Atomic Physics (PHY2005)

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1   *Introduction to PHY2005 Atomic Physics*

What is atomic physics?

Atomic physics is the study of the properties of atoms. We will focus on understanding their bound states and the radiative transitions between them.

What is an "atom"?

Throughout this course, we use "atom" to mean a system of particles bound by the Coulomb potential. As you know, the most common examples involve a heavy, positively-charged nucleus and one or more bound electrons. However, the theories we discuss can apply to more exotic material (e.g. *positronium*). Although we will almost always refer to "atoms", most of our discussion also applies to *ions* (i.e. we do not limit ourselves to systems in which the total electric charge is zero).

Why study atomic physics, and why now?

A personal view: I would suggest three reasons:

1. **Atomic physics is important in its own right.**
   - Atoms are the building blocks of matter: physics, astrophysics and chemistry applications require that we understand them.
2. **Atomic physics is a staging point** for learning about quantum mechanics in real systems.
   - Atomic Physics provides an excellent introduction to many-body quantum mechanics. A good understanding of Atomic Physics is great preparation for topics including Nuclear Physics, Particle Physics and Molecular Physics.
3. **Real physics problems cannot always be solved exactly.**
   - Motivating and using approximations to tackle real physics problems is a vital part of being a physicist. Atomic Physics provides some excellent examples of this skill in action.

2 *Introduction to single-electron atoms and the Bohr model*

Context

Why single-electron atoms? Single-electron atoms are the simplest, and most familiar from previous courses. We cannot understand multi-electron atoms without a solid understanding of the one-electron case.

Why the Bohr model? The Bohr model should be a familiar starting point for students. Although limited, it is successful and its results are common points of reference later in the theory.

Learning goals

1. To revise the observed properties of the spectrum of the hydrogen atom.
2. To revise the postulates of the Bohr model, including how quantization is introduced to the model via a quantum number.
3. To revise the application of the Bohr model to calculate energy levels (and radii) in single-electron atoms.
4. To understand how the Bohr model can be applied to single-electron atoms with differing nuclear mass and/or differing nuclear charge.
5. To assess the quantitative accuracy of the Bohr model.
6. To understand limitations of the Bohr/Sommerfeld model of single-electron atoms.

2.1   The spectrum of the hydrogen atom

"The spectrum of the hydrogen atom has proved to be the Rosetta stone of modern physics: once this pattern of lines had been deciphered much else could be understood" – Hänsch, Schawlow & Series (Scientific American, 1979)

The history and development of atomic physics has always been intimately linked to the study of spectra. Figure 1 shows the famous Balmer series of lines in the optical spectrum of hydrogen: this can be observed either as a spectrum of emission from e.g. a hydrogen lamp, or as a series of absorption lines imprinted on a continuum spectrum.
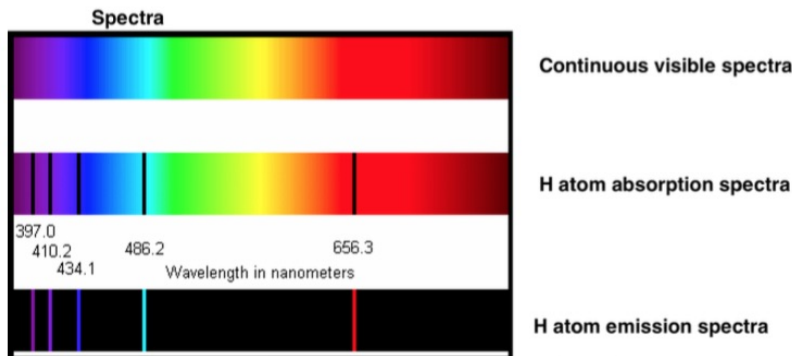

Figure 1: Optical emission line spectrum of hydrogen (bottom) and absorption line spectrum (middle), as measured against a continuum source (top).

The study of spectra is vital in atomic physics because we understand that spectral lines are associated with transitions between atomic states. So accurate spectroscopic measurements allow us to determine (to high precision) the energy states of electrons in atoms and test the theories of quantum mechanics that predict these energy levels. Conversely, given a good understanding of atomic physics, we can interpret spectra that we record. This has a very wide range of applications, including laboratory plasma physics and astrophysics.

2.2   Empirical formulae for the hydrogen spectrum

In the 1880s, Balmer produced a simple empirical[1] formula to describe the wavelengths of the optical emission lines in the hydrogen spectrum. This formula was reworked by Rydberg into the now familiar form

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad \text{for } n \geq 3 \tag{1}$$

where $R \approx 1.097 \times 10^7$ m^{-1} is called the Rydberg constant (and is known to 1 part in 10^8).

[1] *Empirical* means obtained by fitting the data, not from theoretical consideration.
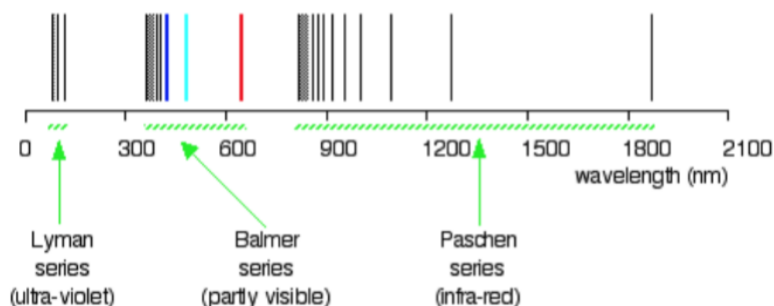
Figure 2: Ultraviolet to infrared series of hydrogen emission line spectra. From chemguide.co.uk.

Gradually technical developments of detectors allowed access to other regions of the electromagnetic spectrum and new hydrogen lines were found (see Table 1 and Figure 2). These lines were found to fall in various *series*, which were usually named after their discoverer. Rydberg and Ritz produced a formula that could match all the series

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{for } n_2 > n_1 \, , \tag{2}$$

which is a simple generalisation of the Rydberg formula above. Since we interpret the lines in the spectrum as being due to electron transitions, the initial goal of developing a theory for hydrogen-like atoms was to explain how a set of electron energy levels could arise that would be consistent with this empirical result.

Series name	Region	n_1	n_2
Lyman	Ultraviolet	1	2 to ∞
Balmer	Visible	2	3 to ∞
Paschen	Infrared	3	4 to ∞
Brackett	Far IR	4	5 to ∞
Pfund	Far IR	5	6 to ∞

Table 1: Series of lines in the hydrogen spectrum.

Within each of the series, the lines are **named using a greek letter** that identifies the change in n. If $\Delta n = n_2 - n_1 = 1$, it is the α transition (e.g. $n = 3$ to $n = 2$ is called Balmer α), if $\Delta n = 2$ it is called β (e.g. $n = 4$ to $n = 2$ is Balmer β) and so on.

2.3   *The Bohr model of the hydrogen atom*

Bohr theory relies on a simple semi-classical picture of an orbiting electron in an atom that allows us to calculate a set of allowed energy levels. In this section we will briefly review the assumption underlining this model and remind ourselves of how some of the important predictions of the model can be derived.

Electron

Proton

Figure 3: Bohr model of the hydrogen atom as described by Postulate 1.

Postulates of the Bohr model:
Bohr's model is based on four postulates (i.e. assumptions):

1. The electron moves around the nucleus in a (classical) circular orbit (Figure 3) in which there is a balance between the attractive Coulomb force and the "repulsive centrifugal" force, much like classical bodies in circular gravitational orbits. The total energy then depends on the kinetic energy K and the potential energy V.
2. The magnitude of the electron **angular momentum** (L) is **quantized** according to

$$L = m_e v r = nh/2\pi = n\hbar \tag{3}$$

where m_e is the electron mass, v its velocity and r its distance from the nucleus. n is any positive *integer*, and is usually called the *principal quantum number*.
3. An electron in such an orbit does not radiate.
4. Radiation is emitted or absorbed during transitions from one stable state to another with frequency given by $\nu = \frac{E_i - E_f}{h}$, where E_i and E_f are the energies of the initial and final states.

Postulate 2 is the most widely discussed (and radical) of the postulates in the model: it is by insisting that n is an integer that quantization is imposed.

Postulate 3 is not always given the attention it deserves: it is vital, but contradicts the classical expectation that an accelerating charged particle should always radiate.

Postulate 4 is related to the Planck/Einstein relation which connects the energy carried by a photon to its frequency, $E_{\text{photon}} = h\nu$.

Derivation of energy and radius in the Bohr model:
Let us assume that the nucleus has charge $+Ze$. From the 1st of the postulates we can then show (Exercise 2.1) that the radius of the orbit is related to the angular momentum by

$$r = \frac{4\pi\epsilon_0 L^2}{m_e Z e^2} \tag{4}$$

If we know the radius of the orbit, we can easily obtain the Coulomb potential energy

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{m_e Z^2 e^4}{(4\pi\epsilon_0)^2 L^2} \ .$$

Also, since the velocity is related to the radius and the angular momentum, we know the kinetic energy

$$K = \frac{1}{2}m_e v^2 = \frac{1}{2}m_e \left(\frac{L}{m_e r}\right)^2 = \frac{m_e Z^2 e^4}{2(4\pi\epsilon_0)^2 L^2} = -\frac{1}{2}V(r) \ .$$
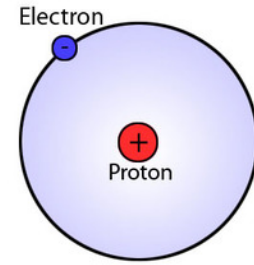
Thus the total energy is

$$E = V + K = V/2 = -\frac{m_e Z^2 e^4}{2(4\pi\epsilon_0)^2 L^2}$$

Using the second postulate, $L = n\hbar$ then gives us the famous Bohr model energy-level formula:

$$E_n = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{m_e Z^2 e^4}{2\hbar^2 n^2} \approx -13.6 \text{ eV} \frac{Z^2}{n^2} , \qquad (5)$$

which predicts the energy levels in the hydrogen atom ($Z = 1$) as shown in Figure 4.

Using $L = n\hbar$ in Eqn 4, we can also calculate the allowed values for the radius

$$r = \frac{4\pi\epsilon_0 n^2 \hbar^2}{m_e Z e^2} = a_0 \frac{n^2}{Z} , \qquad (6)$$

where the constant $a_0 \approx 5.3 \times 10^{-11}$ m is known as the *Bohr radius*.

Exercise 2.1: Bohr orbit (classical treatment)

Verify that, according to the first postulate of the Bohr model, Eqn 4 is correct.

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For a particle of mass m_e in circular motion at radius r with speed v, the classical (repulsive) centrifugal force is

$$\frac{m_e v^2}{r} .$$

The attractive Coulomb force between a nucleus of charge $+Ze$ and an electron of charge $-e$ at radius r is

$$\frac{Z e^2}{4\pi\epsilon_0 r^2} .$$

Classically, the condition of mechanical stability (i.e. effective force balance) is therefore

$$\frac{m_e v^2}{r} = \frac{Z e^2}{4\pi\epsilon_0 r^2}$$

Using $L = m_e v r$, this can be written

$$\frac{L^2}{m_e r^3} = \frac{Z e^2}{4\pi\epsilon_0 r^2} ,$$

which rearranges to

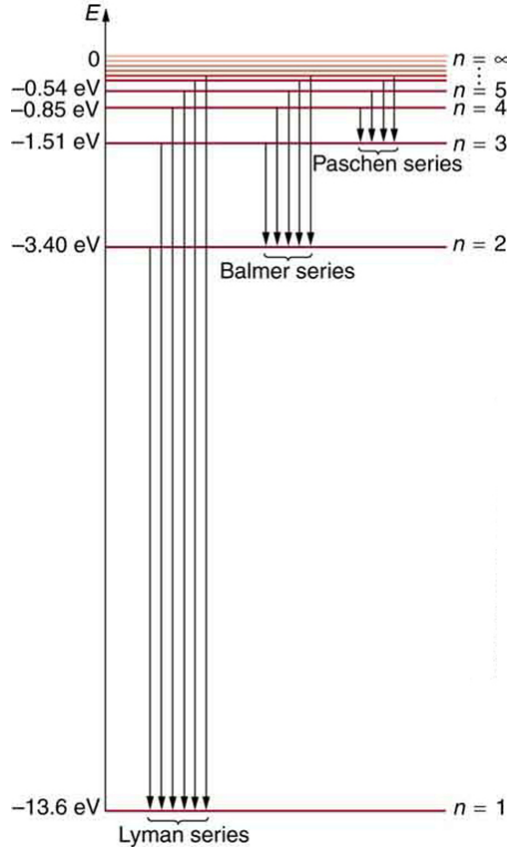$$r = \frac{4\pi\epsilon_0 L^2}{m_e Z e^2} ,$$

as required.

Figure 4: Representation of the energy levels in hydrogen (horizontal lines) according to the Bohr model, and the transitions between them (indicated by arrows) giving rise to the various emission line series.

Spectral lines in the Bohr model:

From postulate 4, it follows that transitions will occur between pairs of energy levels such that radiation (photons) are emitted with frequencies

$$\nu = \frac{1}{h}(E_i - E_f) = -\frac{1}{h}(E_f - E_i)$$

or

$$\frac{1}{\lambda} = \frac{\nu}{c} = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{m_e Z^2 e^4}{4\pi\hbar^3 c} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R_\infty Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) . \quad (7)$$

This agrees with the form of the Ritz-Rydberg formula (Eqn 2), and provides a very good match to the wavelengths of the series of emission lines observed from the hydrogen atom if we adopt $Z = 1$. The coefficient derived here (for $Z = 1$) is the *Rydberg constant for an infinitely heavy nucleus* (because so far we assumed the nucleus was so much more massive than the electron that it remains stationary),

$$R_\infty = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{m_e e^4}{4\pi\hbar^3 c} . \quad (8)$$

In the next section we shall see how the formulae may be altered to account for the finite mass of nuclei.

Important note on energy scales

Throughout this section we have used an energy scale in which $E = 0$ corresponds to the electron being infinitely far from the nucleus. The origin of this lies in the form we used for the Coulomb potential

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \, ,$$

where it is easy to see that $r \to \infty$ corresponds to there being zero energy. This choice of energy scale is convenient for simple one-electron atoms, and can be best thought of as giving *energy relative to ionization*.[2]

Throughout this Chapter, and the next, we will continue to work with this choice of energy scale (i.e. *relative to ionization* for single-electron atoms). However, in our later discussion of multi-electron atoms we will encounter some subtleties and different choices.

In particular, for multi-electron atoms, when considering an energy scale *relative to ionization*, one must choose whether to define $E = 0$ as corresponding to removing *all* the electrons from the atom or removing *only one* electron. The first of these choices effectively given a scale where the energy of a state is related (by a minus sign) to the total binding energy of the electron cloud. The second gives a scale *relative to first ionization*, where the energy of a state is related (again by a minus sign) to the energy needed to remove one electron from the system.

In addition, another common choice is to shift the energy scale so that the ground state has $E = 0$. This choice is common in most advanced applications of atomic physics, and is often what you will encounter in databases of atomic structure.

The reason that a variety of different energy scales can be adopted stems from a very fundamental aspect of our theory. Specifically, when calculating the wavelengths of transitions (e.g. Eqn 7) we are always concerned with *energy differences*. Thus adding any arbitrary constant to shift the energy scale in e.g. Eqn 5 will not change the predications of our theory. For this reason, a shifted energy scale may be chosen as convenient for any particular application or calculation, provided that the scale is treated consistently within that calculation.

[2] We say "relative to ionization" because if the electron is infinitely far from the nucleus we have effectively removed the electron and left behind the bare nucleus, which is a charged *ion*. The value of the energy given by e.g. Eqn 5 is the energy *relative* to that situation.

The "ground state" always means the state with lowest energy.

2.4   *The effect of finite nuclear mass*

Our treatment of the Bohr model in Section 2.3 assumed that the electron orbits a stationary nucleus. However, in a classical two-body orbit, both bodies really orbit their common centre of mass.

Fortunately, the mechanics of the two-body rotation problem can be reduced to the same equations as used in Section 2.3 if we replace all instances of the electron mass m_e with the reduced mass of the system

$$\mu = \frac{m_e M}{m_e + M} \, ,$$ (9)

where M is the mass of the nucleus. (You should be able to prove this for yourself if you wish: try it and see!) With this alteration, Eqn 7 becomes

$$\frac{1}{\lambda} = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\mu Z^2 e^4}{4\pi\hbar^3 c} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R_M Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$ (10)

i.e. if the finite mass of the nucleus is taken into account the appropriate Rydberg constant is given by

$$R_M = \frac{\mu}{m_e} R_\infty = \frac{M}{m_e + M} R_\infty \, .$$ (11)

Although the difference between R_M and R_∞ is small (for hydrogen, μ/m_e is ~ 0.9995), its consequence is measurable and using R_M leads to significantly better agreement with experiment (see Exercise 2.2).

Wavelengths can be measured to about 1 part in 10^8 thus spectroscopic measurement do provide very accurate tests of our theory!

Exercise 2.2: Accuracy of the Bohr model

The Rydberg constant for hydrogen is measured to have a value of 10967757.6 ± 1 m^{-1}. Compare this to (i) the value for R_∞ predicted by the Bohr model when the proton is assumed to be stationary (ii) the value for R_M when the finite mass of the nucleus is taken into account.

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(i) Using the fundamental constants,

$$R_\infty = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{m_e e^4}{4\pi\hbar^3 c} \approx 10973731.6 \text{ m}^{-1}$$

which differs from the experimental value by around 0.05%. I.e. accuracy of roughly 1 part in 2000. Although this may seem accurate, the difference is considerably larger than the stated measurement uncertainty.

(ii) If instead we use R_M with M given by the proton mass (as appropriate for the hydrogen nucleus), we obtain

$$R_M = \frac{M}{m_e + M} R_\infty \approx 10967758.3 \text{ m}^{-1}$$

which agrees with the quoted experimental value (to the given accuracy).

Because the Rydberg constant depends on the reduced mass, different isotopes of hydrogen have their spectral lines at slightly different wavelengths. Deuterium ($^2_1$H) and Tritium ($^3_1$H) (see Figure 5) have reduced mass differences of about 1 part in 10^3 – so differences in their emission line spectra are easily resolved with spectrographs. This is know as an *isotope shift* and it was this effect that led to the discovery of deuterium.
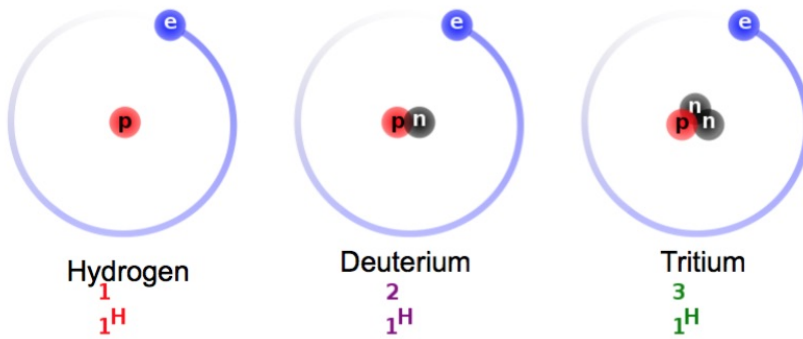
Recall that *isotopes* of an element differ in the number of neutrons in their nuclei.

Figure 5: Isotopes of hydrogen. Figure from Wikipedia (en.wikipedia.org/wiki/Isotopes_of_hydrogen).

2.5   *Further applications of the Bohr model*

Provided that the reduced mass, μ, and the nuclear charge Z are correctly taken into account, Eqn 10 can be applied to a wide range of one-electron systems apart from hydrogen.

For example, in the first assignment you will be asked to consider positronium: this is a single-electron atom where a positron replaces the proton. Although positronium only has a lifetime of $\sim$ 142 ns, while it lasts it behaves as an atom and can emit radiation (first observed in 1975).

The positron is the antiparticle of the electron. It has the same mass as the electron but opposite charge.

Other single-electron "atoms" for which the Bohr model works well include the single-electron ions of heavier elements, provided that the correct nuclear charge (Z) is used (see Table 2) and that the electron velocity does not become relativistic. The Bohr model can also be adapted fairly easy for atoms of the neutral Alkali Metals (e.g. Li, Na, K...).

Table 2: Some single-electron ions and their nuclear charge.

single-electron ion	nuclear charge
He$^+$	$Z = 2$
Li^{2+}	$Z = 3$
Be^{3+}	$Z = 4$

Shortcomings of the Bohr model

Despite its success, the Bohr model is not entirely satisfactory. In particular the postulates are a somewhat odd mix of classical physics with quantization imposed, and the third postulate appears to contradict classical electromagnetism.

Of more practical importance, the version of the model discussed above fails to account for the observed *fine structure* in the spectrum of hydrogen. According to Eqn 5, the allowed energies of the bound electron depend only on fundamental constants and the quantum number n. Consequently, it predicts that the wavelength of photons emitted in the transition between a pair of n-values (e.g. for the Balmer α transition between $n = 3$ and $n = 2$) will always be the same. However, high-resolution measurements of the lines in the hydrogen series show that they are not exactly single-wavelength. Instead they are composed of several closely spaced, but distinct lines (see Table 3, Figure 6). Understanding the origin of this fine structure was one of the driving forces for developing more sophisticated models of the hydrogen atom. Of particular note is the Sommerfeld model, which extended the semi-classical treatment of the Bohr model to include elliptical orbits. This model was very successful and able to address many aspects of the observed fine structure.

We will not discuss Sommerfeld's model of the hydrogen atom here, but it is described in detail in Chapter 4 of Eisberg & Resnick, should you wish to know more.

Transition	principle quantum number change	Fine-structure components (nm)	Bohr theory (nm)
Balmer α	$n = 3 \rightarrow n = 2$	656.4522552	656.4696
		656.4537684	
		656.4584404	
		656.466464	
Balmer β	$n = 4 \rightarrow n = 2$	486.264130281	486.2737
		486.264488967	
		486.265465436	
		486.265570391	

Table 3: Vacuum wavelengths for the main fine structure components in selected lines in the hydrogen spectrum. Fine-structure data taken from the *National Institute of Standards and Technology (NIST)* Atomic Spectra Database (physics.nist.gov). The "Bohr theory" values are those obtained from Eqn 10.

Ultimately, the fundamental limitation of the approach we have discussed so far is that the Bohr model, and semi-classical extensions to it, fail for multi-electron atoms, even the simplest: neutral helium. We will therefore not consider further developments to the semi-classical model here but instead turn to the more complete theories of quantum mechanics in the next sections.
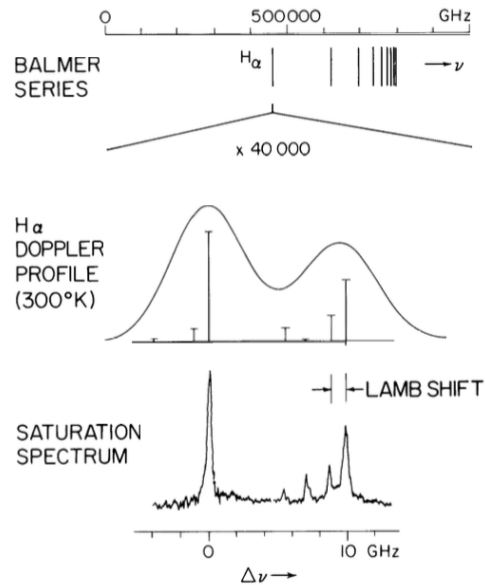
Figure 6: The Balmer α transition of hydrogen resolved into multiple fine-structure components. Figure from Arthur Schawlow's *Nobel* Lecture.

Summary/Revision:

- The spectra of single-electron atoms consist of regular series of lines with wavelengths described by the Rydberg formula.
- Bohr's semi-classical model describes the *quantized* energy and radii of electron orbits in the hydrogen atom and introduces a *quantum number*, *n*.
- The pattern of spectral lines predicted by the Bohr model agrees with the general observed properties of the hydrogen spectrum very well.
- The Bohr model makes simple, testable predictions for how the spectra of other single-electron atoms will behave, depending on the reduced mass and the nuclear charge.
- The simple Bohr model does not account for all properties of the hydrogen spectrum, however. In particular, more sophisticated approaches are need to understand *fine structure* in the spectral lines.

3 Single-electron atoms: Quantum Mechanics and the Schrödinger equation

Context

Why quantum mechanics? In the last section we showed that, while semi-classical models (such as the Bohr model) are very successful for single-electron atoms, they are not entirely satisfactory and are not developed for multi-electron atoms.

Why Schrödinger mechanics? Students have met Schrödinger mechanics already, making it a convenient entry point. Although more sophisticated theories of quantum mechanics exist, much of atomic physics can be understood from a solid foundation in Schrödinger mechanics (with modest extensions when needed).

Learning goals

1. To revise the principles of quantum mechanics, including the wavefunction and the time-independent Schrödinger equation.
2. To revise and elaborate the concepts of operators, eigenfunctions and eigenvalues in quantum mechanics.
3. To appreciate the concepts of *compatible* and *incompatible* quantities in quantum mechanics.
4. To revise the description of angular momentum in quantum mechanics, including operators for components and magnitude (in Cartesian and spherical polar representations).
5. To establish the compatibility of angular momentum operators.
6. To introduce the vector model for angular momentum.

3.1   Introduction

For a true quantum model we must consider wave-particle duality (i.e. the electron in the hydrogen atom can be considered to have wave-like properties) and acknowledge that the Uncertainty Principle means that the idea of electrons following discrete specific orbits (as proposed in the Bohr model) needs to be revised.

Students will have already studied the quantum mechanics of the hydrogen atom in PHY2001. However, since much of our discussion will stem from this, some of main points will be elaborated in this Section, and the next. For further information, students should look back over their own notes, lecture notes and textbooks for the Quantum Mechanics part of PHY2001.

3.2   The wavefunction (revision)

The fundamental quantity in quantum mechanics is the wavefunction $\Psi(\mathbf{r}, t)$ which, for a single particle system, can generally be a function of position ($\mathbf{r}$) and time (t). As students have learned already, the interpretation of Ψ, following Born and others, is that

$$|\Psi|^2 = \Psi^* \Psi$$

We will specify position using a three-dimensional position vector $\mathbf{r}$. Later we will sometimes be more specific and chose to express $\mathbf{r}$ either in Cartesian coordinates (x, y, z) or spherical polar coordinates (r, θ, ϕ).

gives a probability density (i.e the probability of finding a particle in a small region around $\mathbf{r}$ is proportional to $|\Psi|^2$). It then follows that, if summed (i.e. integrated) over all volume (τ), the total probability must be one

Recall that, although $|\Psi|^2$ is necessarily real, Ψ can be complex.

We follow Eisberg & Resnick is using τ for volume (so that we can use V for potential energy without ambiguity).

$$\int_0^\infty |\Psi|^2 \, \mathrm{d}\tau = 1 \ .$$

Since $|\Psi|^2$ is real and represents a physical quantity a consequence is that Ψ and and its derivatives (e.g. $\nabla \Psi$) must:

1. everywhere be finite;
2. everywhere be single valued;
3. everywhere be continuous; and
4. vanish at ∞.

Revise PHY1002 if you are unfamiliar with the meaning of these mathematical properties.

This interpretation of quantum mechanics puts constraints on solutions for the wavefunction which in turn lead to quantisation.

Although the interpretation of the wavefunction as relating to a probability density is of great importance, there is more to the wavefunction than this alone. In fact, the *complete* wavefunction contains *all* the information about the quantum state it represents, not just the *position* information specified by the probability density. Other physical quantities (e.g. momentum, angular momentum etc.) can be obtained

We stress "complete" here since, as we shall see later, the spatial component of the wavefunction you have met in PHY2001 is not quite the full story.

from the wavefunction by application of suitable operators. We will discuss particular examples of this later in this section.

3.3 *The Schrödinger equation*

For a single, non-relativistic particle (mass m) in 3D, the time-dependent Schrödinger equation (which governs the wavefunction) can be written

$$\frac{-\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t} \ . \tag{12}$$

Recall that in e.g. Cartesian coordinates $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. Revise PHY1002 if in doubt.

If, as for the Coulomb potential in atomic physics, V is not a function of time then we can find solutions to Eqn 12 that are *separable* in space and time coordinates: i.e. Ψ can be written

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})T(t) \ , \tag{13}$$

where $\psi(\mathbf{r})$ and $T(t)$ are the space and time parts of the wavefunction, respectively. In this case it is easy to show (PHY2001) that the solution for $T(t)$, is

$$T(t) = \exp\left(-iEt/\hbar\right) \tag{14}$$

while the spatial part of the wavefunction ψ must obey **the time-independent Schrödinger equation**

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{15}$$

Students will have seen all this before, but it is worth emphasising a few points:

1. Given the form of $T(t)$ obtained, although Ψ will retain time dependence, $|\Psi|^2$ will be time independent, provided that E is a real number (because $|\exp(ia)|^2 = 1$ for all real values of a). Thus the probability densities for states described by spatial wavefunctions ψ obeying Eqn 15 will not depend on time. These are sometimes called *stationary states* and it is with their properties that most of this course will be concerned.

