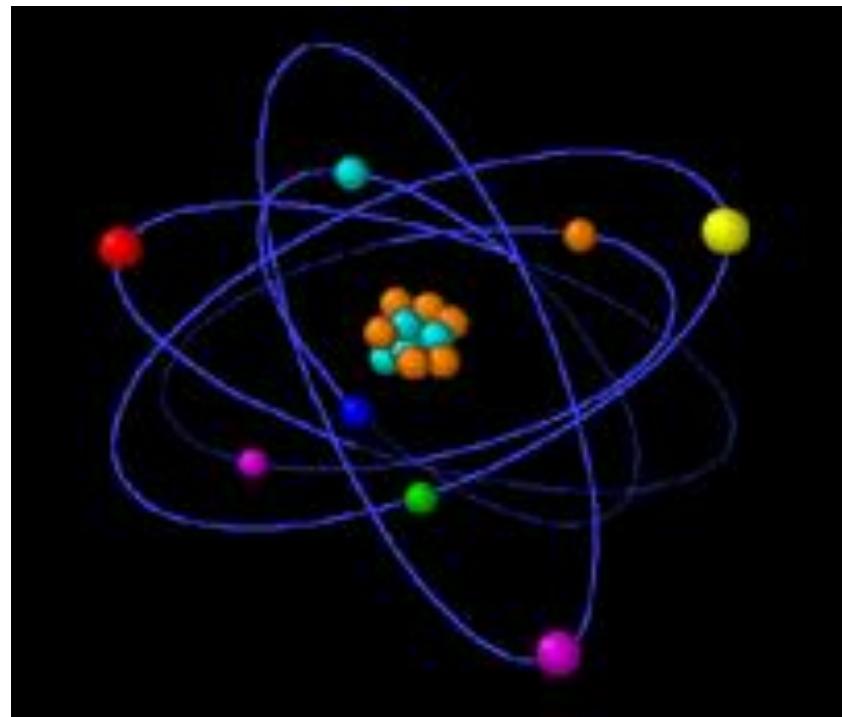


(Take home messages from last class)

## Multi-Electronic Atoms



More than 1e: Can not be solved exactly!  
(Assume same symmetry as H-atom)

# He-atom (2e): 3-particle system!

Kinetic Energy  
Of Electron 1      Nucleus-Electron 1  
Attraction      Electron-Electron  
Repulsion  
 $\hat{H} \equiv \frac{\hat{\mathbf{p}}_1^2}{2m_e} + \frac{\hat{\mathbf{p}}_2^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\hat{r}_1} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\hat{r}_2} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}$   
 Kinetic Energy  
Of Electron 2      Nucleus-Electron 2  
Attraction

$$\hat{H}\Psi(\vec{r}_1, \vec{r}_2) \equiv \left[ \left( -\nabla_{r_1}^2 - \frac{Z}{r_1} \right) + \left( -\nabla_{r_2}^2 - \frac{Z}{r_2} \right) + \frac{1}{r_{12}} \right] \Psi(\vec{r}_1, \vec{r}_2)$$

$$\hat{H}_{He}^{electronic} = \hat{H}_1(\vec{r}_1) + \hat{H}_2(\vec{r}_2) + \frac{1}{r_{12}}$$

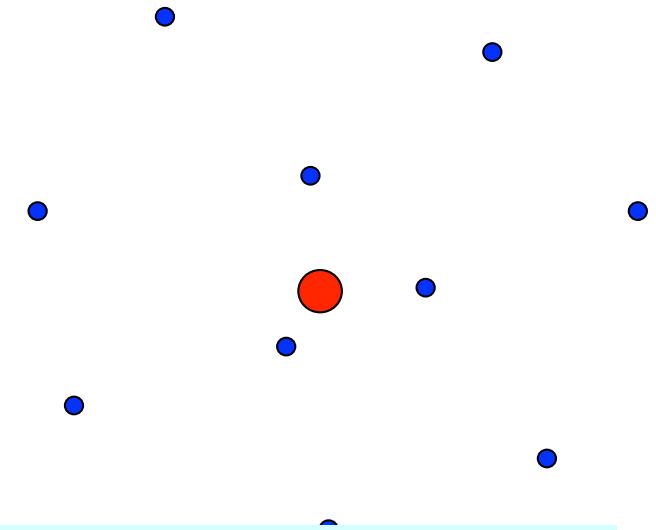
$$\Rightarrow \hat{H}_{He}\Psi(\vec{r}_1, \vec{r}_2) = \hat{H}_1(\vec{r}_1)\Psi(\vec{r}_1, \vec{r}_2) + \hat{H}_2(\vec{r}_2)\Psi(\vec{r}_1, \vec{r}_2) + \boxed{\frac{1}{r_{12}}\Psi(\vec{r}_1, \vec{r}_2)}$$

In atomic units (for convenience) constants  $m_e, e', 4\pi\epsilon_0, h/2\pi \rightarrow X$

# Multi-electron atoms

Assume nucleus to be STATIC

$$\hat{H}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N) \equiv -\sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} + \sum_{i < j} \frac{1}{r_{ij}}$$



$$\hat{H}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2, \dots, r_N, \theta_N, \phi_N) \equiv \sum_{i=1}^N \hat{H}_i(r_i, \theta_i, \phi_i) + \sum_{i < j} \frac{1}{r_{ij}}$$

$\hat{H}_i \rightarrow$  1 electron hydrogenic Hamiltonian for the i-th electron

$$\frac{1}{r_{ij}} \neq f\left(\frac{1}{r_i}\right) + g\left(\frac{1}{r_j}\right) \Rightarrow \text{Not Separable}$$

Inter-electronic interaction terms mess things up!

