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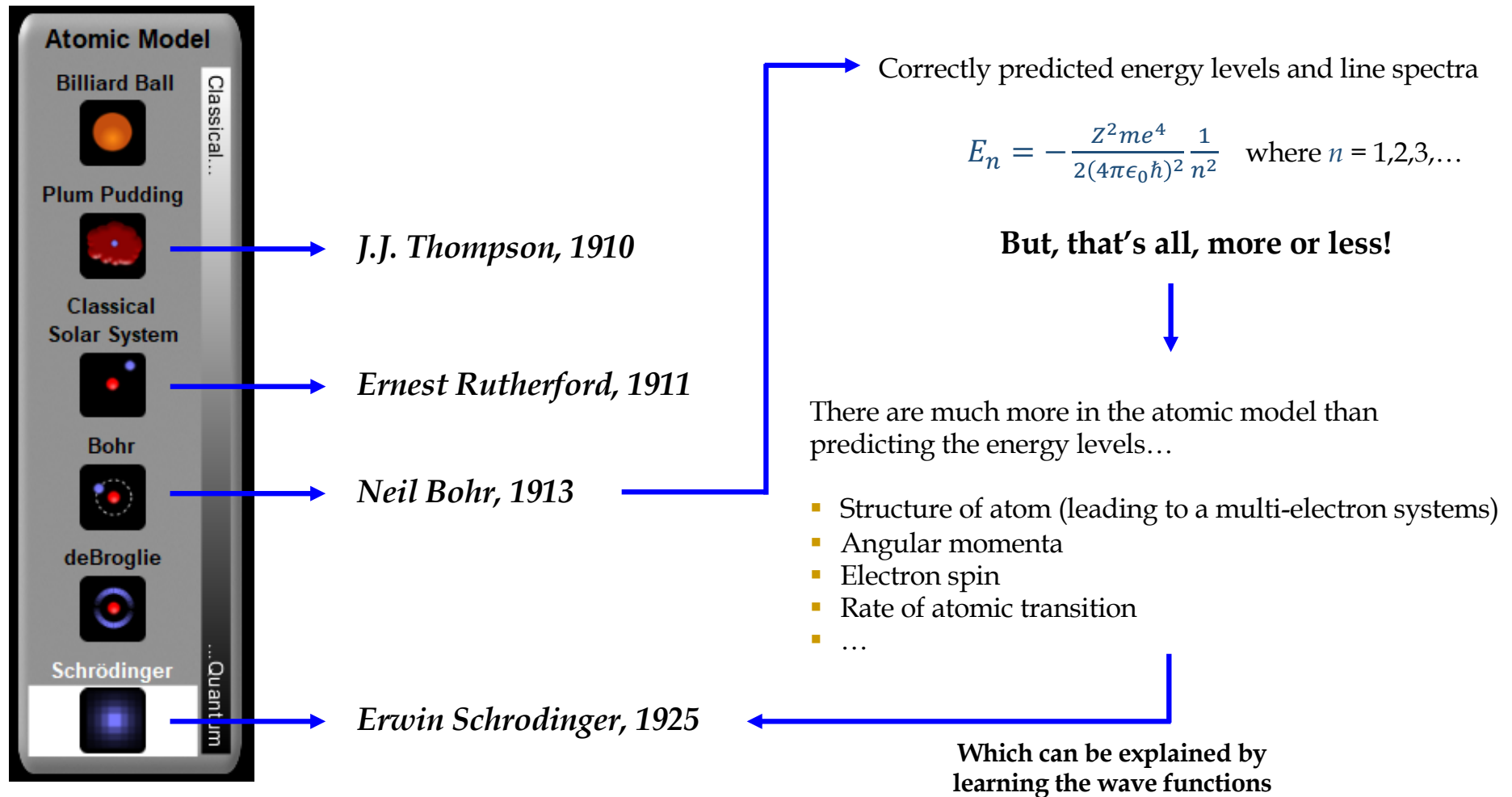
# Part-4

