Ministry of Higher Education and Scientific Research

Al-Muthanna University

Inorganic Pharmaceutical chemistry

For the 3rd year students of the «faculty of Pharmacy»

Lecture (3)
Electronic Structure of Molecules

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Electronic Structure of Molecules

When atoms are incorporated into molecules, there are three major forces that are involved in the overall combinations:

- The attraction forces occur between the negatively charged electrons in the valence orbitals on one atom and the positively charged nucleus of another atom.

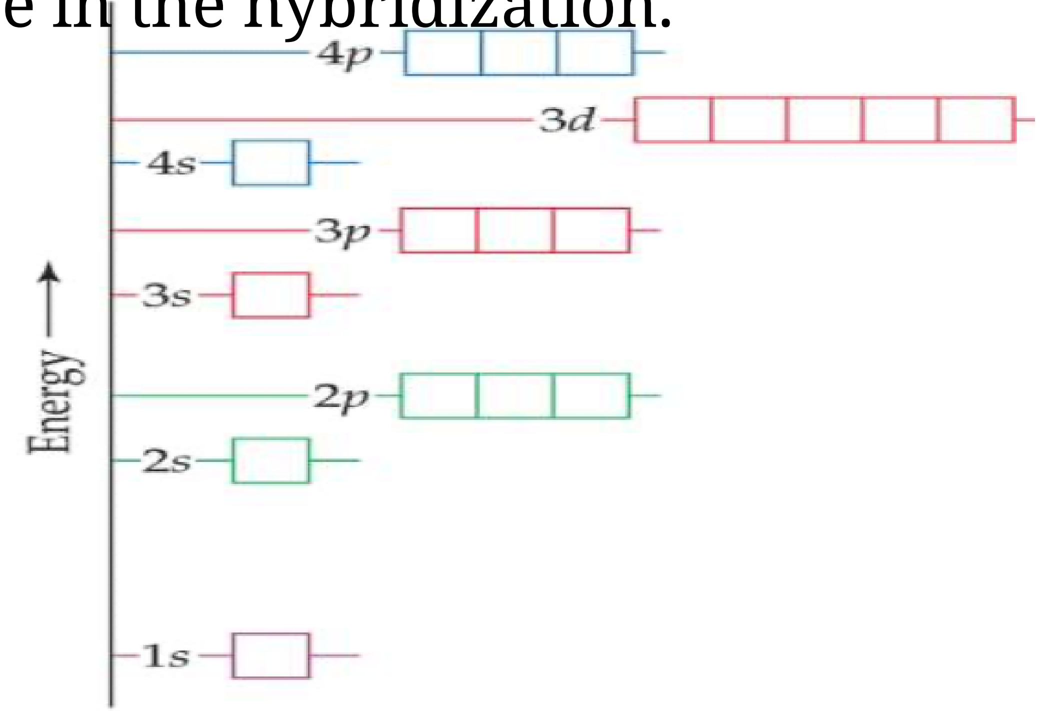
As atoms approach each other, there are two repulsive forces that tend to “push” the atoms away:

- Electron – electron repulsion between valence electrons on neighbor atoms.
- Nuclear repulsion between neighboring nuclei.

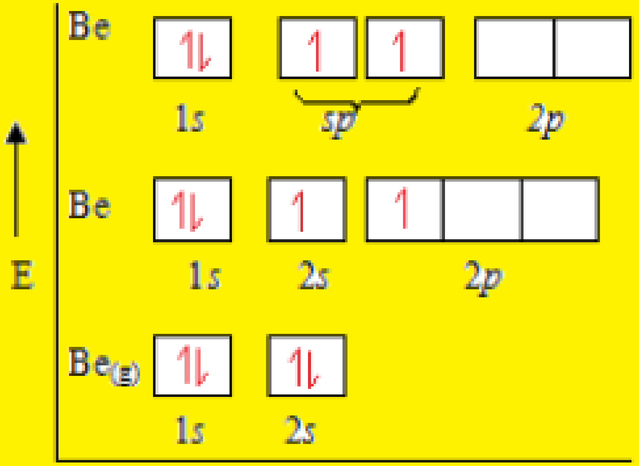
A stable molecule, is possible when the proper balance between these forces exists. The equilibrium distances that are evident between atoms in molecules (bond distances) are established largely by the interaction of these forces.

Hybridization of atomic orbitals

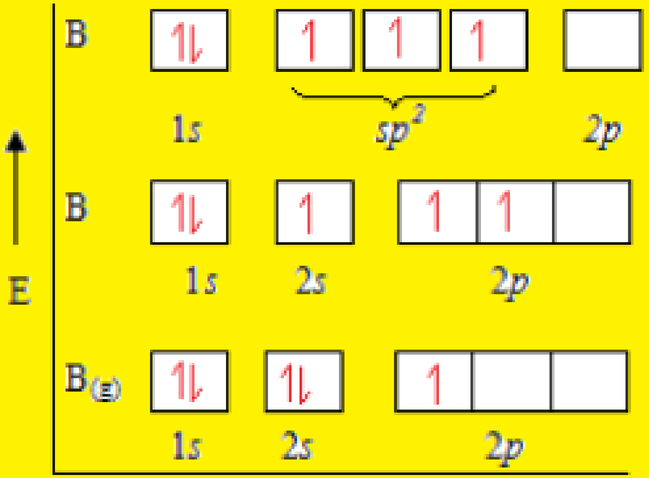
Hybridization is the concept of mixing atomic orbitals into a new set of degenerate (energetically equivalent) orbitals having different spatial orientations and directional properties than the original atomic orbitals. The number of hybrids orbitals produced is equal to the number of atomic orbitals involve in the hybridization.



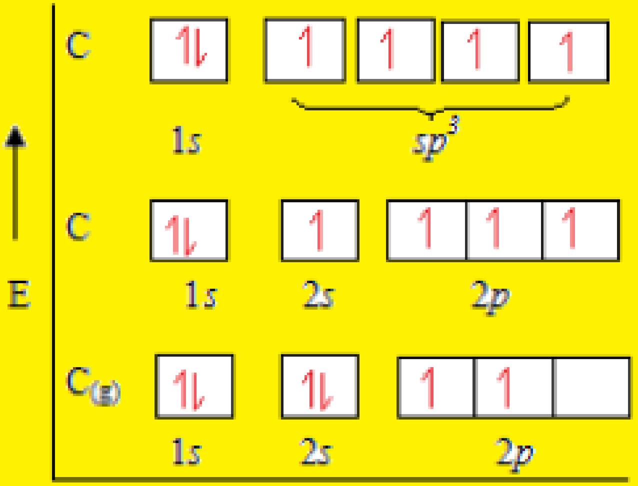
Orbital Hybridization



(a)



(b)



