

## Chapter 9

# Atomic structure

Previously, we have seen that the quantum mechanics of atomic hydrogen, and hydrogen-like atoms is characterized by a large degeneracy with eigenvalues separating into multiplets of  $n^2$ -fold degeneracy, where  $n$  denotes the principle quantum number. However, although the idealized Schrödinger Hamiltonian,

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} + V(r), \quad V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}, \quad (9.1)$$

provides a useful platform from which develop our intuition, there are several important effects which mean that the formulation is a little too naïve. These “corrections”, which derive from several sources, are important as they lead to physical ramifications which extend beyond the realm of atomic physics. Here we outline some of the effects which need to be taken into account even for atomic hydrogen, before moving on to discuss the quantum physics of multi-electron atoms. In broad terms, the effects to be considered can be grouped into those caused by the internal properties of the nucleus, and those which derive from relativistic corrections.

To orient our discussion, it will be helpful to summarize some of key aspects of the solutions of the non-relativistic Schrödinger equation,  $\hat{H}_0\psi = E\psi$  on which we will draw:

### Hydrogen atom revisited:

- ▷ As with any centrally symmetric potential, the solutions of the Schrödinger equation take the form  $\psi_{\ell m}(\mathbf{r}) = R(r)Y_{\ell m}(\theta, \phi)$ , where the spherical harmonic functions  $Y_{\ell m}(\theta, \phi)$  depend only on spherical polar coordinates, and  $R(r)$  represents the radial component of the wavefunction. Solving the radial wave equation introduces a radial quantum number,  $n_r \geq 0$ . In the case of a Coulomb potential, the energy depends on the principal quantum number  $n = n_r + \ell + 1 \geq 1$ , and not on  $n_r$  and  $\ell$  separately.
- ▷ For atomic hydrogen ( $Z = 1$ ), the energy levels of the Hamiltonian (9.1) are given by

$$E_n = -\frac{\text{Ry}}{n^2}, \quad \text{Ry} = \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{m}{2\hbar^2} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a_0} = \frac{1}{2}mc^2\alpha^2,$$

where  $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m}$  is the Bohr radius,  $\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c}$  denotes the **fine structure constant**, and strictly speaking  $m$  represents the reduced mass of the electron and proton. Applied to single electron ions with higher atomic weight, such as  $\text{He}^+$ ,  $\text{Li}^{2+}$ , etc., the Bohr radius is reduced by a factor  $1/Z$ , where  $Z$  denotes the nuclear charge, and the energy is given by  $E_n = -\frac{Z^2}{n^2}\text{Ry} = -\frac{1}{2n^2}mc^2(Z\alpha)^2$ .

The fine structure constant is known to great accuracy and is given by,

$$\alpha = 7.297352570(5) \times 10^{-3} \\ = \frac{1}{137.035999070(9)}.$$

- ▷ Since  $n \geq 1$  and  $n_r \geq 0$ , the allowed combinations of quantum numbers are shown on the right, where we have introduced the conventional notation whereby values of  $\ell = 0, 1, 2, 3, 4 \dots$  are represented by letters  $s, p, d, f, g \dots$  respectively.
- ▷ Since  $E_n$  depends only on  $n$ , this implies, for example, an exact degeneracy of the  $2s$  and  $2p$ , and of the  $3s, 3p$  and  $3d$  levels.

$n$	$\ell$	Subshell(s)
1	0	1s
2	0, 1	2s 2p
3	0, 1, 2	3s 3p 3d
4	0, 1, 2, 3	4s 4p 4d 4f
$n$	$0 \dots (n - 1)$	$ns \dots$

These results emerge from a treatment of the hydrogen atom which is inherently non-relativistic. In fact, as we will see later in our discussion of the Dirac equation in chapter 15, the Hamiltonian (9.1) represents only the leading term in an expansion in  $v^2/c^2 \simeq (Z\alpha)^2$  of the full relativistic Hamiltonian (see below). Higher order terms provide relativistic corrections, which impact significantly in atomic and condensed matter physics, and lead to a lifting of the degeneracy. In the following we will discuss and obtain the hierarchy of leading relativistic corrections.<sup>1</sup> This discussion will provide a platform to describe multi-electron atoms.

To see that  $v^2/c^2 \simeq (Z\alpha)^2$ , we may invoke the **virial theorem**. The latter shows that the average kinetic energy is related to the potential energy as  $\langle T \rangle = -\frac{1}{2}\langle V \rangle$ . Therefore, the average energy is given by  $\langle E \rangle = \langle T \rangle + \langle V \rangle = -\langle T \rangle \equiv -\frac{1}{2}mv^2$ . We therefore have that  $\frac{1}{2}mv^2 = Ry \equiv \frac{1}{2}mc^2(Z\alpha)^2$  from which follows the relation  $v^2/c^2 \simeq (Z\alpha)^2$ .

## 9.1 The “real” hydrogen atom

The relativistic corrections (sometimes known as the **fine-structure corrections**) to the spectrum of hydrogen-like atoms derive from three different sources:

- ▷ relativistic corrections to the kinetic energy;
- ▷ coupling between spin and orbital degrees of freedom;
- ▷ and a contribution known as the Darwin term.

In the following, we will discuss each of these corrections in turn.

### 9.1.1 Relativistic correction to the kinetic energy

Previously, we have taken the kinetic energy to have the familiar non-relativistic form,  $\frac{\hat{\mathbf{p}}^2}{2m}$ . However, from the expression for the relativistic energy-momentum invariant, we can already anticipate that the leading correction to the non-relativistic Hamiltonian appears at order  $\mathbf{p}^4$ ,

$$E = (p_\mu p^\mu)^{1/2} = \sqrt{\mathbf{p}^2 c^2 + m^2 c^4} = mc^2 + \frac{\mathbf{p}^2}{2m} - \frac{1}{8} \frac{(\mathbf{p}^2)^2}{m^3 c^2} + \dots$$

As a result, we can infer the following perturbation to the kinetic energy of the electron,

$$\hat{H}_1 = -\frac{1}{8} \frac{(\hat{\mathbf{p}}^2)^2}{m^3 c^2}.$$

When compared with the non-relativistic kinetic energy,  $\mathbf{p}^2/2m$ , one can see that the perturbation is smaller by a factor of  $p^2/m^2 c^2 = v^2/c^2 \simeq (Z\alpha)^2$ , i.e.  $\hat{H}_1$  is only a small perturbation for small atomic number,  $Z \ll 1/\alpha \simeq 137$ .

<sup>1</sup>It may seem odd to discuss relativistic corrections in advance of the Dirac equation and the relativistic formulation of quantum mechanics. However, such a discussion would present a lengthy and unnecessarily complex digression which would not lead to further illumination. We will therefore follow the normal practice of discussing relativistic corrections as perturbations to the familiar non-relativistic theory.

We can therefore make use of a perturbative analysis to estimate the scale of the correction.

In principle, the large-scale degeneracy of the hydrogen atom would demand an analysis based on the degenerate perturbation theory. However, fortunately, since the off-diagonal matrix elements vanish,<sup>2</sup>

$$\langle n\ell m | \hat{H}_1 | n\ell' m' \rangle = 0 \quad \text{for } \ell \neq \ell' \quad \text{or} \quad m \neq m',$$

degenerate states are uncoupled and such an approach is unnecessary. Then making use of the identity,  $\hat{H}_1 = -\frac{1}{2mc^2} [\hat{H}_0 - V(r)]^2$ , the scale of the resulting energy shift can be obtained from first order perturbation theory,

$$\langle \hat{H}_1 \rangle_{n\ell m} \equiv \langle n\ell m | \hat{H}_1 | n\ell m \rangle = -\frac{1}{2mc^2} (E_n^2 - 2E_n \langle V(r) \rangle_{n\ell} + \langle V^2(r) \rangle_{n\ell})^2.$$

Since the calculation of the resulting expectation values is not particularly illuminating, we refer to the literature for a detailed exposition<sup>3</sup> and present here only the required identities (right). From these considerations, we obtain the following expression for the first order energy shift,

$$\langle \hat{H}_1 \rangle_{n\ell m} = -\frac{mc^2}{2} \left( \frac{Z\alpha}{n} \right)^4 \left( \frac{n}{\ell + 1/2} - \frac{3}{4} \right). \quad (9.2)$$

From this term alone, we expect the degeneracy between states with different values of total angular momentum  $\ell$  to be lifted. However, as we will see, this conclusion is a little hasty. We need to gather all terms of the same order of perturbation theory before we can reach a definite conclusion. We can, however, confirm that (as expected) the scale of the correction is of order  $\frac{\langle \hat{H}_1 \rangle_{n\ell m}}{E_n} \sim \left( \frac{Z\alpha}{n} \right)^2$ . We now turn to the second important class of corrections.

### 9.1.2 Spin-orbit coupling

As well as revealing the existence of an internal spin degree of freedom, the relativistic formulation of quantum mechanics shows that there is a further relativistic correction to the Schrödinger operator which involves a coupling between the spin and orbital degrees of freedom. For a general potential  $V(r)$ , this spin-orbit coupling takes the form,

$$\hat{H}_2 = \frac{1}{2m^2c^2} \frac{1}{r} (\partial_r V(r)) \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}.$$

For a hydrogen-like atom,  $V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$ , and

$$\hat{H}_2 = \frac{1}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}.$$

▷ INFO. Physically, the **origin of the spin-orbit interaction** can be understood from the following considerations. As the electron is moving through the electric field of the nucleus then, in its rest frame, it will experience this as a magnetic field. There will be an additional energy term in the Hamiltonian associated with the orientation of the spin magnetic moment with respect to this field. We can make an estimate of the spin-orbit interaction energy as follows: If we have a central field determined by an electrostatic potential  $V(r)$ , the corresponding electric field is given

<sup>2</sup>The proof runs as follows: Since  $[\hat{H}_1, \hat{\mathbf{L}}^2] = 0$ ,  $\hbar^2 [\ell'(\ell' + 1) - \ell(\ell + 1)] \langle n\ell m | \hat{H}_1 | n\ell' m' \rangle = 0$ . Similarly, since  $[\hat{H}_1, \hat{L}_z] = 0$ ,  $\hbar(m' - m) \langle n\ell m | \hat{H}_1 | n\ell' m' \rangle = 0$ .

<sup>3</sup>see, e.g., Ref [1].

By making use of the form of the radial wavefunction for the hydrogen atom, one may obtain the identities,

$$\left\langle \frac{1}{r} \right\rangle_{n\ell} = \frac{Z}{a_0 n^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle_{n\ell} = \frac{Z^2}{a_0^2 n^3 (\ell + 1/2)}.$$

by  $\mathbf{E} = -\nabla V(r) = -\mathbf{e}_r(\partial_r V)$ . For an electron moving at velocity  $\mathbf{v}$ , this translates to an effective magnetic field  $\mathbf{B} = \frac{1}{c^2}\mathbf{v} \times \mathbf{E}$ . The magnetic moment of the electron associated with its spin is equal to  $\boldsymbol{\mu}_s = g_s \frac{q}{2m}\mathbf{S} \equiv -\frac{e}{m}\mathbf{S}$ , and thus the interaction energy is given by

$$-\boldsymbol{\mu}_s \cdot \mathbf{B} = \frac{e}{mc^2}\mathbf{S} \cdot (\mathbf{v} \times \mathbf{E}) = -\frac{e}{(mc)^2}\mathbf{S} \cdot (\mathbf{p} \times \mathbf{e}_r(\partial_r V)) = \frac{e}{(mc)^2} \frac{1}{r}(\partial_r V) \mathbf{L} \cdot \mathbf{S},$$

where we have used the relation  $\mathbf{p} \times \mathbf{e}_r = \mathbf{p} \times \frac{\mathbf{r}}{r} = -\frac{\mathbf{L}}{r}$ . In fact this isn't quite correct; there is a relativistic effect connected with the precession of axes under rotation, called **Thomas precession** which multiplies the formula by a further factor of  $\frac{1}{2}$ .

