4E : The Quantum Universe

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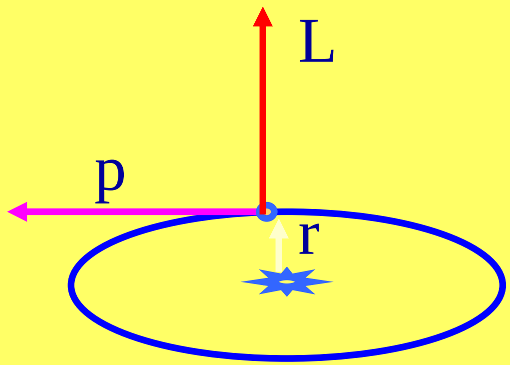
Interpreting Orbital Quantum Number (l)

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

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

what remains is a differential equation 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

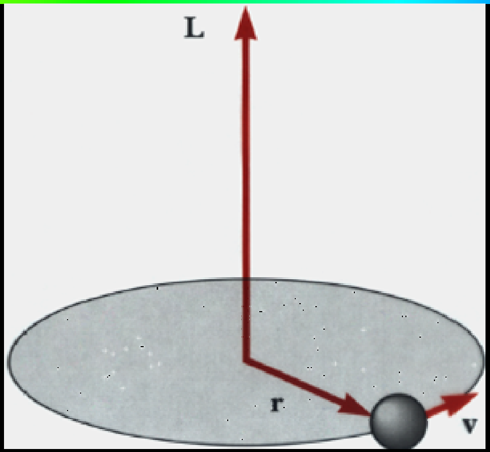
Further, we also know that $K_{ORBITAL}=\frac{1}{2}mv_{orbit}^2$; $\vec{L}=\vec{r}\times\vec{p}$; $|L| = mv_{orb}r \Rightarrow \boxed{K_{ORBITAL}=\frac{L^2}{2mr^2}}$

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 $\boxed{|L|=\sqrt{l(l+1)}\hbar = \textit{discrete values}}$

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

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

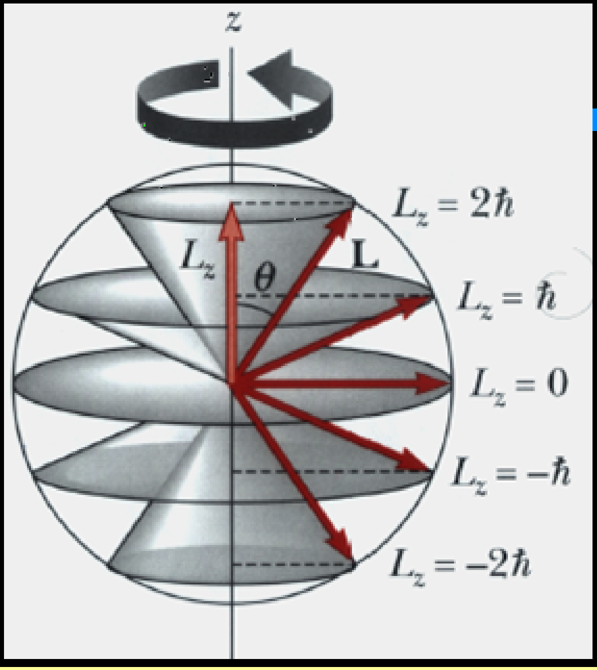
So, in Hydrogen atom, $\vec{L}$ can not have precise measurable value

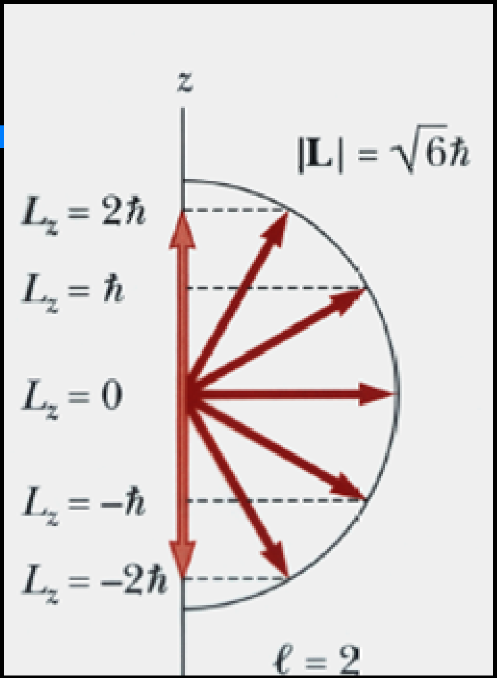
Uncertainty Principle & Angular Momentum : $\boxed{\Delta L_z \Delta \phi \sim \hbar}$

Magnetic Quantum Number m_l

Consider $\ell = 2$

$|L| = \sqrt{\ell(\ell+1)} = \sqrt{6}\hbar$





In Hydrogen atom, $\vec{L}$ can not have precise measurable value

Arbitararily picking Z axis as a reference direction:

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

The Z component of $\vec{L}$: $|L_Z| = m_l\hbar; \quad m_l = \pm 1, \pm 2, \pm 3 \ldots \pm l$

