
Unit#2
AP Chem
Topic#10
Structure (Atomic)

Student Edition

Atomic Theory
Topic#10

Light

Electromagnetic Radiation (EM Radiation)

- $c = \lambda \times \nu$ = wavelength (λ , lambda) x frequency (ν , nu)
- $c = \lambda \times \nu = 2.998 \times 10^8 \text{m/s}$

Max Planck

- Energy can only be gained/lost in whole number multiples of the quantity, $h\nu$
 - where h is Planck's constant, $6.626 \times 10^{-34} \text{J-s}$
 - $\Delta E = n h \nu$ (or $E_{\text{photon}} = h \nu = hc/\lambda$)
 - where n is an integer (1,2,3...)
 - quantization of energy (discrete packets called quanta)

Photoelectric Effect

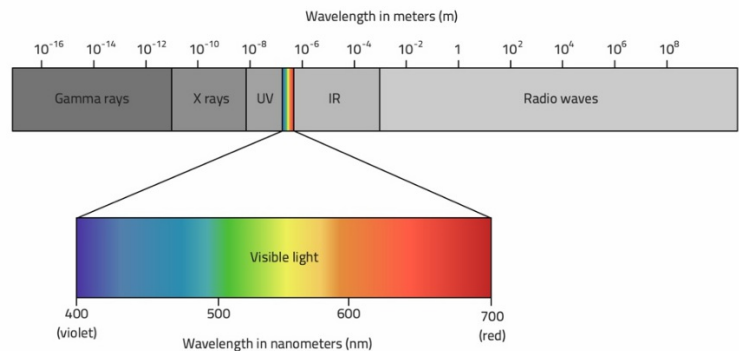
- Einstein proposed light can be thought of as a stream of "massless particles" called photons.
- Electrons are emitted from the surface of a metal when light of a specific frequency hits it.
 - De Broglie's equation, $\lambda = h/mv$
- Dual nature of light - particle and wave

gamma rays

short wavelength (λ)
high frequency (ν)
high energy (E)

radio waves

long wavelength (λ)
low frequency (ν)
low energy (E)



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Sample WS#1 - Atomic Frequency of EM Radiation

1. Calculate the frequency of red light of wavelength $6.50 \times 10^2 \text{ nm}$.

(Ans: $4.61 \times 10^{14} \text{ Hz}$ (1/s))

GUN
 $\lambda = 6.50 \times 10^2 \text{ nm}$

NTK
 $c = \lambda \cdot \nu$
 $c = 2.998 \times 10^8 \text{ m/s}$

UNK
 $\nu = \underline{4.61 \times 10^{14} \text{ 1/s or Hz}}$

SOLVE: $6.50 \times 10^2 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}} = 6.50 \times 10^{-7} \text{ m}$

$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{6.50 \times 10^{-7} \text{ m}} = \boxed{4.61 \times 10^{14} \text{ 1/s}}$

2. What is the increment of energy (the quantum) that is emitted at $4.50 \times 10^2 \text{ nm}$ by CuCl?

(Ans: $4.41 \times 10^{-19} \text{ J}$)

GUN
 $\lambda = 4.50 \times 10^2 \text{ nm}$
 $(4.50 \times 10^{-7} \text{ m})$
 $(450 \times 10^{-9} \text{ m})$
 $\frac{\omega}{\eta}$

NTK
 $E = \frac{hc}{\lambda}$ where $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$

UNK
 $E = \underline{4.41 \times 10^{-19} \text{ J}}$

SOLVE: $E = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{(4.50 \times 10^{-7} \text{ m})} = \boxed{4.41 \times 10^{-19} \text{ J}}$

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3. Using de Broglie's equation, $\lambda = h/mv$, compare the wavelength for an electron (mass = 9.11×10^{-31} kg) traveling at a speed of 1.0×10^7 m/s with that of a ball (mass = 0.10 kg) traveling at 35 m/s (Ans: 7.27×10^{-11} m vs. 1.9×10^{-34} m)

$$\lambda = \frac{h}{mv}$$

$$m_{e^-} = 9.11 \times 10^{-31} \text{ kg}$$

$$m_{bb} = 0.10 \text{ kg}$$

$$v_{e^-} = 1.0 \times 10^7 \text{ m/s}$$

$$v_{bb} = 35 \text{ m/s}$$

$$h = 6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}$$

$$\lambda_{e^-} = \frac{h}{m_{e^-} v_{e^-}} = \frac{6.626 \times 10^{-34}}{(9.11 \times 10^{-31})(1.0 \times 10^7)} = 7.27 \times 10^{-11} \text{ m}$$

$$\lambda_{bb} = \frac{h}{m_{bb} v_{bb}} = \frac{6.626 \times 10^{-34}}{(0.10)(35)} = 1.9 \times 10^{-34} \text{ m}$$

