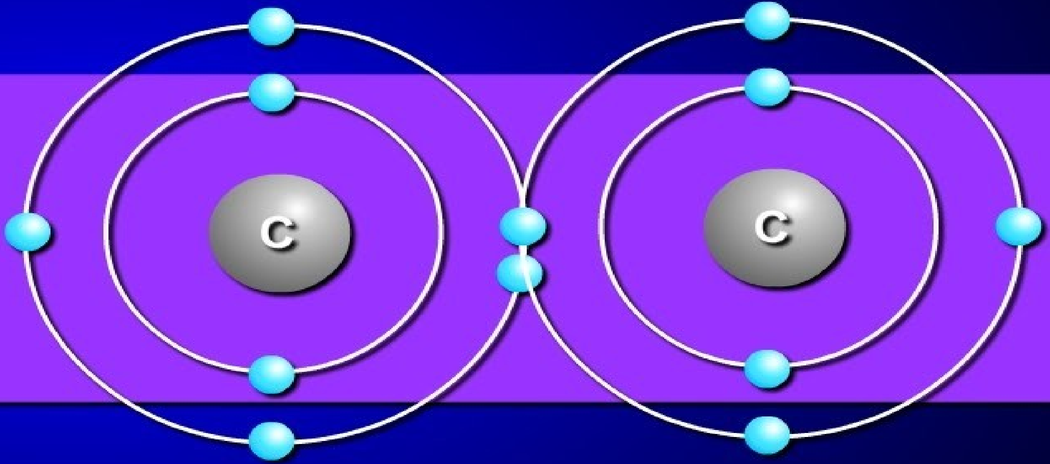
Chemical Bonding



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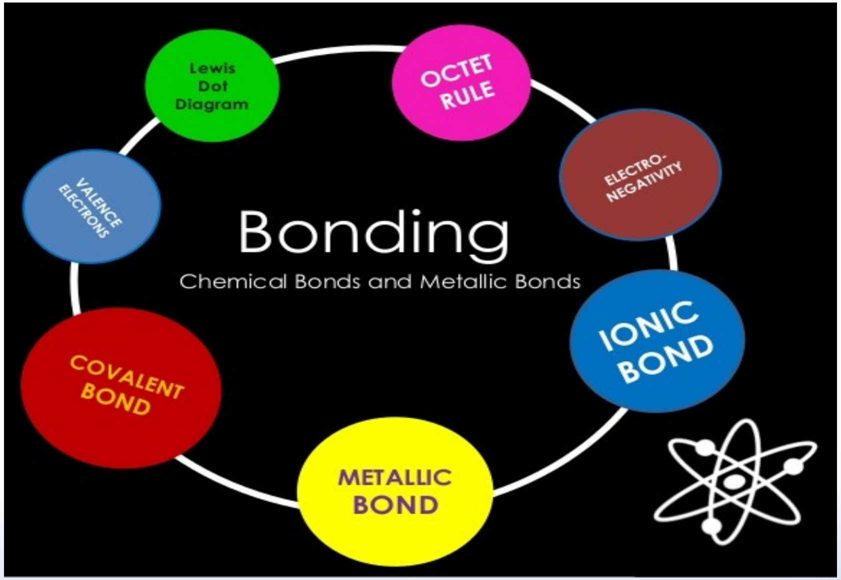
CHEMICAL BOND

The attractive force which holds various constituents together in different chemical species is called a chemical bond.

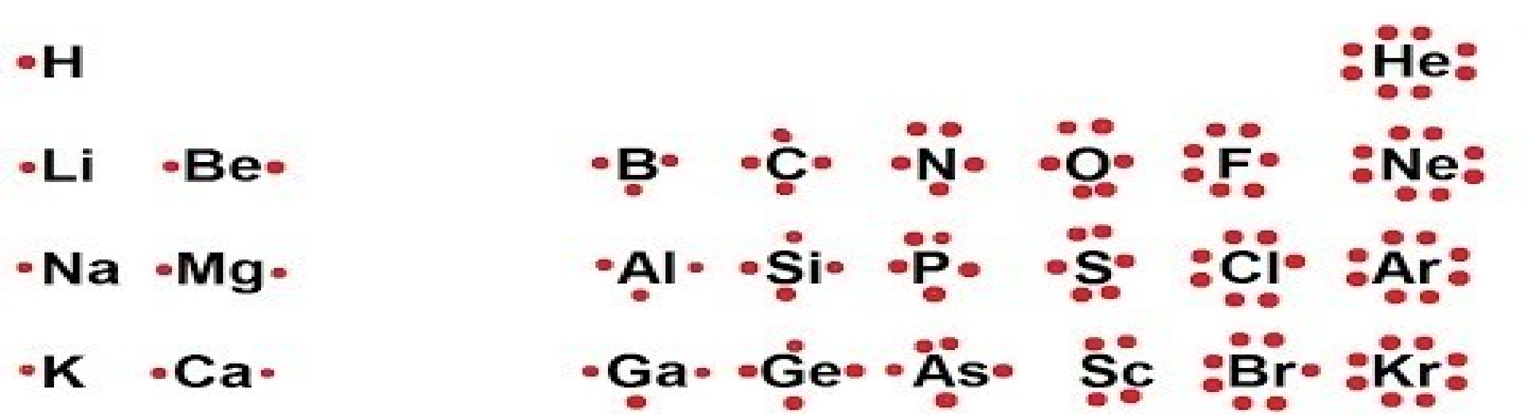


KOSSEL-LEWIS APPROACH

- Kossel and Lewis explained the formation of chemical bonds in terms of electrons.
- Atom is a positively charged ‘Kernel’ (Nucleus + Inner electrons).
- The outer shell could accommodate a maximum of eight electrons.
- These eight electrons occupy the corners of a cube which surround the kernel.
- Eg: The single outer electron of sodium would occupy one corner of the cube.
- In noble gases, all the eight corners would be occupied.

LEWIS SYMBOLS

- G.N Lewis introduced simple notations to represent valence electrons in an atom.
- These notations are called Lewis symbols or Lewis notations.
- According to Lewis symbols, the symbol of the element represents the nucleus.
- The valence electrons are represented as dots (.) or crosses (x) around the Symbol.



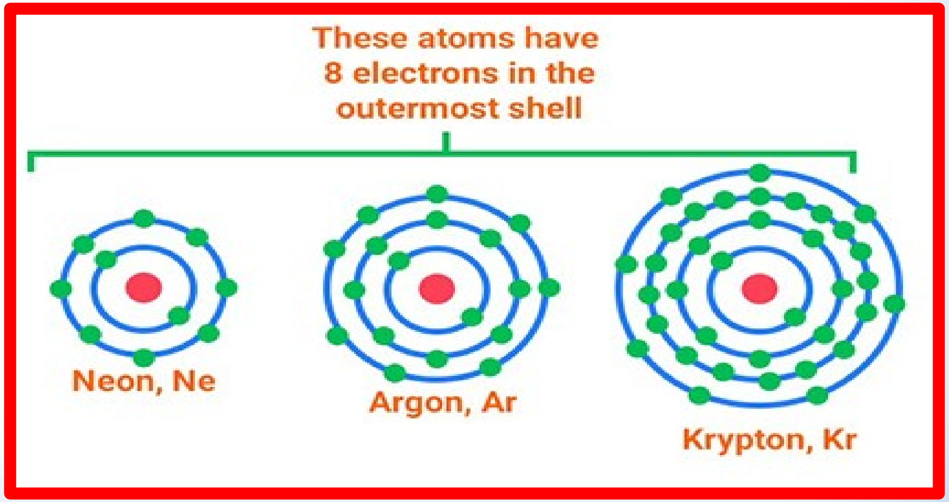
- **The valency of Li, Be, B and C are 1, 2, 3, and 4 respectively.**
- **The valencies of N, O, and F are 3, 2, and 1 respectively.**

SIGNIFICANCE OF LEWIS SYMBOLS

- **The number of dots around the symbol represents the number of valence electrons.**
- **The number of valence electrons helps to calculate the common or group valency of the element.**
- **The group valency of the elements is either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.**

OCTET RULE

- Atoms can combine either by the transfer of valence electrons from one atom to another or by sharing of valence electrons in order to have an octet in their valence shells.
- This is known as Octet Rule.



IONIC BOND OR ELECTROVALENT BOND

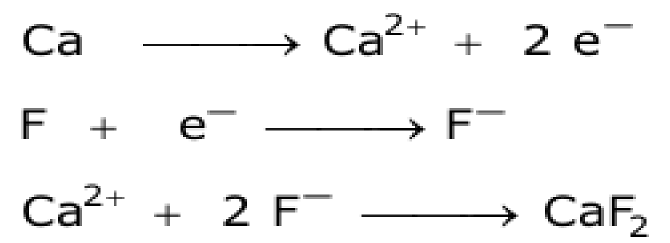
- When an electronegative element combines with an electropositive element, one or more electrons are transferred from the valence shell of an electropositive element to the valence of the electronegative element.
- As a result, the electropositive atom becomes a +ve ion and the electronegative atom becomes a —ve ion.

- The electrostatic force of attraction between positive and negative ions is called electrovalent bond or ionic bond.
- Ionic bond may also be defined as the electrostatic force of attraction holding the oppositely charged ions.
- Eg: Formation of NaCl

$$Na + Cl \longrightarrow Na^{+} + Cl^{-}$$

$$Na^{+} + Cl^{-} \longrightarrow NaCl$$

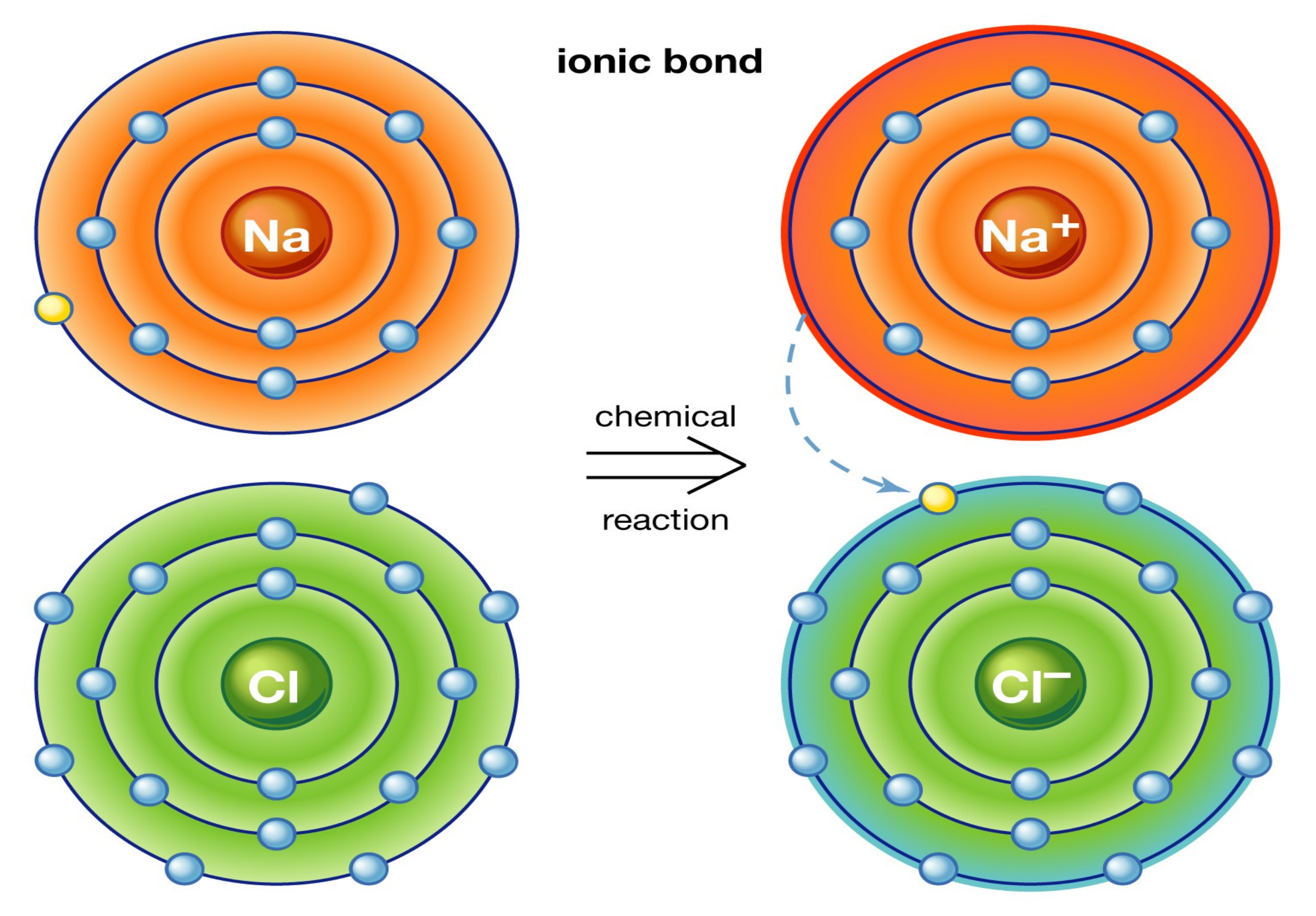
- Eg: Formation of CaF_2



$$Ca \longrightarrow Ca^{2+} + 2\,e^{-}$$

$$F + e^{-} \longrightarrow F^{-}$$

$$Ca^{2+} + 2\,F^{-} \longrightarrow CaF_2$$


ionic bond
Na
Na+
Cl
Cl−
chemical
reaction

ELECTROVALENCY

- **The number of electrons gained or lost by an atom during the formation of an Ionic bond is called electrovalency of the atom.**
- **Electrovalency is equal to the charge on the atom.**

ENERGY CHANGES DURING THE FORMATION OF AN IONIC BOND

- **Formation of gaseous cation:**

$$A_{(g)} \quad + \quad IE \quad \longrightarrow \quad A^{+} \quad + \quad e^{-}$$

- **The energy required for this step is called Ionisation energy.**
- **Formation of gaseous anion:**

$$B_{(g)} \quad + \quad e^{-} \quad \longrightarrow \quad B^{-} \quad + \quad EA$$

- **The energy released during this step is called Electron affinity.**
- **The packing of positive and negative ions to form the solids.**
- **The energy released in this step is called Lattice Energy.**

FACTORS FAVOURING IONIC BOND FORMATION

- Low Ionisation Energy of the electropositive atom.
- High Electron Affinity of the electronegative atom.
- High Lattice Energy of the compound formed.

LATTICE ENERGY

The amount of energy released when one gram mole of an ionic solid is formed from gaseous ions.

It is represented as $A^{+}_{(g)} + B^{-}_{(g)} \longrightarrow A^{+}B^{-}_{(S)} + \text{Lattice Energy}$

LATTICE ENTHALPY

- It is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.
- The lattice enthalpy is equal to lattice energy with reverse sign.