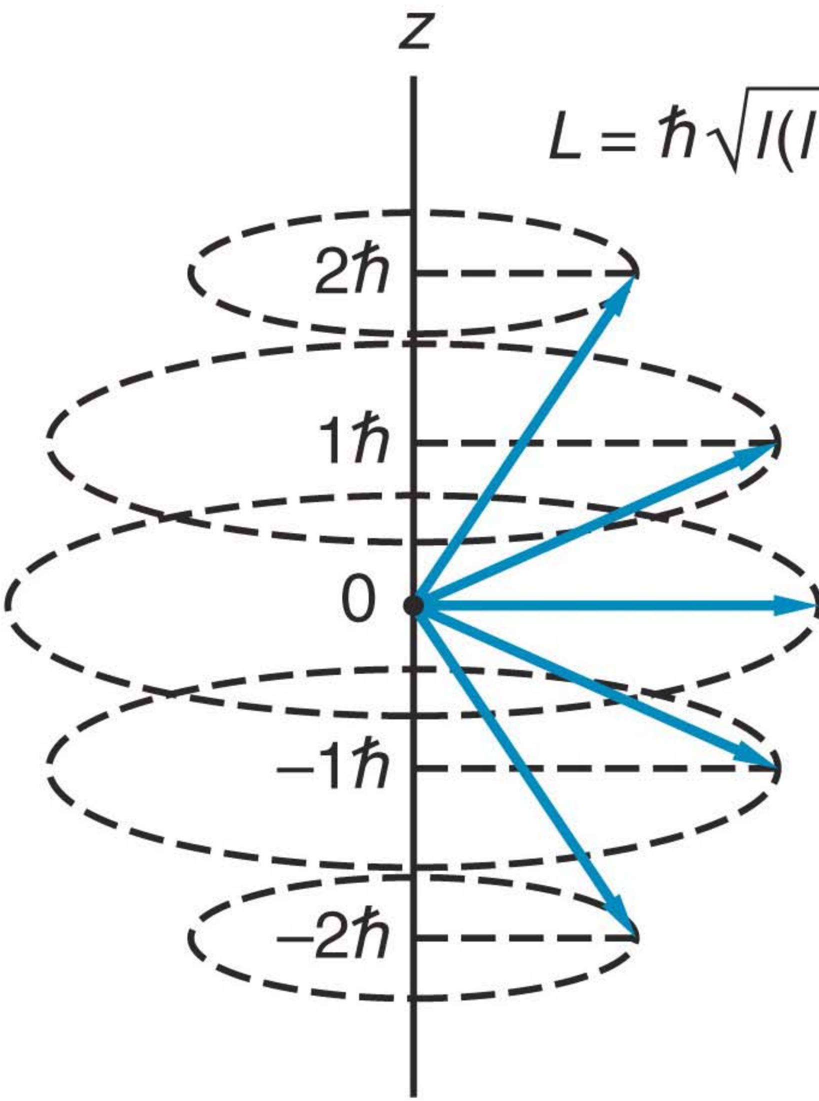
Note: since $|L_Z| < |L|$ (always)

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......the Electron's dance has begun !

L=2, m_l=0,±1, ± 2 : Pictorially



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

Electron “sweeps” conical paths of different ϑ:

$$\cos \vartheta = L_Z/L$$

On average, the angular momentum component in x and y cancel out

$$\langle L_X \rangle = 0$$

$$\langle L_Y \rangle = 0$$

Where is it likely to be ? → 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

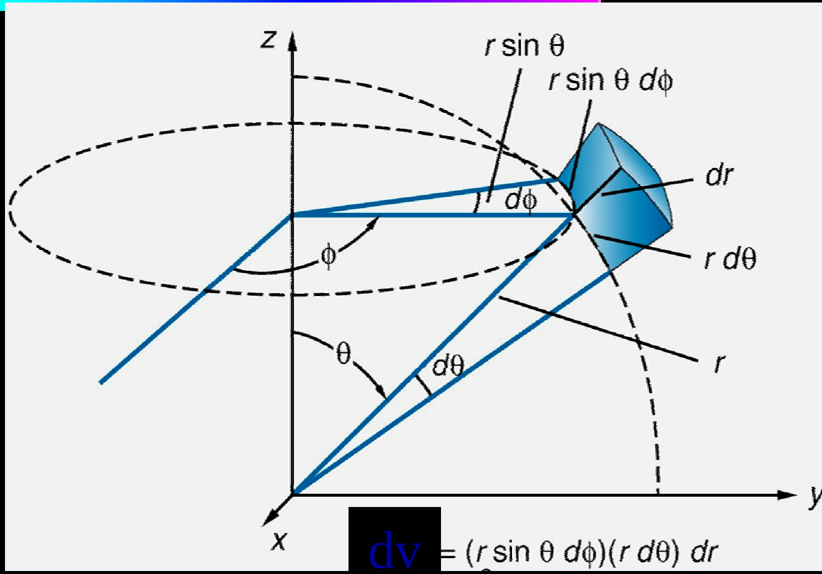
$$P(r)dr = |R_{nl}|^2\,.r^2 dr\int_0^{\pi}|\Theta_{lm_l}(\theta)|^2 d\theta\int_0^{2\pi}|\Phi_{m_l}(\phi)|^2\, d\phi$$

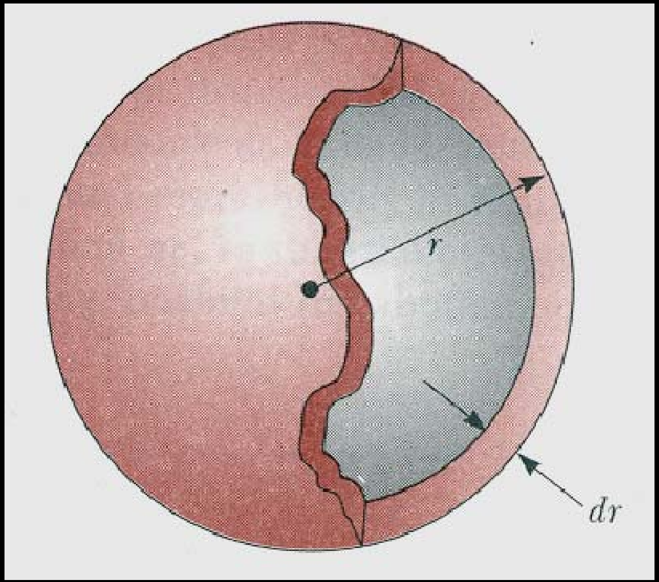
When $\Theta_{lm_l}(\theta)$ & $\Phi_{m_l}(\phi)$ are auto-normalized then

