

Chemical Bond

■ A chemical bond is defined as a force that acts between two or more atoms to hold them together as a stable molecule.

There are three different types of bonds recognized by chemists:

(1) **Ionic or Electrovalent bond**

(2) **Covalent bond**

(3) **Coordinate covalent bond**

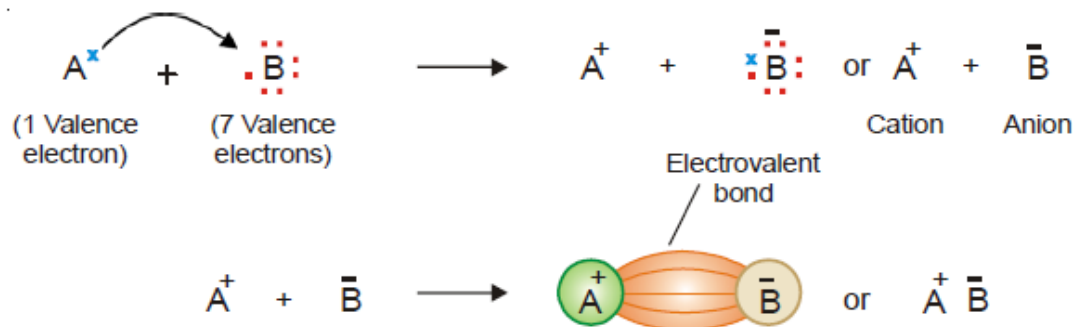
There is a fourth type of bond, namely, the **metallic bond**.

Chemical Bond

■ Ionic Bond

→ This type of bond is established by transfer of an electron from one atom to another.

→ Let us consider a general case; when an atom A has one electron in the valence shell and another atom B has seven electrons. A has one electron in excess and B has one electron short than the stable octet. Therefore, A transfers an electron to B and in this transaction both the atoms acquire a stable electron octet. The resulting positive ion (cation) and negative ion (anion) are held together by electrostatic attraction.



Chemical Bond

■ The electrostatic attraction between the cation (+) and anion (–) produced by electron-transfer constitutes an Ionic or Electrovalent bond.

The compounds containing such a bond are referred to as Ionic or Electrovalent Compounds.

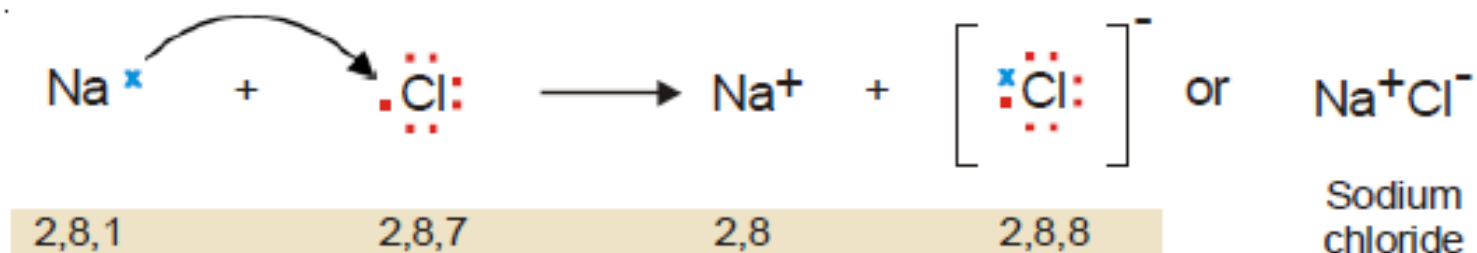
■ **Example:**

A simple sodium chloride molecule is formed from an atom of sodium (Na) and one atom of chlorine (Cl).

Na (2, 8, 1) has one valence electron, while Cl (2, 8, 7) has seven. Na transfers its valence electron to Cl, and both achieve stable electron octet.

Thus Na gives Na^+ and Cl gives Cl^- ion, and the two are joined by an ionic bond.

Chemical Bond



■ Characteristics of Ionic Compounds

- Solids at Room Temperature.
- High Melting Points.
- Hard and brittle.
- Soluble in water.
- Conductors of electricity.
- Do not exhibit isomerism.
- Ionic reactions are fast.

Chemical Bond

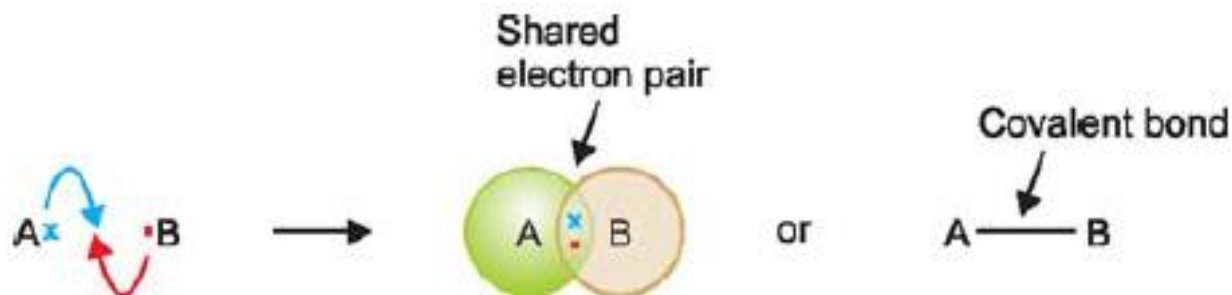
■ Covalent Bond

→ The electron transfer theory could not explain the bonding in molecules such as H_2 , O_2 , Cl_2 etc., and in organic molecules, that had no ions.

It was G.N. Lewis who suggested that two atoms could achieve stable 2 or 8 electrons in the outer shell by sharing electrons between them.

Let us consider a general case where an atom A has one valence electron and another atom B has seven valence electrons. As they approach each other, each atom contributes one electron and the resulting electron pair fills the outer shell of both the atoms. Thus A acquires stable 2 electrons and B, 8 electrons in the outer shell.

Chemical Bond



■ The shared pair is indicated by a dash (—) between the two bonded atoms. A shared pair of electrons constitutes a Covalent bond or Electron-pair bond.

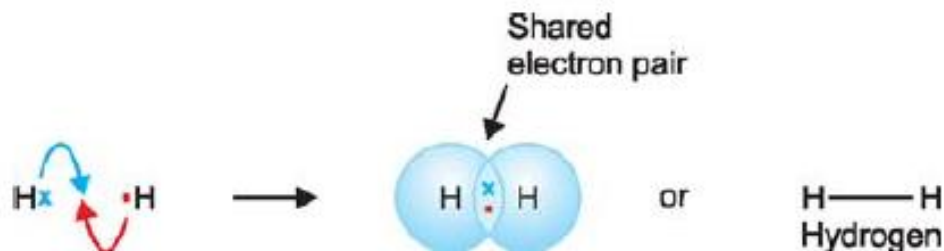
■ The attractive force between atoms created by sharing of an electron-pair.

■ The compounds containing a covalent bond are called **covalent compounds**.

Chemical Bond

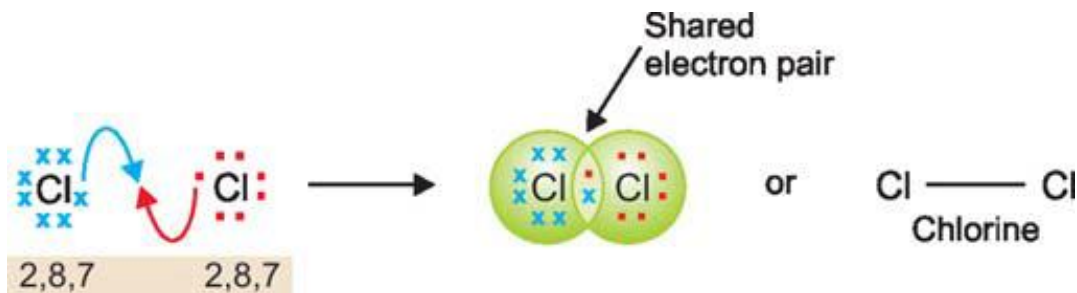
■ Hydrogen, H_2

Hydrogen molecule is made of two H atoms, each having one valence electron. Each contributes an electron to the shared pair and both atoms acquire stable helium configuration. Thus stable H_2 molecule results.



■ Chlorine, Cl_2

Each Cl atom (2, 8, 7) has seven valence electrons. The two Cl atoms achieve a stable electron octet by sharing a pair of electrons and forms Cl_2 .



Chemical Bond

■ Characteristics of Covalent Compounds:

- Gases, liquids or solids at room temperature.
- Low melting points and boiling points.
- Neither hard nor brittle.
- Soluble in organic solvents.
- Non-conductors of electricity.
- Exhibit Isomerism.
- Molecular reactions.

Chemical Bond

■ Co-ordinate Covalent Bond:

→ In a normal covalent bond, each of the two bonded atoms contributes one electron to make the shared pair. In some cases, a covalent bond is formed when both the electrons are supplied entirely by one atom. Such a bond is called co-ordinate covalent or dative bond.

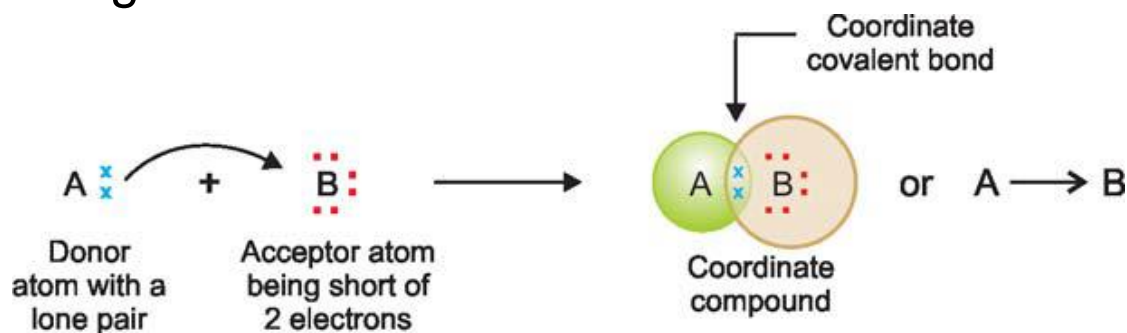
→ **It may be defined as : a covalent bond in which both electrons of the shared pair come from one of the two atoms (or ions).**

→ The compounds containing a coordinate bond are called coordinate compounds.

Chemical Bond

■ Co-ordinate Covalent Bond:

■ If an atom A has an unshared pair of electrons (lone pair) and another atom B is short of two electrons than the stable number, coordinate bond is formed. A donates the lone pair to B which accepts it. Thus both A and B achieve the stable 2 or 8 electrons, the lone pair being held in common.



■ The atom A which donates the lone pair is called the donor, while B which accepts it the acceptor.

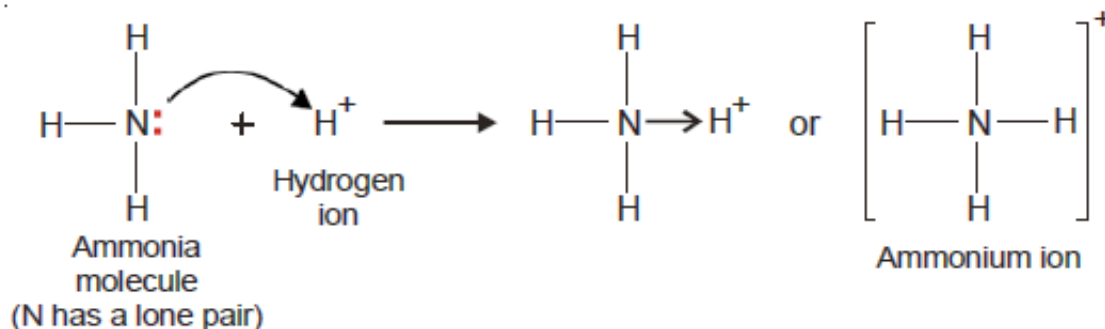
■ The bond thus established is indicated by an arrow pointing from A to B.

Chemical Bond

■ Example:

■ Ammonium ion, NH_4^+

In ammonia molecule, the central N atom is linked to three H atoms and yet N has an unshared pair of electrons. The H^+ ion furnished by an acid has no electron to contribute and can accept a pair of electrons loaned by N atom. Thus, NH_3 donates its unshared electrons to H^+ forming ammonium ion.



■ All the N–H bonds in NH_4^+ are identical, once the coordinate bond $\text{N} \rightarrow \text{H}^+$ is established.

Chemical Bond

■ Lewis Dot Symbols:

→ To keep track of valence electrons in a chemical reaction, and to make sure that the total number of electrons does not change, chemists use a system of dots devised by Lewis called Lewis dot symbols.

→ **A Lewis dot symbol consists of the symbol of an element and one dot for each valence electron in an atom of the element.**

→ A formula using dots to represent valence electrons is called a Lewis electron-dot formula. An electron pair represented by a pair of dots in such a formula is either a bonding pair (an electron pair shared between two atoms) or a lone, or nonbonding, pair (an electron pair that remains on one atom and is not shared).

Chemical Bond

■ Lewis Dot Symbols:

Step 1: Calculate the total number of valence electrons for the molecule by summing the number of valence electrons (group number) for each atom. If you are writing the Lewis formula of a polyatomic anion, you add the number of negative charges to this total.

Step 2: Write the skeleton structure of the molecule or ion, connecting every bonded pair of atoms by a pair of dots (or a dash).

Step 3: Distribute electrons to the atoms surrounding the central atom (or atoms) to satisfy the octet rule for these surrounding atoms.

Chemical Bond

■ Lewis Dot Symbols:

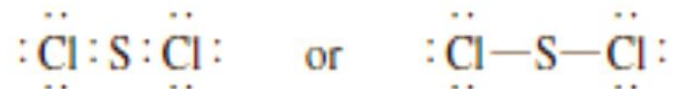
Step 4: Distribute the remaining electrons as pairs to the central atom (or atoms), after subtracting the number of electrons already distributed from the total found in Step 1. If there are fewer than eight electrons on the central atom, this suggests that a multiple bond is present. (Two electrons fewer than an octet suggests a double bond; four fewer suggests a triple bond or two double bonds.) To obtain a multiple bond, move one or two electron pairs (depending on whether the bond is to be double or triple) from a surrounding atom to the bond connecting the central atom. Atoms that often form multiple bonds are C, N, O, and S.

Chemical Bond

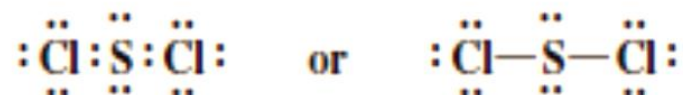
→ **Write the Lewis formula for the molecule SCl_2 :**

- (1) Calculate the total number of valence electrons.
- (2) Write the skeleton structure with two electrons to each bond between atoms.
- (3) Distribute electrons to the outer atoms to satisfy the octet rule.
- (4) Distribute the remaining electrons to the central atom.

