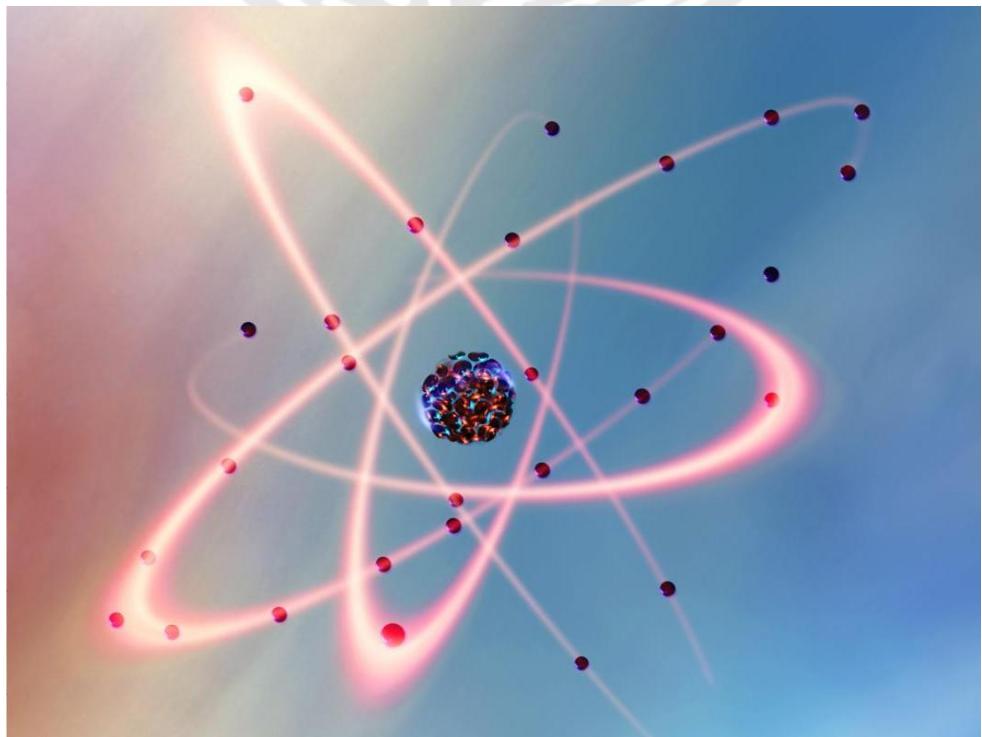


Atomic Physics

2022/2023 PH20013/60 Notes + Problems

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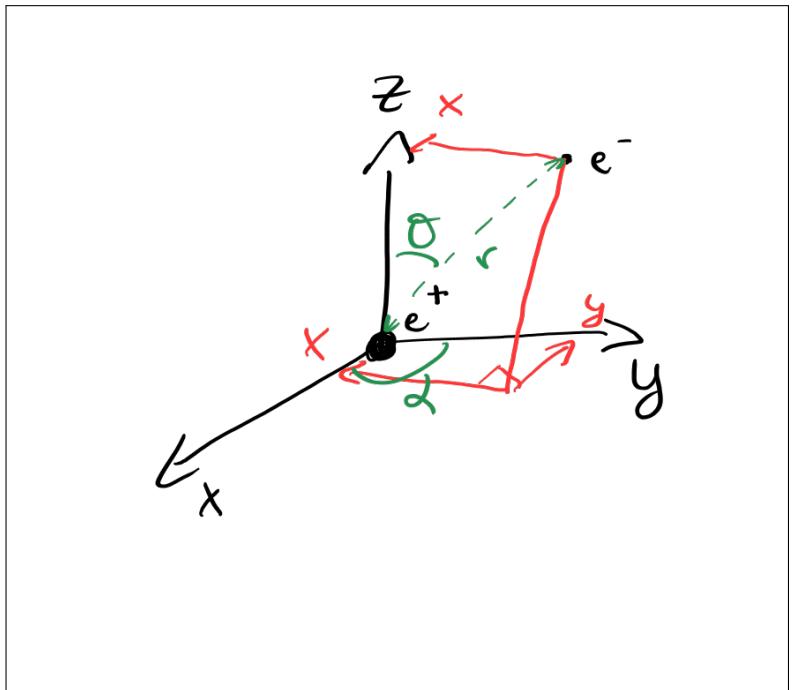
Section 1

The Schrödinger hydrogen atom

To really get to grips with atoms we turn to Erwin Schrödinger's wave mechanics in 3 spatial dimensions. We can write the potential energy between a proton and an electron as

✓
we only care about Coulomb interactions

Figure 1.1: Spherical polar coordinates.



Coulomb potential

$$V(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0 r} \quad (1.1)$$

$$= -\frac{e^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}} \quad (1.2)$$

which is spherically symmetric hence we use spherical polar coordinates (r, θ, ϕ) and now need to solve the time independent Schrödinger equation in 3D fig. 1.1

$$\hat{H}\Psi = E\Psi \quad (1.3)$$

where \hat{H} is the so-called Hamiltonian, that it, the mathematical operation that acts on the wavefunction to give the energy of the wavefunction.

operator

1.1 Operators, eigenvalues and eigenfunctions

It is important to be relaxed with the notation, i.e., how we write things down in the natural language of quantum mechanics.

- Schrödinger's wave mechanics imposes constraints on the wavefunction properties (along with the boundary conditions)
- The natural mathematical formulation is the eigenvalue equation.

⇒ We have a mathematical operator, say, \hat{K} with a hat on to show it's an operator.

⇒ Then we have the eigenvalue equation:

$$\hat{K} \Psi_K = \kappa \Psi_K \quad (1.4)$$

⇒ With K being an eigenvalue of the operator.

⇒ With Ψ_K being an eigenfunction of the operator.

⇒ Things with 'hats' are operators, the same thing with no 'hat' is an eigenvalue of that operator.

⇒ If there are many eigenvalues let's label them n therefore we have a family

$$\hat{K} \Psi_{Kn} = \kappa_n \Psi_{Kn} \quad (1.5)$$

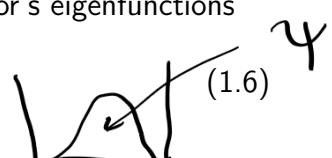
of eigenvalue equations and hence eigenvalues and eigenfunctions.

⇒ Any function ψ can be expressed as a superposition of the operator's eigenfunctions

$$\psi = \sum c_n \Psi_{Kn}$$

where the amplitude term

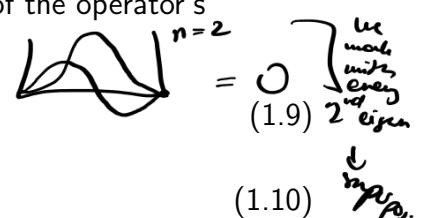
$$c_n = \text{overlap} \\ = \int \psi^* \Psi_{Kn} d\tau \quad (1.8)$$



where this integral runs over all dimensions of the wavefunctions.

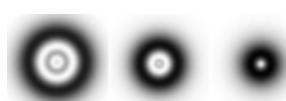
⇒ Therefore given the linearity of operators etc. we can act with an operator on the wavefunction, given that we can express it as a superposition of the operator's eigenfunctions.

$$\hat{K}\psi = \hat{K} \sum c_n \Psi_{Kn} \\ = c_1 K_1 \psi_{K1} + c_2 K_2 \psi_{K2} + c_3 K_3 \psi_{K3} + \dots \quad (1.10)$$



$$\hat{K} \psi = \sum c_n \kappa_n \Psi_{Kn} \quad (1.11)$$

- We will deal with eigenfunctions of operators mostly, but will discuss superpositions and what quantum measurement (sort of) really means.



1.2 Energy

The energy is made up from potential and kinetic so we have two terms in the Hamiltonian

$$\left(\underbrace{-\frac{\hbar^2}{2m} \nabla^2}_{\text{kinetic}} + \underbrace{V(\vec{r})}_{\text{potential}} \right) \psi = E_{\text{kinetic}} \psi + E_{\text{potential}} \psi \quad (1.12)$$

$$= E \psi \quad (1.13)$$

where in Cartesian coordinates

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (1.14)$$

and in spherical polar coordinates

$$\nabla^2 \equiv \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}. \quad (1.15)$$

where

$$r = 0 \rightarrow \infty \quad (1.16)$$

$$\theta = 0 \rightarrow \pi \quad (1.17)$$

$$\text{and } \phi = 0 \rightarrow 2\pi \quad (1.18)$$

Therefore in its full glory the time independent Schrödinger equation for a hydrogen atom is

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi(r, \theta, \phi) - \frac{e^2}{4\pi\epsilon_0 r} \psi(r, \theta, \phi) = E \psi(r, \theta, \phi). \quad (1.19)$$

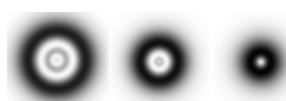
1.3 Separation of variables

Because the potential depends only on r , we can use the technique of separation of variables and look for solutions of the form

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \quad (1.20)$$

where

- $R(r)$ is the radial part of the wavefunction
- $Y(\theta, \phi)$ is the angular part of the wavefunction

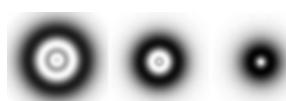


You (you!) can Substitute this into the time independent Schrödinger to give separate equations for $R(r)$ and for $Y(\theta, \phi)$

$$\begin{aligned} -\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} (V(r) - E) &= \\ = \frac{1}{Y} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right) \quad (1.21) \end{aligned}$$

- Since no R dependence on right-hand-side.
- And since no θ, ϕ dependence on left-hand-side

\Rightarrow Both = *The same must*
c.f. $\hat{H}\psi = E\psi$ $\frac{1}{\psi} \hat{H}\psi = E$ \curvearrowright *cancel with your operators*



Section 2

Angular wavefunction

For the angular part we have

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} = \text{constant} \times Y(\theta, \phi) \quad (2.1)$$

which is an eigenvalue problem. Acting on the wavefunction give back a constant times the wavefunction. Hence we get a family of eigenvalues (the constant) and eigenfunctions (the wavefunctions).

2.1 Boundary conditions

And we want solution that are finite for

$$0 \leq \theta \leq 2\pi \quad (2.2)$$

$$0 \leq \phi \leq \pi \quad (2.3)$$

and since wavefunctions are single valued

$$Y(\theta, \phi) = Y(\theta, \phi + 2\pi) \quad (2.4)$$

as these coordinates are the same point in space.

2.2 Quantum Numbers (I)

It turns out that this equation with boundary conditions can only be solved if

$$\text{constant} = -l(l+1) \quad (2.5)$$

$$\text{where } l = 0, 1, 2, 3, \dots \quad \text{hyperphysics} \quad (2.6)$$

and since

$$Y(\theta, \phi) = Y(\theta, \phi + 2\pi) \text{ see } \text{hyperphysics} \quad (2.7)$$



the azimuthal ϕ dependence is

$$\propto e^{im_e \phi} \quad (2.8)$$

with

$$m_e = -\ell, -\ell+1, \dots, 0, \dots \ell-1, \ell \quad (2.9)$$

therefore all solutions are labelled by 2 integers, ℓ and m_e which, the same manner as n , are also quantum numbers. They arise from the boundary conditions imposed by Schrödinger quantum mechanics.

There are restrictions on the quantum numbers such that

$$\begin{cases} \ell=0, m_e=0 \end{cases} \quad (2.10)$$

$$\begin{cases} \ell=1, m_e=-1, 0, +1 \end{cases} \quad (2.11)$$

$$\begin{cases} \ell=2, m_e=-2, -1, 0, +1, +2 \end{cases} \quad (2.12)$$

2.3 Eigenfunctions

The solutions $Y_{\ell,m_e}(\theta, \phi)$ are the orthonormal family of functions called the 'spherical harmonics' and the first few are shown in table 2.1a and in figure 2.1. The spherical harmonics determine the angular shape of the wavefunction (more of that later).

And we have that the functions are normalized hence the overlap integral,

$$S = \int \int Y_{\ell,m_e}^* Y_{\ell',m'_e} dV \quad (2.13)$$

$$= \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} Y_{\ell,m_e}^* Y_{\ell',m'_e} \sin \theta d\theta d\phi \quad (2.14)$$

$$= 1 \quad (2.15)$$

and they are orthogonal

$$\text{if } \ell \neq \ell' \quad (2.16)$$

$$\text{or } m_e \neq m'_e \quad (2.17)$$

$$\text{then } S = \int Y_{\ell,m_e}^* Y_{\ell',m'_e} dV \quad (2.18)$$

$$= 0 \quad (2.19)$$

ANALOGY

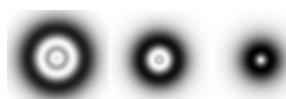
DOT PRODUCT

$$\vec{r} \cdot \vec{j} = 0 \quad (2.17)$$

$$\vec{r} \cdot \vec{e} = 0 \quad (2.18)$$

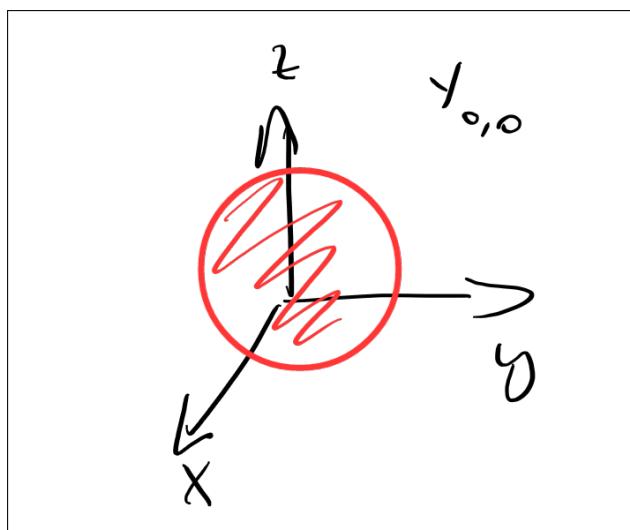
$$\vec{r} \cdot \vec{j} = 1$$

orthonormal basis vectors for 3D space

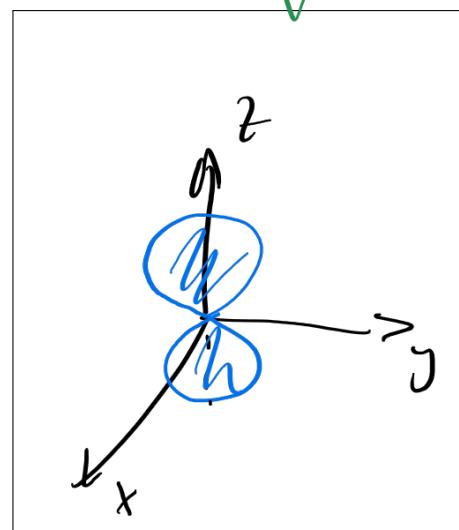


ℓ	m_ℓ	name(s)	Y_{ℓ,m_ℓ} varies as
0	0	S	const
1	0 1, -1	P_z p_x, p_y	$\cos(\theta)$ $e^{\pm i\phi} \sin \theta$
2	0 1, -1 2, -2	d_{z^2} d_{xz}, d_{yz} $d_{xy}, d_{x^2-y^2}$	$3 \cos^2 \theta - 1$ $e^{\pm i\phi} \sin \theta \cos \theta$ $e^{\pm 2i\phi} \sin^2 \theta$

(a) The angular wavefunctions of the first 3 principal quantum numbers.

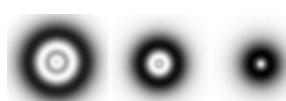


(b) $Y_{0,0} = \text{constant}$: a spherically symmetric orbital



(c) $Y_{1,0} \propto \cos \theta$: note zero probability of finding electron at $x = y = z = 0$ or $\theta = \frac{\pi}{2}$.

Figure 2.1: Spherical harmonics.



Section 3

Radial wavefunction

We now return to the Radial wavefunction. By re-arranging equation (1.21) for $R(r)$ we get

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R - \frac{e^2}{4\pi\epsilon_0 r} R + \frac{\hbar^2 \ell(\ell+1)}{2m r^2} R = E R. \quad (3.1)$$

Another eigenvalue equation! But unfortunately you don't yet know how to solve this directly. So instead let's 'guess' a solution and see if that works.

3.1 Ground state: $\ell = 0$

Let's take the $\ell = 0$ state so that

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R - \frac{e^2}{4\pi\epsilon_0 r} R = E R \quad (3.2)$$

Try solution

$$R(r) = A e^{-r/\alpha} \quad (3.3)$$

and you (you!) can show,

$$-\frac{\hbar^2}{2m} \left(\frac{1}{\alpha^2} - \frac{2}{\alpha r} \right) R - \frac{e^2}{4\pi\epsilon_0 r} R - E R = 0 \quad (3.4)$$

$$R \left[\frac{1}{r} \left(\frac{\hbar^2}{m\alpha} - \frac{e^2}{4\pi\epsilon_0} \right) - \left(\frac{\hbar^2}{2m\alpha^2} + E \right) \right] = 0 \quad (3.5)$$

which must be true for all r , so both brackets must be zero. Therefore the guess $R(r) = A e^{-r/\alpha}$ is a solution of the time independent Schrödinger equation for $\ell = 0$ provided that

$$\frac{\hbar^2}{m\alpha} = \frac{e^2}{4\pi\epsilon_0} \quad (3.6)$$

$$\Rightarrow \alpha = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} \quad (3.7)$$



$$= a_0 \quad (\text{the Bohr radius!}) \quad (3.8)$$

$$\therefore R(r) = \quad (3.9)$$

and

$$E(\ell = 0) = \quad (3.10)$$

$$= -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \quad (3.11)$$

$$= \quad (3.12)$$

So remarkably we have taken a quantum route and derived the same properties for the ground-state orbital that we did using the Bohr model. We can finally write the ground-state wavefunction for a hydrogen atom as

$$\psi_{\text{Ground State}} = \quad (3.13)$$

$$= \quad (3.14)$$

where $Y_{0,0}(\theta, \phi)$ is constant for the state $\ell = 0$ and A is a constant of normalisation. The total probability of finding the electron anywhere must be unity. We can calculate this from the integrated total probability ($\psi^*\psi$) of find the electron at any location in space,

$$S = \quad (3.15)$$

$$= \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} \int_{r=0}^{r=\infty} \psi^*\psi r^2 \sin\theta dr d\theta d\phi \quad (3.16)$$

$$= 4\pi \int_{r=0}^{r=\infty} \psi^*\psi r^2 dr \quad (3.17)$$

$$= \quad (3.18)$$

$$\therefore A = \frac{1}{\sqrt{\pi a_0^3}} \quad (3.19)$$

$$= \quad (3.20)$$

3.2 Radial probability distribution function

For the ground state the probability density is

$$= \quad (3.21)$$

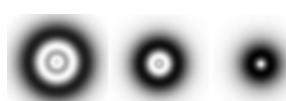


Figure 3.1: Radial dependence of probability density $|\psi|^2$ and of the probability distribution function $P(r)$.