CONSEQUENCE OF LATTICE ENERGY

- **The greater the lattice energy, the more stable is the ionic compound.**
- **Ions having higher charge and smaller radii will have greater lattice energy.**
- **The value of lattice energy affects the solubilities of ionic compounds.**

COVALENT BOND

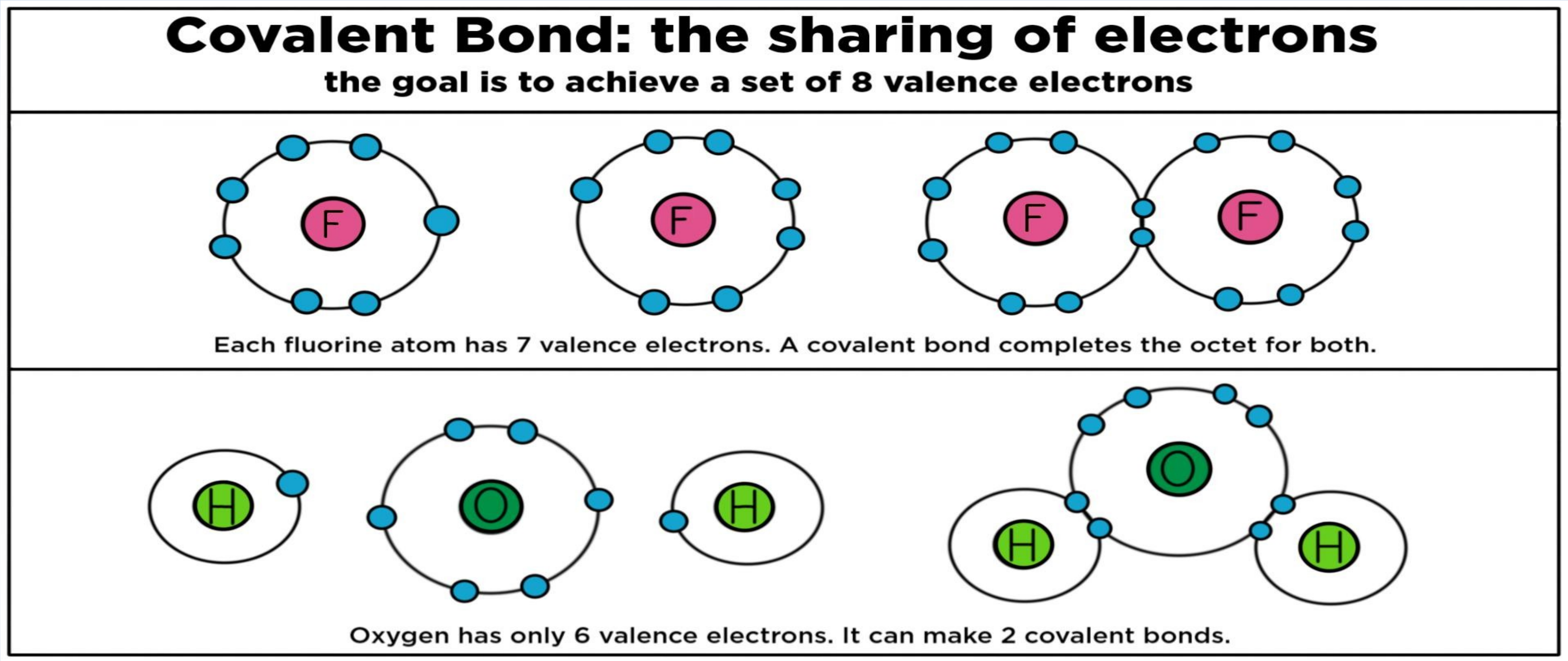
- **A covalent bond is formed by the mutual sharing of electrons between atoms.**
- **The atoms involved in the covalent bond formation contribute equal number of electrons for sharing.**
- **The shared electrons become common to both the atoms.**
- **This shared pair of electrons is called bond pair.**

- If the atoms shared one pair of electrons, the bond formed is called a single covalent bond.
- If the atoms shared two pairs of electrons, the covalent bond is called a double bond.
- If the atoms shared three pairs of electrons, the bond is called a triple bond.

$$Cl + Cl \longrightarrow Cl - Cl \quad \text{or } Cl - Cl$$

$$N + N \longrightarrow N \equiv N \quad \text{or } N \equiv N$$

$$O + O \longrightarrow O = O \quad \text{or } O = O$$



Covalent Bond: the sharing of electrons

the goal is to achieve a set of 8 valence electrons

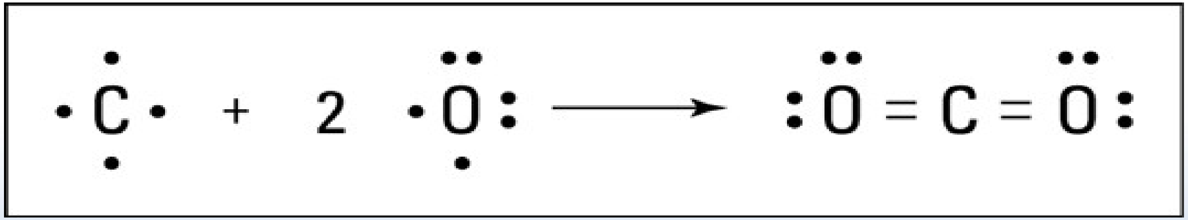
Each fluorine atom has 7 valence electrons. A covalent bond completes the octet for both.

Oxygen has only 6 valence electrons. It can make 2 covalent bonds.

COVALENCY

- The number of electron pairs shared by an atom or the number of electrons contributed by an atom for the formation of covalent bonds is called covalency.
- Eg:- Covalency of chlorine is one, oxygen is two, and that of nitrogen is three.

DOUBLE BONDS IN CO_2 MOLECULE



$$\cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot + 2\ \cdot\overset{\cdot\cdot}{\underset{\cdot}{O}}: \longrightarrow\ :\overset{\cdot\cdot}{O}=C=\overset{\cdot\cdot}{O}:$$

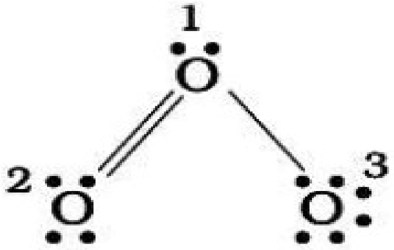
FORMAL CHARGE

- In the case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom.
- The formal charge is defined as the difference between the number of valence electrons of that atom in the free State and the number of electrons assigned to that atom in the Lewis Structure.

Formal Charge = [Total No. of valence electrons in the free atom] — [Total No. of lone pair of electrons] — ½ [Total No. of bonding electrons]

Eg:- Consider ozone molecule

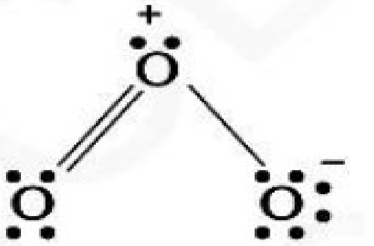
The Lewis structure of ozone may be drawn as

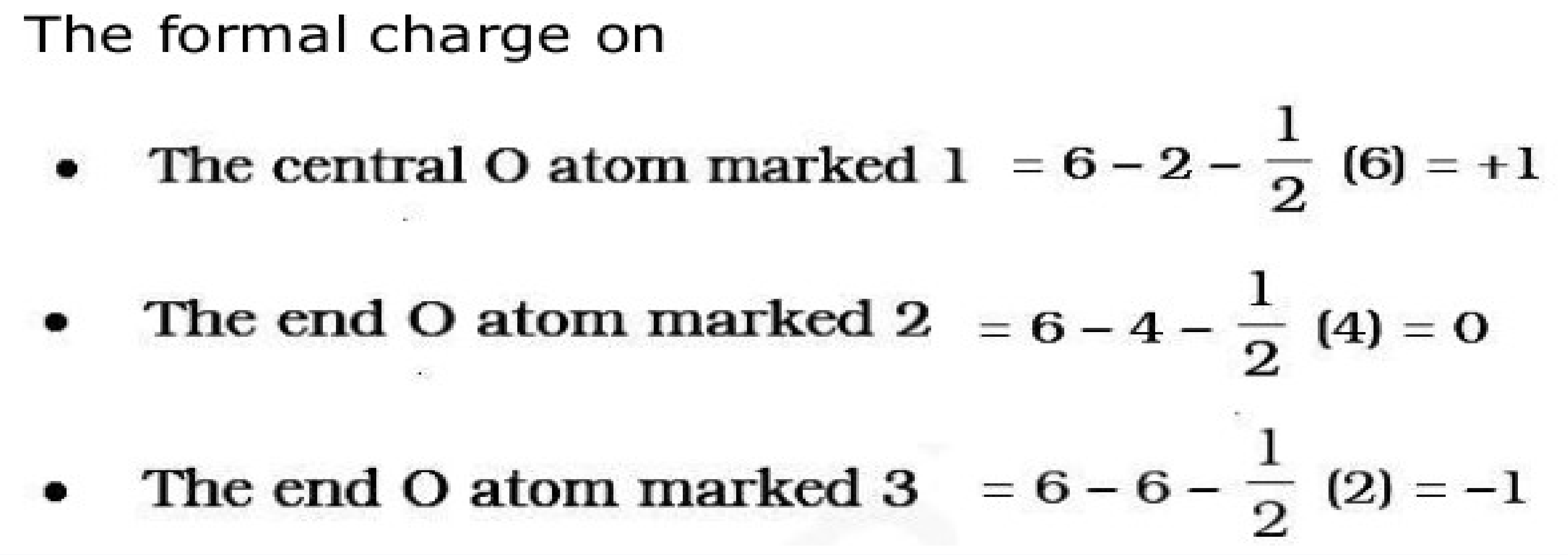


The formal charge on

- The central O atom marked 1 $= 6 - 2 - \frac{1}{2}(6) = +1$
- The end O atom marked 2 $= 6 - 4 - \frac{1}{2}(4) = 0$
- The end O atom marked 3 $= 6 - 6 - \frac{1}{2}(2) = -1$

Therefore, ozone molecule along with formal charge is represented as





The formal charge on

- The central O atom marked 1 $= 6 - 2 - \frac{1}{2}(6) = +1$
- The end O atom marked 2 $= 6 - 4 - \frac{1}{2}(4) = 0$
- The end O atom marked 3 $= 6 - 6 - \frac{1}{2}(2) = -1$

LIMITATIONS OF OCTET RULE

1. THE INCOMPLETE OCTET OF THE CENTRAL ATOM

- In some compounds, the number of electrons surrounding the central atom is less than eight.
- i.e., elements having less than four valence electrons.
- Eg:- LiCl, BeH_2 and BCl_3

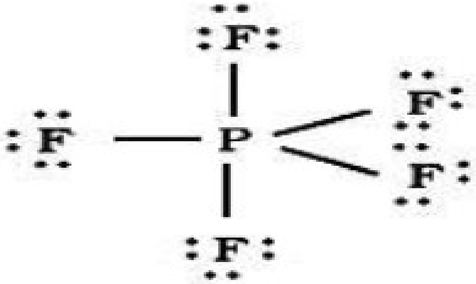
$$\mathrm{Li:Cl} \qquad \mathrm{H:Be:H} \qquad \mathrm{Cl:\overset{Cl}{\ddot{B}}:Cl}$$

2. ODD ELECTRON MOLECULES

In molecules with an odd number of electrons like nitric oxide (NO) and nitrogen dioxide (NO_2), the octet rule is not satisfied for all the atoms.

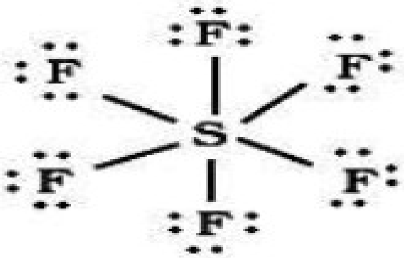
3. THE EXPANDED OCTET

- Elements in and beyond the third period of the periodic table have apart from 3s and 3p orbitals, 3d orbitals also available for bonding.
- Here there are more than eight valence electrons around the central atom.
- This is termed as the expanded octet.
- Eg:- PF_5 , SF_6 , H_2SO_4



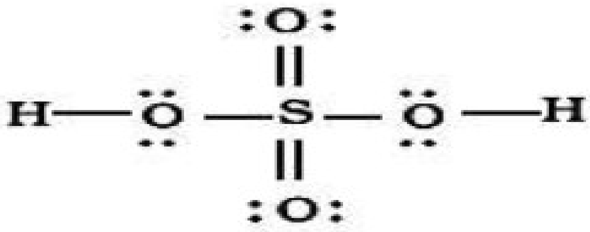
PF_5

10 electrons around the P atom



SF_6

12 electrons around the S atom



H_2SO_4

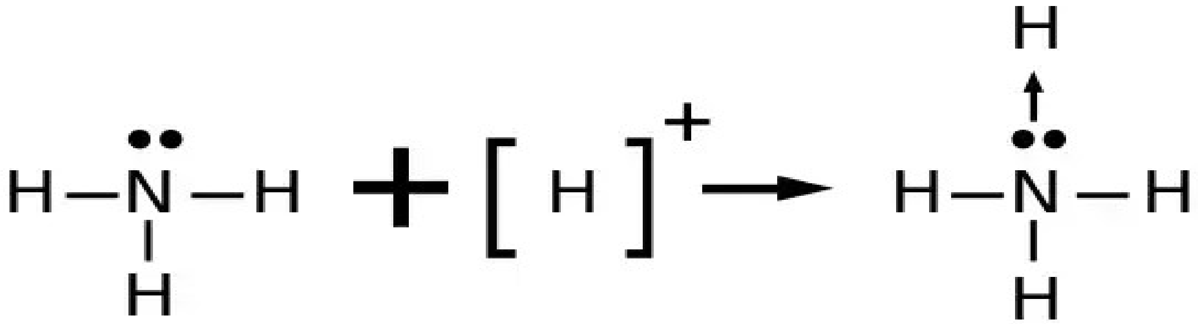
12 electrons around the S atom

COORDINATE OR DATIVE BOND

- A covalent bond in which both the electrons in the shared pair is contributed by only one of the two atoms is called a coordinate covalent bond.
- The atom which contributes the electron pair is called the donor.
- The atom which shares the electron pair is called an acceptor.

- This bond is also called a donor acceptor bond.
- This bond is usually represented by an arrow pointing from donor to the acceptor atom.
- During the formation of coordinate bond, slight polarity develops in the molecule.
- Eg:- Formation of NH_4^+

FORMATION OF NH_4^+



CHARACTERISTICS OF COORDINATE COVALENT COMPOUNDS

- ✓ The electrons in coordinate covalent compounds are held firmly by the nuclei and therefore they do not form ions in water.
- ✓ The coordinate compounds are sparingly soluble in water.
- ✓ A coordinate covalent bond resides a semi polarity in the molecule.
- ✓ Because the shared electron pairs is contributed by one of the atoms only.

