



Adama Science and Technology University

General Chemistry (Chem1011) for Pre-engineering

Chemical Bonding and Molecular Structure

Course instructor: Eneyew Tilahun(M.Sc.)

Email: Eneyew.tilahun@astu.edu.et

ASTU/ASTU/ASTU

QUANTUM MECHANICS

- In the late seventeenth century, Isaac Newton discovered classical mechanics, the laws of motion of macroscopic objects.
- But physicists found that classical mechanics does not correctly describe the behavior of very small particles, such as the electrons and nuclei of atoms and molecules.
- The equations that govern the motion of electrons and of nuclei are not the familiar Newton equations, $F = ma$

- ❖ The behavior of such particles is described by a set of laws called quantum mechanics.
- ❖ **Quantum mechanics:** deals with atomic and molecular properties and behavior of matter on a microscopic scale.
- ❖ **Quantum mechanics** is the branch of physics that mathematically describes the wave properties of submicroscopic particles. it is a collection of postulates based on a huge number of experimental observations.
- ❖ **Quantum chemistry:** applies quantum mechanics to problems in chemistry.

Failures of classical mechanics

It doesn't explain about:

- ✓ Black body radiation (by Planck)
- ✓ Photoelectric effect (Einstein)
- ✓ Heat capacities (Einstein and Debye)
- ✓ Atomic and molecular spectroscopy
- ✓ Uncertainty Principle (Heisenberg)
- ✓ Does not correctly describe the behavior of very small particles such as the electrons and nuclei of atoms and molecules

Applications of Quantum mechanics

- ✓ To calculate thermodynamic properties of gases
- ✓ To interpret molecular spectra
- ✓ To analyze NMR spectra of a molecule

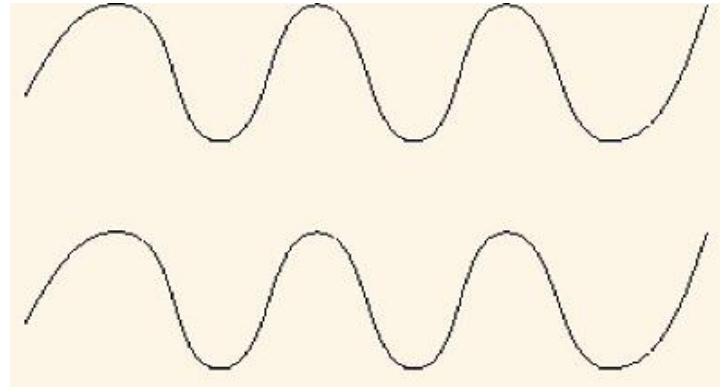
- ✓ to calculate molecular properties theoretically
- ✓ to understand intermolecular forces
- ✓ to deal with bonding in solids
- ✓ to estimate the relative stabilities of molecules
- ✓ to investigate the mechanisms of chemical reactions
- ✓ to calculate properties of reaction intermediates and
- ✓ to predict and explain the properties of transition-metal complex ions.

Background of Quantum Mechanics

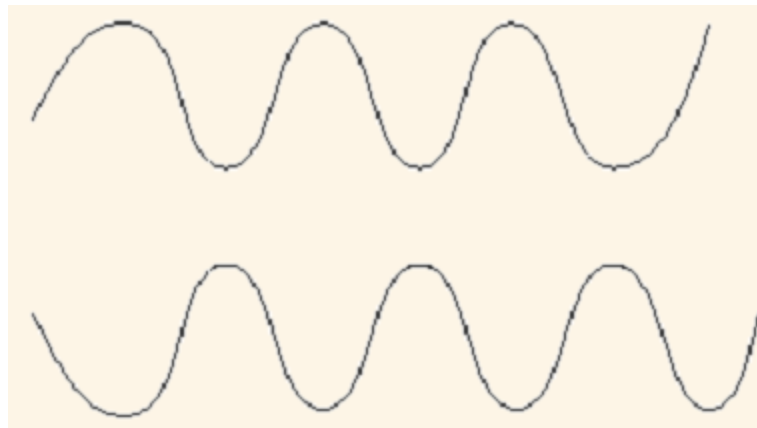
- ✓ Thomas Young gave convincing experimental evidence for the wave nature of light by observing **diffraction** and **interference** phenomenon.
- ✓ **Diffraction** is the bending of a wave around an obstacle or
- ✓ is the scattering of a wave as it passes an obstruction/gap.
- ✓ **Interference** is the combining of two waves of the same frequency to give a wave whose disturbance at each point in space is the algebraic or vector sum of the disturbances at that point resulting from each interfering waves.

❖ Interference can be classified as:-

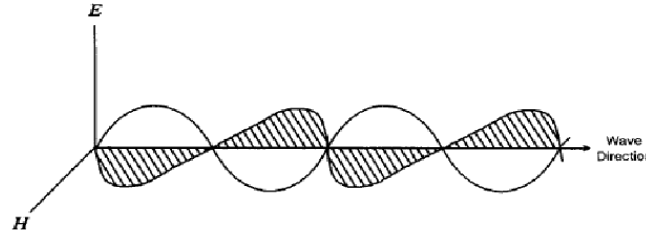
a) **Constructive:** occurs when the phase difference between the waves is even, 2π , 4π , 6π



b) **Destructive:** the phase difference between the waves is odd i.e. π , 3π , 5π



- Maxwell predicted the electromagnetic property of light.



- Heinrich Hertz detected radio waves produced by accelerated electric charges in a spark, as predicted by Maxwell's equations.
- This convinced physicists that light is indeed an electromagnetic wave.
- All electromagnetic waves travel at speed $c = 2.998 \times 10^8$ m/s in vacuum. The frequency & wavelength of an electromagnetic wave are related by $\lambda\nu = c$

SOLVED PROBLEM. The frequency of strong yellow line in the spectrum of sodium is $5.09 \times 10^{14} \text{ sec}^{-1}$. Calculate the wavelength of the light in nanometers.

SOLUTION. We know that wavelength, $\lambda = \frac{c}{\nu}$

Here $c = 3.0 \times 10^8 \text{ m sec}^{-1}$

$$\nu = 5.09 \times 10^{14} \text{ sec}^{-1} \text{ (given)}$$

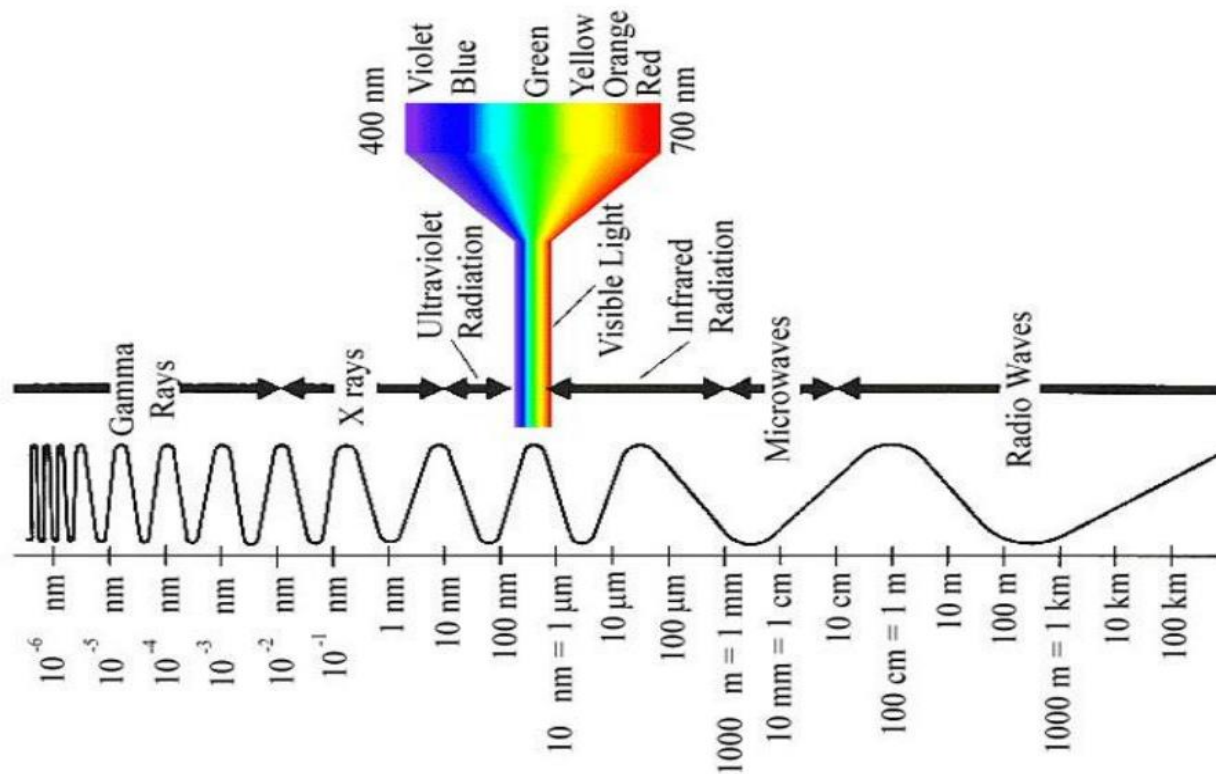
Wavelength $\lambda = \frac{3.0 \times 10^8 \text{ m sec}^{-1}}{5.09 \times 10^{14} \text{ sec}^{-1}}$

$$= \frac{3000}{5.09} \times 10^{-9} \text{ m}$$

$$= 589 \times 10^{-9} \text{ m}$$

$$= 589 \text{ nm}$$

$$[\because 1 \text{ nm} = 10^{-9} \text{ m}]$$



Regions of electromagnetic spectrum

Black Body Radiation

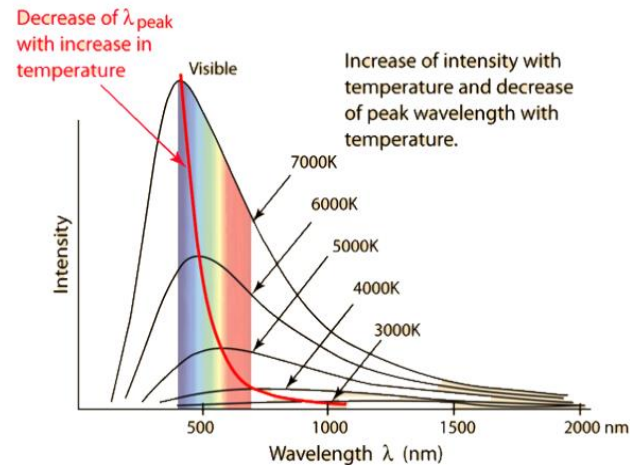
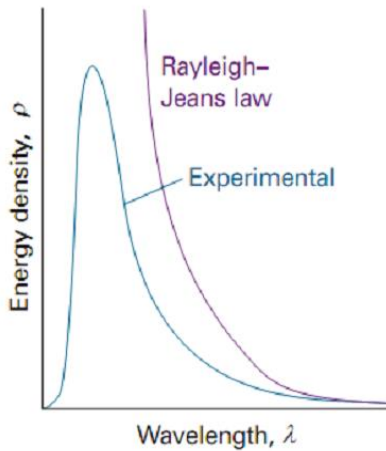
- In the late 1800s, physicists measured experimentally the intensity of light at various frequencies emitted by a heated blackbody at given temperature.

- A **blackbody** is an idealized physical body that absorbs and emits all incident electromagnetic radiation fall on it, regardless of frequency or angle of incidence, with no reflecting power.
- The radiation emitted by a blackbody is called blackbody radiation.
- When physicists used statistical mechanics and the electromagnetic-wave model of light to predict the intensity-versus-frequency curve for emitted blackbody radiation theoretically,
- they found a result in complete disagreement with the high-frequency portion of the experimental curves.

- **Classical Mechanics** assumed that the radiation emitted by the blackbody is caused by the oscillations of the electrons in the constituent particles of the material body.
- At a fixed temperature Rayleigh used equipartition principle to calculate the average energy of each oscillator as kT . Then, with minor help from James Jeans, he arrived at the Rayleigh-Jeans law,

$$dE = \rho d\lambda \quad \rho = \frac{8\pi kT}{\lambda^4}$$

- ρ (rho) the density of states, is the proportionality constant between $d\lambda$ and the energy density, k is Boltzmann's constant.
- The Rayleigh-Jeans law is quite successful at long wavelengths (low frequencies), it fails badly at short wavelengths (high frequencies).



- ❖ In 1900, Max Planck developed a theory that gave excellent agreement with the observed black body radiation curves.
- ❖ Planck assumed that the radiation emitted by the blackbody was caused by the oscillations of the electrons in the constituent particles of the material body.
- ❖ Energy of photon is given by $E = nh\nu$, $n = 0, 1, 2, \dots$
- ❖ Using this quantization of energy and some statistical thermodynamic ideas, Planck derived the equation.

SOLVED PROBLEM. Calculate the magnitude of the energy of the photon (or quantum) associated with light of wavelength 6057.8 Å. (Å = 10^{-8} cm)

SOLUTION

(a) Calculation of Frequency :

$$\begin{aligned} \nu &= \frac{c}{\lambda} = \frac{3.0 \times 10^{10} \text{ cm sec}^{-1}}{6057.8 \times 10^{-8} \text{ cm}} \\ &= 4.952 \times 10^{14} \text{ sec}^{-1} \end{aligned}$$

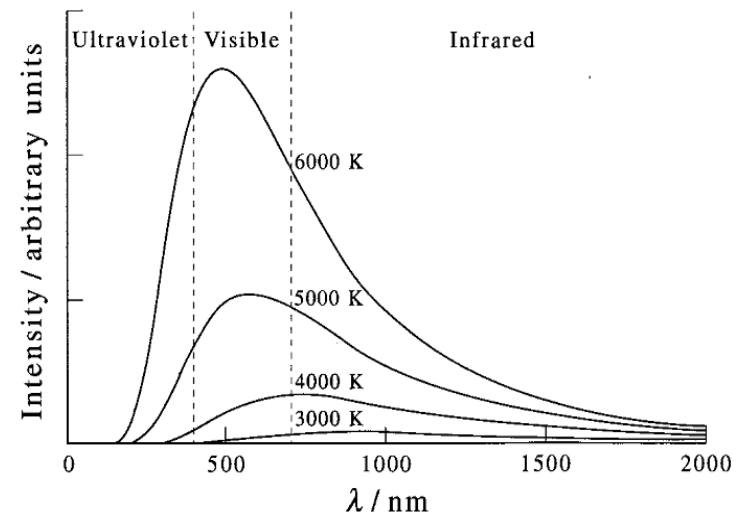
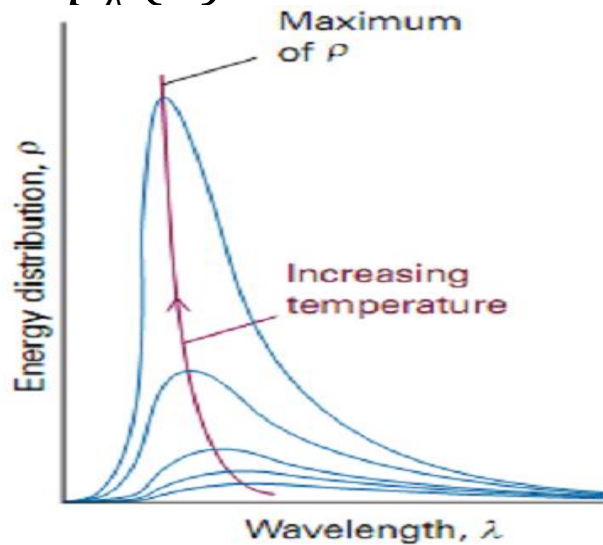
(b) Calculation of Energy :

$$\begin{aligned} E &= h\nu = (6.625 \times 10^{-27} \text{ erg sec}) (4.952 \times 10^{14} \text{ sec}^{-1}) \\ &= 3.281 \times 10^{-12} \text{ erg} \end{aligned}$$

$$dE = \rho d\lambda \quad \rho = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)}$$

Wien's Displacement Law

- We can use the above equation to justify an empirical relationship known as the Wien displacement law.
- The Wien displacement law says that if λ_{\max} is the wavelength at which $p_{\lambda}(T)$ is a maximum, then $\lambda_{\max} T = 2.90 \times 10^{-3} \text{ m} \cdot \text{K}$



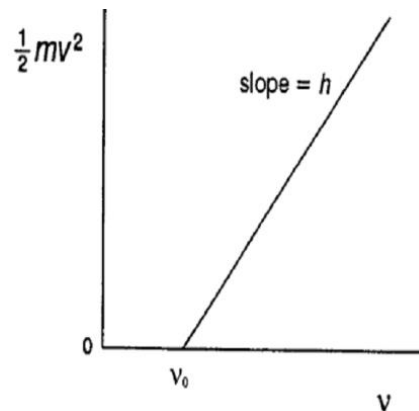
Photoelectric Effect

- ❖ When an electron in the metal absorbs a photon, part of the absorbed photon energy is used to overcome the forces holding the electron in the metal, and the remainder appears as kinetic energy of the electron after it has left the metal.
- ❖ Conservation of energy gives $h\nu = \phi + \text{KE}$, where ϕ is the metal's work function, and KE is the maximum kinetic energy of an emitted electron.
- ❖ The photoelectric effect shows that light can exhibit particle-like behavior in addition to the wavelike behavior it shows in diffraction experiments.

➤ Electrons are bound to the surface of a metal with an energy called the work function, ϕ .

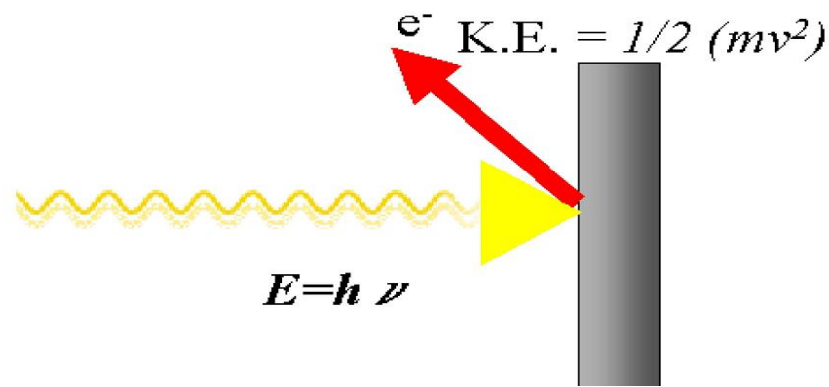
➤ When the electron is ejected from the surface of the metal, $\rightarrow \underline{KE = h\nu - \phi}$

➤ Therefore, we can write, $\frac{1}{2}mv^2 = h\nu - \phi$



$$\phi = h\nu_0$$

Photoelectric Effect



SOLVED PROBLEM. What is the minimum energy that photons must possess in order to produce photoelectric effect with platinum metal? The threshold frequency for platinum is $1.3 \times 10^{15} \text{ sec}^{-1}$.

SOLUTION

The threshold frequency (ν_0) is the lowest frequency that photons may possess to produce the photoelectric effect. The energy corresponding to this frequency is the minimum energy (E).

$$\begin{aligned} E &= h\nu_0 \\ &= (6.625 \times 10^{-27} \text{ erg sec}) (1.3 \times 10^{15} \text{ sec}^{-1}) \\ &= 8.6 \times 10^{-12} \text{ erg} \end{aligned}$$

SOLVED PROBLEM. Calculate the kinetic energy of an electron emitted from a surface of potassium metal (work function = 3.62×10^{-12} erg) by light of wavelength 5.5×10^{-8} cm.

SOLUTION

$$v = \frac{c}{\lambda} \text{ where } c = \text{velocity of light } (3.0 \times 10^{10} \text{ cm sec}^{-1})$$

For

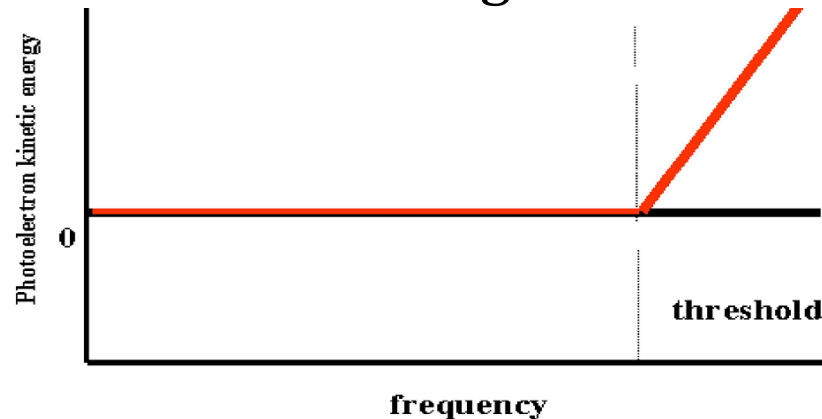
$$\lambda = 5.5 \times 10^{-8} \text{ cm}$$

$$v = \frac{c}{\lambda} = \frac{3.0 \times 10^{10} \text{ cm sec}^{-1}}{5.5 \times 10^{-8} \text{ cm}} = 5.5 \times 10^{17} \text{ sec}^{-1}$$

$$\begin{aligned} \frac{1}{2}mv^2 &= h\nu - W \\ &= (6.6 \times 10^{-27} \text{ erg sec}) (5.5 \times 10^{17} \text{ sec}^{-1}) - 3.62 \times 10^{-12} \text{ erg} \\ &= 3.63 \times 10^{-9} \text{ erg} - 3.62 \times 10^{-12} \text{ erg} \\ &= 3.63 \times 10^{-9} \text{ erg} \end{aligned}$$

Thus the electron will be emitted with kinetic energy of 3.63×10^{-9} erg.

Consider the diagram below



- No electrons are ejected, regardless of the intensity of the radiation, unless its frequency exceeds a **threshold value** characteristic of the metal, i.e. $V > V_0$
- The kinetic energy of the electron increases linearly with the frequency of the incident radiation but is independent of the intensity of the radiation.
- Even at low intensities, electrons are ejected immediately if the frequency is above the threshold.
- In general to eject an electron from the surface of a metal,

$$h\nu > \phi \quad \text{i.e. } h\nu > h\nu_0.$$

Example:

■ Given that the work function of sodium metal is 1.82 eV. Then calculate V_0 for sodium metal.

Solution: convert eV to Joule, since $1\text{eV} = 1.602 \times 10^{-19} \text{ J}$ then 1.82 eV becomes: $1.602 \times 10^{-19} \text{ J} \times 1.82 \text{ eV}/1 \text{ eV} = 2.92 \times 10^{-19} \text{ J} = \phi$

And again $\phi = h\nu_0$ where $h = 6.626 \times 10^{-34} \text{ J.s}$

$$\nu_0 = \phi/h.$$

Particle-Wave Duality

- Because light behaved as both waves (diffraction, as proved by Young in 1801) and particles (the photoelectric effect shown by Einstein in 1905), the nature of light was debated for many years.
- Light has characteristics of both a wave and a particle, the so-called particle-wave duality.
- For electromagnetic radiation, De-Broglie has showed the consequence of relativity theory, EMR has, $E = h\nu = \frac{hc}{\lambda}$,
- He proposed that all moving objects have wave properties. Thus
 - For light characteristics: $E = h\nu = \frac{hc}{\lambda}$ (plank)
 - For particles: $E = mc^2$ (Einstein).

- The photon also has an energy given by the relationship from relativity theory, $E = mc^2$.
- A particular photon has only one energy, so given by $mc^2 = \frac{hc}{\lambda}$,
- This can be re-write as $\lambda = \frac{h}{mc}$.
- Therefore, according to De Broglie, a particle with mass, m , and moving with speed, v , has a wave wavelength given by
$$\lambda = \frac{h}{mv},$$
- Using beam of electrons in electron microscope instead of light beam to investigate the structures of materials is one of the application of wave property of electron.

Example:

Find de Broglie wavelength of an electron traveling at 1.00% of speed of light.

Solution: speed of light, $C = 3 \times 10^8 \text{ m/s}$ and so 1% of speed of light is equivalent to $3 \times 10^6 \text{ m/s} = v$.

So use the formula $\lambda = \frac{h}{mv}$, use value of h and mass of electron as $6.626 \times 10^{-34} \text{ J.s}$ and $9.106 \times 10^{-31} \text{ Kg}$, respectively.

Heisenberg Uncertainty Principle

- In order to locate the particle we must use “light” having a wavelength about the same length as the size of the particle.
- Radiation of 10^{-8} cm (very short) wavelength has very high energy since, $E = \frac{hc}{\lambda}$.
- In the process of locating (observing) the particle with high-energy radiation, we have changed its momentum and energy.
- Therefore, it is impossible to determine both the position and momentum simultaneously to greater accuracy than some fundamental quantity.

➤ That quantity is h and the relationship between the uncertainty in position (distance) and that in momentum is $\Delta x \cdot \Delta (mv) \geq h$.

Exercise

1. Explain the difference and similarity between classical mechanics and quantum mechanics.
2. Find the wavelength (in nm) of a baseball of mass 0.14 kg moving at 85 mph.
3. An FM radio station broadcasts at a frequency of $9.87 \times 10^7 \text{ s}^{-1}$ (98.7 MHz). Calculate the wavelength of the radio waves. What is the energy of one photon of this radiation?
4. Calculate the number of photons in a 2.00 mJ light pulse at $1.06 \mu\text{m}$.
5. When a clean surface of silver is irradiated with light of wavelength 230 nm, the kinetic energy of the ejected electrons is found to be 0.805 eV. Calculate the work function and the threshold frequency of silver.

6. What is the DeBroglie wavelength of an electron that are accelerated via a potential difference of 100 V?
7. Determine the de Broglie wavelength (in nm) associated with a neutron traveling at a speed of 5.0×10^3 m/s. The mass of a neutron is 1.67×10^{-24} g.
8. Calculate the de Broglie wavelength for an electron with kinetic energy of 1 eV.
9. Hydrogen has a red emission line at 656.3 nm, what is the energy and frequency of a photon of this light? Use planks constant and speed of light.

- 10.** What is the uncertainty in velocity of an electron if the uncertainty in position is 100 pm? ($m.e^- = 9.101 \times 10^{-31} \text{ kg}$ and $h = 6.626 \times 10^{-34} \text{ J.S}$).
- 11.** When lithium is irradiated with light, the kinetic energy of the ejected electrons is $2.935 \times 10^{-19} \text{ J}$ for $\lambda = 300.0 \text{ nm}$ and $1.280 \times 10^{-19} \text{ J}$ for $\lambda = 400.0 \text{ nm}$. Calculate
- (a) the Planck constant, (b) the threshold frequency, and (c) the work function of lithium from these data.
- 12.** Radiation in the infrared region is often expressed in terms of wave numbers, $\tilde{\nu} = 1/\lambda$. A typical value of $\tilde{\nu}$ in this region is 10^3 cm^{-1} . Calculate the values of ν , λ , and E .
- 13.** Sirius, one of the hottest known stars, has approximately a blackbody spectrum with $\lambda_{\text{max}} = 260 \text{ nm}$. Estimate the surface temperature of Sirius.

14 Past the infrared region, in the direction of lower energies, is the microwave region. In this region, radiation is usually characterized by its frequency, ν , expressed in units of megahertz (MHz), where the unit, hertz (Hz), is a cycle per second. A typical microwave frequency is 2.0×10^4 MHz. Calculate the values of ν , λ , and E for this radiation.

15 The fireball in a thermonuclear explosion can reach temperatures of approximately 10^7 K. What value of λ_{max} does this correspond to? In what region of the spectrum is this wavelength found.

❖ **Wave function (ψ):** function describing the probability of a particles quantum state as a function of position, momentum or spin.

❖ **ψ in quantum mechanics,** variable quantity that mathematically describes the **wave** characteristics of a particle.

➤ **Importance of wave function:-**

A) To describe the property of the system.

B) To determine any observable property of a system, eg energy

C) Wave function completely defines the system (e.g **electrons in an atom**).

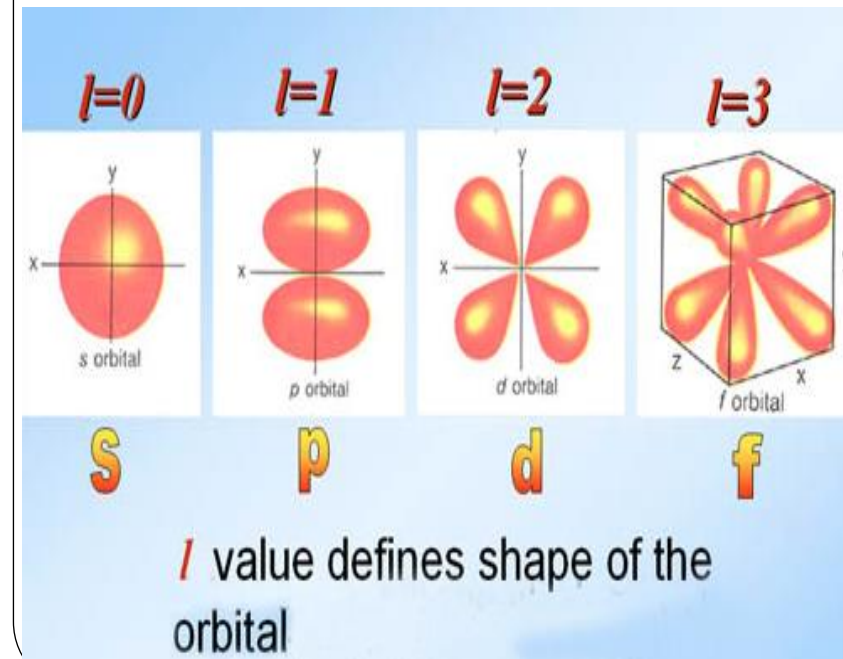
- In radial wave-function, two quantum numbers are defined. One is the principal quantum number (n), corresponding to a shell.
- For example, electrons with $n=2$ belong to the L shell.
- The other is orbital angular momentum quantum number (ℓ), corresponding to a sub-shell, $\ell = n-1, 0, 1, 2, 3, \dots$

When $n = 1$, there is only one s -type subshell ($l = 0$). Quantum numbers of $n = 1$ and $l = 0$ stand for 1s atomic orbital. When $n = 2$, there are s -type ($l = 0$) and p -type ($l = 1$) subshells. Quantum numbers of $n = 2$ and $l = 0$ stand for 2s atomic orbital, and $n = 2$ and $l = 1$ stand for 2p atomic orbital.

❖ Relationship between quantum numbers, shell and subshell in hydrogenic atom .

n	Shell	l	Subshell	Atomic orbital
1	K	0	s	1s
2	L	0	s	2s
2	L	1	p	2p
3	M	0	s	3s
3	M	1	p	3p
3	M	2	d	3d

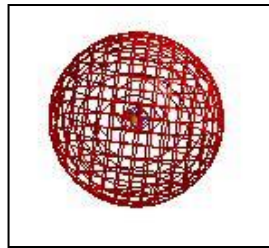
- ❖ That is why 2s and 2p atomic orbitals of hydrogenic atom are degenerated.
- ❖ Number of electron in subshell = $2(2\ell + 1)$. In shell = $2n^2$
- ❖ The angular momentum quantum number, ℓ (also referred to as the secondary quantum number or azimuthal quantum number) describes the shape of the orbital that an electron occupies.



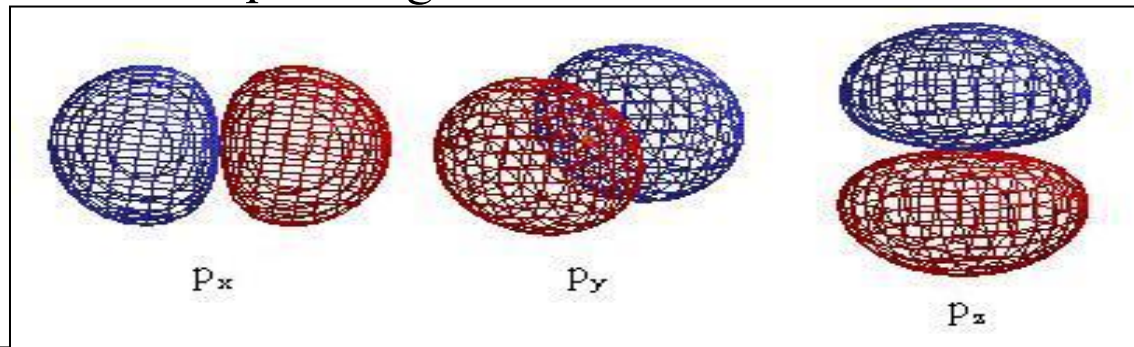
Angular Momentum Quantum Number, ℓ	Name of Subshell	Shape	
0	s	Sphere	
1	p	Dumbbell	
2	d	Complex/double dumbbell	
3	f	More complex/multiple lobes	

Atomic Subshells

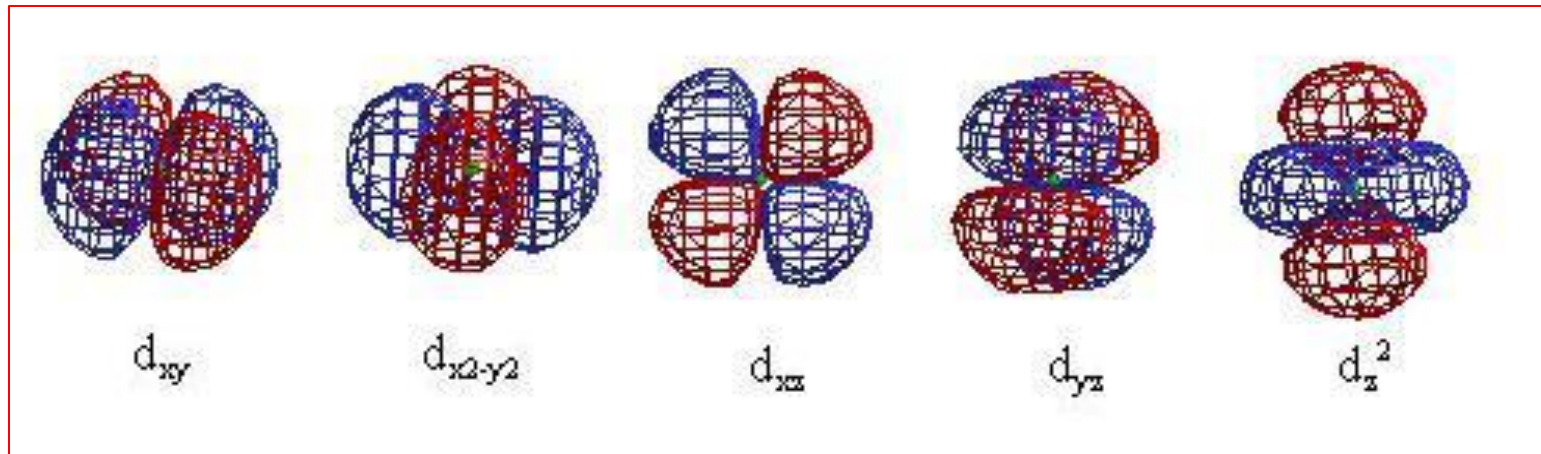
- ❖ **S subshell** (Spherical shape): There is one S orbital in an s subshell. The electrons can be located anywhere within the sphere centered at the atom's nucleus.



- ❖ **P orbitals** (Shaped like two balloons tied together): There are 3 orbitals in a p subshell that are denoted as p_x , p_y , and p_z orbitals. These are higher in energy than the corresponding s orbitals.



- ❖ **d orbitals:** The d subshell is divided into 5 orbitals (d_{xy} , d_{xz} , d_{yz} , d_z^2 and $d_{x^2-y^2}$). These orbitals have a very complex shape and are higher in energy than the s and p orbitals.



Quantum Numbers, Their Properties, and Significance

Name	Symbol	Allowed values	Physical meaning
principle quantum number	n	1, 2, 3, 4,	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	l	$0 \leq l \leq n - 1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \leq m_l \leq l$	orientation of the orbital
spin quantum number	m_s	$\frac{1}{2}, -\frac{1}{2}$	direction of the intrinsic quantum "spinning" of the electron

- The magnetic quantum number m_ℓ , specifies the orbital orientations.
- For the quantum number ℓ values below, how many possible values are there for the quantum number m_ℓ ? (a) 5; (b) 3; (c) 2; (d) 1.
- A) Give the maximum number of electrons in an atom that can have $n = 5$, $m_\ell = +1$.
- m_s specifies how many electrons can occupy that orbital is.

Atomic Orbital is a mathematical function that describes the wave-like behavior of either one electron or a pair of electrons in an atom.

- This function can be used to calculate the probability of finding any electron of an atom in any specific region around the atom's nucleus.

