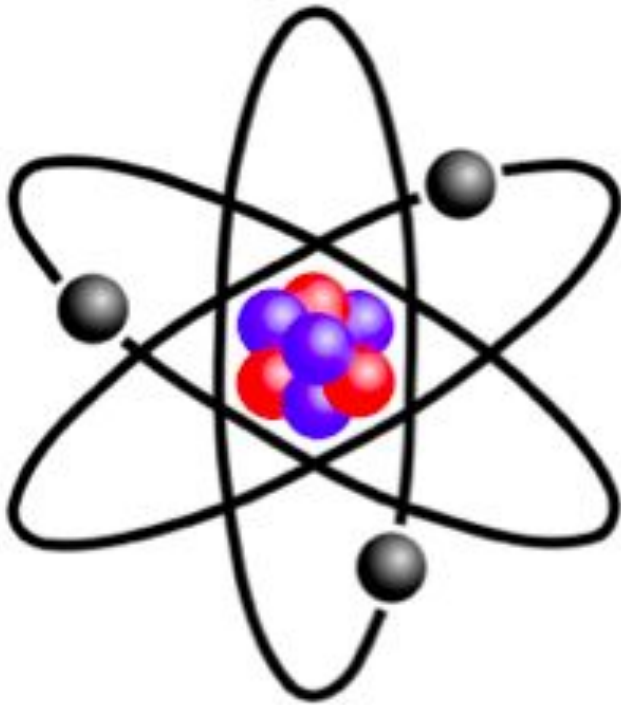


# Lecture 12: Many electron Atoms –Spin and Slater Determinants



$$\psi = \frac{1}{\sqrt{N!}}$$

$$\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1)\dots & \phi_m(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2)\dots & \phi_m(2)\beta(2) \\ \vdots & \ddots & \vdots \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n)\dots & \phi_m(n)\beta(n) \end{vmatrix}$$

# Recapitulation: Many Electron Atoms

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_N} \nabla_N^2}_{\text{Nucleus kinetic energy}} - \frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 - QZ_N e^2 \sum_{i=1}^n \frac{1}{r_i} + Qe^2 \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}$$

$\sum_{i=1}^n H_i$ , 1-electron Hamiltonians

$$\hat{H}_e = \underbrace{-\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 - QZ_N e^2 \sum_{i=1}^n \frac{1}{r_i}}_{\text{Electron kinetic and nuclear attraction}} + Qe^2 \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}$$

$$\hat{H}_e = \sum_{i=1}^n H_i + \underbrace{Qe^2 \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}}_{\text{Inter-electron repulsion}}$$

**Inter-electron repulsion terms:  
CANNOT be ignored**

Hamiltonian is no longer spherically symmetric and the Time-Independent Schrodinger Equation (**TISE**) cannot be solved using analytical techniques

Numerical methods must be used solve the **TISE**

# Recapitulation: Effective Nuclear Charge

$$Z_{\text{eff}} = Z - \sigma$$

$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 - QZ_N e^2 \sum_{i=1}^n \frac{1}{r_i} + Qe^2 \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}$$

$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 - QZ_N^{\text{eff}} e^2 \sum_{i=1}^n \frac{1}{r_i}$$

For Helium atom

$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{QZ_N^{\text{eff}} e^2}{r_1} - \frac{QZ_N^{\text{eff}} e^2}{r_2}$$

$$\psi_e = \left( \frac{1}{\sqrt{\pi}} \left( \frac{Z_{\text{eff}}}{a_o} \right)^{3/2} e^{-Z_{\text{eff}} r / a_o} \right) \cdot \left( \frac{1}{\sqrt{\pi}} \left( \frac{Z_{\text{eff}}}{a_o} \right)^{3/2} e^{-Z_{\text{eff}} r / a_o} \right) = \psi'_{1s}(1) \cdot \psi'_{1s}(2)$$

