#44 Notes   **Unit 6: Atomic Structure and Periodicity**
                Ch. Atomic Structure & Periodicity

I. Emission Spectra

When a substance is exposed to a certain intensity of light or some other form of energy, the atoms absorb some of the energy (**excited state** atoms).

As the atom absorbs energy, one or more electrons change their orbit(s). Since this excited state is not stable, the electrons will return to their stable **ground state**, by releasing energy in the form of light (**emission spectra**).

The emission spectra of each element is unique, since certain bands of light (at certain energies) are produced. The energy is **quantized**, since only certain energies are allowed.

II. Electromagnetic Spectrum

A. Light

$$c = \lambda \upsilon$$

c = the speed of light (3.00×10^8 m/s)

λ (Gr. letter lambda) = wavelength (meters)

υ (Gr. letter nu) = frequency ($\underline{\text{waves}}$ =sec^{-1} = Hertz = Hz)
                                                         sec

** 1 nm = 1 $\times 10^{-9}$ m

B. Max Planck

In 1900 he measured the heat from glowing objects and realized the energy was **quantized**. (The energy was gained/lost in only certain amounts.)

$$\Delta E = nh\upsilon$$

ΔE = change in energy (J/quanta)

n = whole number of quanta , n= 1 for 1 quantum

h = Planck's Constant (6.626×10^{-34} J/Hz)

υ (nu) = frequency (Hz)

C. Einstein's Photoelectric Effect

Electrons can be ejected from metals, when light shines on the metal.

Einstein found that this light energy is quantized: A certain amount of energy must be absorbed to eject each electron.

Light, therefore, all electromagnetic radiation must be quantized and consists of particles, named photons.

$$\Delta E = nh\upsilon$$ applies to all electromagnetic radiation,
                                    where **n = the number of photons**.

Ex. 1) A certain red light has a wavelength of 690 nm. What is its frequency?

$\dfrac{690 \text{ nm}}{} \bigg| \dfrac{1 \text{ X}10^{-9} \text{ m}}{1 \text{ nm}} = 6.90 \text{ X}10^{-7} \text{ m}$

$c = \lambda \upsilon \qquad (3.00 \text{ X}10^8 \text{ m/s}) = (6.90 \text{ X}10^{-7} \text{ m}) \upsilon$

$\mathbf{4.35 \text{ X}10^{14} \text{ Hz} = \upsilon}$

Ex. 2) Find the energy of one quantum of light (**one photon**), having a frequency of 2.76 X10^{15} Hz.

$\Delta E = nh\upsilon$
$\Delta E = (1 \text{ photon}) (6.626 \text{ X}10^{-34} \text{ J /Hz}) (2.76 \text{ X}10^{15} \text{ Hz})$
$\mathbf{\Delta E = 1.83 \text{ X}10^{-18} \text{ J/photon}}$

$\rightarrow$J/mol : $\quad \dfrac{1.83 \text{ X}10^{-18} \text{ J}}{\text{photon}} \bigg| \dfrac{6.022 \text{ X}10^{23} \text{ photons}}{1 \text{ mol}} = \mathbf{1.10 \text{ X}10^6 \text{ J/mol}}$

Ex. 3) It takes 4.42 X10^{-19} J to remove an electron from an unknown atom. Is light with a wavelength of 470 nm strong enough to remove an electron? (like Einstein's experiment)

$\dfrac{470 \text{ nm}}{} \bigg| \dfrac{1 \text{ X}10^{-9} \text{ m}}{1 \text{ nm}} = 4.70 \text{ X}10^{-7} \text{ m}$

$c = \lambda \upsilon \qquad (3.00 \text{ X}10^8 \text{ m/s}) = (4.70 \text{ X}10^{-7} \text{ m}) \upsilon$

$\mathbf{6.38 \text{ X}10^{14} \text{ Hz} = \upsilon}$

$\Delta E = nh\upsilon = (1 \text{ photon}) (6.626 \text{ X}10^{-34} \text{ J/Hz}) (6.38 \text{ X}10^{14} \text{ Hz})$
$\mathbf{\Delta E = 4.23 \text{ X}10^{-19} \text{ J/photon}}$

$\mathbf{4.23 \text{ X}10^{-19} \text{ J/photon} \qquad\qquad < 4.42 \text{ X}10^{-19} \text{ J}}$
(smaller than the needed amount)
This light is not strong enough.

