Physics 2D Lecture Slides
Lecture 30: March 9th 2005

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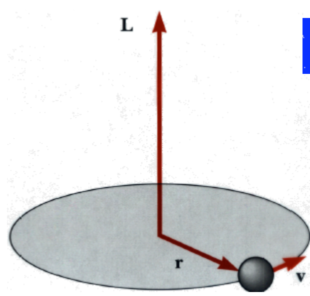
Magnetic Quantum Number m_l



$\vec{L} = \vec{r} \times \vec{p}$ (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 ($\vec{L} \parallel \hat{z}$)

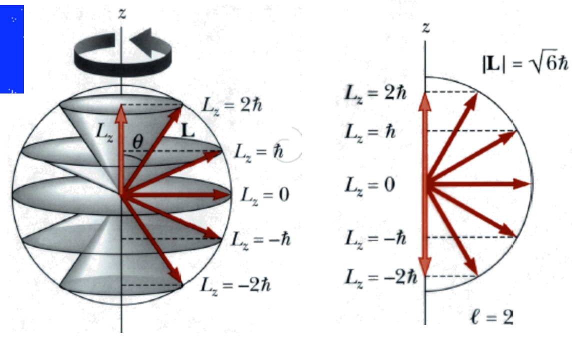
Since $\vec{L} = \vec{r} \times \vec{p} \Rightarrow$ Electron MUST be in x-y orbit plane

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

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

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

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

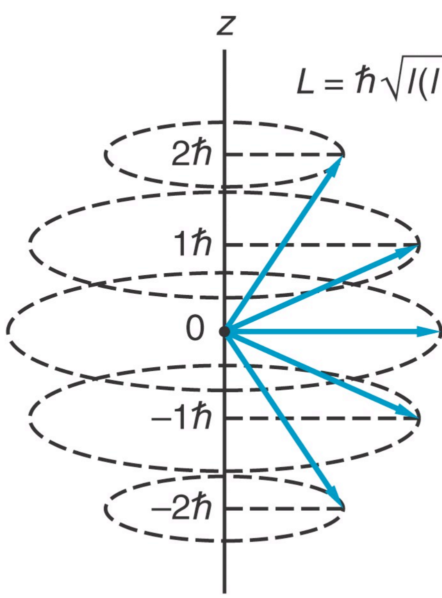
Note: since $|L_Z| < |L|$ (always)

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:

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

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

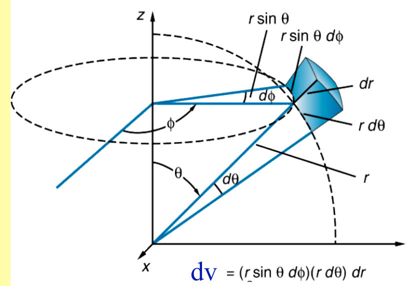
$$P(r)dr = |R_{nl}|^2 .r^2 dr \int_0^{\pi} |\Theta_{lm_l}(\theta)|^2 d\theta \int_0^{2\pi} |\Phi_{m_l}(\phi)|^2\ d\phi$$

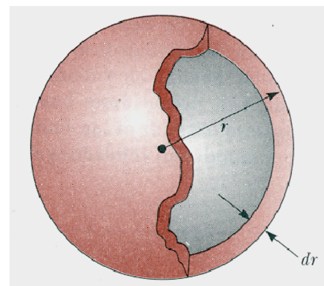
When $\Theta_{lm_l}(\theta)$ & $\Phi_{m_l}(\phi)$ are auto-normalized then

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

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

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





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 $r > a_0$

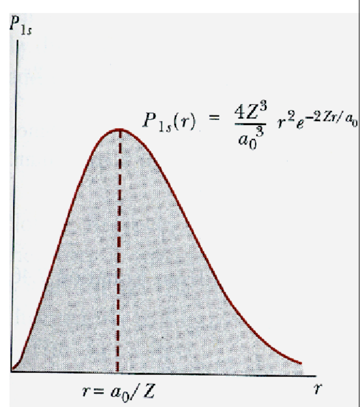
$$P_{r>a_0} = \int_a^{\infty} \frac{4}{a_0^3} r^2 e^{-2\frac{r}{a_0}} dr$$

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

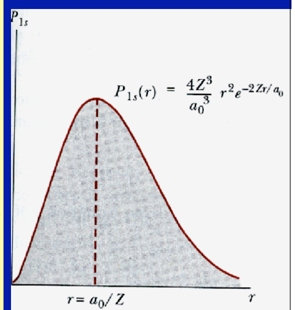
Most probable distance r from Nucleus $\Rightarrow$ What value of r is P(r) max?