Solution The number of valence electrons from an atom equals the group number: 6 for S, 7 for each Cl, for a total of 20 electrons. You expect the skeleton structure to have S as the central atom, with the more electronegative Cl atoms bonded to it. After connecting atoms by electron pairs and distributing electrons to the outer atoms, you have



This accounts for 8 electron pairs, or 16 electrons. Subtracting this from the total number of electrons (20) gives 4 electrons, or 2 electron pairs. You place these on the central atom (S). The final Lewis formula is



Chemical Bond

■ Geometries of Molecules:

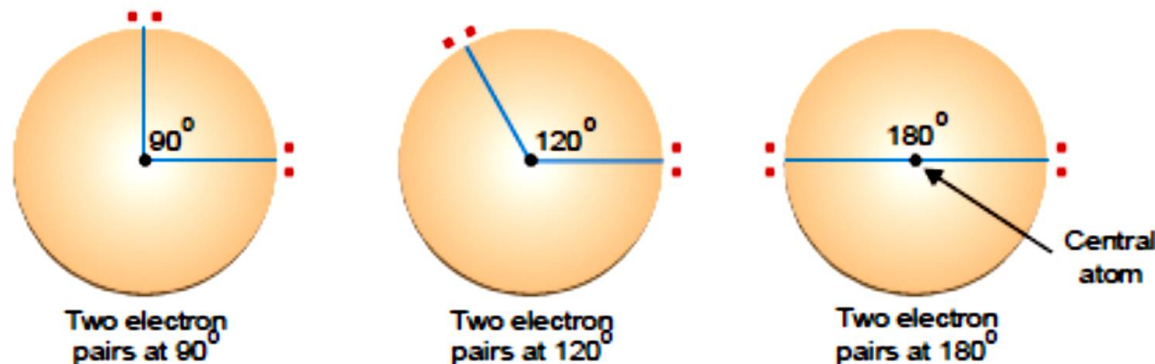
→ So far we have depicted molecules by Lewis structures in the flat plane of paper. But all molecules containing three or more atoms are three-dimensional. The shape of a particular molecule is determined by the specific arrangement of atoms in it and the bond angles. Molecular shapes may be linear, bent (or angular), trigonal planar, pyramidal or tetrahedral.

→ The shapes of molecules can be determined in the laboratory by modern methods such as X-ray and electron diffraction techniques. Molecular shapes are important because they are helpful in the investigation of molecular polarity, molecular symmetry or asymmetry. Physical and chemical properties of compounds depend on these factors.

Chemical Bond

■ Vsepr Theory:

→ Valence-Shell Electron Pair Repulsion or VSEPR (pronounced as 'Vesper') theory. It states that : The electron pairs (both lone pairs and shared pairs, surrounding the central atom will be arranged in space as far apart as possible to minimise the electrostatic repulsion between them.



→ Arrangement of two electron pairs on circle at 90° , 120° and at 180° . Placement of electron pairs at 180° puts them the farthest apart, thereby minimising the electrostatic repulsion.

Chemical Bond

■ Geometries of Molecules:

→ VSEPR theory is simple but remarkably powerful model for predicting molecular geometries and bond angles. While working out the shapes of molecules from this theory, it must be remembered:

(1) Multiple bonds behave as a single electron-pair bond for the purpose of VSEPR. They represent a single group of electrons.

(2) Order of repulsions between lone pair and lone pair (lp - lp), lone pair and bonding pair (lp - bp), and bonding pair and bonding pair (bp - bp) is;

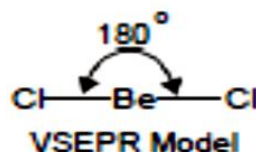
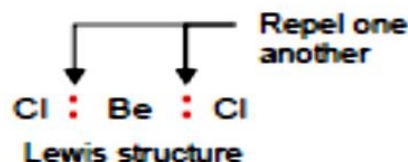
$$\text{lp} - \text{lp} > \text{lp} - \text{bp} > \text{bp} - \text{bp}$$

When a molecule has lone pairs of electrons, the bonding electron pairs are pushed closer and thus the bond angle is decreased.

Chemical Bond

(1) Linear Molecules

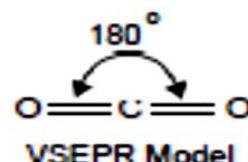
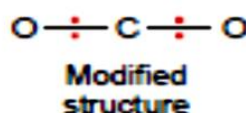
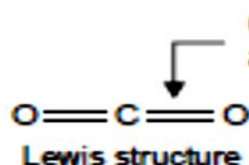
(a) Beryllium chloride, BeCl_2 . It has the Lewis structure



■ **Figure 5.15**
Geometry of BeCl_2 molecule.

The central atom Be has two bonding electron pairs and no unshared electron. According to VSEPR theory, the bonding pairs will occupy positions on opposite sides of Be forming an angle of 180° . An angle of 180° gives a straight line. Therefore, BeCl_2 molecule is linear. In general, all molecules as A-B-A which have only two bonds and no unshared electrons are linear.

(b) Carbon dioxide, CO_2 . It has the structure



■ **Figure 5.16**
Geometry of CO_2 molecule.

The central C atom has no unshared electron. We know that a double bond counts the same as a single bond in VSEPR model. Thus CO_2 is a linear molecule.

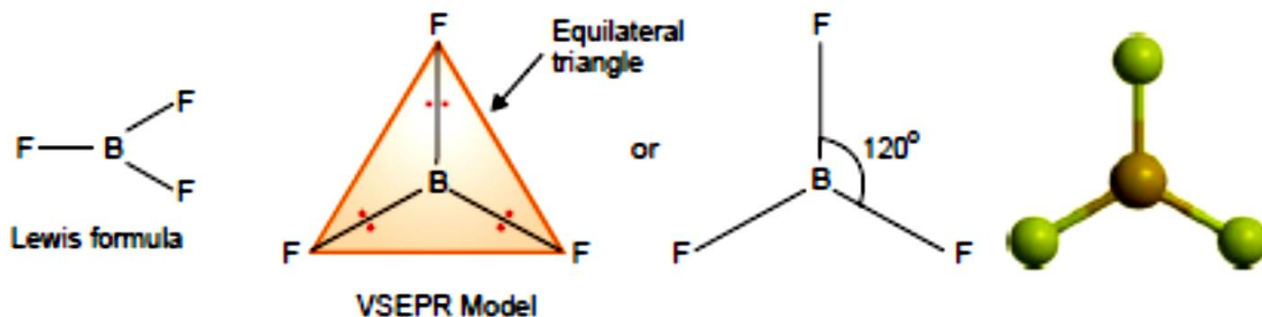
Similarly, it can be shown that hydrogen cyanide ($\text{H} - \text{C} \equiv \text{N}$) and acetylene ($\text{H} - \text{C} \equiv \text{C} - \text{H}$) are linear molecules.



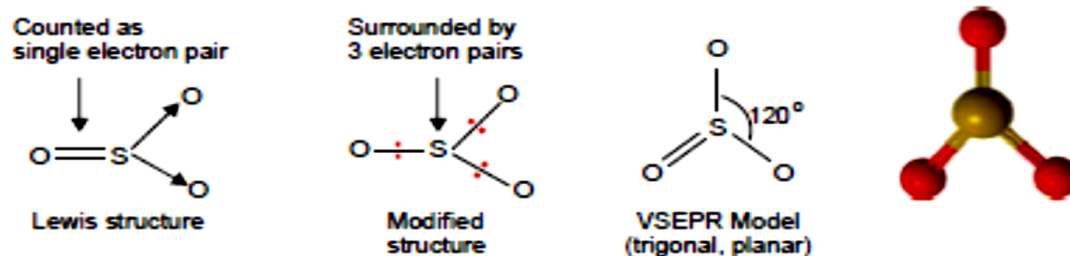
Chemical Bond

(2) Trigonal Planar Molecules

(a) **Boron trifluoride, BF_3 .** Its Lewis structure shows that the central atom B has three bonding electron pairs and no unshared electrons. VSEPR theory says that the three bonding electron pairs will be as far apart as possible. This can be so if these electron pairs are directed to the corners of an equilateral triangle. Thus VSEPR model of BF_3 molecule has three F atoms at the corners of the triangle with B atom at its centre. All the four atoms (three F and one B) lie in the same plane. Therefore, the shape of such a molecule is called trigonal planar. The bond angle is 120° .



(b) **Sulphur trioxide, SO_3 .** In the Lewis structure of SO_3 , the central S atom is joined with two O atoms by covalent bonds. The third O atom is joined with S by a double bond. But a double bond is counted as a single electron pair for the purpose of VSEPR model. Therefore, in effect, S has three electron pairs around it. Thus like BF_3 , SO_3 has trigonal planar geometry.

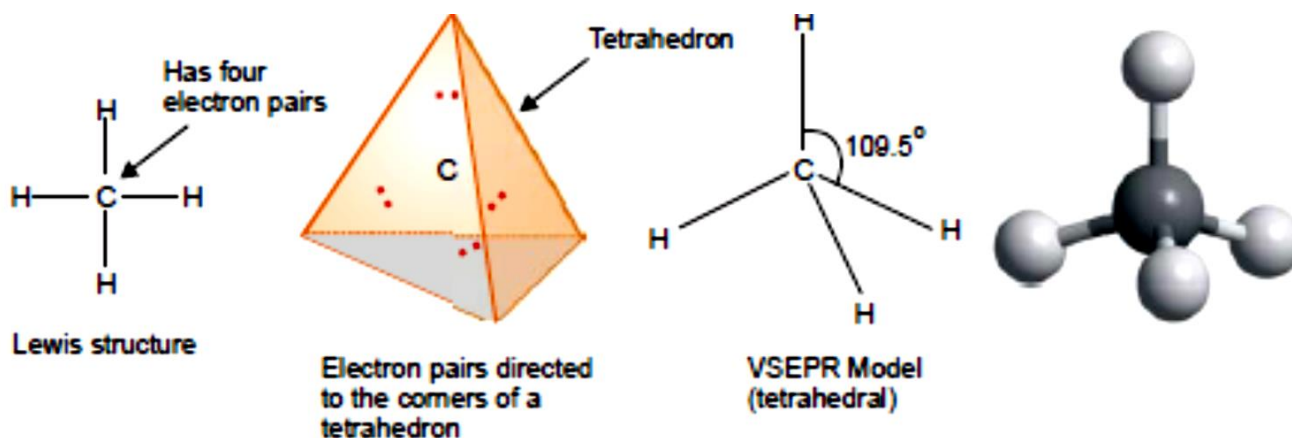


Chemical Bond

■ Tetrahedral Molecules:

→ (a) **Methane, CH₄:**

Lewis structure of methane shows that the central C atom has four bonding electron pairs. These electron pairs repel each other and are thus directed to the four corners of a regular tetrahedron. A regular tetrahedron is a solid figure with four faces which are equilateral triangles. All bond angles are 109.5°.

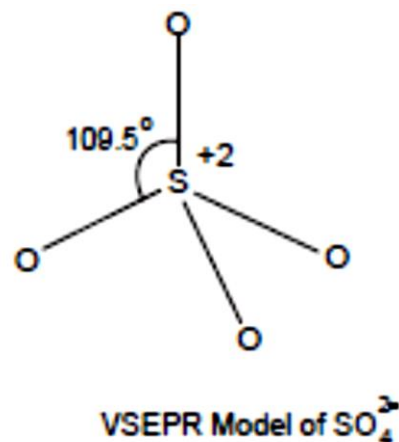
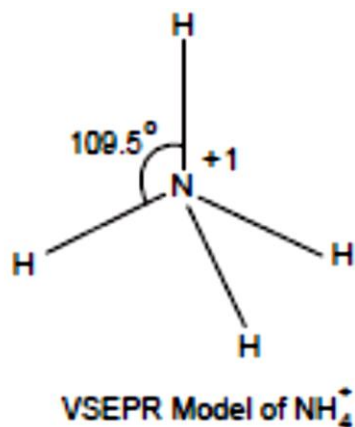


Chemical Bond

■ Tetrahedral Molecules:

→ (b) **Ammonium ion, NH_4^+ , and Sulphate ion, SO_4^{2-} :**

The N atom in NH_4^+ and S atom in SO_4^{2-} have four electron pairs in the valence shell. These are directed to the corners of a tetrahedron for maximum separation from each other. Thus both NH_4^+ and SO_4^{2-} have tetrahedral shape.



Chemical Bond

■ (4) Pyramidal Molecules:

→ (a) Ammonia molecule:

According to VSEPR theory, a lone pair exerts greater repulsion on the bonding electron pairs than the bonding pairs do on each other. As a result, the bonds of NH_3 molecule are pushed slightly closer. This explains why the observed bond angle $\text{H}-\text{N}-\text{H}$ is found to be 107.3° instead of 109.5° predicted from tetrahedral geometry.

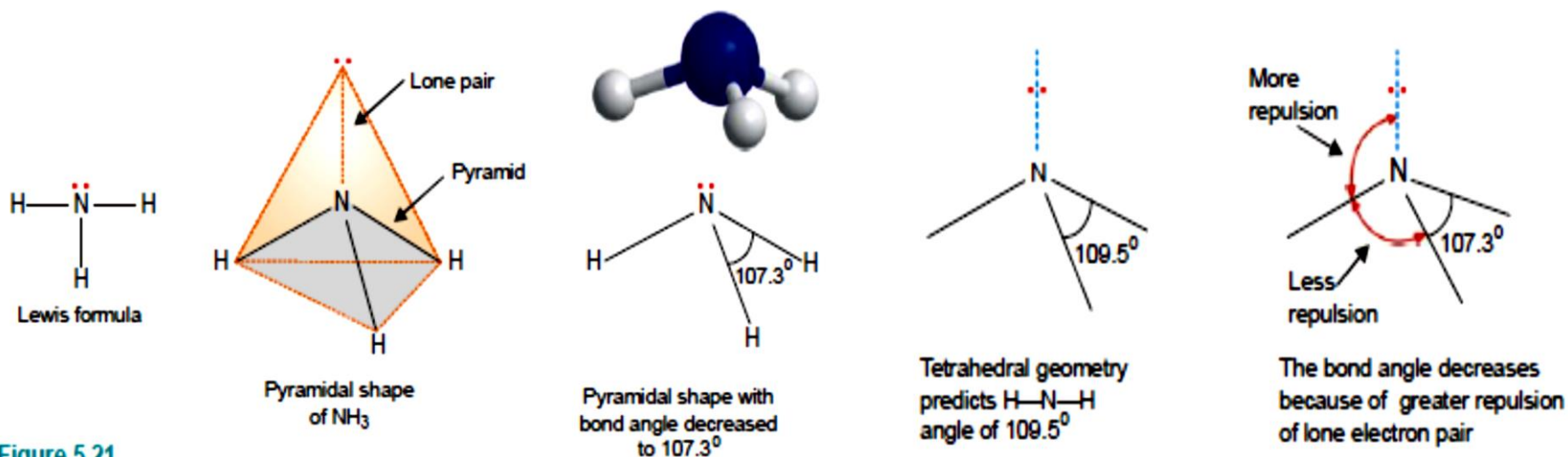


Figure 5.21

Chemical Bond

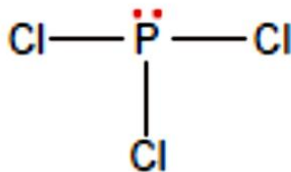
■ (4) Pyramidal Molecules:

All molecules in which the N atom is joined to three other atoms by covalent bonds, have pyramidal shape.

