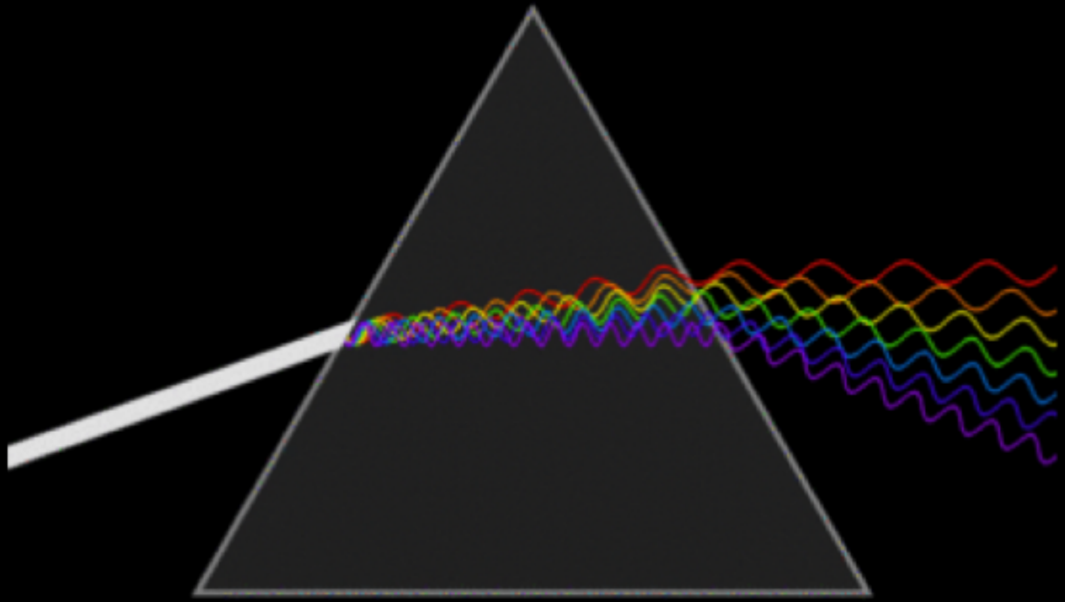
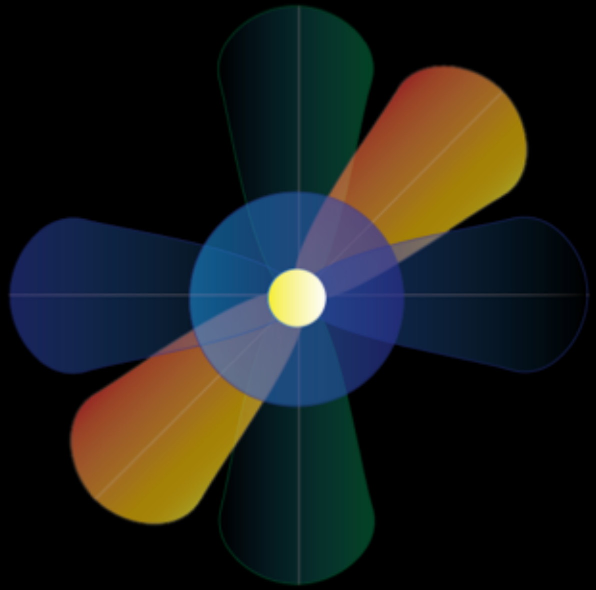




CH301 Unit 2

EXAM REVIEW: ELECTROMAGNETIC RADIATION, QUANTUM MECHANICS, ELECTRON CONFIGURATIONS, PERIODIC TRENDS, INTRODUCTORY BONDING

Tips for a Successful Exam 2

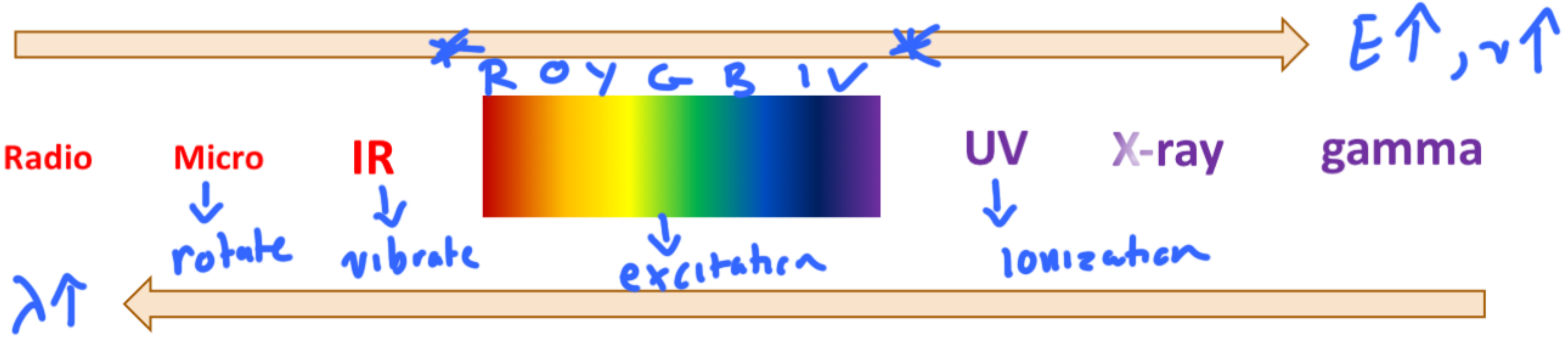
- Exam 2 is VERY conceptual: refer to lecture content, gchem, and my early reviews
- Draw all polyatomics, except those involving transition metals (chromate, for example)
- I have heard of a very good (very difficult) Dr. McCord Exam 2 on Koofers
- Blank homework assignments are available
- Additional worksheets can be found on gchem
- Jimmy Wadman ← YouTube channel (photoelectric effect, quantum numbers, Lewis structure intuition, and more)

Electromagnetic Spectrum

LIGHT IN THE CONTEXT OF QUANTUM MECHANICS

The Electromagnetic Spectrum

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



- 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)

Quantifying Light

↓↑

- Modern physics defines light as photon particles exhibiting wave-like properties:

$$c = \lambda\nu$$

  - This equation states that the **speed of light** (c) is equal to the **frequency** (ν) times the **wavelength** (λ)
  - Remember this relationship: **wavelength and frequency are inversely proportional**

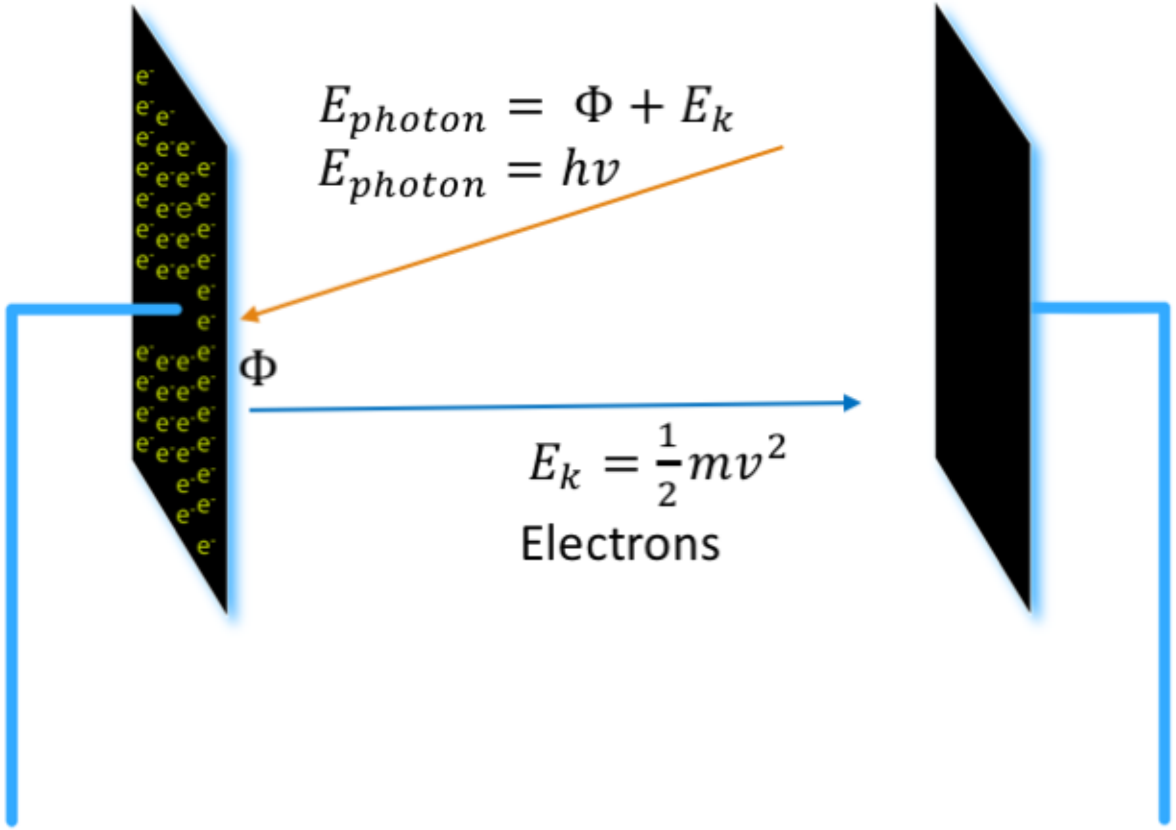
- You can also calculate the **energy per photon**:

$$\left[E_{photon} = h\nu\right] \text{ or } \left[E_{photon} = \frac{hc}{\lambda}\right] \xrightarrow{\times N_A} J/mol$$

