Physics 2D Lecture Slides
Lecture 29: March 8th 2005

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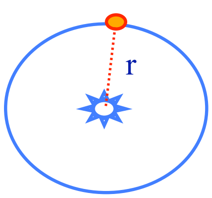
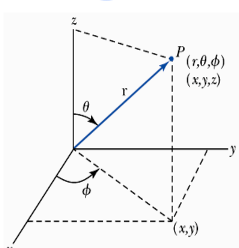
The Hydrogen Atom In Its Full Quantum Mechanical Glory





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 ∇^2 for spherical polar coordinates:

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

Thus the T.I.S.Eq. for $\psi(x,y,z) = \psi(r,\theta,\phi)$ becomes

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

with $U(r) \propto \frac{1}{r} = \frac{1}{\sqrt{x^2+y^2+z^2}}$

So What do we have after all the shuffling!

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

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

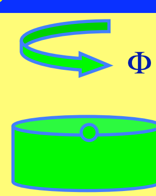
$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2mr^2}{\hbar^2}(E+\frac{ke^2}{r})-\frac{l(l+1)}{r^2}\right]R(r)=0\ldots.(3)$$

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

And Now the Solutions of The S. Eqns for Hydrogen Atom



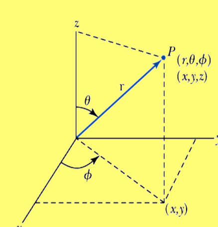
The Azimuthal Diff. Equation : $\boxed{\frac{d^2\Phi}{d\phi^2}+m_l^2\Phi=0}$

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

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

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

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



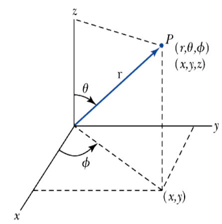
Solutions : go by the name of "Associated Legendre Functions"

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

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

l: Orbital Quantum Number

Wavefunction Along Azimuthal Angle ϕ and Polar Angle θ



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

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

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

$[l=2, m_l=0] \Rightarrow \Theta(\theta)=\frac{\sqrt{10}}{4}(3\cos^2\theta-1)$

....*and* so on and so forth (see book for more Functions)

Radial Differential Equations and Its Solutions

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

$$\boxed{\mathrm{E}=-\frac{\mathrm{ke}^2}{2\mathrm{a}_0}\left(\frac{1}{n^2}\right)};\quad \text{with } a_0=\frac{\hbar^2}{mke^2}=\text{Bohr Radius}$$

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

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

The Hydrogen Wavefunction: ψ(r,θ,φ) and Ψ(r,θ,φ,t)

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

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

Quantum # appear only in Trapped systems

The Spatial part of the Hydrogen Atom Wave Function is:

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

$Y_l^{m_l}$ are known as Spherical Harmonics. They define the angular structure in the Hydrogen-like atoms.

The Full wavefunction is $\boxed{\Psi(r,\theta,\varphi,t) = \psi(r,\theta,\phi)e^{-\frac{iE}{\hbar}t}}$

Radial Wave Functions For n=1,2,3

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:

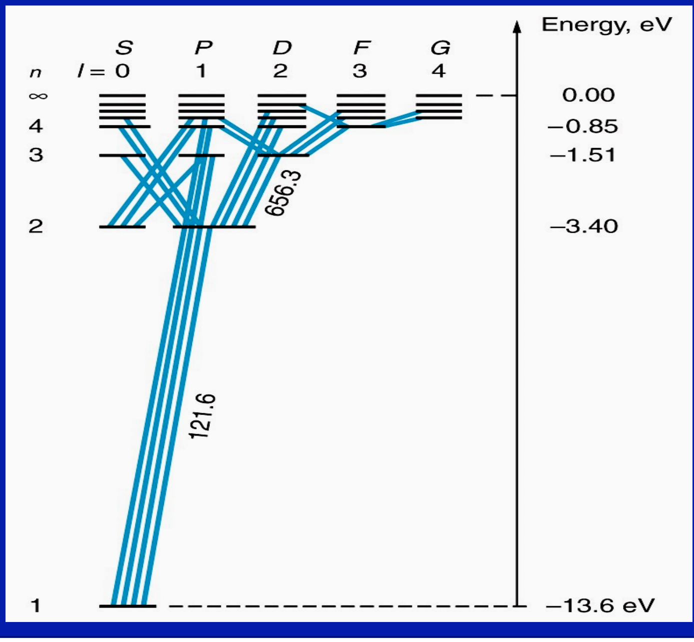
- n =1 is a non-degenerate system
- n>1 are all degenerate in l and m_l