Exercise-2

- 1) Give the maximum number of electrons & orbitals in an atom that can have the following quantum numbers: a) $n = 4$ b) $n = 5$ and $m_s = +1/2$
- 2) Explain why electrons never fall in to the nucleus?
- 3) Give the orbital designation (1s, 2p, 3d, etc.) of electrons with the following combination of principal and azimuthal quantum numbers,
 - (a) $n = 1, m_\ell = 0$
 - (b) $n = 2, m_\ell = 1$
 - (c) $n = 5, \ell = 2$

4) Define the following words and phrases:

- a) Orbital
- b) Wave function
- c) Principal quantum number

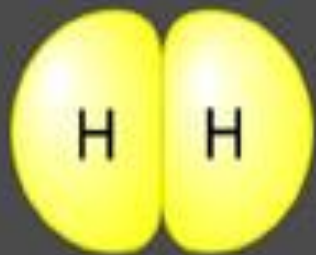
5) How do u calculate the following :

- a) Total number of electrons
- b) Total number of orbitals
- c) Total m_ℓ value

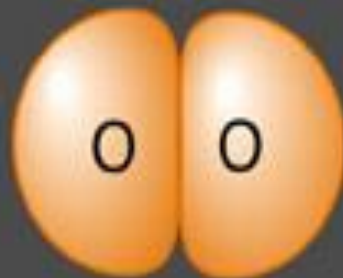
6) What does a set of four quantum numbers tell you about an electron?

Compare and contrast the locations and properties of two electrons with quantum number sets $(4, 3, 1, +\frac{1}{2})$ and $(4, 3, -1, +\frac{1}{2})$.

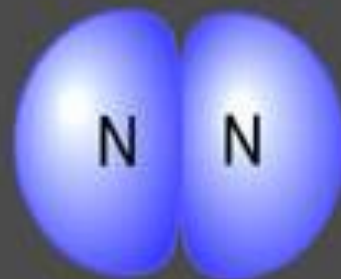
Chemical Bonding



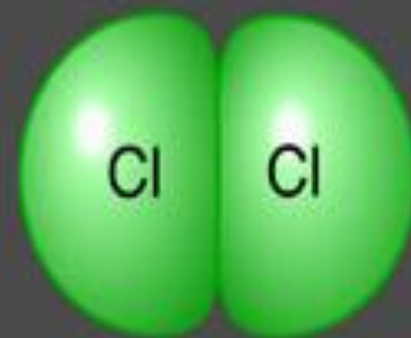
H_2
hydrogen



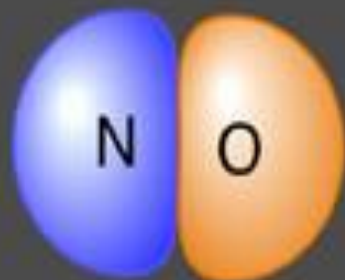
O_2
oxygen



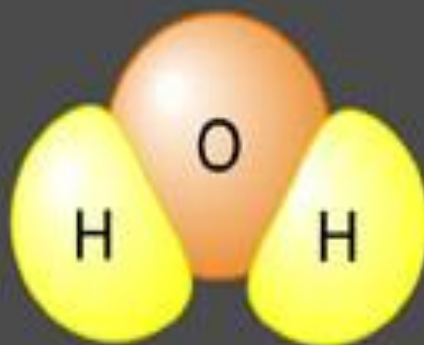
N_2
nitrogen



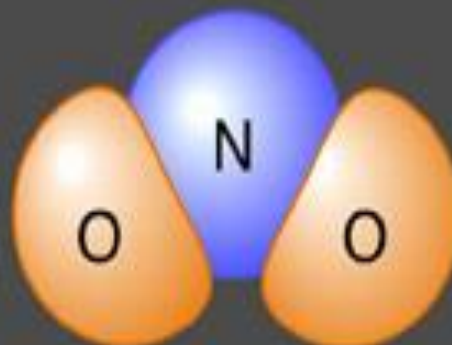
Cl_2
chlorine



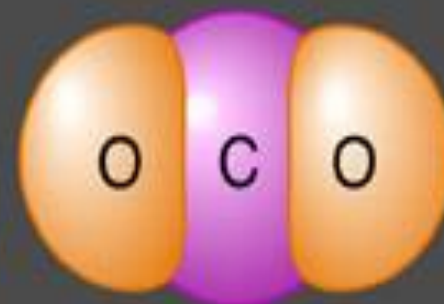
NO
nitrogen oxide



H_2O
water



NO_2
nitrogen dioxide



CO_2
carbon dioxide

CHEMICAL BONDING

- **Bond** a force that holds two or more atoms and/or molecules together.
- A **chemical bond** is the attraction between atoms, ions or molecules that enables the formation of chemical compounds.
- The valence electrons are outer shell electrons that participate in chemical bonding.

<u>Group</u>	<u>e⁻ configuration</u>	<u># of valence e⁻</u>
1A	ns ¹	1
2A	ns ²	2
3A	ns ² np ¹	3
4A	ns ² np ²	4
5A	ns ² np ³	5
6A	ns ² np ⁴	6
7A	ns ² np ⁵	7

The classical description

- ❖ By classical, we mean models that do not take into account the quantum behavior of small particles, notably the electron.
- ❖ Lewis structures use Lewis symbols to show valence electrons in molecules and ions of compounds.
- ❖ In Lewis symbols, valence electrons for each element are shown as a dot.

[illegible]

- ❖ Atoms bond because it results in a more stable electron configuration
- ❖ Atoms bond together by either transferring or sharing electrons so that all atoms obtain an outer shell with 8 electrons

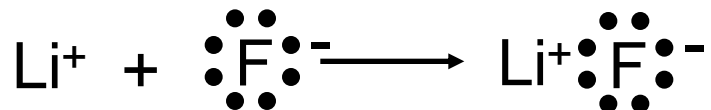
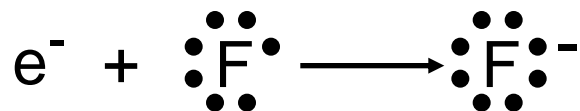
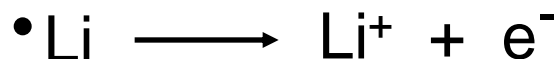
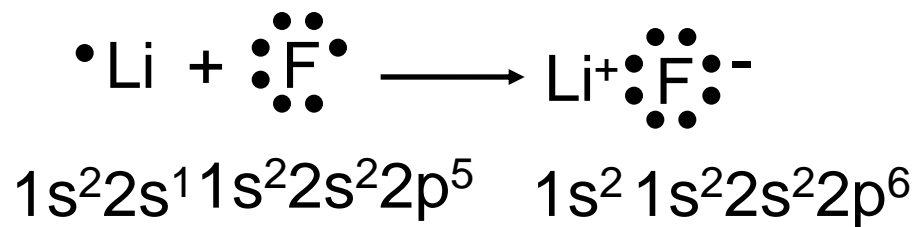
Octate Rule

- ❖ There are some exceptions to this rule, the key to remember is to try to get an electron configuration like a noble gas.
- ❖ Cations have Lewis symbols without valence electrons.
 - ✓ Lost in the cation formation
- ❖ Anions have Lewis symbols with 8 valence electrons
 - ✓ Electrons gained in the formation of the anion

Ionic Bond

- metal to nonmetal
- metal loses electrons to form cation
- nonmetal gains electrons to form anion
- ionic bond results from $+$ to $-$ attraction
- larger charge = stronger attraction
- smaller ion = stronger attraction
- Lewis theory allow us to predict the correct formulas of ionic compounds

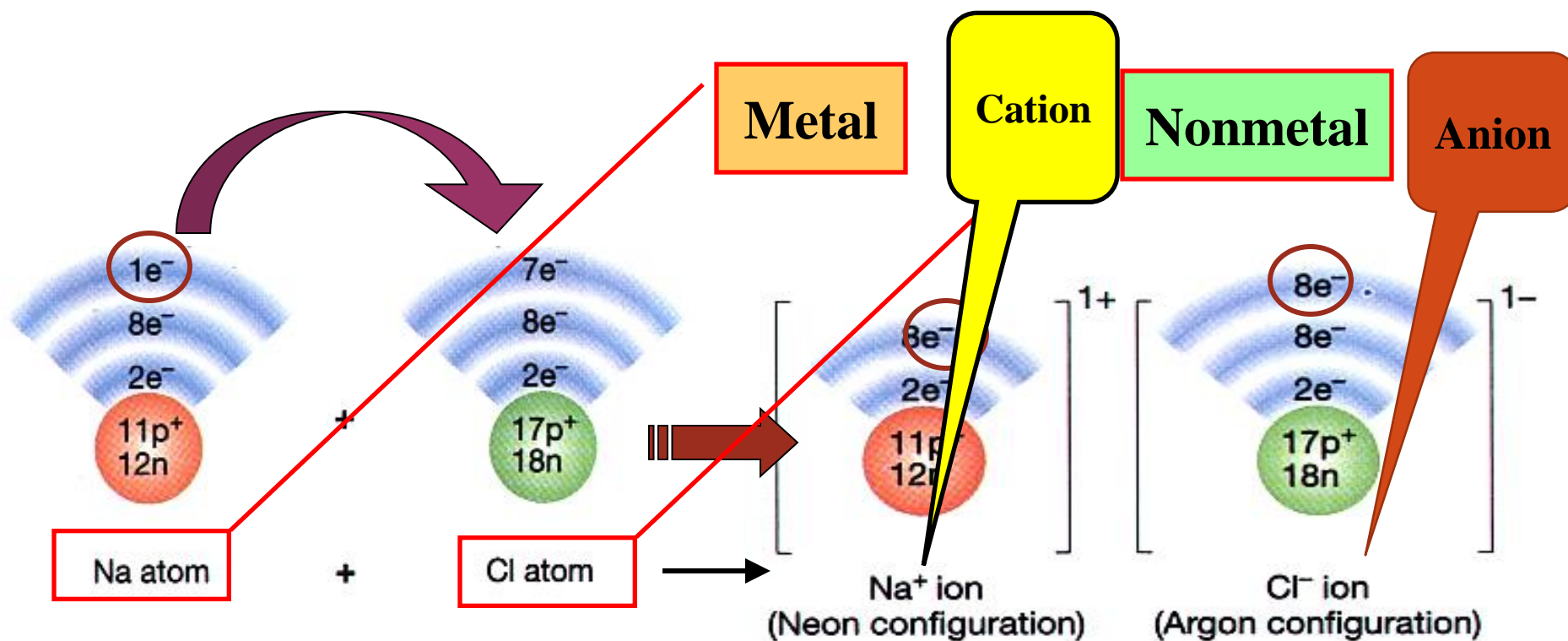
Ionic bond: the electrostatic force that holds ions together in an ionic compound also called **electrovalent bond**



Condition for the formation of Ionic bonds

1. Low ionization energy for metal atom ($\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$)
2. High electron affinity for non-metal atom ($\text{F} > \text{O} > \text{N} > \text{C}$)
3. High Lattice energy
 - a. Size of the ions
 - b. Charge on the ions
4. Large differences of electro negativities between the electro positive element (metal) and electro negative element (non-metal)
 - After bonding, each atom achieves a complete shell (noble gas configuration).

- ❑ The smallest particles of ionic compounds are ions (not atoms).
- ❑ Atoms that lose electrons (metals) form positive ions (cations).
- ❑ Atoms that gain electrons (non-metals) form negative ions (anions).

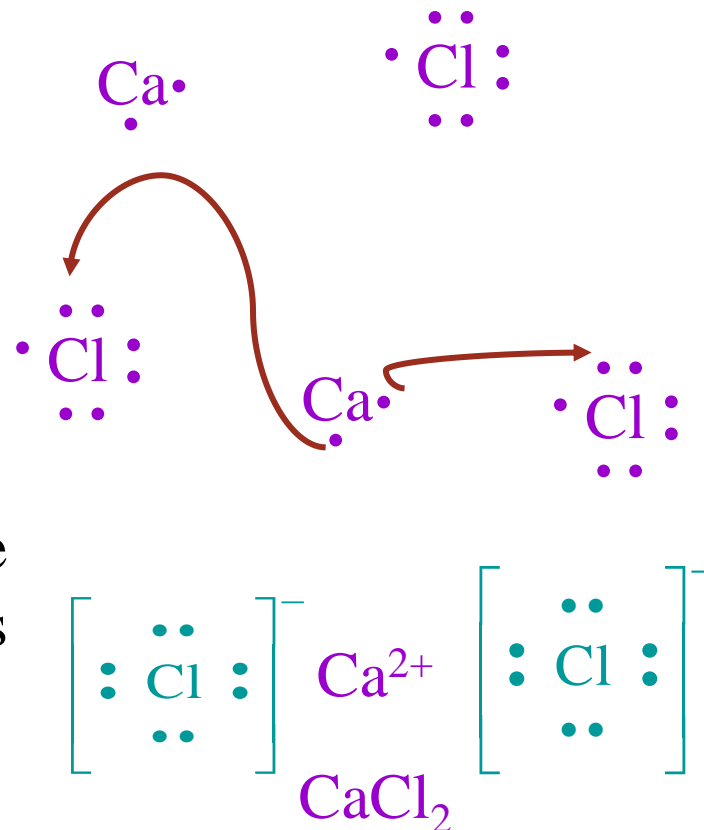


Using Lewis Theory to Predict Chemical Formulas of Ionic Compounds

Predict the formula of the compound that forms between calcium and chlorine.

Draw the Lewis dot symbols of the elements

- ✓ Transfer all the valance electrons from the metal to the nonmetal,
- ✓ adding more of each atom as you go, until all electrons are lost from the metal atoms and all nonmetal atoms have 8 electrons



The element $\cdot\dot{X}:$ could be

(a) Sulfur

(b) Iodine

(c) Aluminum

(d) Silicon

Electrostatic (Lattice) Energy

Lattice energy (U) is the energy required to completely separate one mole of a solid ionic compound into gaseous ions.

$$E = k \frac{Q^+ Q^-}{r}$$

E is the potential energy

Q^+ is the charge on the cation

Q^- is the charge on the anion

r is the distance between the ions

<u>Compound</u>	<u>Lattice Energy</u> (kJ/mol)
-----------------	-----------------------------------

Lattice energy increases as **Q increases** and/or as **r decreases**.

MgF₂

2957

Q: +2,-1

MgO

3938

Q: +2,-2

LiF

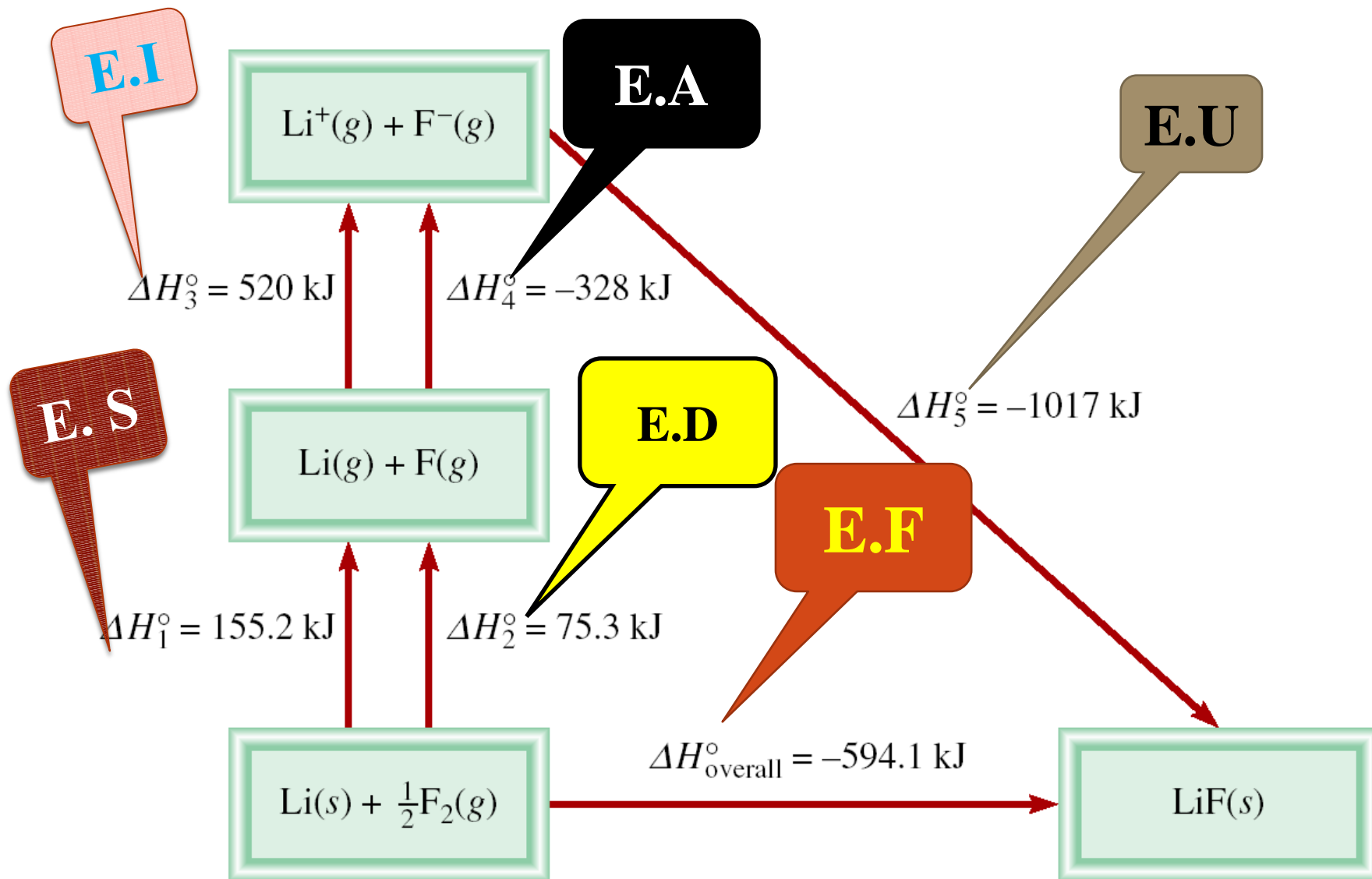
1036

$r \text{ F}^- < r \text{ Cl}^-$

LiCl

853

Born-Haber Cycle for Determining Lattice Energy



$$\Delta H_{\text{overall}}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ + \Delta H_5^\circ$$

- Born-Haber cycle relates the lattice energy of a crystal to other thermochemical data such as enthalpies of sublimation and dissociation, electron affinity, ionization energy involved in building a crystal.
- The lattice energy and electron affinity are negative while enthalpies of sublimation and dissociation and the ionization energy are positive.

$$\Delta H_f (\text{NaCl}) = \Delta H_{\text{sub}} + I + \Delta H_{\text{dis}} + \Delta H(\text{E.A}) + U$$

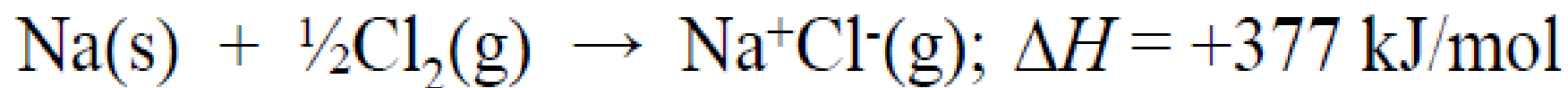
$$U = \Delta H_f (\text{NaCl}) - \Delta H_{\text{sub}} - I - \Delta H_{\text{dis}} - \Delta H(\text{E.A})$$

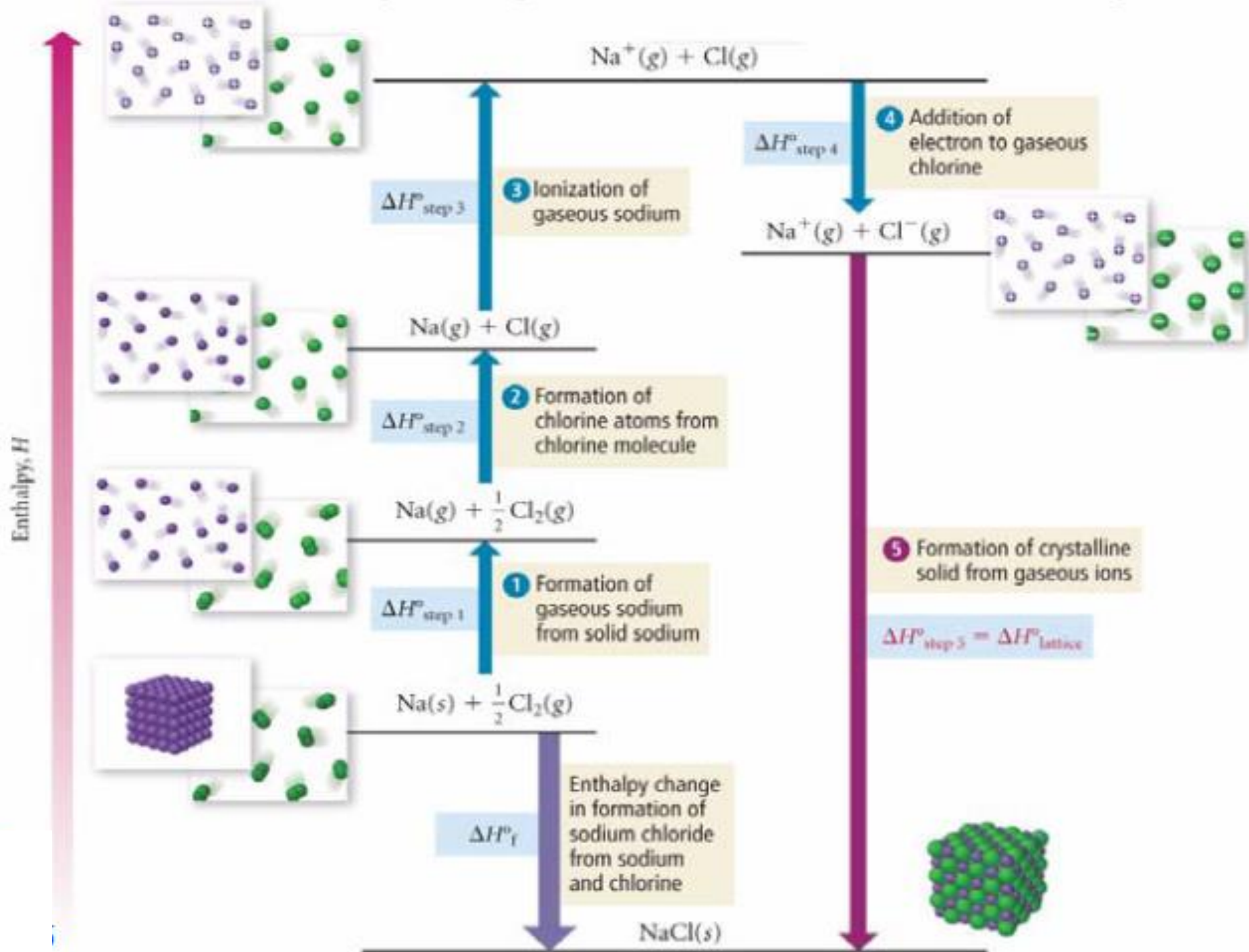
$$= -381.8 \text{ kJ} - 108.5 \text{ kJ} - 121.5 \text{ kJ} - 495.2 \text{ kJ}$$

$$\mathbf{U = -758.7 \text{ kJ}}$$

- The energy changes in the formation of NaCl from Na(s) and Cl₂(g) are shown in Figure
 - **Step 1:** sublimation of Na(s) to Na(g):
 $\Delta H = +107.3 \text{ kJ/mol}$
 - **Step 2:** dissociation of Cl₂(g) molecules into 2Cl(g) atoms:
 $\Delta H = +122 \text{ kJ/mol}$
 - **Step 3:** ionization of Na(g) into Na⁺(g) ions:
 $\Delta H = +495.8 \text{ kJ/mol}$
 - **Step 4:** addition of an electron to Cl(g) to form Cl⁻(g) ions:
 $\Delta H = -348.6 \text{ kJ/mol}$

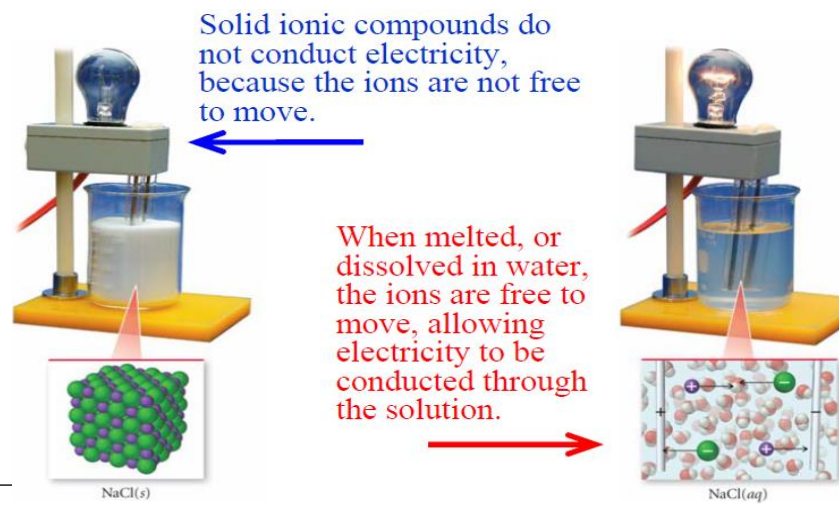
- The total so far:





Properties of ionic compounds

- Ionic compounds are usually crystalline solids that are hard and brittle.
- They are freely soluble in polar solvents like water and are insoluble in solvents like benzene, CS_2 , CCl_4 etc., [H_2O has high dielectric constant]
- Do not conduct electricity in solid state but act as good conductors in fused state.



- The chemical reactions between ionic compounds in solutions are very fast.
- They do not exhibit spacial isomerism due to non-directional nature of ionic bond.
- The lattice energy (U) of crystals is the energy evolved when one mole of ionic crystal is formed from gaseous ions.
- Example:

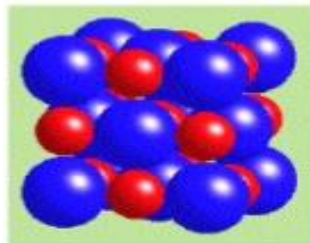
$$Na^{+}(g) + Cl^{-}(g) \longrightarrow NaCl (crystal) \quad \Delta H = -758.7 \text{ kJ mol}^{-1}$$
$$Li^{+}(g) + F^{-}(g) \longrightarrow LiF (crystal) \quad \Delta H = -1004 \text{ kJ mol}^{-1}$$
- Lattice energies cannot be measured directly, but experimental values are obtained from thermodynamic data using the Born-Haber cycle.

- ❖ **Ionic bonding** is **non-directional** because an **ion** has the same attraction from all directions for an **ion** of opposite charge.
- ❖ This means that packing efficiency in the crystal lattice determines the arrangement of **ions** in a crystal. There is no preferred direction for the **bonds**.

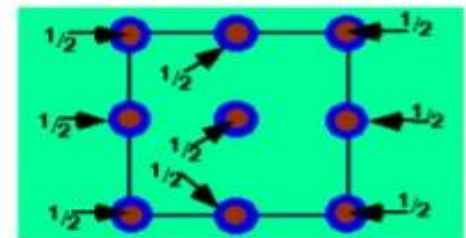
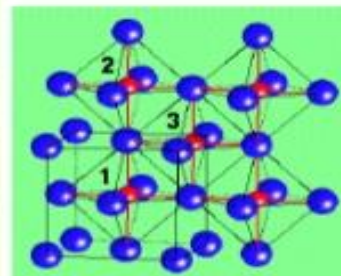
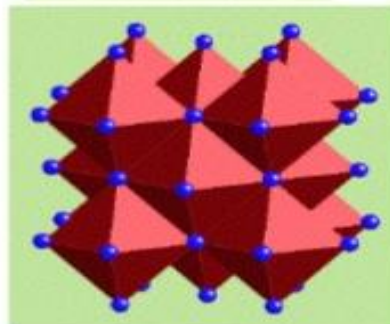
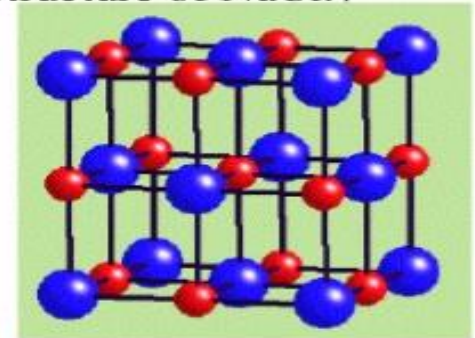
Geometric Arrangement of Ions in an Ionic Solid

Because the ionic bond is nondirectional the ions pack together in a solid in ways which are governed by their relative sizes.

Another important factor is that the ions must be arranged so that their is local charge neutrality. [Note the structure of NaCl.]



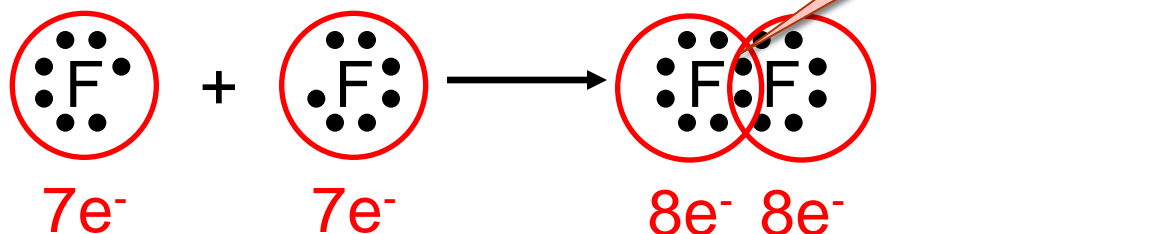
NaCl
Rock Salt
(Halite)



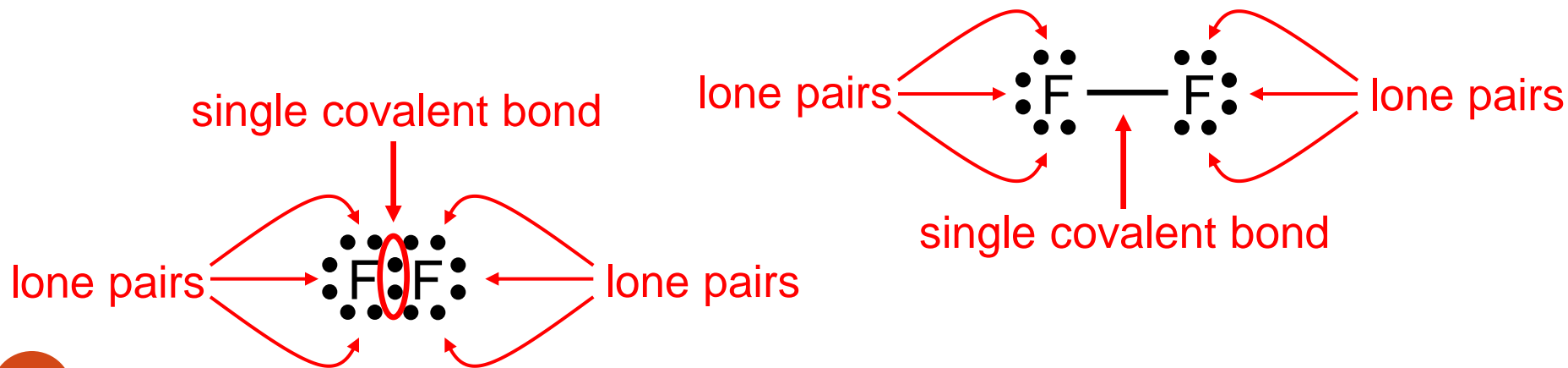
covalent bond

Is a chemical bond in which two or more electrons are shared by two atoms.

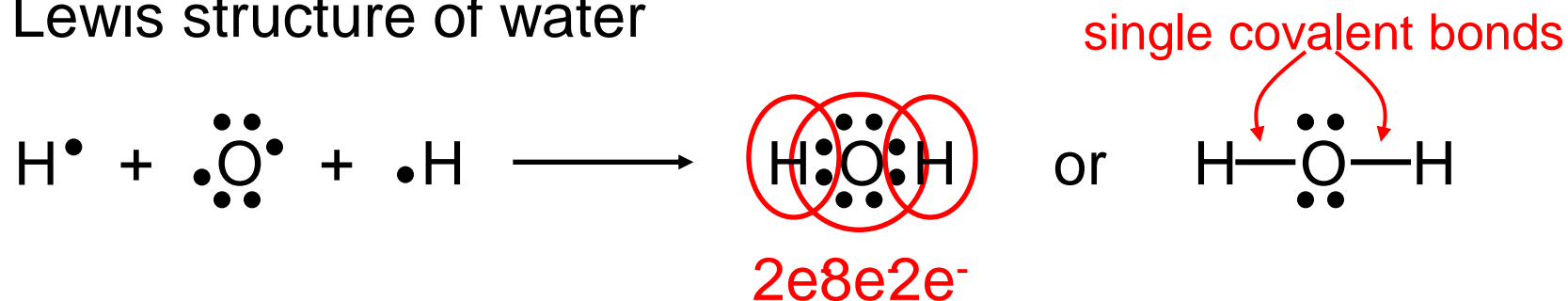
Why should two atoms share electrons?



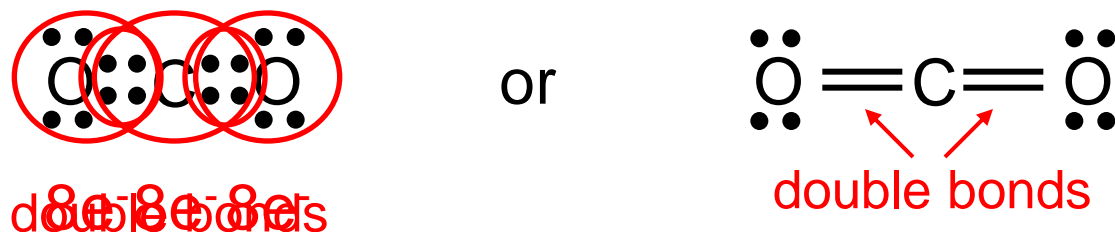
Lewis structure of F_2



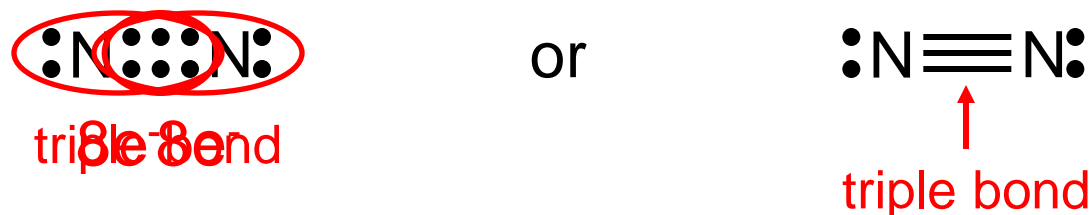
Lewis structure of water



Double bond – two atoms share two pairs of electrons

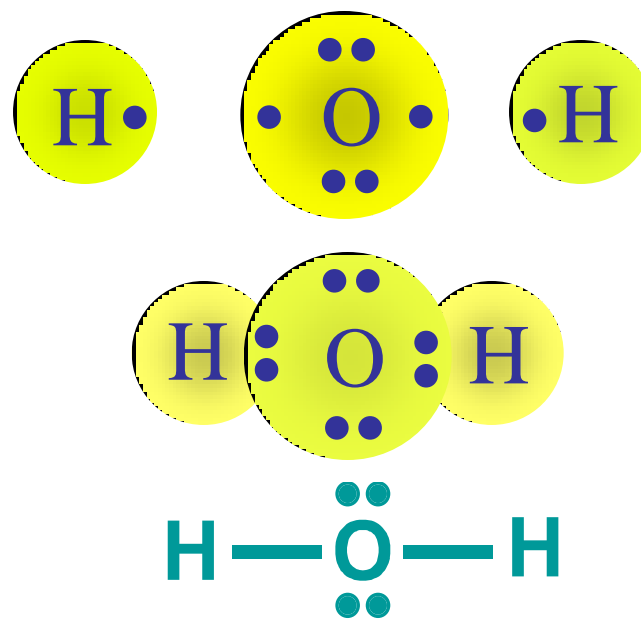
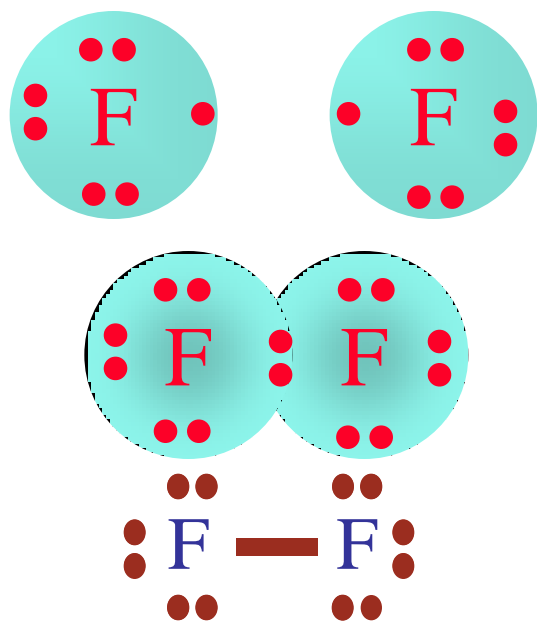


Triple bond – two atoms share three pairs of electrons



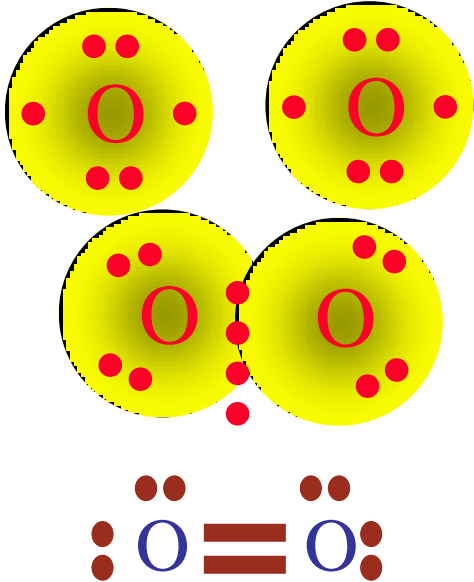
Single Covalent Bonds

- two atoms share one pair of electrons, 2 electrons
- one atom may have more than one single bond



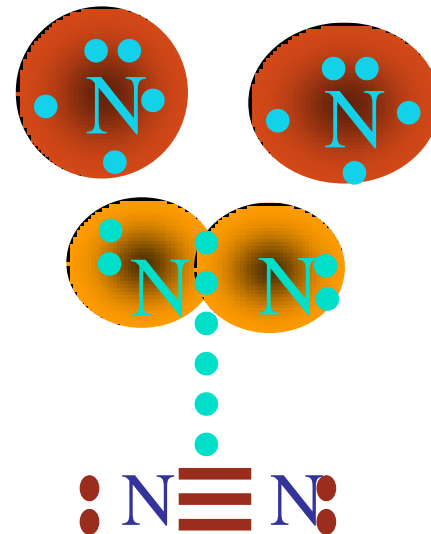
Double Covalent Bond

- two atoms sharing two pairs of electrons, 4 electrons
- shorter and stronger than single bond

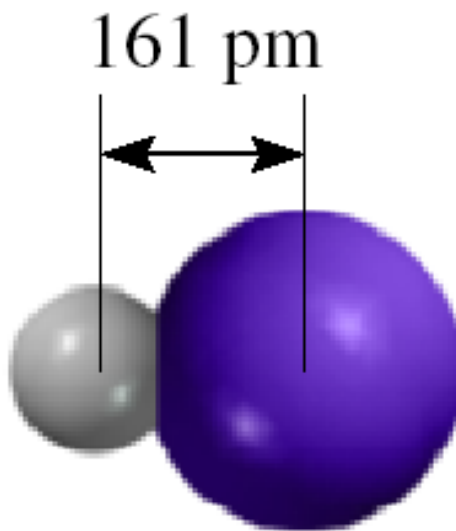
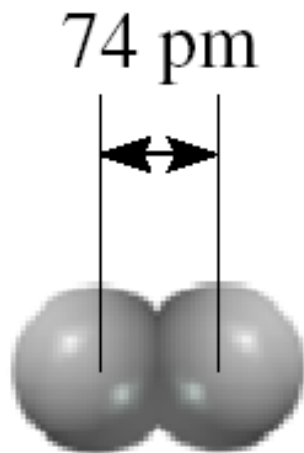


Triple Covalent Bond

- two atoms sharing 3 pairs of electrons, 6 electrons
- shorter and stronger than single or double bond



Lengths of Covalent Bonds



Average Bond Lengths of
Some Common Single,
Double, and Triple Bonds

Bond Type	Bond Length (pm)
C—H	107
C—O	143
C=O	121
C—C	154
C=C	133
C≡C	120
C—N	143
C=N	138
C≡N	116
N—O	136
N=O	122
O—H	96

Bond Lengths

Triple bond < Double Bond < Single Bond

Polar & Non-polar Covalent Bonds

❑ Two types of covalent bonds exist:

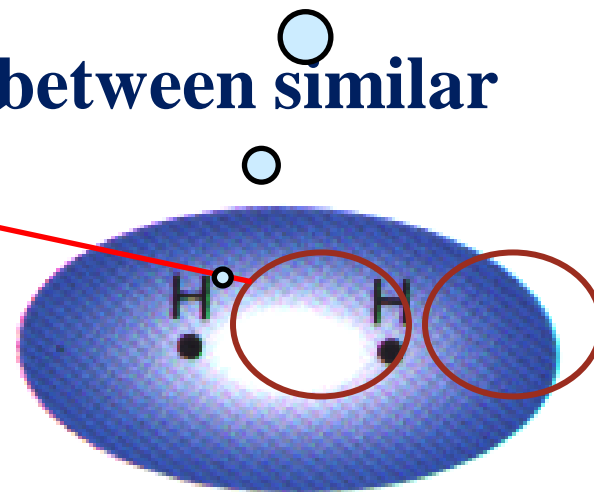
Polar

&

Nonpolar

Electrons
shared
equally

❑ Non-polar covalent bonds occur between similar atoms.



