



Physics 2D Lecture Slides  
Dec 3 : The End !

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

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

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

These 3 "simple" diff. eqn describe the physics of the Hydrogen atom. All we had to do was figure out (with help of French mathematicians) the solutions of the diff. equations

Each part, clearly, has a different functional form and gave clues to behaviour of the Hydrogen atom in its Ground state and excited states

# Solutions of The S. Eq for Hydrogen Atom

In Summary : 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

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

$$= R_{nl} Y_l^{m_l} \text{ (Spherical Harmonics)}$$

NOW we are going to take the Hydrogen atom and  
“ Kick it up a Notch !”

# 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

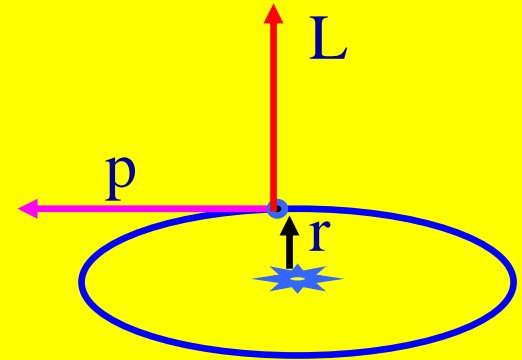
$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} [K_{\text{RADIAL}}] R(r) = 0 \text{ which depends only on radius } r \text{ of orbit}$$

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 $m_l$

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

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  $\vec{L}$

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

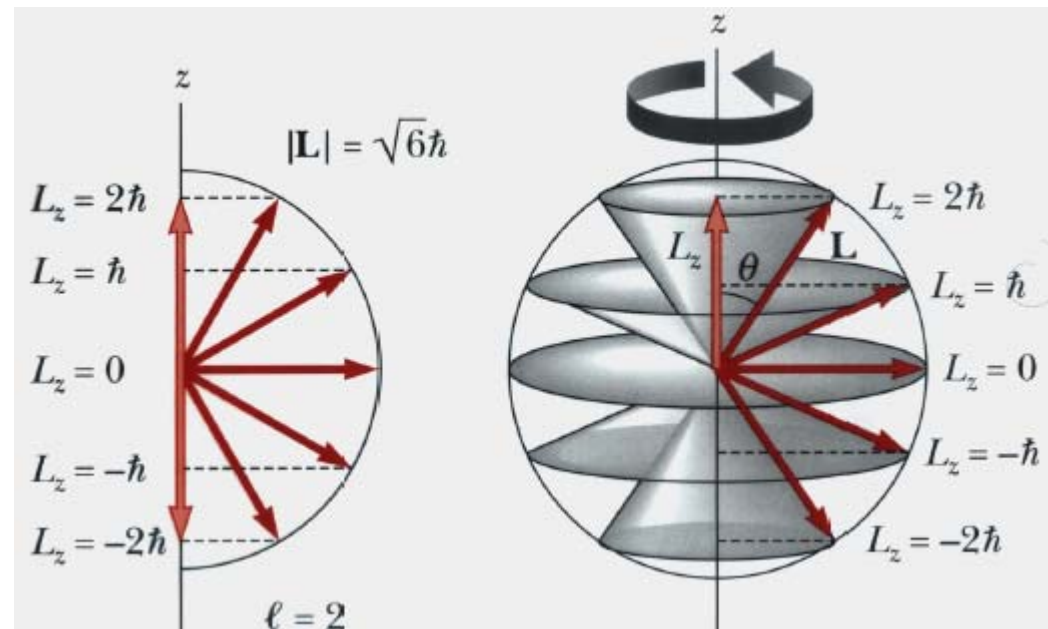
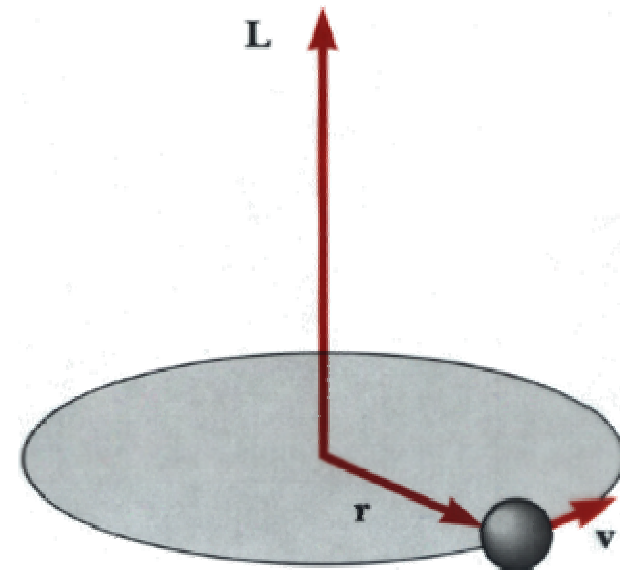
Note :  $|L_z| < |L|$  (always)

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 !

**DANCING IN THE DARK !**



# 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

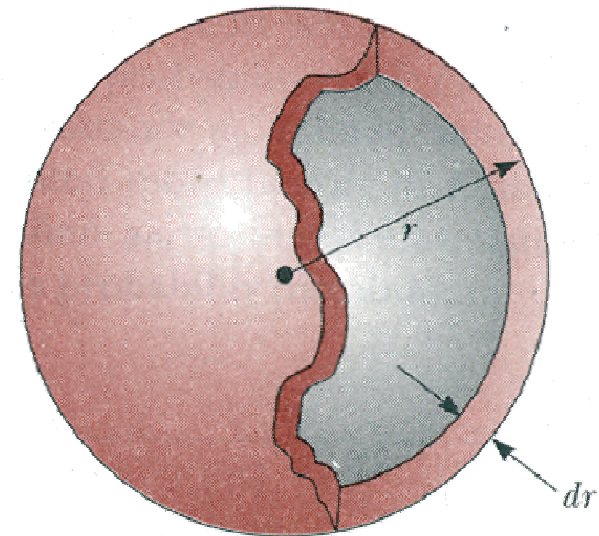
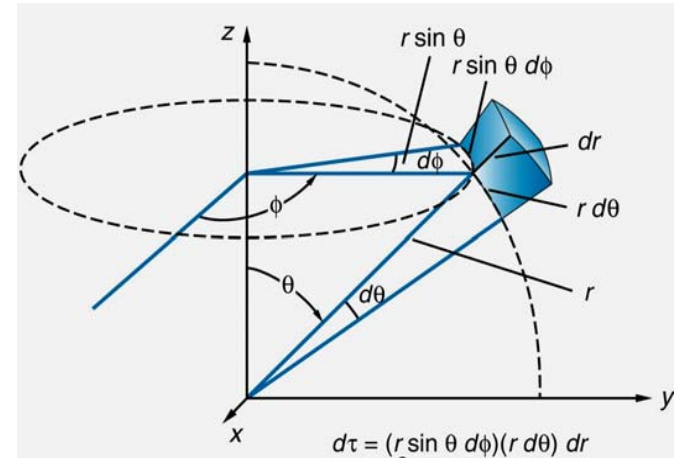
$$P(r)dr = |R_{nl}|^2 \cdot r^2 dr; \text{ in other words } P(r) = r^2 |R_{nl}|^2$$

