6 Schroedinger in 3D - spherical polar coordinates

so we really need to put the proper potential in. but $1/R = 1/(x^2 + y^2 + z^2)^{1/2}$ which is NOT separable as $V(x) + v(y) + V(z)$. we cannot use cartesian coordinates - and in fact we would expect to be using spherical polars as they follow the symmetry of the potential.

In spherical polars we have $r = \sqrt{x^2 + y^2 + z^2}$, $\cos\theta = z/r$ and $\tan\phi = y/x$. and then our potential $U(r, \theta, \phi) = U(r)$. Then the wavefunction can be separated into $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$ similarly to the cartesian problem above where we had $\psi(x, y, z) = X(x)Y(y)Z(z)$. After a LOT of maths (that you will tangle with in 2nd year) we get three differential equations:

$$\frac{-\hbar^2}{2\mu r^2}\frac{d}{dr}\Big(r^2\frac{dR}{dr}\Big) + \Big(\frac{\hbar^2 l(l+1)}{2\mu r^2} + U(r)\Big)R(r) = ER(r)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\Big(\sin\theta\frac{d\Theta(\theta)}{d\theta}\Big) + \Big(l(l+1) - \frac{m_l^2}{\sin^2\theta}\Big)\Theta(\theta) = 0$$

$$\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi(\phi) = 0$$

where l, m_l are quantized constants and we are calling mass μ to distinguish it from m_l. Essentially the boundary conditions produce 3 integer quantum numbers (one for each direction!) which are n, l, and m_l.

For any radial potential then we can get these wavefunctions - and only the first equation changes with changing the shape of the potential. it is this equation which sets the third quantum number n, while l, m_l are talking about the angular dependence which is set by the assumption that the potential is radial.

For hydrogen we need to solve these equations (horrible maths) for the specific potential $U(r) = -e^2/(4\pi\epsilon_0 r)$.

When we do this (second year!) we find that the energy E_{n,l,m_l} is actually only a function of n

$$E_n = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = -\frac{13.6}{n^2}\ \text{eV}$$

so it reproduces what we see in Hydrogen!! which is what the Bohr atom did for us but this time we're getting here via a wave equation.

n is called the principle quantum number. Ground state is $n = 1$

l is called the orbital quantum number and runs from $0, 1 \ldots n - 1$
    This appears alongside the potential in the radial Schroedinger equation

$$\frac{-\hbar^2}{2\mu r^2}\frac{d}{dr}\Big(r^2\frac{dR}{dr}\Big) + \Big(\frac{\hbar^2 l(l+1)}{2\mu r^2} + U(r)\Big)R(r) = ER(r)$$

in classical mechanics, we'd associate cetripetal force $F = \mu v^2/r$ - but angular momentum is $L = \mu v r$ and this is conserved. so $F = L^2/(\mu r^3)$. this is associated with a potential as $U = \int F dr$ so the conservation of angular momentum means that there is an additional potential term $U = L^2/(2\mu r^2)$

this suggests that we should associate $L^2 = \hbar^2 l(l+1)$, ie that l is talking about angular momentum. This is quantised as l is an integer - which just comes out of the maths now rather than being Bohrs assumptions. and in fact this differs from Bohr as the magnitude of the angular momentum is $|L| = \hbar\sqrt{l(l+1)}$ whereas Bohr has $|L| = n\hbar$

m_l is called the magnetic quantum number and runs from $= -l, -l + 1 \ldots l - 1, l$
m_l: magnetic quantum number
    total angular momentum $L^2 = L_x^2 + L_y^2 + L_z^2$ and we can know this as its quantised into a definite value.
    But it should also have a direction - which I'm going to talk about in terms of cartseian coordinates as its easier
    $\vec{L} = L_x\mathbf{i} + L_y\mathbf{j} + L_z\mathbf{k} = \vec{r} \times \vec{p}$
    so in here there will be problems - this is about position and momentum! and we know from heisenburg that we can't constrain these to arbitrary accuracy simultaneously. so we can't know all the individual components of $\vec{L}$. But we can know the magnitude of ONE of them along with the total angular momentum. we pick the projection onto the z axis (as it makes the maths easier). see the linked picture to visualise this.

6.1   Wavefunctions

The radial wavefunction $R(r)$ is set by BOTH n, l so better to write it as $R_{nl}(r)$

$$R_{10} = \frac{2}{\sqrt{a^3}} e^{-r/a}$$

$$R_{20} = \frac{1}{\sqrt{2a^3}} a^{-3/2} (1 - \frac{r}{2a}) e^{-r/(2a)}$$

$$R_{21} = \frac{1}{\sqrt{24a^3}} \frac{r}{a} e^{-r/(2a)}$$

The angular wavefunctions are $\Theta(\theta)$ which depends on l, m_l and $\Phi(\phi)$ which depends only on m_l. The combination $Y_l^{m_l} = \Theta_{l,m_l} \Phi_{m_l}$ are called spherical harmonics and are the same for ANY radially symmetric potential (eg the 2D harmonic oscillator $U = \frac{1}{2} k'(x^2 + y^2 + z^2) = \frac{1}{2} K' r^2$)

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

hence the ground state is $\psi_{100} = R_{10} Y_0^0 = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$

6.2 probability densities

BEWARE THE VOLUME ELEMENT $dV = r^2 \sin\theta dr d\theta d\phi \neq dr d\theta d\phi$

probability of finding the electron within volume element dV is

$$P(r, \theta, \phi) dV = \psi^* \psi dV = |R_{nl}|^2 |Y_l^{m_l}|^2 r^2 \sin\theta dr d\theta d\phi$$

radial probability density distribution - probability to find within dr of r

$$P(r) dr = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} P(r, \theta, \phi) dV = r^2 |R|^2 dr \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} |Y_l^{m_l}|^2 \sin\theta d\theta d\phi = |R_{nl}|^2 r^2 dr$$

but both R and ψ are really nasty maths functions - use wolfram alpha to visualise the radial probability distribution and see the links from the website for visualisation of the wavefunctions and probability densities

6.3   Degeneracies

for each n, the energy level is determined, but there are other quantum numbers associated with the angle symmetries so there are degeneracies!

so for n=1, we can only have l=0 and $m_l = 0$. single level, non degenerate

$n = 2$, so $l = 0$ and $m_l = 0$ AND $l = 1$ which can have $m_l = -1, 0, 1$ so 4 distinct states all with the SAME ENERGY - degeneracy 4.

$n = 3$, so $l = 0$ and $m_l = 0$ AND $l = 1$ which can have $m_l = -1, 0, 1$ AND $l = 2$ so $m_l = -2, -1, 0, 1, 2$, so 9 distinct states all with the SAME ENERGY - degeneracy 9.

6.4   spectroscopic notation

spectra were studied long before quantum mechanics! so the terminology just has to be learnt!

spectroscopic notation - think chemistry!
$l = 0$ s states
$l = 1$ p states
$l = 2$ d states
$l = 3$ f states states with same principle quantum number n are in the

same 'shell'
$n = 1$ called K shell
$n = 2$ called L shell
$n = 3$ called M shell
$n = 4$ called N shell
(at least these are alphabetic!)

Table 41.1 Quantum States of the Hydrogen Atom

n	l	m_l	Spectroscopic Notation	Shell
1	0	0	$1s$	K
2	0	0	$2s$	L
2	1	$-1, 0, 1$	$2p$	
3	0	0	$3s$	
3	1	$-1, 0, 1$	$3p$	M
3	2	$-2, -1, 0, 1, 2$	$3d$	
4	0	0	$4s$	N

and so on

Figure 1:

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