Lecture #7

Reading:
1.12- Orbital Energies
1.13- The building up principle

Topics: Multi-electron atoms
  I. Wavefunctions for multi-electron atoms
  II. Binding energies
  III. Electron configurations (Aufbau principle)

I. WAVEFUNCTIONS FOR MULTIELECTRON ATOMS
(Describing atoms with Z=2 or higher)

The Schrödinger equation correctly describes the electronic structure for all atoms, not just 1-e⁻ atoms.

Hydrogen: $\hat{H}\Psi(r\theta\phi) = E\Psi(r\theta\phi)$

Helium (2 e⁻s): $\hat{H}\Psi(r_1\theta_1\phi_1 r_2\theta_2\phi_2) = E\Psi(r_1\theta_1\phi_1 r_2\theta_2\phi_2)$

Lithium (3 e⁻s): $\hat{H}\Psi(r_1\theta_1\phi_1 r_2\theta_2\phi_2 r_3\theta_3\phi_3) = E\Psi(r_1\theta_1\phi_1 r_2\theta_2\phi_2 r_3\theta_3\phi_3)$

The equations becomes much more complicated. Approximations are needed!

Hartree orbitals: Assume we can write a multi-electron Ψ as the product of 1-electron Ψs:

Helium: $\Psi(r_1\theta_1\phi_1 r_2\theta_2\phi_2) = \Psi (r_1\theta_1\phi_1) \cdot \Psi (r_2\theta_2\phi_2)$
  Ψ for _____ • Ψ for _____
  $\Psi_{100+1/2}$ $\Psi_{100-1/2}$
  1s(1)   1s(2)

Lithium: $\Psi (r_1\theta_1\phi_1 r_2\theta_2\phi_2 r_3\theta_3\phi_3) = \Psi (r_1\theta_1\phi_1) \cdot \Psi (r_2\theta_2\phi_2) \cdot \Psi (r_3\theta_3\phi_3)$
  1s(1)   _____   _____

Electron configuration is the shorthand notation for electron wavefunctions.

H $1s^1$
He $1s^2$
Li $1s^2 2s^1$

Be _____   B   _____

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HOW DO THE MULTI-ELECTRON WAVEFUNCTIONS COMPARE TO THE H-ATOM WAVEFUNCTIONS?

Let's consider Ar as an example: $1s^2 2s^2 2p^6 3s^2 3p^6$

Similarities to H atom wavefunctions:

- Each orbital obtained is similar in shape to the corresponding H 1-e⁻ orbital.

- The nodal structure is the same (nodes occur at values of r, θ and Φ which give Ψ and $\Psi^2 = 0$).

Differences to H atom wavefunctions:

- Each multi-electron orbital is _____ than the corresponding hydrogen atom orbital.

  Why? Stronger pull from the nucleus with higher Z (Z=18 for Ar , Z=1 for H).

- In multi-electron atoms, orbital energy depends on both the shell (n) and the subshell (l).