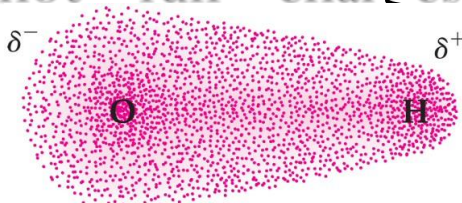
In these bonds the electron pair is shared equally between the two protons.

- ✓ Polar covalent bonds occur between different atoms.
- ✓ In these bonds the electron pair is shared unequally between the two atoms.



As a result there is a charge separation in the molecule, and partial charges on each atom.

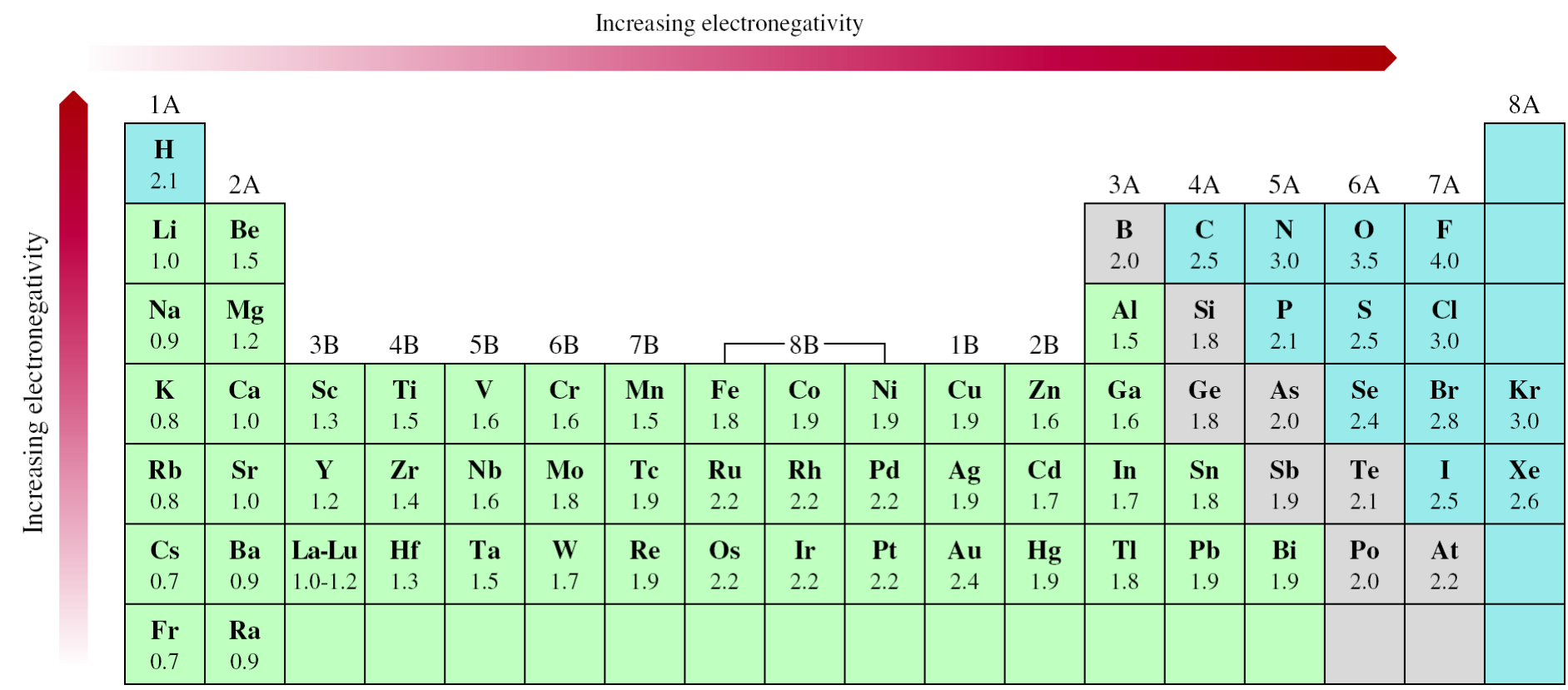
Dipole Moment

- A **dipole** is a material with positively and negatively charged ends
- Polar bonds or molecules have one end slightly positive, δ^+ and the other slightly negative, δ^- not “full” charges, come from nonsymmetrical electron distribution. 
- Dipole Moment, μ , is a measure of the polarity of covalent bond/molecules measured in Debye, D.

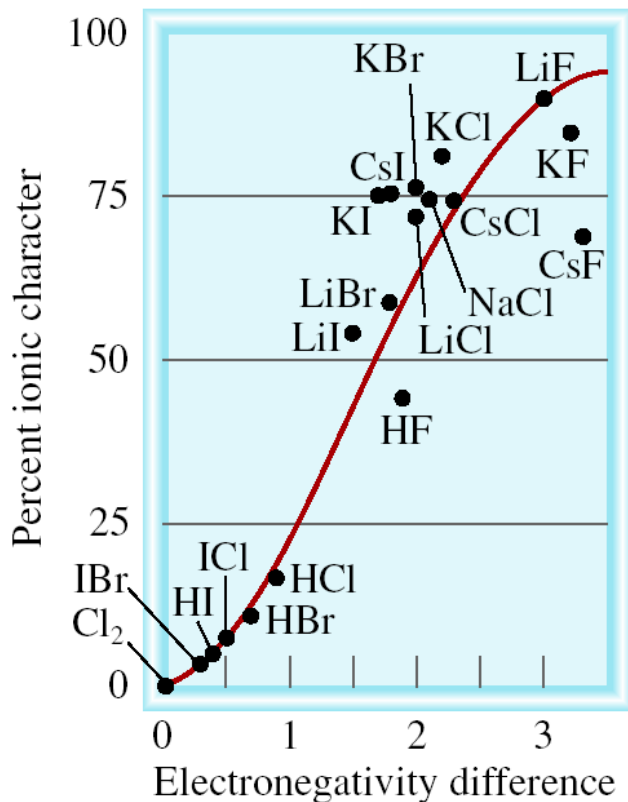
Which one of the following arrangements of molecules is correct on the basis of their dipole moments?

(a) $\text{BF}_3 > \text{NF}_3 > \text{NH}_3$ (b) $\text{NF}_3 > \text{BF}_3 > \text{NH}_3$ (c) $\text{NH}_3 > \text{BF}_3 > \text{NF}_3$ (d) $\text{NH}_3 > \text{NF}_3 > \text{BF}_3$

- Electronegativity (E.N) is the ability of an atom involved in a covalent bond to attract the bonding electrons to itself.
- The electronegativities of common elements



Classification of bonds by difference in electronegativity



Difference

0

≥ 2

$0 < \text{and} < 2$

Bond Type

Covalent

Ionic

Polar Covalent

Increasing difference in electronegativity

Covalent

Polar Covalent

Ionic

share e^-

partial transfer of e^-

transfer e^-

Classify the following bonds as ionic, polar covalent, or covalent: The bond in CsCl; the bond in H₂S; and the NN bond in H₂NNH₂.

Cs – 0.7 Cl – 3.0 $3.0 - 0.7 = 2.3$ **Ionic**

H – 2.1 S – 2.5 $2.5 - 2.1 = 0.4$ **Polar Covalent**

N - 3.0 N - 3.0 3.0 - 3.0 = 0 **Non polar covalent**

A simplified periodic table grid with columns labeled 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A. The grid is 5 rows high and 18 columns wide. The first two columns (1A and 2A) are shaded green, and the last two columns (7A and 8A) are shaded red. The grid is as follows:

1A	2A											3A	4A	5A	6A	7A	8A

BOND POLARITY & ELECTRONEGATIVITY

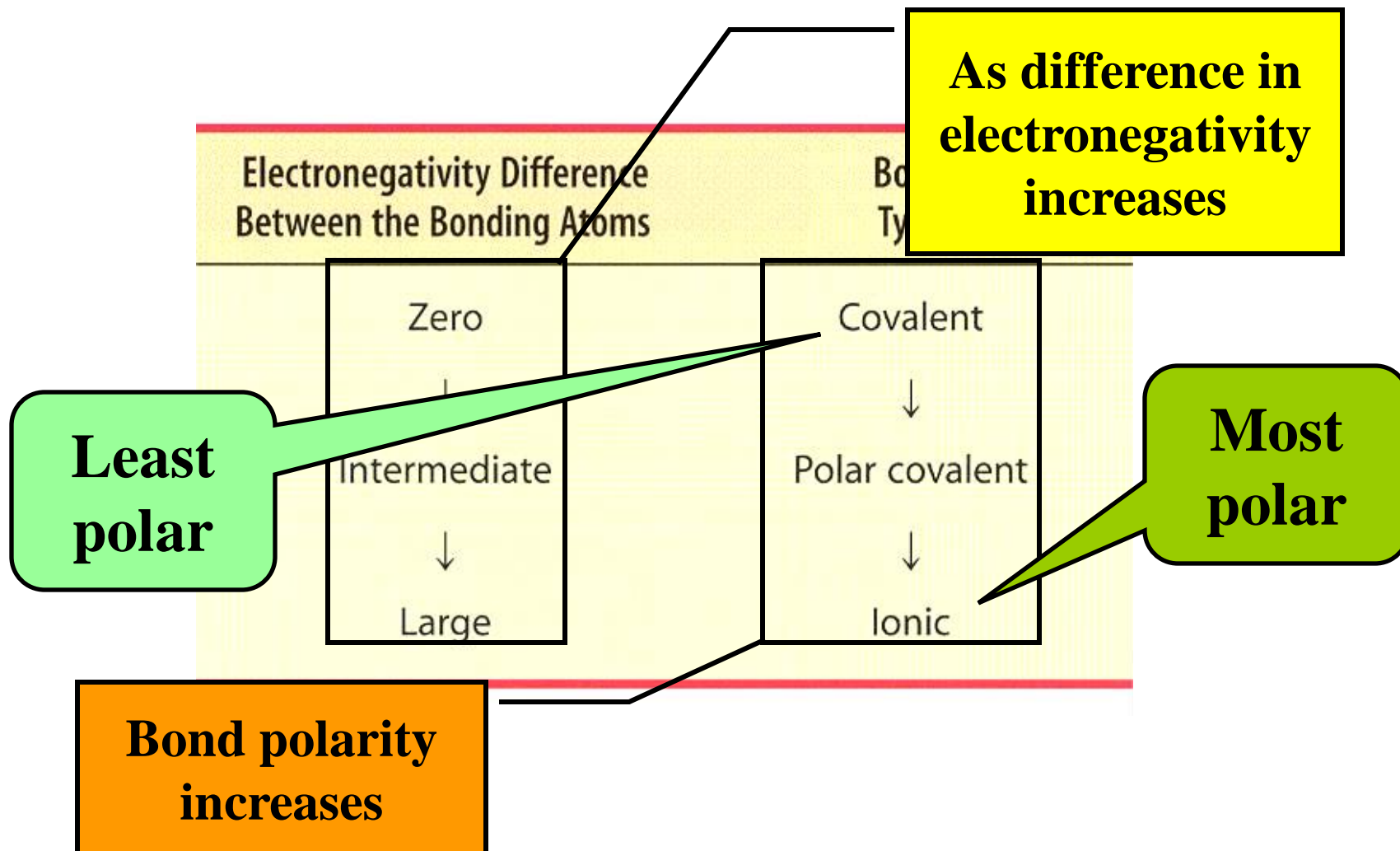
Polarity is a measure of the inequality in the sharing of bonding electrons

**The more different
the
electronegativity of
the elements
forming the bond**

**The larger the
electronegativity
difference
(ΔEN)**

**The more
polar the
bond
formed**

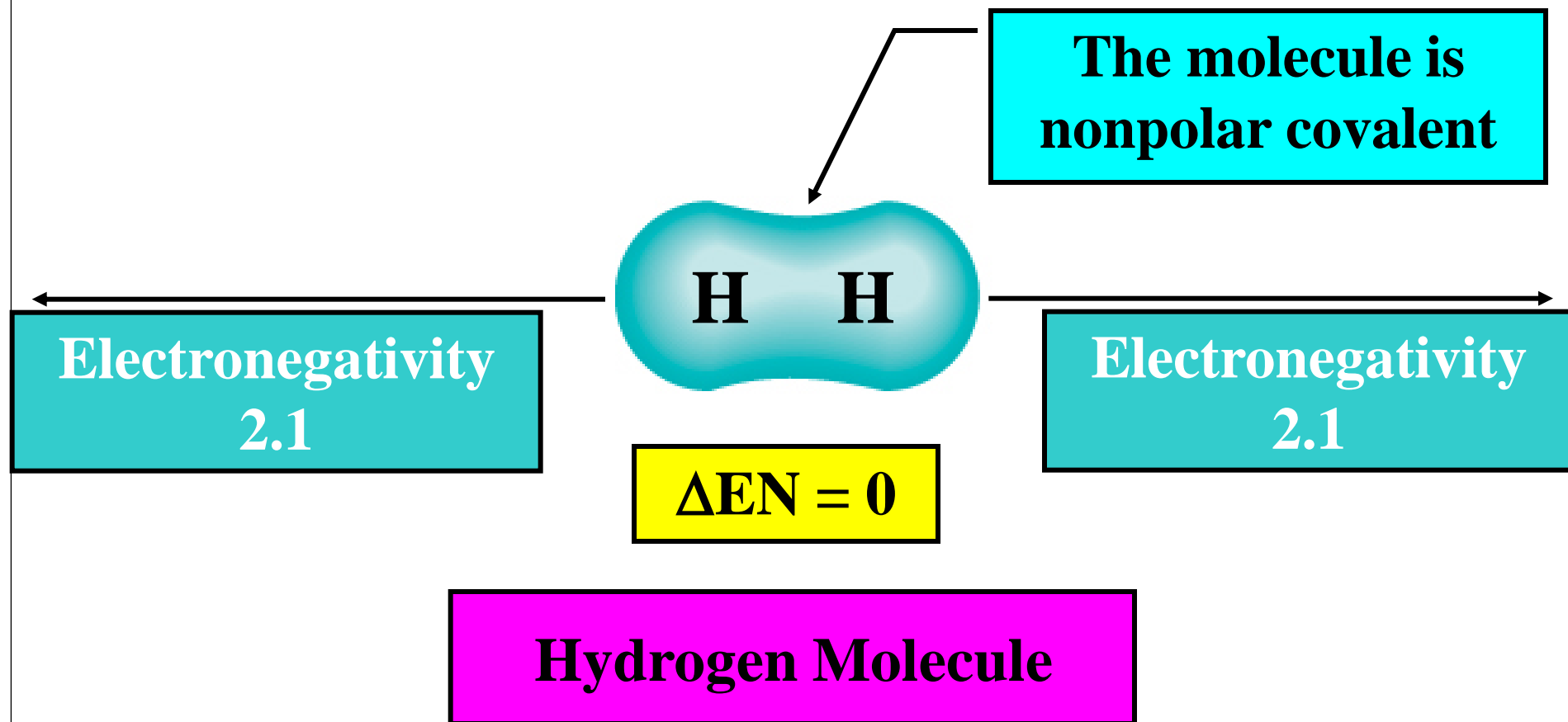
POLARITY & ELECTRONEGATIVITY



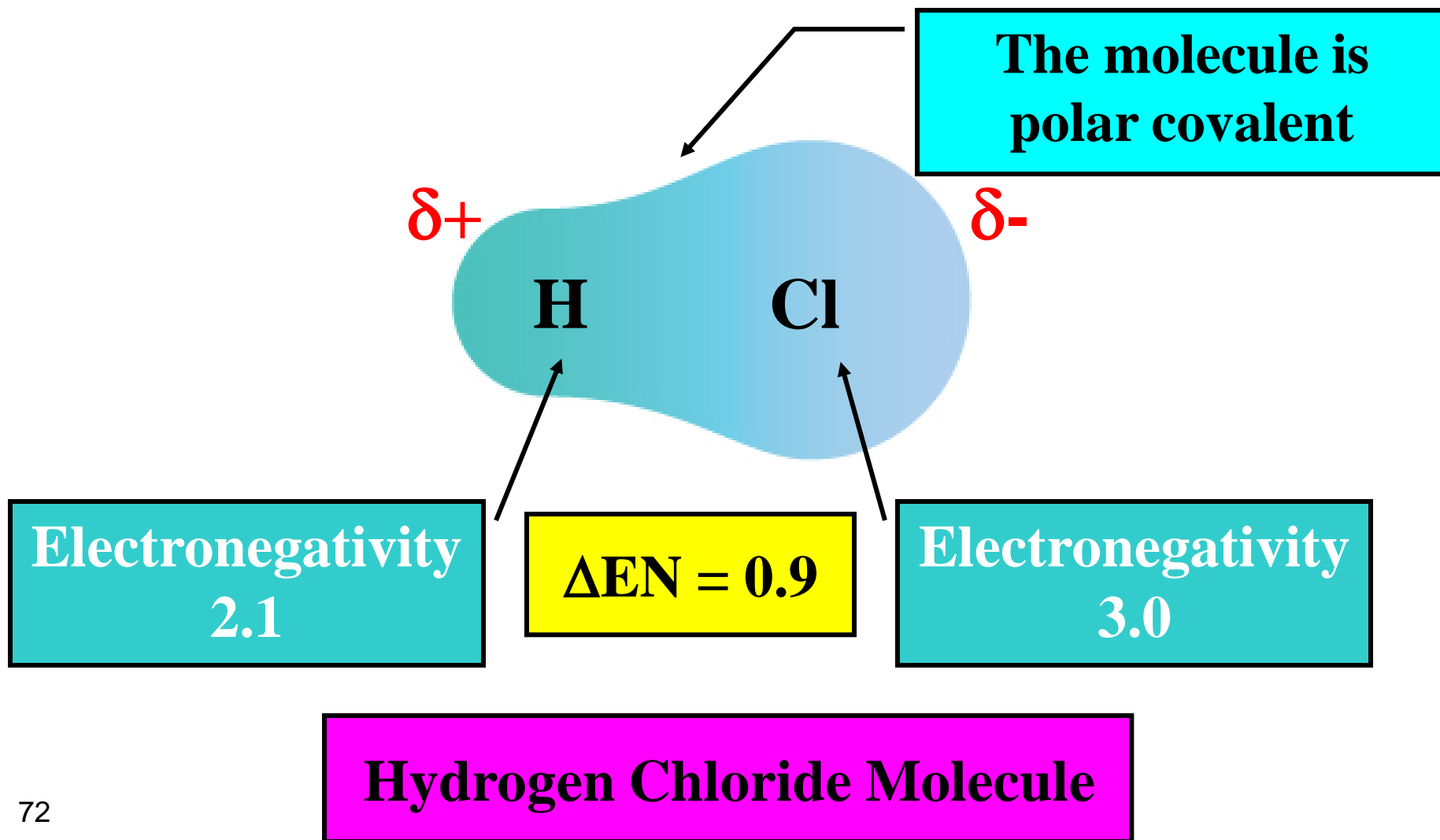
POLARITY & ELECTRONEGATIVITY

Electronegativity difference	Bond Type
$\Delta EN = 0$	Non-polar covalent
$0 < \Delta EN < 1.7$	Polar covalent
$\Delta EN > 1.7$	Ionic

POLARITY & ELECTRONEGATIVITY



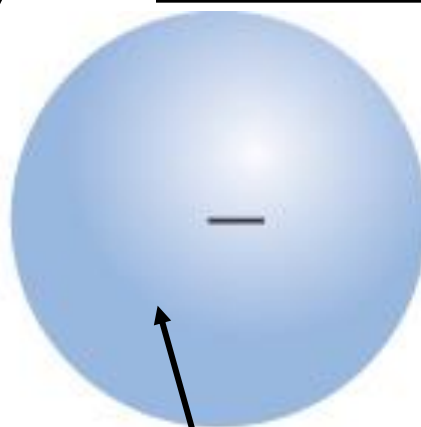
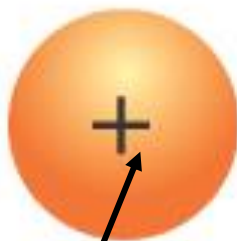
POLARITY & ELECTRONEGATIVITY



POLARITY & ELECTRONEGATIVITY

No molecule exists bond is ionic

Na^+



Cl^-

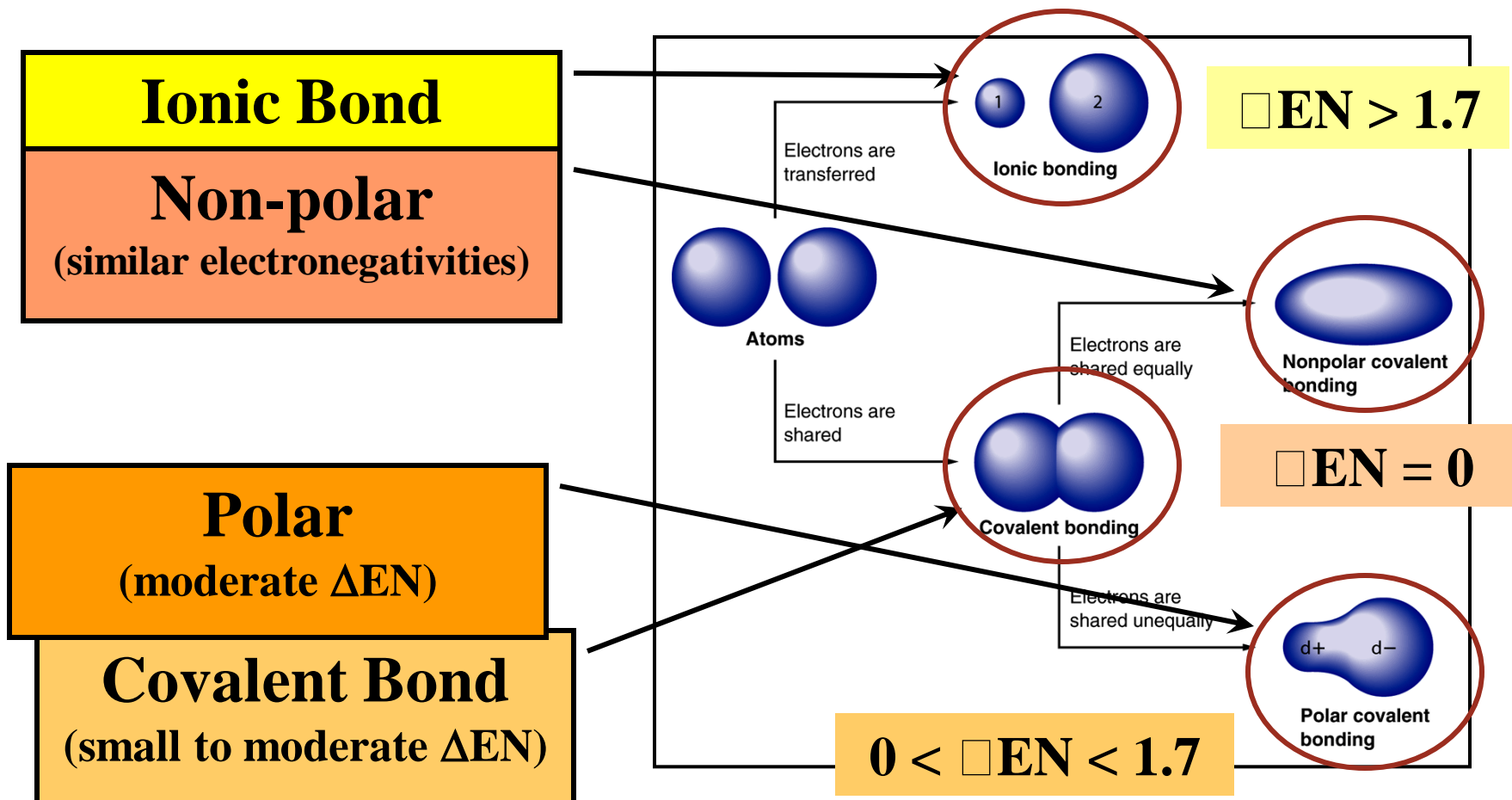
Electronegativity
0.9

$$\Delta \text{EN} = 2.1$$

Electronegativity
3.0

Sodium Chloride

SUMMARY OF BONDING



Bonding & Lone Pair Electrons

- ❑ Electrons that are shared by atoms are called **bonding pairs**
- ❑ Electrons that are not shared by atoms but belong to a particular atom are called **lone pairs** also known as **nonbonding pairs**.

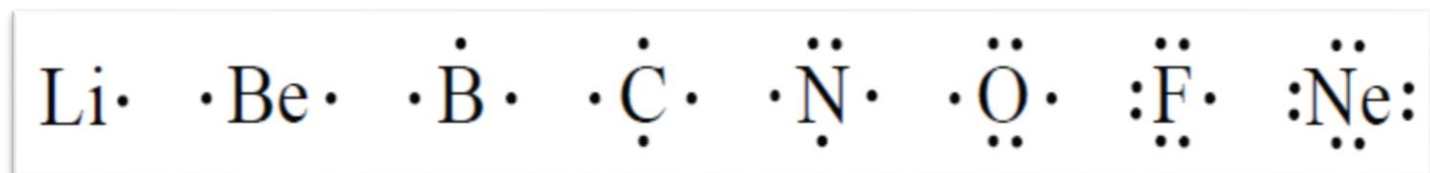
WRITING LEWIS STRUCTURES

1. Draw skeletal structure of compound showing what atoms are bonded to each other. Put least electronegative element in the center.
2. Count total number of valence e^- . Add 1 for each negative charge. Subtract 1 for each positive charge.

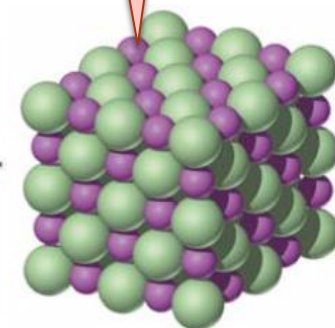
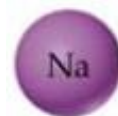
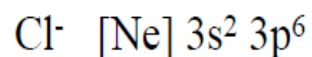
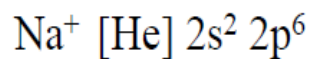
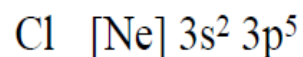
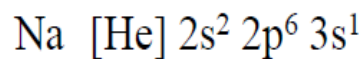
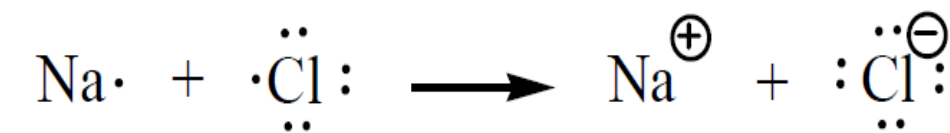
3. Complete an octet for all atoms *except* hydrogen

4. If structure contains too many electrons, form double and triple bonds on central atom as needed.

5. Rules of assigning electrons as dots to the surrounding of the central atom.



Example :



Crystal
lattice

Write the Lewis structure of nitrogen trifluoride (NF₃).

Step 1 – N is less electronegative than F, put N in center

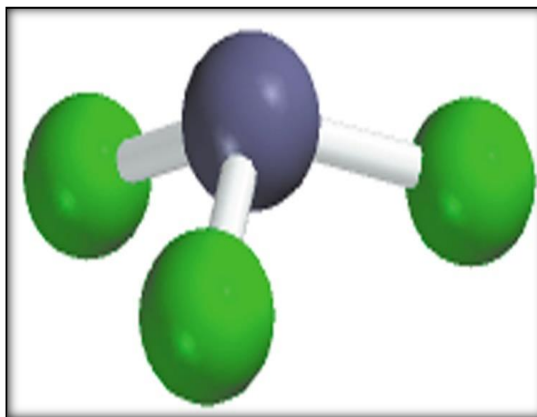
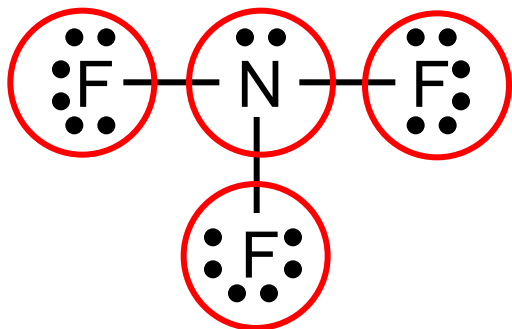
Step 2 – Count valence electrons N - 5 (2s²2p³) and F - 7 (2s²2p⁵)

$$5 + (3 \times 7) = \text{26 valence electrons}$$

Step 3 – Draw single bonds between N and F atoms and complete octets on N and F atoms.

Step 4 - Check, are # of e⁻ in structure equal to number of valence e⁻ ?

$$3 \text{ single bonds } (3 \times 2) + 10 \text{ lone pairs } (10 \times 2) = \text{26 valence electrons}$$



Write the Lewis structure of the carbonate ion (CO_3^{2-}).

Step 1 – C is less electronegative than O, put C in center

Step 2 – Count valence electrons C - 4 ($2s^2 2p^2$) and O - 6 ($2s^2 2p^4$)
-2 charge – $2e^-$

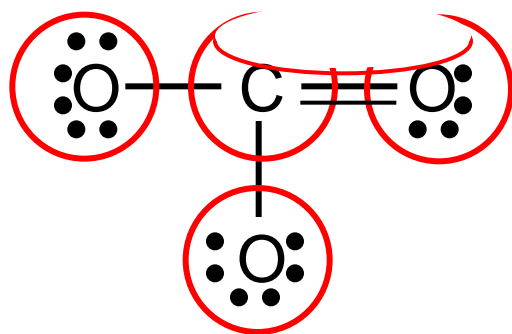
$$4 + (3 \times 6) + 2 = \text{24 valence electrons}$$

Step 3 – Draw single bonds between C and O atoms and complete octet on C and O atoms.

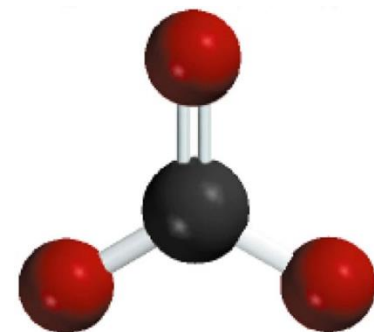
Step 4 - Check, are # of e^- in structure equal to number of valence e^- ?

$$3 \text{ single bonds } (3 \times 2) + 10 \text{ lone pairs } (10 \times 2) = \text{26 valence electrons}$$

Step 5 - Too many electrons, form double bond and re-check # of e^-



$$\begin{array}{rcl} 2 \text{ single bonds } (2 \times 2) & = & 4 \\ 1 \text{ double bond} & = & 4 \\ 8 \text{ lone pairs } (8 \times 2) & = & 16 \\ \hline \text{Total} & = & 24 \end{array}$$



Example 1:

Write Lewis structure for H_2O

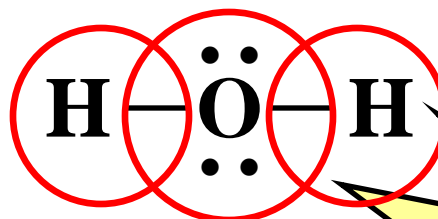
Step 1:



= 8 electrons

$$2(1) + 6 = 8$$

Step 2:



Step 3:

Step 4:

Octet rule is satisfied

4 electrons remaining

Hydrogen has
doublet

symmetrical

Example 2:

Write Lewis structure for CO₂

Step 1:



= 16 electrons

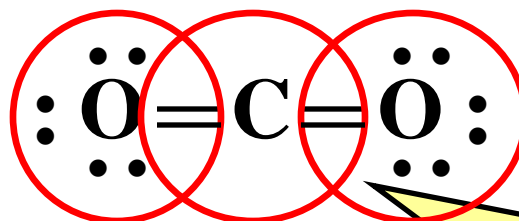
$$4 + 2(6) = 16$$

Step 2:

Step 3:

Step 4:

Step 5:

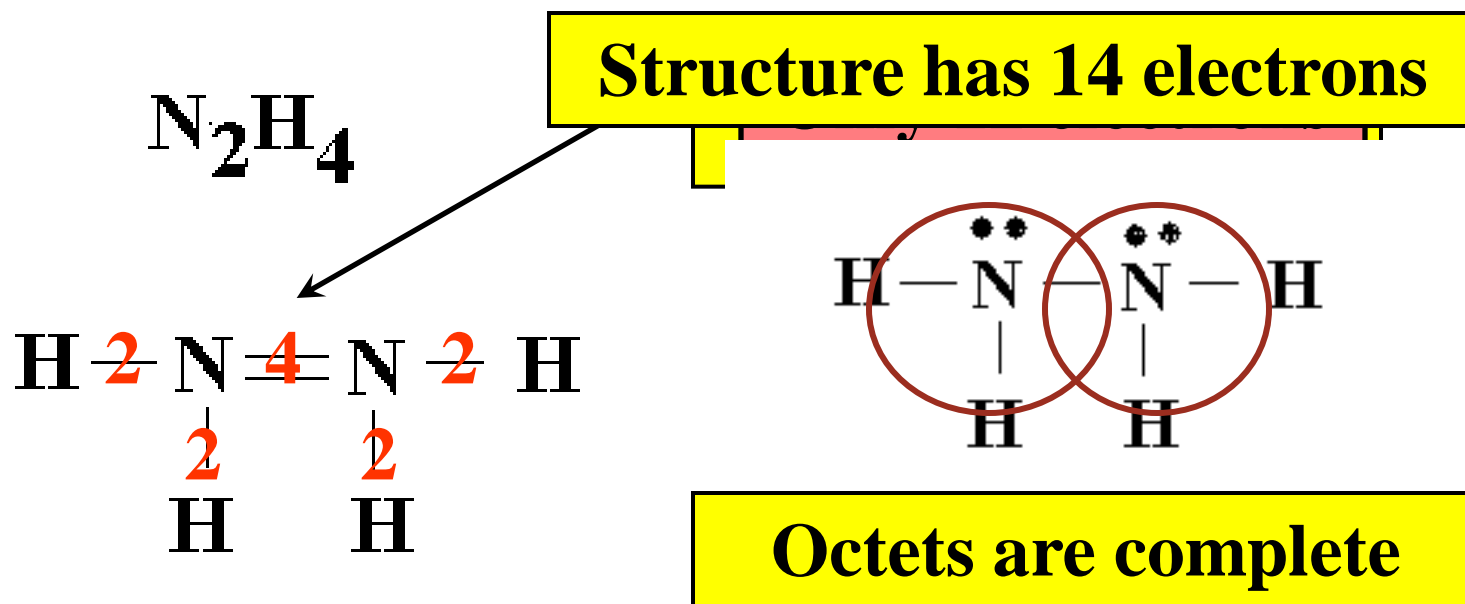


Octet rule is NOT
satisfied

Skeleton
structure
should be
symmetrical

Example 3:

- Determine if each of the following Lewis structures are correct or incorrect. If incorrect, rewrite the correct structure.



