Physics 2D Lecture Slides
Lectures Week of March 1, 2010

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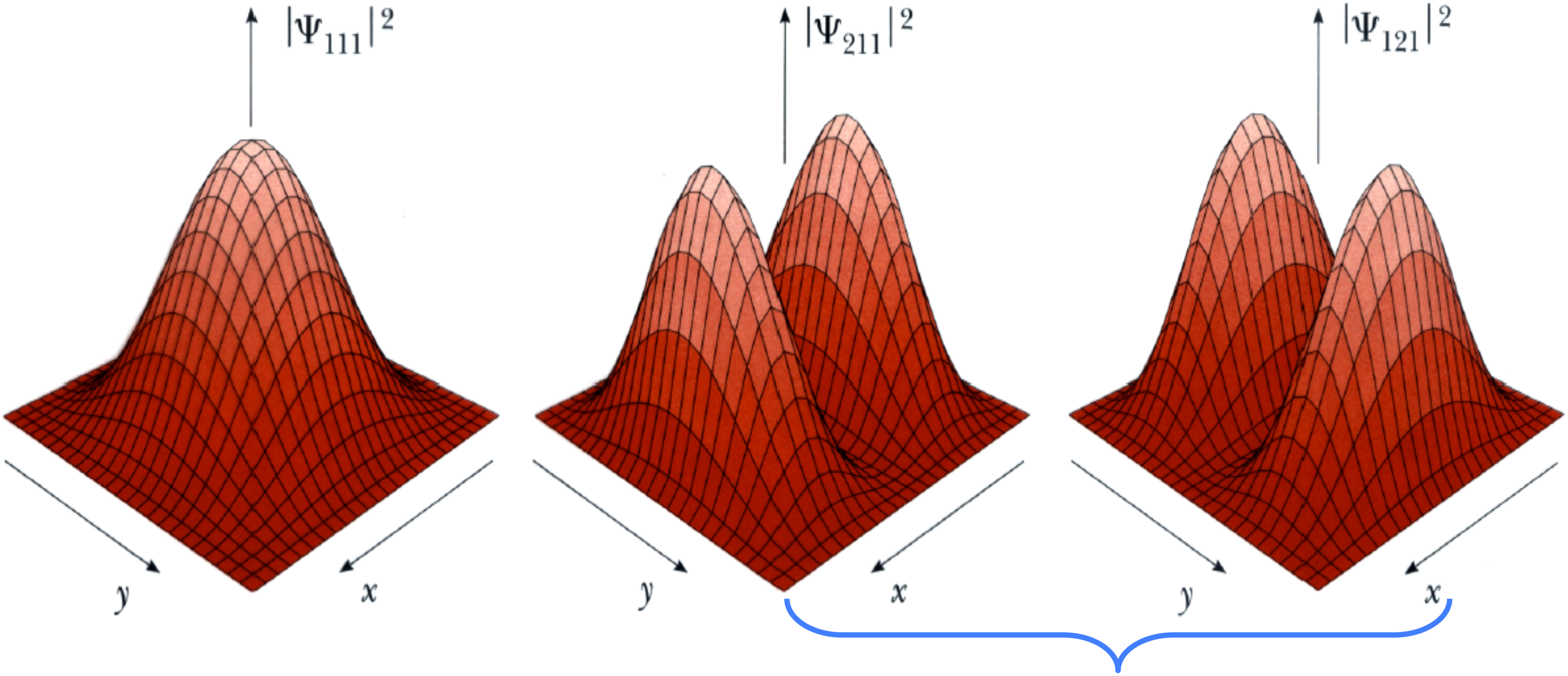
Probability Density Functions for Particle in 3D Box



