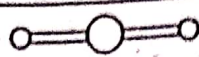
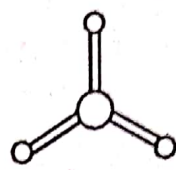
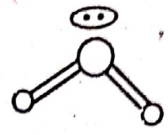
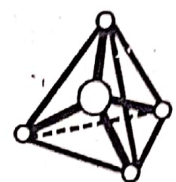
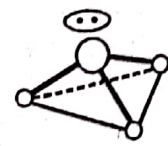
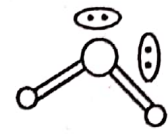
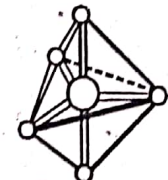
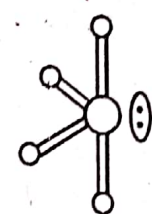



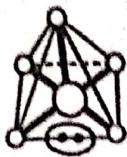
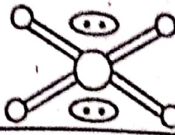


Table 2.2: Molecular geometries according to the VSEPR Theory

NO. of Electron Pairs	Number of lone pairs	Molecular geometry	Examples
2	0	Linear	 $\text{BeCl}_2, \text{HgCl}_2$
3	0	Trigonal Planar	 $\text{BF}_3, \text{BCl}_3, \text{HCHO}$
3	1	Trigonal	 $\text{SO}_2$
4	0	Tetrahedral	 $\text{CH}_4, \text{BF}_4^-$
4	1	Trigonal Pyramidal	 $\text{NH}_3, \text{PCl}_3, \text{PH}_3, \text{AsCl}_3$
4	2	Bent.(angular) V-shaped	 $\text{H}_2\text{O}, \text{H}_2\text{S}$
5	0	Trigonal bipyramidal	 $\text{PCl}_5, \text{SbCl}_5$
5	1	Seesaw (Irregular tetrahedral)	 $\text{SF}_4, \text{TeCl}_4$
5	2	T-shaped	 $\text{ClF}_3, \text{BrF}_3$
5	3	Linear	 $\text{XeF}_2$

NO. of Electron Pairs	Number of lone pairs	Molecular geometry	Examples
6	0	Octahedral	 SF <sub>6</sub>
6	1	Tetragonal Pyramidal (Square Pyramidal)	 BrF <sub>5</sub> , IF <sub>5</sub>
6	2	Square Planar	 ICl <sub>4</sub> <sup>-</sup>

### Example 2.1.

Predict the geometry of the NOCl molecule.

Solution: i. The Lewis structure for NOCl is  $\text{:}\ddot{\text{Cl}}-\ddot{\text{N}}=\ddot{\text{O}}\text{:}$

- ii. The central atom is the N atom.
- iii. There are two atoms and one lone pair on the N atom, so we count three valence shell electron pairs.
- iv. VSEPR theory predicts trigonal planar geometry for three electron pairs.
- v. The atoms lie in the same plane but not on the same line.

A lone pair affects the structure more than a double bond.


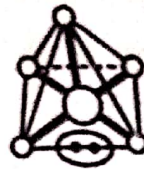
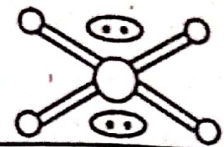
Thus it has angular geometry and the measured angle is 116°



### 2.12 Valence Bond Theory

The VSEPR theory is quite successful in explaining and predicting molecular geometry, but does not describe *how* bonding occurs and *where* bonding occurs, as well as where lone pairs of valence electrons are directed. Also, it does not permit a prediction of bond energies, bond lengths etc. In order to find the answer to these questions, the methods of wave mechanics have been employed. Two approaches have been used for the purpose of describing the covalent bond and electronic structures of molecules. Each approach employed quantum mechanics. The first approach, called the valence bond theory and the second called the molecular orbital theory. Both approaches are based on the concept of orbitals.