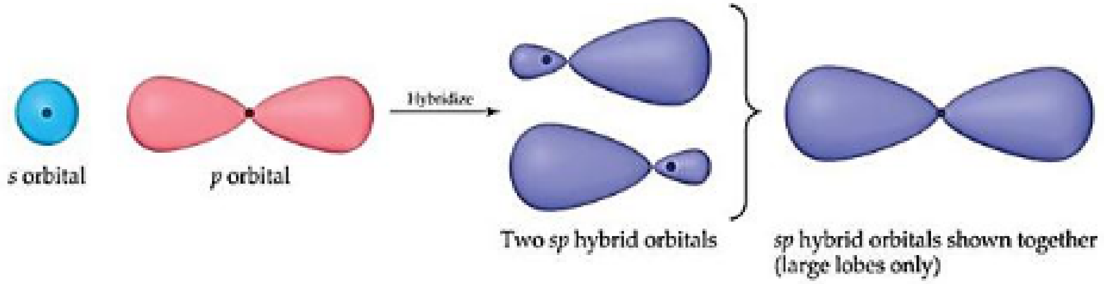
(c)

Orbital Hybridization

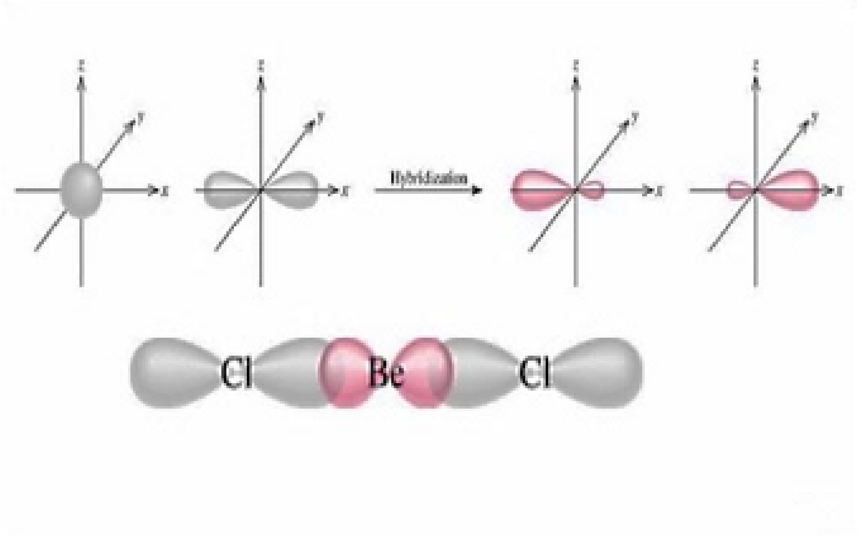
Linear sp hybrids

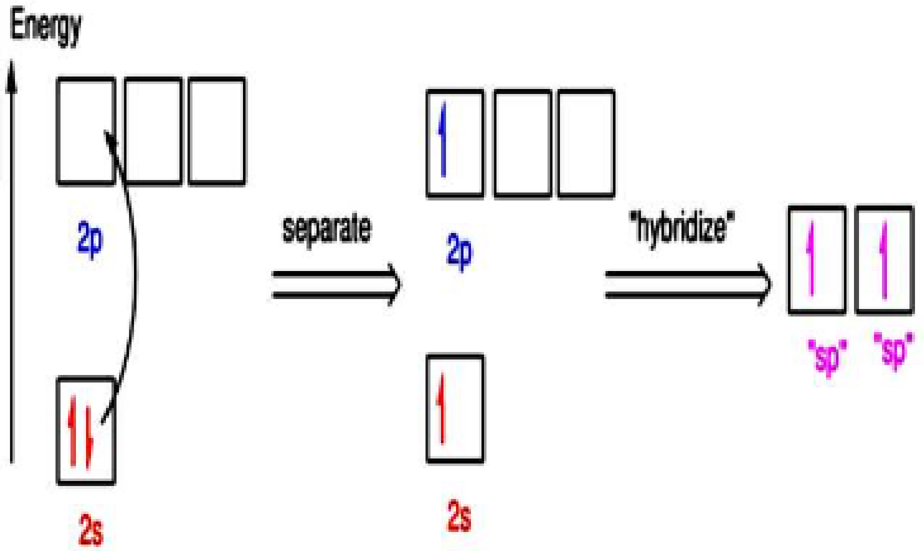
These are composed of the valence shell s-orbital and one of the three porbitals. The other two p-orbitals remain unhybridized. The s orbital has no influence on the orientation due to its spherical symmetry. The two equivalent and symmetrical about the bonding axis and oriented at 180°away from each other. They possess 50% “s” and 50% “p” character.

The largest proportion of electron density is oriented in single direction, thus improving overlap with orbitals from other atoms and increase the strength of the resulting bond. This type of hybridization is seen in the covalent compound of group II elements.



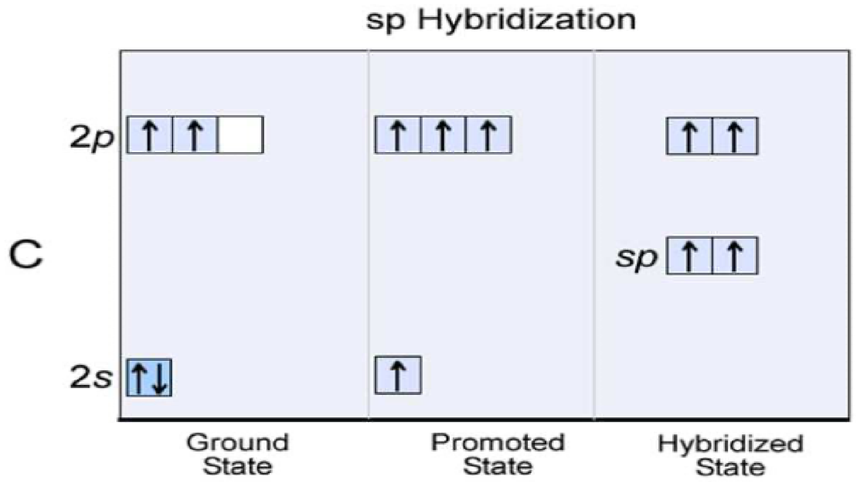
Example: $BeCl_2$



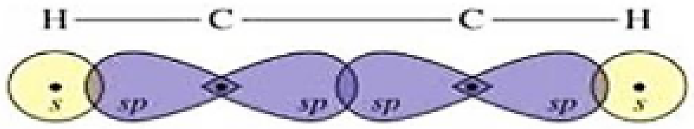


Example: Acetylene or ethyne C_2H_2 :

- In this model, the s orbital is mixed with only one of the three p orbitals resulting in two sp orbitals



Since *sp* orbitals are linear, acetylene will be a linear molecule.



Trigonal sp2 hybrids

These are composed of the valence shell s-orbital and two of the p-orbitals to form three equivalent sp^2 hybrid orbitals.

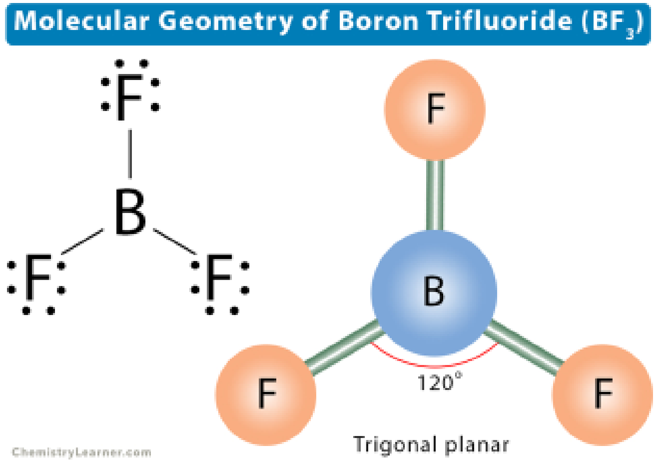
The overall appearance of one of these hybrids is similar to the sp orbital except that the inclusion of an additional p orbital causes the hybrid to be somewhat more elongated.

