

# CH301 Unit 2

---

EXAM REVIEW: ATOMIC THEORY

USEFUL: [HTTP://MCCORD.CM.UTEXAS.EDU/COURSES/FALL2017/CH301/EXAM2.PHP](http://mccord.cm.utexas.edu/courses/fall2017/ch301/exam2.php)

KNOW YOUR POLYATOMICS!

<http://mccord.cm.utexas.edu/courses/fall2017/ch301/exam2.php>

KNOW LYMAN AND BALMER SERIES!

# Learning Objectives – Unit 2

---

Perform quantitative calculations based on the relationship between wavelength, energy, and the speed of light.

Identify and rank the different types of radiation which comprise the electromagnetic spectrum.

Explain why classical mechanics doesn't describe electromagnetic radiation.

Describe the photoelectric effect and relate the energy and/or intensity of the photons to the work function and kinetic energy of the ejected electrons.

Explain the origin of atomic and emission spectra and relate these spectra to discrete energy levels.

Apply the Rydberg formula to predict the energy of transitions between fixed energy levels in the hydrogen atom.

Explain that quantum mechanics is a mathematical model, the solutions of which yield wave functions and energies.

List the possible combinations of quantum numbers that are allowed.

State the atomic orbital names based on quantum numbers.

Explain that a wave function can be used to calculate a radial distribution function that describes the probability of an electron as a function of distance away from the nucleus

Distinguish between one-electron systems and multi-electron systems.

Apply the Aufbau principle to determine the configuration for any atom or ion.

Relate the electronic configuration of an element to its position on the periodic table.

Recognize that there are exceptions to the Aufbau principle and predict where on the periodic table these are likely to occur.

Apply Hund's Rule and the Pauli Exclusion Principle to

determine electron configuration using an orbital diagram (electrons in individual orbitals with spins).

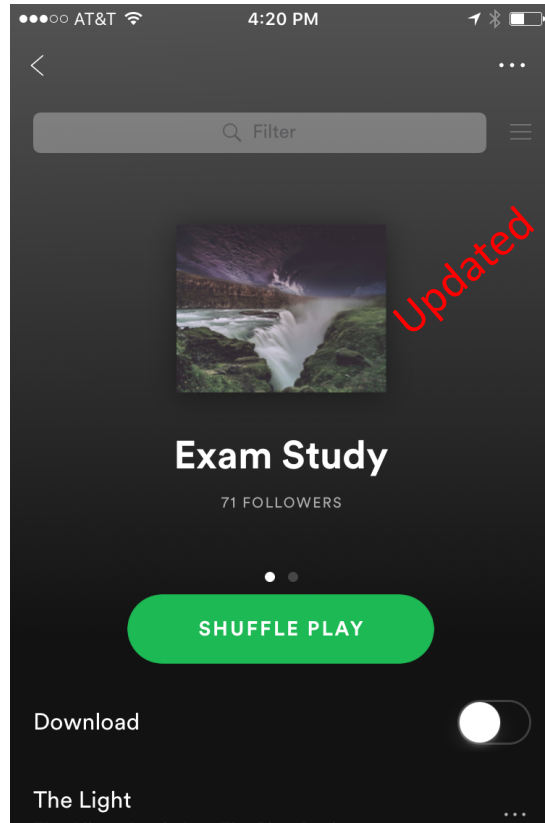
Fill an electron atomic orbital diagram and determine whether the element is paramagnetic or diamagnetic.

Apply the shell model of multi-electron atoms to describe the concept of core vs. valence electrons.

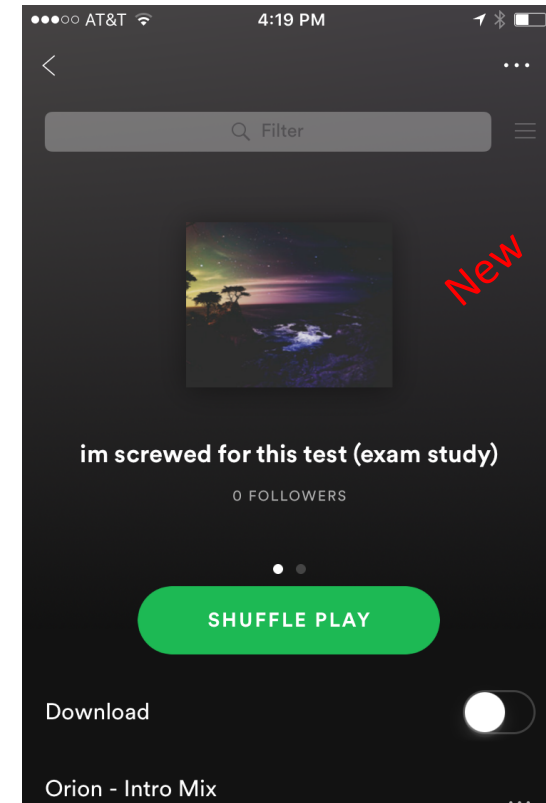
Describe the organization of the periodic table and the characteristics of elements in different regions of the table.

Describe the concept of electronic shielding and effective nuclear charge ( $Z_{\text{eff}}$ ) and their relationship to trends in ionization energy, atomic radii, and ionic radii.

# Most Important Exam Announcement:



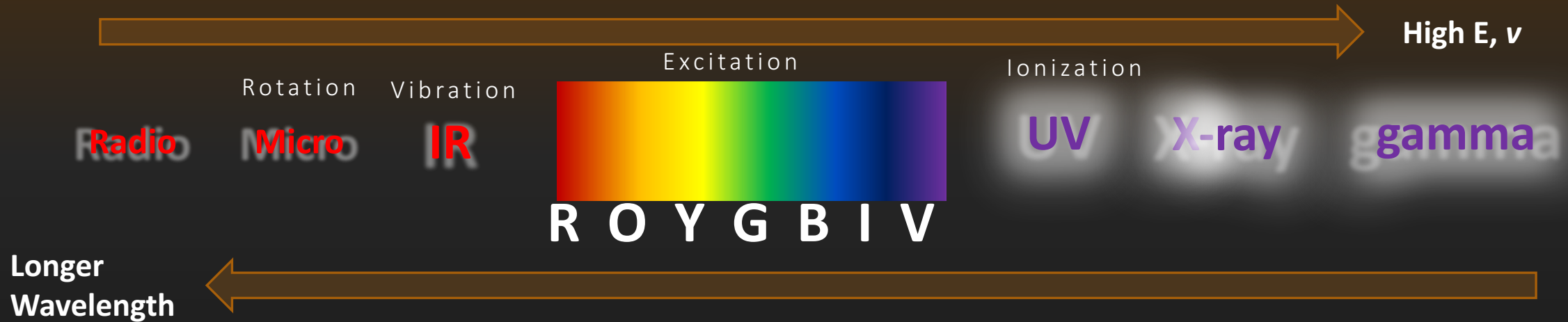
“I’m going to have a chill study session tonight because I’m already prepared”



In case you need to stay away for 4+ hours past your bedtime

$$c = \lambda\nu ; E_{\text{photon}} = h\nu ; E_{\text{photon}} = \frac{hc}{\lambda}$$

## THE ELECTROMAGNETIC SPECTRUM



- Microwaves: enough energy to begin rotating a molecule
- IR: enough energy to begin vibrating a molecule
- Visible (700nm to 400nm): enough energy to begin exciting electrons
- UV and beyond: begins the full ionization (breaking) of electrons/bonds

\*: know how to make calculations  
\*: understand conceptually only  
\*: understand how to model the equation (PIB and RDF)