Solve:

$$e^-: \lambda_{e^-} = \frac{6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}}{(9.11 \times 10^{-31} \text{ kg})(1.0 \times 10^7 \text{ m/s})} = 7.27 \times 10^{-11} \text{ m}$$

$$bb: \lambda_{bb} = \frac{6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}}{(0.10 \text{ kg})(35 \text{ m/s})} = 1.9 \times 10^{-34} \text{ m}$$

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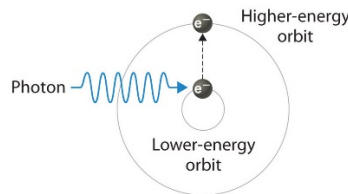
Light

Atomic Spectrum of Hydrogen

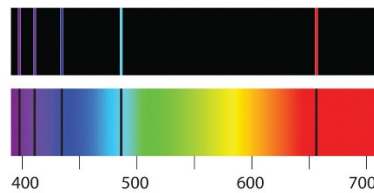
- **Continuous spectrum** - ROY G BIV
- **Line spectrum** - unique to each substance, photons of specific frequency (E) are formed when an electron "falls" from a higher energy state to a lower energy state, the movement "down" releases energy in the form of light (EM spectrum)

Bohr Model

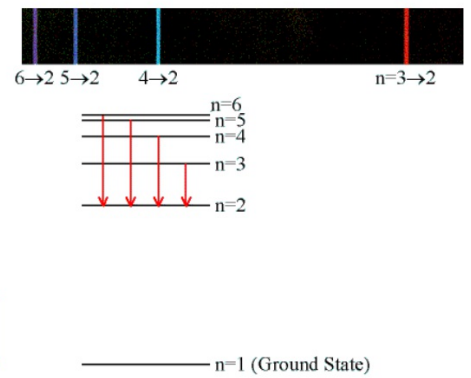
- Developed quantum model for H (a single electron of the H atom could occupy only certain energy states)
- Equation for the energy levels available for an electron in H: $E = -2.178 \times 10^{-18} \text{J} (Z^2/n^2)$
- Ground state – lowest energy state, $n = 1$
- $\Delta E = E_F - E_I$



(a) Electronic absorption transition



(b) H₂ emission spectrum (top), H₂ absorption spectrum (bottom)

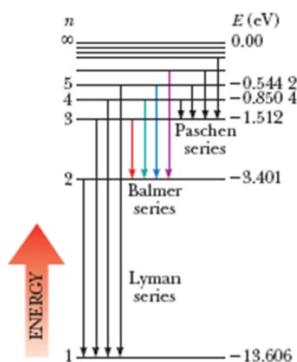


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$$\Delta E = E_F - E_I$$

$$E = -2.178 \times 10^{-18} \text{ J } (Z^2/n^2)$$



3. Calculate the energy required to excite the hydrogen electron from level $n = 1$ to level $n = 2$. Also calculate the wavelength of light that must be absorbed by hydrogen atom in its ground state to reach this excited state.

(Ans: $1.633 \times 10^{-18} \text{ J}$, $1.216 \times 10^{-7} \text{ m}$)

$$E_i = n = 1$$

$$E_f = n = 2$$

Solve:

$$E = \frac{hc}{\lambda} \quad \Delta E = E_f - E_i$$

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

$$E_f = -2.178 \times 10^{-18} \text{ J } \left(\frac{1^2}{2^2} \right) = -5.445 \times 10^{-19} \text{ J}$$

$$\Delta E = -5.445 \times 10^{-19} - (-2.178 \times 10^{-18}) = 1.634 \times 10^{-18} \text{ J}$$

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (2.998 \times 10^8 \text{ m/s})}{(1.634 \times 10^{-18} \text{ J})}$$

$$\lambda = 1.21 \times 10^{-7} \text{ m}$$

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Light

$$\Delta E = E_F - E_1 \quad E = -2.178 \times 10^{-18} \text{J} (Z^2/n^2)$$

5. (OYO) Calculate the energy required to remove the electron from a hydrogen atom in its ground state. (Ans: $2.178 \times 10^{-18} \text{J}$)