Hamiltonian is no longer spherically symmetric due to  $\Sigma (1/r_{ij})$  term and therefore, numerical methods must be used to solve the TISE

# Orbital Approximation for N electrons

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N) \approx \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\psi_3(\vec{r}_3)\dots\psi_N(\vec{r}_N)$$

$$H_{Eff}^{(i)} \psi_i(\vec{r}_i) = \varepsilon_i \psi_i(\vec{r}_i)$$
$$\left( -\frac{\hbar^2}{2m_e} \nabla_i^2 + V_i^{eff}(\vec{r}_i) \right) \psi_i(\vec{r}_i) = \varepsilon_i \psi_i(\vec{r}_i)$$

Many e Wave-F(n) is a product of 1e Wave-F(n)s;

Can solve numerically if  $V^{eff}$  is spherically symmetric

1-e wavefunctions are orbitals:  $E_T = \text{sum of } \varepsilon_i$  (Orbital Energies)

## TISE for He atom: 2 electron system

$$\widehat{H}_{He} \Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = E_{He} \Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$
$$\widehat{H}_{He} = \widehat{H}_1^{1e}(r_1, \theta_1, \phi_1) + \widehat{H}_2^{1e}(r_2, \theta_2, \phi_2) + \frac{1}{r_{12}}$$

$\Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) \approx \Psi_1(r_1, \theta_1, \phi_1)\Psi_2(r_2, \theta_2, \phi_2)$  (product of 1e- $\psi$ s)

# Orbital Approximation (for He)

In order to solve for 1e (orbital) energies : NEGLECT Electron – Electron REPULSION

$$\hat{H}_{He}\Psi = \left[ \boxed{\hat{H}_1^{1e} \Psi_1(r_1, \theta_1, \phi_1)} \right] \Psi_2(r_2, \theta_2, \phi_2) + \Psi_1(r_1, \theta_1, \phi_1) \left[ \boxed{\hat{H}_2^{1e} \Psi_2(r_2, \theta_2, \phi_2)} \right] + \boxed{\frac{1}{r_{12}} \Psi_1(r_1, \theta_1, \phi_1) \Psi_2(r_2, \theta_2, \phi_2)}$$

$$\hat{H}_{He}\Psi = \left[ \boxed{\varepsilon_1^{1e} \Psi_1(r_1, \theta_1, \phi_1)} \right] \Psi_2(r_2, \theta_2, \phi_2) + \Psi_1(r_1, \theta_1, \phi_1) \left[ \boxed{\varepsilon_2^{1e} \Psi_2(r_2, \theta_2, \phi_2)} \right]$$

$$\hat{H}_{He}\Psi = \varepsilon_1^{1e} [\Psi_1(r_1, \theta_1, \phi_1) \Psi_2(r_2, \theta_2, \phi_2)] + \varepsilon_2^{1e} [\Psi_1(r_1, \theta_1, \phi_1) \Psi_2(r_2, \theta_2, \phi_2)]$$

$$\hat{H}_{He}\Psi = (\varepsilon_1^{1e} + \varepsilon_2^{1e}) [\Psi_1(r_1, \theta_1, \phi_1) \Psi_2(r_2, \theta_2, \phi_2)] = E_{He}\Psi \Rightarrow E_{He} = \varepsilon_1^{1e} + \varepsilon_2^{1e}$$

Hydrogenic orbitals → both electrons will be in the 1s orbital!

$$\Psi_{He} \approx \sqrt{\frac{1}{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr_1/a_0} \cdot \sqrt{\frac{1}{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr_2/a_0} \Rightarrow \boxed{\Psi \approx 1s(1)1s(2)}$$

# Effective Nuclear Charge

Let us find out what the ionization energies come out to be:

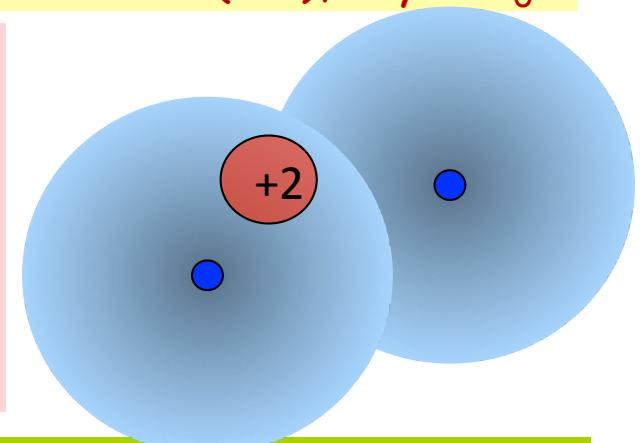
$$E_1(\text{Theory}) = -\frac{Z^2 \mu e^4}{n^2 \hbar^2} = -13.6 \frac{Z^2}{n^2} \text{eV} = 4(-13.6) \text{eV} = E_2 \Leftrightarrow E = E_1 + E_2 = -108.8 \text{eV}$$