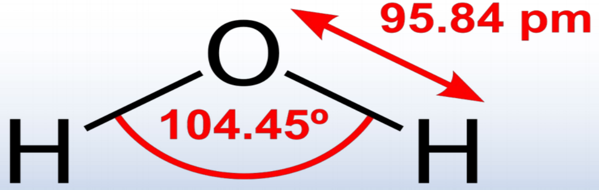
BOND PARAMETERS

BOND LENGTH

- **The equilibrium distance between the nuclei of two bonded atoms in a molecule.**
- **Bond lengths are measured by spectroscopic, x-ray diffraction and electron diffraction techniques.**

BOND ANGLE

- The angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.
- Bond angle is expressed in degrees.
- It can be experimentally determined by spectroscopic methods.
- Eg:- H_2O



BOND ENTHALPY

- **The amount of energy required to break one mole of bonds of a particular type between two atoms in gaseous state.**
- **The unit of bond enthalpy is kJ/mol.**
- **Eg:- The H—H bond enthalpy in hydrogen molecule is 435.8 kJ/mol**

$$H_{2(g)} \longrightarrow H_{(g)} + H_{(g)} \qquad \Delta H = 435.8\ \text{kJ / mol}$$

AVERAGE BOND ENTHALPY

- Average bond enthalpy is used in the case of polyatomic molecules.
- It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken.
- Eg: H_2O

$$H_2O_{(g)} \longrightarrow H_{(g)} + OH_{(g)} \quad \Delta H = 502\ kJ / mol$$

$$OH_{(g)} \longrightarrow H_{(g)} + O_{(g)} \quad \Delta H = 427\ kJ / mol$$

BOND ORDER

Bond order is the number of bonds between the two atoms in a molecule.

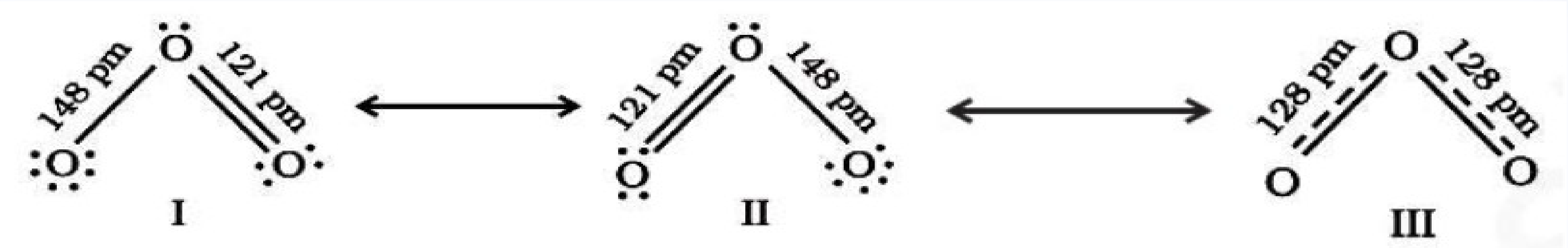
Eg:- H_2 , O_2 and N_2 have bond order 1, 2 and 3 respectively.

RESONANCE STRUCTURES

When a molecule cannot be represented by a single structure, but its characteristic properties can be described by two or more structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons, then the actual structure is said to be a resonance hybrid of these structures.

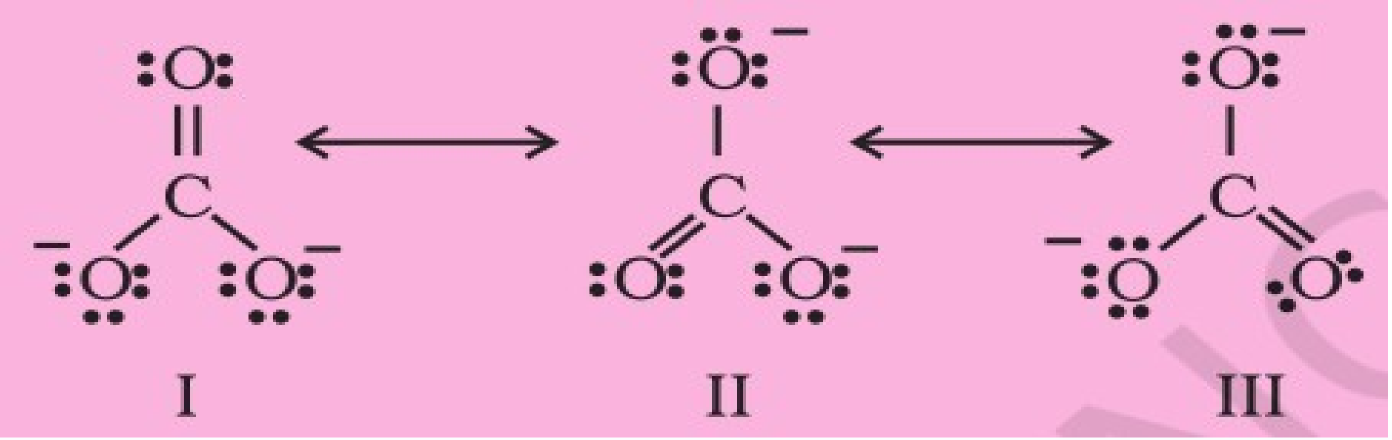
- This phenomenon is called resonance.
- The different possible structures are called contributing or canonical structures.
- Resonance is represented by double headed arrows.
- Eg:- O_3

RESONANCE IN OZONE



RESONANCE IN CO_2

RESONANCE IN CO_3^{2-}



POLARITY OF BONDS

- When a covalent bond is formed between two similar atoms, the shared pair of electrons is equally attracted by the atoms.
- As a result, electron pair is situated exactly between the two identical nuclei.
- The bond so formed is called non polar covalent bond.
- In the case of heteronuclear molecule, the shared electron pair between the atoms gets displaced more towards the more electronegative atom.
- The bond thus formed is called a polar covalent bond.
- As a result of polarization, the molecule possesses the dipole moment.

DIPOLE MOMENT

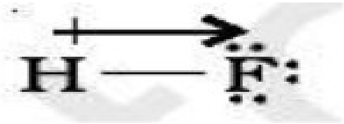
- It is the product of the magnitude of the charge and the distance between the centres of +ve and −ve charges.
- It is usually designated by a Greek letter 'μ'.
- Mathematically it is expressed as

$$\text{Dipole Moment, } \mu = \text{Charge (Q) x Distance of separation (r)}$$

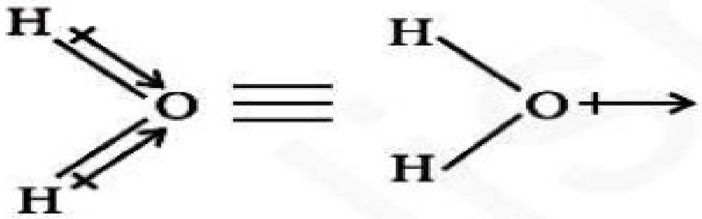
$$\mu = Q \times r$$

- Dipole moment is usually expressed in Debye units. (D)
- $1\ D = 3.33564 \times 10^{-30}$ Cm Where C is Coulomb and m is metre.
- Dipole moment is a vector quantity and it is expressed by a small arrow with tail on the positive centre and head pointing towards the negative centre. (+⟶)

HF



H_2O

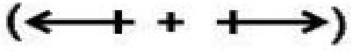


(a)
Bond dipole

(b)
Resultant
dipole moment

- Net dipole moment, μ = 1.85D
- **BeF_2**

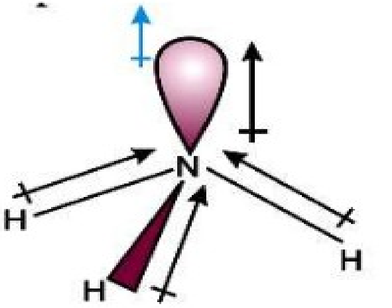
Bond dipoles in BeF_2



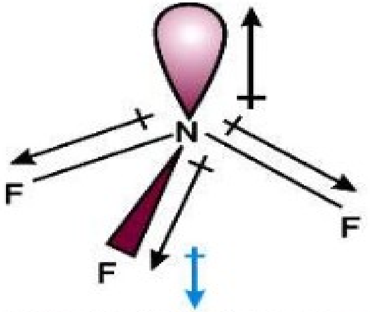
Total dipole moment in BeF_2

- Net dipole moment, μ = o

- **NH_3 and NF_3**



Resultant dipole moment
in $NH_3 = 4.90 \times 10^{-30}$ C m



Resultant dipole moment
in $NF_3 = 0.80 \times 10^{-30}$ C m

- Net dipole moment of NH_3 is 4.90×10^{-30} and Net Dipole moment of NF_3 is 0.80×10^{-30}

FAJAN'S RULES

- Smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- Greater the charge on the cation, greater will be the covalent character of the ionic bond.
- For cations of same size and charge, the one, with electronic configuration $(n-1)d^n\ ns^0$, typical of transition metals, is more polarizing than the one with a noble gas configuration, $ns^2\ np^6$, typical of alkali and alkaline earth metal cations.

EXAMPLES OF FAJAN'S RULES

1. **Which compound should theoretically the most ionic and the most covalent amongst the metal halides?**

- **The smallest metal ion and the largest anion should technically be the most covalent.**
- **Therefore, LiI is the most covalent.**
- **The largest cation and the smallest anion should be the most ionic.**
- **Therefore, CsF should be the most ionic.**

2. Arrange the following according to the increasing order of covalency:

i) NaF, NaCl, NaBr, NaI

ii) LiF, NaF,KF,RbF,CsF

i. Since the cation is the same, compare the anions.

- **Amongst the anions, larger the size more would be the covalency.**
- **Therefore the order is: NaF < NaCl < NaBr < NaI**

ii. Here the anion is the same, so we compare with cations.

- **Smaller the cation more is the covalency.**
- **Therefore, the order is: CsF < RbF < KF < NaF < LiF.**

SUMMARY OF FAJAN’S RULES

IONIC CHARACTERISTIC	COVALENT CHARACTERISTIC
● Large Cation	Small Cation
● Small Anion	Large Anion
● Small Charge	Large Charge

VSEPR THEORY

Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms.

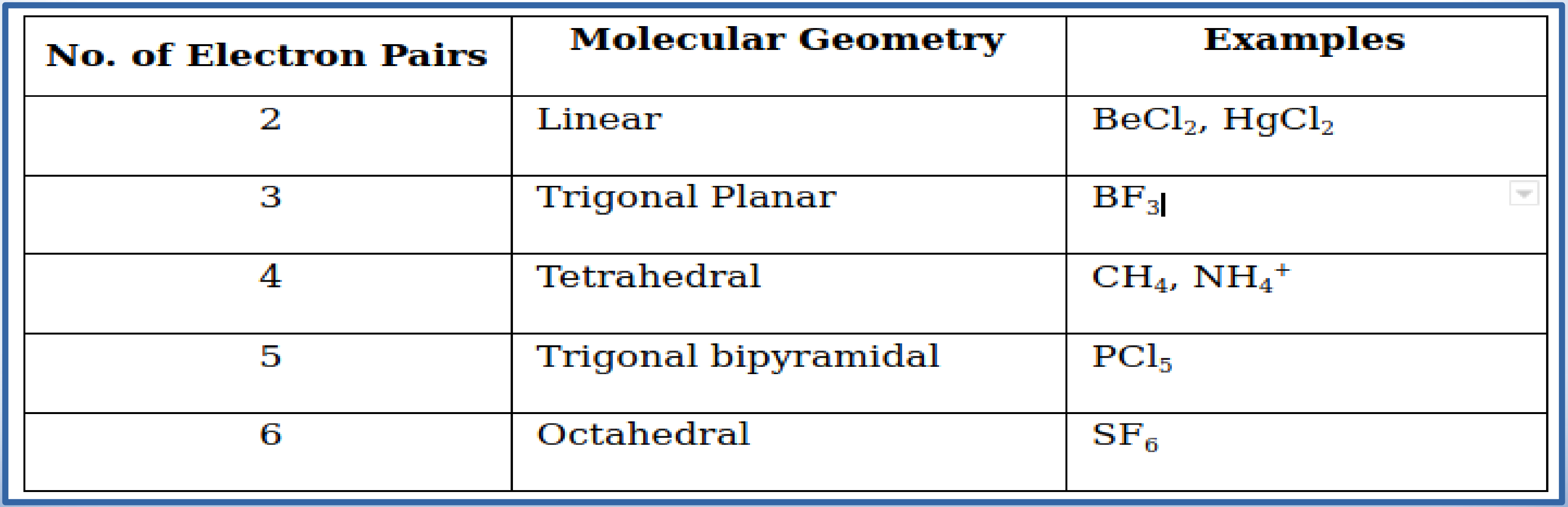
POSTULATES OF VSEPR THEORY

- The shape of a molecule depends upon the number of valence shell electron pairs around the central atom.
- The valence shell electron pairs repel each other.
- In order to reduce the repulsion, the electron pairs stay at a maximum distance.
- Presence of lone pairs of electron causes distortion in the expected geometry of the molecule.

SHAPES OF MOLECULES

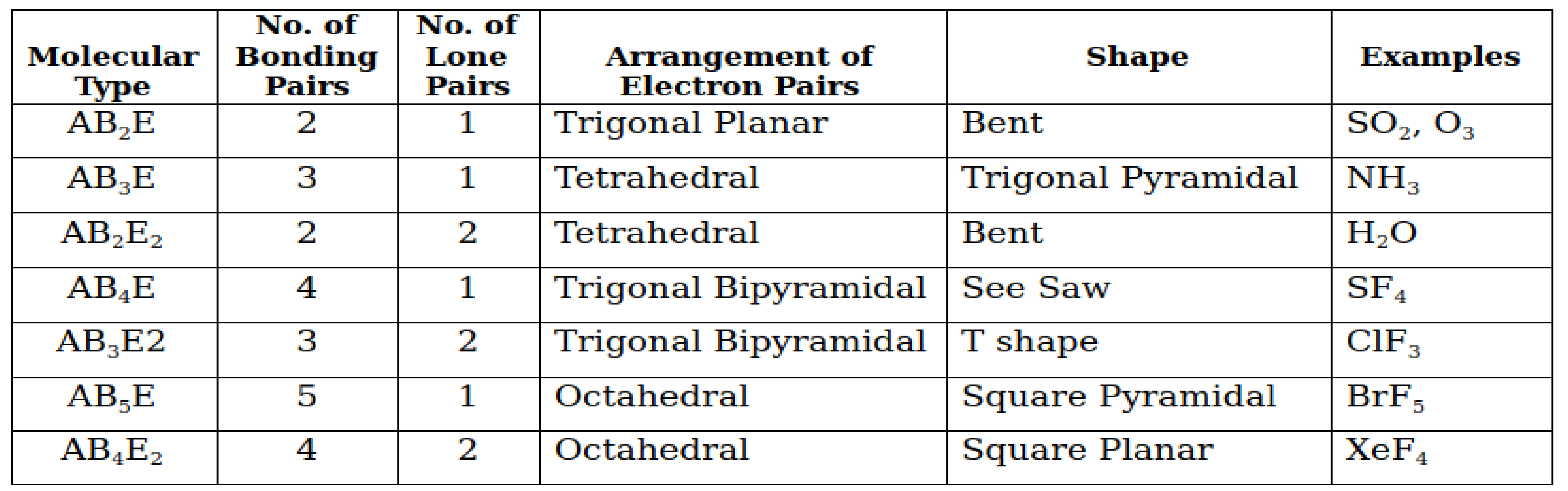
- The definite relative arrangement of the bonded atoms in a molecule is known as geometry or shape of the molecule.
- For the prediction of geometrical shapes of molecules, with the help of VSEPR theory, it is convenient to divide molecules into two categories.
- Molecules in which the central atom has no lone pair.
- Molecules in which the central atom has one or more lone pairs.

