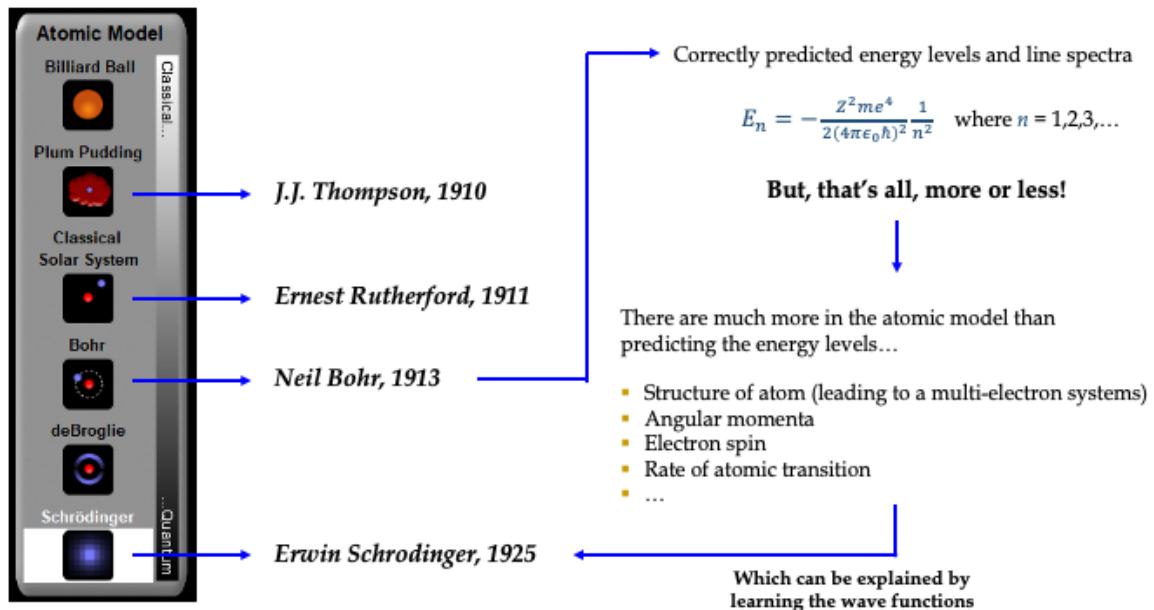


Part-4

Hydrogen Atom

The hydrogen atom – the simplest two body problem. - yet the topic that kept physicists excited for decades

<https://phet.colorado.edu/en/simulation/legacy/hydrogen-atom>



- A little history of quantum mechanics, which we called the “old Quantum Theory”. Most of these has been covered already in the first part.
- The screenshot is taken from the link mentioned in the slide, <https://phet.colorado.edu/en/simulation/legacy/hydrogen-atom> which is an interesting one to check out.
- Most interesting is to note the difference between the representation of electron orbitals between Bohr (classical circular orbit), deBroglie (orbit enclosed by a standing wave) and Schrodinger’s model (3D orbitals and shapes defined by the probability density of electrons). As per the Schrodinger’s model (all earlier models belongs to old quantum theory), an electron in higher energy state may also be found closer to the nucleus, sharing the space with the electrons in the ground state. Very interesting and exhilarating physics which we are now going to look at in detail.

Limitations of the Bohr's Model :

Bohr postulates in a nutshell: (just to remind ourselves)

- Electron moves in circular orbit about a nucleus (nucleus is infinitely heavy and fixed)
- Orbital angular momentum is quantised : $mvr = n\hbar$
- Electrons do not emit radiation (lose energy) if in one of these "stable" orbits.
- Electrons change its orbit by emitting/absorbing photons.

Correctly predicted energy levels and line spectra

$$E_n = -\frac{Z^2 m e^4}{2(4\pi\epsilon_0 \hbar)^2} \frac{1}{n^2} \quad \text{where } n = 1, 2, 3, \dots$$

And reasonably matched the five different series of hydrogen spectra
(Lyman, Balmer, Paschen Brackett and Pfund)

explained many other features of atomic spectra measured very accurately, such as,
difference between spectra between isotopes (for ex. Hydrogen and deuterium) using reduced mass of
electron.

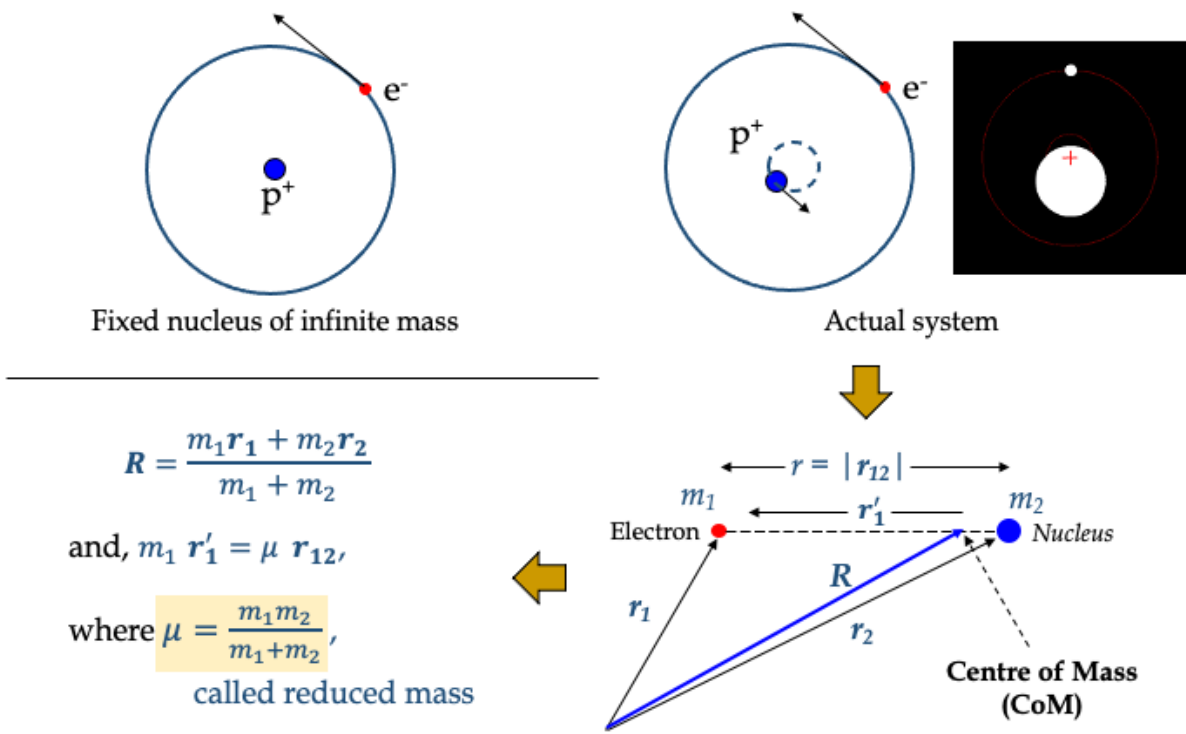
Where are the limitations?