  - This equation states that the **energy of a photon** (E) is equal to the **frequency** (ν) times the **Planck's constant** (h = 6.626 x 10^{-34} J s)
  - You get a tiny value here. Why? → J/mol
  - **Energy and frequency are directly proportional**
  - **Energy and wavelength are inversely proportional**

Photoelectric Effect: Conceptual

- **Photoelectric Effect**: a metal will eject electrons if a beam of light reaches a threshold energy
  - Demonstrates how light can interact with matter (the electrons of a metal)



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

$$E_{photon} = h\nu$$

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

Key points (If *Φ* is reached)

- Increasing photon energy: → λ ↓ ν ↑ frequency
  Ek ↑ velocity ↑
  no effect on # of e^-
- Increasing intensity: → brightness, # of photons
  → # of e- ↑
  no effect on Ek, velocity

Photoelectric Effect: Calculation

$$E_{photon} = \overset{\text{eV} \rightarrow \text{J}}{\underline{\underline{\Phi}}} + E_k$$

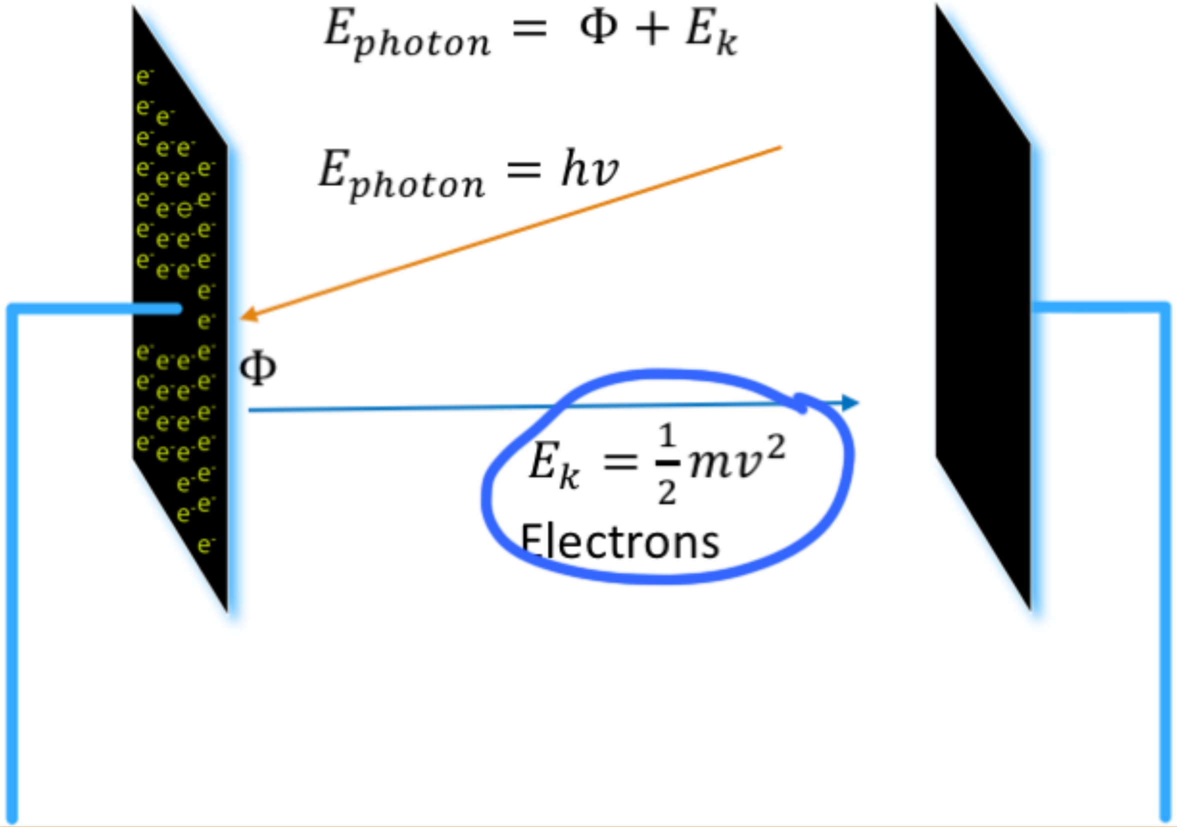
$E = h\nu$

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

$\text{nm} \rightarrow \text{m}$

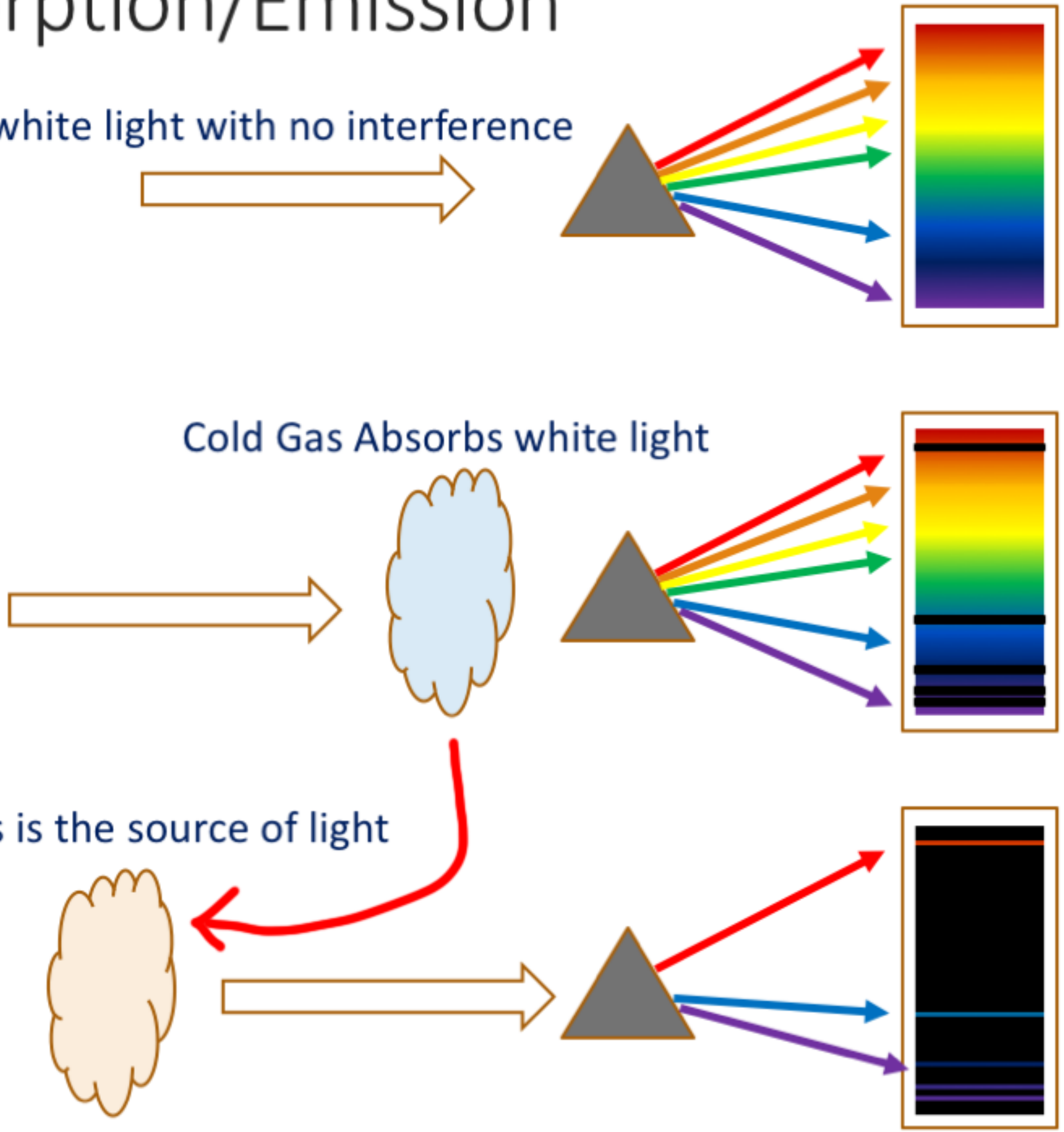
$\hookrightarrow \frac{1}{2}mv^2 \rightarrow$ provided

$\text{m/s} \rightarrow \text{km/s}$



Absorption/Emission

Conceptual Experiments



Pure white light with no interference

Cold Gas Absorbs white light

Hot gas is the source of light

CONTINUOUS

ABSORPTION

EMISSION

Notice how these are opposites for any given gas. This is evidence of the discrete energy levels of electrons

