<u>Quantitative Analysis</u>

Quantitative: How much of the compound of interest (quantity)
Amounts of atoms in a compound

$$\text{Organic compound} \xrightarrow[\Delta \text{ (heat)}]{} CO_2 + H_2O + NO_2 \xrightarrow{[H] = \text{Reduction}} N_2 + H_2O$$

MW (g/mol): 44 (CO_2), 18 (H_2O)

$$\text{Compound (4.34 mg)} \xrightarrow{O_2} \underset{CO_2}{10.35 \text{ mg}} \quad \underset{H_2O}{3.42 \text{ mg}} \quad \underset{NO_2}{0 \text{ mg}}$$

Contains C, H, O

Note: Matter cannot be created or destroyed in a chemical reaction; therefore the amount of carbon in the CO_2 is equal to the amount of carbon in the starting sample.

<u>Percent Composition</u> – how much of each atom is present in the sample

$$\text{Weight of carbon (in sample)} = \frac{12 \text{ g/mol of C}}{44 \text{ g/mol } CO_2} \times 10.35 \text{ mg of } CO_2 = 2.82 \text{ mg of C}$$

Molecular Weight (MW) of CO_2 = 12 (C) + 2×16 (O) = 44 g/mol

$$\text{Weight of hydrogen} = \frac{2(1 \text{ g/mol of H})}{18 \text{ g/mol of } H_2O} \times 3.42 \text{ mg of } H_2O = 0.383 \text{ mg of H}$$

NB: H_2O contains two hydrogen. MW of $H_2O = \underbrace{(2\times1)}_{H_2} + \underbrace{16}_{O}$

Weight of oxygen = 4.34 mg sample – (2.82 mg of C + 0.383 mg of H) = 1.14 mg of O

Now one can calculate percentage composition:

<u>% Composition:</u>

$$\% C = \frac{\text{Mass of carbon}}{\text{Mass of sample}} \times 100\% = \frac{2.82 \text{ mg of C}}{4.34 \text{ mg}} \times 100\% = 65.1\%$$

$$\% H = \frac{0.383 \text{ mg of H}}{4.34 \text{mg}} = 8.83\%$$

% O = 100% - 65.1% - 8.83% = 26.1%

Determining the empirical experimental formula:

Definition: Empirical formula is the ratio of atoms to each other in a molecular formula

There are three steps to calculate the empirical formula:

1) Divide each percentage (%) by the atomic weight of the element → crude ratio
2) Divide each crude ratio by the smallest crude ratio → refined ratio
3) Multiply the refined ratio by an integer value (x2, x3, x4…) → integral ratio

% Composition	Crude Ratio	Refined Ratio	Integral Ratio
65.1 % C	65.1 / 12.0 = 5.42 (% C / At Wt C)	5.42 / 1.63 = 3.34	3.34 x 3 = 10
8.83 % H	8.83 / 1.01 = 8.76	8.76 / 1.63 = 5.39	5.39 x 3 = 16
26.1 % O	26.1 / 16.0 = 1.63	1.63 / 1.63 = 1.00	1.00 x 3 = 3

From the integral ratio, the empirical formula is $C_{10}H_{16}O_3$. Using this formula an empirical weight can be calculated.

C: $10 \times 12 = 120$ g/mol
H: $16 \times 1 = 16$ g/mol
O: $3 \times 16 = 48$ g/mol

$C_{10}H_{16}O_3$ = 184 g/mol

Note: Suppose the molecular weight is given as 368 g/mol, then the molecular formula is obtained by multiplying the integral ratios by a factor of 2 and it would be $C_{20}H_{32}O_6$.

The molecular weight can be independently determined via mass spectrometry.

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

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

Standard conditions for temperature and pressure (STP)
Old definition of STP used in this course
Standard pressure is 1 atmosphere = 760 mmHg; standard temperature is 0°C = 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 3.0 mL at 750 mmHg and room temperature (298 °K). What volume it will occupy at standard pressure and temperature (STP)?

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

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

Solve for V_1

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

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

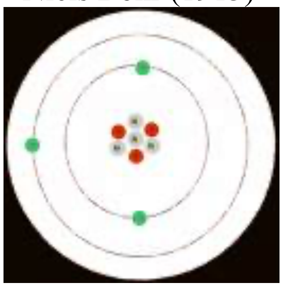
Note: 1 mole of an ideal gas occupies 22.4 L at STP.