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

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

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





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

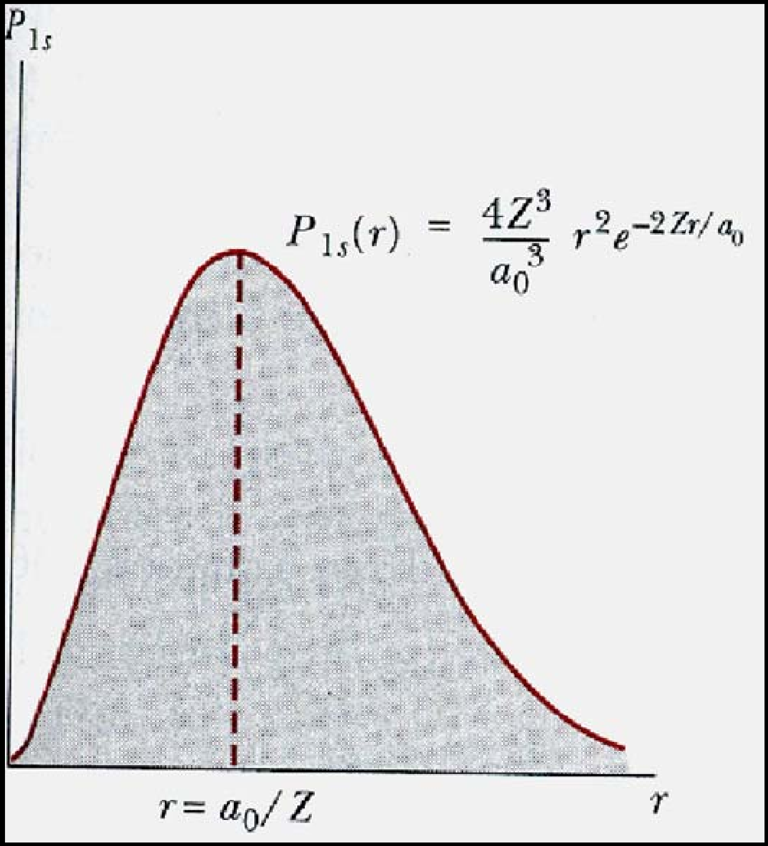
$$P_{r>a_0} = \int_a^\infty \frac{4}{a_0^3} r^2 e^{-2\frac{r}{a_0}} dr$$

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)

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



Most Probable & Average Distance of Electron from Nucleus

Most Probable Distance:

In the ground state $(n=1, l=0, m_l=0)$ $\boxed{P(r)dr = \frac{4}{a_0^3} r^2 e^{-2\frac{r}{a_0}}}$

Most probable distance r from Nucleus $\Rightarrow$ What value of r is P(r) max?

$$\Rightarrow \frac{dP}{dr}=0 \quad \Rightarrow \quad \frac{4}{a_0^3}\cdot\frac{d}{dr}\left[r^2 e^{-2\frac{r}{a_0}}\right] = 0 \Rightarrow \left[\frac{-2r^2}{a_0} + 2r\right] e^{-2\frac{r}{a_0}} = 0$$

$$\Rightarrow \frac{2r^2}{a_0} + 2r = 0 \Rightarrow \boxed{r = 0 \text{ or } r = a_0}$$ ... which solution is correct?

(see past quiz) : Can the electron BE at the center of Nucleus (r=0)?

$P(r=0) = \frac{4}{a_0^3} 0^2 e^{-2\frac{0}{a_0}} = 0! \Rightarrow$ $\boxed{\text{Most Probable distance } r = a_0}$ (Bohr guessed right)

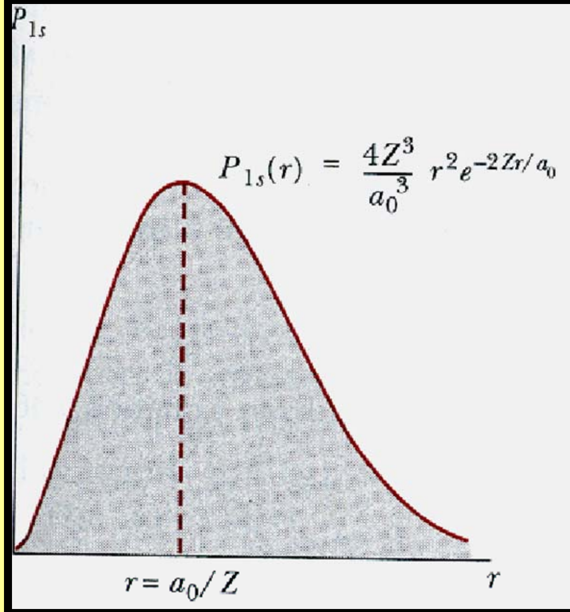
What about the AVERAGE location <r> of the electron in Ground state?

$$<r> = \int_{r=0}^{\infty} rP(r)dr = \frac{4}{a_0^3}\int_0^{\infty} r.r^2 e^{-2\frac{r}{a_0}} dr$$ ...change of variable $z = \frac{2r}{a_0}$

$$\Rightarrow <r> = \frac{a_0}{4}\int_{z=0}^{\infty} z^3 e^{-z} dz.......$$ $\boxed{\text{Use general form } \int_0^{\infty} z^n e^{-z} dz = n! = n(n-1)(n-2)...(1)}$

$$\Rightarrow \quad \boxed{<r> = \frac{a_0}{4} 3! = \frac{3a_0}{2} \neq a_0!}$$ Average & most likely distance is not same. Why?