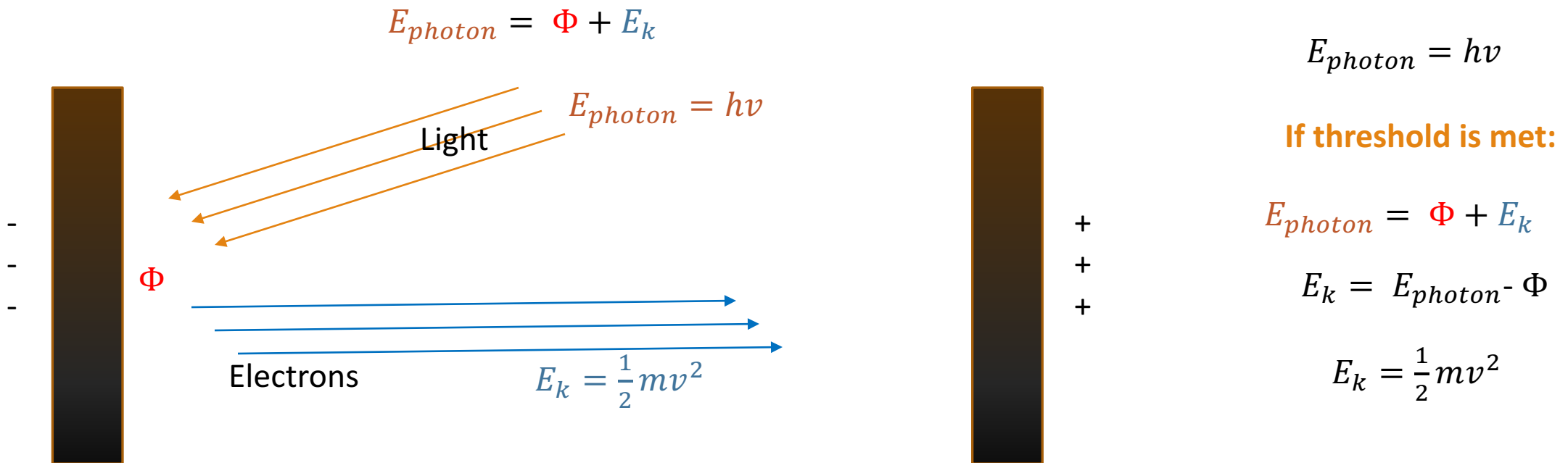
# Quantum Mechanics: Evidence

---

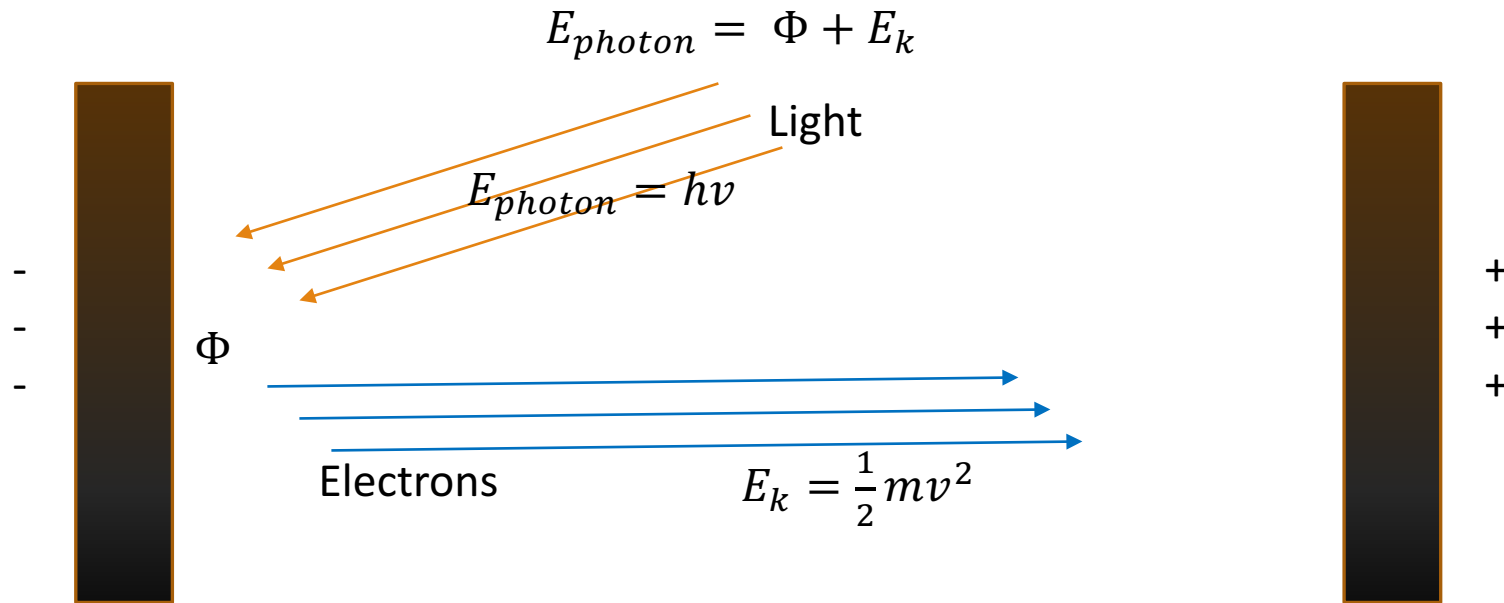
1. Electrons exist in **discrete, quantifiable energy states**.
  - **Absorption/Emission spectra**: The line spectra for a given gas has characteristic wavelengths \*
2. Electrons and light (photons) exhibit **wave-particle duality**.
  - **Photoelectric effect**: Light can act like particles (photons): \*
  - Light of sufficient energy interacts with matter by ejecting electrons from a metal surface
  - **X-Ray diffraction**: Small particles (electrons) can act like waves \*
  - A perfect crystal will scatter incident x-rays into specific interference patterns
3. The location and behavior of electrons can be described only with **probabilities**.
  - **The Schrödinger Equation**: Uses an understanding of probabilities and uncertainty to give us useful information about the electrons of an atom, such as the 4 quantum numbers ( $n$ ,  $l$ ,  $m_l$ , and  $m_s$ ) \*

# Quantum Mechanics: Photoelectric Effect

- **Photoelectric Effect:** a metal will eject electrons if a beam of light reaches a threshold energy
  - Demonstrates how light can act as a particle when interacting with matter (the electrons of a metal)
  - Quantifies this interaction using the equations shown below:



# Quantum Mechanics: Photoelectric Effect



**Unit the work function is reached ( $E_{\text{photon}} < \Phi$ ):**

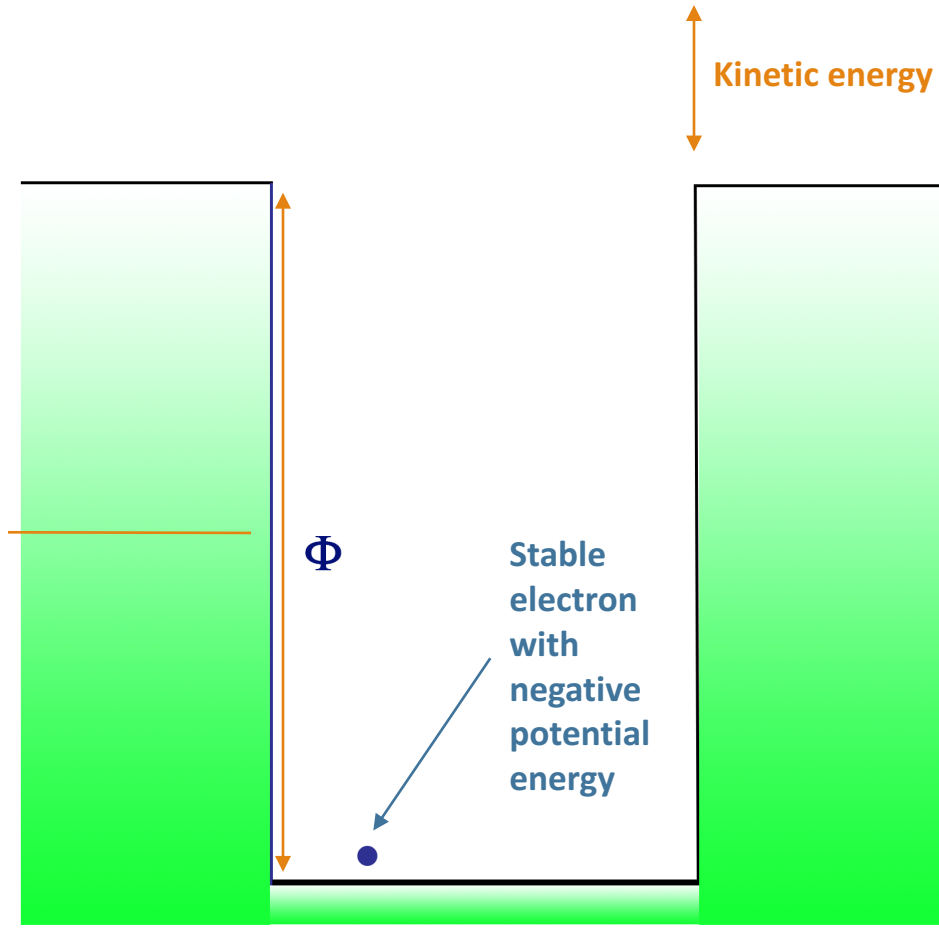
- **Increasing intensity has no effect**
- Note: photon energy is **NOT additive in terms of reaching the work function**. Two 2.5eV photons does NOT equal 5eV overall.

**IF THE WORK FUNCTION IS REACHED:**

- **Increasing intensity:**
  - Increases the number of emitted electrons
  - **Has NO EFFECT** on the kinetic energy/ velocity of the emitted electrons
- **Increasing the energy of the photon** (or increasing the frequency/decreasing the wavelength):
  - Increases the kinetic energy of the emitted electrons
  - Increases the velocity of the emitted electrons
  - **Has NO EFFECT** on the number of electrons

# Potential Energy Well

The “depth” of the potential energy well represents the amount of energy needed to release the electron from the metal



$$E_{\text{photon}} = \Phi + E_k$$

What's the point:

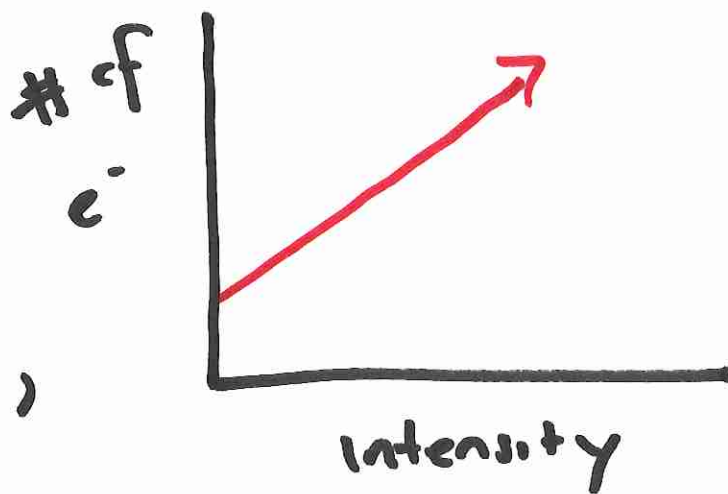
- $\Phi$  = work function; energy necessary to “dig the electron out of the well”
  - Specifically, this is the negative potential energy of the electron
- $E_k$  is the kinetic energy of the released electron AFTER the work function is reached
- $E_{\text{photon}}$  is the energy of the incident light