# Recapitulation: Effective Nuclear Charge

Due to Shielding, the electrons do not see the full nuclear charge  $Z$ , but  $Z_{\text{eff}} = Z - \sigma$  ( $\sigma$  = Shielding Constant)

$$Z_{\text{eff}} = Z - \sigma$$

$$E = E_{\text{Hatom}} \cdot \sum_{i=1}^n \left( \frac{Z - \sigma_i}{n_i} \right)^2$$

$$E_{\text{He}} = E_{\text{Hatom}} \cdot (Z_{\text{eff}}^2 + Z_{\text{eff}}^2)$$

There are methods such as **Perturbation Theory** and **Variational Method** to estimate  $Z_{\text{eff}}$

For Helium atom

$$Z_{\text{eff}} = Z - \sigma = 1.69$$

$$n = 1$$

$$E_{\text{He}} = E_{\text{Hatom}} \cdot \sum_{i=1}^2 \left( \frac{Z_{\text{eff}}}{n_i} \right)^2$$
$$-13.6 \times 5.712 = -77.68 \text{ eV}$$

Compare with  $-78.99$

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

## Orbital Angular Momentum

$L$  = orbital angular momentum

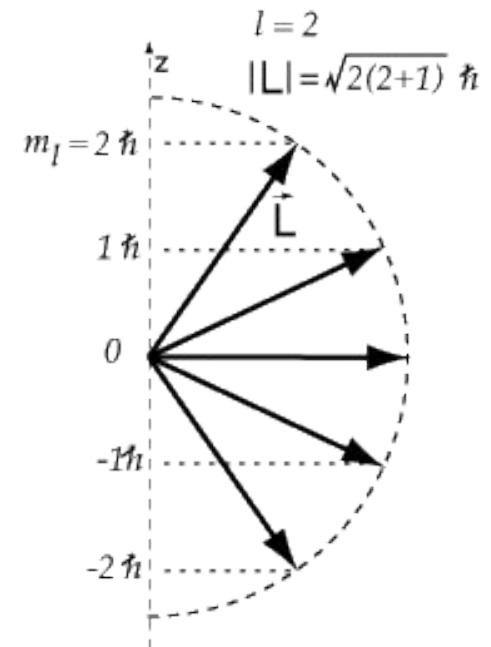
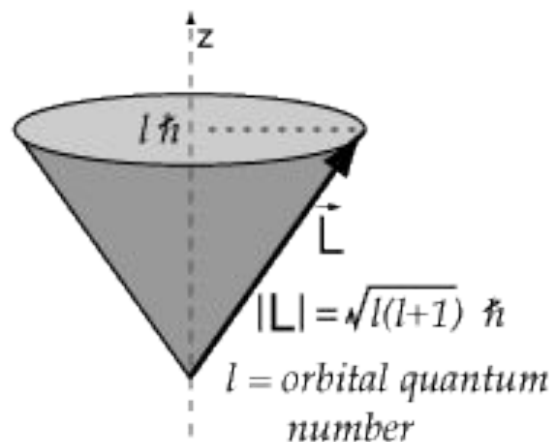
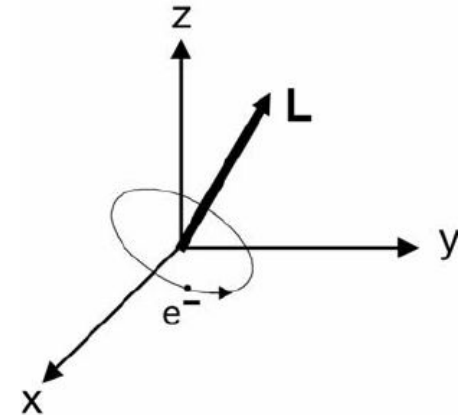
$$|L| = \hbar \sqrt{l(l+1)}$$