Exp. Ionization Energies:  $E_1^{IE} = -24.6 \text{eV}$     $E_2^{IE} = -54.4 \text{eV}$

For He:  $Z=2$ ,  
 $n=1$  (GS), say  $a=a_0$

Electrons must be shielding each other!!!  
Outer electrons feel that the net charge on  
the nucleus is less than what is expected:

Screening of  $Z$   
*"Effective Nuclear Charge"*



Assumption of no inter-electronic interaction is too drastic!  
Electrons stay out of each other's way by undergoing "correlated"  
Motion to ensure electronic repulsion is minimum

$$\boxed{\frac{1}{r_{12}} \Psi_1(r_1) \Psi_2(r_2)} \Rightarrow \text{not small, cannot be neglected!}$$

Need to use other (numerical) approximate methods such as **Variational Method** or **Perturbation Theory** using Central Field Approximation (Not a part of CH107)

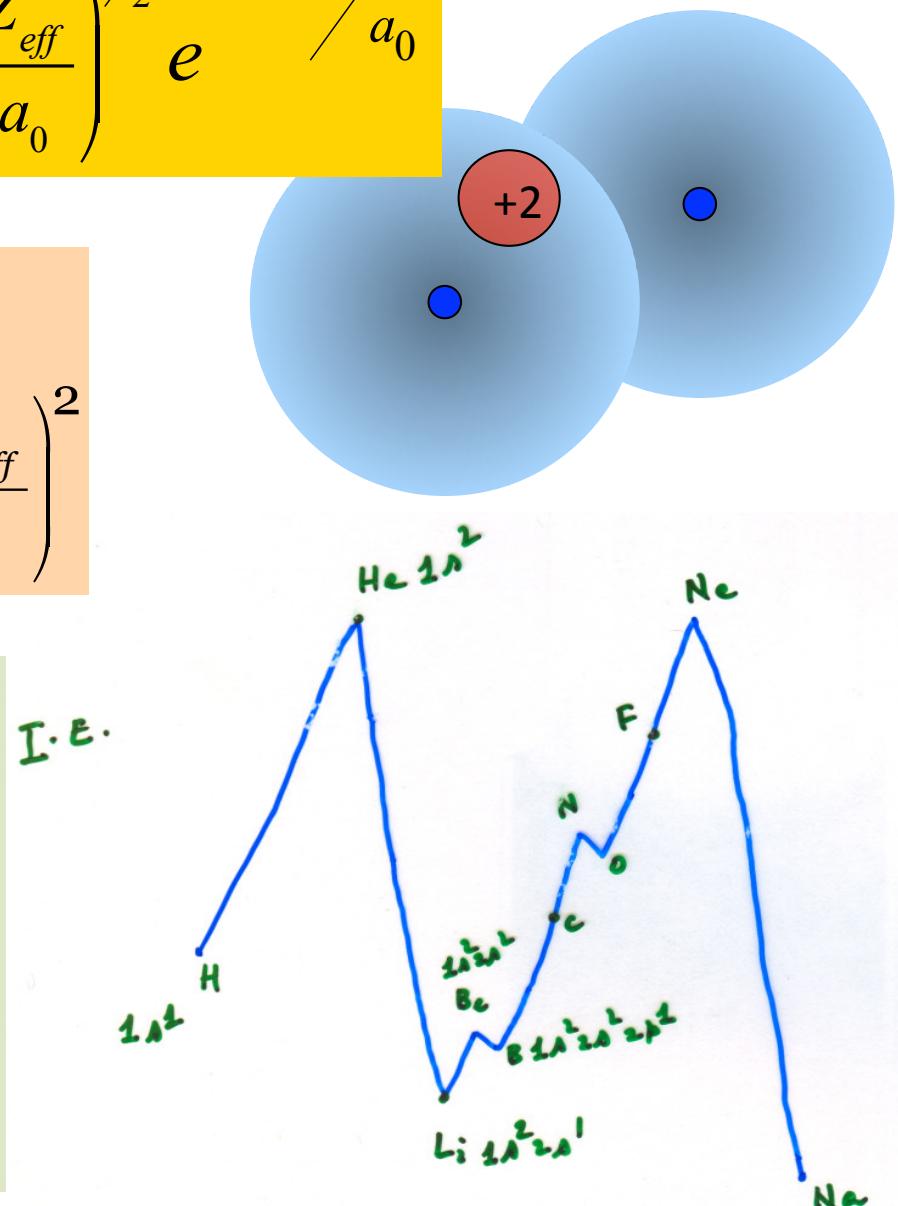
# Electronic Shielding: Effective Nuclear Charge

$$\Psi_{He} \approx 1s(1)1s(2) \approx \left(\frac{Z_{eff}}{a_0}\right)^{3/2} e^{-Z_{eff}r_1/a_0} \cdot \left(\frac{Z_{eff}}{a_0}\right)^{3/2} e^{-Z_{eff}r_2/a_0}$$