** if kJ/mol change to J/photon $\qquad 1 \text{ kJ} = 1 \text{ X}10^3 \text{ J}$

#45 Notes   D. De Broglie's Equation for **Particles**

He hypothesized that since light consisting of photons moves in waves, other small particles must also move in waves.

Einstein: $E = mc^2$ Planck: $E = h\upsilon$ $c = \lambda\upsilon$

$$E = E$$

Therefore $mc^2 = h\upsilon$ $c/\lambda = \upsilon$

↑   ↓

←←←←←←←←←←←←←←←←←←

$mc^2 = h(c/\lambda)$

$mc = h/\lambda$

$\lambda mc = h$

$\lambda = \dfrac{h}{mc}$ → $\lambda = \dfrac{h}{mv}$ m = mass (kg)   **for particles**

v = velocity (m/s)

mass of electron = 9.109×10^{-31} kg
mass of proton = 1.673×10^{-27} kg
mass of neutron = 1.675×10^{-27} kg

Ex. 1) What is the speed of an electron traveling with a wavelength of 432 nm?

$$\dfrac{432 \text{ nm}}{} \bigg| \dfrac{1 \times 10^{-9} \text{ m}}{1 \text{ nm}} = 4.32 \times 10^{-7} \text{ m}$$

$\lambda = \dfrac{h}{mv}$ $(4.32 \times 10^{-7} \text{ m}) = \dfrac{(6.626 \times 10^{-34} \text{ J/Hz})}{(9.109 \times 10^{-31} \text{ kg) v}}$

(3.935×10^{-37}) v $= (6.626 \times 10^{-34}$ J/Hz)

v = 1.68×10^3 m/s

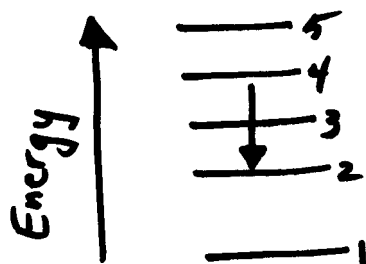**If a problem states: 4% the speed of light = $(0.04)(3.00 \times 10^8$ m/s)

III. Bohr Model
Bohr figured out an equation to calculate the energy given off as an electron in a Hydrogen atom moves between different energy levels. (Only certain orbits/layers are allowed, so it is quantized.)

$\Delta E = -2.178 \times 10^{-18}$ J $\left(\dfrac{1}{n^2_{final}} - \dfrac{1}{n^2_{initial}} \right)$ n = layer number

Ex. 1) Calculate the energy for n=4 → n=2.

Show the transition:

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n^2_{final}} - \frac{1}{n^2_{initial}} \right)$$

$\Delta E = -2.178 \times 10^{-18}$ J $(1/2^2 - 1/4^2)$
$\Delta E = -2.178 \times 10^{-18}$ J $(1/4 - 1/16)$
$\Delta E = -2.178 \times 10^{-18}$ J $(0.25 - 0.0625)$
$\Delta E = -2.178 \times 10^{-18}$ J (0.1875)
$\Delta E = -4.08 \times 10^{-19}$ J of the light → $\Delta E = nh\upsilon$ → $c = \lambda\upsilon$ To find wavelength of light!

IV. Schrodinger's Quantum Mechanics
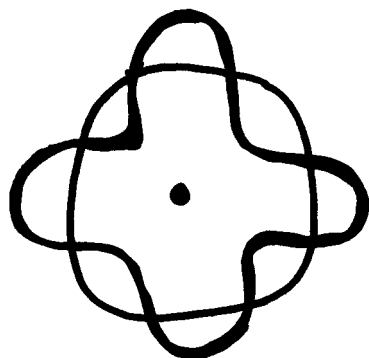Unfortunately Bohr's Model only worked accurately on Hydrogen.
Schrodinger, like De Broglie, believed that the electron showed wave-like features.