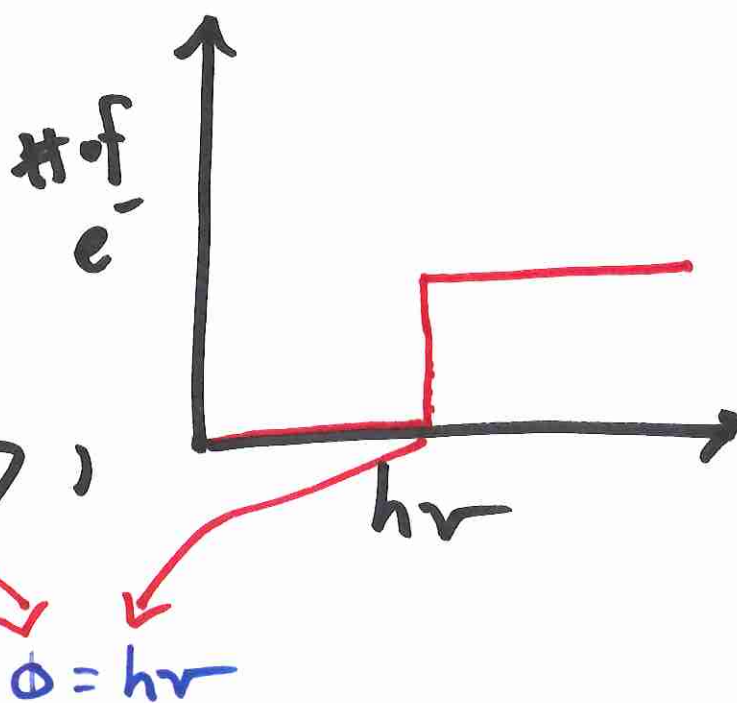
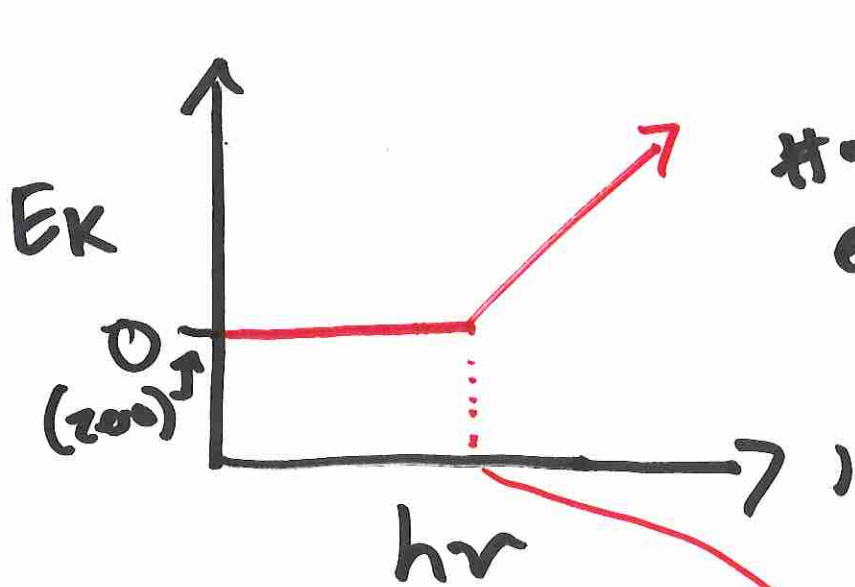
# Effect of brightness / intensity / # of photons

$\Phi$  not reached

$\Phi$  reached



# Effect of increasing Energy / increasing $\nu$ OR decreasing $\lambda$



$\Phi = h\nu$

# P.E. Effect

Photo electric Effect or Photoelectric Effect Effect?

if  $h\nu < \phi$ , nothing happens

↑  
Incident  
light

↑  
work  
function

hz

... MHz

$\times 10^9$

nm

$\times 10^{-9}$

m

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

$$E_{\text{photon}} = h\nu = \phi + E_k$$

Needs to be in J,  
provided as eV  
always

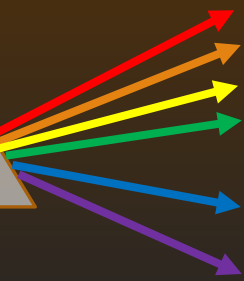
$$= \frac{1}{2}mv^2$$

kg

m/s

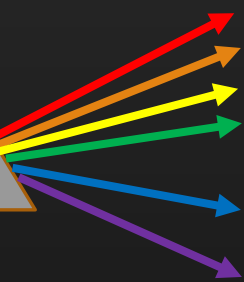
Point: Know your units; Practice

Pure white light with no interference



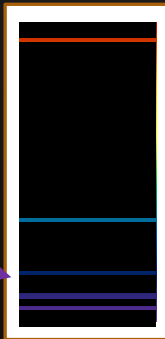
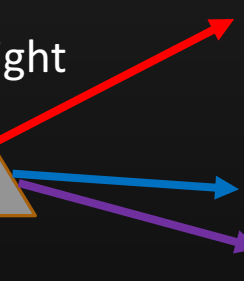
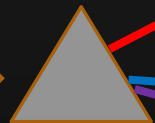
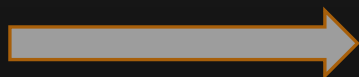
CONTINUOUS

Cold Gas Absorbs white light



ABSORPTION

Hot gas is the source of light



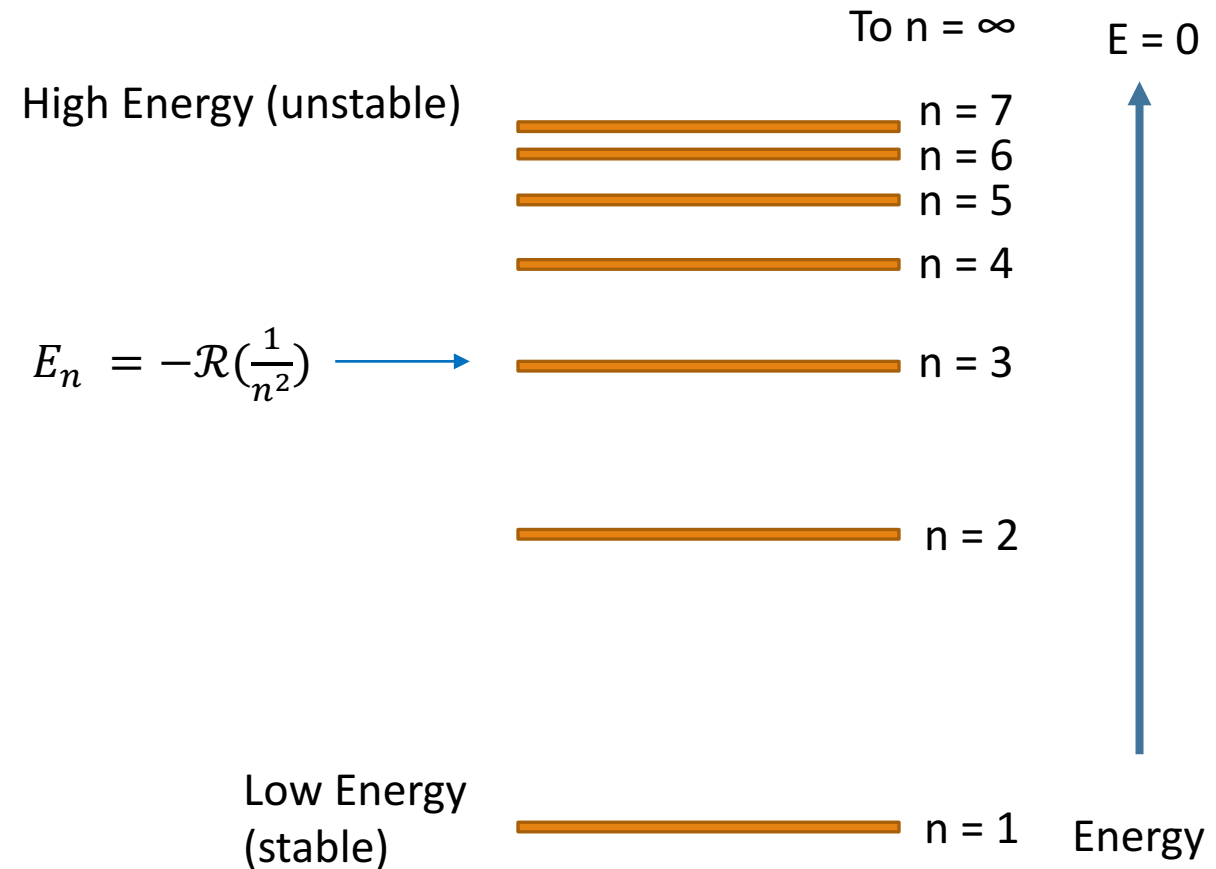
EMISSION

NOTICE HOW THESE ARE OPPOSITES FOR ANY GIVEN GAS. THIS IS EVIDENCE OF THE DISCRETE ENERGY LEVELS OF ELECTRONS

SPECIFIC GASES HAVE THEIR OWN DISCRETE ENERGY PATTERNS

# Quantum Mechanics: The Bohr Model

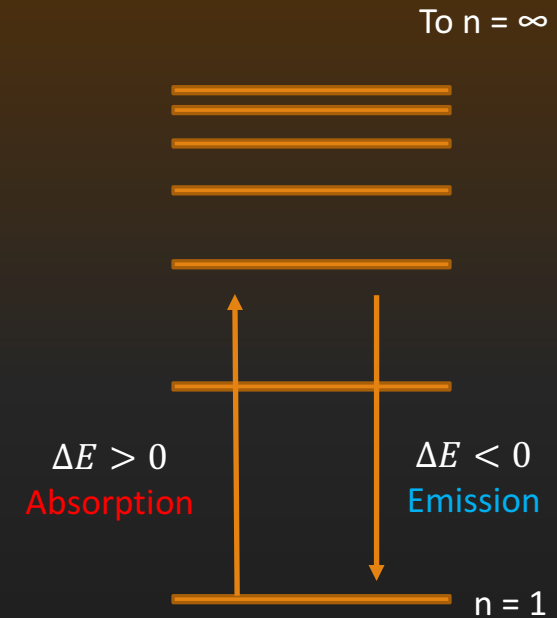
- The Bohr Model of the atom explained that electrons exist in “energy states,” which we now designate the letter “n.”
- You can understand n values by following these rules:
  1. n values begin at 1 (closest to the nucleus) and go to infinity (completely out of the influence of the nucleus/ free in space)
  2. The lower n value means more stable (most negative potential energy)
  3. The greatest energy difference between two **consecutive** numbers is 1 and 2.
- This model works only for one-electron systems (the hydrogen atom), and collapses due to electron repulsions for more complex atoms