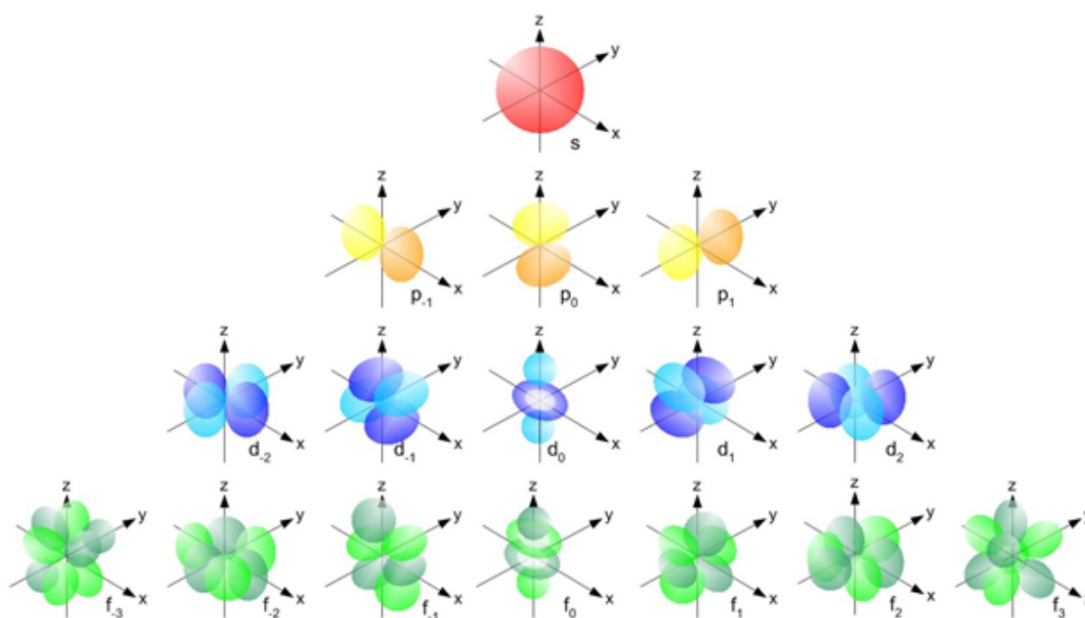
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Quantum-Mechanical Model of the Atom

Quantum Wave Mechanical Model of Atom

- Heisenberg Uncertainty Principle - cannot know position and momentum of a particle at the same time.
- Orbital - energy level where an electron can exist
- Quantum numbers
 - Principal quantum number, $n = 1$ to 7
 - Angular momentum quantum number (l) - shape (type) of orbital $l = 0$ (s), $l = 1$ (p), $l = 2$ (d), $l = 3$ (f)
 - Magnetic quantum number (m_l) - orientation of orbital in space
 - s -orbital - $m_l = 0$ 1 orbital with a maximum of 2 electrons
 - p -orbital - $m_l = -1, 0, 1$ 3 orbitals with a maximum of 6 electrons
 - d -orbital - $m_l = -2, -1, 0, 1, 2$ 5 orbitals with a maximum of 10 electrons
 - f -orbital - $m_l = -3, -2, -1, 0, 1, 2, 3$ 7 orbitals with a maximum of 14 electrons
 - Spin quantum number (m_s) - an electron spins clockwise (+1/2) or counterclockwise (-1/2)
 - Each electron has a unique set of four quantum numbers (n, l, m_l, m_s)



Different Shapes of Orbitals

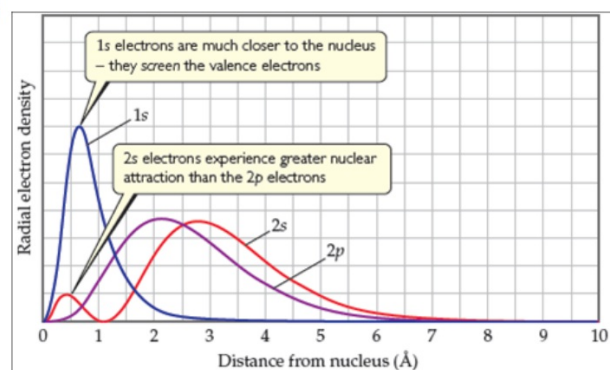
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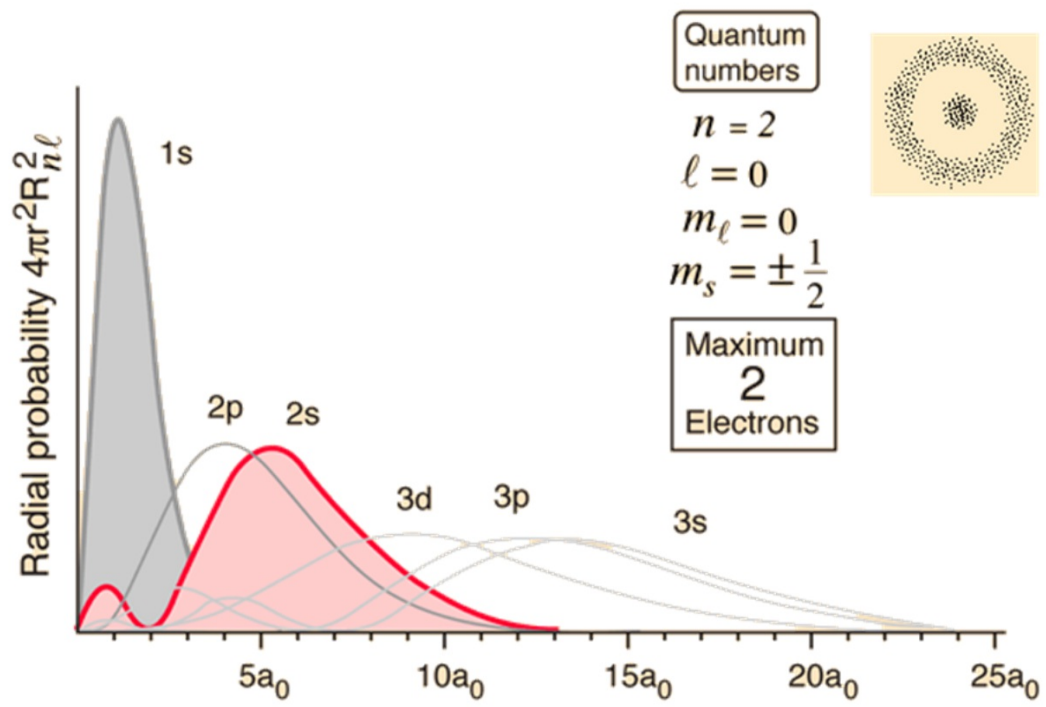
Quantum-Mechanical Model of the Atom