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

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

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

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

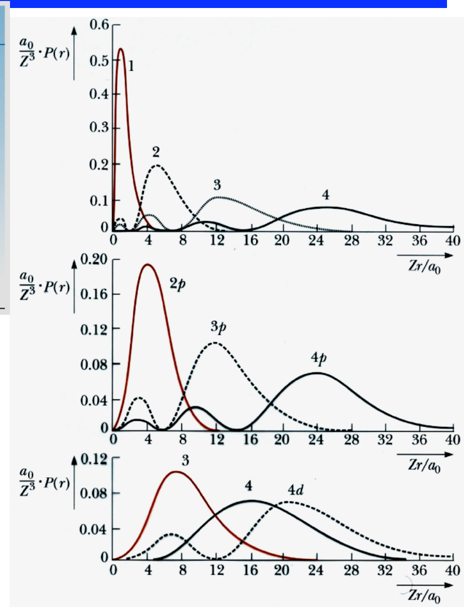
$\Rightarrow$ $\boxed{\langle r \rangle = \frac{a_0}{4} 3! = \frac{3a_0}{2} \neq a_0!}$ Average & most likely distance is not same. Why?

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

$n=1$	$l=0$	$R_{10} = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$
$n=2$	$l=0$	$R_{20} = \frac{1}{\sqrt{2a_0^3}}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$
	$l=1$	$R_{21} = \frac{1}{2\sqrt{6a_0^3}} \frac{r}{a_0} e^{-r/2a_0}$
$n=3$	$l=0$	$R_{30} = \frac{2}{3\sqrt{3a_0^3}}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$
	$l=1$	$R_{31} = \frac{8}{27\sqrt{6a_0^3}} \frac{r}{a_0}\left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0}$
	$l=2$	$R_{32} = \frac{4}{81\sqrt{30a_0^3}} \frac{r^2}{a_0^2} e^{-r/3a_0}$



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

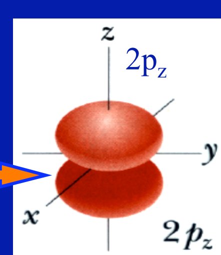
What about ($n=2$, $\ell=1$, $m_l = 0$)

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

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

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 !

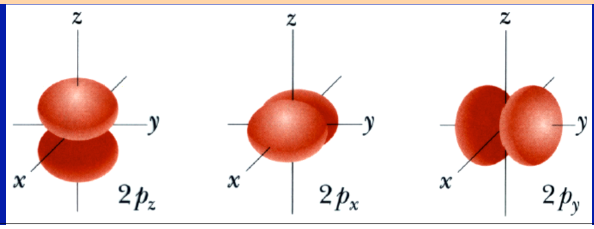
Linear Superposition Principle means allows me to "cook up" wavefunctions

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

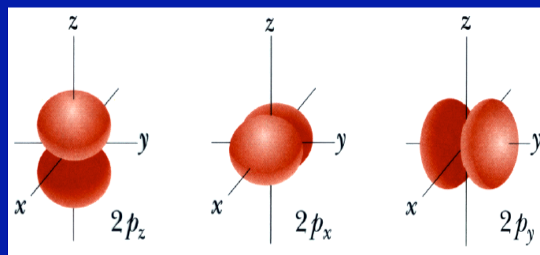
$\psi_{2p_y} = \frac{1}{\sqrt{2}}[\psi_{211} - \psi_{21-1}]$ ......has electron "cloud" oriented along y axis

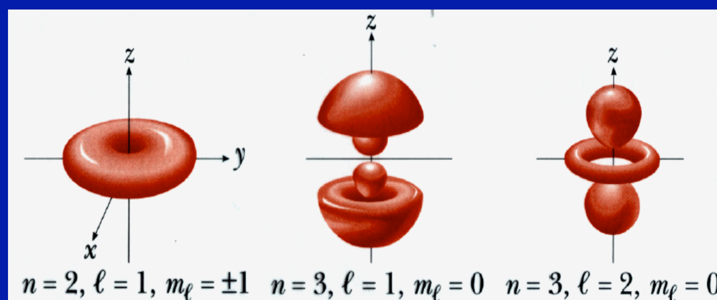
So from 4 solutions $\psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1} \rightarrow 2s, 2p_x, 2p_y, 2p_z$

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 !