# RYDBERG EQUATION

$$\Delta E = \mathcal{R} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad R = 2.18 \times 10^{-18} \text{J}$$

$$|\Delta E| = E_{\text{photon}} = h\nu = \frac{hc}{\lambda}^*$$



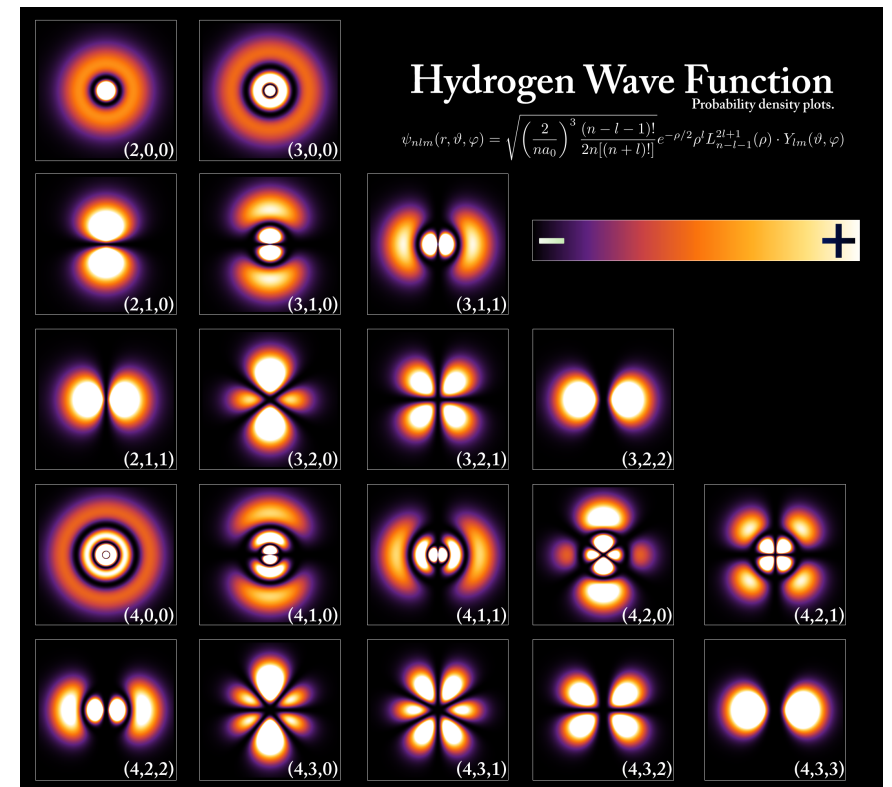
Electron energy level transition	Sign of $\Delta E$	Absorption/Emission ( $ \Delta E $ ) (Cause/Effect)
Low $n$ to high $n$	Positive (increasing energy)	Light absorbed
High $n$ to low $n$	Negative (decreasing energy)	Light emitted

\* The energy, wavelength, and frequency of the light are always positive

# Conceptual look into the Schrödinger Equation

$$\underbrace{-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2}}_{\text{kinetic energy}} + \underbrace{V(x)\psi}_{\text{potential energy}} = \underbrace{E\psi}_{\text{total energy}}$$

- The Schrödinger Equation gives us infinite wave functions (solutions) for the Hydrogen atom.
- The wave functions are classified by the quantum numbers:
  - Principle Quantum Number,  $n$  (Energy)
  - Angular Momentum Quantum Number,  $l$  (Shape)
  - Magnetic Quantum Number,  $m_l$  (Orientation)
- **This ultimately tells us the energy of an electron and the probable location of that electron in three dimensional space.**



# Schrödinger Equation

## Solutions:

□  $n, l, m_l$

Energy, Probability  
of location

## Equation

## Modeling the Equation:

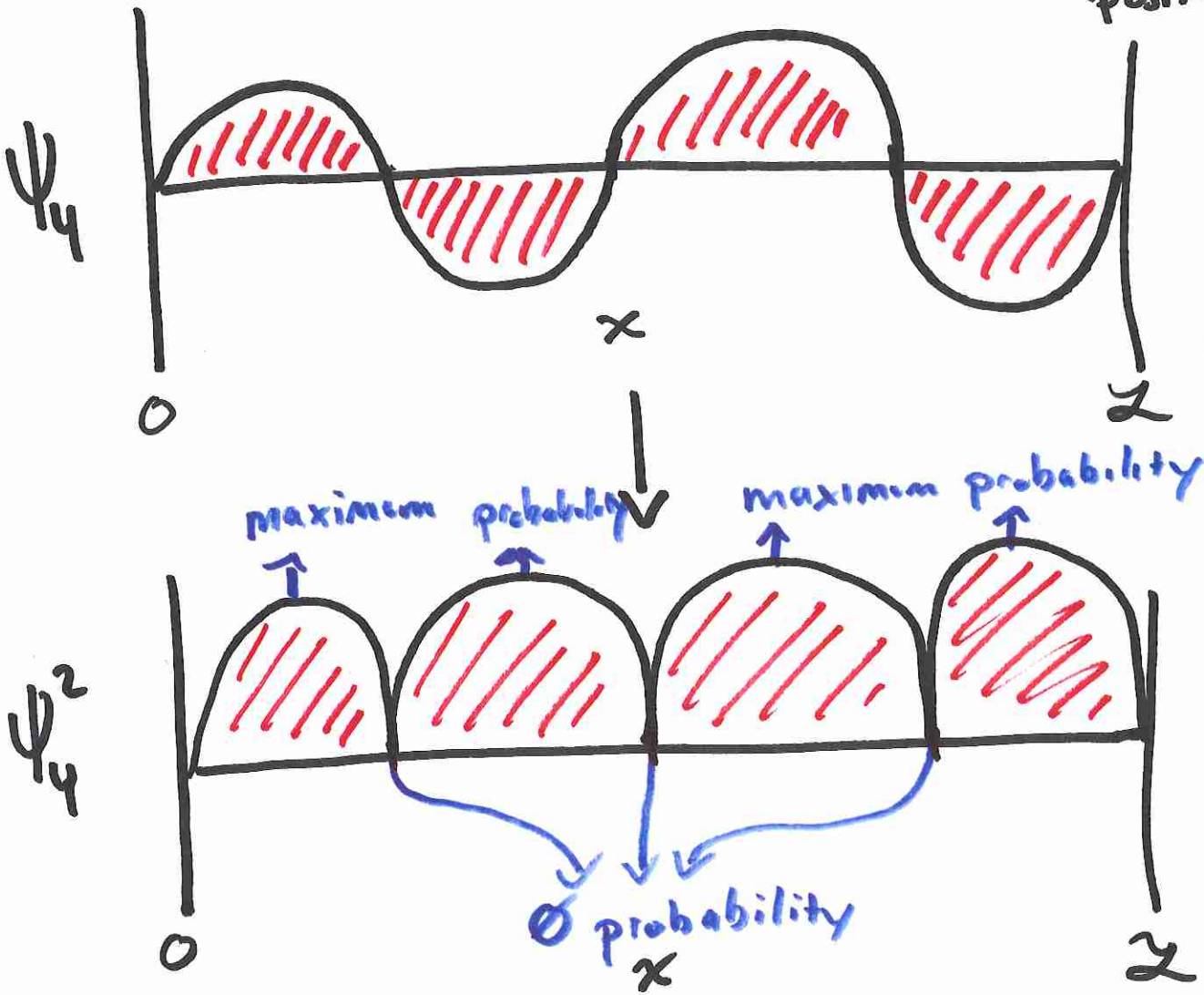
□ • Particle in a box  
(1D, 1 particle)

□ • Radial Distribution  
(Hydrogen atom,  
s-orbitals)

PIB: 1 particle, 1 dimension

# nodes =  $n-1$   
 # humps =  $n$

$\infty$  solutions,  
 positive, negative



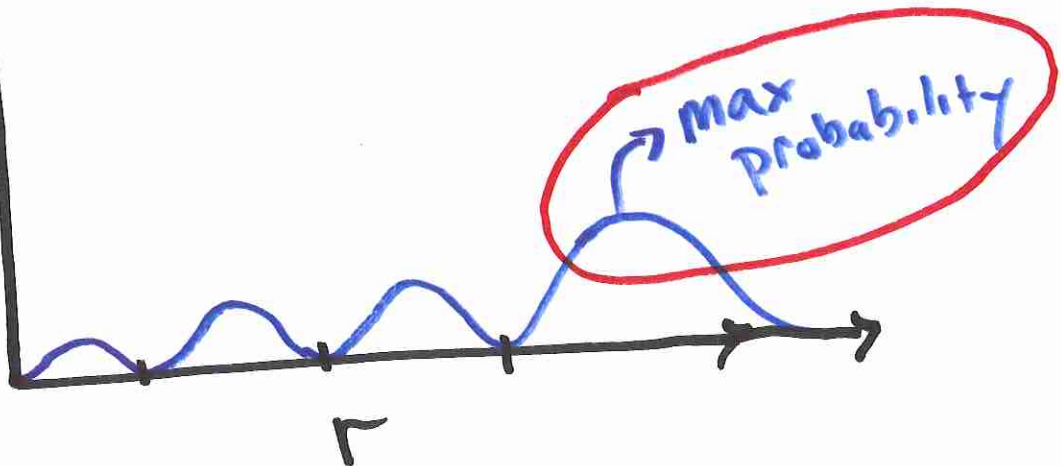
\* if you are given a value for  $L$ , give exact values for the nodes and peaks \*