The electron moves around the nucleus in a motion resembling a <u>standing wave</u> (waves that do not travel).
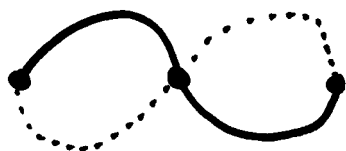
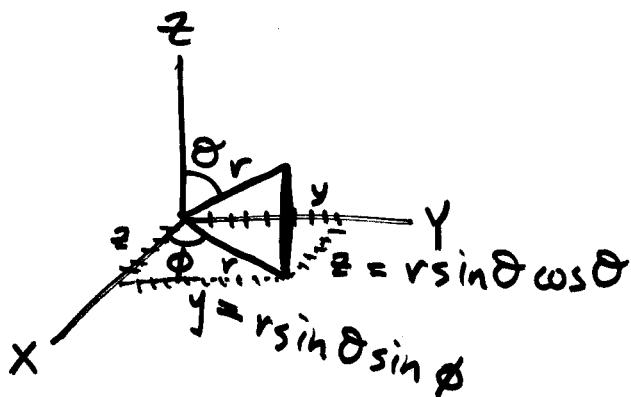Ex. Guitar string, Tacoma Narrows Bridge Collapse

Around the atom:

n = 4

Schrodinger created an equation to describe this.

$\hat{H}\ \overset{\wedge}{\Psi} = \hat{E}\ \overset{\wedge}{\Psi}$ H = mathematical operator, E = the energy operator
                        Ψ = wave function describing the electrons orbit

For Hydrogen:

$$\frac{\delta^2 \psi}{\delta x^2} + \frac{\delta^2 \psi}{\delta y^2} + \frac{\delta^2 \psi}{\delta z^2} + \frac{2\mu}{h^2}\left(E + \frac{ze^2}{r}\right)\psi = 0$$

z = r sinϑ cosϑ
y = r sinϑ sin∅

$$\frac{1}{r^2}\frac{\delta}{\delta r}\left(r^2 \frac{\delta\psi}{\delta r}\right) + \frac{1}{r^2 sin^2\theta}\frac{\delta^2\psi}{\delta\phi^2} + \frac{1}{r^2 sin\theta}\frac{\delta}{\delta\theta}\left(sin\theta \frac{\delta\psi}{\delta\theta}\right) + 2\left(E + \frac{z}{r}\right)\psi = 0$$

**From this we know where the electron is, but not it's path.

V. Heisenburg's Uncertainty Principle

$\Delta x \cdot \Delta(mv) \geq \dfrac{h}{4\pi}$ x = uncertainty in position (meters)
                        mv = uncertainty in momentum
                              (m = mass (kg), v = velocity (m/s))

If Δx is small, then Δ(mv) is large.
(If we know its position, we don't know about its motion.)
**Either we know its position, or its motion. Not Both!

Ex. 1) Using the Heisenburg Uncertainty Principle, calculate Δx for an electron with $\Delta v = 5.79 \times 10^{-3}$ m/s. How does Δx of the electron compare with a hydrogen atom (diameter of 1×10^{-10} m)? {electron mass = 9.109×10^{-31} kg}

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta(9.109 \times 10^{-31} \text{ kg})(5.79 \times 10^{-3} \text{ m/s}) \geq \frac{(6.626 \times 10^{-34} \text{ J/Hz})}{(4)(3.14)}$$

$$\Delta x \cdot \Delta(5.274 \times 10^{-33}) \geq (5.275 \times 10^{-35})$$
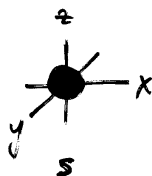
$$\Delta x = 1.00 \times 10^{-2} \text{ m}$$

This means that the position of the electron is known within 0.0100 m, but the size of the hydrogen atom is 1×10^{-10} m (10^8 times smaller). The electron's uncertainty in position is 10^8 larger than hydrogen atom's size of 1×10^{-10} m. We would not know where the electron was in the hydrogen atom. (We <u>know</u> the electron's velocity, but do <u>not</u> have a good idea of the electron's position.)
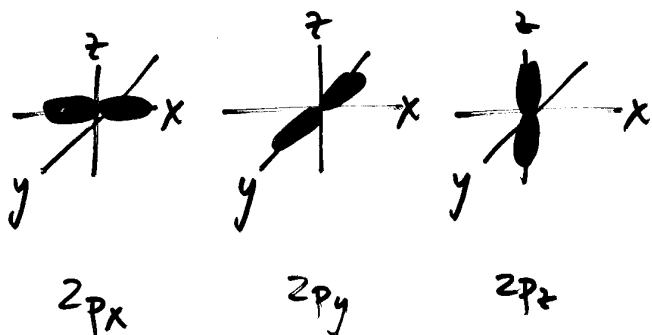
By using the square of the wave function, a probability map can be drawn to show where the electrons are located at specific times.

