PHY2005
Atomic Physics

Lecturer: Dr. Stuart Sim

Room: 02.019

E-mail: s.sim@qub.ac.uk

(4) Single-electron atoms: space wavefunctions

Learning goals

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

Single-electron atom TISE

For single electron atom, the TISE is:

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

where the potential is given by

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

We can find solutions that are separable in the three space coordinates:

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Separated equations

Separation of variables (see also PHY2001) leads to

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

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

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

Separated equations: implications

Comparing to the angular momentum operators (last section):

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m_l^2\Phi \qquad\qquad \hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

implies that

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

Separated equations: implications

Similarly, comparing:

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

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

implies that

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

Separated equations: implications

So solutions are simultaneous eigenfunctions of energy, of $\hat{\mathbf{L}}^2$ and of $\hat{L}_z$.

It is convenient to identify the states by their eigenvalues of these quantities, or equivalently the associated quantum numbers…

Separated equations: quantisation

Solving the separated equations leads to quantisation: results are summarised in the table:

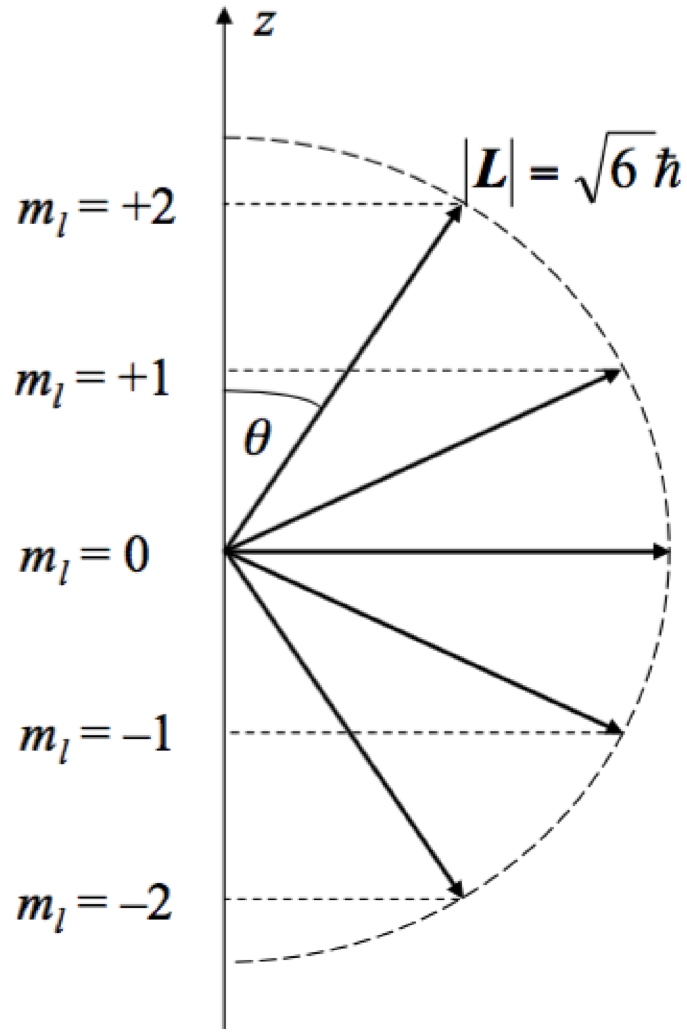
Physical quantity	Eigenvalue	Quantum number	Quantization
E	$-\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$	n	$n > 0$
$\lvert\mathbf{L}\rvert$	$\sqrt{l(l+1)}\hbar$	l	$0 \leq l < n$
L_z	$m_l\hbar$	m_l	$-l \leq m_l \leq l$

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

The quantum numbers *n, l* and m_l are used as labels to identify particular states.