Absorption/Emission Conceptual Overview

Experiment	Light Source	Observation	ΔE (electrons)
Continuous Spectrum	White Light	Continuous spectrum (rainbow)	N/A
Absorption	White Light	Continuous spectrum minus discrete black lines	(+)
Emission	Hot Gas	Black plus the same colored lines	(−)

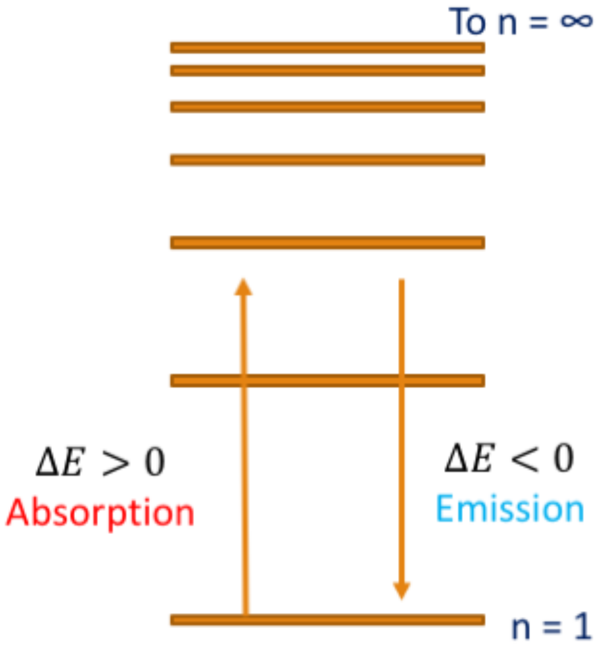
Rydberg Equation

✓ $$\Delta E = \mathcal{R}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

R = 2.18 X 10^{-18}J

↓

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



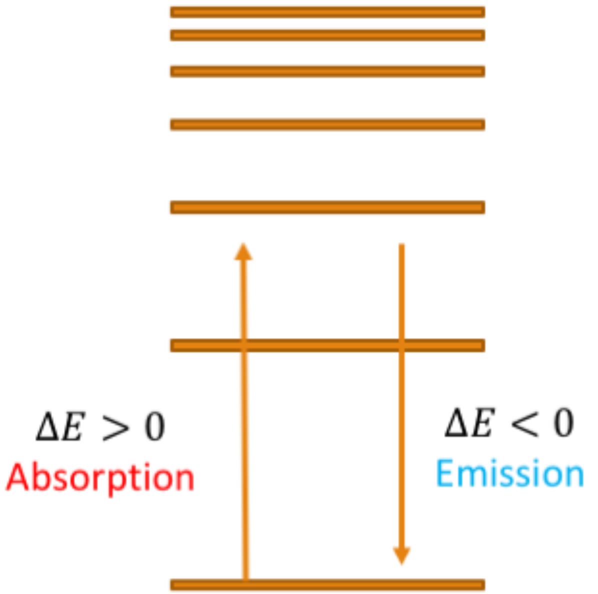
- This equation calculates the energy difference of an electron going from n_i to n_f
- This equation will always work so long as you follow one conceptual trick: The value for photon energy will always be positive.
- If you are undergoing absorption, ΔE is positive. If you are undergoing emission ΔE is negative. Either way, your photon energy is the absolute value of these energy transitions.

Rydberg Equation

$$\Delta E = \mathcal{R}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$R = 2.18 \times 10^{-18} J$

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

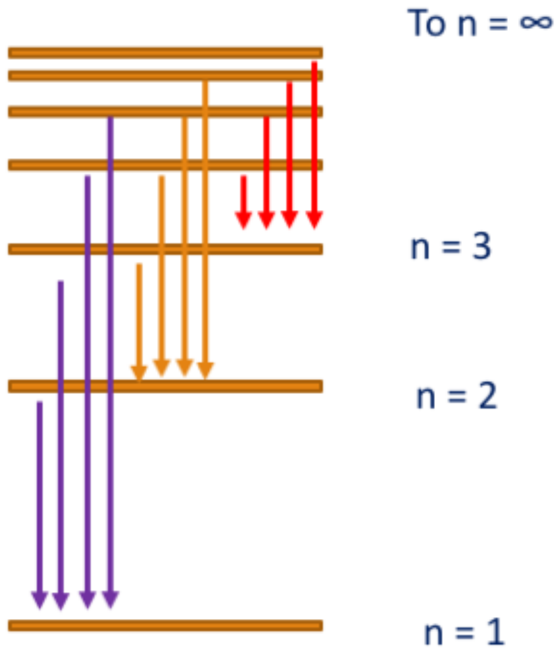


Electron energy level transition	Sign of ΔE	Absorption/Emission ($\|\Delta E\|$) (Cause/Effect)
Low n to high n	Positive (increasing energy)	Light absorbed
High n to low n	Negative (decreasing energy)	Light emitted

IR → visible → UV

Rydberg Equation

- **Lyman Series: $n_f = 1$, UV emission**
  - This is the highest energy emission series
- **Balmer Series: $n_f = 2$, visible spectrum**
  - This is what we **see** in our emission experiments
- **Paschen Series: $n_f = 3$, IR emission**
  - This is the lowest energy emission series of the three we have you memorize



Quantum Mechanics

MODELING THE SCHRÖDINGER EQUATION, ELECTRON CONFIGURATIONS

The Schrödinger Equation “Math”

- **Particle in a Box and Radial Distribution model the Schrödinger Equation in a way that we can understand the solutions without doing the math**

- 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?

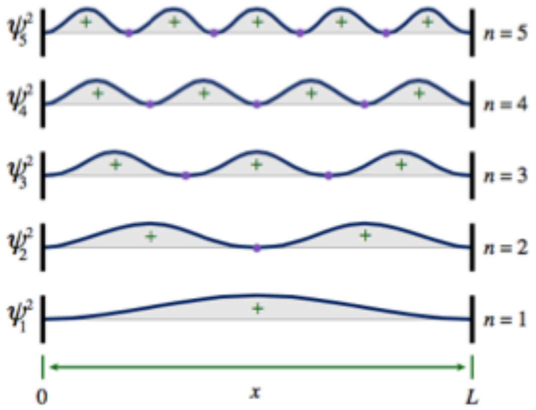
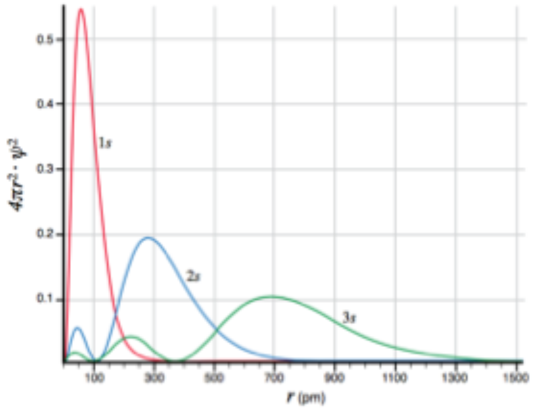


figure 2



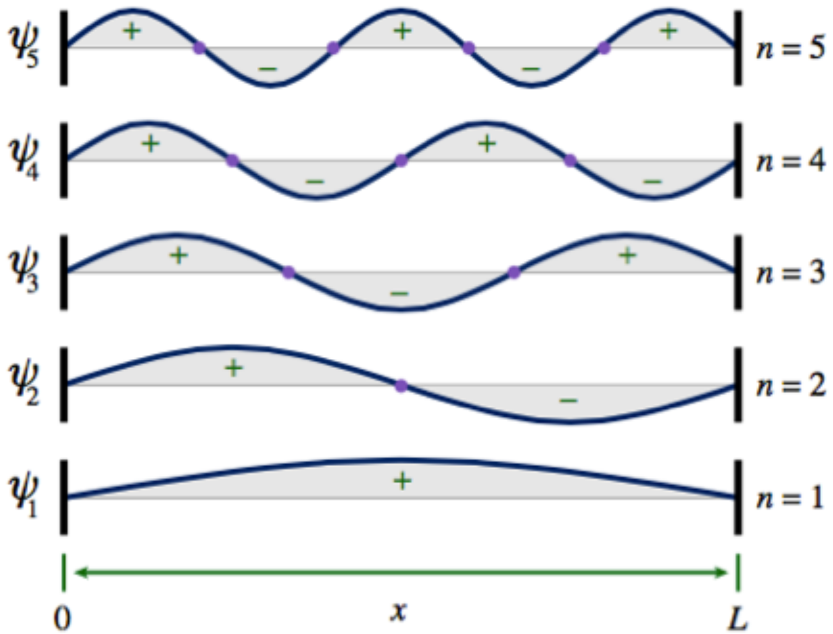
✓ **Some helpful rules:**

- # of distributions ("humps") = n
- # of nodes = n-1

Particle in a Box

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

- 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 (y=0)