II. BINDING ENERGIES FOR MULTI-ELECTRON ATOMS

All orbitals in a multi-electron atom are lower in energy (_____) than the corresponding energy in a hydrogen atom.
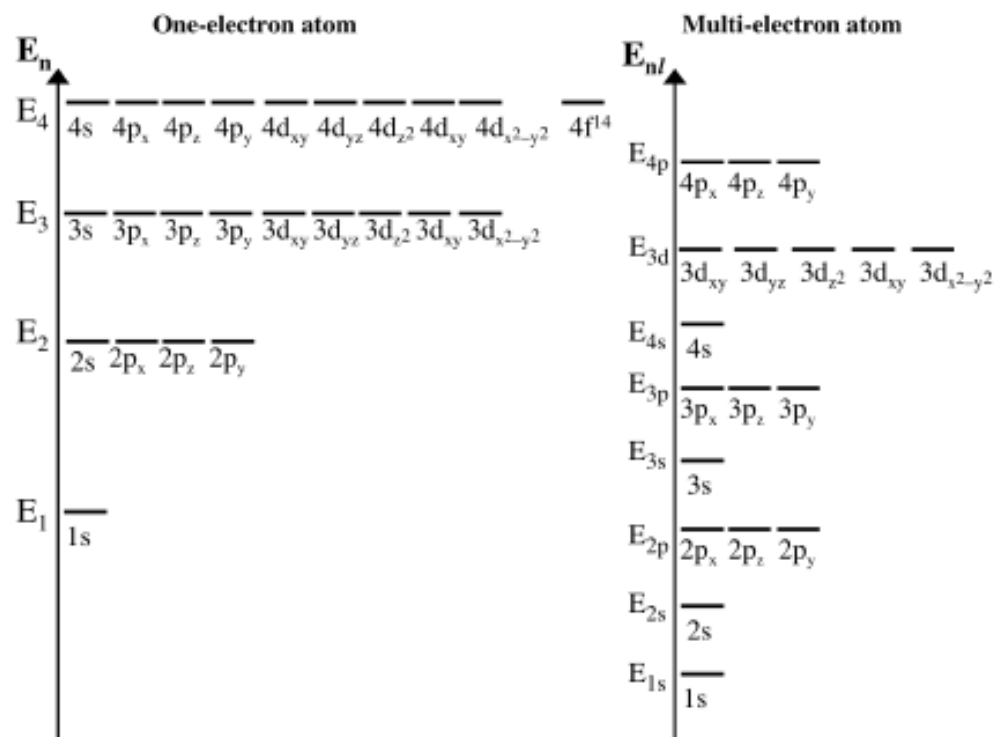
The lower energy results in multi-electron atoms results from a higher Z--- a stronger pull from the nucleus.

The principal quantum number, n, is no longer the sole determining factor for the orbital energies of multi-electron atoms. Energy now depends on n and _____ .

$$E_n = -IE_n = -\frac{Z^2 R_H}{n^2} \qquad\qquad E_{nl} = -IE_{nl} = -\frac{(Z_{eff}^{nl})^2 R_H}{n^2}$$

For _____-electron atoms   For _____-electron atoms

Where Z_{eff} is the effective charge experienced by the electron in the n,l state.

Z_{eff} _____ the same as Z for the nucleus. Z_{eff} differs from Z because of _____ .

Shielding and Z_{eff}

To illustrate the effect of shielding, consider the two extreme shielding situations possible for the He atom (Z = 2).

EXTREME CASE A: electron #1 is very far from nucleus; electron #2 close to nucleus

electron _____

ⓔ

electron _____

ⓔ

Z = 2

He nucleus (charge= _____)

- Electron #2 cancels part of the charge experienced by electron #1.

- Electron #1 experiences a force on average of $Z_{eff} =$ _____ , not $Z_{eff} = +2e$.

- The energy of electron #1 is that of an electron in a H (1-electron) atom.

$$E_{e-\#1} = \underline{\qquad}_{e-\#1} = -\frac{(Z_{eff})^2 R_H}{n^2} = \underline{\qquad} = \underline{\qquad} \text{ J}$$

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EXTREME CASE B: electron #1 close to nucleus; electron #2 very far from nucleus

electron _____

$\textcircled{e}$

electron _____

$\textcircled{e}$

$\left(\overset{Z = 2}{}\right)$

He nucleus (charge = +2e)

- Electron #1 experiences a force on average of Z_{eff} = _____.
- The energy of electron #1 is that of an electron in a _____ (1-electron) ion.

$$E_{e-\#1} = - IE_{e-\#1} = -\frac{(Z_{eff})^2\ R_H}{n^2} = \underline{\hspace{2cm}} = \underline{\hspace{2cm}} J$$

Extreme case A: $Z_{eff} = 1$, $IE_{He} = 2.18 \times 10^{-18}$ J   _____ shielding
Extreme case B: $Z_{eff} = 2$, $IE_{He} = 8.72 \times 10^{-18}$ J   _____ shielding
Experimentally determined IE_{He}:

Experimental $IE_{He} = 3.94 \times 10^{-18}$ J

So the reality is somewhere between total shielding and no shielding.

