathrm{D}_2,\ \ ^3\mathrm{D}_3\,.$$

We thus have a confusing array of *ten* terms in the energy spectrum for the (2p,np) configuration.

The situation in the ground state configuration $(2p, 2p)$ is simplified by the fact both of the electrons are in the *same* shell. The Pauli exclusion principle forbids the possibility that two or more electrons have

	m_l		
m_s	−1	0	+1
+1/2		↑	↑
−1/2			

Table 5.2: Distribution of the two valence electrons of carbon ground state within the m_s and m_l states of the 2p shell.

Z	Element	Configuration	Ground state
1	H	$1s^1$	$^2S_{1/2}$
2	He	$1s^2$	$^1S_0$
3	Li	$1s^2\ 2s^1$	$^2S_{1/2}$
4	Be	$1s^2\ 2s^2$	$^1S_0$
5	B	$1s^2\ 2s^2\ 2p^1$	$^2P_{1/2}$
6	C	$1s^2\ 2s^2\ 2p^2$	$^3P_0$
7	N	$1s^2\ 2s^2\ 2p^3$	$^4S_{3/2}$
8	O	$1s^2\ 2s^2\ 2p^4$	$^3P_2$
9	F	$1s^2\ 2s^2\ 2p^5$	$^2P_{3/2}$
10	Ne	$1s^2\ 2s^2\ 2p^6$	$^1S_0$
11	Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$	$^2S_{1/2}$

Table 5.3: Electronic configurations and ground state terms of the first 11 elements in the periodic table.

the same set of quantum numbers. This means that only five of the ten terms listed above are possible, namely those that have $L + S$ equal to an even number, that is:[8]

$$^1\mathrm{S}_0,\ \ ^1\mathrm{D}_2,\ \ ^3\mathrm{P}_0,\ \ ^3\mathrm{P}_1,\ \ ^3\mathrm{P}_2\,.$$

We can now apply Hund's rules to find out which of these is the ground state. The two electrons can go into six possible (m_s, m_l) sub-levels of the 2p shell.

1. To get the largest value of M_S we must have both electron spins aligned with $m_s = +1/2$. This gives $M_S = 1$ and hence $S = 1$

2. Having put both electrons into spin up states, we cannot now put both electrons into $m_l = +1$ states because of Pauli's exclusion principle. The best we can do is to put one into an $m_l = 1$ state and the other into an $m_l = 0$ state, as illustrated in Table 5.2. This gives $M_L = 1$ and therefore $L = 1$.

3. The shell is less than half full, and so we have $J = |L - S| = 0$.

The ground state is thus the $^3\mathrm{P}_0$ term. All the others are excited states.

The ground state terms for the first 11 elements are listed in Table 5.3. Note that full shells always give $^1\mathrm{S}_0$ terms with no net angular momentum: $S = L = J = 0$.

5.11 jj coupling

The spin-orbit interaction gets larger as Z increases. (See, for example, eqn 5.51.) This means that in some atoms with large Z (eg tin with $Z = 50$) we can have a situation in which the spin-orbit interaction is much stronger than the residual electrostatic interaction. In this regime, **jj coupling** coupling occurs. The spin-orbit interaction couples the orbital and spin angular momenta of the individual electrons

[8] There is no easy explanation of why $L + S$ must be even for equivalent electrons. The derivation of the allowed states for the (np, np) configuration of a group IV atom is considered, for example, in Woodgate, *Elementary Atomic Structure*, 2nd Edition, Oxford University Press, 1980, Section 7.2.

together first, and we then find the resultant $\boldsymbol{J}$ for the whole atom by adding together the individual $\boldsymbol{j}$s:

$$\begin{aligned} \boldsymbol{j}_i &= \boldsymbol{l}_i + \boldsymbol{s}_i \\ \boldsymbol{J} &= \sum_{i=1}^{N} \boldsymbol{j}_i \end{aligned} \tag{5.62}$$

These J states are then split by the weaker residual electrostatic potential, which acts as a perturbation.