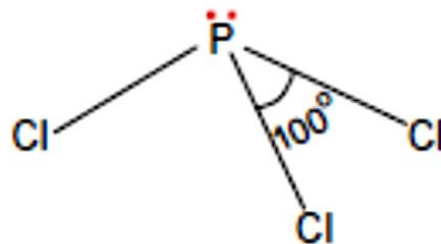
For example, amines RNH_2 , R_2NH and R_3N have pyramidal shape.

→ (b) **Phosphorus trichloride, PCl_3 :**

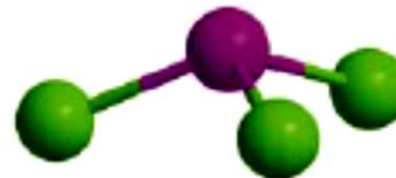
The structural formula indicates that the central phosphorus atom has three bonding electron pairs and one lone electron pair. Thus, like NH_3 it has pyramidal shape and the observed bond angle $Cl-P-Cl$ is 100° .



Lewis formula



Pyramidal PCl_3 molecule



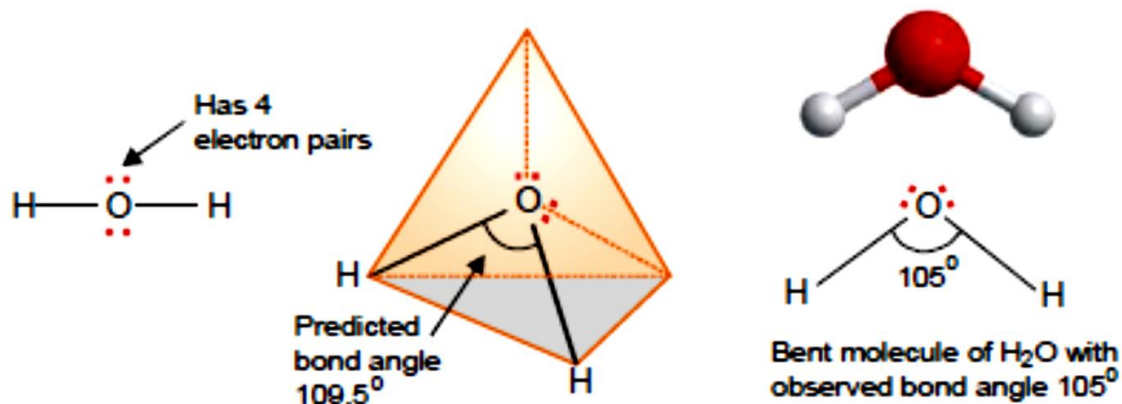
Chemical Bond

■ (5) Bent or Angular Molecules:

→ (a) **Water, H_2O :**

In the structural formula of H_2O , the O atom is bonded to two H atoms by covalent bonds and has two lone pairs. Thus O is surrounded by two bonding electron pairs and two unshared electron pairs. VSEPR theory says that in order to secure maximum separation between them, the four electron pairs are directed to the corners of a tetrahedron. If we look at the three atoms (and ignore the unshared pairs), the atoms HOH lie in the same plane and the predicted bond angle is 109.5° . But with two unshared pairs repelling the bonding pairs, the bond angle is compressed to 105° , the experimental value. Thus the H_2O molecule is flat and bent at an angle at the O atom.

Chemical Bond



→ (b) **Sulphur dioxide, SO_2 :**

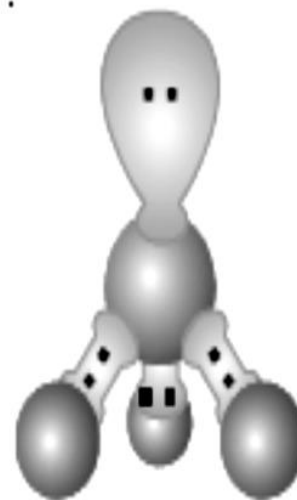
(b) In VSEPR model a double bond is counted as a single electron pair. That way, the S atom is surrounded by three electron pairs, two bonding pairs and one unshared pair. For maximum separation the three electron pairs are directed to the corners of an equilateral triangle. The predicted bond angle is 120° . But with the unshared electron pair repelling the bonding electron pairs, the bond angle is actually reduced somewhat. Thus SO_2 has a planar bent molecule with the observed bond angle 119.5° .

Chemical Bond

HOW TO WORK OUT THE SHAPE OF A MOLECULE

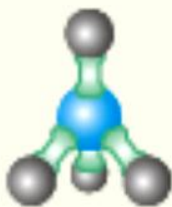


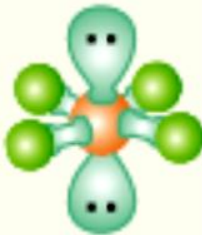
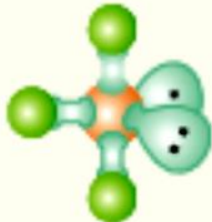
It is possible to work out the shape of a small molecule that has a formula XY_n by applying a few simple rules. We will use ammonia as an example to illustrate the idea.

- Rule 1 First find the number of bonding pairs of electrons in the molecule. The number of bonding pairs of electrons in the molecule NH_3 can be seen in the formula. There must be three bonding pairs of electrons holding the three hydrogens onto the nitrogen.
- Rule 2 Find the number of valence electrons (electrons in the outer energy level) on an atom of the central atom (The one of which there is only one.) Nitrogen is in group V, so the nitrogen has five electrons in the outer energy level.
- Rule 3 Find the number of lone pairs on the central atom by subtracting the number of bonding pairs (3) from the valence electrons (5) to find the number of electrons (2) that will make up lone pairs of electrons. Divide this number by 2 to find the number of lone pairs, $2/2 = 1$.
- Rule 4 Distribute all the electron pairs around the central atom and learn the angles they will make from molecules with no lone pairs.
- Rule 5 Learn that the repulsion between lone pairs of electrons is greater than the repulsion between bonding pairs, and subtract 2° from the bond angles for every lone pair.
- Rule 6 Learn the names of the shapes. The shapes are named from the position of the atoms and not the position of the orbitals.



Chemical Bond

SOME MORE EXAMPLES

Formula	NH_4^+	PCl_5	SF_6	XeF_4	ICl_3
Bonding Pairs	4	5	6	4	3
Valence Electrons	5	5	6	8	7
Rule 2(a)	$5 - 1 = 4$				
Lone Pairs	0	0	0	2	2
Angles between bonding pairs	109.5°	90° & 120°	90°	90°	90°
Name of shape	Tetrahedral	Trigonal Bipyrimid	Octahedron	Square	T shape
					

Chemical Bond

■ Bond Formation (Valence Bond Theory):

Bond formation between atoms to give chemical compounds can be interpreted admirably in terms of the orbital theory of atomic structure.

Heitler and London believed that electron cloud of the valence orbital on one atom 'overlaps' the electron cloud of the other bonding atom to form a covalent linkage. On the contrary, the electrovalent bond formation involves a physical transfer of the electron and the orbital concept is not very useful for their explanation. The theory of 'maximum overlap', affords an excellent interpretation of covalent bond formation. The essential conditions for the overlap of electron waves of orbitals are:

Chemical Bond

■ Bond Formation (Valence Bond Theory):

(1) The orbitals entering into combination must have only one electron.

The orbitals containing a pair of electrons are not capable of combination. In fact, half-filled orbitals on one atom have a tendency to combine with half-filled orbitals on other atom, and the resulting orbital acquires a pair of electrons of opposite spins.

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

The strength of a covalent bond depends upon the extent of overlapping. Greater the overlapping between the atomic orbitals stronger is the bond formed between the two atoms.

Chemical Bond

■ Bond Formation (Valence Bond Theory):

→ The amount of energy given off or released per mole at the time of overlapping of atomic orbitals to form a bond is termed as **Bond Energy or Stabilization Energy**

→ Since the overlapping of atomic orbitals involves a release of energy, it must produce a stabilizing effect on the system. The merger or overlapping of the atomic orbitals halts at a stage when the atomic nuclei have come close enough to exercise a repulsive force on one another, which exactly balances the force of merger. **This equilibrium distance at which the two atomic nuclei are now held is called the Bond length.**

Chemical Bond

■ Bond Formation (Valence Bond Theory):

→ In the bond formation, greater the overlap greater is the energy set free, *i.e.*, the higher will be the bond strength. This implies that for a bond to be stronger, greater should be the overlap which in turn shortens the distance between the nuclei. **A stronger bond has, therefore, a shorter bond length.**

■ Formation of H₂ molecule:

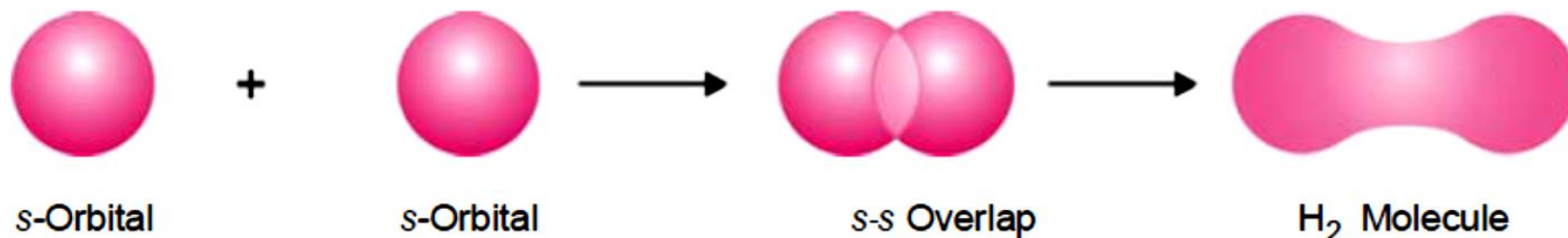
Let us consider the formation of hydrogen molecule (H₂) from two isolated H atoms each having an electron in its 1s orbital. When two H atoms approach each other, their 1s orbitals overlap, resulting in the formation of a bigger electron cloud known as molecular orbital. This new molecular orbital contains both the electrons.

Chemical Bond

■ Bond Formation (Valence Bond Theory):

→ Formation of H_2 molecule:

As a result, the two H atoms are held together in the form of Hydrogen molecule ($H-H$). This overlapping of atomic orbitals of hydrogen atoms is shown following Fig.



Chemical Bond

■ Types of overlapping and Nature of Covalent Bond

A covalent bond is of two types depending on the type of overlapping between the two atoms

(1) Sigma (σ) bond

(2) Pi (π) Bond

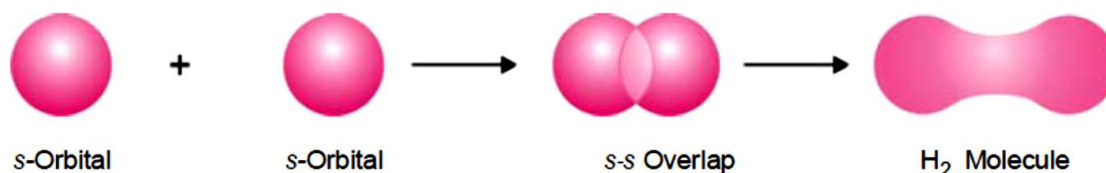
(1) Sigma (σ) Bond

When there is end to end overlapping of atomic orbitals along the internuclear axis, the bond resulted is called sigma (σ) bond. This type of overlapping between the atomic orbitals is also called “head-on” overlapping or “axial” overlapping. It results when one of the following types of overlapping takes place:

Chemical Bond

(a) s – s overlapping

Here s-orbital of one atom overlaps with the s-orbital of other atom. An example of this type of overlapping is the formation of hydrogen molecule from two H-atoms.



(b) s – p overlapping

In this type of overlap s-orbital of one atom overlaps with the half filled p-orbital of the other atom as shown below :

Examples : HF, HCl etc.

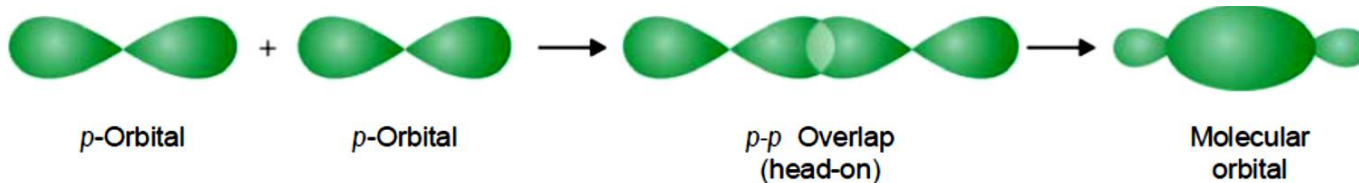


Chemical Bond

(c) p – p overlapping

Here p-orbital of one atom overlaps with the p-orbital of the other atom on internuclear axis. It is shown below :

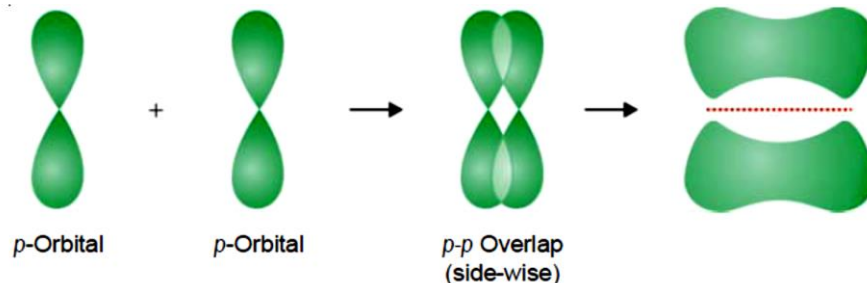
Examples : F_2 , Cl_2 , Br_2 etc.



(2) Pi (π) Bond

This type of covalent bond is formed by the sidewise overlap of the half filled atomic orbitals. It is also called lateral or sidewise overlap.

This type of overlapping takes place perpendicular to the internuclear axis as shown below :



Chemical Bond

■ Strength of σ and π bonds

As mentioned earlier, the strength of a covalent bond depends upon the extent of overlapping between the atomic orbitals of participating atoms. During the formation of σ bond the extent of overlapping is more and hence a Sigma bond is stronger than Pi bond.

Chemical Bond

Sigma (σ) Bond

1. It is formed by *end to end* overlapping of half filled atomic orbitals.
2. Overlapping takes place along internuclear axis.
3. The extent of overlapping is large and bond formed is *stronger*.
4. The molecular orbital formed as a result of overlapping is symmetrical about the internuclear axis.
5. There is free rotation about σ bond and no geometrical isomers are possible.
6. The bond can be present alone.
7. *s* and *p* orbitals can participate in the formation of σ bond.