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  $r > a_0$

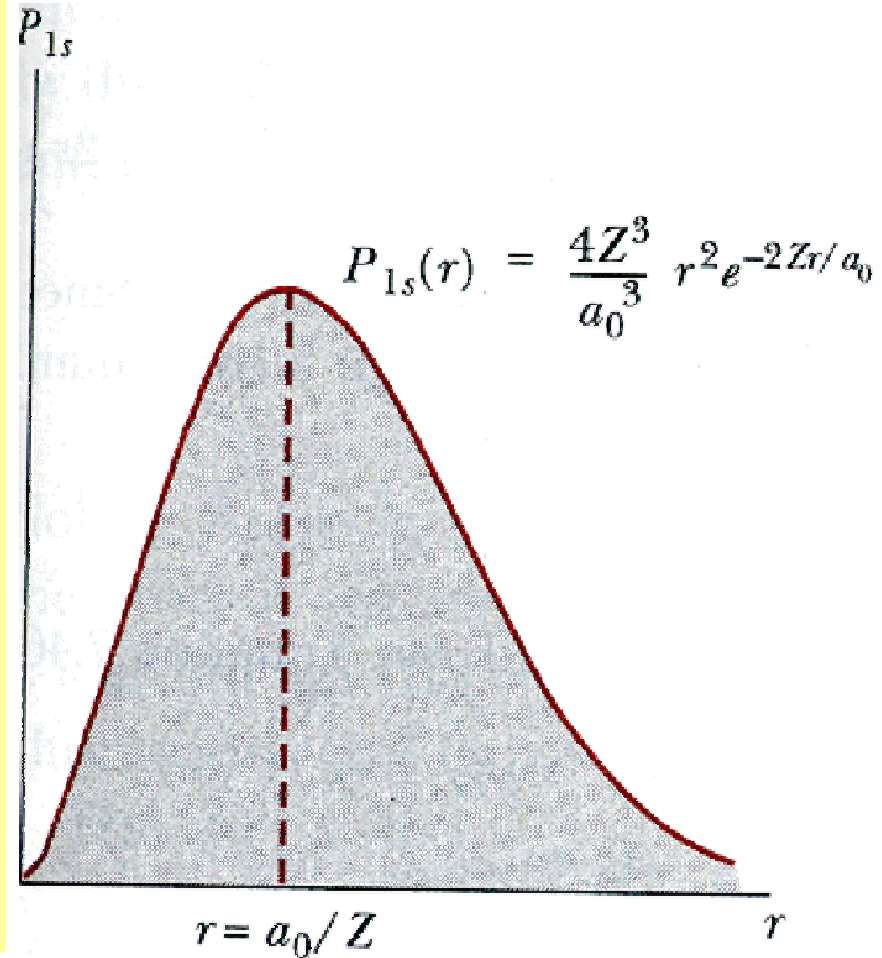
$$P_{r>a_0} = \int_{a_0}^{\infty} \frac{4}{a_0^3} r^2 e^{-2\frac{r}{a_0}} dr$$

To solve, employ change of variable

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

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

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



# Most Probable & Average Distance of Electron from Nucleus

Most Probable Distance:

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

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

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

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

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

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

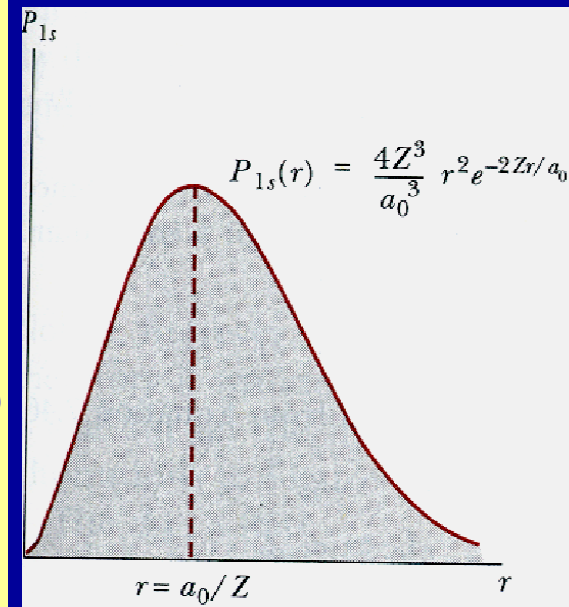
What about the AVERAGE location  $\langle r \rangle$  of the electron in Ground state?

$$\langle r \rangle = \int_{r=0}^{\infty} rP(r)dr = \frac{4}{a_0^3} \int_0^{\infty} r^3 e^{-\frac{2r}{a_0}} dr \dots \text{change of variable } z = \frac{2r}{a_0}$$