Multiply by Ψ to get all positive values

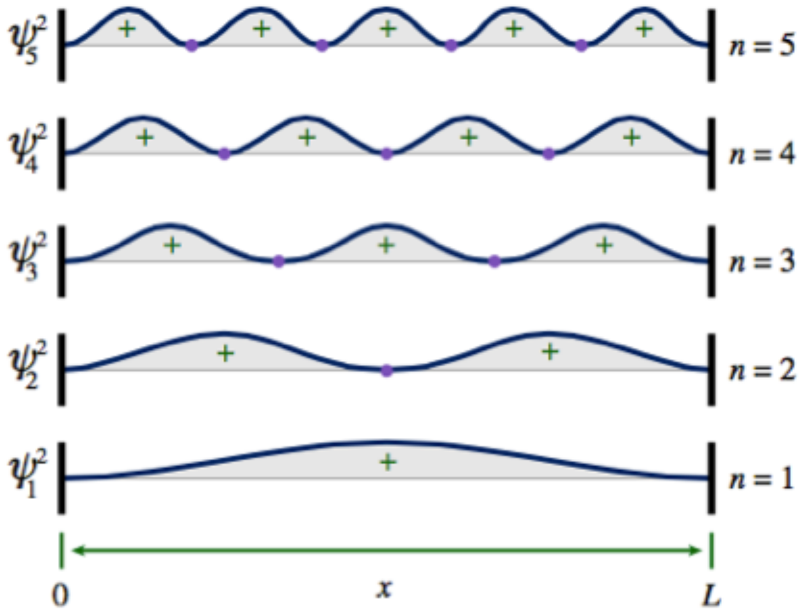
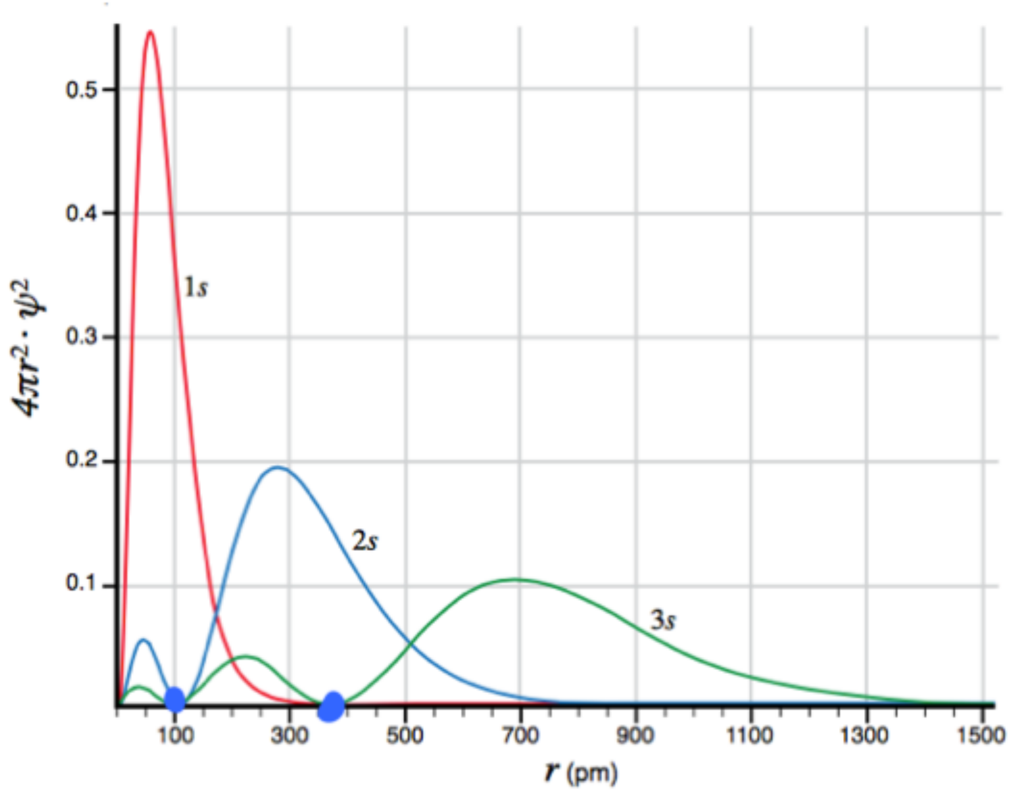


figure 2

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

Radial Distribution Function

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

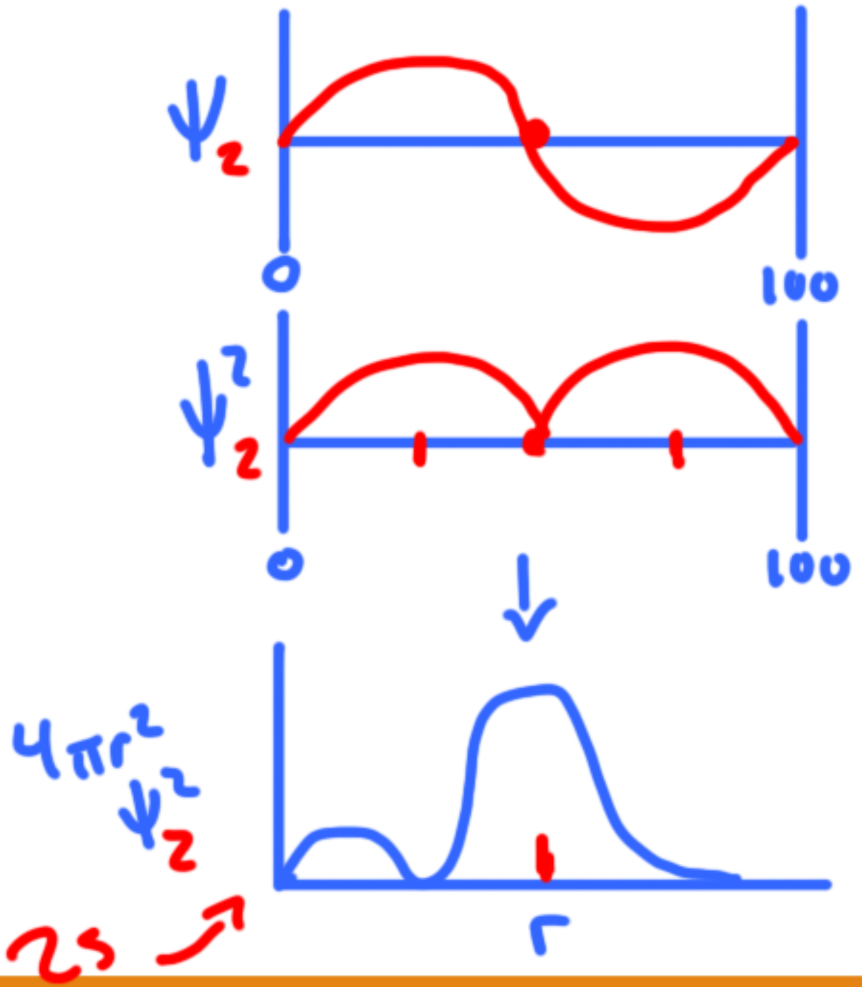


- Radial distribution curves show the same number of nodes as particle in a box, but they also show the actual probability of finding an electron in **three-dimensional space**.
- The number of distributions is equal to the n-value. It is always most probably that electrons are found in the furthest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

PIB to Radial Distribution Example

Suppose you have a single particle confined to a one-dimensional "box" of length 100 pm.

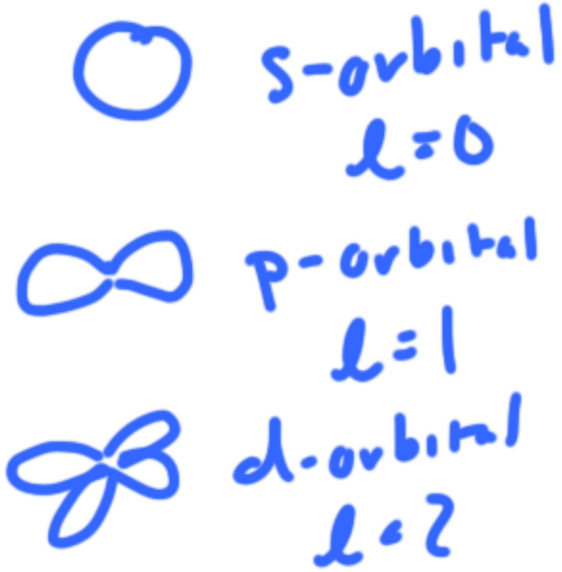
1. At what distances are you most likely to find the particle if n = 2? 25, 75
2. At what distance(s) do you have zero probability of finding this particle? 50
3. Lastly, if this particle is a hydrogen atom electron in the 2s orbital, what does the radial distribution function tell you about the location of the electrons?
4. What type of nodes are depicted in these plots?



Schrödinger Solutions: 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. **Principal 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 fundamental 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 ½ or - ½, but all that really matters is that no two electrons in the same orbital have the same value

Angular Nodes = ℓ



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:

Principal Quantum Number (n) = 1,2,3, …to n = ∞

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

Example:

If you have a 4p orbital…

ℓ MUST equal 1

m_l can equal -1,0,1,

m_s = +/- 1/2

Exception One: D-Block Exceptions

✓ $[Ag] = [\cancel{A}Kr]5\overset{1/2}{s^1}4\overset{\text{full}}{d^{10}}$

~~↳ = [Ar]$5s^2 4d^9$~~

✓ $[Mo] = [\cancel{A}Kr]5\overset{1/2}{s^1}4\overset{1/2}{d^5}$

~~↳ [Ar]$5s^2 4d^4$~~

Why?