See figure 3.1. This suggests that it is most probable to find the electron at $r = 0$, but this is somewhat misleading. We should consider the probability of finding an electron in a small volume dV , that is, we should consider $|\psi|^2 dV$. We define the radial probability distribution function $P(r)$ as

- $P(r)dr$ is the probability of finding the electron surrounding a hydrogen nucleus between a radius r and $r + dr$ from the nucleus.

The question then is, what is dV ? Well, it's the volume of the shell between r and $r + dr$, see figure 3.2.

Figure 3.2: Volume of a thin shell. [1]

$$dV = \quad (3.22)$$

$$= \text{area of shell} \quad (3.23)$$

$$= \text{thickness of shell} \quad (3.24)$$

$$\therefore P(r)dr = \quad (3.25)$$



Here we swap to R since the $4\pi r^2$ takes care of the angular part. Therefore for the ground state of hydrogen we have

$$P(r)dr = \quad (3.26)$$

as shown in [figure 3.1](#).

- Therefore you are most likely to find an electron at $r = a_0$.
- Therefore, although the wavefunction has a maximum at the origin, since we live in 3D space there is little chance of finding the electron at the nucleus.
- As we get away from the core the probability drops exponentially towards zero, but never quite getting there.
- So there is, it turns out, a small chance of finding the electron that is predominantly bound to one of your hydrogen atoms that is bound to a water molecule inside you, anywhere in the Universe. Odd.

3.3 Full radial solutions: Quantum Numbers (II)

The radial equation

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{e^2}{4\pi\epsilon_0 r} R + \frac{\hbar^2 \ell(\ell+1)}{2m r^2} R = ER. \quad (3.27)$$

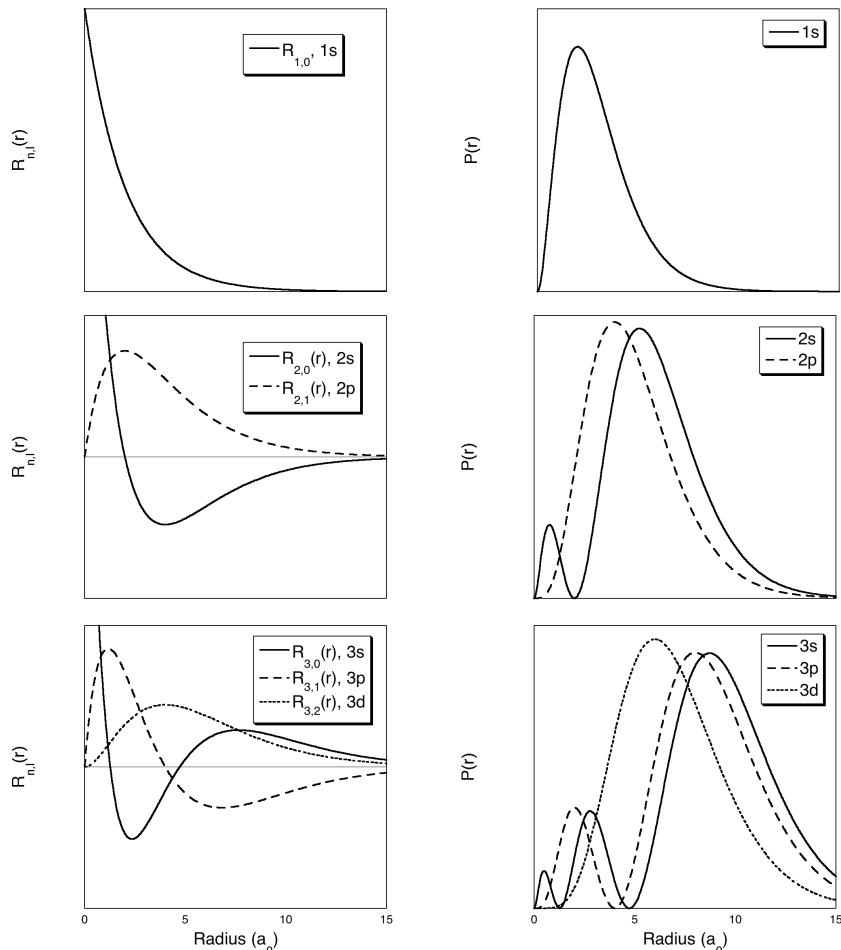
can, in fact, be solved for any value of the quantum number ℓ .

- We find that solutions that stay finite between $r = 0$ and $r = \infty$ can be labelled by an integer (Quantum Number!) n where $n > \ell$.
- Radial states can therefore be labelled by $R_{n,\ell}(r)$.
- [Table 3.3a](#) presents the radial parts of the first 3 principle quantum number states
- [figure 3.3b](#) shows plots of these radial wavefunctions.
 - ⇒ Wavefunction have
 - ⇒ $P(r)$ plots show that, for a given ℓ an electron is found further from the nucleus as n increases
 - ⇒ $P(r)dr$ plots show that for a given n an electron is more likely to be found near the nucleus for small ℓ , c.f., $2s$ and $2p$



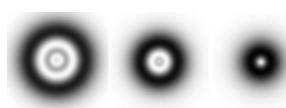
n	ℓ	name	$R_{n,\ell}$ varies as
			$e^{-\frac{r}{a_0}}$
			$\left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$ $\left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$
			$\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-\frac{r}{3a_0}}$ $\left(6\frac{r}{a_0} - \frac{r^2}{a_0^2}\right) e^{-\frac{r}{3a_0}}$ $\left(\frac{r^2}{a_0^2}\right) e^{-\frac{r}{3a_0}}$

(a) The radial wavefunctions of the first 3 principal quantum numbers.



(b) Radial wavefunction as per table 3.3a and radial probability distributions. Note the energy for 1s = -13.6 eV, for 2s and 2p the same energy of -3.4 eV, and 3s, 3p and 3d at -1.5 eV. The energy operator has no dependence on the angular momentum.

Figure 3.3: Hydrogen states.



Section 4

Full solution: Angular + Radial

4.1 Quantum Numbers (III)

As we saw the angular part has solution of the form $Y_{\ell,m_\ell}(\theta, \phi)$ and for the radial part we have $R_{n,\ell}(r)$. So all full solutions of the Schrödinger equation are defined by three quantum numbers:

- n : principal quantum number
- ℓ : orbital angular quantum number
- m_ℓ : orbital magnetic quantum number

giving

$$= \quad (4.1)$$

and you may know each orbital angular momentum number has its own special name

$$\ell = 0 : \text{-orbital} \quad (4.2)$$

$$\ell = 1 : \text{-orbital} \quad (4.3)$$

$$\ell = 2 : \text{-orbital} \quad (4.4)$$

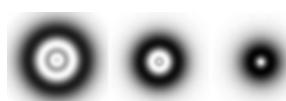
$$\ell = 3 : \text{-orbital} \quad (4.5)$$

4.2 Another Quantum number: Pauli exclusion and a bit of spin

Pauli says that

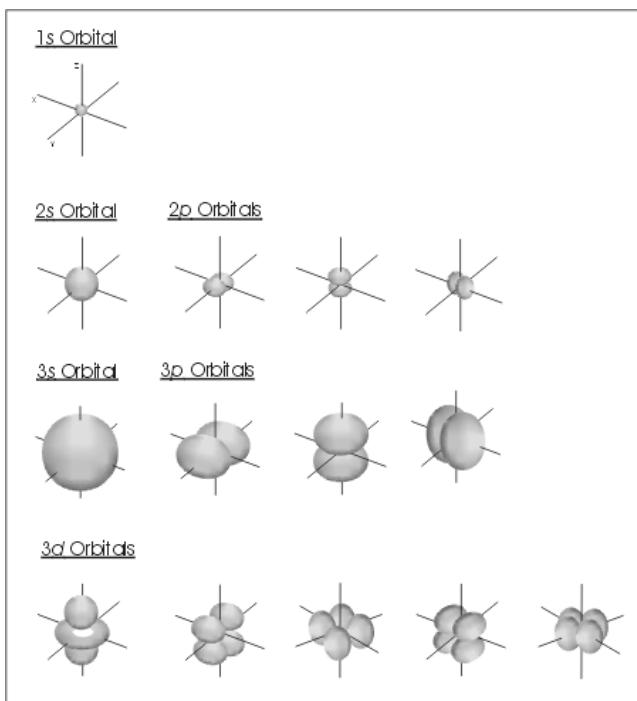
- No two electrons of the same atom can have the same quantum numbers.

There is another degree of freedom for an electron, spin. This is another quantum number but can take only two values, crudely, spin-up or spin-down. Hence each state defined by n, ℓ and m_ℓ can have two electrons, one spin up and spin down.

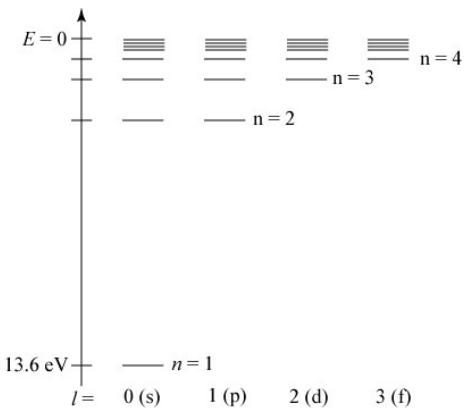


n	ℓ	m_ℓ	Orbital name(s)	energy (eV)	states	electrons
			1s			
			2s 2p _y , 2p _z , 2p _x			
			3s 3p _y , 3p _z , 3p _x 3d _{x²-y²} , 3d _{yz} , 3d _{z²} , 3d _{xz} , 3d _{xy}			

(a) The orbitals and energies of the first 3 principal quantum numbers.



(b) Probability plots of an s -orbital ($\ell = 0$), the three p -orbitals ($\ell = 1$), and the five d -orbitals ($\ell = 2$).



(c) Energy level diagram for a hydrogen atom.

Figure 4.1: Hydrogenic Quantum States [2].

4.3 Hydrogen quantum states.

We can construct table 4.1a and the spatial probability plots of figure 4.1b.



Section 5

Self-Study: Energy and atomic spectra

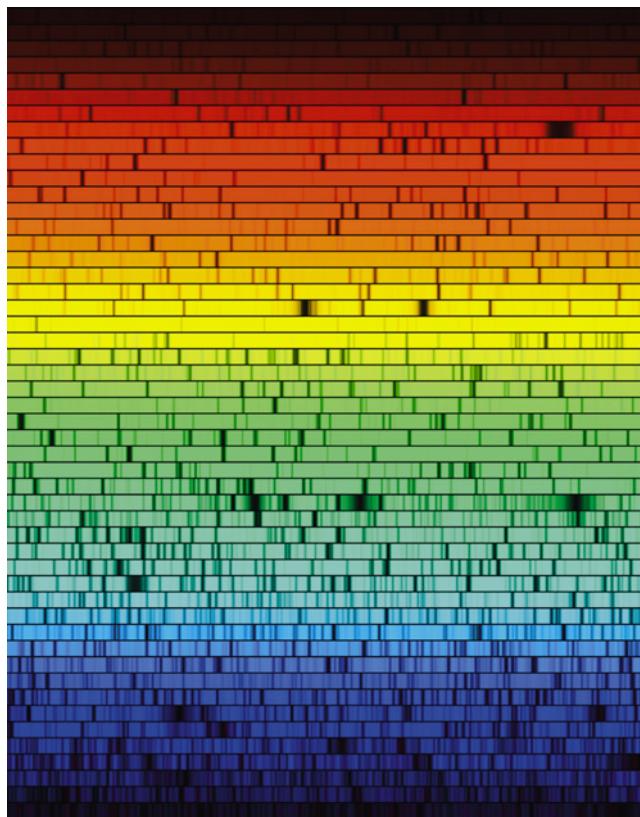
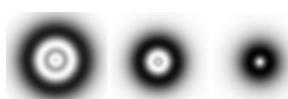


Figure 5.1: A solar absorption spectrum with many missing lines, where light has been absorbed by elements undergoing optical excitation [3].

- How do we measure the energy of the electronic states? By spectroscopy.
- Emission spectra arise from electrons excited into higher energy levels that then relax back into lower energy state emitting a photon with a precise energy.
- Excitation can occur thought thermal excitation (as in stars), collisions with electrons and ions in a discharge tube (e.g., a sodium lamp) or through optical excitation or collision with an excited atom.



- Absorption spectra arise from the absorption of light with a precise energy, promoting an electron from one energy state to a higher energy state,

5.1 Energy eigenvalues

If you work it out (don't bother, long and tedious), the energy of the n th state is given by

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2n^2} \quad (5.1)$$

$$= -\frac{13.6}{n^2} \text{ eV} \quad (5.2)$$

exactly as for the Bohr model. The [figure 5.2] shows the energy levels.

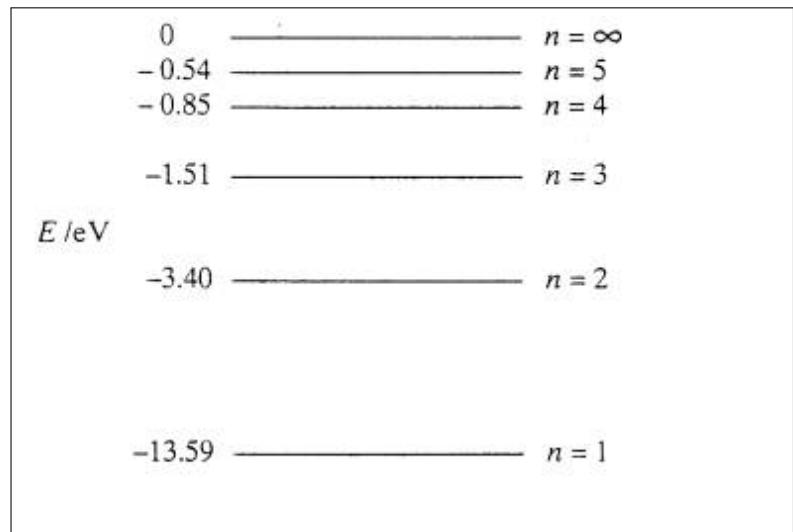


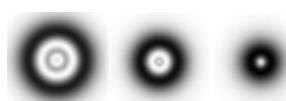
Figure 5.2: Energy level diagram of a hydrogen atom [4].

- The energies are negative, they are bound states
- The ground state, the lowest energy state, has $n = 1$
- States with $n = 2, 3, 4, \dots$ are excited states
- Zero energy corresponds to $n = \infty$
- Higher energies are unbound and form a continuum of allowed energies: no quantisation.
- An energy of +13.6 eV is required to excite an electron from the ground 1s state to infinity (escape!). This is called the ionization energy.

5.1.1 Other 1-electron atoms: Hydrogenic atoms

The results for hydrogen atoms can be extended to other 1-electron atoms. That is atoms that have lost all but 1 of their electrons, e.g., He^+ , Li^{2+} , ..., and so the Coulomb potential becomes

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad (5.3)$$



where Z is the atomic number and so

$$E_n = -\frac{Z^2 \times 13.6}{n^2} \text{ eV} \quad (5.4)$$

if we write as before for the 1s orbital

$$R(r) \propto Ae^{-\frac{r}{\alpha}} \quad (5.5)$$

then

$$\alpha = \frac{a_0}{Z} \quad (5.6)$$

Smaller orbitals, so more closely held and lower (more bound) energies.

5.1.2 Energies of lines.

What we measure experimentally is spectral lines, the emission or absorption of light at particular frequencies or energies. Their presence, or absence are related to the energy difference $|\Delta E_{i \rightarrow f}|$ between two states in hydrogen. The and initial state i and a final state f (more about this in section 5):

$$|\Delta E_{i \rightarrow f}| = |E_{n_i} - E_{n_f}| \quad (5.7)$$

$$= 13.6 \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right| \text{ eV} \quad (5.8)$$

If the final state is $n = 2$ then these transitions form part of the 'Balmer' series as shown in figure 5.3 which are transition with light in the visible spectrum.

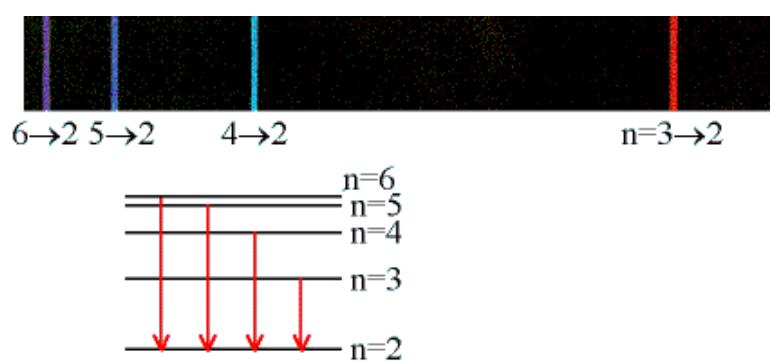


Figure 5.3: Balmer series adsorption spectrum and schematic of energy levels and transitions [5].

————— n=1 (Ground State)



5.1.3 Selection rules

For spectral lines there are selection rules that determine whether a transition from one state to another, is allowed (a strong line) or forbidden (a weak line).

- Here we just wrote down (see text books for more info if you wish):
- There is no restriction on Δn .
- Allowed transitions are

$$\Delta \ell = -1, \text{ or } +1 \quad (5.9)$$

$$\Delta j = -1, \text{ or } 0, \text{ or } +1 \quad (5.10)$$

but not from $j = 0 \rightarrow j = 0$.

$$\Delta m_j = -1, \text{ or } 0, \text{ or } +1 \quad (5.11)$$

- Learn these selection rules.

Note j is the total angular momentum quantum number. We'll discuss it later, but have to include it here for completeness (sorry).

5.2 Width of spectral lines

So far we have assumed that energy levels are perfectly well defined, leading to perfectly sharp spectral lines. In practice there are 3 factors that broaden spectral lines in energy (or in wavelength, or frequency if you prefer).

