



Physics 2D Lecture Slides

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Vivek Sharma
UCSD Physics

The Hydrogen Atom In Its Full Quantum Mechanical Glory

$$U(r) \propto \frac{1}{r} = \frac{1}{\sqrt{x^2 + y^2 + z^2}} \Rightarrow \text{More complicated form of } U \text{ than box}$$

By example of particle in 3D box, need to use separation of variables (x,y,z) to derive 3 independent differential eqns.

This approach will get very ugly since we have a "conjoined triplet"

To simplify the situation, use appropriate variables

Independent Cartesian (x,y,z) \rightarrow Inde. Spherical Polar (r, θ , ϕ)

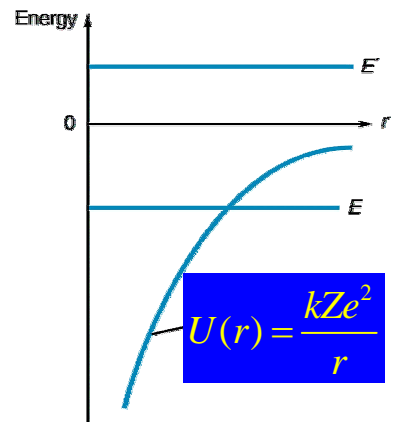
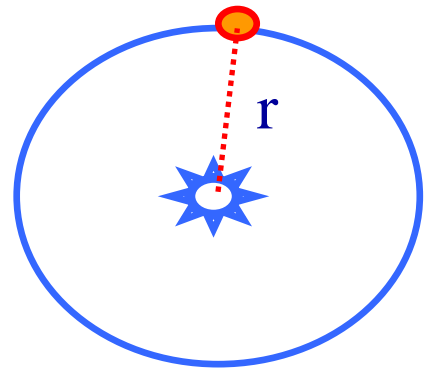
Instead of writing Laplacian $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, write

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

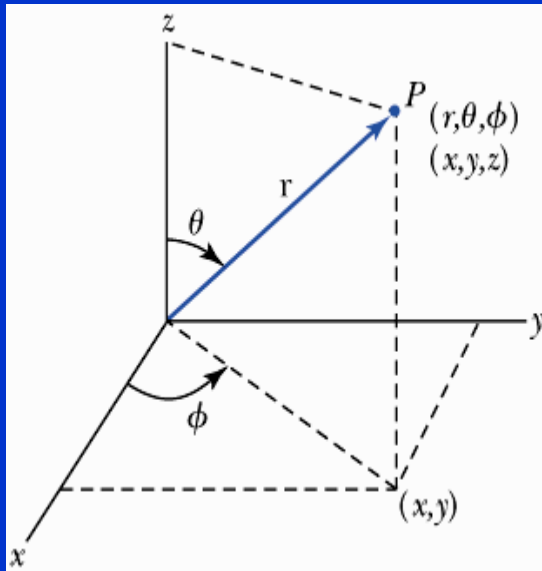
TISE for $\psi(x,y,z) = \psi(r, \theta, \phi)$ becomes

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi(r, \theta, \phi)}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi(r, \theta, \phi)}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - U(r)) \psi(r, \theta, \phi) = 0$$

!!!! fun!!!!



Spherical Polar Coordinate System

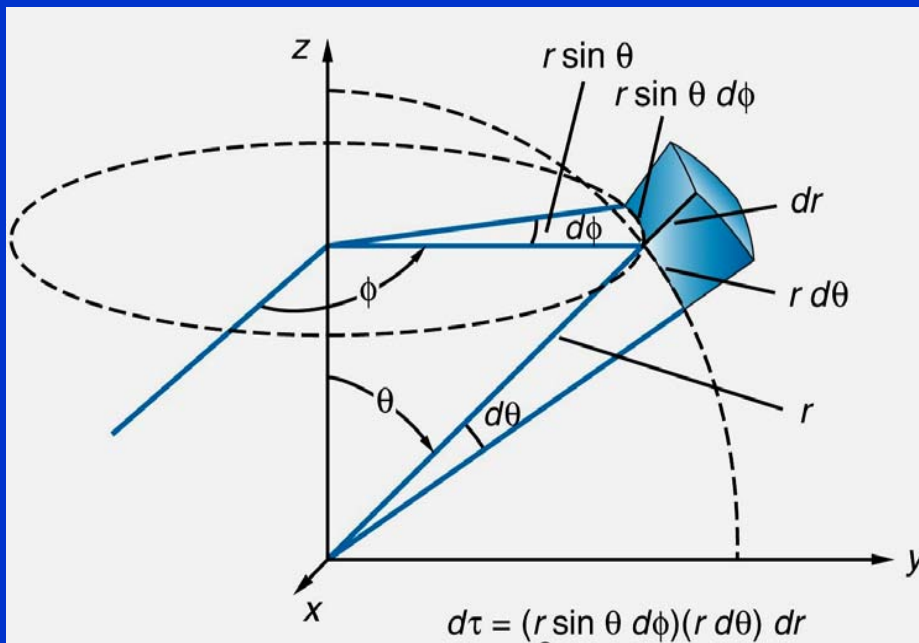


$$\begin{aligned}x &= r \sin \theta \cos \phi \\y &= r \sin \theta \sin \phi \\z &= r \cos \theta\end{aligned}$$