# 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>



# 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)

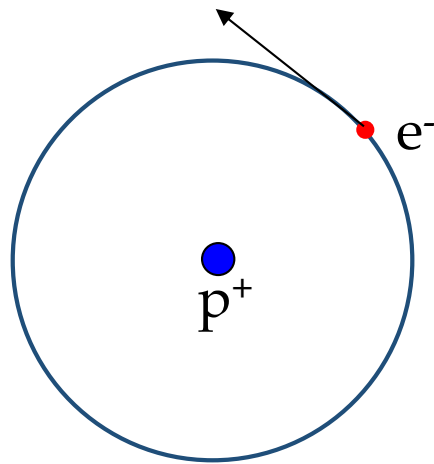
explained many other features of atomic spectra measured very accurately, such as,  
difference between spectra between isotopes (for ex. Hydrogen and deuterium) using reduced mass of electron.

## Where are the limitations?

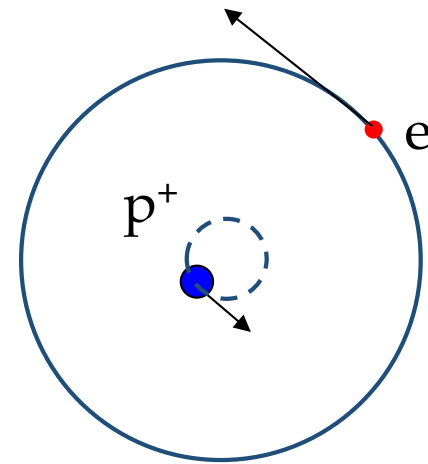
- Could not provide a detailed picture of the atom (probability density distribution). The system should better represented in 3D – Bohr only considered radial component,  $mvr = n\hbar$
- Did not account for Electron spin, could not explain rates of atomic transitions.
- could not be applied to multi-electron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

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

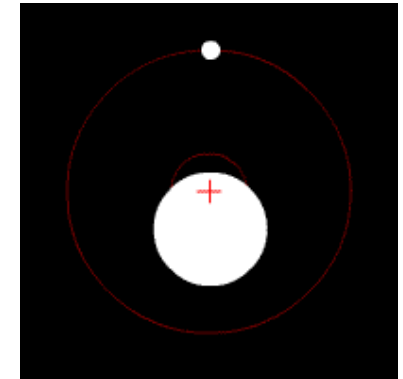
## Reduced mass instead of actual mass of electron :