- The Heisenberg uncertainty principle can be rewritten as:

$$\Delta t \Delta E \sim \hbar \quad (5.12)$$

Consider a array of N_0 atoms in an excited state (not the ground state). There is a probability per unit time k of each one relaxing back to the ground state. Why? We'll see below. We can write at

$$t = 0 \quad (5.13)$$

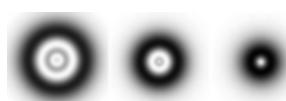
$$N = N_0 \quad (5.14)$$

where N is the number of excited atoms at time t , then the change in N , written as ΔN , between time t and $t + \Delta t$

$$\Delta N = -k \cdot \Delta t \cdot N \quad (5.15)$$

where k is the probability per unit time of an atom decaying back to its ground state. In the limit we can write

$$\frac{dN}{N} = -k dt \quad (5.16)$$



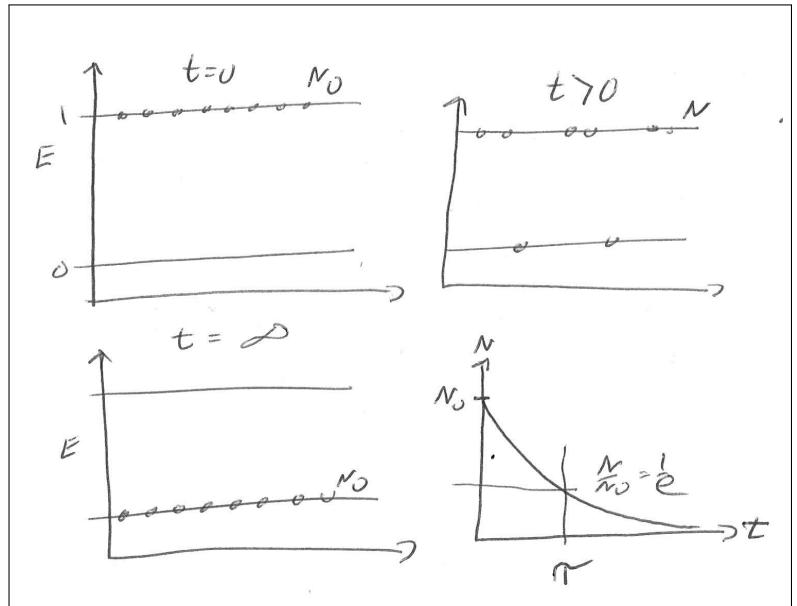


Figure 5.4: Excited state population.

solve this differential equation

$$\ln N = -kt + C \quad (5.17)$$

with the initial conditions $N(t = 0) = N_0$

$$\frac{N}{N_0} = e^{-t/\tau} \quad (5.18)$$

where τ is the lifetime of the excited state

$$1/k = \tau \quad (5.19)$$

this is nothing more than the probability of an atom that was initially excited still being in the excited state after time t

$$P(t) = \frac{1}{\tau} e^{-t/\tau} \quad (5.20)$$

When does the atom decay? The mean value of this exponential probability distribution

$$\langle t \rangle = \int_0^\infty t \frac{1}{\tau} e^{-t/\tau} dt = \tau \quad (5.21)$$

and the uncertainty? We can now compute the standard deviation

$$\sigma = \sqrt{\int_0^\infty (t - \tau)^2 \frac{1}{\tau} e^{-t/\tau} dt} = \tau \quad (5.22)$$

so the atom decays in a time $\tau \pm \tau$ and hence we have an uncertainty in the decay time and an uncertainty in the energy.

$$\Delta E \times \Delta t \sim \hbar \quad (5.23)$$

$$\therefore \Delta E \sim \frac{\hbar}{\tau} \quad (5.24)$$

Long lifetimes, narrow lines, short lifetime, wide lines. Note also, that because each decay is an independent event with a mean time of τ the decay process is in fact a homogeneous Poisson process.



5.2.1 Natural or lifetime broadening

This is the most fundamental mechanism and derives from the uncertainty principle that links the uncertainty in energy ΔE_N (N for natural broadening) with the uncertainty in time Δt ,

$$\Delta E_N \Delta t \sim \hbar. \quad (5.25)$$

- A perfectly defined energy level for which $\Delta E = 0$ must have an infinite lifetime.
- This may be true of the ground state, but not the excited states where given time they relax back to the ground state, hence $\Delta t < \infty$ and so $\Delta E > 0$.
 - ⇒ Why does it relax?
 - ⇒ Space is frothing with particle-antiparticle pairs. It costs $\Delta E = mc^2$ to create them, which is OK so long as they live for a short $\Delta E \Delta t \sim \hbar$ time, but in that time they can perturb our excited state and knock it back to the ground state.
- Natural broadening shows up when we examine the width of the spectra line associated with a particular transition.

Say we have a transition between some initial to final state with lifetimes of τ_i and τ_f then the broadening of each state is

$$\Delta E_i \sim \frac{\hbar}{\tau_i} \quad (5.26)$$

$$\Delta E_f \sim \frac{\hbar}{\tau_f}. \quad (5.27)$$

Therefore the total broadening for a transition between the two, as shown in figure 5.5 becomes

$$\Delta E_{i \rightarrow f} \sim \Delta E_i + \Delta E_f \quad (5.28)$$

$$\Delta E_{i \rightarrow f} \sim \hbar \left(\frac{1}{\tau_i} + \frac{1}{\tau_f} \right). \quad (5.29)$$

For a transition between the 2p and the 1s state of a Hydrogen atoms

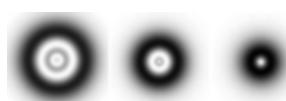
$$\tau_{2p} = 1.6 \times 10^{-9} \text{ s} = 1.6 \text{ ns} \quad (5.30)$$

$$\tau_{1s} = \infty \quad (5.31)$$

$$\therefore \Delta E_{2p \rightarrow 1s} = 0.4 \times 10^{-6} \text{ eV} \quad (5.32)$$

and we know from section 5.1.2 that $E_{2 \rightarrow 1} = 10.2 \text{ eV}$ therefore we have

$$E_{2 \rightarrow 1} = 10.2 \text{ eV} \pm 0.4 \mu\text{eV} \quad (5.33)$$



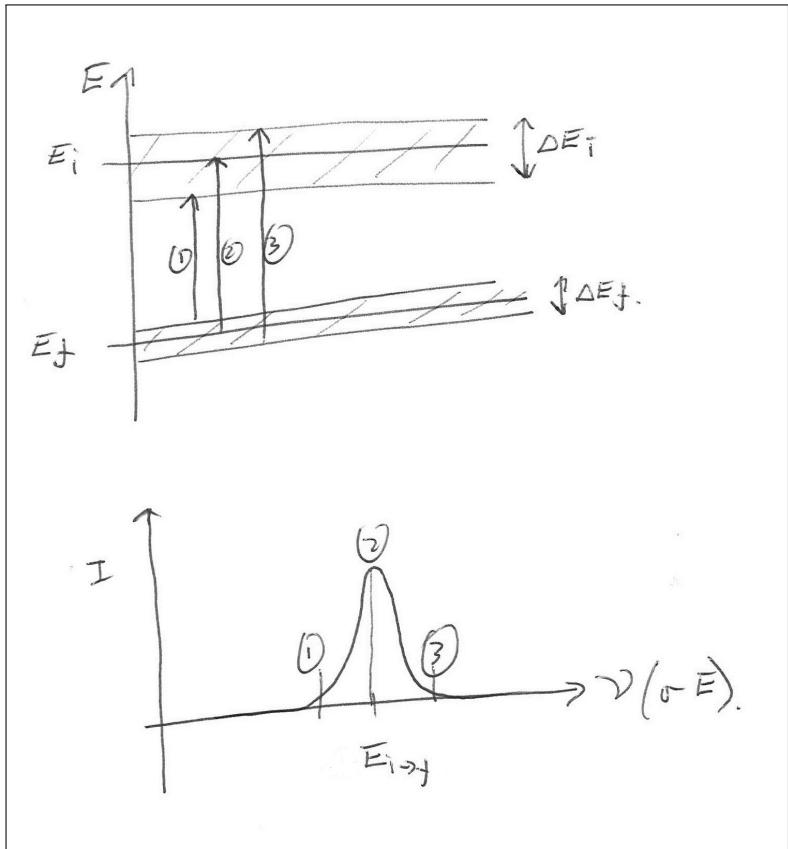


Figure 5.5: Transitions and line-widths

5.2.2 Pressure or collision broadening

The time between collisions of gas atoms can be shorter than the natural lifetime. This can cause premature relaxation and emission of a photon. This reduces the lifetime and hence increases the uncertainty ΔE_C in the energy.

$$\Delta E_C \sim \frac{\hbar}{\tau_C}. \quad (5.34)$$

At higher pressures the time τ_C between collision will be shorter than at lower pressures.

5.2.3 Doppler broadening

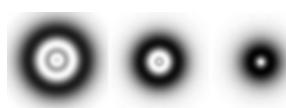
Atoms of mass M in thermal equilibrium have a Maxwell-Boltzmann velocity distribution

$$P(v) \propto \exp\left(-\frac{Mv^2}{2k_B T}\right). \quad (5.35)$$

If a transition of an atom that is stationary with respect to a photo detector has frequency f_0 then atoms travelling towards (+) and away from (-) a detector with a velocity v will have an apparent Doppler modified emission frequency resulting in an uncertainty in the energy of

$$\Delta E_D = \frac{2hf_0}{c} \sqrt{\frac{2k_B T \ln 2}{M}}. \quad (5.36)$$

For the $2p \rightarrow 1s$ transition in Hydrogen we get that at 300 K $\Delta E_D = 125 \mu\text{eV}$. So we see that Doppler broadening is usually dominant, but can be controlled by lowering the temperature of the gas of atoms.



Section 6

Problems for part A

P1: Bohr's Theory [comprehension, easy]

In Bohr's theory, the energy levels of the electron in hydrogen are discrete and correspond to orbits of different radius. Which of the following statements is/are correct?

- (a) To make a transition from a state of small radius to one of the next larger radius, a photon of exactly corresponding energy difference must be absorbed.
- (b) When an electron loses energy in making a transition from one state to another, energy is conserved by several photons being emitted.
- (c) When a photon whose energy is greater than the energy difference between the lowest two states in energy is incident upon the hydrogen atom, a transition is made, and the energy is conserved by emitting a photon of lower energy.
- (d) Although the energy of the electron is constant in the orbit of smallest radius ($n = 1$), it is not constant in states of larger orbital radius such as $n = 2$ or $n = 3$.

P2: Separate variables [application, medium]

Since we can write

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

show that

$$\begin{aligned} -\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} (V(r) - E) &= \text{constant} \\ &= \frac{1}{Y} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right) \end{aligned}$$



P3: Spherical harmonics [application, medium]

Show that the following normalised spherical harmonics $Y_{\ell,m_\ell}(\theta, \phi)$

$$(a) Y_{0,0} = \sqrt{\frac{1}{4\pi}}$$

$$(b) Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$(c) Y_{1,1} = \sqrt{\frac{3}{8\pi}} \sin \theta \exp(i\phi)$$

$$(d) Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin \theta \exp(-i\phi)$$

satisfy the equation

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} = -\ell(\ell+1)Y(\theta, \phi)$$

with the relevant value of ℓ .

P4: Overlap (or not) [synthesis, hard]

Complete the following grid for the overlap S between two normalized angular wavefunctions,

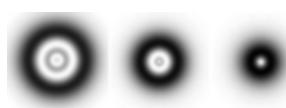
$$S = \int_0^{2\pi} \int_0^\pi Y_{\ell,m_\ell}^* Y_{\ell',m'_\ell} \sin \theta d\theta d\phi$$

where Y_{ℓ,m_ℓ}^* is the complex conjugate. You should not need to undertake any major mathematics.

	$\ell = 0, m_\ell = 0$	$\ell = 1, m_\ell = 0$	$\ell = 1, m_\ell = -1$	$\ell = 1, m_\ell = 1$
$\ell' = 0, m'_\ell = 0$				
$\ell' = 1, m'_\ell = 0$				
$\ell' = 1, m'_\ell = -1$				
$\ell' = 1, m'_\ell = 1$				

P5: Quantization [analysis, medium]

If quantum states of the hydrogen atom have a ϕ dependence of the form $\exp(i\alpha\phi)$ where α is a constant, explain why α must be an integer (i.e., the quantum number m_ℓ).



P6: Radial wavefunction [application, medium]

Given,

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{e^2}{4\pi\epsilon_0 r} R = ER.$$

show that the solution

$$R(r) = Ae^{-\frac{r}{\alpha}}$$

gives

$$R \left[\frac{1}{r} \left(\frac{\hbar^2}{m\alpha} - \frac{e^2}{4\pi\epsilon_0} \right) - \left(\frac{\hbar^2}{2ma^2} + E \right) \right] = 0$$

P7: Is it a solution? What's its energy? [application, medium]

Show that the radial function of the 2p state of the hydrogen atom $R_{2,1}(r) = r \exp(-r/2a_0)$ obeys the radial equation with the relevant value of ℓ and find the associated energy E .

P8: Maximum Probabilitus [analysis, medium]

Show that for the 1s state of hydrogen, the radial probability distribution function $P(r)$ has its maximum at $r = a_0$. Where is the radial maximum for the 2p state?

P9: Exponential lifetime [application, hard]

- (a) Show that the mean value of the exponential distribution

$$\langle t \rangle = \int_0^\infty t \frac{1}{\tau} e^{-t/\tau} dt$$

is τ .

[3]

- (b) Evaluate the integral

$$\sigma = \sqrt{\int_0^\infty (t - \tau)^2 \frac{1}{\tau} e^{-t/\tau} dt}$$

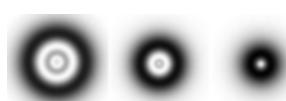
to confirm that the standard deviation of an exponential distribution is τ .

[5]

P10: Line widths [knowledge, easy]

Briefly describe two processes that can broaden the width of spectral lines and what steps, if any, could be taken to minimise them.

[3]



P11: Collision broadening [evaluation, medium]

The time between collisions of gas atoms can be shorter than the natural lifetime. This can cause premature relaxation and emission of a photon. By assuming an ideal gas and considering the volume swept out by a particle as it moves, show that the time between collision τ_C is typically,

$$\tau_C = \frac{1}{\pi d^2 n_v} \sqrt{\frac{m}{3kT}}$$

where d is the diameter of the gas particle, n_v the number of gas particles per unit volume, m the particles mass, k Boltzmann's constant and T the absolute temperature of the gas. So that the uncertainty ΔE_C caused by pressure broadening is

$$\Delta E_C \sim \frac{\hbar}{\tau_C}.$$

P12: Symmetric? [analysis, medium]

An emission spectrum for hydrogen can be obtained by analyzing the light from hydrogen gas that has been heated to very high temperatures (the heating populates many of the excited states of hydrogen). An absorption spectrum can be obtained by passing light from a broadband incandescent source through hydrogen gas. If the absorption spectrum is obtained at room temperature, when all atoms are in the ground state, the absorption spectrum will

- (a) be identical to the emission spectrum.
- (b) contain some, but not all, of the lines appearing in the emission spectrum.
- (c) contain all the lines seen in the emission spectrum, plus additional lines.
- (d) look nothing like the emission spectrum.



Part B: Angular momentum

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Section 7

Quantised orbital angular momentum

Earlier in the course you saw how observable quantities, e.g., momentum and kinetic energy are associated with operations on wavefunctions. The Bohr model (see 1st year) assumes angular momentum comes in integer units of \hbar , that is, $L = n\hbar$.

7.1 Why is angular momentum so important?

It allows us to understand the spin of electrons and the connection between orbital and spin angular momentum. It allows us to understand the magnetic properties of atoms.

7.2 Classical angular momentum

Figure 7.1: Classical angular momentum.

Angular momentum \vec{L} is defined as

$$\vec{L} = \quad (7.1)$$

$$= \quad (7.2)$$

as depicted in figure 7.1. It has units Js. For circular motion about an origin in the x, y plane we have

$$\vec{L} = \quad (7.3)$$



where m is the mass of the orbiting particle, v is its speed and r is the radius of orbit. In classical mechanics a twisting force, a torque $\vec{\Gamma}$, causes a change of angular momentum

$$\vec{\Gamma} = \quad (7.4)$$

$$= \quad (7.5)$$

$$= \quad (7.6)$$

So, if a torque is zero (as we would expect for a H-atom) the angular momentum is constant in time.

7.3 Orbital angular momentum

In a similar way we can find operators that correspond to angular momentum, its total magnitude and its z -component.

- Angular momentum

$$\Rightarrow \text{Classical: } \vec{L} = \vec{r} \times \vec{p}$$

\Rightarrow Quantum:

- Radial position

$$\Rightarrow \text{Classical: } \vec{r}$$

\Rightarrow Quantum:

- Linear momentum

$$\Rightarrow \text{Classical } \vec{p} = m \times \vec{v}$$

\Rightarrow Quantum:

7.3.1 Magnitude of orbital angular momentum: L^2

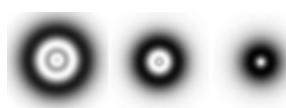
In spherical polar coordinates we have an operator (see Rae 5.2 for derivation) for the square of the total angular momentum.

$$= -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad (7.7)$$

$$= \quad (7.8)$$

From the previous analysis (Section 2) of the H-atom we now know that

$$\underbrace{-\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)}_{Y_{\ell,m_\ell}(\theta, \phi)} = \underbrace{\hbar^2 \ell (\ell + 1)}_{Y_{\ell,m_\ell}(\theta, \phi)} \underbrace{Y_{\ell,m_\ell}(\theta, \phi)}_{(7.9)}$$



$$= \quad (7.10)$$

Hence the *magnitude* of the angular momentum has discrete values of

$$|L| = \quad (7.11)$$

$$= \quad (7.12)$$

so angular momentum is quantised (as Bohr assumed). Note due to the linearity of the operators and the radial wavefunction independence on angle we can write

$$= \quad (7.13)$$

$$= \quad (7.14)$$

$$= \quad (7.15)$$

$$= \quad (7.16)$$

We can act on Y or ψ to get the eigenvalue L^2 .