Vector model of quantised angular momentum

Example for l=2: magnitude and z-component quantised



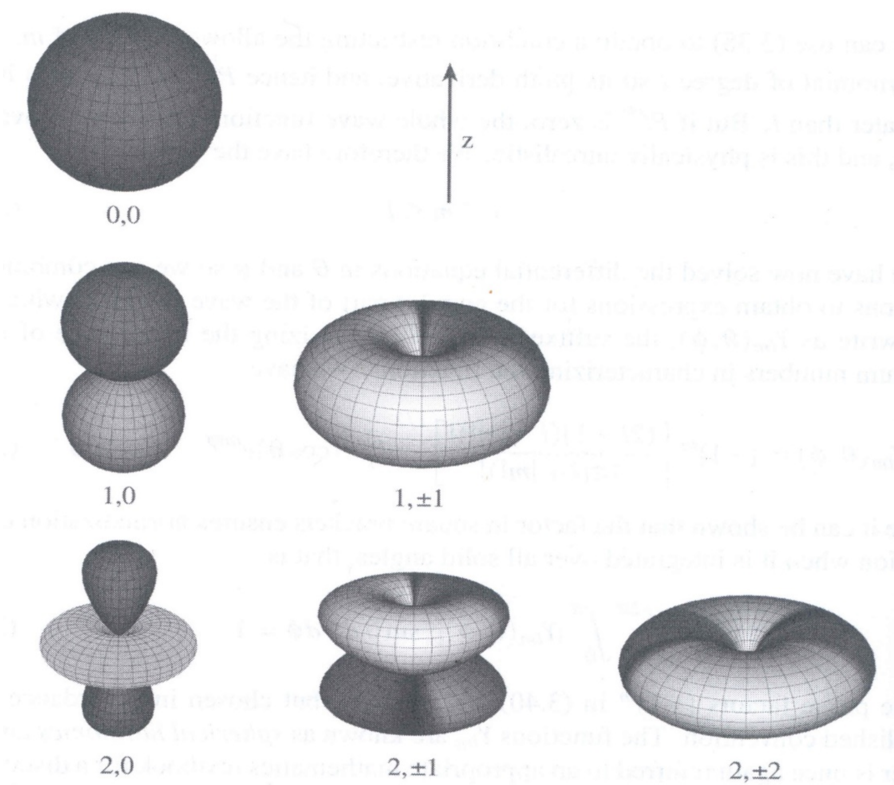
Example solutions

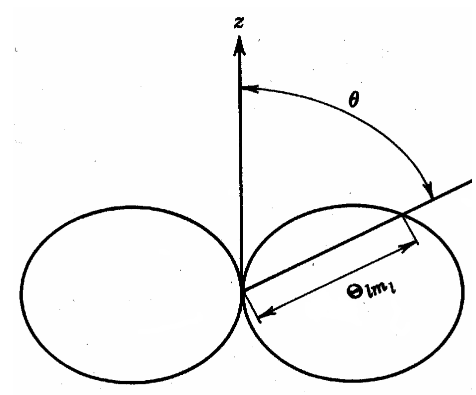
Quantum Numbers			
n	l	m_l	Eigenfunctions
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2}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

From PHY2001 notes

Visualising Spherical Harmonics

- Some Y_{lm} orbitals are below. For $m_l = 0$ the dark and light regions are of opposite sign; when $m_l \neq 0$ the function is complex and its phase changes by $2m_l\pi$ during a complete circuit of the z axis.



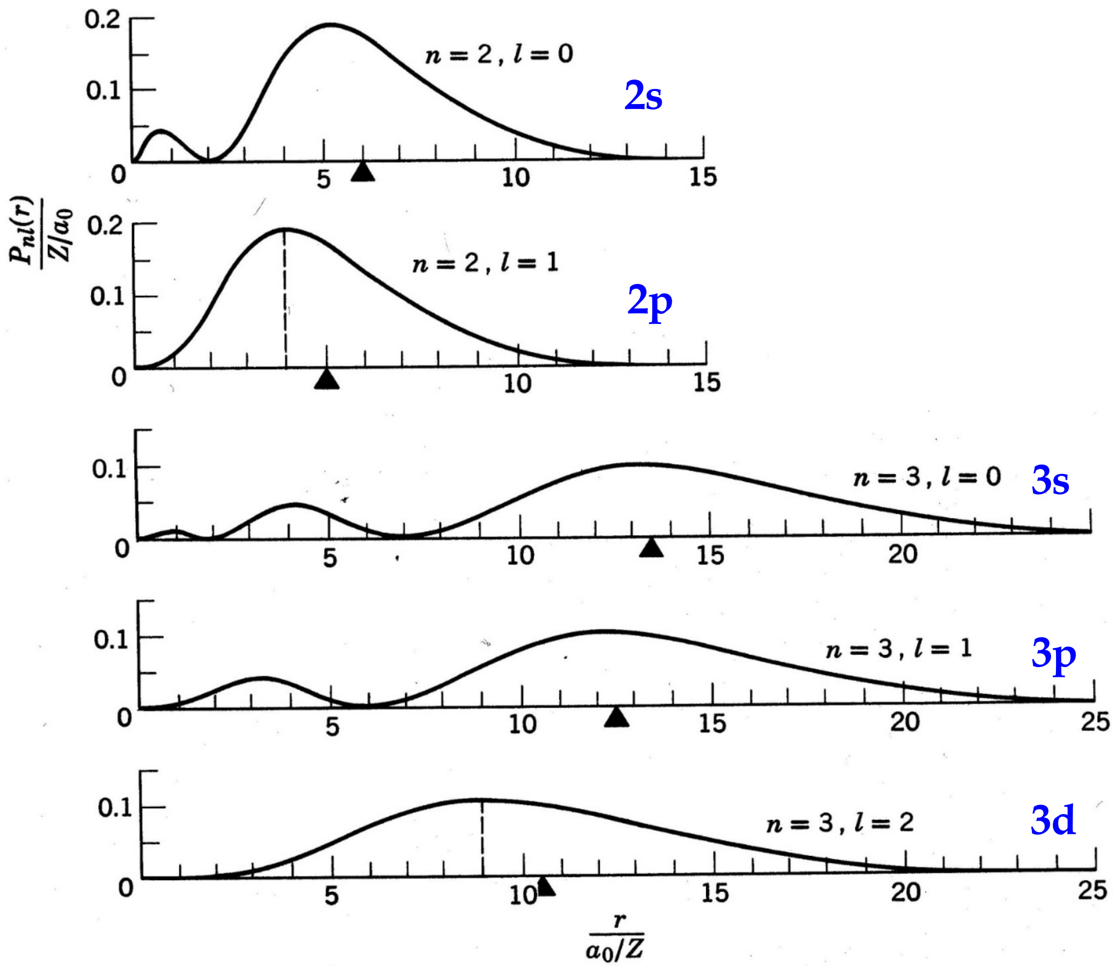


The best way to visualise angular functions is using a polar plot above. On the left are 3D polar plots

From PHY2001 notes

Radial Probability Distributions in Hydrogen

$$\boxed{P_{nl}(r)dr = 4\pi r^2 |R_{nl}(r)|^2 dr}$$



- Note
  - For larger l (higher angular momentum) there is lower probability of being close to zero
  - Number of nodes ($P(r) = 0$) equal to $n - l - 1$

Summary/Revision

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