



Physics 2D Lecture Slides

Lecture 31: March 11th 2005

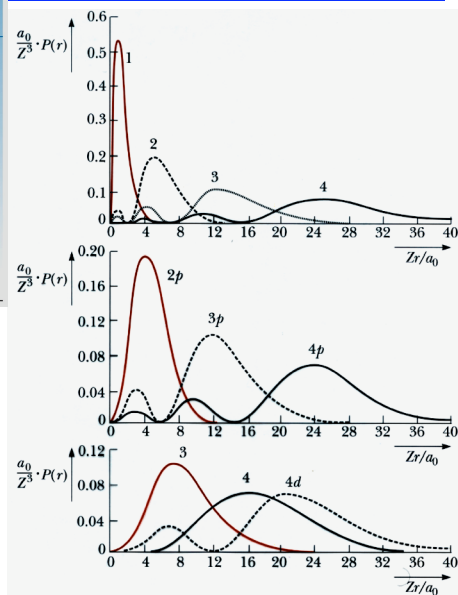
Vivek Sharma
UCSD Physics



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 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

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

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

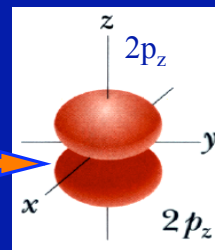
What about ($n=2, l=1, m_1 = 0$)

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

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

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

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

The diversity in Chemistry and Biology DEPENDS on this superposition rule

Designer Wave Functions: Solutions of S. Eq !

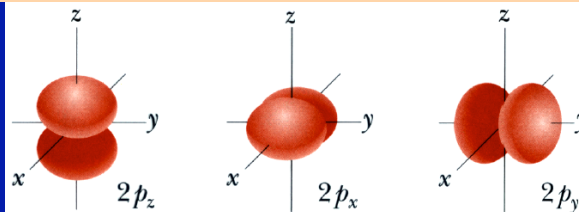
Linear Superposition Principle means allows me to "cook up" wavefunctions

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

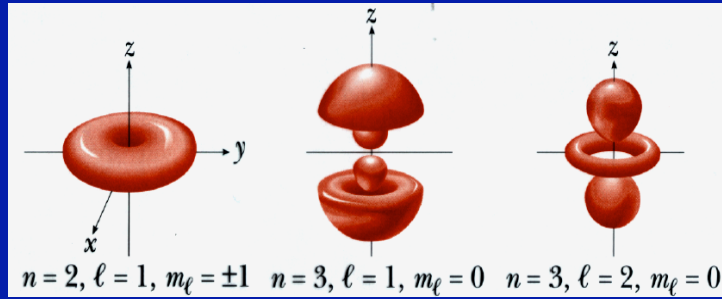
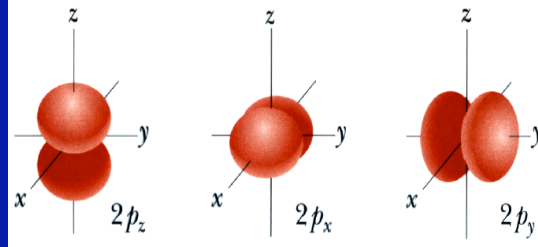
$$\psi_{2p_y} = \frac{1}{\sqrt{2}}[\psi_{211} - \psi_{21-1}] \dots\dots\text{has electron "cloud" oriented along y axis}$$

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 & ϕwhich 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 !