$$Z_{eff}^i = Z - \sigma^i, \text{ where } i = s, p, d, f \dots$$

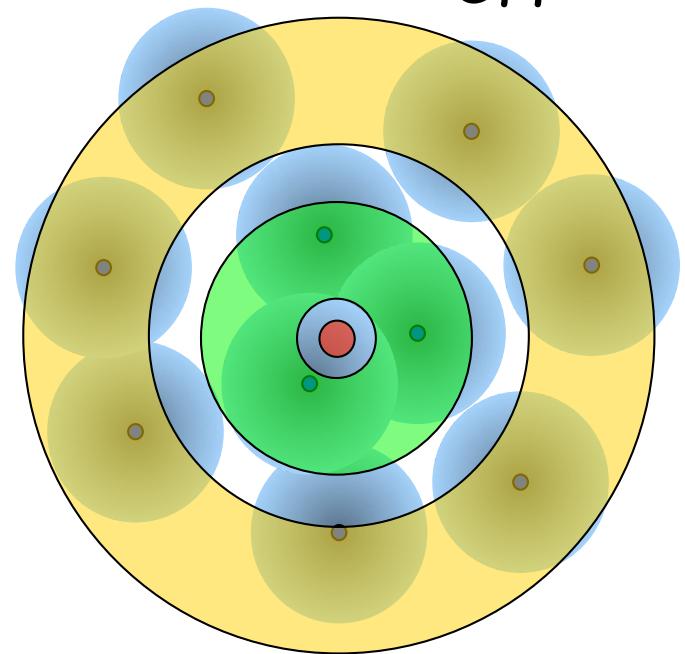
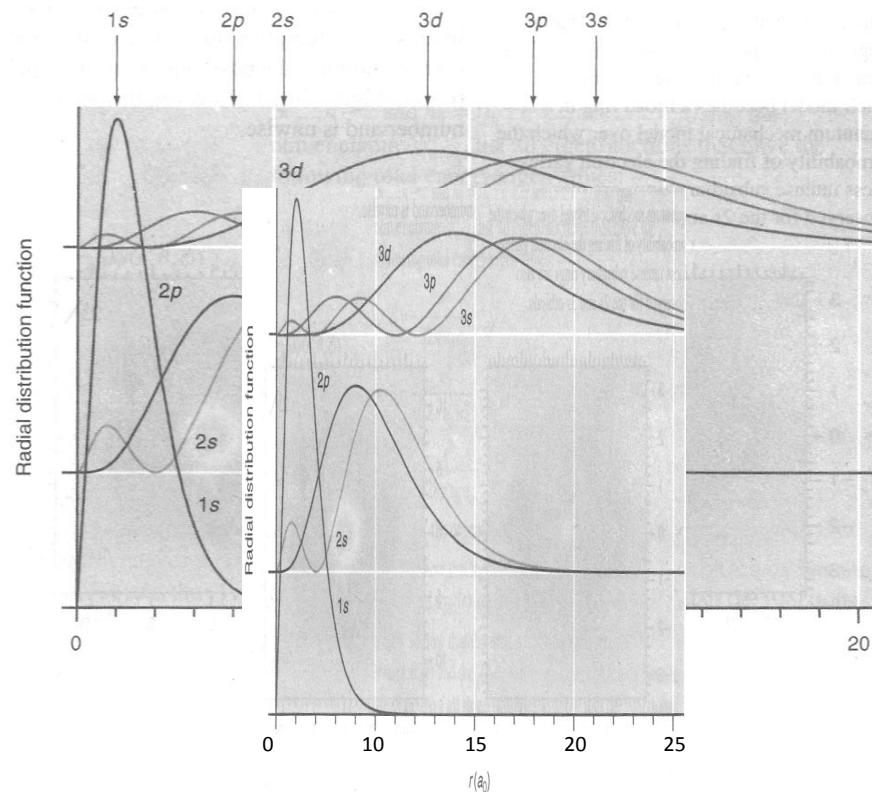
$$\langle IE_z \rangle (\text{avg, per } e') = IE_H (-13.6 \text{ eV}) \times \left(\frac{Z_{eff}^i}{n_i}\right)^2$$

Effective nuclear charge is same for electrons in the same orbital, but greatly varies for electrons of different orbitals (s,p,d,f) and n.  $Z_{eff}$  determines several physical and chemical properties of multi-electron systems



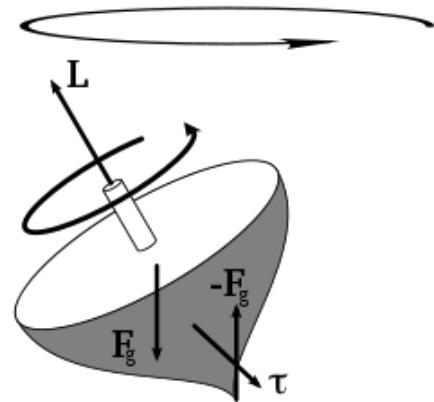
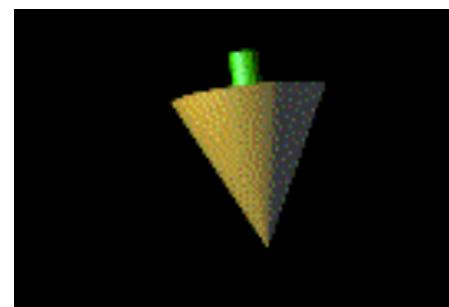
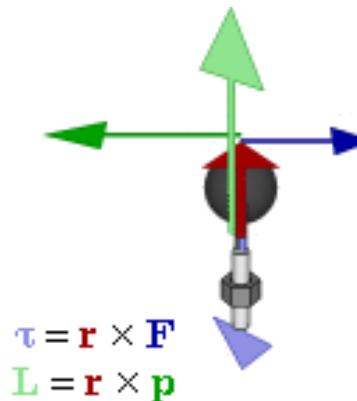
# Many-electrons: Consequences of $Z_{\text{eff}}$

- Why is 2p energy higher than 2S?
- How does Radial distributions change?
- How does  $Z_{\text{eff}}$  affect atomic properties?