Pi (π) Bond

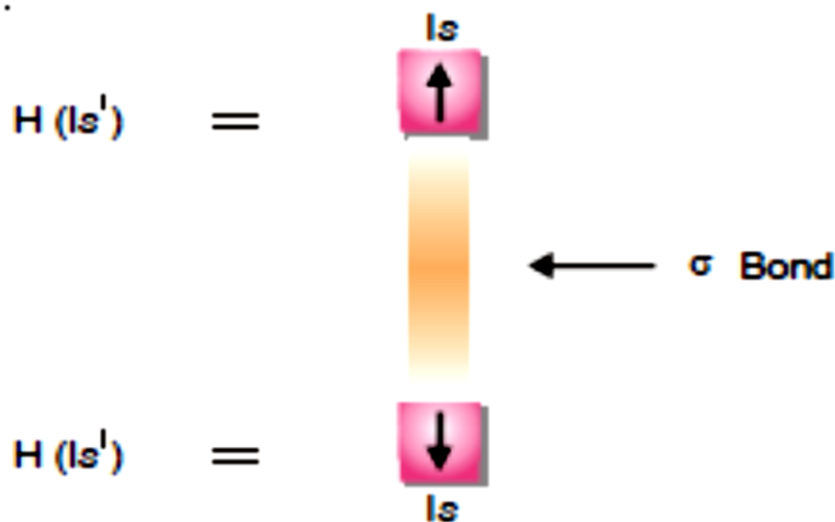
1. It is formed by the sidewise overlapping of half filled *p*-orbitals only.
2. Overlapping takes place perpendicular to internuclear axis.
3. The extent of overlapping is small and bond formed is *weaker*.
4. The molecular orbital formed as a result of overlapping consists of two lobes above and below the internuclear axis.
5. There is no free rotation about π bond and geometrical isomers are possible.
6. The bond is always formed in addition to sigma (σ) bond.
7. Only *p*-orbitals participate in the formation of π bond.

Chemical Bond

■ Orbital Representation of Molecules:

→ (a) Formation of H_2 molecule:

Each hydrogen atom has one electron in 1s-orbital. Two such atoms join to form a molecule of hydrogen. In this case s-s overlapping between two 1s-orbitals of hydrogen atoms takes place resulting in the formation of hydrogen;

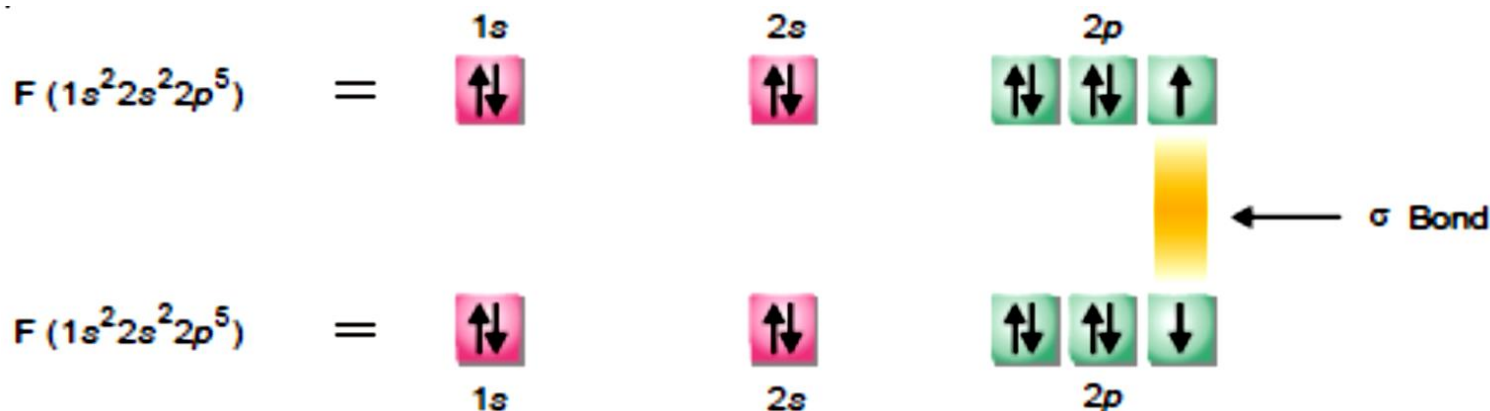


Chemical Bond

■ Orbital Representation of Molecules:

→ (b) Formation of F_2 molecule:

Fluorine (at. no. 9) atom has electron configuration $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$. The unpaired electron in $2p_z$ orbital of one atom overlaps with similar orbital of other Fluorine atom along internuclear axis leading to the formation of σ bond. It is represented as follows :

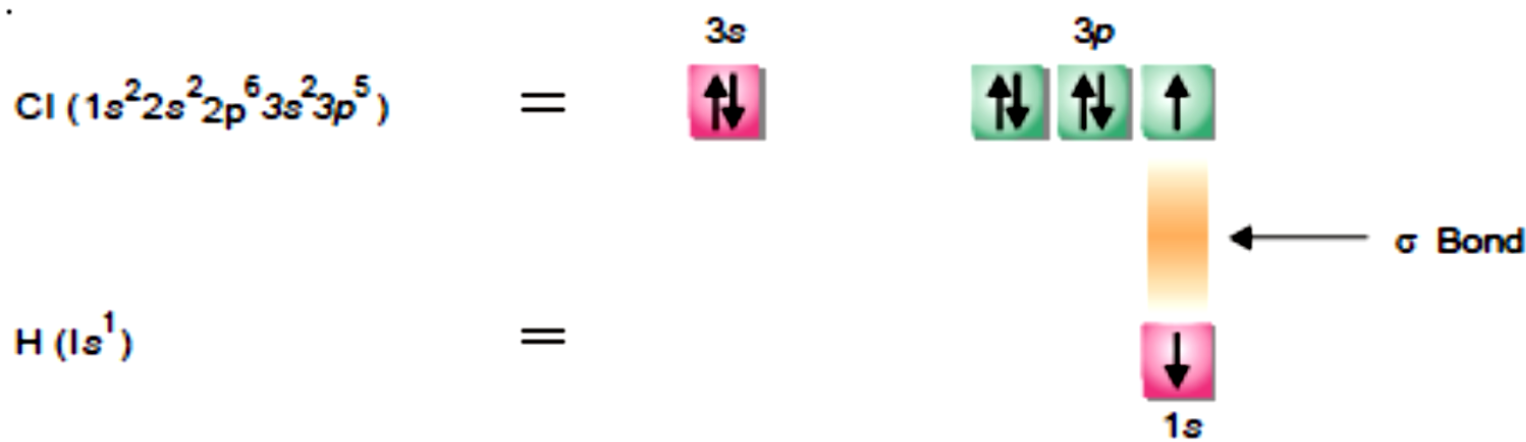


Chemical Bond

■ Orbital Representation of Molecules:

→ (c) Formation of HCl molecule:

During the formation of HCl molecule, 1s orbital of Hydrogen atom having an unpaired electron overlaps with 3p_z orbital of chlorine atom having electronic configuration 1s² 2s² 2p_x² 2p_y² 2p_z¹. This overlapping takes place along internuclear axis leading to the formation of σ bond as shown below :



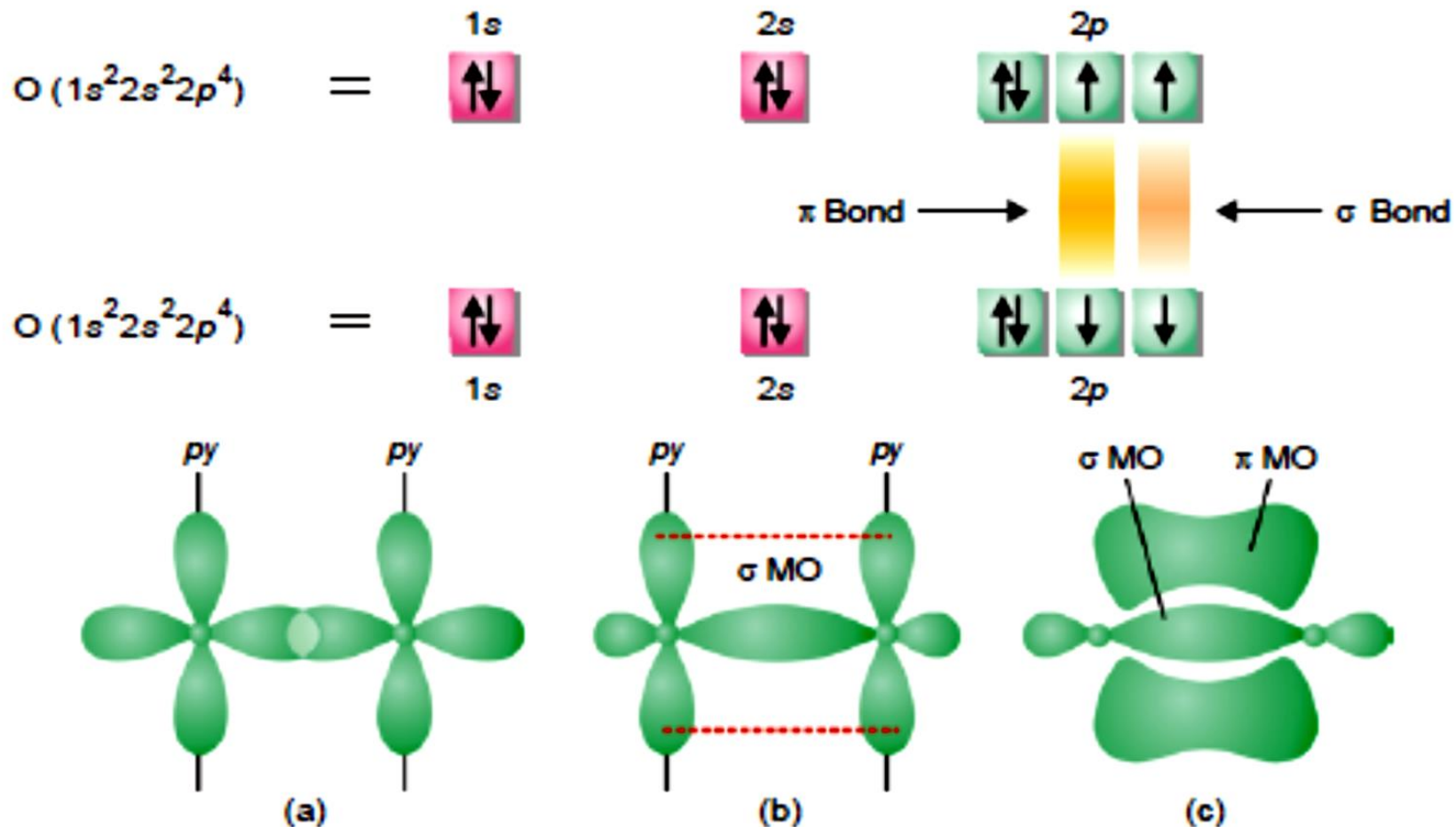
Chemical Bond

■ Orbital Representation of Molecules:

→ (d) Formation of Oxygen molecule

Oxygen (at. no. 8) atom has electronic configuration $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. In the formation of O_2 molecule $2p_z$ orbital of one oxygen atom overlaps with the similar orbital of the other atom along internuclear axis leading to the formation of a sigma (σ) bond. The other $2p_y$ orbital of one oxygen atom overlaps with the similar orbital of the another oxygen atom in sidewise manner forming a pi (π) bond. Thus an oxygen molecule contains a double bond consisting of a sigma (σ) bond and a pi (π) bond. The orbital overlap is represented below :

Chemical Bond



Schematic overlaps of atomic orbitals of the two oxygen atoms in the formation of O_2 molecule (inner filled orbitals are not shown). (a) represents a head on overlap forming; (b) the σ bond; and (c) represents a π MO enveloping a σ MO.

Chemical Bond

■ Concept of Hybridization:

→ While formation of simple molecules could be explained adequately by overlap of atomic orbitals, the formation of molecules of Be, B and C present problems of greater magnitude having no solution with the previous theory.

→ To explain fully the tendency of these atoms to form bonds and the shape or geometry of their molecules, a new concept called Hybridization is introduced.

→ Rules of Hybridization:

For hybridization to occur, it is necessary for the atom to satisfy the following conditions :

- (1) Orbitals on a single atom only would undergo hybridization.
- (2) There should be very little difference of energy level between the

Chemical Bond

(3) Number of hybrid orbitals generated is equal to the number of hybridizing orbitals.

(4) **The hybrid orbitals assume the direction of the dominating orbitals.** For example, if s and p orbitals are to hybridize, the s orbital having no directional character, does not contribute towards the direction when p orbitals determine the directional character of the hybrid orbitals.

(5) **It is the orbitals that undergo hybridization and not the electrons.** For example, four orbitals of an oxygen atom ($2s^2$, $2p_x^2$, $2p_y^1$, $2p_z^1$) belonging to second level (*i.e.*, $2s$, $2p_x$, $2p_y$, $2p_z$) can hybridize to give four hybrid orbitals, two of which have two electrons each (as before) and the other two have one electron each.

(6) **The electron waves in hybrid orbitals repel each other and thus tend to be farthest apart.**

Chemical Bond

■ Types of Hybridization:

→ Since hybridization lends an entirely new shape and orientation to the valence orbitals of an atom, it holds a significant importance in determining the shape and geometry of the molecules formed from such orbitals. Depending upon the number and nature of the orbitals undergoing by hybridization, we have various types of hybrid orbitals. For instance s, p, and d orbitals of simple atoms may hybridize in the following manner.

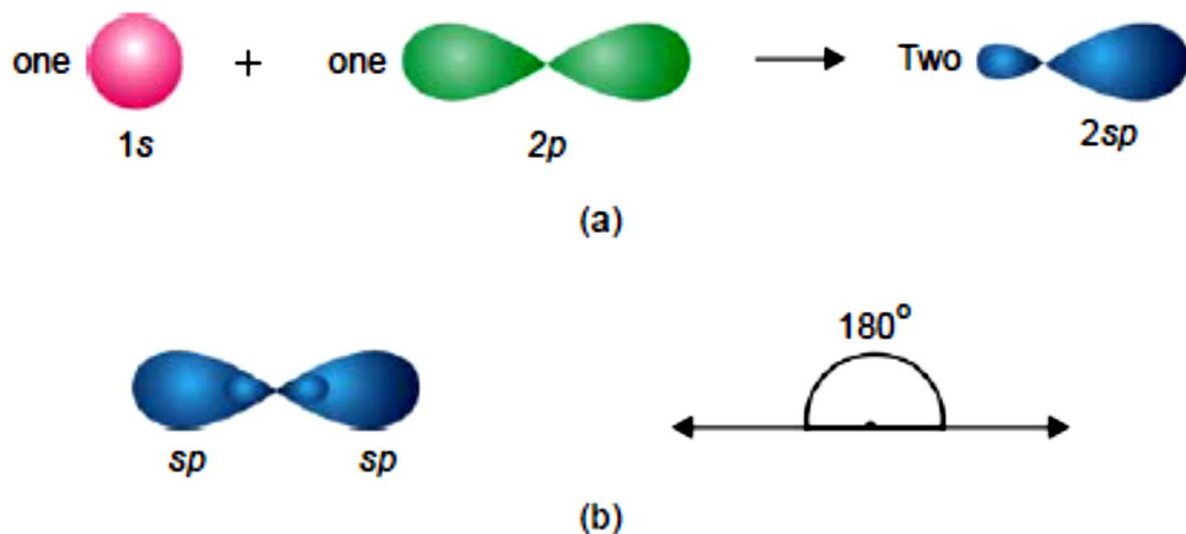
→ (a) **sp Hybridization:**

The mixing of an s and a p orbital only leads to two hybrid orbitals known as sp hybrid orbitals after the name of an s and a p orbital involved in the process of hybridization. The process is called sp hybridization. Each sp orbital has 50%, s-character and 50% p-character.