- Could not provide a detailed picture of the atom (probability density distribution). The system should better be represented in 3D - Bohr only considered radial component, $mvr = n\hbar$
- Did not account for Electron spin, could not explain rates of atomic transitions.
- could not be applied to multi-electron systems (non-periodic systems)

How to resolve : Find wave function using T.I.S.E using reduced mass of electrons

- A recap of Bohr's model and what it can or can't explain. The Schrodinger's model is nothing but a combination of Bohr's and deBroglie concepts, with a lot of maths...
- Please take a look at the sections of Eisberg book (chapter 4 and 7) for more details around this topic.

Reduced mass instead of actual mass of electron :



- Since the nucleus is not of infinite mass, it is not stationary. Both the nucleus and electron orbit around a center of mass, very similar to a planetary motion. Therefore, if we use the reduced mass of electron in the Schrodinger's equation, instead of its rest mass, it automatically fixes the problem.
- The reduced mass of the electron can be found out by considering the moments, as shown in the slide. The 'R' points to the center of mass of the system. The concept of center of mass and two-body system, as shown in this slide, must be familiar to you from Level 1. You can watch the nice video here to refresh...

<https://www.youtube.com/watch?v=ayv0MoCgtlk>

(From beginning to ~3 min, then from 5.3 min onwards)

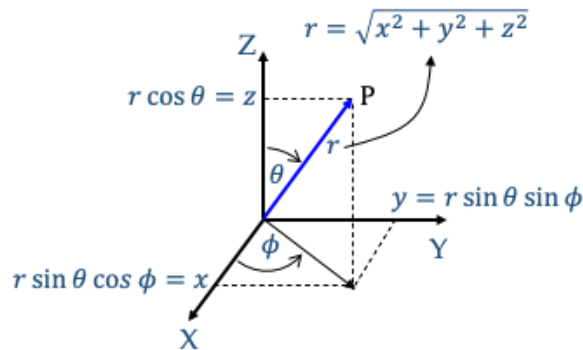
There are also many webpages with full derivations, for instance,

http://eng-web1.eng.famu.fsu.edu/~dommelen/quantum/style_a/nt_mred.html

Degrees of freedom and Co-ordinate system

- One electron atom is the simplest bound system in nature, yet not perfectly symmetrical from all sides.
- Must assume, at least to start with, 3 degrees of freedom !
- Best would be to use spherical polar co-ordinate system instead of cartesian !!!
(although it implies some mathematical complexity ☹)

Spherical polar coordinate system (r, θ, ϕ)



$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

- Here to say we need to consider the problem in 3 dimensions and more importantly using a spherical polar coordinate system. This is because of the coulomb potential, which is radially symmetrical.
- In fact, we can use the cartesian co-ordinate system, while defining the Coulomb's potential as

$$V(x, y, z) = \frac{1}{4\pi\epsilon_0} \frac{-Ze^2}{\sqrt{x^2 + y^2 + z^2}}$$

But it will make the mathematics very difficult due to the term $\sqrt{x^2 + y^2 + z^2}$ in the denominator. We cannot decouple the coordinates when we try to split the partial differential equations.

On the other hand, if we use the spherical polar co-ordinate system, the Laplacian operator becomes too complicated, but it not too bad to handle as, at least, we can use the separation of variable method. And this is possible as the coulomb potential has θ and ϕ symmetry (only a function of r)

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{-Ze^2}{r}$$

(in cartesian coordinate system we can not split the potential into terms, each of which involve only one coordinate)

Solution to T.I.S.E. for hydrogenic atom

Aim: to find out the eigen function and eigen values (energy states) of the electron.

- define potential :

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

- write down T.I.S.E : (in 3D and spherical polar)

$$\frac{\hbar^2}{2\mu} \nabla^2 \psi(r, \theta, \phi) + [E - V(r)] \psi(r, \theta, \phi) = 0,$$

$$\text{where, } \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

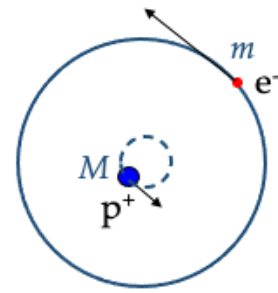
- define general expression for the eigen function :

Since the potential is a function of 'r' only, we can use separation of variable technique to solve the T.I.S.E.