The **valence Bond (VB) theory** is based upon the assumption that half-filled atomic orbitals of combining atoms interact to form bigger new orbitals called *molecular orbitals*. These new orbitals are responsible for making the system to be a stable one. Heitler and London (1927) proposed that the electron wave of the valence orbital on one atom 'overlaps' the electron wave of the other bonding orbital to form a covalent bond. The essential conditions for the overlap of electron waves of orbitals are:

0	Octahedral		$SF_6$
1	Tetragonal Pyramidal (Square Pyramidal)		$BrF_5, IF_5$
2	Square Planar		$ICl_4$

### Example 2.1.

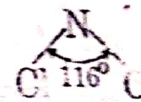
Predict the geometry of the NOCl molecule.

**Solution:** i. The Lewis structure for NOCl is  $:\ddot{Cl}-\ddot{N}=\ddot{O}$

- ii. The central atom is the N atom.
- iii. There are two atoms and one lone pair on the N atom, so we count three valence shell electron pairs.
- iv. VSEPR theory predicts trigonal planar geometry for three electron pairs.
- v. The atoms lie in the same plane but not on the same line.

A lone pair affects the structure more than a double bond.

Thus it has angular geometry and the measured angle is  $116^\circ$ .



## 2.12 Valence Bond Theory

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1. The two overlapping orbitals must be valence orbitals, must be half-filled and must retain their identities. All other orbitals on the atoms remain undisturbed.

2. The half-filled valence orbitals of the atoms should approach sufficiently close to one another with the axis of their orbitals in proper alignment.

Let us see how valence bond theory explains the formation of  $H_2$  molecule starting from H atoms. We begin when two hydrogen atoms are far apart so that no interaction occurs. They are each described as either  $1s_A$  or  $1s_B$  and if electron 1 occupies atom A and electron 2 occupies atom B, the wave function for the pair is:

$$\psi = \psi_{1s_A}(1) \psi_{1s_B}(2) \quad (1)$$

Note that the wave functions of separate systems are multiplied to produce the overall function. This is an accurate description when the atoms are infinitely separated.

As the two hydrogen atoms approach each other, the electron of one atom is attracted to the nucleus of the other. The electrostatic attraction increases steadily as the distance shortens. However, repulsion between electron-electron and nucleus-nucleus also become important. The attractive and repulsive forces are balanced at an internuclear distance of 0.074 nm, the actual distance between two hydrogen nuclei in an  $H_2$  molecule and the system has its lowest (minimum) energy -436 kJ/mol corresponding to the most stable arrangement. The plot of potential

energy versus internuclear distance for two hydrogen atoms is shown in Fig. 2.22. The valence bond theory assumes that it is also an adequate description when the atoms are at their equilibrium separation in the molecule. In the electrostatic analysis, we treat the electrons as distinguishable particles. It turns out that we really do not know which electron is which i.e., it is impossible to say whether it is electron 1 that is in  $1s_A$  and electron 2 in  $1s_B$ , or vice versa. When we take this into account, the electrons are given a little more freedom, which leads to a lower energy. In quantum mechanics, this effect is described in terms of