Chemical Bond

→ (a) **sp Hybridization:**

The new orbitals arrange themselves along a line and are, therefore, often referred to as Linear hybrid orbitals. This gives an angle of 180° between the axes of the two orbitals.



(a) sp Hybridization. (b) Disposition of a sp hybrid orbitals along a line.

Example: BeF_2 , BeCl_2 , etc.

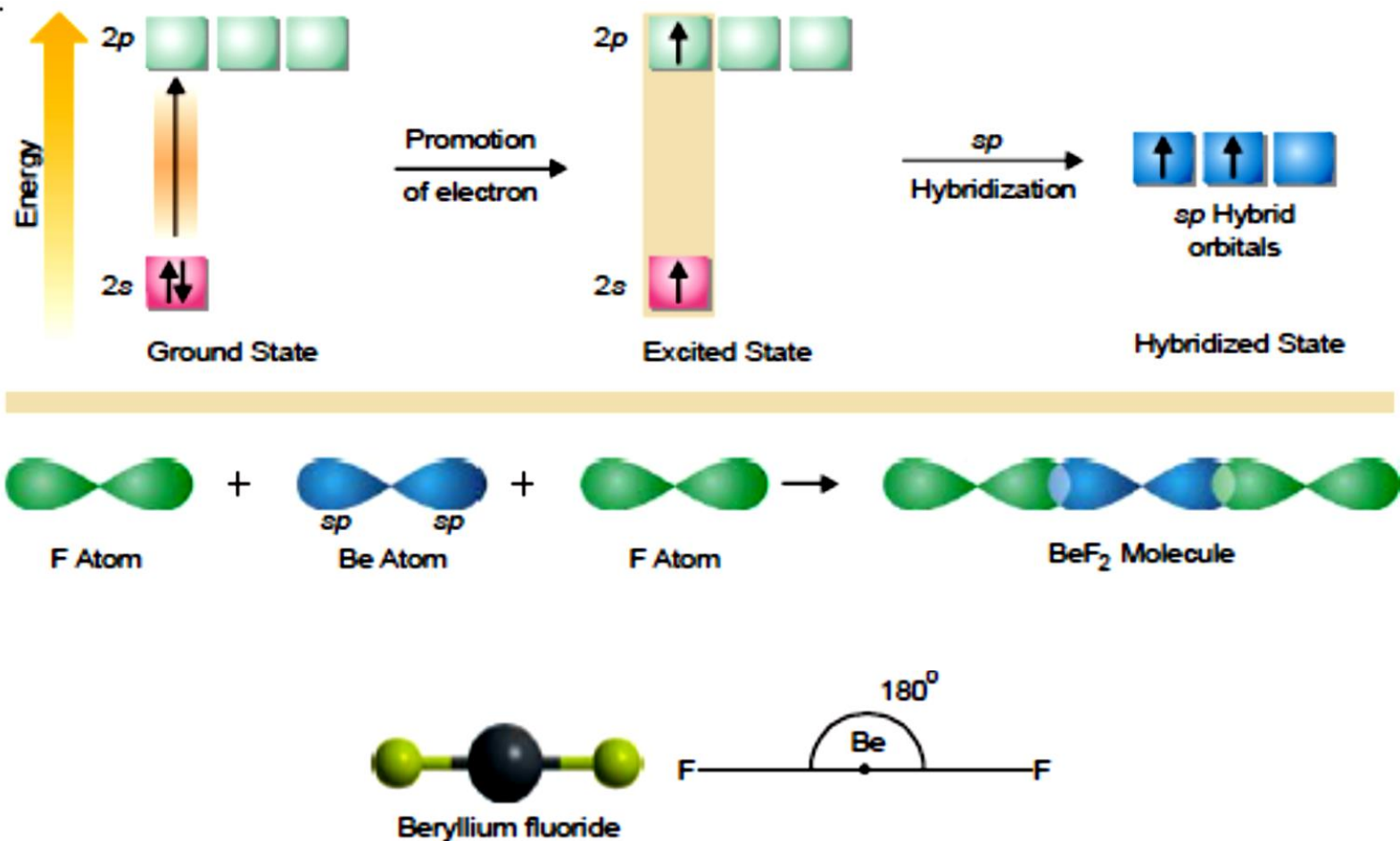
Chemical Bond

Hybridization of BeF_2 :

→ An isolated Be atom in its ground state has the electronic configuration $1s^2, 2s^2$. The Be atom, therefore, gets excited so that one of its $2s^2$ electrons is 'promoted' to the next available $2p_x$ orbital before the atom participates in chemical bonding. Now the excited atom acquires the structure $1s^2, 2s^1, 2p_x^1$. Thus the s and p orbitals first hybridize to form two new and completely equivalent sp hybrid orbitals. These hybrid orbitals of Be are now capable of forming bonds. The two sp hybrid orbitals overlap two 2p orbitals from two fluorine atoms in the 'head on' manner to form two σ bonds. The two sp orbitals being linear, lend a linear shape to BeF_2 molecule with Be atom lying in the center and two F atoms on its either side so that F—Be—F angle is equal to 180° .

Chemical Bond

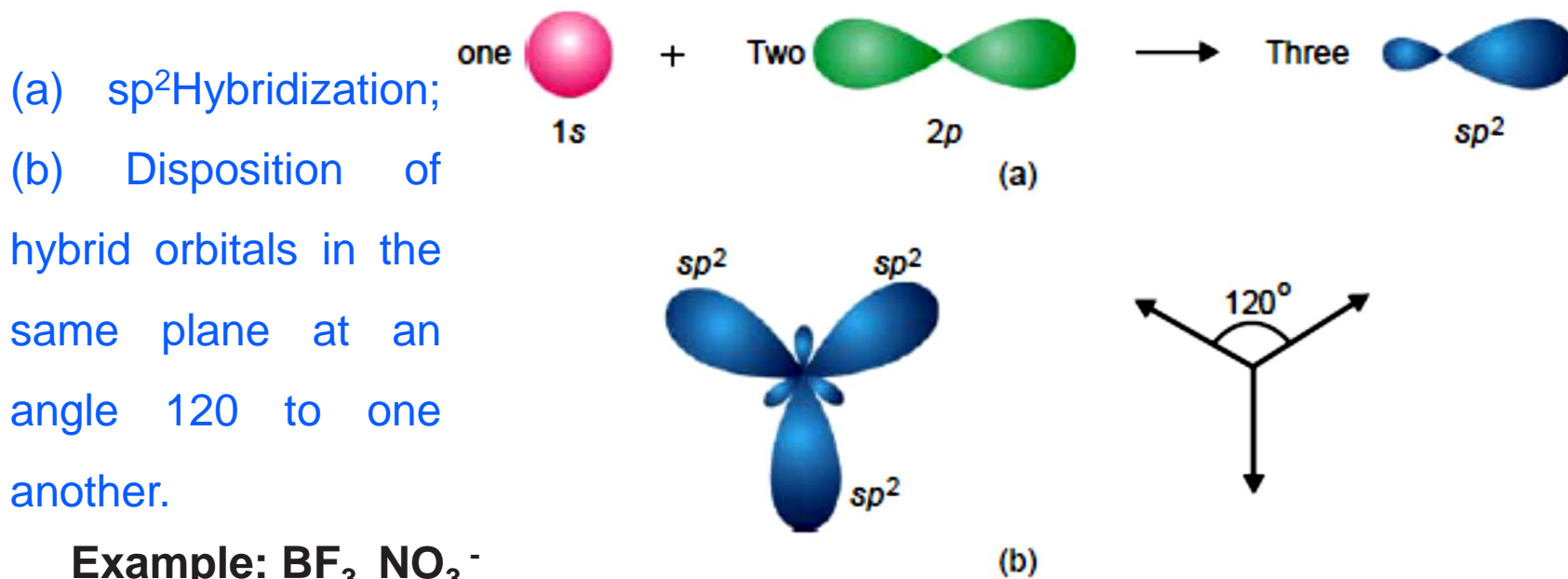
Hybridization of BeF_2 :



Chemical Bond

(b) sp^2 Hybridization:

→ When an s and two p orbitals mix up to hybridize, there result three new orbitals called sp^2 hybrid orbitals (spoken as 'sp two'). Each sp^2 hybrid orbital has 33% s-character and 67% p-character. As the three orbitals undergoing hybridization lie in a plane, so do the new orbitals. They have to lie farthest apart in a plane which can happen if they are directed at an angle 120° to one another.



Chemical Bond

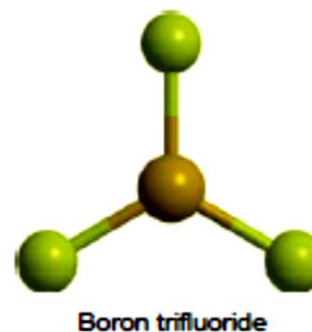
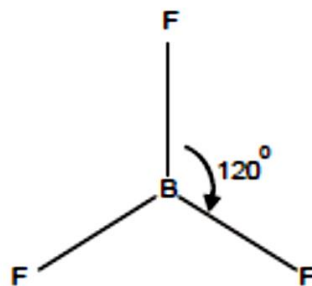
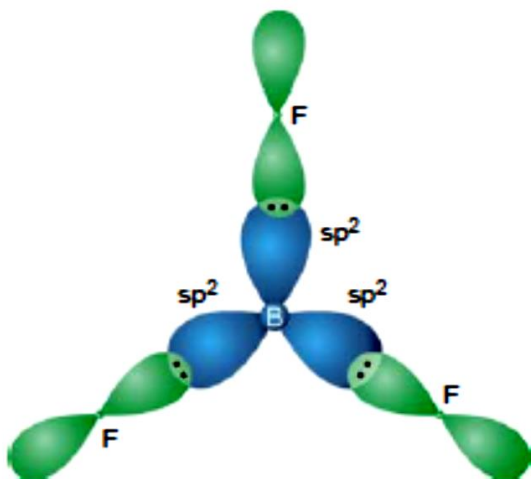
Hybridization of BF_3 :

→ The orbital electronic configuration of Boron (B) is $1s^2, 2s^2, 2p_x^1, 2p_y^0, 2p_z^0$. As there is only one bonding orbital $2p_x$, B is expected to form only one bond. Boron, in fact, is known to form compounds such as BCl_3 , BF_3 , BH_3 etc., indicating its capacity to form three bonds.

Thus in the excited state of Boron there are three half-filled orbitals available for bonding. If as such it were to form bonds by overlap, the nature of these bonds would be different owing to their different types. One $2s$ and two $2p$ orbitals undergo sp^2 hybridization giving three sp^2 hybrid orbitals lying in one plane with an angle 120° . The equivalent hybrid orbitals can now enter into bond formation by overlapping with three $2p$ orbitals of three fluorine atoms

Chemical Bond

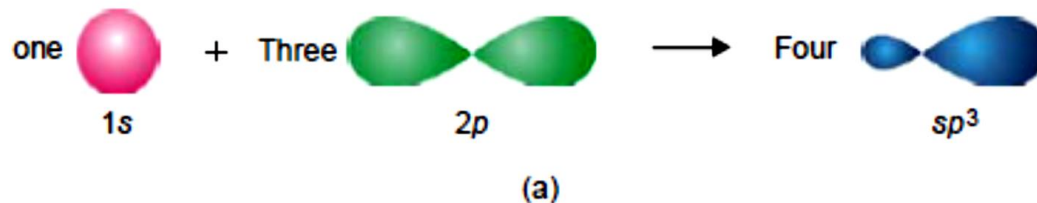
Hybridization of BF_3 :



Chemical Bond

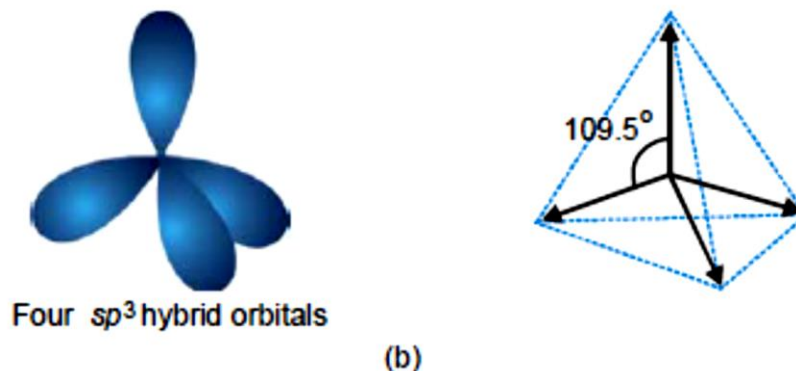
(c) sp^3 Hybridization:

→ The four new orbitals formed by mixing an s and three p orbitals of an atom are known as sp^3 hybrid orbitals. Each sp^3 hybrid orbital has 25% s-character and 75% p-character. Since mixing of orbitals takes place in space, the four hybrid orbital would also lie in space. An arrangement in space that keeps them farthest apart is that of a tetrahedron. They are disposed in manner such that the angle between them is 109.5°



(a) sp^3 Hybridization; (b)

The four hybrid orbitals are directed towards the four corners of a tetrahedron and are at an angle of 109.5° to one another.