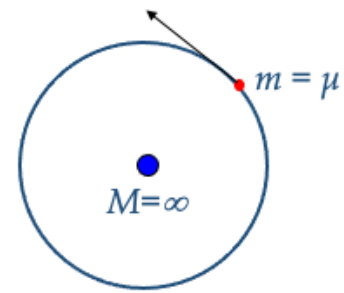
$$\psi(r, \theta, \phi) = R(r) \times \Theta(\theta) \times \Phi(\phi)$$

Hence, the T.I.S.E. can be written as

$$\frac{\hbar^2}{2\mu} \left[\frac{\Theta(\theta)\Phi(\phi)}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{R(r)\Phi(\phi)}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{R(r)\Theta(\theta)}{r^2 \sin^2 \theta} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} \right] + [E - V(r)] R(r)\Theta(\theta)\Phi(\phi) = 0$$



Actual system



Modelled system

- Here is starting of a tedious mathematics, but most of the complicated bits are removed and you will not be asked in exams to derive in full. But you must understand and conceptualise all steps and should be able to explain or derive small section of it. Please refer to past papers for the type of questions asked from this derivation.
- The recipe is again exactly the same as we used for the problems before. The things to change here are – (1) use reduced mass and (2) use spherical polar.
- As mentioned in the slide, the eigenfunction can be expressed as the product of three function, each one function of one coordinate only.
- Then you get the last equation in the slide, which has all these changes incorporated, and we now need to solve this to get the expression for eigen function ($\psi = R\Theta\Phi$), which will tell us how the electron exist in the atom in 3D, what are its energy levels, and any further interesting aspects we can find (and we will...). Looking at this last equation of the slide, it seems a very, very.... difficult task, but actually, it is not 😊.

c.f.
$$\frac{\hbar^2}{2\mu} \left[\frac{\Theta(\theta)\Phi(\phi)}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{R(r)\Phi(\phi)}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{R(r)\Theta(\theta)}{r^2 \sin^2 \theta} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} \right] + [E - V(r)]R(r)\Theta(\theta)\Phi(\phi) = 0$$

dividing by $R(r)\Theta(\theta)\Phi(\phi) \dots$

$$\Rightarrow \frac{\hbar^2}{2\mu} \left[\frac{1}{R(r)r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{1}{\Theta(\theta)r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{1}{\Phi(\phi)r^2 \sin^2 \theta} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} \right] + [E - V(r)] = 0$$

multiplying by $r^2 \sin^2 \theta$,

$$\Rightarrow \frac{\hbar^2}{2\mu} \left[\frac{\sin^2 \theta}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{\sin \theta}{\Theta(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} \right] + [E - V(r)] r^2 \sin^2 \theta = 0$$

$$\Rightarrow \underbrace{\frac{\sin^2 \theta}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{\sin \theta}{\Theta(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] r^2 \sin^2 \theta}_{\text{Function of } r \text{ and } \theta} = \underbrace{-\frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2}}_{\text{Function of } \phi \text{ only}} = \alpha \quad (\text{a constant}) \quad (1)$$

Let's first consider the ϕ component.

$$\frac{-1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = \alpha \Rightarrow \frac{d^2 \Phi(\phi)}{d\phi^2} + \alpha \Phi(\phi) = 0 \quad (2)$$

This is a nice differential equation, with general solution of the form

$$\Phi(\phi) = A \exp(i\sqrt{\alpha}\phi) \quad (3)$$

- Ok, some complicated looking, long expressions, but quite trivial algebra. Follow the steps as indicated in the slide, and we will arrive at equation (1). At this stage you see that there is no relation between the left and right hand side. They are functions of different variables, yet are equal. This can only be possible (as both sides are valid expressions) if they both yield a same constant value, as we assumed α here.
- By doing so, we immediately make two short equations. We can first consider the Φ part, which seems the simplest one ☺. Indeed, as you simplify it, you see a very familiar differential equation, which immediately suggest a general form for the Φ .

▪ **apply boundary conditions to the $\Phi(\phi)$:**

- The eigen functions should be single valued!

$\Rightarrow \Phi(\phi)$ and $\Phi(\phi + 2\pi)$ should be the same
(as the azimuthal angles ϕ and $\phi + 2\pi$ are actually the same angles.)

i.e. $\Phi(\phi) = \Phi(\phi + 2\pi)$

$$\Rightarrow \exp[i\sqrt{\alpha}\phi] = \exp[i\sqrt{\alpha}(\phi + 2\pi)]$$

$$= \exp[i\sqrt{\alpha}\phi] \exp[i\sqrt{\alpha} 2\pi]$$

$$\Rightarrow \exp[i\sqrt{\alpha} 2\pi] = 1$$

$$\Rightarrow \cos [\sqrt{\alpha} 2\pi] + i \sin [\sqrt{\alpha} 2\pi] = 1$$

$$\Rightarrow \sqrt{\alpha} \text{ is an integer, say } m_l = 0, \pm 1, \pm 2, \dots \text{ is called the "magnetic quantum number"}$$

(explanation later)

Hence the azimuthal part of the eigen function can be written as

$$\Phi(\phi) = \Phi_{m_l}(\phi) = A \exp(im_l\phi), \text{ where } m_l = 0, \pm 1, \pm 2, \dots \quad (4)$$

We'll come back to its normalisation once we find the r and θ components of the eigen function.

- Now Φ is a function of ϕ (azimuth) only, which is periodic over 2π . So if we use this boundary condition, we can see that the constant α we used has a particular set of values. We can define the term m_l that we will see soon responsible for quantizing the angular momentum of the electron.
- So we now have a definite expression for the Φ , which takes very discrete set of expression.
- Now we will try to find similar level of details for the other two parts of the eigen function, i.e. $R(r)$ and $\Theta(\theta)$.

Now, let's go back to equation (1)

$$\frac{\sin^2 \theta}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{\sin \theta}{\Theta(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] r^2 \sin^2 \theta = -\frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = \alpha = m_l^2$$

$$\Rightarrow \frac{\sin^2 \theta}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{\sin \theta}{\Theta(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] r^2 \sin^2 \theta = m_l^2$$

dividing by $\sin^2 \theta$...

$$\Rightarrow \frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{1}{\Theta(\theta) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] r^2 = \frac{m_l^2}{\sin^2 \theta}$$

$$\Rightarrow \underbrace{\frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] r^2}_{\text{Function of } r} = \underbrace{\frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta(\theta) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right)}_{\text{Function of } \theta} = \beta \quad (\text{another constant}) \quad (5)$$

Let's now consider the θ component.

$$\frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta(\theta) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) = \beta$$

$$\Rightarrow \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left(\beta - \frac{m_l^2}{\sin^2 \theta} \right) \Theta(\theta) = 0 \quad (6)$$

- Lets first simplify a a bit the left hand side of equation (1) in the slide 43.
- This wont be difficult as we can separate out the terms depends on r and θ .
- And we arrive at equation 5, where split the equation in two parts – left hand side depends on r only, and the right hand side depends on θ , yet they give the same result. Hence we can assign another constant term β for instance.
- If we now take the right hand side, we can solve it to get an expression for $\Theta(\theta)$. It does not look as simple as we had for $\Phi(\phi)$, nevertheless, it can be solved analytically using some special polynomial functions.