  All states have same energy

  But different angular configuration

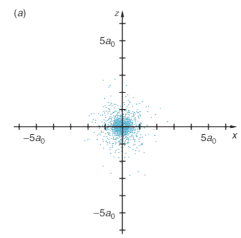
$$E=-\frac{ke^2}{2a_0}\left(\frac{1}{n^2}\right)$$

Energy States, Degeneracy & Transitions



Facts About Ground State of H Atom

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

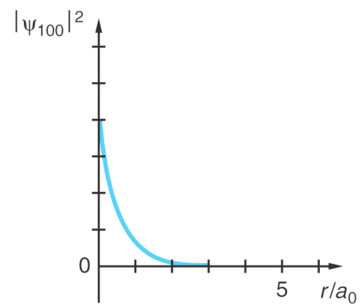


$\boxed{\Psi_{100}(r,\theta,\phi)=\frac{1}{a_0\sqrt{\pi}}e^{-r/a}}$......look at it carefully

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

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

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*

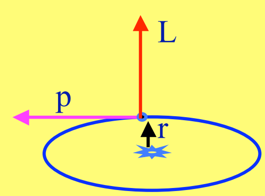
Not much chemistry or Biology could develop if there was only the ground state of the Hydrogen Atom!

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

Interpreting Orbital Quantum Number *(l)*

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

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

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

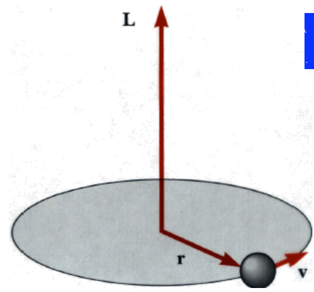
Further, we also know that $K_{ORBITAL}=\frac{1}{2}mv^2_{orbit}$; $\vec{L}=\vec{r}\times\vec{p}$; $|L|=mv_{orb}r \Rightarrow \boxed{K_{ORBITAL}=\frac{L^2}{2mr^2}}$

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

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

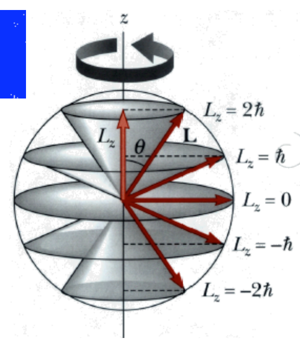
So, in Hydrogen atom, $\vec{L}$ can not have precise measurable value

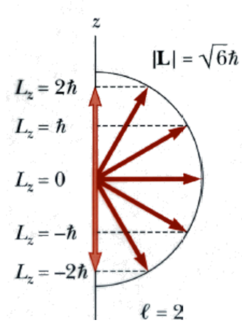
Uncertainty Principle & Angular Momentum : $\boxed{\Delta L_z \Delta\phi \sim \hbar}$

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

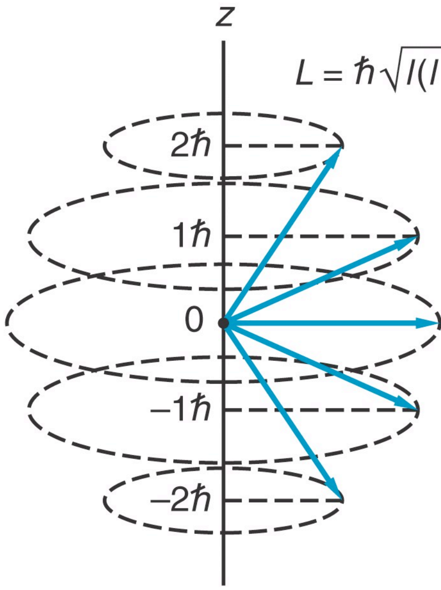
Note: since $|L_Z| < |L|$ (always)

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 !

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

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

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

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

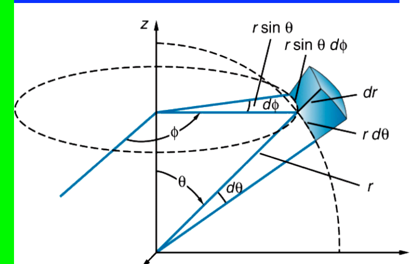
$$P(r)dr = |R_{nl}|^2\,.r^2dr\int_0^{\pi}|\Theta_{lm_l}(\theta)|^2 d\theta\int_0^{2\pi}|\Phi_{m_l}(\phi)|^2\,d\phi$$

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

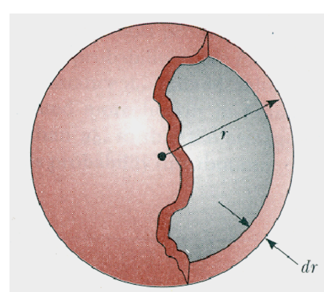
$P(r)dr = |R_{nl}|^2\,.r.^2dr;$ in other words $\boxed{P(r) = r^2\,|R_{nl}|^2}$