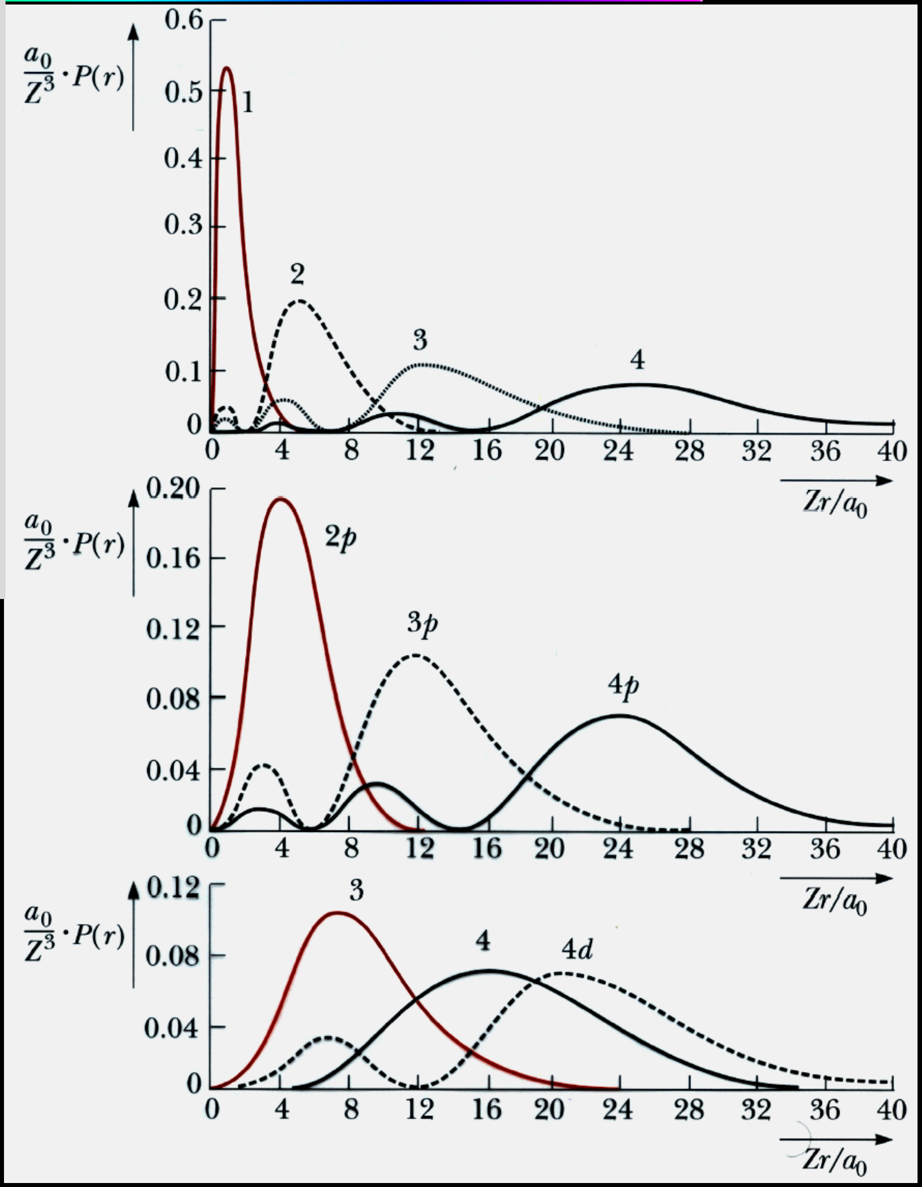
Asnwer is in the form of the radial Prob. Density: Not symmetric



Radial Probability Distribution P(r)= $r^2R(r)$

TABLE 7-2 Radial functions for hydrogen

$n = 1$	$l = 0$	$R_{10} = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$
$n = 2$	$l = 0$	$R_{20} = \frac{1}{\sqrt{2a_0^3}}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0}$
	$l = 1$	$R_{21} = \frac{1}{2\sqrt{6a_0^3}} \frac{r}{a_0} e^{-r/2a_0}$
$n = 3$	$l = 0$	$R_{30} = \frac{2}{3\sqrt{3a_0^3}}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$
	$l = 1$	$R_{31} = \frac{8}{27\sqrt{6a_0^3}} \frac{r}{a_0}\left(1 - \frac{r}{6a_0}\right)e^{-r/3a_0}$
	$l = 2$	$R_{32} = \frac{4}{8\sqrt{30a_0^3}} \frac{r^2}{a_0^2} e^{-r/3a_0}$



Because P(r)=r^2R(r); No matter what R(r) is for some n,

The prob. Of finding electron inside the nucleus = 0 !!

Normalized Spherical Harmonics & Structure in H Atom

TABLE 7-1 Spherical harmonics

$l = 0$	$m = 0$	$Y_{00} = \sqrt{\frac{1}{4\pi}}$
$l = 1$	$m = 1$	$Y_{11} = -\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\phi}$
	$m = 0$	$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$
	$m = -1$	$Y_{1-1} = \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{-i\phi}$
$l = 2$	$m = 2$	$Y_{22} = \sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{2i\phi}$
	$m = 1$	$Y_{21} = -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta\, e^{i\phi}$
	$m = 0$	$Y_{20} = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$
	$m = -1$	$Y_{2-1} = \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta\, e^{-i\phi}$
	$m = -2$	$Y_{2-2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{-2i\phi}$

Excited States (n>1) of Hydrogen Atom : Birth of Chemistry !

Features of Wavefunction in θ & ϕ :

Consider $n = 2,\ l = 0 \Rightarrow \psi_{200}$ = Spherically Symmetric (last slide)

Excited States (3 & each with same E_n) :

$\psi_{211}, \psi_{210}, \psi_{21\text{-}1}$ are all 2p states

$$\psi_{211} = R_{21} Y_1^1 = \left(\frac{1}{\pi}\right) \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Z}{8}\right)\left(\frac{r}{a_0}\right) e^{\frac{-Zr}{a_0}} .\sin\theta . e^{i\phi}$$

$|\psi_{211}|^2 = |\psi^*_{211}\psi_{211}| \propto \sin^2\theta$ Max at $\theta = \frac{\pi}{2}$, min at $\theta = 0$; Symm in ϕ

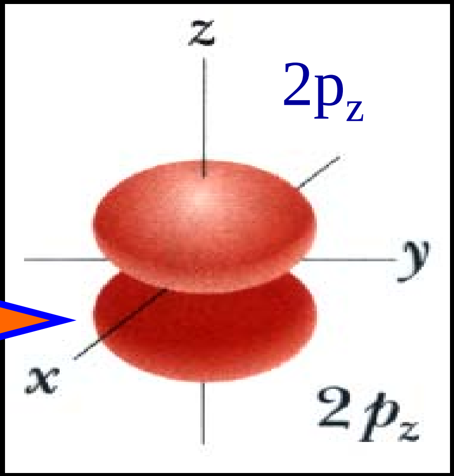
What about $(n=2, \ell=1, m_l = 0)$

$\psi_{210} = R_{21}(r)\, Y_1^0(\theta,\phi)$;

$Y_1^0(\theta,\phi) \propto \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$;

Function is max at $\theta = 0$, min at $\theta = \frac{\pi}{2}$

We call this $2p_z$ state because of its extent in z



Excited States (n>1) of Hydrogen Atom : Birth of Chemistry !

Remember Principle of Linear Superposition

for the TISE which is basically a simple differential equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U\psi = E\psi$$

Principle of Linear Superposition $\Rightarrow$ If ψ_1 *and* ψ_2 are sol. of TISE

then a "designer" wavefunction made of linear sum

$\psi' = a\psi_1 + b\psi_2$ is also a sol. of the diff. equation !

To check this, just substitute ψ' in place of ψ

& convince yourself that

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi' + U\psi' = E\psi'}$$

The diversity in Chemistry and Biology DEPENDS

on this superposition rule

Designer Wave Functions: Solutions of S. Eq !