We can calculate the Z_{eff} from the experimentally determined IE:

$$IE = \frac{(Z_{eff})^2\ R_H}{n^2}$$ $R_H = 2.180 \times 10^{-18}$ J

$$Z_{eff} = \left(\underline{\hspace{2cm}}\right) = \left(\underline{\hspace{3cm}}\right) = \underline{\hspace{2cm}}$$

Note: Our calculated Z_{eff} is a reasonable value, since it falls between ___ (total shielding) and ___ (no shielding).

Why is E2s < (more negative than) E2p and E3s < E3p < E3d

For a given n state (shell), electrons in orbitals with lower values of l _____ closer to the nucleus (even though r_{mp} decreases with increasing l!).

2p   2s

RPD

radius
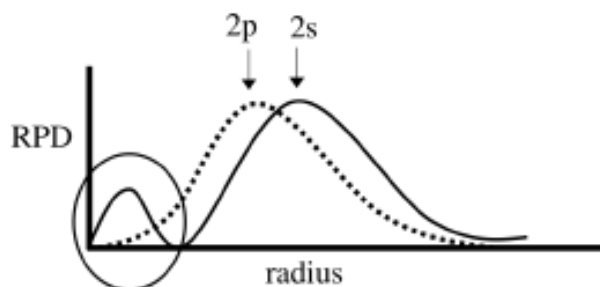
This means (for the same n):

- s-electrons are _____ shielded than p electrons.

- p-electrons are less shielded than ____-electrons

Consider why the electron configuration for Li is $1s^2\ 2s^1$ and not $1s^2\ 2p^1$.

The s-orbital is less shielded. Averaging over the RPD yields _____ < _____ .

Since $E_{nl} = - (Z_{eff})^2 R_H\ /\ n^2$, E_{2s} _____ E_{2p}

III. ELECTRON CONFIGURATIONS

Electron configuration describes the electronic structure of an atom by specifying which orbitals are occupied. This is very useful notation, since electron structure dictates the chemical properties and reactivity of a given atom.

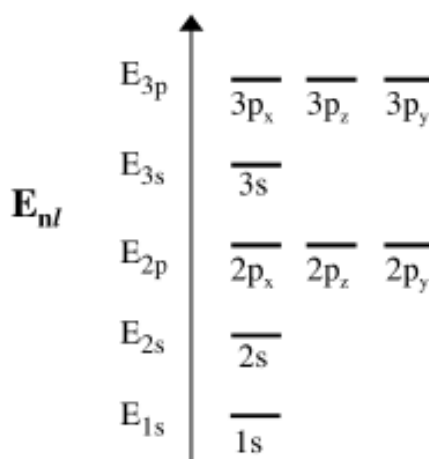How do we determine the electron configuration of an atom?

AUFBAU PRINCIPLE
Fill energy states (which depend on ___ and ___) one electron at a time, starting with the lowest energy state and following:

1) The Pauli exclusion principle

2) Hund's rule: when electrons are added to states of the same E, a single electron enters each state before a second electron enters any state. Spins remain _____ prior to adding a second electron to any state.
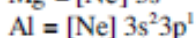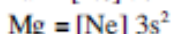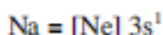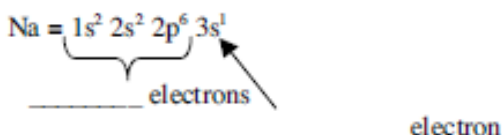
   Let's try this for O (Z = 8).