GEOMETRY OF MOLECULES IN WHICH THE CENTRAL ATOM HAS NO LONE PAIR OF ELECTRONS



No. of Electron Pairs	Molecular Geometry	Examples
2	Linear	$BeCl_2$, $HgCl_2$
3	Trigonal Planar	BF_3
4	Tetrahedral	CH_4, NH_4^+
5	Trigonal bipyramidal	PCl_5
6	Octahedral	SF_6

SHAPE OF SOME SIMPLE MOLECULES/IONS WITH CENTRAL IONS HAVING ONE OR MORE LONE PAIR OF ELECTRONS



Molecular Type	No. of Bonding Pairs	No. of Lone Pairs	Arrangement of Electron Pairs	Shape	Examples
AB_2E	2	1	Trigonal Planar	Bent	SO_2, O_3
AB_3E	3	1	Tetrahedral	Trigonal Pyramidal	NH_3
AB_2E_2	2	2	Tetrahedral	Bent	H_2O
AB_4E	4	1	Trigonal Bipyramidal	See Saw	SF_4
AB_3E2	3	2	Trigonal Bipyramidal	T shape	ClF_3
AB_5E	5	1	Octahedral	Square Pyramidal	BrF_5
AB_4E_2	4	2	Octahedral	Square Planar	XeF_4

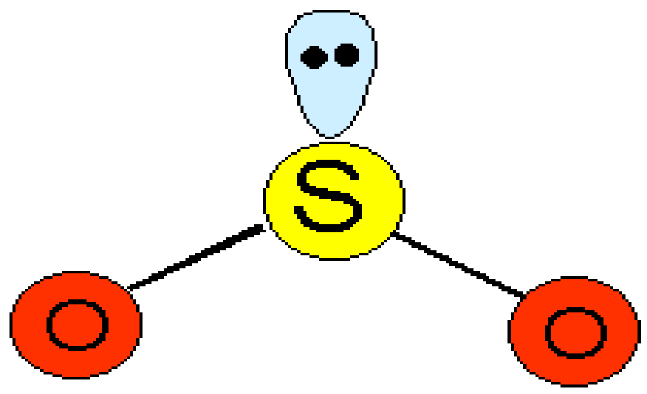
SHAPES OF MOLECULES CONTAINING BOND PAIR AND LONE PAIR

1. MOLECULAR TYPE AB_2E

No. of bonding pairs : 2

No. of lone pairs : 1

Shape : Bent



REASON FOR THE SHAPE ACQUIRED

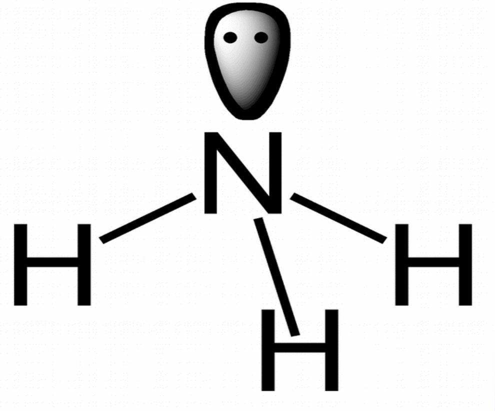
- Theoretically the shape should have been triangular planar.
- Actually it is found to be bent or V shaped.
- The reason is that the lone pair—bond pair repulsion is much more as compared to the bond pair— bond pair repulsion.
- So the bond angle is reduced to 119.5^0 from 120^0.
- Eg: SO_2

2. MOLECULAR TYPE AB_3E

No. of bonding pairs : 3

No. of lone pairs : 1

Shape : Trigonal Pyramidal



REASON FOR THE SHAPE ACQUIRED

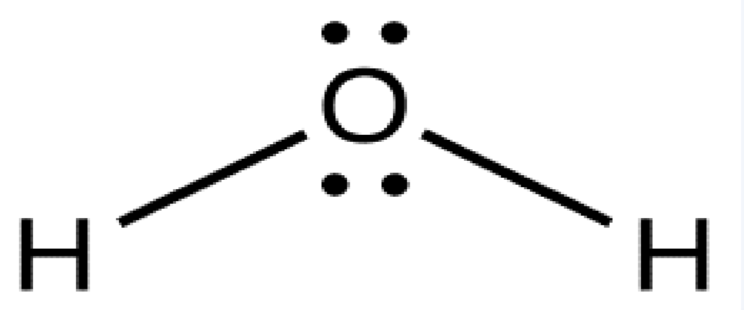
- **Here one lone pair of electron is present.**
- **Lone pair—Bond pair repulsion is greater than bond pair—bond pair repulsion.**
- **The angle between the bond pairs is reduced to 107^0 from 109.5^0.**
- **Eg: NH_3**

3. MOLECULAR TYPE AB_2E_2

No. of bonding pairs : 2

No. of lone pairs : 2

Shape : Bent



REASON FOR THE SHAPE ACQUIRED

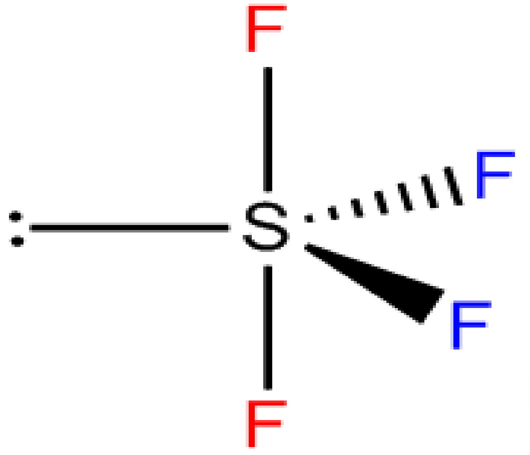
- The shape should have been tetrahedral if there were all bond pairs.
- Here two lone pairs are present.
- So the shape is distorted tetrahedral or angular.
- The reason is lone pair—lone pair repulsion is more than lone pair—bond pair repulsion which is more than bond pair—bond pair repulsion.
- Thus the angle is reduced to 104.5^0 from 109.5^0 .
- Eg: H_2O

4. MOLECULAR TYPE AB_4E

No. of bonding pairs : 4

No. of lone pairs : 1

Shape : See Saw



REASON FOR THE SHAPE ACQUIRED

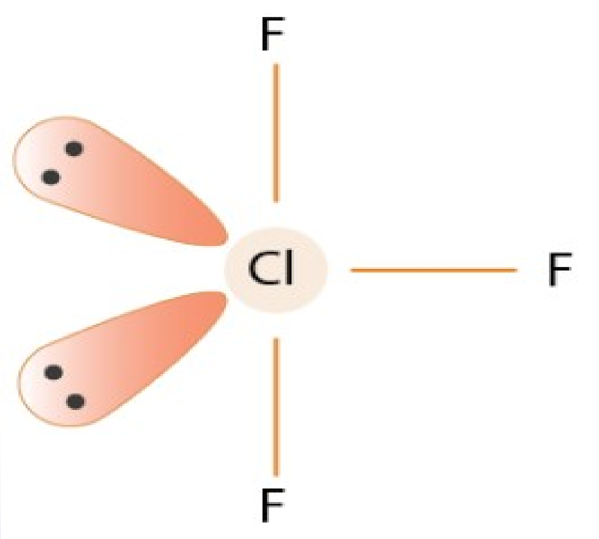
- **Here the lone pairs are in an equatorial position.**
- **There are two Lone Pair—Bond Pair repulsions.**
- **Hence this arrangement is more stable.**
- **Shape is distorted tetrahedron or see saw.**
- **Eg: SF_4**

5. MOLECULAR TYPE AB_3E_2

No. of bonding pairs : 3

No. of lone pairs : 2

Shape : T Shape



REASON FOR THE SHAPE ACQUIRED

- **Here the lone pairs are present at equatorial position.**
- **So there are less lone pair—bond pair repulsions as compared to others in which the lone pair are at axial position.**
- **So this structure is the most stable.**
- **Eg: ClF_3**

VALENCE BOND THEORY (VBT)

- Valence Bond Theory was developed by Heitler and London in 1927.
- Developed further by Pauling and others.
- A covalent bond is formed by the overlapping of half-filled orbitals present in the valence shell of the combining atoms.
- The overlapping orbitals must contain electrons with opposite spins.

- As a result of overlapping, energy is released and hence stability is increased.
- The strength of the bond depends on the extent of overlapping.
- The greater the overlap, the stronger is the bond.
- The number of covalent bonds formed by an atom is equal to the number of half-filled orbitals in it.
- The direction of the bond is the same as the direction of the overlap of half-filled orbitals.

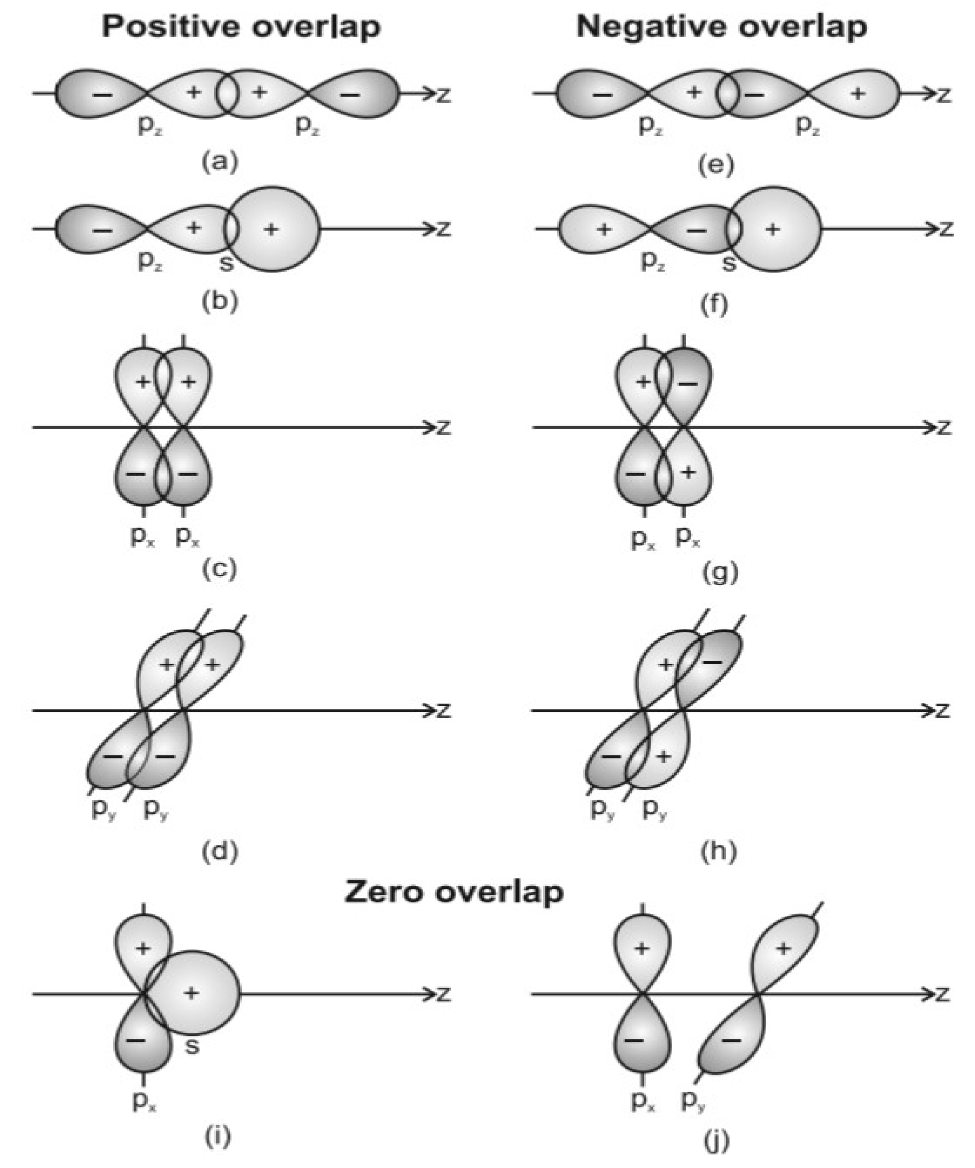
FORMATION OF HYDROGEN MOLECULE

- **Consider two hydrogen atoms A and B having the nuclei H_A and H_B and the corresponding electrons e_A and e_B respectively.**
- **When the two atoms are at large distance from each other, there is no interaction between them.**
- **The potential energy of the system at this stage is taken as Zero.**
- **As the two atoms come closer and closer, they will begin to interact with each other.**

- As a result new attractive and repulsive forces begin to operate.
- The new forces are attraction between the nucleus of one atom and the electron of the other atom
- i.e., (i) the attraction between H_A and e_B
- (ii) the attraction between H_B and e_A .
- Repulsive forces between their electrons and their nuclei i.e.,
- (i) repulsion between e_A and e_B
- (ii) repulsion between H_A and H_B .

ORBITAL OVERLAP CONCEPT FOR COVALENT BOND

- The main ideas of orbital overlap concept of forming covalent bonds are:
- Covalent bonds are formed by the overlapping of half-filled atomic orbitals present in their valence shell.
- The orbital undergoing overlapping must have electrons with opposite spins.
- The overlapping results in pairing of the electrons.
- Overlapping of atomic orbitals results in the decrease of energy and formation of covalent bond.
- The strength of a covalent bond depends on the extent of overlapping.
- The greater the overlapping, the stronger is the bond formed between the atoms.


Positive overlap
Negative overlap
– + + – z
p_z p_z
(a)
– + – + z
p_z p_z
(e)
– + + z
p_z s
(b)
+ – + z
p_z s
(f)
+ + – – z
p_x p_x
(c)
+ – – + z
p_x p_x
(g)
+ + – – z
p_y p_y
(d)
+ – – + z
p_y p_y
(h)
Zero overlap
+ + – z
p_x s
(i)
+ – + – z
p_x p_y
(j)

Why He_2 Molecule is not formed?

- He atom has two electrons in its 1s orbital.
- The 1s orbital of one He atom cannot overlap with the 1s orbital of another He atom, because it violates the Pauli's Exclusion Principle.
- Hence, He atoms do not form bonds between them.
- Therefore, He_2 molecule is not formed.

TYPES OF ORBITAL'S OVERLAPPING

- **Depending upon the extent and type of overlapping, the covalent bonds may be of two types.**
- **They are sigma bonds(σ) and Pi (π) bonds.**

SIGMA BOND

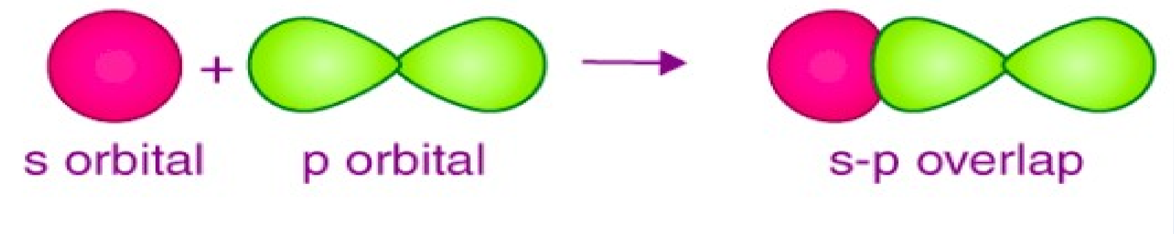
- The covalent bond formed by axial overlapping or end to end overlapping of half filled atomic orbitals along the internuclear axis is known as sigma bond.
- The electrons involved in sigma bond formation are called sigma electrons.
- Single bonds present in all molecules are always of sigma type.
- The sigma bond is formed by any one of the following types of combination of atomic orbitals.

s-s OVERLAPPING

In this type, two half-filled s orbitals overlap along the inter-nuclear axis.

s-p OVERLAPPING

This type of overlapping occurs between the half-filled s orbital of one atom and half-filled p orbital of the other atom.