7.3.2 z -component of orbital angular momentum: L_z

The projection of the angular momentum vector onto the z -axis is given by,

$$\underbrace{-i\hbar \frac{\partial}{\partial \phi}}_{\text{operator}} \underbrace{Y_{\ell,m_\ell}(\theta, \phi)}_{\text{wavefunction}} = \underbrace{m_\ell \hbar}_{\text{eigenvalue}} \underbrace{Y_{\ell,m_\ell}(\theta, \phi)}_{\text{wavefunction}} \quad (7.17)$$

$$\widehat{L}_z Y = L_z Y \quad (7.18)$$

which follows from the ϕ dependence of the angular wavefunction $Y_{\ell,m_\ell}(\theta, \phi)$ always having the form $e^{im_\ell \phi}$ and so the z component has discrete values

$$-i\hbar \frac{\partial}{\partial \phi} e^{im_\ell \phi} = \quad (7.19)$$

$$= \quad (7.20)$$

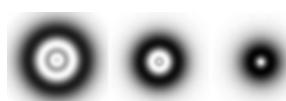
$$L_z = \quad (7.21)$$

$$m_\ell = \quad (7.22)$$

and in similar analysis to the the total we have

$$\widehat{L}_z \psi = L_z \psi \quad (7.23)$$

$$\widehat{L}_z Y R = L_z Y R \quad (7.24)$$



$$\widehat{RL_z}Y = RL_zY \quad (7.25)$$

$$\widehat{L_z}Y = L_zY \quad (7.26)$$

7.3.3 Whither quantization

This quantisation of angular momentum drops out of the analysis because of the boundary conditions, it is not assumed as it was for the case of the Bohr model.

7.4 ‘Semi-classical’ vector model for orbital angular momentum

Figure 7.2: Vector model for angular momentum for $\ell = 1$.

Consider the case $\ell = 1$

$$|L| = \quad (7.27)$$

$$= \quad (7.28)$$

and there are three possible value of L projected onto the z -axis, that is L_z , because there are three m_ℓ quantum numbers

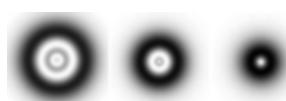
$$m_\ell = \quad (7.29)$$

$$L_z = \quad (7.30)$$

- Hence there are three possible angular momentum vectors.
- We can represent angular momentum \vec{L} as a vector somewhere on the surface of a cone about the z -axis as shown in figure 7.2.

7.4.1 What's so special about the z -axis?

- Nothing!



- The lab frame x , y and z are all identical given the spherical symmetry of atoms,
- When we make a measurement then we define an axis and we usually for convenience label it z . The maths is nicer.
- Or if an \vec{E} or \vec{B} field applied then the symmetry is broken and there are well defined atomic axes.

7.4.2 L_x and L_y : Fundamental Quantum Mechanics

Can I now measure the angular momentum along x and y ?

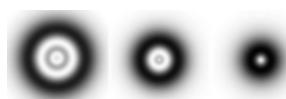
- In the semi-classical picture we drew cones, not single vectors: why?
 - ⇒ The projection onto the x or y axis can take any allowed value of L_x or L_y .
 - ⇒ Why not pick a single momentum vector of well defined L_z , L_y and L_x ?
 - ⇒ Answer: Fundamental Quantum Mechanics!
- A version of the Heisenberg uncertainty principle says that we cannot measure L_x , L_y and L_z simultaneously.
- We can measure any one, but only one, of these components alongside L^2 .
- If we do measure along x then we then know (nearly) nothing about z , see figure 7.3

Figure 7.3: Semi classical vector model of a x measurement

$$\widehat{L^2}\psi_{\ell,m_\ell} \Rightarrow L^2\psi_{\ell,m_\ell}. \quad (7.31)$$

No change in the wavefunction as it's an eigenfunction of the operator. Now measure another,

$$\widehat{L_z}\psi_{\ell,m_\ell} \Rightarrow L_z\psi_{\ell,m_\ell}. \quad (7.32)$$



Again, no change in the wavefunction as it's an eigenfunction of the operator. Now measure another

$$\widehat{L}_x \psi_{\ell, m_\ell} \neq L_x \psi_{\ell, m_\ell}. \quad (7.33)$$

ψ_{ℓ, m_ℓ} is not an eigenfunction of the \widehat{L}_x operator so cannot return exactly the same state. It must change it into an eigenstate of the \widehat{L}_x operator

$$(7.34)$$

- This is a fundamental property of Quantum Mechanics.
 - ⇒ It is not always possible to make measurements of all aspects of a system.
 - ⇒ As we'll see more in section 10, making a measurement of one property totally ruins (right royally **** up) any knowledge about another property.
 - ⇒ For example $\Delta x \Delta p \geq \hbar$.
 - * An accurate measurement of position ($\Delta x = 0$) of a particle means that the uncertainty in momentum is infinite. That position measurement ruins any knowledge we may have had about momentum.
 - * Or vice versa.
- A police man pulls an electron over and asks "Did you know you were travelling at 60 mph?", "Gee thanks" says the electron sarcastically "now I'm lost".



Section 8

Spin angular momentum

8.1 Defining spin

Quantum theory based on the Schrödinger equation cannot explain a number of experimental observations

- the effect of magnetic field on spectral lines - the Zeeman effect (see section 17.1).
- the existence of fine-structure in atomic spectra, e.g., the yellow emission lines from Sodium has 2 components, see figure 21.2.
- the deflection of electron beams by magnetic fields (see section 17.2).

Why?

- Electrons have an intrinsic angular momentum called spin.
- Spin arises naturally in quantum theory that includes special relativity (the Dirac equation - year 4 QM).
- It is not a function of spatial coordinates, it is a purely quantum effect.

Here we just write down its properties, in section 11 we'll take a more indepth look at spin.

8.1.1 Spin quantum number

Electron spin has a quantum number s (analogous to ℓ) but has only one value

$$s = \quad (8.1)$$

- It is a spin 1/2 particle, a Fermion.
- It has a spin angular momentum vector \vec{S} such that

$$|S| = \quad (8.2)$$



$$= \quad (8.3)$$

and in a similar fashion to m_ℓ we have the magnetic spin quantum number m_s with

$$m_s = \quad (8.4)$$

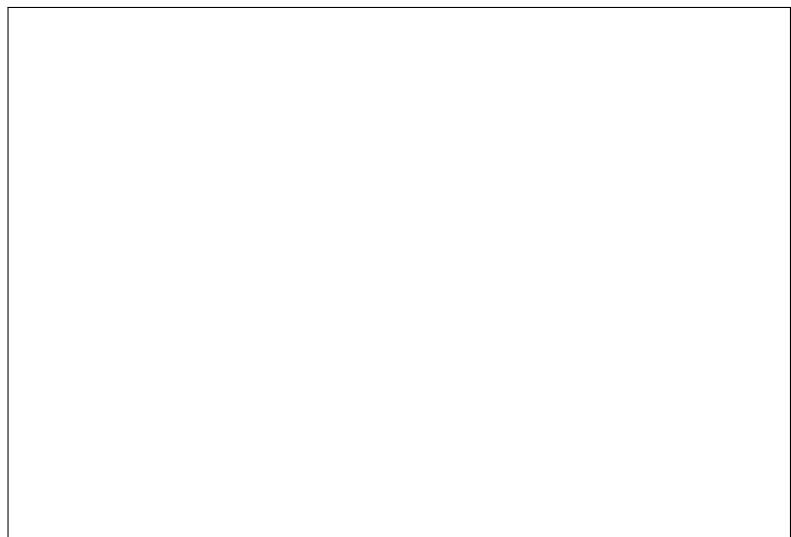
with magnitude

$$S_z = \quad (8.5)$$

which are mostly referred to as spin up and spin down states.

8.1.2 Semi-classical spin

Figure 8.1: Vector model of spin angular momentum.



We can draw a vector model for spin as in figure 8.1. Note we draw cones so know (nearly) nothing about the spin the x or y directions.

8.2 Quantum Numbers (IV)

We now have a hydrogen atom where we can use the following quantum numbers to describe the state of that atom.

- n : principle quantum number
- ℓ : orbital quantum number
- m_ℓ : magnetic orbital quantum number
- s : spin quantum number
- m_s : magnetic spin quantum number



Therefore we should write,

$$\psi = \quad (8.6)$$

We'll produce a neater form for this later.

8.2.1 Uncoupled quantum numbers

Table 8.1 presents the first few uncoupled quantum states of a hydrogen atom. Here we assume no connection between spin and orbital angular momentum (in section 15 we'll see what happens when they are coupled).

n	ℓ	m_ℓ	s	m_s	name	spin
1	0	0	1/2	1/2	1s	↑
	0	0	1/2	-1/2	1s	↓
2	0	0	1/2	1/2	2s	↑
	0	0	1/2	-1/2	2s	↓
2	1	0	1/2	1/2	2p _z	↑
	1	0	1/2	-1/2	2p _z	↓
	1	1	1/2	1/2	2p _x	↑
	1	1	1/2	-1/2	2p _x	↓
	1	-1	1/2	1/2	2p _y	↑
	1	-1	1/2	-1/2	2p _y	↓

Table 8.1: First 10 uncoupled quantum states of the hydrogen atom.

8.2.2 Degeneracy and the Pauli principle

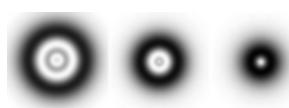
- Two or more quantum states are defined as being degenerate if they have the same energy.
- For a hydrogen atom, states with the same principal n value, but different ℓ , m_ℓ or m_s values all have the same energy and so are degenerate.
- The number of states with the same energy is called the degree of degeneracy g of that level.
- The Pauli exclusion principle states that
 - ⇒ no two electrons (in an atom) can have the same set of quantum numbers.
- g therefore determines the maximum number of electrons in any given n energy level.
- From this we get the shell structure of many-electron atoms.



- For an H atom the degeneracy of the n^{th} level is

$$g_n = \dots \quad (8.7)$$

- $g_{n=1} = \dots$, $g_{n=2} = \dots$, $g_{n=3} = \dots$



Section 9

Revisited notation: Dirac notation

This section closely follows chapter 18 of the book ‘Physics, A student Companion’ by Lowry A. Kirkby. This is a re-stating of the Dirac work from the 1st half of this course. Please read this and the following section.

9.1 Quantum numbers

- We are now in a position to write down a hydrogen wavefunction, just in terms of its quantum numbers.
- $\psi = \psi_{n,\ell,m_\ell,s,m_s}$
- Consider each component of the wavefunction (i.e., quantum number).
- From the quantum numbers we can workout the mathematical form of the wavefunction.
- Really all we need is some rules and the quantum numbers and we can do away with lots of maths.

9.2 Dirac notion

We write the wavefunction as a column vector, and so give it the new notation $|\psi\rangle$

$$= \quad (9.1)$$

where the individual elements are the amplitudes (or weights) of each component represented by that element.



9.2.1 ket: Example

Say we are only interested in the orbital angular part of the wavefunction, and $\ell = 1$, $m_\ell = -1$, then we have

$$\psi = \quad (9.2a)$$

$$= (Y_{0,0}, Y_{1,1}, Y_{1,0}, Y_{1,-1}, Y_{2,2}, Y_{2,1}, \dots) \times \quad (9.2b)$$

Therefore we now can write

$$= \quad (9.2c)$$

which we succinctly write as

$$|\psi\rangle = |\ell, m_\ell\rangle \quad (9.2d)$$

$$|\psi\rangle = \quad (9.2e)$$

We call this a ket.

9.2.2 bra and inner product

we define the bra, $\langle\psi|$

$$= \quad (9.3a)$$

the transpose and complex conjugate of the ket. And we define the inner (dot) product as

$$= \quad (9.3b)$$

Which is the overlap of the two wavefunctions. For our example since the function Y is orthonormal the product

$$\langle 1, -1 | 1, -1 \rangle = \quad (9.3c)$$

$$= \quad (9.3d)$$

and more than that for any other angular wavefunction

$$= \quad (9.3e)$$



9.2.3 Operators

Any operator transforms a ket into another ket. If the ket represents an eigenvector (i.e., an eigenfunction) of the operator then we get the original ket back.

For our example,

$$\widehat{L^2} Y_{1,-1} = \quad (9.4a)$$

$$\widehat{L^2} Y_{1,-1} = \quad (9.4b)$$

$$\widehat{L^2} |\ell = 1\rangle = \quad (9.4c)$$

therefore we can write

$$= \quad (9.4d)$$

We can write similar relationships for the other operators we have used so far. The Schrödinger equation

$$\widehat{H} \psi_n = E_n \psi_n \quad (9.4e)$$

becomes in Dirac notation

$$= \quad (9.4f)$$

$$\widehat{H} |n\rangle = -\frac{me^4}{32\pi\epsilon_0^2\hbar^2 n^2} |n\rangle \quad (9.4g)$$

For the z -component of orbital angular momentum we have

$$= \quad (9.4h)$$

For the total spin we have

$$= \quad (9.4i)$$

which for a 1e system, $s = 1/2$ therefore

$$\widehat{S^2} |s\rangle = \quad (9.4j)$$

Finally for the z -component of the spin we have

$$= \quad (9.4k)$$

9.2.4 Expectation values

If we wanted to know the mean position of say the radial coordinate of an electron we'd compute

$$\langle r \rangle = \quad (9.5a)$$



where the central r is the ‘operator’. What is, in our example, the expectation value of the orbital angular momentum?

$$\langle L^2 \rangle = \quad (9.5b)$$

$$= \quad (9.5c)$$

compute the right hand side bit, $\widehat{L^2} |\ell\rangle = L^2 |\ell\rangle$,

$$= \quad (9.5d)$$

now L^2 is just a number and we can pull it out

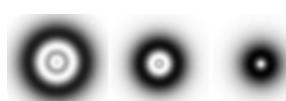
$$= \quad (9.5e)$$

and we know $\langle \ell | \ell \rangle$ is unity

$$\therefore \langle L^2 \rangle = \quad (9.5f)$$

$$= \quad (9.5g)$$

- Since our original wavefunction was an eigenstate of the operator $\widehat{L^2}$ the eigenvalue and expectation value are the same.
- What if the wavefunction is not an eigenstate?



Section 10

Superposition

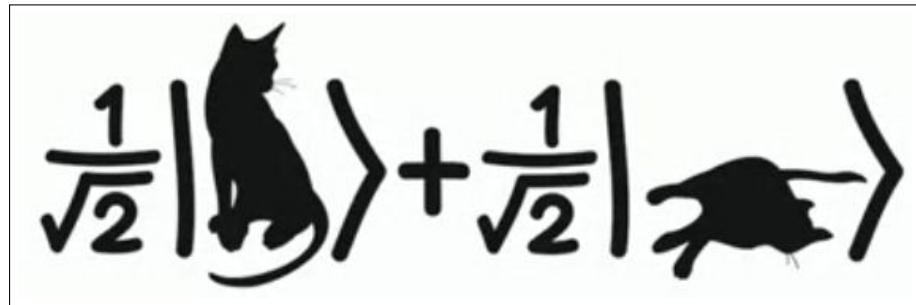


Figure 10.1: Dead or alive? [6]

This is a re-stating (in terms of atoms) the Dirac work from the 1st half of this course. Please read this and the following section. Say we have a state which is a superposition of orbital angular states

$$|\psi\rangle = A \left[|\ell = 2\rangle + \frac{1}{3} |\ell = 1\rangle \right] \quad (10.1a)$$

this superposition is also a solution of the angular operator and so a valid wavefunction. What is A? a normalization constant

$$\langle \psi | \psi \rangle = 1 \quad (10.1b)$$

$$= \left[A^* \langle 2| + \frac{1}{3} A^* \langle 1| \right] \left[A |2\rangle + \frac{1}{3} A |1\rangle \right] \quad (10.1c)$$

$$= A^* A \left[\underbrace{\langle 2 | 2 \rangle}_{\text{}} + \frac{1}{3} \underbrace{\langle 2 | 1 \rangle}_{\text{}} + \frac{1}{3} \underbrace{\langle 1 | 2 \rangle}_{\text{}} + \frac{1}{9} \underbrace{\langle 1 | 1 \rangle}_{\text{}} \right] \quad (10.1d)$$

$$= \quad (10.1e)$$

$$\therefore A = \quad (10.1f)$$



$$\therefore |\psi\rangle = |2\rangle + |1\rangle \quad (10.1g)$$

which we can write as

$$= |2\rangle + |1\rangle \quad (10.1h)$$

where c_2 and c_1 are the amplitudes of the individual eigenvectors that make up the wavefunction. What therefore is the expectation value of L^2 ?

$$= \quad (10.1i)$$

$$= \left[\frac{3}{\sqrt{10}} \langle 2| + \frac{1}{\sqrt{10}} \langle 1| \right] \widehat{L^2} \left[\frac{3}{\sqrt{10}} |2\rangle + \frac{1}{\sqrt{10}} |1\rangle \right] \quad (10.1j)$$

$$= \left[\frac{3}{\sqrt{10}} \langle 2| + \frac{1}{\sqrt{10}} \langle 1| \right] \left[\frac{3}{\sqrt{10}} L_{\ell=2}^2 |2\rangle + \frac{1}{\sqrt{10}} L_{\ell=1}^2 |1\rangle \right] \quad (10.1k)$$

$$= \frac{9}{10} L_{\ell=2}^2 \underbrace{\langle 2 | 2 \rangle}_{+} \frac{3}{10} L_{\ell=2}^2 \underbrace{\langle 1 | 2 \rangle}_{+} \frac{3}{10} L_{\ell=1}^2 \underbrace{\langle 2 | 1 \rangle}_{+} \frac{1}{10} L_{\ell=1}^2 \underbrace{\langle 1 | 1 \rangle}_{} \quad (10.1l)$$

$$= \quad (10.1m)$$

notice

$$= L_{\ell=2}^2 + L_{\ell=1}^2 \quad (10.1n)$$

more later on this

$$= \frac{9}{10} 6\hbar^2 + \frac{1}{10} 2\hbar^2 \quad (10.1o)$$

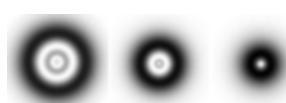
$$= \quad (10.1p)$$

So for this superposition we have EASILY calculated the expectation value, the mean value of a number of experiments. But what do we actually see on the experiment readout?

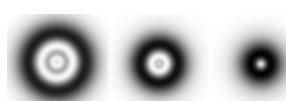
10.1 God and dice

Einstein famously said “God does not play dice”. Why?

- We have calculated the expectation, i.e., mean, value but what do we actually measure in a single experiment?
- You always measure an eigenvalue of the operator!
 - ⇒ For any single measurement $L^2 = 6\hbar^2$ or $= 2\hbar^2$
 - ⇒ Never (ever) do you find $\frac{28}{5}\hbar^2$ in a single measurement.



- ⇒ The system is always found in an eigenstate of the measurement.
- It is as if the wavefunction has two possible values and only upon measurement does it decide upon one, with a probability given by the square of the weighting factors (amplitudes) c .
- Quantum mechanics is probabilistic.
- This is the Copenhagen interpretation of quantum mechanics.
 - ⇒ Out of all the possible eigenstates of an operator that a system can have, the measurement always returns just one state with a probability given by the square of the amplitude of that state within the original superposition.
 - ⇒ The superpositon wavefunction is collapsed onto one of its components.
 - ⇒ The wavefunction is changed by the measurement.
- Copenhagen has a measurement problem, since I can write $|you\rangle$ and just include you in the analysis yet you never find yourself in a superposition.
- Humans are important!?
- Or the many worlds interpretation says that all measurements are found, and the universe splits into two, one where you measure $L^2 = 6\hbar^2$ and the other $= 2\hbar^2$
- Crazy. Please do more physics and fix it.
- For some further reading see the chapter on “Conceptual problems with quantum mechanics” in A. I. M. Rae, Quantum Mechanics, 5th edition.