2. Mathematically, E in introduced somewhat innocently as a separation constant (having units of energy) in solving the equations. However, its physical interpretation as the *total energy of the system* is extremely important, as will be elaborated below.

We will often work in terms of the *Hamiltonian* operator

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V \qquad (16)$$

so that Eqn 15 can be abbreviated to

When necessary (for clarity) we will use the ^ notation to indicate that a symbol represents an operator.

$$\hat{H}\psi = E\psi \ . \qquad (17)$$

3.4   *Eigenfunctions, eigenvalues and measurements in Quantum Mechanics*

Students will recognise Eqn 17 as an *eigenvalue problem*. If ψ satisfies this equation is it said to be an *eigenfunction* (or *eigenstate*) of $\hat{H}$ with *eigenvalue E*. In general, for any physical problem (i.e. any particular choice for the potential energy function inside $\hat{H}$), we expect that there will be multiple possible eigenfunctions of $\hat{H}$, each with their own eigenvalue E.

Revise PHY2001 for more on *eigenvalues* and *eigenfunctions*.

Eigenvalues and eigenfunctions are of great importance in our interpretation of quantum mechanics. Specifically, whenever a wavefunction is an eigenstate of the operator associated with a physical quantity, this means that the state described by that wavefunction has a definite value of that physical quantity. That value is given by the eigenvalue. E.g., if ψ satisfies Eqn 17 then it is an eigenfunction of the Hamiltonian. Since $\hat{H}$ is associated with the *total energy of the system* (Exercise 3.1), this means that the state has a definite value for the total energy, E, and can be interpreted as an "energy level" of the atom.

Note that while each eigenfunction has an eigenvalue, the eigenvalues do not have to be distinct: i.e. it is possible to have more than one eigenfunction with the same value of E. When multiple such eigenfunctions exist they are said to be *degenerate* with respect to $\hat{H}$.

In general, eigenvalue equations such as Eqn 17 will have multiple solutions. Our physical interpretation of these is that each eigenfunction is a possible state for the system and each eigenvalue is an allowed value for the (measurable) physical property. Moreover, if a physical quantity is measured (i.e. the value becomes known), then the wavefunction immediately after measurement should be an eigenstate of the corresponding operator with eigenvalue matching the measured value. This concept, relating to the *collapse of the wavefunction*, is central to the theory of measurement in quantum mechanics.

If there are degenerate eigenstates then, following measurement, the wavefunction can be a linear combination of the degenerate possibilities, but the idea remains the same.

> **Exercise 3.1: The Hamiltonian as an energy operator**
>
> What is the physical interpretation of the two terms in Eqn 16? Clearly, the second term is associated with the potential energy of the system. Given that the momentum operator is $\hat{\mathbf{p}} = -i\hbar\nabla$, give a physical interpretation to the first term, and hence to the sum.
>
> -
>
> Consider the first term in the Hamiltonian acting on a wavefunction ψ
>
> $$-\frac{\hbar^2}{2m}\nabla^2\psi = -\frac{\hbar^2}{2m}\nabla\cdot\nabla\psi$$
>
> Now substitute $\nabla = -\frac{1}{i\hbar}\hat{\mathbf{p}}$
>
> $$-\frac{\hbar^2}{2m}\nabla^2\psi = -\frac{\hbar^2}{2m}\left(-\frac{1}{i\hbar}\right)\hat{\mathbf{p}}\cdot\left(-\frac{1}{i\hbar}\hat{\mathbf{p}}\right)\psi = \frac{\hat{\mathbf{p}}^2}{2m}\psi$$
>
> From this we see that the first term is in fact the momentum-squared operator divided by $2m$. This is just like the non-relativistic kinetic energy in classical mechanics
>
> $$\frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{p}{m}\right)^2 = \frac{p^2}{2m}$$
>
> i.e. the first term in the Hamiltonian is the *kinetic energy* expressed as an operator.
>
> Just as in classical mechanics, for a single particle moving in a potential, the total energy is the sum of its kinetic plus potential energy and so it make sense to associate the complete Hamiltonian with the total energy of the particle, as expected.

Students may be most familiar with the concept/interpretation of eigenvalue equations as applied to the Hamiltonian (i.e. the time-independent Schrödinger equation). However, it applies just as well to other physical quantities that can be represented as operators (so-called *dynamical variables*). For example, in PHY2001, students were introduced to the momentum operator

$$\hat{\mathbf{p}} = -i\hbar\nabla \ . \tag{18}$$

A wavefunction ψ is an eigenstate of momentum (and will therefore have a definite value for the momentum) if it obeys the eigenvalue equation

$$-i\hbar\nabla\psi = \mathbf{p}\psi \tag{19}$$

where $\mathbf{p}$ is a (vector) constant. If Eqn 19 is satisfied, $\mathbf{p}$ will be the result of any measurement of the momentum. On the other hand, if

Be careful not to confuse operators with their eigenvalues. As is customary, we will often use the same letter for both, but distinguish the operator with a ˆ when the distinction is important.

Eqn 19 is *not* satisfied, the state does *not* have a single definite value for the momentum vector and the result of a momentum measurement will be uncertain.

One way of stating the momentum-position *uncertainty principle*, with which students are familiar, is to say that there are no *simultaneous* eigenstates of both position and momentum: if some particular state is an eigenstate of momentum it *cannot* also be an eigenstate of position. Thus there are no quantum states in which the momentum and position are both known. In such cases, the quantities concerned are said to be *incompatible observables*. In contrast, if states exist that are eigenstates of two quantities, then those quantities can both be known simultaneously and are called *compatible observables*. The concepts of *compatible* and *incompatible observables* are important in atomic physics, having special bearing on our understanding of angular momenta in atoms (elaborated below). If unfamiliar with these concepts, Exercises 3.2 and 3.3 may help to clarify.

Exercise 3.2: Energy and momentum: example 1

In 1 dimension, consider a single particle moving in free space ($V = 0$). Show that, if the particle is in an eigenstate of (linear) momentum, it is also in an energy eigenstate.

- -

In 1D, the momentum operator has only one component

$$\hat{p} = -i\hbar \frac{\mathrm{d}}{\mathrm{d}x}$$

If the particle is in a momentum eigenstate it must satisfy the momentum eigenvalue equation

$$\hat{p}\psi = p\psi$$

where p is a constant (the eigenvalue). Thus

$$-i\hbar \frac{\mathrm{d}}{\mathrm{d}x}\psi = p\psi$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\psi = \frac{ip}{\hbar}\psi \;\Rightarrow\; \frac{1}{\psi}\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{ip}{\hbar} \;\Rightarrow\; \frac{\mathrm{d}\ln\psi}{\mathrm{d}x} = \frac{ip}{\hbar}\;.$$

Integrating gives the solution

$$\ln\psi = \frac{ipx}{\hbar} + \text{const.} \;\Rightarrow\; \psi = C\exp\left(\frac{ipx}{\hbar}\right)$$

where C is a normalisation constant, with which we need not concern ourselves here. We can now check whether this state is *also* an eigenstate of the Hamiltonian (i.e. of energy). In 1D, for $V = 0$, the Hamiltonian is simply

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

and so, adopting the momentum eigenstate from above,

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\left[C\exp\left(\frac{ipx}{\hbar}\right)\right]$$

thus

$$\hat{H}\psi = -\frac{\hbar^2}{2m}C\frac{-p^2}{\hbar^2}\exp\left(\frac{ipx}{\hbar}\right) = \frac{p^2}{2m}\psi$$

Since $p^2/2m$ is a constant, this mean ψ is an eigenstate of $\hat{H}$ (with eigenvalue $E = p^2/2m$). So, *in this case*, the eigenstates of momentum *are* also eigenstates of (total) energy.

In this case, it is possible to simultaneously specify both the energy and the momentum of the particle exactly. This is expressed by saying that the momentum and total energy are "compatible observables" in this example.

Exercise 3.3: Energy and momentum: example 2

Consider whether the momentum and the total energy can simultaneously be completely known for a particles in a 1D potential $V = V_0 x^2$, where V_0 is a postitive constant.

- -

This problem is closely related to Exercise 3.2. The question is whether total energy and momentum are still "compatible observables": i.e. can we still find wavefunctions that are eigenstates of both $\hat{p}$ and $\hat{H}$?

The eigenstates of $\hat{p}$ are unchanged from Exercise 3.2. They are wavefunctions of the form

$$\psi = C \exp \left(\frac{ipx}{\hbar} \right)$$

Are these eigenstates of the new Hamiltonian? Consider

$$\hat{H}\psi = \left(-\frac{\hbar^2}{2m} \frac{\mathrm{d}^2}{\mathrm{d}x^2} + V_0 x^2 \right) \psi \, .$$

We can easily evaluate the derivatives for $\psi = C \exp \left(\frac{ipx}{\hbar} \right)$ to find

$$\hat{H}\psi = \left(\frac{p^2}{2m} + V_0 x^2 \right) \psi$$

Since

$$\frac{p^2}{2m} + V_0 x^2$$

is *not* a constant (it depends on x), we conclude that $\psi = C \exp \left(\frac{ipx}{\hbar} \right)$ is *not* an eigenstate of $\hat{H}$ in this case. Thus, in the presence of the simple-harmonic potential, the total energy and the momentum are no longer compatible observables: we cannot simultaneously know both precisely.

3.5   *Angular momentum*

Of particular importance in atomic physics (but also molecular, nuclear and particle physics) is the application of quantum mechanics and the concepts of *compatible observables* to angular momentum. As students have seen in PHY2001, it is possible (and usual) to describe the states of the hydrogen atom in terms of wavefunctions that are (simultaneously) eigenstates of energy (i.e. obey the time-independent Schrödinger equation, as stationary states must) and of appropriate angular momentum operators.

That angular momentum is relevant to the study of particles bound

in the Coulomb potential comes as no surprise: in classical physics, we know that angular momentum is a conserved quantity in the presence of any central force (i.e. force always directed towards the origin), and the classical angular momentum vector $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is used to characterise orbits (e.g., see Figure 7).

In quantum mechanics, the relationship of (orbital) angular momentum, $\mathbf{L}$ to position $\mathbf{r}$, and linear momentum $\mathbf{p}$, is analogous to that in Classical Mechanics. Specifically, since the linear momentum is given by Eqn 18, it follows that we identify orbital angular momentum with an operator

$$\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}} = -i\hbar \mathbf{r} \times \nabla \qquad (20)$$

Expressed in Cartesian coordinates, the three components of this operator can easily be evaluated by writing out the components of the vector product:

$$\hat{L}_z = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \qquad (21)$$

$$\hat{L}_y = -i\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) \qquad (22)$$

$$\hat{L}_x = -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \qquad (23)$$

These three operators may seem simple enough, but they have several important properties that will both fascinate[3] and inconvenience[4] us as we proceed.

In particular, we can show (Exercise 3.4) that $\hat{L}_z$, $\hat{L}_y$ and $\hat{L}_x$ cannot share a set of eigenfunctions: e.g. if a wavefunction is an eigenstate of $\hat{L}_z$, it cannot also be an eigenstate of $\hat{L}_x$ *or* $\hat{L}_y$. Consequently, the three components of the angular momentum vector are *not* compatible observables: we cannot simultaneously have definite values for more than one of the three components. When encountered for the first time, this is a rather surprising property: a physical vector quantity for which we cannot *in principle* know more than one of the components. Nevertheless, this is what our interpretation of quantum mechanics implies, and this property is vital to our quantum treatment of atoms.
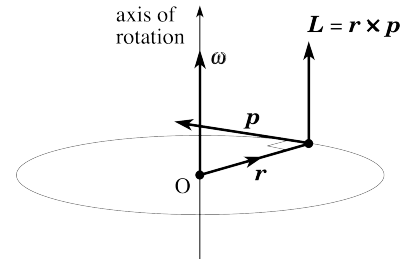

Figure 7: Classically, a particle in a circular orbit of radius $|\mathbf{r}|$ with momentum $\mathbf{p}$ has angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. The magnitude of the vector gives the value of $rp = mvr$, and the vector is oriented perpendicular to the plane of rotation ($\mathbf{L}$ is parallel to the orbital velocity vector ω).

We give the Cartesian expressions here, but note that for most real applications to atomic physics it is more convenient to use spherical polar coordinates. See Appendix M of Eisberg & Resnick, and below.

[3] I hope.

[4] Of this I am sure.

Equivalently, the vector operator $\hat{\mathbf{L}}$ has *no* eigenstates except for the rather uninteresting $L = 0$.

Exercise 3.4: Compatibility of angular momentum components

According to our interpretation of quantum mechanics, physical quantities are compatible (i.e. can be simultaneously known) if there exist wavefunctions that are eigenstates of both. Here we aim to show that this is *not* the case for L_x and L_z (as defined by Eqns 21 and 23). There exist a number of ways to consider this question in quantum mechanics, and students will likely encounter more complete/sophisticated treatments in later courses. Here, we will content ourselves with a fairly simple proof by contradiction, which addresses most of the main points.

Suppose that the $\hat{L}_x$ and $\hat{L}_z$ did share an eigenfunction ψ. By definition, ψ would then obey both the eigenvalue equations

$$\hat{L}_x\psi = \lambda_x\psi \ \text{ and } \ \hat{L}_z\psi = \lambda_z\psi$$

where λ_x and λ_z are the eigenvalues (constants).

(a) For ψ to be an eigenstate of both $\hat{L}_x$ and $\hat{L}_z$, prove that it must satisfy

$$(\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x)\psi = 0$$

(b) Using Eqns 21 and 23, find an expression for $(\hat{L}_x\hat{L}_z \quad - \quad \hat{L}_z\hat{L}_x)$ and use this to explain why it is impossible to satisfy the equation in part (a), except for the trivial case in which all the components of angular momentum are zero.

- -

(a) Consider

$$(\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x)\psi = \hat{L}_x\hat{L}_z\psi - \hat{L}_z\hat{L}_x\psi \ .$$

If ψ obeys the eigenvalue equations given above ($\hat{L}_x\psi = \lambda_x\psi$, $\hat{L}_z\psi = \lambda_z\psi$) we can use these to evaluate each of the operators in turn and obtain the desired result:

$$\hat{L}_x\hat{L}_z\psi - \hat{L}_z\hat{L}_x\psi = \hat{L}_x\lambda_z\psi - \hat{L}_z\lambda_x\psi = \lambda_z\lambda_x\psi - \lambda_x\lambda_z\psi = (\lambda_z\lambda_x - \lambda_x\lambda_z)\psi = 0$$

since the λ-values are just constants.

(b) However, we can substitute our expressions for the operators and evaluate the result:

$$(\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x)\psi = -\hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi + \hbar^2\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\psi$$

$$= -\hbar^2\left[\left(yx\frac{\partial^2\psi}{\partial z\partial y} - y^2\frac{\partial^2\psi}{\partial z\partial x} - zx\frac{\partial^2\psi}{\partial y^2} + zy\frac{\partial^2\psi}{\partial y\partial x} + z\frac{\partial\psi}{\partial x}\right) - \left(xy\frac{\partial^2\psi}{\partial y\partial z} + x\frac{\partial\psi}{\partial z} - xz\frac{\partial^2\psi}{\partial y^2} - y^2\frac{\partial^2\psi}{\partial x\partial z} + yz\frac{\partial^2\psi}{\partial x\partial y}\right)\right]$$

$$= -\hbar^2\left(z\frac{\partial\psi}{\partial x} - x\frac{\partial\psi}{\partial z}\right) \ \left[\text{recall that } \frac{\partial^2\psi}{\partial z\partial y} = \frac{\partial^2\psi}{\partial y\partial z} \ \text{etc.}\right]$$

$$\neq 0 \ \ [\text{at least not in general}]$$

Thus we have a contradiction: if ψ is an eigenstate of both $\hat{L}_x$ and $\hat{L}_z$, then we have to find $(\hat{L}_x\hat{L}_z \quad - \quad \hat{L}_z\hat{L}_x)\psi \quad = \quad 0$, according to part (a). But part (b) tells us that, $(\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x)\psi$ will not generally be zero but a function. Therefore we conclude that our initial assumption, that a set of joint eigenfunctions exists is spurious and conclude that we cannot (in general) have ψ satisfy both $\hat{L}_x\psi \quad = \quad \lambda_x\psi$ and $\hat{L}_z\psi = \lambda_z\psi$.

Note: the argument presented here outlines the principles, but there is some additional subtlety (particularly associated with $L = 0$) which we will not elaborate here.

We can, however, simultaneously specify more about the orbital angular momentum than just one of its components. Although $\mathbf{L}$ is incompatible with any of its own components, $\mathbf{L}^2$ *is* compatible with any of the three components. Physically, we can readily identify $\mathbf{L}^2$ with the square of the **magnitude** of the orbital angular momentum vector, and the associated operator can be obtained from Eqn 20 and/or Eqns 21 – 23

$$\hat{\mathbf{L}}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{24}$$

Students may find it an illustrative, if slightly laborious, exercise to work through a proof to demonstrate that e.g. $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ can have simultaneous eigenstates (and are therefore compatible observables). This, can be done using an approach equivalent to that in Exercise 3.4 but, in this case, leading to the conclusion that joint eigenfunction *do* exist.

In quantum mechanics, the combination of knowing the magnitude of the angular momentum vector (via $|\mathbf{L}| = \sqrt{\mathbf{L}^2}$) and any one of its three components is the most complete specification of the angular momentum of a state that can be given. Throughout this course, as is customary, we will choose to adopt the z-component of the angular momentum as the one to be specified (meaning that the x- and y-components are uncertain). Choosing the z-component is merely a convention, adopted for mathematical convenience.

Vector model of angular momentum

Many of the important properties of angular momentum in quantum mechanics can be represented via a simple *vector* model, as illustrated in Figure 8 – the magnitude and z-component of the vector $\mathbf{L}$ are known, but the x- and $y-$components are uncertain: in the diagram this means that the tip of the vector could lie anywhere on the dotted circle.

Angular momentum operators in spherical polar coordinates

Since the Coulomb potential due to the nucleus in atoms is spherically symmetric, is it usual to work in spherical polar coordinates (r, θ, ϕ) rather than Cartesian coordinates (Figure 9). Although slightly tedious, it is a purely mathematical endeavour to use the relationships between Cartesian and spherical polar coordinate systems to re-express the operators introduced above in spherical coordinates. This is discussed e.g. in Appendix M of Eisberg & Resnick and so here we will state only the most important two results, because we will need them in later sections.

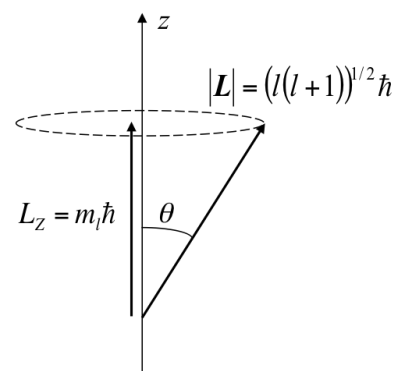A precise expression for the $\hat{\mathbf{L}}^2$ operator in spherical polar coordinates will be given below.

Figure 8: Vector model for the orbital angular momentum $\mathbf{L}$. The magnitude and z-component of the vector are specified but the x and y components are uncertain: thus the vector is confined to lying on a "cone", pointing to a position on the circle indicated by the dashed line. The quantum numbers l and m_l are defined in the next section.
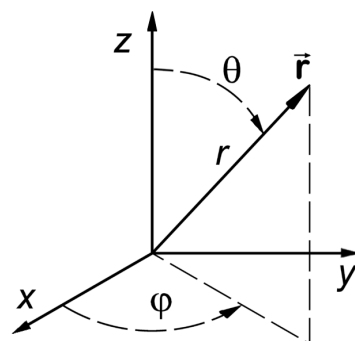

Figure 9: Relationship between Cartesian (x, y, z) and spherical polar (r, θ, ϕ) coordinate systems.

In spherical polar coordinates, the $\hat{L}_z$ operator has a particularly simple form

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \ . \tag{25}$$

It is largely the simplicity of the $\hat{L}_z$ operator that motivates the convention of working with L_z rather than L_x or L_y as our compatible observable.

Notice that this operator involves neither r nor θ. The $\hat{\mathbf{L}}^2$ operator is more complicated but can be expressed as

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \ . \tag{26}$$

In this case, the operator involves both θ and ϕ, but still r does not appear.

Summary/Revision:

- All information about a quantum state is contained in the *wavefunction*.
- Physical quantities (observables) are associated with operators that can be applied to the wavefunction.
- The eigenfunctions of an operator are states with a definite value for the associated physical quantity. The value for the quantity is the eigenvalue.
- The Hamiltonian is associated with the total energy. The time-independent Schrödinger equation is an energy eigenvalue equation: wavefunctions satisfying this equation have definite energy and are *stationary states*.
- Physical quantities are *compatible* if they posses a simultaneous set of eigenstates and *incompatible* if they do not. If two quantities are incompatible they cannot both be specified without uncertainty.
- L_x, L_y and L_z are incompatible with each other, but compatible with $\mathbf{L}^2$.
- The vector model is one means to visualise what we can know about angular momentum in quantum mechanics.
- Operators for the z-component of the angular momentum and for the square of the magnitude of the angular momentum are given by Eqns 25 and 26.

4 *Single-electron atoms: space wave-functions (revision)*

Context

Why revisit the single-electron wavefunctions? Students have considered solutions to the one-electron Schrödinger equation already. However, since the study of multi-electron atoms builds on what has been learned from solving the one-electron case, it will be important to briefly revise the main points for later reference.

Learning goals

1. To revise how the Schrödinger equation is actually solved for one-electron atoms.
2. To clarify that the one-electron states are eigenstates of $\hat{\mathbf{H}}$, $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ (i.e. have definite energy, magnitude of angular momentum and z-component of angular momentum).
3. To revise the manner in which quantisation enters the solution and ensure familiarity with the *quantum numbers n, l and m_l*.

4.1   Solving the time-independent Schrödinger equation for the one-electron atom

Most students will have already seen the process of solving the time-independent Schrödinger equation (Eqn 15)

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

for a one-electron atom (PHY2001), so we will not repeat all the details here. Instead, in the following sub-sections, we will outline the process only and emphasise the physically important points, which will help shape our understanding of multi-electron atoms later.

Details of how the equation can be solved are **not** required for this module. However, Eisberg & Resnick gives an excellent description, which is recommended reading for those curious to see the details of how it works.

4.2   Separation of variables

We start by identifying the particle mass as the reduced mass of the electron-nuclear system ($m = \mu$, just as in the Bohr model) and specifying the form of the potential,

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \,, \tag{27}$$

and we note that V depends only on r (neither θ nor ϕ). We consider a solution in which the wavefunction is written as the product of three functions, each of which depends on only one of the spherical polar coordinates

Technically, we do not really need to specific the exact form of the potential before carrying out the separation of variables, but we do need to agree that it depends only on r.

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) \,. \tag{28}$$

Separation of variables leads to three differential equations, one associated with each coordinate. First, by separating ϕ, we obtain

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m_l^2\Phi \,, \tag{29}$$

second, for θ,

$$\left[-\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\right) + \frac{m_l^2}{\sin^2\theta}\right]\Theta = l(l+1)\Theta \,, \tag{30}$$

and the third equation governs the radial function

$$\left[\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right) + \frac{2\mu}{\hbar^2}\left(E - V(r)\right)\right]R = l(l+1)\frac{R}{r^2} \,. \tag{31}$$

Each of these three equations can be solved to find the appropriate sets of functions Φ, Θ and R (students will have seen these solutions before [PHY2001] and some of their properties are discussed below).

Before considering the solutions, however, there are several points to reinforce from the equations themselves:

1. In carrying out the separation of variables we introduced *two* more separation constants: "$-m_l^2$" and "$l(l+1)$". This is in close analogy to how E entered our framework (Eqn 15) as a separation constant between time and space coordinates. Just as for E, it is natural to examine the separated equations when establishing a physical meaning for the separation constants.

   We write the constants this way because it turns out to be convenient later but, when they first appear here, they are arbitrary constants.

2. Eqns 29, 30 are eigenvalue equations with eigenvalues related to the separation constants.

3. Using Section 3.5, we can give a physical interpretation of Eqn 29 and its eigenvalue. Specifically, Eqn 25 associates ϕ-derivates with L_z. If we operate on the state defined by the wavefunction $\psi = R(r)\Theta(\theta)\Phi(\phi)$ with $\hat{L}_z$ twice we obtain

$$\hat{L}_z\hat{L}_z\psi = \left(-i\hbar\frac{\partial}{\partial\phi}\right)\left(-i\hbar\frac{\partial}{\partial\phi}\right)R(r)\Theta(\theta)\Phi(\phi) = -\hbar^2 R(r)\Theta(\theta)\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}\ .$$

   However, we know that Φ must obey Eqn 29, so even without solving equations Eqns 29 – 31, we can see that

$$\hat{L}_z\hat{L}_z\psi = -\hbar^2 R(r)\Theta(\theta)(-m_l^2)\Phi = \hbar^2 m_l^2\psi\ .$$

   Thus $\psi = R\Theta\Phi$ must be an eigenstate of $\hat{L}_z\hat{L}_z$ (with eigenvalue $\hbar^2 m_l^2$). In fact we can choose it to be an eigenstate of $\hat{L}_z$ itself, with corresponding eigenvalue $\hbar m_l$.

   Formally, there is some subtlety here – but loosely we can think of this in the following way: we have shown that if we act on ψ with $\hat{L}_z$ twice, this is equivalent to multiplying ψ by $\hbar m_l$ twice. So we anticipate that acting on ψ with $\hat{L}_z$ once will be equivalent to multiplying by $\hbar m_l$ once.

$$\hat{L}_z\psi = \hbar m_l\psi \tag{32}$$

   Thus ψ has a definite value for the z-component of angular momentum, and that value is $m_l\hbar$. m_l is known as the *magnetic quantum number*, because of its relevance to how atoms behave in the presence of an applied magnetic field.

4. In a similar way, Eqn 30 is closely related to the $\hat{\mathbf{L}}^2$ operator (Eqn 26): see Exercise 4.1. This leads to the conclusion that $\psi = R\Theta\Phi$ is *also* an eigenstate of $\hat{\mathbf{L}}^2$:

$$\hat{\mathbf{L}}^2\psi = l(l+1)\hbar^2\psi \tag{33}$$

   Again, the eigenvalue is related to the separation constant: it is $l(l+1)\hbar^2$, from which we conclude that a measurement of the

magnitude of the orbital angular momentum vector will yield $\sqrt{l(l+1)}\hbar$. l is often called the *orbital angular momentum* quantum number and sometimes (e.g. in Eisberg & Resnick) the *azimuthal* quantum number.

Exercise 4.1: Eigenstates of $\hat{\mathbf{L}}^2$.

Show that, if $\psi = R\Theta\Phi$ satisfies Eqn 30 and Eqn 29 then it is an eigenstate of $\hat{\mathbf{L}}^2$ with eigenvalue $l(l+1)\hbar^2$.

- -

Apply the $\hat{\mathbf{L}}^2$ operator (Eqn 26) to ψ:

$$\hat{\mathbf{L}}^2\psi = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] R(r)\Theta(\theta)\Phi(\phi)$$

$$= -\hbar^2 \left[\frac{R\Phi}{\sin\theta} \frac{\mathrm{d}}{\mathrm{d}\theta} \left(\sin\theta \frac{\mathrm{d}\Theta}{\mathrm{d}\theta} \right) + \frac{R\Theta}{\sin^2\theta} \frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} \right]$$

using Eqn 29 to simplify the last term

$$\hat{\mathbf{L}}^2\psi = -\hbar^2 \left[\frac{R\Phi}{\sin\theta} \frac{\mathrm{d}}{\mathrm{d}\theta} \left(\sin\theta \frac{\mathrm{d}\Theta}{\mathrm{d}\theta} \right) - \frac{R\Theta}{\sin^2\theta} m_l^2 \Phi \right]$$

$$= R\Phi\hbar^2 \left[-\frac{1}{\sin\theta} \frac{\mathrm{d}}{\mathrm{d}\theta} \left(\sin\theta \frac{\mathrm{d}}{\mathrm{d}\theta} \right) + \frac{m_l^2}{\sin^2\theta} \right] \Theta \ .$$

Eqn 30 allows us to replace the term in square brackets, leading to

$$\hat{\mathbf{L}}^2\psi = R\Phi\hbar^2 \left(l(l+1)\Theta \right) = \hbar^2 l(l+1)\psi \ .$$

Thus, as required, ψ is an eigenfunction of $\hat{\mathbf{L}}^2$ with eigenvalue $l(l+1)\hbar^2$.

4.3   *Solving for the eigenstates and quantisation*

To find suitable combinations of functions $(R(r), \Theta(\theta), \Phi(\phi))$, Eqns 29 – 31 can all be solved by standard mathematical techniques. Students will have seen elements of this before (PHY2001) and the details are presented (for Eqns 30 and 31) in Appendix N of Eisberg & Resnick.