Exceptions to the Octet Rule

- H & Li, lose one electron to form cation

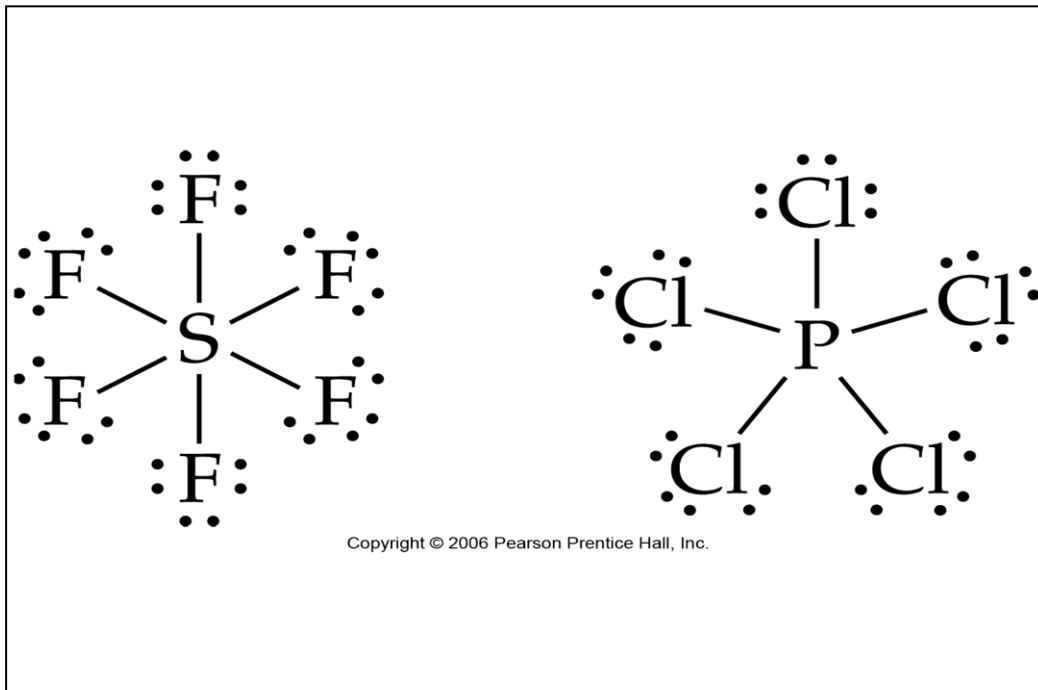
Li now has electron configuration like He

H can also share or gain one electron to have configuration like He

- Be shares 2 electrons to form two single bonds
- B shares 3 electrons to form three single bonds
- expanded octets for elements in Period 3 or below using empty valence *d* orbitals,
- some molecules have odd numbers of electrons. Example: NO

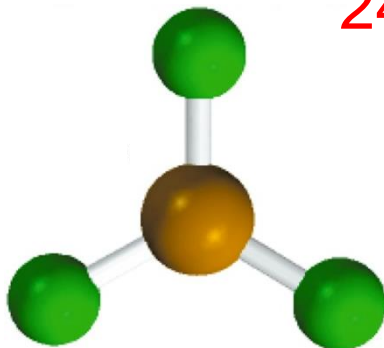
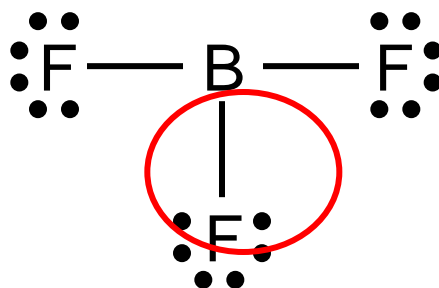
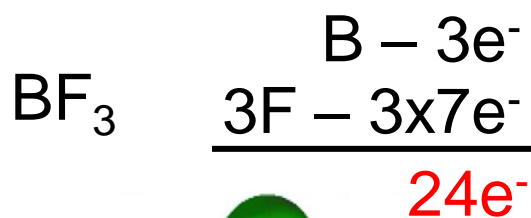
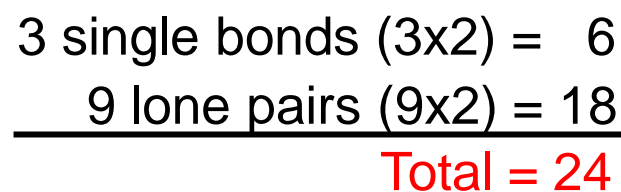
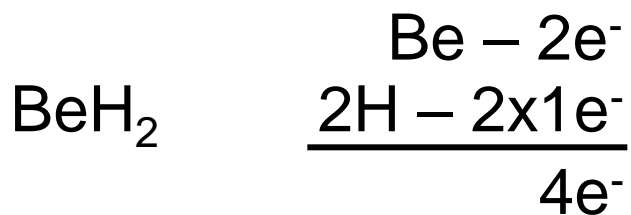


Some molecules, such as SF_6 and PCl_5 have more than 8 electrons around a central atom in their Lewis structure.

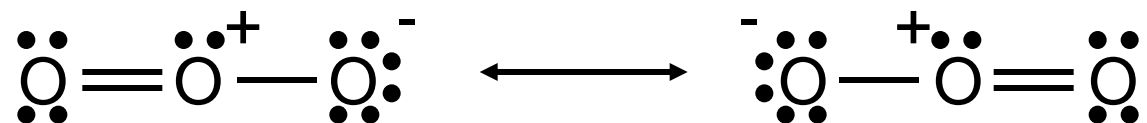


SF_6 and PCl_5 can violate the octet rule through the use of empty d orbitals: both S and P can utilize empty d orbitals to hold pairs of electrons that help bond halogen atoms.

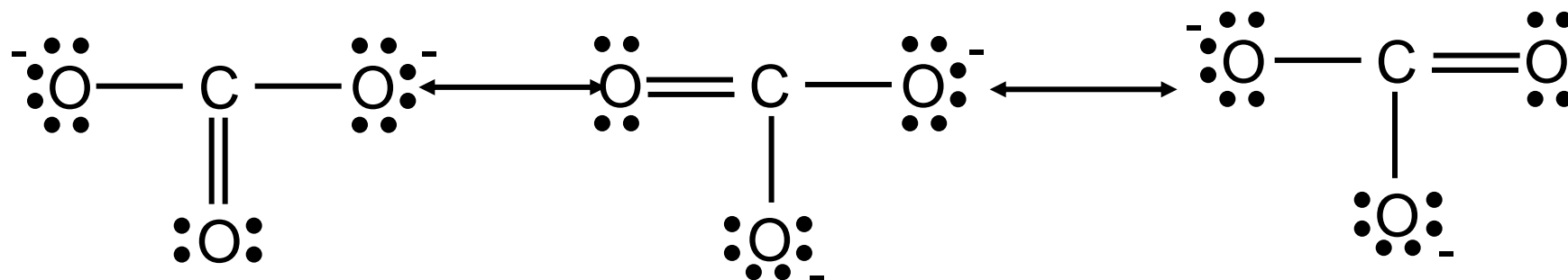
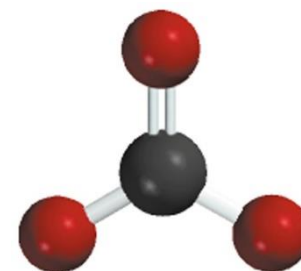
The Incomplete Octet



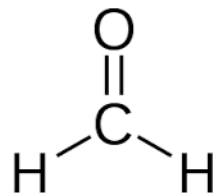
A **resonance structure** is one of two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure.



What are the resonance structures of the carbonate (CO_3^{2-}) ion?



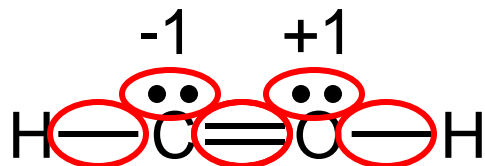
Two possible skeletal structures of formaldehyde (CH₂O)



- An atom's **formal charge** is the difference between the number of valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

$$\text{formal charge} = \# \text{ valence shell electrons (free atom)} - \# \text{ lone pair electrons} - \frac{1}{2} \# \text{ bonding electrons}$$

- The sum of the formal charges of the atoms in a molecule or ion must equal the charge on the molecule or ion.
- The sum of the formal charges of all atoms in a molecule must be **zero**; the sum of the formal charges in an ion should equal the charge of the ion.



$$\begin{array}{r}
 \text{C} - 4 \text{ e}^- \\
 \text{O} - 6 \text{ e}^- \\
 2\text{H} - 2 \times 1 \text{ e}^- \\
 \hline
 12 \text{ e}^-
 \end{array}$$

$$\begin{array}{r}
 2 \text{ single bonds } (2 \times 2) = 4 \\
 1 \text{ double bond} = 4 \\
 2 \text{ lone pairs } (2 \times 2) = 4 \\
 \hline
 \text{Total} = 12
 \end{array}$$

$$\begin{array}{l}
 \text{formal charge} \\
 \text{on an atom in} \\
 \text{a Lewis} \\
 \text{structure}
 \end{array}
 =
 \begin{array}{l}
 \text{total number} \\
 \text{of valence} \\
 \text{electrons in} \\
 \text{the free atom}
 \end{array}
 -
 \begin{array}{l}
 \text{total number} \\
 \text{of nonbonding} \\
 \text{electrons}
 \end{array}
 -
 \frac{1}{2}
 \left(
 \begin{array}{l}
 \text{total number} \\
 \text{of bonding} \\
 \text{electrons}
 \end{array}
 \right)$$

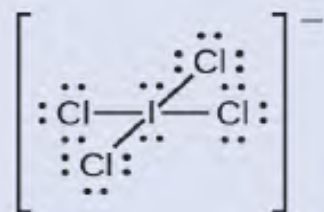
$$\begin{array}{l}
 \text{formal charge} \\
 \text{on C}
 \end{array}
 = 4 - 2 - \frac{1}{2} \times 6 = -1$$

$$\begin{array}{l}
 \text{formal charge} \\
 \text{on O}
 \end{array}
 = 6 - 2 - \frac{1}{2} \times 6 = +1$$

Assign formal charges to each atom in the interhalogen ion ICl_4^- .

Solution

Step 1. We divide the bonding electron pairs equally for all I–Cl bonds:



Step 2. We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Step 3. Subtract this number from the number of valence electrons for the neutral atom:

$$\text{I: } 7 - 8 = -1$$

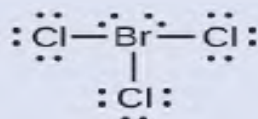
$$\text{Cl: } 7 - 7 = 0$$

The sum of the formal charges of all the atoms equals -1 , which is identical to the charge of the ion (-1).

Assign formal charges to each atom in the interhalogen molecule BrCl_3 .

Solution

Step 1. Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:



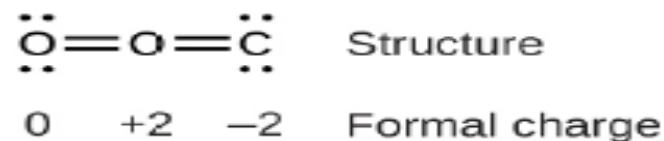
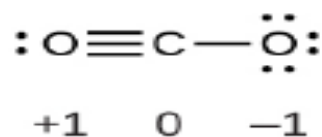
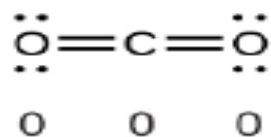
Step 2. Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons.

Step 3. Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:

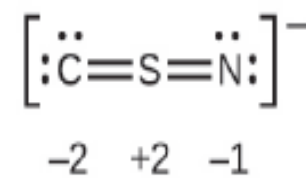
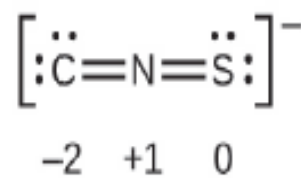
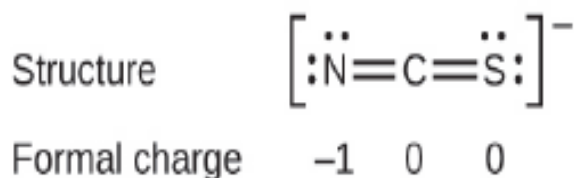
$$\text{Br: } 7 - 7 = 0$$

$$\text{Cl: } 7 - 7 = 0$$

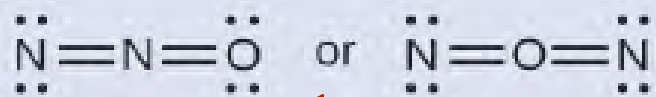
All atoms in BrCl_3 have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.



Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero



Note that the sum of the formal charges in each case is equal to the charge of the ion (-1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element



Which structure is most preferable and why

The enthalpy change required to break a particular bond in one mole of gaseous molecules is the ***bond enthalpy***.

Bond Enthalpy



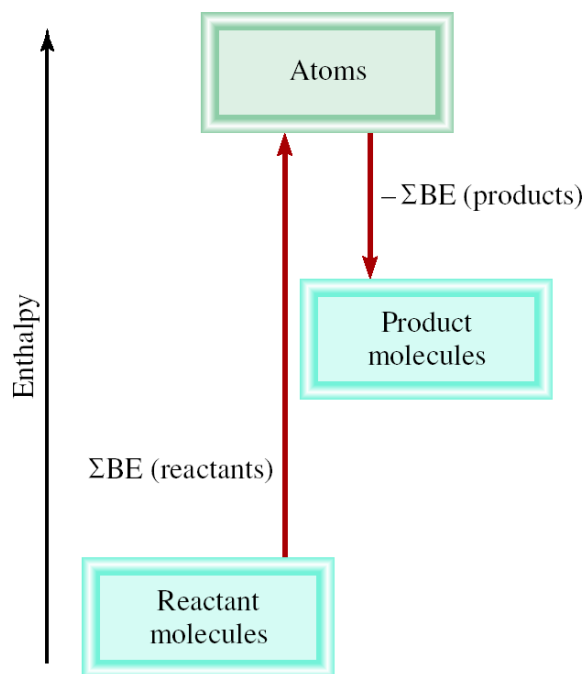
Bond Enthalpies

Single bond < Double bond < Triple bond

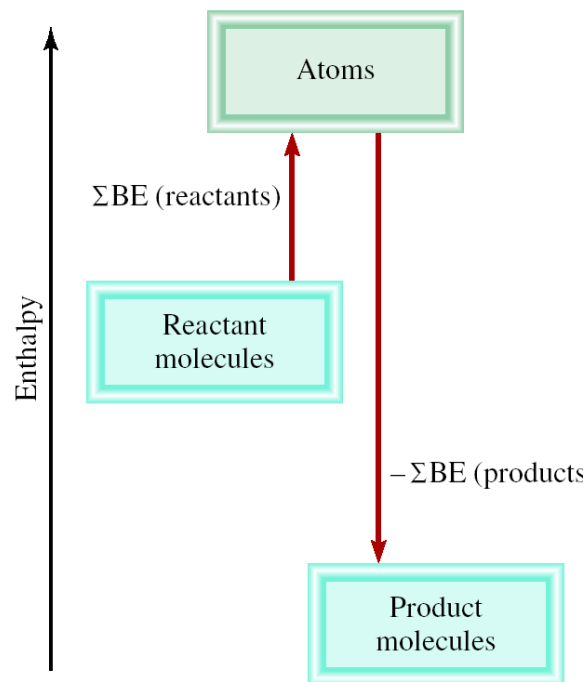
Bond Enthalpies (BE) and Enthalpy changes in reactions

Imagine reaction proceeding by breaking all bonds in the reactants and then using the gaseous atoms to form all the bonds in the products.

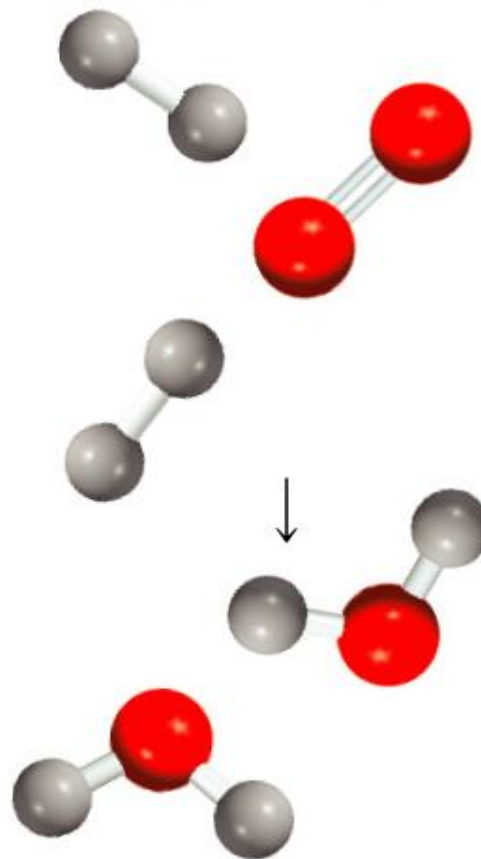
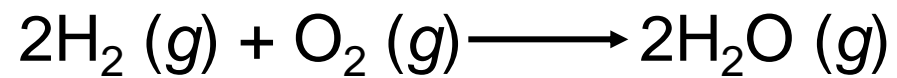
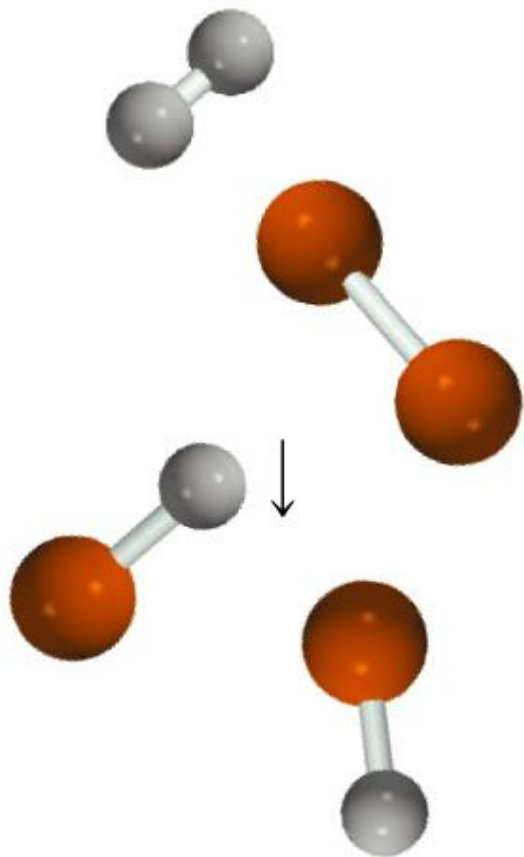
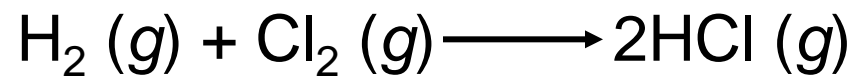
$$\begin{aligned}\Delta H^0 &= \text{total energy input} - \text{total energy released} \\ &= \Sigma \text{BE}(\text{reactants}) - \Sigma \text{BE}(\text{products})\end{aligned}$$



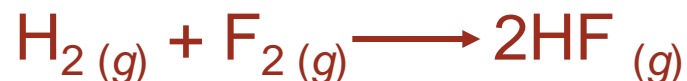
endothermic



exothermic



Use bond enthalpies to calculate the enthalpy change for:

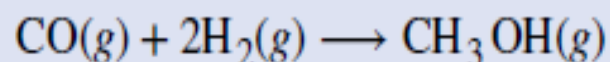


$$\Delta H^0 = \Sigma \text{BE}(\text{reactants}) - \Sigma \text{BE}(\text{products})$$

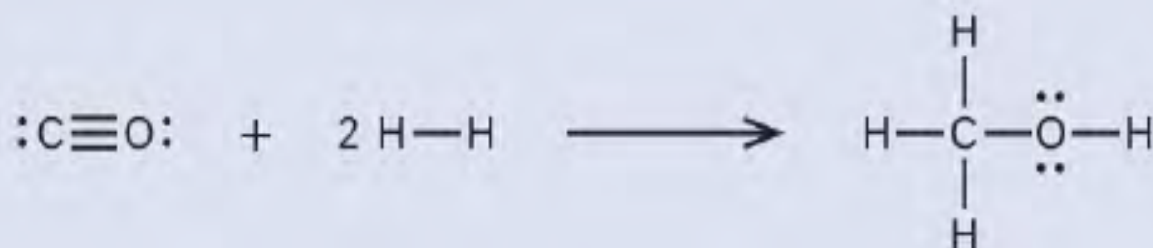
Type of bonds broken	Number of bonds broken	Bond enthalpy (kJ/mol)	Enthalpy change (kJ/mol)
H — H	1	436.4	436.4
F — F	1	156.9	156.9
Type of bonds formed	Number of bonds formed	Bond enthalpy (kJ/mol)	Enthalpy change (kJ/mol)
H — F	2	568.2	1136.4

$$\Delta H^0 = 436.4 + 156.9 - 2 \times 568.2 = -543.1 \text{ kJ/mol}$$

Methanol, CH_3OH , may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO , and hydrogen, H_2 , from which methanol can be produced. Using the bond energies calculate the approximate enthalpy change, ΔH , for the reaction here:



First, we need to write the Lewis structures of the reactants and the products:



From this, we see that ΔH for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows:

$$\Delta H = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$$

$$\Delta H = [D_{\text{C}\equiv\text{O}} + 2(D_{\text{H}-\text{H}})] - [3(D_{\text{C}-\text{H}}) + D_{\text{C}-\text{O}} + D_{\text{O}-\text{H}}]$$

$$\begin{aligned} \Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107 \text{ kJ} \end{aligned}$$

Estimate the enthalpy change for the combustion of hydrogen gas:



Strategy Note that H_2O is a polyatomic molecule, and so we need to use the average bond enthalpy value for the O—H bond.

Solution We construct the following table:

<i>Type of bonds broken</i>	<i>Number of bonds broken</i>	<i>Bond enthalpy (kJ/mol)</i>	<i>Energy change (kJ/mol)</i>
H—H (H_2)	2	436.4	872.8
O=O (O_2)	2	498.7	498.7
<i>Type of bonds formed</i>	<i>Number of bonds formed</i>	<i>Bond enthalpy (kJ/mol)</i>	<i>Energy change (kJ/mol)</i>
O—H (H_2O)	4	460	1840

Next, we obtain the total energy input and total energy released:

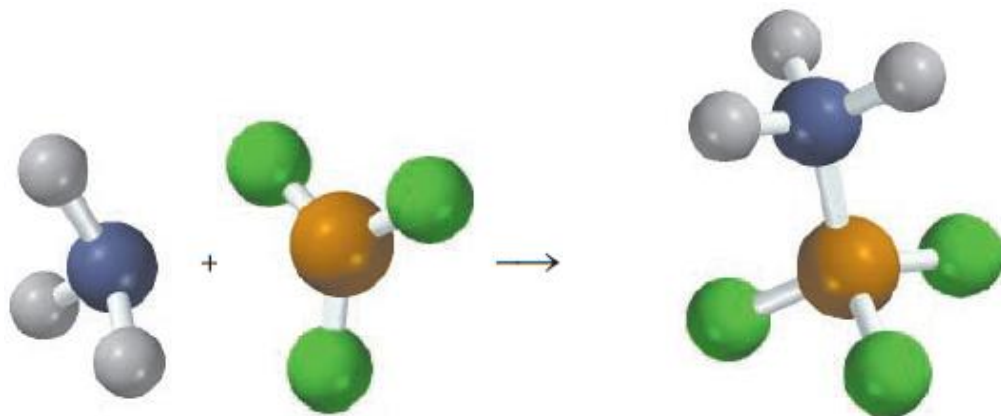
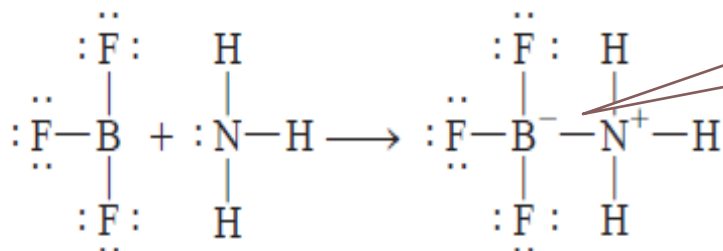
$$\begin{aligned}\text{total energy input} &= 872.8 \text{ kJ/mol} + 498.7 \text{ kJ/mol} = 1371.5 \text{ kJ/mol} \\ \text{total energy released} &= 1840 \text{ kJ/mol}\end{aligned}$$

$$\Delta H^\circ = 1371.5 \text{ kJ/mol} - 1840 \text{ kJ/mol} = -469 \text{ kJ/mol}$$

COORDINATE COVALENT BOND

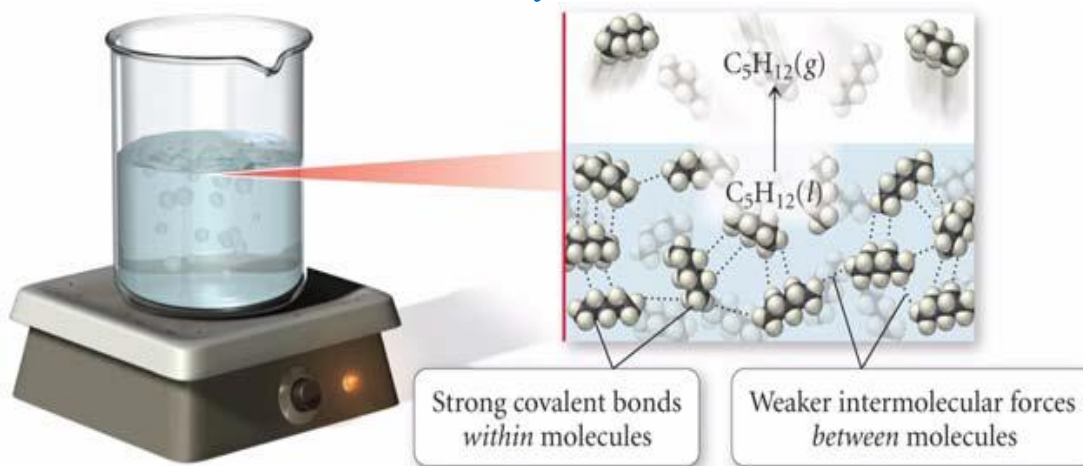
❖ Also referred to as a dative bond), defined as a covalent bond in which one of the atoms donates both electrons

**COORDINATE
COVALENT
BOND**



Properties of Molecular Compounds

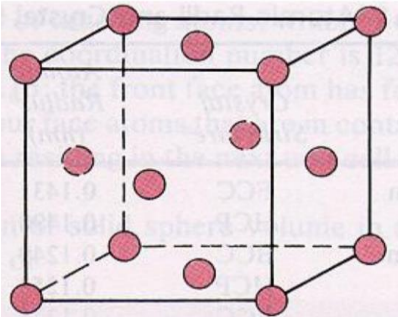
- ❖ Covalent bonds are directional, and hold specific atoms together in a molecule.
- ❖ In polar bonds, one atom has a **partial negative charge** (δ^-) and the other atom has a **partial positive charge** (δ^+).
- ❖ Molecular compounds are generally gases, liquids, or low-melting solids.
- ❖ The covalent bonds within molecules are very strong, but the attractive forces between the separate molecules are fairly weak.



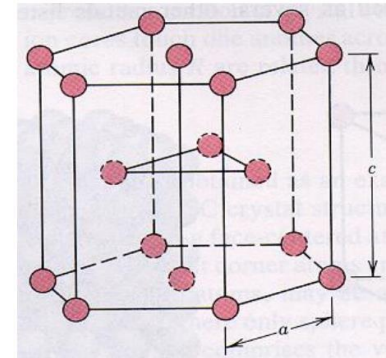
Metallic Bond

❖ Metals are made up of positive ions packed together, usually in one of the three following geometrical arrangements:

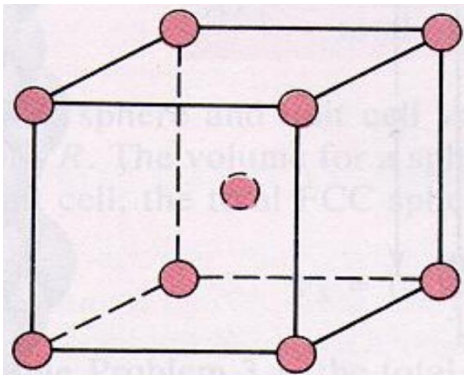
➤ Face centered cubic (FCC)



Hexagonal close packed (HCP)



➤ Body centered cubic (BCC)



- ❖ The outstanding feature of metals is their very high electrical conductivity, which is due to the mobility of these electrons through the lattice.

❑ General properties of metals

- ✓ Metals have close packed structures.
 - ✓ Metals are good conductor of heat and electricity-**due to movement of electrons.**
 - ✓ Metals possess a characteristic **luster**- they are bright, shiny and highly reflective. It arises b/c the mobile electrons in the lattice absorb visible light.
 - **Promotion of free electrons into excited states.**
 - **Re-emission of energy in the form of visible light**
- Makes the metal shiny .**

- ✓ **Metals are malleable and ductile**- these characteristics are depend on mobile electrons
- **Metals are malleable**-they may be deformed in to various shapes.
- **Metals are ductile**- they may be drawn into wires.
- ✓ **Metals possess a large cohesive force in their lattice.**
- A large cohesive force holds the metal atoms together in a metallic lattice. Increases across a period and reflected in melting point and boiling point of the metal.
- **What do u think its relationship with size?**

✓ Metals form alloys.

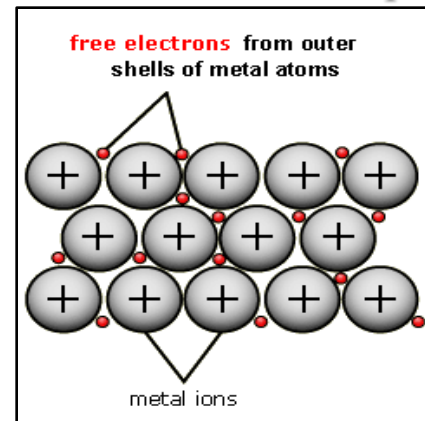
- A metal can mix with another metal, often over a wide range of composition to give a variety of alloys.

□ Metallic Bond

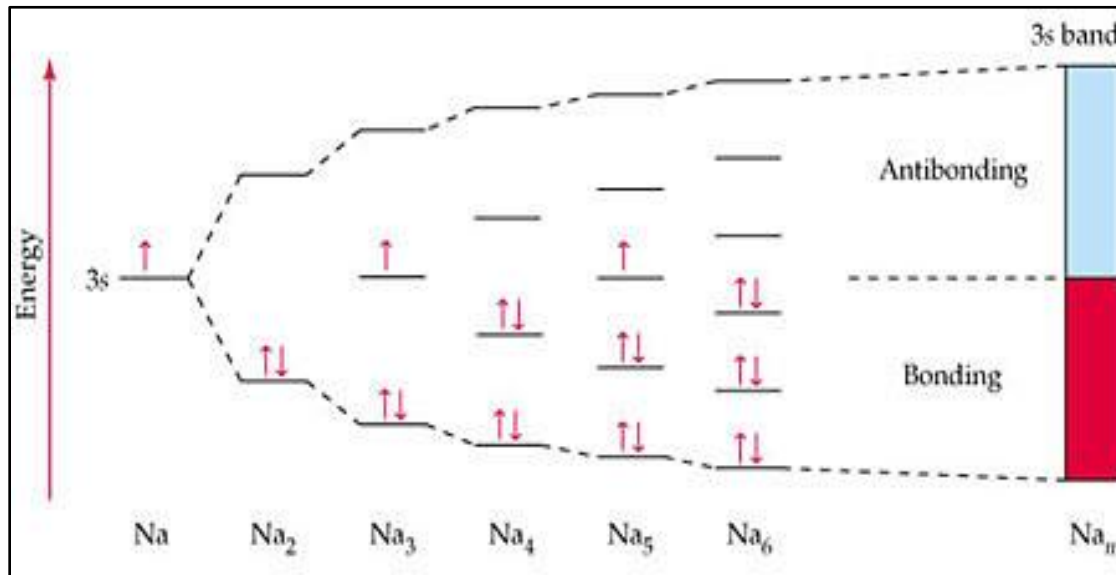
- Theories of bonding in metals-attempts to explain the physical characteristics of metals in terms of valence electrons.

1. **Sea of electrons theory**- a metallic lattice consists of a rigid positive ions, arranged in close packed array , with their valence electrons spread throughout the crystal.

The valence electrons are distributed amongst the
Interstices.



❑ **Band theory**- based on the molecular orbital concept.



❑ **Metallic bond**- Is electrostatic force of attraction between delocalized electron called conduction electron gathered in an “sea of the electron” and metallic nuclei with in metals. Is the sharing of free electron among a lattice positively charged metal ion.