Section 11

Spin revisited

11.1 Pauli matrices



Figure 11.1: Pauli, Heisenberg and Fermi [7].

There is no way to represent spin with spatial coordinates (x, y, z or r, ϕ, θ). Spin doesn't exist in the Schrödinger wave mechanics. But we have written down the relations

$$= \quad (11.1)$$

$$= \quad (11.2)$$

Wolfgang Ernst Pauli determined a simple matrix mechanics of dimension 2×2 that exactly described spin through the Pauli spin matrices,

$$= \qquad \widehat{S}_x = \frac{1}{2}\hbar\sigma_x \qquad \widehat{S}_y = \frac{1}{2}\hbar\sigma_y \quad (11.3)$$

where the Pauli spin matrices are

$$\sigma_z = \qquad \sigma_x = \qquad \sigma_y = \quad (11.4)$$

and the magnitude of the spin is given by

$$\widehat{S}^2 = \quad (11.5)$$



and you (you!) can show that

$$\widehat{S^2} = \quad (11.6)$$

11.2 Eigenvectors and eigenvalues

Using your mathematical powers you (you!) can show that the eigenvectors of $\widehat{S_z}$ etc. are

$$= = \quad (11.7)$$

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad |\downarrow_x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (11.8)$$

$$|\uparrow_y\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \quad |\downarrow_y\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \quad (11.9)$$

- Spin-up the eigenvalue is $\hbar/2$
- Spin-down the eigenvalue is $-\hbar/2$.

11.2.1 Example

Let's take the eigenstate of z -spin-up.

$$|\psi\rangle = \quad (11.10a)$$

Let's find the spin projected onto the z axis

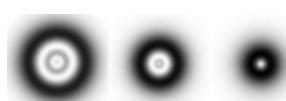
$$= \quad (11.10b)$$

$$\underbrace{\frac{1}{2}\hbar}_{\text{operator}} \underbrace{\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}}_{\text{matrix}} \underbrace{\begin{pmatrix} 1 \\ 0 \end{pmatrix}}_{\text{vector}} = \quad (11.10c)$$

it really is an eigenvalue equation!

$$\therefore S_z = \quad (11.10d)$$

We have stated that we can know the magnitude and the projection of the spin. let's check this is true.



11.2.2 Sequential measurements

- If we can know both S^2 and S_z then this implies we must be able to make multiple measurements of these quantities in any order and always get the same answers.
⇒ Measuring one doesn't mess up the next measurement and so on.
- Which means that whatever wavefunction we start the experiment with better be the same as the one at the end of the exp, otherwise next time around we'd measure something different.
- We've just seen this for a measurement of S_z , what about S^2 ?
- Really the question is: is $|\uparrow_z\rangle$ an eigenvector of \widehat{S}^2 ?

$$\widehat{S}^2 |\uparrow_z\rangle = \quad (11.11a)$$

$$= \quad (11.11b)$$

$$= \frac{3}{4}\hbar^2 \quad (11.11c)$$

- so we can measure the magnitude of the spin and we do not alter the wavefunction.
- As you find out next year more formally, those two operators are said to mathematically 'commute'.

11.3 Expectation values

The expectation value, in this matrix mechanics, is given by (in another example)

$$\langle \uparrow_x | \widehat{S}_x | \uparrow_x \rangle = \quad (11.12)$$

which you (you!) can show is

$$= \quad (11.13)$$

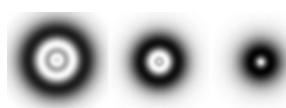
as expected since this wavefunction is an eigenvector of the operator. What if it isn't?

11.4 Superposition of spin states

Keeping the same wavefunction, what happens when we now measure S_z ?

$$\widehat{S}_z |\uparrow_x\rangle = \underbrace{\frac{1}{2}\hbar \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}}_{\text{underbrace}} \underbrace{\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}}_{\text{underbrace}}$$

$$= \quad (11.14)$$



$$= \quad (11.15)$$

This is not an eigenvalue equation. Instead we can write the x -spin state as a superposition of z -spin states

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \left[\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right] \quad (11.16)$$

$$|\uparrow_x\rangle = \quad (11.17)$$

$$= \quad (11.18)$$

the expectation value is therefore

$$= \left[\frac{1}{\sqrt{2}} \langle \uparrow_z | + \frac{1}{\sqrt{2}} \langle \downarrow_z | \right] \widehat{S}_z \left[\frac{1}{\sqrt{2}} |\uparrow_z\rangle + \frac{1}{\sqrt{2}} |\downarrow_z\rangle \right] \quad (11.19)$$

$$= \quad (11.20)$$

as for the previous superposition we can write

$$= \quad (11.21)$$

$$= \quad (11.22)$$

$$= \quad (11.23)$$

There is equal chance of spin up or down, so an average of no spin.

Some quantum conclusions.

- If we measure x -spin of an electron to form a pure state of $|\uparrow_x\rangle$ what can we say about the z component?
- The z -spin component has a 50/50 chance of being either $|\uparrow_z\rangle$ or $|\downarrow_z\rangle$.
- So we know nothing about the z -spin component until we make a measurement of it.
- if we then take the $|\uparrow_z\rangle$ state and measure the x component what do we get?
- The x -spin component now has a 50/50 chance of being either $|\uparrow_x\rangle$ or $|\downarrow_x\rangle$.
- Even although we started with pure $|\uparrow_x\rangle$!
- measurement can really mess things up.
- See section 17.2 for how to make measurements.



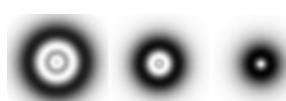
11.4.1 Spinning top

Classical spinning top.

- Set a small spinning top spinning at some angle.
 - ⇒ Measure the angular momentum component in the x -direction.
 - ⇒ Measure the angular momentum component in the y -direction.
 - ⇒ Measure the angular momentum component in the z -direction.
- We now have a 3D vector for the angular momentum and can work out its magnitude.
- Go back and take multiple readings of the components. All return the same as the initial experimental result.

Quantum spinning top.

- Isolate an electron
 - ⇒ Measure the angular momentum (spin) component in the x -direction.
 - ⇒ Measure the spin in the y -direction.
 - ⇒ Measure the spin in the z -direction.
- We now have a 3D vector for the angular momentum and can work out its magnitude?
- No.
- All we'll know is the magnitude and the spin in the last direction we measured.
- Say the quantum-toy spins by an amount in x . Then we measure the y component. If we subsequently measure in x we can find it now spinning in $-x$!
- W.T.F.?
- Measurements matter.



Section 12

Problems for part B

P13: Pauli magnitude [analysis, medium]

The magnitude of the spin is given by

$$\widehat{S^2} = \widehat{S_x}^2 + \widehat{S_y}^2 + \widehat{S_z}^2$$

show that

$$\widehat{S^2} = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

P14: Spin expectation [application, medium]

Calculate the expectation values

(a) $\langle \downarrow_y | \widehat{S_y} | \downarrow_y \rangle.$

(b) $\langle \uparrow_y | \widehat{S_y} | \uparrow_y \rangle.$

(c) $\langle \downarrow_y | \widehat{S_z} | \downarrow_y \rangle.$

(d) $\langle \downarrow_y | \widehat{S_x} | \downarrow_y \rangle.$



Part C: Magnetic properties

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Section 13

Magnetic Moments

Associated with both orbital and spin angular momentum there is a magnetic moment. This leads to atoms acting as small magnets and underlies all magnetism in material. See youtube video from [minute physics](#).

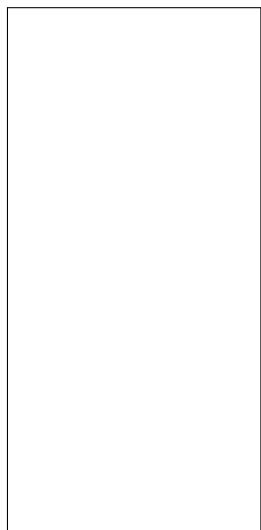
13.1 Definitions

Magnets have a magnetic moment $\vec{\mu}$. For example figure 13.1a shows a bar magnet with magnetic moment $\vec{\mu}$ and its associated magnetic field \vec{B} . Where we know that

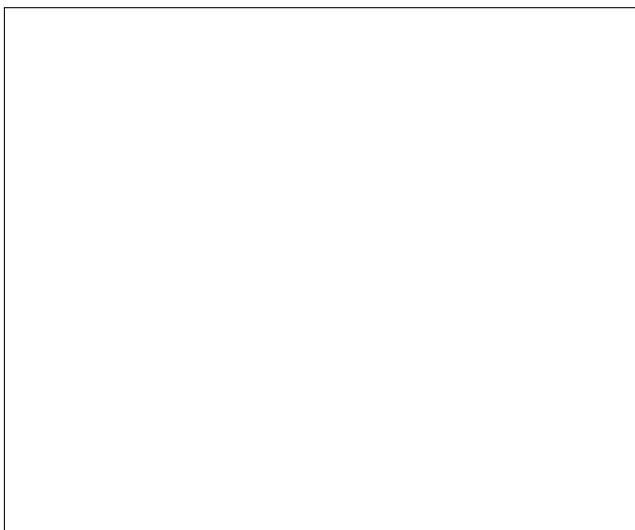
$$\vec{\mu} = \quad (13.1)$$

and that

$$\vec{A} = \quad (13.2)$$



(a) A simple bar magnet.



(b) A simple current loop.

Figure 13.1: Magnetic moments and fields



where I is the current in the loop, A is the area of the loop and \hat{n} is a unit vector normal to the plane of the loop. Furthermore in a uniform magnetic field \vec{B} we know that

$$\text{Energy of magnetic moment: } E = \quad (13.3)$$

$$\text{Torque on magnetic moment: } \vec{\Gamma} = \quad (13.4)$$

and that the units of $\vec{\mu}$ are JT^{-1} .

13.2 Classical model of orbital magnetic moment

Figure 13.2: Classical orbit model for an electron orbiting a proton.



Figure 13.2 shows the classical picture for a single electron orbiting a proton. The electron orbit acts as a current loop of radius r and with angular velocity ω . So we can write

$$\vec{\mu} = \quad (13.5)$$

$$= \quad (13.6)$$

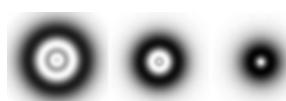
$$= \quad (13.7)$$

and since

$$\vec{L} = mvr\hat{n} \quad (13.8)$$

$$= mr^2\omega\hat{n} \quad (13.9)$$

$$\therefore \vec{\mu} = \quad (13.10)$$



Although this is a classical derivation, a proper quantum analysis gives the same result. This is usually written as

$$\vec{\mu}_L = \dots \quad (13.11)$$

Here

- $\vec{\mu}_L$ is to show that this is the orbital (L) magnetic moment.
- g_L is the orbital ‘ g -factor’ = 1
- and μ_B is a constant, the Bohr magneton:

$$\mu_B = \dots \quad (13.12)$$

and is the fundamental unit of atomic magnetism.

Therefore since the magnitude of the orbital angular momentum is given by

$$|L| = \hbar\sqrt{\ell(\ell+1)} \quad (13.13)$$

$$\Rightarrow |\mu_L| = \dots \quad (13.14)$$

13.3 Spin magnetic moment

Dirac’s relativistic quantum theory shows that there is also a magnetic moment $\vec{\mu}_S$ associated with the spin angular momentum \vec{S} :

$$\vec{\mu}_S = \dots \quad (13.15)$$

where g_S is the spin ‘ g -factor’ and is 2 as shown in Dirac theory (not here!). Since the magnitude of the spin angular momentum is given by

$$|S| = \hbar\sqrt{s(s+1)} \quad (13.16)$$

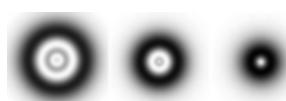
$$= \hbar \frac{\sqrt{3}}{2} \quad (13.17)$$

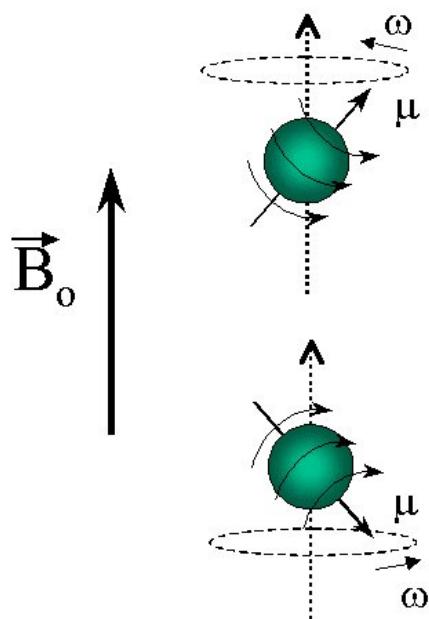
$$\Rightarrow |\mu_s| = \dots \quad (13.18)$$

In general atoms have both orbital and spin contributions to their total magnetic moments.

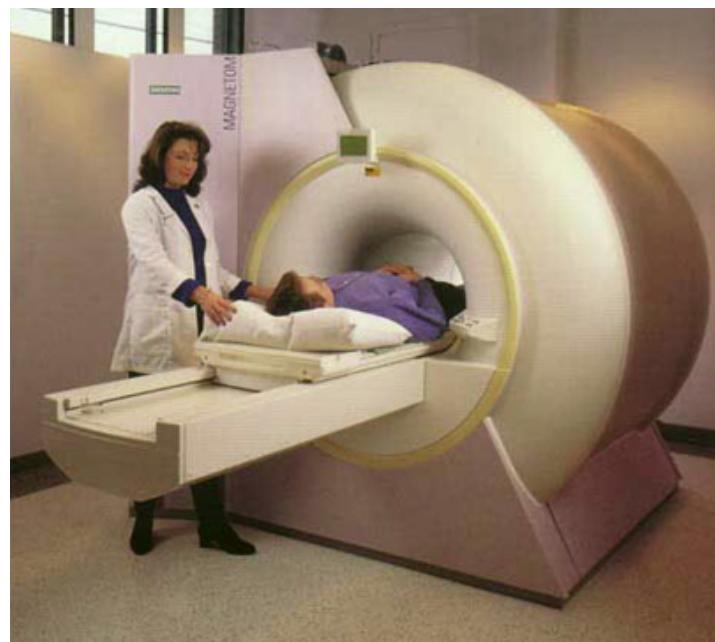
13.3.1 Application: Electron spin resonance

Imagine a single electron all on its own. Now apply a small magnetic field along the z -axis. This is equivalent to making a measurement of the spin in the z -axis. The electron will be either spin up $S_z = \hbar/2$ or spin down $S_z = -\hbar/2$ as in figure (fig. 8.1). But the spin is not aligned with





(a) ESR.



(b) MRI.

Figure 13.3: Electrons and protons in a spin [8, 9].

the field it gets 'stuck' at some angle. The magnetic moment of the spin is therefore not aligned with the magnetic field and there is a resulting torque felt by the electron's magnetic moment. What happens? The Torque makes the magnetic moment rotate about the z -axis, it precesses at a particular frequency. If you now shine light on the electron with the same frequency (radio frequencies) as it is rotating it can absorb the light which results in it flipping from spin up to down (or vice versa) - (fig. 13.3a). This is known as electron spin resonance. You can also do the same thing with the nucleus, and so you invent NMR (Nuclear magnetic resonance) or in more general-public-friendly terms MRI (Medical Resonance Imaging - figure 13.3b - and [video](#)).



Section 14

Total angular momentum: j

We have seen how orbital \vec{L} and spin \vec{S} angular momentum arise, and how they have associated magnetic moments, μ_L and μ_S . In practice we find that \vec{L} and \vec{S} are magnetically coupled (they interact) to produce a total angular momentum \vec{J} , from the superposition

$$\vec{J} = \quad (14.1)$$

Associated with the total angular momentum is the total angular momentum quantum number j with the resulting magnitude

$$\widehat{J^2} |n, \ell, s, j\rangle = \hbar^2 j(j+1) |n, \ell, s, j\rangle \quad (14.2)$$

$$\therefore |J| = \quad (14.3)$$

As with all angular quantum numbers consecutive values of j must differ by 1. j also obeys

$$\leq \leq \quad (14.4)$$

furthermore the projection of \vec{J} onto the z -axis is also quantized

$$= \quad (14.5)$$

$$J_z = \quad (14.6)$$

$$m_j \quad (14.7)$$

14.1 More quantum numbers?

- Does this coupling lead to more quantum numbers in total?
- That is, have we created more states?
- So far we have n , ℓ , m_ℓ , s and m_s .
- Now we have added j and m_j .
- Have we created more possible states?
- In short no.



14.1.1 Coupled regime

When we couple \vec{L} and \vec{S} it turns out that the values of L_z and S_z are no longer conserved (the eigen-function of one are not eigen-functions of the other) and so m_ℓ and m_s are no longer allowed (good) quantum numbers. So in the coupled regime we have

•

Let's do some adding to make sure. For an $\ell = 1$ state we can have in the uncoupled basis,

$$m_\ell = \quad , \quad m_s = \quad (14.8)$$

$$m_\ell = \quad , \quad m_s = \quad (14.9)$$

$$m_\ell = \quad , \quad m_s = \quad (14.10)$$

so 6 electronic states in total. In the coupled regime we have

$$j = \quad , \quad (14.11)$$

$$j = \quad , \quad m_j = \quad (14.12)$$

$$j = \quad , \quad m_j = \quad (14.13)$$

which is again 6 electron states. So all we've done is change the basis set used to describe the problem, not changed the problem itself.