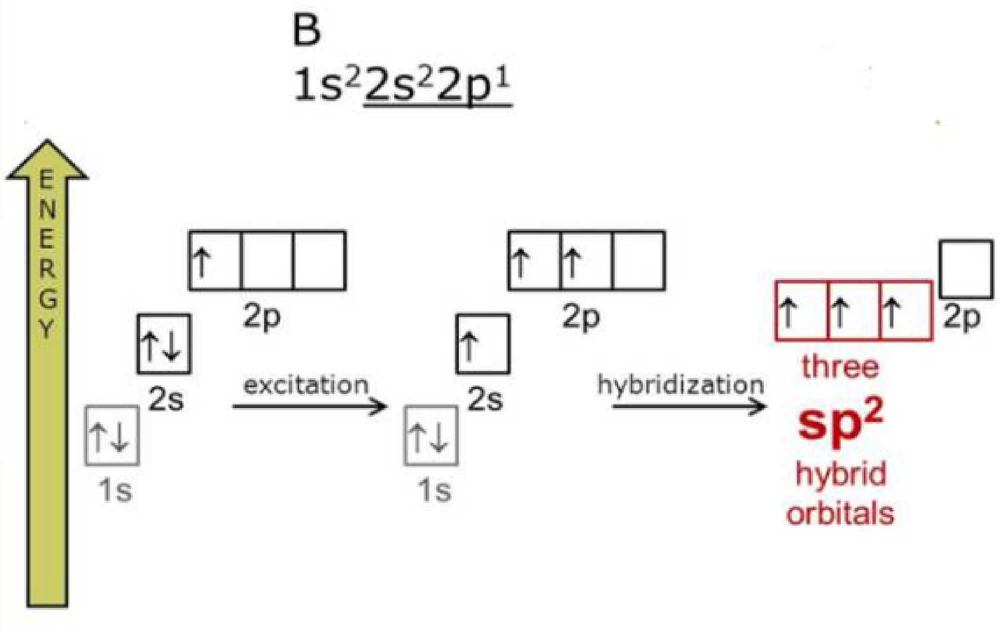
The three orbitals are located in the same plane and oriented to the points of equilateral triangle 120° apart. The sp2 hybride orbitals have 33.3% „s‟ character and 66.6% „p‟ character.

This type is seen in the covalent compound of group III elements (B, Al, …etc.), as well as unsaturated “ethylenic” compounds of carbon.

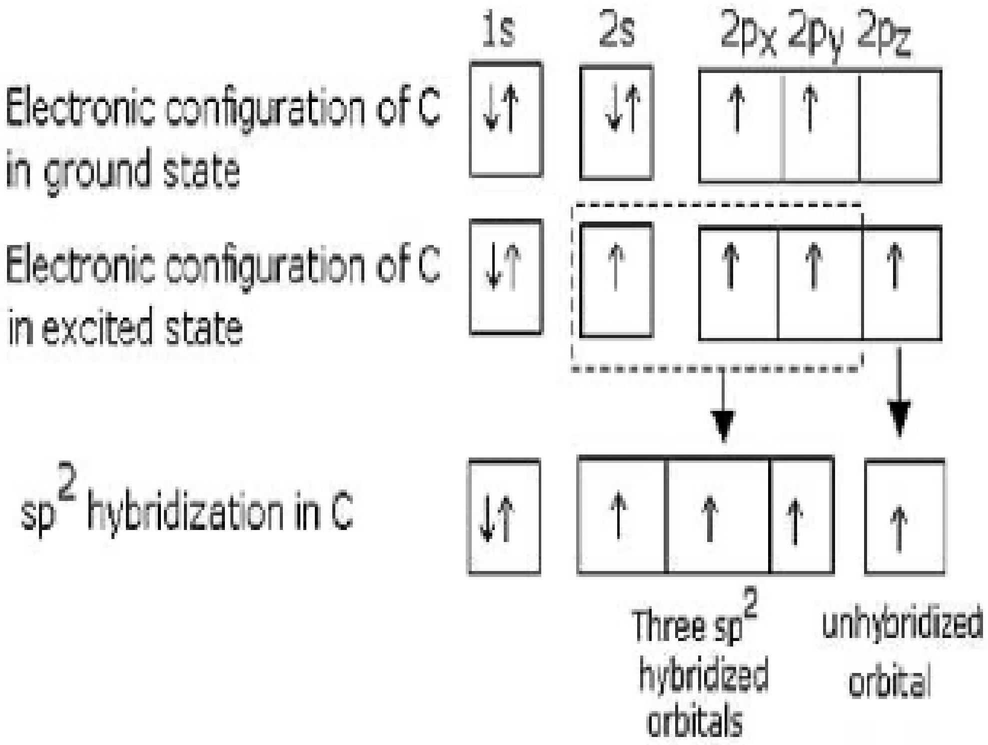
These orbitals provide improved overlap due to a concentration of the electron density of each hybride in a single direction. This result in increased stabilization in the molecular energy of the compound.

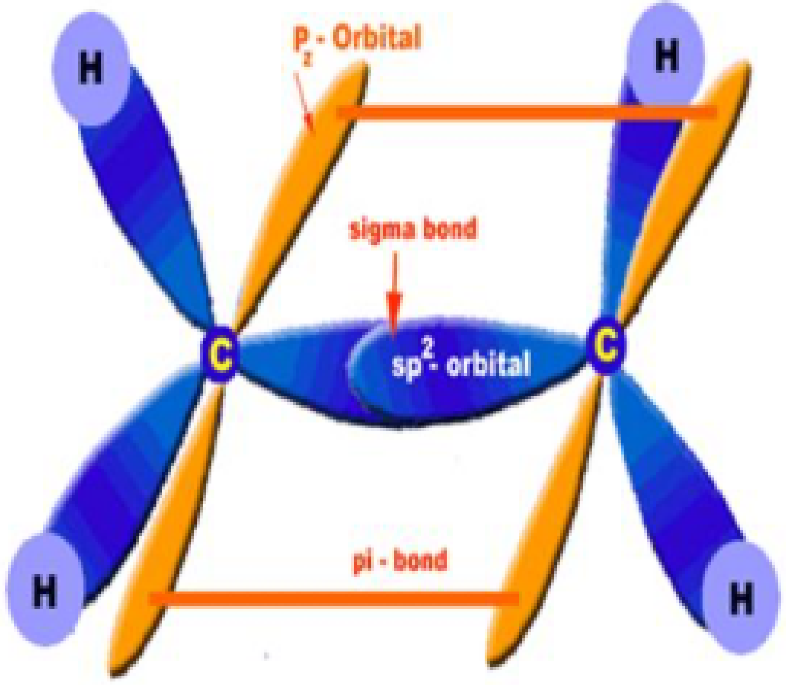
Example BF_3 :


Molecular Geometry of Boron Trifluoride (BF_3)
F
B
F
F
F
B
F
F
120°
Trigonal planar
ChemistryLearner.com