Fixed nucleus of infinite mass



Actual system

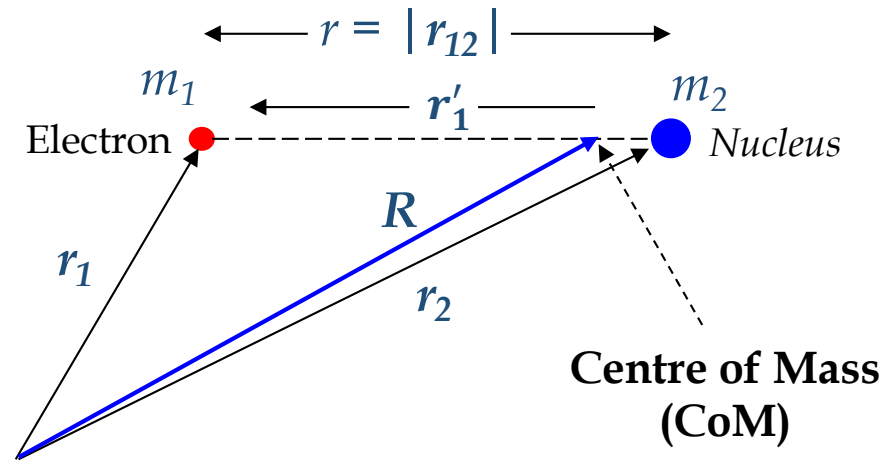


$$\mathbf{R} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}$$

and,  $m_1 \mathbf{r}'_1 = \mu \mathbf{r}_{12}$ ,

where  $\mu = \frac{m_1 m_2}{m_1 + m_2}$ ,

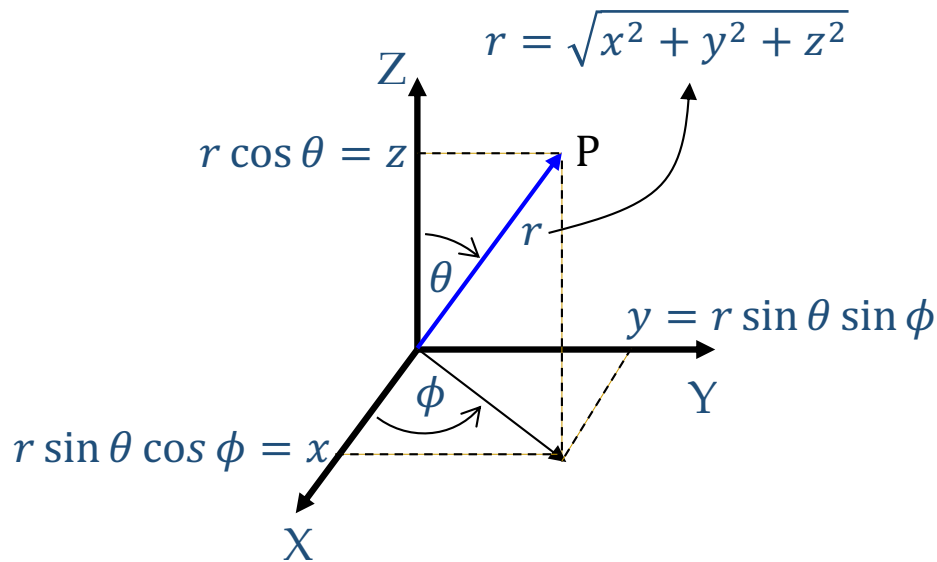
called reduced mass



# 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 $(r, \theta, \phi)$



$$\begin{aligned}\nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \\ &\quad + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}\end{aligned}$$

# 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)

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

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

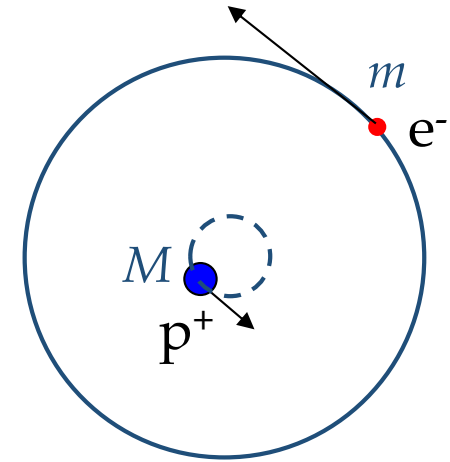
- define general expression for the eigen function :

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

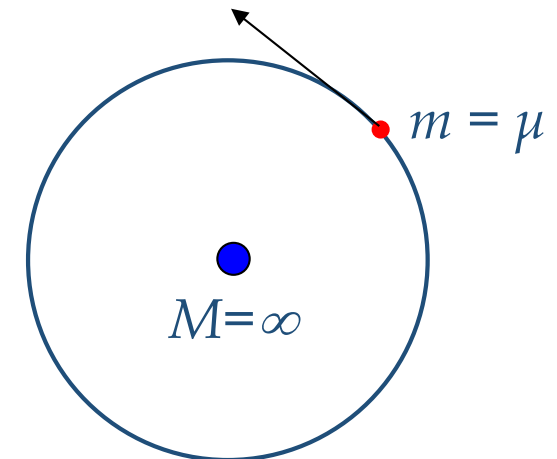
$$\psi(r, \theta, \phi) = R(r) \times \Theta(\theta) \times \Phi(\phi)$$

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

**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  $\phi$  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

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

- **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  $\phi$  and  $\phi + 2\pi$  are actually the same angles.)

