4E : The Quantum Universe

Lecture 30, May 25
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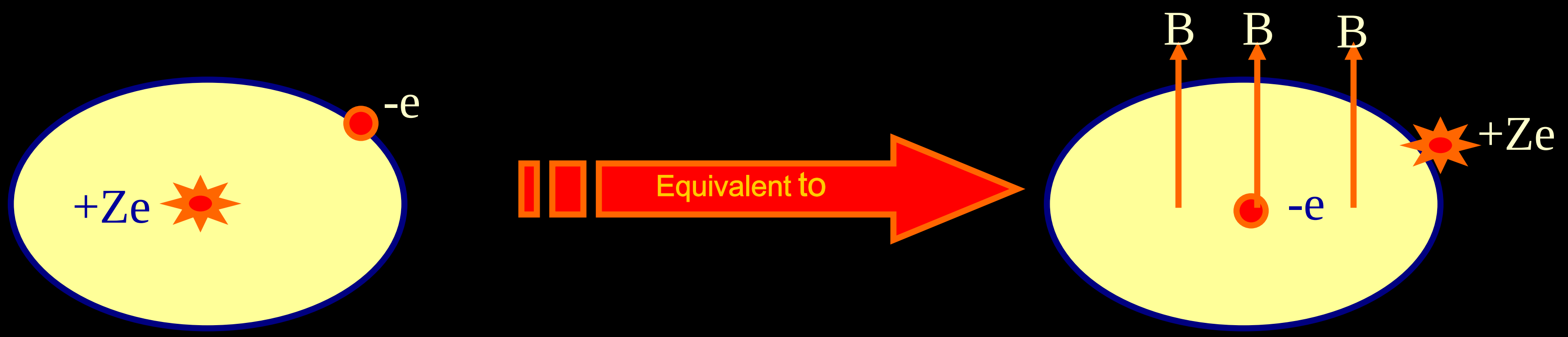
Spin-Orbit Interaction: L and S Momenta are Linked Magnetically



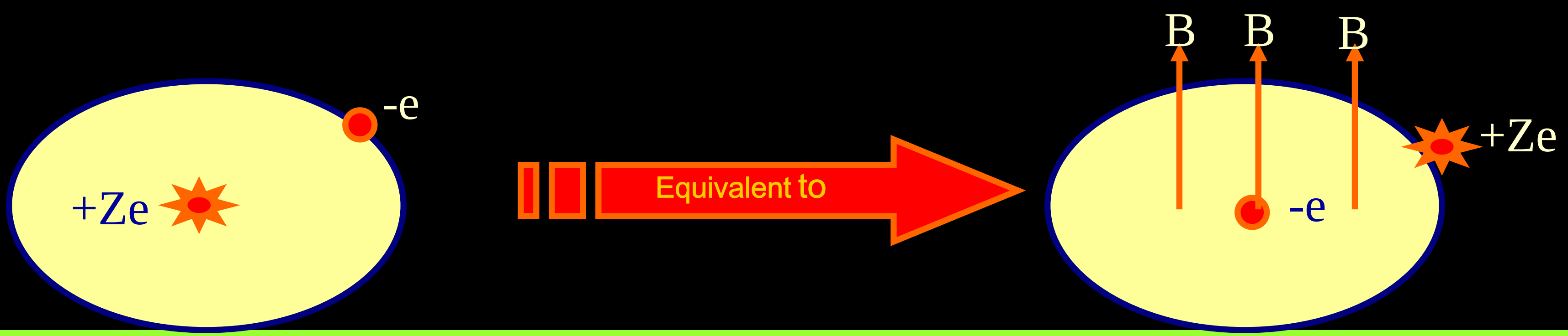
Electron revolving around Nucleus finds itself in a "internal" B field because in its frame of reference, the nucleus is orbiting around it