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

$$\theta = \cos^{-1} \frac{z}{r} \text{ (Polar angle)}$$

$$\phi = \tan^{-1} \frac{y}{x} \text{ (Azimuthal angle)}$$



Volume Element dV

$$dV = (r \sin \theta d\phi)(r d\theta)(dr)$$

$$= r^2 \sin \theta dr d\theta d\phi$$

Don't Panic: Its simpler than you think !

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial^2 \phi} + \frac{2m}{\hbar^2} (E - U(r)) \psi(r, \theta, \phi) = 0$$

Try to free up last term from all except ϕ

This requires multiplying thruout by $r^2 \sin^2 \theta \Rightarrow$

$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial^2 \phi} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(E + \frac{ke^2}{r} \right) \psi = 0$$

For Separation of Variables, Write $\psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$

Plug it into the TISE above & divide thruout by $\psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$

Note that :

$$\frac{\partial \Psi(r, \theta, \phi)}{\partial r} = \Theta(\theta) \cdot \Phi(\phi) \frac{\partial R(r)}{\partial r}$$
$$\frac{\partial \Psi(r, \theta, \phi)}{\partial \theta} = R(r) \Phi(\phi) \frac{\partial \Theta(\theta)}{\partial \theta} \Rightarrow \text{when substituted in TISE}$$
$$\frac{\partial \Psi(r, \theta, \phi)}{\partial \theta} = R(r) \Theta(\theta) \frac{\partial \Phi(\phi)}{\partial \phi}$$

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial^2 \phi} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(E + \frac{ke^2}{r} \right) = 0$$

Rearrange by taking the ϕ term on RHS

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(E + \frac{ke^2}{r} \right) = - \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial^2 \phi}$$

LHS is fn. of r, θ & RHS is fn of ϕ only , for equality to be true for all r, θ, ϕ

$$\Rightarrow \text{LHS} = \text{constant} = \text{RHS} = -m_l^2$$

Now go break up LHS to separate the r & θ terms.....

$$\text{LHS: } \frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(E + \frac{ke^2}{r} \right) = m_l^2$$

Divide Thruout by $\sin^2 \theta$ and arrange all terms with r away from $\theta \Rightarrow$

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} \left(E + \frac{ke^2}{r} \right) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right)$$

Same argument : LHS is fn of r , RHS is fn of θ , for them to be equal for all r, θ

\Rightarrow $\text{LHS} = \text{const} = \text{RHS} = l(l+1)$ What do we have after shuffling!

$$\frac{d^2 \Phi}{d\phi^2} + m_l^2 \Phi = 0 \dots \dots \dots (1)$$

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

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{\partial R}{\partial r} \right) + \left[\frac{2mr^2}{\hbar^2} \left(E + \frac{ke^2}{r} \right) - \frac{l(l+1)}{r^2} \right] R(r) = 0 \dots \dots (3)$$

These 3 "simple" diff. eqn describe the physics of the Hydrogen atom.

All we need to do now is guess the solutions of the diff. equations

Each of them, clearly, has a different functional form

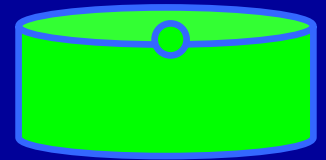
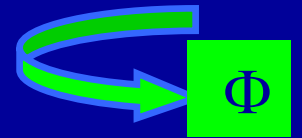
Solutions of The S. Eq for Hydrogen Atom

The Azimuthal Diff. Equation : $\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0$

Solution : $\Phi(\phi) = A e^{im_l\phi}$ but need to check "Good Wavefunction Condition"

Wave Function must be Single Valued for all $\phi \Rightarrow \Phi(\phi) = \Phi(\phi + 2\pi)$

$\Rightarrow \Phi(\phi) = A e^{im_l\phi} = A e^{im_l(\phi+2\pi)} \Rightarrow m_l = 0, \pm 1, \pm 2, \pm 3, \dots$ (**Magnetic Quantum #**)



The Polar Diff. Eq: $\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta} \right] \Theta(\theta) = 0$