Once again, we can estimate the effect of spin-orbit coupling by treating  $\hat{H}_2$  as a perturbation. In the absence of spin-orbit interaction, one may express the eigenstates of hydrogen-like atoms in the basis states of the mutually commuting operators,  $\hat{H}_0$ ,  $\hat{\mathbf{L}}^2$ ,  $\hat{L}_z$ ,  $\hat{\mathbf{S}}^2$ , and  $\hat{S}_z$ . However, in the presence of spin-orbit coupling, the total Hamiltonian no longer commutes with  $\hat{L}_z$  or  $\hat{S}_z$  (exercise). It is therefore helpful to make use of the degeneracy of the unperturbed Hamiltonian to switch to a new basis in which the angular momentum components of the perturbed system are diagonal. This can be achieved by turning to the basis of eigenstates of the operators,  $\hat{H}_0$ ,  $\hat{\mathbf{J}}^2$ ,  $\hat{J}_z$ ,  $\hat{\mathbf{L}}^2$ , and  $\hat{\mathbf{S}}^2$ , where  $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$  denotes the total angular momentum. (For a discussion of the form of these basis states, we refer back to section 6.4.2.)

Making use of the relation,  $\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ , in this basis, it follows that,

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2).$$

Combining the spin and angular momentum, the total angular momentum takes values  $j = \ell \pm 1/2$ . The corresponding basis states  $|j = \ell \pm 1/2, m_j, \ell\rangle$  (with  $s = 1/2$  implicit) therefore diagonalize the operator,

$$\hat{\mathbf{S}} \cdot \hat{\mathbf{L}}|j = \ell \pm 1/2, m_j, \ell\rangle = \frac{\hbar^2}{2} \begin{pmatrix} \ell \\ -\ell - 1 \end{pmatrix} |j = \ell \pm 1/2, m_j, \ell\rangle,$$

where the brackets index  $j = \ell + 1/2$  (top) and  $j = \ell - 1/2$  (bottom). As for the radial dependence of the perturbation, once again, the off-diagonal matrix elements vanish circumventing the need to invoke degenerate perturbation theory. As a result, at first order in perturbation theory, one obtains

$$\langle H_2 \rangle_{n,j=\ell \pm 1/2, m_j, \ell} = \frac{1}{2m^2c^2} \frac{\hbar^2}{2} \begin{pmatrix} \ell \\ -\ell - 1 \end{pmatrix} \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r^3} \right\rangle_{n\ell}.$$

Then making use of the identity (right),<sup>4</sup> one obtains

$$\langle \hat{H}_2 \rangle_{n,j=\ell \pm 1/2, m_j, \ell} = \frac{1}{4}mc^2 \left( \frac{Z\alpha}{n} \right)^4 \frac{n}{j + 1/2} \begin{pmatrix} \frac{1}{j} \\ -\frac{1}{j+1} \end{pmatrix}.$$

Note that, for  $\ell = 0$ , there is no orbital angular momentum with which to couple! Then, if we rewrite the expression for  $\langle \hat{H}_1 \rangle$  (9.2) in the new basis,

$$\langle \hat{H}_1 \rangle_{n,j=\ell \pm 1/2, m_j, \ell} = -\frac{1}{2}mc^2 \left( \frac{Z\alpha}{n} \right)^4 n \begin{pmatrix} \frac{1}{j} \\ \frac{1}{j+1} \end{pmatrix},$$

and combining both of these expressions, for  $\ell > 0$ , we obtain

$$\langle \hat{H}_1 + \hat{H}_2 \rangle_{n,j=\ell \pm 1/2, m_j, \ell} = \frac{1}{2}mc^2 \left( \frac{Z\alpha}{n} \right)^4 \left( \frac{3}{4} - \frac{n}{j + 1/2} \right),$$

while for  $\ell = 0$ , we retain just the kinetic energy term (9.2).

For  $\ell > 0$ ,

$$\left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \left( \frac{m\alpha Z}{\hbar n} \right)^3 \frac{1}{\ell(\ell + \frac{1}{2})(\ell + 1)}.$$

<sup>4</sup>For details see, e.g., Ref [1].

### 9.1.3 Darwin term

The final contribution to the Hamiltonian from relativistic effects is known as the Darwin term and arises from the “**Zitterbewegung**” of the electron – trembling motion – which smears the effective potential felt by the electron. Such effects lead to a perturbation of the form,

$$\hat{H}_3 = \frac{\hbar^2}{8m^2c^2} \nabla^2 V = \frac{\hbar^2}{8m^2c^2} \left( \frac{e}{\epsilon_0} Q_{\text{nuclear}}(\mathbf{r}) \right) = \frac{Ze^2}{4\pi\epsilon_0} \frac{\hbar^2}{8(mc)^2} 4\pi\delta^{(3)}(\mathbf{r}),$$

where  $Q_{\text{nuclear}}(\mathbf{r}) = Ze\delta^{(3)}(\mathbf{r})$  denotes the nuclear charge density. Since the perturbation acts only at the origin, it effects only states with  $\ell = 0$ . As a result, one finds that

$$\langle \hat{H}_3 \rangle_{njm_j\ell} = \frac{Ze^2}{4\pi\epsilon_0} \frac{\hbar^2}{8(mc)^2} 4\pi |\psi_{\ell n}(0)|^2 = \frac{1}{2} mc^2 \left( \frac{Z\alpha}{n} \right)^4 n\delta_{\ell,0}.$$

Intriguingly, this term is formally identical to that which would be obtained from  $\langle \hat{H}_2 \rangle$  at  $\ell = 0$ . As a result, combining all three contributions, the total energy shift is given simply by

$$\boxed{\Delta E_{n,j=\ell\pm 1/2,m_j,\ell} = \frac{1}{2} mc^2 \left( \frac{Z\alpha}{n} \right)^4 \left( \frac{3}{4} - \frac{n}{j+1/2} \right)}, \quad (9.3)$$

a result that is independent of  $\ell$  and  $m_j$ .

To discuss the predicted energy shifts for particular states, it is helpful to introduce some nomenclature from atomic physics. For a state with principle quantum number  $n$ , total spin  $s$ , orbital angular momentum  $\ell$ , and total angular momentum  $j$ , one may use **spectroscopic notation**  $n^{2s+1}L_j$  to define the state. For a hydrogen-like atom, with just a single electron,  $2s + 1 = 2$ . In this case, the factor  $2s + 1$  is often just dropped for brevity.

If we apply our perturbative expression for the relativistic corrections (9.3), how do we expect the levels to shift for hydrogen-like atoms? As we have seen, for the non-relativistic Hamiltonian, each state of given  $n$  exhibits a  $2n^2$ -fold degeneracy. For a given multiplet specified by  $n$ , the relativistic corrections depend only on  $j$  and  $n$ . For  $n = 1$ , we have  $\ell = 0$  and  $j = 1/2$ : Both  $1S_{1/2}$  states, with  $m_j = 1/2$  and  $-1/2$ , experience a negative energy shift by an amount  $\Delta E_{1,1/2,m_j,0} = -\frac{1}{4}Z^4\alpha^2 \text{Ry}$ . For  $n = 2$ ,  $\ell$  can take the values of 0 or 1. With  $j = 1/2$ , both the former  $2S_{1/2}$  state, and the latter  $2P_{1/2}$  states share the same negative shift in energy,  $\Delta E_{2,1/2,m_j,0} = \Delta E_{2,1/2,m_j,1} = -\frac{5}{64}Z^4\alpha^2 \text{Ry}$ , while the  $2P_{3/2}$  experiences a shift of  $\Delta E_{2,3/2,m_j,1} = -\frac{1}{64}Z^4\alpha^2 \text{Ry}$ . Finally, for  $n = 3$ ,  $\ell$  can take values of 0, 1 or 2. Here, the pairs of states  $3S_{1/2}$  and  $3P_{1/2}$ , and  $3P_{3/2}$  and  $2D_{3/2}$  each remain degenerate while the state  $3D_{5/2}$  is unique. These predicted shifts are summarized in Figure 9.1.

This completes our discussion of the relativistic corrections which develop from the treatment of the Dirac theory for the hydrogen atom. However, this does not complete our description of the “real” hydrogen atom. Indeed, there are further corrections which derive from quantum electrodynamics and nuclear effects which we now turn to address.

### 9.1.4 Lamb shift

According to the perturbation theory above, the relativistic corrections which follow from the Dirac theory for hydrogen leave the  $2S_{1/2}$  and  $2P_{1/2}$  states degenerate. However, in 1947, a careful experimental study by Willis Lamb

#### Willis Eugene Lamb, 1913-2008

A physicist who won the Nobel Prize in Physics in 1955 “for his discoveries concerning the fine structure of the hydrogen spectrum”. Lamb and Polykarp Kusch were able to precisely determine certain electromagnetic properties of the electron.



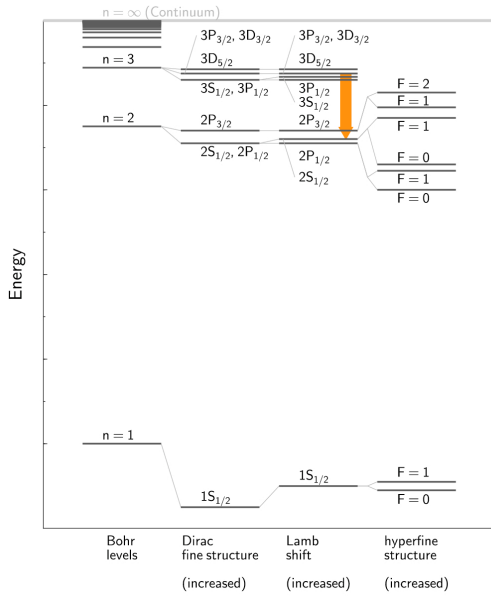


Figure 9.1: Figure showing the heirarchy of energy shifts of the spectra of hydrogen-like atoms as a result of relativistic corrections. The first column shows the energy spectrum predicted by the (non-relativistic) Bohr theory. The second column shows the predicted energy shifts from relativistic corrections arising from the Dirac theory. The third column includes corrections due quantum electrodynamics and the fourth column includes terms for coupling to the nuclear spin degrees of freedom. The H- $\alpha$  line, particularly important in the astronomy, corresponds to the transition between the levels with  $n = 2$  and  $n = 3$ .

and Robert Retherford discovered that this was not in fact the case:<sup>5</sup>  $2P_{1/2}$  state is slightly lower in energy than the  $2S_{1/2}$  state resulting in a small shift of the corresponding spectral line – the Lamb shift. It might seem that such a tiny effect would be deemed insignificant, but in this case, the observed shift (which was explained by Hans Bethe in the same year) provided considerable insight into quantum electrodynamics.