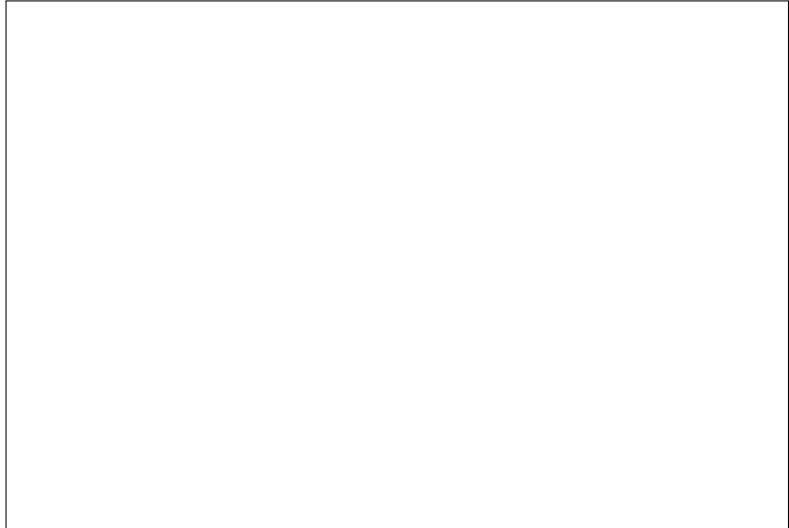
So we can construct a list of j and m_j values as shown in [table 14.1](#).

ℓ	s	j	m_j

Table 14.1: Total angular momentum quantum numbers.



Figure 14.1: Semi-classical vector representation of the total angular momentum vector and projection onto the z axis.



14.2 Semi-classical vector model for \vec{J}

If we now switch on a weak magnetic field along the z -axis, which is the equivalent to making a measurement along the z -axis, we find (as ever) quantisation of the z -projection resulting in the quantization of $|J_z|$, see figure 14.1.



Section 15

Spin-Orbit interaction

Why does all this matter?

- Because magnetic coupling splits the energies of the j states, that is the states $j = \ell + s$ to $j = |\ell - s|$ have slightly different energies.
- We observe this fine structure in atomic spectra.

15.1 Classical derivation of spin-orbit splitting

Consider the frame of reference of the electron.

- It is at rest and the nucleus orbits it.
- We have the nucleus Z orbiting at radius r in a time τ acting as a current $I = Ze/\tau$ loop which produces a magnetic field at the centre of the orbit, exactly at the location of our electron.

$$\vec{B} = \quad (15.1a)$$

and we can write the angular momentum of the electron as

$$\vec{L} = mr^2\omega\hat{n} \quad (15.1b)$$

$$= mr^2\frac{2\pi}{\tau}\hat{n} \quad (15.1c)$$

so that

$$\vec{B} = \quad (15.1d)$$

is the strength of the magnetic field at the position of the electron produced by the ‘orbiting’ proton. So now we can compute the energy of the spin magnetic moment in this magnetic field as

$$E_{so} = \quad (15.1e)$$



$$= \quad (15.1f)$$

substitute in equation (15.1d)

$$= \left(\frac{\mu_B \mu_0 Z e}{2\pi \hbar m} \right) \left(\frac{1}{r^3} \right) \quad (15.1g)$$

We can make an estimation for the value of $1/r^3$ (the expectation value)

$$\frac{1}{r^3} \sim \left(\frac{Z}{a_0} \right)^3 \frac{1}{n^3}. \quad (15.1h)$$

To determine the value of $\vec{L} \cdot \vec{S}$ let's start by squaring \vec{J}

$$\vec{J}^2 = \quad (15.1i)$$

$$= \quad (15.1j)$$

$$\therefore \vec{L} \cdot \vec{S} = \quad (15.1k)$$

and we can substitute the magnitudes of the various vectors with their eigenvalues

$$\vec{J}^2 = \quad (15.1l)$$

$$\vec{L}^2 = \quad (15.1m)$$

$$\vec{S}^2 = \quad (15.1n)$$

to finally give the energy of spin-orbit splitting

$$E_{so} \sim \left(\frac{\mu_B \mu_0 e \hbar}{m a_0^3} \right) \quad (15.1o)$$

Hence only really important for large atoms with high Z numbers.

15.1.1 Example: Spin-Orbit splitting for 2p

For the 2p states of hydrogen we have

$$\ell = , s = , \therefore j = \quad \& \quad j = . \quad (15.2)$$

For

$$j = \quad (15.3)$$

$$E_{so} = C [j(j+1) - \ell(\ell+1) - s(s+1)] \quad (15.4)$$

$$\therefore E_{so} = \quad (15.5)$$



$$= \quad (15.6)$$

For

$$j = \quad (15.7)$$

$$\therefore E_{so} = \quad (15.8)$$

$$= \quad (15.9)$$

So the energy splitting between these two states is

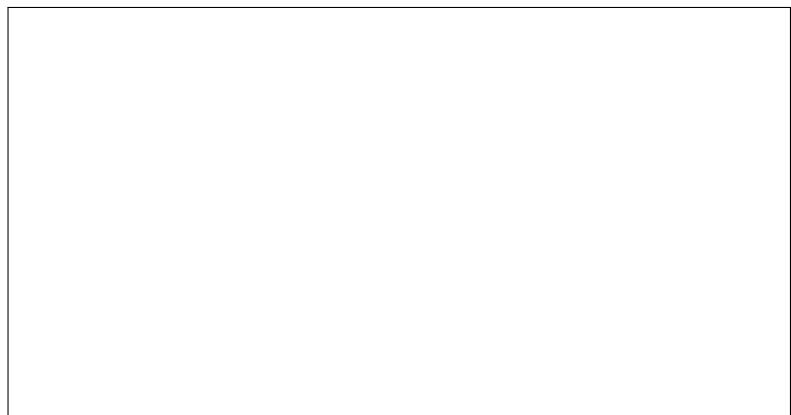
$$\Delta E = \quad (15.10)$$

$$C = \left(\frac{\mu_B \mu_0 e \hbar}{m a_0^3} \right) \left(\frac{Z^4}{n^3} \right) \quad (15.11)$$

$$\approx \quad (15.12)$$

This is very small energy for a hydrogen atom ($Z = 1$). In table 4.1a we showed that the energy

Figure 15.1: Energy level diagram for uncoupled and coupled regime.



for the $n = 2$ state was 3.4 eV, so spin-orbit is really very small. But it does become more important as Z increases.

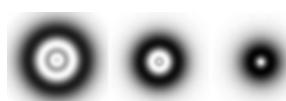
15.1.2 Example: Spin-Orbit splitting for 2s

For the $2s$ state (or any s -state) we have $E_{so} = 0$ and so no splitting. The s -state has no orbital angular momentum so this should not come as a surprise.

15.2 Total magnetic moment

We have already seen that both the orbital and spin angular momenta have associated magnetic moments

$$\vec{\mu}_L = -\frac{g_L \mu_B}{\hbar} \vec{L} \quad (15.13)$$



$$\vec{\mu}_S = -\frac{g_S \mu_B}{\hbar} \vec{S} \quad (15.14)$$

By analogy we can simply write

$$\vec{\mu}_J = \quad (15.15)$$

where g_J is called the Landé g -factor and is given by

$$g_J = \quad (15.16)$$

so

- if $s = 0$ then $j = \ell$ and so $g_J = g_L =$
- if $\ell = 0$ then $j = s$ and so $g_J = g_S =$



Section 16

Time independent perturbation theory

This section closely follows chapter 7 of Mandel “Quantum mechanics” (see library - [link](#)) and Kirkby ([link](#)).

Few systems can be solved exactly in quantum mechanics. Most rely on solving for a known system, then adding in small corrections (perturbations) to describe how the real system differs from the ideal one. We have already encountered this with the spin-orbit interaction adding an energy correction to the ‘solved’ energy of an electronic state of a hydrogen atom.

The aim of this section is to derive probably the most useful results in quantum mechanics and then apply it to the spin-orbit interaction to drive the result of the previous chapter but purely quantum mechanically.

Formally this is 1st order time independent non-degenerate perturbation theory and we’ll only look at energy corrections.

16.1 Derivation of energy correction

16.1.1 Starting points

We can write the energy operator of a system (the Hamiltonian) as the sum of a zeroth order Hamiltonian (the un-perturbed system) and a small perturbation

$$\hat{H} = \quad (16.1)$$

and we write the corresponding wavefunction of a state n

$$\psi_n = \quad (16.2)$$

and we write the corresponding energy as

$$E_n = \quad (16.3)$$

16.1.2 Zeroth order (unperturbed)

$$\hat{H}_0 |\psi_n^0\rangle = \quad (16.4)$$



16.1.3 Full system

$$\hat{H} |\psi_n\rangle = \quad (16.5)$$

16.2 Inner product

Here we start with

$$= \quad (16.6)$$

and now we substitute the expansions of section 16.1.1 to do the derivation, hold on.

16.2.1 Left-hand-side

$$\langle \psi_n^0 | \hat{H} | \psi_n \rangle = \quad (16.7)$$

$$= \underbrace{\langle \psi_n^0 | \hat{H}_0 | \psi_n^0 \rangle}_{1st} + \underbrace{\langle \psi_n^0 | \delta \hat{H} | \psi_n^0 \rangle}_{2nd} + \underbrace{\langle \psi_n^0 | \hat{H}_0 | \delta \psi_n \rangle}_{3rd} + \underbrace{\langle \psi_n^0 | \delta \hat{H} | \delta \psi_n \rangle}_{4th} \quad (16.8)$$

- First term: Just as above we can evaluate

$$\langle \psi_n^0 | \hat{H}_0 | \psi_n^0 \rangle = \quad (16.9)$$

$$= \quad (16.10)$$

$$= \quad (16.11)$$

- 2nd term: This term we leave alone as it is going to be term we'll get when we also do the RHS.

$$\langle \psi_n^0 | \delta \hat{H} | \psi_n^0 \rangle \quad (16.12)$$

- 3rd term: Here, as you'll find out next year, because of various properties of quantum operators we can write

$$\langle \psi_n^0 | \hat{H}_0 | \delta \psi_n \rangle = \quad (16.13)$$

$$= \quad (16.14)$$

$$= \quad (16.15)$$

$$= \quad (16.16)$$

- 4th term: Here we have two terms with δ terms so it is a second order correction, small.

$$\langle \psi_n^0 | \delta \hat{H} | \delta \psi_n \rangle = \quad (16.17)$$

- Finally we have

$$\langle \psi_n^0 | \hat{H} | \psi_n \rangle \approx \quad (16.18)$$



16.2.2 Right-hand-side

$$\langle \psi_n^0 | E_n | \psi_n \rangle = \quad (16.19)$$

$$= \langle \psi_n^0 | E_n^0 | \psi_n^0 \rangle + \langle \psi_n^0 | \delta E_n | \psi_n^0 \rangle + \langle \psi_n^0 | E_n^0 | \delta \psi_n \rangle + \langle \psi_n^0 | \delta E_n | \delta \psi_n \rangle \quad (16.20)$$

- 1st Term: Just as above,

$$\langle \psi_n^0 | E_n^0 | \psi_n^0 \rangle = \quad (16.21)$$

E s are just numbers and since the wavefunction are normalized

$$= \quad (16.22)$$

- 2nd Term: Just as above,

$$\langle \psi_n^0 | \delta E_n | \psi_n^0 \rangle = \quad (16.23)$$

$$= \quad (16.24)$$

- 3rd Term:

$$\langle \psi_n^0 | E_n^0 | \delta \psi_n \rangle = \quad (16.25)$$

- 4th Term: Has two δ terms so

$$\langle \psi_n^0 | \delta E_n | \delta \psi_n \rangle = \quad (16.26)$$

- Finally we have

$$\langle \psi_n^0 | E_n | \psi_n \rangle \approx \quad (16.27)$$

16.2.3 Equate both sides

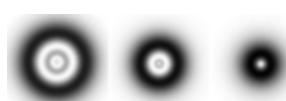
The most useful equation in quantum physics

$$E_n^0 + \langle \psi_n^0 | \widehat{\delta H} | \psi_n^0 \rangle + E_n^0 \langle \psi_n^0 | \delta \psi_n \rangle = E_n^0 + \delta E_n + E_n^0 \langle \psi_n^0 | \delta \psi_n \rangle \quad (16.28)$$

therefore (and the point of all this)

$$\delta E_n = \quad (16.29)$$

To compute the 1st order energy correction due to a small perturbation, we compute the expectation value of the energy of the perturbation acting on the un-perturbed wave-functions.



16.3 Spin-orbit

Now we can use this to compute some useful numbers. How about a proper quantum mechanical description of the Spin-Orbit interaction? Combining equations (15.1g) and (15.1k) for hydrogen atoms

$$\widehat{E}_{so} = \left(\frac{\mu_B \mu_0 e}{2\pi \hbar m} \right) \left(\frac{1}{r^3} \right) \frac{1}{2} \hbar^2 [j(j+1) - \ell(\ell+1) - s(s+1)] \quad (16.30)$$

hence most of this is just constants and we are left with

$$\delta E_{so} = \quad (16.31)$$

$$= \left(\frac{\mu_B \mu_0 e}{2\pi \hbar m} \right) \frac{1}{2} \hbar^2 [j(j+1) - \ell(\ell+1) - s(s+1)] \quad (16.32)$$

so we 'just' need to compute the expectation value for $1/r^3$ for the particular state we are interested in. For the hydrogenic wavefunctions this turns out to be (horrible integral)

$$\langle \psi_n^0 | \frac{1}{r^3} | \psi_n^0 \rangle \sim \quad (16.33)$$

hence for $n = 1$

$$= \quad (16.34)$$

hence we have for hydrogen atoms in the ground state

$$\delta E_{so} \sim \left(\frac{\mu_B \mu_0 e \hbar}{m a_0^3} \right) [j(j+1) - \ell(\ell+1) - s(s+1)] \quad (16.35)$$

We are allowed to use the ψ of the uncoupled Schrodinger equation $|\psi_n^0\rangle$ to compute the small change in energy of a state if we perturb the system in some way. That is, we can use the solutions we know from the ideal system to work out the energies of a non-ideal (perturbed) system.



Section 17

Effects of external magnetic fields

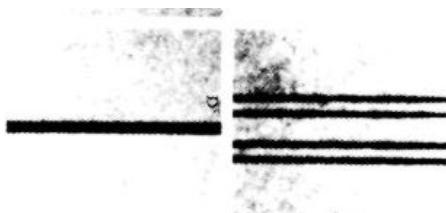
How do we actually know that atomic quantum states have associated magnetic moments? We can perform experiments.

- We do some spectroscopy with the Zeeman effect.
- We pass out atoms through a Stern-Gerlach experiment

17.1 The Zeeman effect



(a) Pieter Zeeman: 25 May 1865 - 9 October 1943 [10].



(b) Photographic plate taken by Zeeman with the magnetic field, on and off [11].

Figure 17.1: The Zeeman effect experiment. When still a student at high school he made a drawing and description of the phenomenon of the Aurora borealis and submitted it to Nature, where it was published. The editor praised “the careful observations of Professor Zeeman from his observatory in Zonnemaire”.

When an external magnetic field is applied to an atom the energy levels may split, leading to a splitting of the spectral lines. This is the Zeeman effect, see figure 17.1. Suppose we have a uniform magnetic field in the z direction $\vec{B} = B\hat{z}$ then the energy of a magnetic moment in this



field is given by

$$E = \quad (17.1)$$

and since

$$\vec{\mu}_J = \quad (17.2)$$

then

$$E = \quad (17.3)$$

which is just the value of the total angular momentum projected onto the B axis which is the z axis, hence

$$= \quad (17.4)$$

and since the allowed values of J_z are $m_j\hbar$ then

$$\Delta E_{\text{Zeeman}} = \quad (17.5)$$

- This is the energy change of a state due to interaction with an external B -field.
- So each j level will split into $2j + 1$ sub-levels with different values of m_j .
- The size of this splitting is given by g_J - see figure 17.2.
- The external magnetic field must be weak compared with the internal field responsible for spin-orbit coupling. So the splitting energy given here must be smaller than that of spin-orbit coupling.

But what we measure are the spectral lines that have the selection rules $\Delta m_j = 0, \pm 1$, so only the transitions indicated will absorb/produce light: 4 lines for the $2P_{1/2} \rightarrow 1S_{1/2}$ and 6 for the $2P_{3/2} \rightarrow 1S_{1/2}$.

17.2 Stern Gerlach experiment

A beam of neutral atoms is deflected by an inhomogeneous magnetic field (a field with a spatially varying amplitude). The figure 17.3 shows the experimental apparatus for this defining experiment. So let's consider an inhomogeneous field in the z -direction $B_z(z)$. So the energy of a magnetic moment in this field will be

$$E = \quad (17.6)$$

and so the force acting on the moment is

$$F = \quad (17.7)$$



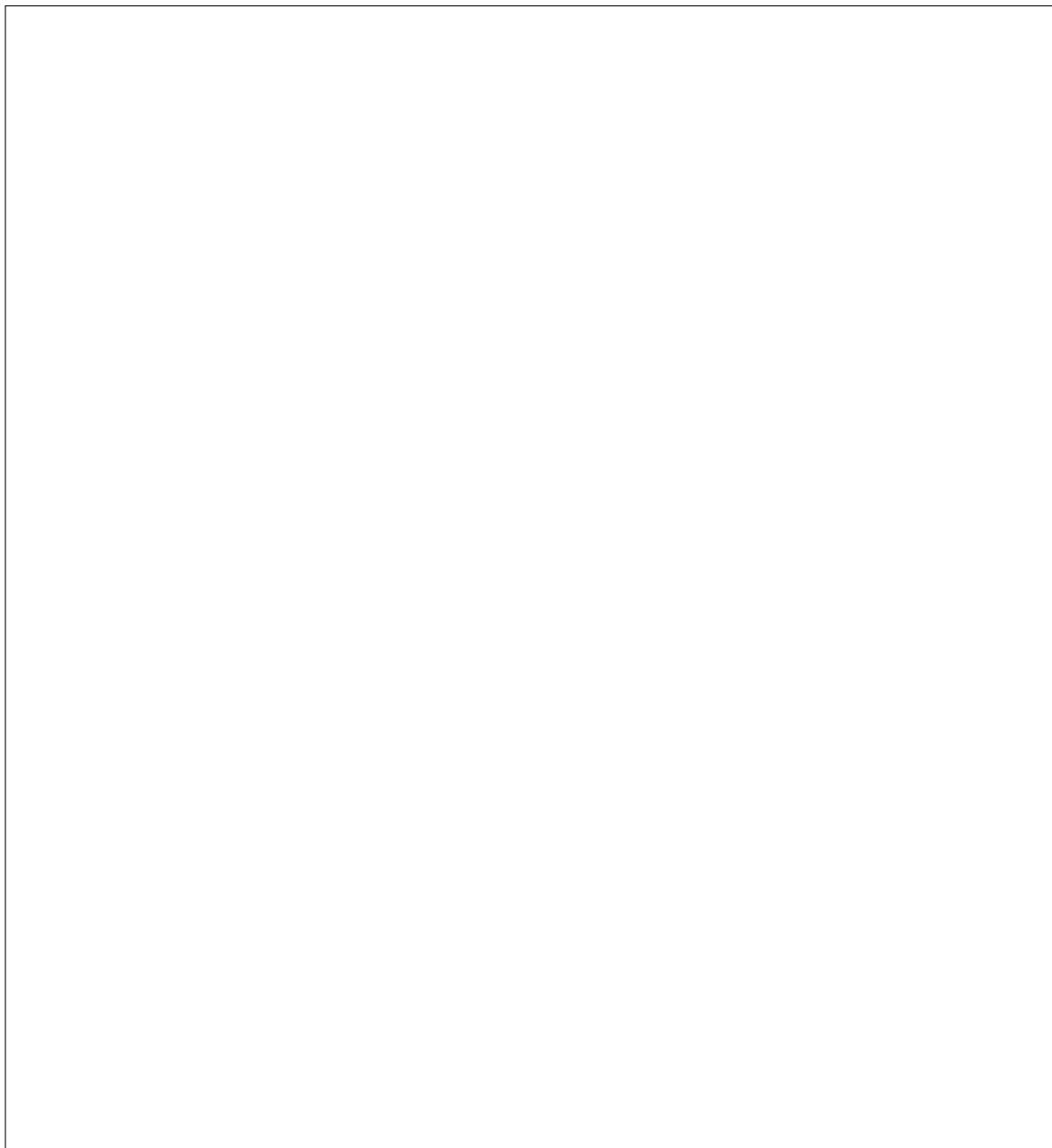


Figure 17.2: Schematic energy level diagram of the Zeeman effect, also showing allowed optical transitions.