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

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

Atomic Theory:

- Niels Bohr (1913) – Won the Nobel prize for his atomic theory – NOT fully correct



- 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
- The atom is mostly made up of empty space

- 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

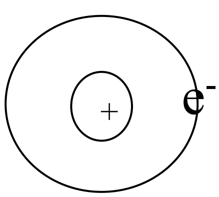
ψ = orbital

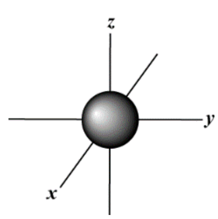
ψ^2 = $(\text{orbital})^2$ = electron density distribution

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

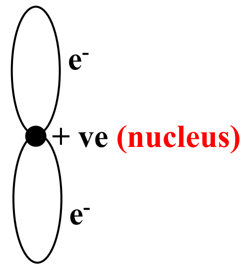
Orbitals:

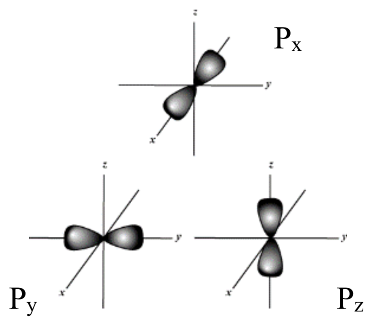
1. *s*-Orbital - Spherical shaped (electron density)



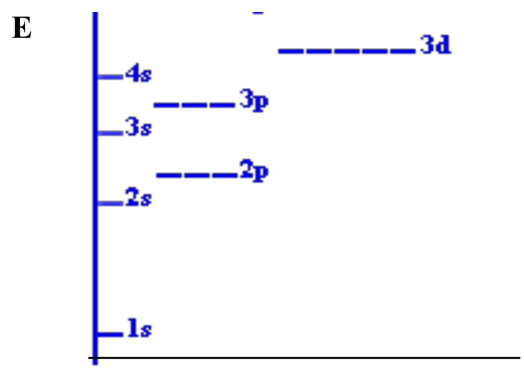


2. *p*-Orbital - Dumbbell-shaped (Three orientations: placed on the x, y and z-axis)





Energy (E) Level Diagram for an Atom:



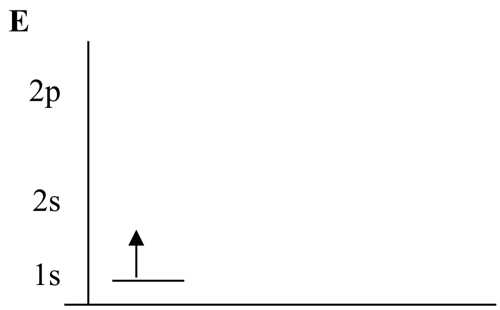
Degenerate orbitals have the same energy
-e.g. all three 2p orbitals have the same energy

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

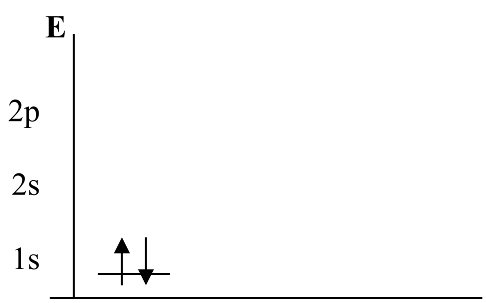
Rules for Filling Electron Orbitals – AUFBAU Rule (Building-Up Principle):

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

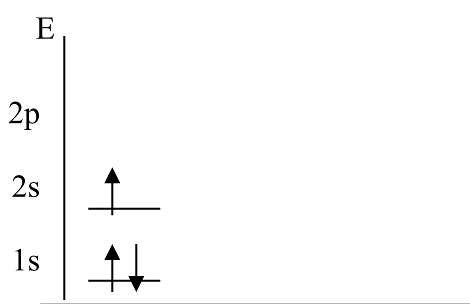
Hydrogen (H) *(atomic no. 1)*



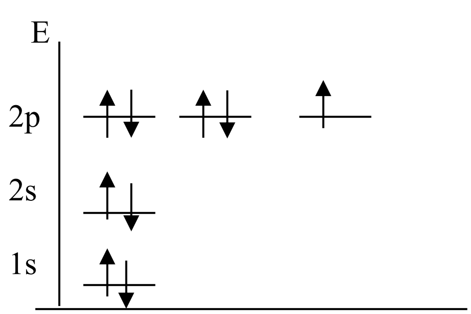
Helium (He) *(atomic no. 2)*



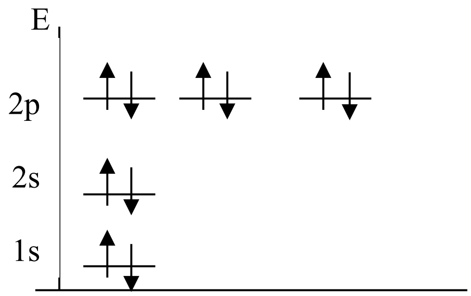
Lithium (Li) *(atomic no. 3)*



Fluorine (F) *(atomic no. 9)*



<u>Neon (Ne)</u> *(atomic no. 10)*



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

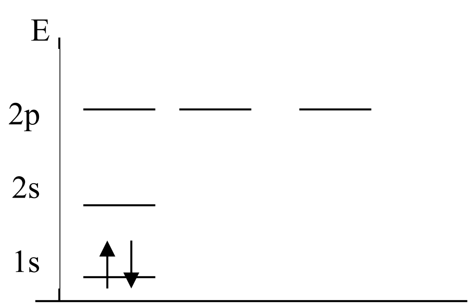
Ionic Bonding

Lithium fluoride (LiF) is an example of <u>ionic bonding</u> 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^-).

