

## Chapter VI :

# Chemical Bonding

### 1- Introduction :

Did you know that the 118 elements on the periodic table combine to make millions and millions of chemical compounds ? This is because chemical bonds between atoms result in new substances that are very different from the elements they are made of. For example, chlorine can be used as a chemical weapon and yet it combines with sodium, a highly reactive element, to make common table salt.

To summarize simply, a chemical bond is the attractive force holding atoms or ions together. This attractive interaction leads to a more stable state for the whole system compared to individual atoms.

Valence electrons play a fundamental role in chemical bonding. In the electron configuration of an atom, the outermost shell is called the valence shell, and the electrons in the valence shell (outermost shell) are known as valence electrons. Take the carbon atom for example: the electron configuration of carbon is  $1s^2 2s^2 2p^2$ . The outermost shell is the 2<sup>nd</sup> principal shell, so there are 4 valence electrons in carbon. Valence electrons are the electrons that are the furthest away from the nucleus, and thus they experience the least attraction from the nucleus and are the most reactive. They play the most important role in chemical bonding.

### 2- Types of chemical bonds :

What are the types of bonds in chemistry? Let's look at three of the most popular types of bonds – covalent bonds, ionic bonds, and metallic bonds.

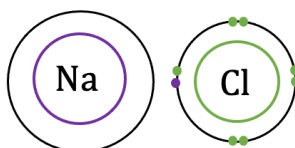
#### 2-1- Ionic bond :

The definition of **ionic bond**, is a bond between atoms where electrons are (mostly) transferred from one atom to another. We say mostly, because there is always some sharing of electrons between atoms, but in Ionic bonds, the sharing is very unequal. The less equal the sharing of the electrons, the more **ionic character** the bond has.

Ionic bonds occur between a metal and a non-metal. Unlike covalent bonds, ionic bonds transfer their valence electrons between atoms. In ionic bonding, the electronegativity difference

between non-metals and metals exceeds 1.7. The metal atom transfers its electrons to the non-metal atom. Therefore, the metal atom becomes a positively charged cation and the non-metal atom becomes a negatively charged anion. Consequently, ionic bonds create two charged ions, the metal always donates its electron, and the non-metal always accepts the electron. An example of an ionic bond is the bond in sodium chloride, which is salt. Sodium's valence electron is transferred to the outer electron shell of chloride.

Ionic Bond

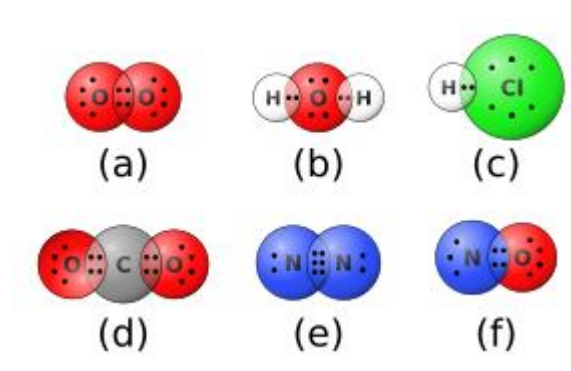


## 2-2- Covalent Bonds :

A covalent bond, or molecular bond, is a chemical bond formed between two atoms that share a pair of electrons; the elements that form these bonds are generally non-metals. Some examples of oxygen, hydrogen and nitrogen in compounds like O<sub>2</sub> and H<sub>2</sub>O). A defining characteristic of a covalent bond is that electron density is high in the middle of the bond. This means that electrons are more likely to be found in between the two atoms than at each end. Chemists sometimes describe and predict the ways that covalent bonds form using a model called molecular orbital theory.