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Polyelectric Atoms - atoms with more than one electron

- $E_s < E_p < E_d < E_f$
- electrons "prefer" the orbitals in the order s, p, d , and then f
- Notice that $2p$ has its maximum probability closer to the nucleus than the $2s$
- But, notice the small hump of the $2s$ electron very close to the nucleus? This small amount of time when a $2s$ electron is near the nucleus.
- The $2s$ electron "penetrates" to the nucleus more than the $2p$
- Therefore, the $2s$ electron has a lower energy than the $2p$ electron.





Atomic Theory

History of the Periodic Table

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6. For principal quantum number $n = 5$, determine the number of allowable subshells (n), orbitals (n^2), and electrons ($2n^2$).

(Ans: 5 (s, p, d, f, and g), 25, and 50)

GVN
 $n = 5$

NTK
subshells = $n = 5$
orbitals = $n^2 = 5^2 = 25$
electrons = $2n^2 = 2(5^2) = 50$

UNK
subshells $\rightarrow 5$ (s, p, d, f, g)
orbitals $\rightarrow 25$
electrons $\rightarrow 50$

Electron Configurations

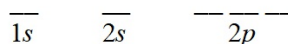
- **Aufbau Principle** - electrons move to lowest energy (Exceptions Cr, Mo, and W and Cu, Ag, and Au)
- **Pauli exclusion principle** - no two electrons can have the same four quantum numbers (two electrons per orbital with one having a +1/2 spin (\uparrow) and the other -1/2 spin (\downarrow))
- **Hund's rule** - lowest energy is when an atom has the lowest number of unpaired electrons (so, 1 electron in each orbital before a second can be added.)
- Elements in the same group have the same number of valence electrons ($ns^{1-2}np^{0-6}$)
- **Isoelectric** - ions that have the same electron configuration as the closest noble gas
 - N^{3-} , O^{2-} , F^{1-} , Ne, Na^{1+} , Mg^{2+} , and Al^{3+} all have the same electron configuration: $1s^2 2s^2 2p^6$ or $[He] 2s^2 2p^6$
- **Valence electrons** - outer s and p electrons of the atom
 - For example, N's valence electrons are $2s^2 2p^3$

Atomic Theory

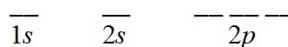
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- **Core electrons** - the inner electrons
 - For example, N's core electrons are $1s^2$
- **Noble Gas Electron Configuration** - replace inner core electrons with the symbol of the Noble gas symbol with brackets: $1s^2 2s^2 2p^3$ or $[He] 2s^2 2p^3$
 - these are the inner core electrons of the element
- **Paramagnetic** - when the species can be affected by a magnetic field.
- **Diamagnetic** - when a species cannot be affected by a magnetic field.

Nitrogen ($Z = 7$)



Nitride, N^{3-} ($7e^- + 3e^- = 10e^-$)



Atomic Theory Topic#10

Electron Configurations

7. Give the electron configuration, Noble gas (abbreviated) electron configuration, valence electrons, electron dot, and ion formed for sulfur, cadmium, hafnium, and radium.

Z	Electron Configuration	Nobel Gas (abbr) e^- configuration	Valence e^-	Electron Dot	Ion
S 16	$1s^2 2s^2 2p^6 3s^2 3p^4$	$[\text{Ne}] 3s^2 3p^4$	$3s^2 3p^4$	$\cdot\ddot{\text{S}}\cdot$	S^{2-}

$\frac{1L}{1s} \frac{1L}{2s} \frac{1L}{2p} \frac{1L}{3s} \frac{1L}{3p} \frac{1}{3p}$ paramagnetic

Zn 30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	$[\text{Ar}] 4s^2 3d^{10}$	$4s^2$	$\text{Zn}\cdot$	Zn^{2+}
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$\frac{1L}{1s} \frac{1L}{2s} \frac{1L}{2p} \frac{1L}{3s} \frac{1L}{3p} \frac{1L}{4s} \frac{1L}{3d} \frac{1L}{3d} \frac{1L}{3d} \frac{1L}{3d} \frac{1L}{3d}$
 diamagnetic

* 57 58 59 60 61 62 63 64 65 66 67 68 69 70
 La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb
 * 89 90 91 92 93 94 95 96 97 98 99 100 101 102
 Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No

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Electron Configurations

7. Give the electron configuration, Noble gas (abbreviated) electron configuration, valence electrons, electron dot, and ion formed for sulfur, cadmium, hafnium, and radium.