B
$1s^2\underline{2s^22p^1}$
ENERGY
2p
2s
1s
excitation
2p
2s
1s
hybridization
2p
three
sp^2
hybrid
orbitals

Example Ethylene C_2H_4



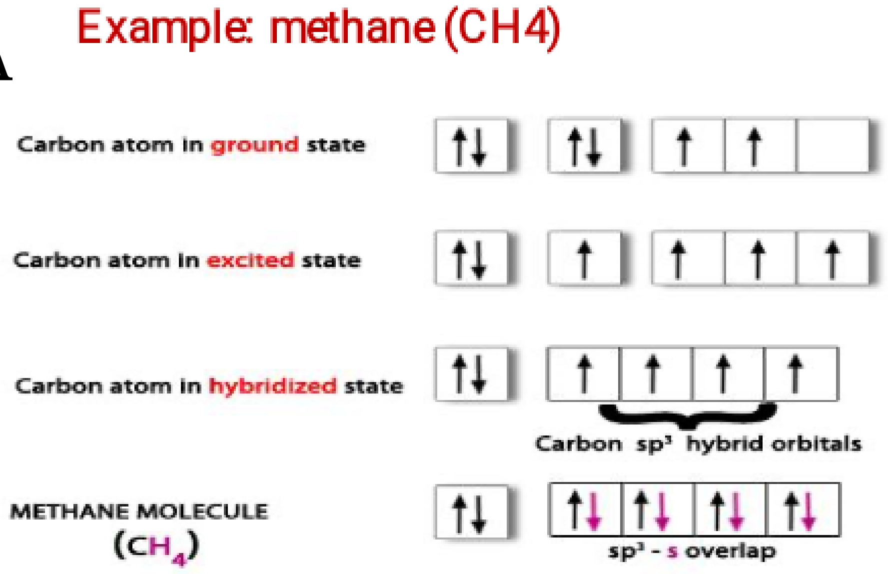


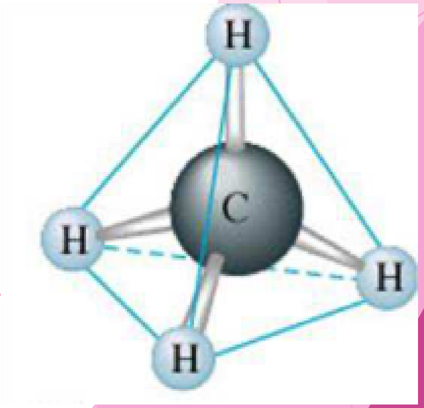
Orbital structure of ethene

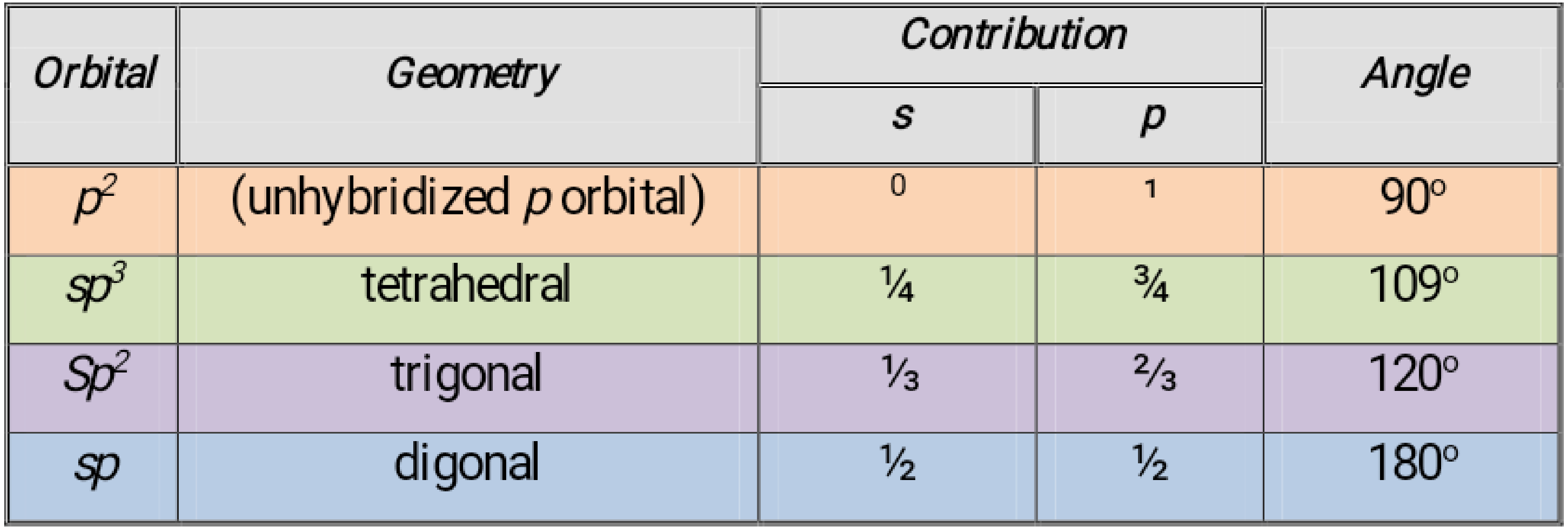
Tetrahedral sp3 hybrids

- These are composed of the valence shell s-orbital and all three p-orbitals. The result is a set of four equivalent sp3 hybrid orbitals pointing to the four corners of a tetrahedron. The geometry of the formed molecule is tetrahedral and the bond angle is 09 . The sp3 hybrid orbitals have 25% „s‟ character and 75% „p‟ character.

- Example: Group IVA


Example: methane (CH4)





Orbital	*Geometry*	*Contribution*		*Angle*
		s	*p*	
p^2	(unhybridized *p* orbital)	0	1	90°
sp^3	tetrahedral	¼	¾	109°
Sp^2	trigonal	⅓	⅔	120°
sp	digonal	½	½	180°

Types of bonding interaction

1. Ionic Bonding :

Ionic bonding is a type of electrostatic force that exists between two chemical entities of opposite charge and have a large difference in electronegativity. The least electronegative entity loses one or more of its valence electrons to the more electronegative entity to produce the respective cation(s) and anion(s)

Cation resembling the inert gas in the period above them in the periodic table and anions resemble the inert gas in the same period.

Ionic bonding is found:

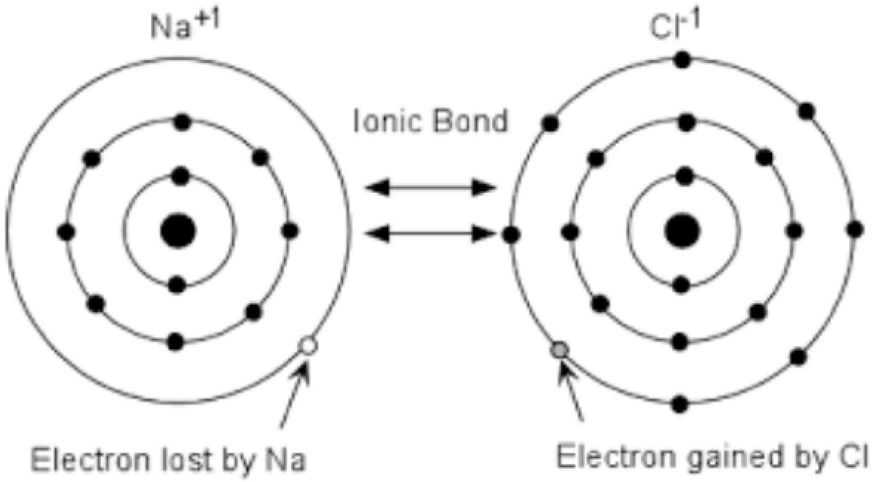
-Between metallic elements Group IA and IIA and nonmetallic elements Group VIIA.