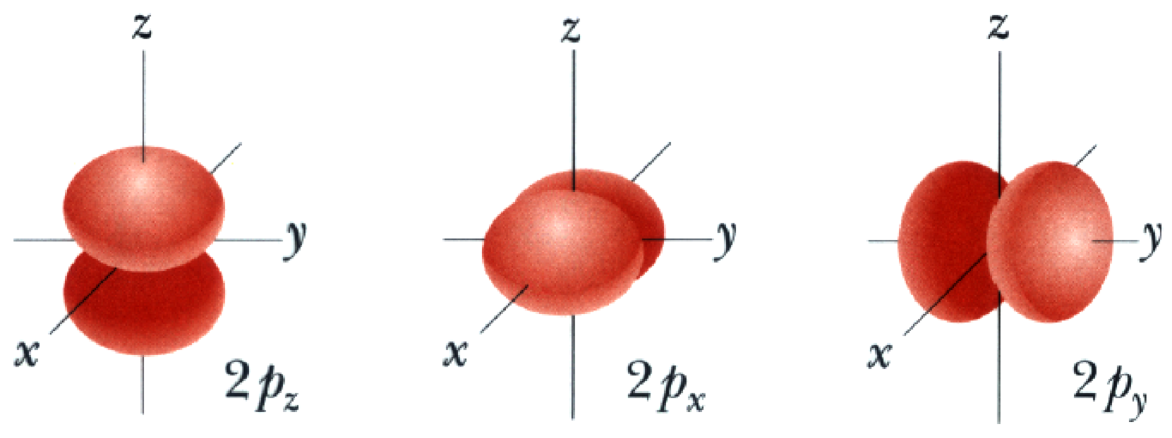
Linear Superposition Principle means allows me to "cook up" wavefunctions

$$\psi_{2p_x} = \frac{1}{\sqrt{2}}[\psi_{211} + \psi_{21-1}]$$ ......has electron "cloud" oriented along x axis

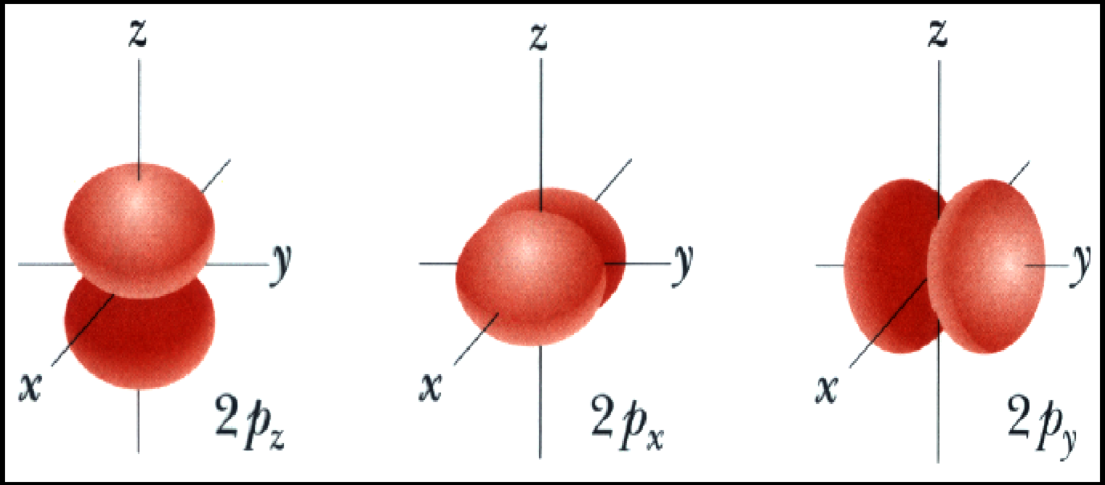
$$\psi_{2p_y} = \frac{1}{\sqrt{2}}[\psi_{211} - \psi_{21-1}]$$ ......has electron "cloud" oriented along y axis

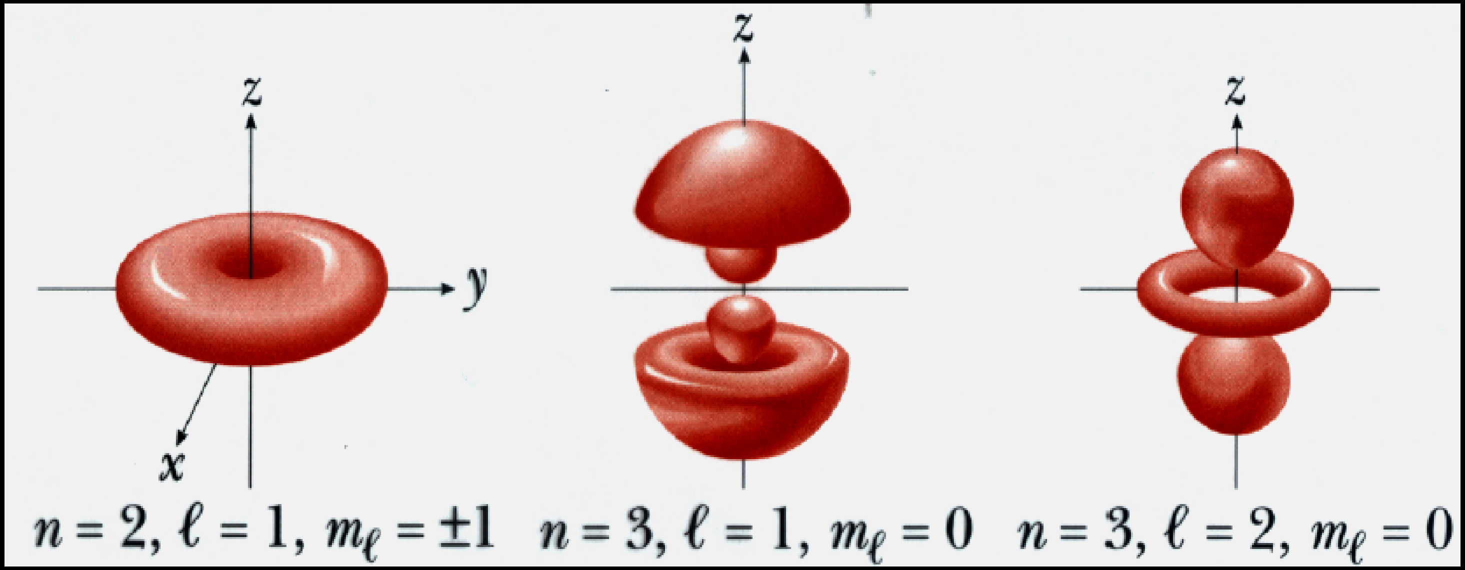
So from 4 solutions $\psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1} \rightarrow 2s, 2p_x, 2p_y, 2p_z$

Similarly for n=3 states ...and so on ...can get very complicated structure in θ & ϕ.......which I can then mix & match to make electrons "most likely" to be where I want them to be !