MOLECULAR SHAPES

- ❑ The three-dimensional shape of the molecules is an important feature in understanding their properties and interactions.
- ❑ Molecular geometry is the three-dimensional arrangement of atoms in a molecule.
- ❑ Molecule's geometry affects its physical and chemical properties
- ❑ Based on VSEPR, the electron pair groups in a molecule will repel one another and seek to minimize their repulsion by arranging themselves around the central atom as far apart as possible.
- ❑ Electron pair groups can be defined as any one of the following:

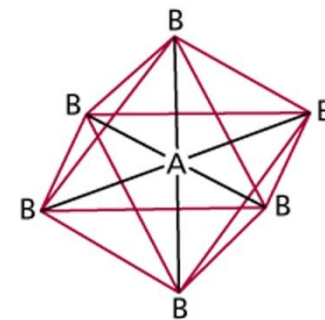
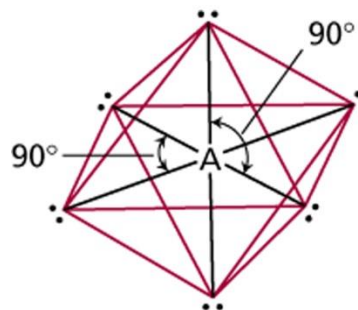
bonding pairs

non-bonding pairs

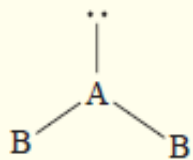
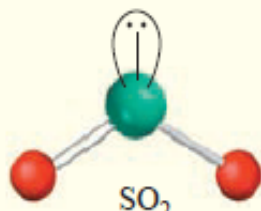
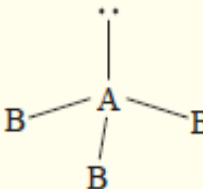
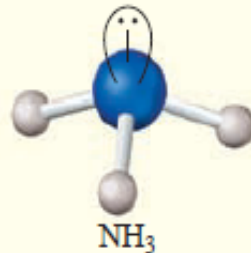
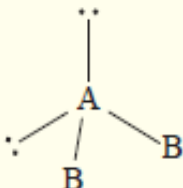
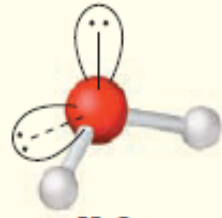
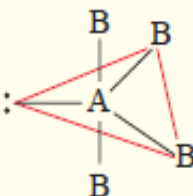
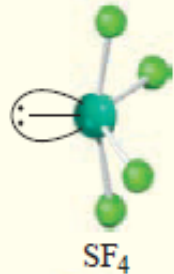
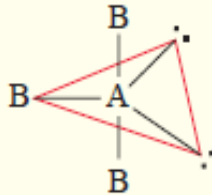
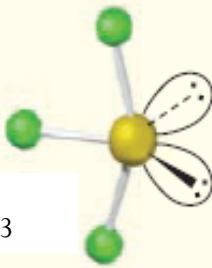
multiple bonds

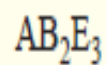
VSEPR

<u>Class</u>	<u># of atoms bonded to central atom</u>	<u># lone pairs on central atom</u>	<u>Arrangement of electron pairs</u>	<u>Molecular Geometry</u>
AB_2	2	0	linear	linear
AB_3	3	0	trigonal planar	trigonal planar
AB_4	4	0	tetrahedral	tetrahedral
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AB_6	6	0	octahedral	octahedral



Number of electron pair groups around central atom		Molecular Shape	Bond Angle	Examples
Bonding	Non-bonding			
2	0	Linear	180	CO ₂
3	0	Trigonal planar	120	BF ₃
2	1	Bent	120	SO ₂
4	0	Tetrahedral	109.5	CH ₄
3	1	Pyramidal	109.5	NH ₃
2	2	Bent	109.5	H ₂ O

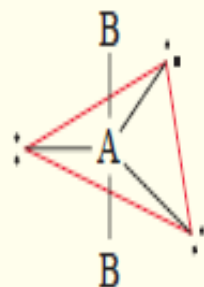
Class of molecule	Total number of electron pairs	Number of bonding pairs	Number of lone pairs	Arrangement of electron pairs*	Geometry	Examples
AB_2E	3	2	1	 Trigonal planar	Bent	 SO_2
AB_3E	4	3	1	 Tetrahedral	Trigonal pyramidal	 NH_3
AB_2E_2	4	2	2	 Tetrahedral	Bent	 H_2O
AB_4E	5	4	1	 Trigonal bipyramidal	Distorted tetrahedron (or seesaw)	 SF_4
AB_3E_2	5	3	2	 Trigonal bipyramidal	T-shaped	 ClF_3



5

2

3



Trigonal bipyramidal

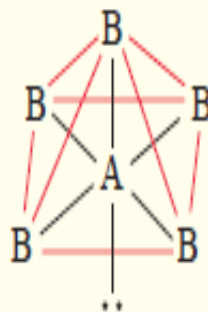
Linear



6

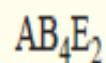
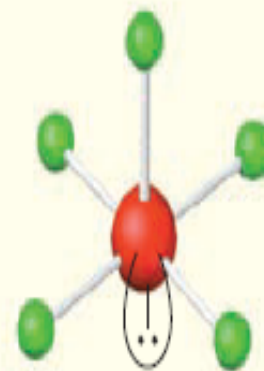
5

1



Octahedral

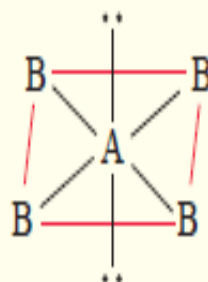
Square pyramidal



6

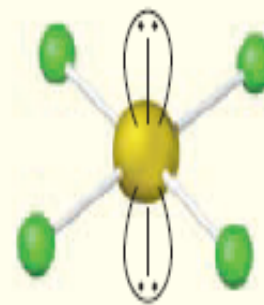
4

2

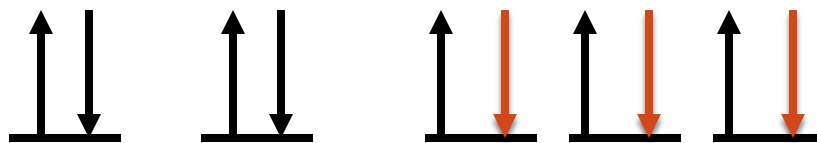
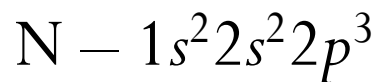


Octahedral

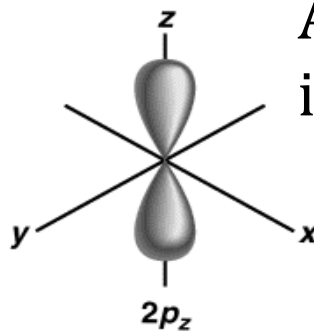
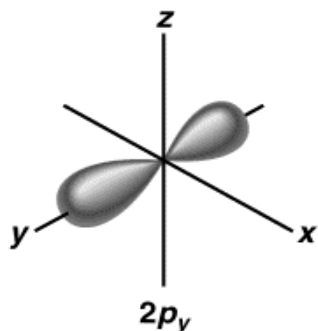
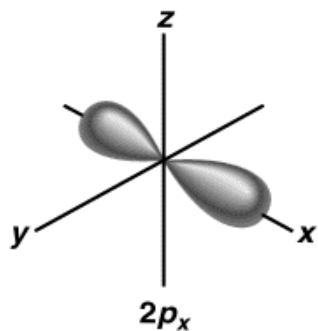
Square planar



Consider the formation of NH_3



If the bonds form from overlap of 3 $2p$ orbitals on nitrogen with the $1s$ orbital on each hydrogen atom, what would the molecular geometry of NH_3 be?



Actual H-N-H bond angle is 107.3°

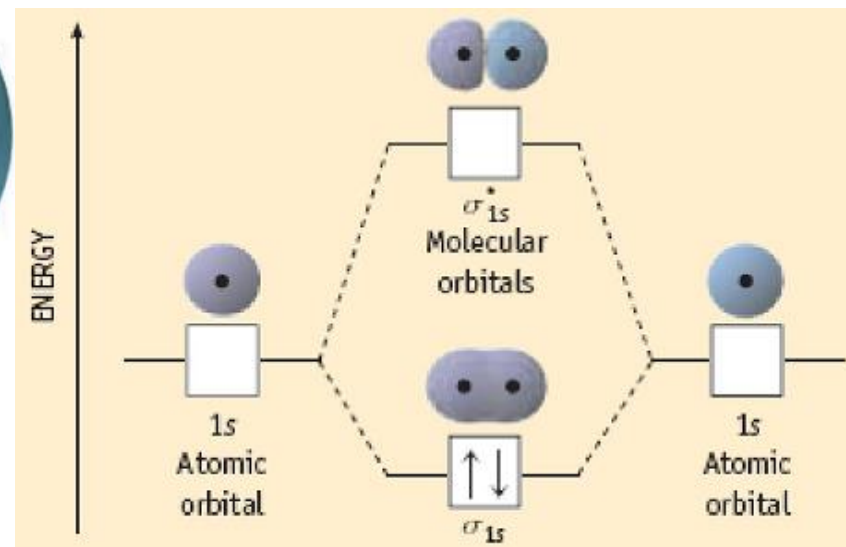
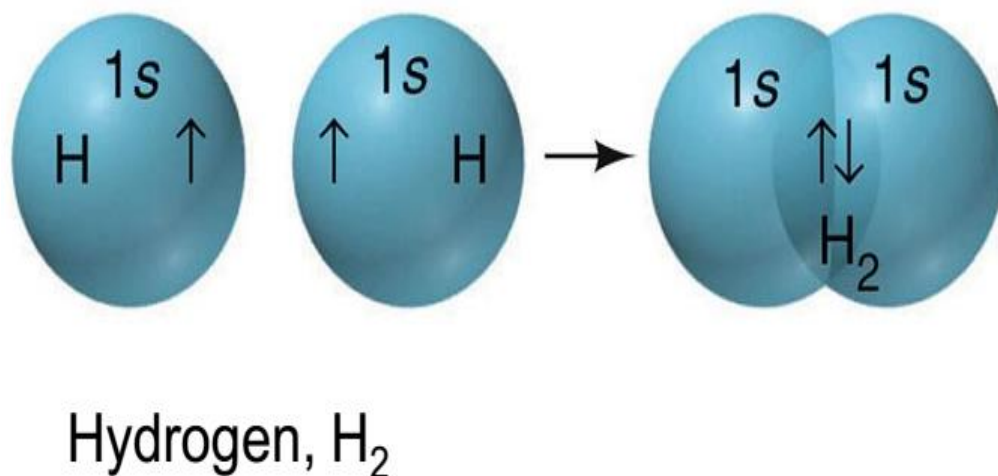
➤ **Hybridization** mixing of two or more atomic orbitals to form a new set of hybrid orbitals.

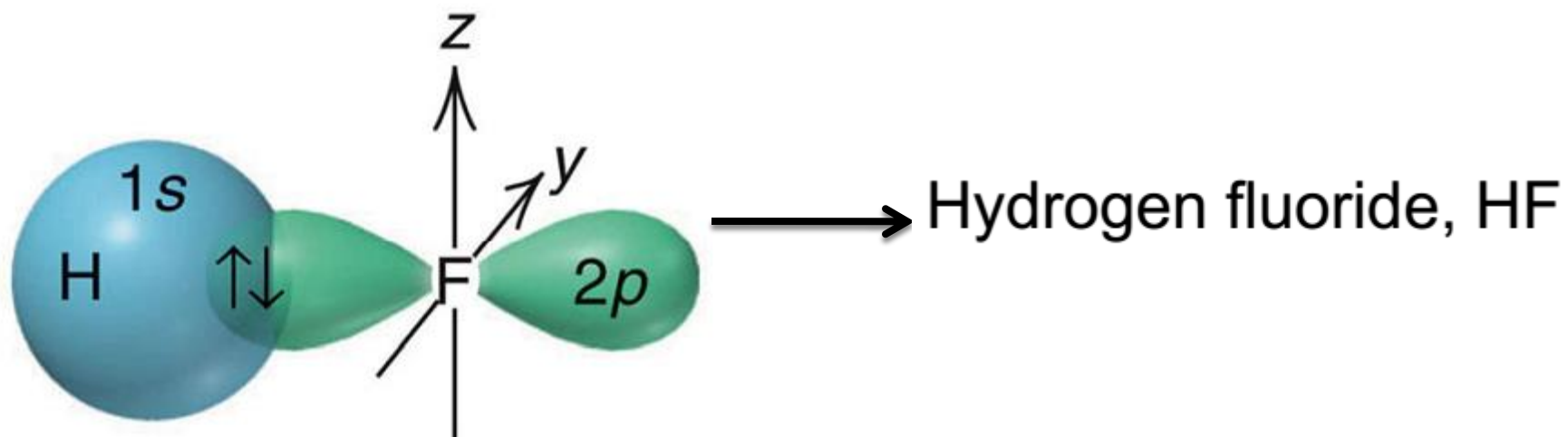
Valency Bond theory

- Valence-bond theory was the first quantum mechanical theory of bonding to be developed.
- In VB theory, a bond is regarded as forming when an electron in an atomic orbital on one atom pairs its spin with that of an electron in an atomic orbital on another atom.
- A set of overlapping orbitals has a maximum of two electrons that must have opposite spins.
- The greater the orbital overlap, the stronger (more stable) the bond.

- The valence atomic orbitals in a molecule are different from those in isolated atoms.
- ❖ There is a hybridization of atomic orbitals to form molecular orbitals.

Orbital overlap and spin pairing in diatomic molecules.





Hybrid Orbitals

- ✓ The number of hybrid orbitals obtained equals the number of atomic orbitals mixed.
- ✓ The type of hybrid orbitals obtained varies with the types of atomic orbitals mixed.

Types of Hybrid Orbitals

sp

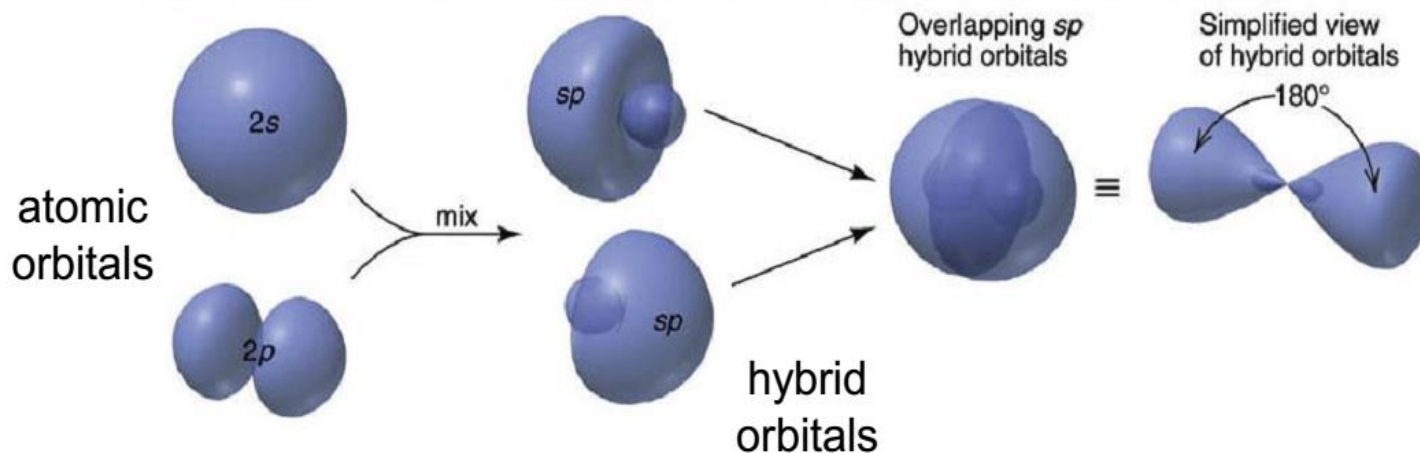
sp²

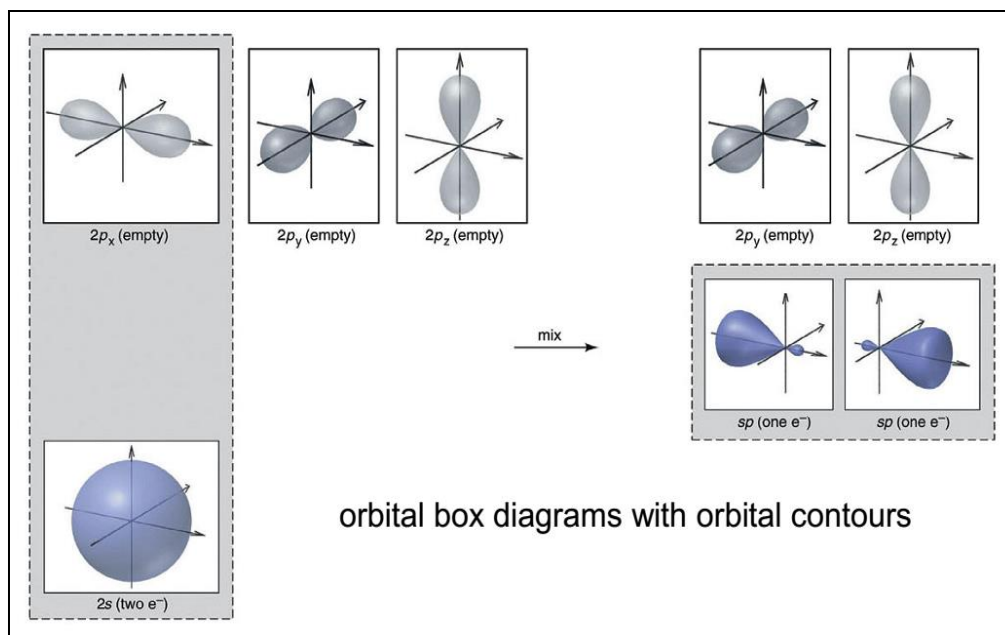
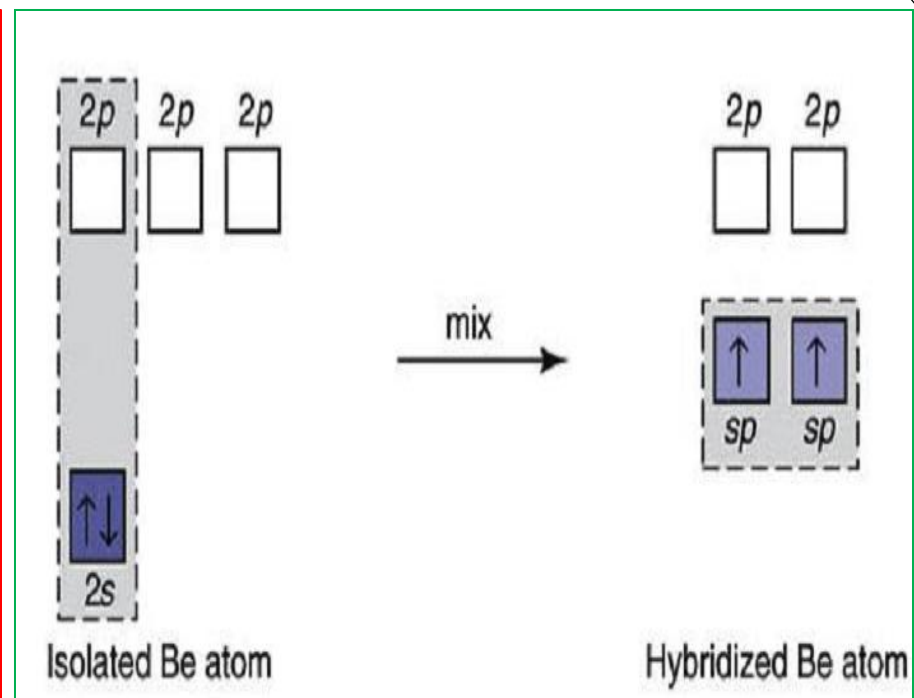
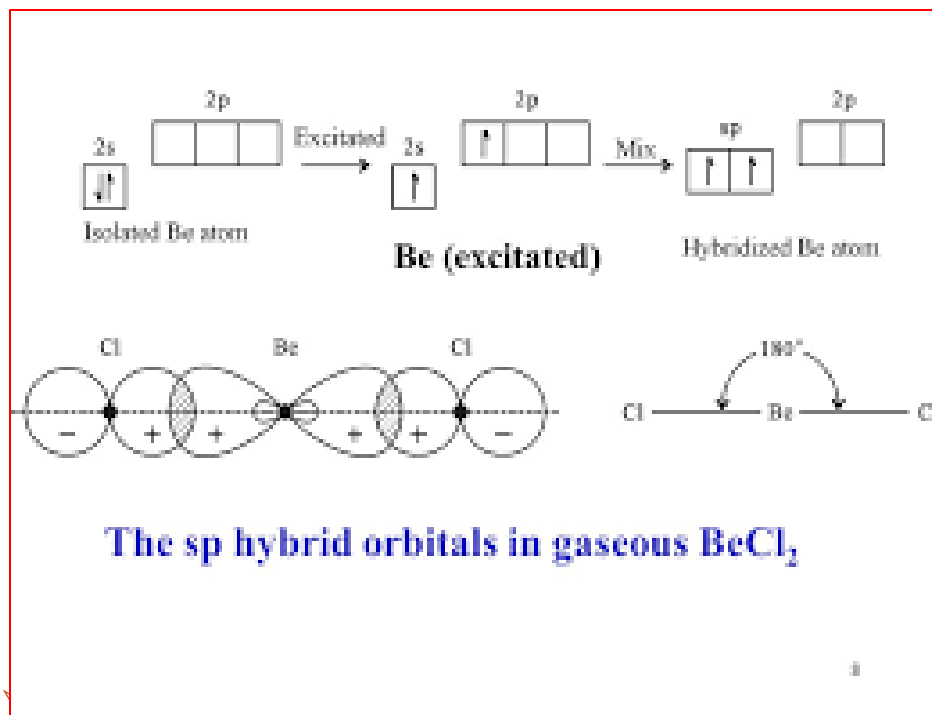
sp³

sp³d

sp³d²

➤ The **sp** hybrid orbitals in gaseous BeCl₂





sp hybridisation for BeH_2 (beryllium hydride) molecule :

It is the process of mixing and recasting of one s and one p orbital of same atom with nearly equal energy to form two sp hybridised orbital having equivalent energy, maximum symmetry and definite orientation in a space.

Need for hybridisation : The observed valency of Be in BeH_2 is two and it has a bond angle of 180° with a linear geometry which can be explained on the basis of hybridisation.

sp hybridisation of Be atom :

Ground state electronic configuration for Be is $1s^2 2s^2$



$1s^2$

$2s^2$

$2p_x$

$2p_y$

$2p_z$

Be in excited state has electronic configuration $1s^2 2s^1 2p^1$



$1s^2$

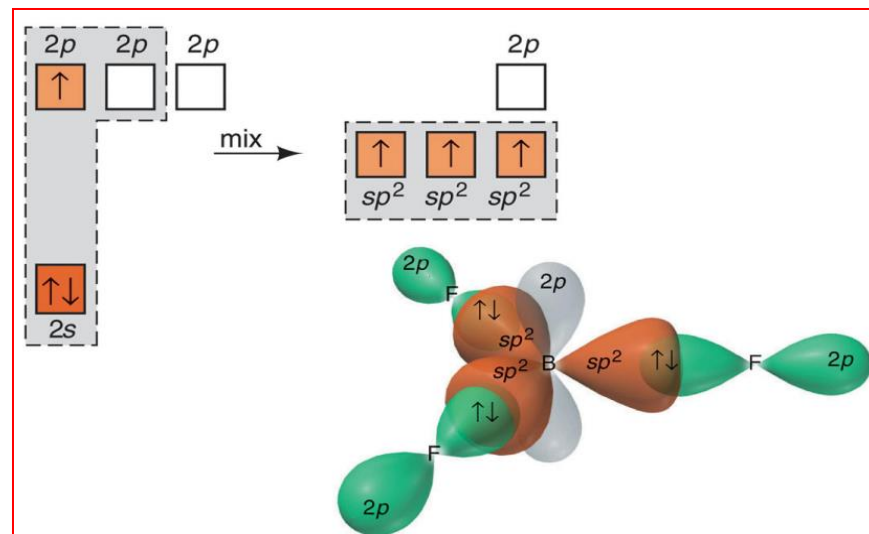
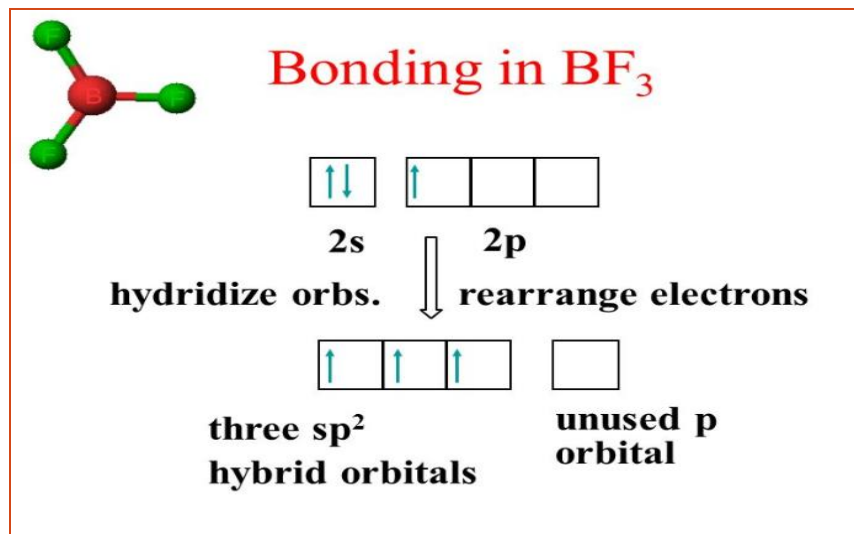
$2s^2$

$2p_x$

$2p_y$

$2p_z$

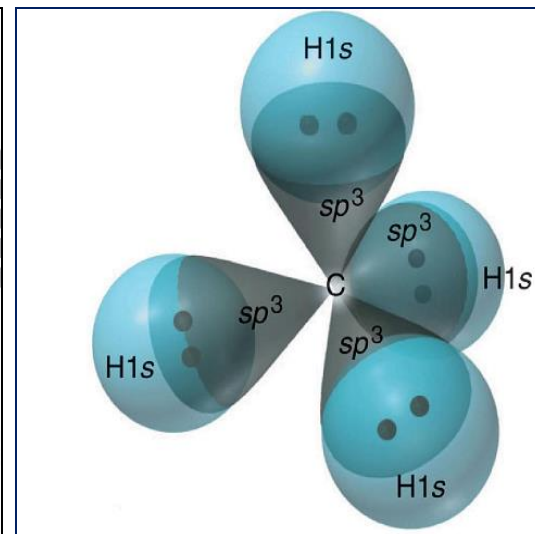
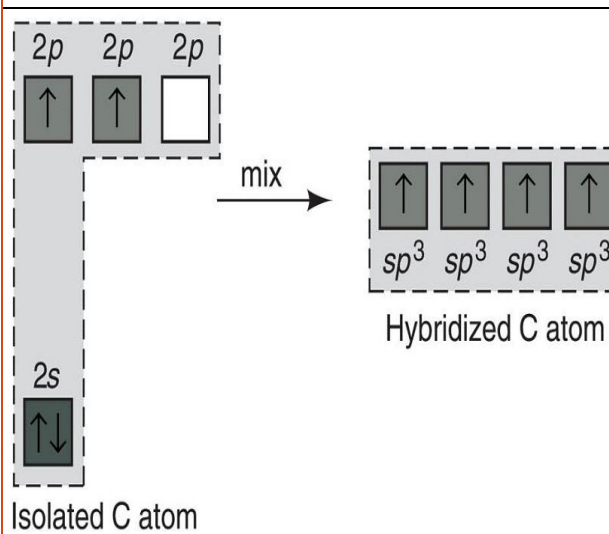
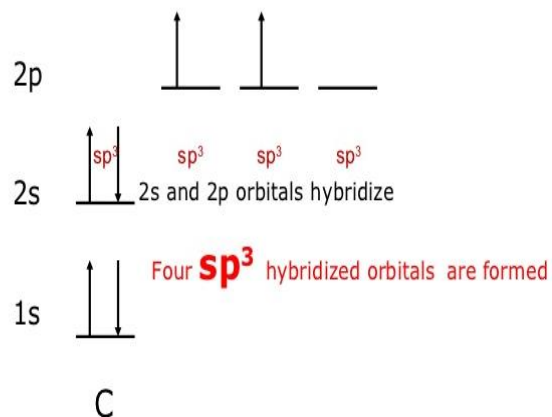
The sp^2 hybrid orbitals in BF_3



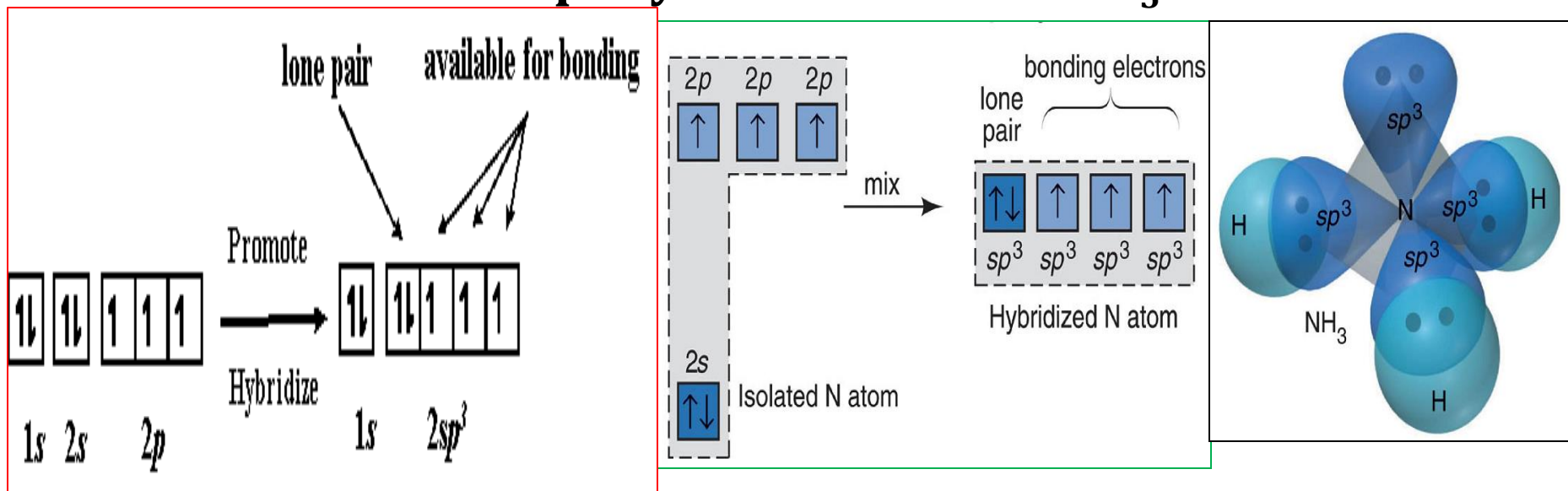
The sp^3 hybrid orbitals in CH_4

Example: Methane (CH_4)

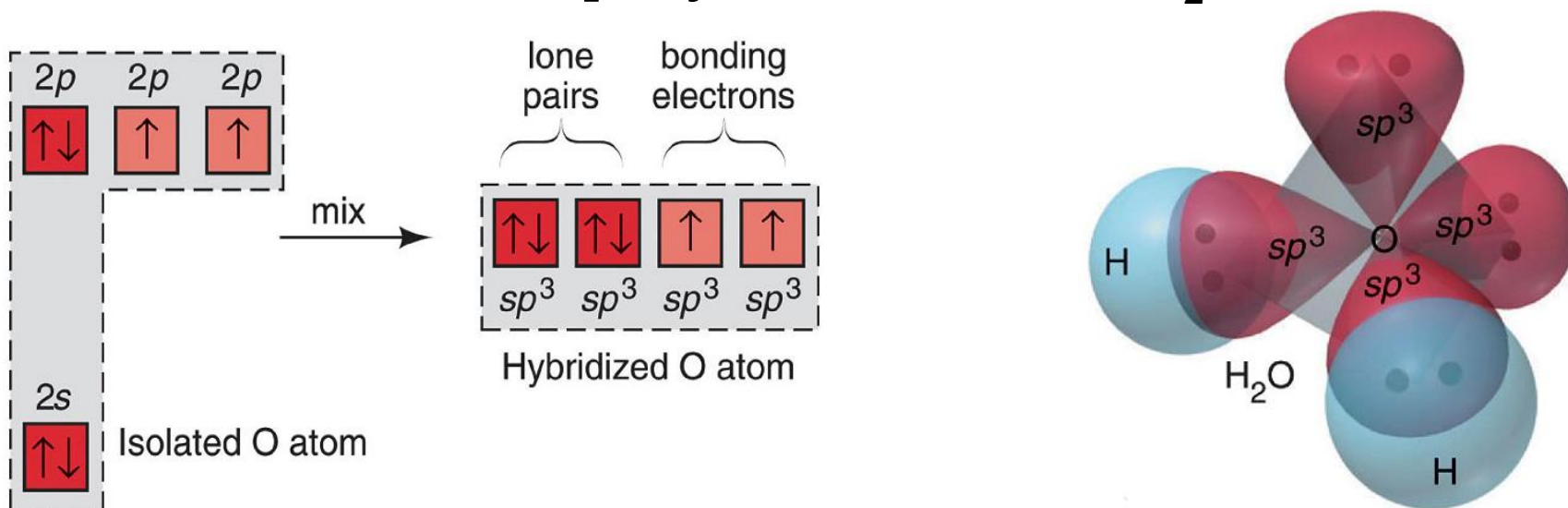
The orbitals can **hybridize** with each other to form 4 bonds:



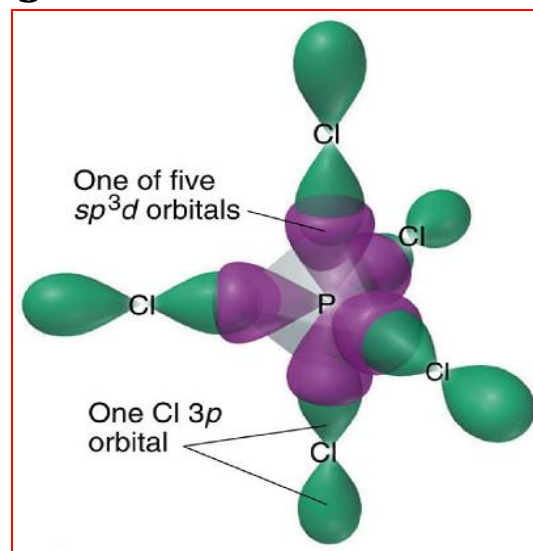
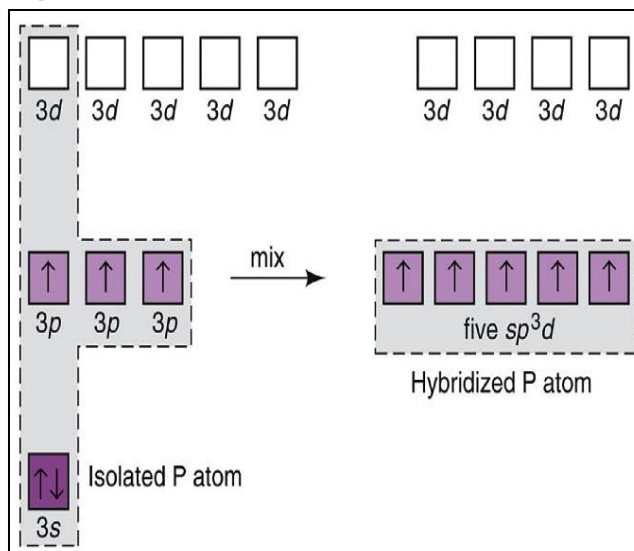
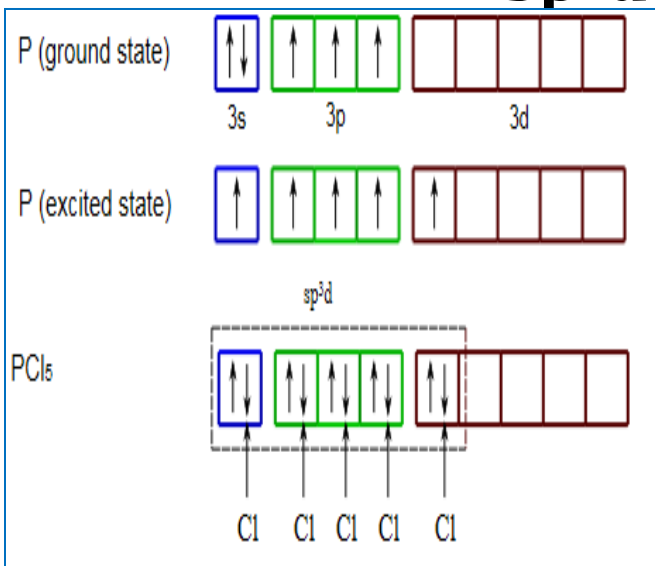
The sp^3 hybrid orbitals in NH_3



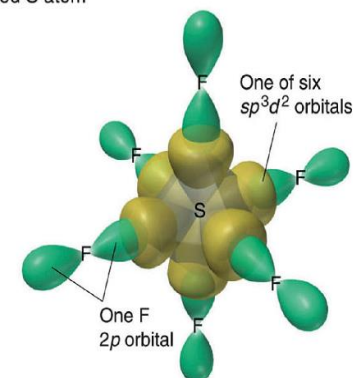
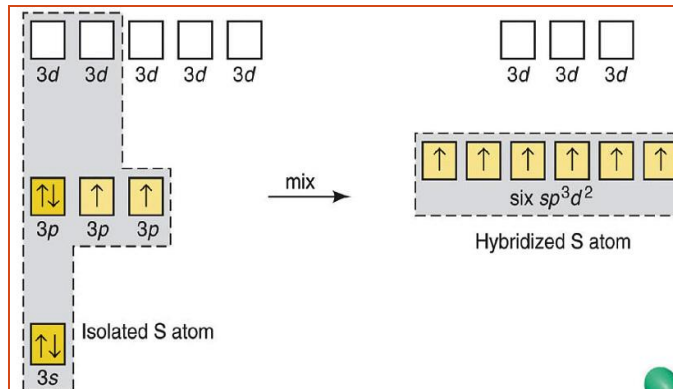
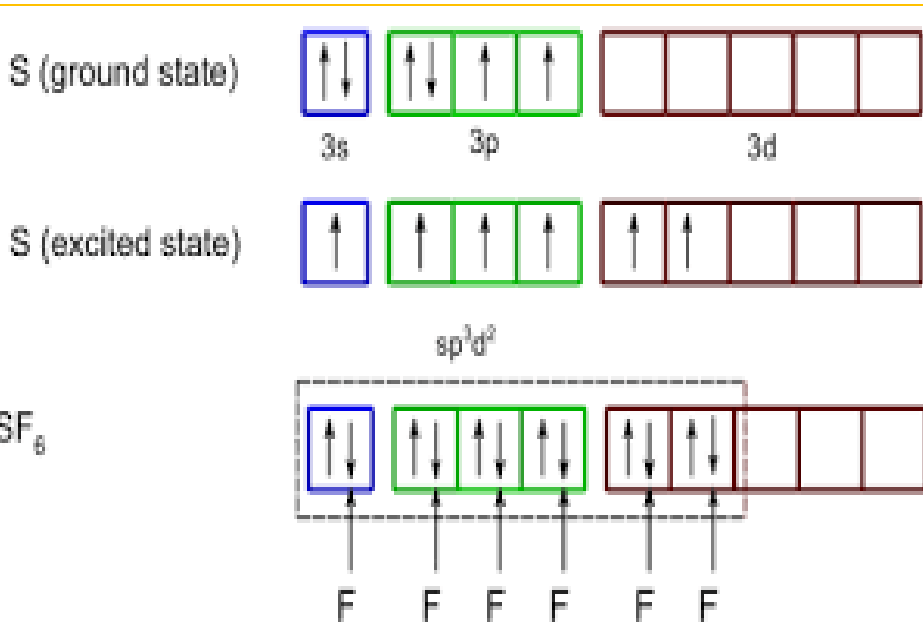
The sp^3 hybrid orbitals in H_2O

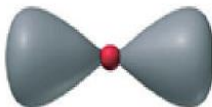
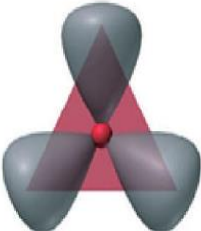


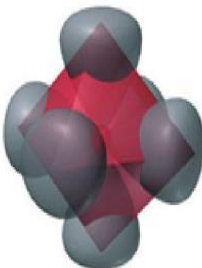


sp^3d hybrid orbitals in PCl_5





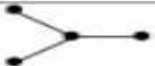
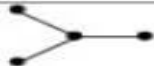




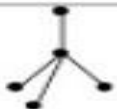




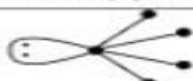




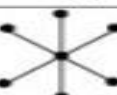

sp^3d^2 hybrid orbitals in SF_6



	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one <i>s</i> one <i>p</i>	one <i>s</i> two <i>p</i>	one <i>s</i> three <i>p</i>	one <i>s</i> three <i>p</i> one <i>d</i>	one <i>s</i> three <i>p</i> two <i>d</i>
Hybrid orbitals formed	two <i>sp</i>	three <i>sp</i> ²	four <i>sp</i> ³	five <i>sp</i> ³ <i>d</i>	six <i>sp</i> ³ <i>d</i> ²
Unhybridized orbitals remaining	two <i>p</i>	one <i>p</i>	none	four <i>d</i>	three <i>d</i>
Orientation					

Hybridization Summary

sp	s + p	= 2-sp	Linear	BeCl₂
sp²	s + 2p	= 3-sp²	Trigonal-Planar	BF₃
sp³	s + 3p	= 4-sp³	Tetrahedral	CH₄
sp³d	s + 3p + d	= 5-sp³d	Trigonal-Bypramidal	PCl₅
sp³d²	s + 2p + 2d	= 6-sp³d²	Octahedral	SF₆

Shape		Tetrahedral		Pyramidal		Bent
Sr. No.	Hybridisation	bp	lp	Gometry	Shape	Examples
1.	sp	2	0	 Linear	 Linear	$\text{BeF}_2, \text{BeCl}_2, \text{CO}_2, \text{C}_2\text{H}_2$
2.	sp^2	3	0	 Planar	 Planar	$\text{BF}_3, \text{BCl}_3, \text{NO}_3, (\text{SiH}_3)_3\text{N}$
3.	sp^3	4	0	 Tetrahedral	 Tetrahedral	$\text{CH}_4, \text{CCl}_4, \text{SO}_4^{2-}, \text{ClO}_4^-$
4.	sp^3	3	1	 Tetrahedral	 Pyramidal	$\text{NH}_3, \text{NF}_3, (\text{CH}_3)_3\text{N}, \text{CH}_3^-$
5.	sp^3	2	2	 Tetrahedral	 Angular or Bent	H_2O
6.	sp^3d	5	0	 Trigonal bipyramidal	 Trigonal bipyramidal	$\text{PF}_5, \text{PCl}_5, \text{PBr}_5, \text{PCl}_3, \text{Br}_2$
7.	sp^3d	4	1	 Trigonal bipyramidal	 See Saw	SF_4
8.	sp^3d	3	2	 Trigonal bipyramidal	 T-shape	$\text{ClF}_3, \text{BrF}_3$
9.	sp^3d	2	3	 Trigonal bipyramidal	 Linear	$\text{ICl}_2^-, \text{I}_3^-, \text{XeF}_2$
10.	sp^3d^2	6	0	 Octahedral	 Octahedral	$\text{SF}_6, \text{PCl}_6^-$

Exercise on VBT

1. In sp hybridization, ____ s orbital(s) hybridize with ____ p orbital(s) to form ____ sp orbital(s). The hybrid orbitals are oriented at ____⁰ to each other to form a _____ electron group geometry. ____ p orbitals remain unhybridized.
2. In sp^2 hybridization, ____ s orbital(s) hybridize with ____ p orbital(s) to form ____ sp^2 orbital(s). The hybrid orbitals are oriented at ____⁰ to each other to form a _____ electron group geometry. ____ p orbitals remain unhybridized.
3. In sp^3 hybridization, ____ s orbital(s) hybridize with ____ p orbital(s) to form ____ sp^3 orbital(s). The hybrid orbitals are oriented at ____⁰ to each other to form a _____ electron group geometry. ____ p orbitals remain unhybridized.