Solutions : go by the name of "Associated Legendre Functions"

only exist when the integers l and m_l are related as follows

$m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l$; $l =$ positive number

l : Orbital Quantum Number

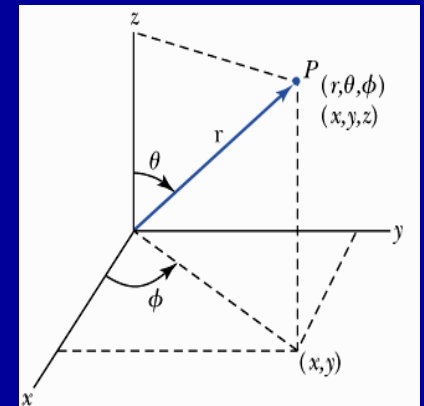
For $l = 0, m_l = 0 \Rightarrow \Theta(\theta) = \frac{1}{\sqrt{2}}$;

For $l = 1, m_l = 0, \pm 1 \Rightarrow$ Three Possibilities for the Orbital part of wavefunction

$$[l = 1, m_l = 0] \Rightarrow \Theta(\theta) = \frac{\sqrt{6}}{2} \cos\theta$$

$$[l = 1, m_l = \pm 1] \Rightarrow \Theta(\theta) = \frac{\sqrt{3}}{2} \sin\theta$$

$$[l = 2, m_l = 0] \Rightarrow \Theta(\theta) = \frac{\sqrt{10}}{4} (3\cos^2\theta - 1) \dots \text{and so on and so forth (see book)}$$



Solutions of The S. Eq for Hydrogen Atom

The Radial Diff. Eqn:
$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{\partial R}{\partial r} \right) + \left[\frac{2mr^2}{\hbar^2} \left(E + \frac{ke^2}{r} \right) - \frac{l(l+1)}{r^2} \right] R(r) = 0$$

Solutions : Associated Laguerre Functions $R(r)$, Solutions exist only if:

1. $E > 0$ or has negative values given by $E = -\frac{ke^2}{2a_0} \left(\frac{1}{n^2} \right)$; $a_0 = \frac{\hbar^2}{mke^2} = \text{Bohr Radius}$

2. And when $n = \text{integer}$ such that $l = 0, 1, 2, 3, 4, \dots, (n-1)$

$n = \text{principal Quantum \# or the "big daddy" quantum \#}$

To Summarize : The hydrogen atom is brought to you by the letters

$$n = 1, 2, 3, 4, 5, \dots, \infty$$

$$l = 0, 1, 2, 3, \dots, (n-1)$$

$$m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l$$

Quantum # appear only in Trapped systems

The Spatial Wave Function of the Hydrogen Atom

$$\Psi(r, \theta, \phi) = R_{nl}(r) \cdot \Theta_{lm_l}(\theta) \cdot \Phi_{m_l}(\phi) = R_{nl} Y_l^{m_l} \text{ (Spherical Harmonics)}$$

Radial Wave Functions & Radial Prob Distributions

$$n \ l \ m_l \ R(r) =$$

$$1 \ 0 \ 0 \ \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

$$2 \ 0 \ 0 \ \frac{1}{2\sqrt{2}a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$$

$$3 \ 0 \ 0 \ \frac{2}{81\sqrt{3}a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-\frac{r}{3a_0}}$$

$n=1 \rightarrow$ K shell

$n=2 \rightarrow$ L Shell

$n=3 \rightarrow$ M shell

$n=4 \rightarrow$ N Shell

.....

$l=0 \rightarrow$ s(harp) sub shell

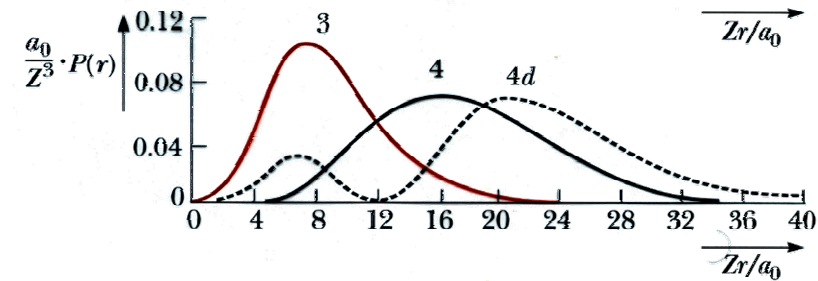
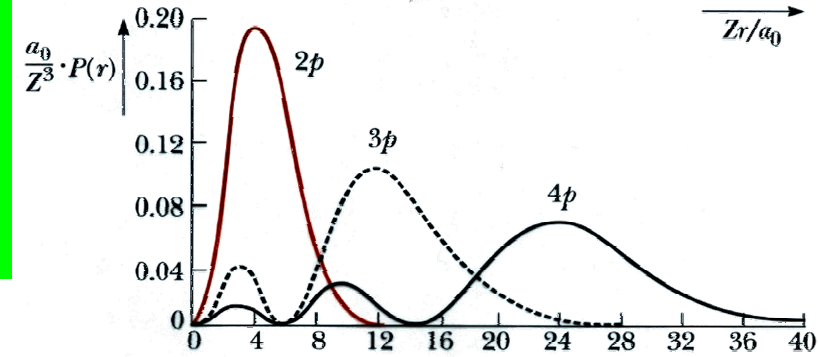
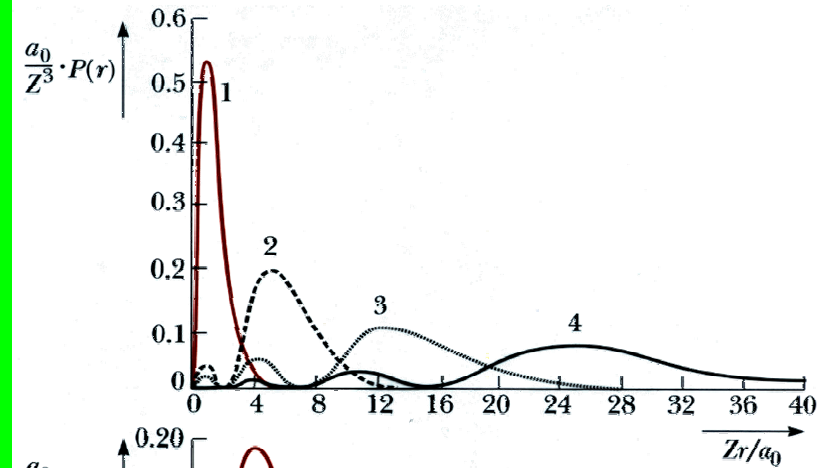
$l=1 \rightarrow$ p(rincipal) sub shell