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

TYPE FIXED

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

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

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

The hydrogen atom brought to you by the letters

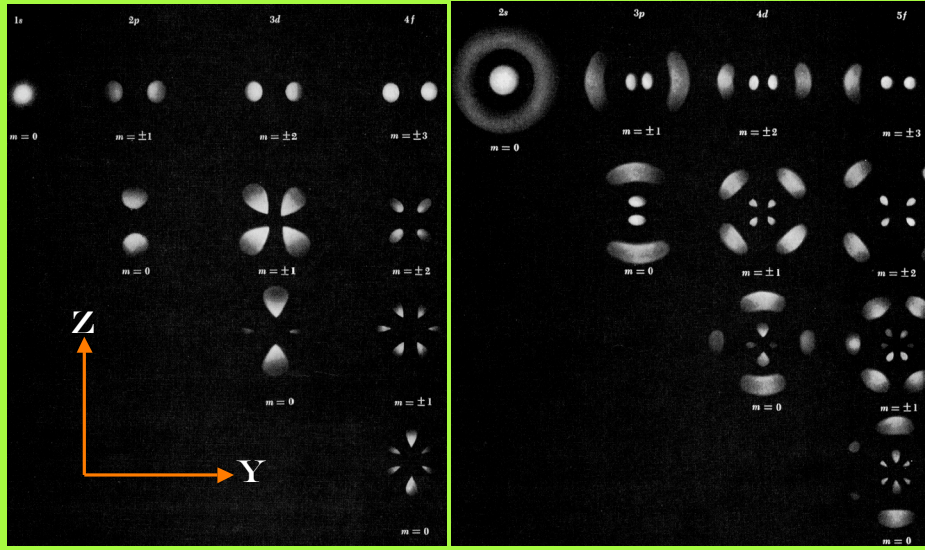
$$\begin{aligned}
 n &= 1, 2, 3, 4, 5, \dots, \infty \\
 l &= 0, 1, 2, 3, \dots, (n-1) \\
 m_l &= 0, \pm 1, \pm 2, \pm 3, \dots, \pm l
 \end{aligned}$$

The Spatial Wave Function of the Hydrogen Atom

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

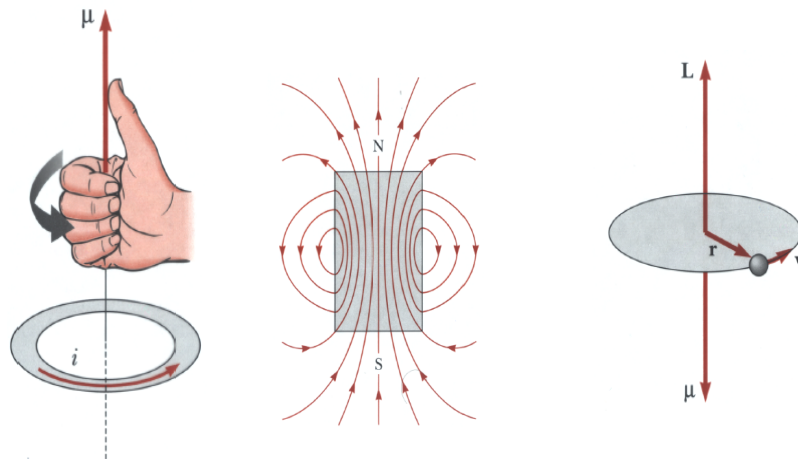
Cross Sectional View of Hydrogen Atom prob. densities in r, θ, ϕ
 Birth of Chemistry (Can make Fancy Bonds \rightarrow Overlapping electron "clouds")

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



What's So "Magnetic" ?

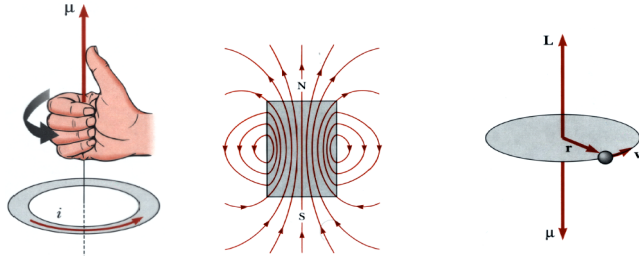
Precessing electron \rightarrow Current in loop \rightarrow Magnetic Dipole moment μ



The electron's motion \rightarrow hydrogen atom is a dipole magnet

The "Magnetism" of an Orbiting Electron

Precessing electron \rightarrow Current in loop \rightarrow Magnetic Dipole moment μ



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

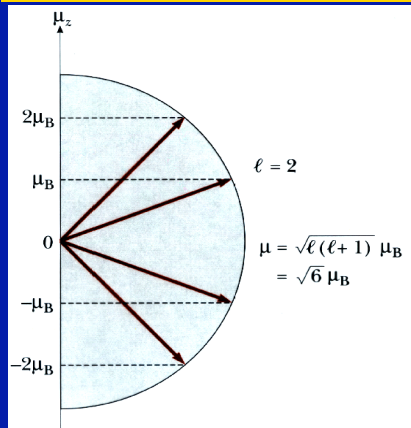
$$i = \frac{-e}{T} = \frac{-e}{\frac{2\pi r}{v}} = \frac{-ev}{2\pi r}; \text{ Area of current loop } A = \pi r^2$$