- The ½ filled s and fully filled d is more stable than the "non-exception" configuration
- The ½ filled s and ½ filled d is stable than the "non-exception" configuration

Know: Cu, Mo, Cr, Ag

Exception Two: Filling versus “Unfilling”

$[Fe] = [Ar]4s^23d^6$

$[Fe^{2+}] = [Ar]3d^6$

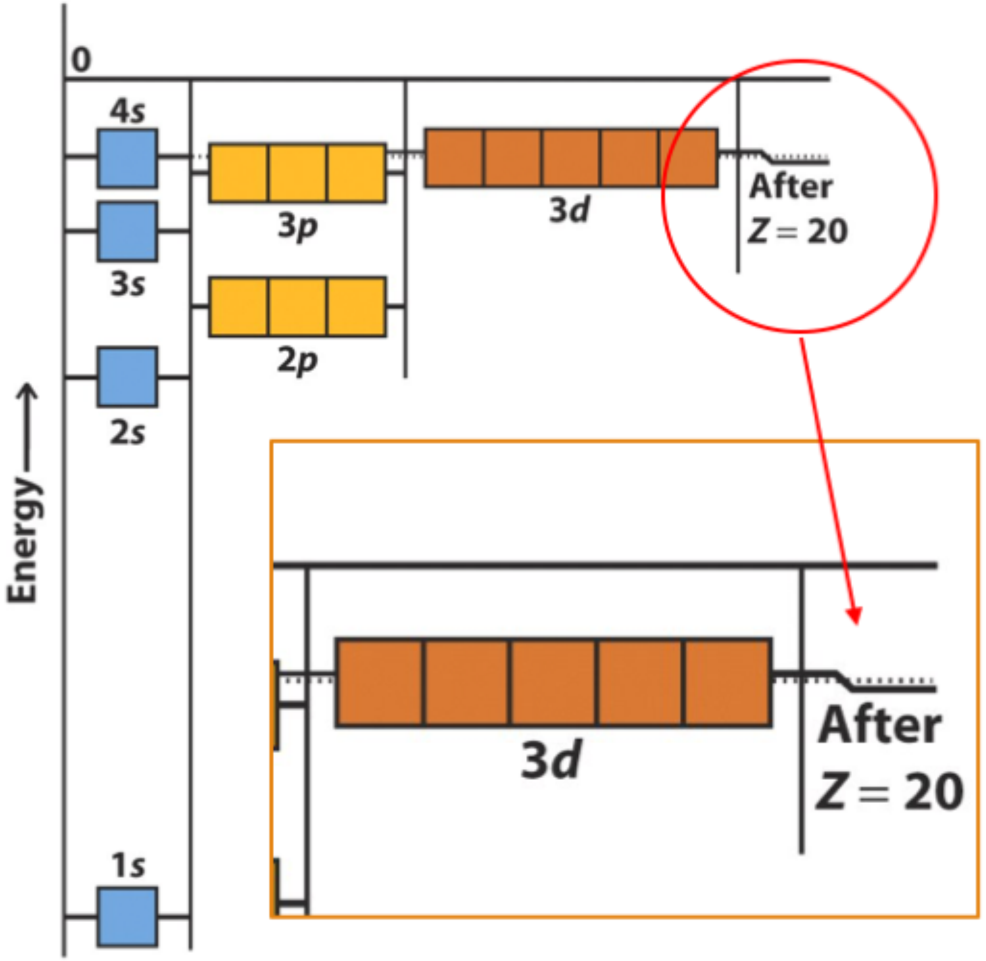
Why?

- **When filling, use the Aufbau Order:**

1s 2s 2p 3s 3p $\underbrace{4s\ 3d}$

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

4s 3d 3p 3s 2p 2s 1s



Periodic Trends

TRENDS AND EXCEPTIONS BASED ON THE STABILITY OF ELECTRONS

* Imperfect Trends! *

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_{eff} is minimized
- Z_{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_{eff} is simply the group number

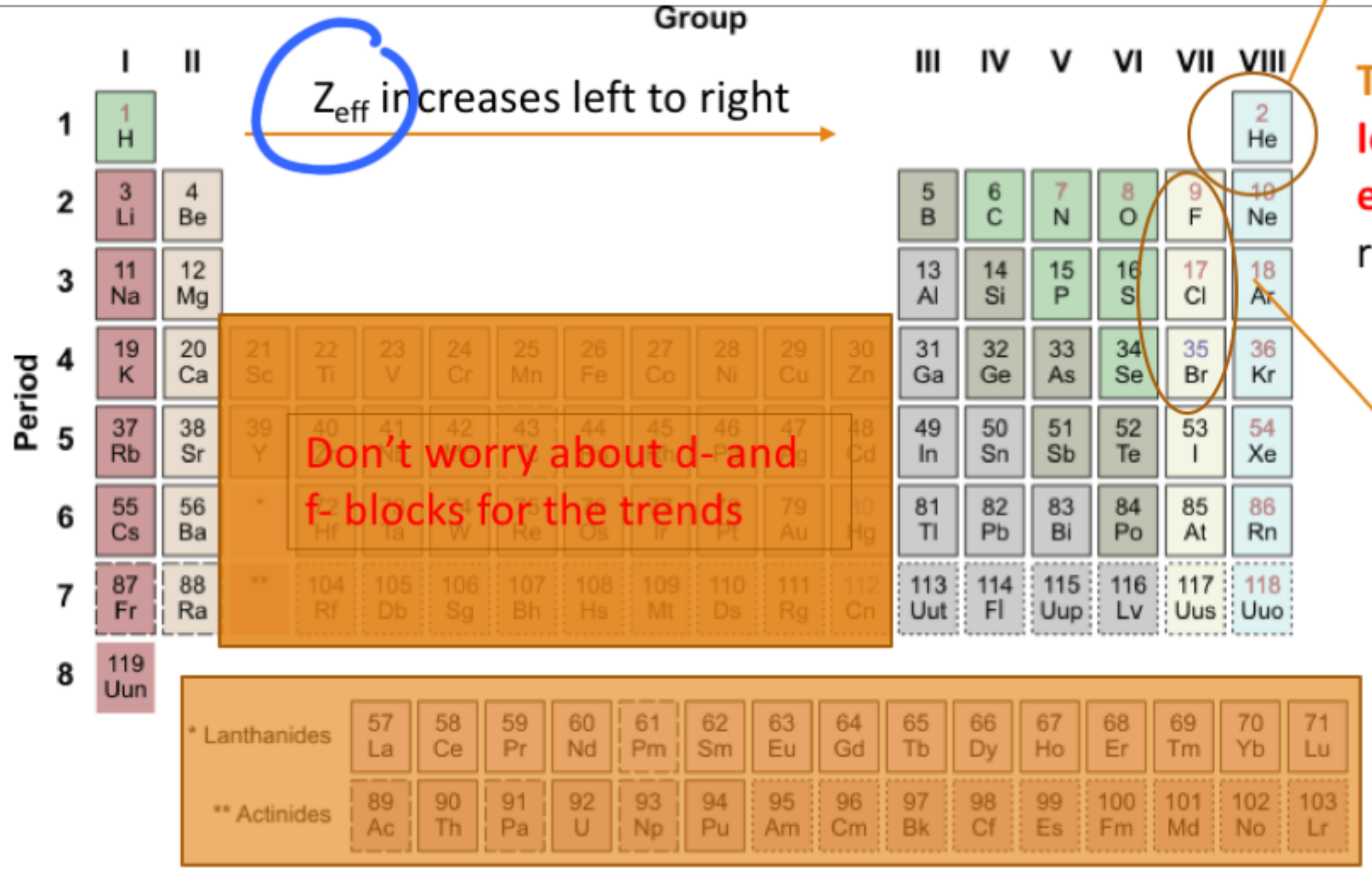
Remember: Periodic Trends explain **why** you get cations, anions, or polarity in chemical bonds