RDF:  $1 e^-$ , Hydrogen

# nodes =  $n-1$   
 # distributions =  $n$

$4s$ :

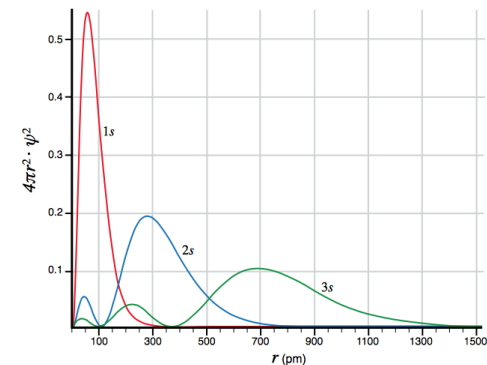
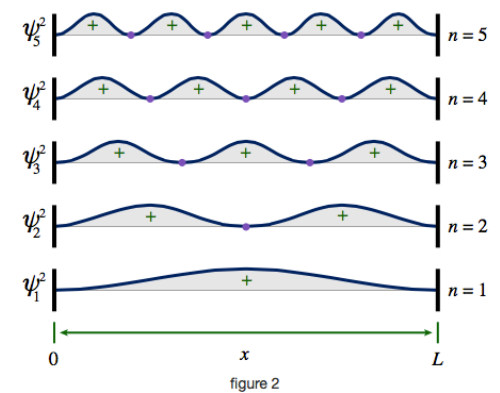
$4\pi r^2 \cdot \psi_4^2$





# Particle in a Box

- The Schrödinger Equation gives us insight to the **energy of an electron** and the **probability of finding that electron** (location, correlates with shape) in a given range of three dimensional space.
- Particle in a Box is useful because it conceptualizes the simplest solutions to the Schrödinger equation (1 particle, 1 dimension, no potential energy):
  - **Given any n-value, where can I find the particle?**  
Where is there zero probability of finding the particle?
- The Radial Distribution Function helps bring it all together in three-dimensional space by answering:
  - **Where are my electrons most likely to be found?**



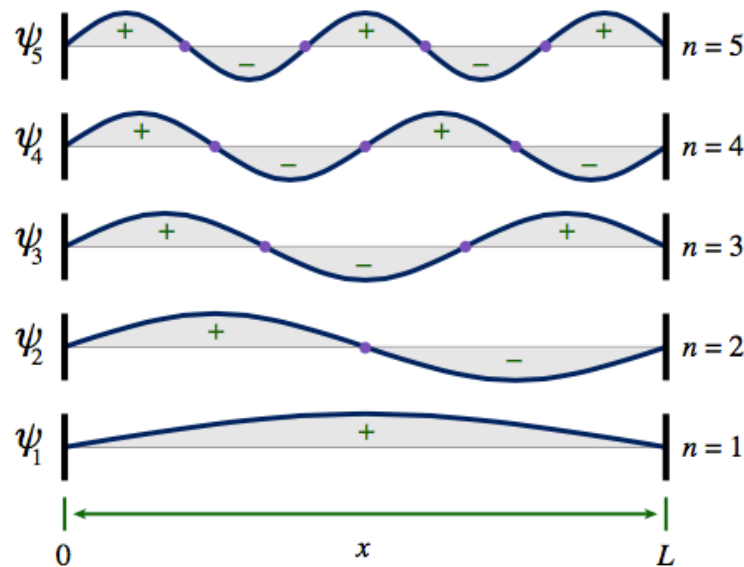
# Particle in a Box

## Some helpful rules:

- # of full wavelengths =  $n/2$
- # of distributions (“humps”) =  $n$
- # of nodes =  $n-1$

- Given any  $n$ -value, where can I find the electrons?
  - Where the graph gives you a non-zero value
- Where is there zero probability of finding an electron?
  - At the nodes ( $\psi=0$ )

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}\right) x$$



Multiply by  $\psi$  to  
get all positive  
values

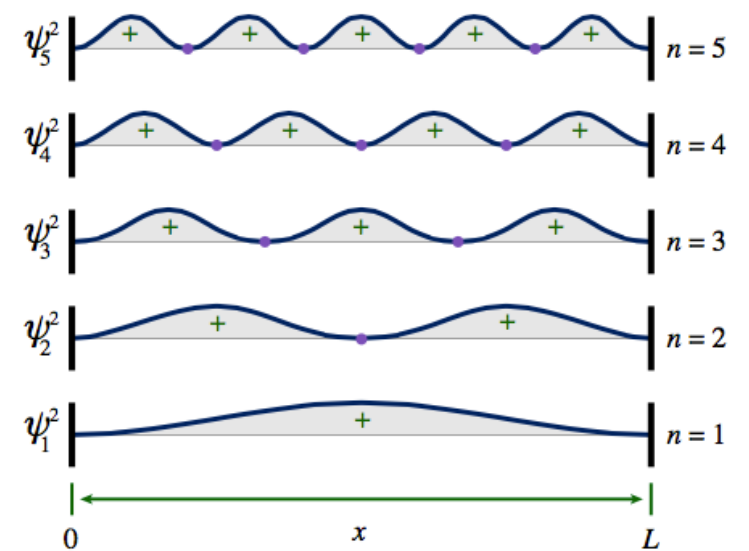
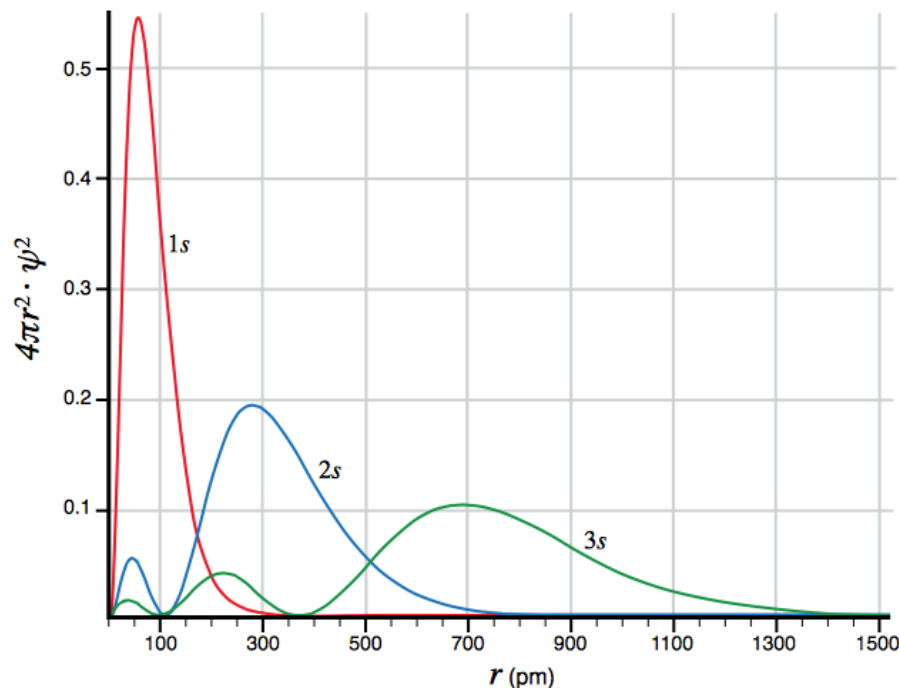


figure 2

**Node:** any time the sinusoidal function crosses from (-) to (+) or (+) to (-)

# Radial Distribution

- If we further apply this concept, we can answer the more specific question: where are the electrons **most likely** to be found?