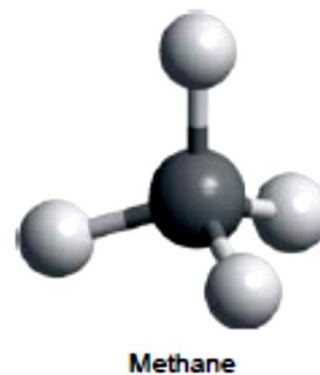
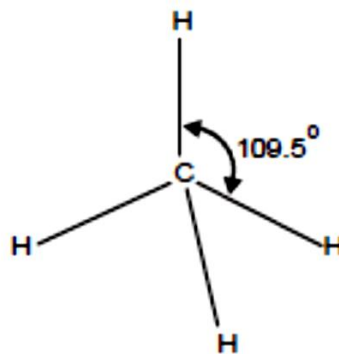
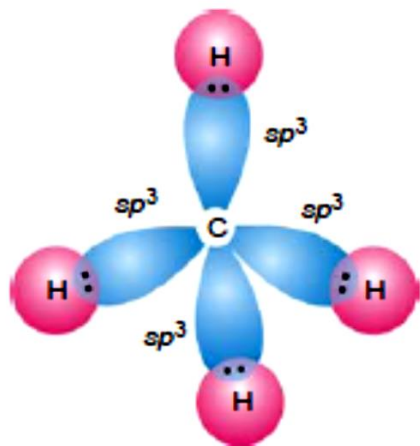
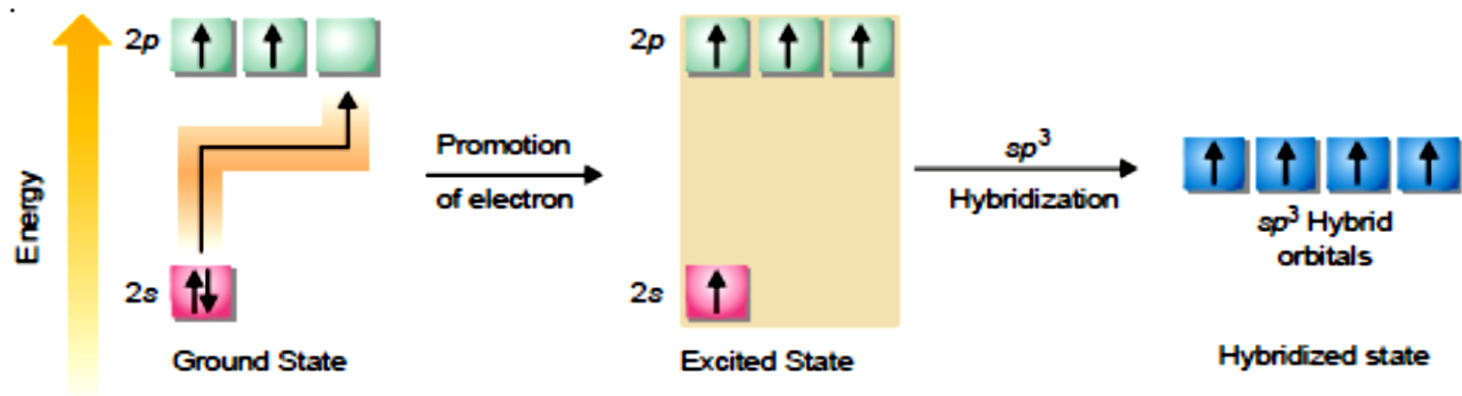
Chemical Bond

Hybridization of CH_4 :

→ It is proposed that from 2s orbital, being quite near in energy to 2p orbitals, one electron may be promoted to the vacant $2p_z$ orbital thus obtaining the excited atom. At this stage the carbon atom undoubtedly has four half-filled orbitals and can form four bonds. In the excited atom all the four valence shell orbitals may mix up to give identical sp^3 hybrid orbitals also four in number. Each of these four sp^3 orbitals possesses one electron and overlaps with 1s orbitals of four H-atoms thus forming four equivalent bonds in methane molecule. Due to the tetrahedral disposition of sp^3 hybrid orbitals, the orbitals are inclined at an angle of 109.5° . Thus all the HCH angles are equal to 109.5° .

Chemical Bond

Hybridization of CH_4 :



Chemical Bond

(d) Hybridization involving d orbitals:

→ There are several types of hybridization involving d orbitals. Since the d orbitals have a relatively complex shape, we will consider here only some of the common types. The most important of these are sp^3d hybridization, sp^3d^2 hybridization and sp^2d hybridization.

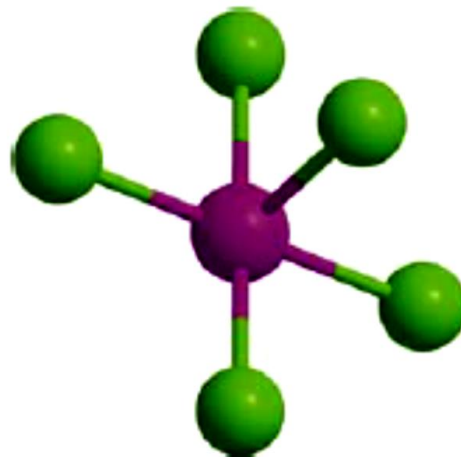
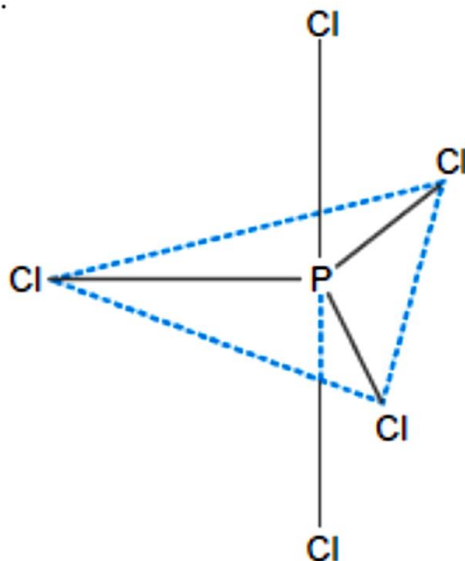
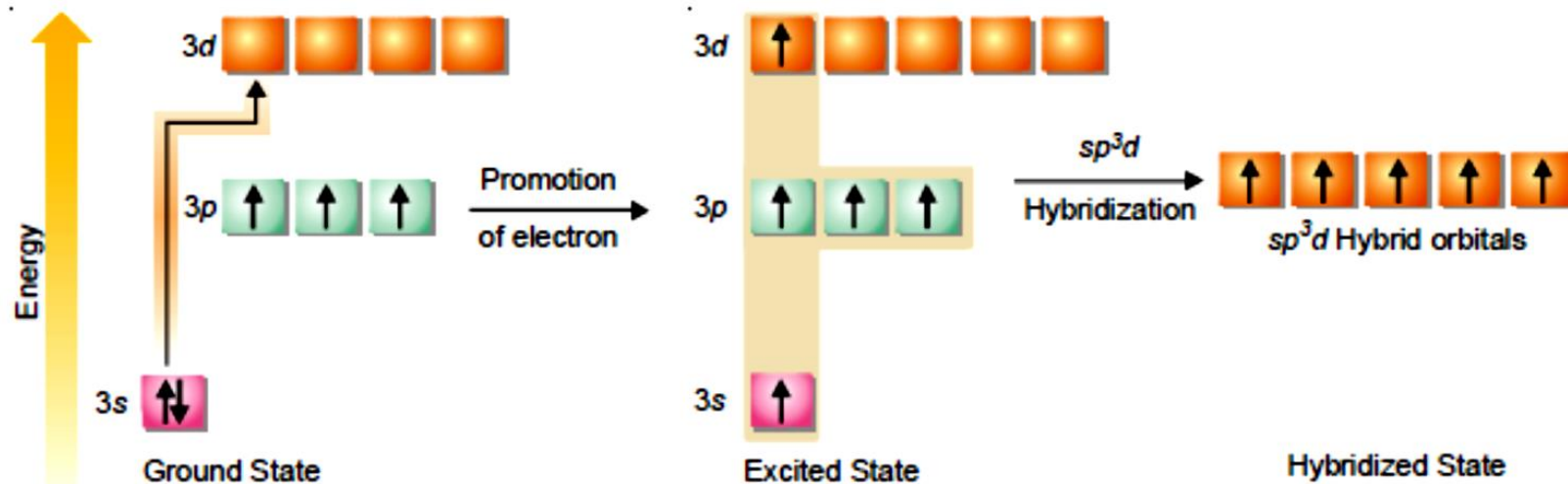
Chemical Bond

(i) sp^3d Hybridization of Phosphorus pentachloride molecule, PCl_5 :

→ In PCl_5 molecule, phosphorus is the central atom which has the electronic configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^3, 3d^0$. In the ground state, it has only three bonding orbitals in the valence shell. One of the two $3s$ electrons uncouples itself and is promoted to the $3d$ orbital. The orbitals now hybridize in accordance with sp^3d type as follows. Three of these five bonding orbitals lie in a plane inclined at an angle of 120° , while the other two are directed above and below the plane in a direction perpendicular to the plane, taking the shape of a trigonal bipyramid. These orbitals of phosphorus atom can overlap with those of five chlorine atoms forming the PCl_5 molecule which will therefore have trigonal bipyramidal shape.

Chemical Bond

Hybridization of PCl_5 :



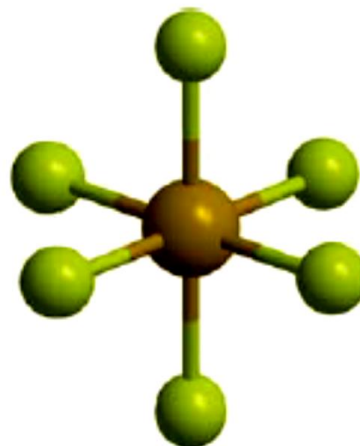
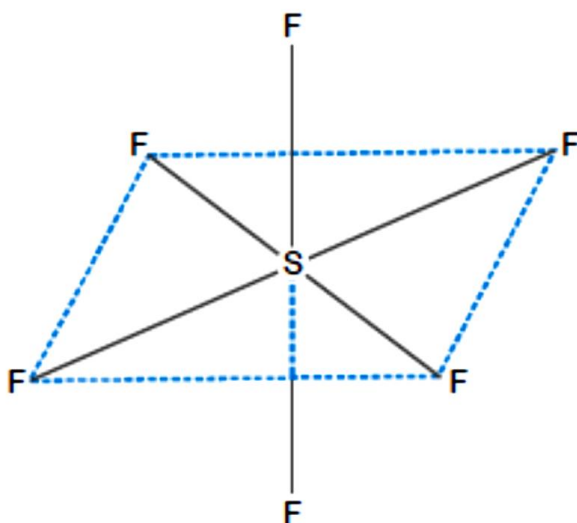
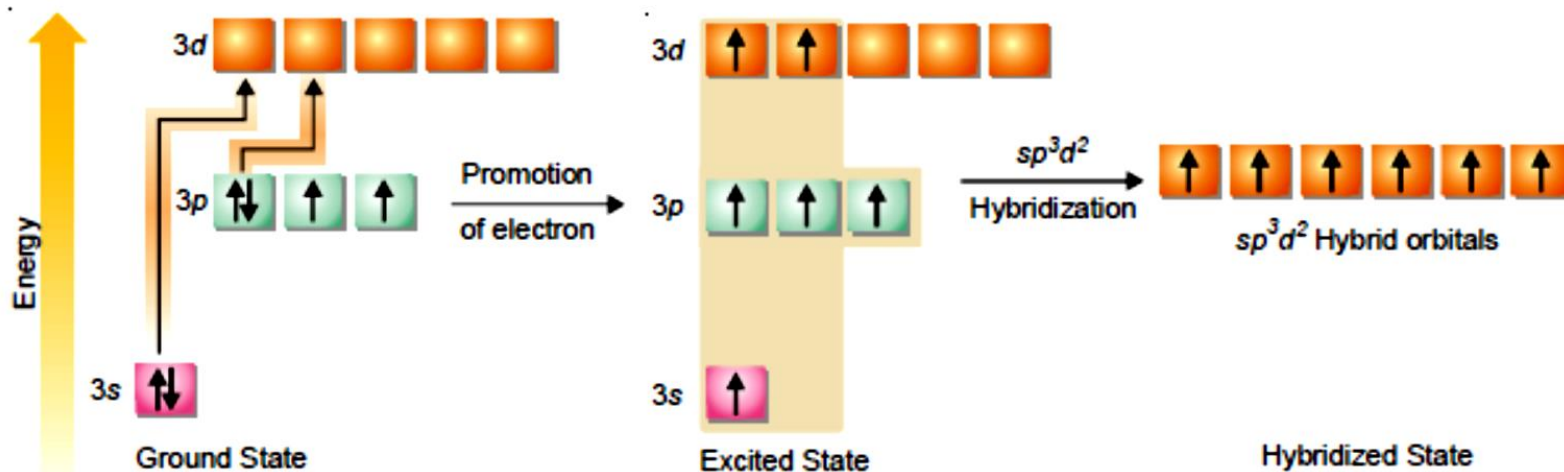
Chemical Bond

ii) sp^3d^2 Hybridization of Sulphur hexafluoride molecule, SF_6 :

→ The sulphur atom has the electronic configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^4, 3d^0$, showing the existence of only two bonding orbitals $3p_y$ and $3p_z$. But sulphur is known to be hexacovalent which may be explained by promoting one electron each from $3s$ and $3p$ orbitals to the vacant d orbitals of the valence shell. The orbitals of the excited atom then undergo sp^3d^2 hybridization to produce six equivalent hybrid orbitals each having one electron. These hybrid orbitals are now available for the overlap after getting octahedrally dispersed (four of them lying in one plane inclined at an angle of 90° while the other two directed above and below the plane perpendicularly). Six fluorine atoms (each having one $2p^1$ bonding orbital) may approach at the corners of the regular octahedron for overlap.

Chemical Bond

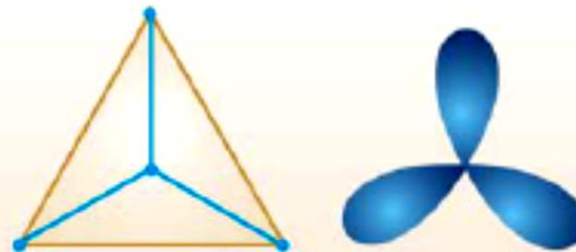
Hybridization of SF_6 :



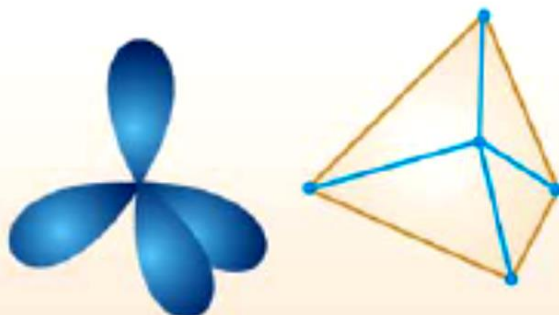
Chemical Bond



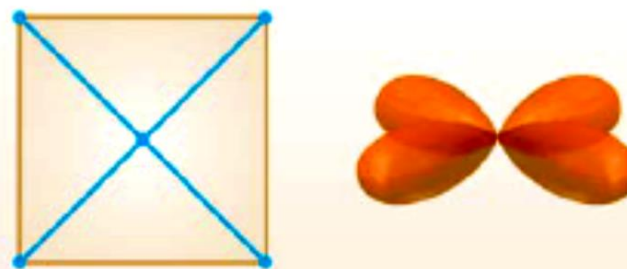
sp Linear



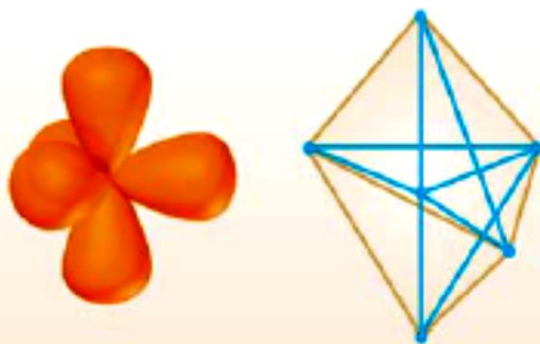
sp^2 Triangular planar



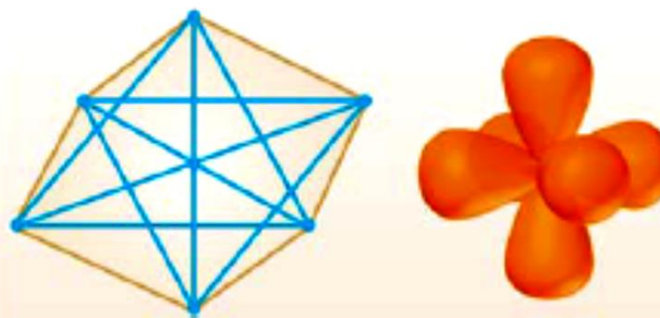
sp^3 Tetrahedral



sp^2d Square planar



sp^3d Trigonal bipyramidal



sp^3d^2 Octahedral

Chemical Bond

■ Limitations of Valence Bond Theory:

- (1) The presence of other nuclei should affect the electronic arrangement of all the atoms in the molecule
- (2) Sometimes a single electronic structure does not explain all known properties of that molecule or ion and we have the many electronic structures called resonating structures.
- (3) Valence Bond theory fails to explain the bonding in electron deficient compounds.
- (4) It fails to explain the paramagnetic character of oxygen molecule.