Periodic Trends

Helium has the maximum ionization energy

Shielding Increases going down

Z_{eff} increases left to right



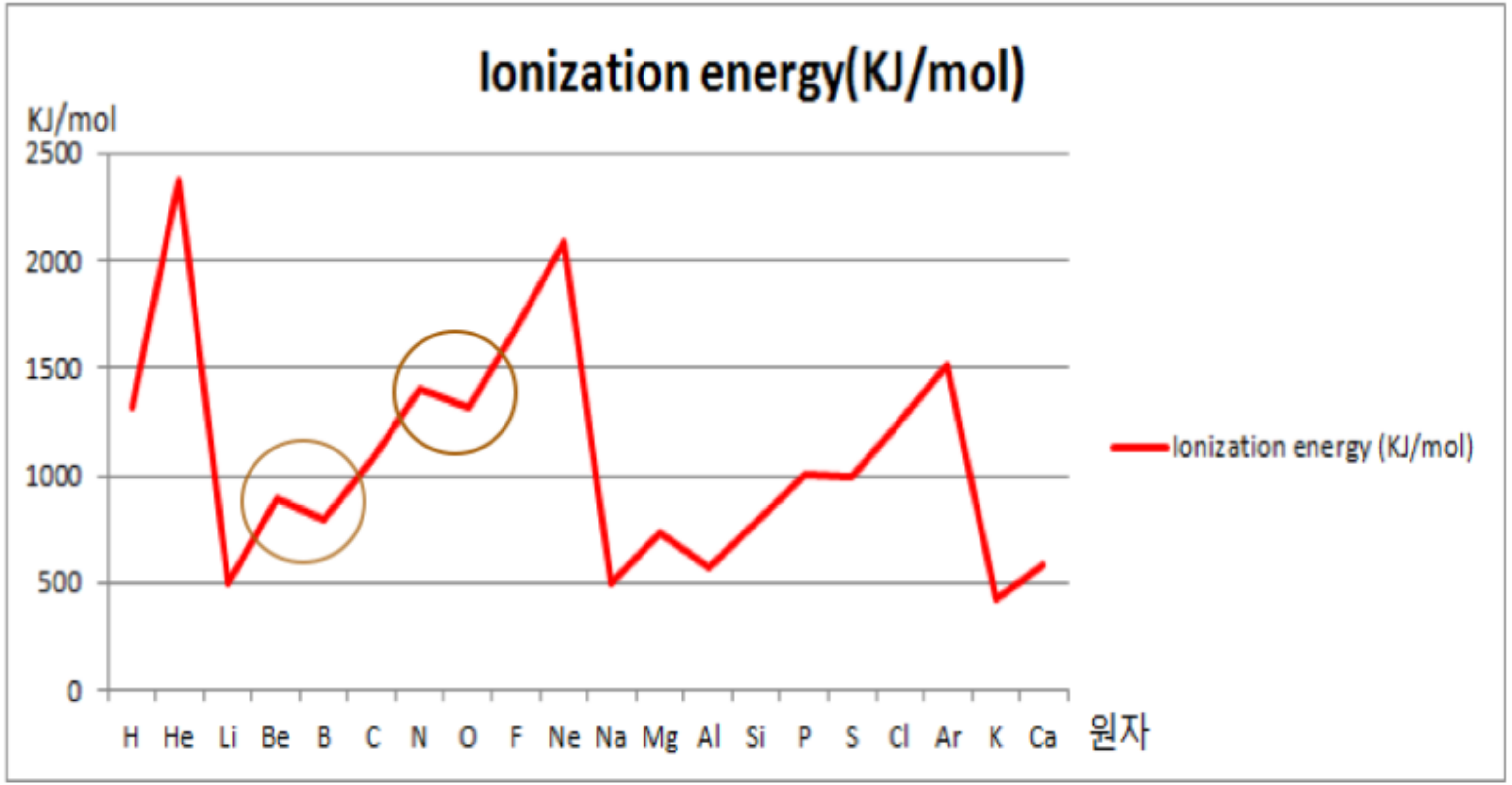
Don't worry about d- and f- blocks for the trends

TOP RIGHT: **High Ionization energy, high electron affinity,** small radius

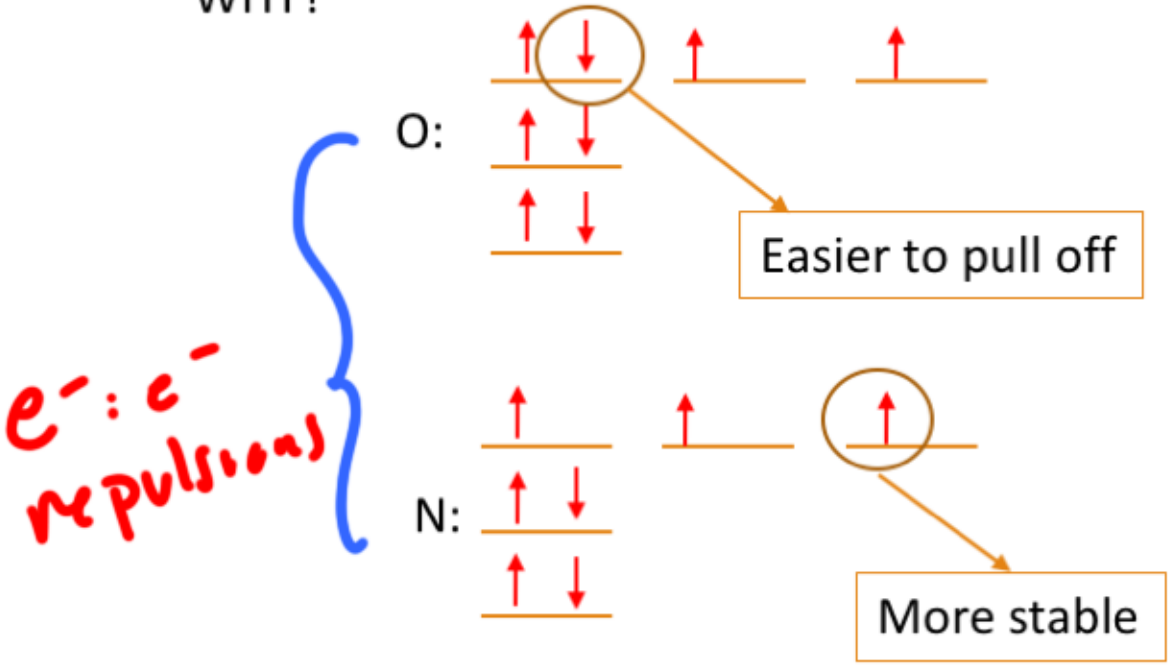
The halogens have the highest electron affinity

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

Ionization Energy Exceptions



WHY?



$e^- : e^-$ repulsions

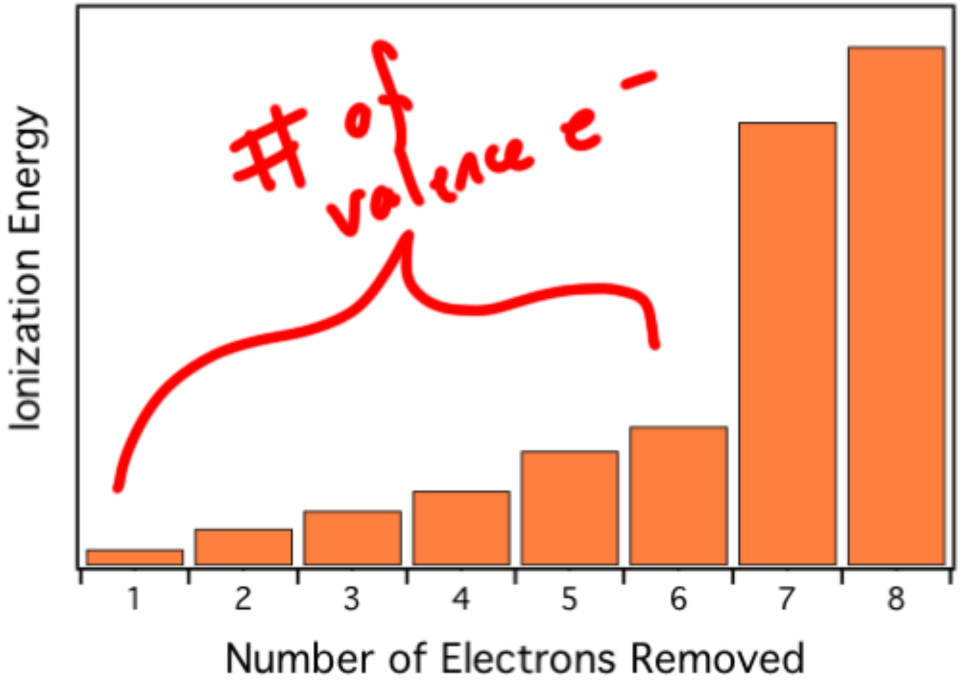
Easier to pull off

More stable

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

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. $S^{7+} \rightarrow S^{8+} + e^{-}$

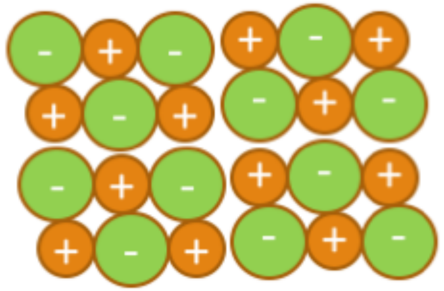
Big jump in IE means S^{6+} is most likely the noble gas configuration

Bonding

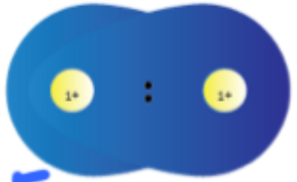
FUNDAMENTALS OF BONDING + LEWIS STRUCTURES