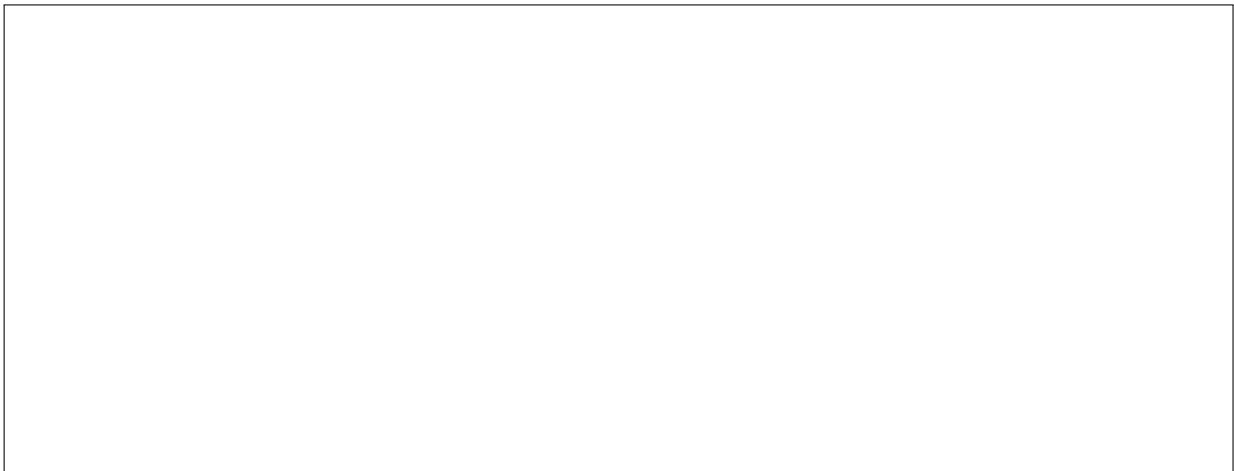


Figure 17.3: Schematic diagram of S-G apparatus.

Now that force will cause a small deflection in z which we want to know. We define the following

$$\Delta t = \text{time spent by atoms in the field} \quad (17.8)$$

$$M = \text{mass of the atom} \quad (17.9)$$

$$V_x = \text{speed of atoms in the } x\text{-direction} \quad (17.10)$$

$$a = \text{length of magnetic field} \quad (17.11)$$

$$b = \text{length of 'drift' region} \quad (17.12)$$

$$\Delta z = \text{deflection in } z. \quad (17.13)$$

We first want to know the z velocity component as an atom leaves the magnetic field region. The field will apply a force and this will change the atom's z momentum. So

$$F_z = \quad (17.14)$$

$$\therefore \Delta P_z = \quad (17.15)$$

$$\text{and } \Delta t = \quad (17.16)$$

$$\therefore \Delta V_z = \quad (17.17)$$

$$\text{and so } \Delta V_z = \quad (17.18)$$

The time of flight of the drift region is simply b/V_x and so the distance travelled in z will be

$$\Delta z = \quad (17.19)$$

$$\text{since } \mu_z \propto \propto \quad (17.20)$$



$$\Delta z \propto \quad (17.21)$$

- So the beam should split into discrete components
- The number of which is determined by the value of j since $-j \leq m_j \leq +j$ and hence there are $2j + 1$ states.
- The Stern-Gerlach experiment was first performed with Ag atoms. These were expected to act as effectively a one-electron atom with $\ell = 0$ and so no deflection.
- But, the beam split into 2 components, which indicated the existence of the spin magnetic moment and won them a Nobel prize



Section 18

Problems for part C

P15: Magneton [knowledge, easy]

Calculate the Bohr magneton.

P16: Orbital and spin [application, medium]

What is the magnitude of the orbital and spin magnetic moments in μ_B of a 1-electron atom in a state with quantum number $\ell = 2$.

P17: Coupled momenta [application, hard]

When the orbital and spin angular momentum of a 1-electron atom in a state with quantum number $\ell = 2$ are coupled

- (a) What are the possible values of the total angular momentum quantum number j ?
- (b) What are the Lande g -factors of the allowed states?
- (c) What is the magnitude of the magnetic moment (in units of μ_B) associated with these allowed states of j ?
- (d) Into how many levels are these states split when a magnetic field is applied?
- (e) What is the spacing (in eV) between the split levels if the field strength is $B = 1$ T?

P18: H-atom in a B-field [analysis, hard, past exam]

Consider the electronic structure of a hydrogen atom.

- (a) For the $3d$ state, draw a fully labelled semi-classical vector model of its angular momentum. This should include all possible m_ℓ values, their associated L_z values and the magnitude of the angular $|L|$. [3]



(b) Given

$$E_n = -\frac{13.6}{n^2} \text{eV}$$

and

$$E_{spin-orbit} \sim \left(\frac{\mu_B \mu_0 e \hbar}{m a_0^3 n^3} \right) [j(j+1) - \ell(\ell+1) - s(s+1)]$$

and that

$$E = m_j g_j \mu_B B,$$

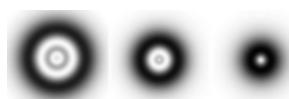
sketch an energy level diagram of the $1s$ and $2p$ states with relevant quantum numbers and energy ordering (there is no need to compute the actual energy) for:

- (i) A Schrödinger wave-mechanics model. [2]
- (ii) A quantum mechanical model that includes spin. [4]
- (iii) A quantum mechanical model that includes spin and with an applied constant magnetic field. [4]



Part D: More than a single electron

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Section 19

Electronic states of many electron atoms

19.1 Assumption

Electrons now feel two forces

- Attraction to the nucleus
- Repulsion from other electrons.
- The time independent Schrödinger equation cannot be solved explicitly.
- We make simplifying assumptions that electrons feel the average effect of repulsion from other electrons, leading to an effective potential energy for each electron that is still a function of the radial distance r only.

We therefore write a two electron wavefunction as

$$\approx \quad (19.1)$$

- Where e_1 represents all the quantum numbers of the first electron (n_1, ℓ_1 etc.) and e_2 represents all the quantum numbers of the second electron.
- where $|e_1\rangle$ and $|e_2\rangle$ are hydrogen-like orbitals, which means we can still use the quantum numbers n and ℓ as labels.
- Note that $Y_{\ell,m_\ell}(\theta, \phi)$ is the angular wavefunction for any central potential $V(r)$ so is still valid here for Z protons.

19.2 Screening and energy ordering

The main effect of the repulsion between electrons is to reduce the effective nuclear charge felt by each electron. This is known as screening.

- Consider the distribution of electron charge $\rho(r)$ inside some radius a
- See figure 19.1 for an example of s orbitals.



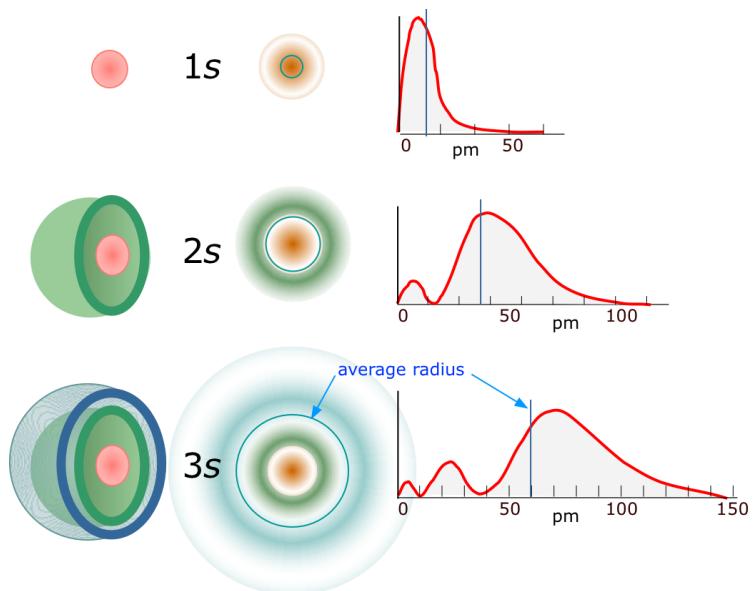


Figure 19.1: 3D pictures and radial distribution for s orbitals [12].

- To an electron outside a the overall effect is as if all of the charge inside a is located at the origin (Gauss' law).
- By analogy with the Hydrogen atom we can write

(19.2)

where Z_{eff} is the effective nuclear charge felt by an electron in the n, ℓ state (other quantum numbers do not alter the physical shape of the orbital).

- $Z_{\text{eff}} \rightarrow 1$ for orbitals with probability density mostly outside the charge sphere of all the other electrons, e.g., Li, Na, K.
- The larger the effective charge the more tightly bound (lower in energy) is that electron.
- Z_{eff} is largest for orbitals with a large probability density near the nucleus (see figure 3.3b)
- Z_{eff} larger for smaller n
- For a given n Z_{eff} larger for smaller ℓ .

Why?

- Orbitals increase in energy (less bound) with increasing ℓ .
- A careful look at figure 19.2 and you can see
 - ⇒ that the $3s$ shell has a small probability density close to the nucleus
 - ⇒ more so than the $3p$
 - ⇒ more so than the $3d$
- This little bump can drop the energy s shell for that level below the energy of some of the sub-shells in a lower n state.
 - ⇒ Hence we get the snake diagram to tell us how to populate energy states.



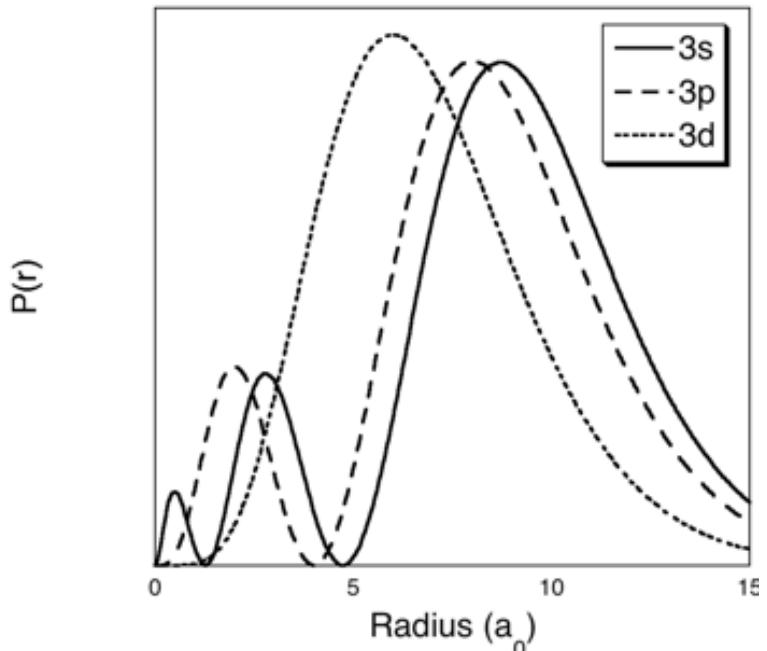


Figure 19.2: Radial probability density for the $n = 3$ state. Note the tails at small r for the s -state.

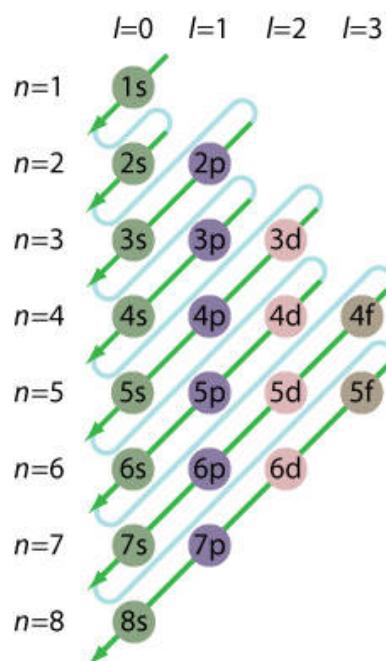
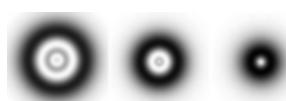


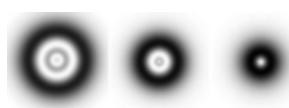
Figure 19.3: How to fill up your energy levels (almost) [13].



19.2.1 Electron configuration

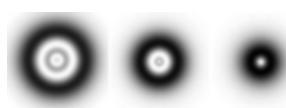
- Many-electron orbitals still carry the n quantum number labels and electrons with the same n tend to be found at similar mean distances from the nucleus. This directly leads to a “shell” structure. The maximum occupancy of a shell is still $2n^2$.
- Electrons with the same ℓ within a given shell are said to be in the same sub-shell. And of course the maximum occupancy of the sub-shell (s , p , d , etc.) is still $2(2\ell + 1)$.
- Electrons in filled shells are called core electrons. They have large ionization energies and are chemically inert.
- Electrons in partially filled shells are called valence electrons and are the ones involved in chemical reactivity, the formation of bonds, and in optical spectra.

Hence we can construct the table (19.1) of electronic configurations for the elements and hence the Periodic table of the elements.



Atomic Number	Name	Symbol	Electron Configuration
1	Hydrogen	H	$1s^1$
2	Helium	He	$1s^2 = [\text{He}]$
3	Lithium	Li	$[\text{He}]2s^1$
4	Beryllium	Be	$[\text{He}]2s^2$
5	Boron	B	$[\text{He}]2s^22p^1$
6	Carbon	C	$[\text{He}]2s^22p^2$
7	Nitrogen	N	$[\text{He}]2s^22p^3$
8	Oxygen	O	$[\text{He}]2s^22p^4$
9	Fluorine	F	$[\text{He}]2s^22p^5$
10	Neon	Ne	$[\text{He}]2s^22p^6 = [\text{Ne}]$
11	Sodium	Na	$[\text{Ne}]3s^1$
12	Magnesium	Mg	$[\text{Ne}]3s^2$
13	Aluminium	Al	$[\text{Ne}]3s^23p^1$
14	Silicon	Si	$[\text{Ne}]3s^23p^2$
15	Phosphorous	P	$[\text{Ne}]3s^23p^3$
16	Sulphur	S	$[\text{Ne}]3s^23p^4$
17	Chlorine	Cl	$[\text{Ne}]3s^23p^5$
18	Argon	Ar	$[\text{Ne}]3s^23p^6 = [\text{Ar}]$
19	Potassium	K	$[\text{Ar}]4s^1$
20	Calcium	Ca	$[\text{Ar}]4s^2$
21	Scandium	Sc	$[\text{Ar}]3d^14s^2$
22	Titanium	Ti	$[\text{Ar}]3d^24s^2$
23	Vanadium	V	$[\text{Ar}]3d^34s^2$
24	Chromium	Cr	$[\text{Ar}]3d^54s^1$: anomaly!
25	Manganese	Mn	$[\text{Ar}]3d^54s^2$
26	Iron	Fe	$[\text{Ar}]3d^64s^2$
27	Cobalt	Co	$[\text{Ar}]3d^74s^2$
28	Nickel	Ni	$[\text{Ar}]3d^84s^2$
29	Copper	Cu	$[\text{Ar}]3d^{10}4s^1$: anomaly!
30	Zinc	Zn	$[\text{Ar}]3d^{10}4s^2$
31	Gallium	Ga	$[\text{Ar}]3d^{10}4s^24p^1$

Table 19.1: Electron configuration of the first 4 rows of elements.



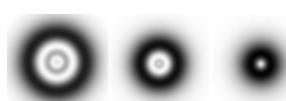
19.3 The Periodic table of the elements

Periodic Table of the Elements

H																			He																																
		Li		Be																				Ne																											
		Na		Mg																				Ar																											
		K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Al		Si		P		S		Cl																	
				Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		As		Se		Br		Kr											
				Cs		Ba		La		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn													
				Fr		Ra		Ac		Unq		104		105		106		107		108		109		110		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb	
				Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr		103																			

Figure 19.4: The periodic table of the elements [14].

The periodic table figure 19.4 is an elegant ordering of the elements into like-minded sets. It is just a consequence of the various quantum numbers n and ℓ and the number of states at their electron configuration. The configuration of the valence electrons determines the column (or group) in the periodic table. Whereas the number of filled shells determines the row (or period).



Section 20

Angular Momentum in Many-Electron Atoms

20.1 Total orbital angular momentum L

The total orbital angular momentum \vec{L} is obtained by the vector addition over all valence electrons, i.e., those in unfilled sub-shells,

$$\vec{L} = \quad (20.1a)$$

We use capital letters to distinguish these total quantum numbers from the quantum numbers for each individual electron (e.g., ℓ, m_ℓ). And we can write

$$|\vec{L}| = \quad (20.1b)$$

and

$$L_z = \quad (20.1c)$$

To find all the possible values of L we add the orbital angular momentum for 2 valence electrons with ℓ_1 and ℓ_2 then

$$\leq L \leq \quad (20.1d)$$

where L is an integer. Therefore if

$$\ell_1 = 1 \text{ and } \ell_2 = 2 \quad (20.1e)$$

then

$$L = \quad (20.1f)$$

These represent all the possible ways of adding the individual angular momentum vectors.