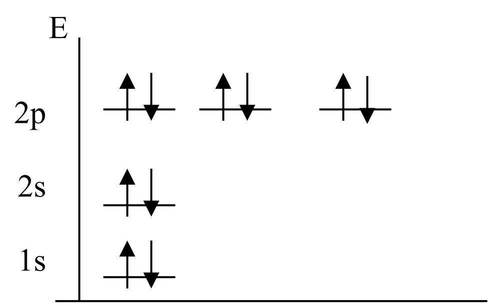
$$\underset{}{Li^o} \quad + \quad F^o \rightarrow \underset{\text{Loss of } 1e^-}{Li^+} \quad + \quad \underset{\text{Gain of } 1e^-}{F^-}$$

Isoelectronic = Same electron configuration

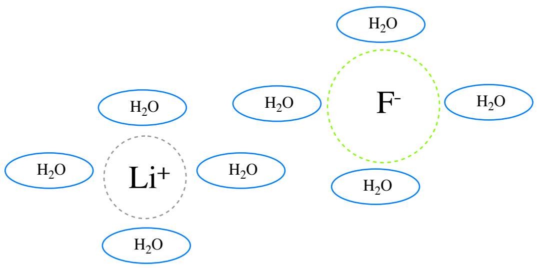
<u>Li^+ (cation)</u> Isoelectronic with He



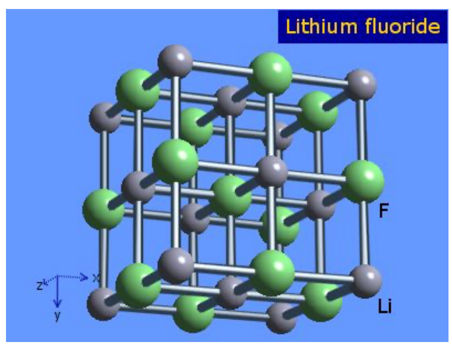
<u>F^- (anion)</u> Isoelectronic with Ne

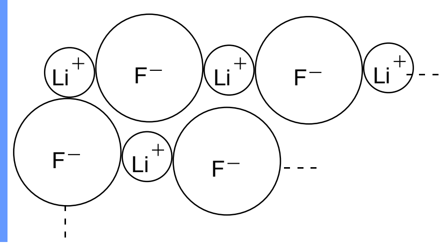


In space, Li^+ and F^- would be attracted to each other
In solution, Li^+ and F^- might be separated due to solvation (e.g. water would surround). Larger ions would have a higher degree of solvation than smaller ions (more water molecules would surround the larger molecule).



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



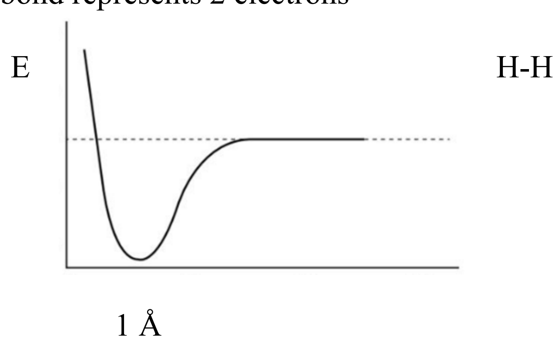


Electronegativity

- 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

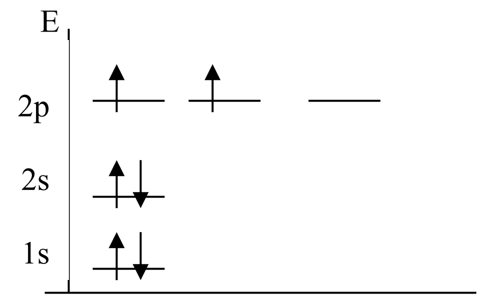
- <u>Sharing</u> of electrons between the atoms
- More common in organic chemistry
- One bond represents 2 electrons



Electronic configuration of carbon (C):

- Atomic number = 6
- Atomic weight = 12

<u>Carbon (C)</u>



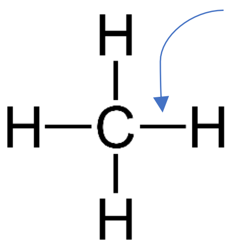
- Carbon needs to gain or lose $4e^-$ to get an inert gas configuration, but this would result in unfavourable charge buildup:

- C^{4+} is isoelectronic with He

- C^{4-} is isoelectronic with Ne

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

Methane (CH_4)



Each line is 2 e- in outer shell

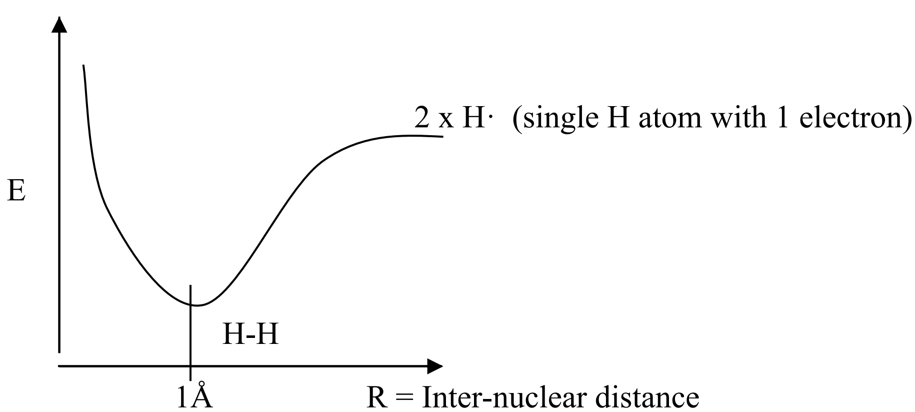
Carbon in methane has 10 e- in total;
- the 2 e- are in 1s and is not shown
- the other 8 e- are the outer shell electrons drawn as line bond

<u>Energetics of Forming Bonds</u>

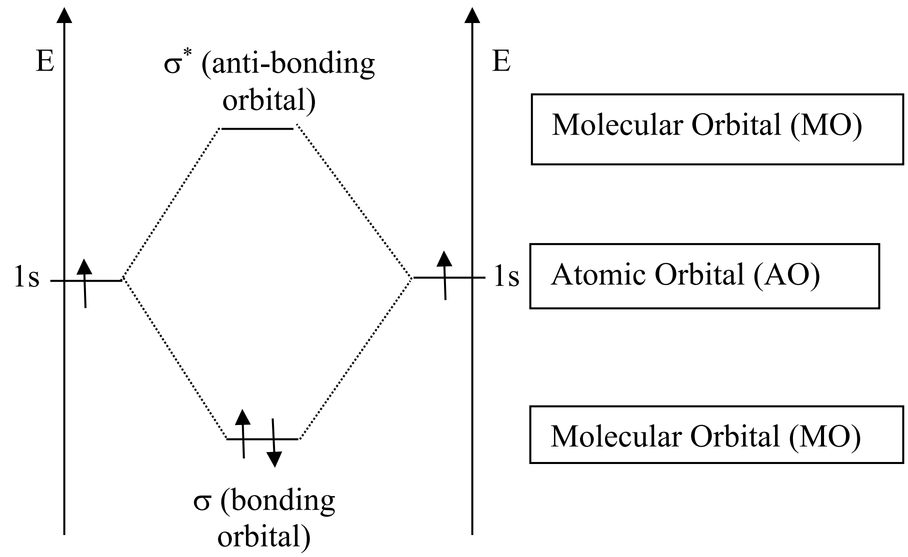
As two hydrogen atoms come together, molecular hydrogen (H_2) is formed

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

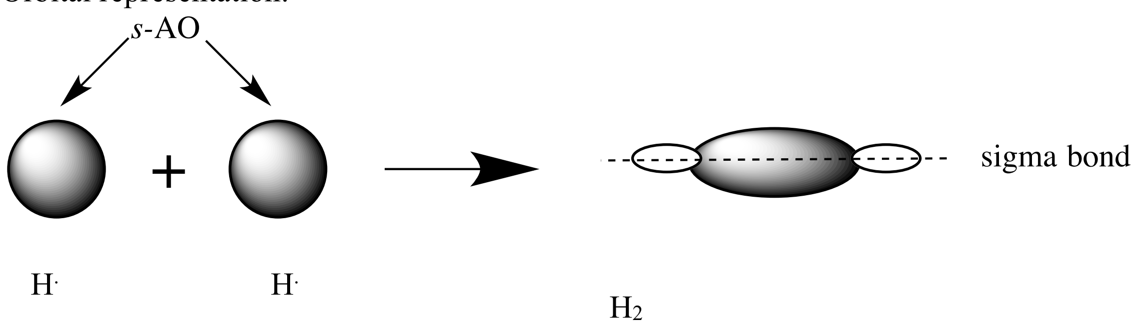
Energy diagram of two hydrogen atoms interacting to form a bond:



1Å is the average H-H bond distance
e.g. H_2



Orbital representation:



LCAO

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