Chem 261 September 7, 2021

Gas Law: (Different kinds of units for pressure and volume can be used provided the value of the gas constant is adjusted to those units)

PV = nRT P = Pressure in atm
V = Volume in L
n = Number of Moles
T = Temperature in °K; K and °C are the same size, but 0 K = - 273 °C
R = Gas Constant

$$R \text{ is } \frac{0.082 \text{ L} \cdot \text{atm.}}{\text{mol . K}}$$

Standard conditions for temperature and pressure (STP)
Old definition of STP used in this course
Standard pressure is 1 atmosphere, or 760 mmHg; standard temperature is 273 K
1 mol of gas occupies 22.4 L at STP. –

Sample Question: A certain amount of N_2 gas occupies a volume of 3 mL at 750 mmHg and room temperature (298 K). What volume it will occupy at standard pressure and temperature (STP)?

$$\frac{P_1V_1}{P_2V_2} = \frac{nRT_1}{nRT_2} \quad \text{divide equations to give} \quad \frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$$

P_1 = 760 mmHg T_1 = 273 °K V_1 = ?
P_2 = 750 mmHg T_2 = 298 °K V_2 = 3 mL

Solve for V_1

$$V_1 = \frac{T_1P_2V_2}{T_2P_1} = \frac{(273\ °\text{K})(750\text{ mmHg})(3\text{ mL})}{(298\ °\text{K})(760\text{ mmHg})} = 2.71\text{ mL}$$

Question: How many moles of N_2 is 2.71 mL at STP and what is its mass?

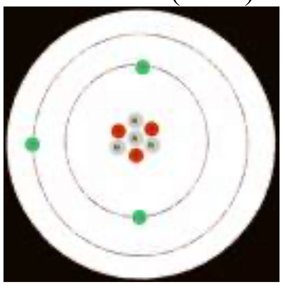
Note: 1 mole of an ideal gas occupies 22.4 L at STP.

$$2.71 \times 10^{-3}\text{ L} \times \frac{1\text{ mole}}{22.4\text{ L}} = 1.21 \times 10^{-4}\text{ moles of } N_2$$

1.21×10^{-4} mol $\times$ 28 g/mol = 3.4 mg of N_2

Atomic Theory:

- Neils Bohr (1913) – Won the Nobel prize for his atomic theory – <u>NOT fully correct</u>



- The neutrons (no charge) and protons (positively charged) occupy a dense central region called the nucleus (p^+ +N)
- The electrons (negatively charged) orbit the nucleus much like planets orbiting the Sun

- de Broglie (1924) – His 12 page PhD thesis won him the Nobel Prize
  - He proposed that ordinary "particles" such as electrons and protons could behave as both particles and waves (wave - particle duality of matter)

Particles ↔ Waves

Often the electron density distribution is called an "orbital" by chemists
- The orbitals of an atom are described by wave functions (mathematical equations)
- These have no direct physical meaning, but when squared describe electron density

ψ = Wave function

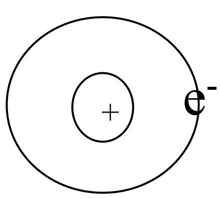
ψ = orbital

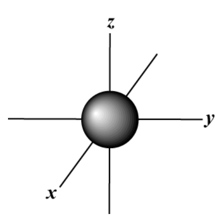
ψ^2 = (orbital)^2 = electron density distribution

For the hydrogen (H) atom: >98% of electron density is found in a sphere with diameter of 1Å (10^{-8} cm)

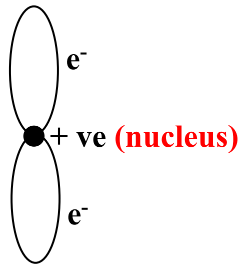
Orbitals:

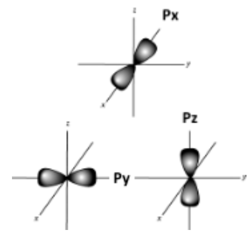
1. *s*-Orbital - Spherical shaped (electron density)