Read up on electronic configuration of multi-electronic atoms:  
Hund's Rules & Aufbau Principle  
(most of you know!)

# Quantization of Spatial (Orbital) Angular Momentum of Electrons in the atom



## Orbital Angular Momentum

$L$  = orbital angular momentum

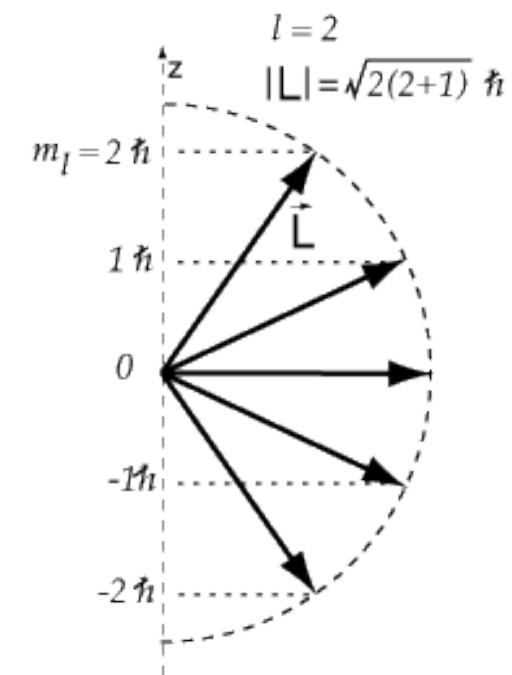
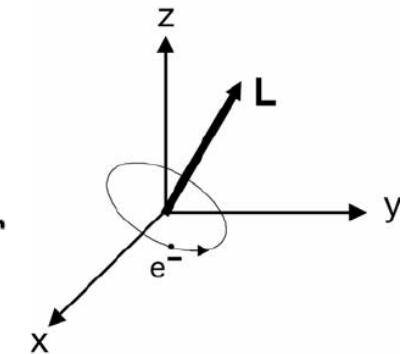
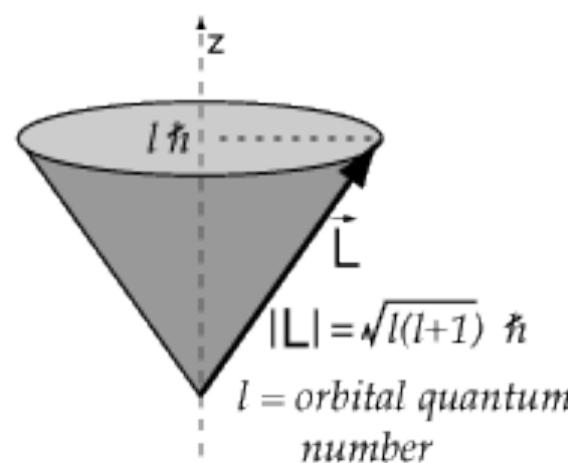
$$|L| = \hbar \sqrt{l(l+1)}$$