$l$  = orbital angular momentum quantum number

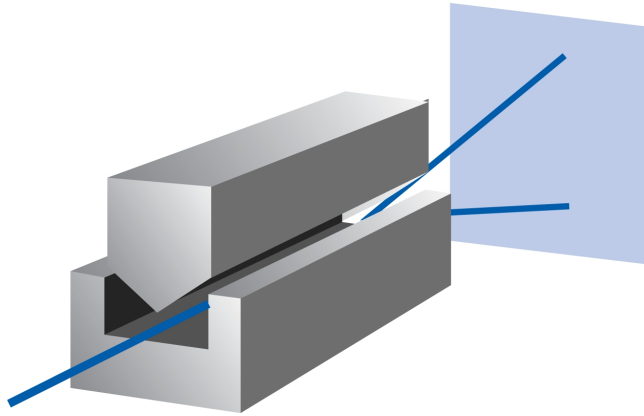
$$l \leq n - 1$$

$$L_z = m\hbar$$

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



# “Spin” of an electron: Later comer to the quantum party



## **Stern-Gerlach Experiment (1922):**

Beam of Ag atoms ( $4d^{10} 5s^1$ ) passed through an inhomogeneous magnetic field: ***TWO*** lines

**Uhlenbeck and Goudsmit (1925):**  
*Two angular momentum states,*  
***Intrinsic to the electron***

**NOT** a result of actual rotation ( $v > c$  !!)

Spin:  $S(\omega)$ ,  $\omega$  is an unknown coordinate

**Dirac:** Relativistic quantum mechanics

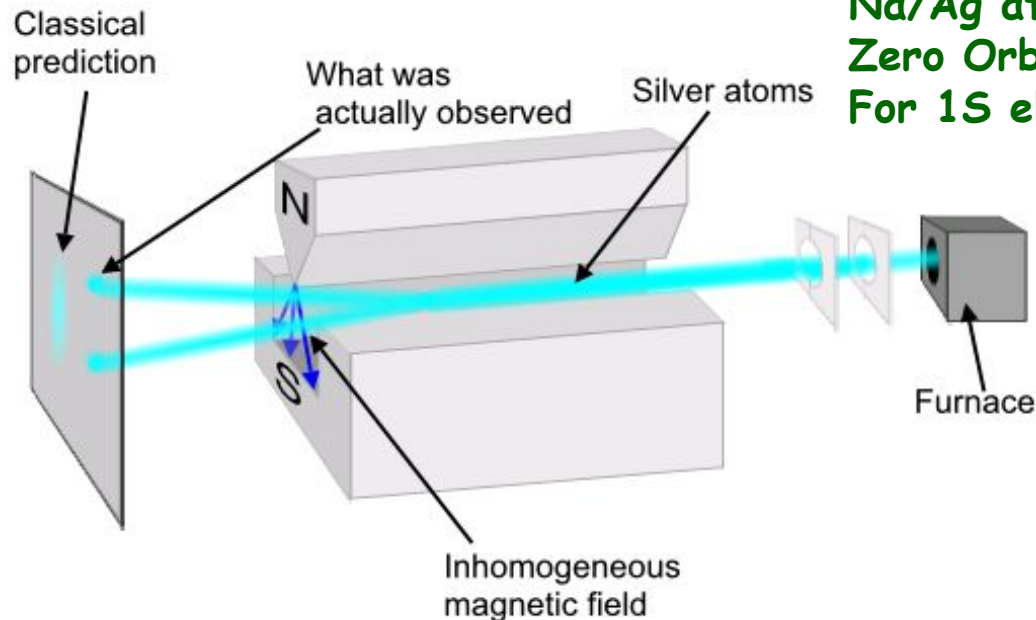


If electrons - classical, "spinning" particles - distribution of their spin angular momentum vectors / magnetic moment in z direction would be random: deflected up or down by a different amount, producing an even distribution.  
**But electrons deflected either up or down by a specific (same) amount!!!**

# Intrinsic Angular Momentum: "Spin"

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

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.



Na/Ag atoms:  $ns^1$ :  $l=0$ :  
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 deflected either up or down by a specific (same) amount!!!