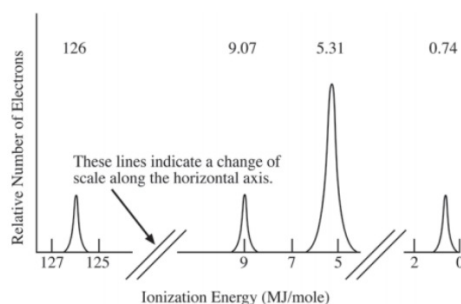
Z	Electron Configuration	Nobel Gas (abbr)	e ⁻ configuration	Valence e ⁻	Electron Dot	Ion																																																				
Hf 72	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^2$	[Xe]	$6s^2 4f^{14} 5d^2$	$6s^2$	Hf [•]	Hf ²⁺																																																				
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Atomic Theory

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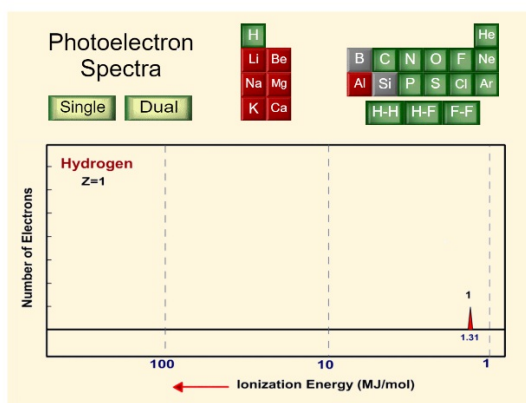
Photoelectron Spectroscopy

- **Photoelectron spectroscopy** is an experimental method used to determine the electronic structure of atoms and molecules.
- Photoelectron spectrometers ionize samples by bombarding them with high-energy radiation, such as UV or x-rays, and detecting the number and kinetic energy of ejected electrons.
- The frequency and energy of incident photons can be used to calculate the binding energy of the ejected electron using the following equation: $BE = h\nu - KE_{\text{electron}}$
 - In other words, $E_{(\text{x-ray photon})} = PE \text{ (BE; ionization } E) + KE \text{ (energy of ejected electron; } 1/2mv^2)$
- The PES spectrum is a graph of **electron count vs. electron binding energy**.
- The peaks in PES spectra correspond to the electrons in different subshells of the atom. The peaks with the lowest binding energy correspond to the valence electrons, while the peaks at the highest binding energy correspond to the inner-shell or core electrons.
- Ionization Energy - the energy needed to remove an electron from a gaseous atom
 - $A(g) + E \rightarrow A^+(g) + e^-$
 - $IE_n > \dots > IE_3 > IE_2 > IE_1$



Photoelectron Spectroscopy

Atomic Theory
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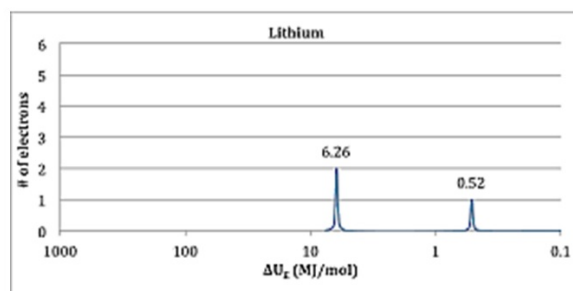
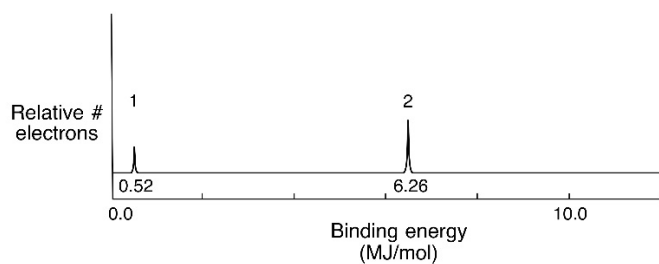


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Photoelectron Spectroscopy

Because electrons in a particular subshell of an atom have approximately the same binding energy, each peak in a PES spectrum corresponds to a subshell. To illustrate, let's first look at a simulated PES spectrum for lithium, Li. As we look at the spectrum, it will be useful to keep in mind the ground-state electron configuration for lithium, which is $1s^2 2s^1$.