$l$  = orbital angular momentum quantum number

$$l \leq n-1$$

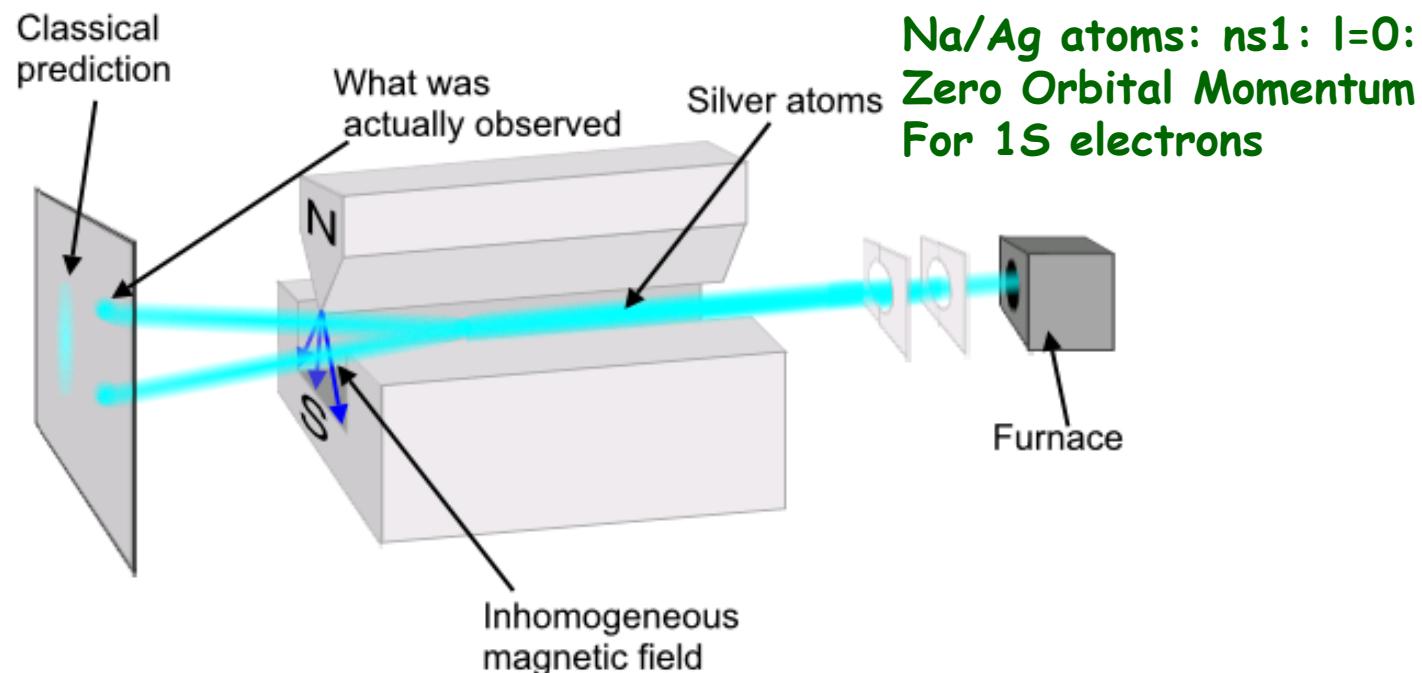
$$L_z = m\hbar$$

$$m = 0, \pm 1, \pm 2, \dots, \pm l$$



Stern-Gerlach Experiment (1922): Passed a beam of silver atoms ( $4d^{10}5s^1$ ) through an inhomogeneous magnetic field and observed that they split into two beams of space quantized components.

Uhlenbeck and Goudsmit (1925) showed that these were two angular momentum states - the electron has intrinsic angular momentum - "SPIN" angular momentum



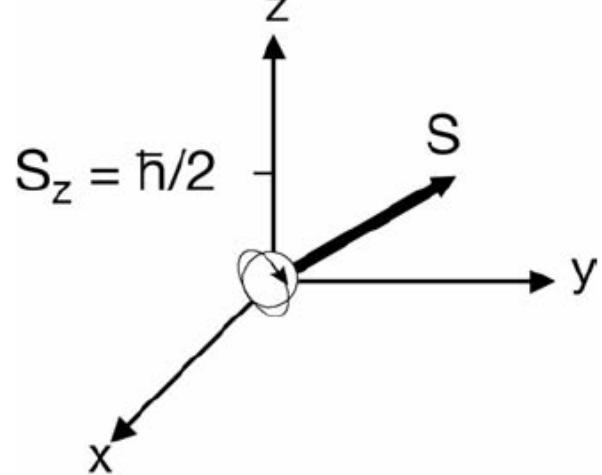
**Na/Ag atoms: ns1: l=0:  
Zero Orbital Momentum  
For 1S electrons**



If electrons are classical, "spinning" particles, then distribution of their spin angular momentum vectors is taken to be truly random and each particle would be deflected up or down by a different amount, producing an even distribution. But electrons are deflected either up or down by a specific amount.

# Intrinsic angular momentum or "Spin" of an electron is quantized

This can only mean that spin angular momentum is quantized!!!



## Spin Angular Momentum

$S \equiv$  spin angular momentum

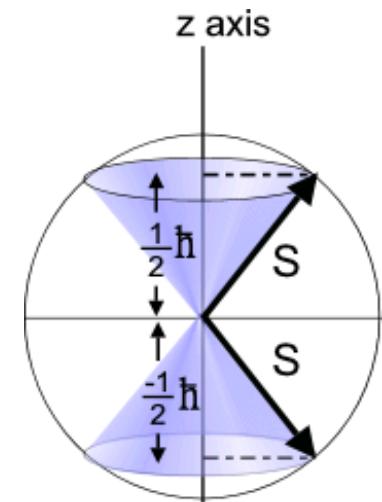
$$|S| = \hbar \sqrt{s(s+1)} = \hbar \sqrt{3}/2$$

$s$  = spin angular momentum quantum number

$$s = 1/2$$

$$S_z = m_s \hbar$$

$$m_s = \pm 1/2$$



Define spin angular momentum operators analogous to orbital angular momentum

Electrons are spin-1/2 particles. Only two possible spin angular momentum, referred to as "spin-up" (or  $\alpha$ ) and "spin-down" (or  $\beta$ ).

The exact value in the z direction is  $m_s = +\hbar/2$  or  $-\hbar/2$ . If this value arises as a result of the rotating particles, then they would have to be spinning impossibly fast

Spin  $S(\omega)$ :  $\omega$  is unknown (internal) coordinate (NON-CLASSICAL)

# Implication of "Spin" on Hydrogen 1-e wavefunctions: Spin Orbitals

Introduce a "spin" component to each of the 1e WFs along with spatial components. This doubles the degeneracy of each level in hydrogenic atoms.