In finding the possible solutions we have to remember that they must meet the conditions laid out in Section 3.2: i.e. be continuous, single-valued etc. Is is these requirements that lead to quantisation: if unfamiliar, Exercise 4.2 illustrates the principle applied to the Φ function. Taken together, finding physical solutions leads to three distinct quantisation conditions (one associated with each equation):

For this module, students are not required to know the details of how to solve equations 30 and 31: you just need to be satisfied that they can be solved and be able to verify specific solutions by substitution.

1. *Energy* quantisation:

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} \tag{34}$$

   where n is a positive integer.
2. *Orbital angular momentum* quantisation:

   l is an integer in the range $0 \le l < n$.
3. L_z quantisation:

   m_l is an integer in the range $-l \le m_l \le l$.

Notice that the quantisation condition on E is exactly the same as predicted by the Bohr model (and the integer n is still called the *principal quantum number*, as in the Bohr model). However, note that there are fundamental differences from the Bohr model. For example, the angular momentum for the $n = 1$ state is $\hbar$ in the Bohr model (by postulate) but zero in the quantum mechanical treatment.

For completeness, Table 4 lists the first few wavefunctions for single-electron atoms, identified by the three defining *quantum numbers n, l* and m_l. Plots of some of these wavefunctions are given in Chapter 7 of Eisberg & Resnick and (as radial and/or angular probability distributions) in the PHY2001 lecture notes (reproduced in the slides accompanying these notes).

The eigenfunctions have several noteworthy properties, including:

1. In all cases, the solution includes an exponential term with negative argument proportional to r. This ensures the wavefunction vanishes at ∞, as it must.
2. For $l = 0$, the wavefunction is independent of both θ and ϕ: i.e. it is spherically symmetric.
3. For $l = 0$ the wavefunction is finite at $r = 0$. For all other values of l, $\psi \to 0$ as $r \to 0$. This means that only $l = 0$ states can place the electron very close to the nucleus.

4. For $m_l = 0$, the wavefunction is independent of ϕ. The probability density $\psi^*\psi$ is always independent of ϕ.

Exercise 4.2: Quantisation: Φ as an example.

Show that physical solutions to Eqn 29 require that m_l be an integer.

- -

We know that Φ obeys:

$$\frac{d^2\Phi}{d\phi^2} = -m_l^2\Phi\,,$$

We should recognise this as the simple harmonic equation, to which the solution is

$$\Phi = Ce^{im_l\phi} \quad \left(\text{or } Ce^{-im_l\phi}\right)$$

where C is a normalisation constant. Mathematically, this is a solution for *any* value of m_l (if unsure, this can be easily verified by direct substitution). However, $\Phi(\phi)$ is part of the wavefunction and so must be single-valued at any point in space (see Section 3.2). In particular, a point described by $\phi = 2\pi$ is exactly the *same* point described by $\phi = 0$. Thus for ψ to be single-valued, it must be that

$$\Phi(\phi = 0) = \Phi(\phi = 2\pi) \rightarrow e^0 = e^{im_l 2\pi} \rightarrow 1 = e^{im_l 2\pi}\,.$$

Euler's relation (PHY1002) tells us that

$$e^{im_l 2\pi} = \cos m_l 2\pi + i\sin m_l 2\pi$$

from which we can see that the requirement $= 1$ is met if (and only if) m_l is an integer. I.e., by imposing the physical condition that the wavefunction is single-valued in space we find that m_l must be an integer.

Quantum Numbers			Eigenfunctions
n	l	m_l	
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$
2	1	± 1	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta \, e^{\pm i\phi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \cos\theta$
3	1	± 1	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \sin\theta \, e^{\pm i\phi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \left(3\cos^2\theta - 1\right)$
3	2	± 1	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin\theta \cos\theta \, e^{\pm i\phi}$
3	2	± 2	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin^2\theta \, e^{\pm 2i\phi}$

Table 4: Some Eigenfunctions for the One-Electron Atom. From Eisberg & Resnick.

It is usual to identify the specific wavefunctions via their values for the three quantum numbers n, l and m_l. These quantum numbers, their associated eigenvalues and their quantisation conditions are all summarised in Table 5. For reference, the common names of the quantum numbers are given in Table 6.

The quantisation of **L** can be represented by a vector model, as in the example shown in Figure 10. Following our discussion of incompatible observables and angular momentum (Section 3), it should come as no surprise that only two quantum numbers are needed to specify the orbital angular momentum as completely as possible: the other two components L_x and L_y are incompatible with L_z and so cannot be used to add further labels to the states: l and m_l tell us as much as we can know!

However, the spatial functions are not the complete specification of the quantum state: for this we must also consider the spin of the electron, which will be discussed more fully in the next section.
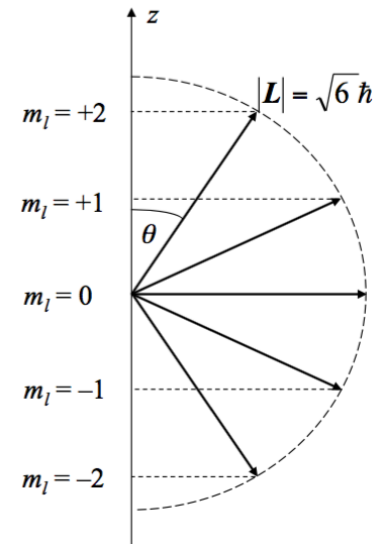

Figure 10: Representation of a vector model for **L** in the case $l = 2$: the magnitude of the vector is known ($\sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$) and the z-component can have discreet allowed values $m_l\hbar$ with $m_l = -2, -1, 0, 1$ or 2.

Summary/Revision:

- The time-independent Schrödinger equation can be solved for single-electron atoms.

Physical quantity	Eigenvalue	Quantum number	Quantization
E	$-\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$	n	$n > 0$
$|\mathbf{L}|$	$\sqrt{l(l+1)}\hbar$	l	$0 \le l < n$
L_z	$m_l \hbar$	m_l	$-l \le m_l \le l$

Table 5: The quantum numbers associated with solving the Schrödinger equation for a one-electron atom. Note that the n, l and m_l quantum numbers must be integers.

Quantum number	Name
n	principal quantum number
l	orbital angular momentum quantum number
m_l	magnetic quantum number

Table 6: Some commonly used names for the quantum numbers.

- The eigenfunctions obtained are identified not only with specific values for the energy (E) but also for the magnitude ($|\mathbf{L}|$) and z-component (L_z) of the orbital angular momentum.
- E, $|\mathbf{L}|$ and L_z are all quantised.
- The quantisation is conveniently expressed in terms of the *quantum numbers n, l and m_l* (see Table 5); these three quantum numbers are commonly used to label or identify states.

5   Single-electron atoms: spin, total angular momentum and spectroscopic notation

Context

Why introduce spin? Spin is a quantum mechanical property distinct from those described by the spatial wavefunction. Spin is very important in explaining atomic structure (and also nuclear and particle physics).

Why use spectroscopic notation? As we extend our theory of atomic physics we will find spectroscopic notation a useful shorthand to identify states in atoms. Spectroscopic notation is also widely used in other topics, including molecular, nuclear and particle physics.

Learning goals

1. To formally introduce the spin part of the wavefunction.
2. To appreciate that spin has many similarities to orbital angular momentum, and has analogous compatible observables.
3. To introduce the total angular momentum **J**.
4. To introduce spectroscopic notation as used in atomic physics.
5. To conclude discussion of one-electron atoms with relativistic results.

5.1   *Electron spin*

Wavefunctions as obtained by solving the Schrödinger equation (e.g. Eqn 15) are expressed in terms of the spatial coordinates (**r**) of the electron. However, we know (e.g. from the Stern-Gerlach experiment; recall last semester labs) that electrons also have a quantum mechanical property known as *spin*. A full specification of the quantum mechanical state of an electron therefore requires that the "coordinates" associated with its spin properties are also specified. This can be done by identifying the complete wavefunction as a product of a "spatial" part (ψ) and a "spin" part (σ):

$$\text{complete wavefunction} = \text{space wavefunction} \times \text{spin wavefunction}$$
$$= \psi(\mathbf{r}) \times \sigma(\mathbf{S})$$

Note that, because the spin does not appear in the simple one-electron Hamiltonian we have considered in Section 4, we expect that the spin part of the wavefunction will not alter the energies of states. However, spin does affect the energy in more advanced theories, and in multi-electron atoms (see later).

Unlike the space coordinates (**r**), the spin "coordinates" for an electron are discreet. Specifically, spin (**S**) is a vector that behaves in a manner very similar to orbital angular momentum (**L**): the spin properties of an electron are described by two quantum numbers

1. All electrons have the same magnitude of their spin: this is specified by the spin quantum number $s = 1/2$, which gives the magnitude of the spin angular momentum: $\mathbf{S}^2 = s(s+1)\hbar^2$;

2. For an isolated electron, the second quantum number, m_s, gives the z-component of the spin $S_z = m_s\hbar$. Similar to the rules for orbital angular momentum, the allowed values for m_s range from $-s$ to s in integer steps, which (since $s = 1/2$) gives only two allowed values: $m_s = +1/2$ and $-1/2$. These two "orientation" states are usually referred to as "up" and "down".

Just like orbital angular momentum, the three components of spin (S_x, S_y, S_z) are *incompatible* with each other: thus if (as is conventional) we identify states by definite S_z-values, those states cannot have definite values of S_x or S_y. Note that all component of **S** are compatible with all components of **L**. In both cases, the incompatibility is between components of the *same* operator.

For a one-electron atom, the electron spin is a fairly simple "bolt-on" to the Schrödinger theory: it just requires that the two spin quantum numbers (see Table 7) are included when defining a state.

Physical quantity	Eigenvalue	Quantum number	Quantization
$\lvert\mathbf{S}\rvert$	$\sqrt{s(s+1)}\hbar$	s	$s = \frac{1}{2}$
S_z	$m_s\hbar$	m_s	$m_s = -\frac{1}{2}$ or $\frac{1}{2}$

Table 7: The spin quantum numbers for a single-electron atom. Note that s is often not really included in "the list" for single-electron atoms since, for such atoms, $s = 1/2$ always.

5.2 *Total angular momentum: addition of **L** and **S**.*

We will often find it useful to work with the **total angular momentum (J)**, which is the sum of the orbital angular momentum and the spin (see Figure 11)

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \qquad (35)$$

Just like **L** and **S**, **J** is an angular momentum vector and its properties are specified by two quantum numbers:

1. the magnitude of **J** is determined by the quantum number j via $|\mathbf{J}| = \sqrt{j(j+1)}\hbar$;
2. the z-component, J_z, is given by a quantum number m_j in the familiar manner: $J_z = m_j\hbar$.

If s is half-integer (as for single-electron atoms), then j is also half-integer[5]. However, in multi-electron atoms the total angular momentum quantum number can be integer (as in e.g. the helium atom, to be discussed later).

In a manner similar to **L** and **S**, the allowed values of m_j form a sequence

$$m_j = -j, -j+1, ..., j-1, j. \qquad (36)$$

Consequently, for each j-value, there are always $2j+1$ distinct states (each with its own m_j-value).

As one might expect, the specific allowed values of j depend on the particular combination of **L** and **S** that are being added. In particular, since **J** is obtained by vector addition, we require that $||\mathbf{L}| - |\mathbf{S}|| \leq |\mathbf{J}| \leq |\mathbf{L}| + |\mathbf{S}|$ (see Figure 12). Expressed in quantum numbers this becomes

$$|\sqrt{l(l+1)} - \sqrt{s(s+1)}| \leq \sqrt{j(j+1)} \leq \sqrt{l(l+1)} + \sqrt{s(s+1)}$$

For the current case of interest (single electron atom), $s = 1/2$ and the above inequality can be satisfied for two half-integer choices of j:

$$j = l + 1/2, \; l - 1/2$$

except for the special case $l = 0$ for which the only solution is

$$j = 1/2.$$

These are specific examples of the general rule for addition of spin and orbital angular momentum quantum numbers, which we will revisit when discussing multi-electron atoms later. Exercise 5.1 gives an example of using the above rules to find the allowed total angular momentum quantum numbers for a single-electron atom.
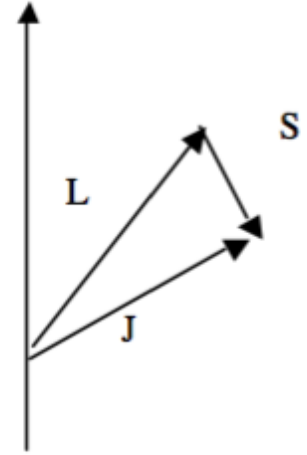

Figure 11: Vector addition of **L** and **S** to form the total angular momentum **J**.

[5] By "half-integer" we mean 1/2, 3/2, 5/2, etc.

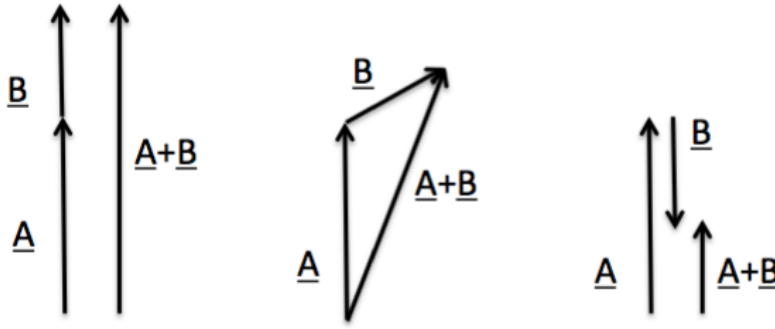Students can verify that these j-values do indeed satisfy the required inequality by substitution.

Exercise 5.1: Total angular momentum quantum numbers

Consider states of a single-electron atom in which $l = 2$. Identify all the possible states by their j and m_j quantum numbers, and verify that the total number of states is given by $2(2l + 1)$.

- -

For a single-electron atom, $s = 1/2$. So, for $l = 2$, the allowed values of j are
$$j = 3/2 \text{ and } 5/2$$

For $j = 3/2$, the allowed values of m_j are $-3/2, -1/2, 1/2$ and $3/2$ (i.e. four distinct states).
For $j = 5/2$ there are six distinct states, corresponding to m_j-values $-5/2, -3/2, -1/2, 1/2, 3/2$ and $5/2$.
Thus, in total, there are 10 states. This is consistent with the statement that the total number of states is $2(2l + 1) = 10$.

The combination of specifying j and m_j rather than m_l and m_s provides an alternative, and usually more convenient, means of identifying states of the atom. In this representation, the full set of quantum numbers describing the state of a single-electron atom is tabulated in Table 8.

Of course, the total number of quantum states does not depend on whether we label them with m_l and m_s or with j and m_j (see Exercise 5.2), and, for the simple Hamiltonian of Section 4, it makes no real difference which labels we use to identify the states. However, when additional physics is considered (in particular the spin-orbit interaction, to be discussed later), it is preferable to use the j-representation introduced here.

$|\mathbf{J}|$ is compatible with neither L_z nor S_z, thus formally we must choose *either* to identify states with j (and m_j) or with m_l and m_s; we cannot use all together.

Physical quantity	Eigenvalue	Quantum number	Quantization
E	$-\dfrac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$	n	$n > 0$
$|\mathbf{L}|$	$\sqrt{l(l+1)}\hbar$	l	$0 \le l < n$
$|\mathbf{S}|$	$\sqrt{s(s+1)}\hbar$	s	$s = \frac{1}{2}$
$|\mathbf{J}|$	$\sqrt{j(j+1)}\hbar$	j	$j = l \pm 1/2$ or $j = 1/2$ for $l = 0$
J_z	$m_j\hbar$	m_j	$-j, -j+1, ..., j-1, j$

Table 8: The quantum numbers for a single-electron atom when described in terms of a total angular momentum. Note that the n and l quantum numbers must be integers while j and m_j will be half-integer in this case.

Exercise 5.2: Total number of quantum states

As in Exercise 5.1, consider the states of a single-electron atom in which $l = 2$. Verify that whether we identify states using m_l and m_s or using j and m_j the total number of such states is the same.

- -

From Exercise 5.1 we know that the j and m_j representation leads to a total of 10 distinct states with $l = 2$ and $s = 1/2$. Considering m_l and m_s instead, we know that the allowed values of m_l would be integers from $-l$ to $+l$: i.e. there are 5 allowed m_l values: $-2, -1, 0, 1$ and 2. For each m_l value there will be 2 distinct states: one with $m_s = -1/2$ and one with $m_s = +1/2$. Thus the total number of states is $5 \times 2 = 10$, consistent with Exercise 5.1.

5.3   *Spectroscopic notation: Terms*

It is standard to identify atomic states by their combination of orbital angular momentum, spin angular momentum and total angular momentum quantum numbers. For the single-electron atom, this mean the l, s and j quantum numbers from Table 8. In spectroscopic notation, this information is written as a *Term*, in the following form:

$$^{2s+1}l_j \tag{37}$$

As we will see, in multi-electron atoms, the *term* gives the angular momentum quantum numbers for the atom as a whole. However, for the single-electron atoms described so far this distinction is unimportant (since there is only one electron to contribute).

When written out, the numerical values are used for $2s + 1$ (often called the *spin multiplicity*) and for j, however, the orbital angular momentum quantum number is represented using a letter (see Table 9). In writing a term, the letter is always *upper case* (i.e. "P" not "p"). Thus, for example, a single-electron atom in the state with $l = 2$ and $j = 5/2$ (and, of course, $s = 1/2$) is identified by the term

We must be very precise when using spectroscopic notation: lowercase letters are used to specify *configurations* (see later), which must not be confused with *terms*.

$$^2\mathrm{D}_{5/2}$$

while the ground state of hydrogen ($l = 0$) has term

Note: when reading terms, it is common to say "singlet", "doublet", "triplet" etc. to express the spin multiplicity (i.e. we might say "doublet dee five-halves" and "doublet ess half" for the two examples here).

$$^2S_{1/2} \, .$$

Exercises 5.3, 5.4 and 5.5 give some additional examples.

Giving the spectroscopic term alone does not fully identify a state of a single-electron atom. To include the principal quantum number n, we often write it as an integer before the term. Thus the ground state is identified by

$$1 \, ^2S_{1/2}$$

while the states making up the $n = 2$ energy levels are

$$2 \, ^2S_{1/2} \, , \ \ 2 \, ^2P_{1/2} \ \text{and} \ 2 \, ^2P_{3/2} \, .$$

The m_j quantum number is not normally specifically identified when naming states because, in the absence of e.g. an applied magnetic field, the m_j states are degenerate. Similarly, states that differ only in their j-values are very nearly degenerate and this label is sometimes dropped from the term. Thus e.g. the name "2 ^2P" in the hydrogen atom would be understood to mean the combination of $^2P_{1/2}$ and $^2P_{3/2}$.

orbital angular momentum quantum number	letter	origin
0	S	sharp
1	P	principal
2	D	diffuse
3	F	fundamental
4	G	alphabetical
5	H	

Table 9: Letters used to identify orbital angular momentum quantum numbers in spectroscopic *terms*. The third column gives the spectroscopic series names from which the convention derives. After "F" alphabetical identification is used.

Exercise 5.3: Constructing terms

Write out all the *terms* that describe states of the hydrogen atom for principal quantum number $n = 4$.

- -

For $n = 4$, the allowed values of l are 0, 1, 2 and 3, which we denote using S, P, D and F, respectively. For $l = 0$, we only have $j = 1/2$ (since $s = 1/2$ for hydrogen) while for all the other l-values we have $j = l - 1/2$ and $j = l + 1/2$. Thus the full list of terms is:
$^2S_{1/2}, \, ^2P_{1/2}, \, ^2P_{3/2}, \, ^2D_{3/2}, \, ^2D_{5/2}, \, ^2F_{5/2}$ and $^2F_{7/2}$

Exercise 5.4: Interpreting terms (1)

What are the angular momentum quantum numbers for states of the hydrogen atom with term $^2H_{11/2}$?

- -

From the term, we can read off $2s + 1 = 2 \rightarrow s = 1/2$ (as expected). H corresponds to $l = 5$, and the j-value can be read off directly as $j = 11/2$.

> **Exercise 5.5: Interpreting terms (2)**
>
> What is the lowest principal quantum number for which a $^2G_{7/2}$ term is possible?
>
> -
>
> A G-term requires $l = 4$. Thus, since $l < n$, the lowest value of n for which this term is allowed is $n = 5$.

Single-electron Dirac theory results

We have now introduced the full quantum mechanical description of the states of a single-electron atom (in terms of n, l, s, j and m_j) and the means by which states can be identified (and counted) using these quantum numbers and spectroscopic terms. Although s, j and m_j matter even in the simplest quantum theories of atoms (since they determine how many distinct states an atom has), the energies of the states of single-electron atoms are unaffected by the values of these three quantum numbers in the simple Schrödinger theory (Section 4).

However, in the more complete theory of relativistic quantum mechanics developed by Dirac, the angular momentum does affect the energy. Specifically, Dirac theory (which accounts for relativistic effects and the *spin-orbit interaction*) predicts energy levels for the hydrogen atom given by

We will discuss the spin-orbit interaction later in this module but focus on its relevance to multi-electron atoms.

$$E = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right] \tag{38}$$

where $\alpha = e^2/4\pi\epsilon_0\hbar c \approx 1/137$ is known as the *fine-structure* constant. I.e. the energy levels are shifted compared to the Bohr values (first term in Eqn 38) and split depending on their j-values (see Figure 13). The effect is small (of order $\alpha^2 \sim 5 \times 10^{-5}$ relative shift) but is measurable and provides an excellent match to the observed fine-structure in the hydrogen spectrum (see Section 2.6).

The accuracy of Dirac theory in matching the fine-structure of the hydrogen spectrum was a great success of quantum mechanical theory, and remains one of the most convincing lines of argument in support of quantum mechanics. In lends great confidence to our use of quantum mechanics to understand more complicated systems and is the foundation of our extension to the physics of multi-electron atoms, which will the topic of most of the rest of this module.

There is another interesting effect that contributes to the fine structure of the hydrogen spectrum: the so-called *Lamb shift* is an observed energy difference between the l-states for given n and j. This shift is about a factor of 10 smaller even than the shifts in the Dirac theory, but it can be measured. The Lamb shift is explained accurately by the theory of *quantum electrodynamics*, but the details of this are well beyond the scope of this module.
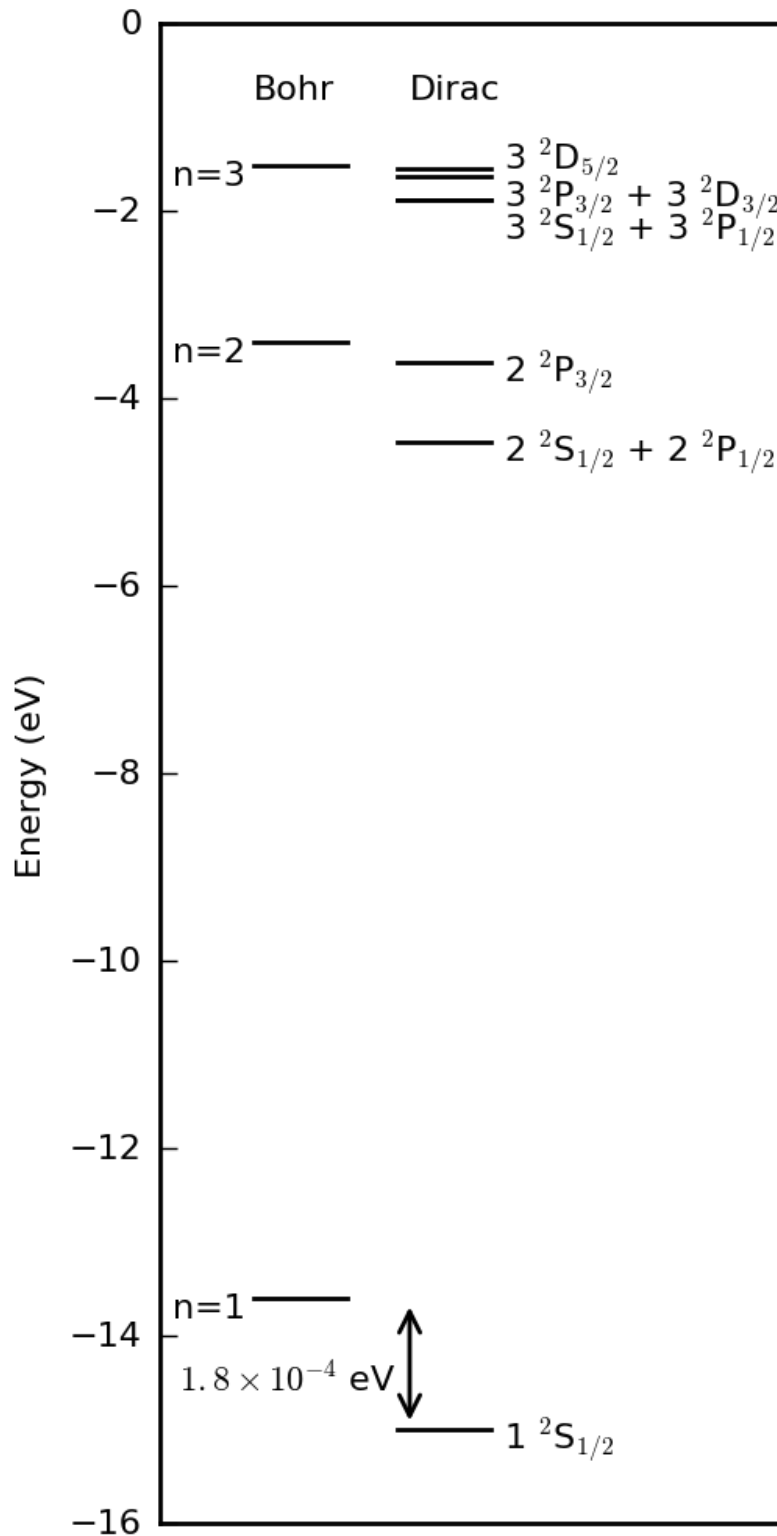
Figure 13: Comparison of $n = 1, 2$ and 3 hydrogen energy levels according to Bohr and Dirac theory. Following Eisberg & Resnick, the splittings of the levels in the Dirac theory are exaggerated by a large factor so that they can be seen (the shifts are all $\sim 10^{-4}$ eV or smaller).

Summary/Revision:

- Spin (**S**) must be included in the theory of atomic physics. It behaves just like an angular momentum vector in quantum mechanics.
- The spin properties of a single electron are specified by two quantum numbers: s and m_s .
- s specifies the magnitude of the spin: $|\mathbf{S}| = \sqrt{s(s+1)}\hbar$; for a single electron $s = 1/2$.
- m_s gives the z-component of the spin: $S_z = m_s\hbar$. For a single electron, $m_s = -1/2$ or $+1/2$.
- The total angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is widely used in identifying states.
- $\mathbf{J}$ is also defined by two quantum numbers, j and m_j. These specify the magnitude $|\mathbf{J}| = \sqrt{j(j+1)}\hbar$ and z-component $J_z = m_j\hbar$.
- For a single-electron atom, the allowed values of j are $l - 1/2$ and $l + 1/2$.
- For given j, allowed values of m_j form a sequence:

$$m_j = -j, -j+1, ..., j-1, j$$

- For the simple one-electron Hamiltonian we considered in Section 4, the energy of a state is independent of l, s, j and m_j. However, in Dirac theory, the energy levels are shifted and split by their j values. These effects are small ($\sim 10^{-4}$eV) but accurately match observed fine structure in hydrogen lines.
- In spectroscopic notation, the quantum numbers for orbital, spin and total angular momenta of a complete atom are indicated by the *term*.

6   *Multi-electron atoms: adding angular momenta*

Context

Why learn how to sum quantised angular momenta? In multi-electron atoms we sometime work with the angular momenta of individual electrons and sometimes with the total angular momenta summed over the electrons: to do this we need to understand the relationship between the two

Learning goals

1. To introduce notation that distinguishes angular momenta of single electrons from the summed angular momenta that apply to multi-electron atoms as a whole.
2. To learn how to sum quantised angular momenta (using quantum numbers).

6.1   *Angular momenta of atoms and spectroscopic terms revisited*

In multi-electron atoms, we need to distinguish between the angular momenta (and quantum numbers) that refer to individual electron orbitals, and the total values that describe the composite atom. We will follow the convention of using upper case letters (**L**, **S**, **J** etc.) to refer to angular momenta that describe the overall state of an atom while using lower cases letter (**l**, **s** etc.) when describing the properties of a single electron. When needed, we will use subscripts to distinguish between electrons. Thus, e.g. for a two-electron atom, the orbital angular momenta of the two electrons will be called $\mathbf{l_1}$ and $\mathbf{l_2}$, while the total orbital angular momentum of the atom will be called $\mathbf{L} = \mathbf{l_1} + \mathbf{l_2}$.