- **Multiple Bonds**

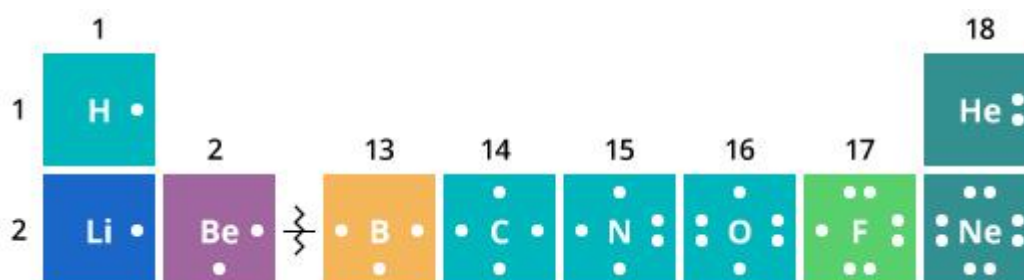
Covalent bonds can be either single or multiple bonds. In a single bond, only one pair of valence electrons are being shared between two atoms. However, sometimes atoms share more than one electron pair, forming what is called a multiple bond. The common types of multiple bonds are double and triple, with higher order bonds forming only in certain exotic compounds of transition metals. The elements that most often participate in multiple bonding are: carbon, nitrogen, oxygen, phosphorus, and sulfur.



Atoms engaging in **single** (b,c), **double** (a,d,f) and **triple** (e) covalent bonding

- **Lewis Theory of Chemical Bonding**

In 1916, the American scientist Gilbert N. Lewis published a now famous paper on bonding entitled “The atom and the molecule” (Lewis, 1916). In that paper he outlined a number of important concepts regarding bonding that are still used today as working models of electron arrangement at the atomic level. Most significantly, Lewis developed a theory about bonding based on the number of outer shell, or valence, electrons in an atom. He suggested that a chemical bond was formed when two atoms shared a pair of electrons (later renamed a covalent bond by Irving Langmuir). His "Lewis dot diagrams" used a pair of dots to represent each shared pair of electrons that made up a covalent bond (following figure).

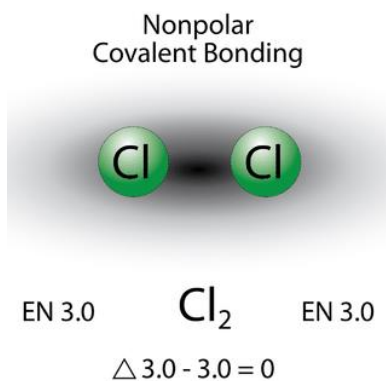


Lewis dot structures for the elements in the first two periods of the periodic table. The structures are written as the element symbol surrounded by dots that represent the valence electrons.

Lewis also championed the idea of ‘octets’ (groups of eight), that a filled valence shell was crucial in understanding electronic configuration as well as the way atoms bond together. The octet had been discussed previously by chemists such as John Newland, who felt it was important, but Lewis advanced the theory.

- **Nonpolar Covalent Bonds**

A bond in which the electronegativity difference is less than 1.7 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.

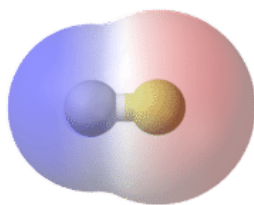


A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the Cl<sub>2</sub> molecule is symmetrical. Note that molecules in which the electronegativity difference is very small (<0.4) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ( $\Delta EN = 3.0 - 2.8 = 0.2$ ).

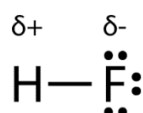
- **Polar Covalent Bonds**

A bond in which the electronegativity difference between the atoms is between 0.4 and 1.7 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons, and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.



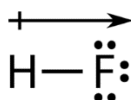
In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta ( $\delta$ )



Use of  $\delta$  to indicate partial charge.

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.



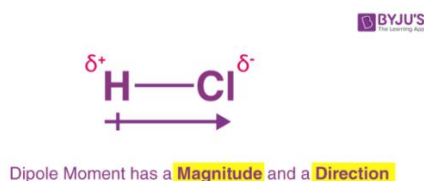
Use of crossed arrow to indicate polarity.

### What is Dipole Moment?

A dipole moment arises in any system in which there is a separation of charge. They can, therefore, arise in ionic bonds as well as in covalent bonds. Dipole moments occur due to the difference in electronegativity between two chemically bonded atoms.

A bond dipole moment is a measure of the polarity of a chemical bond between two atoms in a molecule. It involves the concept of electric dipole moment, which is a measure of the separation of negative and positive charges in a system.

The bond dipole moment is a vector quantity since it has both magnitude and direction. An illustration describing the dipole moment that arises in an HCl ([hydrochloric acid](#)) molecule is provided below.