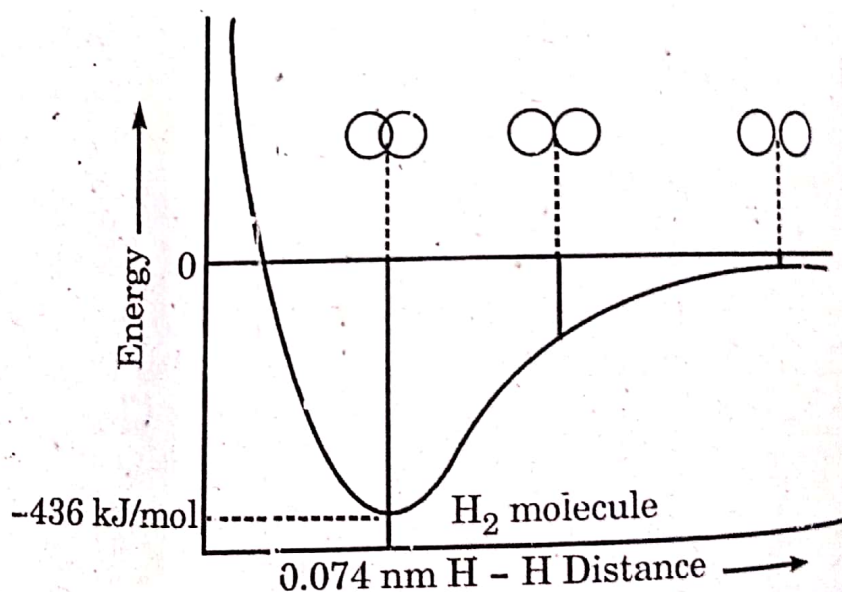


Fig. 2.22. Energy of the  $H_2$  molecule as a function of the distance between the two nuclei. The lowest point on the curve -436 kJ/mol, corresponds to the internuclear distance observed in the  $H_2$  molecule, 0.074 nm. Energy is compared to that of two separated hydrogen atoms, which is defined as zero.

25.2 kJ/mole

"orbital overlap". We say that  $H_2$  molecule is stabilized by the overlap of the two  $1s$  orbitals. Each electron, in effect, is spread over both orbitals. Therefore, the wave function  $\psi_{1s_A}$  (2) and  $\psi_{1s_B}$  (1) is admitted as an equally valid description and the valence bond wave function  $\psi_{1s_{v.b}}$  for the pair of electrons in the molecule may be taken to be a linear combination of the two products and is written as:

$$\psi_{v.b} = \psi_{1s_A} (1) \psi_{1s_B} (2) + \psi_{1s_A} (2) \psi_{1s_B} (1) \quad (2)$$

In  $H_2$  molecule, because of symmetry, the wave function would contribute equally well. The probability density of the electrons in the molecule is proportional to the square of the VB wave function:

$$\psi_{v.b}^2 = \psi_{1s_A} (1)^2 \psi_{1s_B} (2)^2 + \psi_{1s_A} (2)^2 \psi_{1s_B} (1)^2 + 2 \psi_{1s_A} (1) \psi_{1s_B} (1) \psi_{1s_A} (2) \psi_{1s_B} (2) \quad (3)$$

Such an interaction is more like a covalent bond in which one electron is shared equally between the two atoms. The terms  $\psi_{1s_A} (1) \psi_{1s_B} (2)$  and  $\psi_{1s_A} (2) \psi_{1s_B} (1)$  represent enhancement of electron density in the overlap region. Therefore, the strength of the bond in VB theory can be a measure of accumulation of electron density in the internuclear region. The VB approach treats the bond as purely covalent.

The valence bond description of  $H_2$  (and any other diatomic molecule) could be improved by adding terms that permit both electrons to appear in the same atom to some extent. A wave function that puts both electrons into  $1s_A$  is  $\psi_{1s_A} (1) \psi_{1s_A} (2)$ . If both are in  $1s_B$  the wave function contains a term  $\psi_{1s_B} (1) \psi_{1s_B} (2)$ . Since both  $H^+H^+$  and  $H^+H^-$  are equally probable the original valence bond wave function ought to be augmented by an ionic contribution;

$$\psi_{ionic} = \psi_{1s_A} (1) \psi_{1s_A} (2) + \psi_{1s_B} (1) \psi_{1s_B} (2) \quad (4)$$

The new, improved wave function is therefore ;

$$\psi = \psi_{v.b}(\text{Covalent}) + c \psi_{ionic}$$

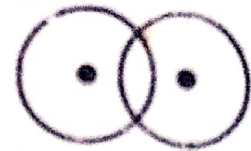
Where the value of  $c$  governs the extent of ionic character mixed into the original purely covalent v.b. structure. The improvement of the wave function by this admixture is called **ionic-covalent resonance**, and the improvement in energy can be traced to the extra freedom it gives to the distribution of the electrons.

The actual value of  $c$  is about 0.25, which indicates that the ionic structures contribute about  $c^2 \sim 0.06$  or 6 per cent to the overall structure of  $H_2$ . In heteronuclear molecules the ionic terms are much more important, and in species like  $NaCl$  they wholly dominate the vestigial covalent character.

