Quantum Mechanics and Atomic Physics Lecture 22: Multi-electron Atoms http://www.physics.rutgers.edu/ugrad/361 Prof. Sean Oh

#### Last Time

- Multi-electron atoms and Pauli's exclusion principle
- Electrons are Fermions (spin 1/2), are indistinguishable and have an antisymmetric total eignefunction

- Helium:
  - For antiparallel spins:
    - s'=0
    - Singlet state in Helium
    - $\chi$  antisymmetric
    - $\Psi$ (space) symmetric
  - For parallel spins:
    - s'=1
    - triplet state in Helium
    - $\chi$  symmetric
    - $\Psi$ (space) antisymmetric.





## Example

- If we put 5 electrons (fermions!) in an infinite square well, what is the ground state energy?
  - Recall the energies for an infinite square well are:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = n^2 E_1$$
, where  $E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$ 

- Since electrons are fermions, 2 electrons will populate n=1, 2 in n=2, and 1 in n=3.
- So, the ground state energy of this system is:

$$E = 2 \cdot (E_1) + 2 \cdot (4E_1) + 1 \cdot (9E_1) = 19E_1$$

- What if we put 5 bosons in the well?
  - All 5 bosons can go into n=1!
  - So ground state energy is  $E=5E_1$

## Example

Construct total (spatial+spin) first excited state configuration of a Helium atom using the spatial hydrogenic wavefunction

If you consider Coulomb repulsion between electrons, will the first excited state be in a singlet state (parahelium) or in a triplet state (orthohelium)?

## **Complex Atoms**

- For complex atoms, S.E. is solved numerically, using:
  - the potential between each electron and the nucleus,
  - and the potential between each electron and all the others.
- Atomic energy levels and chemical properties are then obtained!

| Each value of n corresponds to a shell: |   |   |   |   |       |  |  |
|---|---|---|---|---|-------|--|--|
| n:                                      | 1 | 2 | 3 | 4 | • • • |  |  |
| Shell:                                  | K | L | Μ | Ν | • • • |  |  |

| Eac | Each n and l constitute a subshell: |   |   |   |   |       |  |  |  |  |
|-----|-------------------------------------|---|---|---|---|-------|--|--|--|--|
| l:  | 0                                   | 1 | 2 | 3 | 4 | • • • |  |  |  |  |
|     | S                                   | р | d | f | g | • • • |  |  |  |  |

### **Population of Shells**

| <u>Shell</u> | <u>n</u> | <u>ℓ</u> | <u>m</u> <sub>ℓ</sub> | <u>m</u> <sub>s</sub> | Sub-shell  | <u>Max. Sub-shell</u><br>population | <u>Max. Shell</u><br>population |
|--------------|----------|----------|-----------------------|-----------------------|------------|-------------------------------------|---------------------------------|
| K            | 1        | 0        | 0                     | $\pm 1/2$             | <b>1</b> s | 2                                   | 2                               |
| L            | 2        | 0        | 0                     | ±1/2                  | 2s         | 2                                   |                                 |
|              |          | 1        | $0, \pm 1$            | ±1/2                  | 2p         | 6                                   | } 8                             |
| Μ            | 3        | 0        | 0                     | ±1/2                  | 3s         | 2                                   |                                 |
|              |          | 1        | $0, \pm 1$            | ±1/2                  | 3р         | 6                                   | 18                              |
|              |          | 2        | $0,\pm 1,$            | $\pm 1/2$             | 3d         | 10                                  | J                               |
|              |          |          | <b>±</b> 2            |                       |            |                                     |                                 |

For each  $\ell$ , there are ( $2\ell$ +1) values of  $m_{\ell}$  and 2 values of  $m_s$ , so the maximum subshell population is 2( $2\ell$ +1)

#### **Maximum Shell Population**

For each  $n, \ell = 0, 1, ... (n-1)$ 

• So the maximum shell population is:

$$\sum_{l=0}^{N-1} 2(2l+1) = \sum_{l=0}^{N-1} (4l+2)$$
  
=  $4 \frac{(n-1)n}{2} + 2n = 2n^2 - 2n + 2n = 2n^2$ 

# Shielding/Screening

- Chemical properties of atoms are (mostly) determined by the outermost electrons.
- Outer electrons do not feel the full nuclear charge, because inner electrons partially shield the nucleus.
  - This is called shielding or screening.



- Also radii of complex atoms are within a factor of two of hydrogen!
  - The inner electrons get pulled in closer to the nucleus. (In contrast, note that hydrogenic radius grows fast with n as a<sub>0</sub>\*n<sup>2</sup>)

# **Energy Levels of Helium**

- In Helium one electron is presumed to be in the ground state of a helium atom, the 1s state.
- An electron in an upper state can have spin antiparallel to the ground state electron (s'=0, singlet state) or parallel to the ground state electron (s'=1, triplet state)
- This gives us two sets of states for Helium:
  - 1. <u>Parahelium:</u>
    - electrons have antiparallel spins, s'=0, singlet spin eigenfunctions, antisymmetric χ, symmetric Ψ(space), attractive exchange force, electrons close
  - 2. <u>Orthohelium:</u>
    - electrons have parallel spins, s'=1, triplet spin
       eigenfunctions, symmetric χ, antisymmetric Ψ(space),
       repulsive exchange force, electrons generally far apart.