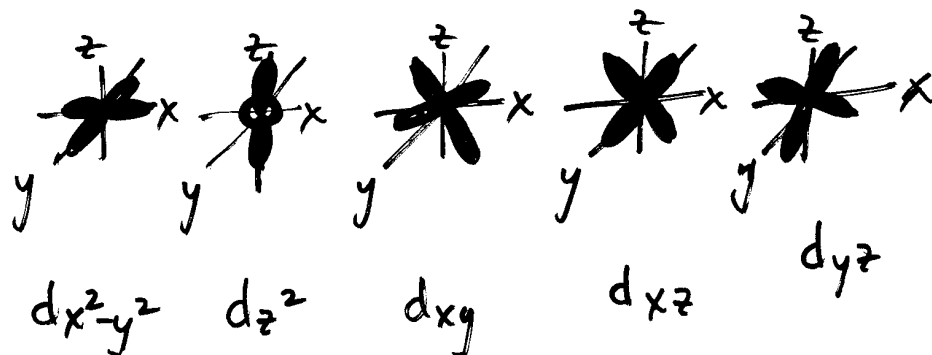## I.   <u>s – orbitals (1 type)</u>

s

II.   <u>p – orbitals (3 types)</u>

$2p_x$ $2p_y$ $2p_z$

III.   <u>d – orbitals (5 types)</u>

$d_{x^2-y^2}$ d_{z^2} d_{xy} d_{xz} d_{yz}

IV.   <u>f – orbitals (7 types)</u>

f_{xyz} $f_{y(x^2-z^2)}$ $f_{x(z^2-y^2)}$ $f_{z(x^2-y^2)}$ $f_{z^3-\frac{3}{5}zr^2}$ $f_{x^3-\frac{3}{5}xr^2}$ $f_{y^3-\frac{3}{5}yr^2}$
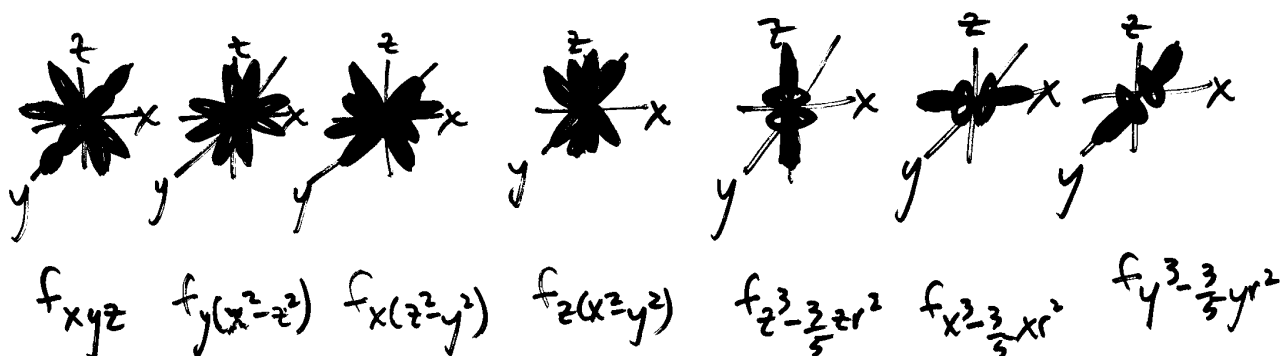
Energy Levels: are the layers of electrons (1, 2, 3, 4, etc.)
Sublevels: are the energy levels and orbital (2s, 3p, etc.)
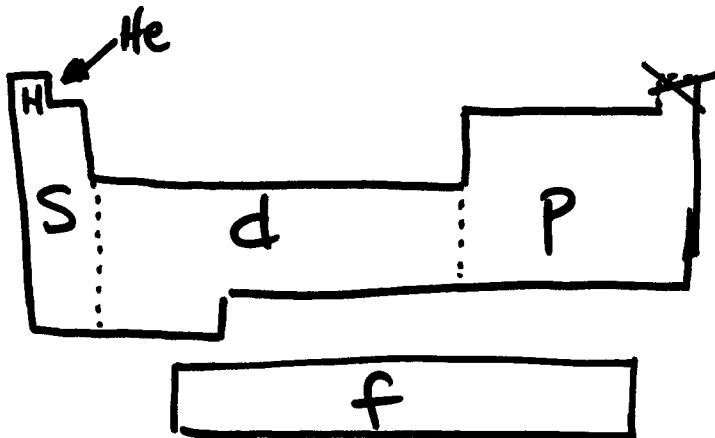
VII. Electron Configurations
Ex. 1a) Mg: $1s^2 \ 2s^2 \ 2p^6 \ 3s^2$
                    ↑↑↑
$1 = 1^{st}$ layer (row #), s = orbital type , power of 2 = the 2 electrons in the 1s orbital