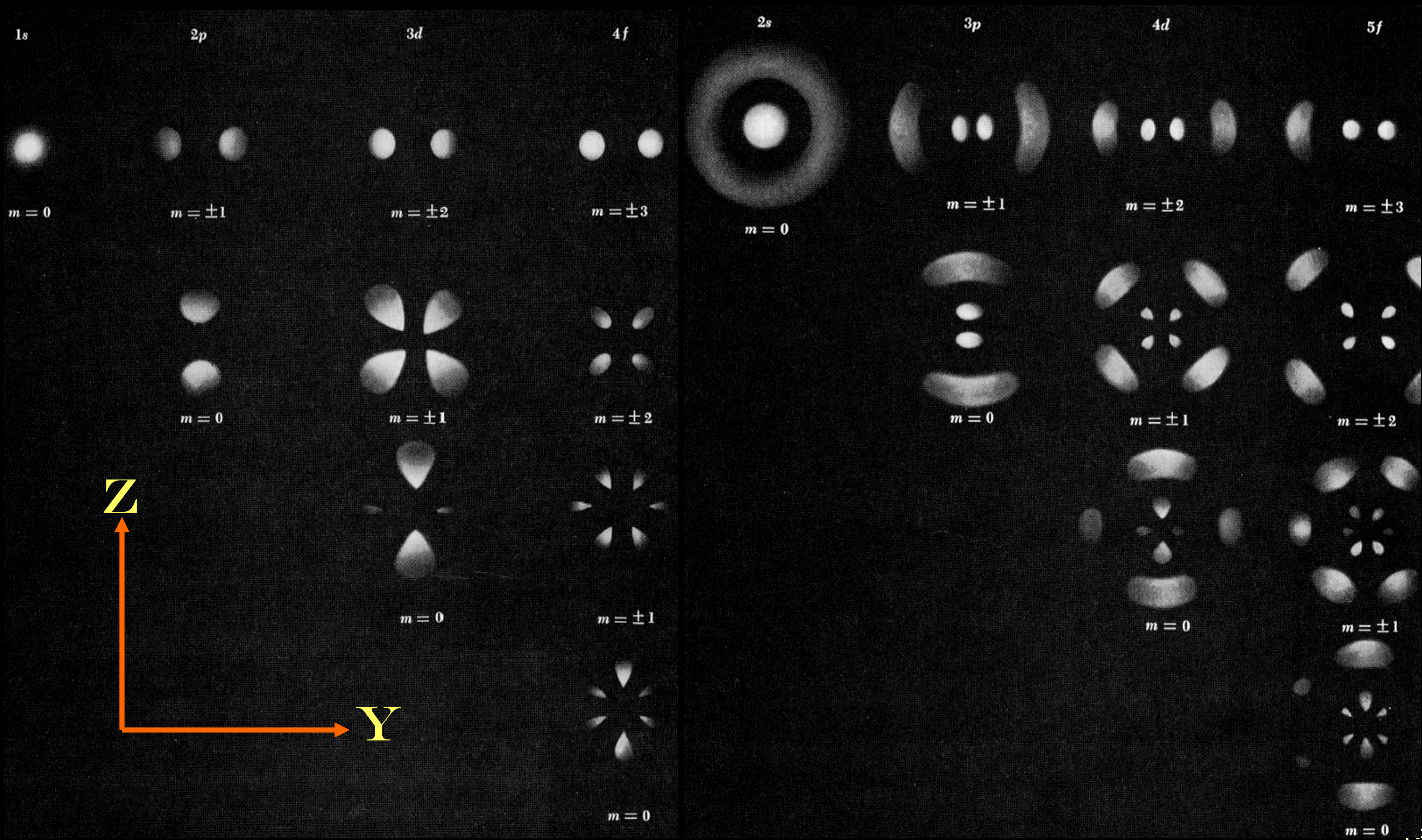
Designer Wave Functions: Solutions of S. Eq !





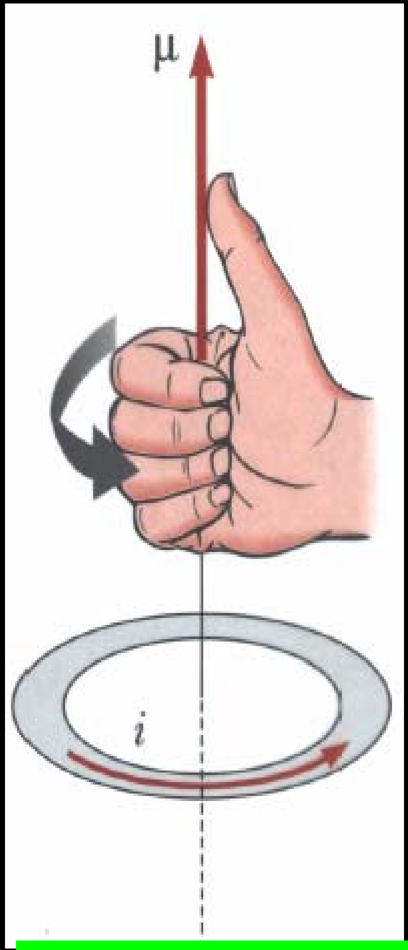
Cross Sectional View of Hydrogen Atom prob. densities in r,θ,φ
Birth of Chemistry (Can make Fancy Bonds→ Overlapping electron "clouds")

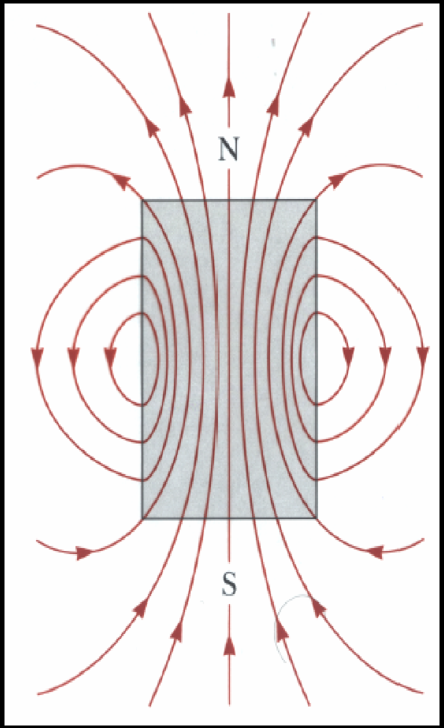
What's the electron "cloud" : Its the Probability Density in r, θ,φ space!

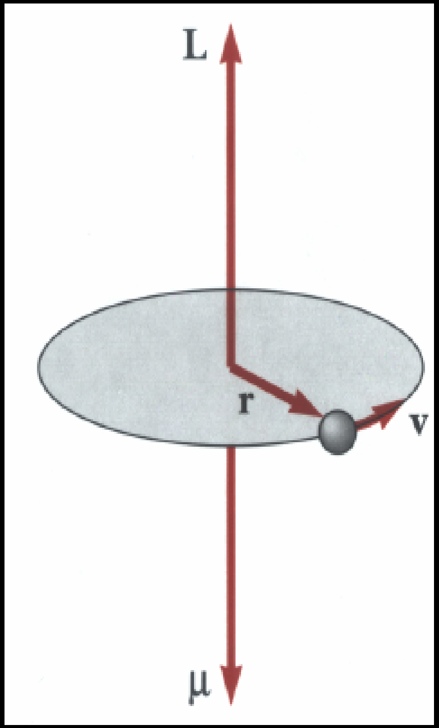


What's So "Magnetic" ?

Precessing electron→ Current in loop → Magnetic Dipole moment μ



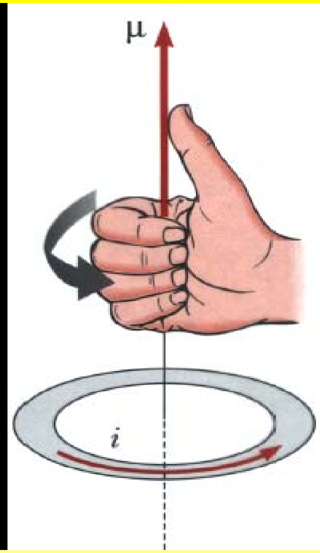


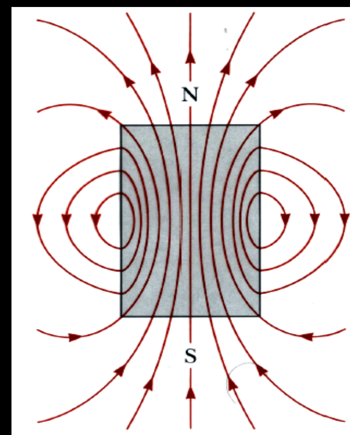


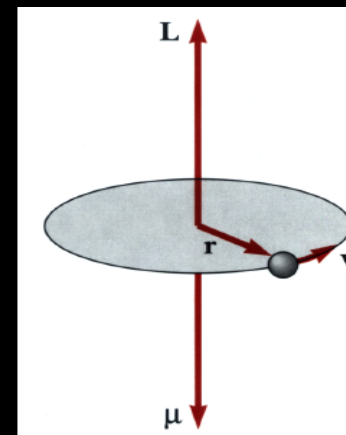
The electron's motion → hydrogen atom is a dipole magnet

The "Magnetism" of an Orbiting Electron

Precessing electron → Current in loop → Magnetic Dipole moment μ







Electron in motion around nucleus ⇒ circulating charge ⇒ curent i

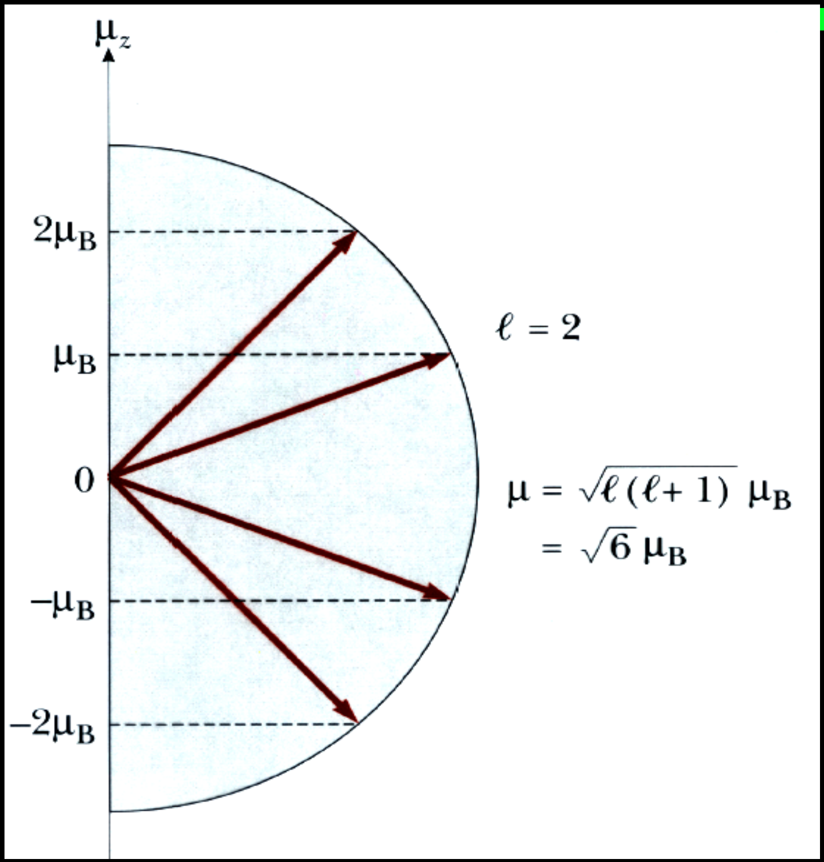
$i = \frac{-e}{T} = \frac{-e}{\frac{2\pi r}{v}} = \frac{-ep}{2\pi m r}$; Area of current loop $A = \pi r^2$