In quantum electrodynamics, a quantized radiation field has a zero-point energy equivalent to the mean-square electric field so that even in a vacuum there are fluctuations. These fluctuations cause an electron to execute an oscillatory motion and its charge is therefore smeared. If the electron is bound by a non-uniform electric field (as in hydrogen), it experiences a different potential from that appropriate to its mean position. Hence the atomic levels are shifted. In hydrogen-like atoms, the smearing occurs over a length scale,

$$\langle(\delta\mathbf{r})^2\rangle \simeq \frac{2\alpha}{\pi} \left(\frac{\hbar}{mc}\right)^2 \ln \frac{1}{\alpha Z},$$

some five orders of magnitude smaller than the Bohr radius. This causes the electron spin  $g$ -factor to be slightly different from 2,

$$g_s = 2 \left(1 + \frac{\alpha}{2\pi} - 0.328 \frac{\alpha^2}{\pi^2} + \dots\right).$$


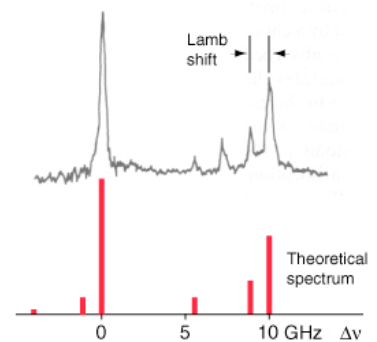
There is also a slight weakening of the force on the electron when it is very close to the nucleus, causing the  $2S_{1/2}$  electron (which has penetrated all the way to the nucleus) to be slightly higher in energy than the  $2P_{1/2}$  electron. Taking into account these corrections, one obtains a positive energy shift

$$\Delta E_{\text{Lamb}} \simeq \left(\frac{Z}{n}\right)^4 n\alpha^2 \text{Ry} \times \left(\frac{8}{3\pi}\alpha \ln \frac{1}{\alpha Z}\right) \delta_{\ell,0},$$

for states with  $\ell = 0$ .

<sup>5</sup>W. E. Lamb and R. C. Retherford, *Fine Structure of the Hydrogen Atom by a Microwave Method*, Phys. Rev. **72**, 241 (1947).

**Hans Albrecht Bethe 1906-2005**  
 A German-American physicist, and Nobel laureate in physics “for his work on the theory of stellar nucleosynthesis.” A versatile theoretical physicist, Bethe also made important contributions to quantum electrodynamics, nuclear physics, solid-state physics and particle astrophysics. During World War II, he was head of the Theoretical Division at the secret Los Alamos laboratory developing the first atomic bombs. There he played a key role in calculating the critical mass of the weapons, and did theoretical work on the implosion method used in both the Trinity test and the “Fat Man” weapon dropped on Nagasaki.

Hydrogen fine structure and hyperfine structure for the  $n = 3$  to  $n = 2$  transition (see Fig. 9.1).

### 9.1.5 Hyperfine structure

So far, we have considered the nucleus as simply a massive point charge responsible for the large electrostatic interaction with the charged electrons which surround it. However, the nucleus has a spin angular momentum which is associated with a further set of **hyperfine corrections** to the atomic spectra of atoms. As with electrons, the protons and neutrons that make up a nucleus are fermions, each with intrinsic spin  $1/2$ . This means that a nucleus will have some total nuclear spin which is labelled by the quantum number,  $I$ . The latter leads to a nuclear magnetic moment,

$$\boldsymbol{\mu}_N = g_N \frac{Ze}{2M_N} \mathbf{I}.$$

where  $M_N$  denotes the mass of the nucleus, and  $g_N$  denotes the gyromagnetic ratio. Since the nucleus has internal structure, the nuclear gyromagnetic ratio is not simply 2 as it (nearly) is for the electron. For the proton, the sole nuclear constituent of atomic hydrogen,  $g_P \approx 5.56$ . Even though the neutron is charge neutral, its gyromagnetic ratio is about  $-3.83$ . (The constituent quarks have gyromagnetic ratios of 2 (plus corrections) like the electron but the problem is complicated by the strong interactions which make it hard to define a quark’s mass.) We can compute (to some accuracy) the gyromagnetic ratio of nuclei from that of protons and neutrons as we can compute the proton’s gyromagnetic ratio from its quark constituents. Since the nuclear mass is several orders of magnitude higher than that of the electron, the nuclear magnetic moment provides only a small perturbation.

According to classical electromagnetism, the magnetic moment generates a magnetic field

$$\mathbf{B} = \frac{\mu_0}{4\pi r^3} (3(\boldsymbol{\mu}_N \cdot \mathbf{e}_r)\mathbf{e}_r - \boldsymbol{\mu}_N) + \frac{2\mu_0}{3} \boldsymbol{\mu}_N \delta^{(3)}(\mathbf{r}).$$

To explore the effect of this field, let us consider just the  $s$ -electrons, i.e.  $\ell = 0$ , for simplicity.<sup>6</sup> In this case, the interaction of the magnetic moment of the electrons with the field generated by the nucleus, gives rise to the hyperfine interaction,

$$\hat{H}_{\text{hyp}} = -\boldsymbol{\mu}_e \cdot \mathbf{B} = \frac{e}{mc} \hat{\mathbf{S}} \cdot \mathbf{B}.$$

For the  $\ell = 0$  state, the first contribution to  $\mathbf{B}$  vanishes while second leads to the first order correction,

$$\langle H_{\text{hyp}} \rangle_{n,1/2,0} = \left(\frac{Z}{n}\right)^4 n\alpha^2 \text{Ry} \times \frac{8}{3} g_N \frac{m}{M_N} \frac{1}{\hbar^2} \mathbf{S} \cdot \mathbf{I}.$$

Once again, to evaluate the expectation values on the spin degrees of freedom, it is convenient to define the total spin  $\mathbf{F} = \mathbf{I} + \mathbf{S}$ . We then have

$$\begin{aligned} \frac{1}{\hbar^2} \mathbf{S} \cdot \mathbf{I} &= \frac{1}{2\hbar^2} (\mathbf{F}^2 - \mathbf{S}^2 - \mathbf{I}^2) = \frac{1}{2} (F(F+1) - 3/4 - I(I+1)) \\ &= \frac{1}{2} \begin{cases} I & F = I + 1/2 \\ -I - 1 & F = I - 1/2 \end{cases} \end{aligned}$$

Therefore, the  $1s$  state of Hydrogen is split into two, corresponding to the two possible values  $F = 0$  and  $1$ . The transition between these two levels has frequency  $1420$  Hz, or wavelength  $21$  cm, so lies in the radio waveband. It

<sup>6</sup>For a full discussion of the influence of the orbital angular momentum, we refer to Ref. [6].

is an important transition for radio astronomy. A further contribution to the hyperfine structure arises if the **nuclear shape** is not spherical thus distorting the Coulomb potential; this occurs for deuterium and for many other nuclei.

Finally, before leaving this section, we should note that the nucleus is not point-like but has a small size. The effect of **finite nuclear size** can be estimated perturbatively. In doing so, one finds that the  $s$  ( $\ell = 0$ ) levels are those most effected, because these have the largest probability of finding the electron close to the nucleus; but the effect is still very small in hydrogen. It can be significant, however, in atoms of high nuclear charge  $Z$ , or for **muonic** atoms.

A **muon** is a particle somewhat like an electron, but about 200 times heavier. If a muon is captured by an atom, the corresponding Bohr radius is 200 times smaller, thus enhancing the nuclear size effect.

This completes our discussion of the “one-electron” theory. We now turn to consider the properties of multi-electron atoms.

## 9.2 Multi-electron atoms

To address the electronic structure of a multi-electron atom, we might begin with the hydrogenic energy levels for an atom of nuclear charge  $Z$ , and start filling the lowest levels with electrons, accounting for the exclusion principle. The degeneracy for quantum numbers  $(n, \ell)$  is  $2 \times (2\ell + 1)$ , where  $(2\ell + 1)$  is the number of available  $m_\ell$  values, and the factor of 2 accounts for the spin degeneracy. Hence, the number of electrons accommodated in shell,  $n$ , would be  $2 \times n^2$ ,

$n$	$\ell$	Degeneracy in shell	Cumulative total
1	0	2	2
2	0, 1	$(1 + 3) \times 2 = 8$	10
3	0, 1, 2	$(1 + 3 + 5) \times 2 = 18$	28
4	0, 1, 2, 3	$(1 + 3 + 5 + 7) \times 2 = 32$	60

We would therefore expect that atoms containing 2, 10, 28 or 60 electrons would be especially stable, and that in atoms containing one more electron than this, the outermost electron would be less tightly bound. In fact, if we look at data (Fig. 9.2) recording the first ionization energy of atoms, i.e. the minimum energy needed to remove one electron, we find that the noble gases, having  $Z = 2, 10, 18, 36 \dots$  are especially tightly bound, and the elements containing one more electron, the alkali metals, are significantly less tightly bound.

The reason for the failure of this simple-minded approach is fairly obvious – we have neglected the repulsion between electrons. In fact, the first ionization energies of atoms show a relatively weak dependence on  $Z$ ; this tells us that the outermost electrons are almost completely shielded from the nuclear charge.<sup>7</sup> Indeed, when we treated the Helium atom as an example of the variational method in chapter 7, we found that the effect of electron-electron repulsion was sizeable, and really too large to be treated accurately by perturbation theory.

<sup>7</sup>In fact, the shielding is not completely perfect. For a given energy shell, the effective nuclear charge varies for an atomic number  $Z$  as  $Z_{\text{eff}} \sim (1 + \alpha)^Z$  where  $\alpha > 0$  characterizes the ineffectiveness of screening. This implies that the ionization energy  $I_Z = -E_Z \sim Z_{\text{eff}}^2 \sim (1 + 2\alpha Z)$ . The near-linear dependence of  $I_Z$  on  $Z$  is reflected in Fig. 9.2.



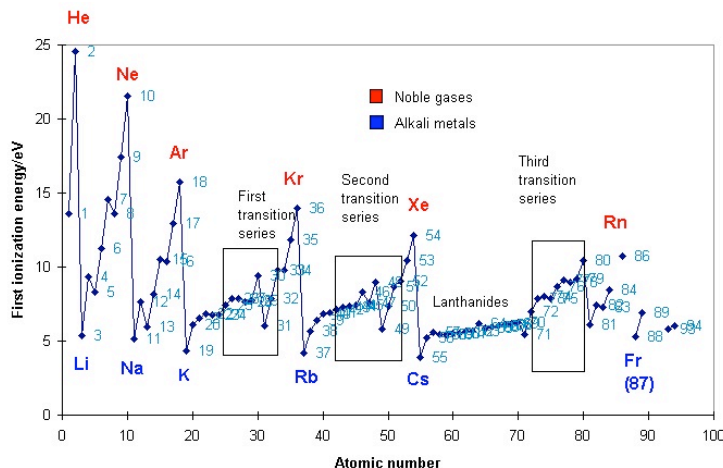


Figure 9.2: Ionization energies of the elements.