Every angular momentum that we consider is quantised and described by the usual pair of quantum numbers: one that specifies the magnitude, and one that gives the z-component. When writing these quantum numbers, we will use the same distinction as in the vector notation above: upper case letters to indicate quantum numbers for the complete state of the atom; lower case letters for the quantum numbers associated with individual electrons. Thus, continuing the two-electron example from the previous paragraph, we would denote the quantum numbers of **L** as L and M_L, where $|\mathbf{L}| = \sqrt{L(L+1)}\hbar$ and $L_z = M_L\hbar$. Similarly, quantum numbers l_1 and l_2 would give the magnitudes of the angular momenta of the two electrons individually ($|\mathbf{l_1}| = \sqrt{l_1(l_1+1)}\hbar$ and $|\mathbf{l_2}| = \sqrt{l_2(l_2+1)}\hbar$) and their z-components would be specified by $m_{l,1}$ and $m_{l,2}$ ($l_{z,1} = m_{l,1}\hbar$ and $l_{z,2} = m_{l,2}\hbar$).

6.2   *Summation of angular momenta*

In multi-electron atoms we will often need to sum angular momenta: i.e. we start from knowning the quantum numbers describing some pair of angular momenta and want to find the possible quantum numbers describing the angular momentum that is the vector sum of that pair:

$$\mathbf{L} = \mathbf{l_1} + \mathbf{l_2} \tag{39}$$

Here we use **l** angular momenta as examples, but note that the principle applies to all angular momenta, where orbital (**l**), spin (**s**) or combined (**j**).

In Section 5.2 we have already encountered one example of the addition of angular momenta ($\mathbf{J} = \mathbf{L} + \mathbf{S}$ for one-electron atoms). The general rule follows from similar principles: provided we know the quantum numbers that specify the magnitudes of the two vectors being summed (l_1 and l_2), we can anticipate that the magnitude of the resultant vector will be constrained by (see Figure 12):

In terms of a vector model, the maximum and minimum cases correspond to the two vectors being summed being as close to parallel/anti-parallel as the quantisation rules allow.

$$\left|\sqrt{l_1(l_1+1)} - \sqrt{l_2(l_2+1)}\right| \leq \sqrt{L(L+1)} \leq \sqrt{l_1(l_1+1)} + \sqrt{l_2(l_2+1)}$$

Usually (but not always) there will be more than one L value that satisfies this inequality. To find the allowed values, the following recipe can always be used:

Addition of angular momenta:
1. Calculate the maximum allowed value of L: this will always be $l_1 + l_2$.
2. Calculate the minimum allowed value of L: this will always be $|l_1 - l_2|$.
3. The full set of allowed values consists of the maximum, the minimum and all values at integer steps between:

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, ..., l_1 + l_2 - 1, l_1 + l_2 \qquad (40)$$

4. If the maximum and minimum values for L calculated in steps (1) and (2) are equal to each other, then only that single value of L is allowed.

For each allowed L-value, there is the usual set of allowed M_L values:

$$M_L = -L, -L+1, ..., L-1, L \qquad (41)$$

One consequence of these rules is that if either one of the angular momenta being summed has half-integer quantum numbers, then the sum will also have half-integer quantum numbers. However, if both quantities being summed have half-integer quantum numbers (e.g. two single-electron spins) the resultant will have integer quantum numbers.

The rules for summing angular momenta are extremely important for the study of multi-electron atoms and should be committed to memory. They apply regardless of whether the angular momenta considered are orbital, spin or total components. Exercises 6.1, 6.2 and 6.3 provide examples of using these rules.

Exercise 6.1: Addition of angular momentum quantum numbers: example 1

Consider a two electron atom in which one electron has $l = 1$ and the other has $l = 2$. What are the allowed values of the quantum number L that specifies the total orbital angular momentum of the atom?

- -

The total orbital angular momentum of the atom is the sum of orbital angular momenta of the two electrons. Thus we can use the rule in Eqn 40 with $l_1 = 1$ and $l_2 = 2$. The smallest allowed value of L is $|l_1 - l_2| = 1$, and the largest is $l_1 + l_2 = 3$. As always, the allowed values are quantised in integer steps. Thus the allowed L-values in this case are: 1, 2 and 3.

Exercise 6.2: Addition of angular momentum quantum numbers: example 2

What are the allowed values of the total spin quantum number for a two-electron atom?

The total spin is the sum of spins of the two electrons:
$\mathbf{S} = \mathbf{s_1} + \mathbf{s_2}$. All electrons have $s = 1/2$, thus $s_1 = s_2 = 1/2$. Then applying the addition rule (Eqn 40), the smallest allowed value of S is $|s_1 - s_2| = 0$, and the largest is $s_1 + s_2 = 1$. So there are two allowed values: $S = 0$ and $S = 1$.

Exercise 6.3: Addition of angular momentum quantum numbers: example 3

What are the allowed values of the total angular momentum quantum number (J) for a two-electron atom with $S = 1$ and $L = 3$?

In this problem we are given the quantum numbers describing the total orbital angular momentum (L) and the total spin (S). Since $\mathbf{J} = \mathbf{L} + \mathbf{S}$, we just need to use the usual rule (Eqn 40) to combine them. The smallest value of J will be $|L - S| = 2$ and the largest $L + S = 4$. Thus the allowed J quantum numbers in this case are 2, 3 and 4.

6.3   *Terms in multi-electron atoms*

For multi-electron atoms, the *term* is used to specify the angular momentum quantum numbers of the complete atom (L, S and J)[6], using the same notation as we met already for the single-electron case:

$$^{2S+1}L_J \ .\tag{42}$$

We will see specific examples of multi-electron terms in the next section.

[6] When possible – it is not always appropriate to specify L and S; this will be elaborated later.

Summary/Revision:

- In multi-electron atoms, we use upper case letters for angular momenta (and associated quantum numbers) that describe the sum over all the electrons in the atom. Lower case letters are used when describing individual electrons.
- Quantised angular momentum vectors can be summed by applying a simple rule for combining the associated quantum numbers.
- It is usually the case that summing angular momenta leads to more than one possible resultant: this can be understood as a consequence of different allowed "orientations" of the vectors being summed. When finding / describing the possible states of atoms it is important to consider *all* the possibilities.
- In multi-electron atoms the spectroscopic *term* is used to identify the angular momentum quantum numbers of the whole atom.

7   Multi-electron atoms: Two-electron atoms

Context

Why study multi-electron atoms? Most atoms have more than one electron, and most related quantum mechanical problems (nuclei, molecules etc.) have more than one constituent. Thus developing theory for multi-particle quantum mechanics has a vast range of applications.

Why the two-electron atom? The two-electron case is the simplest to consider in detail but it successfully illustrates many of the fundamental points that are relevant to more complicated systems too.

Learning goals

1. To study the two-electron atom as the simplest example of the multi-electron case
2. To introduce the Schrödinger equation for a two-electron atom
3. To introduce the concept of *orbitals* in multi-electron atoms and how these are described by a *configuration*
4. To be able to interpret and use spectroscopic notation to describe electron configurations
5. To appreciate that, L and S have significant effects on the energy levels of multi-electron atoms
6. To qualitatively understand how the requirements of particle exchange symmetry give rise to the *exchange force* in helium
7. To formalise how the electron-electron interaction in helium can be expressed in terms of the *Coulomb* and *Exchange* integrals

7.1 Introduction

Our aim throughout this Section will be to determine the states / energy-levels of two electron atoms, often using the helium atom as an example.

Helium was discovered by spectroscopy of the Sun:[7] its spectrum has a particularly strong line in the yellow part of the spectrum ~ 587nm, see Figure 14. It is a very important element: after hydrogen, it is the most abundant element in the Universe, and so of considerable importance to astronomy and cosmology. It is also, however, an excellent laboratory for studying quantum mechanics: probably the best real example to study the quantum mechanics of a system of two identical particles.
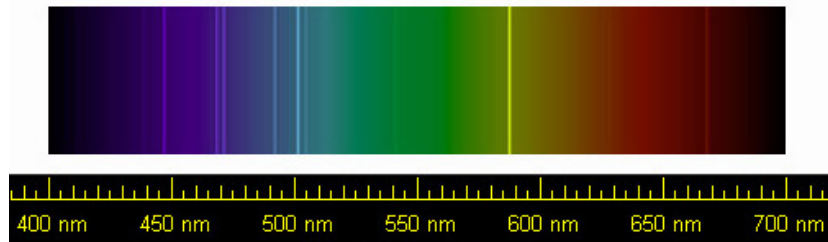
[7] Hence the name.

Figure 14: : Emission line spectrum of helium.

The helium atom is a three-particle system: two electrons and the nucleus, which has charge $Z = +2$ (the nucleus contains two protons and either one or two neutrons; Figure 15). Unfortunately the three-body problem cannot be solved exactly (in either classical or quantum mechanics).

Therefore, our approach is based on making a sequence of physically motivated approximations. We will follow the standard approach of starting by considering the dominant interaction and then increasing the level of sophistication by incorporating more subtle effects.
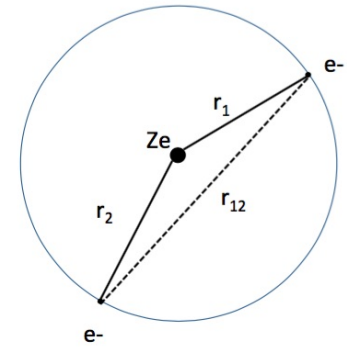

Figure 15: : Schematic diagram of two-electron atom (i.e. for $Z = 2$, the helium atom).

7.2 Two-electron atoms: the Schrödinger equation

It is simple enough to write down the time-independent Schrödinger equation for a two-electron atom. Assuming that the motion of the nucleus is negligible, it is simply

$$-\frac{\hbar^2}{2m_e}\nabla_1^2\psi_T - \frac{\hbar^2}{2m_e}\nabla_2^2\psi_T + V_T\psi_T = E_T\psi_T \qquad (43)$$

where $\psi_T(\mathbf{r_1}, \mathbf{r_2})$ is the wavefunction (which depends on the coordinates of the two electrons, $\mathbf{r_1}$ and $\mathbf{r_2}$), $V_T(\mathbf{r_1}, \mathbf{r_2})$ is the total potential energy and E_T is the total energy. ∇_1^2 and ∇_1^2 are the usual Laplacian

When we studied the one-electron atom we *did* consider the motion of the nucleus (by using the reduced mass). However, we will not pursue this level of accuracy in multi-electron atoms and so content ourselves with using the electron mass here.

Recall the meaning of $\psi_T(\mathbf{r_1}, \mathbf{r_2})$: $|\psi_T^2|$ gives the probability density of finding the electrons at the positions $\mathbf{r_1}$ and $\mathbf{r_2}$.

operator applied to the coordinates of the two particles in 3D; e.g. in terms of Cartesian coordinates (i.e. $\mathbf{r_1} = (x_1, y_1, z_1)$, $\mathbf{r_2} = (x_2, y_2, z_2)$),

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \text{ and } \nabla_2^2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}.$$

Just as in a single-electron atom, solving the time-independent Schrödinger equation is an eigenvalue problem: each ψ_T that satisfies the equation is an eigenfunction of energy and corresponds to an energy state of the system (with energy given by the eigenvalue E_T). Thus, if we can find all the solutions to Eqn. 43 we have found the energy levels of a two-electron atom.

The difficulty in solving Eqn 43 comes from the potential energy V_T, which may be written

$$V_T = -\frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad , \tag{44}$$

Recall: the Coulomb potential energy between two particles with charge q_1 and q_2 is $V = q_1 q_2 / 4\pi\epsilon_0 r$, where r is the distance between them.

where Z is the nuclear charge and $r_{12} = |\mathbf{r_2} - \mathbf{r_1}|$, see Figure 15. The physical interpretation of the three terms in Eqn 44 is straightforward: the first two terms give the potential energy of each electron due to the nucleus; the third term is the energy associated with the Coulomb repulsion between the two electrons. It is this last term that is the source of our troubles: it means that we cannot solve the problem first for one electron and then the other since the potential depends on both. Consequently, an accurate solution will require that we consider the electrons simultaneously.

Mathematically, this is because the last term in Eqn 44 means that Eqn 43 is not *separable*: see below.

7.3   *Independent electron approximation: the simplest place to start*

The simplest approach we might consider is simply to neglect the last term in Eqn 44. This is a drastic simplification, but does allow us to make initial progress. In this case, the remaining two terms in Eqn 44 can be substituted in Eqn 43 leading to

Discussion point: Does this approximation seem reasonable to you (this is one of those places where physics intuition should guide us)?

$$-\frac{\hbar^2}{2m_e}\nabla_1^2\psi_T - \frac{\hbar^2}{2m_e}\nabla_2^2\psi_T - \frac{Ze^2}{4\pi\epsilon_0 r_1}\psi_T - \frac{Ze^2}{4\pi\epsilon_0 r_2}\psi_T = E_T\psi_T$$

which can be neatly re-written as

$$\hat{H}_1\psi_T + \hat{H}_2\psi_T = E_T\psi_T \tag{45}$$

where $\hat{H}_1$ is a Hamiltonian operator associated with particle 1,

$$\hat{H}_1 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1}$$

and $\hat{H}_2$ is the equivalent Hamiltonian for particle 2.

Since all the terms in Eqn 45 depend only on *either* $\mathbf{r_1}$ or $\mathbf{r_2}$, we can solve for the full eigenfunction by considering a product of *one-particle* eigenfunctions

I.e. Eqn 45 is separable, unlike Eqn 43

$$\psi_T = \psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2}) \qquad (46)$$

where $\psi_\alpha(\mathbf{r_1})$ and $\psi_\beta(\mathbf{r_2})$ are chosen to be the functions that satisfy the one-particle time-independent Schrödinger equations

$$\hat{H}_1\psi_\alpha(\mathbf{r_1}) = E_\alpha\psi_\alpha(\mathbf{r_1}) \qquad (47)$$

and

$$\hat{H}_2\psi_\beta(\mathbf{r_2}) = E_\beta\psi_\beta(\mathbf{r_2}) \ . \qquad (48)$$

We use the labels α and β to clarify that there are two distinct one-particle eigenfunctions here: you can think of these labels are shorthand for writing out the full set of quantum numbers needed to identify a one-particle space wavefunction (i.e. n, l and m_l).

It is easy to show (Example 7.1) that provided Eqns 47 and 48 are satisfied, then $\psi_T = \psi_\alpha\psi_\beta$ satisfies the simplified two-electron Schrödinger equation (Eqn 45) yielding a total energy eigenvalue

$$E_T = E_\alpha + E_\beta \ . \qquad (49)$$

Exercise 7.1: Independent electron energies

Verify that Eqn 49 follows from Eqns 45 – 48.

- -

Substitute Eqn 46 into Eqn 45:

$$\hat{H}_1\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2}) + \hat{H}_2\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2}) = E_T\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2})$$

$$\psi_\beta(\mathbf{r_2})\left(\hat{H}_1\psi_\alpha(\mathbf{r_1})\right) + \psi_\alpha(\mathbf{r_1})\left(\hat{H}_2\psi_\beta(\mathbf{r_2})\right) = E_T\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2})$$

Now use Eqns 47 and 48

$$\psi_\beta(\mathbf{r_2})\left(E_\alpha\psi_\alpha(\mathbf{r_1})\right) + \psi_\alpha(\mathbf{r_1})\left(E_\beta\psi_\beta(\mathbf{r_2})\right) = E_T\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2})$$

we can now cancel out the product $\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2})$ from each term, leaving

$$E_\alpha + E_\beta = E_T$$

as required.

Remember that $\hat{H}_1$ contains partial derivates w.r.t. $\mathbf{r_1}$ but not $\mathbf{r_2}$. So $\psi_\beta(\mathbf{r_2})$ can be treated like a constant when dealing with $\hat{H}_1$.

7.4 *Orbitals: spectroscopic notation and configurations for multi-electron atoms*

Although an approximation, the notion of representing multi-electron wavefunctions as a product of single-electron states (see above) is

very useful. We will often refer to single-electron states (such as ψ_α and ψ_β) as *orbitals*, and use this concept as the basis of identifying states in multi-electron atoms.

Definition of **orbital**.

When applying the concept of orbitals in multi-electron atoms, it is standard to use spectroscopic notation to indicate which orbitals the electrons occupy. Single-electron states are identified by their n and l quantum numbers: in spectroscopic notation, these are combined in a particular *nl*-notation, where n is written as a number and l is identified using the same letters as for spectroscopic terms (Section 5.3), except that *lower case* is now used (see Table 10).

l-value	letter	origin
0	s	sharp
1	p	principal
2	d	diffuse
3	f	fundamental
4	g	alphabetical
5	h	

Table 10: Letters used to identify l-values in spectroscopic notation. The third column gives the spectroscopic series names from which the convention derives. After "f" alphabetical identification is used.

Thus, for example, in a single-electron atom, if the electron is in the ground state ($n = 1, l = 0$), this is notated as occupying the 1s orbital. If the electron is in an excited state with $n = 2$ and $l = 1$ it is called 2p.

In multi-electron atoms, we specify the orbitals occupied by each electron. Thus, if one electron in a helium atom occupies an ($n = 1, l = 0$) orbital while the other has ($n = 2, l = 1$), we denote this 1s2p. When specified, this occupation information is known as the *configuration* of the atom.

Definition of **configuration**.

Note that if more than one electron occupies the same orbital, it is conventional to represent this with a superscript: i.e. for the ground state of the helium atom we write $1s^2$ rather than 1s1s.

It is also conventional to neglect fully occupied inner electron shells when specifying the configuration in many cases. More on this later.

The combination of specifying the *configuration* and the *term* is the usual means by which to identify states in multi-electron atoms. For example, the first excited state of the helium atom can be fully specified as

$$1s2s \; ^3S_1 \; .$$

To get used to this notation, Exercise 7.2 gives an example of identifying the next few excited states of the helium atom.

Exercise 7.2: Spectroscopic notation for the helium atom.

Consider helium atoms in which one of the electrons is in an $n = 1$ orbital while the second electron is in one of the $n = 2$ orbitals. Identify all the possible *configurations*, and for each configuration all the possible *terms*.

The first electron has $n = 1$, $l = 0$: i.e. it is a 1s electron. The second electron has $n = 2$ and so is allowed to have either $l = 0$ or $l = 1$: so the configuration is *either* 1s2s or 1s2p.

To find the allowed terms for each configuration, we first find the allowed L and S values, and then combine these to find J.

For 1s2s, the only possible value of L is 0 (the two electrons both have $l = 0$, thus their sum – according to Eqn 40 with $l_1 = l_2 = 0$ – can only have $L = 0$). As in Exercise 6.2, the total spin for two electrons is $S = 0$ or $S = 1$. Combining $L = 0$ and $S = 0$, only $J = 0$ is allowed – this gives one possible term: $^1S_0$. For $L = 0$ and $S = 1$, the only allowed J-value is $J = 1$: this gives the term $^3S_1$. Thus, for the configuration 1s2s, the two possible terms are:

$$^1S_0 \text{ and } ^3S_1$$

For 1s2p, the only possible value of L is 1 (according to Eqn 40, for $l_1 = 0$, $l_2 = 1$). Again, the total spin is either $S = 0$ or $S = 1$. For $L = 1$ and $S = 0$, only $J = 1$ is allowed: $^1P_1$. For $L = 1$ and $S = 1$, however, J can be 0, 1 or 2, allowing the terms $^3P_0$, $^3P_1$ and $^3P_2$. So, to summarise, for the 1s2p configuration there are four allowed terms:

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

Note: using a comma-separated list of J-values, as above, is a common shorthand for listing terms with the same L and S values.

7.5   *Magnitude of electron-electron repulsion*

Although the "independent-electron" approximation of Section 7.3 has given us a useful starting point and led us to the concept of *orbitals*, it has some important problems: neglecting the electron-electron repulsion term gives very inaccurate results compared to experimental measurements. Exercise 7.3 illustrates this for the ground state of He.

Exercise 7.3: Estimating the ground state energy of helium

Estimate the total binding energy of the ground state (i.e. lowest energy state) of the helium atom if it were assumed that the two electrons are completely independent of each other (i.e. each electron occupies an orbital with $n = 1$ but the electron-electron interaction is ignored). Comment on the comparison of your answer to the experimentally measured total binding energy of the ground state electrons of helium, -78.9 eV.

- -

If the electrons were truly independent of each other, then the two-electron case is just the same as solving the one-electron case twice and the total energy is the sum of the two (as in Eqn 49). We already know the energy levels for a single electron atom, they are given by the Bohr formula:

$$E_n = \frac{\mu Z^2 e^4}{8\epsilon_0^2 h^2 n^2} = -13.6 \text{ eV} \frac{Z^2}{n^2}$$

So we can calculate that, if independent, each electron in the lowest state ($n = 1$) of helium ($Z = 2$) would have energy

$$E_1 = -54.4 \text{ eV}$$

and so the total energy (sum of the two, in accordance with Eqn 49), would be

$$E_T = -108.8 \text{ eV}$$

Although of the correct magnitude, this estimate is significantly more negative than the experimental value. I.e. this simple picture predicts that the electrons are significantly more strongly bound than in reality.

Further discrepancies also emerge if excited state energies are compared: Figure 16. Considering these leads to several points:

1. If electron-electron repulsion is ignored, the predicted energies of states are always significantly more negative than observed.

2. States with different terms (i.e. different values of L and S) have significantly different energies from each other: e.g., the six terms belonging to the 1s2s and 1s2p configurations (see Exercise 7.2) span a range of around 1.5 eV in energy. This splitting is orders of magnitude larger than any effects associated with angular momentum in single-electron atoms: the physical origin of these effects must also be a consequence of the electron-electron interaction.

3. It is reasonable to expect that the differences in energy between states with differing L-values can be attributed to different average distances between the two electrons. We already know (Table 4) that the spatial probability distributions for states with different l quantum numbers vary: thus we can anticipate that different pairs of occupied orbitals will have different mean separations between the electrons (and thus different average values for the Coulomb repulsion energy; see Exercise 7.4). That this is relevant, is borne out by detailed calculations.

4. However, simple considerations do not explain the striking difference between the energies of states with different S quantum numbers: e.g. 1s2s $^3S_1$ and 1s2s $^1S_0$ have the same configuration (i.e. same orbitals) and differ only in their spin properties. Nevertheless, the energy separation is large: ~ 0.8 eV. This is a consequence of the *exchange force*, a purely quantum mechanical effect which will be the main subject of the rest of this section.

Important: When studying multi-electron atoms, it is quite common to measure the energy of states relative to the ionization energy of the atom/ion considered (as in Figure 16). This scale should not be confused with the total binding energy of *all* electrons in the atom, as calculated for the example in Exercise 7.3.
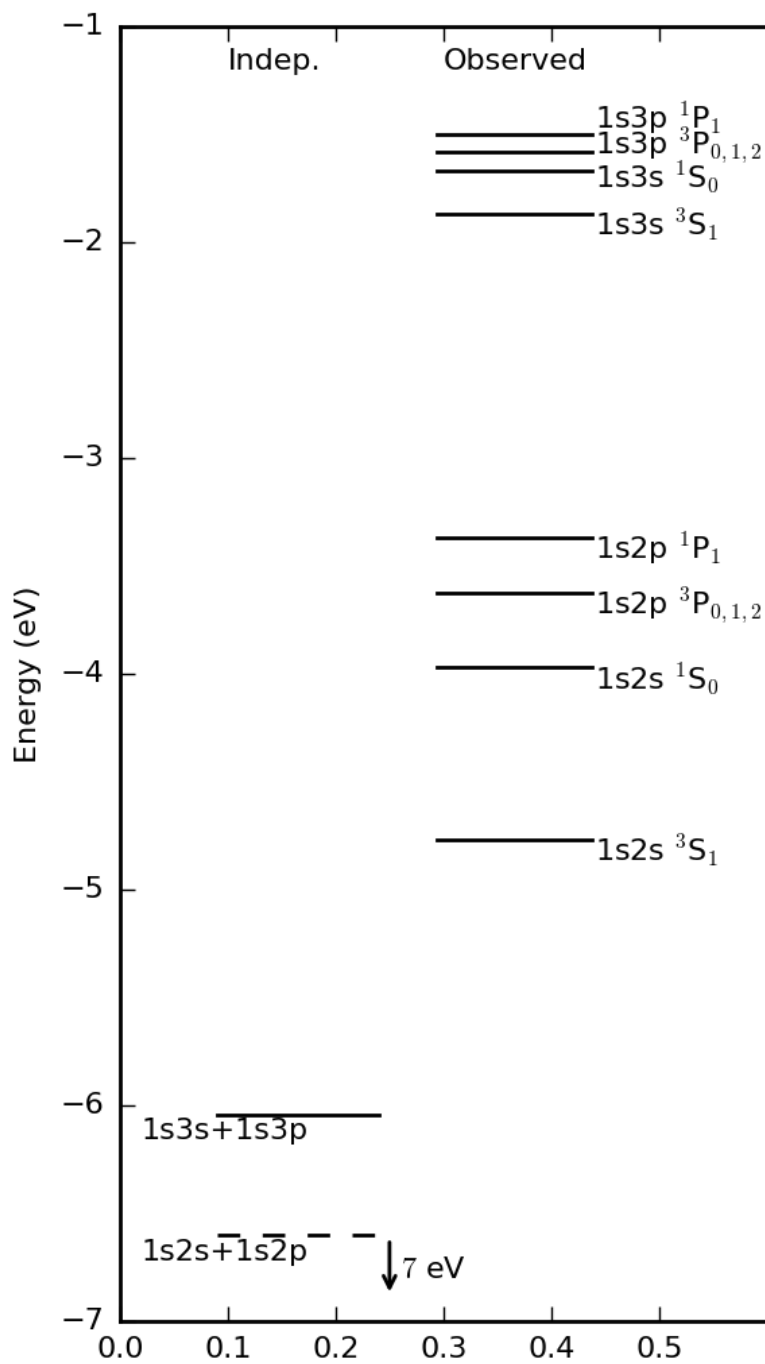
Figure 16: : Energy levels for states with 1s2s, 1s2p, 1s3s and 1s3p configurations of the helium atom. As is conventional, energies are given relative to the ionization potential. Left: expected values if the electron-electron interaction is neglected ("independent electron approximation"). Right: observed energies. Note that the 1s2s + 1s2p level on the left has been shifted up by 7eV.

> **Exercise 7.4: Estimating the electron-electron separation**
>
> Using Figure 16 make a **rough** estimate of the average separation of the two electrons when occupying 1s3s configurations.
>
> -
>
> From Figure 16 we see that the energy of 1s3s would be $\sim$ -6 eV if the electrons were treated as independent. However, the observed 1s3s states have energies of $\sim$ -1.7 and $\sim$ -1.9eV. This is a difference in energy of $\sim$ 4.2 eV (averaging the two states), which we can attribute to the Coulomb interaction between the two electrons. So we can estimate the difference using
>
> $$4.2 \text{ eV} \approx \frac{e^2}{4\pi\epsilon_0 r_{12}} \,, \tag{50}$$
>
> which gives $r \approx 3.4 \times 10^{-10}$m. This seems reasonable: separation on scale of atom.

7.6 *Exchange symmetries of the spatial wavefunction*

A fundamental objection to Section 7.3 is that Eqn 46 does not acknowledge that the two electrons are *indistinguishable* particles. I.e., if we exchange the "labels" on the two electrons in a helium atom, no measurable quantity should be affected. We know that measurable quantities (e.g. the probability density of finding the particles at particular positions) depend on the square of the modulus of the wavefunction:

If in doubt, revise the discussion of identical particles and indistinguishability *from PHY2001.*

$$\text{Prob.density} \propto |\psi_T|^2 = \psi_T \psi_T^* \,.$$

According to Eqn 46, this would yield

$$\text{Prob.density} \propto \psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2})\psi_\alpha^*(\mathbf{r_1})\psi_\beta^*(\mathbf{r_2}) \,.$$

If we exchange the two particles (i.e. swap the particle labels $1 \to 2$, $2 \to 1$)

$$\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2})\psi_\alpha^*(\mathbf{r_1})\psi_\beta^*(\mathbf{r_2}) \to \psi_\alpha(\mathbf{r_2})\psi_\beta(\mathbf{r_1})\psi_\alpha^*(\mathbf{r_2})\psi_\beta^*(\mathbf{r_1})$$
$$\neq \psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2})\psi_\alpha^*(\mathbf{r_1})\psi_\beta^*(\mathbf{r_2})$$

i.e. this wavefunction does not respect the requirement that the probability density is unchanged if we swap the particles. As introduced in PHY2001, the solution is to recognise that, for indistinguishable particles, $\psi_\alpha(\mathbf{r_2})\psi_\beta(\mathbf{r_1})$ must be just as valid a representation as $\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2})$ (since swapping the particles can have no effect). Then,

because the Schrödinger equation is linear, if these are both valid solutions any linear combination of them is also a solution. So we can adopt combinations that satisfy our exchange requirements. In particular, for a two-particle system, there are two valid choices:

$$\psi_S = \frac{1}{\sqrt{2}} \left(\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2}) + \psi_\alpha(\mathbf{r_2})\psi_\beta(\mathbf{r_1}) \right) \tag{51}$$

and

$$\psi_A = \frac{1}{\sqrt{2}} \left(\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_2}) - \psi_\alpha(\mathbf{r_2})\psi_\beta(\mathbf{r_1}) \right) . \tag{52}$$

These solutions, known as the "symmetric" (ψ_S) and "antisymmetric" (ψ_A) total eigenfunctions have the properties that, under particle exchange, $\psi_S \to \psi_S$ and $\psi_A \to -\psi_A$. Thus both satisfy the requirement that particle exchange leaves $\psi\psi^*$ unchanged (see Example 7.5).