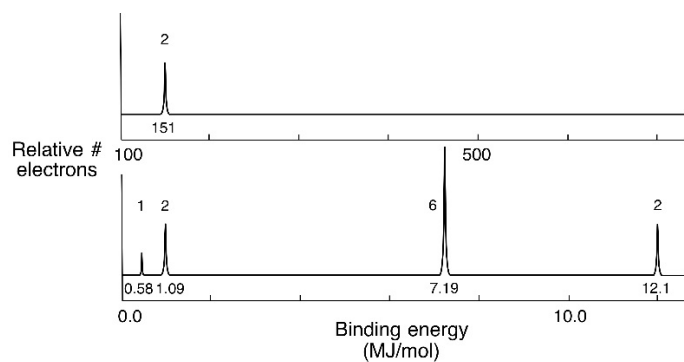
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Photoelectron Spectroscopy

Sample WS#2 - Atomic Frequency of EM Radiation

1. Identify the element represented by the PES spectrum. Write the electron configuration of the element. What is the first ionization energy for this element?



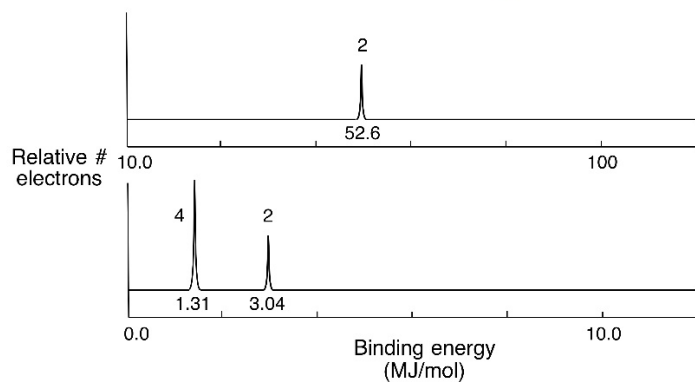
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Photoelectron Spectroscopy

Sample WS#2 - Atomic Frequency of EM Radiation

2. Identify the element represented by the PES spectrum. Write the electron configuration of the element. What is the first ionization energy for this element?



Atomic Theory
Topic#10

Periodic Table

Periodic Table

- History
 - Johann Dobereiner (Triads) < John Newlands (octaves) < Dmitrii Mendeleev & Julius Lothar Meyer (atomic mass) < Mosley (atomic number)
 - Group I (alkali metals, most reactive metals), Group II (alkaline metals), Group 17 (halogens, most active nonmetals), and Group 18 (noble gases, inert (unreactive))
 - Transition metals - fill *d* orbitals (NEVER use half filled sublevels as a reason for stability or energy, SAY instead the half-filled subshell MINIMIZES electron-electron repulsions which LOWERS the energy state of the atom!)
 - Rare Earth Metals (Inner transition metals) - fill *f* orbitals

Atomic Theory

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Periodic Trends

Periodic Trends (ALMOST always a FRQ question!)

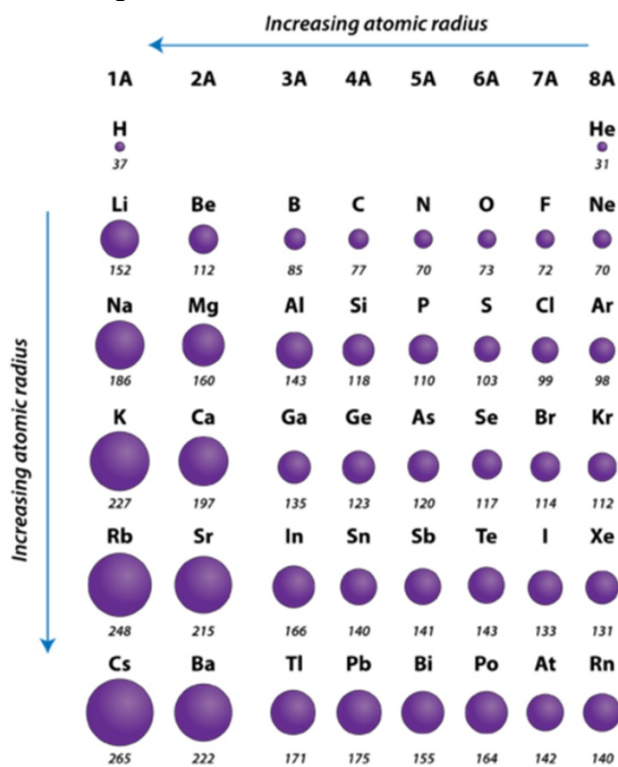
Arguments

1. Effective nuclear charge (Z_{eff}) - equal to group # (Group 1, Z_{eff} is 1) for groups 1 and 2. For groups 13-18, Z_{eff} is equal to group # - 10 (Group 13 is $13-10 = +3$ for core charge), the higher the Z_{eff} , the more positive the nucleus, the greater the positive (attractive) force is on electrons (coulombic force). (the higher the Z_{eff} , the more energy it takes to remove an electron or the smaller the atom's radius due to the nucleus pulling the outer electrons in closer). Used for **ACROSS** a period comparisons.
2. Distance - increased distance from the nucleus weakens the attractive coulombic force on the electron (need a lower amount of energy to remove). Used for **UP/DOWN** a group comparisons.
3. Shielding - the "shielding" of outer electrons from the nucleus by inner electrons. (Use only GOING UP OR DOWN a group NEVER across a period, use Z_{eff} and coulombic force for this). Used for **ACROSS** a period comparisons.
4. Minimize electron-electron repulsions - puts atom at a lower energy state (More stability).