Equation (5) is not easy to solve. A solution including a series term

$$\sum_{j=0}^{\infty} a_j \cos^j \theta$$

is needed, and a recursion relation for the coefficients a_j can be found, where $a_{j+2} \propto a_j$.

- **apply boundary conditions to the $\Theta(\theta)$:**

To ensure the series doesn't diverge there must be a value of $j = l$ for which $a_l = 0$.

This is only possible for the conditions

- $l = 0, 1, 2, 3, \dots$
- $|m_l| \leq l$ i.e. $m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l$
- which gives a value for $\beta = l(l + 1)$

The solution has the following form (see E&R Appendix N for detailed solution)

$$\Theta(\theta) = B \sin^{|m_l|} \theta P_{l,|m_l|}(\cos \theta)$$

(7)

where B is a constant and P is a polynomial in $\cos \theta$

- The derivation to find a solution for the equation (6) in the previous slide is a bit tedious and is skipped for this module. You can however find it in the Appendix N of the Eisberg book.
- What we will get that the $\Theta(\theta)$ is a series, and if we try to make it a well-behaved, using suitable boundary conditions so that the function does not diverge with θ , it will lead us a set of limiting conditions that defines the possible set of values we can assume for the constant β we used in equation (5).
- Since the equation (6), the differential equation of $\Theta(\theta)$, also contains m_l , we will find that the β depends on the value of m_l , i.e. they both have discrete set of values and one depending on other. These conditions are mentioned in the slide - $\beta = l(l + 1)$, where l has to be a +ve integer including zero, and $|m_l| \leq l$. Very peculiar set of conditions, but lets move on without thinking too much about this for the moment. Once we finish the mathematics, we will try to make some sense of these.
- Now with some more algebra (which is skipped here) we can arrive at a descent expression for $\Theta(\theta)$, although involves a polynomial series in terms of the cosine of our variable (the angle θ). You don't have to remember the expression for assessment, it will be provided if there is a question based on this.

Let's now consider the r component in equation (5).

$$\begin{aligned} \frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] r^2 &= \frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta(\theta) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) = \beta = l(l+1) \\ \Rightarrow \frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] r^2 &= l(l+1) \\ \Rightarrow \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{2\mu}{\hbar^2} \left[E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R(r) &= 0 \end{aligned} \quad (8)$$

This radial equation can be solved analytically (see E&R Appendix N) for $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$.

This time an infinite polynomial series in r is used as a solution, of the form $\sum_{j=0}^{\infty} b_j r^j$

for which a recursion relationship between successive coefficients can be found, where $b_{j+1} \propto b_j$

▪ **apply boundary conditions to the $R(r)$:**

- For this polynomial to remain finite, there must be a coefficient $b_j = 0$ when $j = n$

The overall solution for the H atom is

$$R(r) = C \left(\frac{2r}{na_0} \right)^l \exp \left(-\frac{r}{na_0} \right) F_{n-l}^{2l+1} \left(\frac{2r}{na_0} \right) \quad (9)$$

where C is a constant, F are associated Laguerre polynomials and a_0 is the Bohr radius $= 4\pi\epsilon_0 \hbar^2 / \mu e^2$

- Now, the final task, to find out the $R(r)$, which can be done by solving the radial part of the equation (5) in slide 45. Here we can use the expression for $\beta = l(l+1)$, we know while trying to make the $\Theta(\theta)$ well behaved. Hence we will arrive at a better looking expression given in equation (8).
- It is also mathematically tedious to solve this equation to find an expression for $R(r)$ (hence is skipped), but we will end up with the expression given in equation (9), which involves another polynomial series.
- If we apply suitable boundary condition, as mentioned in the slide, we will see there is only a discrete set of solutions to equation (8) in terms of another number, n , that can only take natural numbers (no zero).

OK, let's recap, just to have a clear idea...

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

$R(r) = C \left(\frac{2r}{na_0} \right)^l \exp\left(-\frac{r}{na_0}\right) F_{n_l}^{2l+1}\left(\frac{2r}{na_0}\right)$

involves n and l

$\Theta(\theta) = B \sin^{|m_l|} \theta P_{l, |m_l|}(\cos \theta)$

involves l and m_l

$\Phi(\phi) = A \exp(im_l \phi)$

involves m_l

and, from the derivations in the previous slides, we know,

- $n = 1, 2, 3, \dots$
- $l = 0, 1, 2, \dots, n-1$
- $|m_l| = 0, 1, 2, \dots, l$, i.e. $m_l = -l, -(l-1), \dots, -1, 0, 1, \dots, (l-1), l$

But, what are these numbers n , l and m_l represent?

- So there we go. We done all mathematics and we got what we were after – the expressions for the three components of the eigen function, which can tell all the information we need to know about the electron.
- The most important to note here that each component depend on 1 or 2 discrete set of numbers, hence the eigen function for the electron $\psi(r, \theta, \phi)$ depends on three quantum numbers, n, l, m_l . And furthermore, these quantum numbers cannot be chosen independently – they are bound by a set of rules as shown in the slide.
- This implies, as we expect, the electron can only have a well-defined set of states, each state representing a different configuration for the electron around the nucleus. So it is now important to understand what these quantum numbers represent and what effect they have on the electron's state of existence.

n – Principal Quantum Number

- The Laguerre polynomial expansion must remain finite so solutions only exist for
 - All positive energies E (which corresponds to free electrons)
 - Negative energies (bound electrons), where