It can be noted that the symbols  $\delta^+$  and  $\delta^-$  represent the two electric charges that arise in a molecule which are equal in magnitude but are of opposite signs. They are separated by a set distance, which is commonly denoted by 'd'.

### Important Points

- The dipole moment of a single bond in a polyatomic molecule is known as the bond dipole moment and it is different from the dipole moment of the molecule as a whole.
- It is a vector quantity, i.e. it has magnitude as well as definite directions.
- Being a vector quantity, it can also be zero as the two oppositely acting bond dipoles can cancel each other.
- By convention, it is denoted by a small arrow with its tail on the negative center and its head on the positive center.
- In chemistry, the dipole moment is represented by a slight variation of the arrow symbol. It is denoted by a cross on the positive center and arrowhead on the negative center. This arrow symbolizes the shift of electron density in the molecule.
- In the case of a polyatomic molecule, the dipole moment of the molecule is the vector sum of the all present bond dipoles in the molecule.

### Dipole Moment Formula :

A dipole moment is the product of the magnitude of the charge and the distance between the centers of the positive and negative charges. It is denoted by the Greek letter ' $\mu$ '.

Mathematically,

$$\text{Dipole Moment } (\mu) = \text{Charge } (Q) * \text{distance of separation } (r)$$

It is measured in Debye units denoted by 'D'.  $1 \text{ D} = 3.33564 \times 10^{-30} \text{ C.m}$ , where C is Coulomb and m denotes a metre.

The bond dipole moment that arises in a chemical bond between two atoms of different electronegativities can be expressed as follows:

$$\mu = \delta \cdot d$$

Where:  $\mu$  is the bond dipole moment,

$\delta$  is the magnitude of the partial charges  $\delta^+$  and  $\delta^-$ ,

And  $d$  is the distance between  $\delta^+$  and  $\delta^-$ .

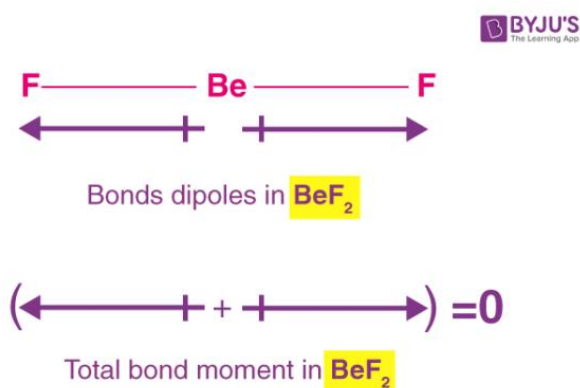
The bond dipole moment ( $\mu$ ) is also a vector quantity, whose direction is parallel to the bond axis. In chemistry, the arrows that are drawn in order to represent dipole moments begin at the positive charge and end at the negative charge.

When two atoms of varying electronegativities interact, the electrons tend to move from their initial positions to come closer to the more electronegative atom. This movement of electrons can be represented via the bond dipole moment.

## Examples

### Dipole moment of $\text{BeF}_2$

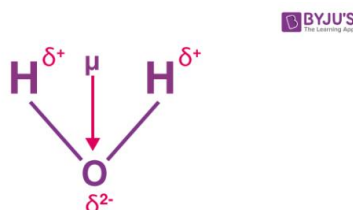
In a beryllium fluoride molecule, the bond angle between the two beryllium-fluorine bonds is  $180^\circ$ . Fluorine, being the more electronegative atom, shifts the electron density towards itself. The individual bond dipole moments in a  $\text{BeF}_2$  molecule are illustrated below.



From the illustration provided above, it can be understood that the two individual bond dipole moments cancel each other out in a  $\text{BeF}_2$  molecule because they are equal in magnitude but are opposite in direction. Therefore, the net dipole moment of a  $\text{BeF}_2$  molecule is zero.

### Dipole moment of H<sub>2</sub>O (Water) :

In a water molecule, the electrons are localised around the oxygen atom since it is much more electronegative than the hydrogen atom. However, the presence of a lone pair of electrons in the oxygen atom causes the water molecule to have a bent shape (as per the [VSEPR theory](#)). Therefore, the individual bond dipole moments do not cancel each other out as is the case in the BeF<sub>2</sub> molecule. An illustration describing the dipole moment in a water molecule is provided below.