Same Energy → Degenerate States

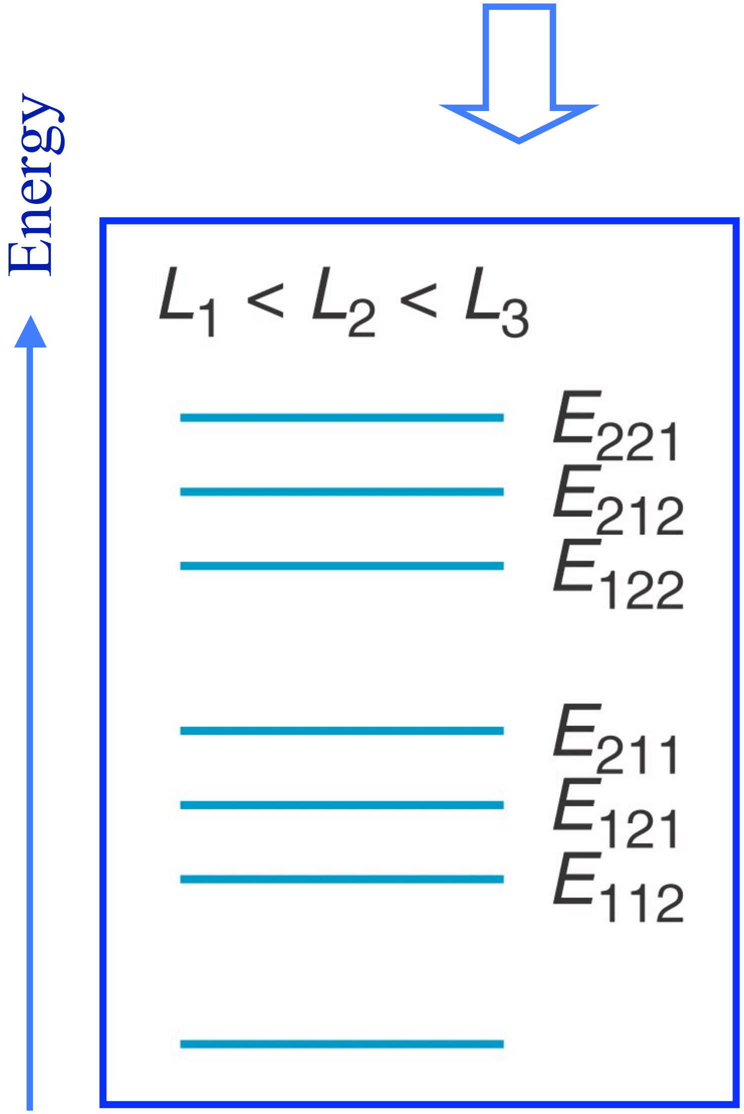
Cant tell by measuring energy if particle is in 211, 121, 112 quantum State

Source of Degeneracy: How to “Lift” Degeneracy

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

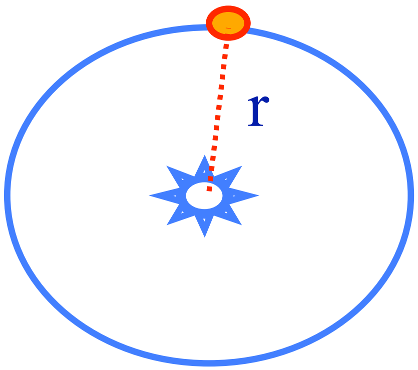
- To Lift (remove) degeneracy → change each dimension such that CUBICAL box → Rectangular Box
  - ($L_x \neq L_y \neq L_z$)
  - Then

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



The Hydrogen Atom In Its Full Quantum Mechanical Glory

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



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

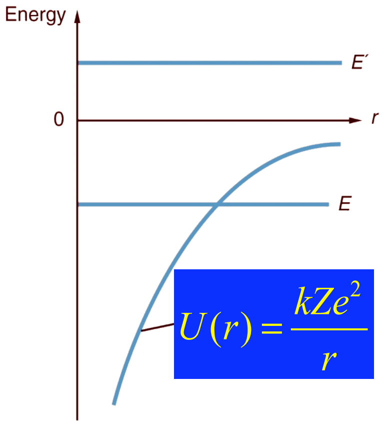
This approach will get very ugly since we have a "conjoined triplet"