20.2 Total Spin Angular Momentum S

In a similar fashion we define the total spin angular momentum \vec{S} as

$$\left| \vec{S} \right| = \quad (20.2a)$$

and

$$S_z = \quad (20.2b)$$

So if there are, say, two valence electrons and we know that $s_1 = s_2 =$ then

$$S = \quad (20.2c)$$

In general S is an integer or half-integer.

20.3 Total Angular Momentum J

Just as above we define the total angular momentum \vec{J} as

$$\vec{J} = \quad (20.3a)$$

$$\left| \vec{J} \right| = \quad (20.3b)$$

and

$$J_z = \quad (20.3c)$$

The possible values of the quantum number J are

$$\leq J \leq \quad (20.3d)$$

with J taking integer steps. Table 20.1 gives a few examples of the possible total angular momentum combinations.

Table 20.1: Total angular momentum quantum numbers.

L	S	J	M_J
2	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}, +\frac{1}{2}$
		$\frac{3}{2}$	$-\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$
		$\frac{5}{2}$	$-\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2}$
		$\frac{7}{2}$	$-\frac{7}{2}, -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2}, +\frac{7}{2}$



20.4 Term Symbols

The values of L , S and J for an atoms are conventionally written as a term symbol.

(20.4)

so the term symbol has

- The number of possible M_S values
- A letter to represent the total orbital angular momentum

\Rightarrow

\Rightarrow

\Rightarrow

\Rightarrow

- And the total angular momentum quantum number

For example, if $L = 1$ and $S = 1$ then we have $J = 0, 1, 2$ and the possible term symbols

(20.5)

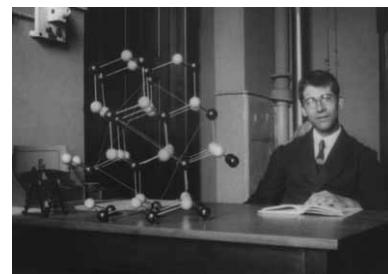
if we have $L = 2$ and $S = 0$ then $J = 2$ and so only 1 term symbol

(20.6)

If there is more than one possible term symbol (i.e., atomic configuration) how do we choose the lowest energy state, the ground state?

20.5 Hund's rules

Figure 20.1: Friedrich Hermann Hund (1896 - 1997) worked with such prestigious physicists as Schrödinger, Dirac, Heisenberg and Max Born. He appears to have had his office in the [steam pipe trunk distribution venue](#).



For an atom with a given number of valence electrons, there are usually several possible values of L , S and J . Which combination gives the lowest energy, i.e., which is the ground state? We use Hund's rules to find out.



20.5.1 Rule 1: arrange m_s to maximise S

This rule will minimise the ‘exchange’ energy (the ‘Exchange interaction’ is beyond this course).

- Put valence electrons into the highest M_s states (consistent with the exclusion principle) so that the ground state S is given by

$$S = \dots \quad (20.7)$$

20.5.2 Rule 2: arrange m_ℓ to maximise L

- Distribute electrons among the m_ℓ states to maximise L .
- This tends to minimise the electrostatic repulsion hence lower the overall energy.
- The average distance between electrons tends to be larger for larger L .
- To apply this rule, add electrons one at a time into the highest m_ℓ states (still consistent with the exclusion principle) then

$$L = \dots \quad (20.8)$$

20.5.3 Rule 3: Maximise or minimise J

- If a sub-shell is less than half filled, then the ground state has the smallest allowed J value.
- If a sub-shell is more than half full, then the ground state has the largest allowed J value.
- These rules minimise the magnetic spin-orbit interaction energy.

20.5.4 Term symbol examples

Phosphorus

Phosphorus has an unfilled sub-shell, with electronic structure [Ne]3s²3p³ (see table 19.1). So it has an unfilled sub-shell p³ and three valence electrons.

- Rule 1: arrange m_s to maximise S
 \Rightarrow All three electrons can sit in different m_ℓ states hence they can all have $m_s = \pm \frac{1}{2}$.
- Rule 2: arrange m_ℓ to maximise L
 \Rightarrow Since all electrons have the same spin, they cannot be in the same m_ℓ state (exclusion). They are in a p sub-shell so possible m_ℓ are -1, 0, 1. So we have but one choice, one electron in each m_ℓ state giving $L = 0$.
 \Rightarrow For a half filled shell L is always 0.



- Rule 3: maximise or minimise J .

⇒ Only one value of J , .

- Term symbol for P is



Figure 20.2: P valence electrons for $^4S_{3/2}$

Argon

Argon has the electronic structure $[Ne]3s^23p^6$ (see table 19.1). So it has a filled sub-shell p^6 and six valence electrons.

- Rule 1: arrange m_s to maximise S

⇒ Since we have 6 electrons and 3 m_ℓ states, we must have a pair in each m_ℓ state and $S = 0$.

- Rule 2: arrange m_ℓ to maximise L

⇒ From rule 1 we have no choice but to put two electrons into each m_ℓ state, giving $L = 0$.

- Rule 3: maximise or minimise J .

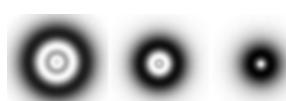
⇒ Only one value of $J = 0$.

⇒ For a filled shell $S = L = J = 0$.

- Term symbol for Ar is 1S_0



Figure 20.3: Ar valence electrons for 1S_0



Section 21

Spectra of Many-Electron Atoms

Here we will illustrate the spectra produced by many-electron atoms by considering two examples, sodium and helium. In both cases, only one electron is excited to a higher energy level since excitations of two electrons costs much more energy.

21.1 Sodium atoms

Sodium has the energy level configuration

(21.1)

And hence the term symbol

(21.2)

Only the electron in the $3s$ is involved in the optical spectrum. [figure 21.1](#) for energy level diagram. The energy of the excited states increases with ℓ for a given n because of screening effects. Screening is greatest for larger n and for large ℓ , since $Z_{\text{eff}} \rightarrow 1$.

We have the new selection rule

= (21.3)

and

= (21.4)

For Sodium, ℓ and L are the same as there is only 1 valence electron. So we can photo-excite our electron from, say, the $3s$ to the $3p$, or an excited atom with the electron in the $3p$ may drop that electron down to the $3s$ and emit a photon. The [figure 21.2](#) shows the spectrum of emitted light from this transition - we see two lines. Why?

21.1.1 Sodium Doublet

There is fine-structure due to spin-orbit splitting. Each excited state is split into two with $J = L \pm 1/2$, except for the s -states which are not split. So for the $3p$ we have (see figure 21.3) a small energy difference between the the $J = 3/2$ and $J = 1/2$ states.



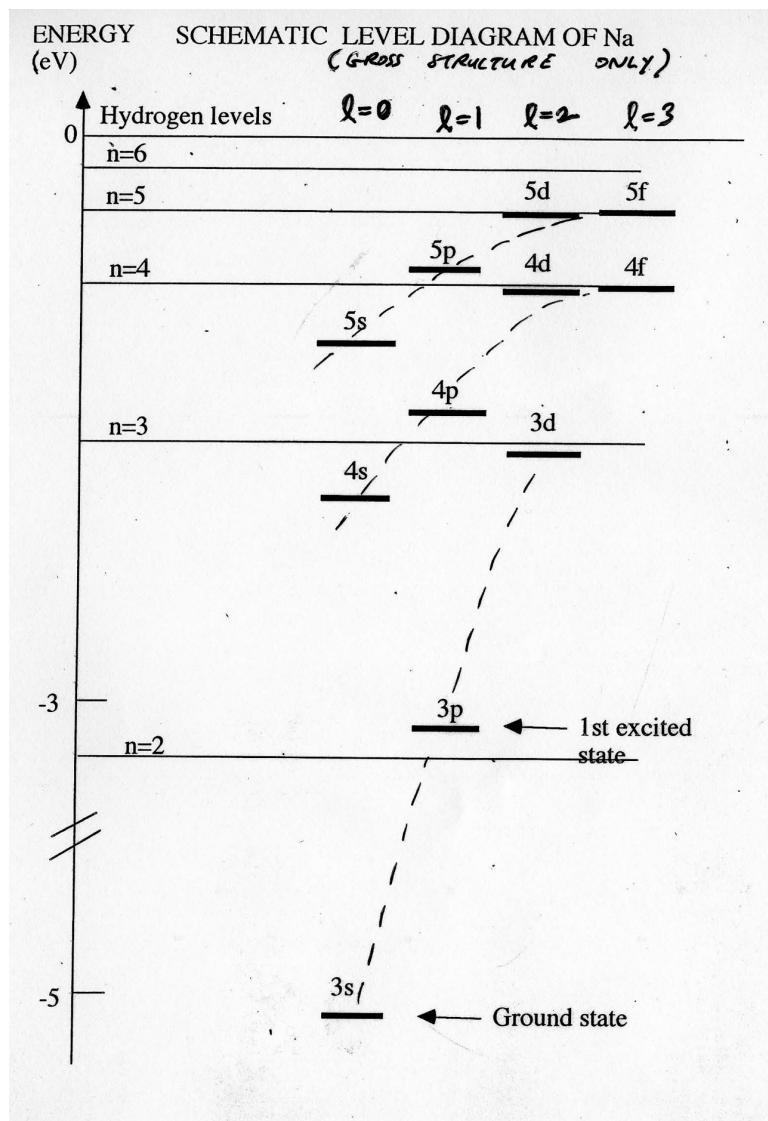


Figure 21.1: Energy level diagram showing gross structure only for Sodium.

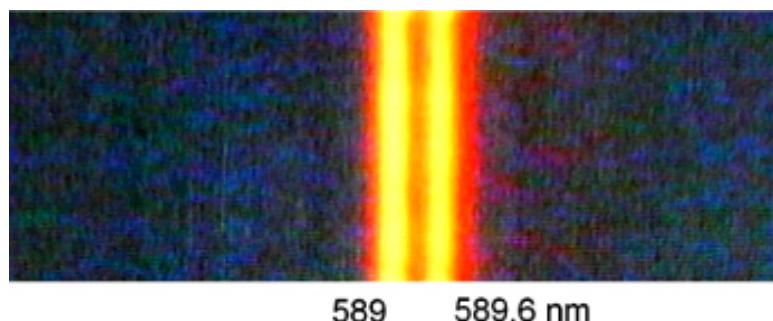
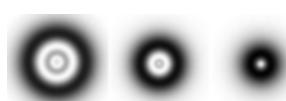


Figure 21.2: Emission spectrum of sodium for $3p \rightarrow 3s$ transition.



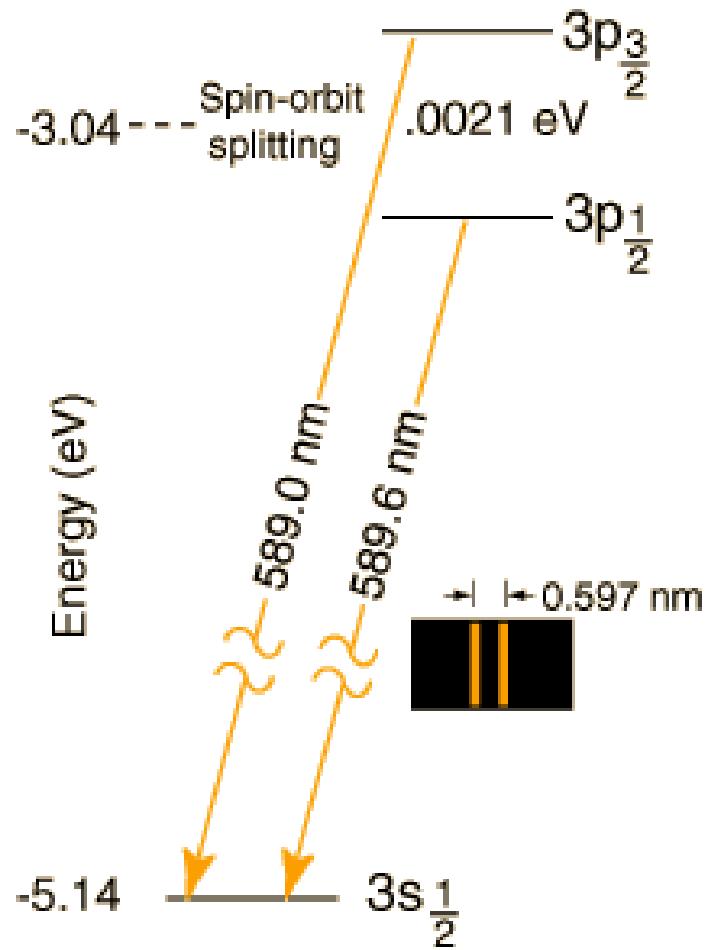
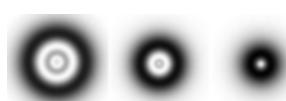
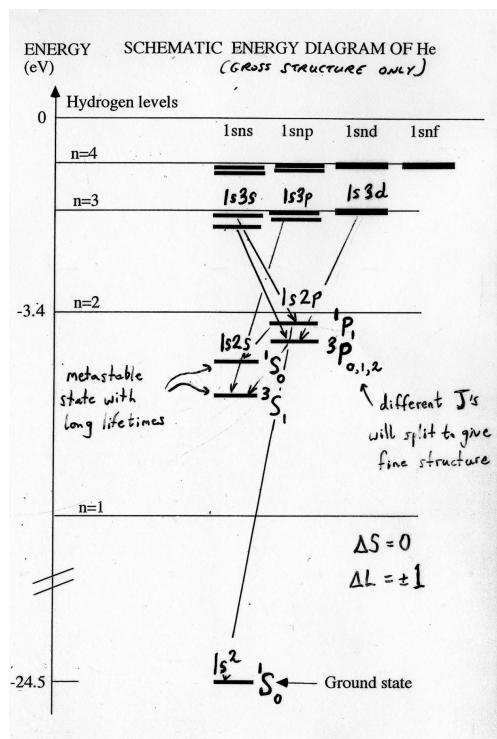


Figure 21.3: Spin orbit splitting of the $3p$ states[15].

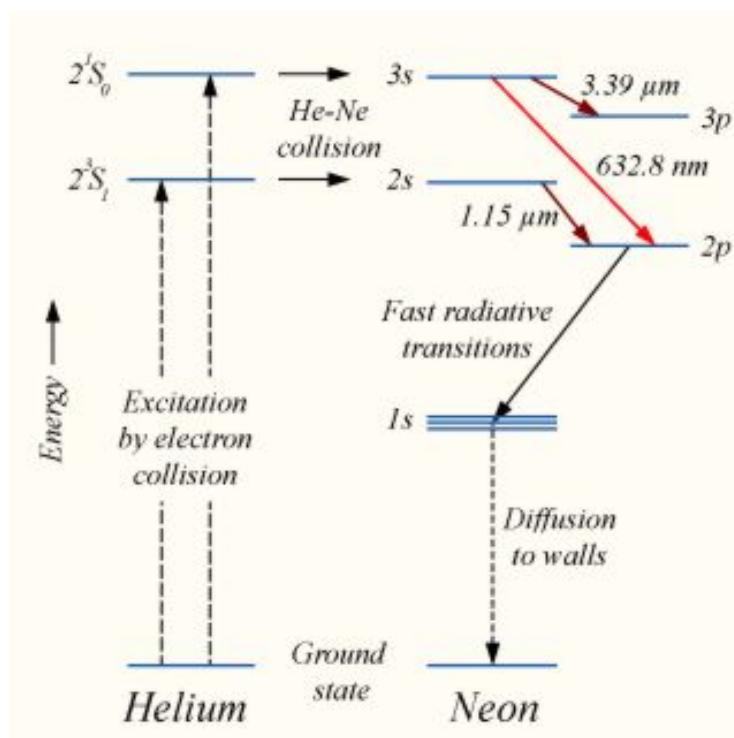
21.2 Helium atoms

The ground state configuration is $1s^2$. Consider excited states where one electron has left the $1s$ orbital. See [figure 21.4a](#) for a sketch of the energy level diagram. Now note that not all transitions are allowed. Not only must $\Delta L = \pm 1$ but also $\Delta S = 0$. Hence there are long lived excited states of S character as these are forbidden to decay into the ground state. In fact these can be used to transfer energy to Neon atoms (fig. 21.4b) which can then emit light and be turned into a HeNe Laser.



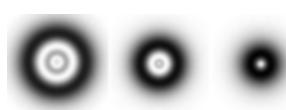


(a) Energy level diagram showing gross structure only for Helium.



(b) Energy level diagram for a He Ne laser [16].

Figure 21.4: He and HeNe



Section 22

Problems for part D

P19: 1s E for Z?

Following a similar recipe to that outlined in the notes, for a one electron atom with a nuclear charge Z , show that the 1s state has the form $\psi(r, \theta, \phi) \propto \exp(-Zr/a_0)$ and that the energy of its 1s state is simply Z^2 times that of hydrogen.

P20: More terms please

Consider a many electron atom

- (a) Describe the three components that make up a term symbol. [2]
- (b) What is the term symbol for the ground state of an oxygen atom? [6]

P21: Term symbol for Iron

Iron has $[\text{Ar}]3\text{d}^64\text{s}^2$. What is its term symbol?

P22: S-G beams

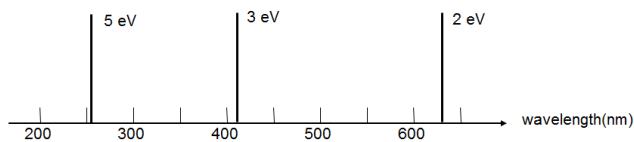
How many beam are generated in a Stern-Gerlach experiment for:

- Si 3P_0 :
- P ${}^4S_{3/2}$:
- Ar 1S_0 :
- Fe 5D_4 :

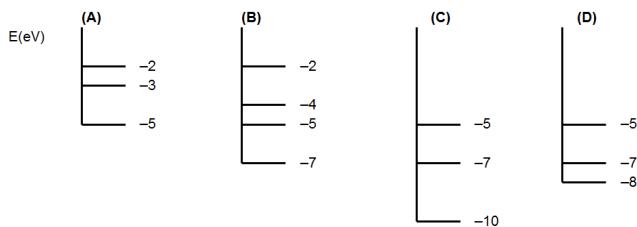


P23: Bathium

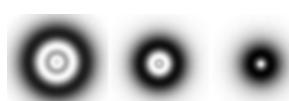
The spectrum of “Bathium” has only 3 emission lines.



Which energy level structure is consistent with the spectrum?

**P24: Na lamp [analysis, hard]**

A low pressure ^{23}Na lamp at an effective temperature of 500 K emits light in transitions between the 3p and 3s states at a wavelength of 589 nm. The natural lifetime of the 3p state is 16 ns. What is the natural and Doppler line widths in eV of this transition?



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