$l=2 \rightarrow$ d(iffuse) sub shell

$l=3 \rightarrow$ f(undamental) ss

$l=4 \rightarrow$ g sub shell

.....



Symbolic Notation of Atomic States in Hydrogen

| | | | | | | |
|-----------------|-----------|-----------|-----------|-----------|-----------|-------|
| $l \rightarrow$ | $s (l=0)$ | $p (l=1)$ | $d (l=2)$ | $f (l=3)$ | $g (l=4)$ | |
| n | | | | | | |
| \downarrow | | | | | | |
| 1 | 1s | | | | | |
| 2 | 2s | 2p | | | | |
| 3 | 3s | 3p | 3d | | | |
| 4 | 4s | 4p | 4d | 4f | | |
| 5 | 5s | 5p | 5d | 5f | 5g | |

Note that:

- $n=1$ non-degenerate system
- $n > 1$ are all degenerate in l and m_l .

All states have **same energy**

But different spatial configuration

$$E = -\frac{ke^2}{2a_0} \left(\frac{1}{n^2} \right)$$

Facts About Ground State of H Atom

$$n = 1, l = 0, m_l = 0 \Rightarrow R(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}; \quad \Theta(\theta) = \frac{1}{\sqrt{2\pi}}; \quad \Phi(\phi) = \frac{1}{\sqrt{2}}$$

$$\Psi_{100}(r, \theta, \phi) = \frac{1}{a_0 \sqrt{\pi}} e^{-r/a_0} \dots \text{look at it carefully}$$

1. Spherically symmetric \Rightarrow no θ, ϕ dependence (structure)

2. Probability Per Unit Volume: $|\Psi_{100}(r, \theta, \phi)|^2 = \frac{1}{\pi a_0^3} e^{-2r/a_0}$

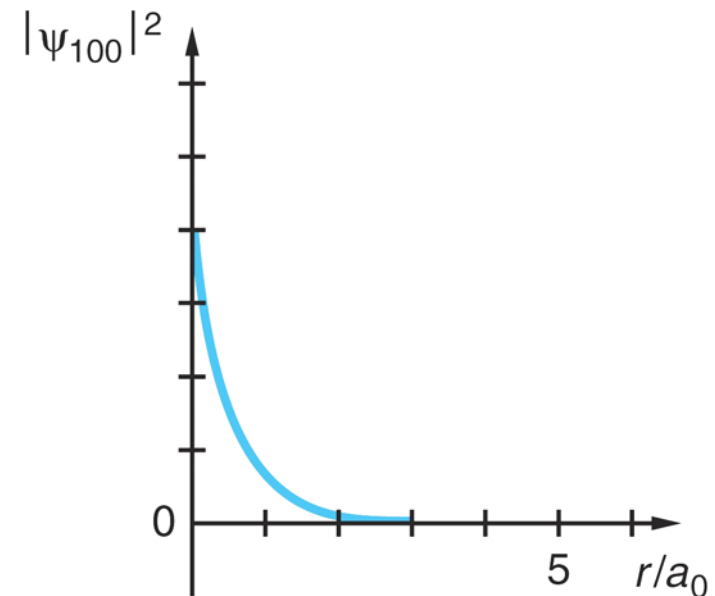
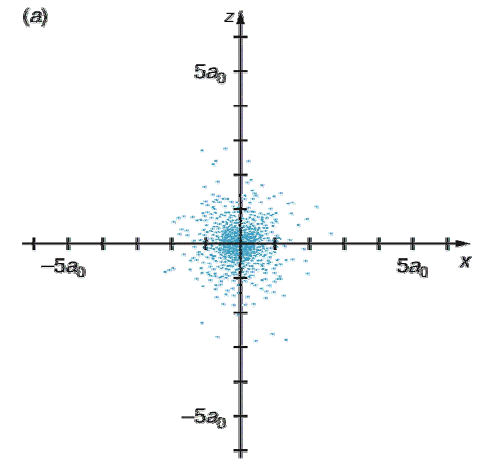
Likelihood of finding the electron is same at all θ, ϕ and depends only on the radial separation (r) between electron & the nucleus.