To simplify the situation, use appropriate variables

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

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

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

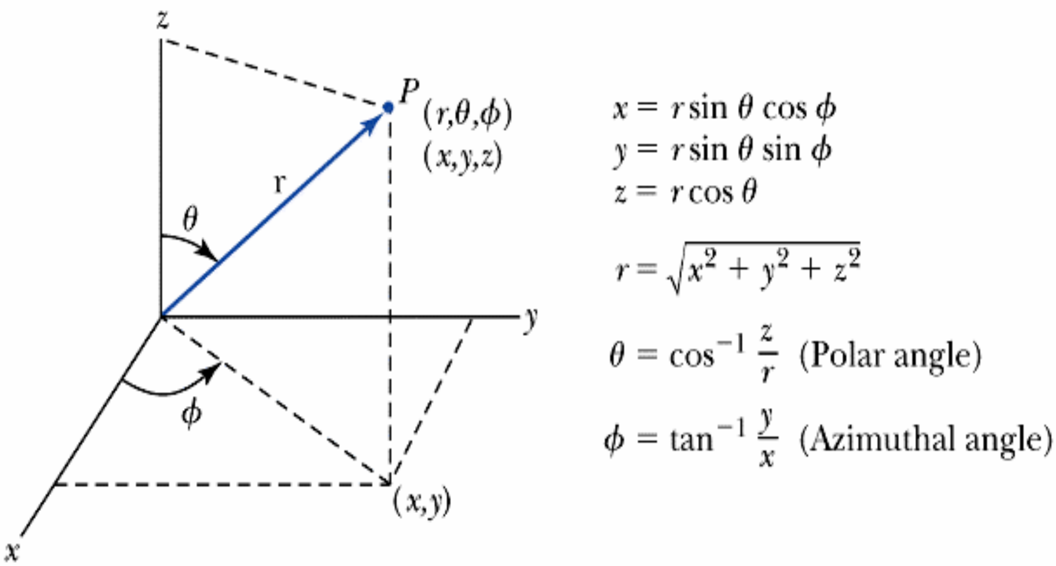


TISE for $\psi(x,y,z)=\psi(r,\theta,\phi)$ becomes

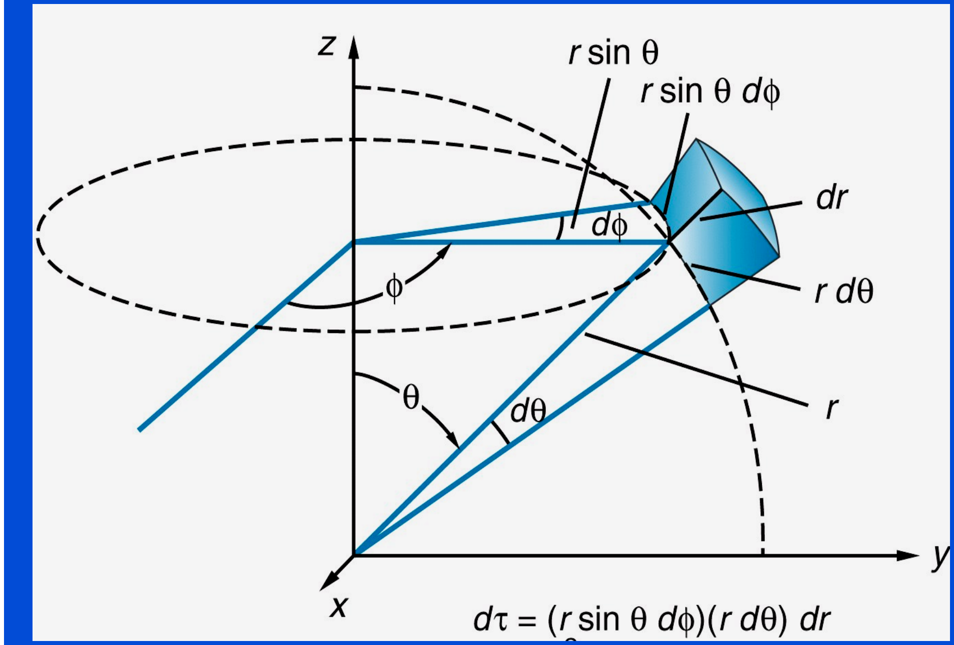
$$\boxed{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial^2\phi}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

!!!! fun!!!