Chemical Bond

■ Molecular Orbital Theory:

The main features of molecular orbital theory are as follows :

- (1) A molecule is quite different from its constituent atoms. All the electrons belongs to the constituent atom and are considered to be moving under the influence of all nuclei.
- (2) Atomic orbitals of individual atoms combine to form molecular orbitals and these Mos are filled up in the same way as atomic orbitals are formed. In other words, Pauli's exclusion principle, Aufbau principle and Hund's rule of maximum multiplicity are followed.
- (3) The molecular orbitals have definite energy levels.
- (4) The shapes of MOs formed depend upon the shape of combining atomic orbitals

Chemical Bond

■ Linear Combination of Atomic orbitals (LCAO method):

According to wave mechanics the atomic orbitals can be expressed as wave functions (ψ_s) which represent the amplitude of electron waves.

According to this method, the molecular orbitals are formed by the linear combination (addition or subtraction) of atomic orbitals of the constituent atoms of the molecule.

Let us consider the simplest case of H_2 molecule consisting of two hydrogen atoms represented by H_A and H_B . The atomic orbitals of these atoms are represented by the wave functions ψ_A and ψ_B . When these atoms approach each other there come two possibilities

Chemical Bond

■ Linear Combination of Atomic orbitals (LCAO method):

(1) Molecular orbital is formed by the **addition** of wave functions of atomic orbitals. It can be represented by

$$\Psi_{(\text{MO})} = \Psi_{\text{A}} + \Psi_{\text{B}} \dots (i)$$

The M.O. formed is called **bonding molecular orbital**. It lowers the energy and brings about the stability in the system.

(2) Molecular orbital is formed by the **subtraction** of wave functions of atomic orbitals. It can be represented by

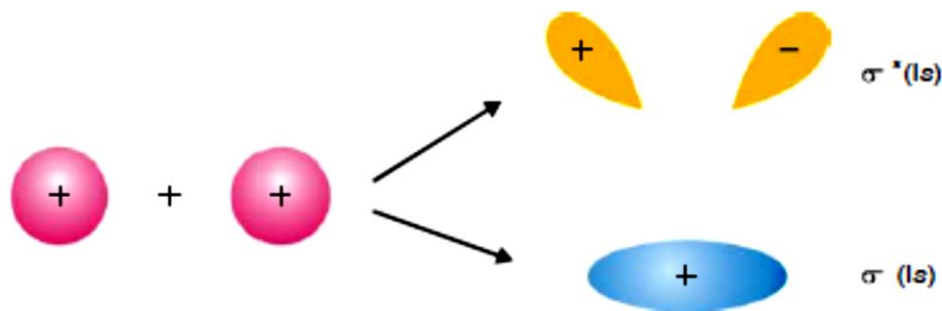
$$\Psi^*_{(\text{MO})} = \Psi_{\text{A}} - \Psi_{\text{B}} \dots (ii)$$

The MO formed is called **antibonding molecular orbital**. This type of MO corresponds to higher energy state.

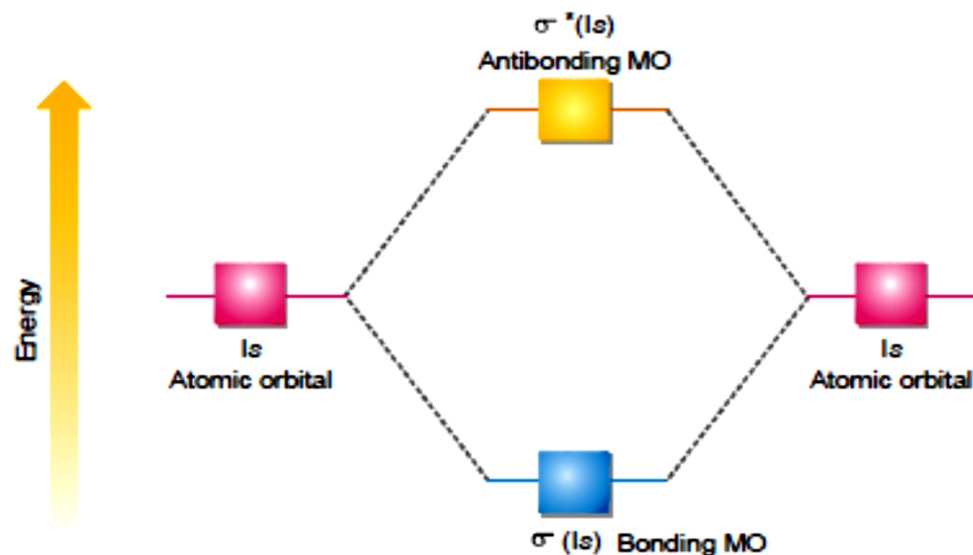
Chemical Bond

■ Linear Combination of Atomic orbitals (LCAO method):

The molecular orbitals formed by the combination of 1s orbitals of two hydrogen atoms is shown below :



■ Relative Energies of bonding and antibonding MOs



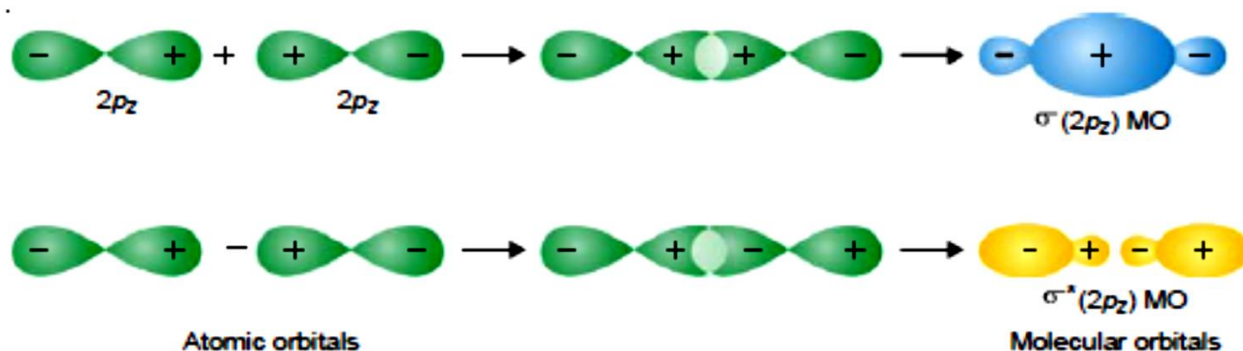
Chemical Bond

■ Molecular Orbitals from p-Atomic Orbitals

Combination of p-orbitals is slightly complicated. There being three types of 2p orbitals namely $2p_x$, $2p_y$ and $2p_z$ directed along the cartesian co-ordinates x, y and z respectively. By convention we assume that z-axis is the intermolecular axis.

(1) Combination of $2p_z$ atomic orbitals

When two $2p_z$ orbitals on two atoms approach each other along the internuclear axis they combine by the addition of electron wave. This results in the formation of bonding $\sigma(2p_z)$ orbital while subtraction of electron waves give rise to antibonding molecular orbital $\sigma^*(2p_z)$. It is represented as:

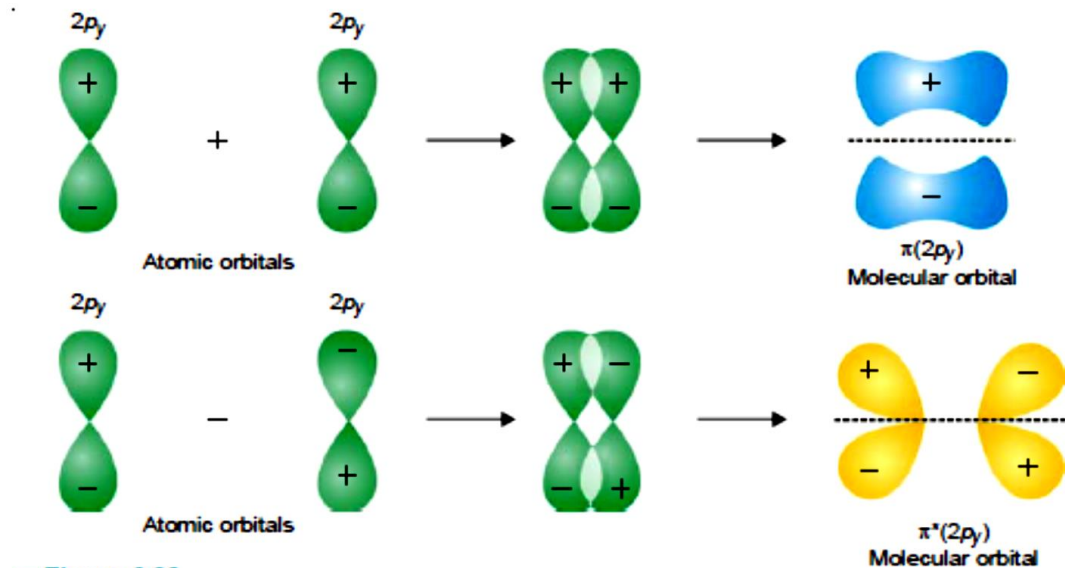


Chemical Bond

■ Molecular Orbitals from p-Atomic Orbitals

When two $2p_y$ or $2p_x$ orbitals on two atoms are approaching in a manner that their axes are mutually parallel, they interact to give rise to the formation of molecular orbitals that are not symmetrical about the internuclear axis and are called molecular orbitals represented by π ($2p_y$) or π ($2p_x$) bonding orbitals. The π^* ($2p_y$) and π^* ($2p_x$) antibonding MOs have higher energy than their corresponding molecular and atomic orbitals. Since $2p_y$ and $2p_x$ atomic orbitals on an atom are degenerate (are of equal energy), the π molecular orbitals arising out of them will also be degenerate *i.e.* π ($2p_y$) and π ($2p_x$) bonding molecular orbitals possess equal energy and the same situation prevails in antibonding molecular orbitals π^* ($2p_y$) and π^* ($2p_x$).

Chemical Bond



Since we are concerned here with few simple molecules, the only molecular orbitals which need to be considered are.

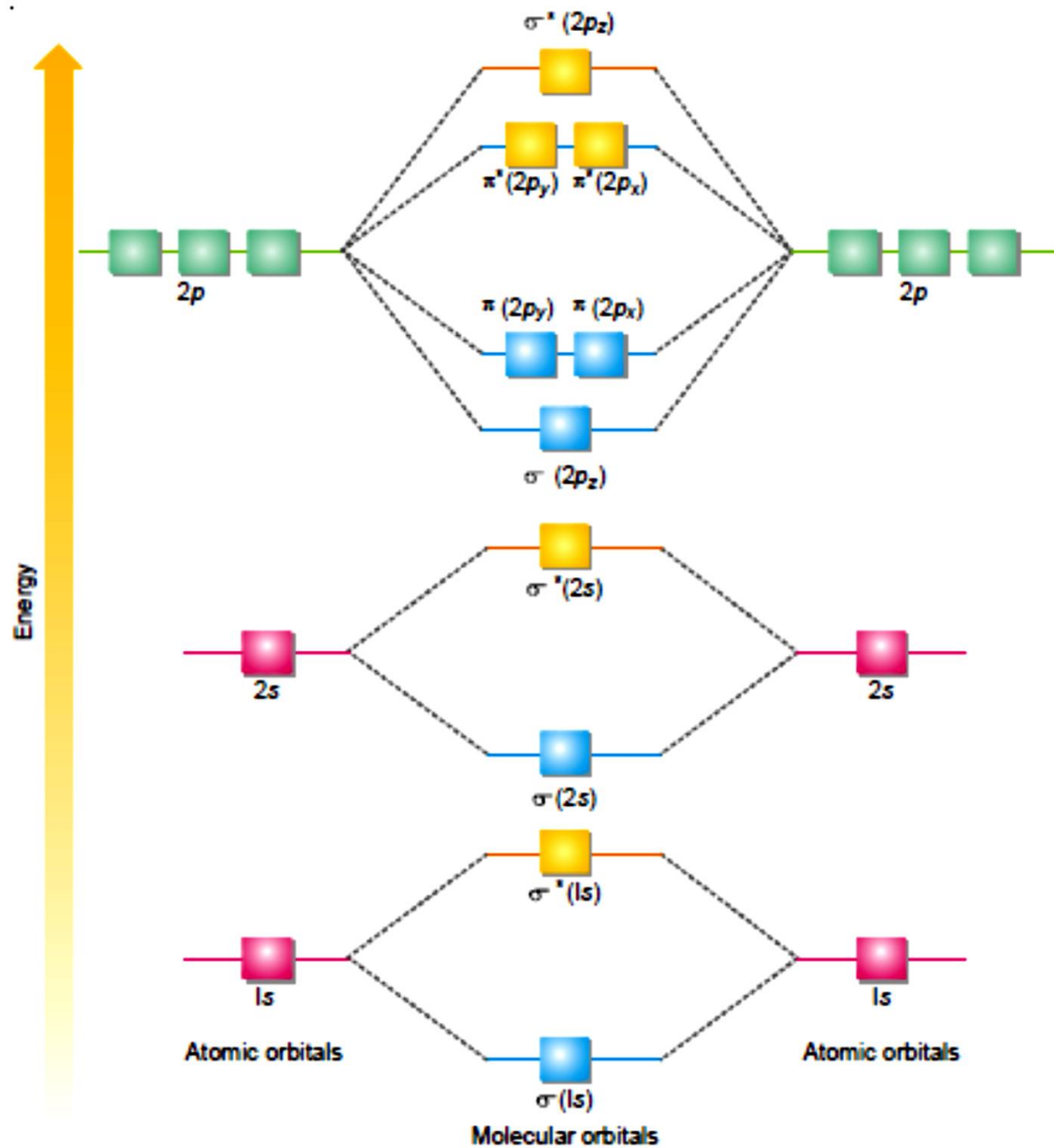
Bonding MOs = $\sigma(1s) \sigma(2s) \sigma 2p_z \pi(2p_y) \pi 2p_x$

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

This order may be written as:

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

Chemical Bond



Chemical Bond

■ Bond Order:

How many are the bonds in a molecule or Bond order is correctly predicted by the Molecular Orbital theory. The number of bonds in a molecule is one-half of the difference of the number of electrons in the bonding molecular orbitals and the number of electrons in the antibonding molecular orbitals. Mathematically,

$$\text{Bond order} = \frac{\left(\begin{array}{c} \text{No. of electrons in} \\ \text{bonding orbitals} \end{array} \right) - \left(\begin{array}{c} \text{No. of electrons in} \\ \text{antibonding orbitals} \end{array} \right)}{2} = \frac{N_b - N_a}{2}$$

■ Information given by Bond order

(1) Stability of the Molecule/ion

A molecule/ion is stable if $N_b > N_a$

A molecule/ion is stable if $N_b < N_a$

Chemical Bond

(2) Bond Dissociation Energy

It depends upon the bond order. Greater the bond order greater is the bond dissociation energy.