- Radial distribution curves show the **same number of nodes** as particle in a box, but they also show the actual probability of finding an electron in **three-dimensional space**.
- The number of distributions is equal to the n-value. It is always most probably that electrons are found in the furthest hump from the nucleus ( $r=0$ )
- **Yes, you absolutely need to know this, but only for the s-orbitals of hydrogen**

# Quantum Numbers

---

- The Quantum Numbers ( $n$ ,  $l$ ,  $m_l$ , and  $m_s$ ) stem from the solutions of the Schrödinger Equation and represent the following:
  1. **Principle Quantum Number ( $n$ )**: the size and energy of the shell; mostly corresponds to the row of the periodic table (exception: d, f block).
  2. **Angular Momentum ( $l$ )**: the shape of the subshell; corresponds to the region on the periodic table.
    - $0 = s$  subshell;  $1 = p$  subshell;  $2 = d$  subshell;  $3 = f$  subshell
    - Depending on the question,  $l$  can signify the shape OR the shape can signify  $l$
    - **How do we get the shape? What  $l$  represents is the number of angular nodes. Knowing this can help determine the basic shape of even the most complicated orbitals (f, g, h, i, etc.)\***
  3. **Magnetic ( $m_l$ )**: the orbitals of the subshell; mathematically indicates the orientation of the subshell shape
    - The number of possible  $m_l$  values is equal to the number of orientations possible in space, which therefore represents the number of orbitals available
  4. **Spin Magnetic ( $m_s$ )**: the spin of the electrons in a subshell
    - Can equal  $\frac{1}{2}$  or  $-\frac{1}{2}$ , but all that really matters is that no two electrons in the same orbital have the same value


Total Nodes =  $n - 1$


Angular Nodes =  $l$

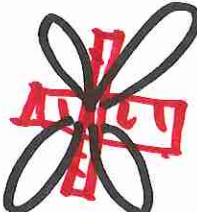
Spherical Nodes =  $n - l - 1$

# l, nodes, shape

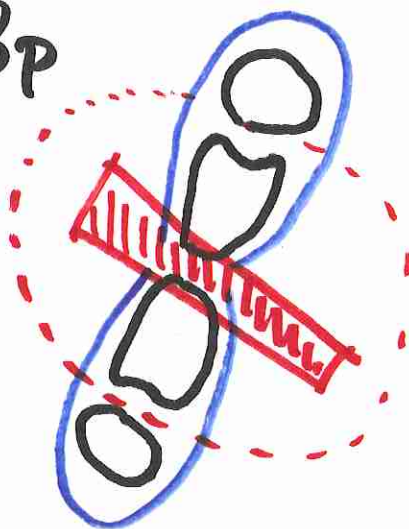
## Fundamental Shape:

1s  0 angular nodes  
sphere

2p  1 angular node  
(plane)  
dumbbell

3d  2 angular nodes  
(plane)  
complex

## Detailed Shape

3p  1 angular node,  
1 spherical node

For complex shapes: 5f, 6g, 7h... etc.

# angular nodes =  $l$

# spherical nodes =  $n - l - 1$

# total nodes =  $n - 1$

# Quantum Numbers: Rules

---

We are mostly interested in assigning possible quantum numbers to the electrons of a given species. To do this, we must understand the rules for assigning quantum numbers:

**Principle Quantum Number (n)** = 1,2,3, ...to  $n = \infty$

**Angular Momentum (l)** = 0,1,2,... to  $n-1$

**Magnetic ( $m_l$ )** = -l to l

**Spin Magnetic ( $m_s$ )** =  $\pm \frac{1}{2}$

**Example:**

If  $n = 4$

l can equal 0,1,2,3

$m_l$  can equal -3,-2,-1,0,1,2,3

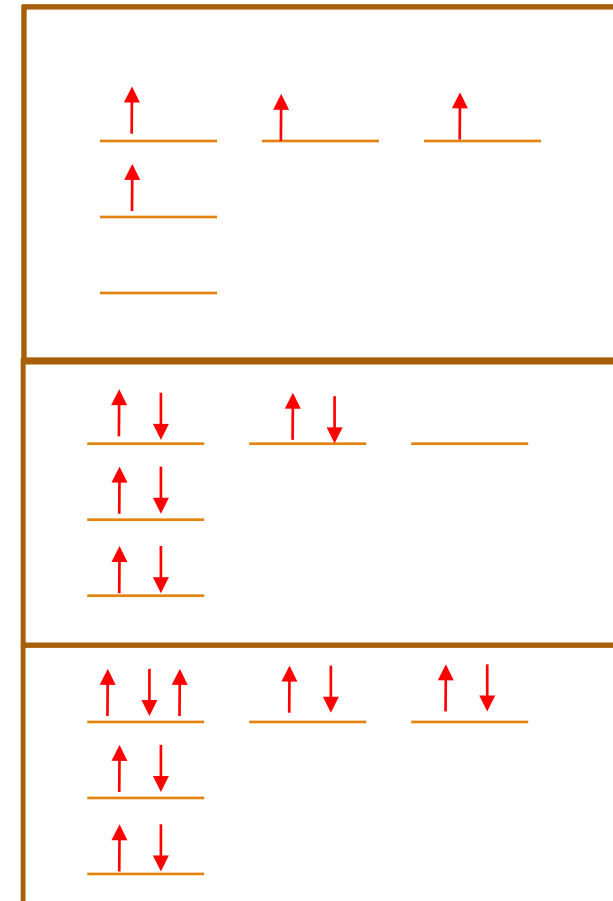
$m_s = +/- 1/2$

Ways to designate quantum numbers without saying it directly:

- “Highest energy electrons” = look at the last filled electrons. This will give you n and l.
- If we say 4s, we are giving you n (4) and l (s= 0)

# Electron Configurations: Rules

- There are three main rules to abide by when filling out electron configurations. It is important to follow these rules when doing your own electron configurations and be able to identify the rule that an incorrect electron configuration breaks
- **Aufbau Principle:** fill electrons from the bottom (lowest energy) up
- **Hund's rule:** fill each orbital in a given subshell with a single electron before doubling up
  - Technically this refers to the idea that you should maximize the multiplicity of your configuration
- **Pauli's Exclusion Principle:** no electrons can occupy the same orbital with the same spin and a maximum of two electrons can exist in a single orbital



Note:  
these are  
all  
examples  
of these  
rules  
violated

# PERIODIC TABLE: S, P, D, F BLOCKS

Exceptions

## Periodic Table of the Elements

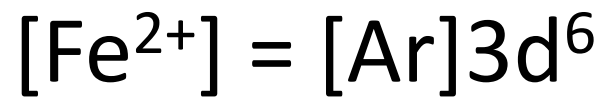
1A 1	2A 2											3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1 1 H 1.008																	2 2 He 4.003
2 3 Li 6.941	4 4 Be 9.012											5 5 B 10.81	6 6 C 12.01	7 7 N 14.01	8 8 O 16.00	9 9 F 19.00	10 10 Ne 20.18
3 11 Na 22.99	12 12 Mg 24.31	3B 3 3d	4B 4	5B 5	6B 6	7B 7	8B 8	9 9	10 10	1B 11	2B 12	13 13 Al 26.98	14 14 Si 28.09	15 15 P 30.97	16 16 S 32.07	17 17 Cl 35.45	18 18 Ar 39.95
4 19 K 39.10	20 20 Ca 40.08	21 21 Sc 44.96	22 22 Ti 47.87	23 23 V 50.94	24 24 Cr 52.00	25 25 Mn 54.94	26 26 Fe 55.85	27 27 Co 58.93	28 28 Ni 58.69	29 29 Cu 63.55	30 30 Zn 65.38	31 31 Ga 69.72	32 32 Ge 72.64	33 33 As 74.92	34 34 Se 78.96	35 35 Br 79.90	36 36 Kr 83.80
5 37 Rb 85.47	38 38 Sr 87.62	39 39 Y 88.91	40 40 Zr 91.22	41 41 Nb 92.91	42 42 Mo 95.94	43 43 Tc (98)	44 44 Ru 101.1	45 45 Rh 102.9	46 46 Pd 106.4	47 47 Ag 107.9	48 48 Cd 112.4	49 49 In 114.8	50 50 Sn 118.7	51 51 Sb 121.8	52 52 Te 127.6	53 53 I 126.9	54 54 Xe 131.3
6 55 Cs 132.9	56 56 Ba 137.3	57 57 La 138.9	72 72 Hf 178.5	73 73 Ta 180.9	74 74 W 183.8	75 75 Re 186.2	76 76 Os 190.2	77 77 Ir 192.2	78 78 Pt 195.1	79 79 Au 197.0	80 80 Hg 200.6	81 81 Tl 204.4	82 82 Pb 207.2	83 83 Bi 209.0	84 84 Po (209)	85 85 At (210)	86 86 Rn (222)
7 87 Fr (223)	88 88 Ra (226)	89 89 Ac (227)	104 104 Rf (267)	105 105 Db (268)	106 106 Sg (271)	107 107 Bh (272)	108 108 Hs (270)	109 109 Mt (276)	110 110 Ds (281)	111 111 Rg (280)							

4f	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
5f	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Yes, there are more exceptions. But not on the test.

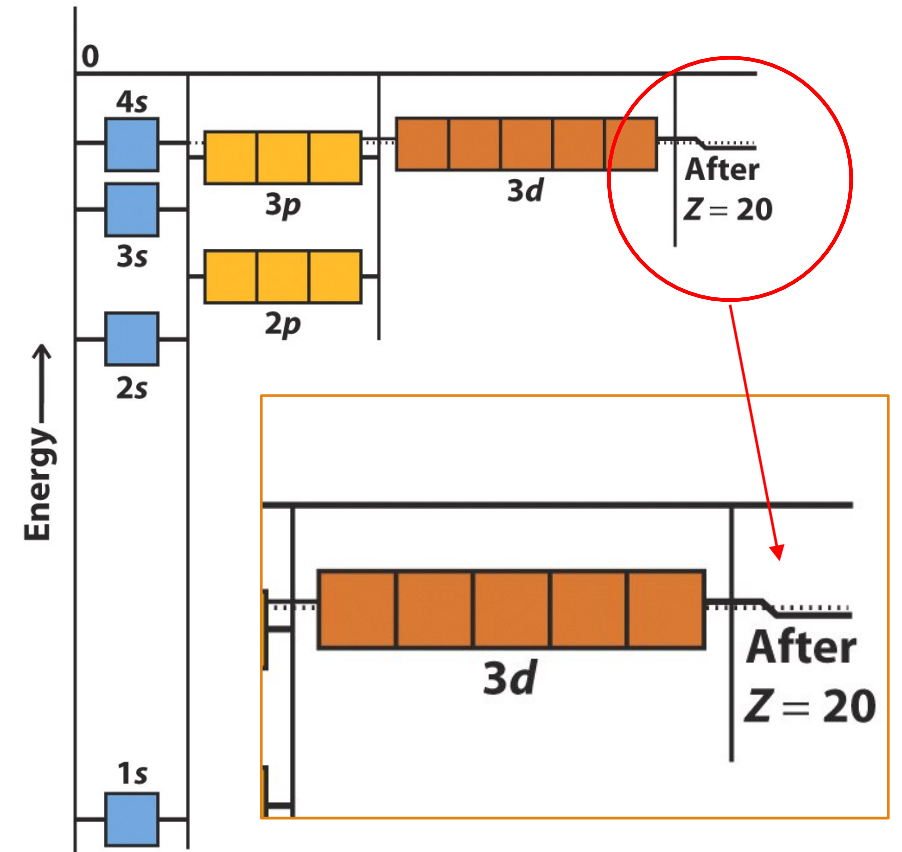


# Filling versus “Unfilling”



Why?