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 $\vec{S}$

Spin-Orbit Interaction: Angular Momenta are Linked Magnetically



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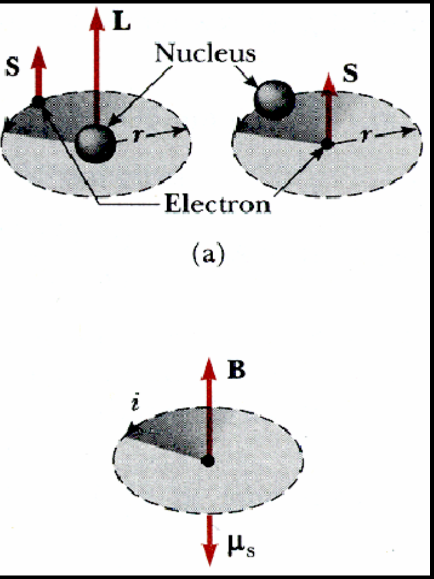
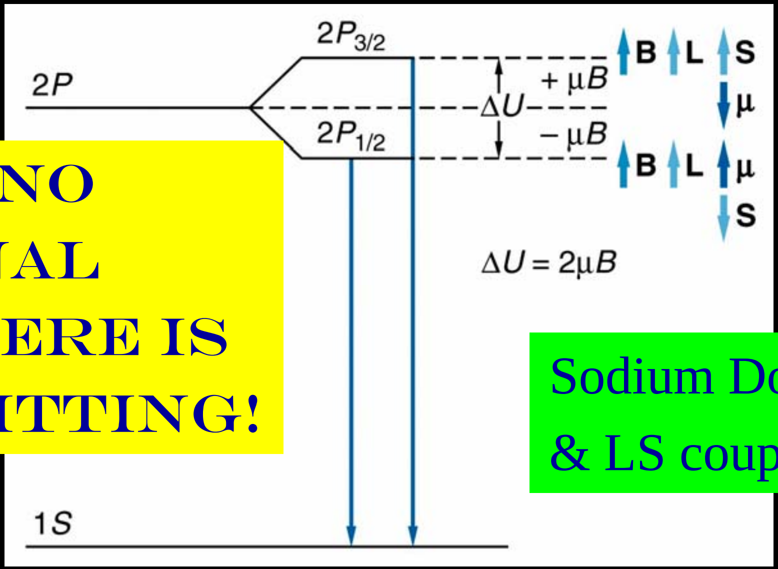
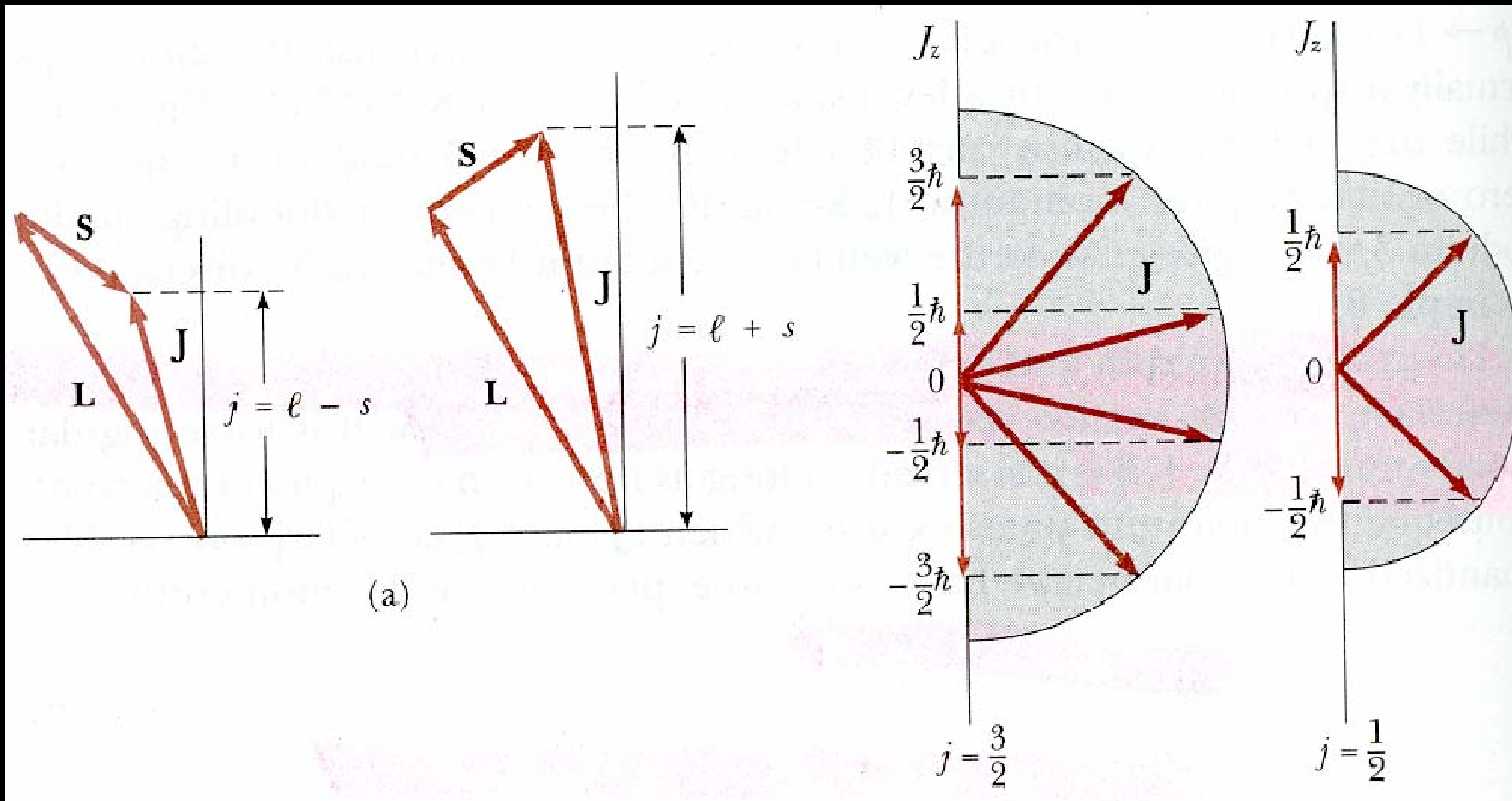