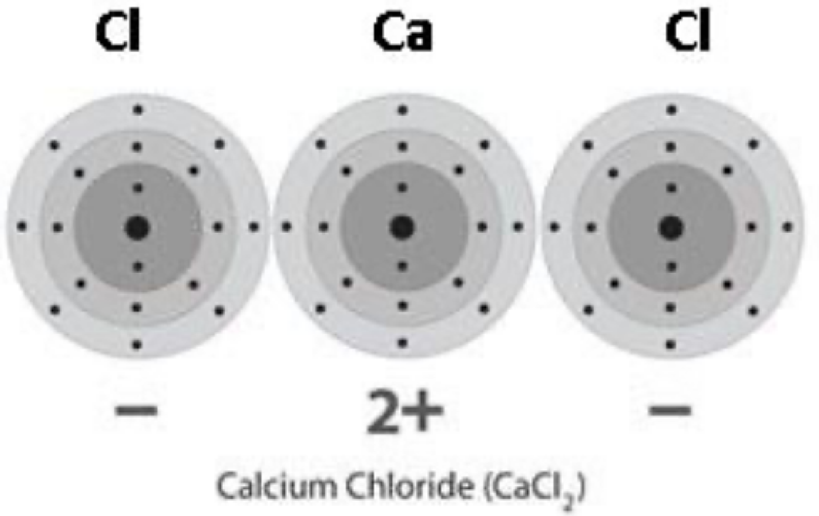
-In most salts, where the anion is complex such as SO_4^{-2} , PO_4^{-3} , NO_3^-

-Also when polar compounds are dissolved in polar solvents.

NaCl

$CaCl_2$


Na^{+1}
Cl^{-1}
Ionic Bond
Electron lost by Na
Electron gained by Cl


Cl
Ca
Cl
−
2+
−
Calcium Chloride ($CaCl_2$)

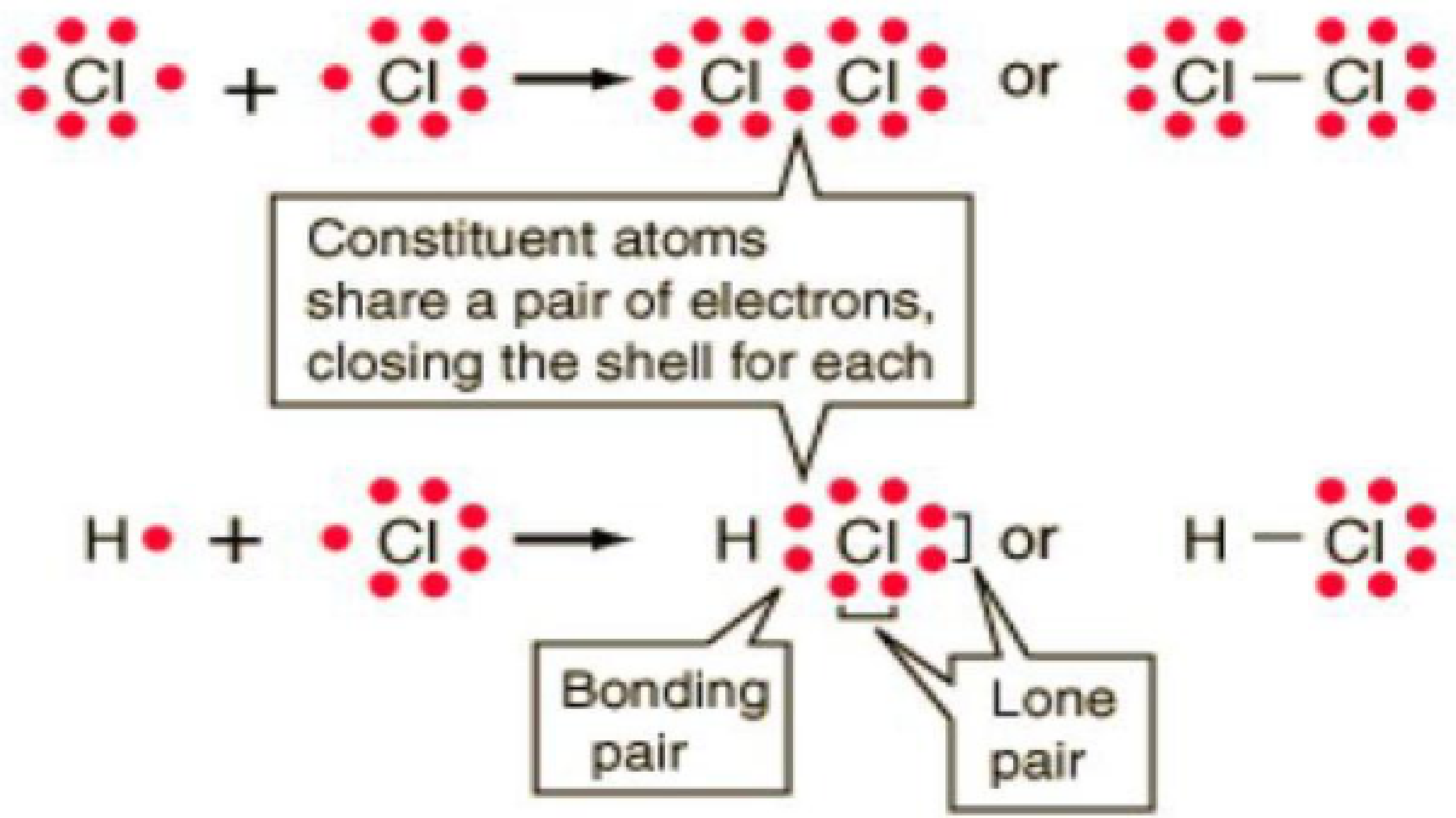
2- Covalent bonding

Is the attractive force that exists between two chemical entities due to their sharing a pair of electrons.

The electronegativity difference between the bonded atoms is small or nonexistent. Bonds within most [organic compound]s are described as covalent although quite common in inorganic compounds.

Occur in homonuclear diatomic molecules such as H_2 , Cl_2 , N_2 , etc. and the electron pair is shared equally by the two bonded atoms.

In most covalent molecules the electron density tend to be shifted towards the more electronegative member of the bond.


Cl + Cl → Cl Cl or Cl – Cl
Constituent atoms share a pair of electrons, closing the shell for each
H + Cl → H Cl] or H – Cl
Bonding pair
Lone pair

Types of Covalent Bonds

1. sigma (δ) bond: single covalent bond, formed by end-to-end overlap of orbitals. in which the molecular orbital or electron distribution are symmetrical about the bond axes.