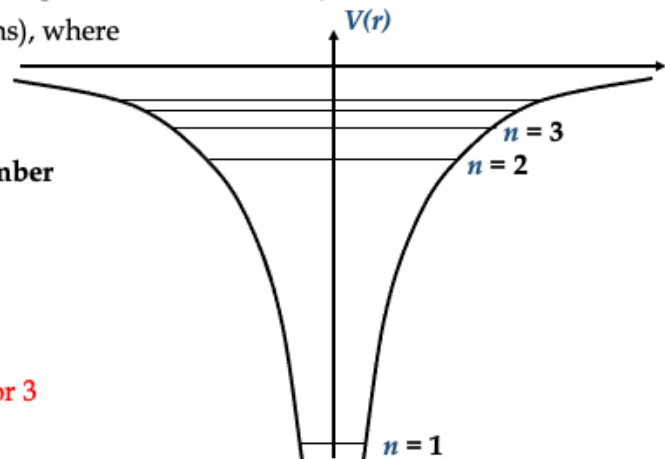
$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2 \hbar^2 n^2}$$

n is called the principal quantum number

and, $n = 1, 2, 3, \dots$ and $n > l$

i.e. for each level n there are n
degenerate states with different l
quantum numbers

for e.g. for $n = 4$, $l = 0, 1, 2$ or 3



- Recall the Bohr model of the atom where it was postulated that the electron has a classical circular orbit and the angular momentum is quantised ($n\hbar$).
- Identical energy levels are found by this derivation by Schrödinger, and it was the first convincing verification of quantum mechanics.

- First, let's look at the number n . There is a particular reason we call it as principal quantum number – it defines the energy (eigen value) of the electron. Simply because this only appears in the radial part, which is the only part of ψ that depends on the potential (as we see from equation (2), (6) and (8)).
- If we try to find the eigen value of ψ (the derivation is skipped), we will also see the energy of the electron does only depend on the n . Another thing to note that the expression for E we get here is exactly the same we get from Bohr's model, which is very convincing as hydrogen atom is a perfectly periodic and symmetrical system.
- Hence we can define the discrete energy levels for the electron, which is shown in the figure. As you see $E \propto \frac{1}{n^2}$, the energy levels get closer together as we go higher in n . If we use the numerical values for the parameters in the expression of E , we will get $E_n \propto \frac{-13.6}{n^2}$ eV.
- Now another interesting aspect – since the eigen value does not depend on the other two quantum numbers, l and m_l , there is a significant level of degeneracy for each energy level. For instance, for the 3rd energy level (or you can say the 2nd excited state, as $n=1$ called the ground state) we can have $l = 0, 1$ and 2 , and for each of these l values, we will have a number of

possible values of m_l . So the list of degenerate states for $n=3$ are (in ψ_{n,l,m_l} format)
: $\psi_{3,0,0}, \psi_{3,1,-1}, \psi_{3,1,0}, \psi_{3,1,1}, \psi_{3,2,-2}, \psi_{3,2,-1}, \psi_{3,2,0}, \psi_{3,2,1}, \psi_{3,2,2}$: 9 fold
degeneracy – n^2 degeneracy.

l – orbital angular momentum quantum number

- If we look again at the radial equation (equation 8)

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{2\mu}{\hbar^2} \left[E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R(r) = 0$$

the terms inside the brackets are energy terms, hence the term $\frac{l(l+1)\hbar^2}{2\mu r^2}$ has unit of energy.

In classical mechanics, rotational energy of a point mass = $\frac{L^2}{2\mu r^2}$,

where L is the angular momentum.

Hence by comparison, $L = \sqrt{l(l+1)} \hbar$

is the angular momentum of the electron, which is quantised.

This is why l is called the “orbital angular momentum quantum number”.

- For historical reasons, the allowed values of l are assigned the following letters

$$l = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6$$

$$s \quad p \quad d \quad f \quad g \quad h \quad i$$

- Note that s -state corresponds to zero angular momentum which is contrary to Bohr's model of an orbiting electron.

- The next to make some sense is the physical significance of the quantum number l . For this let's look at the radial part of the Schrodinger's equation, the equation (8) in slide 47. Each term inside the big square bracket has to be some sort of energy, otherwise you can't add them together. Therefore the term containing l is also a kind of energy – but what type?
- If we remember our classical mechanics, we know the rotational kinetic energy has a similar form – having mass of the object and the r^2 term in the denominator, where the numerator represents the square of angular momentum. Certainly the electron exhibits a circular motion around the nucleus (even though it is represented by a matter wave). Hence it should possess some angular momentum, which has to be quantised – which is the basis of the Bohr's model for a stable atom. Hence the term $\sqrt{l(l+1)} \hbar$ represents the orbital angular momentum of the electron, hence we can call the l as orbital angular momentum quantum number (also called as azimuthal quantum number)

See the embedded video1 (under the section of quantum numbers) in the canvas page (from the beginning until 2.4 min.), to remind the concept of angular momentum.

- The other thing to note here, if $l=0$, which is the only case for the ground state ($n=1$), the angular momentum is zero. This is in contradiction to the Bohr's model, but there is a plenty of expt results to support this. In fact, we will see soon (slide 56), that the ground state is completely θ and ϕ symmetric. So in absence of a preferred axis, electron can precess around the nucleus on any plane in 3D, and the angular momentum being a vector, it can be zero if we take an average.

m_l – Azimuthal quantum number

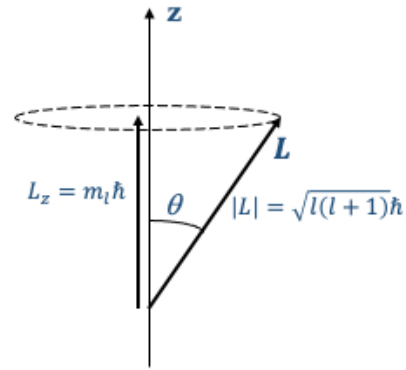
- If we look again at θ equation (equation 6)

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left(\beta - \frac{m_l^2}{\sin^2 \theta} \right) \Theta(\theta) = 0$$

Now, since $\beta = l(l+1) = \frac{L^2}{\hbar^2}$,

$$\frac{m_l^2}{\sin^2 \theta} \text{ should have the dimension of } \frac{L^2}{\hbar^2},$$

i.e. m_l should have the dimension of $\frac{L}{\hbar}$



- More detailed analysis shows it is the component of L along the z axis,

$$\text{i.e. } L_z = m_l \hbar$$

and L (the angular momentum vector) precesses around z like a spinning top.