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

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

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

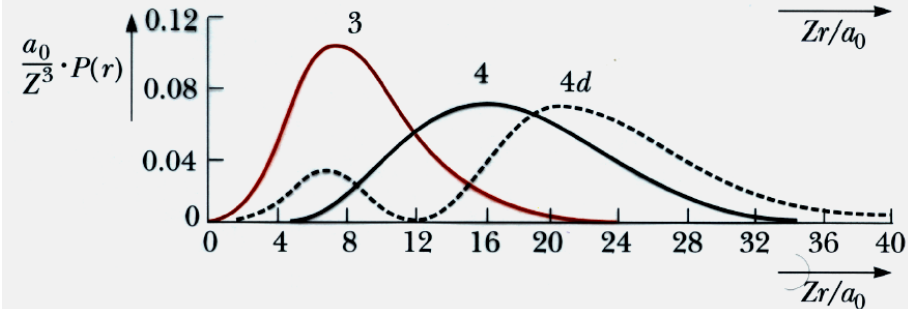
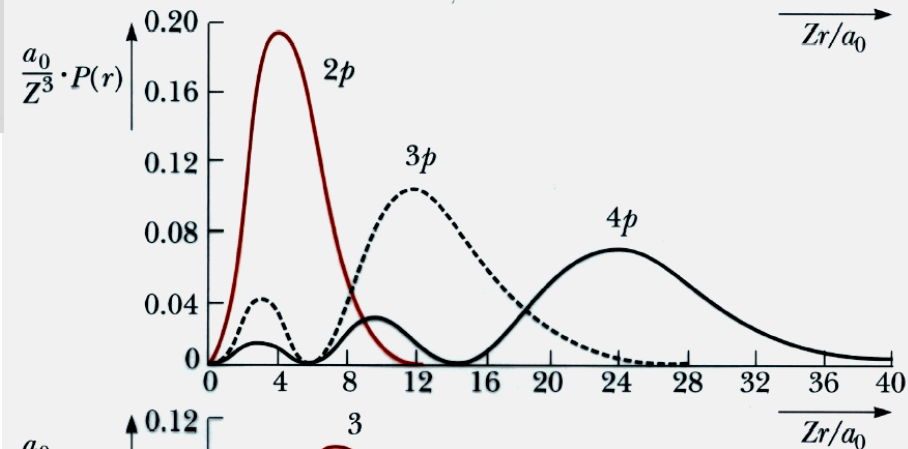
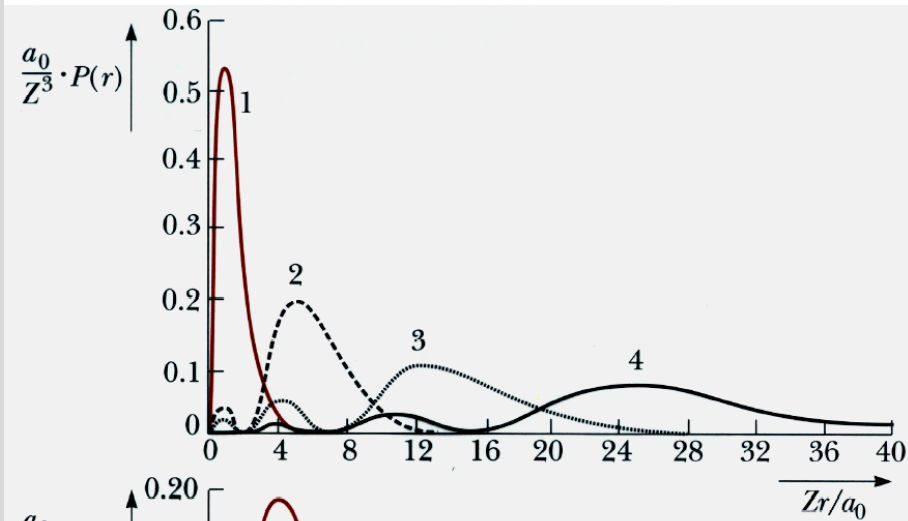




# Radial Probability Distribution $P(r) = r^2 R(r)$

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  $P(r) = r^2 R(r)$

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 in  $\theta$  &  $\phi$  :

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

Excited States (3 & each same  $E_n$ ) :  $\psi_{211}, \psi_{210}, \psi_{21-1}$  are all **2p** states

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

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

$$\psi_{210} = R_{21}(r) Y_1^0(\theta, \phi); Y_1^0(\theta, \phi) \propto \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta; \text{ max at } \theta = 0, \text{ min at } \theta = \frac{\pi}{2}$$

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

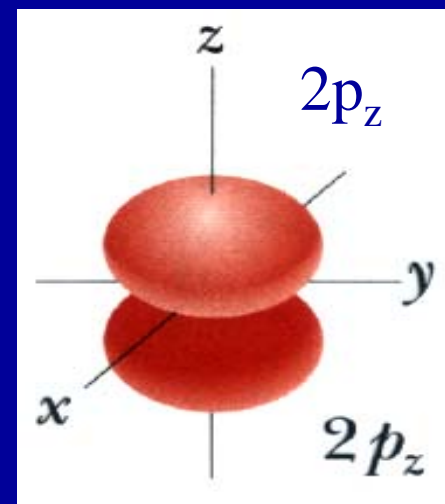
Remember, for a TISE:  $-\frac{\hbar^2}{2m} \nabla^2 \psi + U\psi = E\psi$

Principle of Linear Superposition: If  $\psi_1$  &  $\psi_2$  are sol. of TISE

then a "designer" wavefunction  $\psi' = a\psi_1 + b\psi_2$  is also a sol. of TISE

To check this, substitute  $\psi'$  in place of  $\psi$  & convince yourself that

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



# Designer Wave Functions: Solutions of S. Eq !

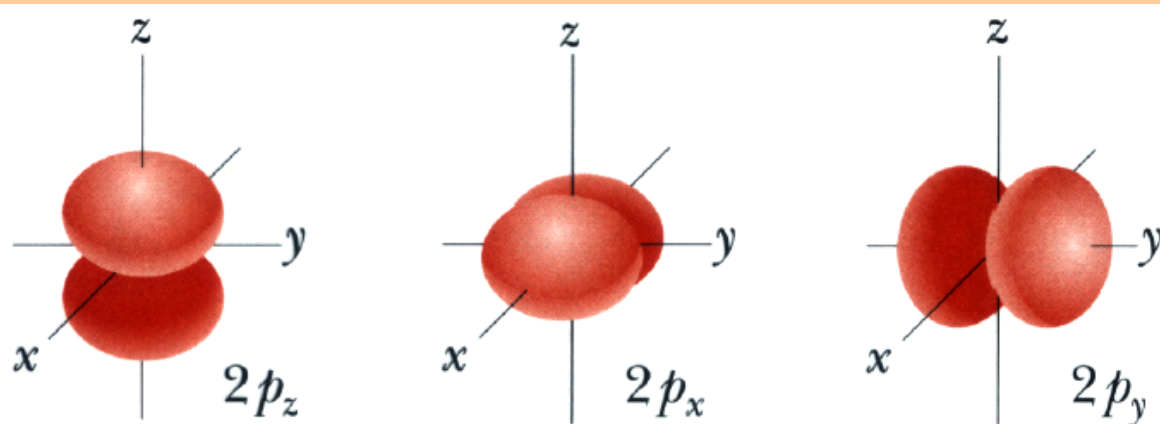
Linear Superposition Principle means allows me to "cook up" wavefunctions