4. In sp^3d hybridization, ____ s orbital(s) hybridize with ____ p orbital(s) and ____ d orbital(s) to form ____ sp^3d orbital(s). The hybrid orbitals are oriented at ____⁰ to each other to form a ____ electron group geometry. ____ p orbitals remain unhybridized and ____ d orbitals remain unhybridized.
5. In sp^3d^2 hybridization, ____ s orbital(s) hybridize with ____ p orbital(s) and ____ d orbital(s) to form ____ sp^3d^2 orbital(s). The hybrid orbitals are oriented at ____⁰ to each other to form a ____ electron group geometry. ____ p orbitals remain unhybridized and ____ d orbitals remain unhybridized.

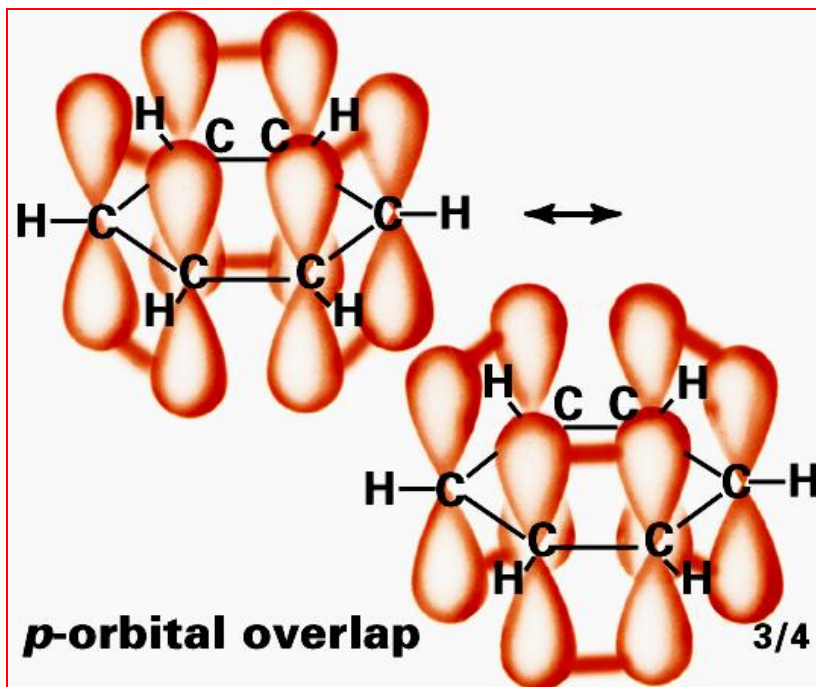
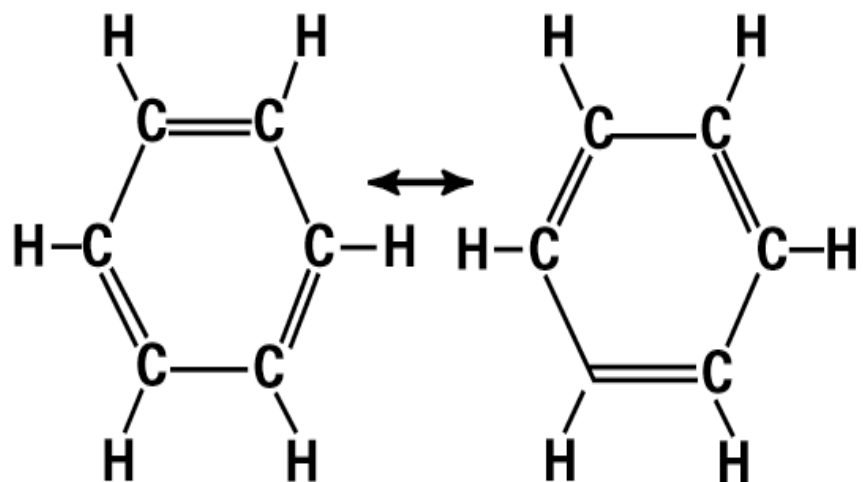
6. For the following molecules, indicate the molecular shape, hybridization of the central atom, the nature of the bonds on the central atom (for example: sp^2 -p), number of sigma and pi bonds, and whether or not the molecule is polar.



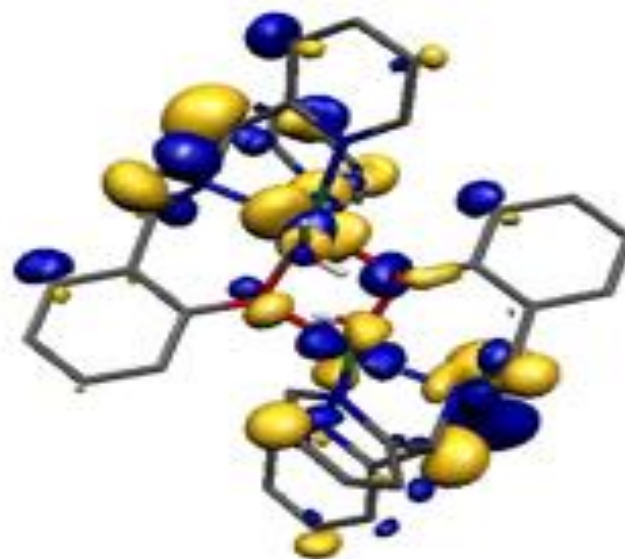
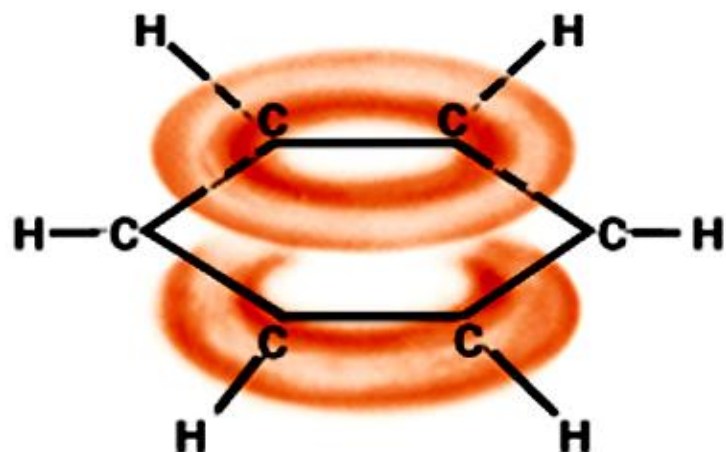
7. Explain briefly the main limitations of valence bond theory.

8. Why we study atomic structure? Explain briefly?

Lewis formulas



Delocalized MO representation



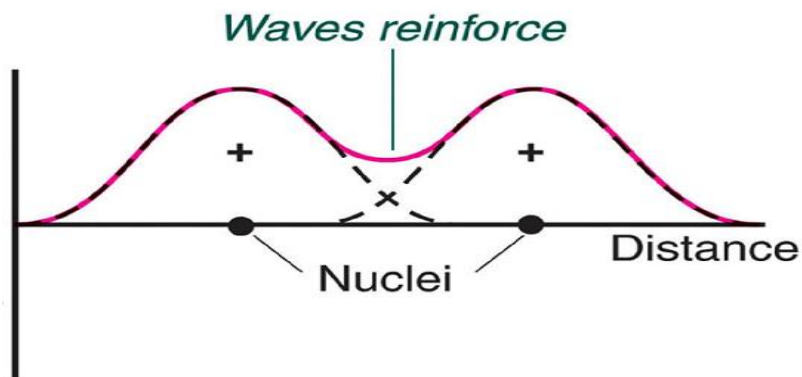
Molecular orbital theory

- **Molecular orbital theory (MOT)** is a method for describing the electronic structure of molecules.
- Hybridized valence bond theory does not explain much of the observed phenomena for small molecules such as paramagnetism or
- UV absorption and a better theory needs to be introduced to rationalize these experimental observations.
- In molecular MO theory, electrons occupy orbitals each of which spans the entire molecule.
- **Ground-rule of MO theory:** number of MOs that can be formed must equal the number of atomic orbitals of the constituent atoms

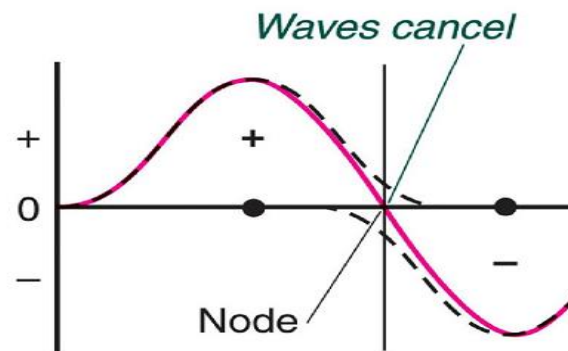
- In MO theory, it is accepted that electrons should not be regarded as belonging to particular bonds but should be treated as spreading throughout the entire molecule.
- A molecule is viewed on a quantum mechanical level as a collection of nuclei surrounded by delocalized molecular orbitals.
- Atomic wave functions are summed to obtain molecular wave functions
- If an electron can be found in an atomic orbital belonging to atom A and also in an atomic orbital belonging to atom B,
- then the overall wave function is a superposition of the two atomic orbitals: $\psi_{\pm} = N(A \pm B)$

- If wave functions reinforce each other, a bonding MO is formed (region of high electron density exists between the nuclei).
- If wave functions cancel each other, an antibonding MO is formed (anode of zero electron density occurs between the nuclei).

An analogy between light waves and atomic wave functions

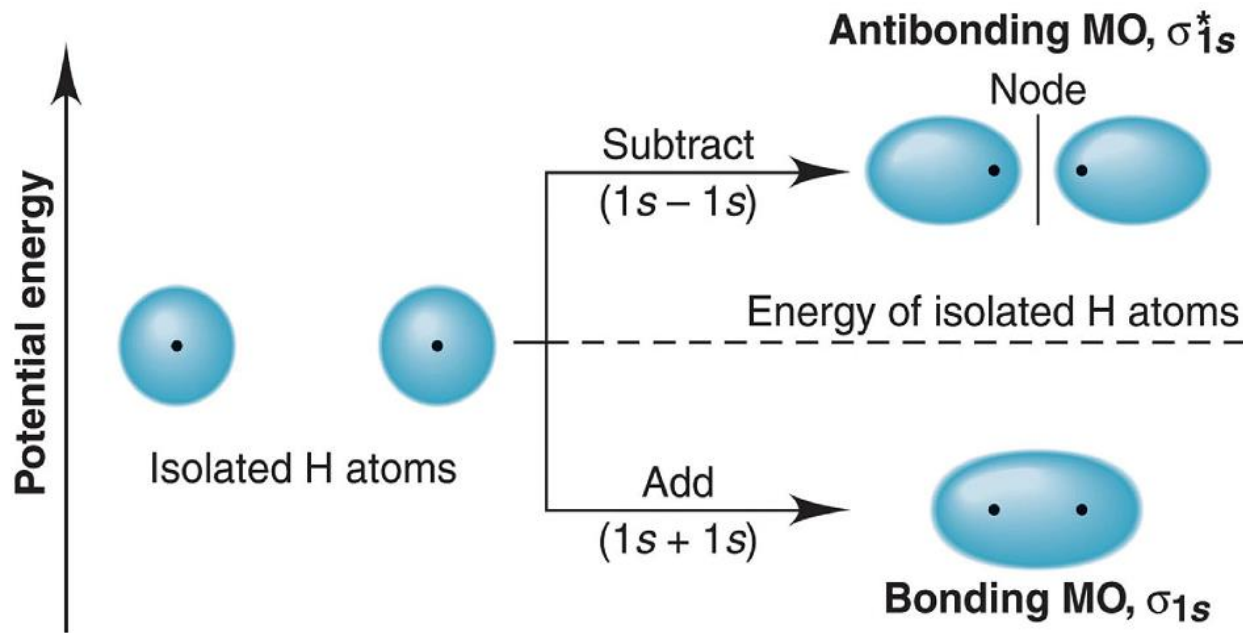


Amplitudes of wave functions added



Amplitudes of wave functions subtracted.

Contours and energies of the bonding and antibonding molecular orbitals (MOs) in H_2 .



- The bonding MO is lower in energy and the antibonding MO is higher in energy than the AOs that combined to form them.

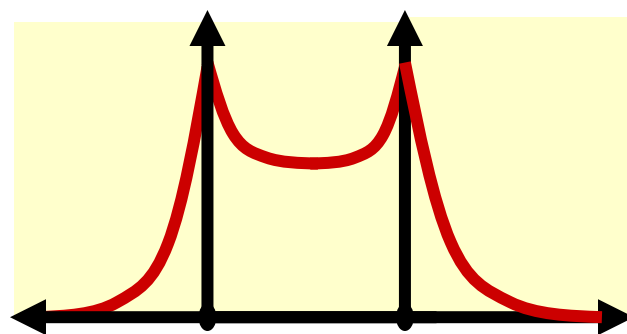
Q. Why this so?

➤ Each of the H atoms has 1s atomic orbital with associated wave functions, Ψ_1 and Ψ_2 and the signs of the wavefunction associated with the 1s orbital may be either + or -.

➤ The possible combinations of the two 1s orbitals are given by equations:

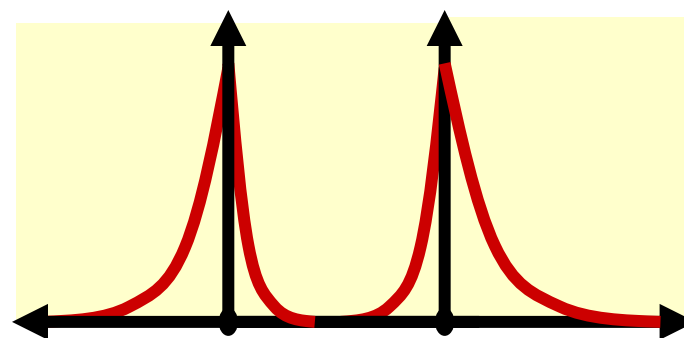
$$\Psi_{\text{MO (in-phase)}} = \Psi_{\text{MO}} = N[\Psi_1 + \Psi_2], \quad \Psi_{\text{MO (out-of-phase)}} = \Psi_{\text{MO}}^* = N^*[\Psi_1 - \Psi_2]$$

➤ where N and N* are the normalization factors, Ψ_{MO} is an in-phase (bonding) interaction and Ψ_{MO}^* is an out-of-phase (antibonding) interaction.



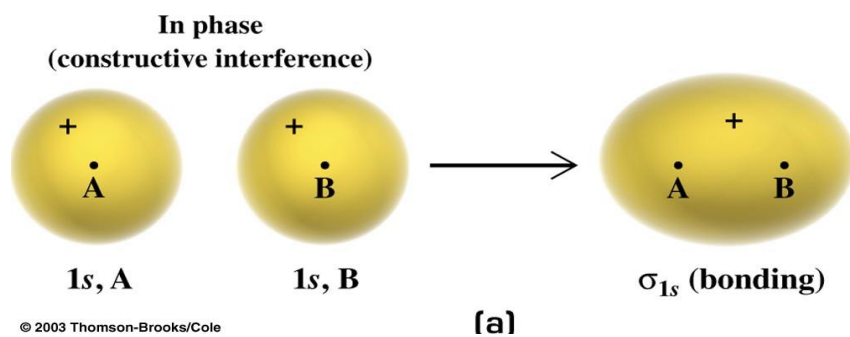
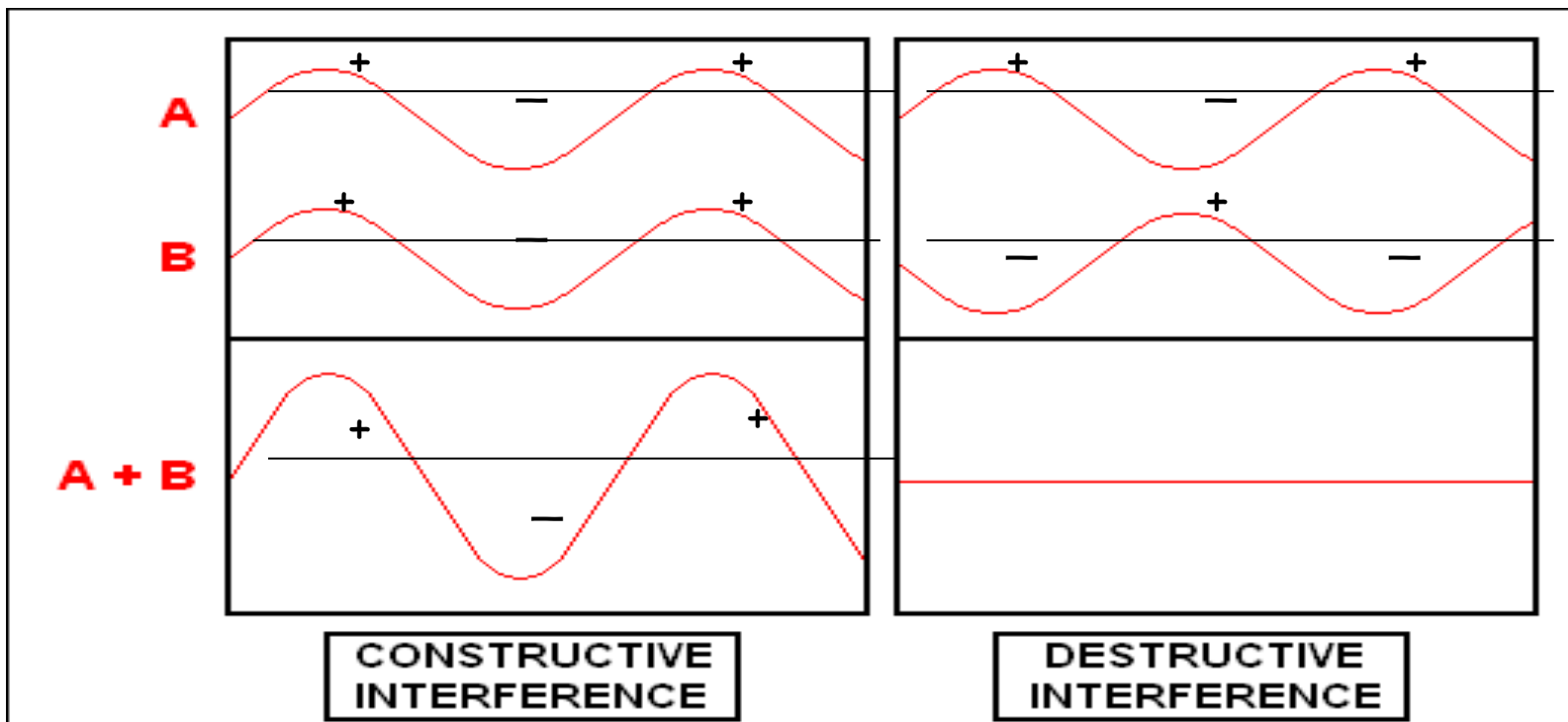
$$1s_A + 1s_B = \text{MO}_1$$

constructive interference

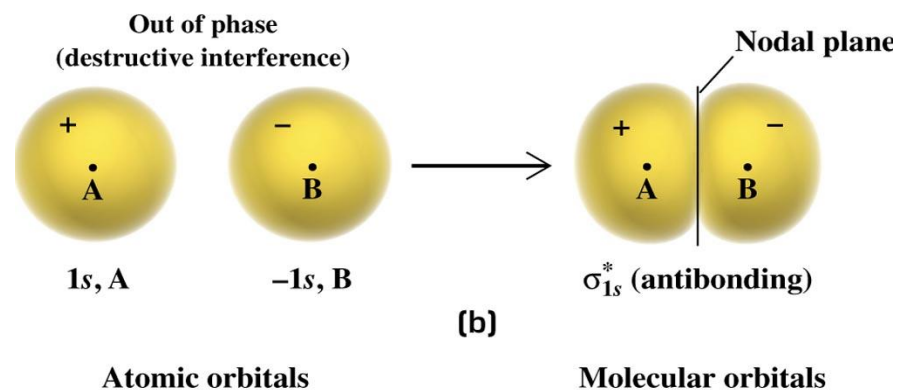


$$1s_A - 1s_B = \text{MO}_2$$

destructive interference

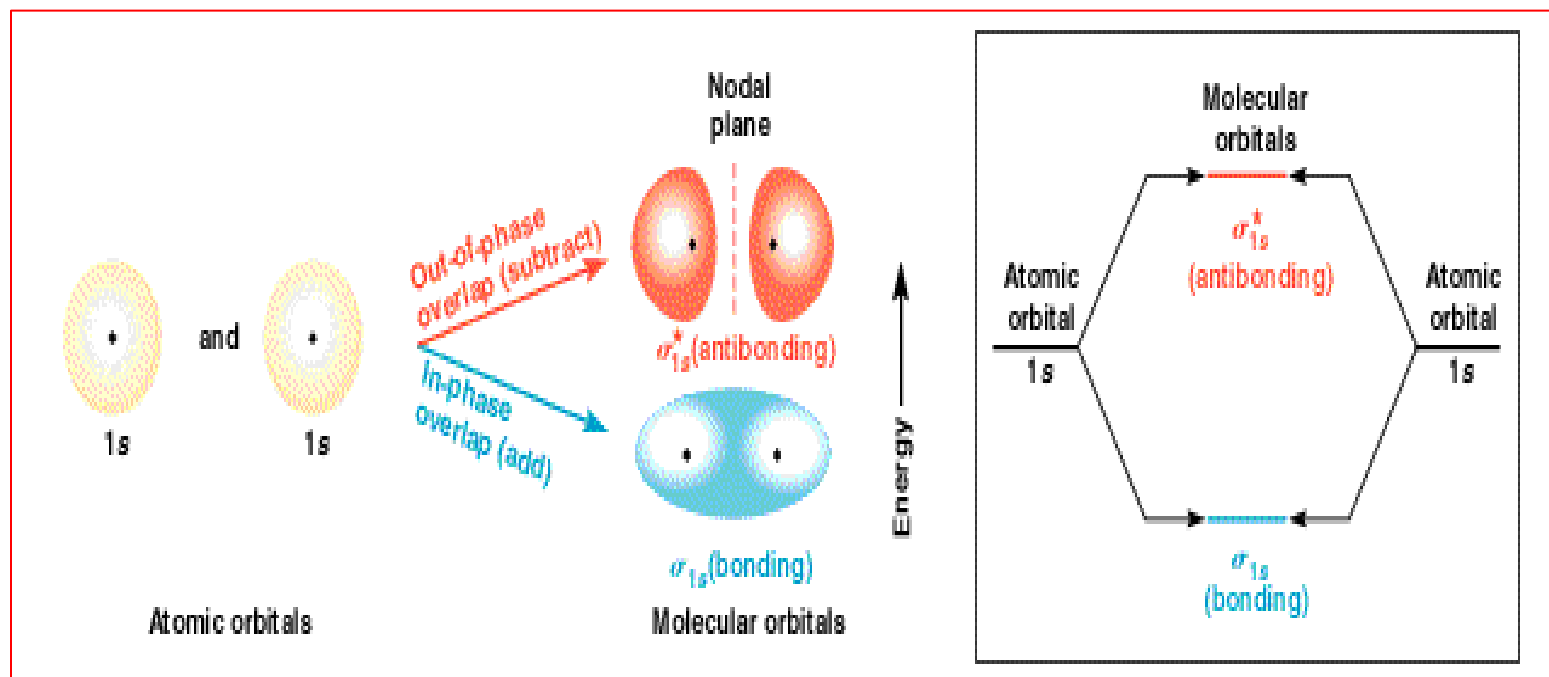


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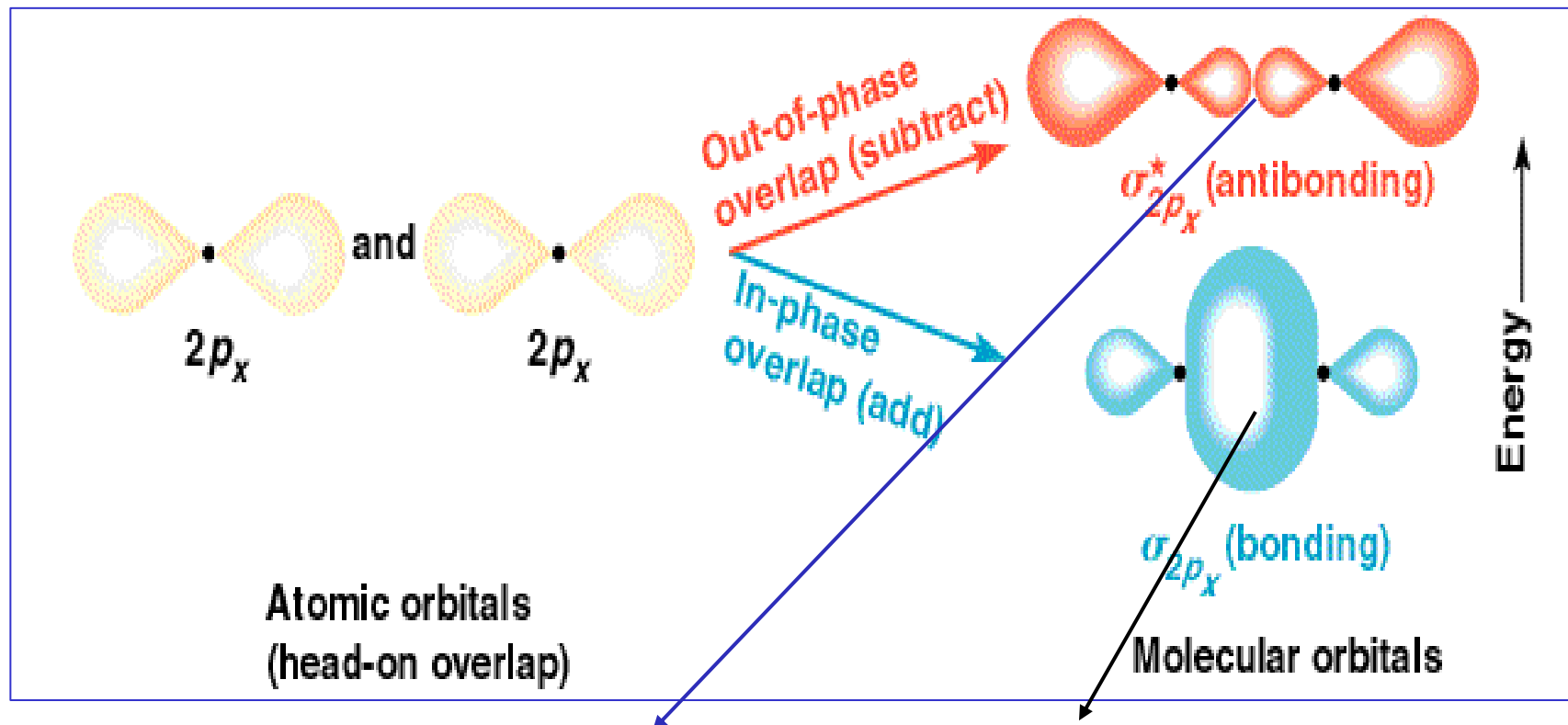
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Overlap of Two 1s Atomic Orbitals



- ✓ Constructive interference from the 1s orbitals (σ_{1s}) while
- ✓ Destructive interference from the 1s orbitals (σ_{1s}^*).