    1b) Br: $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^{10} \ 4p^5$
    1c) Ba: $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^{10} \ 4p^6 \ 5s^2 \ 4d^{10} \ 5p^6 \ 6s^2$

    s-orbitals: column #1-2
    d-orbitals: column #3-12
    p-orbitals: column #13-18
    f-orbitals: elements #57-71 and #89-103

VIII. Orbital Diagrams
A) Pauli Exclusion Principle
An orbital can only hold 2 electrons and they must have opposite spins.

B) Hund's Rule
The lowest energy configuration (most stable) will have the maximum number of unpaired
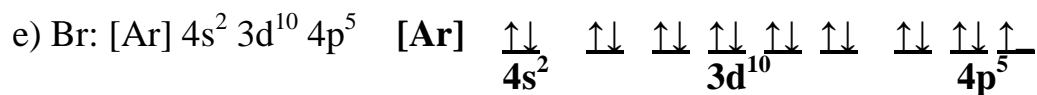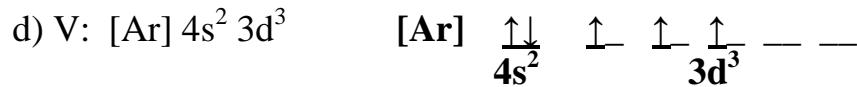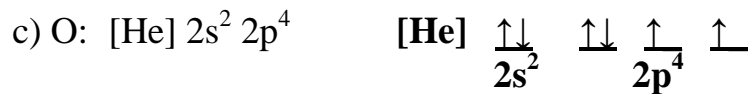electrons allowed by the Pauli Principle.

Ex. 1) Write the orbital diagram for:

a) Al: $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^1$ or [Ne] $3s^2 \ 3p^1$ (short form: start at noble gas before Al)

[Ne] ↑↓   ↑ __ __   These 3 electrons are the <u>outer shell electrons</u>
    3s²   **3p¹**   (<u>valence electrons</u>).

b) N: [He] $2s^2 2p^3$ **[He]** ↑↓   ↑_ ↑_ ↑_   **Hund's Rule: unpaired e⁻ of same type**
               2s²   **2p³**   **have parallel spins.**

c) O: [He] $2s^2 2p^4$ **[He]** ↑↓   ↑↓ ↑_ ↑_
               2s²   **2p⁴**

d) V: [Ar] $4s^2 3d^3$ **[Ar]** ↑↓   ↑_ ↑_ ↑_ — —
               4s²   **3d³**

e) Br: [Ar] $4s^2 3d^{10} 4p^5$ **[Ar]** ↑↓   ↑↓ ↑↓ ↑↓ ↑↓ ↑↓   ↑↓ ↑↓ ↑_
               4s²   **3d¹⁰**   **4p⁵**
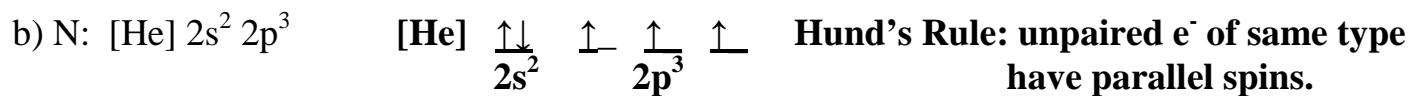
IX. Exceptions