- Now let's take a look at the third quantum number, to see what it represents...
- As shown in slide, $m_l \hbar$ has the same dimension as the angular momentum. But as we know the total angular momentum L , it represents the component of L along a given axis. In this way, we can define the orientation of the plane of electron precession with respect to the axis. So by knowing the l and m_l we can get a full picture of the electron orbitals - l gives the exact magnitude of the total angular momentum ($L = \sqrt{l(l+1)} \hbar$) and m_l gives its z component precisely ($L_z = m_l \hbar$). This is also okay with the uncertainty principle, as we only know one component precisely.
- Note, L_z is always less than L , as m_l can only go up to l . This is a consequence of the uncertainty principle for angular momentum, that implies that no two components of angular momentum can be precisely known simultaneously.

Angle of Precession θ

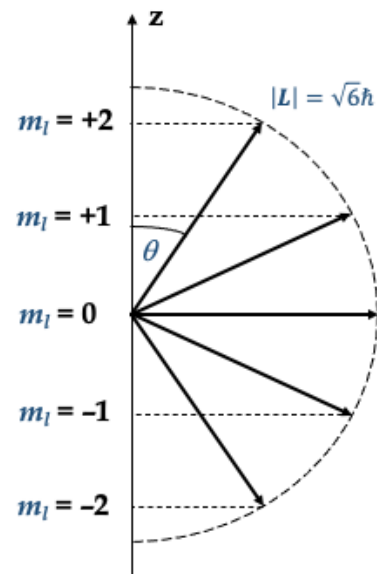
- Consider a d -state (i.e. $l = 2$). The possible values of m_l are $-2, -1, 0, +1, +2$
- The magnitude of the angular momentum is $|L| = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$
- The angle of precession for an eigenstate (l, m_l) is

$$\cos \theta = \frac{L_z}{|L|} = \frac{m_l}{\sqrt{l(l+1)}}$$

Hence,

$$\begin{aligned}\theta(2, +2) &= 35.3^\circ \\ \theta(2, +1) &= 65.9^\circ \\ \theta(2, 0) &= 90^\circ \\ \theta(2, -1) &= 114.1^\circ \\ \theta(2, -2) &= 144.7^\circ\end{aligned}$$

- Note that L is never in along the z direction



- Now, we see that for a given L , the electron orbital can only have a discrete set of orientation, each possible orientation is defined by a given value of m_l . If we know the l and m_l , we can work out the orientation.
- If we don't have a preferred axis defined, for instance a stray hydrogen atom wondering in space ☺, the different planes of orientations does not mean much. Electron in any of these configuration will have the same energy. Hence the m_l states are degenerate states.
- But, the situation will change if we want to define a given axis by some means, for instance applying a magnetic field. In this case the orientation of the precession will make a big difference, as the torque on the electrons due to the magnetic field will depend not only on the magnitude of L , but also the angle between the L and the magnetic field ($\tau = \mu \times B = \gamma J \times B$, where γ is gyromagnetic ratio and $J = L + S$ is the total angular momentum. S stands for spin angular momentum, which is not covered in this course). Hence electron having L closer to the B will have lower energy – which means the m_l states are no longer degenerate. Each will represent a slightly different eigen value for the electron. In this case, when external magnetic field is applied, atomic transition line between two n

levels became multiple lines, as we have now transitions from different m_l states, which vary in energy by a small amount. This is called Zeeman effect (will be covered in more details in other module)

- See the embedded video2 (under the section of quantum numbers) in the canvas page (from 4.58 min to the end) discussing the L , L_z and then Zeeman splitting

Degeneracy of Hydrogen Eigen states

- There are $(2l+1)$ m_l states for each l level
 - e.g. a d level ($l = 2$) has 5 m_l states = 0, ± 1 , ± 2
- There are n orbital angular momentum states for each n level
 - e.g. $n = 3$ has 3 l states = 0, 1, 2 (s, p, d)
 - This degeneracy is a mathematical peculiarity for the H atom (n and l are not degenerate for other atoms)
- Degeneracy can be “raised” when the symmetry is broken
 - e.g. if an external magnetic field is applied (giving a “preferred direction in space” – z axis)
 - The angular momentum of the electron L generates a magnetic dipole moment which interacts with the magnetic field
 - m_l represents the quantisation of L (and hence the magnetic moment) along the z axis
 - Therefore different m_l values give different energies

- A quick few points to note about the degeneracy in hydrogen atom.

- m_l is also called the magnetic quantum number for historical reasons as it was not until an external magnetic field was applied that these degenerate levels could be observed from spectroscopic measurements of light emitted from the atoms (Zeeman Effect – encountered in PHY2005).
- **There are 2 spin states for each m_l state**
 - You will know that for instance a 1s state has a degeneracy of 2 since it can hold 2 electrons.
 - This is due to the electron's intrinsic angular momentum known as spin (more on this later in level 3)

Spherical Harmonics Y_{lm}

- The angular part of the eigenfunctions are known as *spherical harmonics* Y_{lm}