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

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

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

Quantized Magnetic Moment



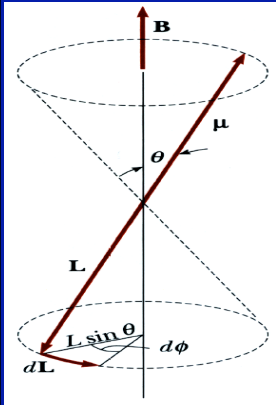
$$\begin{aligned} \mu_z &= \left(\frac{-e}{2m}\right) L_z = \left(\frac{-e\hbar}{2m}\right) m_l \\ &= -\mu_B m_l \\ \mu_B &= \text{Bohr Magnetron} \\ &= \left(\frac{e\hbar}{2m_e}\right) \end{aligned}$$

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:

"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

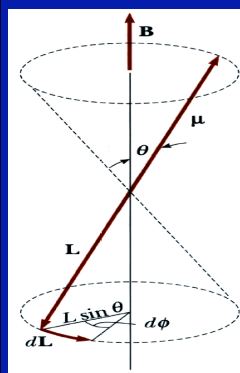
Look at Geometry: |projection along x-y plane : $|dL| = L \sin \theta \cdot d\phi$

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

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

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

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

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

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

Zeeman Effect in Hydrogen Atom

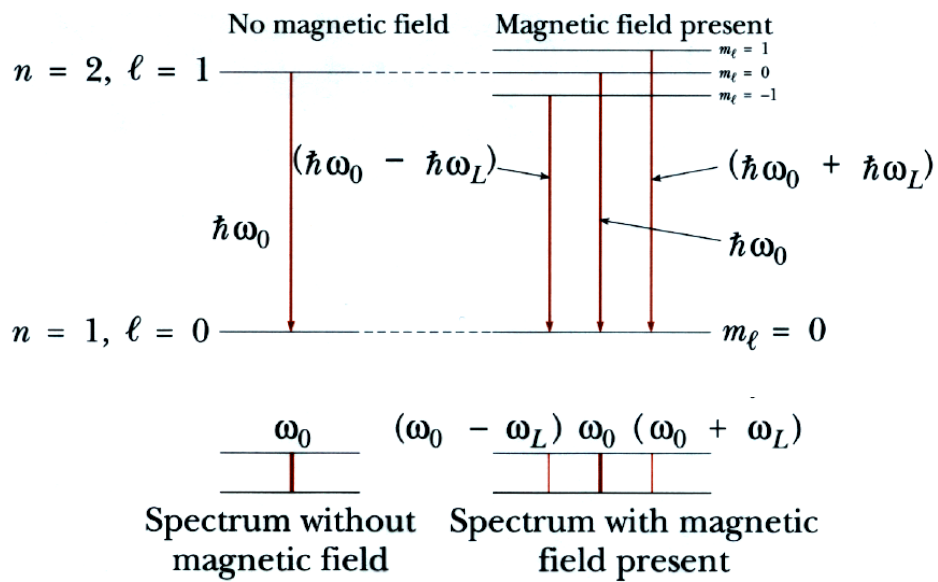
In presence of External B Field, Total energy of H atom changes to

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

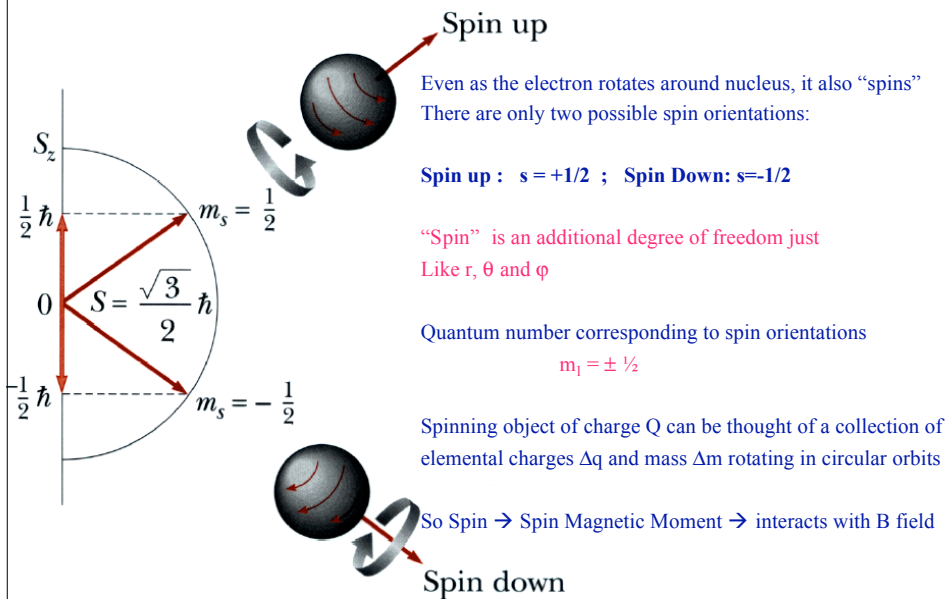
So the Ext. B field can break the E degeneracy "organically" inherent in the H atom. The Energy now depends not just on n but also m_l