TYPO FIXED

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

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

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

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

The hydrogen atom brought to you by the letters

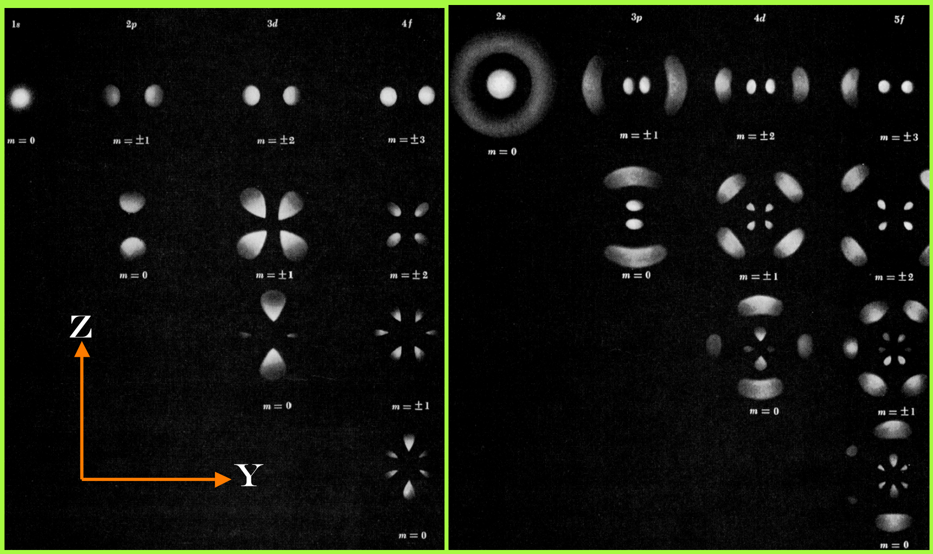
$$\boxed{\begin{aligned} &n = 1,2,3,4,5,....\infty \\ &l = 0,1,2,3,,4....(n-1) \\ &m_l = 0,\pm1,\pm2,\pm3,...\pm l \end{aligned}}$$

The Spatial Wave Function of the Hydrogen Atom

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

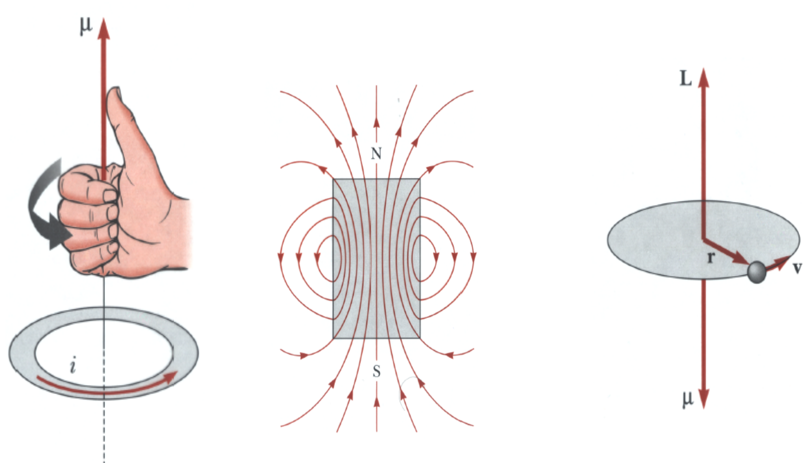
Cross Sectional View of Hydrogen Atom prob. densities in r,θ,ϕ
Birth of Chemistry (Can make Fancy Bonds→ Overlapping electron "clouds")

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



What's So "Magnetic" ?

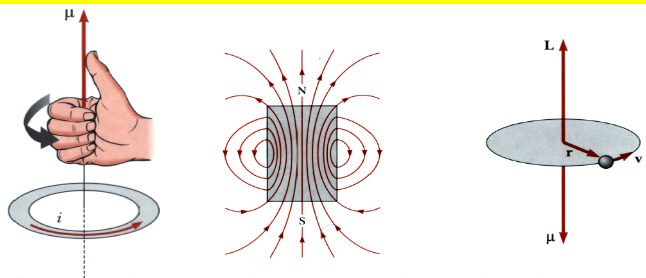
Precessing electron→ Current in loop → Magnetic Dipole moment μ



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

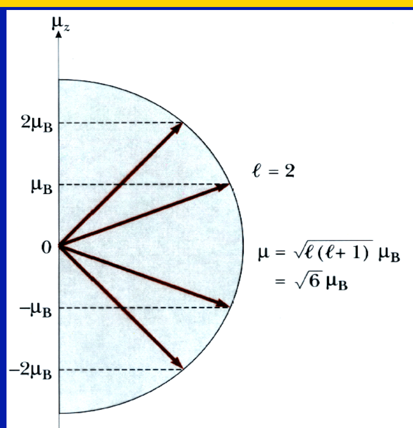
$$i = \frac{-e}{T} = \frac{-e}{\frac{2\pi r}{v}} = \frac{-ep}{2\pi m r};$$ Area of current loop $A=\pi r^2$