Atomic Theory Topic#10

Periodic Trends

- **Atomic Radius** - the distance from center of nucleus to outer electron.
 - **Across** - increase in Z_{eff} results in a more positive charge in the nucleus which attracts electron cloud more strongly and "shrinks" atom (until electron-electron repulsion can overcome the attraction).
 - **Down** - an additional principal (n) energy level is added (attractive force on valence electrons decreases).

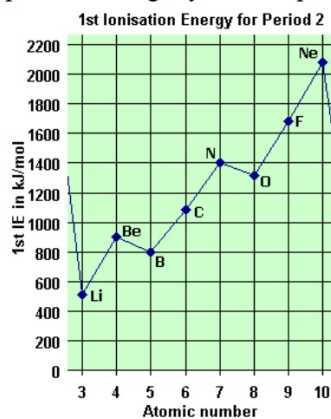


Atomic Theory

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Periodic Trends

- **Ionization Energy (IE)** - energy needed to remove an electron (atom in gas phase!), each electron removed needs more energy.
 - **Across** - increase in Z_{eff} results in a more positive charge in the nucleus which attracts electron cloud more strongly resulting in more energy needed to remove electron (increase of coulombic force of attraction).
 - **Down** - increased distance from nucleus and increased shielding means less energy needed to remove an electron (inner electrons shield outer from nucleus) (decrease of coulombic force of attraction).
 - When electron pairing first occurs in an orbital there is an **increases** electron-electron repulsion which results in a lower energy needed (I_E) to remove an electron. (Look at oxygen vs. nitrogen)
 - Look at s^2 vs p^1 , even though Z_{eff} is greater for the p electron, the removal of a p electron takes less energy than an s electron (Be vs. B).
 - p held less tightly because p electrons do not penetrate the electron cloud as well as an s electron.



Atomic Theory

Topic#10

Periodic Trends

- **Electron Affinity** - energy released when a gaseous neutral atom gains an electron ($A(g) + e^- \rightarrow A^-(g) + E$)
 - **across** - increases (energy released becomes MORE negative). An increase in Z_{eff} results in a more positive charge in the nucleus which attracts the electron cloud more strongly (stronger coulombic force of attraction), resulting in more energy released when an electron is accepted.
 - **down** - due to increased distance from nucleus and shielding of inner electrons with the addition of another energy level (n), the energy released is LESS negative.

1											13	14	15	16	17	18	
1 H -72.8																He ≥0	
2 Li -59.6	Be ≥0											B -27.0	C -121.8	N ≥0	O -141.0	F -328.2	Ne ≥0
3 Na -52.9	Mg ≥0											Al -41.8	Si -134.1	P -72.0	S -200.4	Cl -348.6	Ar ≥0
4 K -48.4	Ca -2.4	Sc -18	Ti -8	V -51	Cr -65.2	Mn ≥0	Fe -15	Co -64.0	Ni -111.7	Cu -119.2	Zn ≥0	Ga -40	Ge -118.9	As -78	Se -195.0	Br -324.5	Kr ≥0
5 Rb -46.9	Sr -5.0	Y -30	Zr -41	Nb -86	Mo -72.1	Tc -60	Ru -101.0	Rh -110.3	Pd -54.2	Ag -125.9	Cd ≥0	In -39	Sn -107.3	Sb -101.1	Te -190.2	I -295.2	Xe ≥0
6 Cs -45.5	Ba -14.0	La -45	Hf ≥0	Ta -31	W -79	Re -20	Os -104.0	Ir -150.9	Pt -205.0	Au -222.7	Hg ≥0	Tl -37	Pb -35	Bi -90.9	Po -180	At -270	Rn ≥0
7 Fr Ra Ac			Rf Db Sg Bh Hs Mt Ds Rg Uub Uut Uuq Uup														
Lanthanides			6	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides			7	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

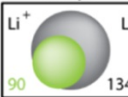
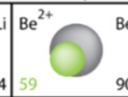
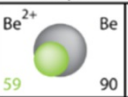
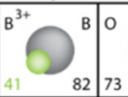
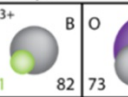
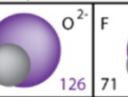
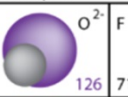
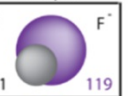
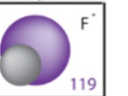


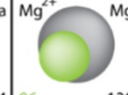
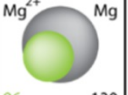
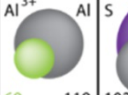
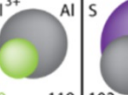
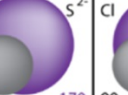
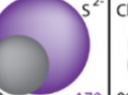