# Spin Angular Momentum : Intrinsic and Quantized

## Spin Angular Momentum “S”

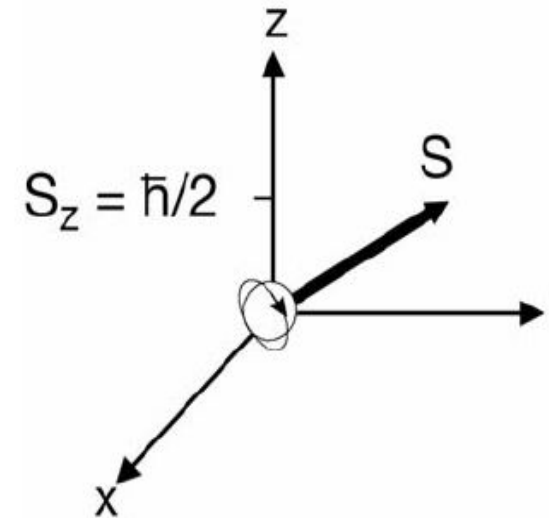
$$|S| = \hbar \sqrt{s(s+1)}$$

$s$  = spin quantum number

$$S_z = m_s \hbar$$

$$m_s = s, s-1, \dots, -s$$

$(2s+1)$  values



For electrons,  $s = 1/2$

$$m_s = \frac{1}{2}, -\frac{1}{2}$$

$$S_z = \frac{1}{2} \hbar, -\frac{1}{2} \hbar$$

“spin-up” (or  $\alpha$ ) and “spin-down” (or  $\beta$ ) two eigenfunctions (spin functions) of the operator, same eigen values but opp sign (S-G observables)

**NOT** a result of actual rotation ( $v > c$  !!)

# Spin

- **Completely quantum mechanical property**
- **No classical analogy**
- **Intrinsic (like charge or mass)**



**Pauli (1924) : “ electron has  
two-valuedness not describable classically  
”**

# Hydrogen Atom Wavefunctions: Redefined

Incorporate “spin” component to each of the 1-electron wavefunctions: **SPIN ORBITALS**

Total wavefunctions = product of spatial and spin parts

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

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

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

Spin o are  $n, l$  e.g. for H atom the ground state total wavefunctions (in atomic units) are

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

**SPIN**  
well a

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

$n/lmm_s$

umbers

tial as

# Hydrogen Atom Wavefunctions: Redefined

**SPIN ORBITAL:** One electron wavefunction containing spatial as well as spin parts

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

# Spin Orbitals and their linear combinations

Two electron system (electron labels: 1 and 2): **four** spin functions

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

1 and 2: **indistinguishable**

**Linear combination**

Wavefunctions must reflect indistinguishability of electrons:  
No known experiments can differentiate between two electrons;  
No **observables** change if co-ords of 2 electrons are interchanged.

Exchange Operator

$$\Psi(1,2) = \pm \Psi(2,1)$$

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

**Symmetric**

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

**Anti-symmetric**

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

The complete wavefunction of a system of identical fermions (e.g. electrons) must be anti-symmetric with respect to interchange of all their coordinates (spatial and spin) of any two particles

$$\Psi(1,2) = -\Psi(2,1)$$

**Pauli's Principle**: Derived using relativistic QM  
independently derived by Dirac and Heisenberg/Pauli

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

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

Space part:  
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

2e spin  
functions are:

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

Total wavefunction of  
He (GS) :anti-symmetric  
wrt exchange of the two  
electronic coordinates

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

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

The complete wavefunction of a system of identical fermions (e.g. electrons) must be anti-symmetric with respect to interchange of all their coordinates (spatial and spin) of any two particles

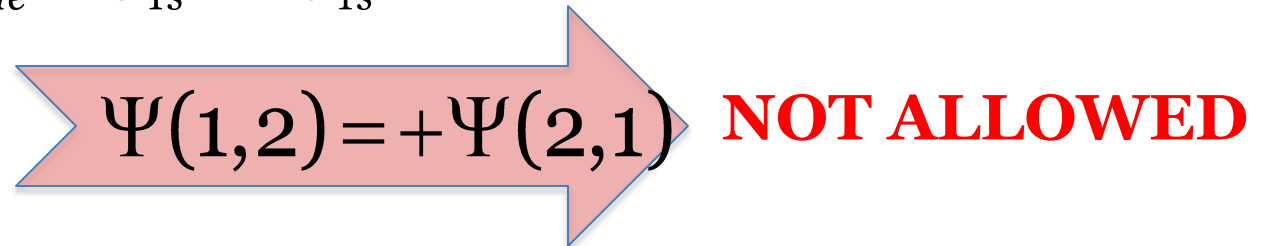
$$\Psi(1,2) = -\Psi(2,1)$$

He atom wavefunction:

$$\psi_{He} = \psi_{1s}(1) \cdot \psi_{1s}(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