**1e WFs with the inclusion of spin are now called SPIN ORBITALS.**

Total electronic wavefunction has both SPATIAL and SPIN parts.  
Each part is normalized so the total wavefunction is normalized

$$\Psi(r, \theta, \phi, \sigma) = \psi(r, \theta, \phi) \alpha(\sigma) \quad \text{or} \quad \psi(r, \theta, \phi) \beta(\sigma)$$

e.g. for H atom the ground state total wavefunctions (in atomic units) are

$$\Psi_{100\frac{1}{2}} = \left( \frac{Z^3}{\pi} \right)^{1/2} e^{-Zr} \alpha \quad \Psi_{100-\frac{1}{2}} = \left( \frac{Z^3}{\pi} \right)^{1/2} e^{-Zr} \beta$$

which are orthogonal and normalized. Note the quantum numbers are now --

$$n/m m_S$$

**Introduction of spin results in the 4th quantum number  
For each electron: 3 spatial, and one for spin (4<sup>th</sup> coordinate)**

# $2e'$ Spin-orbitals: Indistinguishability

Two-Electron Spin Functions for a pair of electrons in  $1s$  (spatial orbital)?

$$\alpha(1)\alpha(2) \quad \beta(1)\beta(2)$$

$$\alpha(1)\beta(2) \quad \beta(1)\alpha(2)$$

Wavefunctions must reflect the indistinguishability of electrons:  
No known experiments can differentiate between two electrons in the same spatial orbital; No observables of the system can change if coordinates of the two electrons are interchanged.

*Indistinguishability ~ Exchange of coordinates ( $\hat{\mathfrak{R}}$ )*

$$|\Psi(1,2)|^2 = |\Psi(2,1)|^2 \Rightarrow \hat{\mathfrak{R}}[\Psi(1,2)] \equiv \boxed{\Psi(2,1) = \pm \Psi(1,2)}$$

$$\hat{\mathfrak{R}}[\alpha(1)\alpha(2)] = [\alpha(2)\alpha(1)] = +[\alpha(1)\alpha(2)]$$

$$\hat{\mathfrak{R}}[\alpha(1)\beta(2)] = [\alpha(2)\beta(1)] \neq \pm [\alpha(1)\beta(2)]$$

# Acceptable Spin Wavefunctions

$$\alpha(1)\alpha(2) \quad \beta(1)\beta(2)$$

$$\alpha(1)\beta(2) \otimes \quad \beta(1)\alpha(2) \otimes$$

Both  $\alpha(1)\beta(2)$  and  $\alpha(2)\beta(1)$  distinguishes between electrons -  
CAN NOT BE ACCEPTABLE Spin functions

What about  $\alpha(1)\beta(2) \pm \beta(1)\alpha(2)$ ?

$$\Re[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = [\alpha(2)\beta(1) + \beta(2)\alpha(1)] \equiv [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\Re[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = [\alpha(2)\beta(1) - \beta(2)\alpha(1)] \equiv -[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\left\{ \begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \end{array} \right\} \text{symmetric - even } f(n)$$

$$\alpha(1)\beta(2) - \beta(1)\alpha(2) \text{ anti-symmetric - odd } f(n)$$

# 6<sup>th</sup> Postulate in Quantum Mechanics

(Pauli's) Exclusion Principle:  
Independently derived by Dirac and Heisenberg

Complete wavefunction (spatial and spin) of system of identical fermions (electrons) must be anti-symmetric with respect to interchange of the coordinates (spatial and spin) of any two particles.

**Postulate 6:** Complete wavefunctions describing a Many-electron system must be antisymmetric under the exchange of coordinates of any two electrons.

# He-atom Wavefunctions for $1S^2$

For He atom ground state (both electron is  $1s$ ):  **$1s(1).1s(2)$**

Space part is SYMMETRIC:

$$\Re[1s(1).1s(2)] = [1s(2).1s(1)] = +[1s(1)1s(2)]$$

How to choose spin part? Must be ANTI-SYMMETRIC function

even\*odd=odd; odd\*even=odd;    even\*even=even; odd\*odd=even

$$\left\{ \begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \\ \alpha(1)\beta(2) - \beta(1)\alpha(2) \end{array} \right\} \text{2e spin functions are:}$$

**symmetric**

**anti - symmetric**

$$[1s(1)\alpha(1)] = \Psi_{100+\frac{1}{2}}^{1e}(r_1, \theta_1, \phi_1, \sigma_1)$$
$$[1s(2)\beta(2)] = \Psi_{100-\frac{1}{2}}^{1e}(r_2, \theta_2, \phi_2, \sigma_2)$$



Total approx.  $\Psi$  of  
He (GS) :**anti-symmetric**  
wrt exchange of the two  
electronic coordinates

$$[1s(1)1s(2)]^* \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

# 2e Wavefunctions as Determinants

Total approx.  $\Psi$  of He (GS)

anti-symmetric wrt exchange  
of two electronic coordinates

$$1s(1)1s(2)^* \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\Psi_{He}^{GS} \approx \frac{1}{\sqrt{2}} [ [1s(1)\alpha(1)] \otimes [1s(2)\beta(2)] - [1s(1)\beta(1)] \otimes [1s(2)\alpha(2)] ]$$

Shows that two electrons in 1s orbitals  $\rightarrow$  OPPOSITE Spins!!!

$$\Psi_{He}^{GS} \approx \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} \Rightarrow \textit{Slater Determinant}$$

Why write the wavefunction as a determinant???  
Exchange of rows and columns - Sign changes! Antisymmetric

# Slater Determinant for Li (3e): $1s^2 2s^1$

$$\Psi_{Li-GS}(1,2,3) \approx \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

What if we put the 3<sup>rd</sup> e of Li in 1s (spatial) orbital?

$$\Psi_{Li-GS}(1,2,3) \approx \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 1s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 1s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 1s(3)\alpha(3) \end{vmatrix}$$

When two columns/rows of determinant are equal,  
Then value of the determinant is....