$$Y_{lm_l} = \Phi_{m_l}(\phi) \cdot \Theta_{lm_l}(\theta)$$

- The normalised spherical harmonics for $l \leq 2$ are

$$Y_{00} = \frac{1}{(4\pi)^{1/2}}$$

$$Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

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

$$Y_{20} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos \theta - 1)$$

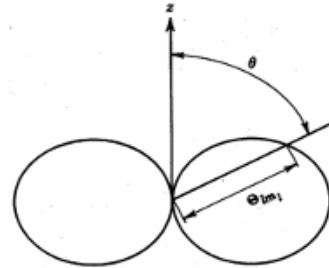
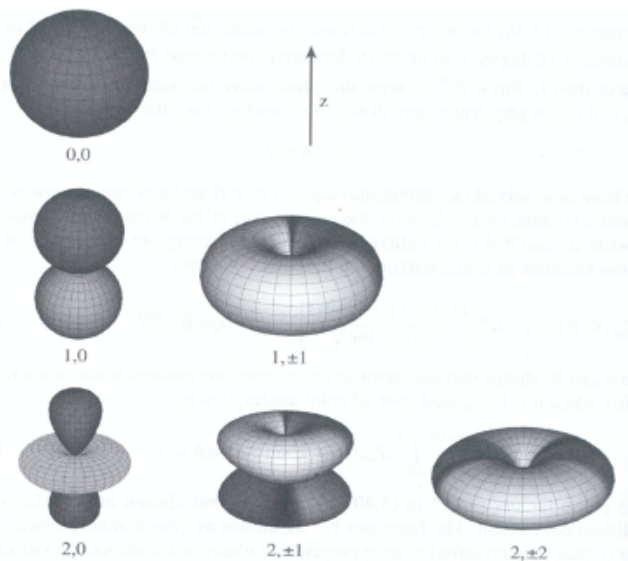
$$Y_{2\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{1/2} \cos \theta \sin \theta \exp(\pm i\phi)$$

$$Y_{2\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta \exp(\pm 2i\phi)$$

- Now let's look at the wavefunction itself. As we seen the eigen function has three components, one for each coordinate of a spherical polar system. The Radial part describes the radial position with respect to the center of mass (not the nucleus, as we used the reduced mass in the Schrodinger equation). But the other two co-ordinates provide the information about the shape and configuration of the orbitals, although they don't contribute towards the eigen value in a isolated system. Combining these two later parts of the eigen function we call spherical harmonics.
- A list of wave functions for different l and m_l values. No need to remember these, just get a overall feeling of how they look.

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

- There are a tons of webpages with more beautiful pictures and animations. The two applets in the canvas page are my favorites. Also refer to the chapter 7 of the Eisberg's book attached in the canvas page (page 249,250).

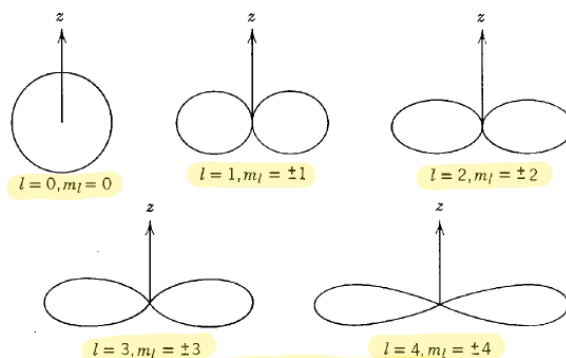


Figure 7-9 Polar diagrams of the directional dependence of the one-electron probability densities for $l = 0, 1, 2, 3, 4$; $m_l = \pm l$.

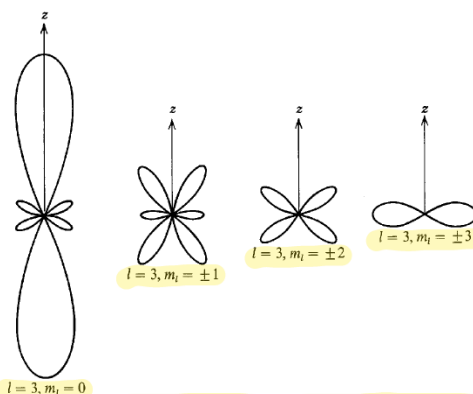


Figure 7-8 Polar diagrams of the directional dependence of the one-electron atom probability densities for $l = 3$; $m_l = 0, \pm 1, \pm 2, \pm 3$.

Radial Probability Densities

- Our time independent solution is $\psi_{nlm_l} = R_{nl}(r) \cdot \Theta_{lm_l}(\theta) \cdot \Phi_{m_l}(\phi)$

- The probability density is given by $\psi^* \psi = R^* R \cdot \Theta^* \Theta \cdot \Phi^* \Phi$

- Let's look at the radial coordinate

Probability electron density $= |R_{nl}(r)|^2$

Probability between r and $r + dr$ $P_{nl}(r)dr = |R_{nl}(r)|^2 dV = 4\pi r^2 |R_{nl}(r)|^2 dr$
 ($dV = 4\pi r^2 dr$ is the shell of radius r and thickness dr)

- The first few radial eigenfunctions are

$$R_{10} = 2 \left(\frac{Z}{a_0} \right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right)$$

$$R_{20} = \frac{1}{\sqrt{8}} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) \exp\left(-\frac{Zr}{2a_0}\right)$$

$$R_{21} = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} \exp\left(-\frac{Zr}{2a_0}\right)$$

- One of the most interesting thing however to know from the wavefunction is the location (in terms of radial distance) of the electron in different energy states. This can be found out by looking at the radial part of the wave function.
- Pretty standard procedure, as you have done in the first part of this module. Since we are operating on a part of the eigen function, the $R_{nl}R_{nl}^*$ is called 'radial' probability density.
- By solving the Schrodinger's equation, we know how to write the R_{nl} - you don't need to remember, will be provided in exam if needed.
- Then it's a matter of some mathematics to find what we want. Typically we want to know how the probability functions look along the radial axis, and the expectation and most probable distance of the electron from the center of mass.

Radial probability distribution

- Consider the 1s ground state of Hydrogen (note no θ or ϕ dependence)

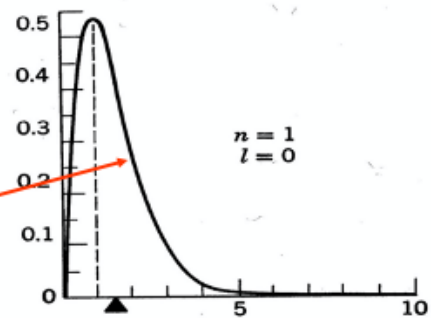
- Eigen function** $R_{n=1,l=0} = \frac{2}{a_0^{3/2}} \exp\left(-\frac{r}{a_0}\right)$

- Radial probability** (between r and $r + dr$)

$$P_{nl}(r)dr = |R_{nl}(r)|^2 dV$$

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

$$P_{10}(r) = \frac{16\pi}{a_0^3} r^2 \exp\left(-\frac{2r}{a_0}\right)$$



- taking the ground state to start with. Although the wavefunction decays exponentially as we go farther away from the CoM, the probability function peaks at a finite distance from the CoM. This is because of the volume integral. Of course, there is zero probability of finding the electron at the centre, even though the wavefunction is maximum there.