### 9.2.1 Central field approximation

Leaving aside for now the influence of spin or relativistic effects, the Hamiltonian for a multi-electron atom can be written as

$$\hat{H} = \sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} \right] + \sum_{i<j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}},$$

where  $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$ . The first term represents the “single-particle” contribution to the Hamiltonian arising from interaction of each electron with the nucleus, while the last term represents the mutual Coulomb interaction between the constituent electrons. It is this latter term that makes the generic problem “many-body” in character and therefore very complicated. Yet, as we have already seen in the perturbative analysis of the excited states of atomic Helium, this term can have important physical consequences both on the overall energy of the problem and on the associated spin structure of the states.

The **central field approximation** is based upon the observation that the electron interaction term contains a large central (spherically symmetric) component arising from the “core electrons”. From the following relation,

$$\sum_{m=-\ell}^{\ell} |Y_{\ell m}(\theta, \phi)|^2 = \text{const.}$$

it is apparent that a **closed shell** has an electron density distribution which is isotropic (independent of  $\theta$  and  $\phi$ ). We can therefore develop a perturbative scheme by setting  $\hat{H} = \hat{H}_0 + \hat{H}_1$ , where

$$\hat{H}_0 = \sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} + U_i(r_i) \right], \quad \hat{H}_1 = \sum_{i<j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r_i).$$

Here the one-electron potential,  $U_i(r)$ , which is assumed central (see below), incorporates the “average” effect of the other electrons. Before discussing how to choose the potentials  $U_i(r)$ , let us note that  $\hat{H}_0$  is separable into a sum of terms for each electron, so that the total wavefunction can be factorized into components for each electron. The basic idea is first to solve the Schrödinger equation using  $\hat{H}_0$ , and then to treat  $\hat{H}_1$  as a small perturbation.

On general grounds, since the Hamiltonian  $\hat{H}_0$  continues to commute with the angular momentum operator,  $[\hat{H}_0, \hat{\mathbf{L}}] = 0$ , we can see that the eigenfunctions of  $\hat{H}_0$  will be characterized by quantum numbers  $(n, \ell, m_\ell, m_s)$ . However,

since the effective potential is no longer Coulomb-like, the  $\ell$  values for a given  $n$  need not be degenerate. Of course, the difficult part of this procedure is to estimate  $U_i(r)$ ; the potential energy experienced by each electron depends on the wavefunction of all the other electrons, which is only known after the Schrödinger equation has been solved. This suggests that an iterative approach to solving the problem will be required.

To understand how the potentials  $U_i(\mathbf{r})$  can be estimated – the **self-consistent field method** – it is instructive to consider a variational approach due originally to Hartree. If electrons are considered independent, the wavefunction can be factorized into the product state,

$$\Psi(\{\mathbf{r}_i\}) = \psi_{i_1}(\mathbf{r}_1)\psi_{i_2}(\mathbf{r}_2)\cdots\psi_{i_N}(\mathbf{r}_N),$$

where the quantum numbers,  $i_k \equiv (n\ell m_\ell m_s)_k$ , indicate the individual state occupancies. Note that this product state is not a properly antisymmetrized Slater determinant – the exclusion principle is taken into account only in so far as the energy of the ground state is taken to be the lowest that is consistent with the assignment of different quantum numbers,  $n\ell m_\ell m_s$  to each electron. Nevertheless, using this wavefunction as a trial state, the variational energy is then given by

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_i \int d^3r \psi_i^* \left( -\frac{\hbar^2 \nabla^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right) \psi_i + \frac{1}{4\pi\epsilon_0} \sum_{i < j} \int d^3r \int d^3r' \psi_i^*(\mathbf{r}) \psi_i^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_j(\mathbf{r}') \psi_i(\mathbf{r}).$$

Now, according to the variational principle, we must minimize the energy functional by varying  $E[\{\psi_i\}]$  with respect to the complex wavefunction,  $\psi_i$ , subject to the normalization condition,  $\langle \psi_i | \psi_i \rangle = 1$ . The latter can be imposed using a set of Lagrange multipliers,  $\varepsilon_i$ , i.e.

$$\frac{\delta}{\delta \psi_i^*} \left[ E - \varepsilon_i \left( \int d^3r |\psi_i(\mathbf{r})|^2 - 1 \right) \right] = 0.$$

Following the variation,<sup>8</sup> one obtains the **Hartree equations**,

$$\left( -\frac{\hbar^2 \nabla^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right) \psi_i + \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r' |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (9.4)$$

Then according to the variational principle, amongst all possible trial functions  $\psi_i$ , the set that minimizes the energy are determined by the effective potential,

$$U_i(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r' |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}.$$

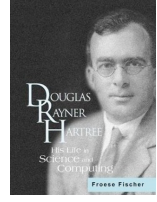
Equation (9.4) has a simple interpretation: The first two terms relate to the nuclear potential experienced by the individual electrons, while the third term represents the electrostatic potential due to the other electrons. However, to simplify the procedure, it is useful to engineer the radial symmetry of the potential by replacing  $U_i(\mathbf{r})$  by its spherical average,

$$U_i(\mathbf{r}) \mapsto U_i(r) = \int \frac{d\Omega}{4\pi} U_i(\mathbf{r}).$$

<sup>8</sup>Note that, in applying the variation, the wavefunction  $\psi_i^*$  can be considered independent of  $\psi_i$  – you might like to think why.

### Douglas Rayner Hartree FRS 1897-1958

An English mathematician and physicist most famous for the development of numerical analysis and its application to atomic physics.



He entered St John's College Cambridge in 1915 but World War I interrupted his studies and he joined a team studying anti-aircraft gunnery. He returned to Cambridge after the war and graduated in 1921 but, perhaps because of his interrupted studies, he only obtained a second class degree in Natural Sciences. In 1921, a visit by Niels Bohr to Cambridge inspired him to apply his knowledge of numerical analysis to the solution of differential equations for the calculation of atomic wavefunctions.

Finally, to relate the Lagrange multipliers,  $\epsilon_i$  (which have the appearance of one-electron energies), to the total energy, we can multiply Eq. (9.4) by  $\psi_i^*(\mathbf{r})$  and integrate,

$$\begin{aligned} \epsilon_i = \int d^3r \psi_i^* \left( -\frac{\hbar^2 \nabla^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right) \psi_i \\ + \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r' d^3r |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\psi_i(\mathbf{r})|^2. \end{aligned}$$

If we compare this expression with the variational state energy, we find that

$$E = \sum_i \epsilon_i - \frac{1}{4\pi\epsilon_0} \sum_{i < j} \int d^3r' d^3r |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\psi_i(\mathbf{r})|^2. \quad (9.5)$$

To summarize, if we wish to implement the central field approximation to determine the states of a multi-electron atom, we must follow the algorithm:

1. Firstly, one makes an initial “guess” for a (common) central potential,  $U(r)$ . As  $r \rightarrow 0$ , screening becomes increasingly ineffective and we expect  $U(r) \rightarrow 0$ . As  $r \rightarrow \infty$ , we anticipate that  $U(r) \rightarrow \frac{1}{4\pi\epsilon_0} \frac{(Z-1)e^2}{r}$ , corresponding to perfect screening. So, as a starting point, we make take some smooth function  $U(r)$  interpolating between these limits. For this trial potential, we can solve (numerically) for the eigenstates of the single-particle Hamiltonian. We can then use these states as a platform to build the product wavefunction and in turn determine the self-consistent potentials,  $U_i(r)$ .
2. With these potentials,  $U_i(r)$ , we can determine a new set of eigenstates for the set of Schrödinger equations,

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} + U_i(r) \right] \psi_i = \epsilon_i \psi_i.$$

3. An estimate for the ground state energy of an atom can be found by filling up the energy levels, starting from the lowest, and taking account of the exclusion principle.
4. Using these wavefunctions, one can then make an improved estimate of the potentials  $U_i(r_i)$  and return to step 2 iterating until convergence.

Since the practical implementation of such an algorithm demands a large degree of computational flair, if you remain curious, you may find it useful to refer to the Mathematica code prepared by Ref. [4] where both the Hartree and the Hartree-Fock procedures (described below) are illustrated.

▷ INFO. An improvement to this procedure, known the **Hartree-Fock** method, takes account of exchange interactions. In order to do this, it is necessary to ensure that the wavefunction, including spin, is antisymmetric under interchange of any pair of electrons. This is achieved by introducing the **Slater determinant**. Writing the individual electron wavefunction for the  $i^{\text{th}}$  electron as  $\psi_k(\mathbf{r}_i)$ , where  $i = 1, 2 \dots N$  and  $k$  is shorthand for the set of quantum numbers ( $n\ell m_\ell m_s$ ), the overall wavefunction is given by

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \psi_1(\mathbf{r}_3) & \cdots \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \psi_2(\mathbf{r}_3) & \cdots \\ \psi_3(\mathbf{r}_1) & \psi_3(\mathbf{r}_2) & \psi_3(\mathbf{r}_3) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix}.$$

Note that each of the  $N!$  terms in  $\Psi$  is a product of wavefunctions for each individual electron. The  $1/\sqrt{N!}$  factor ensures the wavefunction is normalized. A determinant changes sign if any two columns are exchanged, corresponding to  $\mathbf{r}_i \leftrightarrow \mathbf{r}_j$  (say); this ensures that the wavefunction is antisymmetric under exchange of electrons  $i$  and  $j$ . Likewise, a determinant is zero if any two rows are identical; hence all the  $\psi_k$ s must be different and the Pauli exclusion principle is satisfied.<sup>9</sup> In this approximation, a variational analysis leads to the Hartree-Fock equations (exercise),

$$\begin{aligned} \epsilon_i \psi_i(\mathbf{r}) = & \left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon r_i} \right] \psi_i(\mathbf{r}) \\ & + \sum_{j \neq i} \int d^3r_j \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_j^*(\mathbf{r}') \left[ \psi_j(\mathbf{r}') \psi_i(\mathbf{r}) - \psi_j(\mathbf{r}) \psi_i(\mathbf{r}') \delta_{m_{s_i}, m_{s_j}} \right]. \end{aligned}$$

The first term in the last set of brackets translates to the ordinary Hartree contribution above and describes the influence of the charge density of the other electrons, while the second term describes the non-local **exchange** contribution, a manifestation of particle statistics.

The outcome of such calculations is that the eigenfunctions are, as for hydrogen, characterized by quantum numbers  $n, \ell, m_\ell$ , with  $\ell < n$ , but that the states with different  $\ell$  for a given  $n$  are not degenerate, with the lower values of  $\ell$  lying lower. This is because, for the higher  $\ell$  values, the electrons tend to lie further from the nucleus on average, and are therefore more effectively screened. The states corresponding to a particular value of  $n$  are generally referred to as a **shell**, and those belonging to a particular pair of values of  $n, \ell$  are usually referred to as a **subshell**. The energy levels are ordered as below (with the lowest lying on the left):

Subshell name	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	...
$n =$	1	2	2	3	3	4	3	4	5	4	...
$\ell =$	0	0	1	0	1	0	2	1	0	2	...
Degeneracy	2	2	6	2	6	2	10	6	2	10	...
Cumulative	2	4	10	12	18	20	30	36	38	48	...