2. Double and triple covalent bond: two and three pairs of electrons are being shared, respectively, between two atoms.

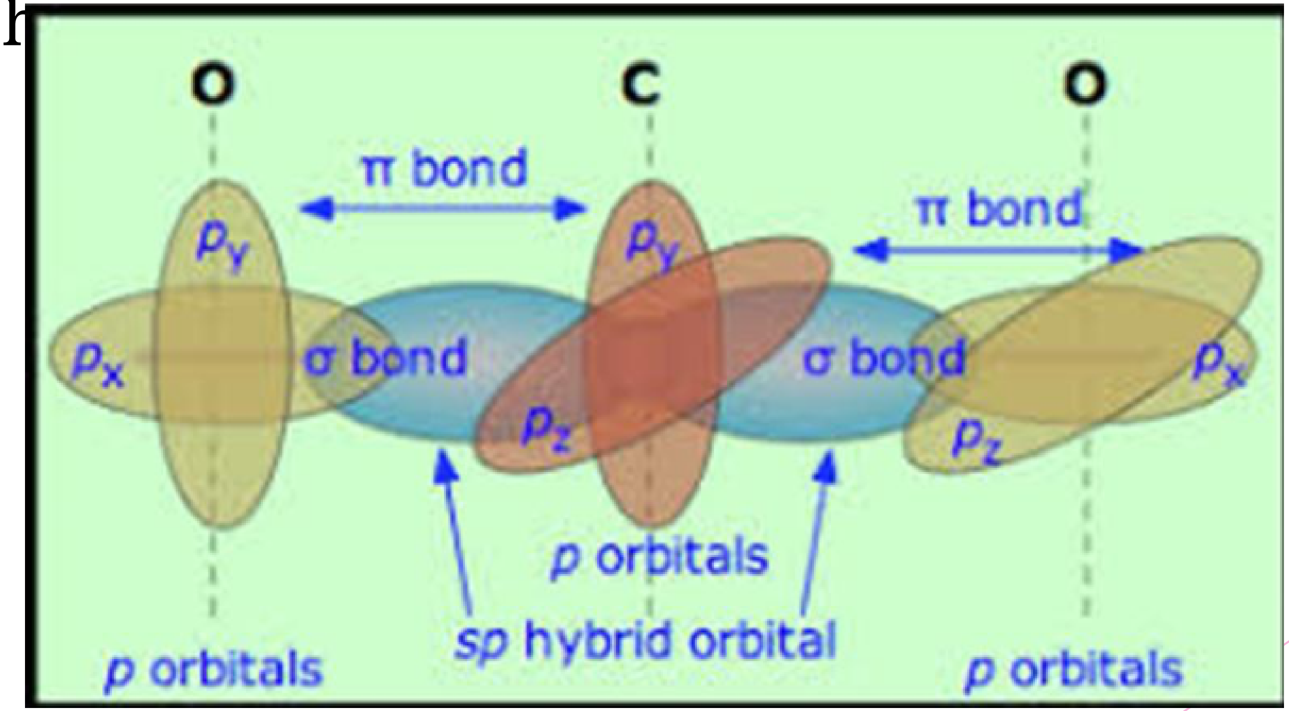
Only one pair of electrons can occupy a single molecular orbital; therefore, atoms bonded in this fashion need to overlap other valence orbitals to form two and three bonding molecular orbitals, respectively.

Only one of the bonds can be a δ bond. The other pairs of electrons will occupy molecular orbitals which are distributed on both sides and perpendicular to a plane passing through a bond axis. This type is called pi bond (π bond).

Example CO_2

Each CO bonds consist of two pairs of electrons, one in the δ bond and one in the π bond.

The δ bonds are formed by overlapping sp orbitals on the carbon with singly occupied p orbitals on the oxygen. This leave two singly occupied p orbitals on carbon and one p orbital on each of the oxygen. The carbon form a π bond with each



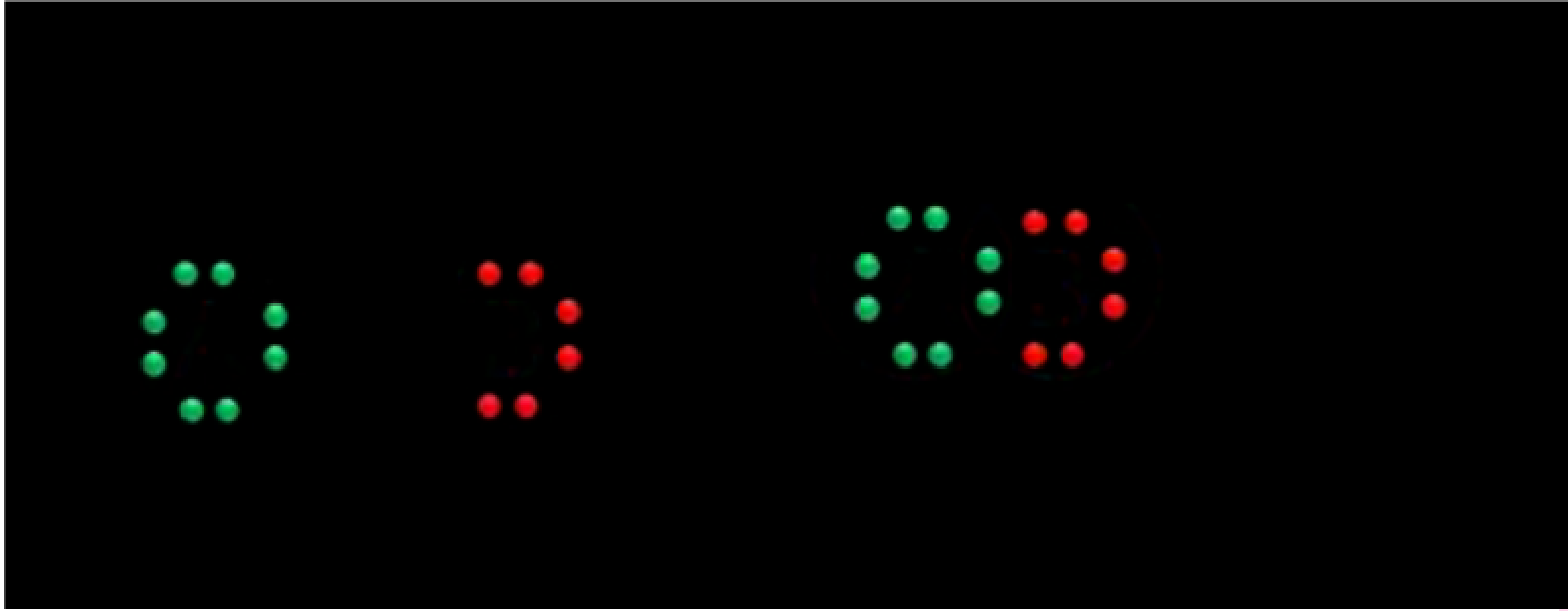
3- Coordinate covalent bond:

A covalent interaction but both electrons in the bond arise from single orbital on one of the atoms forming the bond. It is found most frequently between complex chemical entities.

The entity providing the pair of electrons is referred to as the donor species. The acceptor species is electron deficient and has an empty orbital which can overlap with the orbital from the donor.