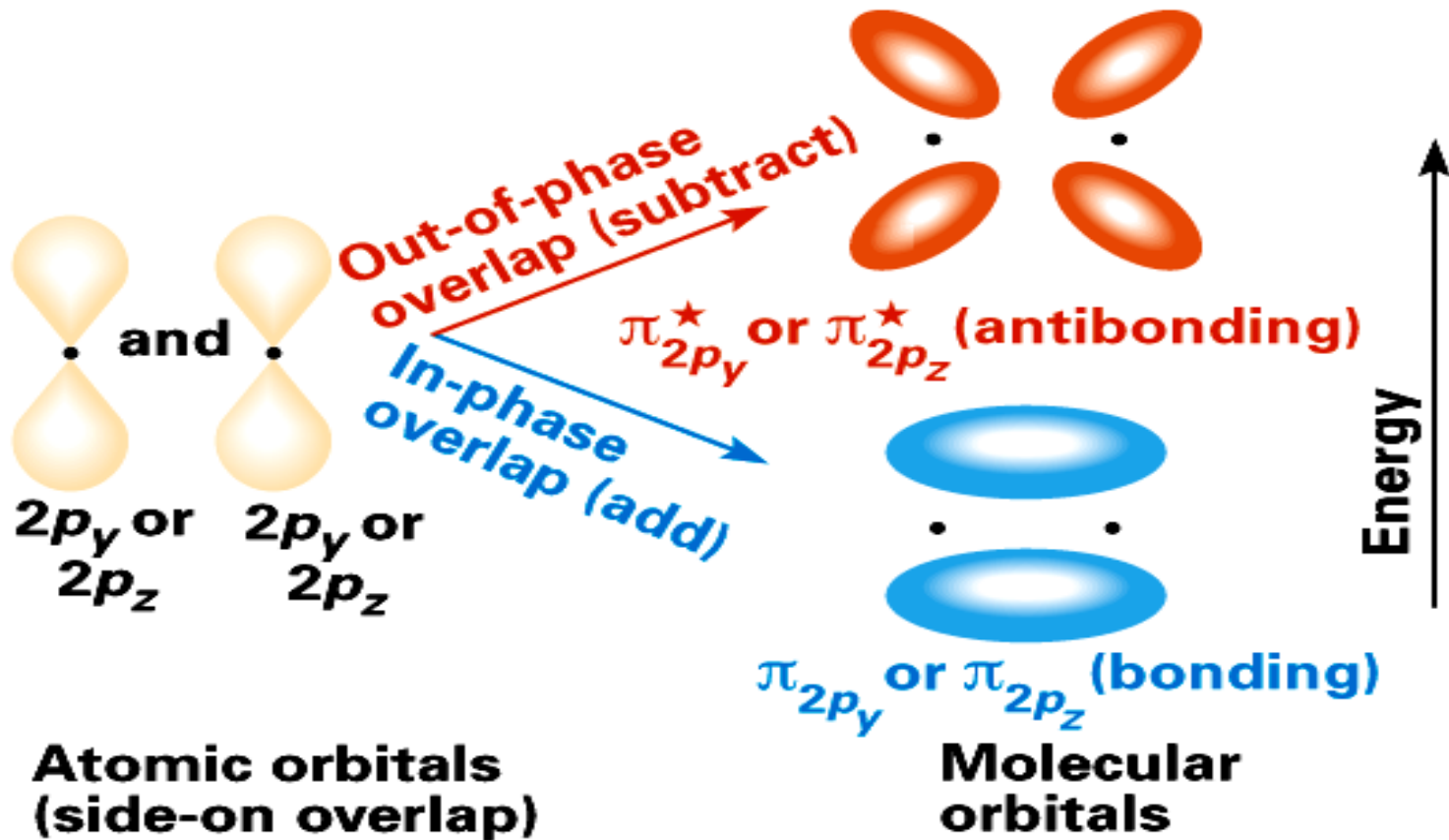
Overlap of $2p_x$ Orbitals



Low electron density/nodal plane

High electron density

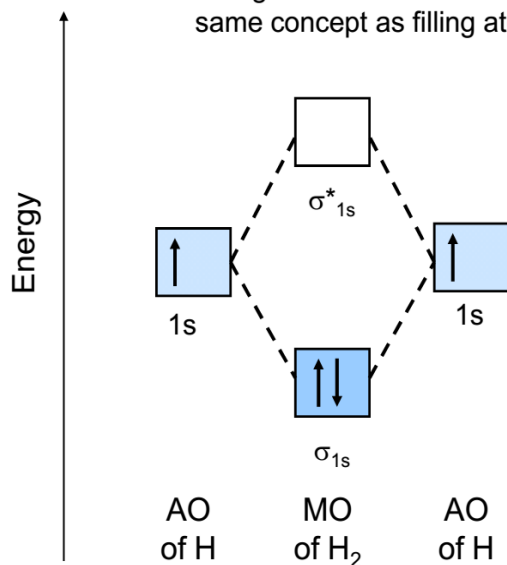
Overlap of $2p_y$ Orbitals



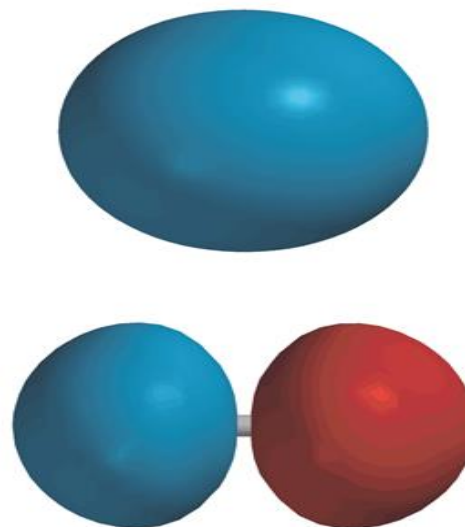
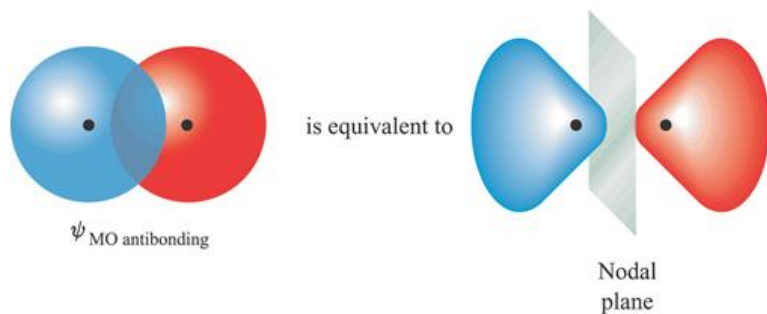
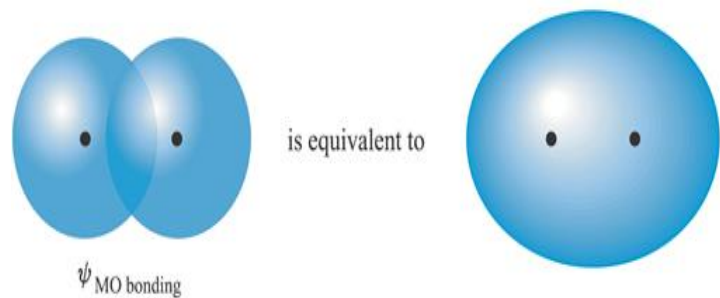
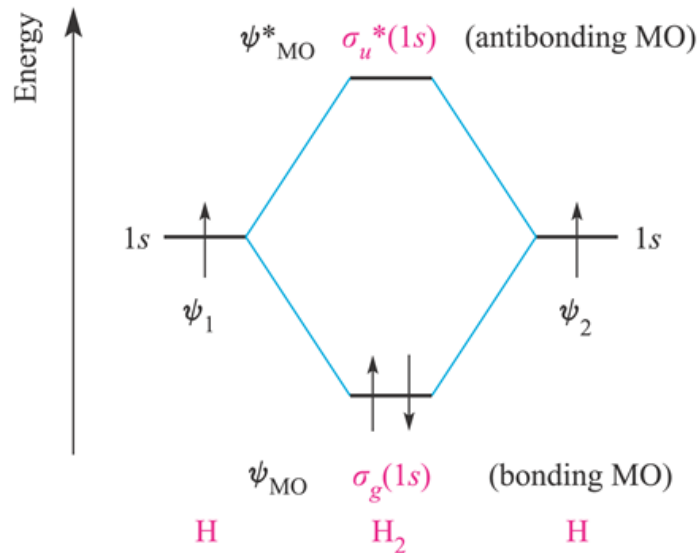
- ✓ Constructive interference from $2p_y$ orbitals
- ✓ Destructive interference from $2p_y^*$ orbitals

The MO diagram for H₂

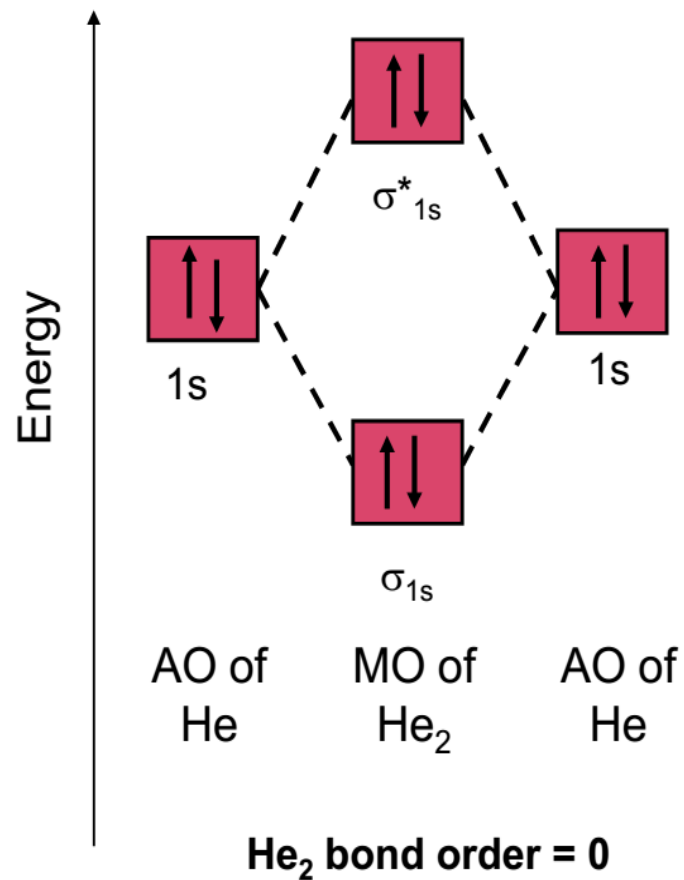
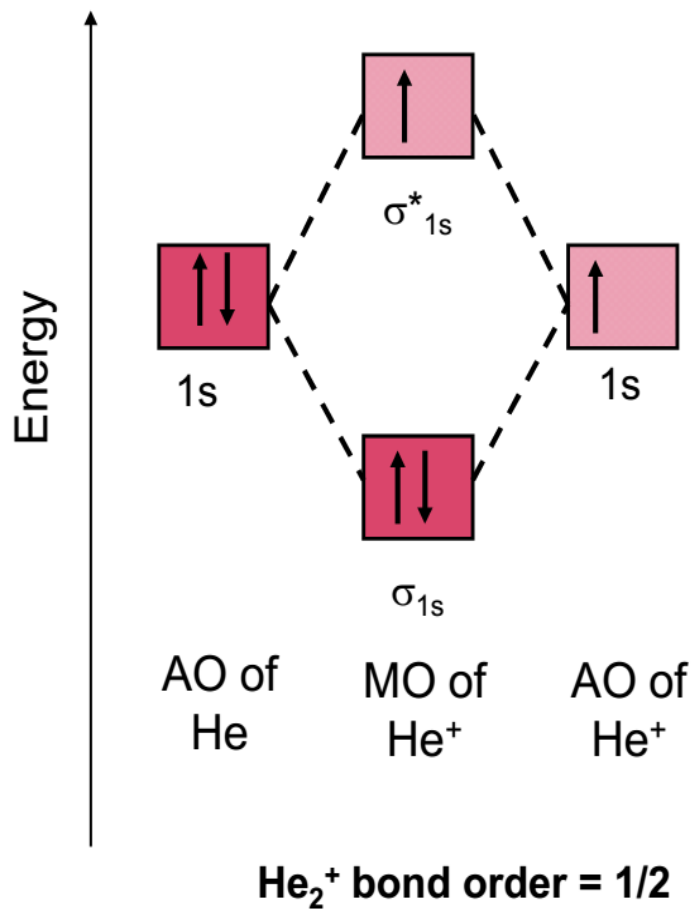
Filling molecular orbitals with electrons follows the same concept as filling atomic orbitals.



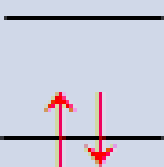
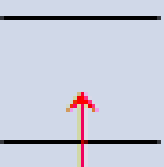
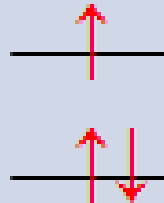
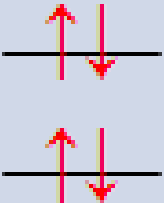
$$\text{H}_2 \text{ bond order} = \frac{1}{2}(2-0) = 1$$



MO diagram for He_2^+ and He_2 .



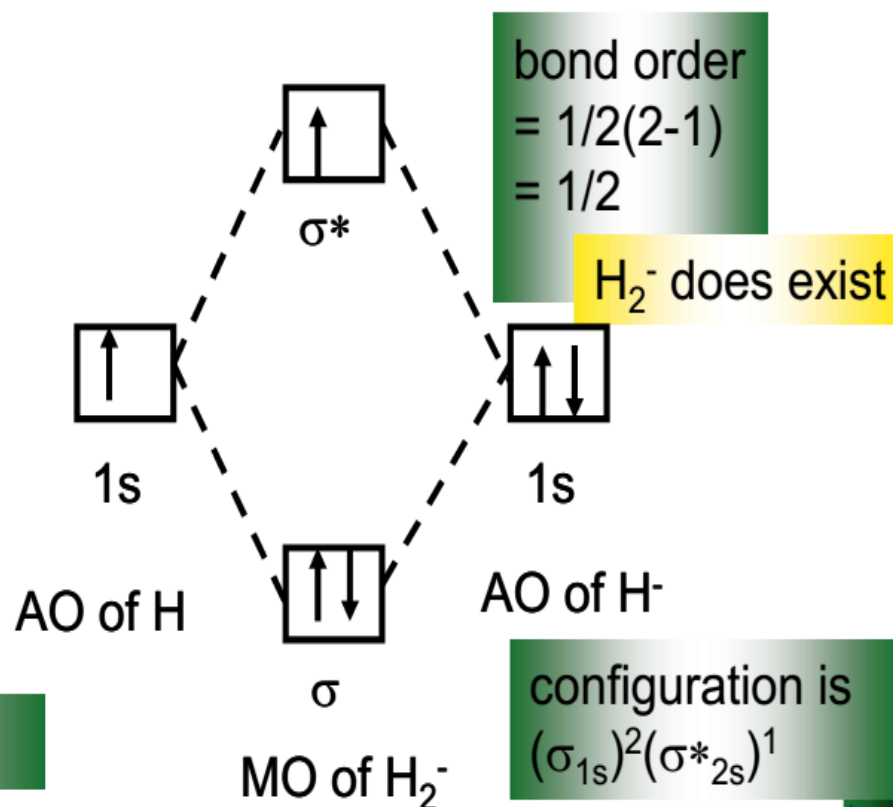
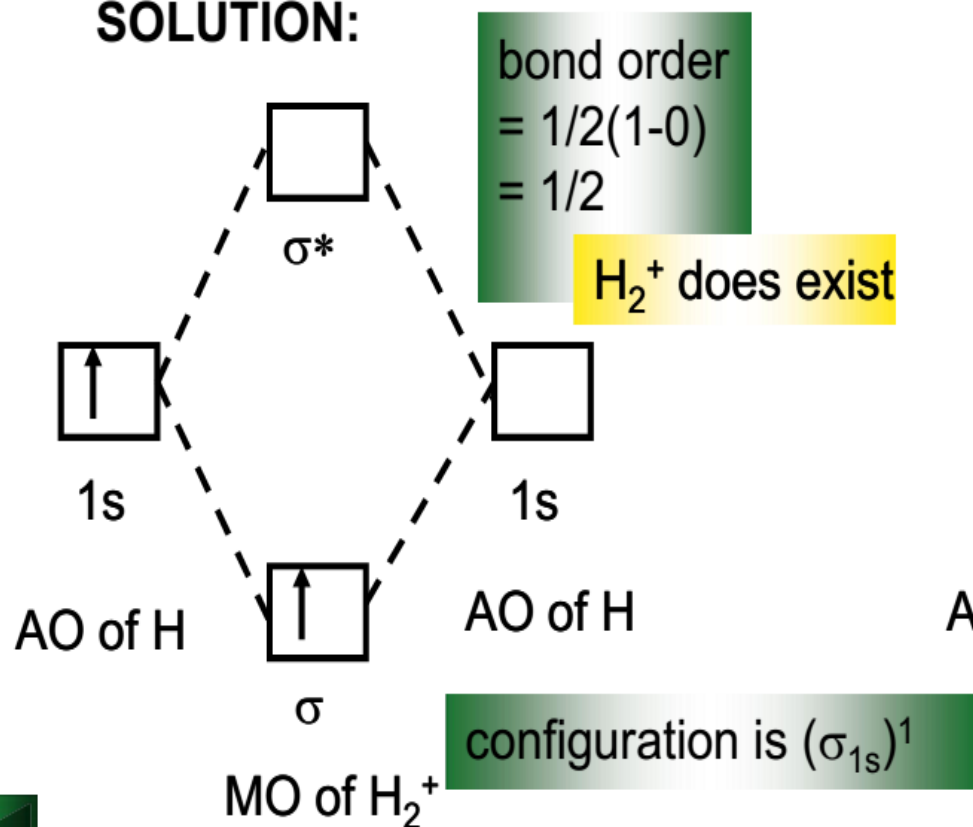
- A high bond order indicates high bond energy and short bond length.
- Consider H_2^+ , H_2 , He_2^+ , He_2 : first row diatomic molecules and ions

	H_2	H_2^+	He_2^+	He_2
$E \uparrow$ $\sigma_g(1s^2)$ $\sigma_u^*(1s^2)$				
Magnetism	<u>Dia-</u>	Para-	Para-	-
Bond order	1	$\frac{1}{2}$	$\frac{1}{2}$	0
Bond energy (<u>kJ/mol</u>)	436	225	251	-
Bond length (pm)	74	106	108	-

PROBLEM: Use MO diagrams to predict whether H_2^+ and H_2^- exist. Determine their bond orders and electron configurations.

PLAN: Use H_2 as a model and accommodate the number of electrons in bonding and antibonding orbitals. Find the bond order.

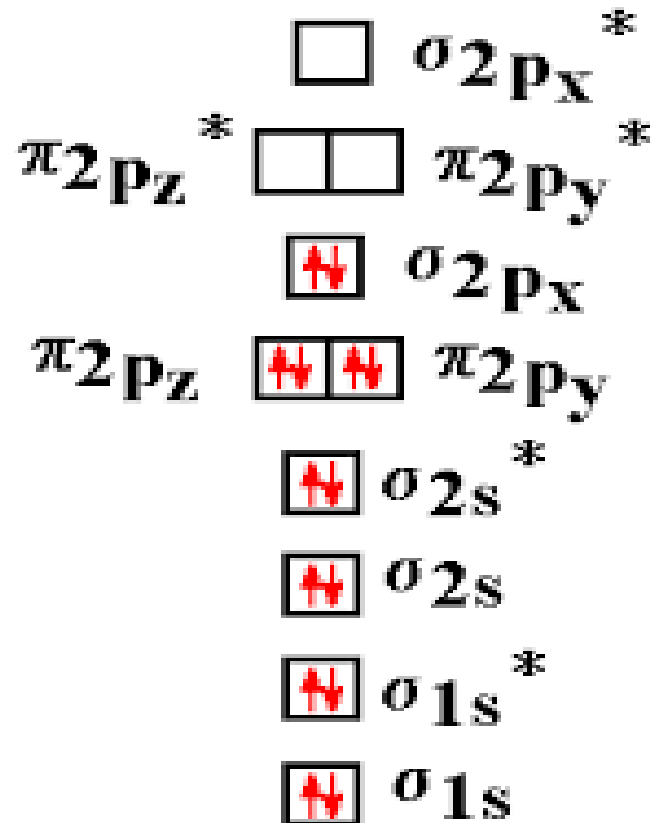
SOLUTION:



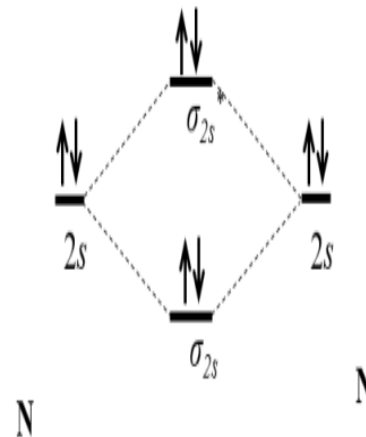
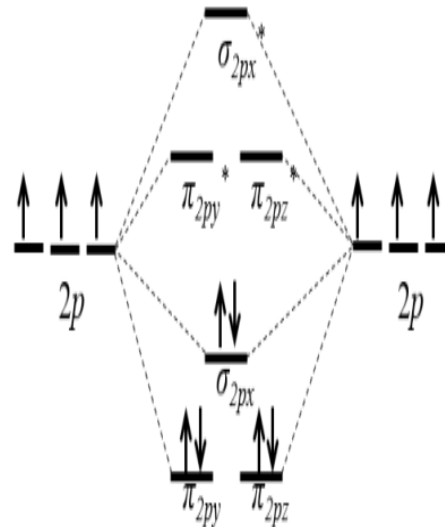
- Another property that MOT can predict is the magnetism of compounds.
- Compounds are classified as diamagnetic or paramagnetic based on their electronic properties.
 - **Diamagnetic compounds** are slightly repulsed by a magnetic field. They contain no unpaired electrons.
 - **Paramagnetic compounds** are slightly attracted to a magnetic field. They contain at least one unpaired electron.

Example: Is N_2 diamagnetic or paramagnetic? Why?

N₂ Orbital Energies



Bond Order = 3

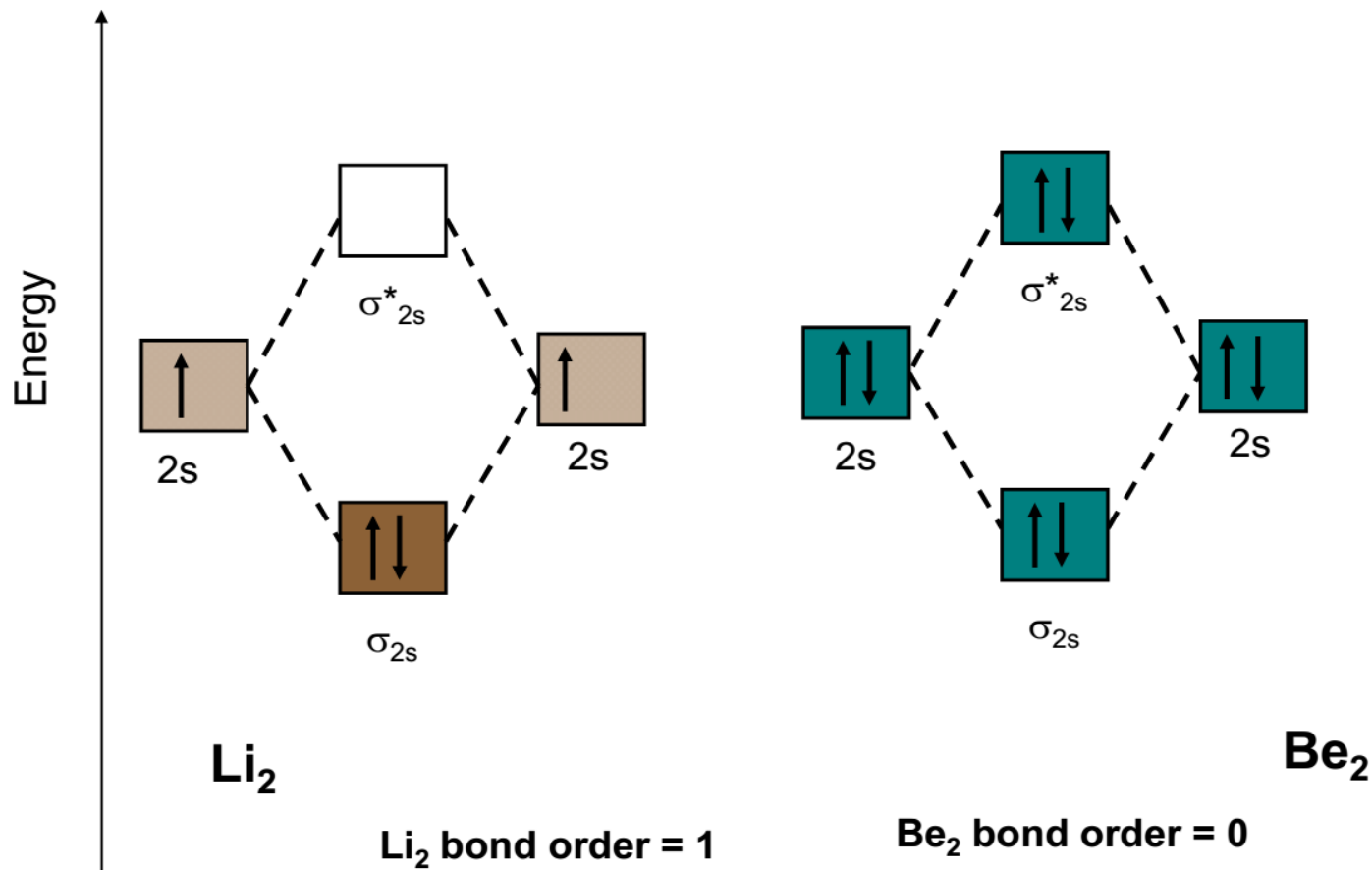


The bond order for N₂ is:

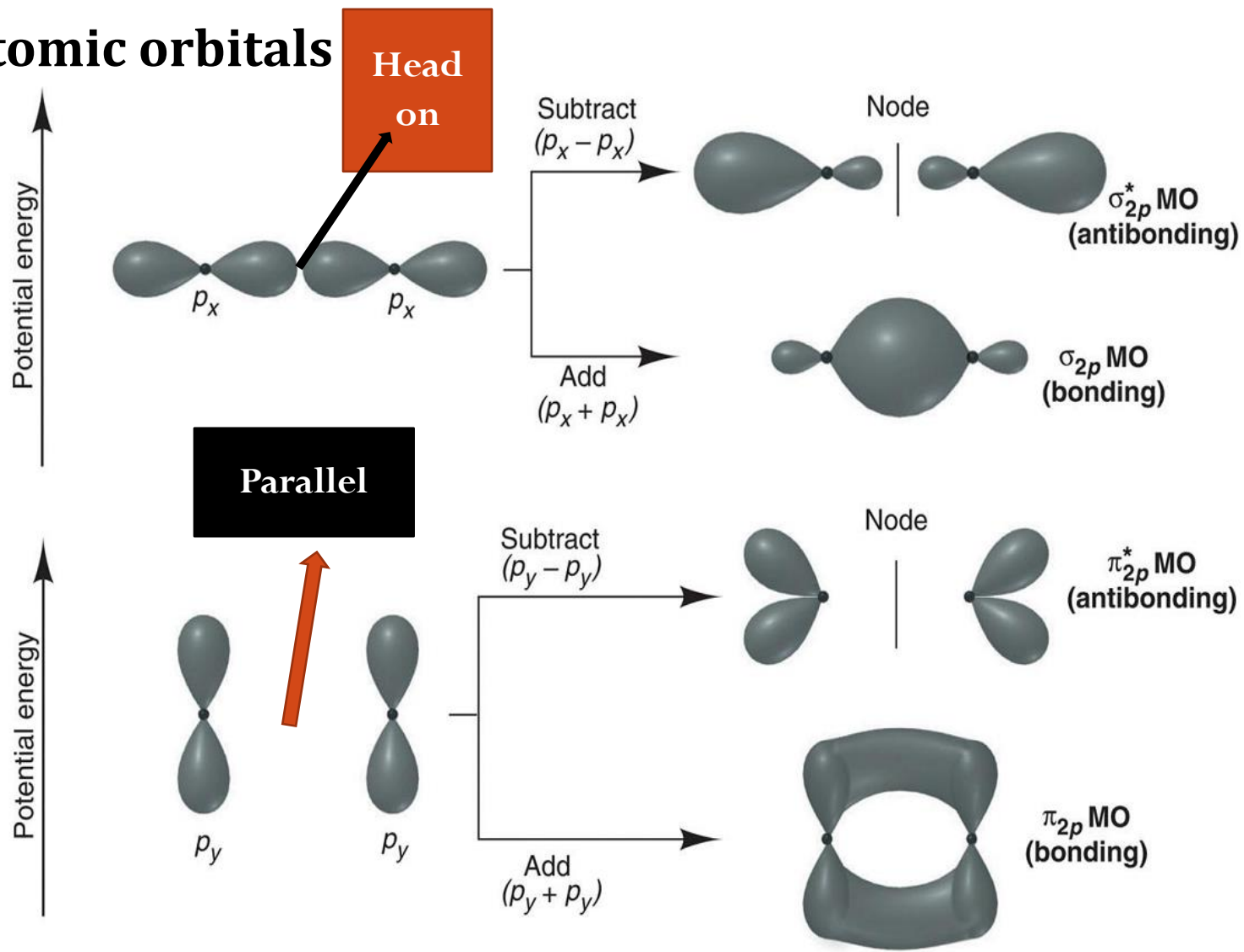
$$\text{Bond Order} = \frac{(8 - 2)}{2} = 3$$

N₂ is diamagnetic since it contains no unpaired electrons.

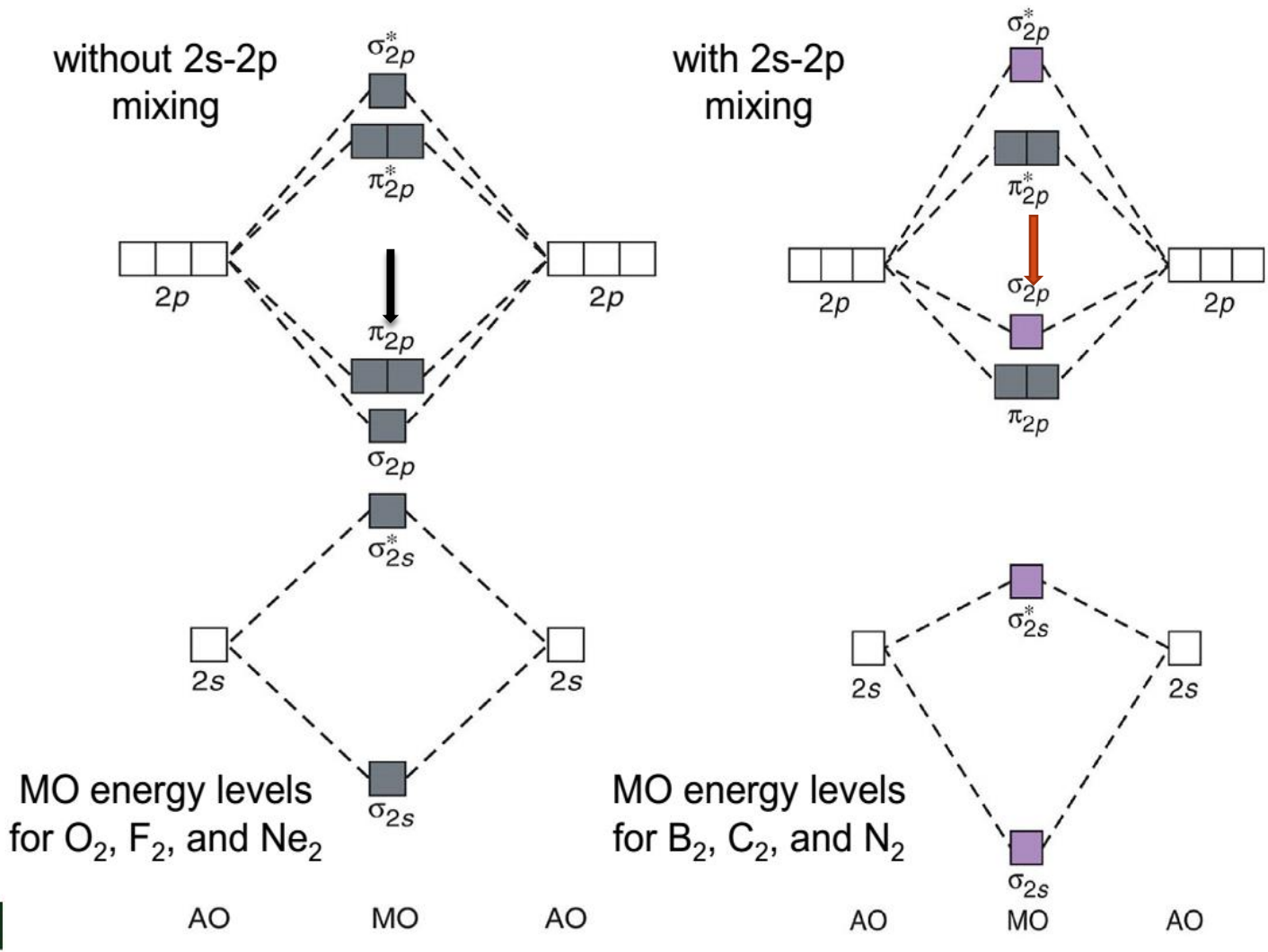
Bonding in homonuclear diatomic molecules



Contours and energies of s and p MOs through combinations of 2p atomic orbitals

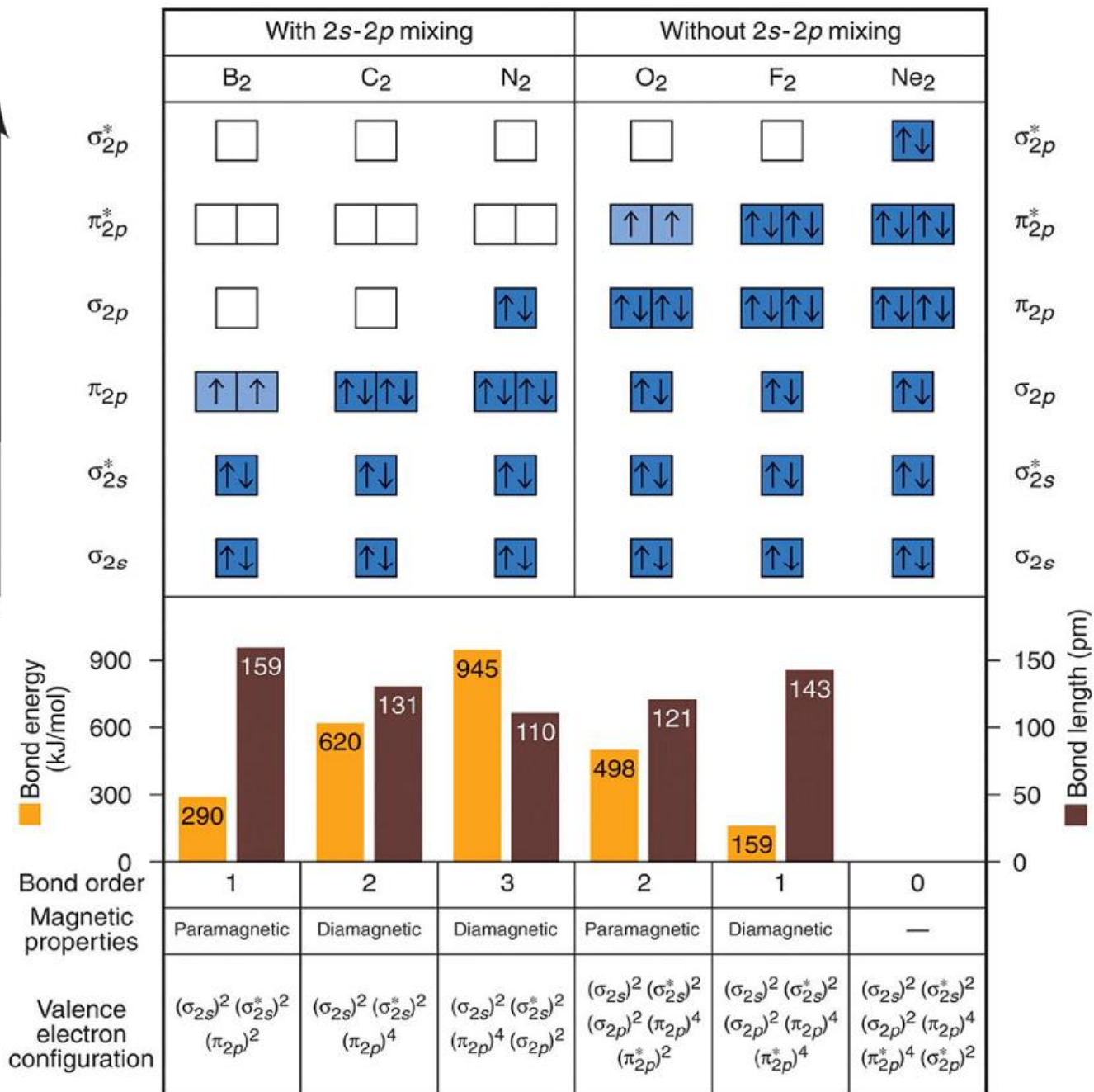


➤ Relative MO energy levels for homonuclear diatomic molecules



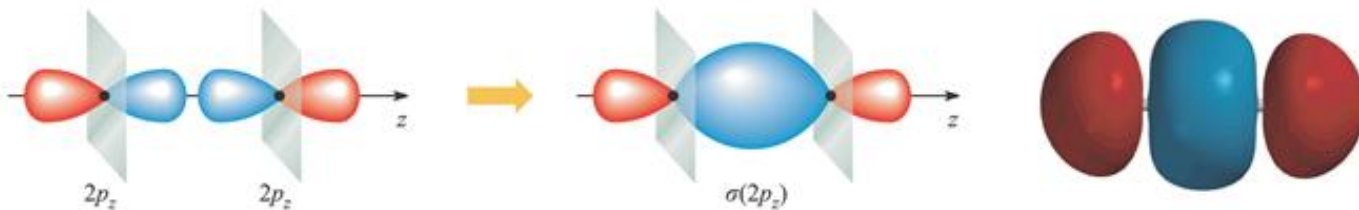
MO occupancy and molecular properties for B₂ through Ne₂

Energy ↑

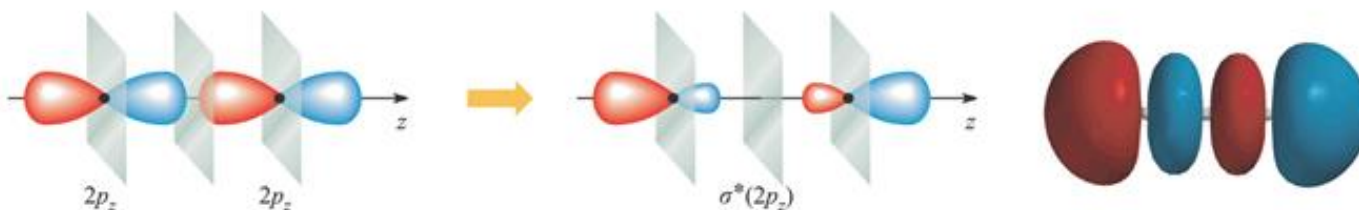


- If the overlap lies along the major bond axis then must constitute a σ bond.

A

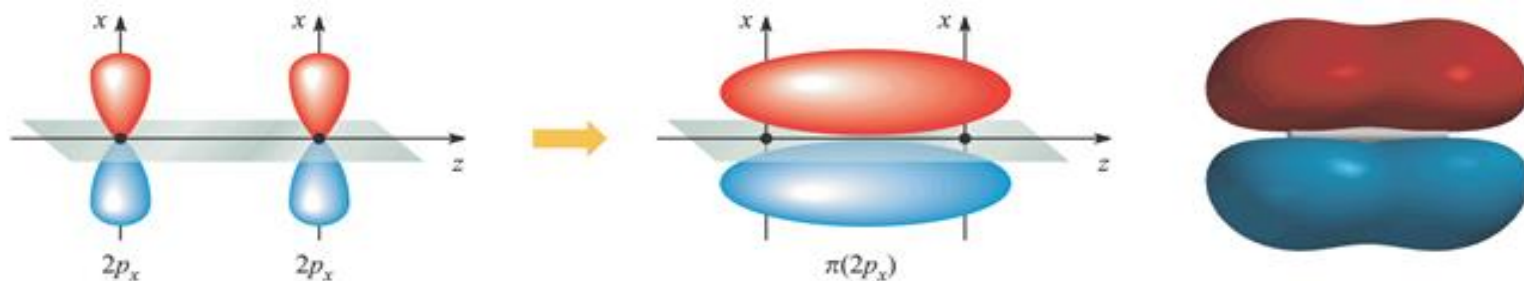


B

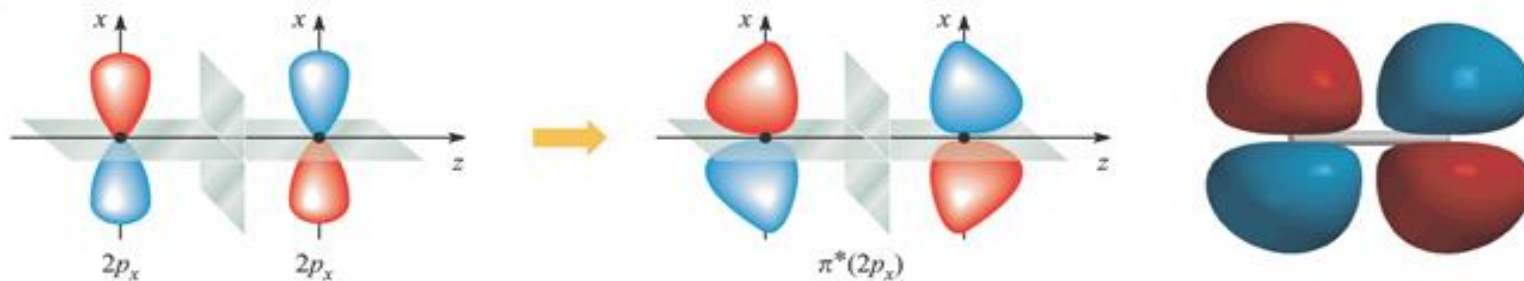


- If they overlap perpendicular to the axis they will form π bonds

C



D



Using MO Theory to Explain Bond Properties

PROBLEM: As the following data show, removing an electron from N_2 forms an ion with a weaker, longer bond than in the parent molecules, whereas the ion formed from O_2 has a stronger, shorter bond:

	N_2	N_2^+	O_2	O_2^+
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

Explain these facts with diagrams that show the sequence and occupancy of MOs.