   Electron configuration: _____

   (specifying m_l): _____

E_{nl}

E_{3p} — $\overline{3p_x}$ $\overline{3p_z}$ $\overline{3p_y}$

E_{3s} — $\overline{3s}$

E_{2p} — $\overline{2p_x}$ $\overline{2p_z}$ $\overline{2p_y}$

E_{2s} — $\overline{2s}$
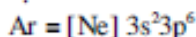
E_{1s} — $\overline{1s}$

You need only provide m_l notation if specifically asked.

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Third Period: Na to Ar

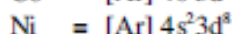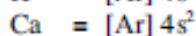$Na = \underbrace{1s^2\ 2s^2\ 2p^6}\ 3s^1$

_____ electrons

_____ electron

$Na = [Ne]\ 3s^1$
$Mg = [Ne]\ 3s^2$
$Al = [Ne]\ 3s^2 3p^1$
.
.
$Ar = [Ne]\ 3s^2 3p^6$

Fourth Period: K to Kr

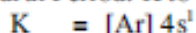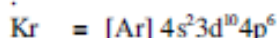|		
K	=	$[Ar]\ 4s^1$
Ca	=	$[Ar]\ 4s^2$
Sc	=	$[Ar]\ 4s^2 3d^1$
Ti	=	$[Ar]\ 4s^2 3d^2$
V	=	$[Ar]\ 4s^2 3d^3$
Cr	**=**	**$[Ar]\ 4s^1 3d^5$** exception to Aufbau*
Mn	=	$[Ar]\ 4s^2 3d^5$
Fe	=	$[Ar]\ 4s^2 3d^6$
Co	=	$[Ar]\ 4s^2 3d^7$
Ni	=	$[Ar]\ 4s^2 3d^8$
Cu	**=**	**$[Ar]\ 4s^1 3d^{10}$** exception to Aufbau*
Zn	=	$[Ar]\ 4s^2 3d^{10}$
Ga	=	$[Ar]\ 4s^2 3d^{10} 4p^1$
		.
Kr	=	$[Ar]\ 4s^2 3d^{10} 4p^6$
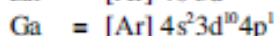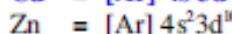
* Exceptions to the Aufbau principle: filled (____) and half-filled (____) d-orbitals have lower energy than simple theory predicts.

Core electrons: electrons in inner shells making up a noble gas configuration.

Valence electrons: electrons in the outer most shell. Valence electrons are the exciting ones- in general, only the valence electrons participate in chemical reactions.

Fifth Period: Rb to Xe. Mo and Ag are counterpart anomalies to Cr and Cu in 4th period. *Additional anomalies and other effects are difficult to predict.*
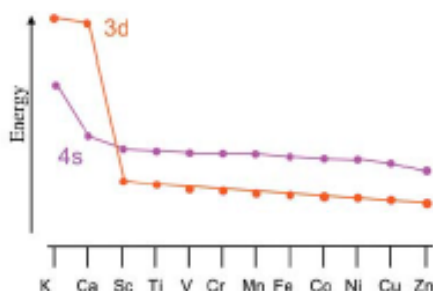
1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f
6s 6p 6d
7s 7p
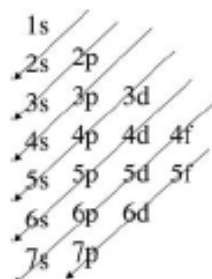
Mnemonic for electon configuration: diagonals

Using this chart, we can write out the correct order of orbitals with increasing energy from left to right

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p

ELECTRON CONFIGURATIONS OF IONS - NOT THE SAME AS NEUTRALS!!!
Once a d orbital is filled, the orbital energy drops to below the corresponding s orbital.

Consider Ti vs. Ti^{2+}

$Ti = [Ar]4s^2 3d^2$ but really $Ti = [Ar]$_____

$Ti^{2+} = [Ar]$_____

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