We note a critical property of the symmetrised wavefunctions (which we will need in Section 7.8): if the two-electron system is described by ψ_A, then the probability of the two electrons being very close together *must* be very small, regardless of α and β:

$$\psi_A \to 0 \text{ as } \mathbf{r_2} \to \mathbf{r_1} .$$

This is not the case for ψ_S, in which the wavefunction remains finite if the electrons are very close to each other:

$$\psi_S \to \sqrt{2}\psi_\alpha(\mathbf{r_1})\psi_\beta(\mathbf{r_1}) \text{ as } \mathbf{r_2} \to \mathbf{r_1} .$$

Since the (positive) electron-electron Coulomb potential depends on the distance between the electrons, it is therefore clear that ψ_S must have higher energy than ψ_A, *even through the occupied orbitals are the same!* This difference in energy is a purely quantum mechanical effect that has no classical analogue. To fully appreciate its significance, however, we must first consider the spin part of the wavefunction in the next section.

> **Exercise 7.5: Particle exchange symmetry**
>
> Verify that ψ_A changes sign if the particles are swapped (i.e. it is antisymmetric with respect to particle exchange) and therefore that $\psi_A \psi_A^*$ is unaffected by particle exchange.
>
> -
>
> From Eqn 52,
>
> $$\psi_A = \frac{1}{\sqrt{2}} \left(\psi_\alpha(\mathbf{r_1}) \psi_\beta(\mathbf{r_2}) - \psi_\alpha(\mathbf{r_2}) \psi_\beta(\mathbf{r_1}) \right)$$
>
> If we swap the particles:
>
> $$\frac{1}{\sqrt{2}} \left(\psi_\alpha(\mathbf{r_1}) \psi_\beta(\mathbf{r_2}) - \psi_\alpha(\mathbf{r_2}) \psi_\beta(\mathbf{r_1}) \right) \rightarrow$$
> $$\frac{1}{\sqrt{2}} \left(\psi_\alpha(\mathbf{r_2}) \psi_\beta(\mathbf{r_1}) - \psi_\alpha(\mathbf{r_1}) \psi_\beta(\mathbf{r_2}) \right)$$
>
> but, taking out a negative sign and swapping the order of the two terms
>
> $$\frac{1}{\sqrt{2}} \left(\psi_\alpha(\mathbf{r_2}) \psi_\beta(\mathbf{r_1}) - \psi_\alpha(\mathbf{r_1}) \psi_\beta(\mathbf{r_2}) \right) =$$
> $$- \frac{1}{\sqrt{2}} \left(\psi_\alpha(\mathbf{r_1}) \psi_\beta(\mathbf{r_2}) - \psi_\alpha(\mathbf{r_2}) \psi_\beta(\mathbf{r_1}) \right) = -\psi_A \ .$$
>
> Thus, under particle exchange,
>
> $$\psi_A \rightarrow -\psi_A$$
>
> as required. From this, the behaviour of the probability density can be easily found: under particle exchange
>
> $$\psi_A \psi_A^* \rightarrow (-\psi_A)(-\psi_A^*) = \psi_A \psi_A^*$$
>
> i.e. the measurable quantity is not affected by particle exchange, as required for indistinguishable particles.

7.7 *Exchange symmetries in the spin wavefunction*

In this section, our goal is to understand how the requirements of *indistinguishability* introduced in Section 7.6 can be applied to the spin of a two-electron system.

It is quite easy to schematically describe the composite spin wave-functions of a two electron atom. We will use a simple notation for the spin part of the wavefunction where:

$$\sigma = (m_{s,1} \ , \ m_{s,2}) \tag{53}$$

is understood to mean that electron "1" has quantum number $m_{s,1}$ and electron "2" has quantum number $m_{s,2}$ (and, of course, both electrons have quantum number $s_1 = s_2 = 1/2$).

Expressed in this simple way, there are four possible spin wavefunctions for a two-electron system:

$$\sigma = (+1/2, +1/2), \ (-1/2, -1/2), \ (+1/2, -1/2) \text{ and } (-1/2, +1/2) \ .$$

Even more simply put, these four states might be called "up-up", "down-down", "up-down" and "down-up", as a reference to the spin orientations.

However, just as for the space wavefunctions described in Section 7.6, the last two are not convenient since they do not respect particle exchange symmetries. Therefore, we instead consider linear combination that do have definite symmetry with respect to particle exchange. We find *three* possibilities (a "triplet") that are symmetric with respect to particle exchange:

$$\begin{aligned}
\text{exchange symmetric} \quad & (+1/2, +1/2) \\
\text{exchange symmetric} \quad & \frac{1}{\sqrt{2}}[(+1/2, -1/2) + (-1/2, +1/2)] \quad (54) \\
\text{exchange symmetric} \quad & (-1/2, -1/2)
\end{aligned}$$

and *one* (a "singlet") that is antisymmetric

$$\text{exchange antisymmetric} \quad \frac{1}{\sqrt{2}}[(+1/2, -1/2) - (-1/2, +1/2)] \ . \quad (55)$$

This division into "triplet" and "singlet" directly corresponds to the total spin S of the atom: as we showed in Exercise 6.2, the total spin quantum number for a two electron atom is either $S = 1$ or $S = 0$. These can be associated with the triplet and singlet, respectively:

– For $S = 1$ we know from the usual quantisation conditions that there must be three distinct states that differ in their S_z values: we expect to find $M_S = 1, 0$ and -1. This is exactly what the triplet of symmetric spin wavefunctions provides:

$(+1/2, +1/2)$ clearly has $M_S = 1$;

$(-1/2, -1/2)$ similarly has $M_S = -1$;

$\frac{1}{\sqrt{2}}[(+1/2, -1/2) + (-1/2, +1/2)]$ has $M_S = 0$ (it is a "mix" of states that are both "one-up one-down").

– For $S = 0$ there is only one total spin "orientation" allowed: this single possibility is the antisymmetric ("singlet") state (which has $M_S = 0$, as required).

Thus we conclude that the total spin quantum number of a two-electron atom (S) effectively distinguishes between states that have

spin wavefunctions that are anti-symmetric (the $S = 0$ singlet) and symmetric (the $S = 1$ triplet) under particle exchange.

7.8 *The Pauli principle and the two-electron atom*

We have now discussed the particle exchange symmetries of both the spatial (Section 7.6) and spin (Section 7.7) parts of two-electron wavefunctions: in this section we will consider how they can be combined.

Electrons are *fermions*: as such they obey the Pauli principle – they always have total wavefunctions that are anti-symmetric under particle change. Recalling that

$$\text{complete eigenfunction} = \psi \times \sigma$$

it follows that wavefunctions for two-electron atoms must always have *either* ψ anti-symmetric and σ symmetric *or* vice versa. Thus, combining what has been discussed in Sections 7.6 and 7.7, we are led to the conclusion that

$$S = 1 \text{ spin states} \quad \text{pair with} \quad \psi_A \text{ spatial wavefunctions}$$

and

$$S = 0 \text{ spin states} \quad \text{pair with} \quad \psi_S \text{ spatial wavefunctions.}$$

This explains qualitatively why the $S = 0$ terms of the helium atom (see Figure 16) always have higher energy than corresponding $S = 1$ terms: they are associated with ψ_S wavefunction, which tend to place the electrons closer together (see Section 7.6) so that the energy of repulsion between them is *larger*. This effect is often called the *exchange force*: the requirements of particle exchange symmetry appears to act as a "force" that pushes the electrons together if the wavefunction is symmetric and apart if antisymmetric. However, there is no real "force" here: the effect is purely quantum mechanical.

You may recall that the other class of fundamental particle, *bosons* are those that have wavefunctions that are symmetric under particle exchange.

I.e. if we exchange the particles we require either ψ or σ to swap sign, but not both.

7.9 *Formal treatment of electron-electron interaction as a perturbation*

In Sections 7.5 to 7.8 we have qualitatively discussed why the electron-electron interaction means that the energies of states in two-electron atoms are significantly affected by the L and S quantum numbers: both quantum numbers affect the mean separation of the two electrons.

A more formal expression for the energy of a state can be obtained by returning to Eqn 49 and adding to it a term to represent the electron-electron interaction energy, which we neglected in Section 7.3:

$$E_T = E_\alpha + E_\beta + < \frac{e^2}{4\pi\epsilon_0 r_{12}} > \quad . \tag{56}$$

Here $< ... >$ indicates the quantum mechanical *expectation value* (i.e. "average value") defined by

Revise PHY2001 for more on expectation values.

$$< \frac{e^2}{4\pi\epsilon_0 r_{12}} >= \iint \psi_T^*(\mathbf{r}_1, \mathbf{r}_2)\frac{e^2}{4\pi\epsilon_0 r_{12}}\psi_T(\mathbf{r}_1, \mathbf{r}_2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \tag{57}$$

where the double integral runs over the the volume elements $\mathrm{d}\tau_1$ and $\mathrm{d}\tau_2$ that correspond to $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively.

Eqn 56 is an example of *first order perturbation theory*: i.e. we first solved the problem ignoring the last term (this allowed us to find expressions for the space wavefunction ψ_T in terms of the orbitals ψ_α and ψ_β) and *then* we correct for the effect we missed by going back and "perturbing" the answer (i.e. adding the average effect of the missing term back in the energy equation). Of course, this is only an approximation (because we ignored the effect of the missing term when calculating ψ_T). Nevertheless, perturbation theory is an invaluable means by which to make progress, and also to develop physical insight.

Introduction of *perturbation theory*.

In fact, it is possible to extend perturbation theory to include corrections to the wavefunctions themselves, but we will not address that here

With the single-electron orbital approximation of Sections 7.3 written as appropriately symmetric combinations (i.e. with $\psi_T = \psi_A$ or ψ_S) it can be shown that

$$< \frac{e^2}{4\pi\epsilon_0 r_{12}} >= J \pm K \tag{58}$$

where J is called the *Coulomb Integral*

Proving this requires only a few lines of mathematics: have a go...it's good practise of using quantum mechanical notation.

We use the standard notation here...but this is one of those unfortunate cases where confusion can arise. The Coulomb integral J is not the same things as the angular momentum quantum number J.

$$J = \iint |\psi_\alpha(\mathbf{r}_1)|^2\frac{e^2}{4\pi\epsilon_0 r_{12}}|\psi_\beta(\mathbf{r}_2)|^2\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \tag{59}$$

and K is the *Exchange Integral*

$$K = \iint \psi_\alpha^*(\mathbf{r}_1)\psi_\alpha(\mathbf{r}_2)\frac{e^2}{4\pi\epsilon_0 r_{12}}\psi_\beta^*(\mathbf{r}_2)\psi_\beta(\mathbf{r}_1)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \; . \tag{60}$$

The physical interpretation of J is clear: it corresponds to the average Coulomb potential energy if one particle were in state α and the other in state β. K, however, has no simple semi-classical interpretation: it is the quantitative expression of the quantum mechanical effect associated with the *exchange force* of Section 7.8. Specifically, the positive sign in Eqn 58 follows from adopting $\psi_T = \psi_S$ (i.e. goes with $S = 0$) and the negative from $\psi_T = \psi_A$ (matching with $S = 1$).

Figure 17 illustrates how J and K shift and split the energies of terms in the helium atom: starting from energies calculated in the independent electron approximation, $E_\alpha + E_\beta$, the Coulomb Integral shifts the energy up and the Exchange Integral separates the state depending on the value of S. The real, observed energy level diagram of helium is shown in Figure 18, where these effects can be seen in action.

Although deriving Eqns 59 and 60 may not be hard, evaluating either integral for any pair of single-electron wavefunctions (i.e. ψ_α and ψ_β chosen from Table 4) is non-trivial. However, hopefully you can convince yourself that – given time! – it can be done.

7.10   *Particle exchange and the ground state of helium*

We conclude our discussion of the two-electron atom with the observation that there is no triplet term for the ground configuration: i.e., in Figure 18, there is no 1 ^{3}S (although there is e.g. a 2 ^{3}S state).

This is because of the Pauli exclusion principle: if $\alpha = \beta$ then $\psi_A = 0$ (see Eqn 52), thus there can be no $\psi_A \times \sigma(S = 1)$ combination if both electrons are in the same orbital. On the other hand, the combination of $\psi_S \times \sigma(S = 0)$ is still valid since $\psi_S \neq 0$, even for $\alpha = \beta$.

This is a nice example of a striking (and measurable) consequence of indistinguishability in quantum mechanics: the "triplet" system of lines in the helium spectrum stops at the 1s2s configuration, while the "singlet" system goes down to 1s^2.
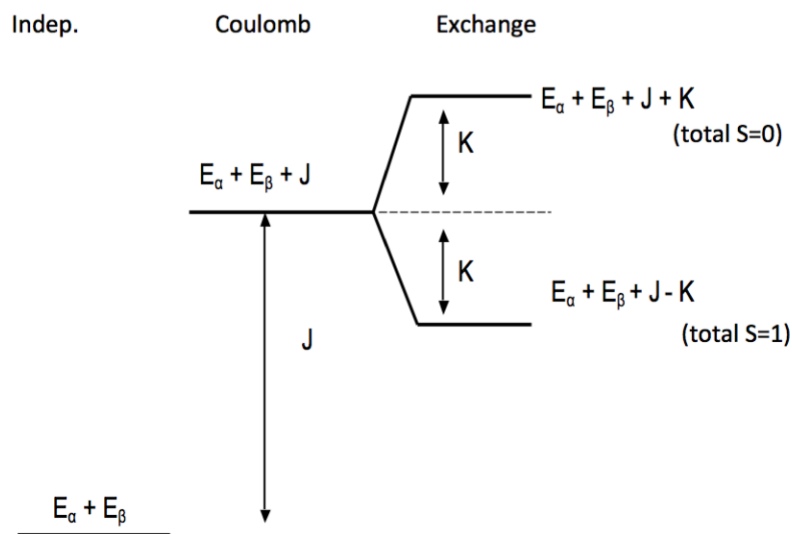
Figure 17: : Schematic diagram of energies in two-electron atom: the energy of a level calculated assuming the electrons are independent (i.e. the electron-electron repulsion is ignored) is shown on the left; when the Coulomb integral is included, the energy is raised (middle); the Exchange integral separates the energies depending on the exchange symmetry (as quantified by the S quantum number, right).
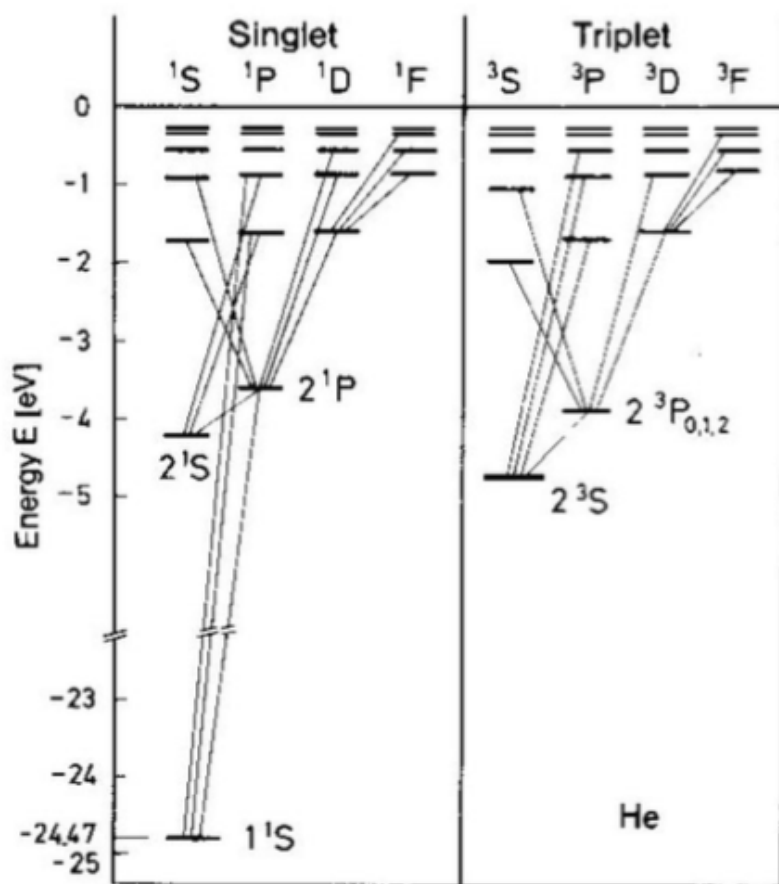

Figure 18: : Energy level diagram for the helium atom (separated with singlets on the left and triplets on the right). Here, configurations are abbreviated to the principle quantum number of the single excited electron.

Summary/Revision:

- For multi-electron atoms, the formulation of the Schrödinger equation is a simple generalisation of what we have seen for single-electron atoms.
- The electron-electron interaction term generally makes analytic solution of the multi-electron Schrödinger equation impossible.
- If the electron-electron interaction is ignored, the wavefunction can be expressed in terms of occupied single-electron *orbitals*.
- For a multi-electron atom, it is usual to indicate which orbitals are occupied by giving the *configuration* in spectroscopic notation.
- The electron-electron interaction has very significant effects on the energy levels of atoms: since this interaction is repulsive, it will raise the total energy compared to a calculation in which it is neglected.
- Since the space distribution of the electrons depends on their l quantum numbers, the value of L affects the strength of the electron-electron repulsion, and therefore the total energy.
- The total wavefunction must be antisymmetric with respect to particle exchange (general expression of the Pauli principle for electrons). This is achieved *either* by having a symmetric space wavefunction and antisymmetric spin wavefunction or *vice versa*.
- For the two-electron atom, if the total spin is $S = 1$ then the spin wavefunction is symmetric under particle exchange. If $S = 0$ the spin wavefunction is antisymmetric.
- Since symmetric space wavefunctions place the electrons closer to each other than antisymmetric wavefunctions, $S = 1$ states have lower energies than $S = 0$ states.
- In the two-electron atom, the electron-electron interaction can be formally expressed in terms of the *Coulomb* and *Exchange* integrals.
- In the two-electron atom, the Pauli principle forbids both electrons occupying the same orbital with an antisymmetric space wavefunction. Thus the ground configuration $1s^2$ has no ^3S term.

8 *Multi-electron atoms: Hartree theory and electron screening*

Context

Why discuss the principles of Hartree theory? To appreciate how real calculations can quantitatively test our theories of multi-electron atoms, we need to understand how they are made.

Why discuss results of Hartree theory and electron screening? The results of *Hartree* calculations form much of the basis upon which our understanding of atomic structure is based. Although performing full numerical calculations is beyond the level of this module, examining the outcome of such calculations is instructive.

Learning goals

1. To introduce the central field approximation
2. To understand how the central field approximation is used in *Hartree* theory to approximately determine the wavefunctions of multi-electron atoms
3. To outline the concepts of the electron shell / sub-shell structure of atoms
4. To introduce the concepts of effective nuclear charge and electron screening
5. To understand how the effective nuclear charge can be used to estimate the energies of electrons in multi-electron atoms
6. To understand how the screening of electrons relates to their principle (n) and orbital angular momentum (l) quantum numbers
7. To appreciate how the *Aufbau* principle can be used to determine the ground state configurations of atoms

8.1   Introduction

In the last section, we introduced the principles of a quantum mechanical treatment of a multi-electron atom, and qualitatively discussed many of the key physical ingredients with specific reference to two-electron atoms. However, the independent electron approximation, upon which much of our discussion was built, could easily be shown to be quantitatively inaccurate and so we must consider how to formulate the treatment of multi-electron atoms if we are to pursue quantitative results.

In this Section we will focus on the *Hartree Theory* of atomic structure and some of its important results. Aside from its practical value in atomic physics, the development of *Hartree Theory* is an excellent example of how quantitative theoretical physics is really done (as opposed to the idealised problems often encountered in undergraduate physics).

8.2   Central field approximation

For a multi-electron atom with nuclear charge Z, the Hamiltonian can be expressed as

$$\hat{H} = \sum_i \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right] \tag{61}$$

where the indices i and j label all electrons in the atom. This is an obvious generalisation of the Hamiltonian we wrote down for the two-electron atom: in particular, the potential energy consists of a central (radial) interaction of each electron with the nucleus (2nd term) and the electron-electron interaction summed over all pairs of electrons (3rd term).

In Section 7.3, we proceeded by ignoring the electron-electron interaction, and from this gained insight into the relationship between the multi-electron and single-electron wavefunctions. However, as discussed in the later sub-sections of Section 7, the electron-electron interaction cannot really be neglected, even if only the qualitative features of two-electron energy level diagram are to be understood. To study atoms with even more electrons, we need to find a means by which to incorporate the effects of the electron-electron interaction.

This can be done rather effectively by introducing a *central field ap-*

proximation. This means we write the Hamiltonian as

$$\hat{H} = \sum_i \left[-\frac{\hbar^2}{2m_e}\nabla_i^2 + U(r_i) \right] \tag{62}$$

where $U(r_i)$ is a central potential that accounts for the net radial contribution of both the nuclear attraction and the electron-electron repulsion. This is only an approximation, since the electron-electron repulsion is not only radial (i.e. an accurate representation would also involve θ and ϕ), but it can be hoped that such an approach can capture many of the main effects of the net repulsion.[8]

The huge practical advantage of a central field approximation is that the solution of the corresponding time-independent Schrödinger equation can still be done by separation of variables. I.e., just like in the *independent electron approximation*, Eqn 62 is a sum of single-particle Hamiltonians that can be solved to produce a set of orbitals (ψ_α, ψ_β etc.). The complete wavefunction of the atom can then be constructed from appropriate products of those orbitals. Moreover, because U depends only on radius, the single-particle time-independent Schrödinger equation for each particle can still be solved by separation of variables: i.e. $\psi_\alpha = R(r)\Theta(\theta)\Phi(\phi)$ (as in Section 4). Indeed the angular parts of the orbitals ($\Theta(\theta)\Phi(\phi)$) will still be *the same* as for the single-electron atom with which we are familiar.[9] The radial parts of the orbital wavefunctions, however, are expected to be different from the single-particle case since the form of the central potential is no longer simply the Coulomb potential of the nucleus. Nevertheless, provided $U(r)$ is known, the radial differential equation can be solved and provide us with a useable set of orbital wavefunctions.

[8] One of the main reasons for optimism here is to recognise than the total probability density (and therefore charge distribution) is spherically symmetric for any filled (sub-)shell of the configuration: e.g. although individual 2p orbitals have probability distributions that are not spherically symmetric, the combined distribution *is* spherical if all are occupied (i.e. for $2p^6$). This matters because the sub-shells are systematically filled up in multi-electron atoms so that (usually) only one or two sub-shells have unfilled orbitals in any given case.

[9] Thus the orbitals are still eigenstates of the same angular momentum operators as the single-electron wavefunctions.

8.3   *The Hartree (and Hartree-Fock) methods*

The challenge in using the *central field approximation* is deducing the form of $U(r)$ to be used: this potential depends on the shape of the wavefunctions (since this determines the probability distribution for the electrons inside the atom and therefore the extent to which they repel each other). But the wavefunctions also depend on the potential (since $U(r)$ appears in the eigenvalue problem for which the orbital functions are the eigenstates). The solution requires a self-consistent calculation of both the wavefunctions and the potential: this can be done using the *Hartree* (later *Hartree-Fock*) method, which dates from the 1920s.

In outline, the Hartree method is an iterative process:

1. Begin with a sensible guess for the form of $U(r)$ (see e.g. Exercise 8.1).
2. Solve for the radial components of the orbitals using $U(r)$ as the potential energy in the time-independent Schrödinger equation. In general, the solution to the differential equation will not be analytic but must be found using computational methods.
3. Calculate the probability density $\psi^*\psi$ associated with the resulting wavefunctions and, from that, the predicted charge distribution ($-e\psi^*\psi$ for each occupied orbital).
4. Apply Gauss's law to the spherically-averaged charge distribution to find an improved approximation for $U(r)$.
5. If the new $U(r)$ differs substantially from that used in step 2, repeat steps 2, 3, and 4 using the improved value of $U(r)$. Continue to repeat this process until a self-consistent $U(r)$ distribution is found.

Just like solutions to the single-electron time-independent Schrödinger equation, the orbitals found via this process will be characterised by three quantum numbers (n, l and m_l), and we can add (as a "bolt-on") the spin (specified by m_s). As noted above, the angular parts of the orbitals will be just the same as for the hydrogenic case (and depend on l and m_l), and the angular momentum eigenvalues will also be the same (i.e. $|\mathbf{l}| = \sqrt{l(l+1)}\hbar$, $l_z = m_l\hbar$). The radial part of the wavefunction, however, will be different and the energy eigenvalues will also change. Of particular note is that the energy eigenvalues E will no longer depend only on n but also on l (notice that l does appear in the separated radial equation, Eqn 31, and so we should not be surprised that it can influence the energy eigenvalue in general).

Calculations of this sort have been done for a wide variety of atoms/ions and they guide our understanding of multi-electron systems (some of the most important results will be elaborated below). The majority of such calculations were initially done (the *Hartree method*) using total wavefunctions (ψ_T) that were simply products of electron orbitals. In this approach the *weak* version of the Pauli principle can be applied (i.e. not more than one electron with the same set of quantum numbers), but the full requirement of particle exchange symmetries (see Sections 7.6 to 7.8) is not addressed.[10] In subsequent studies, when more computational power was available, the exchange symmetries could be included (*Hartree-Fock* method). In most respects, these more sophisticated calculations substantiate the results of the simpler *Hartree theory*, and so we will focus on conclusions drawn from the former.

[10] The reason for this simplification was the computational challenge associated with handling the large number of terms needed to account for exchange symmetries in multi-electron atoms.

Exercise 8.1: Making an initial guess for the central potential.

Hartree Theory requires that we make an initial guess for the form of the central potential $U(r)$. One way to do this is to consider how $U(r)$ should behave at large r and at small r, and then smoothly join the two up.

(a) Consider a neutral atom with nuclear charge Z. Explain why $U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$ is an appropriate form for $U(r)$ as $r \to \infty$.

(b) Give a suitable form for $U(r)$ as $r \to 0$.

- -

(a) Recall that $U(r)$ represents the combined effect of the nuclear potential energy and the net potential energy of interaction of a particular electron with all the *other* electrons in the atom. Also recall that Gauss's law of electrostatics tells us that, if assumed to be spherically symmetric, the Coulomb potential felt at radius r depends only on the charge internal to that radius. If a particular electron were located at very large r (i.e. $r \to \infty$) it will be external to all the other electrons and the total charge internal to its position will be $+e$. [The nucleus has charge $+Ze$ while the combined charge of the other $Z - 1$ electrons is $(-Z + 1)e$.] Thus the effective charge at large r will be $Z_{\text{eff}} = 1$ so that the potential is

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

(b) For $r \to 0$, the electron in question will eventually be closer to the nucleus than any of the other electrons. Thus the charge internal to the electron position will just be the nuclear charge $+Ze$, and so the effective potential for $r \to 0$ could be expected to be

$$U(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

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8.4   *Hartree results: electron screening and effective nuclear charge*

As an example, Fig 19 shows the radial probability distribution for electron orbitals in neutral argon ($Z = 18$), as calculated using *Hartree* Theory. This example illustrates several important conclusions that are of general applicability:

1. Qualitatively, the pattern is similar to that of the single-electron orbitals: in particular, orbitals with the same principle quantum number n have peaks in their probability distribution covering fairly narrow ranges of radii. Thus multi-electron atoms are expected to have a **shell-like structure** in their electron probability (and therefore electric charge) distributions.
2. As one might expect, the most probable radius associated with a given n-value is smaller than in hydrogen (for hydrogen, the $n = 1$ distribution would peak at $r = a_0$; the inner most "shell" here is at substantially smaller radius).
3. The radius of the outermost electron shell is only slightly larger than the most probable $n = 1$-radius of hydrogen (in this case, $\sim 40\%$ larger, despite the atomic number being $Z = 18$). Thus, contrary to common expectations, multi-electron atoms are not substantially larger than hydrogen (more on this below).

The shell-like structure of the overall electron probability density (and therefore charge density) is clearly illustrated in Fig 20: peaks in the distribution can be clearly associated with $n = 1$, $n = 2$ and $n = 3$ shells. As explained in Section 8.3, the net radial potential $U(r)$ follows from the charge distribution inside the atom. In light of Gauss's Law of electrostatics, the central potential can conveniently be expressed in terms of an *effective nuclear charge* $Z(r)$ via

$$U(r) = -\frac{Z(r)e^2}{4\pi\epsilon_0 r} \ . \tag{63}$$

This effective charge is also plotted in Fig 20. As expected (see Exercise 8.1), $Z(r) \to 1$ as $r \to \infty$ but rises steeply inside the atom, approaching the value of the true nuclear charge as $r \to 0$.