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

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

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

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

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

(explanation later)

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

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

(4)

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



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  $\sin^2 \theta$  ...

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

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

(5)

Let's now consider the  $\theta$  component.

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

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

(6)

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  $\cos \theta$

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  $= 4\pi\epsilon_0 \hbar^2 / \mu e^2$

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

$$\begin{array}{ccc} \psi(r, \theta, \phi) = R(r) \times \Theta(\theta) \times \Phi(\phi) & & \\ \swarrow \quad \downarrow \quad \searrow & & \\ \underbrace{R(r) = C \left( \frac{2r}{na_0} \right)^l \exp \left( -\frac{r}{na_0} \right) F_{n_l}^{2l+1} \left( \frac{2r}{na_0} \right)}_{\text{involves } n \text{ and } l} & \underbrace{\Theta(\theta) = B \sin^{|m_l|} \theta P_{l, |m_l|}(\cos \theta)}_{\text{involves } l \text{ and } m_l} & \underbrace{\Phi(\phi) = A \exp(im_l \phi)}_{\text{involves } m_l} \end{array}$$

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?

# $n$ – 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

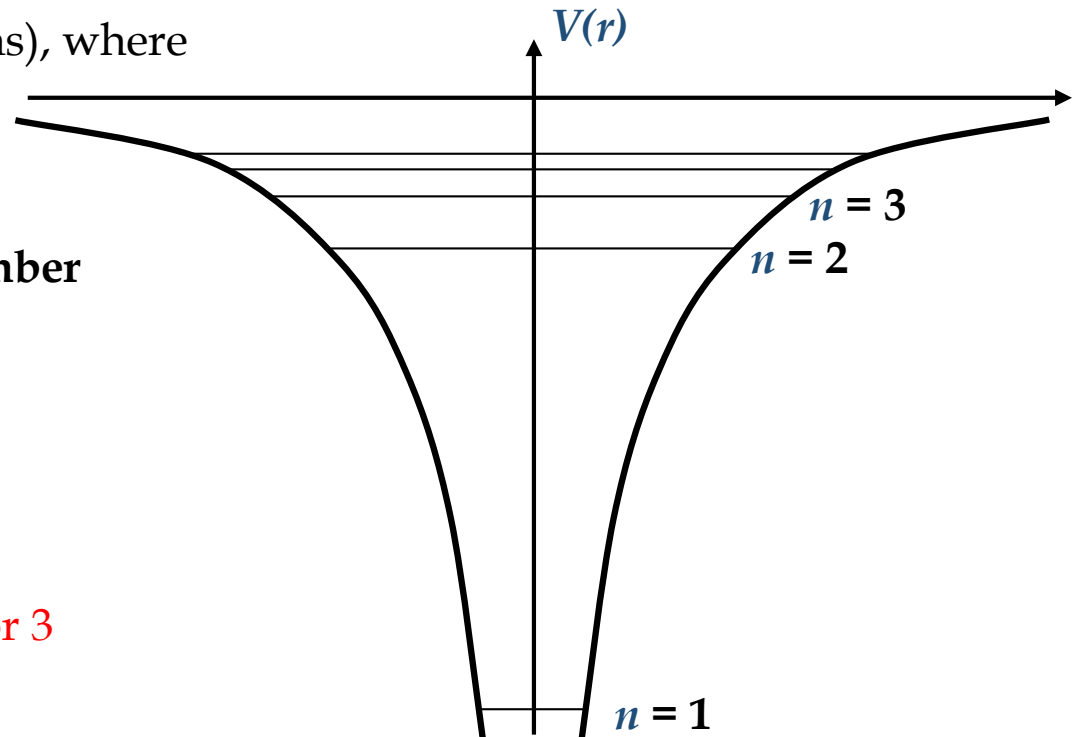
$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2 \hbar^2 n^2}$$

$n$  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.