- When filling, use the “Aufbau” Order
- When “unfilling,” use the “Energy” Order
  - What’s the rule? Unfill the HIGHEST n value FIRST



# D-Block Exceptions

---



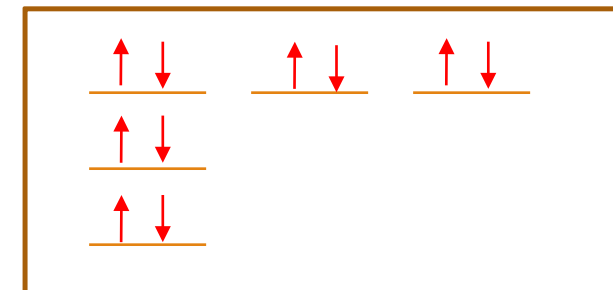
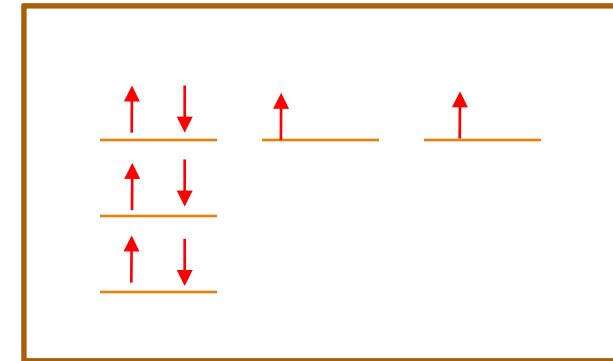
Why?

- The  $\frac{1}{2}$  filled s and fully filled d is more stable than the “non-exception” configuration
- The  $\frac{1}{2}$  filled s and  $\frac{1}{2}$  filled d is stable than the “non-exception” configuration

Know: Cu, Mo, Cr, Ag

# Magnetic Susceptibility

- **Paramagnetic:** If an atom or molecule has unpaired electrons, **it will be attracted to a magnetic field**
  - Remember: “un”-para = unpaired.
- **Diamagnetic:** if an atom or molecule has all paired electrons, **it will be repelled from a magnetic field**
  - Remember: “di” means “two” or “double” in Latin. Think two electrons in each orbital.
  - All odd number atoms are paramagnetic, but not all even number atoms are diamagnetic



# Basic Periodic Table Trends

---

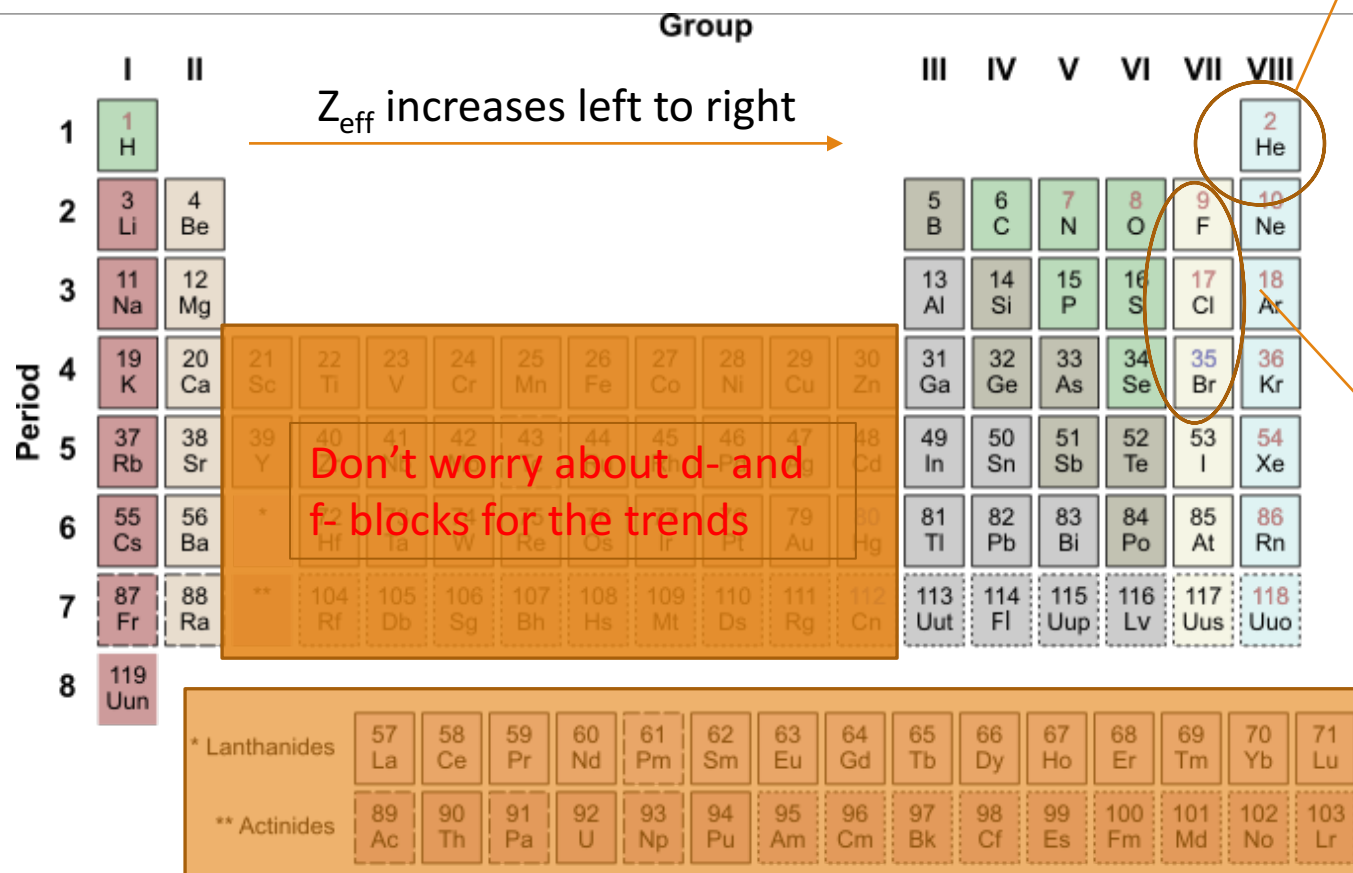
- Ionization Energy: the energy **required** to **remove an electron** from an atom in the gas phase \*
- Trend: generally increases going to the top right of the periodic table (**has notable exceptions**)
- Increases with each successive ionization (the second ionization energy is greater than the first, and so on)
- Electron Affinity: electron affinity is the energy **released** to **add an electron** to an atom in the gas phase \*
- Trend: Electron affinity does not follow a stable trend; however, it generally trends toward the top right of the periodic table.
- Atomic Radius: size of the nucleus and its electrons (most of the size is in the space taken up by the electron clouds)
  - Trend: increases as you go to the bottom left where shielding is maximized and  $z_{\text{eff}}$  is minimized
- $Z_{\text{eff}}$ : a measurement of the **pull of the outer (valence) electrons by the nucleus**
  - Trend: increases as you go from left to right across a period
  - For ground state atoms,  $Z_{\text{eff}}$  is simply the group number

# Periodic Trends

Helium has the maximum ionization energy

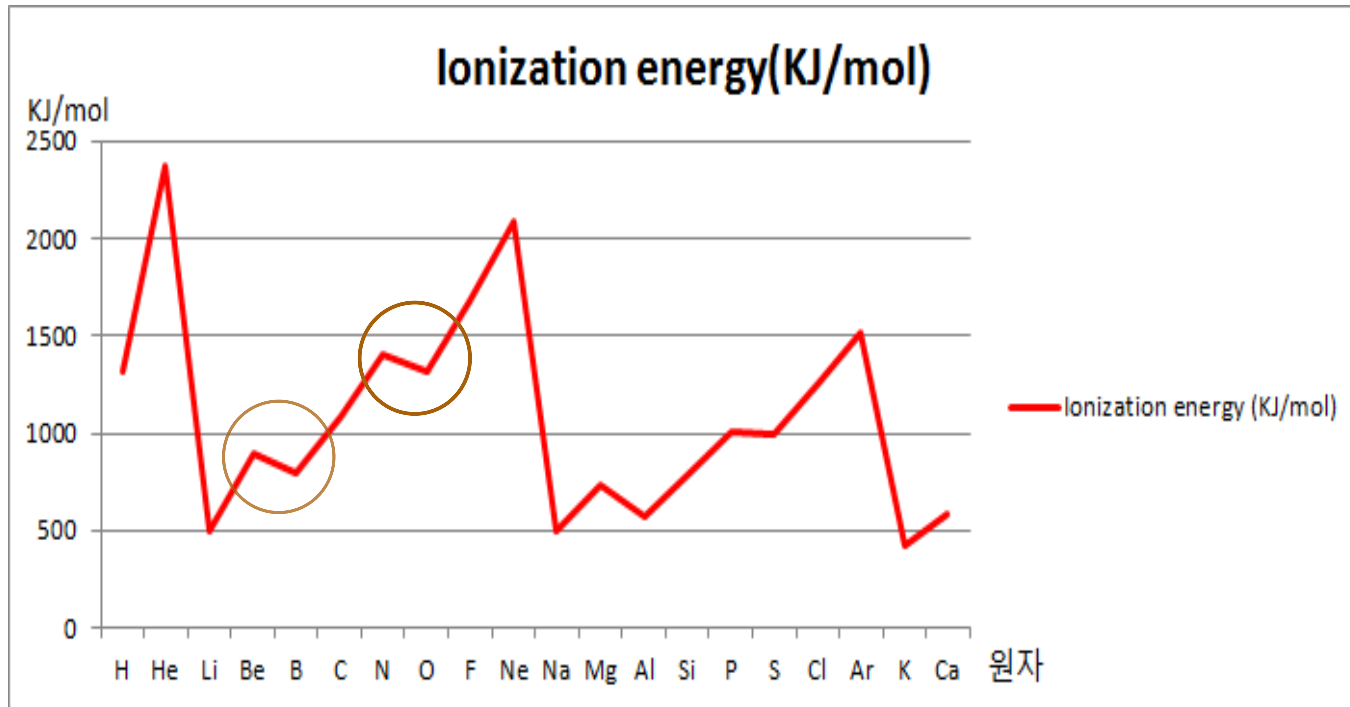
TOP RIGHT: High ionization energy, high electron affinity, small radius