Recall L1 electrostatics: if a charge distribution is assumed to be spherically symmetric (as here), the potential energy at radius r depends only on the total charge enclosed by a Gaussian sphere of radius r. I.e., it is completely independent of the charge distribution outside r and of the shape of the distribution internal to r.

The shell structure combined with the smooth variation of $Z(r)$ lends itself to a very simple (but useful!) way of understanding the energies of electrons in multi-electron atoms. Very crudely, we can consider that the electrons in a specific n shell are moving in a Coulomb potential

$$V(r) = -\frac{Z_n e^2}{4\pi\epsilon_0 r} \tag{64}$$

where the value of Z_n will lie somewhere between $Z_n = Z$ (i.e. equal to the true nuclear charge) and $Z_n = 1$.
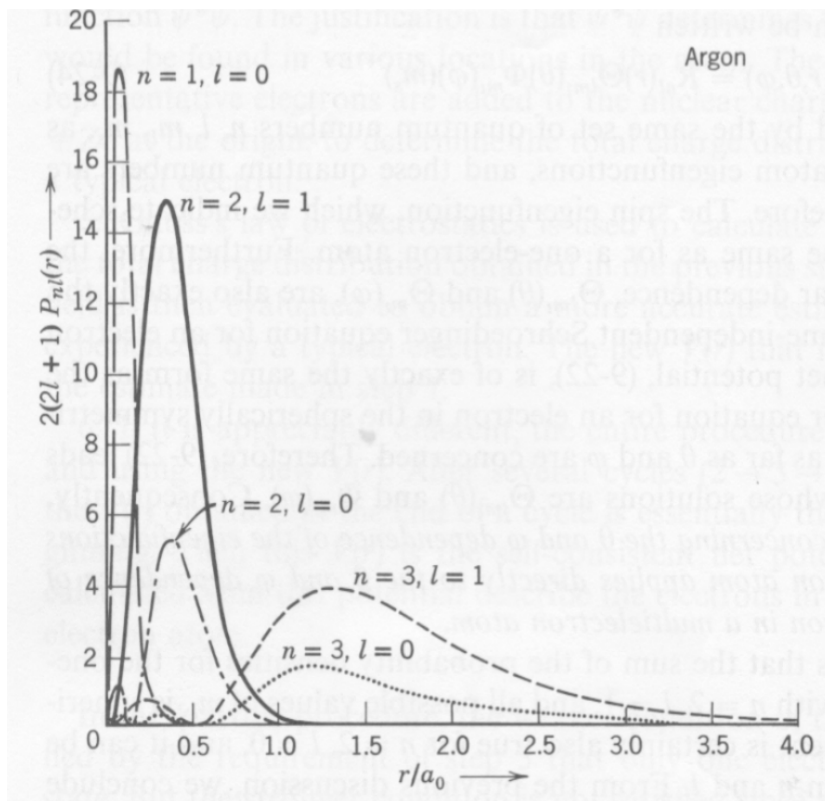
Figure 19: Radial probability distribution for orbitals in the argon atom. From Eisberg & Resnick. Note that the radius is given in units of the Bohr radius.
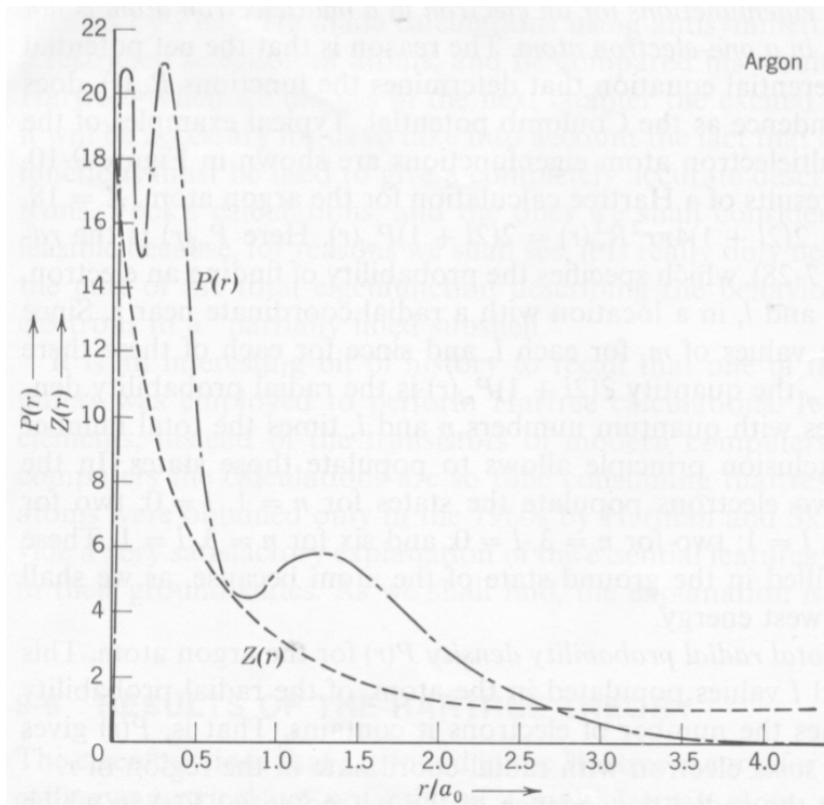
Figure 20: Shape of the total radial probability density ($P(r)$) and the effective charge ($Z(r)$) of argon. From Eisberg & Resnick. Note that the radius is given in units of the Bohr radius.

The variation of Z_n inside an atom is commonly understood in terms of *screening*: from Gauss's law, the effective charge "seen" at a particular point is determined by the net charge internal to that position: thus electrons in interior shells can be expected to "screen out" some of the nuclear charge as seen from a point further out. Of course, because the electron distributions are extended,[11] screening by "internal" electrons is usually imperfect and even electrons that are most probably "exterior" to a given point can make some contribution to the screening (because they may have a small but finite probability of being at smaller radius).

Concept of screening.

[11] I.e. the positions of the electrons are not precisely fixed

If Z_n is known for each shell in the atom, we can estimate the energy of each electron using the usual formula for an electron bound in a Coulomb potential of known charge (see Exercise 8.2):

$$E_n \approx -\frac{\mu Z_n^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} \approx -13.6 \text{ eV } \frac{Z_n^2}{n^2} \quad . \tag{65}$$

It is therefore useful to summarise some general principles related to Z_n that emerge from Hartree calculations applied to neutral atoms:

1. Hartree calculations show that, for $n = 1$ electrons (i.e. innermost shell) in multi-electron atoms, $Z_1 \sim Z - 2$. I.e. the net screening of the 1s electrons by all other electrons in the atom is approximately two units. This has important consequences:
    a. the $n = 1$ shell is smaller than in the hydrogen atom by a factor[12] of roughly $1/(Z - 2)$, up to the point where relativistic effects become important; and
    b. the energy of an electron in the $n = 1$ shell is a factor of $(Z - 2)^2$ times that of an $n = 1$ electron in the hydrogen atom (this follows from Eqn 65 with $n = 1$ and $Z_1 = Z - 2$).

[12] Recall that the most probable radius is inversely proportional to the charge in single-electron atoms.

2. Electrons in outer shells with large n are *almost* completely shielded from the nucleus by the inner shell electrons. In particular, for the outer shell $Z_n \approx n$ is roughly appropriate. This means:
    a. the typical radius of the outermost electron shell is, very approximately $\tilde{r} = \frac{n^2 a_0}{Z_n} \sim n a_0$: thus atomic radii do not grow very rapidly with atomic number (even for atomic number 80, only the $n = 6$ shell is reached, implying a radius only ~ 6 times that of hydrogen);
    b. the energy of an electron in the outermost shell is expected to be of the same order of magnitude as in atomic hydrogen (i.e., since $E_n \propto Z_n^2/n^2$, if $Z_n \sim n$ then E will not vary very much for outer shell electrons across a wide range of atomic number).

The points listed above are very approximate (no better than factor of ~ 2 accuracy) but they do provide important guidance for our

understanding of atomic properties across a wide range of atomic number.

> **Exercise 8.2: Estimating electron energies in argon.**
>
> Use Fig 20 to estimate values of the effective nuclear charge (Z_n) for the $n = 1$, $n = 2$ and $n = 3$ shells of argon. Use these values to calculate the energies of electrons in each of the three shells.
>
> -
>
> From Fig 20 we can read off $Z_1 \approx 16$, $Z_2 \approx 8$ and $Z_3 \approx 3$. Then, using Eqn 65, the energies can be estimated as roughly $E_1 \approx -3500$ eV, $E_2 \approx -220$ eV and $E_3 \approx -14$ eV (see Eisberg & Resnick) for electrons in each shell.

8.5   *l-dependence of screening*

The degree of screening (i.e. the effective nuclear charge that can be used in Eqn 65) does also vary between the various l sub-shells. In particular, since the probability density of states with small values of l are always higher at small r, the screening of outer electrons in orbitals with low l-values is always less effective than for high l. Thus, for a given n-value, an electron in an np orbital will be more effectively screened (and therefore have less negative energy) compared to a ns orbital. This effect can be easily seen in the energy levels of *alkali* atoms, as illustrated for the sodium (Na) atom in Fig 21.
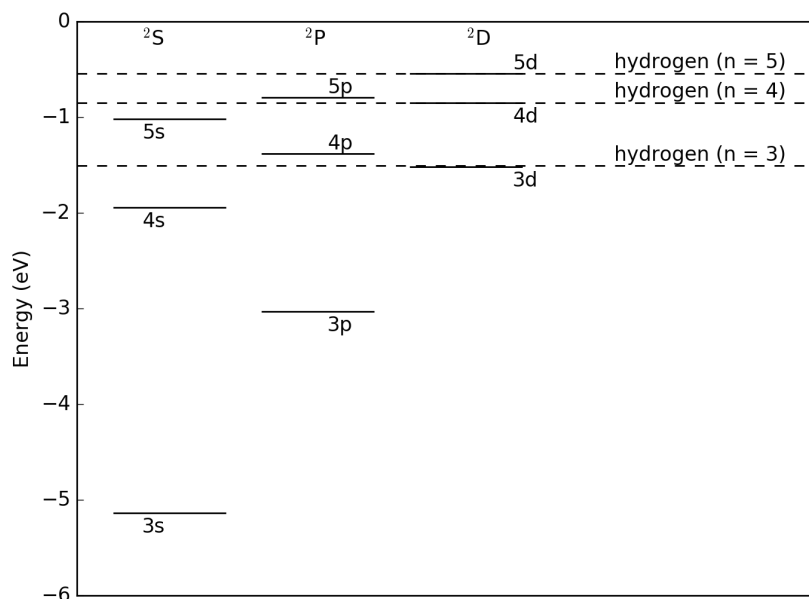
We noted this property for the single-electron wavefunctions in Section 4: only $l = 0$ wavefunctions remain finite as $r \to 0$. This remains true in multi-electron atoms.

Alkali atoms (e.g. Li, Na, K ...) are those in which a number of inner electron shells are filled while a single left-over electron occupies an outer shell.

Figure 21: Some energy levels of the sodium atom, labelled by the orbital occupied by the outermost electron (in all cases, the states shown have fully occupied inner shells: $1s^2 2s^2 2p^6$). The hydrogenic energy levels for $n = 3$, 4 and 5 are indicated by the dashed lines. Notice that, for larger l-values, the states have energies increasingly close to the hydrogenic cases while s-states (i.e. $l = 0$) have significantly more negative energy. This can be attributed to the relatively incomplete screening of outer s-orbitals by the inner electrons.

Depending on the nuclear charge and n-values considered, the l-dependence of screening can be sufficiently large that the energy associated with occupying e.g. an outer nd orbital actually lies above an $(n + 1)$s orbital. This effect is apparent in the ordering of the excited states of sodium (see Fig 21). It is also illustrated in Fig 22, which shows how the energy ordering of the sub-shells for atoms **in their ground states** changes with atomic number.

The changes in order shown in Fig 22 are consequences of changes in the effective screening of each sub-shell.
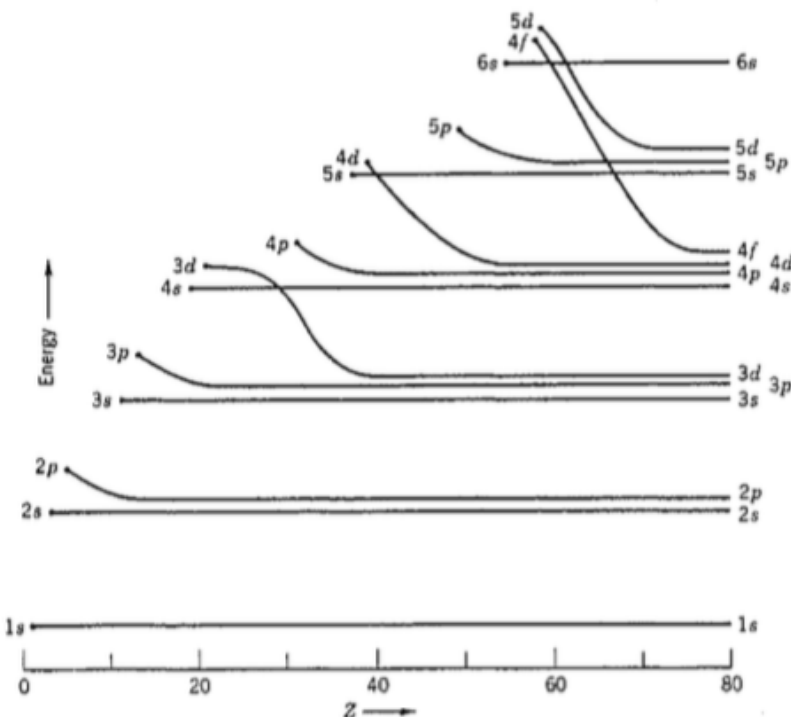
Figure 22: Representation of the energy ordering of sub-shells in the ground states of neutral atoms, as a function of atomic number Z. From Eisberg & Resnick. The energy scale is chosen to schematically illustrate the ordering of the shells only (true energy values vary significantly with Z). Notice how, e.g. the 3d sub-shell lies above 4s when it is first occupied, but drops below in high-Z atoms.

8.6   *Ground state configurations: the Aufbau principle*

The energy ordering of the sub-shells shown in Fig 22 allows us to identify the ground state configurations for atoms. In particular, the **Aufbau principle** states that the ground state (i.e. lowest energy state) will have a configuration in which orbitals are occupied from the lowest energy up, subject to the exclusion principle. Thus, e.g. carbon ($Z = 6$) must have a ground configuration

$$1s^2 2s^2 2p^2$$

while Ti ($Z = 22$) has configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2 \ .$$

Notice that, for Ti, the 4s sub-shell is filled *before* the 3d, in accordance with Fig 22. Exercise 8.3 provides some additional examples.

Exercise 8.3: Ground state configurations of atoms.

Write out the ground state configurations for neutral atoms of (a) Ni ($Z = 28$) and (b) Cd ($Z = 48$).

- -

(a) The first 18 electrons will fill up the 1s, 2s, 2p, 3s and 3p sub-shells (recall that s sub-shells can hold two electrons, and p sub-shells up to 6). According to Fig 22, the next two will occupy 4*s* (which lies at the next lowest energy for $Z = 28$), leaving 8 electrons for 3*d*. Thus the ground configuration will be:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2 \ .$$
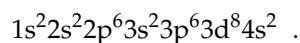
(b) Again, the first 18 electrons will fill up the 1s, 2s, 2p, 3s and 3p sub-shells. At $Z = 48$, the next sub-shell to fill will be 3d, which can accommodate 10 electrons. Next come 4s, 4p and 4d, which accommodate an additional 18 electrons between them, taking us to a total of 46 so far. The remaining two electrons will occupy the 5s orbitals, since these are at lower energy than 4f. Thus the Cd ground configuration will be:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 \ .$$
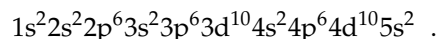
The order in which sub-shells are normally filled according to the *Aufbau* principle can be conveniently remembered with the mnemonic shown in Fig 23. In practise, this works for most elements although there are some exceptions, usually associated with cases where the energies of two sub-shells are very similar in Fig 22.[13]

The chemical properties of elements are directly related to the properties of their partially filled outer electron shells. Thus understanding the order in which the sub-shells are filled is the foundation of interpreting the periodic table of the elements, with which students will be familiar from previous studies. For further reading, see Section 9.7 of Eisberg & Resnick.
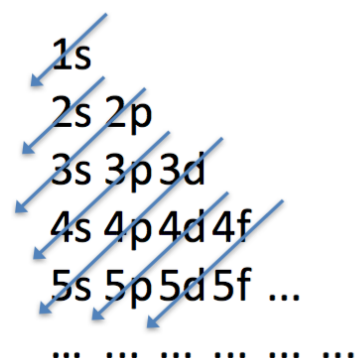

Figure 23: Mnemonic for the ordering in which shell are filled in the ground states of atoms (used to apply the *Aufbau* principle). Starting from the top left, sub-shells are filled in the order indicated by arrows "striking through" the table of orbital configurations.

[13] E.g. Cu ($Z = 29$) has ground state configuration $3d^9 4s$, rather than $3d^8 4s^2$.

Summary/Revision:

- The *central field approximation* to the potential energy allows us to capture many of the important effects of the electron-electron repulsion terms in multi-electron atoms.
- In the central field approximation we include a radial charge distribution in the calculation of the potential energy to account for

the average properties of the electrons in the atom.

- In *Hartree Theory* the central potential is determined self-consistently by iteration and electron orbital wavefunctions can then be calculated.

- *Hartree Theory* explains the approximate localisation of electrons in shells and sub-shells within the atom and can roughly be described in terms of effective values for the potential energy in the region of each shell.

- Electrons in multi-electron atoms are *screened* from the full nuclear charge by the net charge distribution of all the other electrons. Inner shell electrons are most effective at shielding outer shell electrons, although the extended charge distributions mean that screening is imperfect.

- Screening of electrons with low l quantum numbers (particularly $l = 0$) is relatively ineffective compared to screening of high-l electrons with the same value of n.

- The configurations of the ground states of atoms can be determined from the *Aufbau* principle: the available sub-shells in that atom are filled systematically, starting with the lowest energy.

- The energy ordering of sub-shells varies from one atom to the next owing to difference in the effectiveness of screening for atoms with differing numbers of electrons.

9 Spin-orbit interaction, residual Coulomb interaction, and Hunds rules

Context

Why consider spin-orbit and residual Coulomb interactions? These effects, which are not captured in the central field approximation, explain why different *terms* of a given configuration have different energies in a multi-electron atom.

Why learn Hund's rules? These allow us to identify the energy ordering of terms. This is particularly useful since finding the true ground state of an atom is key to understanding many of its properties.

Learning goals

1. To describe the *residual Coulomb interaction* in multi-electron atoms
2. To introduce the *spin-orbit interaction*
3. To discuss the relevance of the *spin-orbit interaction* to multi-electron atoms
4. To become familiar with the Landé interval rule for the *spin-orbit interaction*
5. To be able to use Hund's rules to predict the energy ordering of *terms* in multi-electron atoms

9.1   *Introduction*

In Section 8, we discussed how the net contribution of the electron-electron repulsion terms to the radial potential could be described using a central field approximation. The *Hartree Theory* results arising from this demonstrate how this radial potential alters the energies and eigenstates (orbitals) for electrons inside the atom. Such effects explain why the energies of states in multi-electron atoms depend on which sub-shells of the configuration are occupied, and also why the energies of most shells are significantly shifted compared to their hydrogenic values. However, our discussion of *Hartree Theory* has not addressed how the spectroscopic *term* relates to the energy in multi-electron atoms. To appreciate this we need to introduce (or re-introduce) effects that have been neglected by the *central field approximation*. This is the topic of this Section.

In Section 7 we have already qualitatively discussed why the quantum numbers of the orbital angular momentum (*L*) and spin (*S*) of the complete atom (i.e. the spectroscopic *term*) affect the energy of the state. We will briefly revisit this here and then introduce the *spin-orbit* interaction (Section 9.3), which is responsible for the energy-dependence of states on the *J* quantum number.

9.2   *The residual Coulomb interaction*

The *Hartree* approach only accounts for the radial contribution of the Coulomb repulsion between the electrons. Since filled atomic sub-shells produce spherical charge distributions, this is expected to be a good description of the contribution of electrons occupying filled shells. However, most atoms have at least one partially un-filled shell, which means that there can be a left-over contribution to the Coulomb repulsion, even once the best match to the radial component is found. This *residual Coulomb interaction* can easily be associated with the quantum numbers *L* and *S*, which characterise the total orbital angular momentum (*L*) and spin (*S*) of the atom (see Exercise 9.1).

Exercise 9.1: Angular momentum of filled shells.

Using a simple representation based on the quantum numbers n, l, m_l and m_s (as in *Hartree Theory*), make a table of the quantum numbers of all the electrons in a (filled) $2p^6$ sub-shell. Calculate the resulting M_L and M_S quantum numbers and explain why the *term* corresponding to that sub-shell can only be ^1S. This means that the completely filled shell contributes no net S or L for the atom. Since the same conclusion is drawn for any filled sub-shell, we can conclude that the S and L values for an atom are really determined by the electrons in partially-filled shells.

- -

The Pauli principle means that each electron in the shell must have a different set of quantum numbers. Since there are only six sets available, each of the six electrons must have one of the available sets, as in the Table below:

n	l	m_l	m_s
2	1	-1	-1/2
2	1	-1	+1/2
2	1	0	-1/2
2	1	0	+1/2
2	1	+1	-1/2
2	1	+1	+1/2

In this representation, the z-components of the total spin and the total orbital angular momentum will just be the sum of the z-components of the occupied orbitals. I.e. the M_L and M_S quantum numbers are obtained by summing the m_l and m_s columns of the table, giving the results $M_L = 0$ and $M_S = 0$. Since these are the *only* allowed values for M_L and M_S (no other arrangements of occupied states are permitted), this can correspond only to $L = 0$ and $S = 0$. I.e., the term must be ^1S ,meaning that the filled shell make *no net contribution to the angular momentum of the atom*.

We have already discussed the influence of L and S on the energy levels of the two-electron atom (see Section 7); their role in larger electron systems is complicated but qualitatively similar. In particular,

1. Similar to our treatment of helium, exchange symmetry must be respected. Because the repulsion amongst the outer shell electrons is different depending on whether the space part of the wavefunc-

tion is symmetric or antisymmetric, this makes the energy depend on S. It is usually the case that, as in helium, the larger the value of S, the lower the energy of the state.

2. The value of L also affects the energy (since differing l-states have different orbital shapes). Again, as in helium, the lowest energy state is usually found for the largest allowed value of L. This principle can be approximately justified semi-classically (see Fig 24).

These two principles are the first two of *Hund's rules* (see Section 9.5), and can usually be used to determine the energy ordering of terms in atoms for a wide range of atomic number.[14] The third of Hund's rules governs the energy order of J-states (for given S and L). Before we can understand this, however, we must first investigate the *spin-orbit* interaction.
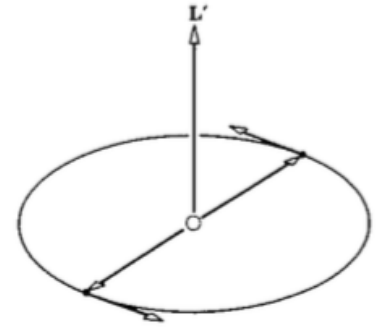

Figure 24: In a semi-classical picture of two electrons orbiting inside at atom, it is clear that the Coulomb repulsion between them will be *lowest* if they orbit at opposite ends of a diameter, as shown. In this circumstance, their orbital angular momentum vectors will be parallel. Figure from Eisberg & Resnick.

[14] So long as *LS coupling* is valid. See later.

9.3   *The spin-orbit interaction*

So far we have considered only Hamiltonians in which the energy is a sum of kinetic and electrostatic potential energies. For low-to-intermediate atomic numbers, these contributions to the energy are certainly dominant, motivating our approach thus far. Up to this point, our discussion of multi-electron atoms has also predicted no effects that explicitly depend on the J quantum number, which specifies the magnitude of the total angular momentum of the atom ($|\mathbf{J}| = \sqrt{J(J+1)}\hbar$ where $\mathbf{J} = \mathbf{L} + \mathbf{S}$).

Note that we *did* already mention that j affects energy levels of the *single-electron* atom in Dirac theory.

As for the hydrogen spectrum, spectroscopic measurements show that transitions in multi-electron atoms can show fine structure, and this fine structure is often far more pronounced than in hydrogen (see Fig 25).
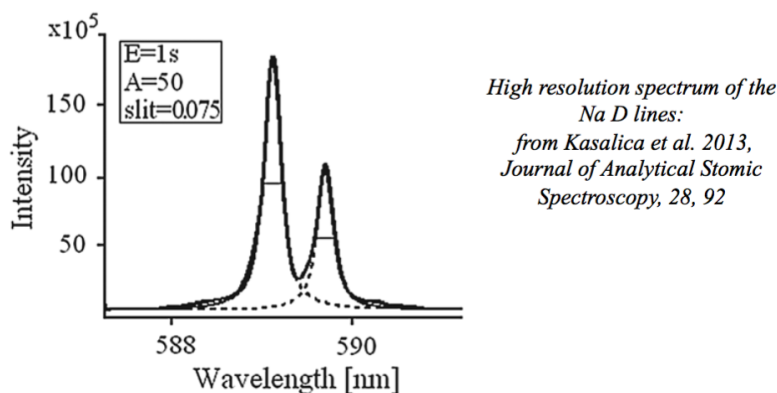
Recall: we actually used this example in PHY2001 Statistical Mechanics!

High resolution spectrum of the Na D lines: from Kasalica et al. 2013, Journal of Analytical Stomic Spectroscopy, 28, 92

Figure 25: Emission line of the sodium (i.e. alkali metal) atom (so called "D" line) in the optical. This transition is 3p ^{2}P – 3s ^{2}S but it is clearly separated into two components (different by more than 0.5nm, much larger than the fine structure splitting of e.g. the Hα line).

In most cases, the observed fine structure of multi-electron atoms can be primarily attributed to lifting of the energy degeneracy of states

with differing *J*-values within a term.

E.g., in the example shown in Fig 25, the two spectral lines can be associated with separate transitions: 3p $^2P_{3/2}$ – 3s $^2S_{1/2}$ and 3p $^2P_{1/2}$ – 3s $^2S_{1/2}$; the difference in wavelength then implies a small (but discernable) splitting of energy between the $^2P_{3/2}$ and $^2P_{1/2}$ terms (see Fig 26).

The origin of this effect is known as the *spin-orbit* interaction. It differs from all the effects we have considered so far since, from a semi-classical viewpoint,[15] it is not associated with the electrostatic potential but rather with a magnetic interaction inside atoms: specifically, it is an new term that we should add to the energy, which represents the magnetic interaction between spin and the magnetic field associated with the angular momentum of the electrons.

Students will recall from PHY2001 (labs.) that electron *spin* corresponds to an intrinsic *magnetic dipole moment*. For a single electron, the magnetic dipole moment associated with *spin* is given by

$$\boldsymbol{\mu}_s = -\frac{g_s \mu_B}{\hbar} \mathbf{S} \tag{66}$$

where $\mu_B = \frac{e\hbar}{2m_e} = 0.927 \times 10^{-23} \mathrm{Am}^2$ is the Bohr magneton and $g_s \approx 2$ is the *spin g-factor*. We also know that, in the presence of a magnetic flux density **B**, a magnetic dipole has an energy of interaction with that field given by

$$\Delta E = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{67}$$

Now, inside an atom, the orbital motion of the electrons (characterised by **L**) gives rise to a magnetic field. To illustrate why this is so, we briefly return to the one-electron atom and consider the simplest (Bohr-like) interpretation: an electron moves in a circular orbit around the nucleus (see Fig 27, left). From the perspective of the electron, the nucleus appears to be in circular orbit around it, and thus constitutes a current loop (see Fig 27, right). If the orbit has radius r and the circular velocity is v, then the magnitude of the current flowing in the loop is

$$I = \frac{Zev}{2\pi r} \quad . \tag{68}$$

We know from elementary electromagnetism that a circular current loop of radius r and current I generates a magnetic flux density of magnitude
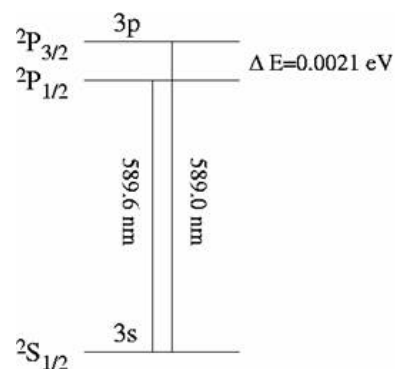

Figure 26: Energy levels for the fine structure in the Na D transition.

[15] If you go on to study relativistic quantum mechanics, you will see that this is actually something of a false dichotomy: but in our non-relativistic framework it is broadly true.

Recall that we discussed magnetic dipole moments and spin when studying the Stern-Gerlach experiment in labs.

A slightly more sophisticated version of this argument is given in Eisberg & Resnick.