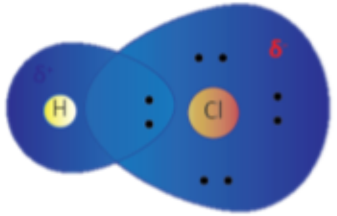
Ionic vs. Covalent Bonds

- Ionic bonds are the electrostatic interaction between discrete fully positive and fully negative charges.
  - Metal – Nonmetal (typically) --> NH_4Cl
  - Ionic bonds are quantified by lattice energy
  - Ionic compounds are almost always a metal (+) and nonmetal (-)
  - The ions can be elements or polyatomic ions (which are, themselves, covalent compounds)
  - **Results in an alternating lattice of discrete positive and negative charges**



- Covalent bonds are the sharing of electrons between two species
  - Nonmetal – Nonmetal (typically) → BeX_2 .... BeH_2, $BeCl_2$, BeF_2
  - Covalent bonds are quantified by bond length, bond strength, bond order, and polarity (Δen)
  - Nonpolar covalent bonds result from equal sharing of electrons between two nuclei
  - Polar covalent bonds result from the electrostatic interaction between partial charges (∂^+, ∂^-)
  - Results in molecules

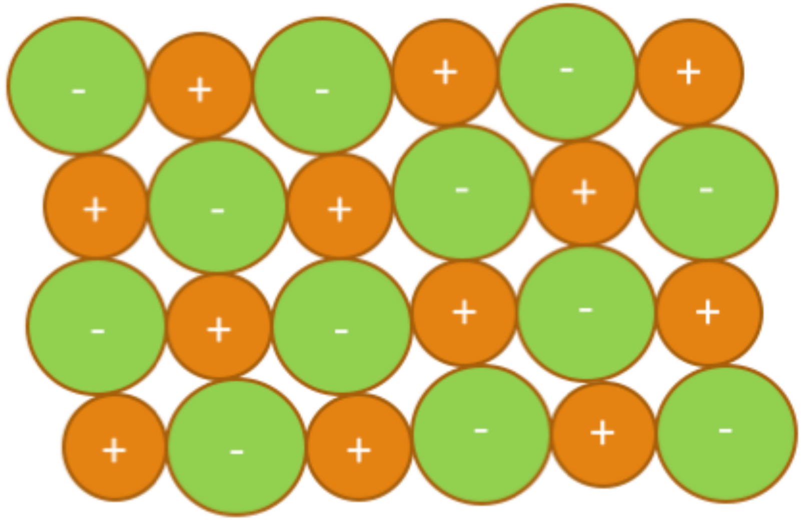




Lattice Energy

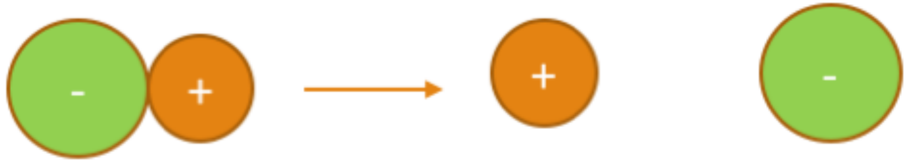
- Lattice Energy: is directly proportional to the charges of the ions (q_1 and q_2) and inversely proportional to the size of the ions (r)

$$\Delta H_{lattice} \propto \frac{q_1 q_2 \rightarrow \text{charge}}{r \rightarrow \text{radius}}$$



- This describes the energy required for the following reaction:

$$NaCl \rightarrow Na^+ + Cl^-$$



+ Energy

When Ranking Lattice Energies:

1. Prioritize **charge first**
2. If two ionic compounds have the same charge, the **smaller one will have a greater lattice energy**
3. Polyatomic ions are **big**

Lattice Energy

List the following in terms of increasing lattice energy:

2, -1

~~LiF~~, MgO, $MgBr_2$, ~~LiBr~~, $MgSO_4$

1. Rank based on charge:

LiF
LiBr , $MgBr_2$, MgO
$MgSO_4$

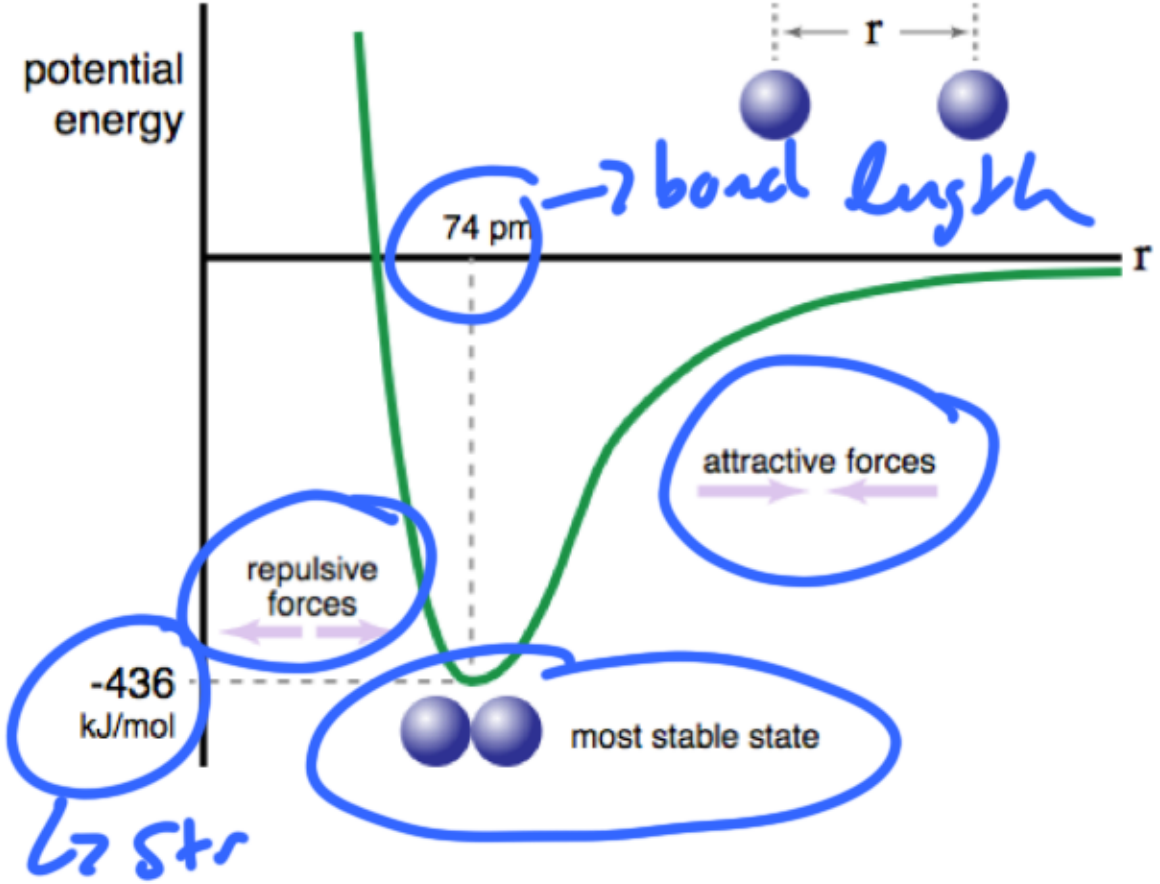
2. Settle everything else based on size:

LiBr < LiF < $MgBr_2$ < $MgSO_4$ < MgO

str ↑, order ↑, length ↓

Covalent Bond Strength and Stability

- **Bond strength**: the energy required to break a covalent bond (also known as Bond Dissociation Enthalpy)
- **Bond order**: a measurement of the average number of chemical bonds between two atoms in a species
- **Bond length**: the distance between atoms in a bond
- **KEY: stronger bonds are shorter; higher order bonds are stronger (and thus shorter)**

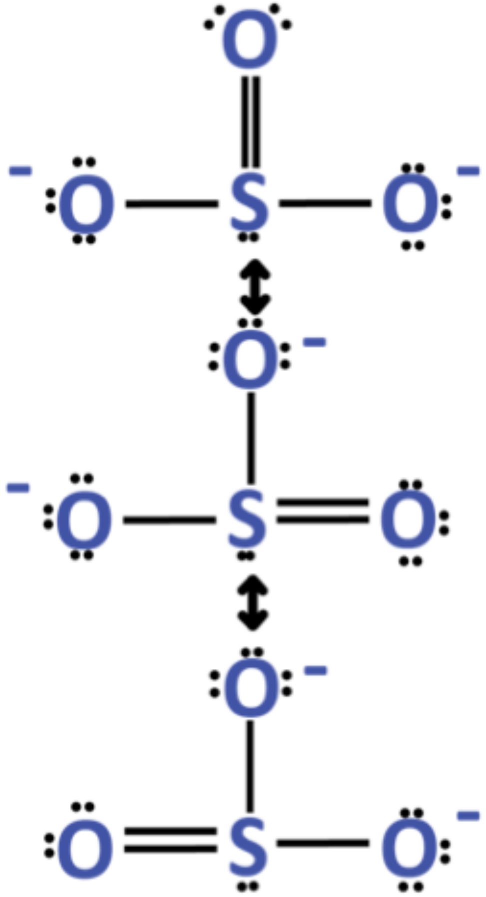


Notice how when a covalent bond gets just right, your potential energy is **most negative** just like lattice energy!