Note that the values of  $Z$  corresponding to the noble gases, 2, 10, 18, 36, at which the ionization energy is unusually high, now emerge naturally from this filling order, corresponding to the numbers of electrons just before a new shell ( $n$ ) is entered. There is a handy mnemonic to remember this filling order. By writing the subshells down as shown right, the order of states can be read off along diagonals from lower right to upper left, starting at the bottom.

We can use this sequence of energy levels to predict the ground state electron configuration of atoms. We simply fill up the levels starting from the lowest, accounting for the exclusion principle, until the electrons are all accommodated (the **aufbau principle**). Here are a few examples:

Z	Element	Configuration	$^{2S+1}L_J$	Ioniz. Pot. (eV)
1	H	(1s)	$^2S_{1/2}$	13.6
2	He	(1s) <sup>2</sup>	$^1S_0$	24.6
3	Li	He (2s)	$^2S_{1/2}$	5.4
4	Be	He (2s) <sup>2</sup>	$^1S_0$	9.3
5	B	He (2s) <sup>2</sup> (2p)	$^2P_{1/2}$	8.3
6	C	He (2s) <sup>2</sup> (2p) <sup>2</sup>	$^3P_0$	11.3
7	N	He (2s) <sup>2</sup> (2p) <sup>3</sup>	$^4S_{3/2}$	14.5
8	O	He (2s) <sup>2</sup> (2p) <sup>4</sup>	$^3P_2$	13.6
9	F	He (2s) <sup>2</sup> (2p) <sup>5</sup>	$^2P_{3/2}$	17.4
10	Ne	He (2s) <sup>2</sup> (2p) <sup>6</sup>	$^1S_0$	21.6
11	Na	Ne (3s)	$^2S_{1/2}$	5.1

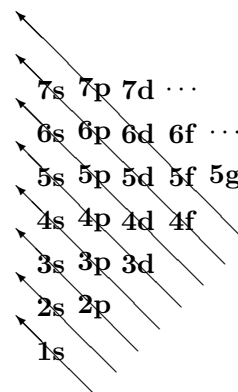
<sup>9</sup>Note that for  $N = 2$ , the determinant reduces to the familiar antisymmetric wavefunction,  $\frac{1}{\sqrt{2}}[\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)]$ .

**Vladimir Aleksandrovich Fock**  
1898-1974

A Soviet physicist, who did foundational work on quantum mechanics and quantum electrodynamics. His primary scientific contribution lies



in the development of quantum physics, although he also contributed significantly to the fields of mechanics, theoretical optics, theory of gravitation, physics of continuous medium. In 1926 he derived the Klein-Gordon equation. He gave his name to Fock space, the Fock representation and Fock state, and developed the Hartree-Fock method in 1930. Fock made significant contributions to general relativity theory, specifically for the many body problems.



**PERIODIC TABLE OF THE ELEMENTS**

http://www.kj-split.hr/periodic/en/

Legend:

- Metal (blue)
- Semimetal (orange)
- Nonmetal (green)
- Alkali metal (yellow)
- Alkaline earth metal (light blue)
- Transition metals (dark blue)
- Lanthanide (light purple)
- Actinide (dark purple)
- Chalcogens element (light green)
- Halogens element (yellow-green)
- Noble gas (light yellow)

Standard State (25 °C, 101 kPa):

- Ne - gas
- Fe - solid
- Br - liquid
- Li - solid
- Te - synthetic

(1) Pure Appl. Chem., 73, No. 4, 697-683 (2001)  
Relative atomic mass is shown with five significant figures. For elements with no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.  
However, these last elements (Tl, Pb, and Bi) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (advvar@rediffmail.com)

Figure 9.3: Periodic table of elements.

Since it is generally the outermost electrons which are of most interest, contributing to chemical activity or optical spectra, one often omits the inner closed shells, and just writes O as  $(2p)^4$ , for example. However, the configuration is not always correctly predicted, especially in the heavier elements, where levels may be close together. It may be favourable to promote one or even two electrons one level above that expected in this simple picture, in order to achieve a filled shell. For example, Cu ( $Z = 29$ ) would be expected to have configuration  $\dots(4s)^2(3d)^9$ , and actually has configuration  $\dots(4s)^1(3d)^{10}$ . There are several similar examples in the transition elements where the  $d$  subshells are being filled, and many among the lanthanides (rare earths) and actinides where  $f$  subshells are being filled.

▷ INFO. Since the assignment of an electron configuration requires only the enumeration of the values of  $n$  and  $\ell$  for all electrons, but not those of  $m_\ell$  and  $m_s$ , each configuration will be accompanied by a **degeneracy**  $g$ . If  $\nu_{n\ell}$  denotes the number of electrons occupying a given level  $E_{n,\ell}$ , and  $\delta_\ell = 2 \times (2\ell + 1)$  is the degeneracy of that level, there are

$$d_{n\ell} = \frac{\delta_\ell!}{\nu_{n\ell}!(\delta_\ell - \nu_{n\ell})!} \quad (9.6)$$

ways of distributing the  $\nu_{n\ell}$  electrons among the  $\delta_\ell$  individual states. The total degeneracy,  $g$ , is then obtained from the product.

This scheme provides a basis to understand the **periodic table of elements** (see Fig. 9.3). We would expect that elements which have similar electron configurations in their outermost shells (such as Li, Na, K, Rb, Cs, Fr which all have  $(ns)^1$  or F, Cl, Br, I, which all have  $(np)^5$ ) would have similar chemical properties, such as valency, since it is the unpaired outer electrons which especially participate in chemical bonding. Therefore, if one arranges the atoms in order of increasing atomic number  $Z$  (which equals the number of electrons in the atom), periodic behaviour is seen whenever a new subshell of a given  $\ell$  is filled.

### 9.3 Coupling schemes

The procedure outlined above allows us to predict the occupation of subshells in an atomic ground state. This is not in general sufficient to specify the ground state fully. If there are several electrons in a partially filled subshell, then their spins and orbital angular momenta can combine in several different ways, to give different values of total angular momentum, with different energies. In order to deal with this problem, it is necessary to consider the spin-orbit interaction as well as the residual Coulomb interaction between the outer electrons.

Schematically we can write the Hamiltonian for this system as follows:

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2},$$

where  $\hat{H}_0$  includes the kinetic energy and central field terms,  $\hat{H}_1$  is the residual Coulomb interaction, and (with  $\xi_i(r_i) = \frac{1}{2m^2c^2} \frac{1}{r} (\partial_r V(r))$ )  $\hat{H}_2$  is the spin-orbit interaction. We can then consider two possible scenarios:

$\hat{H}_1 \gg \hat{H}_2$ : This tends to apply in the case of light atoms. In this situation, one considers first the eigenstates of  $\hat{H}_0 + \hat{H}_1$ , and then treats  $\hat{H}_2$  as a perturbation. This leads to a scheme called **LS** (or **Russell-Saunders coupling**).

$\hat{H}_2 \gg \hat{H}_1$ : This can apply in very heavy atoms, or in heavily ionized light atoms, in which the electrons are moving at higher velocities and relativistic effects such as the spin-orbit interaction are more important. In this case, a scheme called ***jj* coupling** applies.

It is important to emphasise that both of these scenarios represent approximations; real atoms do not always conform to the comparatively simple picture which emerges from these schemes, which we now discuss in detail.

#### 9.3.1 LS coupling scheme

In this approximation, we start by considering the eigenstates of  $\hat{H}_0 + \hat{H}_1$ . We note that this Hamiltonian must commute with the total angular momentum  $\hat{\mathbf{J}}^2$  (because of invariance under rotations in space), and also clearly commutes with the total spin  $\hat{\mathbf{S}}^2$ . It also commutes with the total orbital angular momentum  $\hat{\mathbf{L}}^2$ , since  $\hat{H}_1$  only involves internal interactions, and must therefore be invariant under global rotation of all the electrons. Therefore the energy levels can be characterised by the corresponding total angular momentum quantum numbers  $L$ ,  $S$ ,  $J$ . Their ordering in energy is given by **Hund's rules**:

1. Combine the spins of the electrons to obtain possible values of total spin  $S$ . The largest permitted value of  $S$  lies lowest in energy.
2. For each value of  $S$ , find the possible values of total angular momentum  $L$ . The largest value of  $L$  lies lowest in energy.
3. Couple the values of  $L$  and  $S$  to obtain the values of  $J$  (hence the name of the scheme). If the subshell is less than half full, the smallest value of  $J$  lies lowest; otherwise, the largest value of  $J$  lies lowest.

In deciding on the permitted values of  $L$  and  $S$ , in addition to applying the usual rules for adding angular momenta, one also has to ensure that the exclusion principle is respected, as we will see later when considering some examples.

These rules are empirical; there are exceptions, especially to the  $L$  and  $J$  rules (2 and 3). Nevertheless, Hund's rules are a useful guide, and we should try to understand their physical origin.

1. Maximising  $S$  makes the spin wavefunction as symmetric as possible. This tends to make the spatial wavefunction antisymmetric, and hence reduces the Coulomb repulsion, as we saw when discussing the exchange interactions in Helium.
2. Maximising  $L$  also tends to keep the electrons apart. This is less obvious, though a simple classical picture of electrons rotating round the nucleus in the same or different senses makes it at least plausible.
3. The separation of energies for states of different  $J$  arises from treating the spin-orbit term  $\hat{H}_2$  as a perturbation (fine structure). It can be shown (using the Wigner-Eckart theorem – beyond the scope of these lectures) that

$$\begin{aligned} \langle J, m_J, L, S | \sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i | J, m_J, L, S \rangle \\ = \zeta(L, S) \langle J, m_J, L, S | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | J, m_J, L, S \rangle \\ = \frac{\zeta(L, S)}{2} [J(J+1) - L(L+1) - S(S+1)], \quad (9.7) \end{aligned}$$

where the matrix element  $\zeta(L, S)$  depends on the total  $L$  and  $S$  values. Since one may show that the sign of  $\zeta(L, S)$  changes according to the whether the subshell is more or less than half-filled, the third Hund's rule is established.

To understand the application of LS coupling, it is best to work through some examples. Starting with the simplest multi-electron atom, **helium**, the ground state has an electron configuration  $(1s)^2$ , and must therefore have  $L = S = J = 0$ . In fact, for any completely filled subshell, we have  $L = S = 0$  and hence  $J = 0$ , since the total  $m_L$  and  $m_S$  must equal zero if all substates are occupied. Consider now an excited state of helium, e.g.  $(1s)^1(2p)^1$ , in which one electron has been excited to the  $2p$  level. We can now have  $S = 1$  or  $S = 0$ , with the  $S = 1$  state lying lower in energy according to Hund's rules. Combining the orbital angular momenta of the electrons yields  $L = 1$  and thus, with  $S = 0$ ,  $J = 1$ , while with  $S = 1$ ,  $J = 0, 1, 2$  with  $J = 0$  lying lowest in energy.