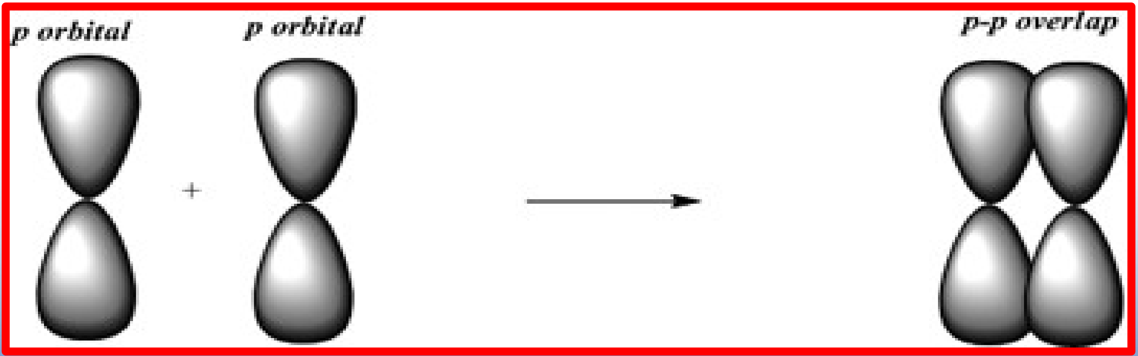


p-p OVERLAPPING

This type of overlapping occurs between the half-filled p orbital of one atom and half-filled p orbital of the other atom.

Pi BOND

- **The covalent bond formed by the side wise or lateral overlap of the half-filled atomic orbitals is known as pi bond.**
- **The electrons involved in pi bond formation are called pi electrons.**
- **The π bond is always present in molecules having multiple bonds.**
- **i.e., double or triple bonds.**



STRENGTH OF SIGMA BONDS AND PI BONDS

- **The strength of a covalent bond depends on the extent of overlapping of atomic orbitals forming the bond.**
- **During the formation of a sigma bond, the overlapping of orbitals takes place to a large extent.**
- **On the other hand, during the formation of a π bond, the overlapping occurs to a smaller extent.**
- **Therefore, a sigma bond is stronger than a pi bond.**

HYBRIDISATION

- **The phenomenon of intermixing of atomic orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new sets of orbitals of equivalent energies and shape.**
- **The new orbitals formed as a result of hybridization are called hybrid orbitals.**

SALIENT FEATURES OF HYBRIDISATION

- The number of hybrid orbitals formed is equal to the number of atomic orbitals that get hybridized.
- The hybrid orbitals are always equivalent in energy and shape.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.

- **These hybrid orbitals are directed in space in some preferred directions to have minimum repulsion between the electron pairs and thus a stable arrangement is obtained.**
- **Therefore, the type of hybridization indicates the geometry of the molecule.**

CONDITIONS FOR HYBRIDISATION

- The orbitals present in the valence shell of the atom are hybridized.
- The orbitals undergoing hybridization should have almost equal energy.
- Promotion of electron is not essential condition prior to hybridization.
- It is not necessary that only half filled orbitals participate in hybridization.
- In some cases, even filled orbitals of valence shell take part in hybridization.

TYPES OF HYBRIDISATION

sp HYBRIDISATION

- The intermixing of one ‘s’ orbital and one ‘p’ orbital of an atom to form two equivalent orbitals is known as sp hybridization.
- The resulting orbitals are known as sp hybrid orbitals.
- These orbitals are directed along a line.

- **So it is also called linear hybridization.**
- **The suitable orbitals for sp hybridization are s and Pz , if the hybrid orbitals are to lie along the z-axis.**
- **Each sp hybrid orbitals has 50% s-character and 50% p-character.**

sp^2 HYBRIDISATION

- The intermixing of one s and two p orbitals of an atom to form three equivalent orbitals is known as sp^2 hybridization.
- The resulting orbitals are called sp^2 hybrid orbitals.
- These sp^2 hybrid orbitals lie in a plane and are directed towards the three corners of an equilateral triangle.
- So it is called trigonal hybridization.

sp^3 HYBRIDISATION

- The intermixing of one s and three p orbitals of an atom to form four orbitals.
- The four orbitals have equivalent energy.
- These orbitals are directed to the four corners of a regular tetrahedron.
- It is called sp^3 hybridization.

- The resulting orbitals are called sp^3 hybrid orbitals.
- The angle between sp^3 hybrid orbitals is 109^0 28ˈ.
- There is 25% s-character and 75% p-character in each sp^3 hybrid orbital.

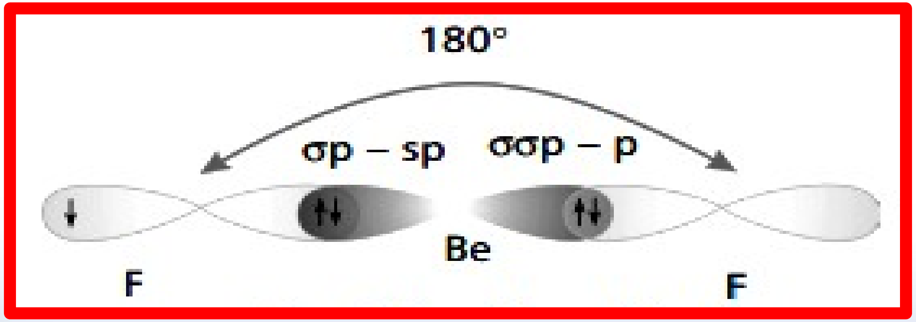
EXAMPLES

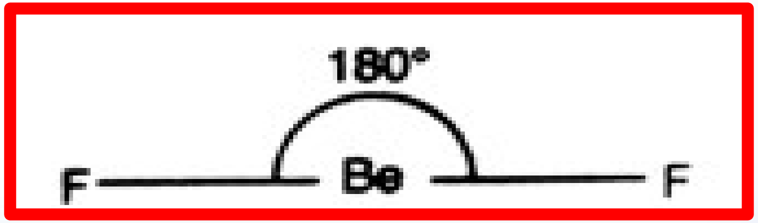
sp HYBRIDISATION

BERYLLIUM FLUORIDE (BeF_2)

- The ground state electronic configuration of Be is $1s^2$ $2s^2$.
- To account for the divalency of Be, one of the 2s electron is promoted to a vacant 2p orbital.
- Now the two half-filled orbitals (2s and 2p) hybridize to form two sp hybrid orbitals.

- These hybrid orbitals overlap with half-filled p orbitals of two fluorine atoms to form two Be—F sigma bonds.
- Thus BeF_2 is linear in shape and the bond angle is 180^0

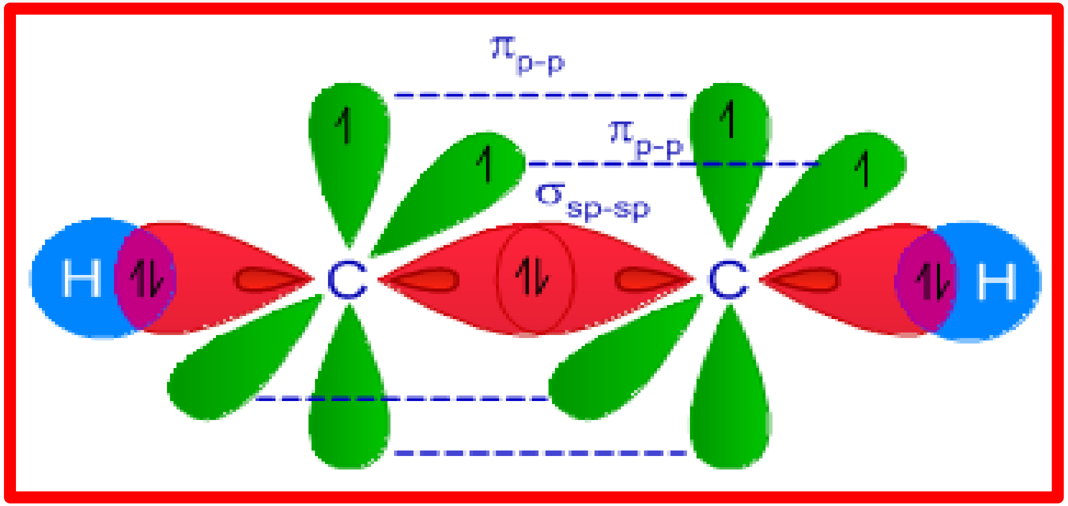




ACETYLENE ($CH\equiv CH$)

- In the formation of acetylene, both the carbon atoms undergo sp hybridization leaving two 2p orbitals (2Py and 2Px) in the unhybridized state.
- One sp hybrid orbital of one carbon atom overlaps axially with sp hybrid orbital of the other carbon atom to form C—C sigma bond.

- The other sp hybrid orbital of each carbon atom overlaps axially with the half filled s orbital of hydrogen atoms forming σ bonds.
- Each of the two unhybridized p orbitals of both the carbon atoms overlaps sidewise to form two π bonds between the carbon atoms.
- So the triple bond between the two carbon atoms is made up of one sigma and two π bonds.

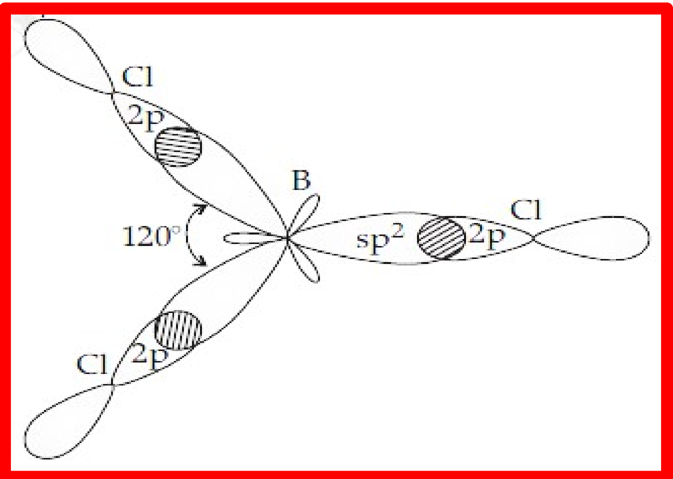

π_{p-p}
π_{p-p}
σ_{sp-sp}
H
C
C
H
↿⇂
↿⇂
↿⇂
↿
↿
↿
↿

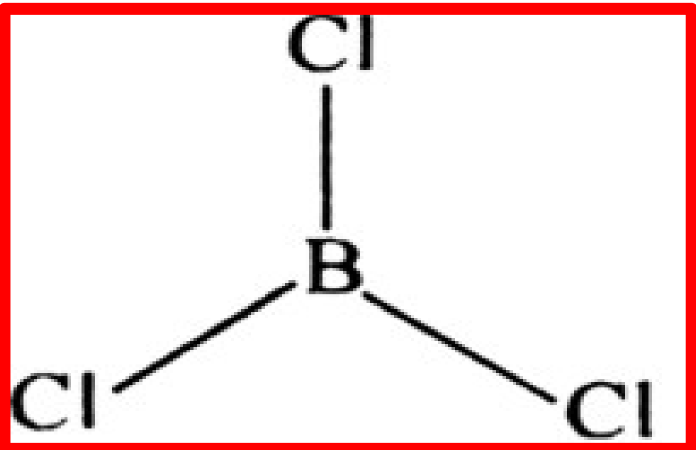
sp^2 HYBRIDISATION

BORON TRICHLORIDE (BCl_3)

- The ground state electronic configuration of boron atom is $1s^2$ $2s^2$ $2p^1$.
- In the excited state, one of the 2s electrons is promoted to vacant 2p orbital.
- As a result, boron has three unpaired electrons.
- These three orbitals (one 2s and two 2p) hybridize to form three sp^2 hybrid orbitals.

- **The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B—Cl bonds.**
- **Therefore, in BCl_3 , the geometry is trigonal planar with bond angle 120^0 .**

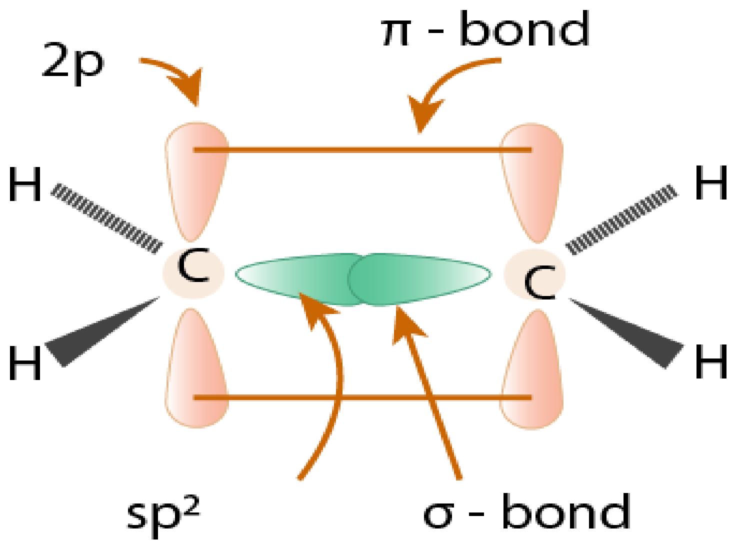


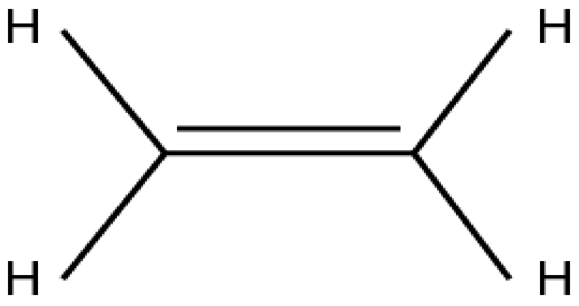


ETHYLENE (CH_2=CH_2)

- In the excited state, carbon atom has four unpaired electrons in the valence shell.
- In the formation of ethylene, each carbon atoms undergo sp^2 hybridization leaving one of the 2p orbitals in the unhybridized state.
- Two hybrid orbitals of each carbon atom overlap with 1s orbitals of two hydrogen atoms to form C—H sigma bonds.

- The third hybrid orbital of one carbon atom overlaps with the sp^2 hybrid orbital of other carbon atom to form C—C sigma bond.
- The unhybridized 2p orbital of one carbon atom overlap sidewise with the similar orbital of the other carbon to form a C—C Pi bond.
- Thus in ethylene, the C—C bond consists of one σ and one π bond.
- Ethylene is a planar molecule with bond angle 120^0.