This expression for I follows from the charge of the nucleus being $+Ze$ and the period of its orbit being $2\pi r/v$. I.e., on average, a charge of $+Ze$ flows past each $2\pi r/v$ seconds.

This can be easily proven from the Biot-Savart law; revise L1 electromagnetism

$$B = \frac{\mu_0 I}{2r} \tag{69}$$

at its centre. Thus, the apparent rotation of the nucleus about the electron cause the electron to experience a field of magnitude

$$B = \frac{\mu_0 Z e v}{4\pi r^2} \quad . \tag{70}$$

Recalling that the angular momentum of the electron in a circular orbit is $|\mathbf{L}| = m_e v r$, this is simply

$$B = \frac{\mu_0 Z e |\mathbf{L}|}{4\pi m_e r^3} \quad . \tag{71}$$

Moreover, since $\mathbf{B}$ and $\mathbf{L}$ are both perpendicular to the plane of orbit we can express the relationship in vector form

$$\mathbf{B} = \frac{\mu_0 Z e}{4\pi m_e r^3} \mathbf{L} \quad . \tag{72}$$

Thus, the energy of interaction (Eqn 67) between the *spin* magnetic dipole moment and the field induced by $\mathbf{L}$ can be expressed

$$\Delta E = -\boldsymbol{\mu}_S \cdot \mathbf{B} = \frac{g_s \mu_B}{\hbar} \frac{\mu_0 Z e}{4\pi m_e r^3} \mathbf{S} \cdot \mathbf{L} = \frac{g_s e^2}{8\pi \epsilon_0 m_e^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L} \tag{73}$$

where we have made use of the fact that $\mu_0^{-1} = \epsilon_0 c^2$.

Eqn 73 shows that the *spin* and *orbital* angular momenta can be expected to interact magnetically with energy proportional to the scalar product of the vectors: **this** *spin-orbit* **interaction will affect the energies of states inside atoms**.

The expression for the spin-orbit interaction that we have motivated using semi-classical arguments here is not accurate: even for a single-electron atom, a correction factor of $1/2$ is needed to properly account for the transformation of frames (between the nucleus rest frame and the electron rest frame; see Eisberg & Resnick). More importantly, it can be anticipated that its application to multi-electron atoms will involve complications since the concept of a single orbiting charge is clearly inadequate. In particular, the relatively simple means to estimate the pre-factor obtained above cannot easily be extended to multi-electron atoms. Nevertheless, it does remain true that the magnetic *spin-orbit* interaction has the form

$$\Delta E = \frac{2K}{\hbar^2} \mathbf{S} \cdot \mathbf{L} \tag{74}$$
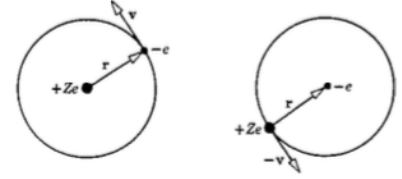

Figure 27: In the semi-classical (Bohr) model, the electron orbits the nucleus at radius r and speed v (left). From the perspective of the electron, the nucleus is in orbit at the same radius and with the same speed but opposite sense of rotation (right). Figure from Eisberg & Resnick.

and, although the pre-factor K is not an absolute constant, it does have the same value for all states of a given *configuration* and combination of L and S.

To understand how the interaction (Eqn 74) affects the energy levels of a multi-electron atom (see also Exercise 9.2), we make use of the fact that

$$\mathbf{J}^2 = \mathbf{J} \cdot \mathbf{J} = (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{S} \cdot \mathbf{L} \tag{75}$$

so that

$$\Delta E = \frac{K}{\hbar^2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) \tag{76}$$

or, in terms of quantum numbers

$$\Delta E = K\left[J(J+1) - L(L+1) - S(S+1)\right] \ . \tag{77}$$

Eqn 77 demonstrates that the *spin-orbit* interaction will lift the degeneracy thus-far associated with the J quantum number: depending on the sign of the coefficient K, states will either shift up or down in energy. This effect accounts for the small difference of energy between e.g. the $^2P_{3/2}$ and $^2P_{1/2}$ state of sodium and, more generally, for the fine structure observed in transitions of multi-electron atoms.

Note that the spin-orbit interaction certainly also occurs in single-electron atoms: it is partly responsible for the fine-structure observed in hydrogen (as explained in the Dirac theory). However, the spin-orbit effect is much stronger in multi-electron atoms, which is why our discussion has focussed on the multi-electron application.

Exercise 9.2: Introducing J to describe the *spin-orbit* interaction.

Explain why we introduce J to handle the spin-orbit interaction: why not use $\mathbf{S} \cdot \mathbf{L} = S_x L_x + S_y L_y + S_z L_z$?

- -

We cannot express $\mathbf{S} \cdot \mathbf{L}$ readily in component form because the components are incompatible with each other: e.g. we cannot simultaneously know L_x, L_y and L_z, so we have to switch to a representation that allows the *spin-orbit* term to be expressed in terms of something else. Fortunately, J^2 is compatible with L^2 and S^2.

9.4 *The Landé interval rule*

Aside from being an important element of understanding the spectra of multi-electron atoms, the simple form of the spin-orbit interaction

(Eqn 77) is widely used in spectroscopy since it can greatly help understand and identify the quantum numbers associated with an observed multiplet (i.e. set of fine-structure transitions). Of particular utility is the Landé interval rule:

> **The Landé interval rule**:
> *The energy difference between two adjacent levels of a multiplet is proportional to the higher of the two J quantum numbers of the levels concerned.*

This rule can be easily obtained from Eqn 77 (Exercise 9.3) and can be used to directly infer the values of J by examining the observed separations of components of spectroscopic multiplets (e.g. Exercise 9.4 should be considered carefully to understand the power of this rule).

Exercise 9.3: Deriving the Landé interval rule.

Use Eqn 77 to derive the Landé interval rule.

- -

Within a multiplet (i.e. given values for L and S), the allowed values of J will always be separated by integers. Thus, for a pair of adjacent levels, if one level has quantum number J, the level adjacent to it will have $J + 1$. According to Equation 77, the spin-orbit energy shift of the first level will be

$$\Delta E_J = K\left[J(J+1) - L(L+1) - S(S+1)\right]$$

while the other will be shifted by

$$\Delta E_{J+1} = K\left[(J+1)(J+2) - L(L+1) - S(S+1)\right]$$

Thus the energy *difference* between the two levels will be

$$\Delta E_{J+1} - \Delta E_J = K\left[(J+1)(J+2) - J(J+1)\right] = 2K(J+1)$$

which is proportional to $J+1$ (the larger of the two total angular momentum quantum numbers), as required.

Exercise 9.4: Using the Landé interval rule.

Analysis of the fine-structure components of a particular spectroscopic multiplet indicates that three levels are present. These differ only in the value of their J quantum number, and it is measured that the energy separations between the adjacent pairs of states are in the ratio of 3 to 5. Use Landé's interval rule to find the J, L and S quantum numbers of the energy levels concerned.

- -

Let us start by calling the (unknown) lowest J-value of the levels concerned J_0. The other two levels will have $J_0 + 1$ and $J_0 + 2$. Landé interval rule tells us that the energy separation between the state with this lowest value and the adjacent state with J higher by 1 will be

$$2K(J_0 + 1) \ .$$

The energy separation between the next pair of states, which have $J_0 + 1$ and $J_0 + 2$, will be

$$2K(J_0 + 2) \ .$$

These two energy separations are in the ratio

$$\frac{2K(J_0 + 1)}{2K(J_0 + 2)} = \frac{J_0 + 1}{J_0 + 2}$$

which can be equated to the measured ratio given in the question

$$\frac{J_0 + 1}{J_0 + 2} = \frac{3}{5} \ .$$

This rearranges to give

$$5J_0 + 5 = 3J_0 + 6 \ \rightarrow \ J_0 = 1/2$$

Thus the J values for the three levels must be

$$J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \ .$$

To find L and S we need to "invert" the quantum number addition formula. I.e., since $\mathbf{J} = \mathbf{L} + \mathbf{S}$, the allowed values of J must be the sequence

$$|L - S|, |L - S| + 1, ..., L + S - 1, L + S \ .$$

Thus $L + S = 5/2$ and $|L - S| = 1/2$. Since L must be an integer, the only valid solution is $L = 1$ and $S = 3/2$. Hence we now know L, S and J for the set of three levels.

9.5   *Hund's Rules*

Hund's Rules provide the means by which to determine the energy ordering of terms within a configuration of a multi-electron atom. Somewhat as for the mnemonic we discussed for the *Aufbau* principle, these rules are not always obeyed, but they are widely applicable.

We already alluded to the first two of *Hund's Rules* in Section 9.2. Having discussed the *spin-orbit* interaction we can now add the third, which relates to the ordering of states by their J quantum number.

> **Hund's Rules:**
> 1. Terms with largest S quantum number lie at lowest energy.
> 2. For given S, the terms are ordered by L, with the largest value lying at lowest energy.
> 3. If the outer electron shell is less than half-filled, the state with lowest J value has lowest energy. If the outer electron shell is more than half-filled, the state with highest J has lowest energy.

Remembering Hund's rules is an effective way to construct energy level digrams for the terms belonging to a given electron configuration and they are a great aid to spectroscopists in interpreting observed transitions from complex atoms. For example, they can be used to predict the ordering of terms even for a fairly complicated case, as shown in Figure 28.
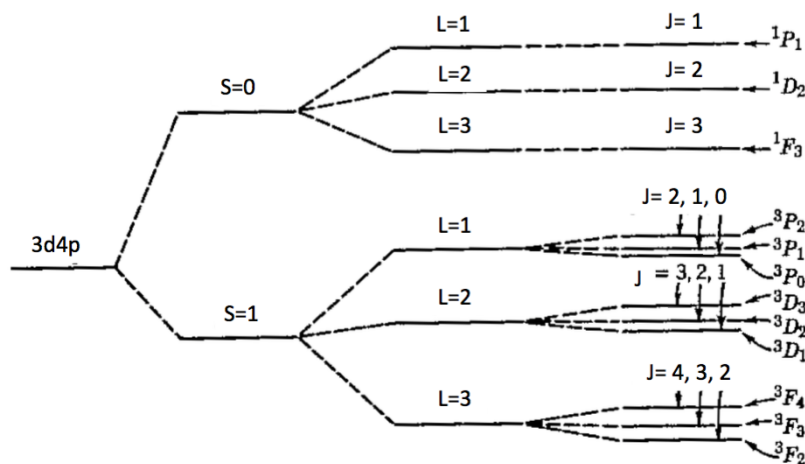

Figure 28: Example of the splittings and energy orderings (according to Hund's rules) for a 3d4p configuration. Thanks to the combined influence of the residual Coulomb interaction and the spin-orbit interaction, the configuration separates into a total of 12 energy levels. Figure from Eisberg & Resnick.

Summary/Revision:

- The *Hartree* method provides improved orbitals and energies for configurations in multi-electron atoms. Nevertheless, we still need to consider residual effects to understand the energy-dependence of *terms* in multi-electron atoms.
- The *residual Coulomb interaction* is associated with the part of the electron-electron repulsion that is not captured by the *central field approximation*. It manifests as changes in energy that involve the S and L quantum numbers of the atom.
- The effects of the *residual Coulomb interaction* can be understood as being similar to the effects of S and L on the energy levels of the two electron atom (see earlier discussion of e.g. *exchange force*).
- Energy levels also depend on their J quantum number, a consequence of the *spin-orbit interaction*.
- The *spin-orbit interaction* is a magnetic effect that depends on the relative orientation of the spin and orbital angular momentum vectors of an atom. It shifts the energies of *terms* depending on the J, L and S quantum numbers.
- Although the absolute magnitude of the *spin-orbit interaction* in multi-electron atoms is hard to predict, the Landé interval rule allows the relative energy differences between adjacent J-levels to be calculated. This is particularly useful when identifying *terms* from spectroscopy.
- Hund's rules allow us to predict the relative energy ordering of the terms associated with a *configuration*. These do not always work, but they are sufficiently general to provide very useful estimates.

10 *Emission and absorption of photons, allowed transitions and selection rules.*

Context

Why consider how atoms absorb and emit photons? Spectroscopy is the key means to test and utilize atomic theory. Analysing spectra depends on our understanding of the ways in which photons are absorbed and emitted.

Why learn the selection rules? To interpret spectra or experimentally test energy level diagrams, we have to known which pairs of energy levels will give rise to strong spectral lines.

Learning goals

1. To qualitatively understand the processes of *spontaneous emission*, *absorption* and *stimulated emission* for transitions between bound states of atoms/ions.
2. To become familiar with the *Einstein coefficients*.
3. To know the *selection rules* that are obeyed by *permitted* (electric dipole) transitions.

Introduction

We have now discussed many of the principles that allow us to formulate theories for the structure of atoms. However, as already demonstrated in several examples, practical applications of our theory very often require us to supplement our knowledge of the states of atoms with rules that govern the emission and absorption of photons: after all, it is mainly via spectroscopic studies that our theory can be used.

A full quantum mechanical treatment of the interaction of atoms with radiation goes beyond the scope of this module. Therefore, in this short section, we will focus on an overview of the relevant processes and examples of how to apply the *selection rules* for *permitted* radiative transitions.

Spontaneous emission

There are three distinct types of interaction between photons and atoms that involve changes in the energy level of the atom. The first is so-called *spontaneous emission* (see Fig 29). This is the process by which an atom deexcites from some upper energy level to some lower energy level by emitting a photon. The frequency of the photon is related to the energies of the two states by

$$h\nu_{lu} = E_u - E_l \tag{78}$$

where E_u and E_l are the energies of the upper and lower state respectively.

The rate at which spontaneous emission occurs is independent of the environment and is determined by the *Einstein A-coefficient (A_{ul}) for spontaneous emission*. A_{ul} has dimensions of s^{-1} and gives the number of photons emitted per second per atom in the upper energy state. I.e.

$$\text{\# photon emissions per second} = N_u A_{ul}$$

where N_u is the number of atoms that are in the upper energy state.

Quantum mechanical calculations of A_{ul} values can be made, but are complex and have accuracy limited by the variety of approximations needed to make their evaluation tractable. *A*-values can also be determined empirically from laboratory experiments.
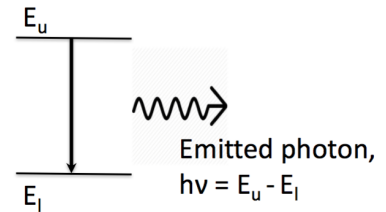

Figure 29: Spontaneous emission of a photon.

10.3 Absorption

Atoms can also absorb photons that have the correct frequency to stimulate a transition of the atom from a lower energy state to an upper state (see Fig 30).

Figure 30: Absorption of a photon in an atomic transition.

In this process, the absorbed photon is destroyed: thus absorption is usually studied via the sharp dark regions that appear in the spectrum of a source of continuous radiation illuminating a target.

The rate at which transitions are stimulated by absorption of radiation depends on the *Einstein B-coefficient (B_{lu}) for stimulated absorption* and on both the number of available atoms in the lower level, and the number of incoming photons of the correct frequency:

$$\text{\# absorptions per second} = N_l \rho(\nu_{lu}) B_{lu}$$

where $\rho(\nu_{lu})$ is the energy density of photons with frequency ν_{lu}.

10.4 Stimulated emission

The third process is likely to be less familiar: *stimulated emission* is the process by which a photon with frequency in resonance with the atomic transition stimulates the emission of a second photon (the emitted photon is identical to the stimulating photon; see Fig 31).

Figure 31: Stimulated emission of a photon in an atomic transition.

Similar to absorption, the rate at which this process occurs is determined by a coefficient (the *Einstein B-coefficient (B_{ul}) for stimulated emission*), by the number of available photons and by the number of atoms in the *upper* energy level:

$$\text{\# stim. emissions per second} = N_u \rho(\nu_{lu}) B_{ul} \ .$$

Under most circumstances, stimulated emission is less important than spontaneous emission (indeed, for many applications it can be neglected). However, stimulated emission is the basis on which *lasers*[16] operate.

[16] Clue in the name: "Light Amplification by Stimulated Emission of Radiation".

10.5 Relations between the Einstein coefficients

Although quantum mechanical calculations are needed to determine A_{ul}, the Einstein B-coefficients can both be derived from the A-value, using arguments from statistical physics and the black-body photon distribution. We will not address this argument in detail in this module, but interested students can find the details in Chapter 11 of
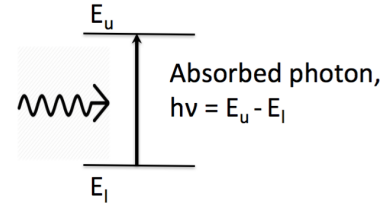
Eisberg & Resnick. The results, however, are easily summarised in the *Einstein relationships*:

$$B_{ul} = A_{ul}\frac{8\pi h\nu_{lu}}{c^3}$$

$$B_{lu} = \frac{g_u}{g_l}B_{ul}$$

where g_u and g_l are the degeneracies of the upper and lower energy states, respectively.

10.6   *Selection rules for permitted transitions*

Quantum mechanical calculations can provide A_{ul} values for most transitions of interest to laboratory plasma physics and astrophysics. The values of A vary across many orders of magnitude but obey certain principles, some of which can be understood semi-classically.

Most importantly, only a restricted subset of possible transitions have large A-values (i.e. have a high probability of occurring). These transitions are usually called *allowed* or *permitted* transitions and are the ones we can usually observe in experiments. Other transitions are said to be *forbidden*, and are usually not observed.

In many cases, *forbidden* transitions are not really completely forbidden but rather are just so unlikely to occur that they are not normally observed.

The *allowed* transitions can partly be understood semi-classically. Specifically, it is known from classical electromagnetism that a charge distribution with an oscillating *electric dipole moment* generates electromagnetic waves. Thus it is reasonable to expect that a transition between two atomic states that involves an appropriate change in the electric dipole moment of the atom can occur by emitting a photon (i.e. a quantum of the electromagnetic field).

The electric dipole moment of a charge distribution can be defined by $\mathbf{d} = \sum_i \mathbf{r_i}q_i$ where $\mathbf{r_i}$ and q_i are the positions and charges of the particles that make up the distribution.

Additional constraints on allowed transitions are imposed by the properties of the photon: in particular, photons carry angular momentum (circularly polarised photons have angular momenta of $-\hbar$ or $+\hbar$). Whatever angular momentum is carried by the photon must correspond to the allowed changes in the angular momentum quantum numbers of the atom.

Detailed consideration (i.e. changes in electric dipole moment and photon properties) of transitions between atomic states leads to the following *selection rules* that can be applied to determine whether any particular transition is *permitted*. These rules are most easily cast in terms of the allowed *changes* in the quantum numbers used to specify the configuration and term of the atomic state:

Selection rules:

1. **Single electron jump**: the transition must involve a change in the configuration that corresponds to a single electron changing its shell (or sub-shell).

2. $\Delta l = \pm 1$: the change in the electron configuration must involve the angular momentum quantum number of the "jumping" electron changing by one.

3. $\Delta L = 0, \pm 1$ **but** $L = 0 \rightarrow L = 0$ **is forbidden**.

4. $\Delta S = 0$.

5. $\Delta J = 0, \pm 1$ **but** $J = 0 \rightarrow J = 0$ **is forbidden**.

6. $\Delta M_J = 0, \pm 1$.
   Note that, under many circumstances, this rule is not explicitly considered (since the M_J states remain degenerate). However, it is relevant to the study of the Zeeman effect (L2 labs).

These selection rules should be committed to memory and can then be readily used to determine which transitions are permitted between any particular set of states. Exercises 10.1 and 10.2 give examples of applying these rules.

**Exercise 10.1: Identifying permitted transitions**

Which of the following transitions are permitted? If forbidden, state which of the rules are violated.
(a) $3p\ ^2P_{1/2} \rightarrow 2p\ ^2P_{1/2}$
(b) $3d\ ^2D_{3/2} \rightarrow 2p\ ^2P_{1/2}$
(c) $2s^2 2p3p\ ^1P_1 \rightarrow 2s^2 2p^2\ ^3P_1$
(d) $1s^2 2s2p\ ^1P_1 \rightarrow 1s^2 2s^2\ ^1S_0$
(e) $3d^2 4s^2\ ^1G_4 \rightarrow 3d^2 4s^2\ ^1D_2$

- -

(a) forbidden since $\Delta l = 0$
(b) permitted
(c) forbidden since $\Delta l = 0$ and $\Delta S = 1$
(d) permitted
(e) forbidden since no electron jump, $\Delta L = 2$, $\Delta J = 2$.

Exercise 10.2: Identifying transitions

The figures below shows the energy levels of sodium (from Fig. 21). Mark all the allowed transitions on this figure.
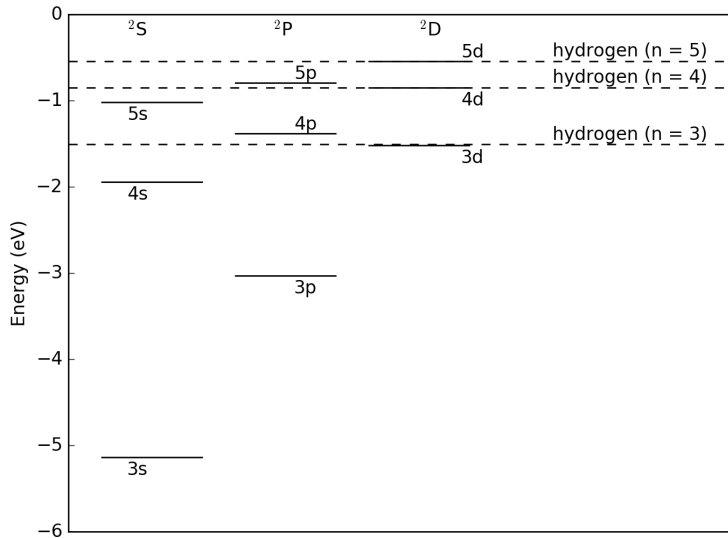
There are permitted transitions between each pair of s and p states, and between each pair of p and d states. Transitions between d and s are forbidden.
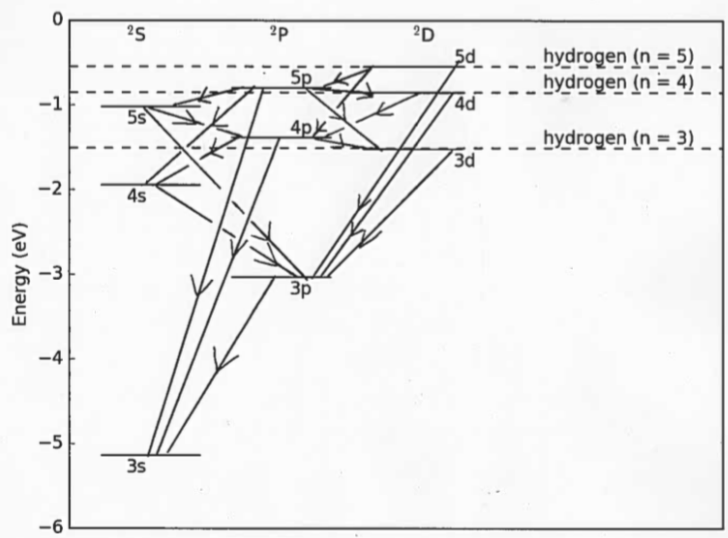
Summary/Revision:

- Transitions between atomic states involving photons have three types: *spontaneous emission*, *absorption* and *stimulated emission*.
- The rates of these three classes of transition depend on the corresponding *Einstein coefficients*.
- Permitted transitions must obey *selection rules* that govern the changes in the quantum numbers that occur during the transition. **Students are expected to know the selection rules.**

11 *The Zeeman effect*

Context

Why investigate the Zeeman effect? The Zeeman effect lifts the last of the degeneracies among the quantum numbers we have used: it allows us to explore the role of M_J.

Learning goals

1. To understand that the magnetic dipole moment of an atom depends on both the orbital angular momentum and the spin
2. To be able to justify (with semi-classical arguments) the relationship between orbital angular momentum and the associated component of the magnetic dipole moment
3. To understand the *normal* Zeeman effect as the interaction between the magnetic dipole moment associated with **L** and an external field
4. To understand, and be able to demonstrate, that spectral lines are split into three components by the *normal* Zeeman effect
5. To appreciate the distinction between the *normal* and *anomalous* Zeeman effects, and to be able to express the magnetic dipole moment appropriate to the *anomalous* Zeeman effect in terms of the L, S and J quantum numbers
6. To be familiar with the Landé g-factor and the splittings of Zeeman components for both the *normal* and *anomalous* Zeeman effects in an externally applied magnetic field
7. To understand the polarisation states of photons emitted in Zeeman effect experiments

Introduction

When the spectra of atoms (or ions) are studied in the presence of externally applied magnetic fields, it is observed that the spectral lines split into multiple distinct components.

This is known as the *Zeeman effect*, and students will have the opportunity to study it experimentally in the L2 laboratory sessions associated with this module.

The magnetic dipole moment

The *Zeeman effect* is a consequence of the interaction of the magnetic dipole moment of the atom with the externally applied magnetic field. Thus, before we can discuss the Zeeman effect itself, we must first discuss the complete magnetic dipole moment of atoms.

Both the orbital angular momentum **L** and the spin **S** contribute to the total magnetic dipole moment μ of an atom:

Recall: We have already considered the spin contribution to μ in our discussion of the spin-orbit interaction (see Section 9.3).

$$\mu = \mu_L + \mu_S \tag{79}$$

The μ_L contribution can be understood semi-classically, similar to the magnetostatic argument we made to justify the form of the spin-orbit interaction (Section 9.3). Specifically, consider a single electron in a Bohr-like circular orbit around the nucleus (see Fig 32). This constitutes a current loop in which the magnitude of the current can be determined from the circular speed and the radius of the orbit:

The distinction from the discussion in Section 9.3 is only that we do now consider the current in the frame where the nucleus is stationary.

$$I = \frac{ev}{2\pi r} = \frac{e|\mathbf{L}|}{2\pi m_e r^2} , \tag{80}$$

where $|\mathbf{L}| = m_e v r$ is the magnitude of the orbital angular momentum. It is known from magnetostatics that a simple current loop generates a dipole magnetic field. The strength of that field is governed by the value of the magnetic dipole moment which, for a circular current loop, has magnitude given by the product of the current I and the area of the loop A
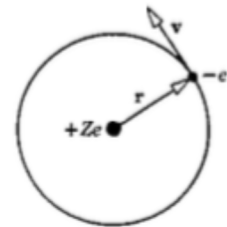
Figure 32:   An electron in circular orbit around the nucleus.

$$|\mu_L| = AI \tag{81}$$

and the vector μ_L points in the direction perpendicular to the current loop (see Figure 33).
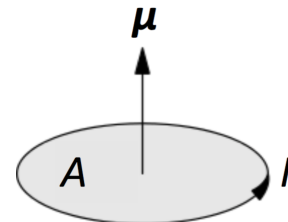

Figure 33:   A current I flowing in a circular loop of surface areas A constitutes a magnetic dipole moment μ that is orientated perpendicular to the plane of the loop.

It then follows that

$$|\boldsymbol{\mu}_L| = \pi r^2 \frac{e|\mathbf{L}|}{2\pi m_e r^2} = \frac{e}{2m_e}|\mathbf{L}| \ . \tag{82}$$

Now, both $\boldsymbol{\mu}_L$ and $\mathbf{L}$ are perpendicular to the plane of orbit, but they are antiparallel (this is because the negative sign of the electron charge actually means that the current – defined as a flow of *positive* charge – is in the opposite sense of rotation to the electron velocity). Thus we can equate

$$\boldsymbol{\mu}_L = -\frac{e}{2m_e}\mathbf{L} \ . \tag{83}$$

Although we have justified Eqn 83 by considering only a simple current loop, it is generally valid. Moreover, we note that it can be readily recast in a form very similar to the relationship we already used for the spin (i.e. Eqn 66): i.e.

$$\boldsymbol{\mu}_L = -\frac{g_L \mu_B}{\hbar}\mathbf{L} \ . \tag{84}$$

While for spin the g-factor was $g_s \approx 2$, here we have $g_L = 1$.

Combining the spin and orbit contributions (Eqns 66 and 84), we then conclude that the total magnetic dipole moment

$$\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S = -\frac{\mu_B}{\hbar}(g_L\mathbf{L} + g_S\mathbf{S}) \approx -\frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S}) \ . \tag{85}$$

11.3   *Interaction with external magnetic field*

When an atom is placed in an external magnetic field (which, for simplicity, we assume to be oriented along the z-direction, i.e. $\mathbf{B} = (0,0,B)$ in Cartesian components), the energy of interaction between the field and the magnetic dipole moment is given by

$$\Delta E = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B \tag{86}$$

Provided that the magnetic field is not too strong, this interacton can be treated as a *perturbation* and its effect accounted for as a shift in the energies of states that depends on their values of μ_z. These shifts in energy correspond to changes in the wavelengths of photons emitted in transitions between the levels and so leads to splitting of the spectral lines, i.e. the *Zeeman effect*.