Magnetic Moment $|\mu| = iA = \left(\frac{-e}{2m}\right) rp$; $\vec{\mu} = \left(\frac{-e}{2m}\right) \vec{r} \times \vec{p} = \left(\frac{-e}{2m}\right) \vec{L}$

Like the $\vec{L}$, magnetic moment $\vec{\mu}$ also precesses about "z" axis

z component, $\mu_z = \left(\frac{-e}{2m}\right) L_z = \left(\frac{-e\hbar}{2m}\right) m_l = -\mu_B m_l = quantized!$

Quantized Magnetic Moment



$$\mu_z = \left(\frac{-e}{2m}\right) L_z = \left(\frac{-e\hbar}{2m}\right) m_l$$

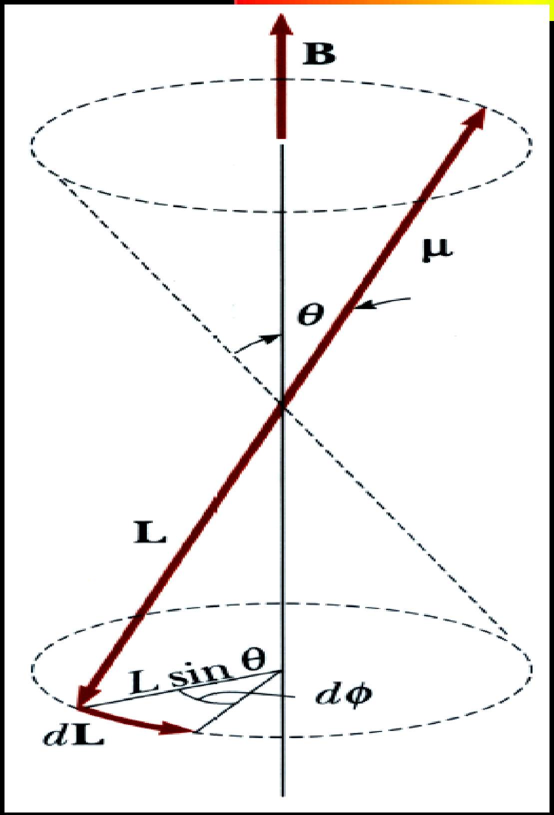
$$= -\mu_B m_l$$

$$\mu_B = \text{Bohr Magnetron}$$

$$= \left(\frac{e\hbar}{2m_e}\right)$$

Why all this ? Need to find a way to break the Energy Degeneracy & get electron in each (n, l, m_l) state to identify itself, so we can "talk" to it and make it do our bidding:
" Walk this way, talk this way!"

"Lifting" Degeneracy : Magnetic Moment in External B Field



Apply an External $\vec{B}$ field on a Hydrogen atom (viewed as a dipole)

Consider $\vec{B} \parallel \vec{Z}$ axis (could be any other direction too)

The dipole moment of the Hydrogen atom (due to electron orbit)

experiences a Torque $\vec{\tau} = \vec{\mu} \times \vec{B}$ which does work to align $\vec{\mu} \parallel \vec{B}$

but this can not be (same Uncertainty principle argument)

$\Rightarrow$ So, Instead, $\vec{\mu}$ precesses (dances) around $\vec{B}$... like a spinning top

The Azimuthal angle ϕ changes with time : calculate frequency

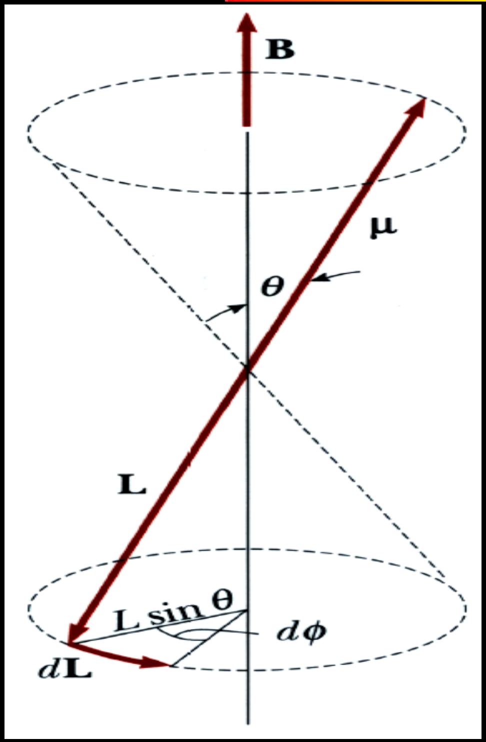
Look at Geometry: |projection along x-y plane : $|dL| = L\sin\theta . d\phi$

$\Rightarrow d\phi = \frac{|dL|}{L\sin\theta}$; Change in Ang Mom. $|dL| = |\tau|\, dt = \left|\frac{q}{2m} LB\sin\theta\right| dt$

$$\Rightarrow \boxed{\omega_L = \frac{d\phi}{dt} = \frac{1}{L\sin\theta}\frac{|dL}{dt} = \frac{1}{L\sin\theta}\frac{q}{2m} LB\sin\theta = \frac{qB}{2m_e}}$$ Larmor Freq

ω_L depends on B, the applied external magnetic field

"Lifting" Degeneracy : Magnetic Moment in External B Field



WORK done to reorient $\vec{\mu}$ against $\vec{B}$ field: $\boxed{dW=\tau d\theta=-\mu B\sin\theta d\theta}$

$dW = d(\mu B\cos\theta)$: This work is stored as orientational Pot. Energy U

$$dW= -dU$$

Define Magnetic Potential Energy $U=-\vec{\mu}.\vec{B} = -\mu\cos\theta.B = -\mu_z B$

Change in Potential Energy $U = \frac{e\hbar}{2m_e} m_l B = \boxed{\hbar\omega_L m_l}$

Zeeman Effect in Hydrogen Atom

In presence of External B Field, Total energy of H atom changes to

$$\boxed{E=E_0 + \hbar\omega_L m_l}$$

So the Ext. B field can break the E degeneracy "organically" inherent in the H atom. The Energy now depends not just on *n* but also m_l

Zeeman Effect Due to Presence of External B field

Energy Degeneracy Is Broken