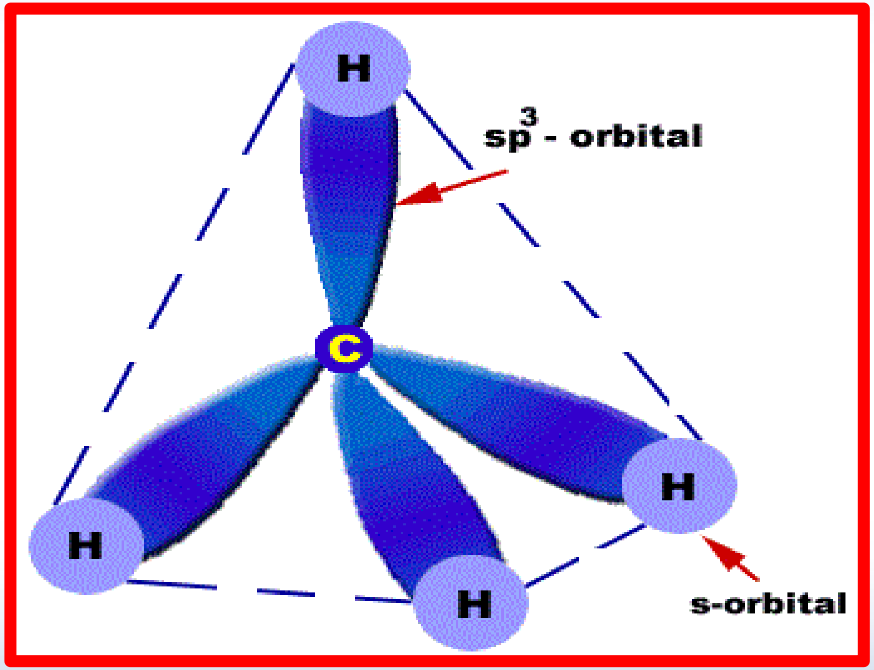


Ethene

sp^3 HYBRIDISATION

METHANE (CH_4)

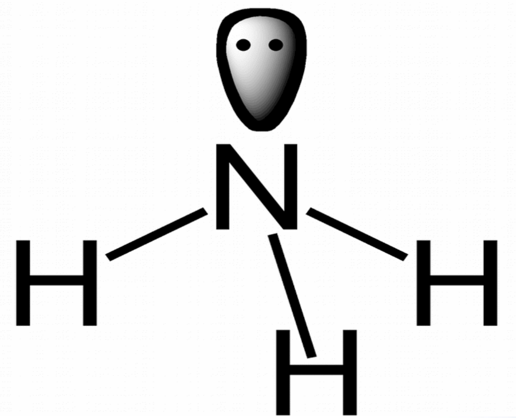
- In the formation of methane, carbon undergoes sp^3 hybridization.
- All the four sp^3 hybrid orbitals overlap with the 1s orbitals of four hydrogen atoms.
- It gives rise to four σ bonds.
- Thus, CH_4 is tetrahedral in shape and the bond angle is $109^0\ 28'$.


H
sp^3 - orbital
C
H
H
H
s-orbital

AMMONIA (NH_3)

- The ground state electronic configuration of nitrogen atom is $1s^2$ $2s^2$ $2px^1$ $2py^1 2pz^1$.
- Nitrogen has three unpaired electrons in the sp^3 hybrid orbitals and a lone pair of electron is present in the fourth one.
- These hybrid orbitals overlap with 1s orbitals of hydrogen atoms to form three N—H sigma bonds.

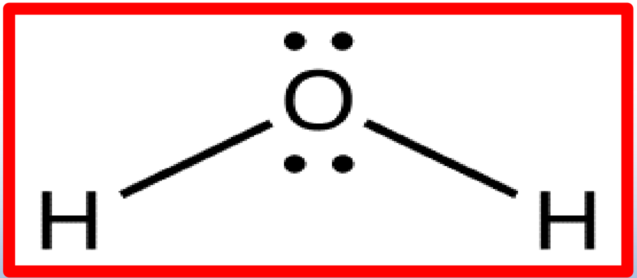
- **Here lone pair bond pair repulsion is greater than the two bond pairs of electrons.**
- **The molecule thus gets distorted and the bond angle is reduced to 107^0 from 109.5^0 .**
- **The geometry of the molecule is pyramidal.**

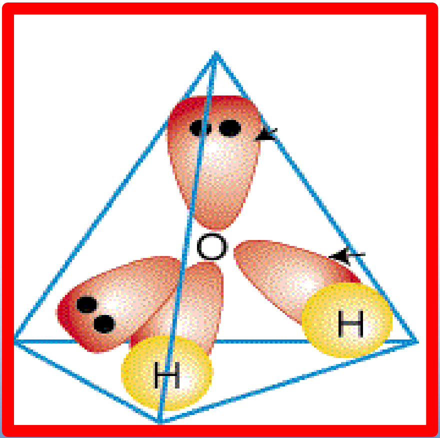


WATER (H_2O)

- **In the case of water molecule, the four orbitals of oxygen (one 2s and three 2p) undergo sp^3 hybridization.**
- **It forms four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons.**

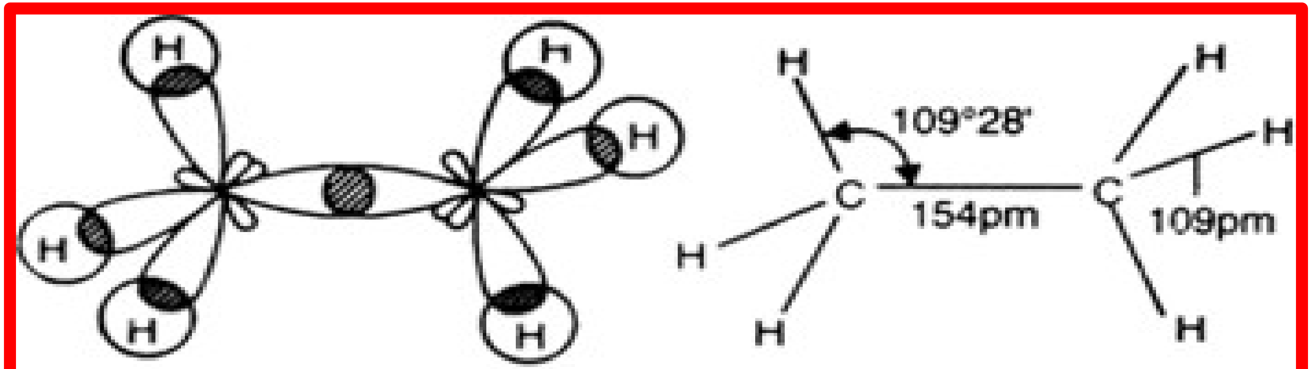
- These four Sp^3 hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by the lone pair.
- The bond angle in this case is reduced to 104.5^0 from 109.5^0
- The molecule acquires a V-shape or angular geometry.





ETHANE (CH_3-CH_3)

- In the formation of ethane, both the carbon atoms undergo sp^3 hybridization.
- One of the sp^3 hybrid orbitals of one carbon atom overlaps with one of the sp^3 hybrid orbitals of the other to establish a C—C sigma bond.
- The remaining sp^3 hybrid orbitals of each carbon atom overlap axially with the 1s orbital of hydrogen atoms to form C—H sigma bonds.

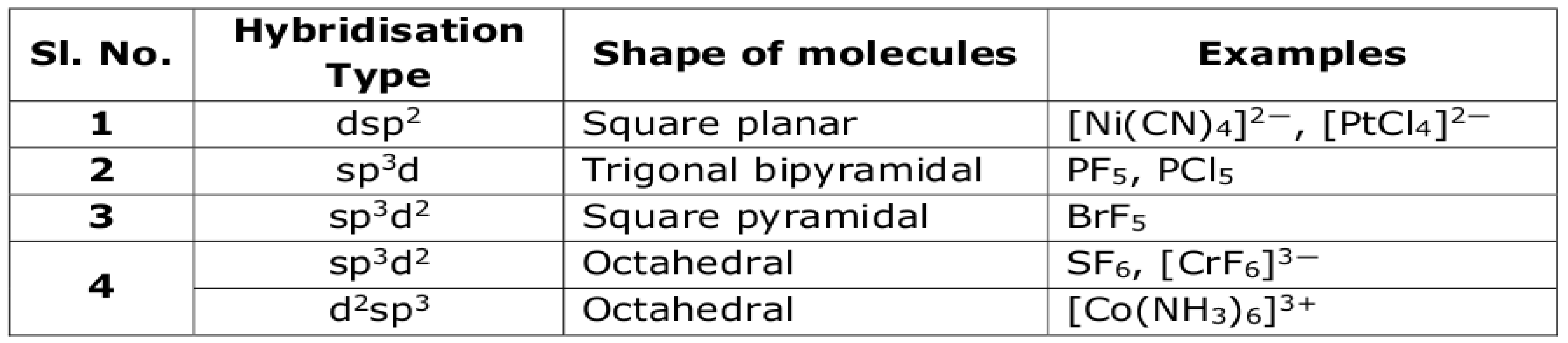


Molecular orbital picture of ethane

HYBRIDISATION OF ELEMENTS INVOLVING d-ORBITALS

- **The elements present in the third period contain d orbitals in addition to s and p orbitals.**
- **The energy of the 3d orbitals are comparable to the energy of the 3s and 3p orbitals.**
- **The energy of 3d orbitals are also comparable to those of 4s and 4p orbitals.**

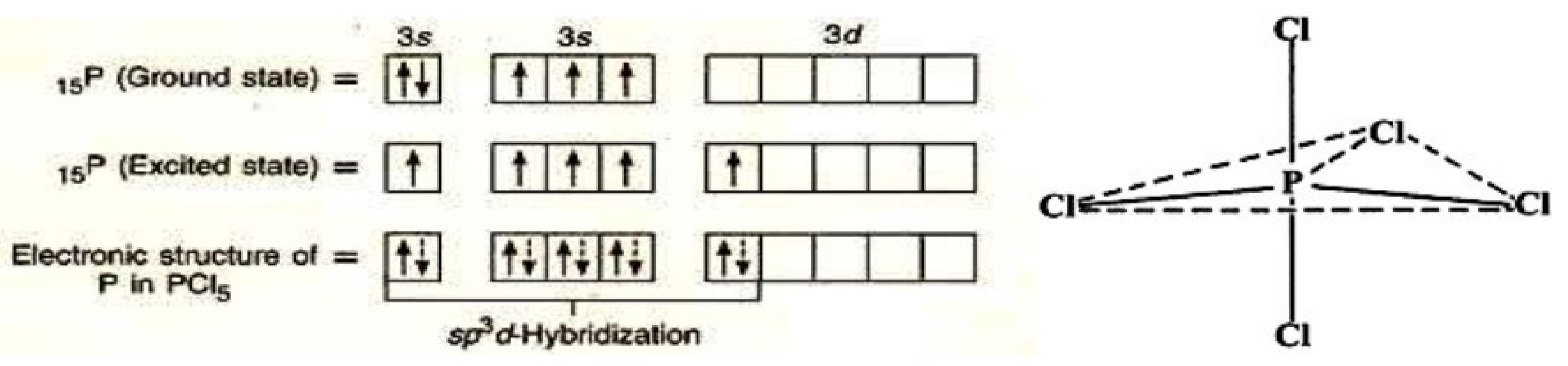
The important hybridization schemes involving s, p and d orbitals are summarized below.



Sl. No.	Hybridisation Type	Shape of molecules	Examples
1	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$
2	sp^3d	Trigonal bipyramidal	PF_5, PCl_5
3	sp^3d^2	Square pyramidal	BrF_5
4	sp^3d^2	Octahedral	SF_6, $[CrF_6]^{3-}$
	d^2sp^3	Octahedral	$[Co(NH_3)_6]^{3+}$

PHOPHOROUS PENTACHLORIDE (PCl_5)

The ground state and the excited state outer electronic configuration of phosphorous (z = 15) is represented below.



- In PCl_5 , the five sp^3d orbitals of phosphorous overlap with singly occupied p orbitals of chlorine atoms to form five P—Cl sigma bonds.
- The three P—Cl bonds lie in one plane and make an angle of 120^0 with each other.
- These bonds are called equatorial bonds.

- The remaining two P—Cl bonds, one lying above and one lying below the equatorial plane make an angle of 90^0 with the plane.
- These bonds are called axial bonds.
- In order to keep the five electron pairs as far apart as possible, PCl_5 adopts trigonal bipyramidal shape.

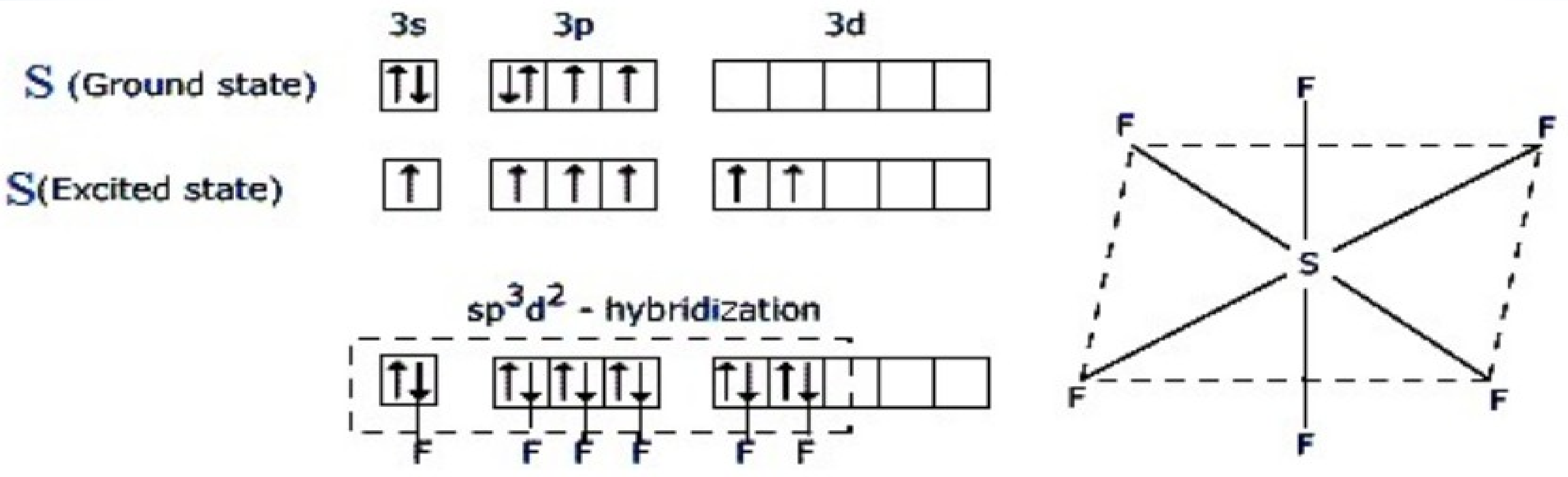
PCl_5 is more reactive. Why?

- In PCl_5 , the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs.
- Therefore, axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds.
- Hence PCl_5 molecule is more reactive.

SULPHUR HEXA FLUORIDE (SF_6)

- In SF_6 , the central atom sulphur has six pairs of electrons in the valence shell.
- The ground state and the excited state electronic configurations of sulphur are represented below.
- In the excited state, the available six orbitals (one s, three p and two d) are singly occupied by electrons.