# $l$ – 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   p   d   f   g   h   i

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

# $m_l$ – Azimuthal quantum number

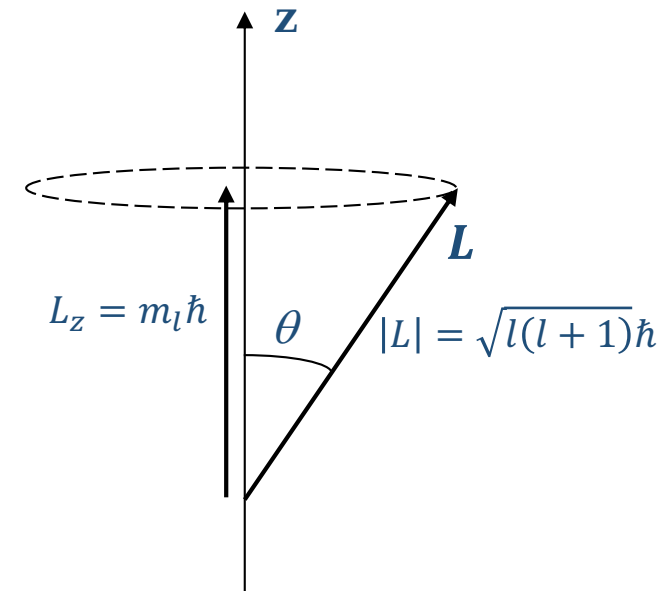
- If we look again at  $\theta$  equation (equation 6)

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

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

$\frac{m_l^2}{\sin^2 \theta}$  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.

# Angle of Precession $\theta$

- 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,

$$\theta(2, +2) = 35.3^\circ$$

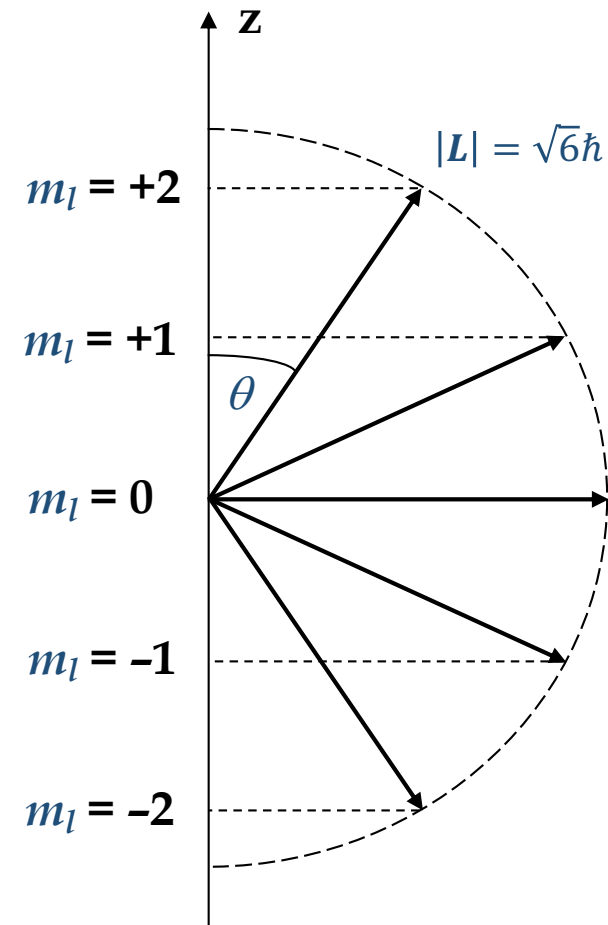
$$\theta(2, +1) = 65.9^\circ$$

$$\theta(2, 0) = 90^\circ$$

$$\theta(2, -1) = 114.1^\circ$$

$$\theta(2, -2) = 144.7^\circ$$

- Note that  $L$  is never in along the  $z$  direction





# 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 =  $0, \pm 1, \pm 2$
- 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