What if the two electrons in **1s** orbital had same spin?

$$\psi_{He} = \psi_{1s}(1) \cdot \psi_{1s}(2) \alpha(1)\alpha(2)$$


$$\Psi(1,2) = +\Psi(2,1) \quad \text{NOT ALLOWED}$$

**Pauli exclusion principle**



# He Atom Wavefunction: Writing anti-sym. wavefunctions

$$\begin{aligned}\psi_{He} &= \psi_{1s}(1) \cdot \psi_{1s}(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ &= \frac{1}{\sqrt{2}} [\psi_{1s}(1) \cdot \psi_{1s}(2) \alpha(1) \beta(2) - \psi_{1s}(1) \cdot \psi_{1s}(2) \beta(1) \alpha(2)] \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(1) & \psi_{1s}(2) & \alpha(1) & \beta(2) \\ \psi_{1s}(1) & \psi_{1s}(2) & \beta(1) & \alpha(2) \end{vmatrix} \quad \text{Slater determinant}\end{aligned}$$

- Exchange of two rows/ columns: **Change in sign**  
**Antisymmetric**
- If any two rows/columns are **same**, then the determinant becomes **zero**.  
no two electrons occupy the same spin orbital.  
***Pauli Exclusion Principle***

# Many Electron Atoms: Determinantal Wavefunctions

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1)\dots & \phi_m(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2)\dots & \phi_m(2)\beta(2) \\ \vdots & \ddots & \vdots \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n)\dots & \phi_m(n)\beta(n) \end{vmatrix}$$

**Slater determinant**

If any two rows/columns are **same**, then the determinant becomes **zero**.

⇒ no two electrons occupy the same spin orbital.

***Pauli Exclusion Principle***

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

Spin orbitals change across columns

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

↓ Electrons

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

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

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

**□ No more than two electrons occupy a spatial orbital**

## Helium Atom: Excited States

If the second electron is in the **2s** orbital then it could have the same spin or the opposite spin.

He excited state  **$1s^1.2s^1$**

$$1s(1) \cdot 2s(2)$$

## Helium Atom: Excited States

If the second electron is in the **2s** orbital then it could have the same spin or the opposite spin.

He excited state ***1s<sup>1</sup>.2s<sup>1</sup>***

$$\frac{1}{\sqrt{2}} \left[ 1s(1) \cdot 2s(2) + 1s(2) \cdot 2s(1) \right] \left[ \alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \frac{1}{\sqrt{2}} \quad (S=0; M_s=0)$$

He excited state ***1s<sup>1</sup>.2s<sup>1</sup>***

$$\left. \frac{1}{\sqrt{2}} \left[ 1s(1) \cdot 2s(2) - 1s(2) \cdot 2s(1) \right] \right\}$$

## Helium Atom: Excited States

If the second electron is in the **2s** orbital then it could have the same spin or the opposite spin.

He excited state  **$1s^1.2s^1$**

$$\frac{1}{\sqrt{2}} \left[ 1s(1) \cdot 2s(2) + 1s(2) \cdot 2s(1) \right] \left[ \alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \frac{1}{\sqrt{2}} \quad (S=0; M_s=0)$$

He excited state  **$1s^1.2s^1$**

$$\frac{1}{\sqrt{2}} \left[ 1s(1) \cdot 2s(2) - 1s(2) \cdot 2s(1) \right] \left\{ \begin{array}{ll} \alpha(1)\alpha(2) & (S=1; M_s=1) \\ \left[ \alpha(1)\beta(2) + \beta(1)\alpha(2) \right] \frac{1}{\sqrt{2}} & (S=1; M_s=0) \\ \beta(1)\beta(2) & (S=1; M_s=-1) \end{array} \right.$$

## Helium Atom: Excited States

If the second electron is in the **2s** orbital then it could have the same spin or the opposite spin.