3 Energy of Ground State $= -\frac{ke^2}{2a_0} = -13.6eV$

Overall The Ground state wavefunction of the hydrogen atom is quite *boring*

Not much chemistry or Biology could develop if there was only the ground state of the Hydrogen Atom!

We need structure, we need variety, we need some curves!



Interpreting Orbital Quantum Number (l)

Radial part of S.Eqn: $\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2mr^2}{\hbar^2} \left(E + \frac{ke^2}{r} \right) - \frac{l(l+1)}{r^2} \right] R(r) = 0$

For H Atom: $E = K + U = K_{\text{RADIAL}} + K_{\text{ORBITAL}} - \frac{ke^2}{r}$; substitute this form for E

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[K_{\text{RADIAL}} + K_{\text{ORBITAL}} - \frac{\hbar^2 l(l+1)}{2m r^2} \right] R(r) = 0$$

Examine the equation, if we set $K_{\text{ORBITAL}} = \frac{\hbar^2 l(l+1)}{2m r^2}$ then get a diff. eq. in r

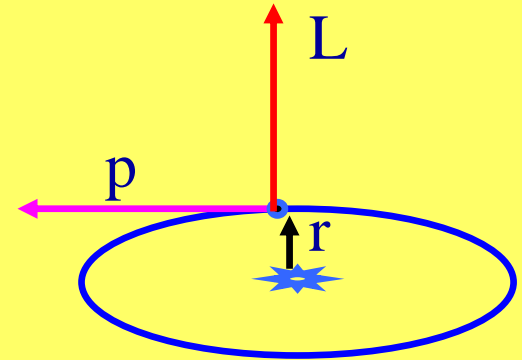
$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} [K_{\text{RADIAL}}] R(r) = 0 \quad \text{which depends only on radius } r \text{ of orbit}$$

Further, we also know that $K_{\text{ORBITAL}} = \frac{1}{2} m v_{\text{orbit}}^2$; $\vec{L} = \vec{r} \times \vec{p}$; $|L| = m v_{\text{orb}} r \Rightarrow K_{\text{ORBITAL}} = \frac{L^2}{2mr^2}$

Putting it all together: $K_{\text{ORBITAL}} = \frac{\hbar^2 l(l+1)}{2m r^2} = \frac{L^2}{2mr^2} \Rightarrow$ magnitude of Ang. Mom $|L| = \sqrt{l(l+1)}\hbar$

Since $l = \text{positive integer} = 0, 1, 2, 3, \dots, (n-1) \Rightarrow$ angular momentum $|L| = \sqrt{l(l+1)}\hbar = \text{discrete values}$

$|L| = \sqrt{l(l+1)}\hbar$: QUANTIZATION OF Electron's Angular Momentum



Magnetic Quantum Number m_l

$\vec{L} = \vec{r} \times \vec{p}$ (Right Hand Rule)

Classically, direction & Magnitude of \vec{L} always well defined

QM: Can/Does \vec{L} have a definite direction ? Proof by Negation:

Suppose \vec{L} was precisely known/defined ($\vec{L} \parallel \hat{z}$)

Since $\vec{L} = \vec{r} \times \vec{p} \Rightarrow$ Electron MUST be in x-y orbit plane

$\Rightarrow \Delta z = 0$; $\Delta p_z \Delta z \sim \hbar \Rightarrow \Delta p_z \sim \infty$; $E = \frac{p^2}{2m} \sim \infty$!!!

So, in Hydrogen atom, \vec{L} can not have precise measurable value

Uncertainty Principle & Angular Momentum : $\Delta L_z \Delta \phi \sim \hbar$

Arbitrarily picking Z axis as a reference direction:

\vec{L} vector spins around Z axis (precesses).