- $m_l$  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

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

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

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

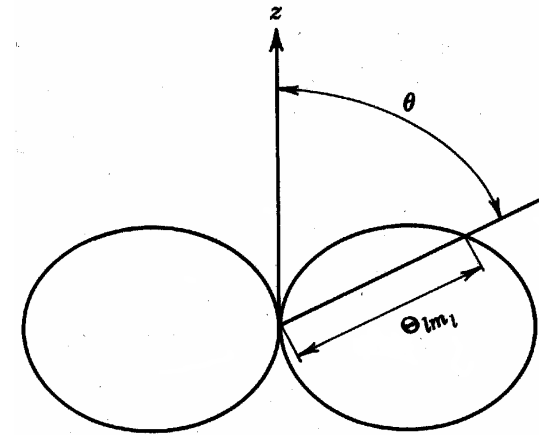
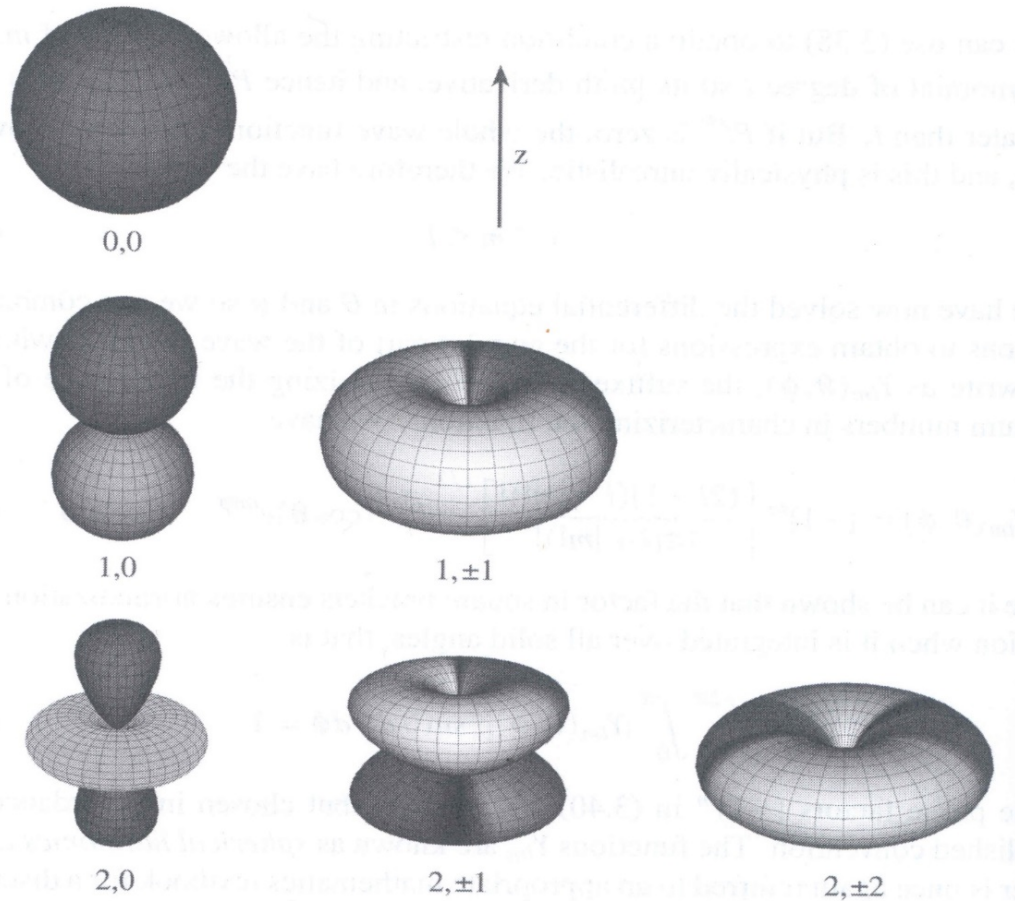
$$Y_{20} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos \theta - 1)$$