Once again, as with the hydrogen-like states, we may index the states of multi-electron atoms by spectroscopic term notation,  $^{2S+1}L_J$ . The superscript  $2S + 1$  gives the multiplicity of  $J$  values into which the level is split by the spin-orbit interaction; the  $L$  value is represented by a capital letter,  $S, P, D$ , etc., and  $J$  is represented by its numerical value. Thus, for the  $(1s)^1(2p)^1$  state of helium, there are four possible states, with terms:

$${}^3P_0 \quad {}^3P_1 \quad {}^3P_2 \quad \quad {}^1P_1,$$

where the three  ${}^3P$  states are separated by the spin-orbit interaction, and the singlet  ${}^1P$  state lies much higher in energy owing to the Coulomb interaction. The separations between the  ${}^3P_2$  and  ${}^3P_1$  and the  ${}^3P_1$  and  ${}^3P_0$  should be in the

ratio 2:1. This is an example of the **Landé interval rule**, which states that the separation between a pair of adjacent levels in a fine structure multiplet is proportional to the larger of the two  $J$  values involved. This is easily shown using Eq. (9.7) – the separation in energy between states  $J$  and  $J - 1$  is

$$\propto J(J+1) - (J-1)J = 2J.$$

Actually in the case of helium the situation is a bit more complicated, because it turns out that the spin-orbit interaction between *different* electrons makes a non-negligible additional contribution to the fine structure. Other excited states of helium, of the form  $(1s)^1(n\ell)^1$ , can be handled similarly, and again separate into singlet and triplet states.

▷ EXERCISE. For the case of **boron**, with the electron configuration  $(1s)^2(2s)^2(2p)$ , use Hund's rules to show that the ground state is  ${}^2P_{1/2}$ .

We next consider the case of **carbon**, which has ground state electron configuration  $(1s)^2(2s)^2(2p)^2$ . This introduces a further complication; we now have two *identical* electrons in the same *unfilled* subshell, and we need to ensure that their wavefunction is antisymmetric with respect to electron exchange. The total spin can either be the singlet  $S = 0$  state, which has an antisymmetric wavefunction  $\frac{1}{\sqrt{2}}[|\uparrow_1\rangle \otimes |\downarrow_2\rangle - |\downarrow_1\rangle \otimes |\uparrow_2\rangle]$ , or one of the triplet  $S = 1$  states, which are symmetric,  $\frac{1}{\sqrt{2}}[|\uparrow_1\rangle \otimes |\downarrow_2\rangle + |\downarrow_1\rangle \otimes |\uparrow_2\rangle]$ ,  $|\uparrow_1\rangle \otimes |\uparrow_2\rangle$  or  $|\downarrow_1\rangle \otimes |\downarrow_2\rangle$ . We must therefore choose values of  $L$  with the appropriate symmetry to partner each value of  $S$ . To form an antisymmetric state, the two electrons must have different values of  $m_\ell$ , so the possibilities are as shown right. Inspecting the values of  $m_L$  we can deduce that  $L = 1$ .<sup>10</sup> By contrast, to form a symmetric total angular momentum state, the two electrons may have any values of  $m_\ell$ , leading to the possibilities shown right. Inspecting the values of  $m_L$  we infer that  $L = 2$  or  $0$ .

We must therefore take  $S = 1$  with  $L = 1$  and  $S = 0$  with  $L = 2$  or  $0$ . Finally, to account for the fine structure, we note that the states with  $S = 1$  and  $L = 1$  can be combined into a single  $J = 0$  state, three  $J = 1$  states, and five  $J = 2$  states leading to the terms  ${}^3P_0$ ,  ${}^3P_1$ , and  ${}^3P_2$  respectively. Similarly the  $S = 0$ ,  $L = 2$  state can be combined to give five  $J = 2$  states,  ${}^1D_2$ , while the  $S = 0$ ,  $L = 0$  state gives the single  $J = 0$  state,  ${}^1S_0$ . Altogether we recover the  $1 + 3 + 5 + 5 + 1 = 15$  possible states (cf. Eq. (9.6) with the ordering in energy given by Hund's rules (shown to the right). The experimental energy values are given using the conventional spectroscopic units of inverse wavelength. Note that the Landé interval rule is approximately obeyed by the fine structure triplet, and that the separation between  $L$  and  $S$  values caused by the electron-electron repulsion is *much* greater than the spin-orbit effect.

In an excited state of carbon, e.g.  $(2p)^1(3p)^1$ , the electrons are no longer equivalent, because they have different radial wavefunctions. So now one can combine any of  $S = 0, 1$  with any of  $L = 0, 1, 2$ , yielding the following terms (in order of increasing energy, according to Hund's rules):

$${}^3D_{1,2,3} \quad {}^3P_{0,1,2} \quad {}^3S_1 \quad {}^1D_2 \quad {}^1P_1 \quad {}^1S_0.$$

For **nitrogen**, the electron configuration is given by  $(1s)^2(2s)^2(2p)^3$ . The maximal value of spin is  $S = 3/2$  while  $L$  can take values 3, 2, 1 and 0. Since

<sup>10</sup>This result would also be apparent if we recall that angular momentum states are eigenstates of the parity operator with eigenvalue  $(-1)^L$ . Since there are just two electrons, this result shows that both the  $L = 0$  and  $L = 2$  wavefunction must be symmetric under exchange.

$m_\ell^{(1)}$	$m_\ell^{(2)}$	$m_L$
1	0	1
1	-1	0
0	-1	-1
$m_\ell^{(1)}$	$m_\ell^{(2)}$	$m_L$
1	1	2
1	0	1
1	-1	0
0	0	0
0	-1	-1
-1	-1	-2
$E / \text{cm}^{-1}$		
${}^1S_0$		20649
${}^1D_2$		10195
${}^3P_2$		43
${}^3P_1$		16
${}^3P_0$		0



the spin wavefunction (being maximal) is symmetric, the spatial wavefunction must be completely antisymmetric. This demands that all three states with  $m_\ell = 1, 0, -1$  must be involved. We must therefore have  $L = 0$ , leading to  $J = 3/2$  and the term,  $^4S_{3/2}$ .

▷ EXERCISE. Construct the  $L = 0$  state involving the addition of three  $\ell = 1$  angular momentum states. Hint: make use of the total antisymmetry condition.

As a final example, let us consider the ground state of **oxygen**, which has electron configuration  $(2p)^4$ . Although there are four electrons in the  $(2p)$  subshell, the maximum value of  $S = 1$ . This is because there are only three available values of  $m_\ell = \pm 1, 0$ , and therefore one of these must contain two electrons with opposite spins. Therefore, the maximum value of  $m_S = 1$ , achieved by having electrons with  $m_s = +\frac{1}{2}$  in both the other  $m_\ell$  states. By pursuing this argument, it is quite easy to see that the allowed values of  $L, S$  and  $J$  are the same as for carbon  $(2p)^2$ . This is in fact a general result – the allowed quantum numbers for a subshell with  $n$  electrons are the same as for that of a subshell with  $n$  “holes”. Therefore, the energy levels for the oxygen ground state configuration are the same as for carbon, except that the fine structure multiplet is inverted, in accordance with Hund’s third rule.

### 9.3.2 $jj$ coupling scheme

When relativistic effects take precedence over electron interaction effects, we must start by considering the eigenstates of  $\hat{H}_0 + \hat{H}_2 = \hat{H}_0 + \sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i$ . These must be eigenstates of  $\hat{\mathbf{J}}^2$  as before, because of the overall rotational invariance, and also of  $\hat{\mathbf{J}}_i^2$  for each electron. Therefore, in this case, the coupling procedure is to find the allowed  $j$  values of individual electrons, whose energies will be separated by the spin-orbit interaction. Then these individual  $j$  values are combined to find the allowed values of total  $J$ . The effect of the residual Coulomb interaction will be to split the  $J$  values for a given set of  $js$ . Sadly, in this case, there are no simple rules to parallel those of Hund.

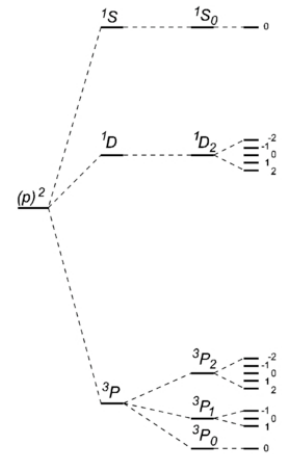
As an example, consider a configuration  $(np)^2$  in the  $jj$  coupling scheme, to be compared with the example of carbon which we studied in the LS scheme. Combining  $s = 1/2$  with  $\ell = 1$ , each electron can have  $j = 1/2$  or  $3/2$ . If the electrons have the same  $j$  value, they are equivalent, so we have to take care of the symmetry of the wavefunction. We therefore have the following possibilities:

- ▷  $j_1 = j_2 = 3/2 \Rightarrow J = 3, 2, 1, 0$ , of which  $J = 2, 0$  are antisymmetric.
- ▷  $j_1 = j_2 = 1/2 \Rightarrow J = 1, 0$ , of which  $J = 0$  is antisymmetric.
- ▷  $j_1 = 1/2, j_2 = 3/2 \Rightarrow J = 2, 1$ .

In  $jj$  coupling, the term is written  $(j_1, j_2)_J$ , so we have the following terms in our example:

$$(1/2, 1/2)_0 \quad (3/2, 1/2)_1 \quad (3/2, 1/2)_2 \quad (3/2, 3/2)_2 \quad (3/2, 3/2)_0$$

in order of increasing energy. Note that both LS and  $jj$  coupling give the same values of  $J$  (in this case, two states with  $J = 0$ , two with  $J = 2$  and one with  $J = 1$ ) and in the same order. However, the pattern of levels is different; in LS coupling we found a triplet and two singlets, while in this ideal  $jj$  scenario, we have two doublets and a singlet. The sets of states in the two coupling



Level scheme of the carbon atom  $(1s)^2(2s)^2(2p)^2$ . Drawing is not to scale. On the left the energy is shown without any two-particle interaction. The electron-electron interaction leads to a three-fold energy splitting with  $L$  and  $S$  remaining good quantum numbers. Spin-orbit coupling leads to a further splitting of the states with  $J$  remaining a good quantum number. Finally on the right, the levels show Zeeman splittings in an external magnetic field. In this case, the full set of 15 levels become non-degenerate.

schemes must be expressible as linear combinations of one another, and the physical states for a real atom are likely to differ from either approximation.