11.4 *The "normal" Zeeman effect*

The *normal Zeeman effect* is observed for transitions between states in which $S = 0$, i.e. when $\mu_S = 0$. This implies

$$\mu = \mu_L = -\frac{\mu_B}{\hbar} \mathbf{L} \ . \tag{87}$$

Using the usual quantum numbers, L and M_L, we can then give the magnitude of the magnetic dipole moment,

$$|\mu| = \mu_B \sqrt{L(L+1)} \tag{88}$$

and

$$\mu_z = -\mu_B M_L \ . \tag{89}$$

So, if we consider a particular energy level with quantum numbers $S = 0$ and $L = L$, in the presence of an applied magnetic field, it will split into $2L + 1$ distinct levels that correspond to the $2L + 1$ allowed values of M_L. The degree of splitting depends on the magnetic field and is given by (see Eqn 86)

$$\Delta E = \mu_B M_L B \tag{90}$$

Exercise 11.1 provides an example of applying this to a level of calcium.

Exercise 11.1: Zeeman splitting (normal Zeeman effect)

The 3d4s configuration of Calcium ($Z = 20$) has a $^1D_2$ term at energy -3.404 eV. (a) If placed in a magnetic field of 0.2 T, calculate how many different energy levels this term will split into and calculate the shift in energy of each as a percentage of the total energy. (b) In the absence of an applied magnetic field, the Ca 3d4s $^3D_2$ and 3d4s $^3D_3$ terms are separated by an fractional energy shift of 7.5×10^{-2} %. Comment on the comparison of this value to the result of part (a).

- -

(a) For $^1D_2$, we can read off the spin multiplicity is 1 and therefore $S = 0$: i.e. the normal Zeeman effect applies. We can also read off from the term symbol ("D") that $L = 2$. Thus the allowed values of M_L are:

$$M_L = -L, -L+1, ..., L-1, L = -2, -1, 0, 1, 2$$

so there will be 5 different energy levels following the Zeeman splitting. To estimate the energy shifts we can use Eqn 11.1 with $B = 0.2$ T to estimate the five energy shifts corresponding to the allowed M_L values. They are

$$\Delta E = (-2.3, -1.2, 0, 1.2, 2.3) \times 10^{-5} \text{ eV}$$

corresponding to percentage change in energy of

$$\Delta E = (6.8, 3.4, 0, -3.4, -6.8) \times 10^{-4} \text{ \%}$$

respectively.

(b) The splitting here are much smaller than the splittings between the J-states within the corresponding triplet term. We know that the splittings associated with different J values (for a given L and S) are due to the spin-orbit interaction inside the atom: i.e. they are associated with the interaction of the spin magnetic moment and the internal B field associated with the orbital angular momentum. Since μ_S and μ_L are of similar order of magnitude, this implies that the internal magnetic field must be much stronger than the external applied field (of 0.2 T in this case).

The energy splittings described by Eqn 90 can be identified by observing the splitting of a spectral line between two levels that both have $S = 0$. One good example of this is the splitting of the 643.8 nm line of cadmium ($Z = 48$) that students will study when carrying out the *Zeeman effect experiment* in L2 labs. This is a transition between an upper $^1D_2$ term and a lower $^1P_1$; when placed in an external magnetic field, these terms are split into five and three distinct energy levels, respectively (see Fig 34). Transitions between these split levels give rise to three distinct spectral lines, associated with the allowed transitions in the M_L quantum number

$$\Delta M_L = -1, 0, +1 \tag{91}$$

As students will find in the L2 lab experiment, it can be verified that the separation of the three components does indeed depend on the applied magnetic field in the manner expected.

Note: in general, the transition rule (Section 10.6) would be written as $\Delta M_J = -1, 0, +1$. However, for the specific case here ($S = 0$, $M_S = 0$), it is easily translated to a rule for M_L.

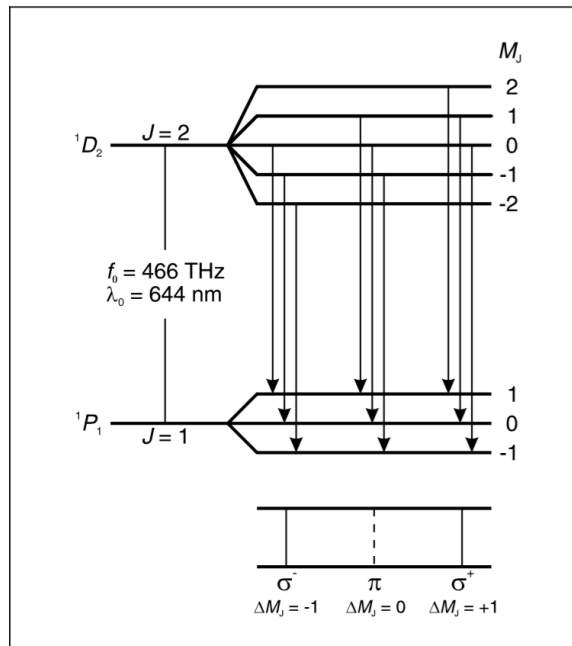Figure 34: Example of the normal Zeeman effect in Cd. On the left are shown energy states in the absence of an applied field. On the right are the energy splittings in an applied field, and the transitions allowed by the usual rule ($\Delta M_J = \pm 1, 0$). Transition at three distinct wavelengths are predicted (lower right), corresponding to the three allowed ΔM_J values. From L2 *Zeeman Effect* laboratory manual.

11.5   *The "anomalous" Zeeman effect*

In the normal Zeeman effect, the splitting of spectral lines is always into three components (also known as the *Lorentz triplet*). However, in the general case, $S \neq 0$, and a wider variety of spectral components is observed. This is known as the *anomalous* Zeeman effect. However, once spin in included in the theory, these "anomalous" splittings can also be readily understood.

We return to Eqn 85 (with $g_s = 2$)

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S})$$

and consider how to express μ_z, as needed to calculate energy shifts from Eqn 86. Recalling that, in order to treat the spin-orbit interaction, we label states with their J and M_J values, we can anticipate that the z-component of the magnetic dipole moment will depend on M_J.

To appreciate how to calculate the relationship between μ_z and M_J it is useful to consider the vector model for angular momenta shown in Fig 35. This illustrates how the relative orientations of $\mathbf{L}$, $\mathbf{S}$ and $\mathbf{J}$ are specified: in order that $|\mathbf{J}|$ is fixed, we chose the "known" components[17] of $\mathbf{L}$ and $\mathbf{S}$ to be those in the $\mathbf{J}$ direction. Thus we first have to find the corresponding "known" components of $\boldsymbol{\mu}_L$ and $\boldsymbol{\mu}_S$; i.e. their components along the $\mathbf{J}$ direction. We can then sum these to obtain the total component of $\boldsymbol{\mu}$ along $\mathbf{J}$, which we denote μ_J. I.e.,

$$\mu_J = \frac{\boldsymbol{\mu}_L \cdot \mathbf{J}}{|\mathbf{J}|} + \frac{\boldsymbol{\mu}_S \cdot \mathbf{J}}{|\mathbf{J}|} = \frac{\boldsymbol{\mu} \cdot \mathbf{J}}{|\mathbf{J}|} = -\frac{\mu_B}{\hbar}\frac{(\mathbf{L} + 2\mathbf{S}) \cdot (\mathbf{L} + \mathbf{S})}{|\mathbf{J}|}$$
$$= -\frac{\mu_B}{\hbar}\frac{|\mathbf{L}|^2 + 3\mathbf{S} \cdot \mathbf{L} + 2|\mathbf{S}|^2}{|\mathbf{J}|} \tag{92}$$

Now, using the same approach as in Section 9.3 (see Eqn 75), the scalar product $\mathbf{S} \cdot \mathbf{L}$ can be written

$$\mathbf{S} \cdot \mathbf{L} = \frac{1}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right) \tag{93}$$

leading to

$$\mu_J = -\frac{\mu_B}{\hbar}\frac{3|\mathbf{J}|^2 + |\mathbf{S}|^2 - |\mathbf{L}|^2}{2|\mathbf{J}|} \tag{94}$$

This gives us the strength of the magnetic dipole moment along the direction of the *J*-vector. We already know that the allowed projections of J on the z-direction are given by the M_J quantum number: i.e.
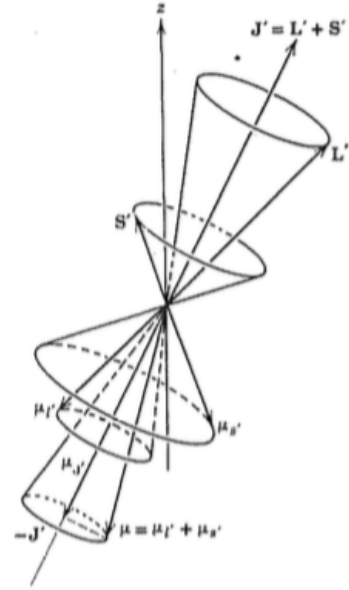

Figure 35: Vector model for $\mathbf{L}$, $\mathbf{S}$, $\mathbf{J}$ and $\boldsymbol{\mu}$. Figure from Eisberg & Resnick.

[17] Recall that, for all angular momentum vectors, we can known the component in one direction, but not simultaneously specify either of the perpendicular components.

$$\mathbf{J} \cdot \hat{\mathbf{z}} = \hbar M_J$$

Thus we can convert from μ_J to the allowed values of μ_z using

$$\mu_z = \mu_J \frac{\mathbf{J} \cdot \hat{\mathbf{z}}}{|\mathbf{J}|} = -\mu_B \frac{3|\mathbf{J}|^2 + |\mathbf{S}|^2 - |\mathbf{L}|^2}{2|\mathbf{J}|^2} M_J \quad . \qquad (95)$$

This can finally be expressed in terms of the L, S, J and M_J quantum numbers:

$$\mu_z = -\mu_B \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} M_J = -\mu_B g_J M_J \ , \qquad (96)$$

where

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \qquad (97)$$

is known as the Landé g-factor. Now that we have an expression for μ_Z, we can readily evaluate the energy shifts that will occur in the presence of an external magnetic field (from Eqn 86):

The Landé g-factor here plays a similar role to g_S (in our description of the spin-orbit interaction) or g_L (in our discussion of the normal Zeeman effect).

$$\Delta E = -\mu_z B = \mu_B g_J M_J B \quad . \qquad (98)$$

An example is given in Exercise 11.2.

Since

1. the energy splitting in the anomalous Zeeman effect will be different for different levels (i.e. g_J depends on the L, S and J quantum numbers involved[18]) and
2. some atoms have integer values of M_J while others have half-integer values,

[18] In the "normal" Zeeman effect the spitting only depends on g_L, which is always equal to one.

the number of distinct wavelengths into which transitions can be split varies from case to case (i.e. we do not always observe three components, as in the normal Zeeman effect). Exercise 11.3 investigates this for an example transition in the sodium atom.

Exercise 11.2: Zeeman splitting (anomalous Zeeman effect)

Let us return to the example of Exercise 11.1 but this time consider the splitting of the 3d4s $^3D_3$ term of Ca. Calculate how many energy levels this will split into and give the energies by which each state is shifted (in eV) in an applied field of 0.2 T.

- -

For $^3D_3$, we can read off $S = 1$, $L = 2$ and $J = 3$. Thus the Landé g-factor is

$$g_J = 1 + \frac{12 + 2 - 6}{24} = \frac{4}{3}.$$

For $J = 3$, the allowed values of M_J are

$$M_J = -3, -2, -1, 0, 1, 2, 3$$

i.e. there are seven possibilities, and therefore the term will be split into seven distinct energy levels. The energy shifts will be given by

$$\Delta E = \mu_B g_J M_J B = (-4.6, -3.1, -1.5, 0, 1.5, 3.1, 4.6) \times 10^{-5} \text{ eV},$$

for $B = 0.2$ T.

Exercise 11.3: Anomalous Zeeman effect components

Consider the 3p $^2P_{1/2}$ $\rightarrow$ 3s $^2S_{1/2}$ transition in the sodium atom. Calculate the number of components into which this transition will be split in an applied magnetic field, and the shift in photon energy of each component for an applied magnetic field of 0.3 T.

It is useful to start by sketching an energy level diagram to identify the expected splittings:
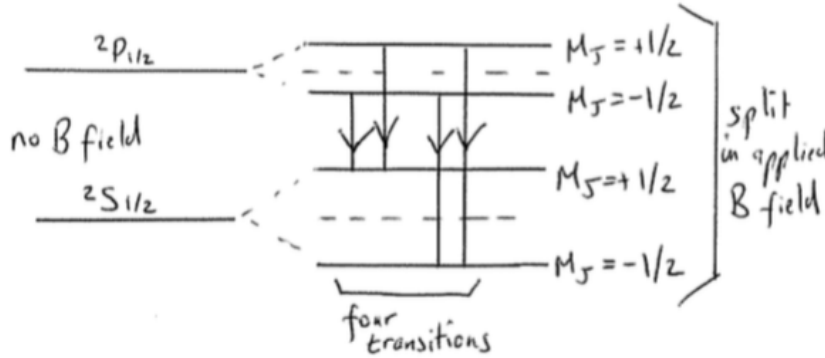
Both the $^2P_{1/2}$ and $^2S_{1/2}$ levels have $J = 1/2$ and so both will be split into two energy levels (for both, the allowed values of M_J are $-1/2$ and $+1/2$). The transition rule ($\Delta M_J = \pm 1, 0$) allows all four of the possible transitions between these two pairs of states to occur: so we need to calculate the energy shift for each of them.

First, before we can calculate the energy shifts, we need to known the g_J factors for both levels. With $L = 1$, $S = 1/2$ and $J = 1/2$, the $^2P_{1/2}$ state has

$$g_J = 1 + \frac{3/4 + 3/4 - 2}{3/2} = \frac{2}{3} \, .$$

The lower state, $^2S_{1/2}$ has $L = 0$ and so can easily be shown to have

$$g_J = g_S = 2 \, .$$

So, for the upper state, the two levels are shifted in energy by $\frac{2}{3}\mu_B B M_J$, and for the lower level by $2\mu_B B M_J$. Thus the energy shifts of the four transitions (these are differences in the energies of the emitted photons compared to the $B = 0$ case) will be (from left to right in the diagram):

$$\Delta E = -\frac{1}{3}\mu_B B - \mu_B B = -\frac{4}{3}\mu_B B$$

$$\Delta E = +\frac{1}{3}\mu_B B - \mu_B B = -\frac{2}{3}\mu_B B$$

$$\Delta E = -\frac{1}{3}\mu_B B + \mu_B B = \frac{2}{3}\mu_B B$$

$$\Delta E = +\frac{1}{3}\mu_B B + \mu_B B = \frac{4}{3}\mu_B B$$

Therefore, four distinct components are expected and, for $B = 0.3$ T, their energy shifts will be

$$\Delta E = (-2.3, -1.2, +1.2, +2.3) \times 10^{-5} \text{ eV} \, .$$

Notice that, for this case, there is no unshifted component (i.e. no component remains with $\Delta E = 0$).

11.6   *Photon polarisation in the Zeeman effect*

Experiments show that the different Zeeman components into which spectral lines are split have polarisation states that depend on the orientation from which measurements are made.

σ^- $(\Delta M_J = -1)$ π $(\Delta M_J = 0)$ σ^+ $(\Delta M_J = +1)$
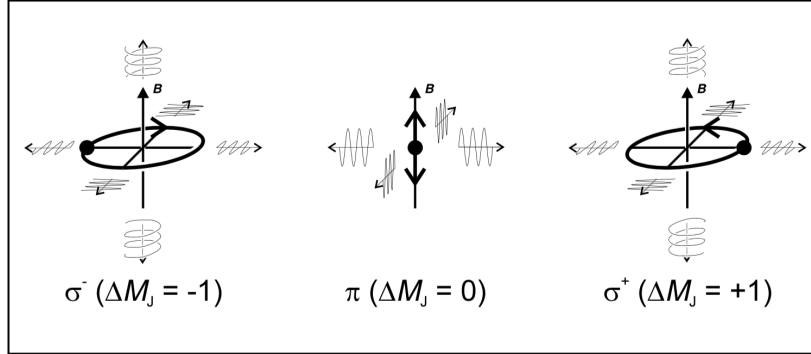
Figure 36: Photon polarisation in the Zeeman effect. The three panels show the polarisation states of emitted photons in the three cases allowed by the *selection rules*: $\Delta M_J = -1$, $\Delta M_J = 0$ and $\Delta M_J = +1$. The magnetic field is vertical.

In particular (see Fig 36), components with $\Delta M_J = \pm 1$ are observed to be circularly polarised (in opposite senses to each other) when viewed along the direction of the field. From this orientation, $\Delta M_J = 0$ components are found to be absent.

Recall from Section 10.6, that components are only allowed for $\Delta M_J = 0, \pm 1$.

In contrast, when observed, perpendicular to the applied field, all components ($\Delta M_J = 0, \pm 1$) are observed, and all are linearly polarised (although the plane of polarisation is 90° rotated for $\Delta M_J = 0$ transitions compared to $\Delta M_J = \pm 1$).

$\Delta M_J \pm 1$ Zeeman components are often referred to as σ components, while those with $\Delta M_J = 0$ are denoted π.

A full understanding of these polarisation states requires more sophisticated theory, but the elements can be understood within the framework we have developed. In particular, we know that transitions with $\Delta M_J = \pm 1$ involve a change in the z-component of the angular momentum of the atom. Thus it makes sense that photons emitted in the z-direction by such transitions should carry net angular momentum about their direction of propagation: this manifests as the photons being circularly polarised, with handedness depending on the sign of the angular momentum they carry.

From a semi-classical view point, the emission of circularly polarised electromagnetic waves can be associated with an electric dipole moment that is rotating in the plane perpendicular to the direction of wave propagation. Such a picture immediately explains why the ΔM_J components are then linearly polarised when viewed perpendicular to the field: viewed along e.g. the x-direction, the projection of an electric dipole that rotates in the xy-plane will be a dipole oscillation in the y direction. This will produce linearly polarised light (with

plane of polarisation in the xy-plane).

We can take the semi-classical analogy one step further and identify the $\Delta M_J = 0$ transitions with an electric dipole moment that oscillated perpendicular to that of the $\Delta M_J = \pm 1$ cases, i.e. oscillating in the z-direction. If viewed along the xy-plane, such a dipole will generate linearly polarised light, with plane of polarization parallel to z. However, if viewed down the z axis, this case leads to no projected oscillation of the electric dipole moment and thus no emission of electromagnetic waves.

11.7   *Applications of the Zeeman effect*

In a similar spirit to the spin-orbit interaction, the *anomalous Zeeman effect* is very useful for spectroscopists when trying to determine the quantum numbers associated with a state of an atom:

– by identifying how many energy levels a given state is split into, the value of J can be constrained;
– by measuring the splitting between those energy levels (in a B field of known strength), an experimental value for the Landé g-factor can be found and used to confirm an identification of L and S.

The Zeeman effect (normal or anomalous) also has a variety of uses in other disciplines. For example, it provides one of only a handful of methods to determine the strength of magnetic fields in astronomical objects.

Summary/Revision:

- The *Zeeman effect* occurs when atoms (or ions) are placed in an external magnetic field.
- In the *Zeeman effect*, the interaction with the external magnetic field lifts the degeneracy of states that differ only in their M_J quantum numbers. The shifts in energy are proportional to the M_J quantum number and to the strength of the applied magnetic field.
- The splitting of energy levels manifests as the splitting of spectral lines into multiple components. Observing these components is both a test of our quantum mechanical theory and a means by which to measure the strength of magnetic fields.
- The *normal* Zeeman effect occurs when the levels have $S = 0$. In this case spectral lines are always split into a triplet.
- The *anomalous* Zeeman effect occurs when $S \neq 0$ and can lead to more or fewer components than the *normal* Zeeman effects.
- The Landé g-factor, which depends on the L, S and J quantum numbers, determines the magnitude of the splitting of energy levels in the *anomalous* Zeeman effect.

12 Advanced topics – angular momentum coupling schemes, the Paschen-Bach effect and hyperfine structure

Concluding thoughts

In this module we have laid the foundations of the theory of atomic structure, atomic transitions and the quantum mechanics of multi-body systems. However, there is much more to the topic than we have been able to address.

Important: For assessment purposes, students are not expected to know details of any of the topics discussed below. However, a basic familiarity may occasionally help with the most advanced parts of questions, and will be useful in further studies.

Learning goals

1. To appreciate that this module has not exhaustively covered all of atomic physic: there is much more than can be studied and understood to demonstrate the effectiveness of the underlying quantum mechanical model.

12.1   *Introduction*

In the sub-sections below, we briefly summarise some important topics that lie just beyond the level of the material we have discussed. These are by no means exhaustive, but are intended as an indication of how "the story" would continue.

12.2   **LS**, **jj** *and intermediate coupling schemes*

Throughout this module we have been working (tacitly) under what is known as the *LS*-coupling approximation (also known as Russell-Saunders coupling). *LS*-coupling is the name given to the scheme where we obtain the total angular momentum of a multi-electron atom by first summing the **l** vectors for all the electrons

$$\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 + \mathbf{l}_3 + \dots \,,$$

then summing the spins

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \dots \,,$$

and finally obtaining the total angular momentum via

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \,.$$

In this "coupling scheme", well-defined values of both L and S can be stated. Because of the way in which the addition rules for quantised angular momenta behave, this comes at the expense of being able to identify unique j_1, j_2, j_3, ... quantum numbers that specify private angular momenta for each of the electrons (i.e. none of the components of $\mathbf{j}_1 = \mathbf{l}_1 + \mathbf{s}_1$ are generally compatible with L and S).

This is often expressed by saying that "L and S are good quantum numbers".

LS coupling is a good means to describe the states of atoms with low-to-intermediate atomic number: in these, the energy of interaction associated with the residual Coulomb interaction is large compared to the spin-orbit interaction. Thus L and S (which we have already associated with the residual Coulomb interaction) provide a good means to label atomic states.

However, the strength of spin-orbit interactions grows with increasing atomic number.[19] Thus, for sufficiently high atomic number the spin-orbit interactions will dominate the residual Coulomb interaction and it becomes better to describe states via a coupling scheme in which the interaction between l and s is described for each electron and a private **j** is assigned to each electron

[19] This is readily apparent if e.g. the fine structure of hydrogen and sodium are compared; see Section 5.4 and 9.3.

$$\mathbf{j}_1 = \mathbf{l}_1 + \mathbf{s}_1 \,, \;\; \mathbf{j}_2 = \mathbf{l}_2 + \mathbf{s}_2 \,, \;\; \mathbf{j}_3 = \mathbf{l}_3 + \mathbf{s}_3 \,, \; \dots$$

and these are combined to give the complete

$$\mathbf{J} = \mathbf{j}_1 + \mathbf{j}_2 + \mathbf{j}_3 + \dots \ .$$

This scheme is known as *jj-coupling*, and is used for high atomic-number atoms. In *jj*-coupling L and S are no longer "good quantum numbers" and the manner in which spectroscopic terms are written is altered so that the *j* quantum numbers are given (rather than L and S).

Unfortunately, there are few good examples of pure *jj* coupling. In reality, most examples for which *LS* coupling is not a good approximation actually involve so-called *intermediate coupling*, which is a complicated mix of the two schemes.

In this module we have not had time to quantitatively discuss *jj* or *intermediate coupling* schemes, but most of the principles we have learned from *LS* coupling do still apply[20] and the interested student will find further reading on these topics in advanced textbooks.

[20] Note, however, that most of the radiative *selection rules* (Section 10.6) are necessarily different when a different scheme applies.

12.3   *The Paschen-Bach effect*

Our discussion of atoms in external magnetic fields has been limited to the normal and anomalous *Zeeman effects* (Section 11). However, the *anomalous Zeeman effect* is only observed for relatively weak magnetic fields: for very strong fields the behaviour of many atoms is rather different and described instead by the *Paschen-Bach effect*.

Details of the *Paschen-Bach effect* are given in Eisberg & Resnick (section 10.6): in many ways it is simpler than the *Zeeman effect*. In essence, a sufficiently strong external magnetic field will dominate the internal magnetic field generated by **L** and effectively break the spin-orbit coupling. In this case, **L** and **S** both couple directly to the external field (rather than to each other) and the magnetic interaction is described in terms of M_L and M_S quantum numbers, rather than M_J (see discussion of anomalous *Zeeman effect*). The consequence is that, for very strong applied fields, the *anomalous* Zeeman effect is effectively destroyed and all transitions are split into three components, similar to the *normal* Zeeman effect.

12.4   *Hyperfine structure and the nuclear spin*

Nucleons (protons and neutrons) also posses spin and an associated magnetic dipole moment. The magnitude of nuclear magnetic dipole moments is approximately three orders of magnitude smaller than the magnetic dipole moment of the electron. Nevertheless, the coupling of the nuclear magnetic moment to the angular momentum of

the electrons does have an effect and can be described using a theoretical framework very similar to that employed for the electron spin-orbit interaction.

Specifically, if we use $\mathbf{I}$ to denote the orbital angular momentum associated with the nuclear spin, we can introduce a new "total" angular momentum $\mathbf{F}$ via

$$\mathbf{F} = \mathbf{I} + \mathbf{J} \, .$$

Following arguments very similar to those we employed to formulate the spin-orbit interaction in Section 9.3, this leads to a hyperfine-structure splitting that be written

$$\Delta E = C[F(F+1) - I(I+1) - J(J+1)] \ .$$

The magnitude of the coupling constant C is approximately three orders of magnitude smaller than that of the spin-orbit K in Section 9.3. Nevertheless, the effect can be detected and provides one means to determine properties of nuclei.

Hyperfine splitting of spectral lines rarely has observable consequences, but there are cases where it is extremely important. For example the famous 21 cm line of hydrogen is associated with the "forbidden" transition between the two hyperfine energy levels into which the ground 1s $^2S_{1/2}$ state of hydrogen is split. Observations of this line are used in astronomy: it provides a unique probe of galactic dynamics and is one of the very few observational signatures that can be used to map out the structure of the early Universe from the so-called "dark ages" that occurred before the first epochs of star formation.

Notation used

m_e	electron rest mass
h	Planck's constant
$\hbar$	$h/2\pi$
e	electron charge
ϵ_0	permittivity of free space
a_0	Bohr radius
ψ	wavefunction (lower case often used for time independant)
Ψ	wavefunction (upper case often used for time dependent)
σ	spin part of the wavefunction
T	time part of the wavefunction
$*$	indicates the complex conjugate of a quantity
$\char`\^$	indicates that the quantity is an operator
$r, \mathbf{r}$	position coordinate
x, y, z	Cartesian coordinates
θ	spherical polar coordinate (polar angle)
ϕ	spherical polar coordinate (azimuthal angle)
t	time
∇	vector differential operator (3D)
∇^2	Laplacian differential operator (3D)
R, R_∞, R_M	Rydberg constant in various forms
E	(total) energy
V	potential energy
Z	atomic number / nuclear charge (in units of +e)
m	particle mass
M	mass of nucleus
τ	volume
μ	reduced mass of electron/nucleus system
ν	frequency of radiation
λ	wavelength of radiation
n	principle quantum number
L	orbital angular momentum (Bohr model)
l, L	orbital angular momentum quantum number (Schrödinger QM)
v	speed
$\hat{H}$	Hamiltonian operator
$\mathbf{p}, \hat{\mathbf{p}}$	momentum, momentum operator
$\mathbf{L}$	orbital angular momentum vector
L_x, L_y, L_z	component of the orbital angular momentum vector
$\hat{L}_x, \hat{L}_y, \hat{L}_z$	operators corresponding to components of the orbital angular momentum vector
$\mathbf{L}^2, \hat{\mathbf{L}}^2$	square of the magnitude of the orbital angular momentum vector, associated operator
m_l	quantum number giving L_z in units of $\hbar$

S	spin vector
s, S	spin quantum number
m_s, M_S	quantum number giving S_z in units of $\hbar$
J	total angular momentum vector
j, J	total angular momentum quantum number
m_j, M_J	quantum number giving J_z in units of $\hbar$
α	fine-structure constant
< ... >	indicates an expectation value
J, K	*Coulomb* and *Exchange Integrals* for two-electron atoms
α, β ...	labels used as sub-scripts to distinguish orbitals in multi-electron atoms
s, p, d, f ...	spectroscopic notation designating *l*-values for electrons in configuration
S, P, D, F ...	spectroscopic notation designating *L*-values in terms
$\boldsymbol{\mu}$	magnetic dipole moment
g_s	spin g-factor
μ_B	Bohr magneton
B, B	Magnetic flux density; its magnitude
I	electric current
μ_0	permittivity of free space
A_{ul}, B_{lu}, B_{ul}	Einstein coefficients
ρ	photon energy density
d	electric dipole moment
N_u, N_l	numbers of atoms in upper and lower states of a transition
g_u, g_l	degeneracies of upper and lower states of a transition
g_S, g_L	g-factors for spin and orbital angular momenta ($g_S \approx 2$, $g_L = 1$)
g_J	Landé g-factor
I; I	Nuclear spin angular momentum; its quantum number
F; F	Total angular momentum (including nuclear spin); its quantum number