- These orbitals hybridize to form six new sp^3d^2 hybrid orbitals.
- These orbitals are projected towards the six corners of a regular octahedron.
- The six sp^3d^2 hybrid orbitals overlap with singly occupied orbitals of fluorine atom to form six S—F sigma bonds.
- Thus SF_6 molecule has a regular octahedral geometry.


3s
3p
3d
S (Ground state)
S(Excited state)
sp^{3}d^2 - hybridization
F
F
F
F
F
F
F
F
F
F
F
F
S

MOLECULAR ORBITAL THEORY (MOT)

- **Molecular Orbital Theory was developed by F. Hund and R.S. Mulliken in 1932.**
- **The salient features of this theory are**
- **The electrons in a molecule are present in the various molecular Orbitals.**
- **The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.**

- A molecular orbital, is influenced by two or more nuclei depending up on the number of atoms in the molecule.
- An atomic orbital is monocentric while a molecular orbital is polycentric.
- The number of molecular orbital formed is equal to the number of atomic orbitals combined.

- **When two atomic orbitals combine, two molecular orbitals are formed.**
- **One is known as bonding molecular orbital while the other is called Antibonding molecular orbital.**
- **The bonding molecular orbital has lower energy and hence greater stability than the corresponding Antibonding molecular orbital.**

- **The electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.**
- **The molecular orbitals are filled in accordance with the Aufbau Principle obeying the Pauli's Exclusion Principle and the Hund's Rule.**

DIFFERENCES BETWEEN ATOMIC ORBITALS AND MOLECULAR ORBITALS

- **An atomic orbital is monocentric.**
- **i.e., an electron in an atomic orbital is influenced by only one nucleus.**
- **A molecular orbital is polycentric.**
- **i.e., an electron in a molecular orbital is influenced by two or more nuclei.**

FORMATION OF MOLECULAR ORBITALS

LINEAR COMBINATION OF ATOMIC ORBITALS

- **Molecular orbitals are formed by the combination of atomic orbitals.**
- **The atomic orbitals can combine by addition and subtraction of their wave functions.**
- **This is called Linear Combination of atomic orbitals, LCAO.**

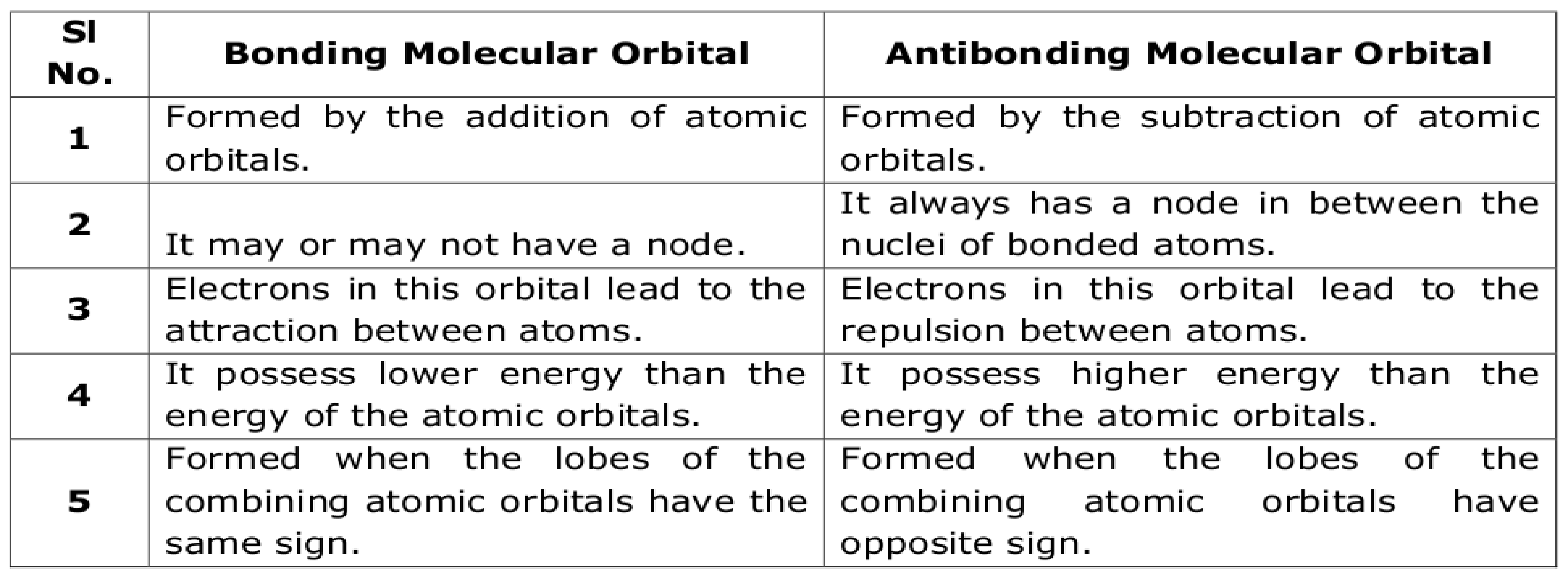
- If ψ_A and ψ_B are the orbital wave functions of two atoms A and B, they can combine by addition or subtraction to form a molecular orbital.
- Therefore the two molecular orbitals σ and σ* are formed as
- The molecular orbital σ formed by the addition of atomic orbitals is called the bonding molecular orbital.

$$\psi_{MO} = \psi_A \pm \psi_B$$

- The molecular orbital σ* formed by the subtraction of atomic orbital is called Antibonding molecular orbital.

$$\begin{aligned} \sigma &= \psi_A + \psi_B \\ \sigma^* &= \psi_A - \psi_B \end{aligned}$$

DIFFERENCE BETWEEN BONDING AND ANTIBONDING MOLECULAR ORBITALS



Sl No.	Bonding Molecular Orbital	Antibonding Molecular Orbital
1	Formed by the addition of atomic orbitals.	Formed by the subtraction of atomic orbitals.
2	It may or may not have a node.	It always has a node in between the nuclei of bonded atoms.
3	Electrons in this orbital lead to the attraction between atoms.	Electrons in this orbital lead to the repulsion between atoms.
4	It possess lower energy than the energy of the atomic orbitals.	It possess higher energy than the energy of the atomic orbitals.
5	Formed when the lobes of the combining atomic orbitals have the same sign.	Formed when the lobes of the combining atomic orbitals have opposite sign.

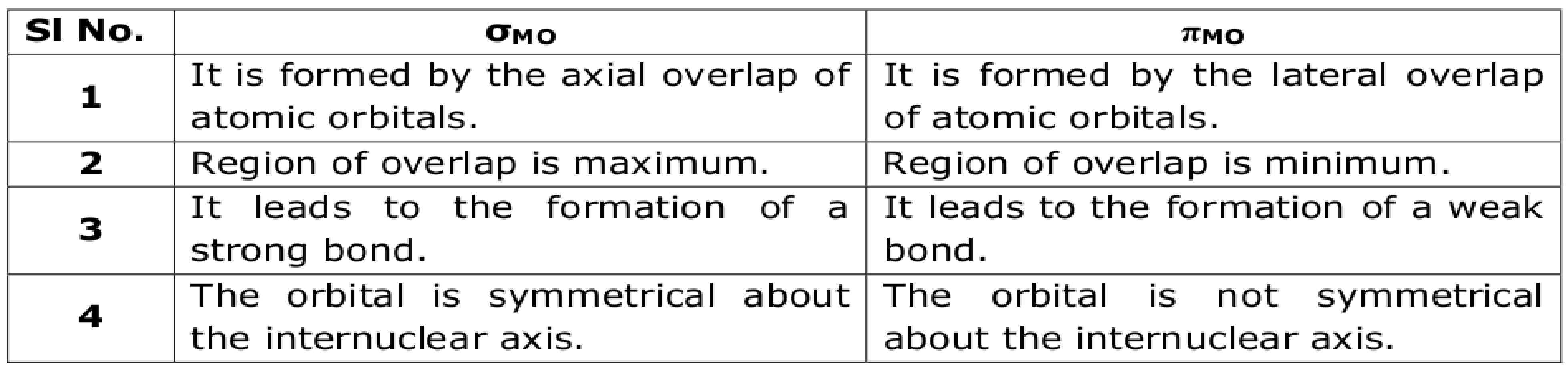
CONDITIONS FOR THE COMBINATION OF ATOMIC ORBITALS

- **The combining atomic orbitals must have the same or nearly the same energy.**
- **The combining atomic orbitals must have the same symmetry about the molecular axis.**
- **The combining atomic orbitals must overlap to the maximum extent.**

TYPES OF MOLECULAR ORBITALS

- **Molecular orbitals of diatomic molecules are designated as sigma (σ) and Pi (π).**
- **A σ MO is formed by the axial overlap of atomic orbitals.**
- **A π MO is formed by the lateral overlap.**

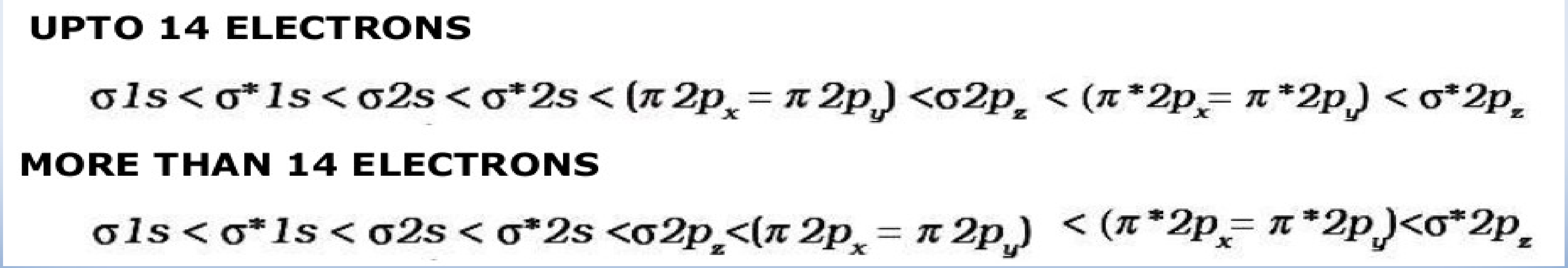
COMPARISON OF SIGMA AND PI MOLECULAR ORBITALS



Sl No.	σ_{MO}	π_{MO}
1	It is formed by the axial overlap of atomic orbitals.	It is formed by the lateral overlap of atomic orbitals.
2	Region of overlap is maximum.	Region of overlap is minimum.
3	It leads to the formation of a strong bond.	It leads to the formation of a weak bond.
4	The orbital is symmetrical about the internuclear axis.	The orbital is not symmetrical about the internuclear axis.

ELECTRONIC CONFIGURATION

The distribution of electrons among various molecular orbitals is called the electronic configuration of the molecule.



UPTO 14 ELECTRONS

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

MORE THAN 14 ELECTRONS

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

STABILITY OF MOLECULES

- N_b is the number of electrons present in bonding molecular orbitals.
- N_a is the number of electrons present in antibonding molecular orbitals.
- If $N_b > N_a$, the molecule is stable.
- If $N_b < N_a$, the molecule is unstable.

BOND ORDER

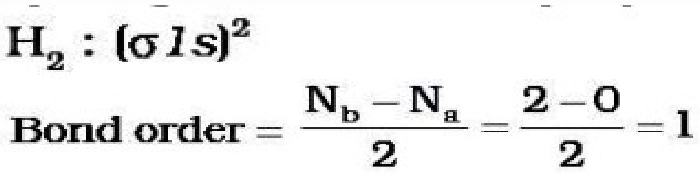
- Bond Order is defined as one half of the difference between the number of electrons present in the bonding and antibonding molecular orbitals.
- $\text{Bond Order} = \frac{1}{2} N_b - N_a$ or $\text{Bond Order} = \frac{N_b - N_a}{2}$
- Bond Order gives the following information.

- **If the value of bond order is +ve, the molecule is stable.**
- **If the bond order is –ve or zero, the molecule is unstable.**
- **Greater the bond order, greater is the dissociation energy.**
- **Greater the bond order, shorter is the bond length.**
- **The bond order of a diatomic molecule is equal to the number of covalent bonds in the molecule.**

MAGNETIC BEHAVIOUR

- A molecule will be paramagnetic if it has unpaired electrons in its Molecular Orbital.
- A molecule will be diamagnetic if it has no unpaired electrons in its Molecular Orbital.

HYDROGEN MOLECULE (H_2)



$H_2 : (\sigma 1s)^2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

- **H_2 molecule is stable.**
- **It is diamagnetic.**
- **The two hydrogen atoms are bonded by a single covalent bond.**

HELIUM MOLECULE (He_2)

$$He_2 : (\sigma 1s)^2 (\sigma^* 1s)^2$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-2}{2} = 0$$

- He_2 molecule is unstable and does not exist.

LITHIUM MOLECULE (Li_2)

$$Li_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{4 - 2}{2} = 1$$

- Li_2 molecule is stable.
- It is diamagnetic.
- The two Li atoms are joined by single covalent bonds.

CARBON MOLECULE (C_2)

$$C_2 : (\sigma 1s)^2(\sigma * 1s)^2(\sigma 2s)^2(\sigma * 2s)^2(\pi 2p_x^2 = \pi 2p_y^2)$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{8-4}{2} = 2$$

- C_2 molecule is stable.
- It is diamagnetic.
- The two carbon atoms are joined by means of a double bond.

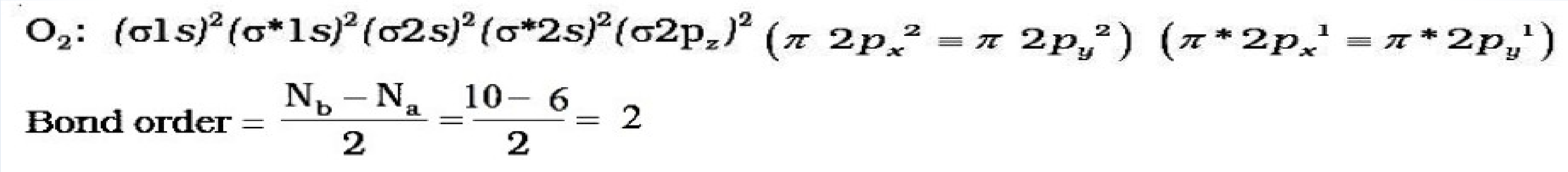
NITROGEN MOLECULE (N_2)

$$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x^2 = \pi 2p_y^2)(\sigma 2p_z)^2$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

- N_2 molecule is stable.
- It is diamagnetic.
- The two nitrogen atoms are joined by triple bonds.

OXYGEN MOLECULE (O_2)



$$O_2:\ (\sigma 1s)^2(\sigma^*1s)^2(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2\ (\pi\ 2p_x{}^2 = \pi\ 2p_y{}^2)\ \ (\pi^*2p_x{}^1 = \pi^*2p_y{}^1)$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$$

- O_2 molecule is stable.
- It is paramagnetic.
- The two oxygen atoms are joined by double bonds.