Spherical Polar Coordinate System



$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$
$$r = \sqrt{x^2 + y^2 + z^2}$$
$$\theta = \cos^{-1}\frac{z}{r} \quad \text{(Polar angle)}$$
$$\phi = \tan^{-1}\frac{y}{x} \quad \text{(Azimuthal angle)}$$



$$d\tau = (r\sin\theta\, d\phi)(r\, d\theta)\, dr$$

Volume Element dV

$$dV = (r\sin\theta d\phi)(rd\theta)(dr)$$
$$= \mathrm{r}^2 \sin\theta drd\theta d\phi$$

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 second 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 Separation 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 : $$\boxed{\begin{array}{l}\frac{\partial\Psi(r,\theta,\phi)}{\partial r}=\Theta(\theta).\Phi(\phi)\frac{dR(r)}{dr}\\ \frac{\partial\Psi(r,\theta,\phi)}{\partial\theta}=R(r)\Phi(\phi)\frac{d\Theta(\theta)}{d\theta}\\ \frac{\partial\Psi(r,\theta,\phi)}{\partial\theta}=R(r)\Theta(\theta)\frac{d\Phi(\phi)}{d\phi}\end{array}}\Rightarrow$$ when substituted in TISE

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

Rearrange by taking the ϕ term on RHS

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

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 separate the r & θ terms.....

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

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

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

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

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

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

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

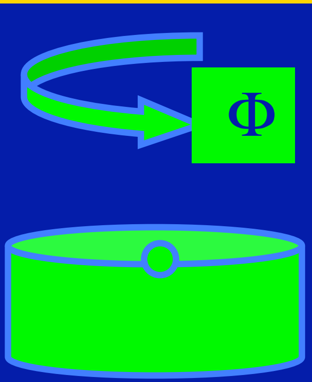
$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2m}{\hbar^2}(E+\frac{ke^2}{r})-\frac{l(l+1)}{r^2}\right]R(r)=0....(3)$$

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 : $\boxed{\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0}$

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

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

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

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

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

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

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

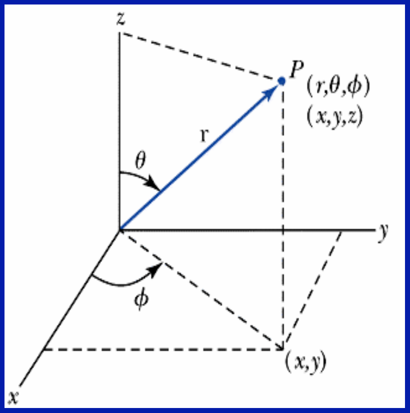
$\boxed{l:\ \text{Orbital Quantum Number}}$