Zeeman Effect Due to Presence of External B field

Energy Degeneracy Is Broken

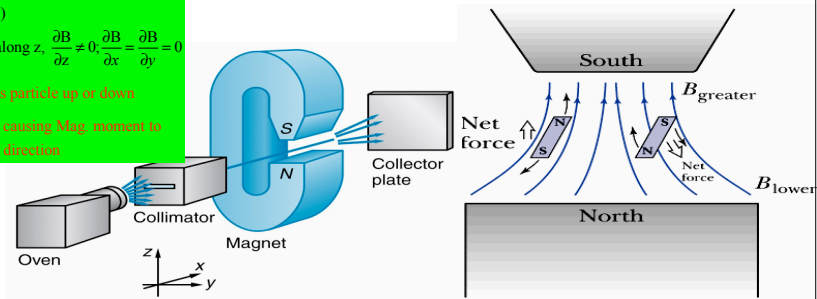


Electron has "Spin": An additional degree of freedom

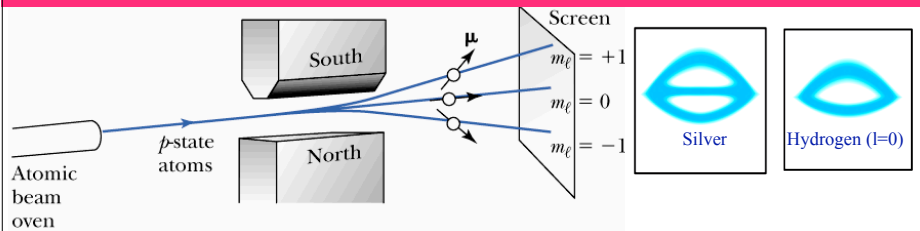


Stern-Gerlach Expt ⇒ An additional degree of freedom: "Spin" for lack of a better name

μ in inhomogeneous B field, experiences force F
 $\vec{F} = -\nabla U_{\mu} = -\nabla(-\vec{\mu} \cdot \vec{B})$
 When gradient only along z, $\frac{\partial B}{\partial z} \neq 0$, $\frac{\partial B}{\partial x} = \frac{\partial B}{\partial y} = 0$
 $F_z = -\mu_z \left(\frac{\partial B}{\partial z}\right)$ moves particle up or down
 In addition to torque causing M_{net} , 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

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

Imagine (semi-classically, *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 $\vec{\mu}_s$

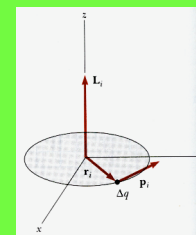
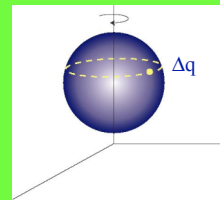
$$\vec{\mu}_s = \left(\frac{q}{2m_e}\right) \sum_i \vec{\mu}_{s_i} = g \left(\frac{q}{2m_e}\right) \vec{S}$$

In a Magnetic Field \vec{B} ⇒ magnetic energy due to spin $U_s = \vec{\mu}_s \cdot \vec{B}$