PLAN: Find the number of valence electrons for each species, draw the MO diagrams, calculate bond orders, and then compare the results.

SOLUTION:

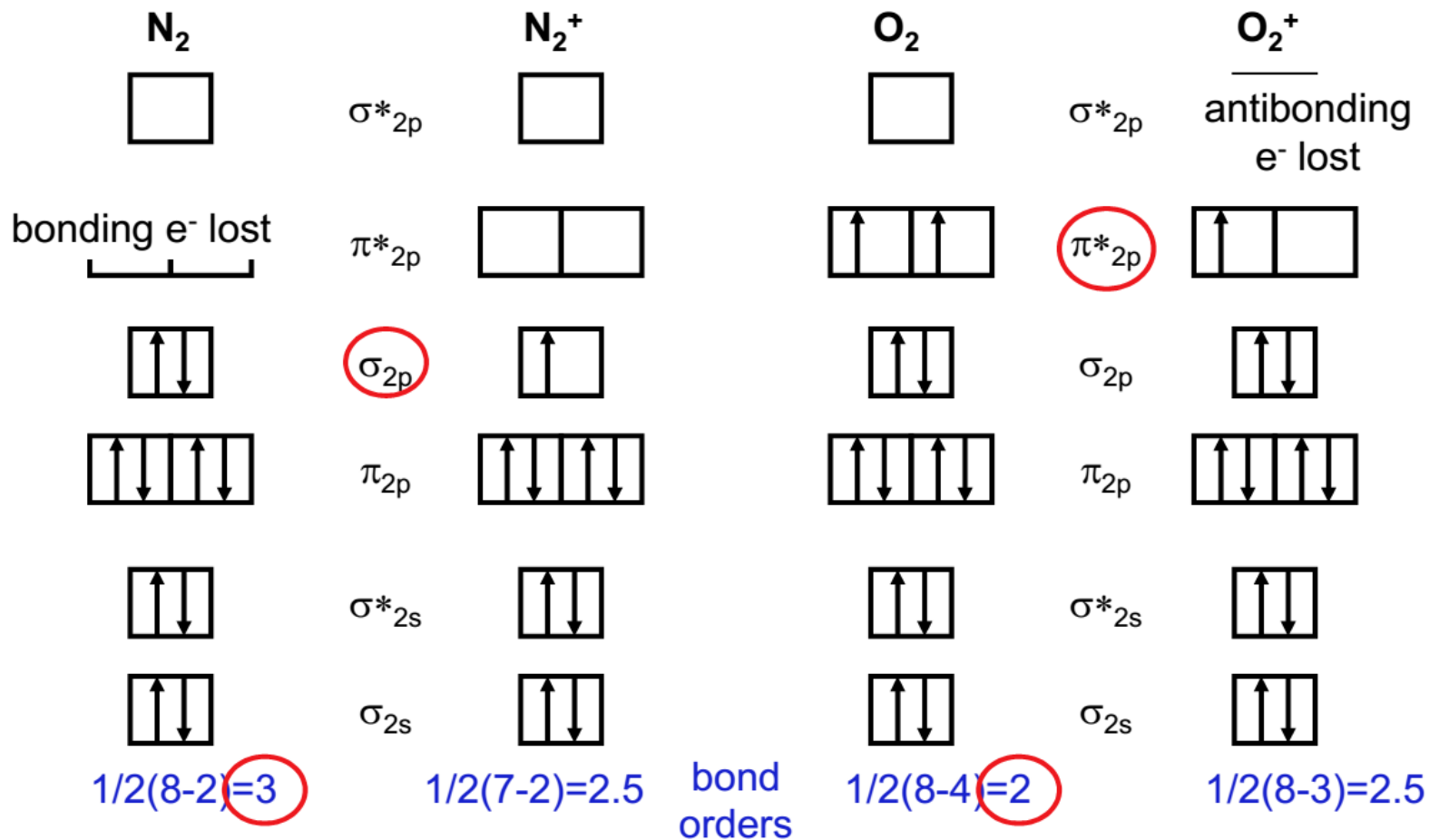
N_2 has 10 valence electrons, so N_2^+ has 9.

O_2 has 12 valence electrons, so O_2^+ has 11.

SAMPLE PROBLEM

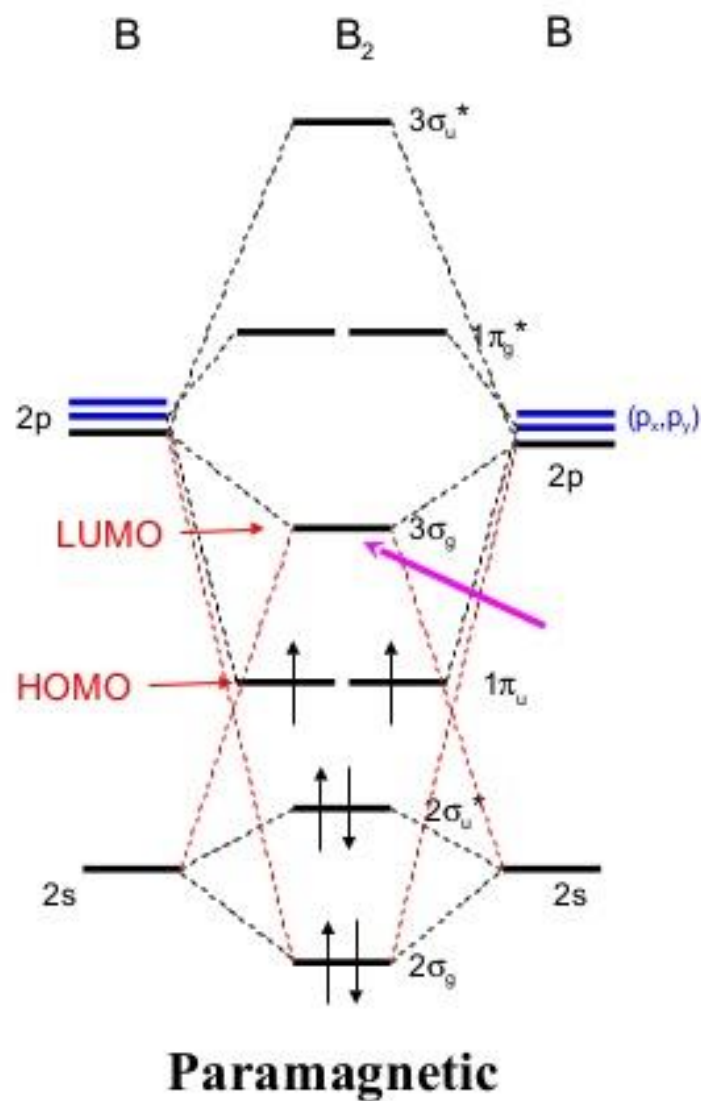
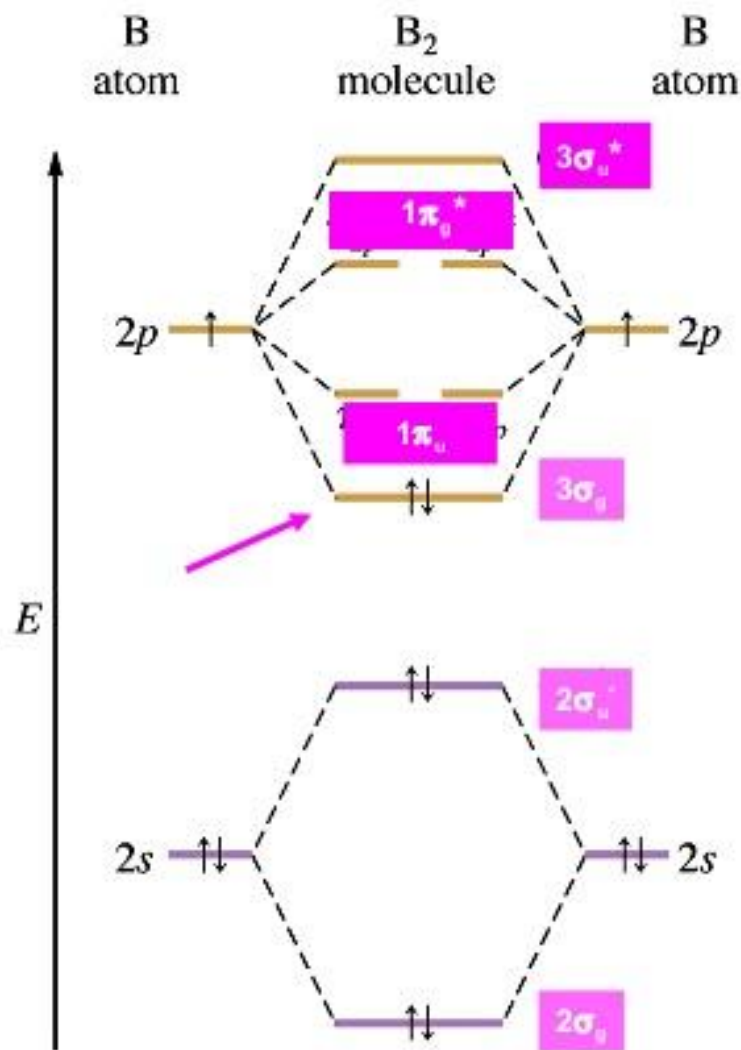
Using MO Theory to Explain Bond Properties

continued





MO diagram for B₂



$$\text{B.O} = \frac{1}{2} (4 - 2) = 1$$

1. Which statement is false? A sigma molecular orbital

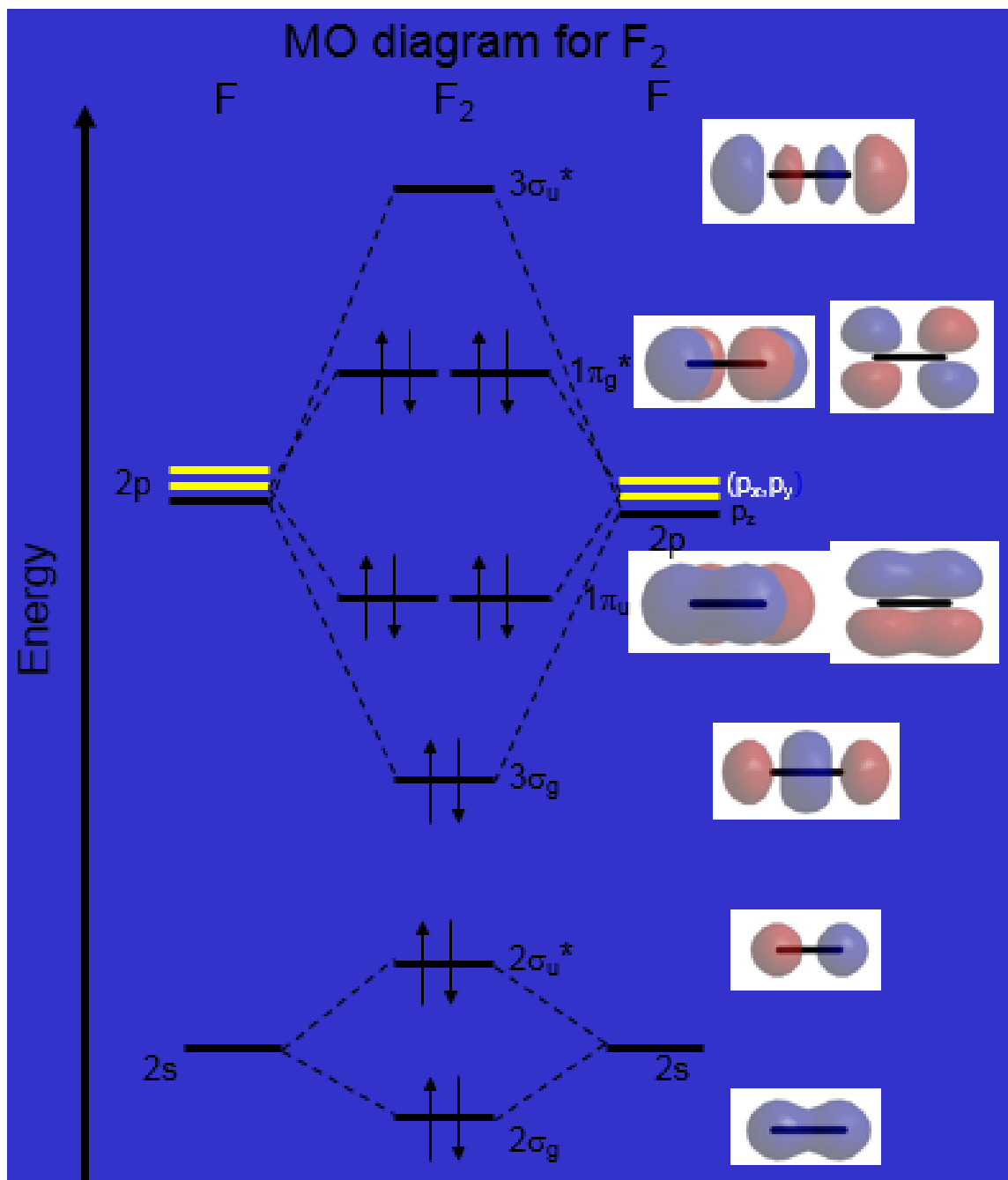
- (a) may result from side-on overlap of p-orbitals.
- (b) may result from head-on overlap of p-orbitals
- (c) may result from overlap of an s atomic orbital with a p atomic orbital
- (d) may be either bonding or antibonding

2. The concept of an antibonding orbital is unique to the:

- (a) theory of bond hybridization
- (b) valence bond theory
- (c) molecular orbital theory.
- (d) concept of resonance,

3. According to molecular orbital theory, which statement is true?

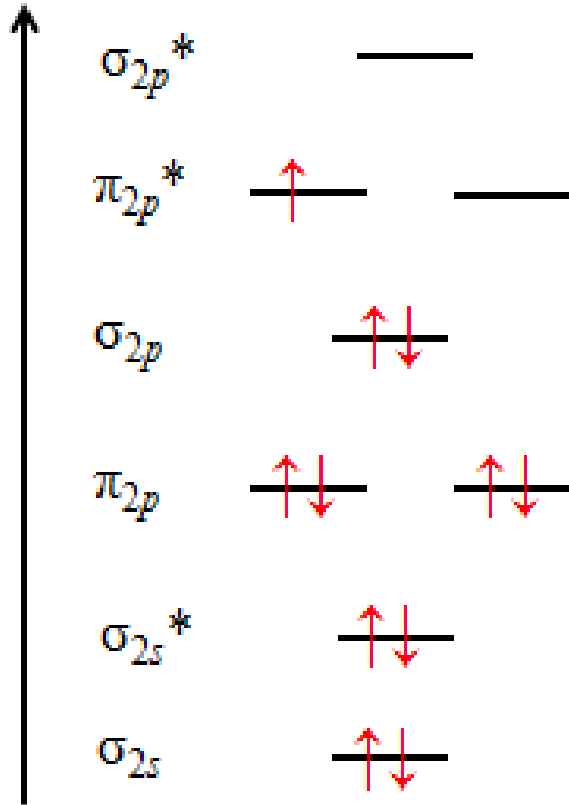
- (a) A molecule with an even number of electrons must be diamagnetic
- (b) There are as many sigma bonds as pi bonds in a molecule
- (c) There are as many molecular orbitals as there are atomic orbitals.
- (d) There are as many bonding as antibonding electrons in a molecule



❖ Notice that there is no mixing of AO's of the same symmetry from a single F atom because there is a sufficient difference in energy between the $2s$ and $2p$ orbitals in F.

Heteronuclear Diatomic Molecules

- Even when the atoms in a diatomic molecule are different, we use the homonuclear diatomic diagram with the **s-p** interaction.
- Nitric Oxide (NO) : Valence electrons = $5 + 6 = 11$



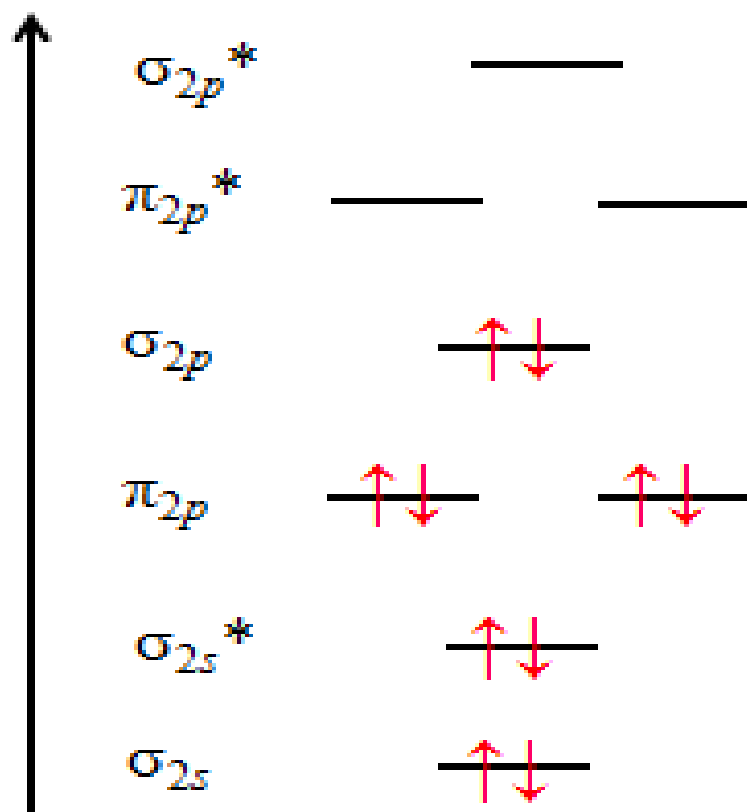
Bond order = 2.5

Molecule is stable and paramagnetic – agrees with experimental data.

NO⁺: Number of valence electrons: $5 + 6 - 1 = 10$

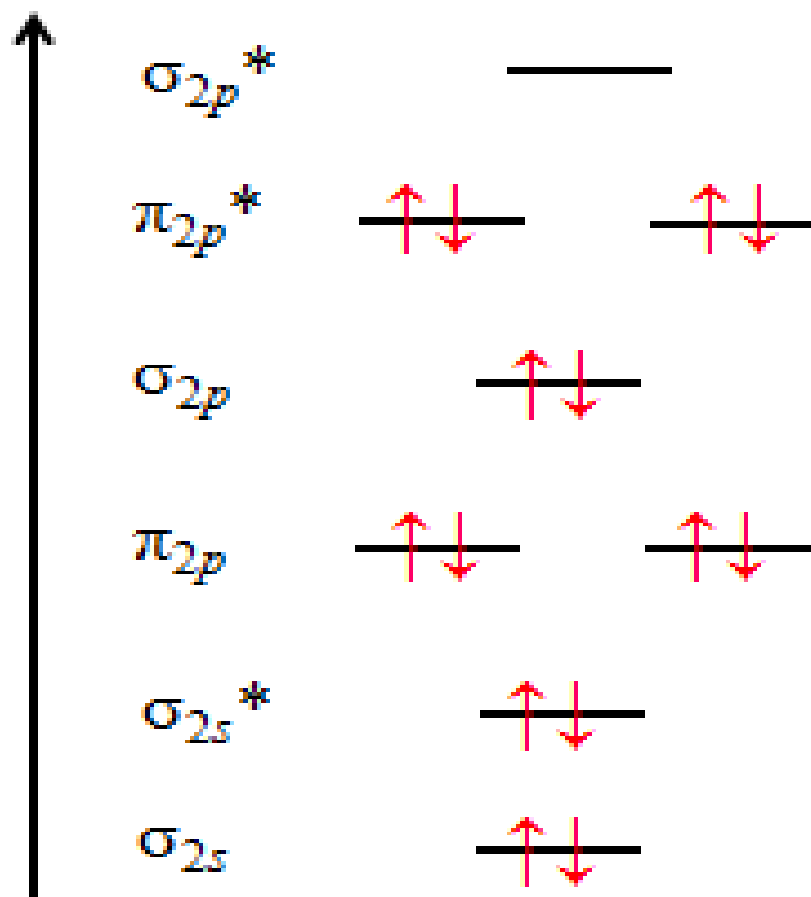
CN⁻: Number of valence electrons: $4 + 5 + 1 = 10$

These structures are **isoelectronic**



Bond order = 3.0

➤ NeO: Number of valence electrons: $8 + 6 = 14$



Bond order = 1.0

Explain briefly each of the following questions

1. Why antibonding molecular orbital has higher energy than bonding molecular orbital? Explain.
2. Which type of bond has higher energy, sigma or pi? And why? Explain.

Exercise on MOT

- 1) Do valence bond theory (hybridization) and MO theory for both O_2 and O_2^{2-} . Which theory works better to explain the molecule and ion?
- 2) For N_2 , N_2^+ and N_2^- compare
 - a. Magnetic character
 - b. Bond Order
 - c. Bond length.
 - d. Bond strength

3. Draw the MO energy diagram for peroxide (O_2^{2-}) and calculate the bond order. Based on this, do you expect the O-O bond in peroxide to be longer or shorter than in oxygen gas (O_2)?
4. Draw the MO energy diagram for F_2^+ ion and determine the ion's bond order.
5. H_2 , N_2 , O_2 and F_2 are all gases under standard conditions. Which of these gases are paramagnetic? Which do you expect will have the strongest bond?
6. Explain why the antibonding $\sigma 2s^*$ orbital will fill before the bonding $\sigma 2p_x$ orbital.
7. Explain the advantage of MOT over VBT.

Bonding in Organic Molecules

Hybridization

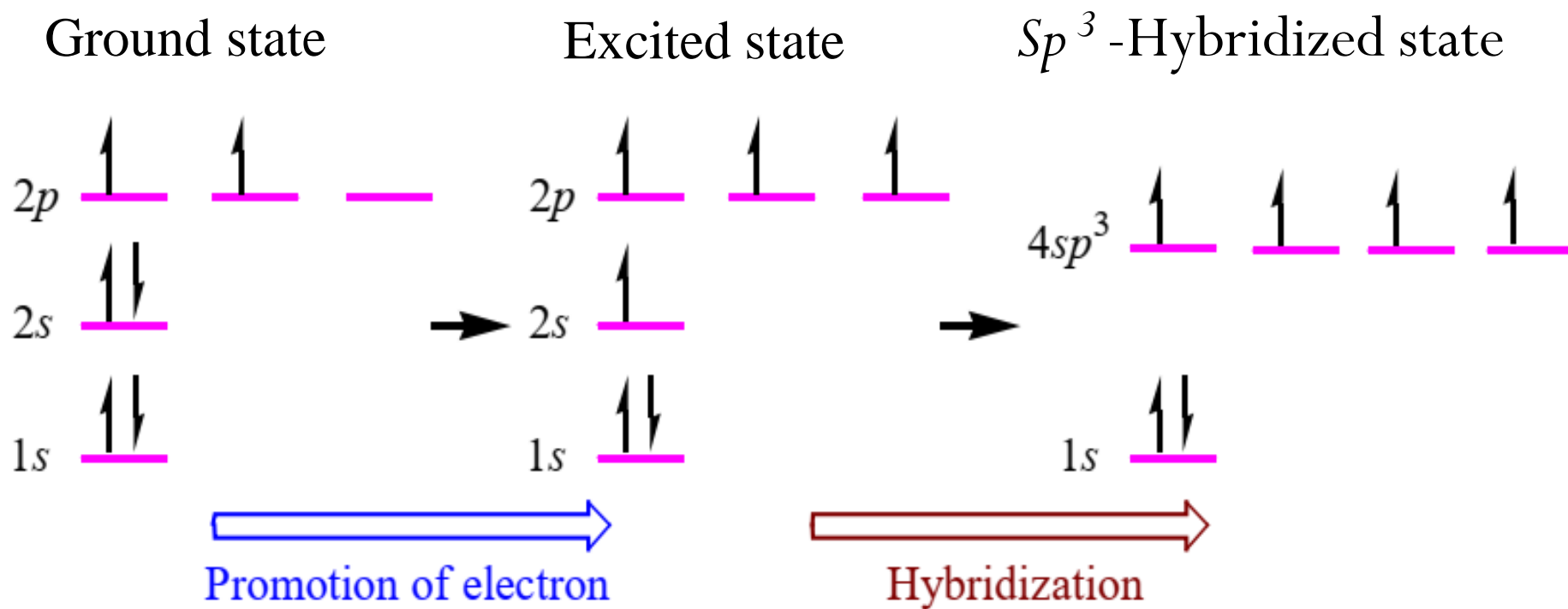
- Hybridization is the mixing of atomic orbitals in to new hybrid orbital to form chemical bond.
- Number of hybrid orbitals produced is equal to the number of atomic orbitals which undergo hybridization.

Types of Hybridization in organic molecules

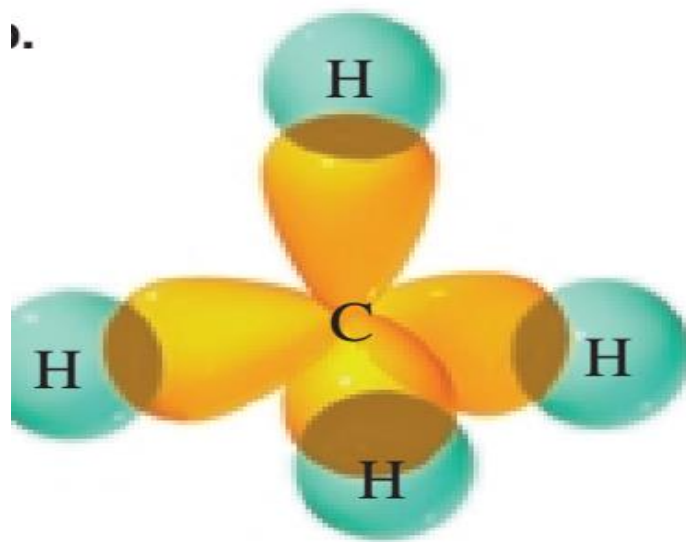
- Tetrahedral or sp^3 -hybridization.
- Trigonal or sp^2 -hybridization.
- Linear or sp -hybridization.

Bonding In Methane: SP^3

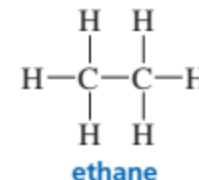
- Methane has four covalent bonds. Because all four bonds have the same length and all the bond angles are the same (109.5°), we can conclude that the four bonds in methane are identical.



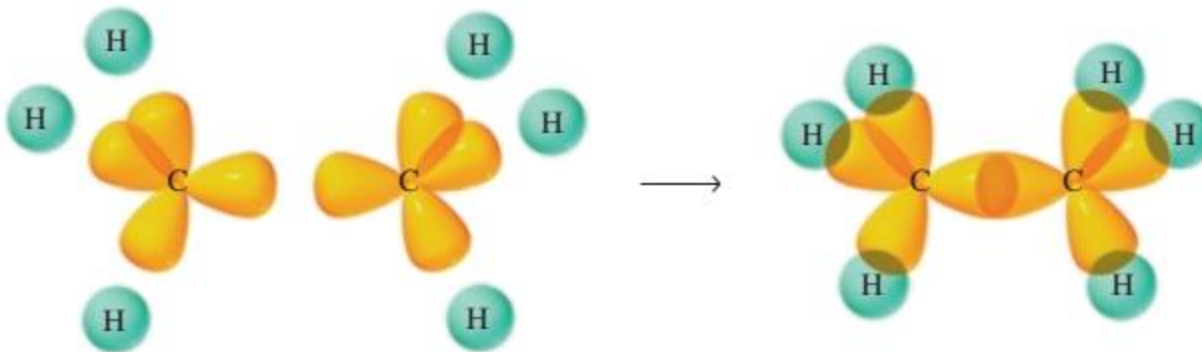
- Each sp^3 orbital has 25% s character and 75% p character.
- The four sp^3 orbitals are degenerate, they have the same energy.
- The angle formed between any two bonds of methane is 109.5° .
- This bond angle is called the **tetrahedral bond angle**.



Bonding in Ethane: SP^3



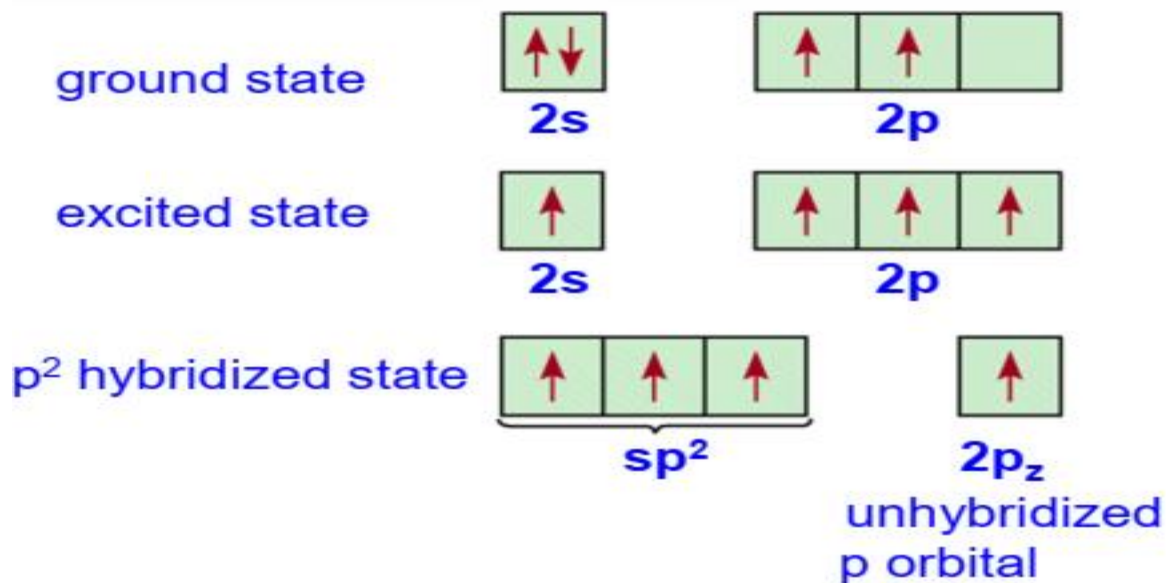
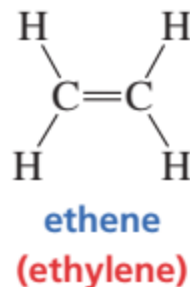
- The two carbon atoms in ethane are tetrahedral. Each carbon uses four orbitals to form four covalent bonds:

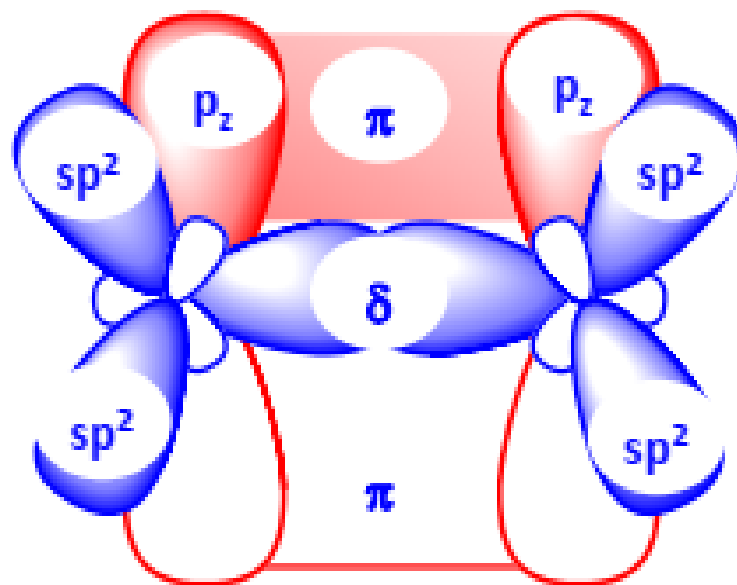


- All the bonds in methane and ethane are sigma bonds because they are all formed by **the end-on overlap** of atomic orbitals.
- All single bonds** found in organic compounds are sigma bonds

Bonding in Ethene- SP^2

- Each of the carbon atoms in ethene forms four bonds, but each is bonded to only three atoms:



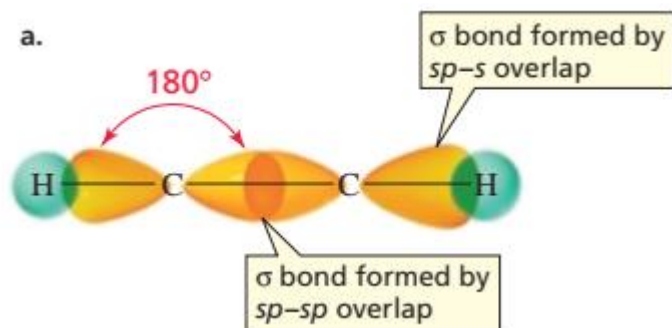
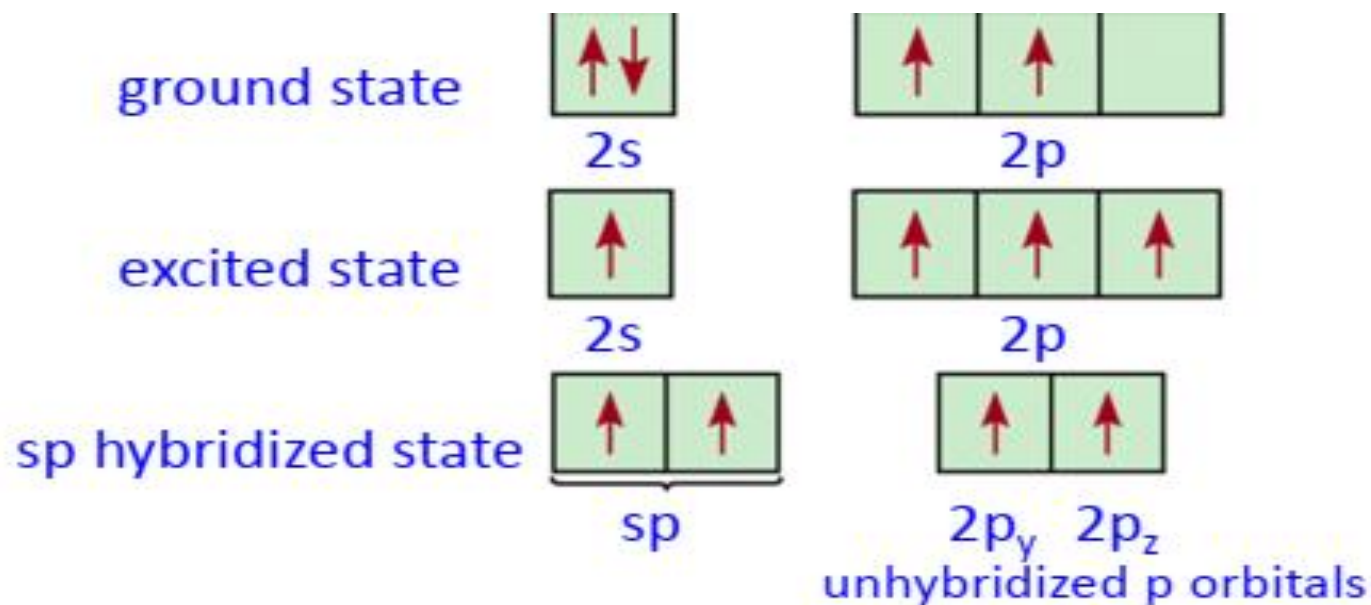


δ Bond are formed by end-on overlap of two sp^2 hybrid orbitals. π bond are formed by side-by-side overlap of two $2p$ orbitals.

A **double bond** consists of one sigma and one pi bond.

Bonding in Ethyne, $\text{HC}\equiv\text{CH}$ SP type

- The carbon atoms in ethyne are each bonded to only two atoms.



A **triple bond** consists of one sigma bond and two pi bonds.

Generally

- All single bonds are σ bonds.
- All double bonds are composed of one σ bond and one π bond.
- All triple bonds are composed of one σ bond and π two bonds.
- Sigma bonds are formed from head-to-head overlap or end-on overlap and π formed from side-to-side overlap of atomic orbitals.
- What is the hybridization of the carbon atom in each of the following molecules and describe the sigma and π bond?