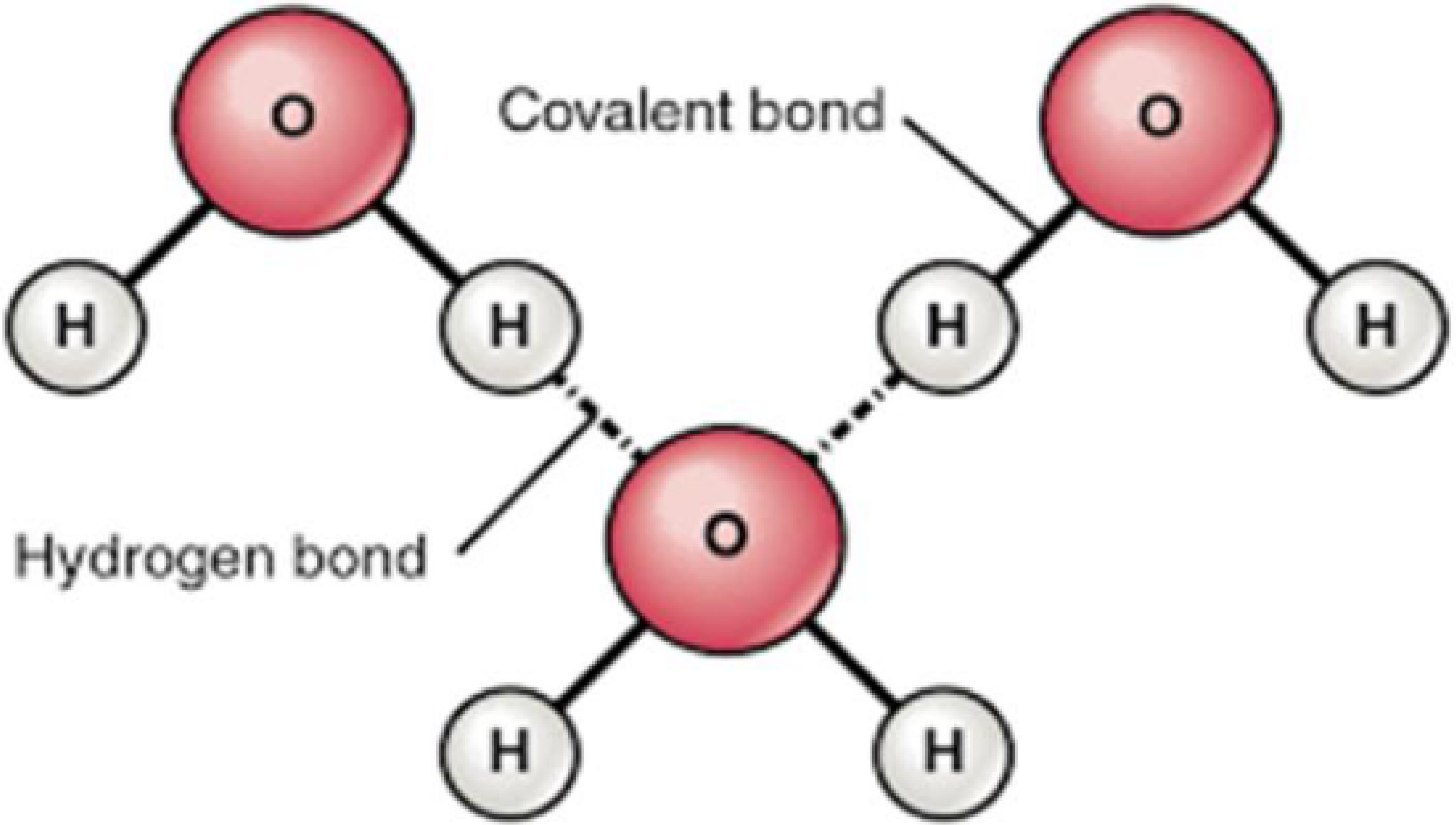
Represented as arrow from the donor atom to the acceptor atom.

Occur in acid –base chemistry between sulfur and oxygen (sulfuric, nitric, phosphoric, and chloric acids).



4-Hydrogen Bonding

- Hydrogen bonding is a force of attraction between a hydrogen atom in one molecule and a small atom of high electronegativity in another molecule.
- When hydrogen is covalently bonded to a more electronegative elements, such as O, F or N, it become electron deficient , taking on a partial positive charge.
- This partially positively charged hydrogen has an increase affinity to the nonbonded electrons on other electronegative atoms in neighbouring molecules. This bond is known as hydrogen bond and not sufficient to cause the original covalent bond to break.
- Its weaker than covalent bond.
- Hydrogen bonding has a very important effect on the physical and chemical properties of water and ice (ex: high boiling point of water). Hydrogen bonding is also very important in complex molecule, secondary structure of proteins and in life processes. It‟s a secondary binding force in drug-receptor interaction.

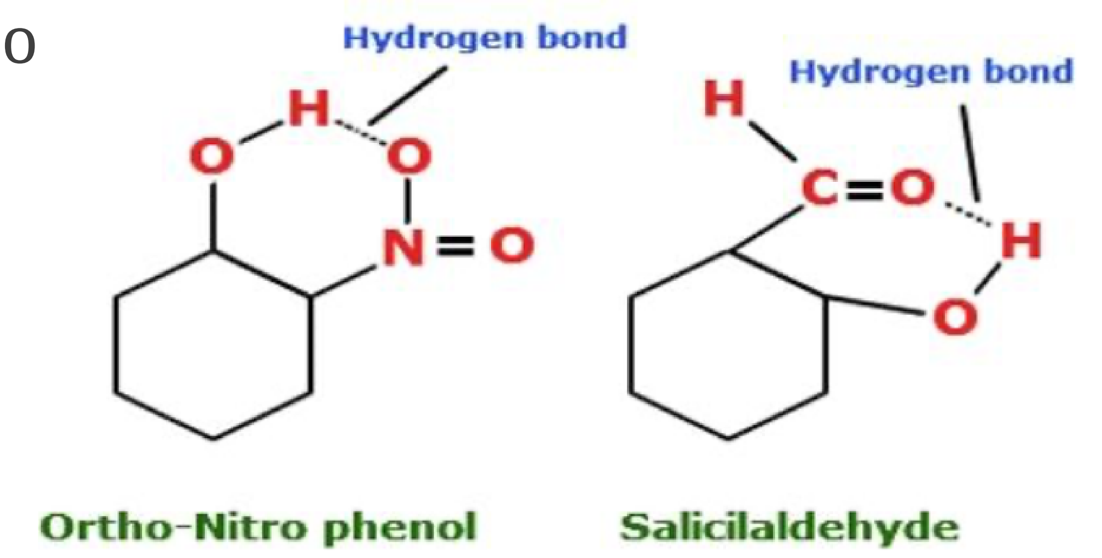

O
Covalent bond
O
H
H
H
H
O
Hydrogen bond
H
H

Types of H-Bonds

(1) Intermolecular hydrogen bond : It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF molecule, alcohol or water molecules, etc.