5.12 Nuclear effects in atoms

For most of the time in atomic physics we just take the nucleus to be a heavy charged particle sitting at the centre of the atom. However, careful analysis of the spectral lines can reveal small effects that give us direct information about the nucleus. The main effects that can be observed generally fall into two categories, namely **isotope shifts** and **hyperfine structure**.

5.12.1 Isotope shifts

There are two main processes that give rise to isotope shifts in atoms, namely mass effects and field effects.

Mass effects The mass m that enters the Schrödinger equation is the *reduced* mass, not the bare electron mass m_e (cf. eqn 1.9). Changes in the nuclear mass therefore make small changes to m and hence to the atomic energies.

Field effects Electrons in s shells have a finite probability of penetrating the nucleus, and are therefore sensitive to its charge distribution.

Both effects cause small shifts in the wavelengths of the spectral lines from different isotopes of the same element. The heavy isotope of hydrogen, namely deuterium, was discovered in this way through its mass effect.

5.12.2 Hyperfine structure

In high–resolution spectroscopy, it is necessary to consider effects relating to the magnetic interaction between the electron angular momentum ($\boldsymbol{J}$) and the nuclear spin ($\boldsymbol{I}$). The angular momentum of the electrons creates a magnetic field at the nucleus which is proportional to $\boldsymbol{J}$. The spin of the nucleus gives it a magnetic dipole moment which is proportional to $\boldsymbol{I}$, and we therefore have an interaction energy term of the form:

$$\Delta E_{\text{hyperfine}} = -\boldsymbol{\mu}_{\text{nucleus}} \cdot \boldsymbol{B}_{\text{electron}} \propto \langle \boldsymbol{I} \cdot \boldsymbol{J} \rangle \,. \tag{5.63}$$

This gives rise to **hyperfine** splittings in the atomic terms. The magnitude of the splittings is very small because the nuclear dipole is about 2000 times smaller than that of the electron. This follows from the small gyromagnetic ratio of the nucleus, which is inversely proportional to its mass. (See eqn 5.4.) The splittings are therefore about three orders of magnitude smaller than the fine structure splittings: hence the name "hyperfine".

Hyperfine states are labelled by the total angular momentum $\boldsymbol{F}$ of the whole atom (i.e. nucleus plus electrons), where

$$\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}. \tag{5.64}$$

In analogy with the $|LSJ\rangle$ states of fine structure, the electric dipole selection rule for transitions between hyperfine states is:

$$\Delta F = 0, \pm 1 \,, \tag{5.65}$$

with the exception that $F = 0 \rightarrow 0$ transitions are forbidden. Let us consider two examples to see how this works.