He excited state **1s<sup>1</sup>.2s<sup>1</sup>** (**singlet**)

$$\frac{1}{\sqrt{2}} \left[ 1s(1) \cdot 2s(2) + 1s(2) \cdot 2s(1) \right] \left[ \alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \frac{1}{\sqrt{2}} \quad (S=0; M_s=0)$$

He excited state **1s<sup>1</sup>.2s<sup>1</sup>** (**triplet**)

$$\frac{1}{\sqrt{2}} \left[ 1s(1) \cdot 2s(2) - 1s(2) \cdot 2s(1) \right] \left\{ \begin{array}{ll} \alpha(1)\alpha(2) & (S=1; M_s=1) \\ \left[ \alpha(1)\beta(2) + \beta(1)\alpha(2) \right] \frac{1}{\sqrt{2}} & (S=1; M_s=0) \\ \beta(1)\beta(2) & (S=1; M_s=-1) \end{array} \right.$$

# Helium Atom: Excited States

He excited state  $1s^1.2s^1$  (triplet)

$$\frac{1}{\sqrt{2}} [1s(1) \cdot 2s(2) - 1s(2) \cdot 2s(1)] \left\{ \begin{array}{l} \alpha(1)\alpha(2) \quad (S=1; M_s=1) \\ [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \frac{1}{\sqrt{2}} \quad (S=1; M_s=0) \\ \beta(1)\beta(2) \quad (S=1; M_s=-1) \end{array} \right.$$

$$\Psi^{3,1} = 1/\sqrt{2} \left| \begin{array}{cc} & 2s \\ & 2s \end{array} \right|$$



# Helium Atom: Excited States

He excited state  $1s^1.2s^1$  (triplet)

$$\frac{1}{\sqrt{2}} [1s(1) \cdot 2s(2) - 1s(2) \cdot 2s(1)]$$

$$\alpha(1)\alpha(2)$$

$$(S=1; M_s=1)$$

$$[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \frac{1}{\sqrt{2}} (S=1; M_s=0)$$

$$\beta(1)\beta(2)$$

$$(S=1; M_s=-1)$$

$$\Psi^{3,1} = 1/\sqrt{2} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix} = \Psi^{3,-1}$$

# Helium Atom: Excited States

He excited state  $1s^1.2s^1$  (triplet)

$$\frac{1}{\sqrt{2}} [1s(1) \cdot 2s(2) - 1s(2) \cdot 2s(1)]$$

$$\alpha(1)\alpha(2)$$

$$(S = 1; M_s = 1)$$

$$\left[ \alpha(1)\beta(2) + \beta(1)\alpha(2) \right] \frac{1}{\sqrt{2}} (S = 1; M_s = 0)$$

$$\beta(1)\beta(2)$$

$$(S = 1; M_s = -1)$$

$$\Psi^{3,1} = 1/\sqrt{2} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$$

$$\Psi^{3,-1} = 1/\sqrt{2} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix}$$

# Helium Atom: Excited States

He excited state  $1s^1.2s^1$  (triplet)

$$\frac{1}{\sqrt{2}} [1s(1) \cdot 2s(2) - 1s(2) \cdot 2s(1)]$$

$$\alpha(1)\alpha(2)$$

$$(S=1; M_s=1)$$

$$\left[ \alpha(1)\beta(2) + \beta(1)\alpha(2) \right] \frac{1}{\sqrt{2}}$$

$$(S=1; M_s=0)$$

$$\beta(1)\beta(2)$$

$$(S=1; M_s=-1)$$

$$\Psi^{3,1} = 1/\sqrt{2}$$

$$\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$$

$$\Psi^{3,-1} = 1/\sqrt{2}$$

$$\begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix}$$

# Helium Atom: Excited States

He excited state  $1s^1.2s^1$  (triplet)

$$\left. \frac{1}{\sqrt{2}} [1s(1) \cdot 2s(2) - 1s(2) \cdot 2s(1)] \right\} \begin{cases} \alpha(1)\alpha(2) & (S=1; M_S=1) \\ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] & (S=1; M_S=0) \\ \beta(1)\beta(2) & (S=1; M_S=-1) \end{cases}$$

$$\Psi^{3,1} = \frac{1}{2} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix} \quad \Psi^{3,-1} = \frac{1}{2} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix}$$

$$\Psi^{3,0} = \frac{1}{2} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix} + \frac{1}{2} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}$$