The halogens have the highest electron affinity

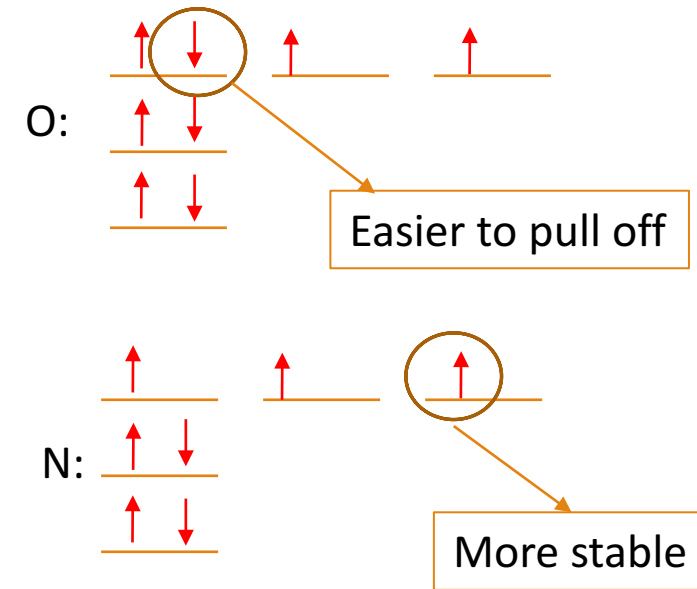


Bottom Left: Low ionization energy, low electron affinity, large radius

# Ionization Energy Exceptions



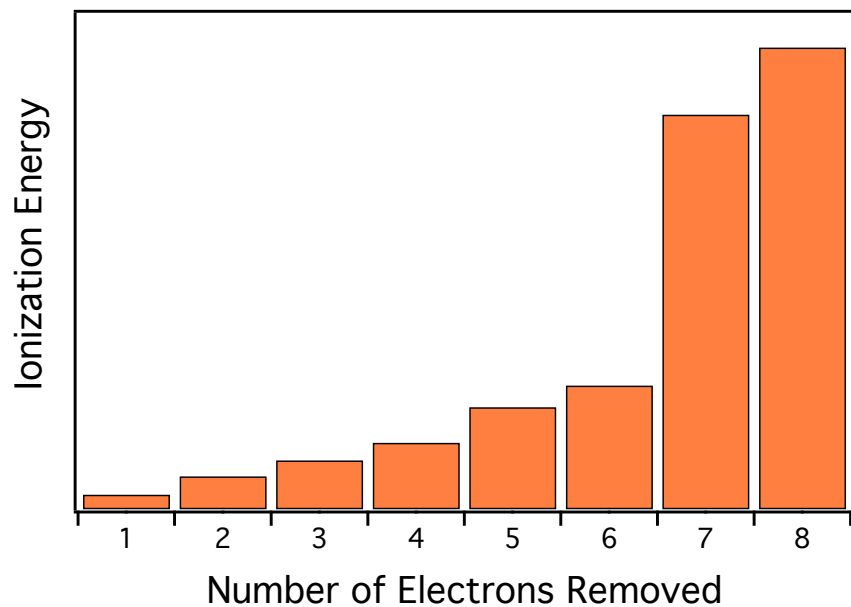
WHY?



The "special" quantum mechanical stability of a fully filled s or p orbital, or a half-filled p orbital, causes exceptions to the trend of ionization energy

Note: all S atoms in these equations are in the gas state

# Successive Ionization Energies



Energy increases for each successive ionization energy for the same atom

Big jump in IE means  $M^{6+}$  is most likely the noble gas configuration

1.  $S \rightarrow S^+ + e^-$
2.  $S^+ \rightarrow S^{2+} + e^-$
3.  $S^{2+} \rightarrow S^{3+} + e^-$
4.  $S^{3+} \rightarrow S^{4+} + e^-$
5.  $S^{4+} \rightarrow S^{5+} + e^-$
6.  $S^{5+} \rightarrow S^{6+} + e^-$
7.  $S^{6+} \rightarrow S^{7+} + e^-$
8.  $S^{7+} \rightarrow S^{8+} + e^-$

# Ionic Radius

Note on this diagram:  
 Neutral atoms are grey  
 Cations are red  
 Anions are blue

## Last year's exam:

For an isoelectronic series of ions, the ion that is the smallest is always

1. the ion with the highest atomic number.  
**correct**
2. the ion with the most electrons.
3. the ion with the most neutrons.
4. the ion with the fewest protons.
5. the least positively (or most negatively) charged ion.

Sizes of atoms and their ions in pm

Group 1		Group 2		Group 13		Group 16		Group 17	
Li <sup>+</sup> 90	Li 134	Be <sup>2+</sup> 59	Be 90	B <sup>3+</sup> 41	B 82	O <sup>2-</sup> 73	O <sup>2-</sup> 126	F <sup>-</sup> 71	F <sup>-</sup> 119
Na <sup>+</sup> 116	Na 154	Mg <sup>2+</sup> 86	Mg 130	Al <sup>3+</sup> 68	Al 118	S <sup>2-</sup> 102	S <sup>2-</sup> 170	Cl <sup>-</sup> 99	Cl <sup>-</sup> 167
K <sup>+</sup> 152	K 196	Ca <sup>2+</sup> 114	Ca 174	Ga <sup>3+</sup> 76	Ga 126	Se <sup>2-</sup> 116	Se <sup>2-</sup> 184	Br <sup>-</sup> 114	Br <sup>-</sup> 182
Rb <sup>+</sup> 166	Rb 211	Sr <sup>2+</sup> 132	Sr 192	In <sup>3+</sup> 94	In 144	Te <sup>2-</sup> 135	Te <sup>2-</sup> 207	I <sup>-</sup> 133	I <sup>-</sup> 206

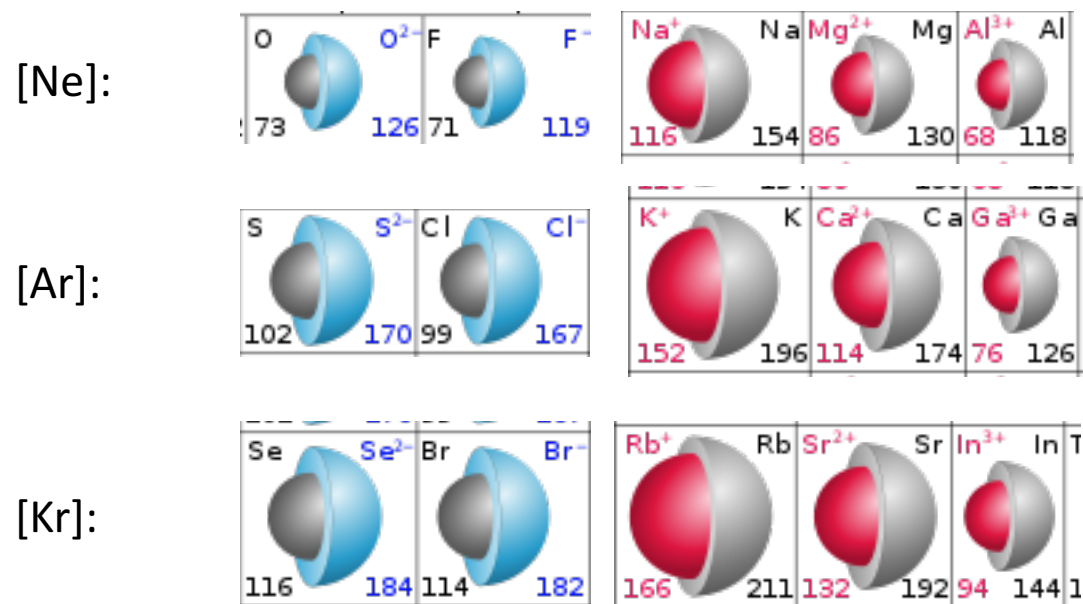
Ionic radii are pretty difficult to compare if you just try to memorize a trend.

- For isoelectronic ions, the larger the Z (positive nuclear charge), the smaller the radius
- So the real trend looks like this:



# Comparing Isoelectronic Ions

Same electronic configuration; **increasing Z**; **decreasing radius**



Note on this diagram:  
Neutral atoms are grey  
**Cations are red**  
**Anions are blue**