✓ $$B.O. = \frac{total\ \#\ of\ bonds\ in\ resonance}{total\ \#\ of\ bonding\ regions\ in\ resonance}$$

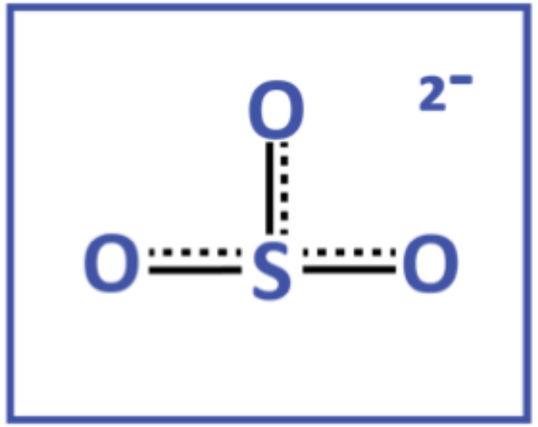
Bonding and Lewis Structures

- Resonance: multiple acceptable Lewis Structures are available for a given compound, meaning that the compound actually exists as the average of all acceptable structures
- Delocalized electrons: in the case of resonance, electrons are not confined to a single bond. Instead the electron charge is distributed over multiple bonds. We call this delocalization.
- **If you have multiple acceptable Lewis Structures in resonance, your actual structure will have the bonding character of the average. Example: Sulfite (SO_3^{2-})**



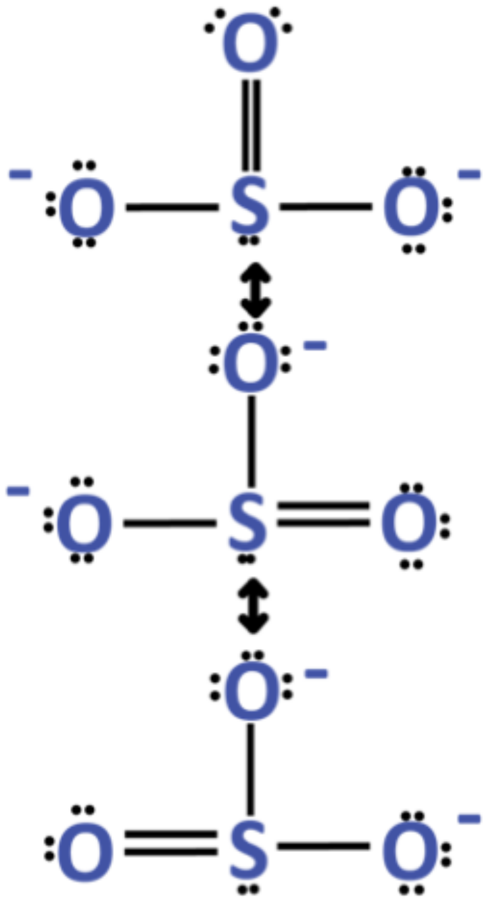
“Acceptable” Structures: double and single bonds

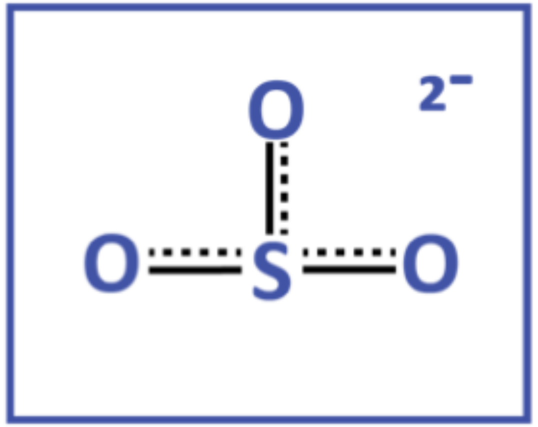
Correct Structure: three 1.33 bonds



Rules for an Acceptable Structure

- What constitutes an "acceptable" Lewis Structure?
  1. The negative charge is placed on only the electronegative or peripheral atoms, unless no better structure is possible (for example, CO and CN^-). Positive charges on the central atom are possible; however….
  2. Any individual charge should not exceed +/- 1
  3. Put your charges on as few atoms as possible
  4. Carbon, nitrogen, oxygen, and fluorine cannot disobey the octet rule
  5. **Your structure accurately reflects the number of available electrons in your atoms**





Lewis Structures

- Lewis structures are the main form of drawing molecules. There are two important equations to know when drawing Lewis Structures:

$$S = N - A$$

- The number of shared electrons is equal to the total electrons **needed** to fill the valence (2 for hydrogen, 8 for other non-exception elements) minus the electrons **available** (valence electrons). Account for positive charge by subtracting from available; account for negative charge by adding to available.
- ✓ **You can then calculate the number of bonds by dividing the shared electrons by two (bonds = S/2)**

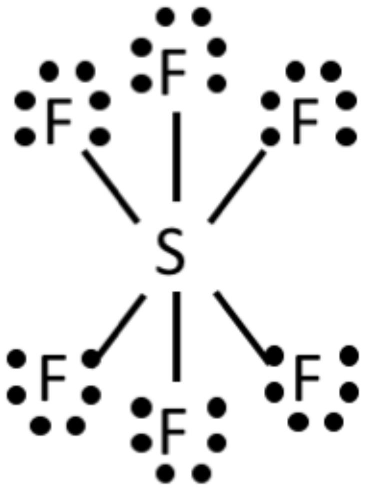
$$FC = \text{Valence} - (\text{lone electrons} + \text{bonds})$$

- **The formal charge of any atom in a molecule is equal to the the valence electrons of the atom (as seen on the periodic table) minus the "things it's touching" in the Lewis structure (the lone electrons and the number of bonds)**

$$FC = \text{Valence} - (\text{"things it's touching"})$$

Solving For Lewis Structure Exceptions

1. Find the number of electrons **available** (valence electrons plus the charges – subtract for positive charge, add for negative).
2. Add your bonds create the lowest possible formal charges possible.*
3. Add lone pairs to your peripheral atoms
4. If you have any electrons left based on your **available** electrons from step 1, add them to your central atom.
5. **Confirm your molecule's structure by checking the formal charge**



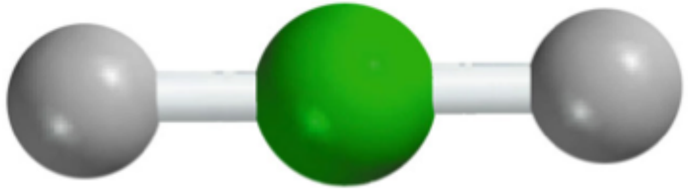
*By this I mean be smart about adding your bonds. The more you practice, the easier this step will be to make a sensible first-attempt at a structure (use the chart in the next slide if necessary)

Incomplete Octet

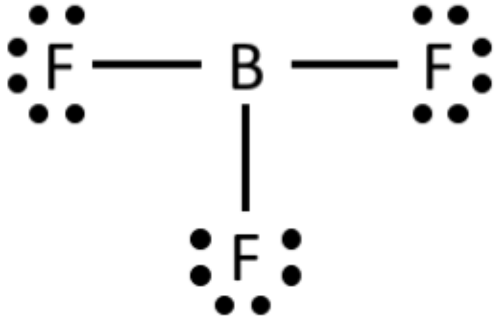
Exam Tip: there are only a few good examples of the incomplete octet: BeX_2 and BX_3, where X is either Hydrogen or a Halogen.

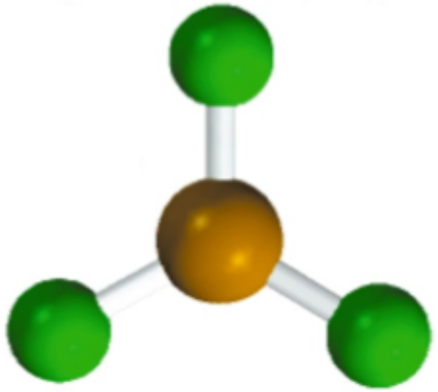
- The octet rule will also be useless for central atoms with fewer than 4 valence electrons (ex: **Boron** and **Beryllium**).
- Beryllium (Be) is satisfied making **2 bonds** (4 valence e^-).
- Boron is satisfied making **3 bonds** (6 valence e^-)
- Boron and beryllium don't have many valence electrons and they have low electronegativies, so we consider them to be **electron-poor** elements with little desire to fill their octets.

H — Be — H



Be (2 e^-) + 2H (1e^-) = 4 total e^-





B (3 e^-) + 3F (7e^-) = 24 total e^-

$C_9H_{11}NO_2$

Organic Molecules

- ✓ What is the formula for this compound?
- How many lone pairs are in this molecule?

A few rules go a long way when drawing organic molecules:

1. Each turn and terminal on a line structure is an implied carbon
2. All neutral carbons make 4 bonds, so you should add hydrogens until each carbon has a filled octet
3. If there is an electronegative atom (such as O, N, F, Cl, etc.), add lone pairs until they have a full octet