The formation of an electron pair covalent bond in  $H_2$  molecule is based on the following assumption s.

1. Each hydrogen atom has a partially filled  $1s$  atomic orbital, each having one electron.

2. Heitler and London pointed out that the electrons are indistinguishable and the wave function must express this fact.
3. The molecular wave function  $\psi_{c.b.}$  is obtained by the linear combination of the wave functions of the atomic orbitals using the concept of resonance.
4. The pairing of electrons in the molecule should satisfy the Pauli's exclusion principle and the two electrons should have different values of spin quantum numbers.
5. An attractive force (bond energy) is the result of electron pairing.
6. The electron pair is localized between the two nuclei.
7. The overlapping orbitals have similar symmetry and energy. The orbitals overlap each other to an appreciable extent. Greater the overlap stronger will be the bond formed.



Overlap of 1s orbitals in  $H_2$  ( $\sigma$  bond)

The description of the  $H_2$  molecule may be generalized that a covalent bond arises from the exchange forces between a pair of electrons with opposite spin.

### 2.13 Sigma ( $\sigma$ ) and Pi ( $\pi$ ) Bonds

A molecular orbital (MO) which is symmetrical about the line joining the two nuclei and is occupied by a pair of electrons, is called a sigma ( $\sigma$ ) molecular orbital ( $\sigma$ -MO) and the linkage thus established is called a sigma bond. Although the electrons have freedom within the entire region of MO, the probability of finding these electrons is greatest between the two nuclei on the bond axis. A straight line joining the two nuclei of bonded atoms is called bond axis. All single bonds are sigma bonds and they are formed by end-to-end or head on overlap of the atomic orbitals. A single bond is formed by the overlap of two s-orbitals, an s-orbital with one p-orbital, or two p orbitals as shown in Fig. 2.23. A bond in which the electron distribution is concentrated along the internuclear axis and possesses axial symmetry is called sigma ( $\sigma$ ) bond.

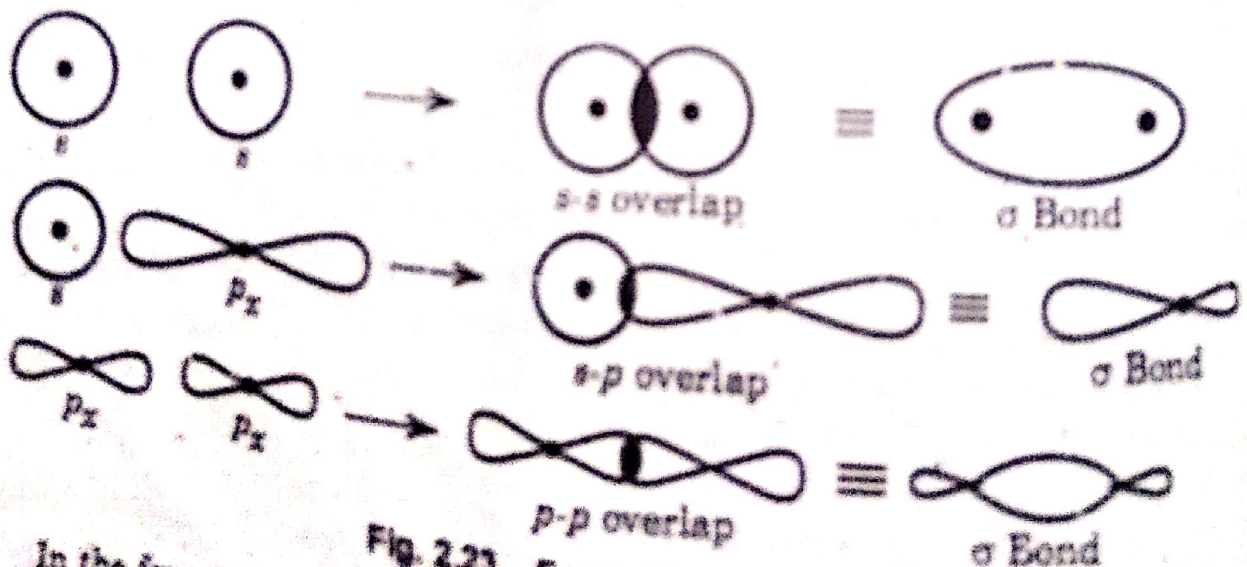
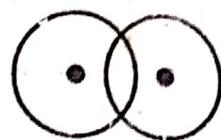


Fig. 2.23. Formation of  $\sigma$  bonds

In the formation of hydrogen fluoride molecule, the half-filled 1s orbital of hydrogen overlaps with the half-filled 2p orbital of fluorine.