The Z component of \vec{L}

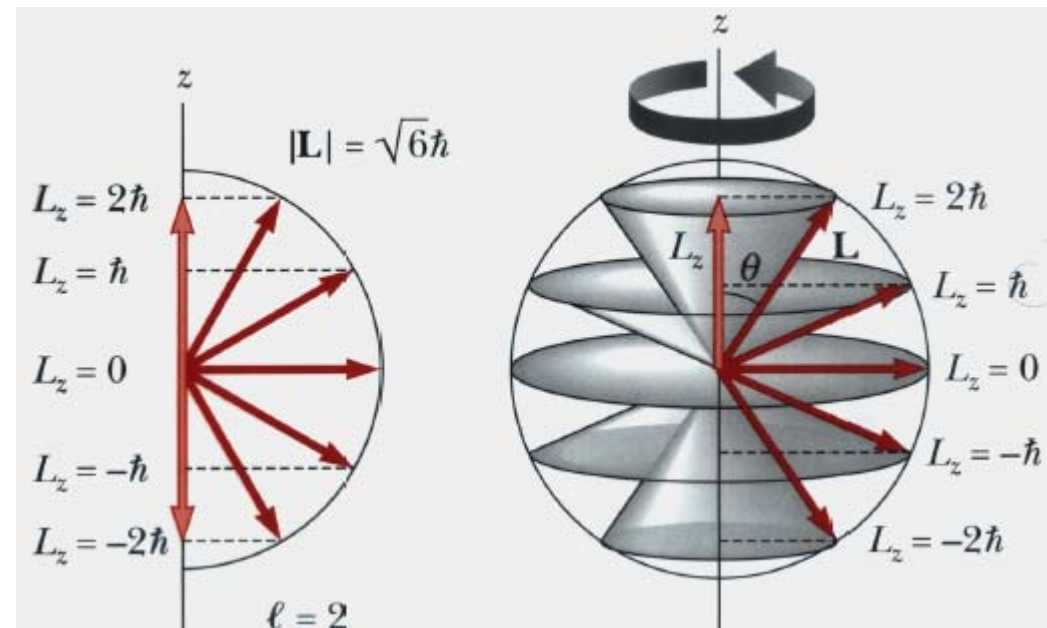
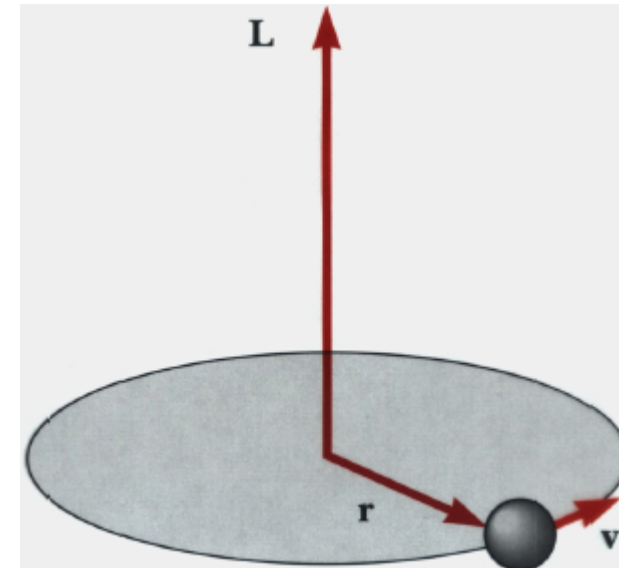
$$|L_z| = m_l \hbar; \quad m_l = \pm 1, \pm 2, \pm 3 \dots \pm l$$

Note: $|L_z| < |L|$ (always)

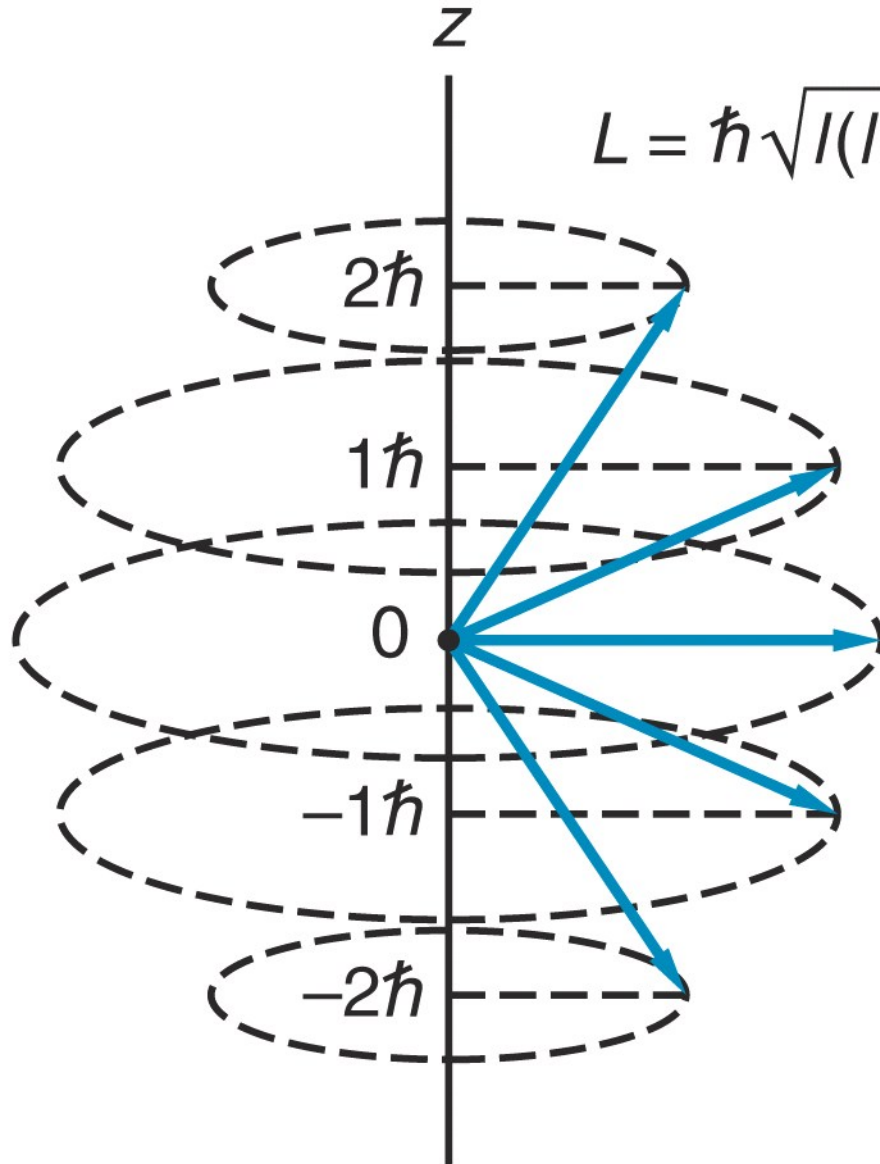
since $m_l \hbar < \sqrt{l(l+1)} \hbar$

It can never be that $|L_z| = m_l \hbar = \sqrt{l(l+1)} \hbar$
(breaks Uncertainty Principle)

So you see, the dance has begun !



$L=2, m_l=0, \pm 1, \pm 2$: Pictorially



$$L = \hbar \sqrt{l(l+1)} = \hbar \sqrt{2(2+1)} = \hbar \sqrt{6}$$

Sweeps Conical paths of different

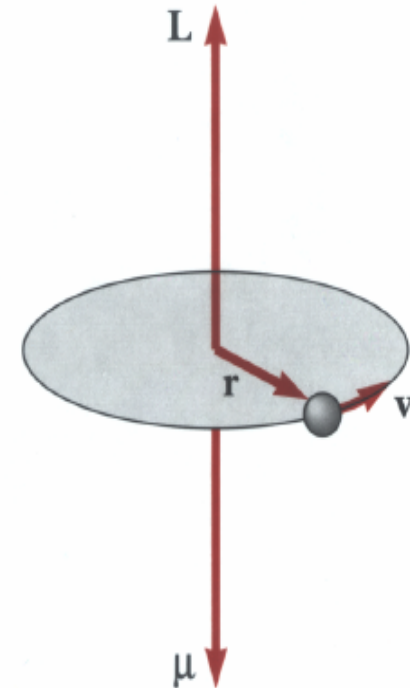
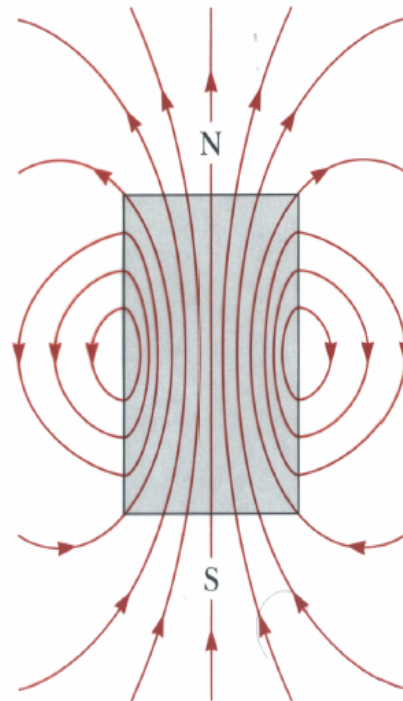
ϑ : $\cos \vartheta = L_z/L$ and average

$$\langle L_x \rangle = 0$$

$$\langle L_y \rangle = 0$$

What's So "Magnetic" ?

Precessing electron \rightarrow Current in loop \rightarrow Magnetic Dipole moment μ



More in this in Tomorrow's lecture when we look at Energy States

Radial Probability Densities

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

Probability Density Function in 3D:

$$P(r, \theta, \phi) = \Psi^* \Psi = |\Psi(r, \theta, \phi)|^2 = |R_{nl}|^2 \cdot |Y_l^{m_l}|^2$$

Note: 3D Volume element $dV = r^2 \cdot \sin \theta \cdot dr \cdot d\theta \cdot d\phi$

Prob. of finding particle in a tiny volume dV is

$$P \cdot dV = |R_{nl}|^2 \cdot |Y_l^{m_l}|^2 \cdot r^2 \cdot \sin \theta \cdot dr \cdot d\theta \cdot d\phi$$

The Radial part of Prob. distribution: $P(r)dr$

$$P(r)dr = |R_{nl}|^2 \cdot r^2 dr \int_0^\pi |\Theta_{lm_l}(\theta)|^2 d\theta \int_0^{2\pi} |\Phi_{m_l}(\phi)|^2 d\phi$$

When $\Theta_{lm_l}(\theta)$ & $\Phi_{m_l}(\phi)$ are auto-normalized then

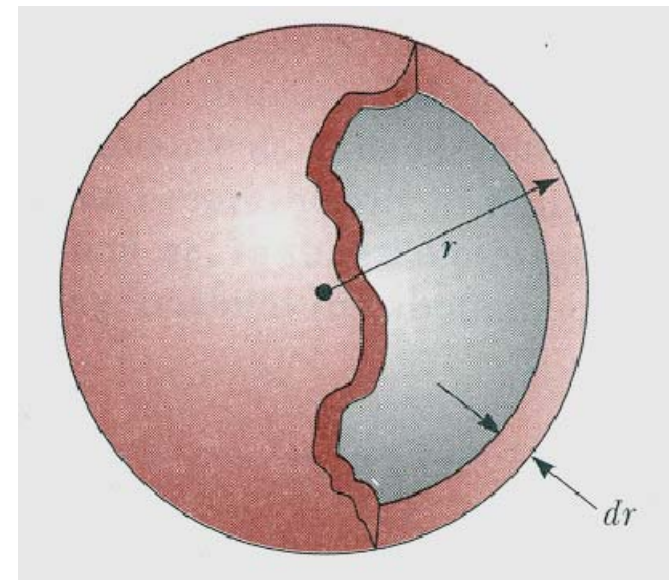
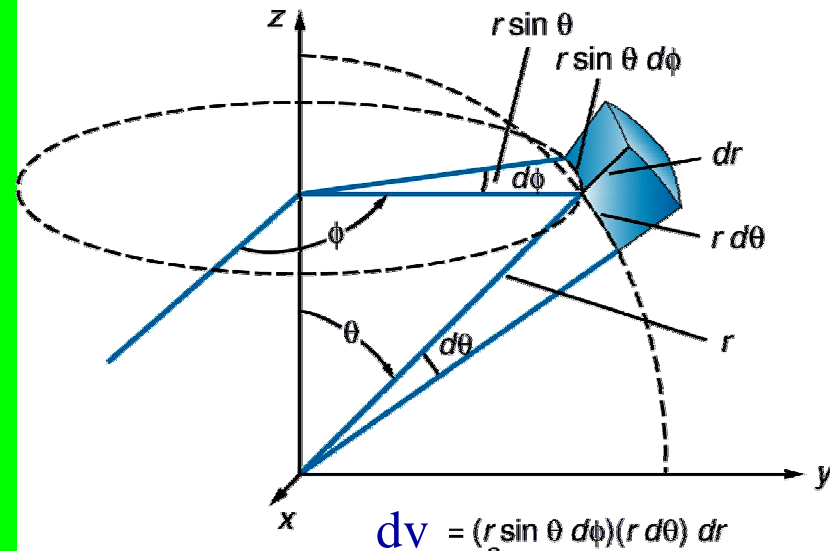
$$P(r)dr = |R_{nl}|^2 \cdot r^2 dr; \text{ in other words } P(r) = r^2 |R_{nl}|^2$$

Normalization Condition:

$$1 = \int_0^\infty r^2 |R_{nl}|^2 dr$$

Expectation Values

$$\langle f(r) \rangle = \int_0^\infty f(r) \cdot P(r) dr$$



Ground State: Radial Probability Density

$$P(r)dr = |\psi(r)|^2 \cdot 4\pi r^2 dr$$

$$\Rightarrow P(r)dr = \frac{4}{a_0^3} r^2 e^{-2\frac{r}{a_0}}$$

Probability of finding Electron for $r > a_0$

$$P_{r>a_0} = \int_{a_0}^{\infty} \frac{4}{a_0^3} r^2 e^{-2\frac{r}{a_0}} dr$$

To solve, employ change of variable

Define $z = \left[\frac{2r}{a_0} \right]$; change limits of integration

$$P_{r>a_0} = \frac{1}{2} \int_2^{\infty} z^2 e^{-z} dz \quad (\text{such integrals called Error. Fn})$$

$$= -\frac{1}{2} [z^2 + 2z + 2] e^{-z} \Big|_2^{\infty} = 5e^{-2} = 0.667 \Rightarrow 66.7\% !!$$