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

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

# 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

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

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

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

# Radial probability distribution

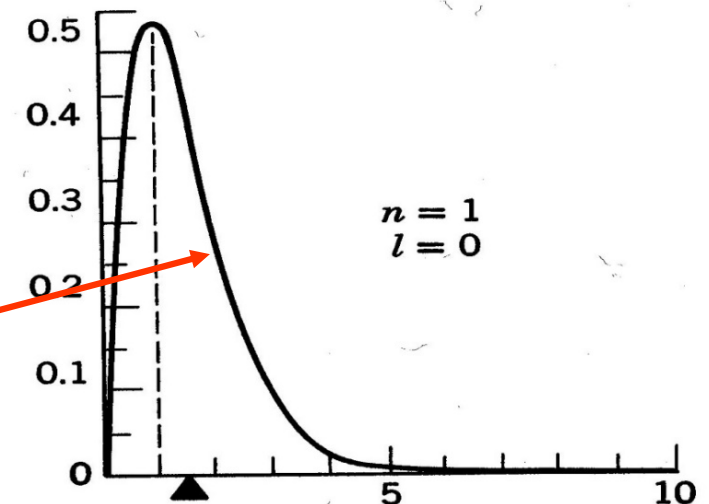
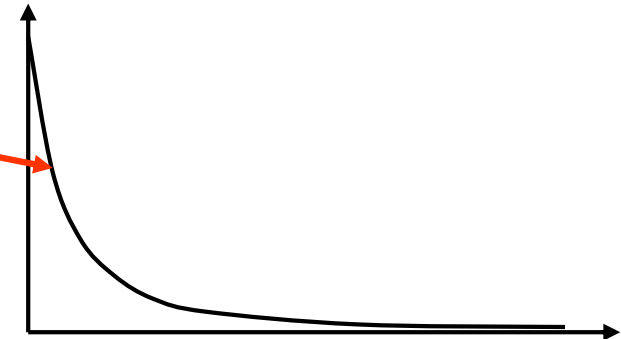
- Consider the 1s ground state of Hydrogen (note no  $\theta$  or  $\phi$  dependence)

- 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  $r + dr$ )