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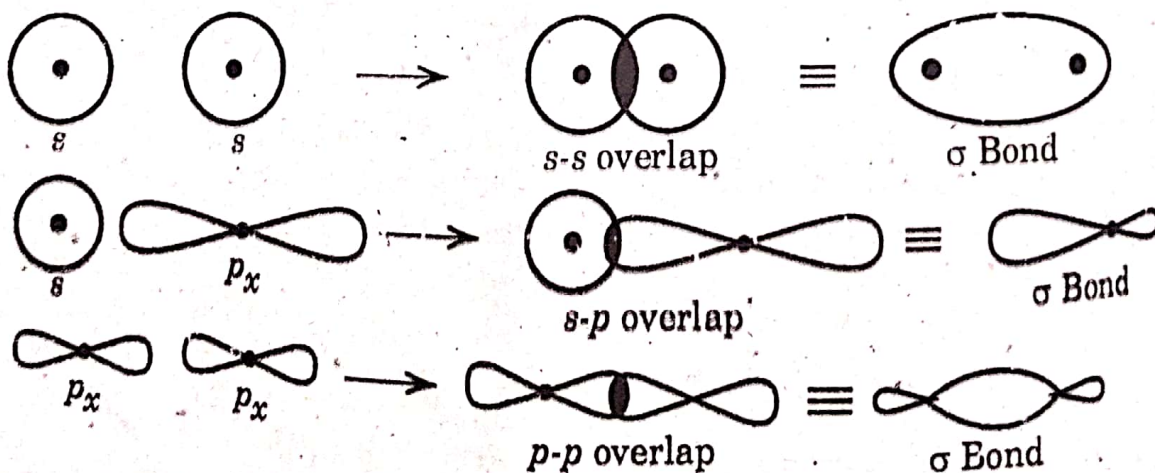
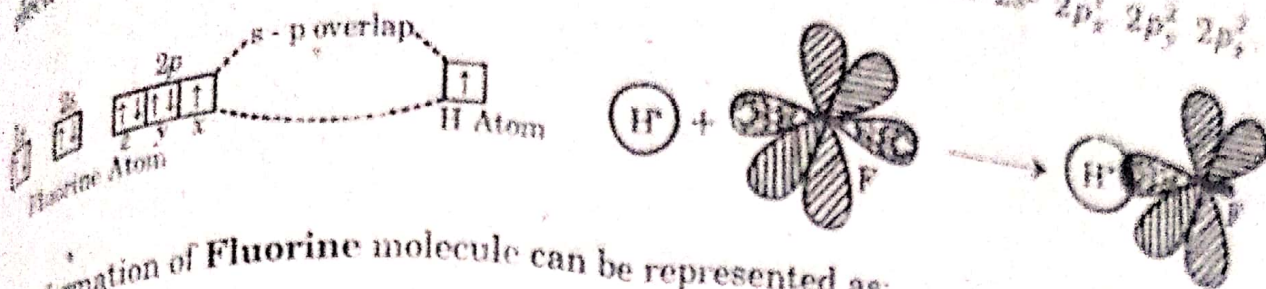