UNDER NO EXTERNAL B FIELD THERE IS STILL A SPLITTING!



Sodium Doublet & LS coupling

*Vector Model For Total Angular Momentum **J***



n → $2P_{3/2}$ ← j

Vector Model For Total Angular Momentum J

Coupling of Orbital & Spin magnetic moments ⇒

Neither Orbital nor Spin angular Momentum are conserved seperately!

$\vec{J} = \vec{L} + \vec{S}$ 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 $(l = 1, s = \dfrac{1}{2})$

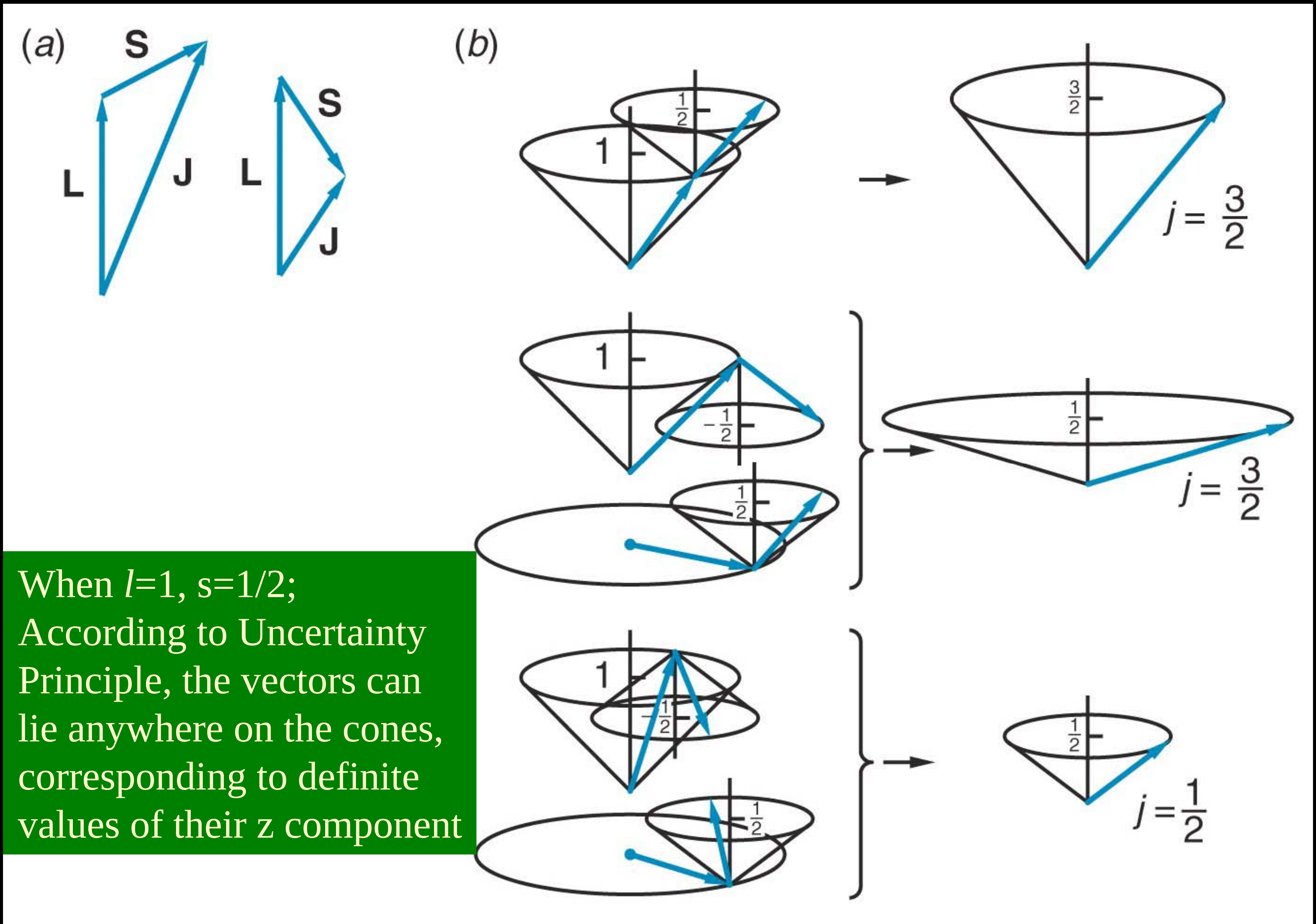
$j = 3/2 \Rightarrow m_j = -3/2, -1/2, 1/2, 3/2$

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

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

⇒ Even # of orientations

Addition of Orbital and Spin Angular Momenta



When *l*=1, s=1/2;
According to Uncertainty Principle, the vectors can lie anywhere on the cones, corresponding to definite values of their z component

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.

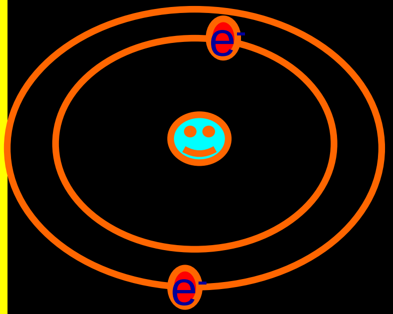
How to describe multi-electrons atoms like He, Li etc?

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



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

complete wavefunction, in "independent"particle approx" :