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

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

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

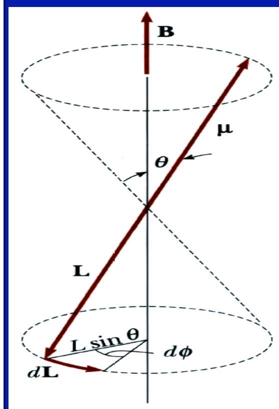
Quantized Magnetic Moment



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

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

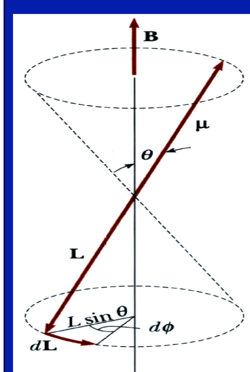
Look at Geometry: |projection along x-y plane : $|dL| = L\sin\theta . d\phi$

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

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

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

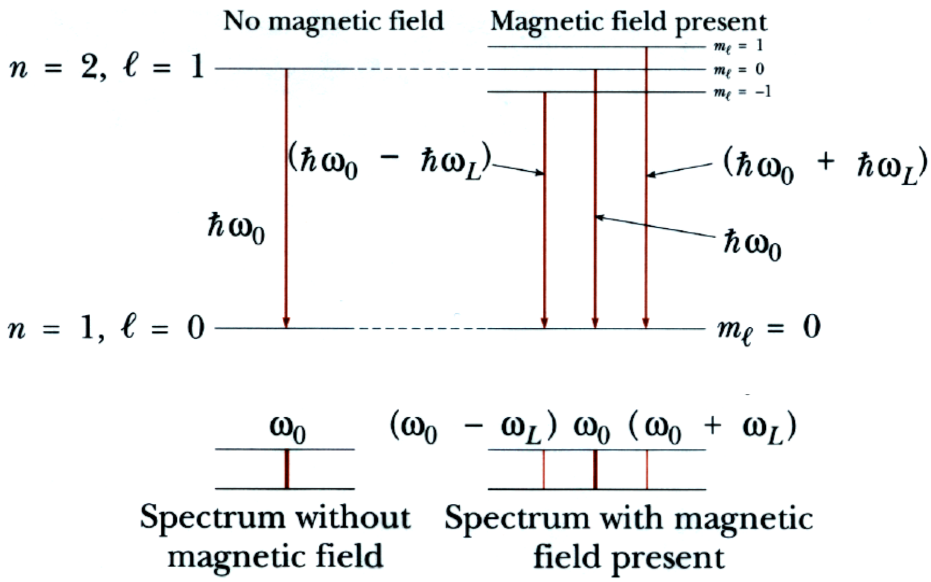
In presence of External B Field, Total energy of H atom changes to

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

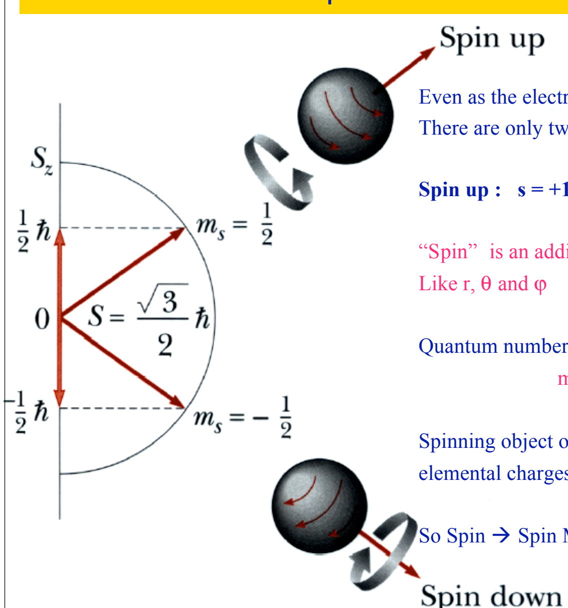
So the Ext. B field can break the E degeneracy "organically" inherent in the H atom. The Energy now depends not just on n but also m_l

Zeeman Effect Due to Presence of External B field

Energy Degeneracy Is Broken



Electron has "Spin": An additional degree of freedom



Even as the electron rotates around nucleus, it also "spins"
There are only two possible spin orientations:

Spin up : s = +1/2 ; Spin Down: s=-1/2

"Spin" is an additional degree of freedom just
Like r, θ and φ

Quantum number corresponding to spin orientations

$m_l = \pm ½$

Spinning object of charge Q can be thought of a collection of elemental charges Δq and mass Δm rotating in circular orbits

So Spin → Spin Magnetic Moment → interacts with B field

Stern-Gerlach Expt⇒ An additional degree of freedom: “Spin” for lack of a better name

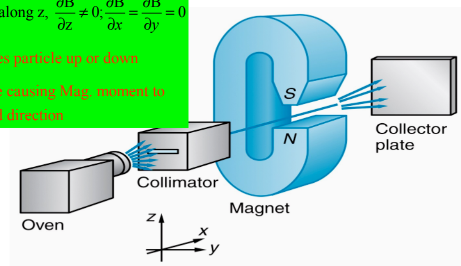
$\vec{\mu}$ in inhomogenous $\vec{B}$ field, experiences force $\vec{F}$