Calculating r_{max} and $\langle r \rangle$

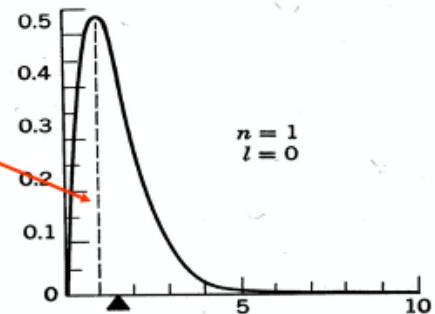
- Most probable radius r_{max}

$$\frac{dP_{10}}{dr} = \frac{16\pi}{a_0^3} \exp\left(-\frac{2r}{a_0}\right) \left(2r - 2\frac{r^2}{a_0}\right) = \frac{32\pi}{a_0^3} r \exp\left(-\frac{2r}{a_0}\right) \left(1 - \frac{r}{a_0}\right)$$

$$\frac{dP_{10}}{dr} = 0 \quad \text{gives} \quad r_{max} = a_0$$

- expectation value of r

$$\langle r \rangle = \frac{\int_0^\infty r P_{nl}(r) dr}{\int_0^\infty P_{nl}(r) dr} = \frac{\int_0^\infty r^3 \exp\left(-\frac{2r}{a_0}\right) dr}{\int_0^\infty r^2 \exp\left(-\frac{2r}{a_0}\right) dr} = \frac{3! / (2/a_0)^4}{2! / (2/a_0)^3} = \frac{3}{2} a_0$$



$$\int_0^\infty x^n \exp(-Kx) dx = \frac{n!}{K^{n+1}}$$

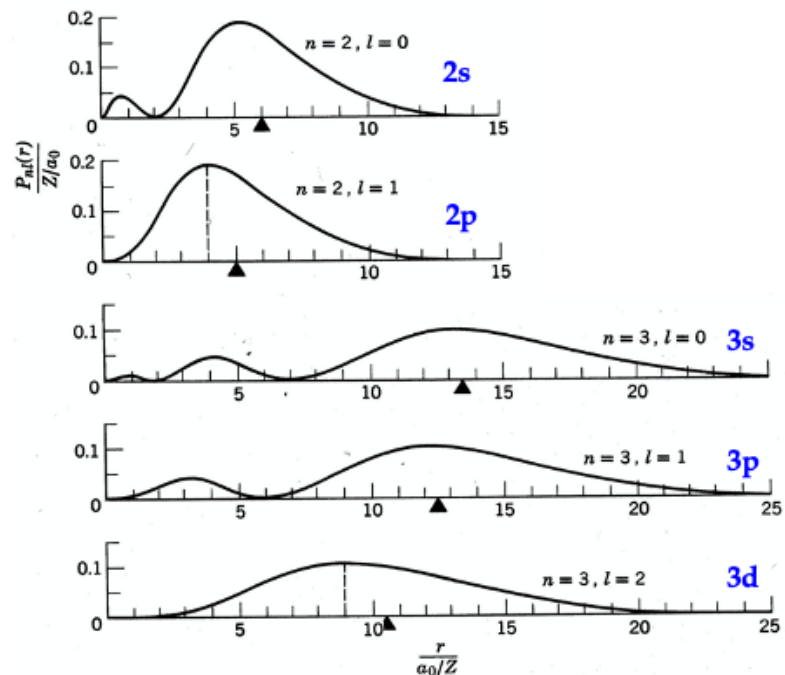
- Trivial algebra, I am sure you are very confident of these. But, any issues, let me know. See the standard integral shown in the bottom right of the slide, that is used in this calculation. However, no need to remember this. Will be given in exam if needed.

Radial Probability Distributions in Hydrogen

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

■ Note

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



- This is one of the most interesting bit. As per Bohr's theory, or as you typically expect, larger the n , farther the electron from the CoM. But in fact, there is a good probability of finding an electron with $n = 3$ near another with $n = 2$. Of course, if we calculate the expectation values (shown by the little black triangle under the axis), it's different and makes a classical sense.
- Another few key points to note here – there are certain radial positions where the probability density is negligible – i.e. you can't find the electron there, even though you can find it on both sides of it. These are called nodal points.
- Other points to note, are the shapes of the function, 3d electron is closer than 3s, no. of nodes depending on n and l

Total Electron Probability Densities

- The electron probability density is

$$P(r, \theta, \phi) = R_{nl}^* R_{nl} \cdot \Theta_{lm_l}^* \Theta_{lm_l} \cdot \Phi_{m_l}^* \Phi_{m_l}$$

- The eigen function has only a phase dependence on the azimuthal coordinate ϕ , so the probability density has no dependence on ϕ

$$\Phi^* \Phi = \frac{1}{\sqrt{2\pi}} \exp(-im_l \phi) \frac{1}{\sqrt{2\pi}} \exp(im_l \phi) = \frac{1}{2\pi}$$

- Visualising the angular dependence is best done with the Y_{lm} orbitals. Factoring in the radial dependence is difficult, try the following web demos
<https://phet.colorado.edu/en/simulation/legacy/hydrogen-atom> or
<http://demonstrations.wolfram.com/HydrogenOrbitals/> or
<http://www.falstad.com/qmatom/>
- There is an apparent discrepancy with these orbitals which have an angular dependence yet the system is isotropic. However for a given value of l , there are $(2l + 1)$ degenerate m_l levels which are indistinguishable by observation. Therefore we can't tell which m_l level is populated. If you do a number of measurements and take an average, the result is isotropic.
- Only if the symmetry is broken, e.g. applying an external field can the m_l levels be observed as they are no longer degenerate, i.e. they have slightly different energy eigenvalues.

- Some final comments...