## Helium Atom: Excited States

He excited state  **$1s^1.2s^1$**  (singlet)

$$\frac{1}{\sqrt{2}} \left[ 1s(1) \cdot 2s(2) + 1s(2) \cdot 2s(1) \right] \frac{1}{\sqrt{2}} \left[ \alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \quad (S=0; M_s=0)$$

## Helium Atom: Excited States

He excited state  **$1s^1.2s^1$**  (singlet)

$$\frac{1}{\sqrt{2}} \left[ 1s(1) \cdot 2s(2) + 1s(2) \cdot 2s(1) \right] \frac{1}{\sqrt{2}} \left[ \alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \quad (S=0; M_s=0)$$

$$\Psi^{1,0} = \frac{1}{2} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix} - \frac{1}{2} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}$$

# Helium Atom: Excited States

Spin-orbital wavefunctions  
are represented as  
**Slater determinants**  
or their **sums**

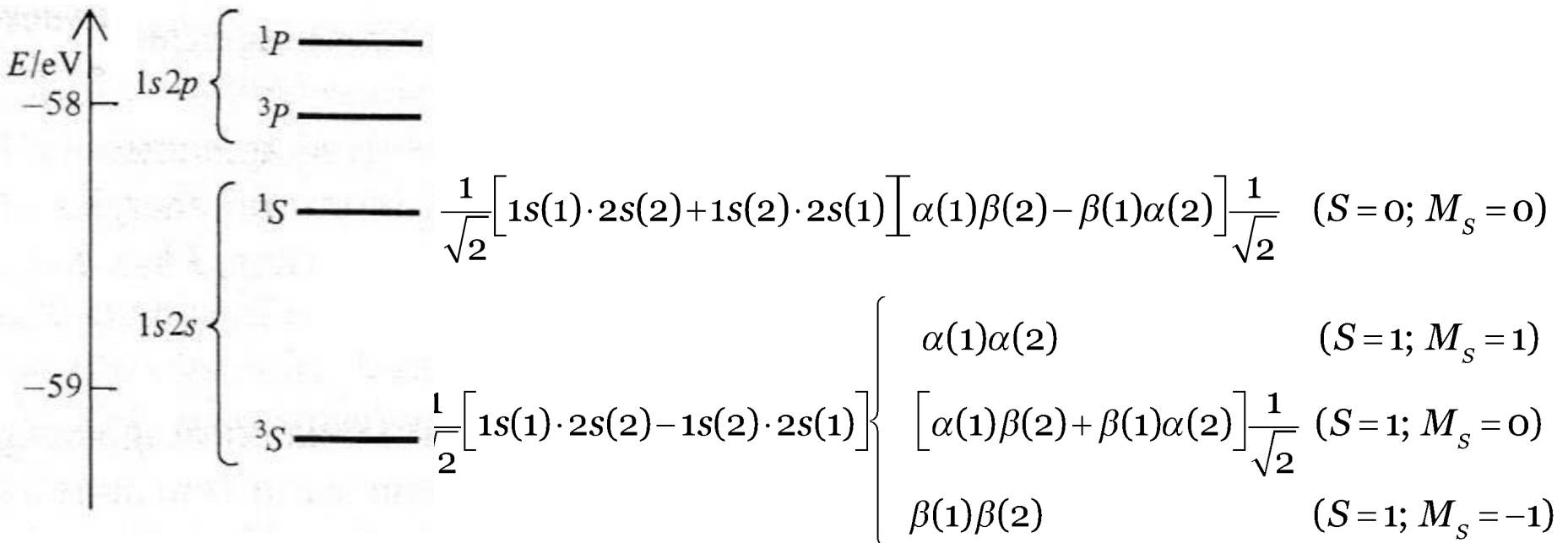
# Helium Atom: Excited States

**$1s(1)1s(2)$**  The spatial part is symmetric

**$1s(1)2s(2)$  or  $1s(2)2s(1)$**  symmetric or anti-symmetric

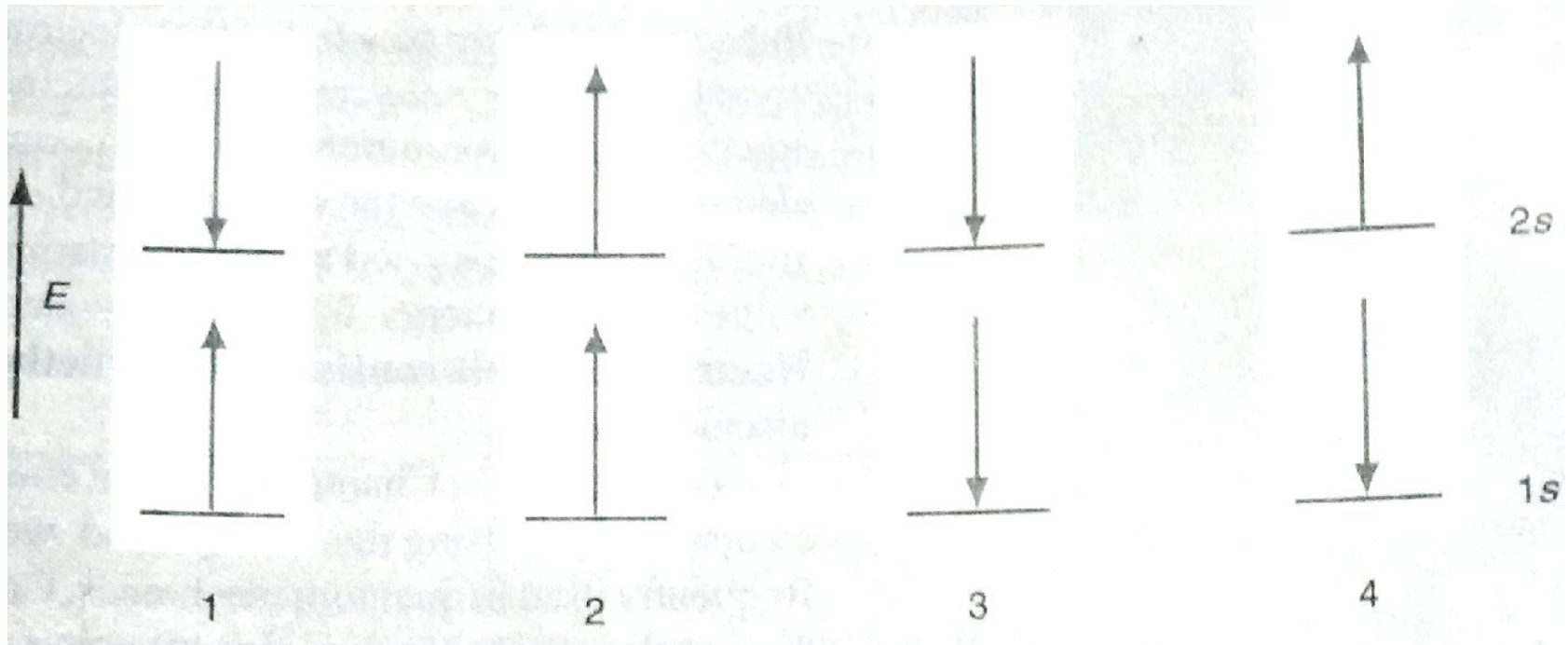
**$1s(1)2s(2) + 1s(2)2s(1)$       Symmetric**

**$1s(1)2s(2) - 1s(2)2s(1)$       Anti-symmetric**





Slater determinants are not just any determinant: There is logic to it...



$$\psi_1(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix} \quad \psi_2(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$$

$$\psi_3(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix} \quad \psi_4(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}$$