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

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

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

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



Solutions of The S. Eq for Hydrogen Atom

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

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

1. E<0 or has negative 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 #

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

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

Quantum # appear only in Trapped systems

The Spatial Wave Function of the Hydrogen Atom

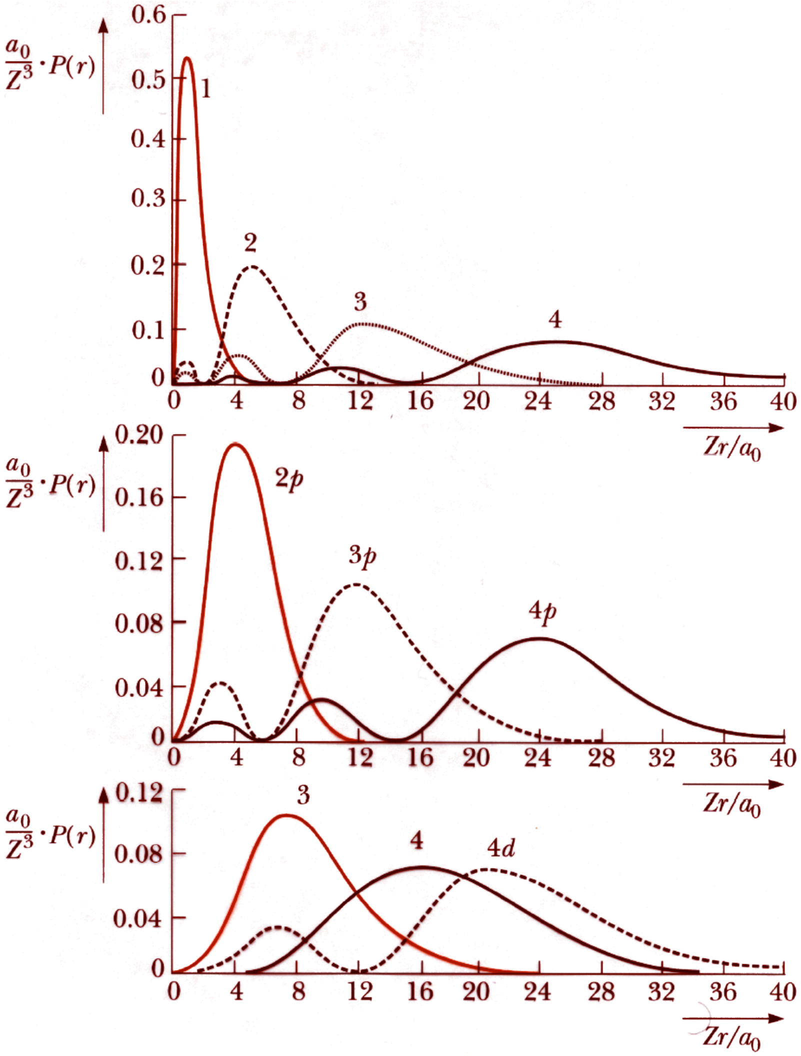
$$\Psi(r,\theta,\phi)=R_{nl}(r)\,.\,\Theta_{lm_l}(\theta)\quad.\,\Phi_{\mathrm{m}_l}(\phi)=R_{nl}\mathrm{Y}_l^{m_l}\text{ (Spherical Harmonics)}$$

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
- n>1 are all degenerate in l and m_l.

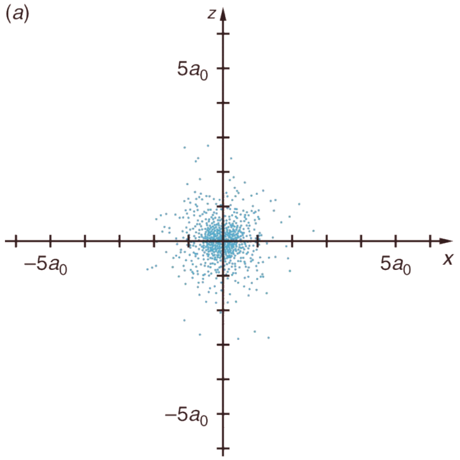
  All states have same energy

  But different spatial configuration

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

Facts About Ground State of H Atom

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



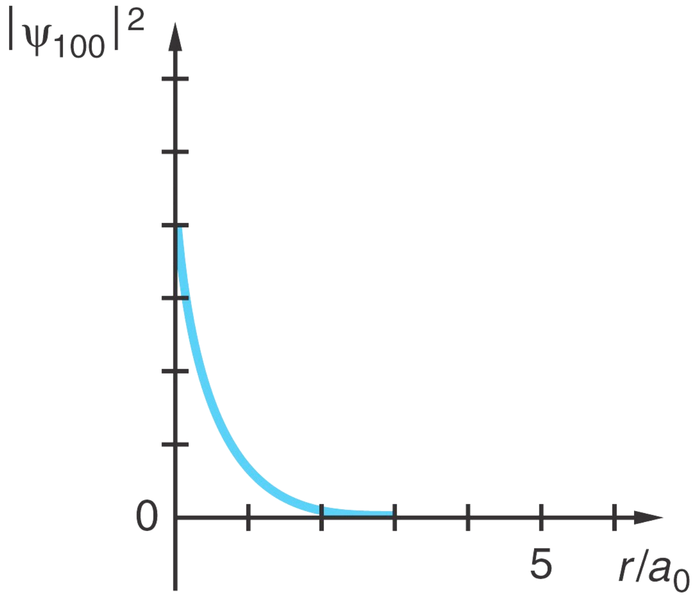
$\boxed{\Psi_{100}(r,\theta,\phi)=\frac{1}{a_0\sqrt{\pi}}\,e^{-r/a}}$......look at it carefully

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 =-$\frac{ke^2}{2a_0}=-13.6eV$