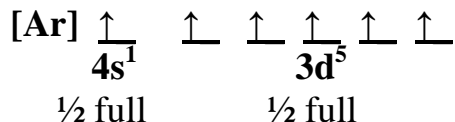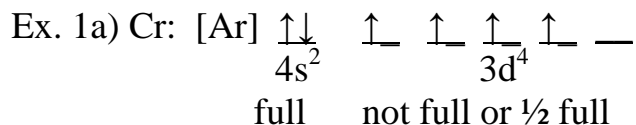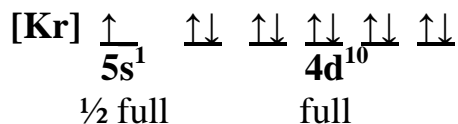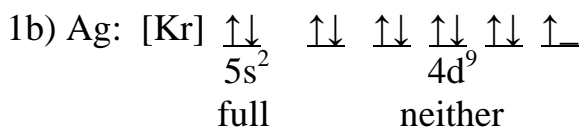Note in textbook, there are many exceptions in the d, f orbitals, since their energies are very similar.

A) Some exceptions can be predicted.
**There is special stability for full and ½ full orbitals.

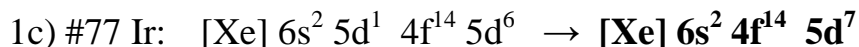Ex. 1a) Cr: [Ar] ↑↓   ↑_ ↑_ ↑_ ↑_ _
              $4s^2$ $3d^4$
          full   not full or ½ full

[Ar] ↑_   ↑_ ↑_ ↑_ ↑_ ↑_
     $4s^1$ $3d^5$
    ½ full   ½ full

** "s" and "d" orbitals are similar in energy, so they can shift an electron from "s" to "d".
    (but not "s" to "p", stop)

1b) Ag: [Kr] ↑↓   ↑↓ ↑↓ ↑↓ ↑↓ ↑_
              $5s^2$ $4d^9$
          full   neither

[Kr] ↑_   ↑↓ ↑↓ ↑↓ ↑↓ ↑↓
     $5s^1$ $4d^{10}$
    ½ full   full

B) f-orbitals:
f-orbitals usually fill before d-orbitals.

Ex. 1a) #60 Nd: [Xe] $6s^2$ $5d^1$ then $4f^3$ **The 1e- alone in the "d" is
                                            lonely and moves to the "**f**" with its **f**riends.
          [Xe] $6s^2$ $4f^4$ $5d^0$

          [Xe] ↑↓   ↑_ ↑_ ↑_ ↑_ _ _ _
               $6s^2$ $4f^4$

    1b) #63 Eu: [Xe] $6s^2$ $5d^1$ $4f^6$ → **[Xe] $6s^2$ $4f^7$ $5d^0$**

    1c) #77 Ir: [Xe] $6s^2$ $5d^1$ $4f^{14}$ $5d^6$ → **[Xe] $6s^2$ $4f^{14}$ $5d^7$**
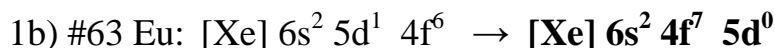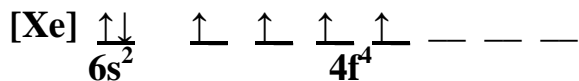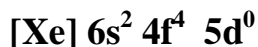
Ex. 2) Ground State or Excited State?

a) $1s^2$ $2s^2$ $3p^1$ **excited state**, should be $1s^2$ $2s^2$ $2p^1$ = **Boron**

b) $1s^2 2s^2 2p^3$ **ground state, = Nitrogen**

X. Quantum Numbers of electrons

A) Principal Quantum Number (n) = 1, 2, 3, 4, 5, 6, 7,
-describes the energy level/layer

B) Angular Momentum Quantum Number (ℓ) = 0, 1, 2, 3, … (n-1)
-relates to the shape/type of orbital

If n = 3, then ℓ = 0, 1, 2
                    ↑ ↑ ↑
Orbital type: s   p   d

C) Magnetic Quantum Number (m_ℓ) = $-\ell$, …0, …, ℓ
-relates to the particular orbital of a type (its orientation in space).