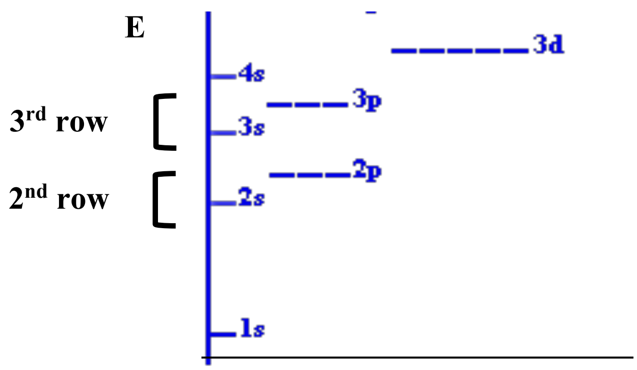


2. *p*-Orbital - Dumbbell-shaped (Three orientations: placed on the x, y and z-axis)





Energy (E) Level Diagram for an Atom:



Degenerate orbitals have the same energy

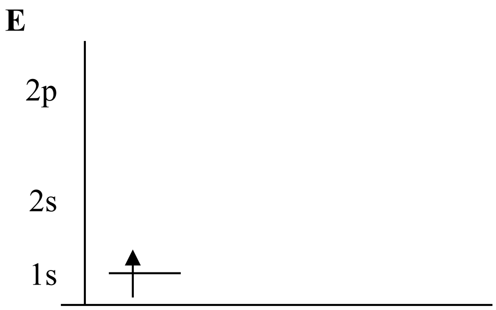
-e.g. all three 2p orbitals have the same energy

Atoms	Protons (+) = Atomic #	Neutrons	1s electrons	2s electrons	2p electrons
H	1	0	1		
He	2	2	2		
Li	3	3	2	1	

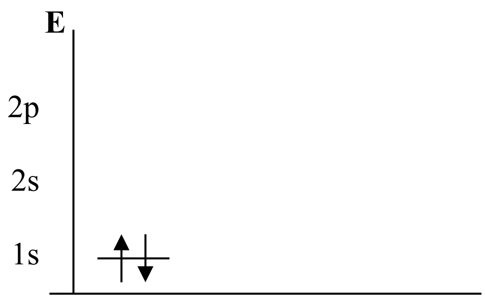
Rules for Filling Electron Orbitals – AUFBAU Rule (Building-Up Principle):

1) Add electron to the lowest energy orbital available
2) Maximum of two electron per orbital (each having opposite spin quantum number)
    - Pauli Exclusion Principle
3) Place one electron into each orbital of the same energy (degenerate orbitals), before adding a second electron
    - Hund's Rule of Maximum Multiplicity

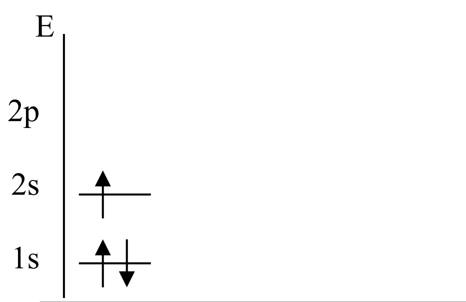
Hydrogen (H)



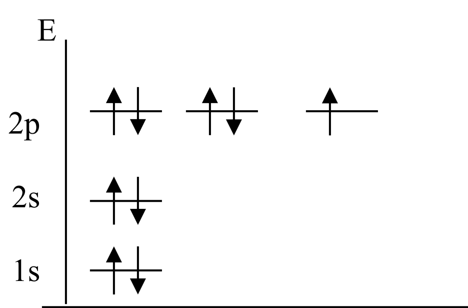
Helium (He)



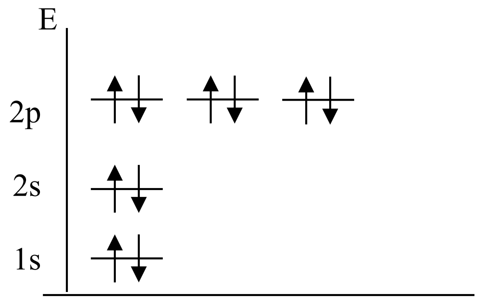
Lithium (Li)



Fluorine (F)



Neon (Ne)



All elements want an inert gas configuration (e.g. Ne) and from the diagrams above, both Li and F are unhappy with unfilled orbitals (not in an inert gas configuration).