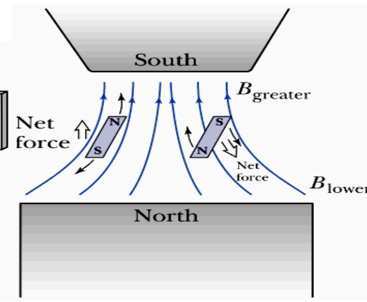
$\vec{F} = -\nabla U_B = -\nabla(-\vec{\mu}.\vec{B})$

When gradient only along z, $\frac{\partial B}{\partial z} \neq 0; \frac{\partial B}{\partial x} = \frac{\partial B}{\partial y} = 0$

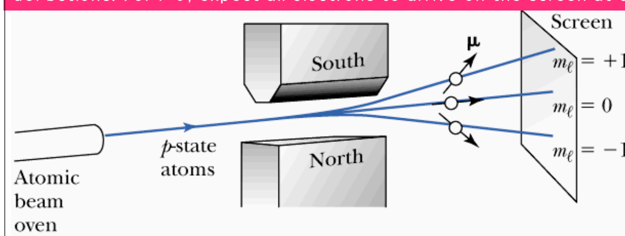
$F_z = m\mu_B(\frac{\partial B}{\partial z})$ moves particle up or down

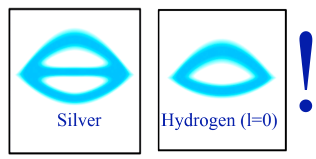
(in addition to torque causing Mag. moment to precess about B field direction





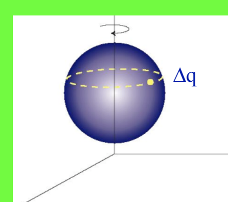
In an inhomogeneous field, magnetic moment μ experiences a force F_z whose direction depends on component of the net magnetic moment & inhomogeneity dB/dz. Quantization means expect *(2l+1)* deflections. For l=0, expect all electrons to arrive on the screen at the center (no deflection)





Four (not 3) Numbers Describe Hydrogen Atom → n, l, m_l, m_s

$\boxed{\text{"Spinning" charge gives rise to a dipole moment } \vec{\mu}_s}$:

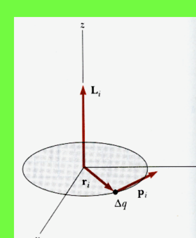


Imagine (semi-clasically,incorrectly!) electron as sphere: charge q, radius r

Total charge uniformly distributed: $q = \sum_i \Delta q_i$;

as electron spins, each "chargelet" rotates ⇒ current ⇒ dipole moment $\vec{\mu}_{s_i}$

$$\boxed{\vec{\mu}_s = \left(\frac{q}{2m_e}\right)\sum_i \vec{\mu}_{s_i} = g\left(\frac{q}{2m_e}\right)\vec{S}}$$



In a Magnetic Field $\vec{B}$ ⇒ magnetic energy due to spin $\boxed{U_S = \vec{\mu}_s.\vec{B}}$

Net Angular Momentum in H Atom $\boxed{\vec{J} = \vec{L} + \vec{S}}$

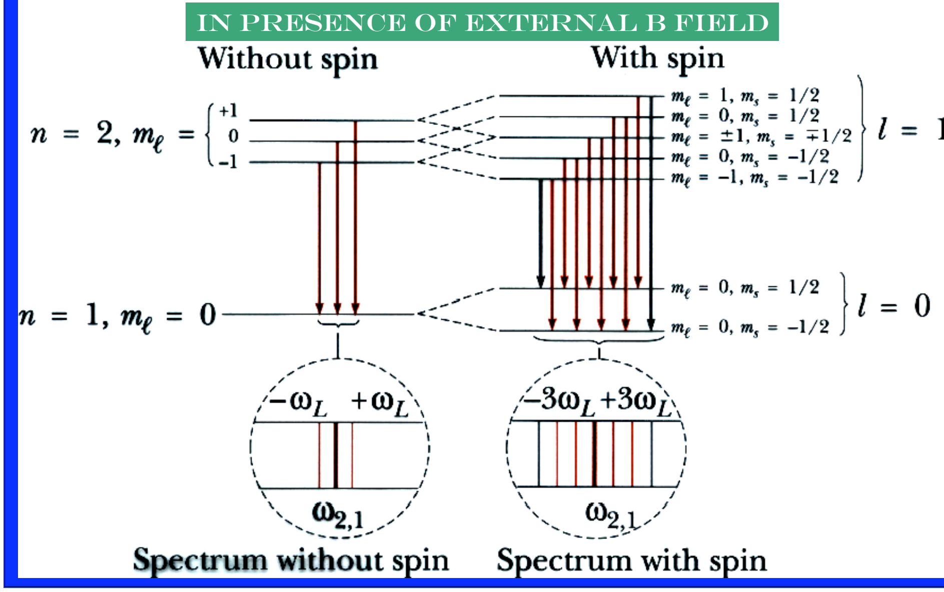
Net Magnetic Moment of H atom: $\boxed{\vec{\mu} = \vec{\mu}_0 + \vec{\mu}_s = \left(\frac{-e}{2m_e}\right)(\vec{L} + g\vec{S})}$