If n = 3, the $\ell = 0$	$\ell = 1$	$\ell = 2$
$m_\ell = 0$	$m_\ell = -1, 0, 1$	$m_\ell = -2, -1, 0, 1, 2$
(1-type of s orbital)	(3-types of p orbital)	(5-types of d orbital)

D) Electron Spin Quantum Number (m_s) = $-\frac{1}{2}, \frac{1}{2}$
-up/down spin on electron

Ex. 1) Is this allowed? n = 2 ℓ = 2 m_ℓ = 1

If n = 2, then ℓ = 0, 1   For ℓ = 0: $m_\ell = 0$
                                    For ℓ = 1: $m_\ell = -1, 0, 1$
ℓ = 2 is not allowed

Ex. 2) What are the maximum number of electrons?

a) n = 3   then ℓ = 0, 1, 2   For ℓ = 0: $m_\ell = 0$ (1 s-orb = 2 e⁻)
                                            For ℓ = 1: $m_\ell = -1, 0, 1$ (3 p-orb = 6 e⁻)
                                            For ℓ = 2: $m_\ell = -2, -1, 0, 1, 2$ (5 d-orb = 10 e⁻)
                                                                                            18 e⁻
b) n = 3, m_ℓ = -1   Above there are two m_ℓ = -1 orbitals, each can hold
                               two electrons, so **4 e⁻**

** See Website for "Quantum Numbers and Electron Orbitals".

#48 Notes   XI. Periodicity
Since an element's position on the periodic table describes its electron configuration, its position allows predictions about certain properties of the element.

A) Atomic Radius (Size)

a) As the number of orbital layers/levels increase (going down a column), the radius will increase.

b) Going to the right across a row, each atom has an extra proton. This will attract the electrons more tightly, decreasing the radius.

c) Anions (-) have gained electrons. Since it will be harder to attract the extra electrons, anions will be larger.

d) Cations (+) have lost electrons. Since it has fewer electrons to attract, its (+) nuclear **charge** can pull the electrons in closer, reducing the radius.

Ex. 1) Which in each pair has a smaller radius?
a) S, Se   b) Ta, Ir   c) Mg, Mg^{2+} d) F, F^{-1} e) Te, Cr
a) S has fewer layers of electrons
b) Ir has more protons to pull in the electrons
c) Mg^{2+} has fewer electrons to attract
d) F has fewer electrons to attract
e) Cr has fewer layers of electrons ***(layers is a larger effect than within a row)
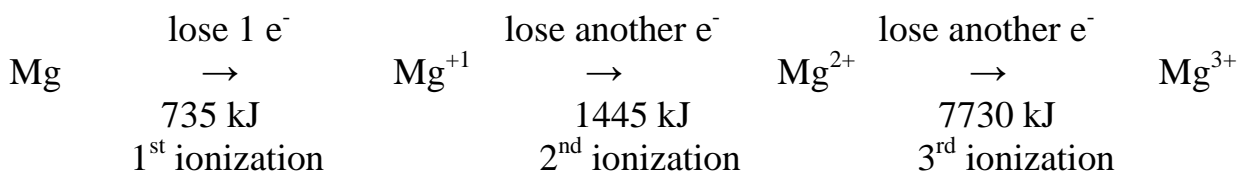
B. Ionization Energy
-is the energy to remove an electron.

a) Generally, the smaller the radius (the electrons are more highly attracted to the nucleus), the harder it is to pull away an electron, the larger the ionization energy.

The larger the radius, the more the inner electrons **shield** the outer electrons from the attraction of the nucleus, making it easier to remove them (small ionization energy).
                                                                                    {Shielding Effect}

b) The larger the (+) **nuclear charge**, the higher the ionization energy. It takes more energy to remove each successive electron.

	lose 1 e⁻		lose another e⁻		lose another e⁻	
Mg	→	Mg^{+1}	→	Mg^{2+}	→	Mg^{3+}
	735 kJ		1445 kJ		7730 kJ	
	1st ionization		2nd ionization		3rd ionization	

3rd ionization is extremely high, since it removes an electron from a stable noble gas configuration.

c) The ionization energy is unusually high to remove an electron from a stable full or ½ full orbital.