→ No more than two electrons occupy spatial orbital ( $n, l, m_l$ )

# Generalized Slater Determinant for N-electron systems

$$\psi(1,2,3,\dots,N) \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) & \dots & \varphi_m(1)\beta(1) \\ \varphi_1(2)\alpha(2) & \varphi_1(2)\beta(2) & \dots & \varphi_m(2)\beta(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(N)\alpha(N) & \varphi_1(N)\beta(N) & \dots & \varphi_m(N)\beta(N) \end{vmatrix}$$

$m = n/2$  if  $n = \text{even}$  and  $m = (n+1)/2$  if  $n = \text{odd}$

# What about excited states of He?

In ground state, both electrons in same orbital  $1s(1)1s(2)$  → Symmetric

Excited states: Electrons in different orbitals means space part:  
 $1s(1)2s(2)$  or  $1s(2)2s(1)$ : neither symmetric nor anti-symmetric!

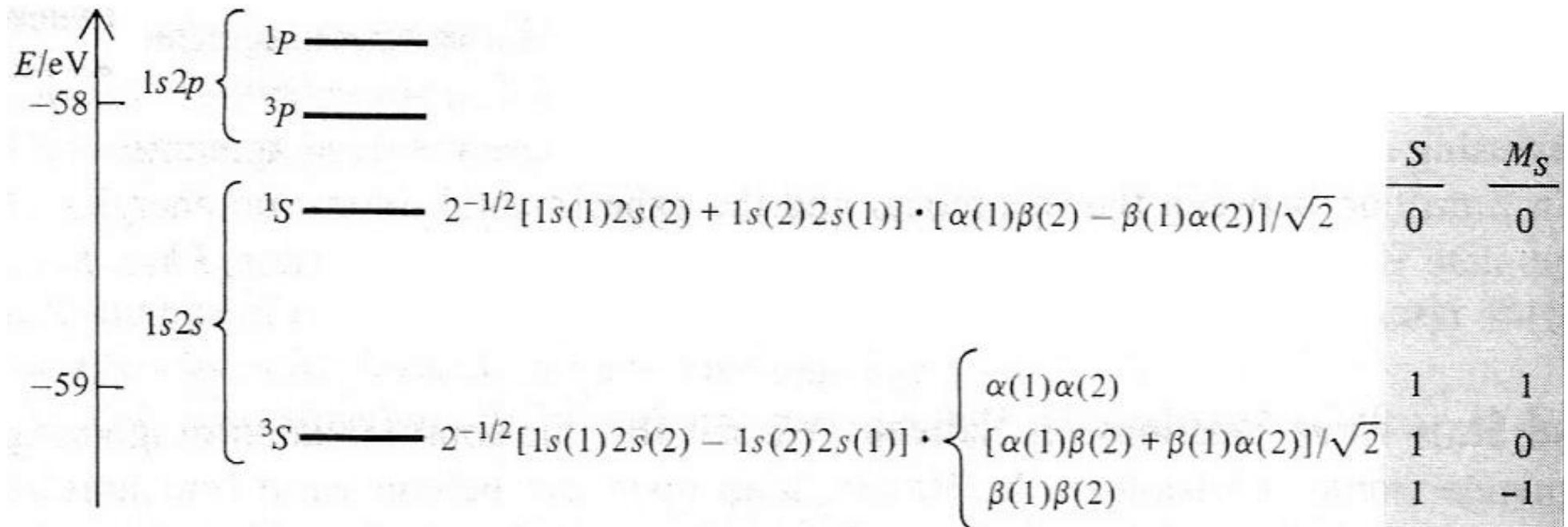
Spatial Part can be:  $1s(1)2s(2) + 1s(2)2s(1)$  (SYMMETRIC)  
or  $1s(1)2s(2) - 1s(2)2s(1)$  (ANTI-SYMMETRIC)

Complete (spatial & spin) wavefunctions for excited states of He  
(Spatial\*Spin part is antisymmetric)

$$[1s(1)2s(2) + 1s(2)2s(1)]^* [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad 1 \text{ state!}$$

$$[1s(1)2s(2) - 1s(2)2s(1)]^* \left\{ \begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \end{array} \right\} \quad 3 \text{ degenerate States!}$$

# Singlet and Triplet excited states of He



$$\Psi_{He-XS}^{3,+1} \approx \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix} \text{ and } \Psi_{He-XS}^{3,-1} \approx \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix}$$

$$\Psi_{He-XS}^{3,0} \approx \frac{1}{2} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix} + \frac{1}{2} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}$$

$\Psi_{He-XS}^{1,0}$  as Slater Determinant?