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

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



dv = (r sin θ dφ)(r dθ) 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

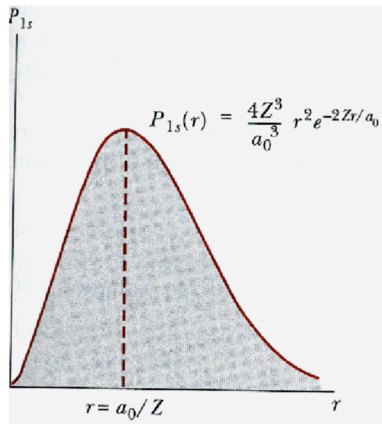
$$P_{r>a_0} = \int_a^\infty \frac{4}{a_0^3} r^2 e^{-2\frac{r}{a_0}} dr$$

To solve, employ change of variable

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

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

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



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?

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

$\Rightarrow \frac{2r^2}{a_0} + 2r = 0 \Rightarrow \boxed{r = 0 \ or\ r = a_0}$... 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)

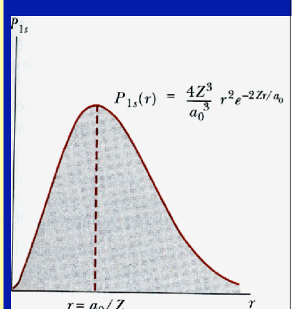
What about the AVERAGE location <r> of the electron in Ground state?

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

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

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

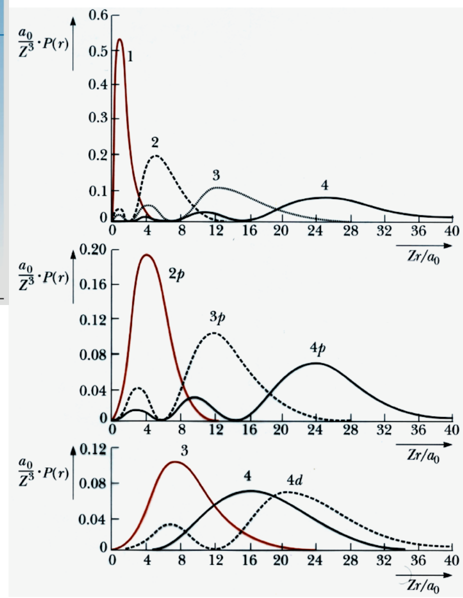
Asnwer is in the form of the radial Prob. Density: Not symmetric



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 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) :

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

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

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

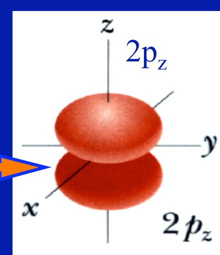
What about ($n=2$, $\ell=1$, $m_l = 0$)

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

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

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 !

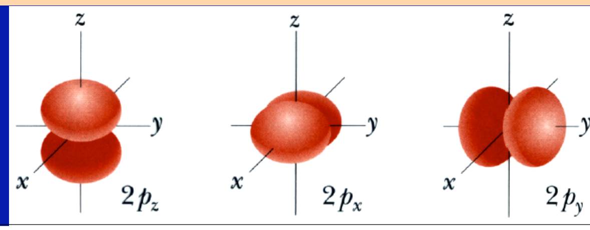
Linear Superposition Principle means allows me to "cook up" wavefunctions

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

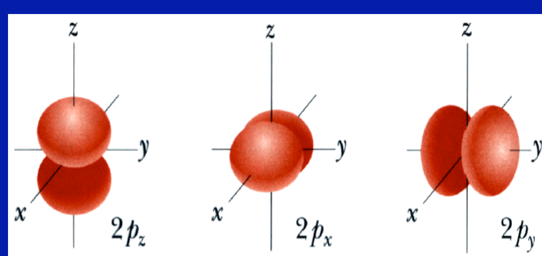
$\psi_{2p_y} = \frac{1}{\sqrt{2}}[\psi_{211} - \psi_{21-1}]$ ......has electron "cloud" oriented along y axis

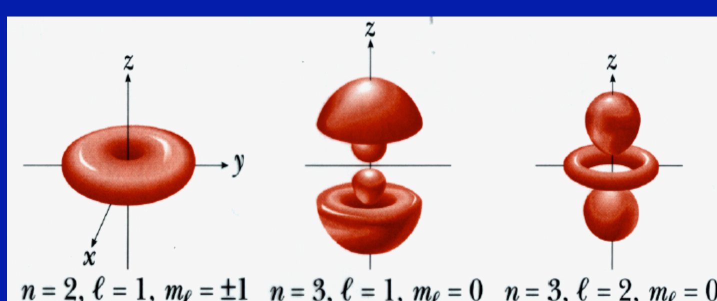
So from 4 solutions $\psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1} \rightarrow 2s, 2p_x, 2p_y, 2p_z$

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 !