#49 Notes   C. Electron Affinity
         -is the attraction energy of an atom for another electron.

The smaller the radius, the stronger the attraction of the electrons, the more it wants to attract more electrons, so the higher the electron affinity.
The larger the radius, the weaker the attraction of electrons, so the smaller the electron affinity.

Atoms that have full or ½ full orbitals will have unusually small electron affinities, since they are already stable and do not need to attract more electrons.
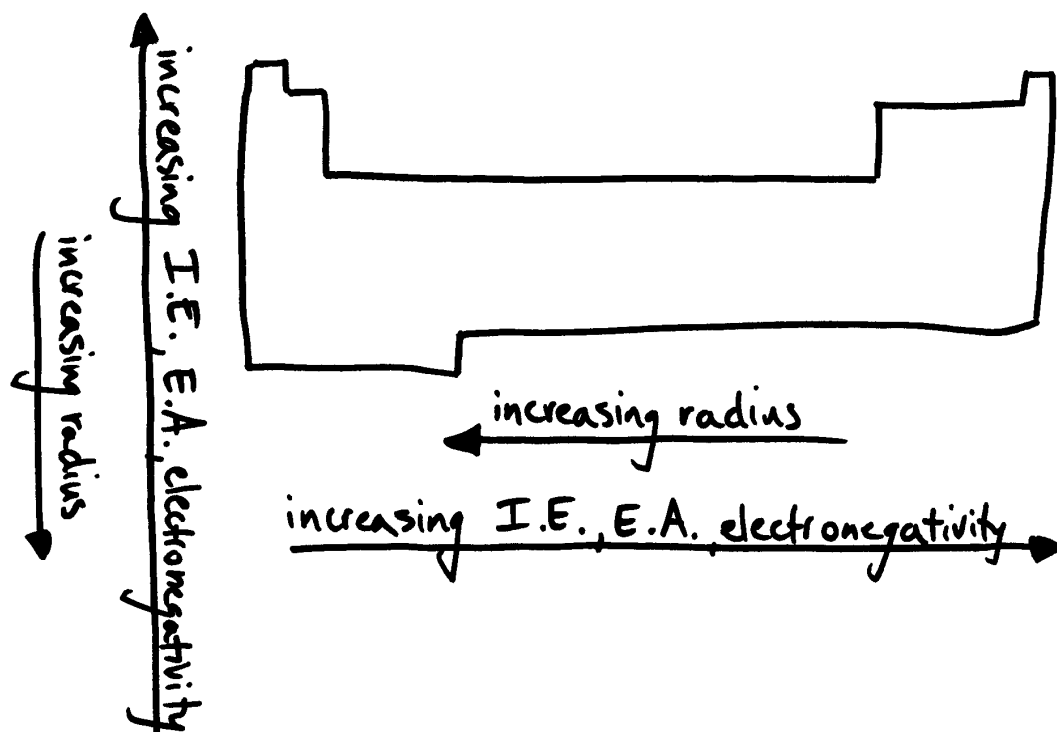
**Electron affinity is (-) {exothermic}, since energy is released as electrons are gained and the atom becomes more stable.
Big (-) # = large electron affinity = highly exothermic

D. Electronegativity
- is the ability of an atom, **in a molecule,** to attract shared electrons to it.

Small radius, strong electron attraction, large electronegativity.

Most Active Metal (Most Metallic)   Most Active Nonmetal (Least Metallic)
(Metals lose electrons)   (Nonmetals gain electrons)
Loses electrons the best!   Gains electrons the best!
Lowest Ionization Energy   Highest Electron Affinity
Largest Radius: Bottom/Left on Table Smallest Radius: Top/Right (excluding noble gases)
         Fr   **F**

Ionization Energy (should be increasing as radius decreases, to the right)

C	N	O	F
1086	1402	1313	1681

N is ½ full, stable and doesn't want to <u>lose any e</u> (<u>very high</u> ionization energy).

Electron Affinity (should be increasing as radius decreases, to the right)

C	N	O	F
-122	0	-141	-328

N is ½ full, stable and doesn't want to <u>gain any e</u> (<u>very low</u> electron affinity).

<u>*End of Notes*</u> (Assignments #50-51 are Review Assignments. There are no notes for these assignments.)