If Li loses an electron to become Li^{+} and obtain inert gas configuration, it becomes isoelectronic with He

-Isoelectronic = same electronic structure

If F gains an electron to become F^{-} and obtain inert gas configuration, it becomes isoelectronic with Ne

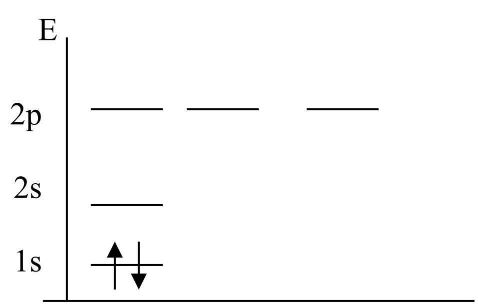
Ionic Bonding

Lithium fluoride is an example of ionic bonding in which positive and negative species are bonded to each other. Li could lose $1e^{-}$ from 2s orbital to become isoelectronic to He (as Li^{+}) and F could gain $1e^{-}$ to become isoelectronic to Ne (as F^{-}).

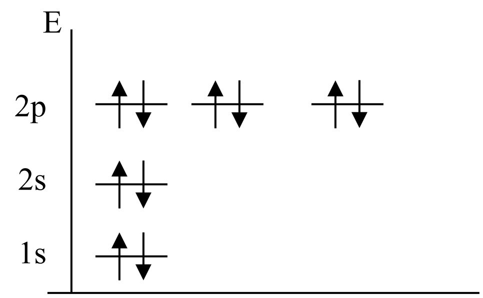
$$\underset{}{Li^{o}} + F^{o} \rightarrow \underset{\text{Loss of } 1e^{-}}{Li^{+}} + \underset{\text{Gain of } 1e^{-}}{F^{-}}$$

Isoelectronic = Same electron configuration

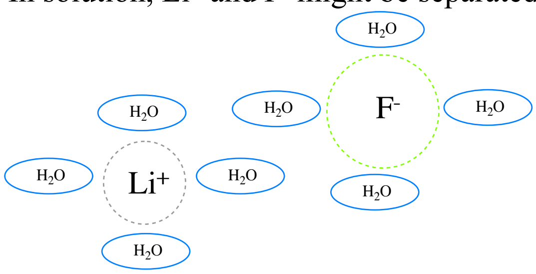
Li^{+} (cation) Isoelectronic with He



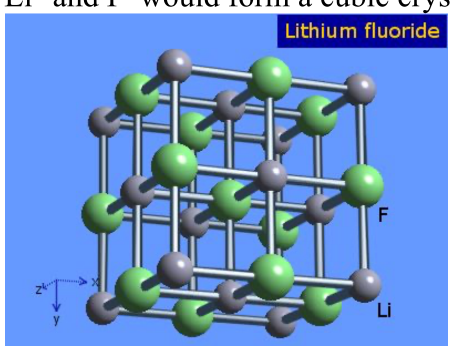
<u>F^- (anion)</u> Isoelectronic with Ne

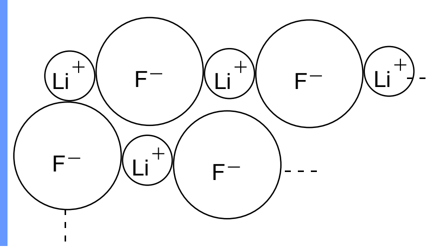


In space, Li^+ and F^- would be attracted to each other
In solution, Li^+ and F^- might be separated due to solvation (e.g. water would surround)