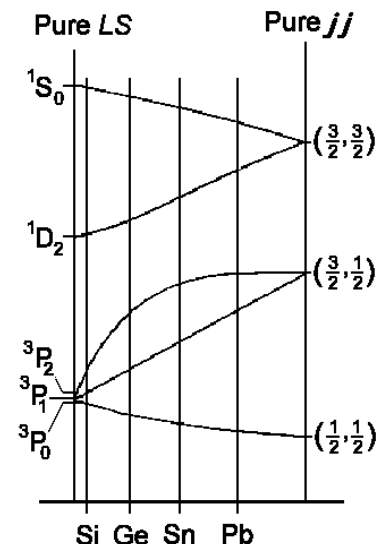
In fact, this idealized form of  $jj$  coupling is not seen in the heaviest such atom in the periodic table, lead  $(6p)^2$ . However, it is seen in some highly ionized states, for example in  $\text{Cr}^{18+}$ , which has the same electron configuration  $(2p)^2$  as carbon, but where, because of the larger unscreened charge on the nucleus, the electrons are moving more relativistically, enhancing the spin-orbit effect. However, a classic example of the transition from LS to  $jj$  coupling is seen in the series C-Si-Ge-Sn-Pb in the excited states  $(2p)(3s)$ ,  $(3p)(4s)$ ,  $\dots$   $(6p)(7s)$  (see figure right). Here, the electrons are not in the same subshell, so their wavefunctions overlap less, and the Coulomb repulsion is reduced compared to the spin-orbit interaction. Analysing this situation in the LS coupling approximation, one expects a triplet and a singlet:

$${}^3P_{0,1,2} \quad {}^1P_1,$$

while in the  $jj$  scheme one expects two doublets:

$$(1/2, 1/2)_{0,1} \quad (1/2, 3/2)_{2,1}.$$

Experimentally, C and Si conform to the LS expectation and Pb to the  $jj$  scheme, while Ge and Sn are intermediate.



## 9.4 Atomic spectra

Atomic spectra result from transitions between different electronic states of an atom via emission or absorption of photons. In **emission spectra**, an atom is excited by some means (e.g. thermally through collisions, or by an electric discharge), and one observes discrete spectral lines in the light emitted as the atoms relax. In **absorption spectra**, one illuminates atoms using a broad waveband source, and observes dark absorption lines in the spectrum of transmitted light. Of course the atoms excited in this process subsequently decay by emitting photons in random directions; by observing in directions away from the incident light this **fluorescence** radiation may be studied. The observation of these spectral lines is an important way of probing the atomic energy levels experimentally. In the case of optical spectra and the nearby wavebands, the excited states responsible generally involve the excitation of a single electron from the ground state to some higher level. In some cases, it may simply involve a different coupling of the angular momenta within the same electron configuration. These are the kinds of excitations which we are about to discuss. However, other types of excitations are also possible. For example, X-ray emission occurs when an electron has been removed from one of the innermost shells of a heavy atom; as electrons cascade down to fill the hole, high energy photons may be emitted.

The basic theory governing stimulated emission and absorption, and spontaneous emission of photons will be outlined in detail when we study radiative transitions in chapter 13. Here we must anticipate some of the basic conclusions of that study. In the **electric dipole approximation**, the rate of transitions is proportional to the square of the matrix element of the electric dipole operator between the initial and final states,  $|\langle\psi_f|\hat{\mathbf{d}}|\psi_i\rangle|^2$ . In addition, the rate of spontaneous transitions is proportional to  $\omega^3$ , where  $\omega = |E_f - E_i|$  denotes the energy separation between the states.

The form of the dipole operator,  $\hat{\mathbf{d}}$  means that the matrix elements may vanish identically. This leads to a set of **selection rules** defining which transitions are allowed. Here we consider the simplest case of a single electron, but

the principles can be generalized. Referring to chapter 13 for a more detailed discussion, one finds that, for a transition to take place:

- ▷ Parity must change;
- ▷  $\Delta J = \pm 1, 0$  (but  $0 \rightarrow 0$  is not allowed) and  $\Delta M_J = \pm 1, 0$ .

Atomic states are always eigenstates of parity and of total angular momentum,  $J$ , so these selection rules can be regarded as absolutely valid in electric dipole transitions. It should be emphasized again, though, that the electric dipole approximation is an approximation, and higher order processes may occur, albeit at a slower rate, and have their own selection rules.

In specific coupling schemes, further selection rules may apply. In the case of ideal LS coupling, we also require:

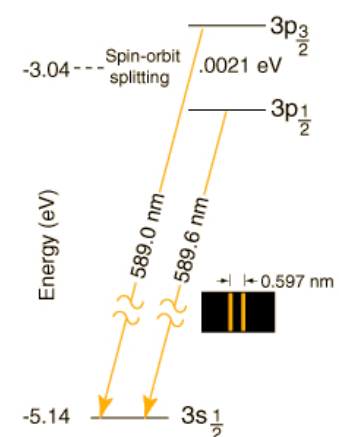
- ▷  $\Delta S = 0$  and  $\Delta M_S = 0$ ;
- ▷  $\Delta L = \pm 1, 0$  (but  $0 \rightarrow 0$  is not allowed) and  $\Delta M_L = \pm 1, 0$ ;
- ▷ and  $\Delta \ell_i = \pm 1$  if only electron  $i$  is involved in the transition.

In LS coupling, the states are eigenstates of total spin; since the dipole operator does not operate on the spin part of the wavefunction, the rules on  $\Delta S$  and  $\Delta M_S$  follow straightforwardly. This, and the absolute rules relating to  $J$ , imply the rules for  $L$  and  $M_L$ . The rule for  $\Delta \ell_i$  follows from the parity change rule, since the parity of the atom is the product of the parities of the separate electron wavefunctions, given by  $(-1)^{\ell_i}$ . However, since LS coupling is only an approximation, these rules should themselves be regarded as approximate. With this preparation, we now turn to the consequences of the selection rules on the atomic spectra of atoms.

### 9.4.1 Single electron atoms

In this context, “single electron atoms” refer to atoms whose ground state consists of a single electron in an  $s$  level, outside closed shells; it is this electron which is active in optical spectroscopy. Our discussion therefore encompasses the **alkali metals**, such as sodium, and also hydrogen. We take **sodium**, whose ground state configuration is  $(3s)^1$ , as our example:

- ▷ The ground state has term  $^2S_{1/2}$ . The excited states are all doublets with  $J = L \pm 1/2$ , except for the  $s$  states, which are obviously restricted to  $J = 1/2$ .
- ▷ The parity is given by  $(-1)^{\ell_i}$ , so the allowed transitions involve changes in  $\ell$  by  $\pm 1$  unit, i.e.  $s \leftrightarrow p$ ,  $p \leftrightarrow d$ ,  $d \leftrightarrow f$ , etc. Changes of more than one unit in  $\ell$  would fall foul of the  $\Delta J$  rule.
- ▷ The  $s \leftrightarrow p$  transitions are all doublets. All the doublets starting or ending on a given  $p$  state have the same spacing in energy. The transition  $3s \leftrightarrow 3p$  gives rise to the familiar yellow sodium “D-lines” at 589 nm (see right).
- ▷ The  $p \leftrightarrow d$  transitions involve two doublets,  $^2P_{1/2,3/2}$  and  $^2D_{3/2,5/2}$ . However, the  $^2P_{1/2} \leftrightarrow ^2D_{5/2}$  transition is forbidden by the  $\Delta J$  rule, so the line is actually a triplet. In practice, the spin-orbit interaction falls quite rapidly with increasing  $\ell$  (and with increasing  $n$ ) as the effect of screening increases, so that the effect of the  $^2D_{3/2,5/2}$  splitting may not be resolved experimentally.



- ▷ As  $n$  increases, the energy levels approach (from below) those for hydrogen, because the nuclear charge is increasingly effectively screened by the inner electrons. This happens sooner for the higher  $\ell$  values, for which the electron tends to lie further out from the nucleus.
- ▷ In an absorption spectrum, the atoms will start from the ground state, so only the  $3s \rightarrow np$  lines will be seen. In emission, the atoms are excited into essentially all their excited levels, so many more lines will be seen in the spectrum.

The comments above for sodium also apply for hydrogen, except that, in this case,  $(2s, 2p)$ ,  $(3s, 3p, 3d)$ , etc. are degenerate. One consequence is that the  $2s$  state in hydrogen is metastable – it cannot decay to the only lower lying level ( $1s$ ) by an electric dipole transition. In fact its favoured spontaneous decay is by emission of two photons; a process which is described by second-order perturbation theory. In practice, hydrogen atoms in a  $2s$  state are more likely to deexcite through collision processes. During an atomic collision, the atoms are subject to strong electric fields, and we know from our discussion of the Stark effect that this will mix the  $2s$  and  $2p$  states, and decay from  $2p$  to  $1s$  is readily possible.

### 9.4.2 Helium and alkali earths

We next discuss atoms whose ground state consists of two electrons in an  $s$  level. Our discussion therefore covers helium  $(1s)^2$ , and the **alkali earths**: beryllium  $(2s)^2$ , magnesium  $(3s)^2$ , calcium  $(4s)^2$ , etc. We start with **helium**.

- ▷ The ground state has term  $^1S_0$ . The excited states are of the form  $(1s)(n\ell)$  (the energy required to excite both of the  $1s$  electrons to higher states is greater than the first ionization energy, and therefore these form discrete states within a continuum of ionized  $\text{He}^+ + e^-$  states). The excited states can have  $S = 0$  or  $S = 1$ , with  $S = 1$  lying lower in energy (Hund).
- ▷ The LS coupling approximation is pretty good for helium, so the  $\Delta S = 0$  selection rule implies that the  $S = 0$  and  $S = 1$  states form completely independent systems as far as spectroscopy is concerned.
- ▷ The lines in the  $S = 0$  system are all singlets. They can be observed in emission, and those starting from the ground state can be seen in absorption.
- ▷ The lines in the  $S = 1$  system are all multiplets. They can be observed in emission only. Transitions of the form  $^3S_1 \leftrightarrow ^3P_{2,1,0}$  are observed as triplets, spaced according to the Landé interval rule. Transitions of the form  $^3P_{2,1,0} \leftrightarrow ^3D_{3,2,1}$  are observed as sextuplets, as is easily seen by application of the  $\Delta J = \pm 1, 0$  rule. Actually, as mentioned above, the fine structure is a little more subtle in the case of helium.

The alkali earths follow the same principles. In the case of calcium, the triplet  $4p$  state is the lowest lying triplet state, and therefore metastable. In fact a faint emission line corresponding to the  $^3P_1 \rightarrow ^1S_0$  decay to the ground state may be observed; this violates the  $\Delta S = 0$  rule, and indicates that the LS coupling approximation is not so good in this case. A more extreme example is seen in Mercury, ground state  $(6s)^2(5d)^{10}$ . Excited states involving promotion of one of the  $6s$  electrons to a higher level can be treated just like the alkali

earths. In this case the “forbidden”  ${}^3P_1 \rightarrow {}^1S_0$  is actually a prominent feature of the emission spectrum in the visible, implying a significant breakdown of the LS approximation.

### 9.4.3 Multi-electron atoms

Similar principles can be used to make sense of the spectra of more complicated atoms, though unsurprisingly their structure is more complex. For example, carbon, with ground state  $(2s)^2(2p)^2$ , corresponds to terms  ${}^3P_{0,1,2}$ ,  ${}^1D_2$  and  ${}^1S_0$  as discussed above. The excited states are of the form  $(2s)^2(2p)^1(n\ell)^1$ , and can be separated into singlets and triplets, and in addition excitations of the form  $(2s)^1(2p)^3$  can arise. Nitrogen, with ground state  $(2s)^2(2p)^3$ , has three unpaired electrons, so the ground state and excited states form doublets ( $S = 1/2$ ) and quartets ( $S = 3/2$ ) with correspondingly complex fine structure to the spectral lines.