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

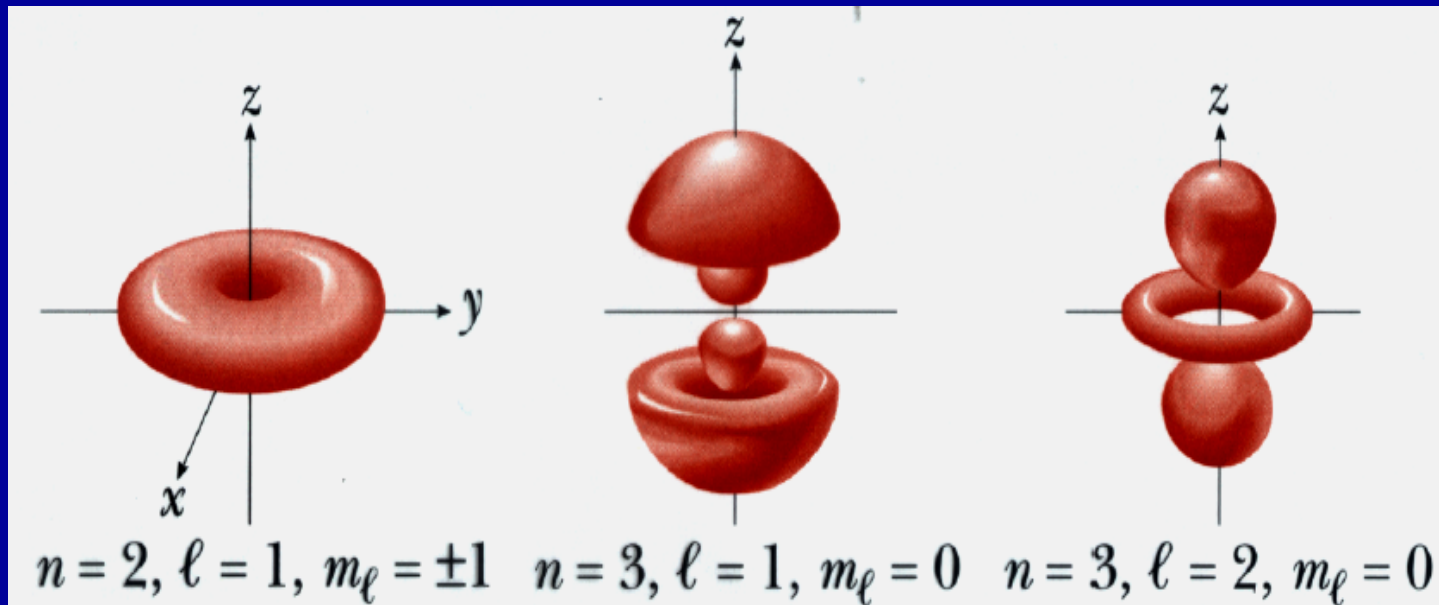
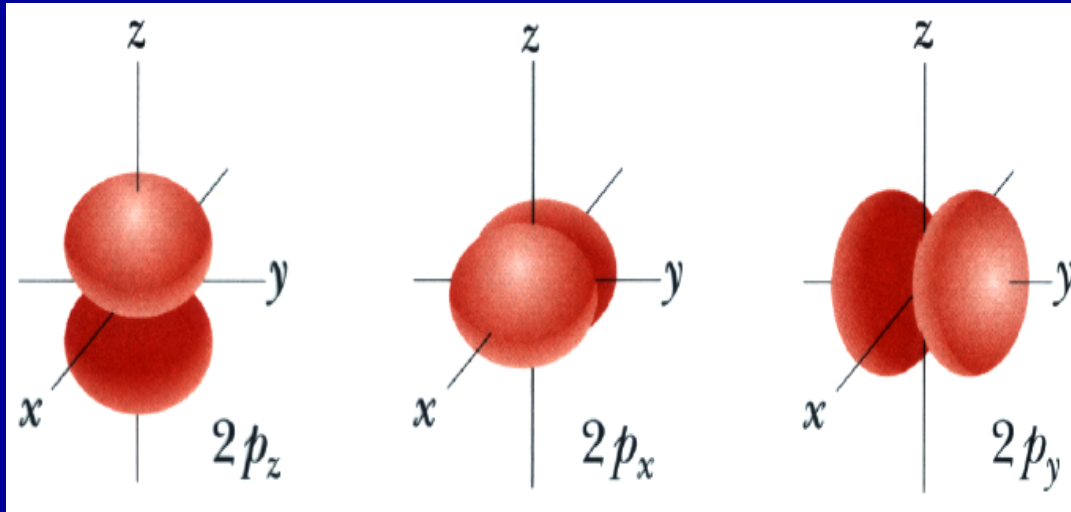
$\psi_{2p_y} = \frac{1}{\sqrt{2}} [\psi_{211} - \psi_{21-1}]$  .....has electron "cloud" oriented along y axis

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

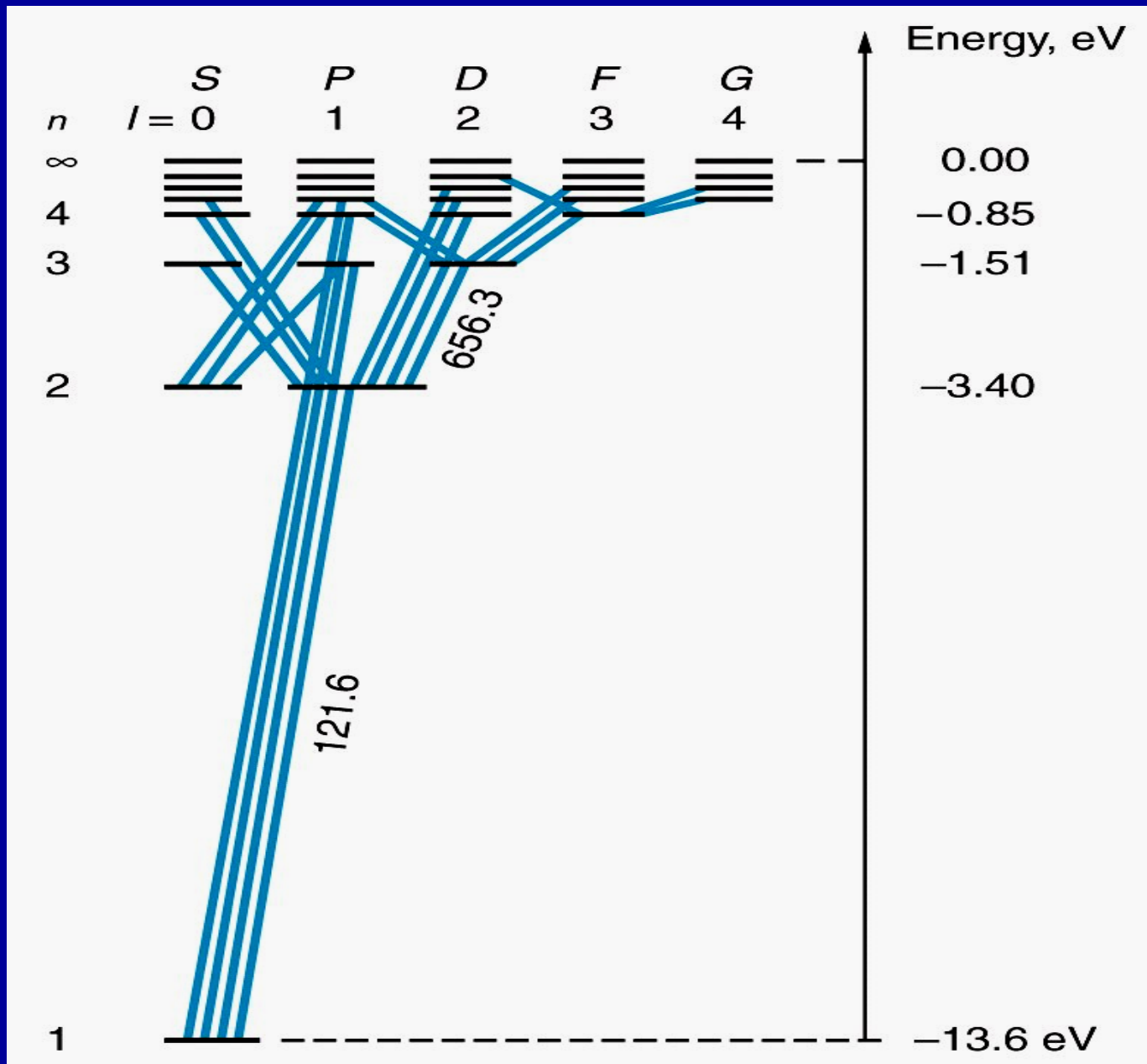
Similarly for n=3 states ...and so on ...can get very complicated structure in  $\theta$  &  $\phi$ .....which I can then mix & match to make electrons "most likely" to be where I want them to be !