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

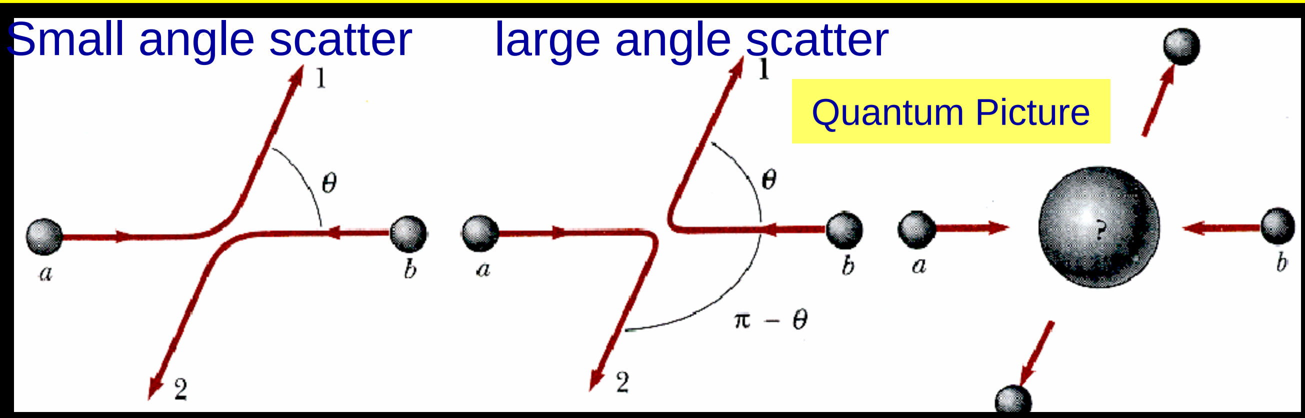
Complication $\rightarrow$ Electrons are identical particles, labeling meaningless!

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



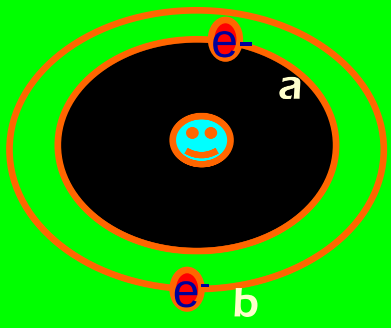
If we cant follow electron path, don't know between which of the two scattering events actually happened

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:

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



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

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

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

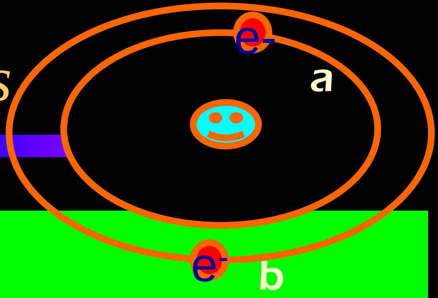
$$H_1\psi_a(r_1).\psi_b(r_2) = E_a\psi_a(r_1).\psi_b(r_2)$$

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

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 ⇒ 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 ⇒ 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

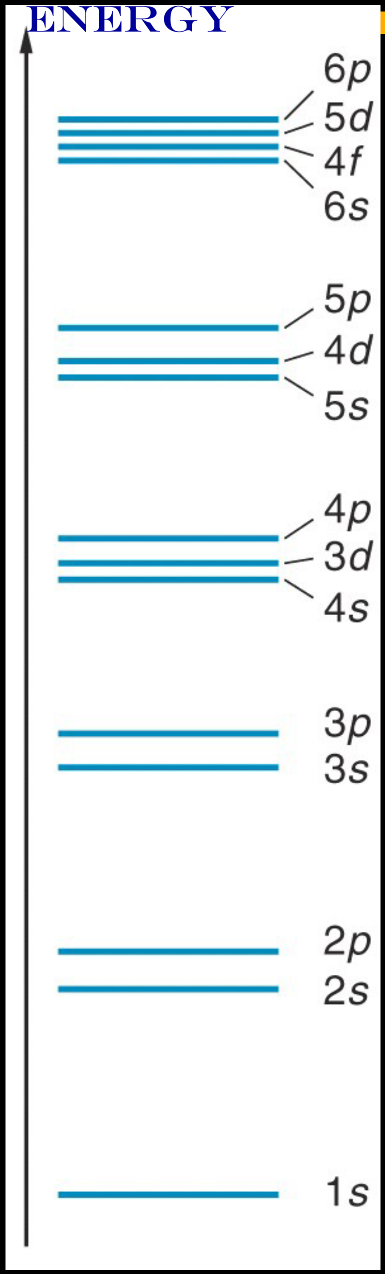
(Effective field: "Seen" Nuclear charge (+Ze) reduced by partial screening due to other electrons "buzzing" closer (in r) to Nucleus)

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 $l \Rightarrow m_l = 0, \pm 1, \pm 2, .. \Rightarrow (2l+1), m_s = \pm\frac{1}{2}$

   $\Rightarrow$ 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 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 configuratio
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	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p^6$