(3) Bond Length

Bond order is inversely proportional to the bond length. Higher the bond order, smaller the bond length.

(4) Magnetic Properties

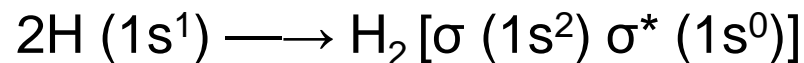
The presence of unpaired electrons in Molecular orbitals of a species makes it paramagnetic in nature. Greater the number of unpaired electrons, the more will be its paramagnetic character. On the other hand, if there are no unpaired electrons in MOs the species will be diamagnetic in nature.

Chemical Bond

■ Homonuclear Diatomic Molecules

(1) Hydrogen, H_2

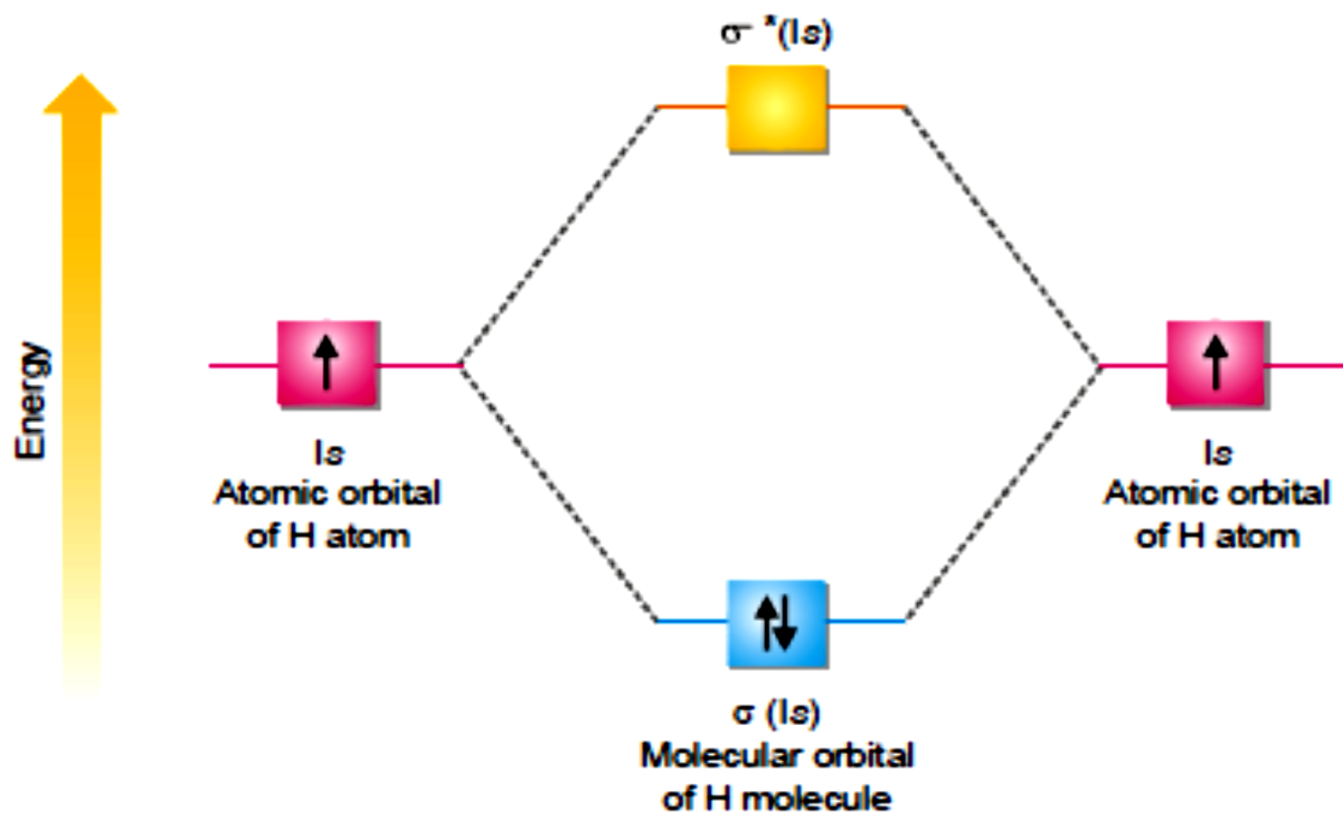
Hydrogen molecule is formed from $1s^1$ atomic orbitals of two atoms. They give rise to two molecular orbitals $\sigma(1s)$ and $\sigma^*(1s)$. The molecule has two electrons to be accommodated in these two molecular orbitals and are filled as desired by Aufbau order of filling. Both these electrons go to the lower energy bonding molecular orbital and the antibonding orbital remains vacant. The electronic configuration of the molecule is represented by the equation :



The number of bonds in the molecule, is $=1/2 (2 - 0) = 1$.

Thus two hydrogen atoms are bonded through only one bond in the molecule.

Chemical Bond



Molecular orbital diagram of H_2 molecule

Chemical Bond

■ Homonuclear Diatomic Molecules

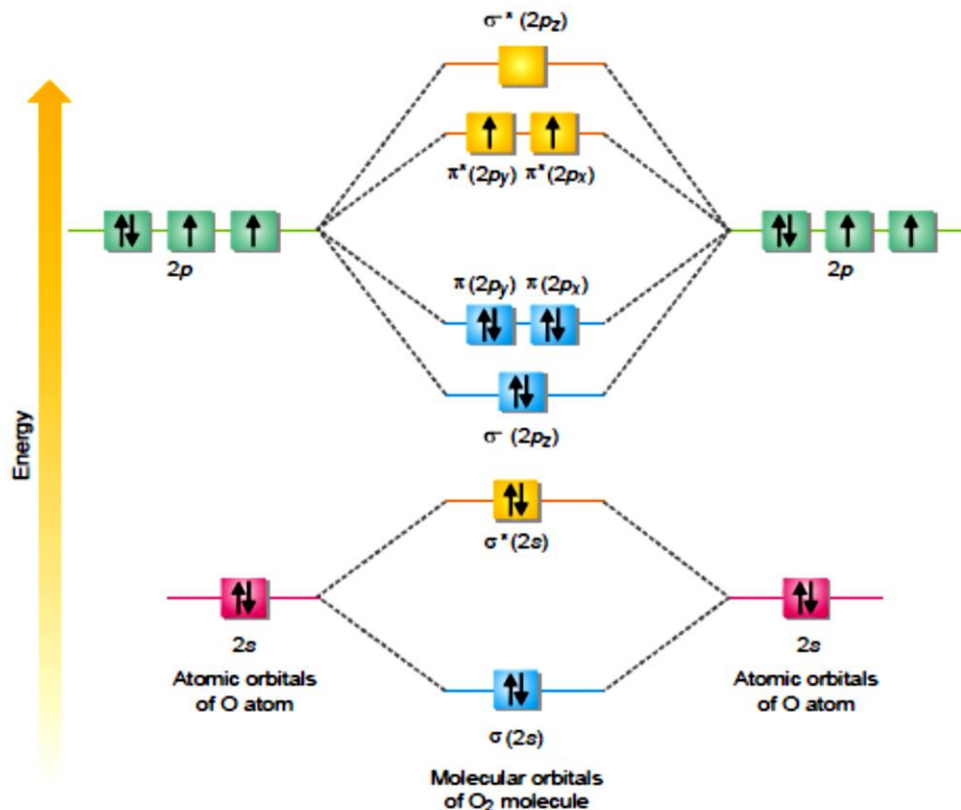
(1) Oxygen, O_2

The two participating oxygen atoms ($1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$) contribute a total of $2(2 + 2 + 1 + 1) = 12$ valence electrons and $2 \times 4 = 8$ atomic orbitals towards the oxygen molecule. There are eight molecular orbitals and 12 electrons are accommodated. The number of bonds in the molecule, is $=1/2 (8 - 4) = 2$.

Thus two oxygen atoms are bonded through two bond in the molecule.

→ Proceeding on these lines, the electronic configurations of other simple species like O_2^+ , O_2^- can be worked out.

Chemical Bond



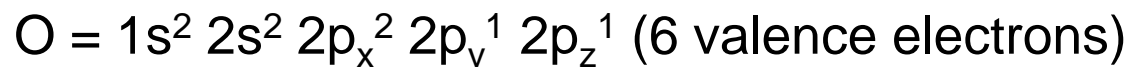
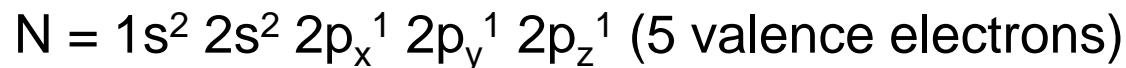
→ Aufbau order of filling of molecular orbital leaves two unpaired electrons in each of degenerate π_y^* ($2p_y$) and π_z^* ($2p_x$) orbitals. The electronic configuration of the molecular orbitals accounts admirably for the paramagnetic behaviour of oxygen molecule.

Chemical Bond

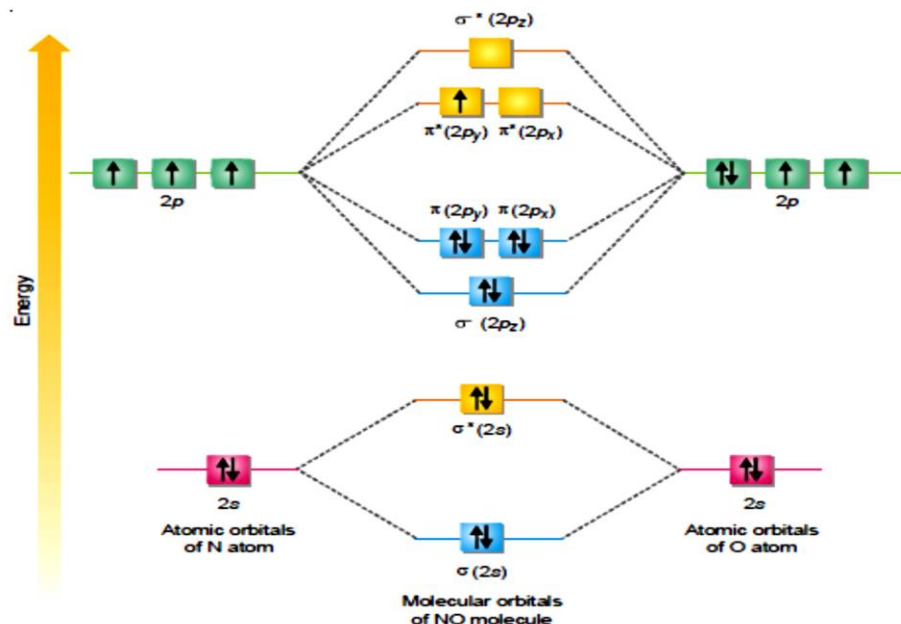
■ Heteronuclear Diatomic Molecules:

(1) Nitric Oxide (NO):

The electronic configuration of participating N and O atoms are



The total number of valence electrons is 11 and molecular orbital diagram of NO molecule can be written as;



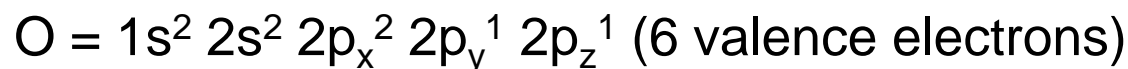
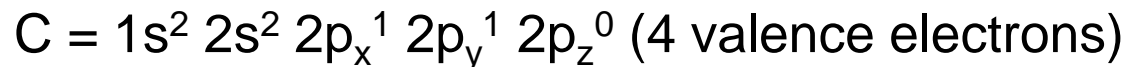
Chemical Bond

→ The bond order = $1/2 (N_b - N_a) = 1/2 (8 - 3) = 2.5$

→ It makes clear that one σ bond and two pi bonds with an unpaired electron in antibonding $\pi^* (2p_y)^1$ molecular orbital are formed. This molecule is less stable than N_2 molecule (Bond order = 3). Due to the presence of one unpaired electron in NO molecule it is paramagnetic in nature.

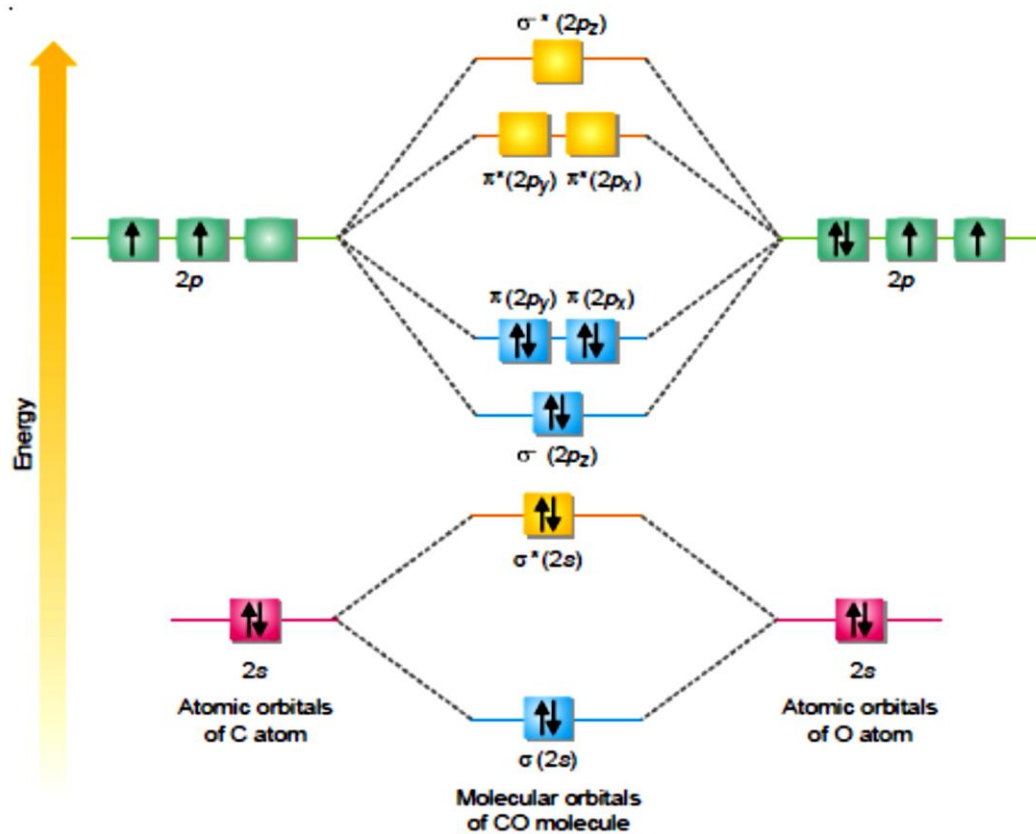
2) Carbon Monoxide (CO)

The electronic configurations of participating C and O atoms are;



The total number of valence electrons is 10 and molecular orbital diagram of CO molecule can be written as;

Chemical Bond



→ The bond order = $\frac{1}{2} (N_b - N_a) = \frac{1}{2} (8 - 2) = 3$

→ This shows that carbon and oxygen atom in CO are bonded to each other by a triple bond (one σ bond and two π bonds). There is no unpaired electron in CO molecule and hence it is diamagnetic in nature.