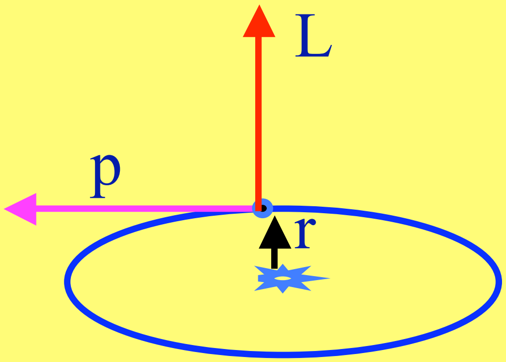


Overall The Ground state wavefunction of the hydrogen atom is quite *boring*

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 $\boxed{K_{ORBITAL}=\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}}$ *then* get a diff. eq. in r

$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left[K_{RADIAL}\right]R(r)=0$ 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: $\boxed{K_{ORBITAL}=\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}=\frac{L^2}{2mr^2}}$ $\Rightarrow$ magnitude of Ang. Mom $|L|=\sqrt{l(l+1)}\hbar$

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

$|L|=\sqrt{l(l+1)}\hbar$: 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 $\vec{L}$

$\boxed{|L_Z| = m_l \hbar; \quad m_l = \pm 1, \pm 2, \pm 3 \ldots \pm l}$

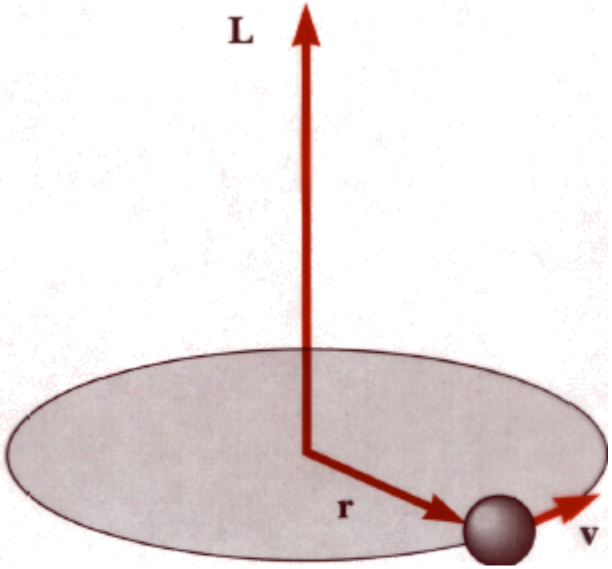
Note : $|L_Z| \ < \ |L|$ (always)

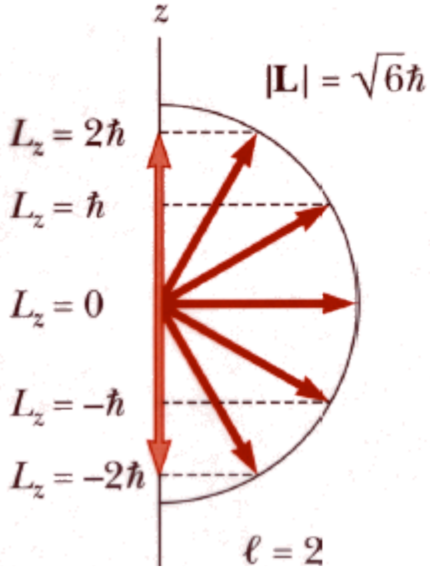
since $m_l \hbar < \sqrt{l(l+1)}\hbar$

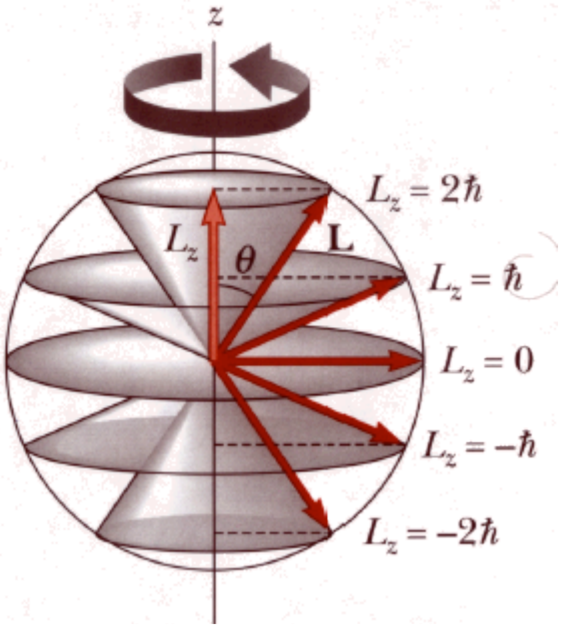
It can never be that $|L_Z| = m_l \hbar = \sqrt{l(l+1)}\hbar$