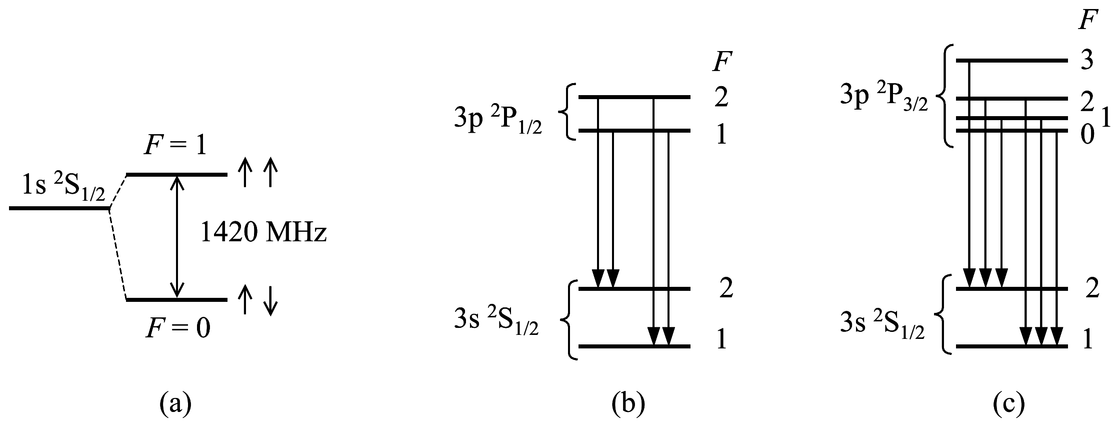

Figure 5.9: (a) Hyperfine structure of the 1s ground state of hydrogen. The arrows indicate the relative directions of the electron and nuclear spin. (b) Hyperfine transitions for the sodium D_1 line. (c) Hyperfine transitions for the sodium D_2 line. Note that the hyperfine splittings are not drawn to scale. The splittings of the sodium levels are as follows: $^2S_{1/2}$, 1772 MHz; $^2P_{1/2}$, 190 MHz; $^2P_{3/2}$ $(3 \to 2)$, 59 MHz; $^2P_{3/2}$ $(2 \to 1)$, 34 MHz; $^2P_{3/2}$ $(1 \to 0)$, 16 MHz.

The hydrogen 21 cm line

Consider the ground state of hydrogen. The nucleus consists of just a single proton, and we therefore have $I = 1/2$. The hydrogen ground state is the 1s $^2S_{1/2}$ term, which has $J = 1/2$. The spins of the electron and the nucleus can be aligned parallel ($F = 1$) or antiparallel ($F = 0$), with different hyperfine energies. These two hyperfine levels are split by 0.0475 cm^{-1} (5.9×10^{-6} eV). (See Fig. 5.9(a).) Transitions between these levels occur at 1420 MHz ($\lambda = 21$ cm), and are very important in radio astronomy. Radio frequency transitions such as these are also routinely exploited in **nuclear magnetic resonance** (NMR) spectroscopy.

Hyperfine structure of the sodium D lines

The sodium D lines originate from 3p→3s transitions. As discussed in Section 5.9, there are two lines with energies split by the spin-orbit coupling, as indicated in Fig. 5.7(b).

Consider first the lower energy D_1 line, which is the $^2P_{1/2} \to^2 S_{1/2}$ transition. The nucleus of sodium has $I = 3/2$, and so we have $F = 1$ and $F = 2$ states for both the upper and lower levels of the transition, as shown in Fig. 5.9(b). Note that the splittings are not drawn to scale, being 190 MHz and 1772 MHz for the upper and lower levels, respectively. All four transitions are allowed by the selection rules, and so we observe four lines. Since the splitting of the upper and lower levels are so different, we obtain two doublets with relative frequencies of (0, 190) MHz and (1772, 1962) MHz. These splittings should be compared to the much larger ($\sim 5 \times 10^{11}$ Hz) splitting between the two J states caused by the spin-orbit interaction. Since the hyperfine splittings are much smaller, they are not routinely observed in optical spectroscopy, and specialized techniques using narrow band lasers are typically employed nowadays.

Now consider the higher energy D_2 line, which is the $^2P_{3/2} \to^2 S_{1/2}$ transition. With $I = 3/2$ and $J = 3/2$, we now have four hyperfine states for the upper level with $F = 3$, 2, 1 or 0, as shown in Fig. 5.9(c). The splittings between these states are not the same, and are much smaller than that of the $^2S_{1/2}$ level. Six transitions are allowed by the selection rules, with the $F = 3 \to 1$ and $F = 0 \to 2$ transitions being forbidden by the $|\Delta F| \leq 1$ selection rule. We thus have six hyperfine lines, which split into two triplets at relative frequencies of (0, 34, 59) MHz and (1756, 1772, 1806) MHz.

Reading

Demtröder, W., *Atoms, Molecules and Photons*, §5.4–8, 6.2–5.
Haken and Wolf, *The physics of atoms and quanta*, chapters 12, 17, 19, 20.
Eisberg and Resnick, *Quantum Physics*, chapters 8, 10.
Foot, *Atomic physics*, §2.3, 4.5–6, chapters 5–6.
Beisser, *Concepts of Modern Physics*, §7.7 – 8.