# Designer Wave Functions: Solutions of S. Eq !

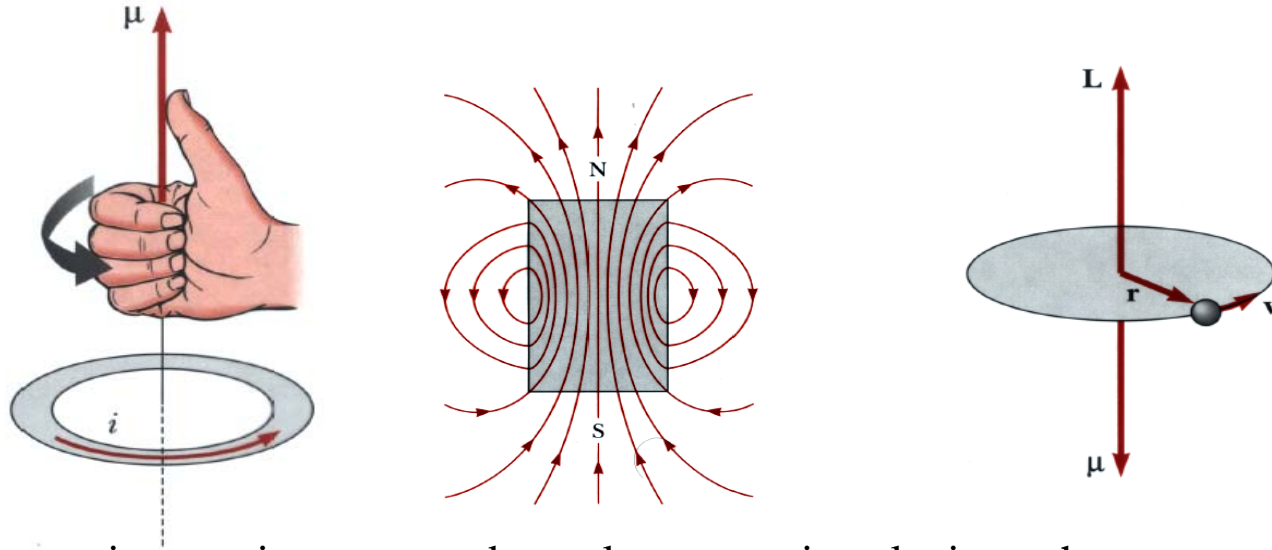


# Energy States, Degeneracy & Transitions



# The "Magnetism" of an Orbiting Electron

Precessing electron  $\rightarrow$  Current in loop  $\rightarrow$  Magnetic Dipole moment  $\mu$



Electron in motion around nucleus  $\Rightarrow$  circulating charge  $\Rightarrow$  current  $i$

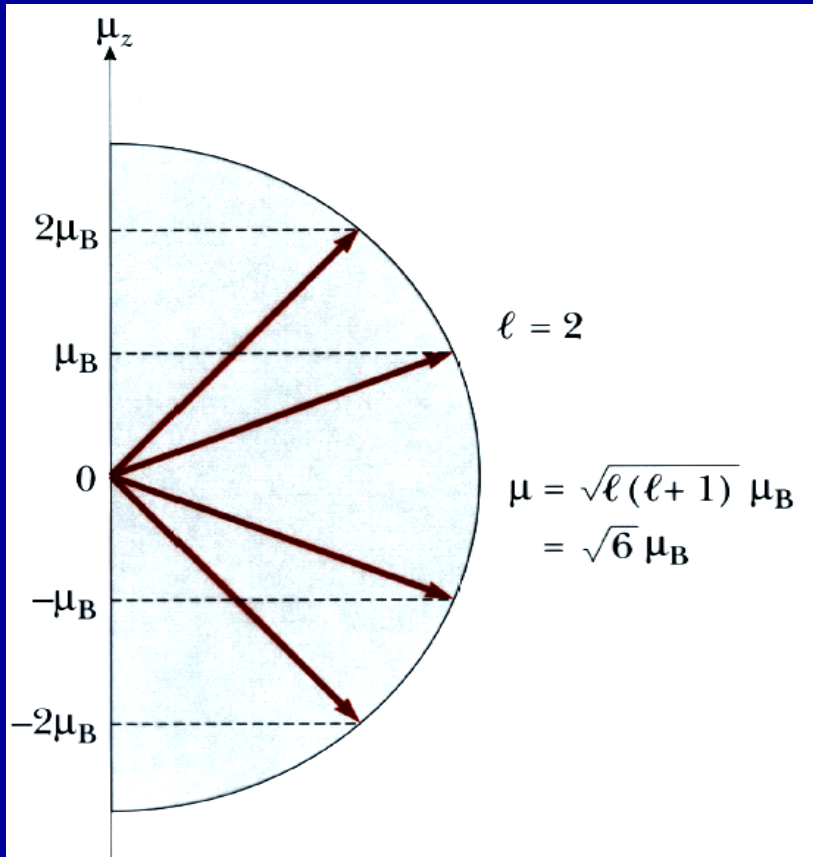
$$i = \frac{-e}{T} = \frac{-e}{\frac{2\pi r}{v}} = \frac{-ev}{2\pi r}; \text{ Area of current loop } A = \pi r^2$$