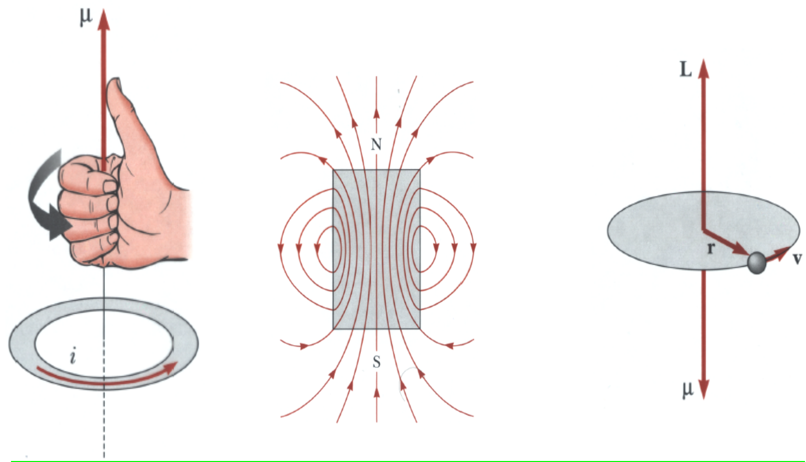
Designer Wave Functions: Solutions of S. Eq !





What's So "Magnetic" ?

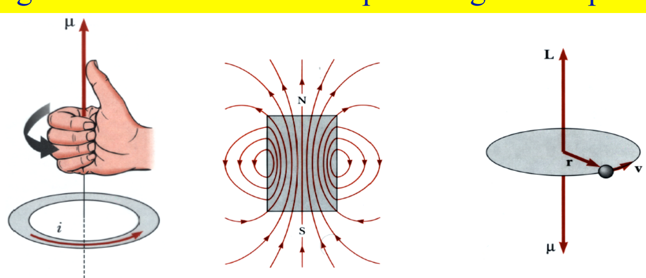
Precessing electron → Current in loop → Magnetic Dipole moment μ



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 $\Rightarrow$ circulating charge $\Rightarrow$ curent i

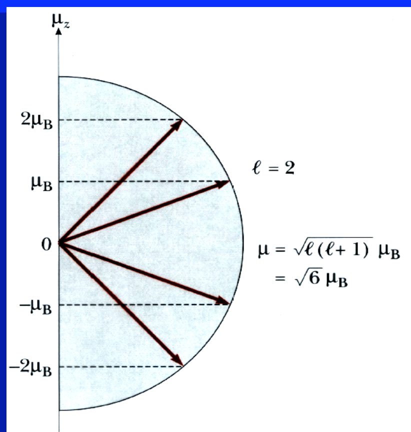
$i = \frac{-e}{T} = \frac{-e}{\frac{2\pi r}{v}} = \frac{-ep}{2\pi mr}$; Area of current loop $A=\pi r^2$

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

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

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

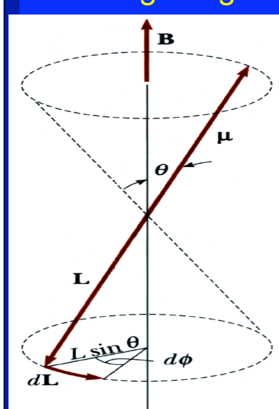
Quantized Magnetic Moment



$$\mu_z = \left(\frac{-e}{2m}\right) L_z = \left(\frac{-e\hbar}{2m}\right) m_l$$
$$= -\mu_B m_l$$
$$\mu_B = \text{Bohr Magnetron}$$
$$= \left(\frac{e\hbar}{2m_e}\right)$$

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



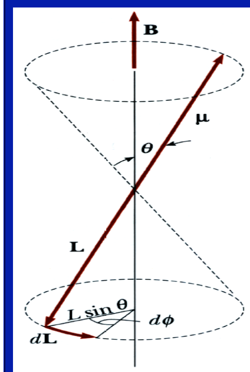
Apply an External $\vec{B}$ field on a Hydrogen atom (viewed as a dipole)
Consider $\vec{B} \parallel \vec{Z}$ axis (could be any other direction too)
The dipole moment of the Hydrogen atom (due to electron orbit) experiences a Torque $\vec{\tau} = \vec{\mu} \times \vec{B}$ which does work to align $\vec{\mu} \parallel \vec{B}$
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 : $|dL| = L\sin\theta . d\phi$

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

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

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