Notice that the $\boxed{\text{net dipole moment vector } \vec{\mu} \text{ is not } \| \text{ to } \vec{J}}$

(There are many such "ubiquitous" quantum numbers for elementary particle but we won't teach you about them in this course !)

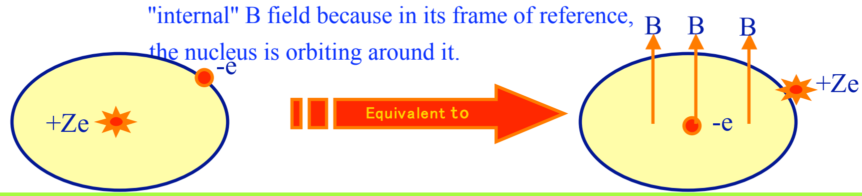
Doubling of Energy Levels Due to Spin Quantum Number

Under Intense B field, each {n , m_l } energy level splits into two depending on spin up or down



Spin-Orbit Interaction: Angular Momenta are Linked Magnetically

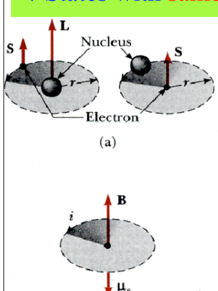
Electron revolving around Nucleus finds itself in a "internal" B field because in its frame of reference, the nucleus is orbiting around it.



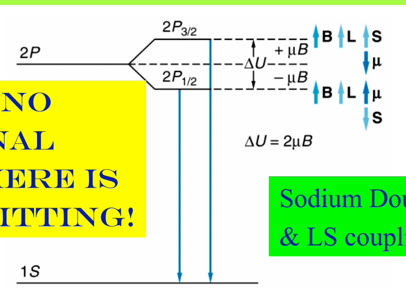
This B field, due to orbital motion, interacts with electron's spin dipole moment $\vec{\mu}_s$

$U_m = -\vec{\mu}.\vec{B} \Rightarrow$ Energy larger when $\vec{S} \parallel \vec{B}$, smaller when anti-parallel

$\Rightarrow$ States with same (n, l, m_l) but diff. spins $\Rightarrow$ energy level splitting/doubling due to $\vec{S}$



UNDER NO EXTERNAL B FIELD THERE IS STILL A SPLITTING!



Sodium Doublet & LS coupling

Vector Model For Total Angular Momentum **J**

$\boxed{\text{Coupling of Orbital \& Spin magnetic moments}} \Rightarrow$

Neither Orbital nor Spin angular Momentum are conserved seperately!

$\boxed{\vec{J} = \vec{L} + \vec{S}}$ is conserved so long as there are no external torques present

Rules for Total Angular Momentum Quantization :

$$|J| = \sqrt{j(j+1)}\,\hbar \quad \text{with} \quad j = |l+s|,\ l+s-1,\ l+s-2......,....,|l-s|$$
$$J_z = m_j \hbar \quad \text{with } m_j = \ j,\ j-1,\ j-2.......,\ -j$$

Example: state with $(l = 1, s = \frac{1}{2})$

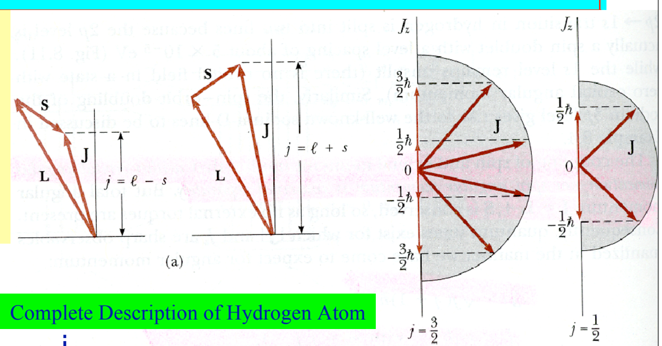
$j = 3/2 \Rightarrow m_j = -3/2, -1/2, 1/2, 3/2$

$j = 1/2 \Rightarrow m_j = \pm 1/2$

In general m_j takes $(2j+1)$ values

$\Rightarrow$ Even # of orientations

Spectrographic Notation: Final Label



n → $1S_{1/2}$

$2P_{3/2}$ ← j

Complete Description of Hydrogen Atom

Complete Description of Hydrogen Atom

Full description of the Hydrogen atom:

$\{n, l, m_l, m_s\}$

$\Downarrow$

LS Coupling

$\Downarrow$

$\{n, l, j, m_s\}$

corresponding to 4 D.O.F.

n → $1S_{1/2}$

$2P_{3/2}$ → j

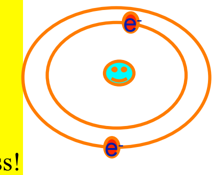
How to describe multi-electrons atoms like He, Li etc?