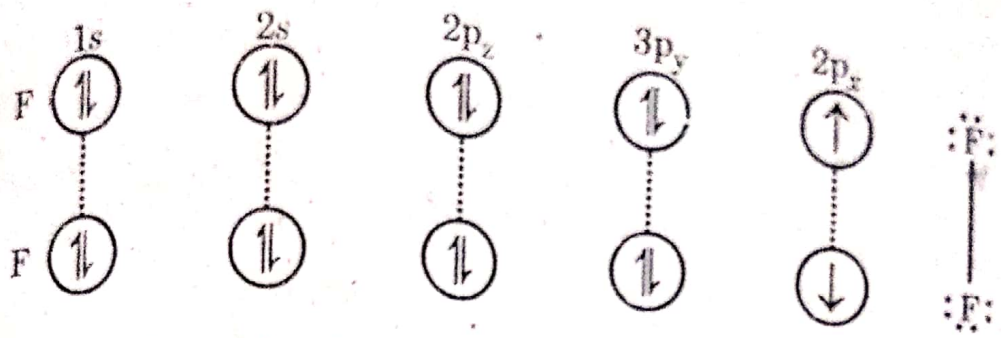
Fig. 2.23. Formation of  $\sigma$  bonds

In the formation of hydrogen fluoride molecule, the half-filled 1s orbital of hydrogen overlaps with the half-filled  $2p_x$  orbital of F atom and this allows pairing of

electrons to form  $\sigma$  bond. The electronic configuration of F atom is  $1s^2 2s^2 2p_x^1 2p_y^2 2p_z^2$ .



The formation of Fluorine molecule can be represented as:



**Pi ( $\pi$ ) Bond:** A bond resulting from the side-wise overlap of two half-filled, parallel  $p$ -orbitals in which the regions of electron density (cloud) are above and below the internuclear axis is called  $\pi$  bond. The internuclear axis lies in the nodal plane. The molecular orbital (MO) thus formed is called Pi ( $\pi$ ) molecular orbital. It should be noted that the  $p$  orbitals have parallel axes and should be coplanar (in one plane). It should be noted that:

- (i) A  $\pi$  molecular orbital involves an overlap at both the lobes of the  $p$ -orbitals, whereas in a sigma bond the overlap takes place in a single region.
- (ii) Sigma ( $\sigma$ ) molecular orbital do not have a nodal plane which contains the nuclear axis, whereas a  $\pi$ MO possesses a nodal plane containing the nuclei and dividing the orbital into two halves.  $\pi$ MO possesses 'sausage-like' regions parallel to the nodal plane passing through the two nuclei.

Let us take the example of oxygen molecule. Oxygen atom has the electronic configuration  $1s^2 2s^2 2p_x^1 2p_y^2 2p_z^2$ . Each oxygen atom has two half-filled  $p$  orbitals. The two  $p_x$  orbitals overlap end to end to form a  $\sigma$  bond. The  $2p_y$  orbitals overlap sidewise to form a  $\pi$  bond. The formation of  $\sigma$  and  $\pi$  bonds in  $O_2$  molecule is shown in Fig. 2.24.

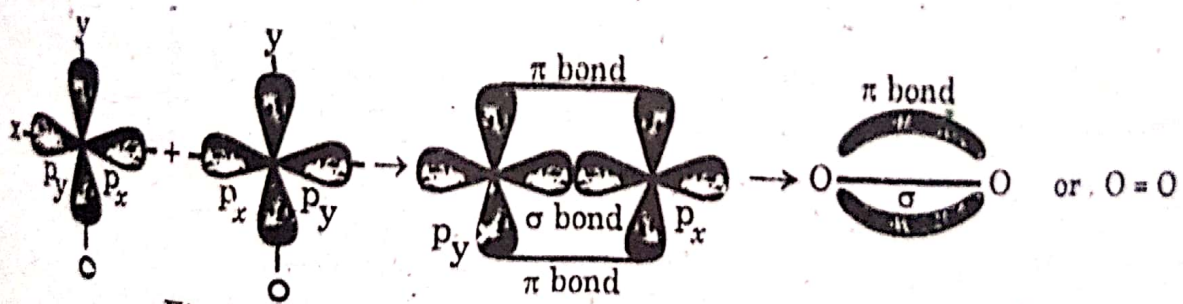


Fig. 2.2  $\sigma$  and  $\pi$ -bonds formation in  $O_2$  molecule

The formation of  $O_2$  molecule based on VB theory can be represented as: