Physics 2D Lecture Slides
Dec 1

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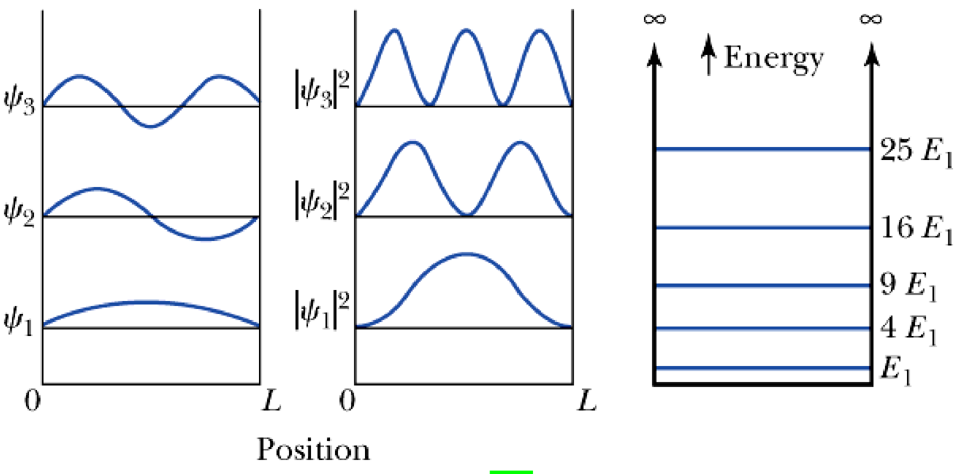
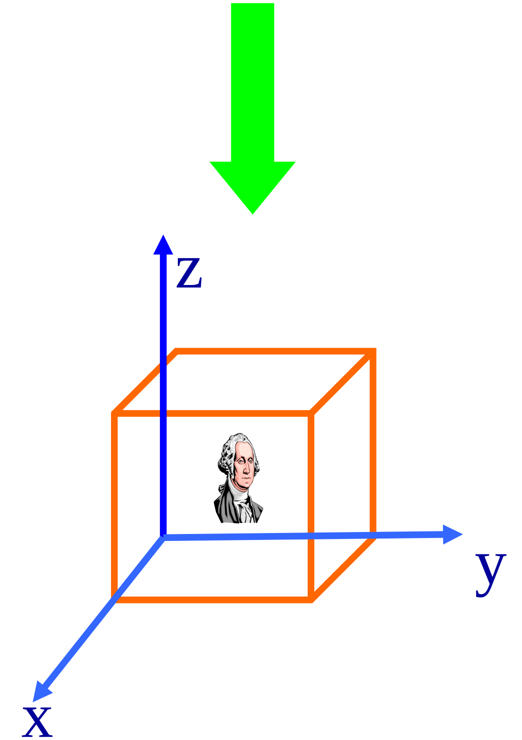
QM in 3 Dimensions

- Learn to extend S. Eq and its solutions from “toy” examples in 1-Dimension (x) $\rightarrow$ three orthogonal dimensions (r ≡x,y,z)

$$\vec{r} = \hat{i}x + \hat{j}y + \hat{k}z$$

- Then transform the systems
  - Particle in 1D rigid box → 3D rigid box
  - 1D Harmonic Oscillator → 3D Harmonic Oscillator
    - Keep an eye on the number of different integers needed to specify system 1→ 3 (corresponding to 3 available degrees of freedom x,y,z)



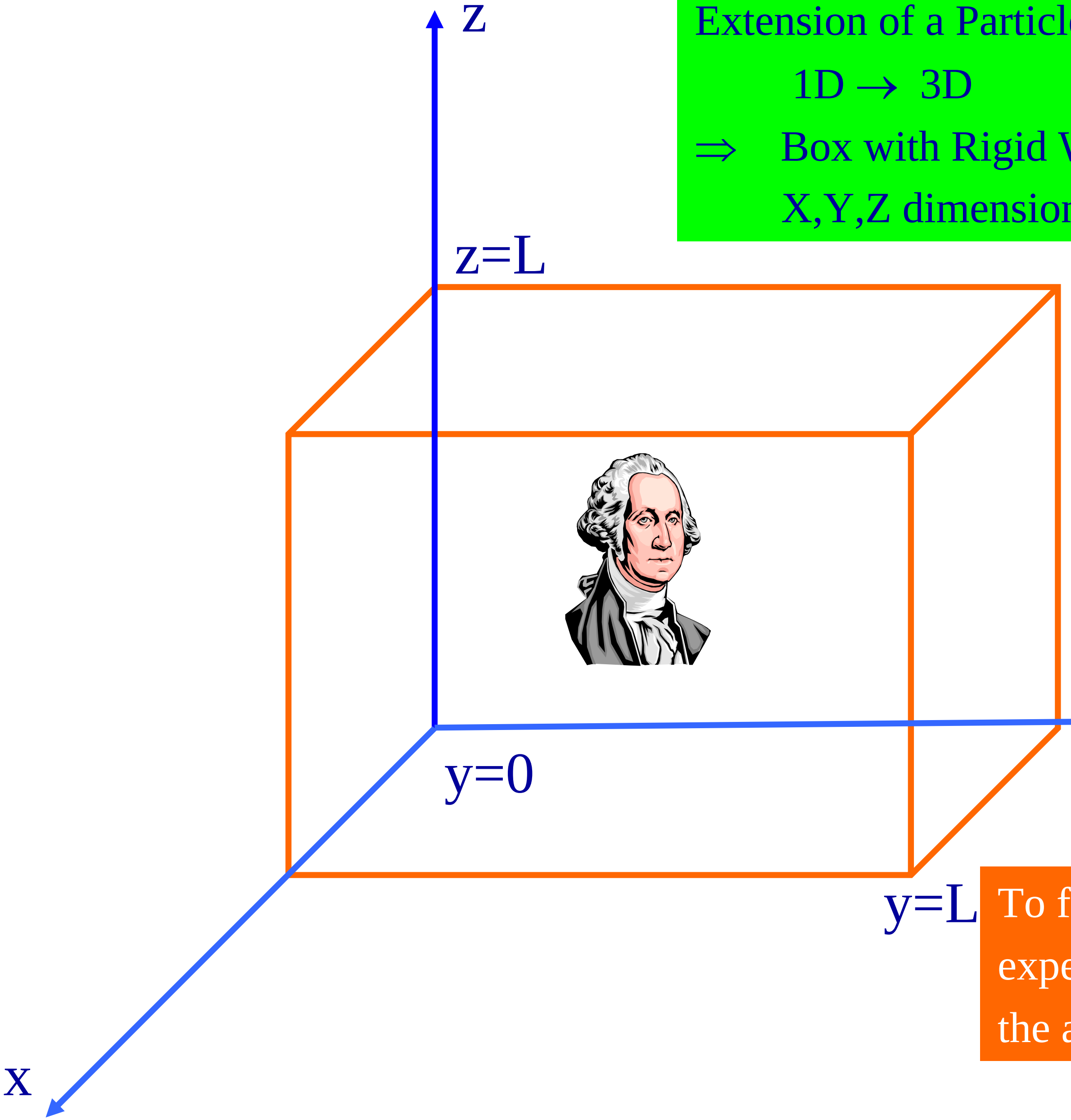


Quantum Mechanics In 3D: Particle in 3D Box

Extension of a Particle In a Box with rigid walls

1D → 3D

⇒ Box with Rigid Walls ($U=\infty$) in X,Y,Z dimensions



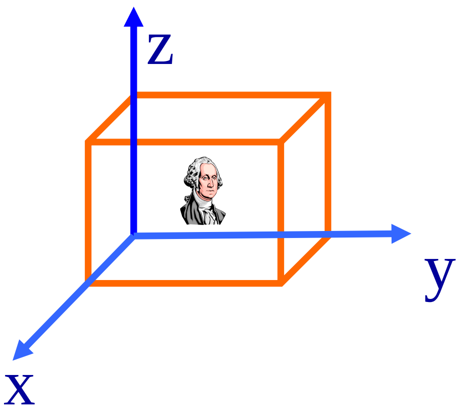
$U(r)=0$ for $(0<x,y,z,<L)$

Ask same questions:

- Location of particle in 3d Box
- Momentum
- Kinetic Energy, Total Energy
- Expectation values in 3D

To find the Wavefunction and various expectation values, we must first set up the appropriate TDSE & TISE

The Schrodinger Equation in 3 Dimensions: Cartesian Coordinates



Time Dependent Schrodinger Eqn:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(x,y,z,t)+U(x,y,z)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t} \quad \text{.....In 3D}$$

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

$$\text{So } -\frac{\hbar^2}{2m}\nabla^2=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)+\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\right)+\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\right)=[K]$$

$$= \quad [K_x] \quad + \quad [K_x] \quad + \quad [K_x]$$

$so\ [H]\Psi(x,t)=[E]\Psi(x,t)$ is still the Energy Conservation Eq

Stationary states are those for which all probabilities are constant in time and are given by the solution of the TDSE in seperable form:

$$\Psi(x,y,z,t)=\Psi(\vec{r},t)=\psi(\vec{r})e^{-i\omega t}$$

This statement is simply an extension of what we derived in case of 1D time-independent potential

Particle in 3D Rigid Box : Separation of Orthogonal Spatial (x,y,z) Variables

TISE in 3D: $-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) + U(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$

x,y,z independent of each other , write $\psi(x,y,z) = \psi_1(x)\psi_2(y)\psi_3(z)$

and substitute in the master TISE, after dividing thruout by $\psi = \psi_1(x)\psi_2(y)\psi_3(z)$

and noting that U(r)=0 for (0<x,y,z,<L) $\Rightarrow$

$$\left(-\frac{\hbar^2}{2m}\frac{1}{\psi_1(x)}\frac{\partial^2\psi_1(x)}{\partial x^2}\right) + \left(-\frac{\hbar^2}{2m}\frac{1}{\psi_2(y)}\frac{\partial^2\psi_2(y)}{\partial y^2}\right) + \left(-\frac{\hbar^2}{2m}\frac{1}{\psi_3(z)}\frac{\partial^2\psi_3(z)}{\partial z^2}\right) = E = Const$$

This can only be true if each term is constant for all x,y,z $\Rightarrow$

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi_1(x)}{\partial x^2} = E_1\psi_1(x)};\ \boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi_2(y)}{\partial y^2} = E_2\psi_2(y)};\ \boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi_3(z)}{\partial z^2} = E_3\psi_3(z)}$$

With $\boxed{E_1 + E_2 + E_3 = E = \text{Constant}}$ (Total Energy of 3D system)

Each term looks like particle in 1D box (just a different dimension)

So wavefunctions must be like $\boxed{\psi_1(x) \propto \sin k_1 x}$, $\boxed{\psi_2(y) \propto \sin k_2 y}$, $\boxed{\psi_3(z) \propto \sin k_3 z}$

Particle in 3D Rigid Box : Separation of Orthogonal Variables

Wavefunctions are like $\psi_1(x) \propto \sin k_1 x$, $\psi_2(y) \propto \sin k_2 y$, $\psi_3(z) \propto \sin k_3 z$

Continuity Conditions for ψ_i and its first spatial derivatives $\Rightarrow$ $n_i \pi = k_i L$

Leads to usual Quantization of Linear Momentum $\vec{p} = \hbar \vec{k}$.....in 3D

$p_x = \left(\frac{\pi\hbar}{L}\right) n_1$; $p_y = \left(\frac{\pi\hbar}{L}\right) n_2$; $p_z = \left(\frac{\pi\hbar}{L}\right) n_3$ $(n_1, n_2, n_3 = 1, 2, 3, ..\infty)$

Note: by usual Uncertainty Principle argument neither of $n_1, n_2, n_3 = 0$! (*why*?)

Particle Energy E = K+U = K +0 = $\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$

Energy is again quantized and brought to you by integers n_1, n_2, n_3 (independent)

and $\psi(\vec{r}) = A \sin k_1 x \sin k_2 y \sin k_3 z$ (A = Overall Normalization Constant)

$$\Psi(\vec{r},t) = \psi(\vec{r})\, e^{-i\frac{E}{\hbar}t} = A\,[\sin k_1 x \sin k_2 y \sin k_3 z]\, e^{-i\frac{E}{\hbar}t}$$

Particle in 3D Box :Wave function Normalization Condition

$$\Psi(\vec{r},t)=\psi(\vec{r})\, e^{-i\frac{E}{\hbar}t} = A\,[\sin k_1 x \sin k_2 y \sin k_3 z]\, e^{-i\frac{E}{\hbar}t}$$

$$\Psi^*(\vec{r},t)=\psi^*(\vec{r})\, e^{i\frac{E}{\hbar}t} = A\,[\sin k_1 x \sin k_2 y \sin k_3 z]\, e^{i\frac{E}{\hbar}t}$$

$$\Psi^*(\vec{r},t)\Psi(\vec{r},t)=A^2\,[\sin^2 k_1 x \sin^2 k_2 y \sin^2 k_3 z]$$

$$\text{Normalization Condition : } 1 = \iiint_{x,y,z} P(r)\,dx\,dydz \Rightarrow$$

$$1 = A^2 \int_{x=0}^{L} \sin^2 k_1 x\, dx \int_{y=0}^{L} \sin^2 k_2 y\, dy \int_{z=0}^{L} \sin^2 k_3 z\, dz = A^2 \left(\sqrt{\frac{L}{2}}\right)\left(\sqrt{\frac{L}{2}}\right)\left(\sqrt{\frac{L}{2}}\right)$$

$$\Rightarrow A = \left[\frac{2}{L}\right]^{\frac{3}{2}} \text{ and } \Psi(\vec{r},t)= \left[\frac{2}{L}\right]^{\frac{3}{2}} [\sin k_1 x \sin k_2 y \sin k_3 z]\, e^{-i\frac{E}{\hbar}t}$$

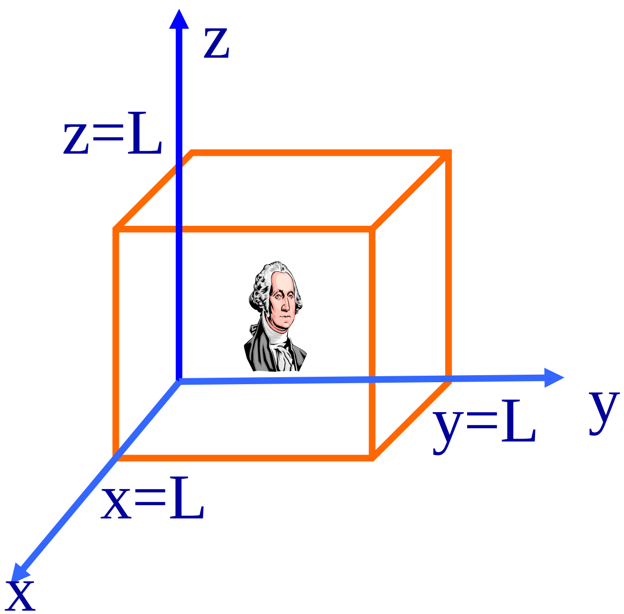
Particle in 3D Box : Energy Spectrum & Degeneracy

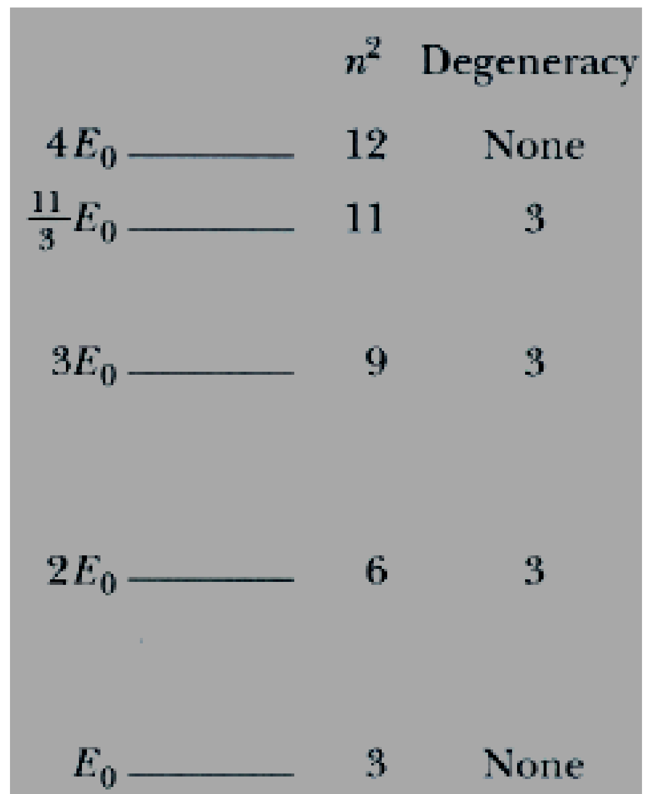
$$E_{n_1,n_2,n_3} = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2+n_2^2+n_3^2); \quad n_i = 1,2,3\ldots\infty, n_i \neq 0$$

Ground State Energy $E_{111} = \dfrac{3\pi^2\hbar^2}{2mL^2}$

Next level $\Rightarrow$ 3 Excited states $E_{211} = E_{121} = E_{112} = \dfrac{6\pi^2\hbar^2}{2mL^2}$

Different configurations of ψ(r)=ψ(x,y,z) have same energy $\Rightarrow$ degeneracy

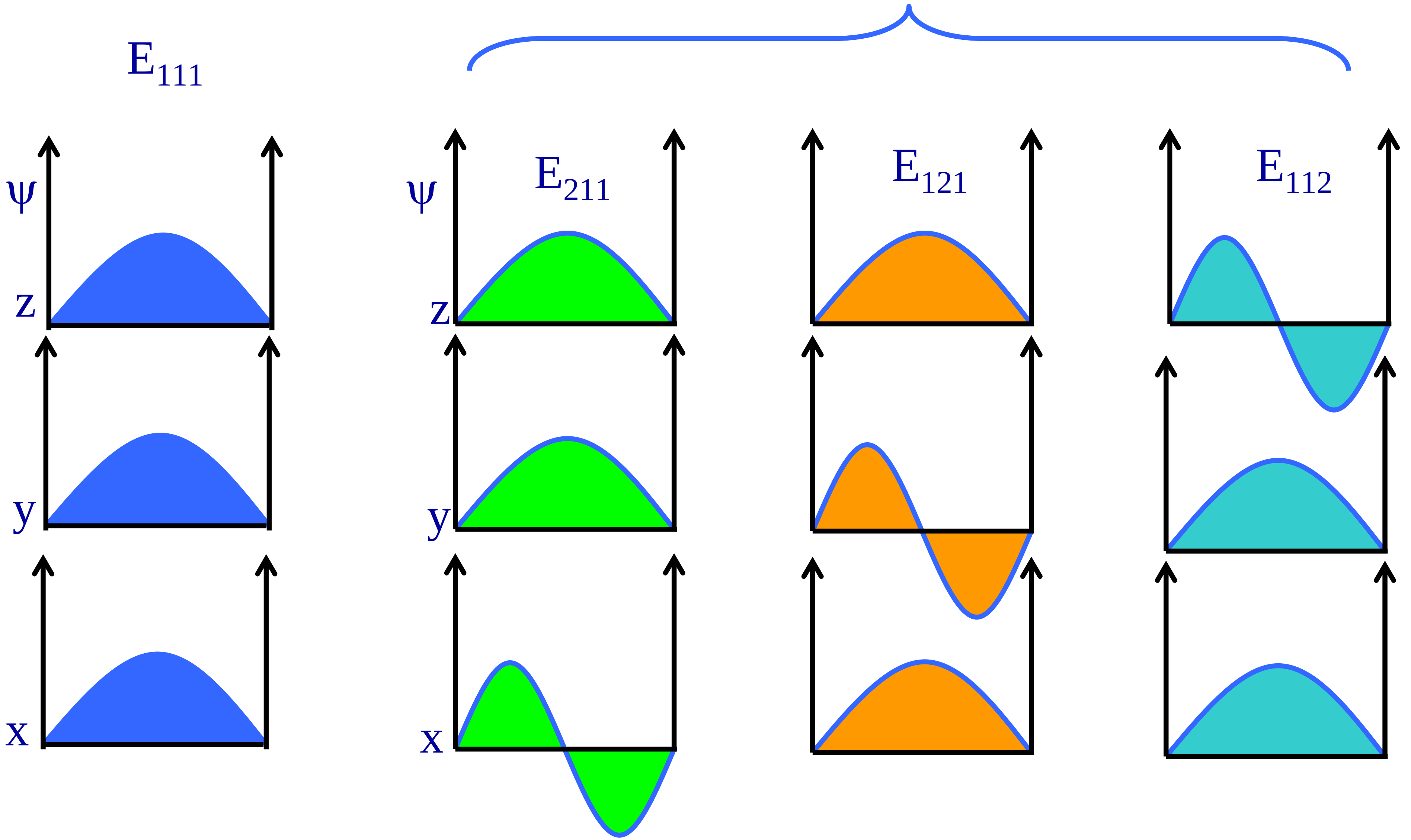




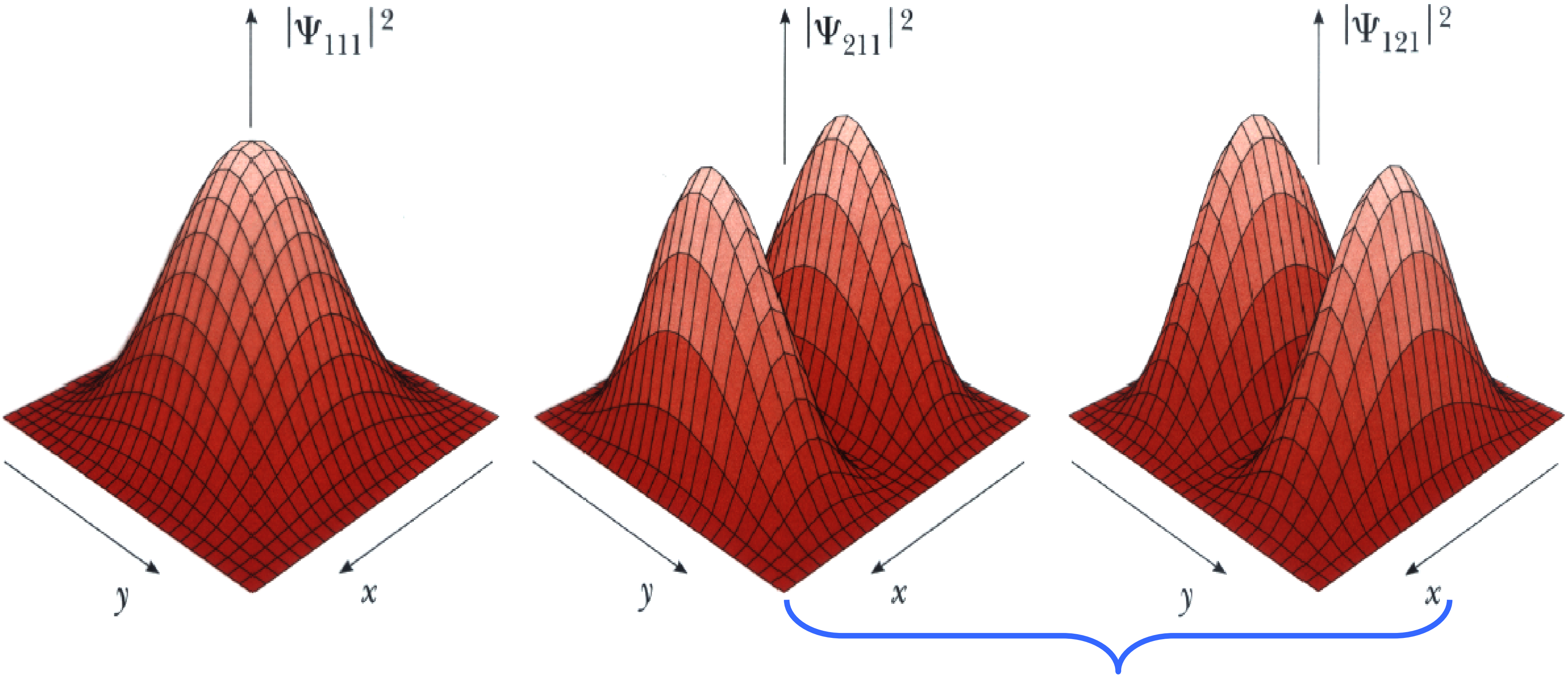
Degenerate States

$$E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2mL^2}$$

Ground State



Probability Density Functions for Particle in 3D Box



Same Energy → Degenerate States

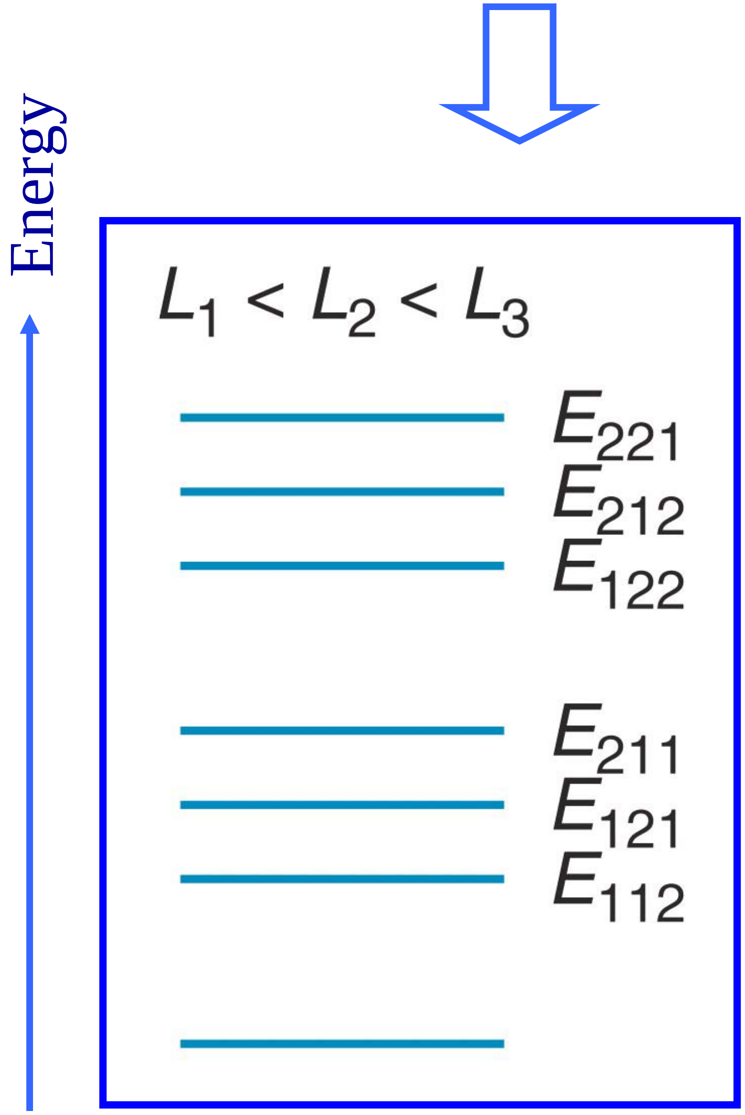
Cant tell by measuring energy if particle is in 211, 121, 112 quantum State

Source of Degeneracy: How to "Lift" Degeneracy

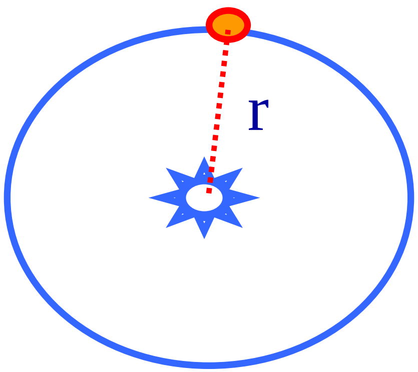
- Degeneracy came from the threefold symmetry of a CUBICAL Box ($L_x = L_y = L_z = L$)

- To Lift (remove) degeneracy → change each dimension such that CUBICAL box → Rectangular Box
  - ($L_x \neq L_y \neq L_z$)
  - Then

$$E = \left(\frac{n_1^2 \pi^2}{2mL_x^2}\right) + \left(\frac{n_2^2 \pi^2}{2mL_y^2}\right) + \left(\frac{n_3^2 \pi^2}{2mL_z^2}\right)$$



The Hydrogen Atom In Its Full Quantum Mechanical Glory



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

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

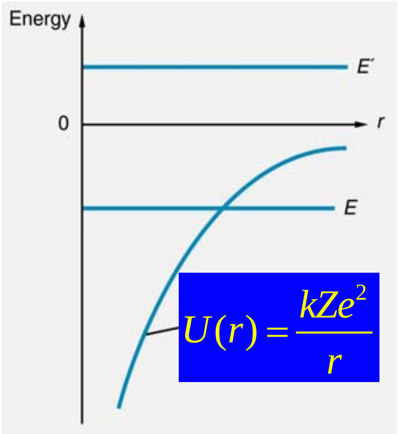
This approach will get very ugly since we have a "conjoined triplet"

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

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

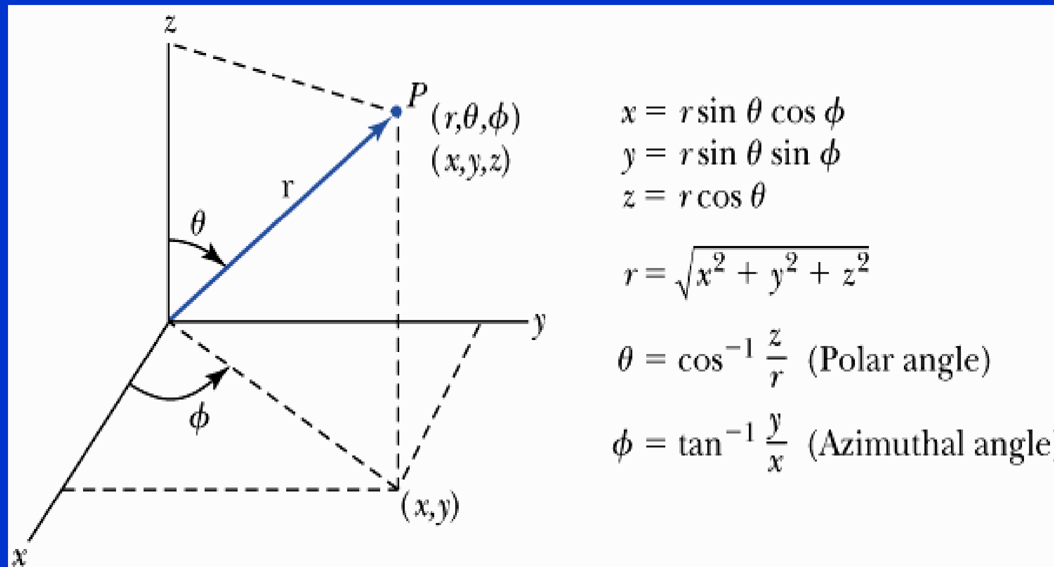


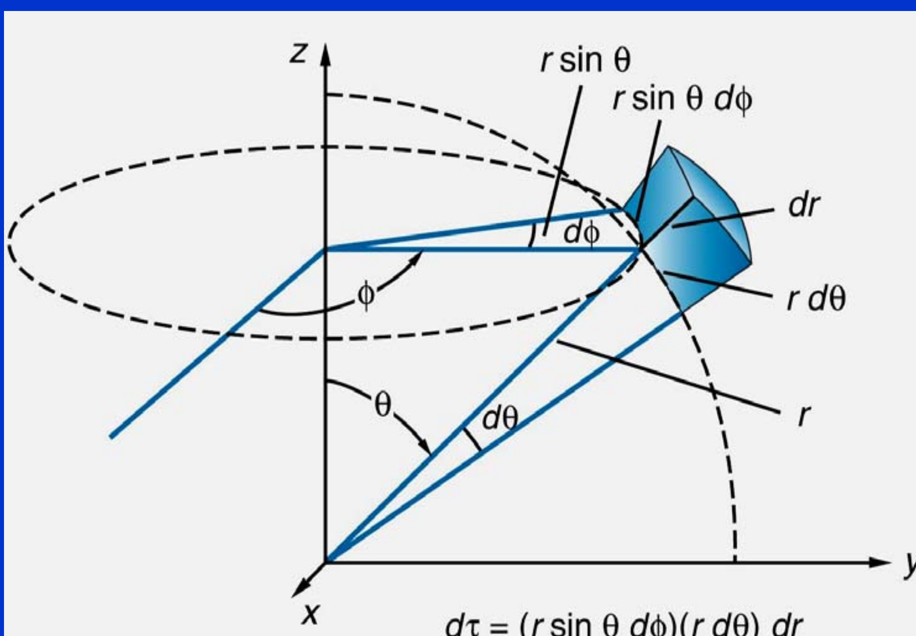
TISE for $\psi(x,y,z)=\psi(r,\theta,\phi)$ becomes

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

!!!! fun!!!

Spherical Polar Coordinate System





Volume Element dV

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

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

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 $\boxed{r^2\sin^2\theta}\Rightarrow$

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

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

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

Note that : $$\boxed{\begin{aligned}\frac{\partial\Psi(r,\theta,\phi)}{\partial r}&=\Theta(\theta).\Phi(\phi)\ \frac{\partial R(r)}{\partial r}\\ \frac{\partial\Psi(r,\theta,\phi)}{\partial\theta}&=R(r)\Phi(\phi)\ \frac{\partial\Theta(\theta)}{\partial\theta}\\ \frac{\partial\Psi(r,\theta,\phi)}{\partial\theta}&=R(r)\Theta(\theta)\ \frac{\partial\Phi(\phi)}{\partial\phi}\end{aligned}}$$ $\Rightarrow$ when substituted in TISE

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

Rearrange by taking the ϕ term on RHS

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

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

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

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

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

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

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

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

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

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

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

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

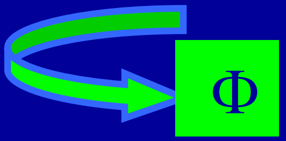
These 3 "simple" diff. eqn describe the physics of the Hydrogen atom.

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

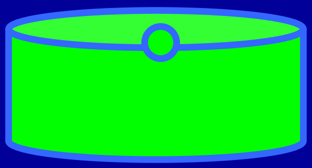
The Azimuthal Diff. Equation : $\boxed{\dfrac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0}$



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

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

$\Rightarrow \Phi(\phi) = A\, e^{im_l\phi} = A\, e^{im_l(\phi+2\pi)} \Rightarrow m_l = 0, \pm1, \pm2, \pm3....($ *Magnetic* Quantum # $)$



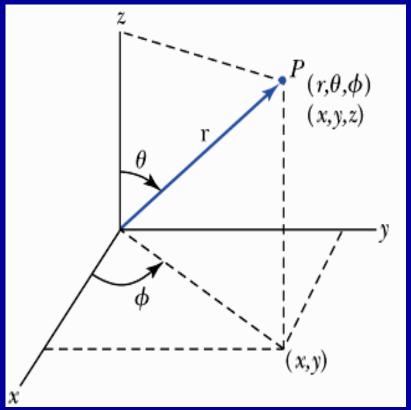
The Polar Diff. Eq: $\boxed{\dfrac{1}{\sin\theta}\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right) + \left[l(l+1) - \dfrac{m_l^2}{\sin^2\theta}\right]\Theta(\theta) = 0}$

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

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

$m_l = 0, \pm1, \pm2, \pm3.... \pm l$; l = positive number

l : Orbital Quantum Number



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

For $l = 1, m_l{=}0, \pm1 \Rightarrow$ Three Possibilities for the Orbital part of wavefunction

$\boxed{[l = 1, m_l = 0] \Rightarrow \Theta(\theta) = \dfrac{\sqrt{6}}{2}\cos\theta}$ $\boxed{[l = 1, m_l = \pm1] \Rightarrow \Theta(\theta) = \dfrac{\sqrt{3}}{2}\sin\theta}$

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

Solutions of The S. Eq for Hydrogen Atom

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

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

1. E>0 or has negtive values given by $\mathrm{E}=-\frac{\mathrm{ke}^2}{2\mathrm{a}_0}\left(\frac{1}{n^2}\right); a_0=\frac{\hbar^2}{mke^2}$ = Bohr Radius

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

n = principal Quantum # or the "big daddy" qunatum #

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

$$\boxed{\begin{array}{l} \mathrm{n} = 1,2,3,4,5,....\infty \\ l=0,1,2,3,,4....(n-1) \\ \mathrm{m}_l=0,\pm1,\pm2,\pm3,...\pm l \end{array}}$$

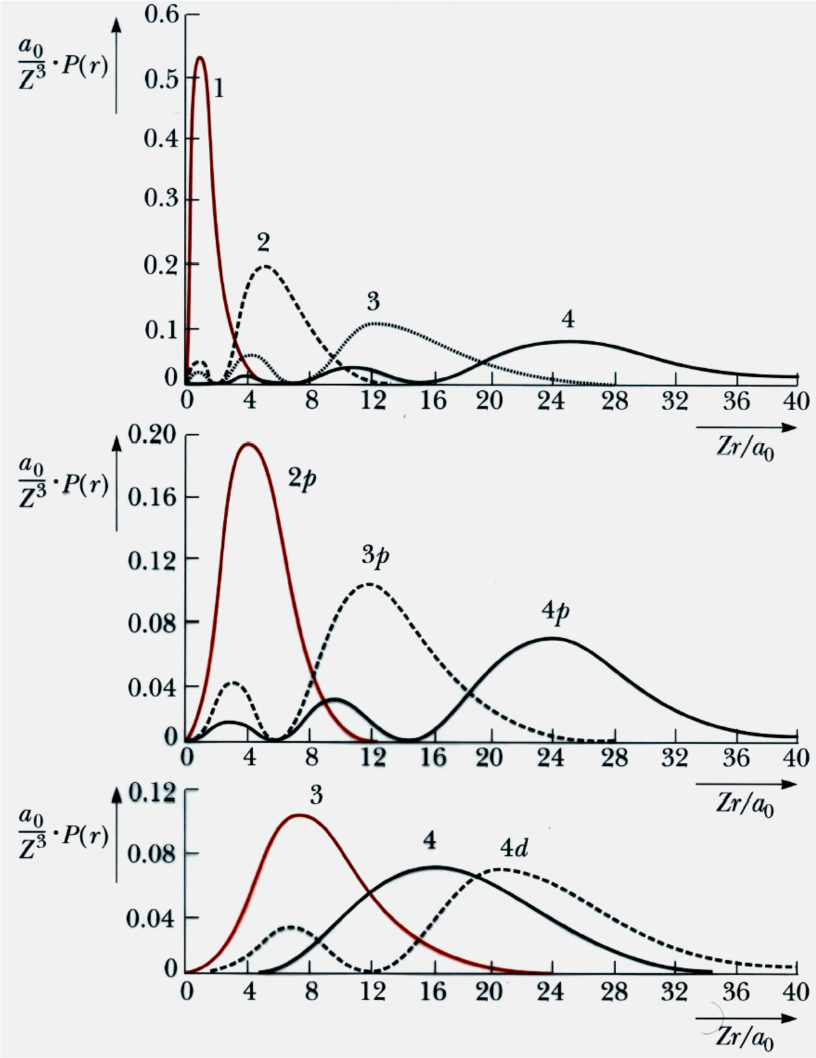
Quantum # appear only in Trapped systems

The Spatial Wave Function of the Hydrogen Atom

$$\Psi(r,\theta,\phi)=R_{nl}(r)\ .\ \Theta_{lm_l}(\theta)\ \ .\ \Phi_{\mathrm{m_l}}(\phi)=R_{nl}\mathrm{Y}_l^{m_l}\ \text{(Spherical Harmonics)}$$

Radial Wave Functions & Radial Prob Distributions

n	l	m_l	$R(r)=$
1	0	0	$\frac{2}{a_0^{3/2}} e^{-r/a}$
2	0	0	$\frac{1}{2\sqrt{2}a_0^{3/2}}(2-\frac{r}{a_0})e^{-\frac{r}{2a_0}}$
3	0	0	$\frac{2}{81\sqrt{3}a_0^{3/2}}(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2})e^{-\frac{r}{3a_0}}$



n=1 → K shell

n=2 → L Shell

n=3 → M shell

n=4 → N Shell

……

l=0 → *s(harp) sub shell*

l=1 → *p(rincipal) sub shell*

l=2 → *d(iffuse) sub shell*

l=3 → *f(undamental) ss*

l=4 → *g sub shell*

………

Symbolic Notation of Atomic States in Hydrogen

$l \rightarrow$ $n \downarrow$	$s\ (l=0)$	$p\ (l=1)$	$d\ (l=2)$	$f\ (l=3)$	$g\ (l=4)$	.....
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
- n1>1 are all degenerate in l and m_l.

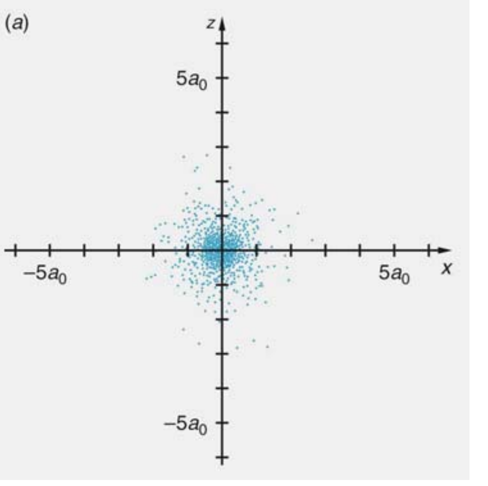
  All states have same energy

  But different spatial configuration

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

Facts About Ground State of H Atom

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



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

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

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

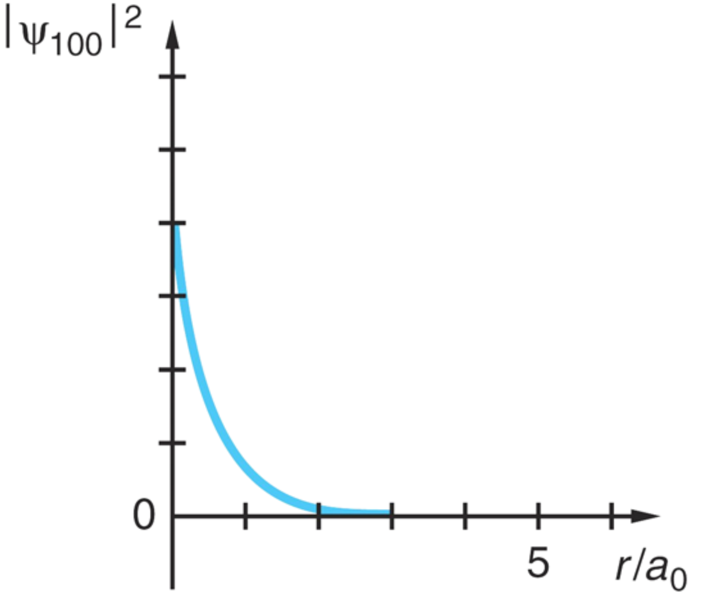
Likelihood of finding the electron is same at all θ,ϕ and depends only on the
radial seperation (r) between electron & the nucleus.

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!

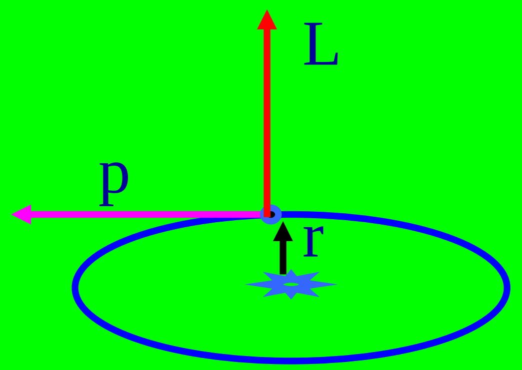


Interpreting Orbital Quantum Number *(l)*

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

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

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



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

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

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

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

Since l = *positive* integer=0,1,2,3...(n-1) $\Rightarrow$ angular momentum $|L|=\sqrt{l(l+1)}\hbar=$ *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:

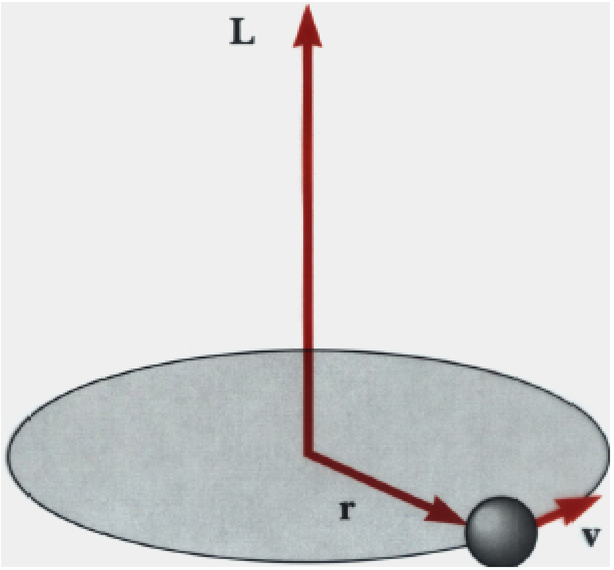
Suppose $\vec{L}$ was precisely known/defined ($\vec{L} \parallel \hat{z}$)

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 : $\boxed{\Delta L_z \Delta\phi \sim \hbar}$



Arbitararily picking Z axis as a reference direction:

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

The Z component of $\vec{L}$

$\boxed{|L_Z| = m_l\hbar; \quad m_l = \pm1, \pm2, \pm3 \ldots \pm l}$

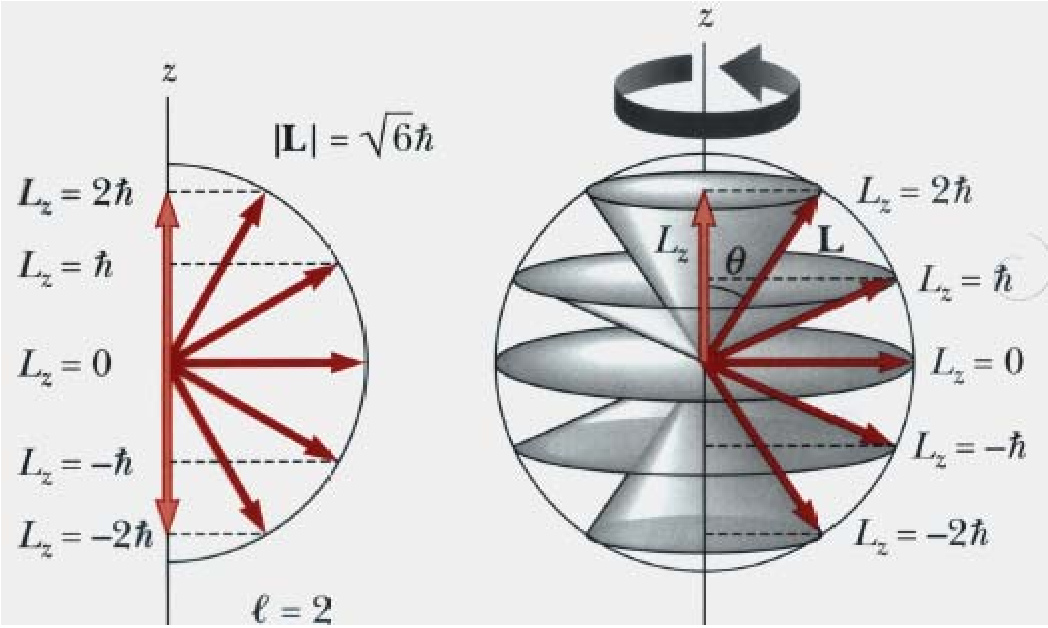
Note : $|L_Z| < |L|$ (always)

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

It can never be that $|L_Z| = m_l\hbar = \sqrt{l(l+1)}\hbar$

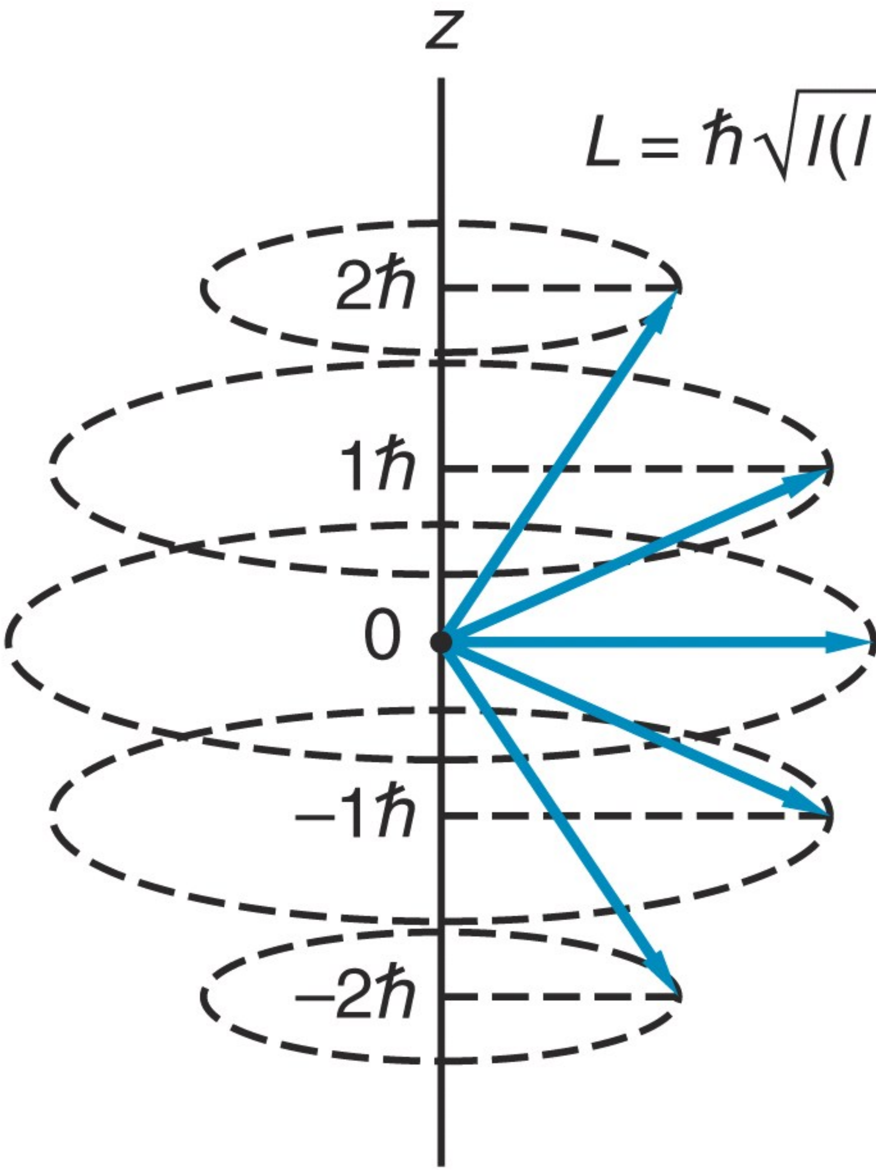
(breaks Uncertainty Principle)

So you see, the dance has begun !



L=2, m_l=0,±1, ± 2 : Pictorially

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



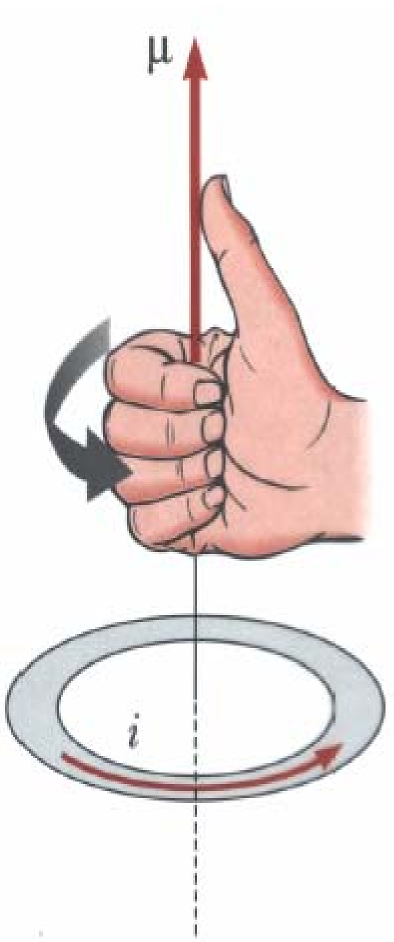
Sweeps Conical paths of different ϑ: Cos $\vartheta = L_Z/L$ and average

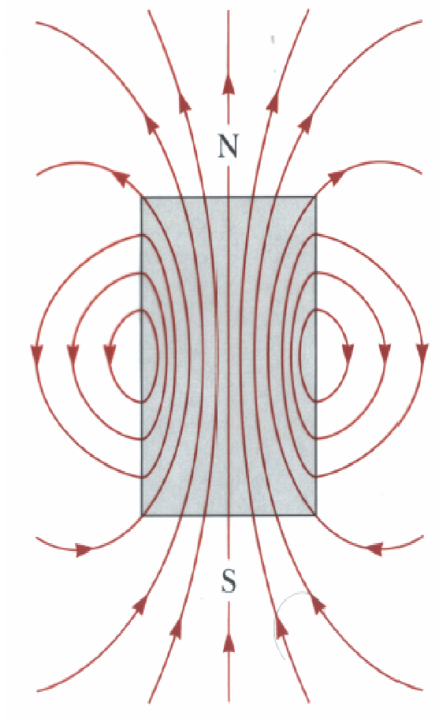
$$\langle L_X \rangle = 0$$

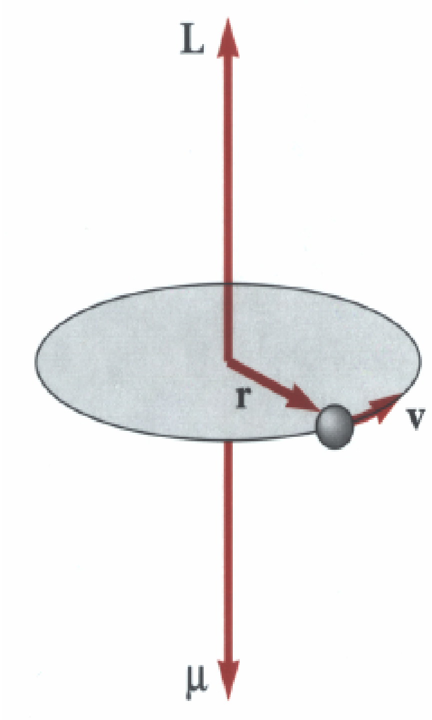
$$\langle L_Y \rangle = 0$$

What's So "Magnetic" ?

Precessing electron→ Current in loop → Magnetic Dipole moment μ







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

Radial Probability Densities

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

Probability Density Function in 3D:

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

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

Prob. of finding particle in a tiny volume dV is

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

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

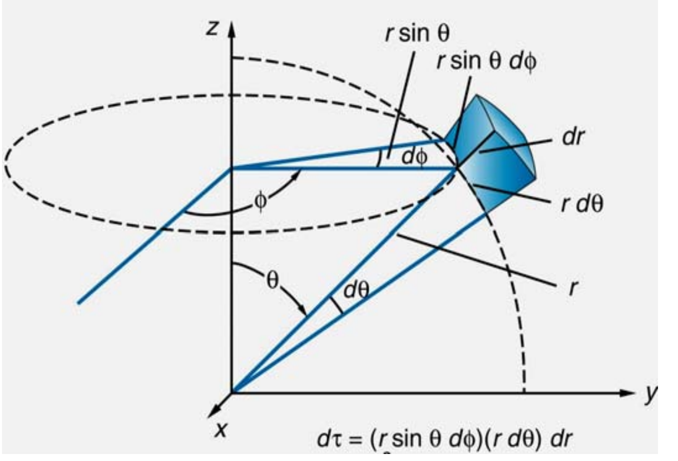
$$P(r)dr = |R_{nl}|^2 .r^2 dr \int_0^{\pi} |\Theta_{lm_l}(\theta)|^2 d\theta \int_0^{2\pi} |\Phi_{m_l}(\phi)|^2\, d\phi$$

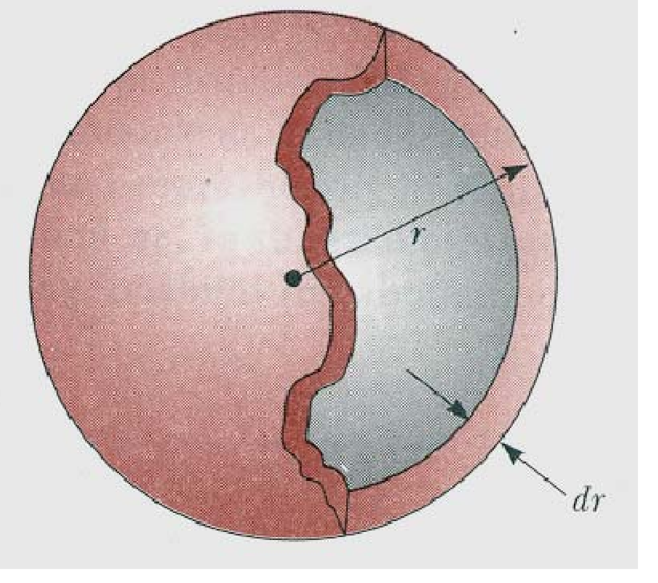
When $\Theta_{lm_l}(\theta)$ & $\Phi_{m_l}(\phi)$ are auto-normalized then

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

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

Expectation Values $\langle f(r)\rangle = \int_0^{\infty} f(r).P(r)dr$





Ground State: Radial Probability Density

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

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

Probability of finding Electron for r>a_0

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

To solve, employ change of variable

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

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

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