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

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

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

# Quantized Magnetic Moment

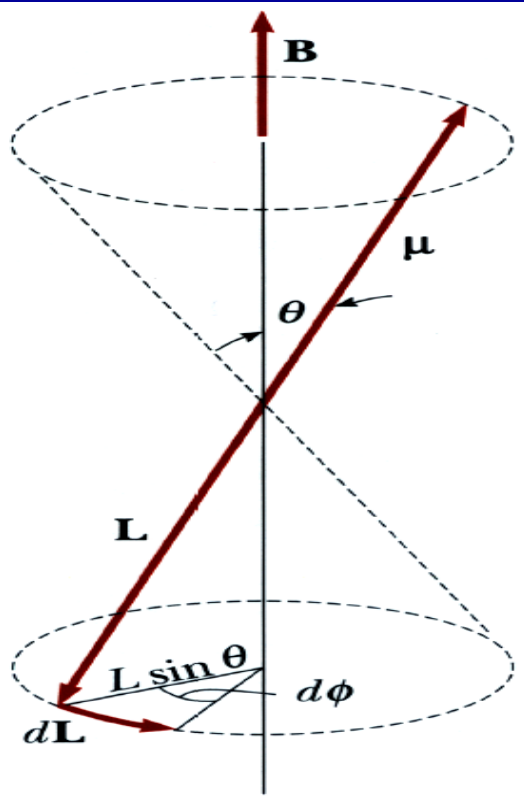


$$\begin{aligned}\mu_z &= \left( \frac{-e}{2m} \right) L_z = \left( \frac{-e\hbar}{2m} \right) m_l \\ &= -\mu_B m_l \\ \mu_B &= \text{Bohr Magnetron} \\ &= \left( \frac{e\hbar}{2m_e} \right)\end{aligned}$$

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: "Puppy training"



# “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  $\phi$  changes with time : calculate frequency

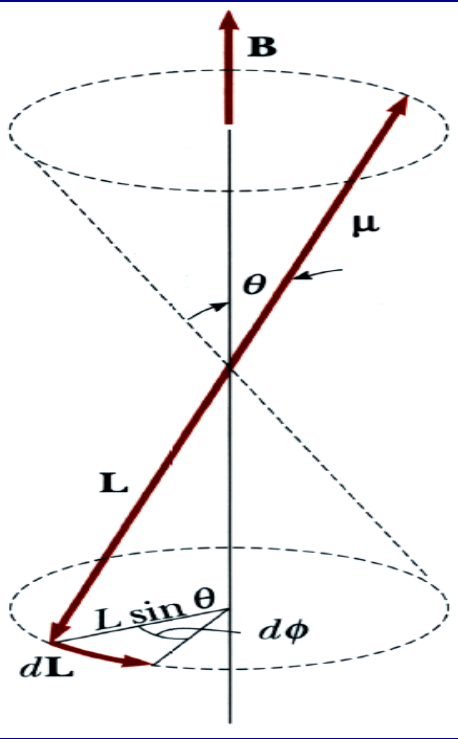
Look at Geometry: |projection along x-y plane :  $|dL| = L \sin \theta \cdot d\phi$

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

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

$\omega_L$  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:  $dW = \tau d\theta = -\mu B \sin\theta d\theta$

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

$$dW = -dU$$

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

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

## Zeeman Effect in Hydrogen Atom

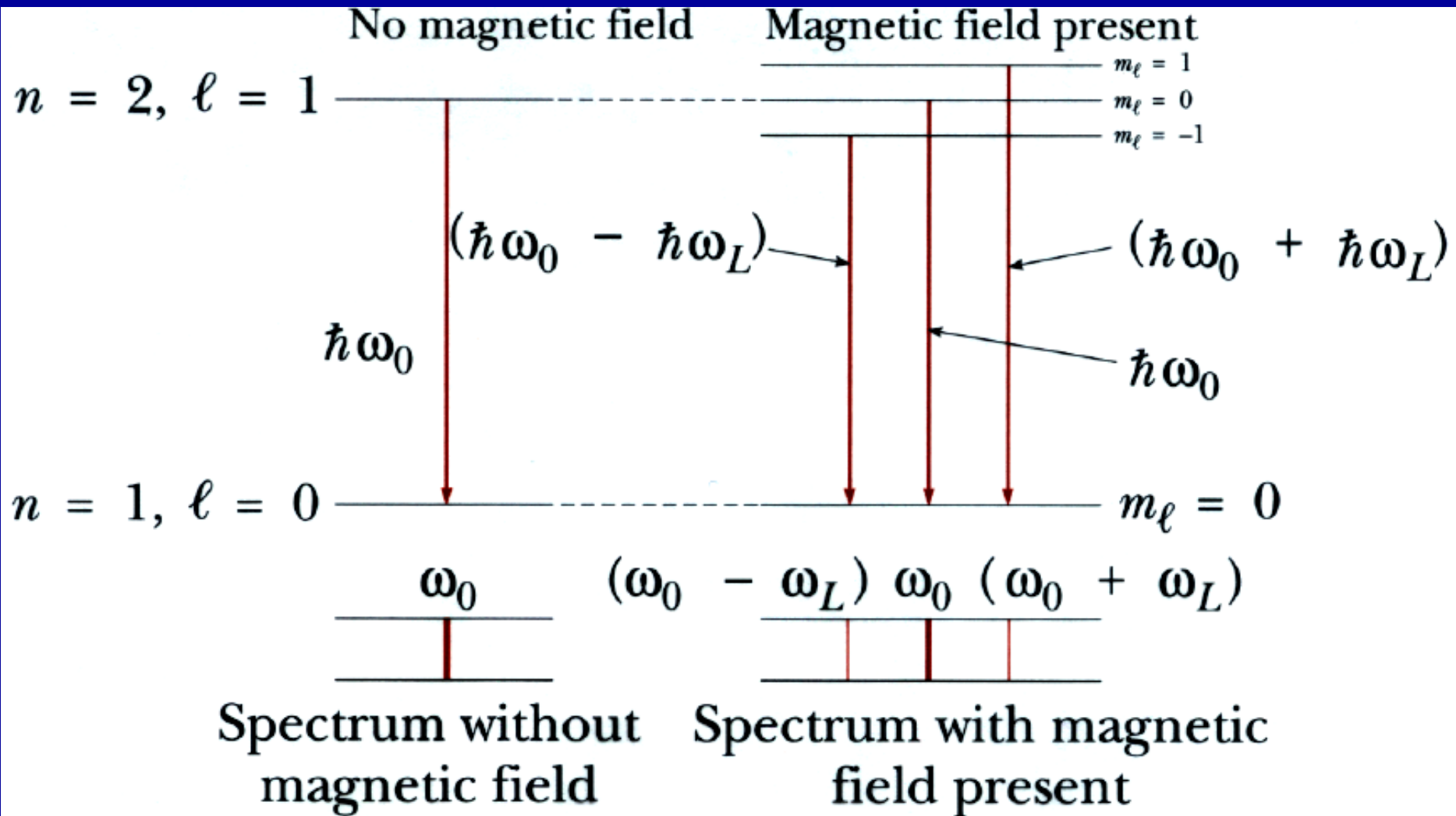
In presence of External B Field, Total energy of H atom changes to