## 9.5 Zeeman effect

### 9.5.1 Single-electron atoms

Before leaving this chapter on atomic structure, we are now in a position to revisit the question of how atomic spectra are influenced by a magnetic field. To orient our discussion, let us begin with the study of hydrogen-like atoms involving just a single electron. In a magnetic field, the Hamiltonian of such a system is described by  $\hat{H} = \hat{H}_0 + \hat{H}_{\text{rel.}} + \hat{H}_{\text{Zeeman}}$ , where  $\hat{H}_0$  denotes the non-relativistic Hamiltonian for the atom,  $\hat{H}_{\text{rel.}}$  incorporates the relativistic corrections considered earlier in the chapter, and

$$\hat{H}_{\text{Zeeman}} = -\frac{eB}{2mc}(\hat{L}_z + 2\hat{S}_z),$$

denotes the Zeeman energy associated with the coupling of the spin and orbital angular momentum degrees of freedom to the magnetic field. Here, since we are dealing with confined electrons, we have neglected the diamagnetic contribution to the Hamiltonian. Depending on the scale of the magnetic field, the spin-orbit term in  $\hat{H}_{\text{rel.}}$  or the Zeeman term may dominate the spectrum of the atom.

Previously, we have seen that, to leading order, the relativistic corrections lead to a fine-structure energy shift of

$$\Delta E_{n,j}^{\text{rel.}} = \frac{1}{2}mc^2 \left(\frac{Z\alpha}{n}\right)^4 \left(\frac{3}{4} - \frac{n}{j+1/2}\right),$$

for states  $|n, j = \ell \pm 1/2, m_j, \ell\rangle$ . For weak magnetic fields, we can also treat the Zeeman energy in the framework of perturbation theory. Here, although states with common  $j$  values (such as  $2S_{1/2}$  and  $2P_{1/2}$ ) are degenerate, the two spatial wavefunctions have different parity ( $\ell = 0$  and  $1$  in this case), and the off-diagonal matrix element of  $\hat{H}_{\text{Zeeman}}$  coupling these states vanishes. We may therefore avoid using degenerate perturbation theory. Making use of the relation (exercise – refer back to the discussion of the addition of angular momenta and spin in section 6.4.2),

$$\langle n, j = \ell \pm 1/2, m_j, \ell | S_z | n, j = \ell \pm 1/2, m_j, \ell \rangle = \pm \frac{\hbar m_j}{2\ell + 1},$$

we obtain the following expression for the first order energy shift,

$$\Delta E_{j=\ell\pm 1, m_j, \ell}^{\text{Zeeman}} = \mu_B B m_j \left(1 \pm \frac{1}{2\ell + 1}\right),$$

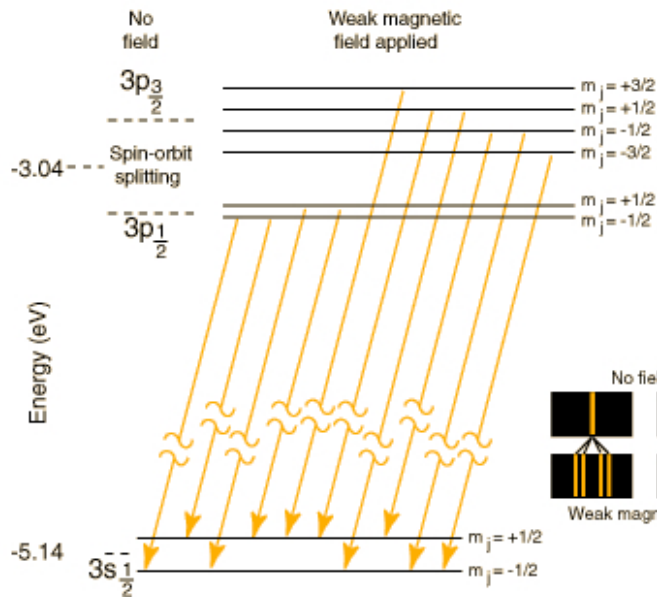


Figure 9.4: The well known doublet which is responsible for the bright yellow light from a sodium lamp may be used to demonstrate several of the influences which cause splitting of the emission lines of atomic spectra. The transition which gives rise to the doublet is from the  $3p$  to the  $3s$  level. The fact that the  $3s$  state is lower than the  $3p$  state is a good example of the dependence of atomic energy levels on orbital angular momentum. The  $3s$  electron penetrates the  $1s$  shell more and is less effectively shielded than the  $3p$  electron, so the  $3s$  level is lower. The fact that there is a doublet shows the smaller dependence of the atomic energy levels on the total angular momentum. The  $3p$  level is split into states with total angular momentum  $J = 3/2$  and  $J = 1/2$  by the spin-orbit interaction. In the presence of an external magnetic field, these levels are further split by the magnetic dipole energy, showing dependence of the energies on the  $z$ -component of the total angular momentum.

where  $\mu_B$  denotes the Bohr magneton. Therefore, we see that all degenerate levels are split due to the magnetic field. In contrast to the “normal” Zeeman effect, the magnitude of the splitting depends on  $\ell$ .

▷ INFO. If the **field is strong**, the Zeeman energy becomes large in comparison with the spin-orbit contribution. In this case, we must work with the basis states  $|n, \ell, m_\ell, m_s\rangle = |n, \ell, m_\ell\rangle \otimes |m_s\rangle$  in which both  $\hat{H}_0$  and  $\hat{H}_{\text{Zeeman}}$  are diagonal. Within first order of perturbation theory, one then finds that (exercise)

$$\Delta E_{n, \ell, m_\ell, m_s} = \mu_B(m_\ell + m_s) + \frac{1}{2}mc^2 \left(\frac{Z\alpha}{n}\right)^4 \left(\frac{3}{4} - \frac{n}{\ell + 1/2} - \frac{nm_\ell m_s}{\ell(\ell + 1/2)(\ell + 1)}\right),$$

the first term arising from the Zeeman energy and the remaining terms from  $\hat{H}_{\text{rel}}$ . At intermediate values of the field, we have to apply degenerate perturbation theory to the states involving the linear combination of  $|n, j = \ell \pm 1/2, m_j, \ell\rangle$ . Such a calculation reaches beyond the scope of these lectures and, for details, we refer to the literature (see, e.g., Ref. [6]. Let us instead consider what happens in multi-electron atoms.

### 9.5.2 Multi-electron atoms

For a multi-electron atom in a weak magnetic field, the appropriate unperturbed states are given by  $|J, M_J, L, S\rangle$ , where  $J$ ,  $L$ ,  $S$  refer to the total angular momenta. To determine the Zeeman energy shift, we need to determine the matrix element of  $\hat{S}_z$ . To do so, we can make use of the following

argument. Since  $2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2$ , this operator is diagonal in the basis of states,  $|J, M_J, L, S\rangle$ . Therefore, the matrix element of the operator (exercise, hint: recall that  $[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{S}_k$  and  $[\hat{L}_i, \hat{S}_k] = 0$ ),

$$-i\hbar\hat{\mathbf{S}} \times \hat{\mathbf{L}} \equiv \hat{\mathbf{S}}(\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}) - (\hat{\mathbf{L}} \cdot \hat{\mathbf{S}})\hat{\mathbf{S}}$$

must vanish. Moreover, from the identity  $[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{\mathbf{J}}] = 0$ , it follows that the matrix element of the vector product,

$$-i\hbar(\hat{\mathbf{S}} \times \hat{\mathbf{L}}) \times \hat{\mathbf{J}} = \hat{\mathbf{S}} \times \hat{\mathbf{J}}(\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}) - (\hat{\mathbf{L}} \cdot \hat{\mathbf{S}})\hat{\mathbf{S}} \times \hat{\mathbf{J}},$$

must also vanish. If we expand the left hand side, we thus find that the matrix element of

$$(\hat{\mathbf{S}} \times \hat{\mathbf{L}}) \times \hat{\mathbf{J}} = \hat{\mathbf{L}}(\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}) - \hat{\mathbf{S}}(\hat{\mathbf{L}} \cdot \hat{\mathbf{J}}) \stackrel{\hat{\mathbf{L}}=\hat{\mathbf{J}}-\hat{\mathbf{S}}}{=} \hat{\mathbf{J}}(\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}) - \hat{\mathbf{S}}\hat{\mathbf{J}}^2,$$

also vanishes. Therefore, it follows that  $\langle \hat{\mathbf{S}}\hat{\mathbf{J}}^2 \rangle = \langle \hat{\mathbf{J}}(\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}) \rangle$ , where the expectation value is taken over the basis states. Then, with  $\hat{\mathbf{S}} \cdot \hat{\mathbf{J}} = \frac{1}{2}(\hat{\mathbf{J}}^2 + \hat{\mathbf{S}}^2 - \hat{\mathbf{L}}^2)$ , we have that

$$\langle \hat{S}_z \rangle = \langle \hat{J}_z \rangle \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}.$$

As a result, we can deduce that, at first order in perturbation theory, the energy shift arising from the Zeeman term is given by

$$\Delta E_{J,M_J,L,S} = \mu_B g_J M_J B,$$

where

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)},$$

denotes the effective **Landé g-factor**, which lies between 1 and 2. Note that, in the special case of hydrogen, where  $S = 1/2$  and  $J = L \pm 1/2$ , we recover our previous result. The predicted Zeeman splitting for sodium is shown in figure 9.4.

▷ INFO. In the **strong field limit**, where the influence of Zeeman term dominates, the appropriate basis states are set by  $|L, M_L, S, M_S\rangle$ , in which the operators  $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$ , and  $\hat{H}_{\text{Zeeman}}$  are diagonal. In this case, the energy splitting takes the form

$$\Delta E_{L,M_L,S,M_S} = \mu_B B(M_L + 2M_S) + \frac{1}{2}mc^2 \left(\frac{Z\alpha}{n}\right)^4 \frac{nM_L M_S}{\ell(\ell+1/2)(\ell+1)},$$

where the second term arises from the spin-orbit interaction.

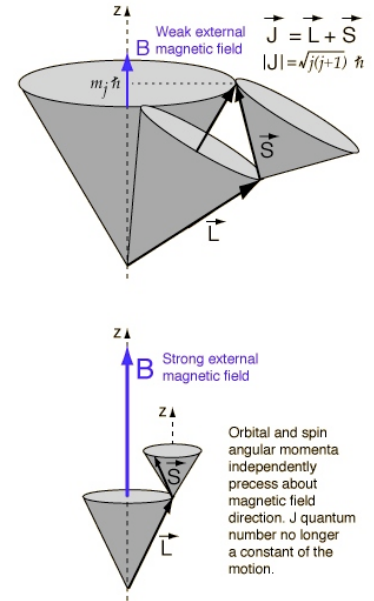


Figure 9.5: In the weak field case, the vector model (top) implies that the coupling of the orbital angular momentum  $\mathbf{L}$  to the spin angular momentum  $\mathbf{S}$  is stronger than their coupling to the external field. In this case where spin-orbit coupling is dominant, they can be visualized as combining to form a total angular momentum  $\mathbf{J}$  which then precesses about the magnetic field direction. In the strong field case,  $\mathbf{S}$  and  $\mathbf{L}$  couple more strongly to the external magnetic field than to each other, and can be visualized as independently precessing about the external field direction.