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

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

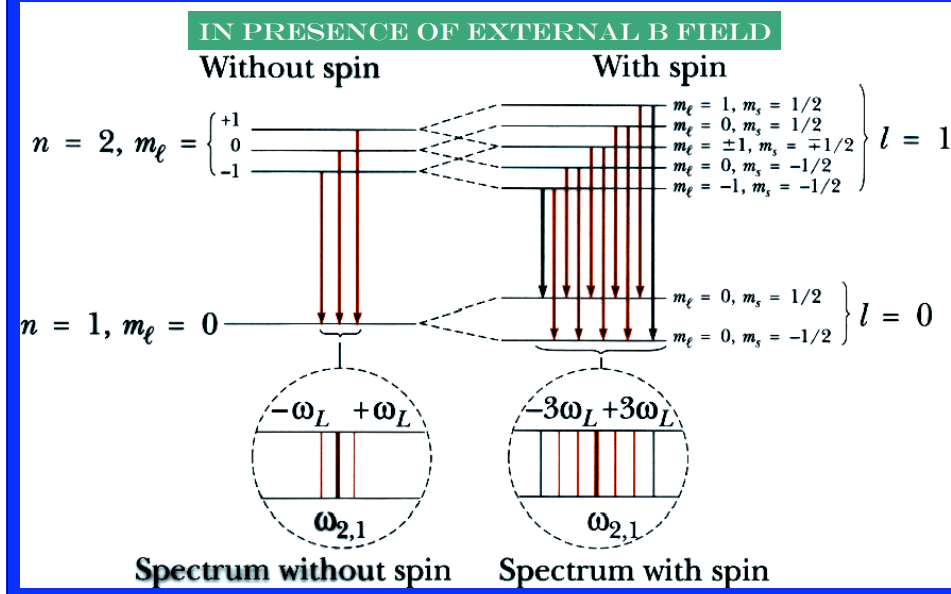
Notice that the net dipole moment vector $\vec{\mu}$ is not || to \vec{J}



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

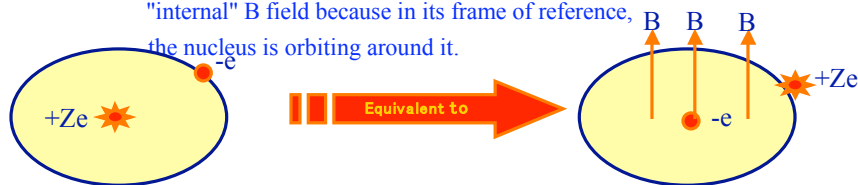
Doubling of Energy Levels Due to Spin Quantum Number

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

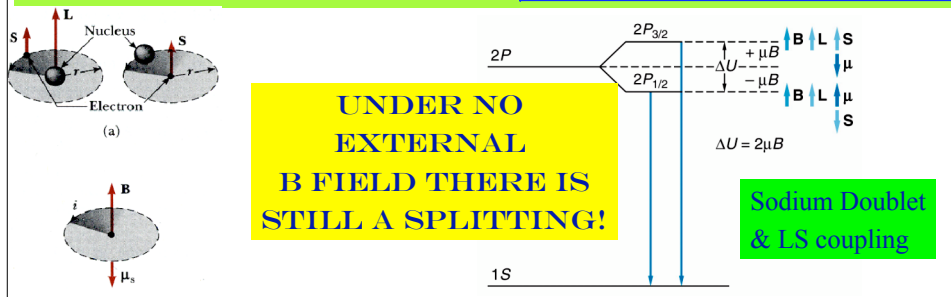
Electron revolving around Nucleus finds itself in a "internal" B field because in its frame of reference, the nucleus is orbiting around it.



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

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

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



Vector Model For Total Angular Momentum \mathbf{J}

Coupling of Orbital & Spin magnetic moments \Rightarrow

Neither Orbital nor Spin angular Momentum are conserved separately!

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

Rules for Total Angular Momentum Quantization :

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

$$J_z = m_j \hbar \quad \text{with } m_j = j, j-1, j-2, \dots, -j$$

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

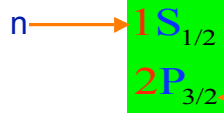
$$j = 3/2 \Rightarrow m_j = -3/2, -1/2, 1/2, 3/2$$