$$E = E_0 + \hbar\omega_L m_l$$

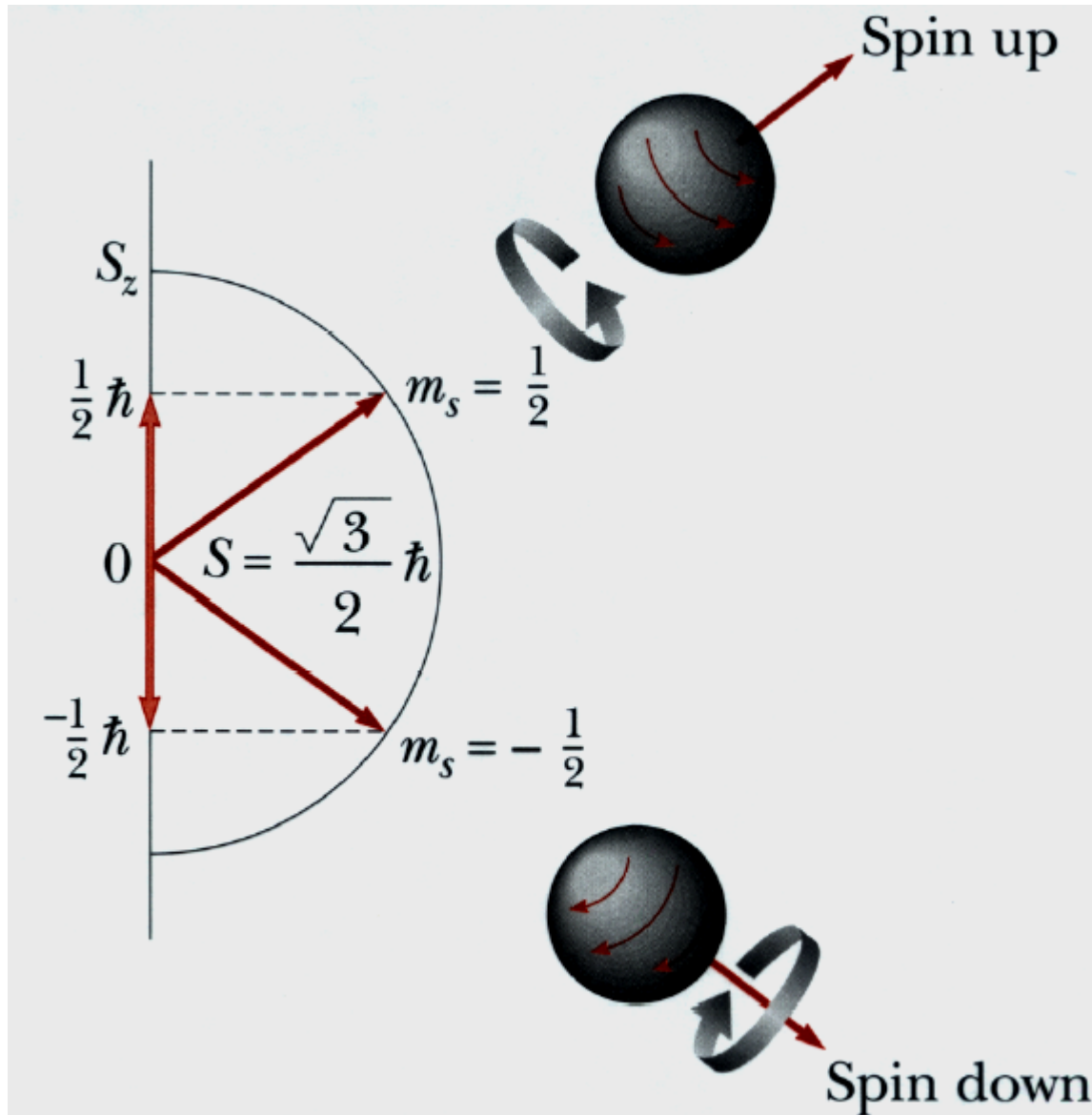
So the Ext. B field can break the E degeneracy "organically" inherent in the H atom. The Energy now depends not just on  $n$  but also  $m_l$