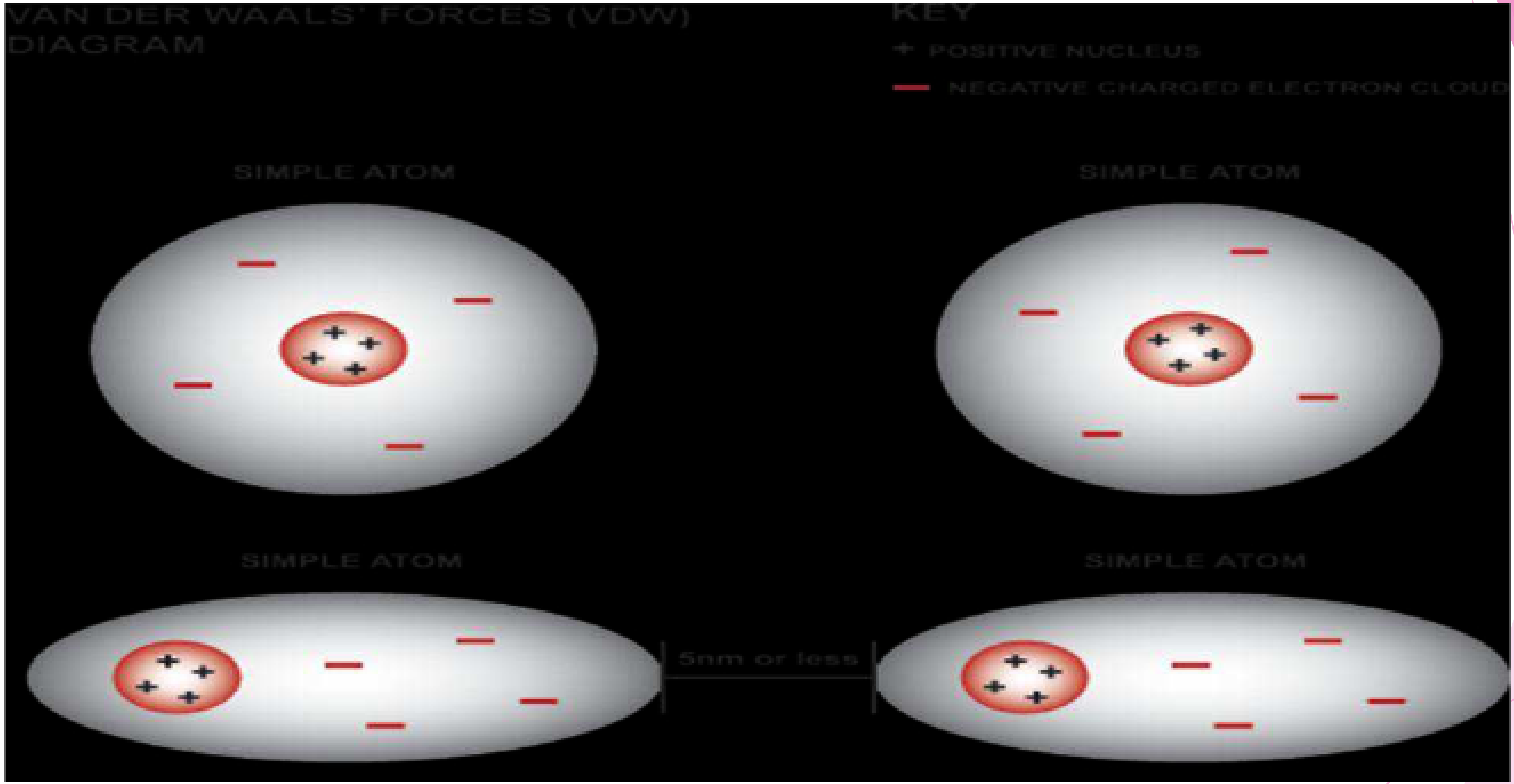
(2) Intramolecular hydrogen bond : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitropheno

two oxygen atoms.



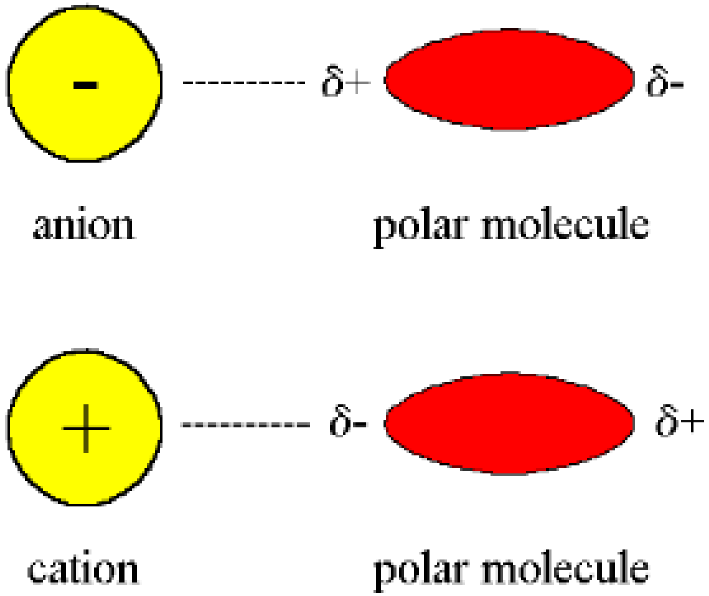
5- Van der Waals (London) forces:

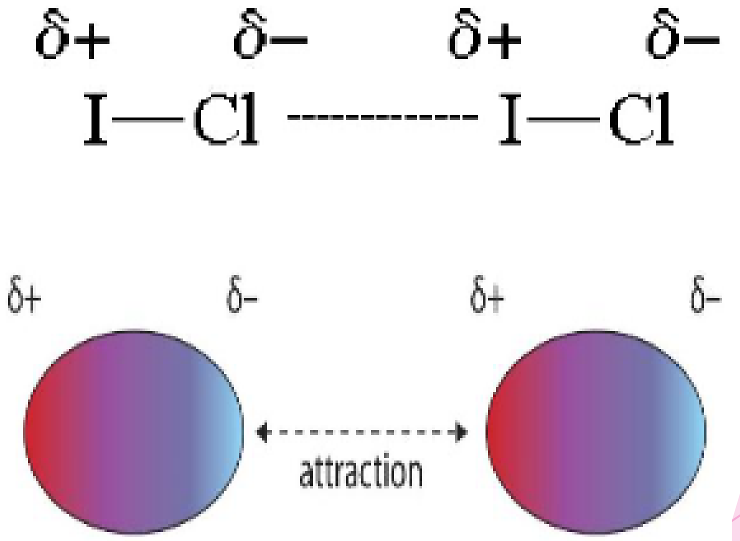
- Relatively weak electrical forces. The electrons in one atomic or molecular species inducing a repulsive distortion in the electron cloud of a neighbouring species. The result is weak induced dipole.
- The positive end of the dipole, which is produced by protons in the nuclei, then has an attraction for the oppositely charged electron in the same or in a neighbouring species.
- This force is active over a very short range, the strength depend upon the polarize-abilities of the interacting entities.
- It"s the only attractive forces between nonpolar molecules.
- The association between aromatic hydrocarbon molecules, such as benzene, are due to van der Waals forces.


VAN DER WAALS' FORCES (VDW) DIAGRAM
KEY
+ POSITIVE NUCLEUS
— NEGATIVE CHARGED ELECTRON CLOUD
SIMPLE ATOM
SIMPLE ATOM
SIMPLE ATOM
SIMPLE ATOM
5nm or less

6- Ion-dipole and dipole-dipole interactions

- Take place between polar molecules and ions or other polar species. They are dependent on phenomenon known as polarization.





Best Regards!

Thank you!