How to order the Periodic table?

- Four guiding principles:
  - Indistinguishable particle & Pauli Exclusion Principle
  - Independent particle model (ignore inter-electron repulsion)
  - Minimum Energy Principle for atom
  - Hund's "rule" for order of filling vacant orbitals in an atom

Multi-Electron Atoms : >1 electron in orbit around Nucleus

In Hydrogen Atom $\psi(r,\theta,\phi)=R(r).\Theta(\theta).\Phi(\phi) \quad \equiv \{n,l,j,m_j\}$



In n-electron atom, to simplify, ignore electron-electron interactions

complete wavefunction, in "independent"particle approx" :

$$\boxed{\psi(1,2,3,..n)=\psi(1).\psi(2).\psi(3)...\psi(n) \quad ???}$$

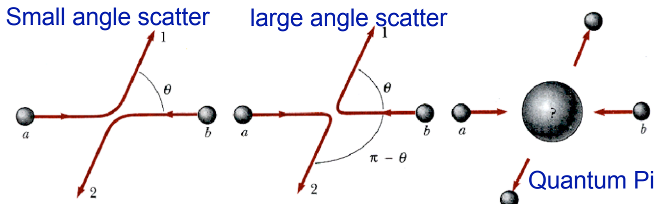
Complication $\rightarrow$ Electrons are identical particles, labeling meaningless!

Question: How many electrons can have same set of quantum #s?

Answer: No two electrons in an atom can have SAME set of quantum#s

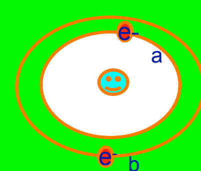
(if not, all electrons would occupy 1s state (least energy)... no structure!!

Example of Indistinguishability: electron-electron scattering



If we cant follow electron path, don't know between which of the two scattering Event actually happened

Helium Atom: Two electrons around a Nucleus



In Helium, each electron has : kinetic energy + electrostatic potential energy

If electron "1" is located at r_1 & electron "2"is located at r_2 then TISE has terms like:

$$H_1 = -\frac{\hbar^2}{2m}\nabla_1^2 + k\frac{(2e)(-e)}{r_1};\ H_2 = -\frac{\hbar^2}{2m}\nabla_2^2 + k\frac{(2e)(-e)}{r_2} \quad \text{such that}$$

$$\boxed{H_1\psi + H_2\psi = E\psi};\ H_1 \text{ \& } H_2 \text{ are same except for "label"}$$

Independent Particle Approx $\Rightarrow$ ignore repulsive $U=k\frac{e^2}{|r_2 - r_1|}$ term

Helium WaveFunction: $\psi=\psi(r_1,r_2)$; Probability $P=\psi^*(r_1,r_2)\psi(r_1,r_2)$

But if we exchange location of (identical, indistinguishable) electrons $\Rightarrow |\psi(r_1,r_2)|=|\psi(r_2,r_1)|$

In general, when $\psi(r_1,r_2)=\psi(r_2,r_1)$.......................Bosonic System (made of photons, e.g)

when $\psi(r_1,r_2)=-\psi(r_2,r_1)$.....................fermionic System (made of electron, proton e.g)

$\Rightarrow$ Helium wavefunction must be ODD; if electron "1" is in state a & electron "2" is in state b

Then the net wavefunction $\psi_{ab}(r_1,r_2)=\psi_a(r_1).\psi_b(r_2)$ satisfies

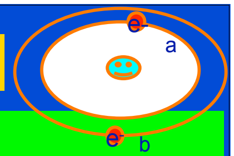
$$H_1\psi_a(r_1).\psi_b(r_2) = E_a\psi_a(r_1).\psi_b(r_2)$$

$$H_2\psi_a(r_1).\psi_b(r_2) = E_b\psi_a(r_1).\psi_b(r_2)$$

and the sum $\quad [H_1+H_2]\psi_a(r_1).\psi_b(r_2) = (E_a + E_b)\psi_a(r_1).\psi_b(r_2)$

Total Helium Energy $E \simeq E_a + E_b$ =sum of Hydrogen atom like E

Helium Atom: Two electrons around a Nucleus



Helium wavefunction must be ODD $\Rightarrow$ anti-symmetric: $\psi_{ab}(r_1,r_2)=-\psi_{ab}(r_2,r_1)$