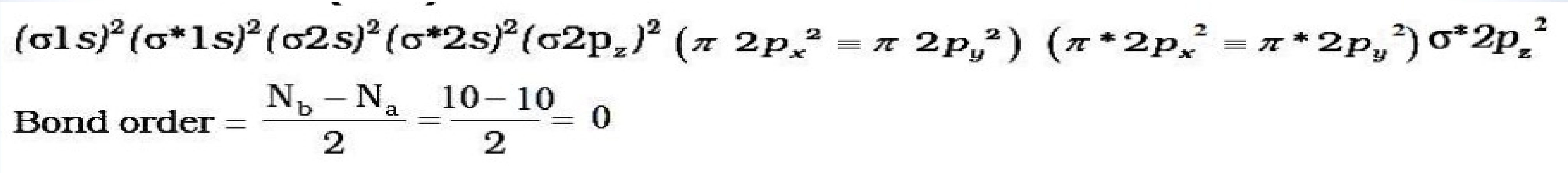
FLUORINE MOLECULE (F_2)

$$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2\ (\pi\ 2p_x{}^2 = \pi\ 2p_y{}^2)\ (\pi^* 2p_x{}^2 = \pi^* 2p_y{}^2)$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-8}{2} = 1$$

- F_2 molecule is stable.
- It is diamagnetic.
- The two fluorine atoms are joined by single covalent bond.

NEON MOLECULE (Ne_2)



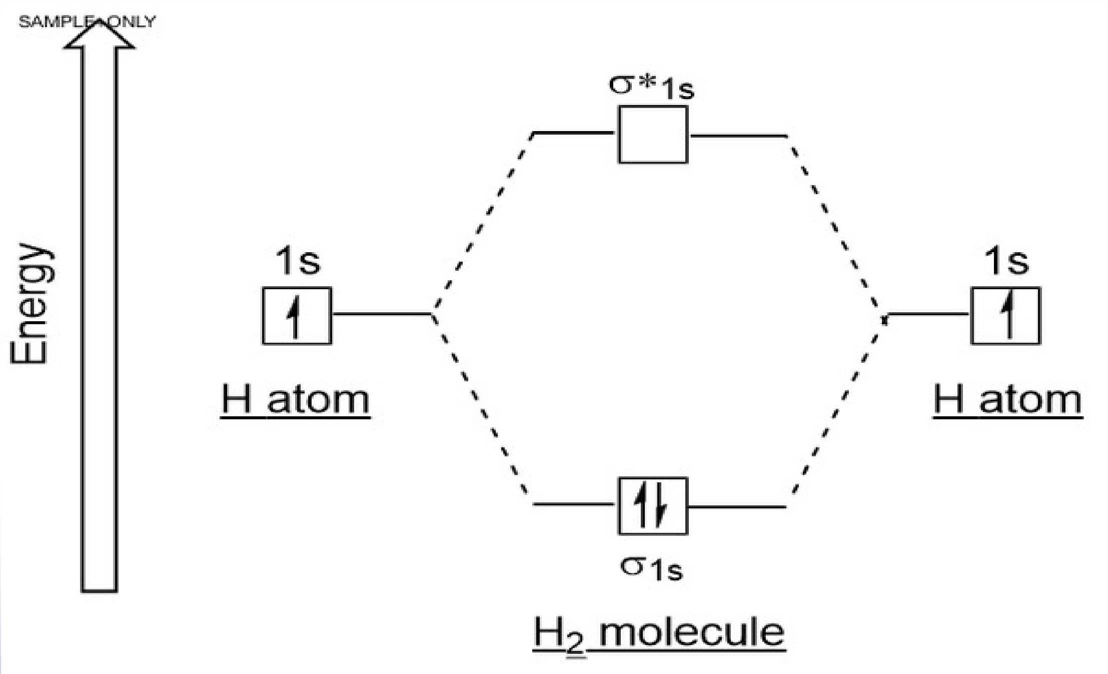
$$(\sigma 1s)^2(\sigma^*1s)^2(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2\ (\pi\ 2p_x{}^2 = \pi\ 2p_y{}^2)\ (\pi^*2p_x{}^2 = \pi^*2p_y{}^2)\,\sigma^*2p_z{}^2$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-10}{2} = 0$$

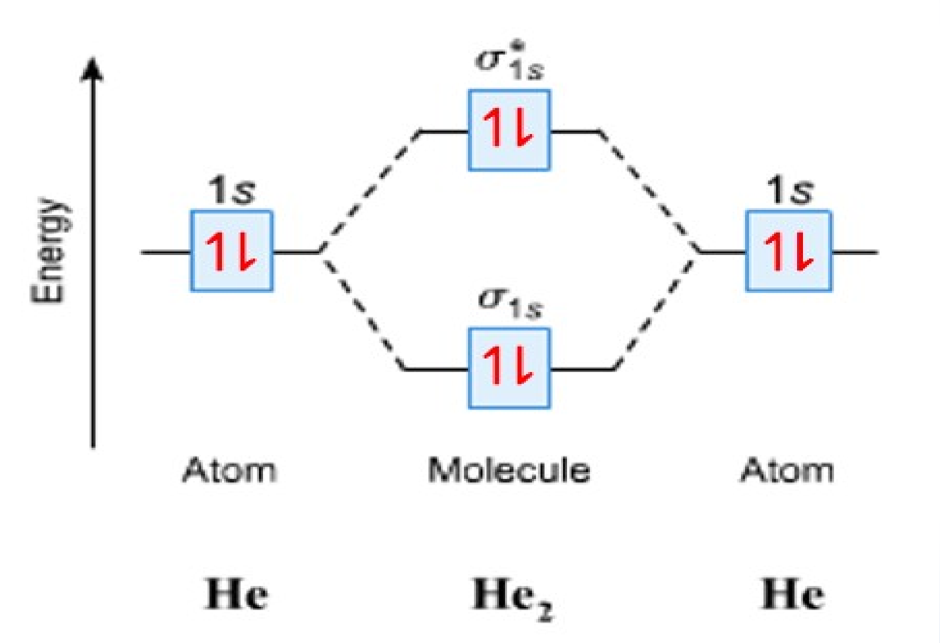
Ne_2 molecule is unstable and does not exist.

MOLECULAR ORBITAL DIAGRAM OF HOMONUCLEAR DIATOMIC MOLECULES

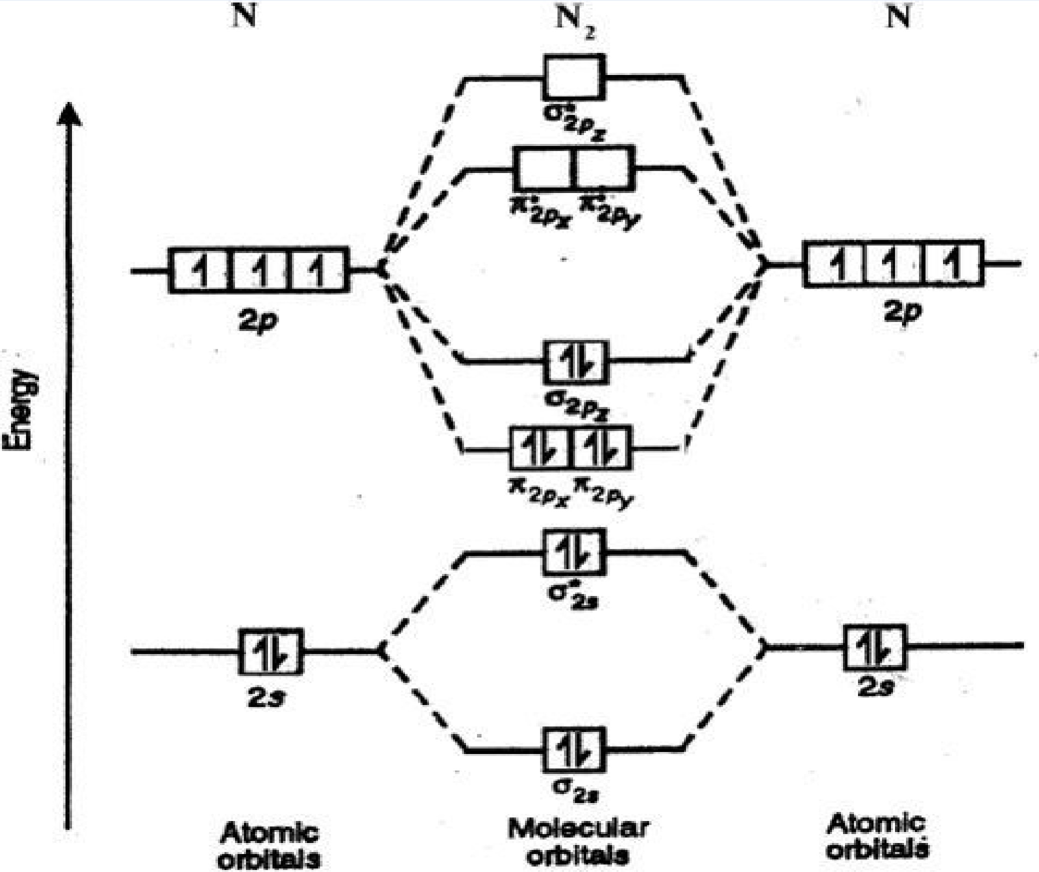
HYDROGEN MOLECULE (H_2)



HELIUM MOLECULE (He_2)



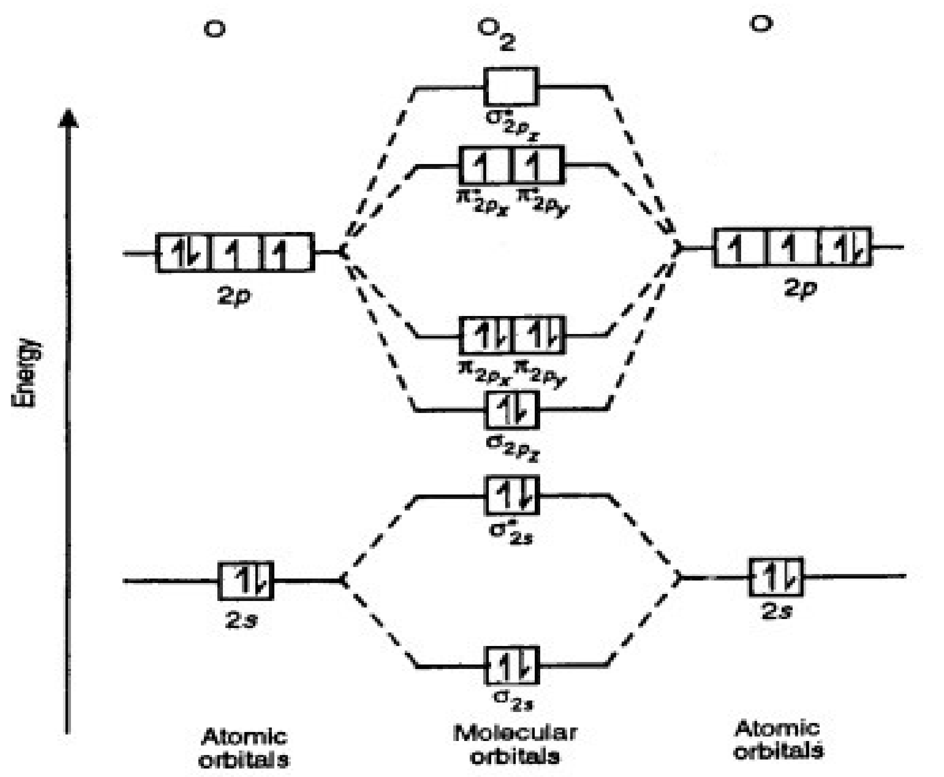
NITROGEN MOLECULE (N_2)



OXYGEN MOLECULE (O_2)

$$O_2:\ (\sigma 1s)^2(\sigma^* 1s)^2(\sigma^* 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2$$

$$\left(\pi 2p_x{}^2 \equiv \pi 2p_y{}^2\right)\ \left(\pi^* 2p_x{}^1 \equiv \pi^* 2p_y{}^1\right)$$



Molecular orbital energy level diagram of O_2 molecule

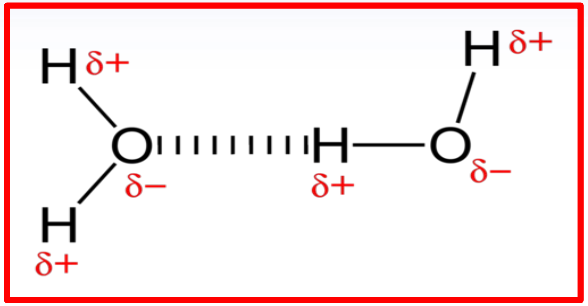
HYDROGEN BOND

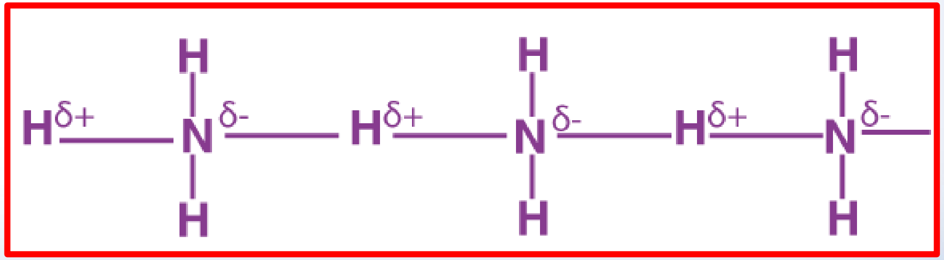
- The attractive force that binds the electronegative atom in one molecule with the hydrogen atom of the neighbouring molecule of the same or different substance is called Hydrogen bond.
- Eg: H_2O, HF, NH_3 etc

INTERMOLECULAR HYDROGEN BOND

If the hydrogen bond is operating between the molecules of same or different substance, it is called Intermolecular Hydrogen Bond.

Eg:- H_2O, HF, NH_3 etc.

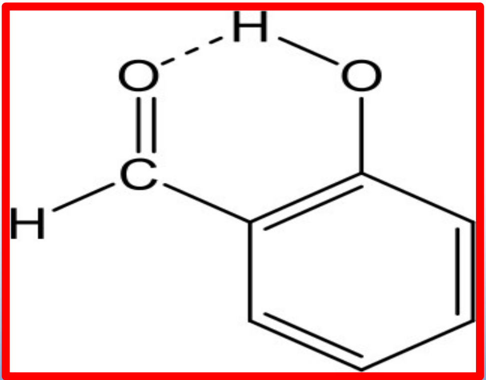


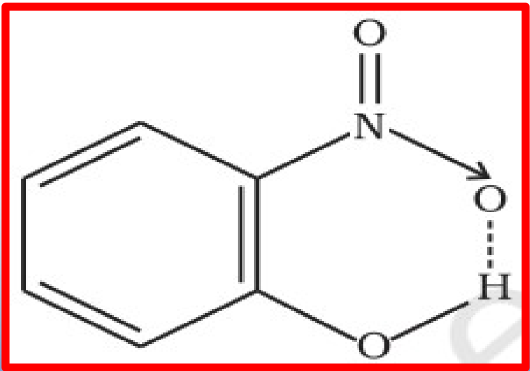


$$---H^{\delta+}-F^{\delta-}---H^{\delta+}-F^{\delta-}---H^{\delta+}-F^{\delta-}$$

INTRAMOLECULAR HYDROGEN BOND

- If the hydrogen bond is operating in a molecule itself, it is called Intramolecular Hydrogen Bond.
- Eg:- Salicylaldehyde, O-nitrophenol





Thank you