In a solid, Li^+ and F^- would form a cubic crystalline solid





Electronegativity

- Desire of atoms for electrons
- Electronegativity increases from left to right across the period in the periodic table (atoms get stronger attraction as the nuclear charge increases
- Electronegativity increases from bottom to top in the group (Distance between nucleus and valence shell decreases)

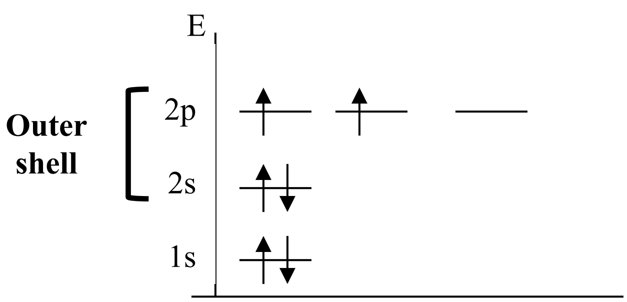
Covalent Bonding

- <u>Sharing</u> of electrons between the atoms
- More common in organic chemistry

Electronic configuration of carbon (C):

- Atomic number = 6
- Atomic weight = 12

Carbon (C)



- Carbon needs to gain or lose $4e^-$ to get an inert gas configuration, but this would result in unfavourable charge buildup:

- C^{4+} is isoelectronic with He

- C^{4-} is isoelectronic with Ne

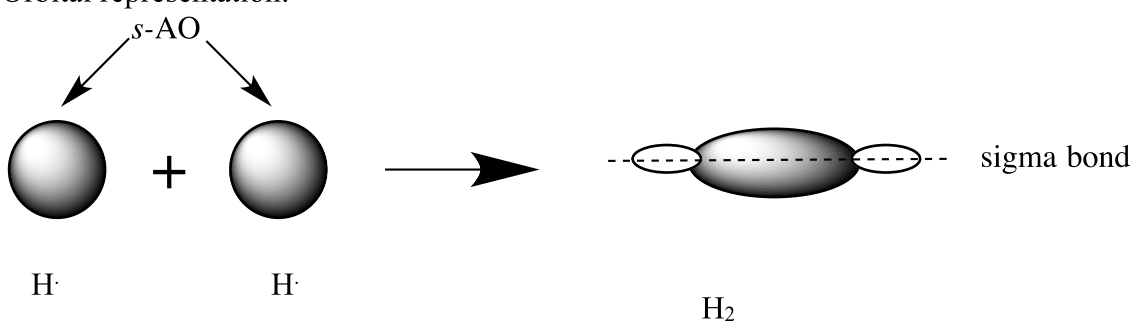
- So, carbon makes up to 4 bonds to share $4e^-$ (covalent bonding)

Energetics of Forming Bonds

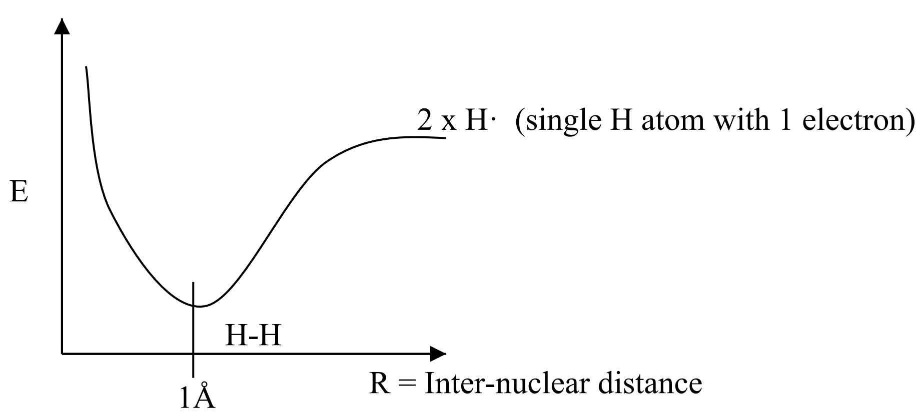
As two hydrogen atoms come together, molecular hydrogen (H_2) is formed (Hydrogen atoms depicted as Lewis dot diagrams)

$$H^{\cdot} \longrightarrow H{:}H \longleftarrow {}^{\cdot}H$$

Orbital representation:

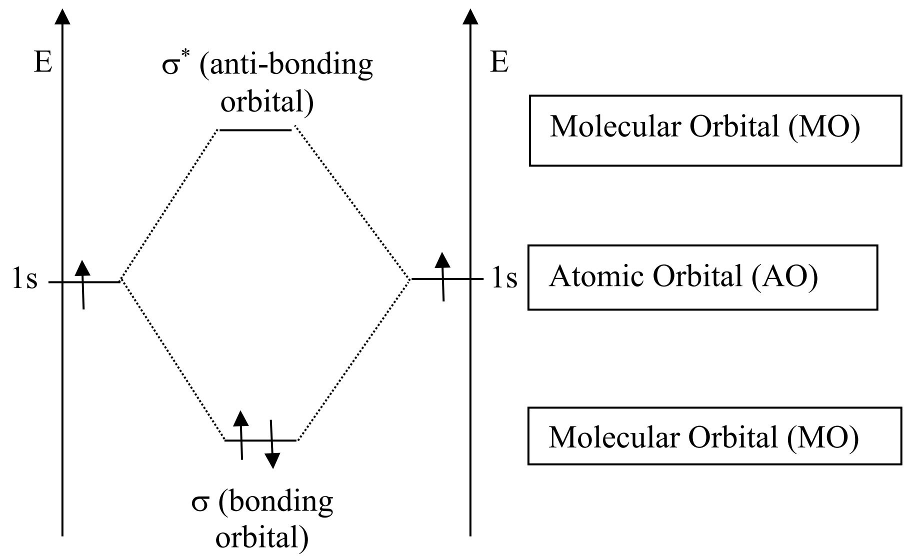


Energy diagram of two hydrogen atoms interacting to form a bond:



1Å is the average H-H bond distance

e.g. H_2

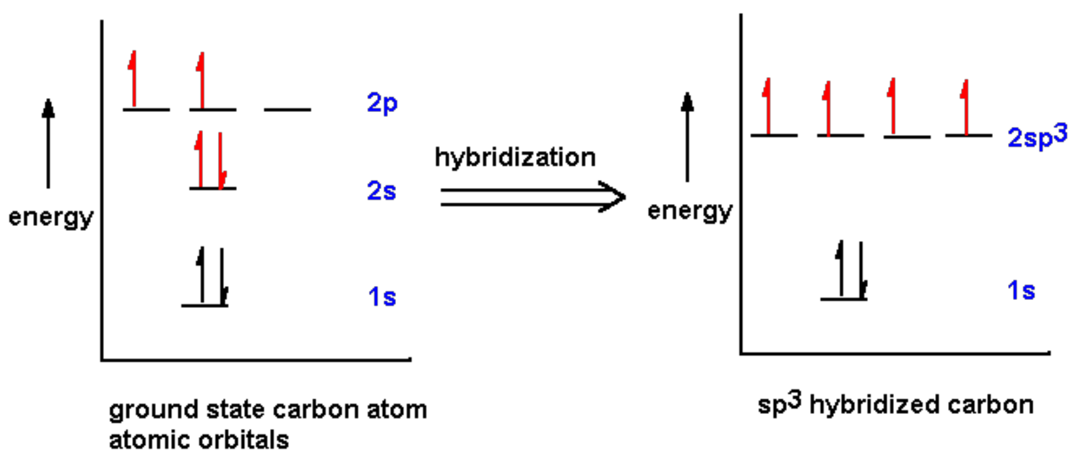


LCAO

- Linear combination of atomic orbitals
- Combination of atomic orbitals of s- character gives molecular orbital called sigma molecular orbital (σ)

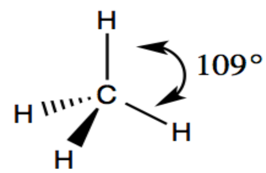
Hybridization:

- Mixing of atomic orbitals (with the wrong geometry for bonding) to form hybrid orbitals with the correct geometry for bonding

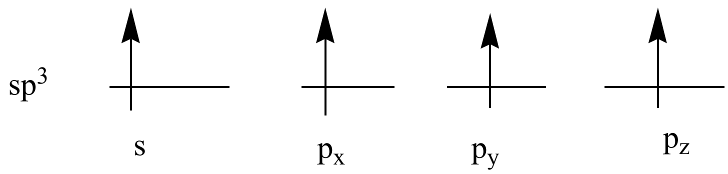


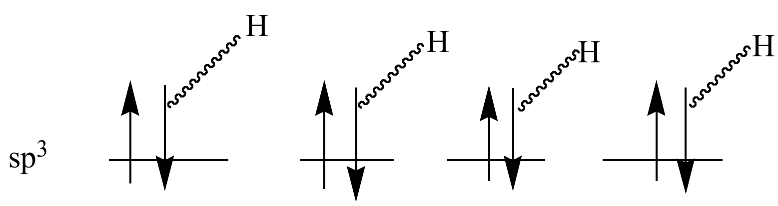
sp^3 Hybridization

- Single bonds
- Tetrahedral geometry
- Angle between two H atoms in methane: 109°, close to that with other elements
- Often free rotation around single bonds
- Overlap of atomic orbitals with s component gives sigma molecular orbital (bond)



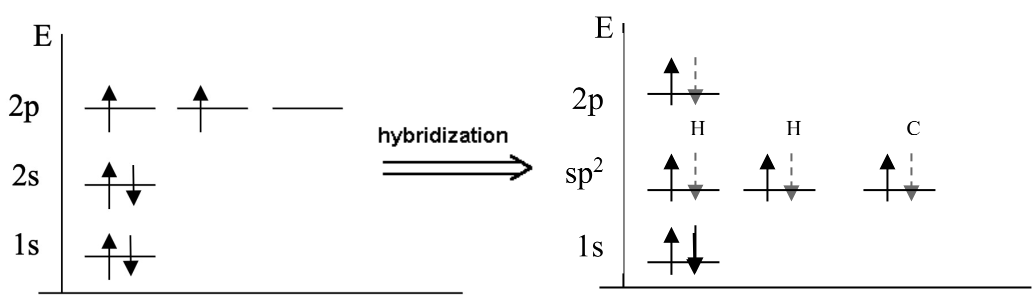
CH_4 - Methane

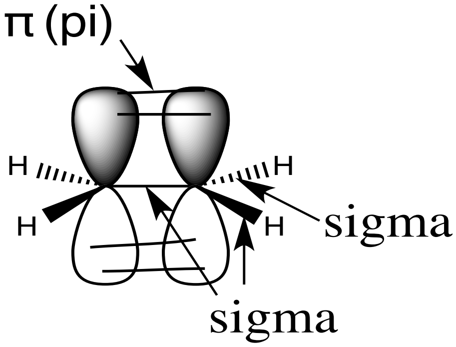


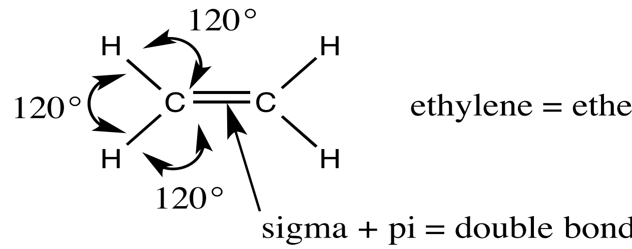


sp² Hybridization

- Double bonds
- Planar geometry
- Angle between two atoms: 120°
- No free rotation around double bonds
- Overlap of atomic orbitals with s component gives sigma molecular orbital (bond)
- Overlap of p atomic orbitals with s component gives pi molecular orbital (bond)







ethylene = ethene

- Each line in a structure represents 2 e^-
- Solid wedge ( ): Toward you / out of the page
- Dashed wedge ( ): Away from you / into the page