#### Parahelium/Orthohelium



- It is observed that the orthohelium states (s'=1) are lower in energy than the parahelium states (s'=0).
- For the same *n*, energy increases with *l*

# Features of Helium Energy Levels

- 1. For an n, energy increases with *l*.
  - Mainly due to increasing shielding as *ℓ* increases.
- 2. Triplet states have a little less energy than corresponding singlet state.
  - Mainly because electrons are farther apart due to exchange forces.
  - Energy of e<sup>-</sup> e<sup>-</sup> interaction is:

$$\frac{1}{4\pi\epsilon_{o}} \frac{(-e)(-e)}{r} = + \frac{1}{4\pi\epsilon_{o}} \frac{e^{2}}{r}$$

# Features of Helium Energy Levels

- 3. Most important: 1<sup>3</sup>S state does not exist!
  - That's because it would violate Pauli exclusion principle: n=1, l=0, m<sub>l</sub>=0, parallel spins (s=1).
- 4. Parahelium: s'=0, so j'= $\ell$ . So singlet states are: 1<sup>1</sup>S<sub>0</sub>, 2<sup>1</sup>S<sub>0</sub>, 2<sup>1</sup>P<sub>1</sub>, etc.

Orthohelium: s'=1, so if  $\ell$ =0, j'=s'=1. 2<sup>3</sup>P is composed of three lines ( $\ell$ =1, j'=0, 1, 2), 2<sup>3</sup>P<sub>0</sub>, 2<sup>3</sup>P<sub>1</sub>, 2<sup>3</sup>P<sub>2</sub>: Nominally these are degenerate, but they get splitted due to spin-orbit coupling, etc.



- The ionization energy: the energy necessary to remove an electron from the neutral atom.
- Ionization energy of hydrogen: 13.6eV
- Other atoms: 5-25 eV
- So within a factor of two or so of hydrogen.
- It is a minimum for the atoms (alkali metals) which have a single electron outside a closed shell.
- It generally increases across a row on the periodic table.
  - maximum for the noble gases which have closed shells.

# **Energy of Complex Atoms**

#### Hydrogen atom:

- In Schrodinger theory, H atom exhibits ℓ-degeneracy
- In Dirac therory: energy depends on n and j
- For complex atoms:

2 electrons in 1s

1 electron in 2s

• For a given n, the energy increases with  $\ell$ 

13.6 eV

Mainly a consequence of screening.

for n=2 and



## **Build-up of Periodic Table**



#### Hund's Rules

- When electrons fill a subshell, do they follow any special ordering of  $m_{\ell}$  and  $m_{s}$ ?
- Yes, they follow Hund's Rules:

## Hund's Rules: Energy Ordering

- 1. Lowest energy for maximum S'
  - Parallel spins  $\Rightarrow$ repulsive exchange force  $\Rightarrow$ electrons apart (large r)  $\Rightarrow$ e-e energy is:

$$V = \frac{1}{4\pi\epsilon_0} + \frac{1}{\epsilon_0} + \frac{1}{\epsilon_0}$$

 $\Rightarrow$  which is low for large r

- 2. Lowest energy for maximum L'.
  - To stay apart, they move in the same direction around the nucleus and maximize L'
- 3. Lowest energy for minimum J' for less than half filled, and maximum J' for more than half-filled: fine structure effect, as in Hydrogen

### **Electron Configurations**

 They follow Pauli's exclusion principle and Hund's rules

|   | Atom | 1.8 | $2_{3}$    |    | 2p |    | configuration                                   |
|---|------|-----|------------|----|----|----|---|
|   | Li   | 1.↓ | 1          |    |    |    | $1s^22s^1$                                      |
| 1 | Be   | †↓  | †↓         |    |    |    | $1s^22s^2$                                      |
|   | В    | 1   | 1↓         | 1  |    |    | $1s^22s^22p^1$                                  |
|   | С    | †↓  | 1↓         | Ť  | †  |    | $1s^{2}2s^{2}2p^{2}$                            |
|   | Ν    | †   | ţţ         | 1  | 1  | 1  | $1r^2s^22p^3$                                   |
|   | 0    | †↓  | <u>†</u>   | †↓ | 1  | †  | $1s^2 2s^2 2p^4$                                |
|   | F    | †↓  | †↓         | †↓ | †↓ | †  | 1s <sup>5</sup> 2s <sup>5</sup> 2p <sup>5</sup> |
|   | Ne   | †↓  | <u>†</u> ↓ | †↓ | †↓ | †↓ | 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> |

Electron

## Electron level filling examples

They should follow both Pauli' exclusion principles and Hund's rules.

Multielectron level filling rules Note Title Electronic configurations of an atom can be written as (15)<sup>2</sup>(25)<sup>2</sup>(2p)<sup>6</sup>(35)<sup>2</sup>.... The filling order is ; 1 p d f g When we fill the orbitals, the total angular momentum values are important in atomic physics. All filled orticals have net zero angubr momentum values, and the partially filled top most orbital determines the total angular momentum values written as "125+11 " 1(25+1 written as We use numbers for s and J, but symbols for L such that  $0 \Rightarrow S , 1 \Rightarrow P , 2 \Rightarrow$ D, 3-) F

(3) 
$$Cl(z=i\eta) = \frac{1}{100} \frac{1}{100} \frac{1}{100} = 5 = \frac{1}{2} \pm 0 \pm 0 = \frac{1}{2}$$
  
=)  $L = -\frac{1}{100} \frac{1}{100} = 5 = \frac{1}{2} \pm 0 \pm 0 = \frac{1}{2}$   
=)  $L = -\frac{1}{100} \frac{1}{100} \frac{1}{100} = \frac{1}{2}$   
=)  $L = -\frac{1}{100} \frac{1}{100} \frac{$ 

# Summary/Announcements

#### Next time:

- Approximation Methods (I)
- HW 12 due on Wed. Dec. 7 (no late submission allowed)
- HW 13 will be due on Mon. Dec. 12 (no late submission allowed)
- Now it's time for Quiz.