(breaks Uncertainty Principle)

So you see, the dance has begun !

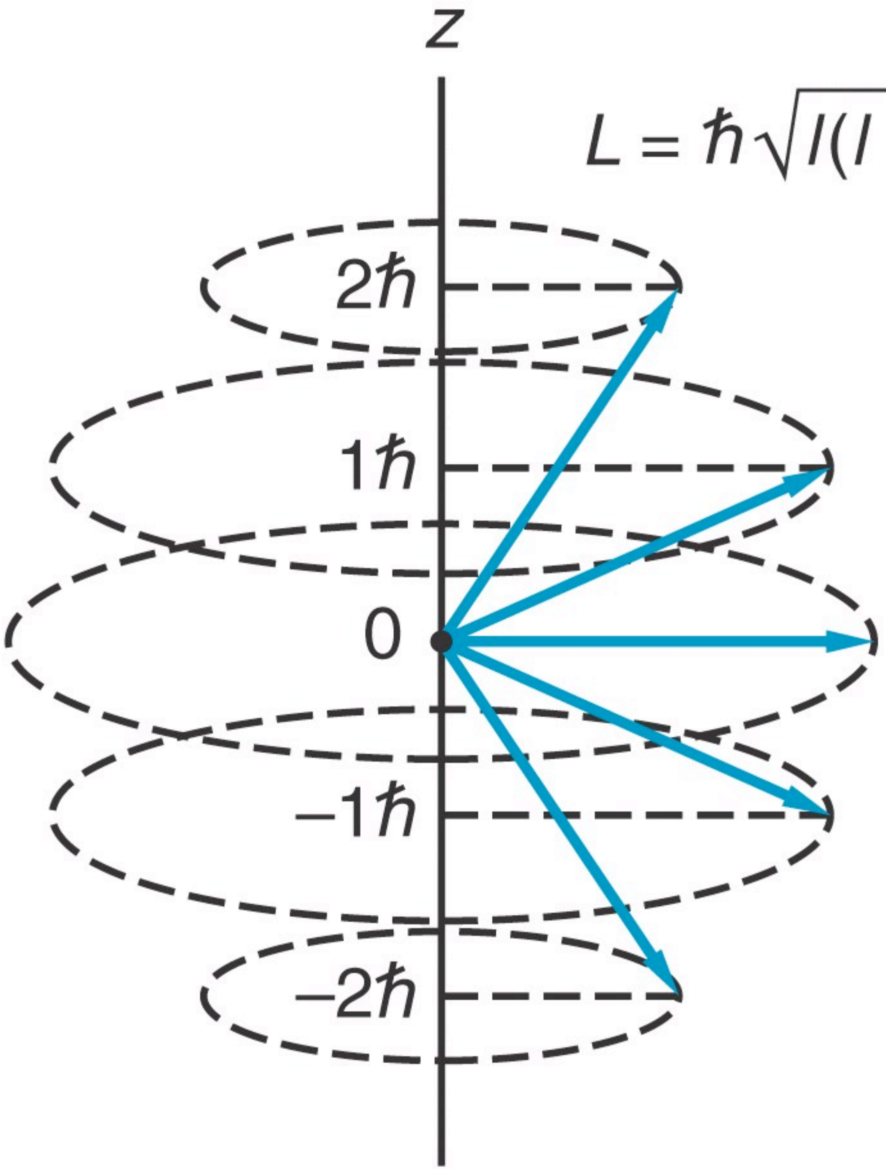






$L=2$, $m_l=0,\pm1, \pm 2$: Pictorially

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



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→ Current in loop → Magnetic Dipole moment μ