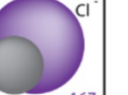

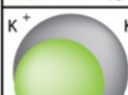
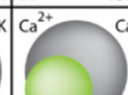
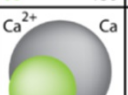
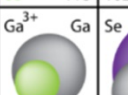
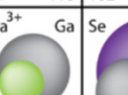
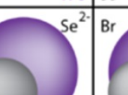
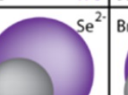
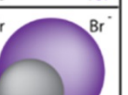
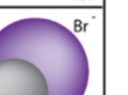

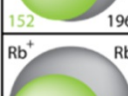
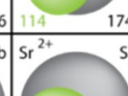

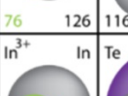
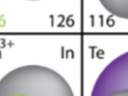
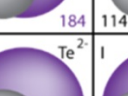
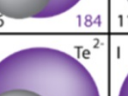
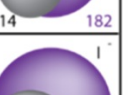
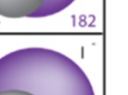

Atomic Theory

Topic#10

Periodic Trends

- **Ionic Radii** (generally follows atomic radius trend, except transition from metal ions to nonmetal ions a BIG jump in radii occurs!)
 - Cations shrink respective to their atoms (nucleus now attracting fewer electrons, Z_{eff} equal for ion and atom)
 - Anions expand respective to their atoms (nucleus now attracting more electrons, Z_{eff} equal for ion and atom and more electron-electron repulsions)
 - Isoelectric - ions containing the same number of electrons.

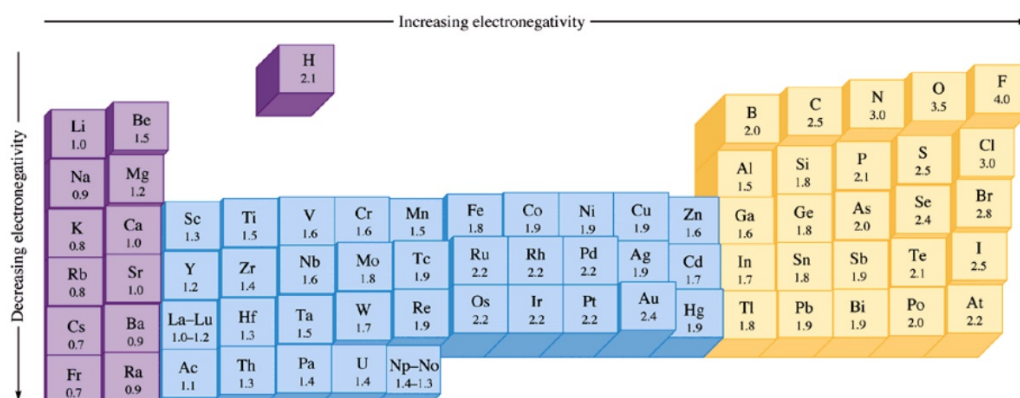
Size of Atoms and Their Ions in PM

Group 1		Group 2		Group 13		Group 16		Group 17	
Li ⁺  90	Li  134	Be ²⁺  59	Be  90	B ³⁺  41	B  82	O 	O ²⁻  126	F 	F ⁻  119
Na ⁺  116	Na  154	Mg ²⁺  86	Mg  130	Al ³⁺  68	Al  118	S 	S ²⁻  170	Cl 	Cl ⁻  167
K ⁺  152	K  196	Ca ²⁺  114	Ca  174	Ga ³⁺  76	Ga  126	Se 	Se ²⁻  184	Br 	Br ⁻  182
Rb ⁺  166	Rb  211	Sr ²⁺  132	Sr  192	In ³⁺  94	In  144	Te 	Te ²⁻  207	I 	I ⁻  206

Atomic Theory Topic#10

Periodic Trends

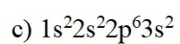
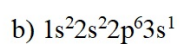
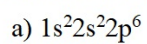
- **Electronegativity** - the ability of an atom in a MOLECULE to attract shared electrons to itself. (generally follows the ionization energy trend)
 - F most (4.0)
 - Why? Highest Z_{eff} and smallest so nucleus is closer to the bound electrons in the bond
 - cesium/francium least (0.7)
 - Why? Lowest Z_{eff} and largest so nucleus is farther away from the bound electrons in the bond.
 - Critical when describing bonding!



Atomic Theory
Topic#10

8. The first ionization energy for phosphorus is 1060kJ/mol, and that for sulfur is 1005kJ/mol. Why?

9. Consider the atoms with the following electron configurations:



Identify each atom. Which atom has the largest first ionization energy, and which one has the smallest second ionization energy? Explain your choices.

10. Predict the trend in radius for the following ions: Be^{2+} , Mg^{2+} , Ca^{2+} , and Ba^{2+} .