So it must be that $\psi_{ab}(r_1,r_2)=\psi_a(r_1).\psi_b(r_2)-\psi_a(r_2).\psi_b(r_1)$

It is impossible to tell, by looking at probability or energy which particular electron is in which state

If both are in the same quantum state $\Rightarrow$ a=b & $\psi_{aa}(r_1,r_2)=\psi_{bb}(r_1,r_2)=0$... Pauli Exclusion principle

General Principles for Atomic Structure for n-electron system:

1. n-electron system is stable when its total energy is minimum
2. Only one electron can exist in a particular quantum state in an atom...not 2 or more !
3. Shells & SubShells In Atomic Structure:

(a) ignore inter-electron repulsion (crude approx.)

(b) think of each electron in a constant "effective" mean Electric field

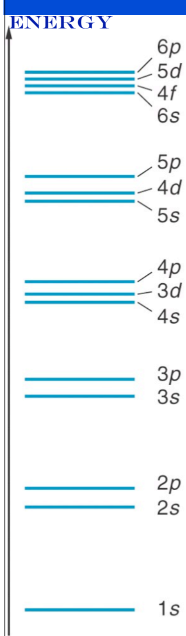
(Effective field: "Seen" Nuclear charge (+Ze) reduced by partial screening due to other electrons "buzzing" closer (in r) to Nucleus)

Electrons in a SHELL: have same n, are at similar <r> from nucleus, have similar energies

Electons in a SubShell: have same principal quantum number n

- Energy depends on l, those with lower l closer to nucleus, more tightly bound
- all electrons in sub-shell have same energy, with minor dependence on m_l, m_s

Shell & Sub-Shell Energies & Capacity



1. Shell & subshell capacity limited due to Pauli Exclusion principle
2. Shell is made of sub-shells (of same principal quantum # n)
3. Subshell $\Leftarrow (n,l)$, given $n \Rightarrow l = 0,1,2,3,..(n-1)$,

for any $l \;\Rightarrow m_l = 0, \pm1, \pm2, .. \Rightarrow (2l+1), m_s = \pm\frac{1}{2}$

$\Rightarrow$ Max. # of electrons in a shell = $\sum$ subshell capacity

$$N_{MAX} = \sum_{l=0}^{n-1} 2.(2l+1) = 2\left[1+3+5+..2(n-1)+1\right] = 2(n)\left[\frac{1}{2}(1+(2n-1))\right] = 2n^2$$

4. The "K" Shell (n=1) holds 2 electrons, "L" Shell (n=1) holds 8 electrons, M shell (n=3) holds 18 electrons ......
5. Shell is closed when fully occupied
6. Sub-Shell closed when

(a) $\sum_i \vec{L}_i = 0, \sum_i \vec{S}_i = 0, \Rightarrow$ Effective charge distribution= symmetric

(b) Electrons are tightly bound since they "see" large nuclear charge

(c) Because $\sum_i \vec{L}_i = 0 \Rightarrow$ No dipole moment $\Rightarrow$ No ability to attract electrons

$\Rightarrow$ *Inert*! *Noble* gas!

6. Alkali Atoms: have a single "s" electron in outer orbit; nuclear charge heavily shielded by inner shell electrons

$\Rightarrow$ very small binding energy of "valence"electron

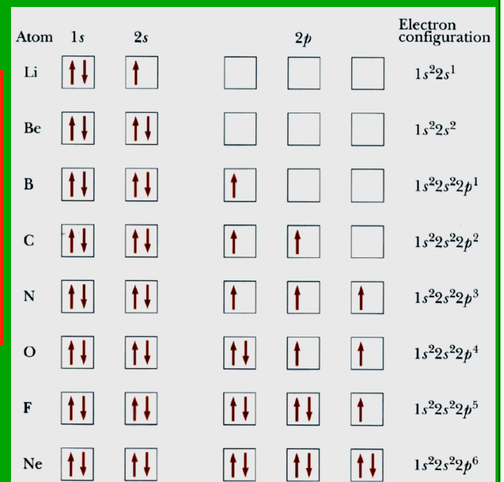
$\Rightarrow$ large orbital radius of valence electron

Electronic Configurations of n successive elements from Lithium to Neon

Hund's Rule: Whenever possible
-electron in a sub-shell remain unpaired

- States with spins parallel occupied first
- Because electrons repel when close together
- → electrons in same sub-shell (l) and same spin
  - -Must have diff. m_l
  - -(very diff. angular distribution)
- Electrons with parallel spin are further apart
  - -Than when anti-parallel ⇒ lesser E state
    - -Get filled first

Periodic table is formed



That's all I can teach you this quarter; Rest is all Chemistry !