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

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

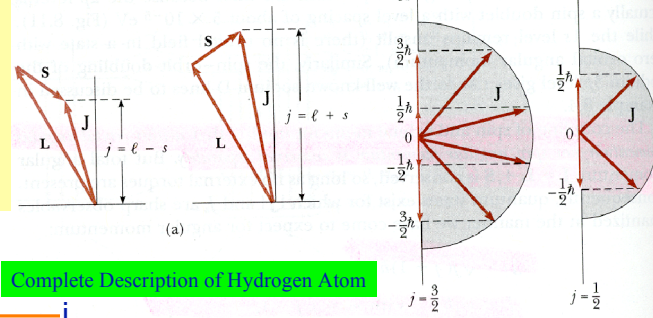
\Rightarrow Even # of orientations

Spectrographic Notation: Final Label



Complete Description of Hydrogen Atom

j



Complete Description of Hydrogen Atom

Full description of the Hydrogen atom:

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

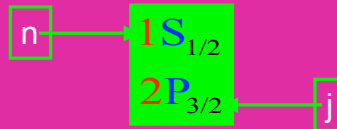
\Downarrow

LS Coupling

\Downarrow

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

corresponding to 4 D.O.F.



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 $\psi(r,\theta,\phi)=R(r)\cdot\Theta(\theta)\cdot\Phi(\phi) \equiv \{n,l,j,m_j\}$

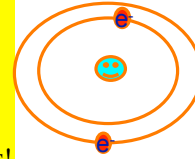
In n-electron atom, to simplify, ignore electron-electron interactions
complete wavefunction, in "independent"particle approx" :

$$\psi(1,2,3,...n)=\psi(1)\cdot\psi(2)\cdot\psi(3)...\psi(n) \quad ???$$

Complication → Electrons are identical particles, labeling meaningless!

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

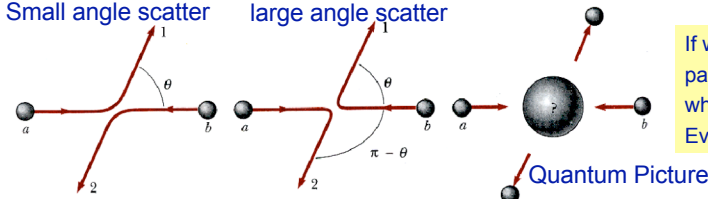
Answer: No two electrons in an atom can have SAME set of quantum #s
(if not, all electrons would occupy 1s state (least energy)... no structure!!)



Example of Indistinguishability: electron-electron scattering

Small angle scatter

large angle scatter



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:

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

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

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 $\Rightarrow \psi(r_1, r_2) = \pm \psi(r_2, r_1)$

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

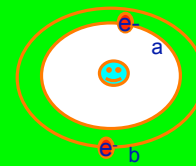
Then the net wavefunction $\psi_{net}(r_1, r_2) = \psi_a(r_1)\psi_b(r_2)$ satisfies

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

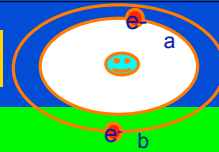
$$H_2\psi_a(r_1)\psi_b(r_2) = E_b\psi_a(r_1)\psi_b(r_2)$$

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

$$\text{Total Helium Energy } E = E_a + E_b = \text{sum of Hydrogen atom like E}$$



Helium Atom: Two electrons around a Nucleus



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

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 $\Rightarrow a=b$ & $\Psi_{ab}(r_1, r_2) = \Psi_{ba}(r_1, r_2) = 0$. **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)

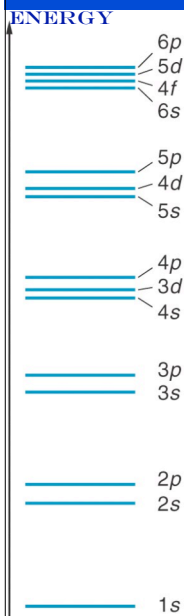
Electrons in a SHELL: have same n , are at similar $\langle r \rangle$ from nucleus, have similar energies

Electrons 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 $n \Rightarrow l = 0, 1, 2, 3, \dots, (n-1)$,

$$\text{for any } l \Rightarrow m_l = 0, \pm 1, \pm 2, \dots \Rightarrow (2l+1), m_s = \pm \frac{1}{2}$$

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

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

4. The "K" Shell ($n=1$) holds 2 electrons, "L" Shell ($n=2$) holds 8 electrons,

M shell ($n=3$) holds 18 electrons, ...

5. Shell is closed when fully occupied

6. Sub-Shell closed when

(a) $\sum L_x = 0, \sum S_x = 0 \Rightarrow$ Effective charge distribution = symmetric

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

(c) Because $\sum L_x = 0 \Rightarrow$ 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

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

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