# Zeeman Effect Due to Presence of External B field

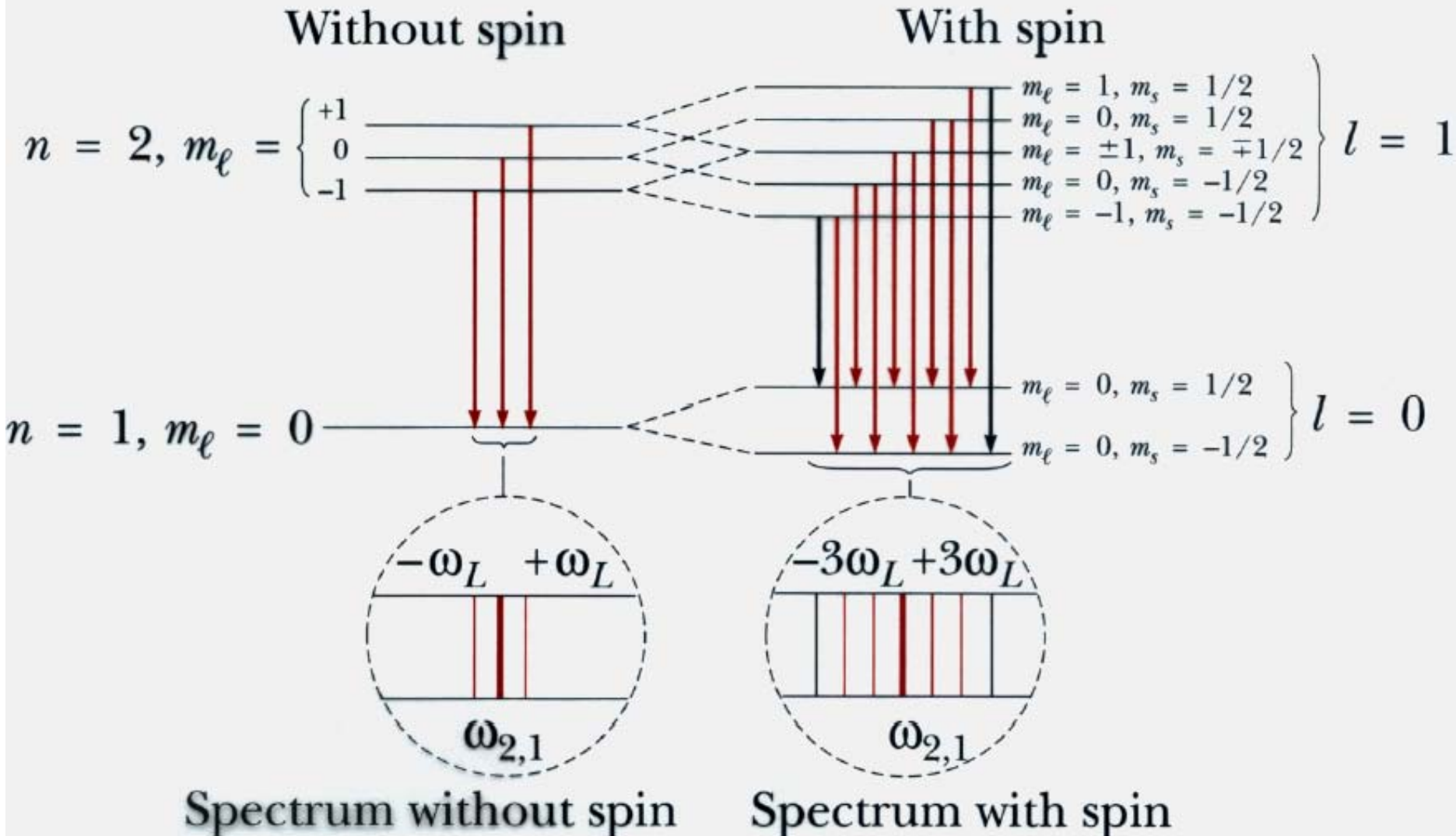
## Bye Bye Energy Degeneracy

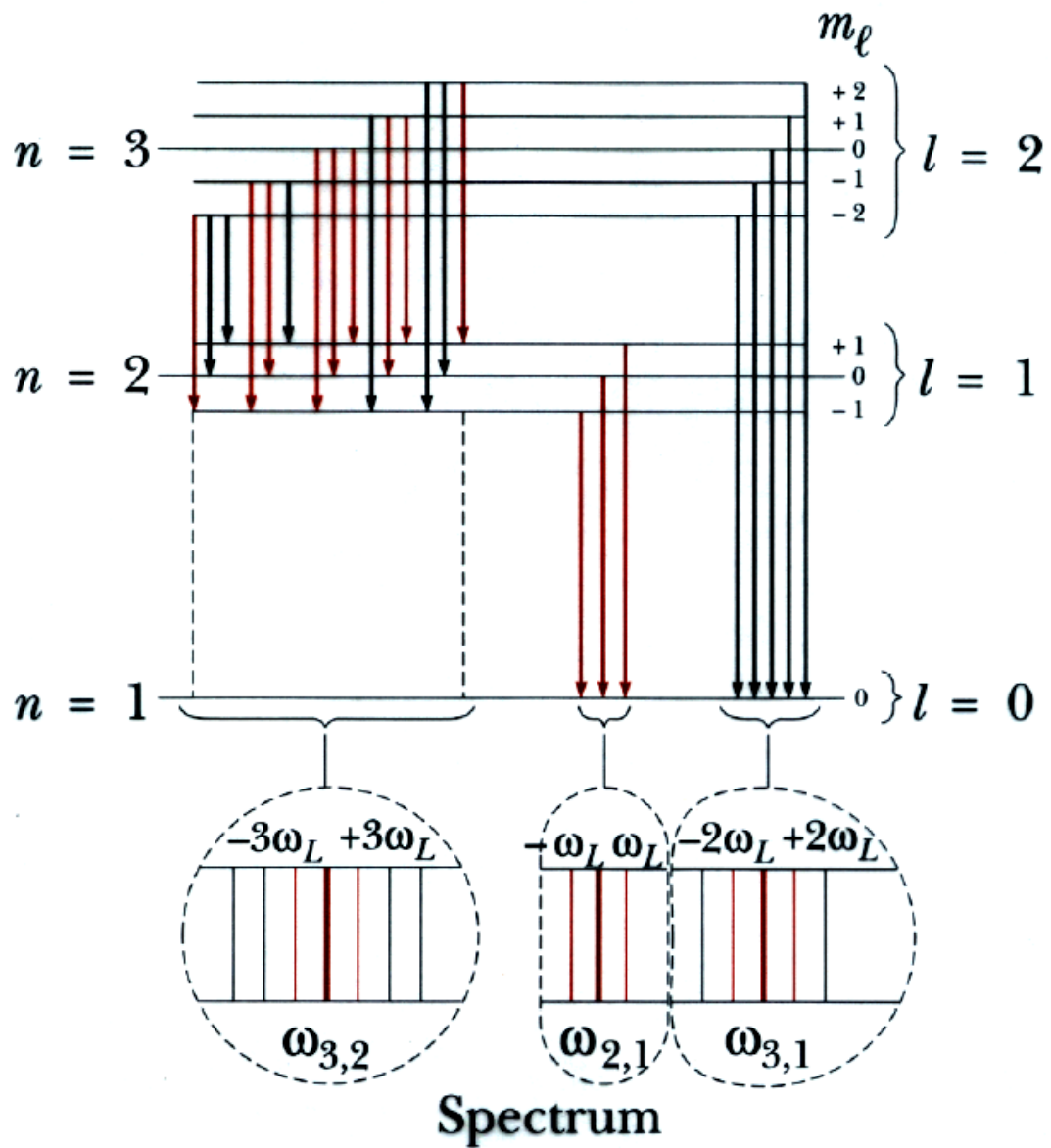


# Electron has "Spin": An additional degree of freedom











































# The Consequence of Spinning Electron





# The Periodic Table based in 4 Quantum numbers

Atom	1s	2s	2p			Electron configuration
Li						$1s^2 2s^1$
Be						$1s^2 2s^2$
B						$1s^2 2s^2 2p^1$
C						$1s^2 2s^2 2p^2$
N						$1s^2 2s^2 2p^3$
O						$1s^2 2s^2 2p^4$
F						$1s^2 2s^2 2p^5$
Ne						$1s^2 2s^2 2p^6$