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

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



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

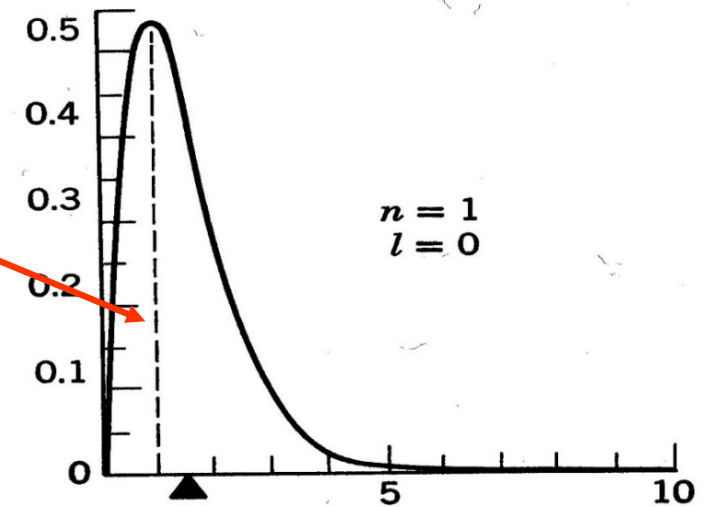
- Most probable radius  $r_{max}$

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

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

- expectation value of  $r$

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



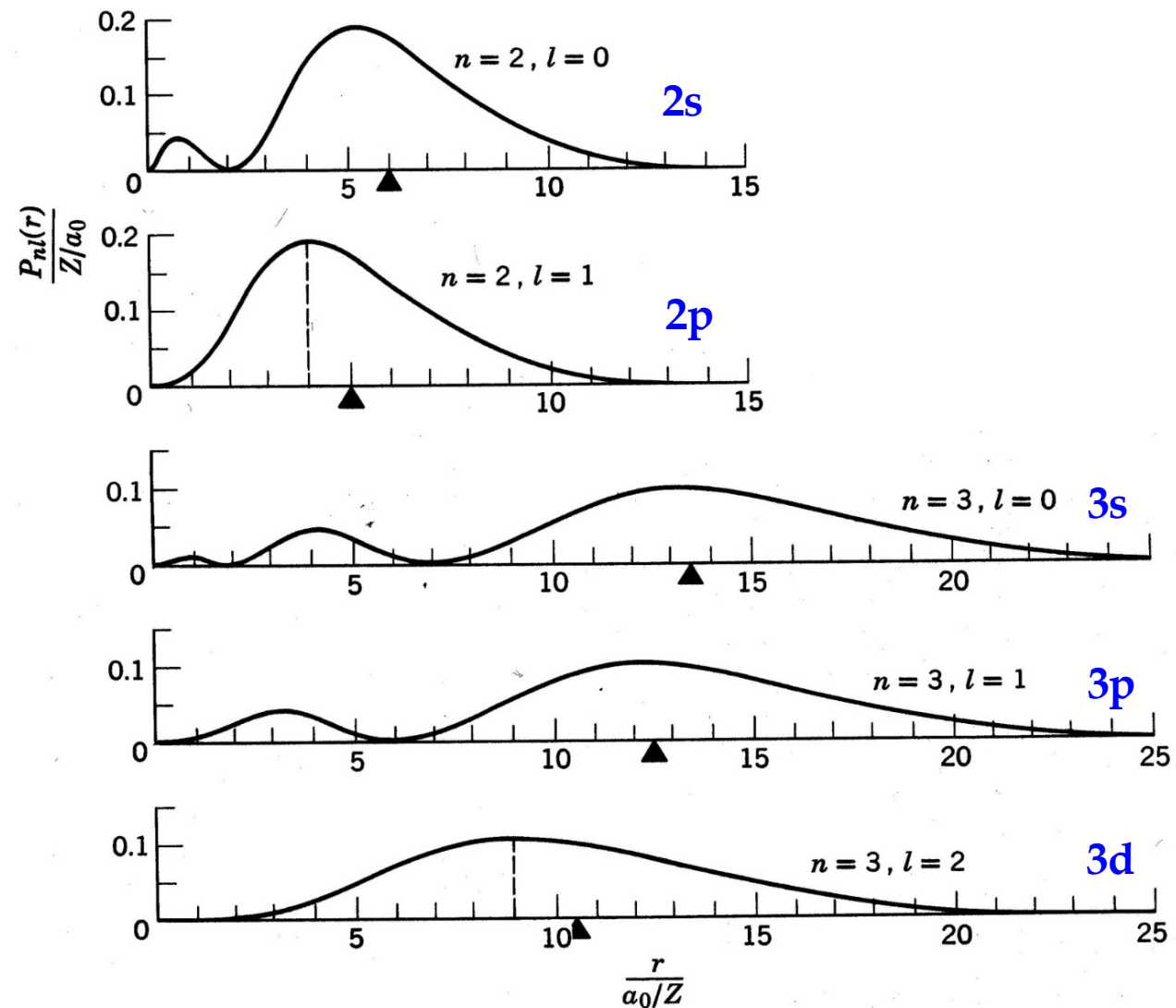
$$\int_0^\infty x^n \exp(-Kx) dx = \frac{n!}{K^{n+1}}$$

# 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  $n - l - 1$





# 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  $\phi$ , so the probability density has no dependence on  $\phi$

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

- 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.