The bond angle in a water molecule is 104.5°. The individual bond moment of an oxygen-hydrogen bond is 1.5 D. The net dipole moment in a water molecule is found to be 1.84D.

- **Dative Covalent (Coordinate) Bonding :**

A **Co-ordinate bond** is a type of alternate covalent bond that is formed by sharing of an electron pair from a single atom. Both shared electrons are donated by the same atom. It is also called a dative bond or dipolar bond.

Co-ordinate covalent bonds are usually formed in reactions that involve two non-metals, such as a hydrogen atom or during bond formation between metal ions and ligands.

#### Characteristics of Coordinate Covalent Bond

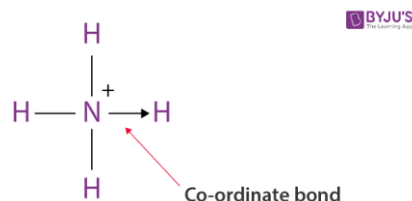
1. In this type of bonding, the atom that shares an electron pair from itself is termed as the donor.
2. The other atom which accepts these shared pair of electrons is known as a receptor or acceptor.
3. The bond is represented with an arrow  $\rightarrow$ , pointing towards the acceptor from the donor atom.
4. After sharing of electron pairs, each atom gets stability.
5. This type of bonding is central to the Lewis theory.



6. Getting a good understanding of co-ordinate covalent bonds can help in properly designing complex organic molecules.

### Coordinate Bond Diagram

Below, we have given a simple diagram of a co-ordinate bond. The bond is shown by an arrow which points in the direction where an atom is donating the lone pair to the atom that is receiving it.

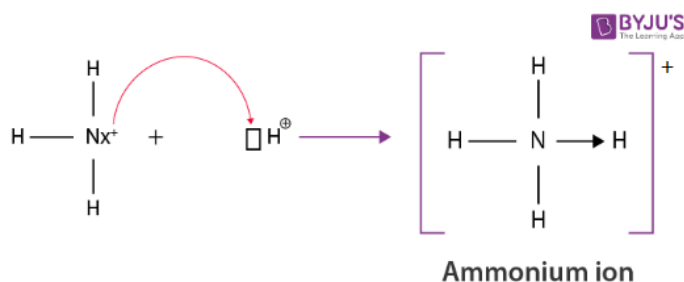


### Co-Ordinate Bond Examples :

Here are a few examples of the coordinate covalent bond.

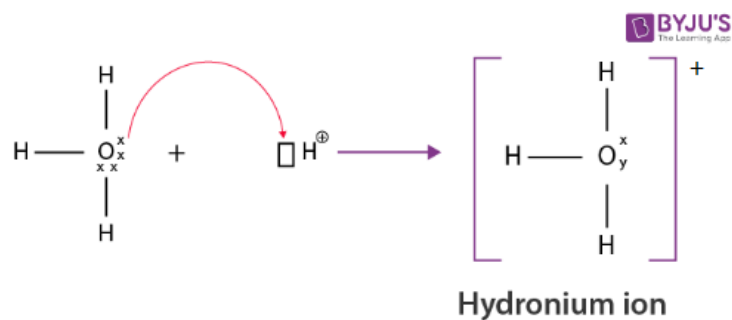
#### Formation of Ammonium Ion

The nitrogen atom in Ammonia donates its electron pair to the empty orbital of the  $H^+$  ion; thus, nitrogen is the donor,  $H^+$  is the acceptor, and a co-ordinate bond is formed



#### Formation of Hydronium Ion

An oxygen atom in water donates its one pair of electrons to the vacant orbital of the  $H^+$  ion; thus, a dative bond is formed oxygen atom is the donor atom and the  $H^+$  is the acceptor atom.



### 2-3-Metallic bonds :

Metallic bonds are chemical bonds among the atoms in a metal. Similar to a sea of freely moving electrons, these bonds connect all the atoms in the metal at once (in contrast to covalent bonds, in which atoms share discrete pairs of electrons over specific parts of a molecule). These chemical bonds are responsible for many properties of bulk metals, including their luster and electrical and thermal conductivity.

### 3- What are intermolecular forces?

Intermolecular forces are electrostatic interactions between permanently or transiently (temporarily) charged chemical species. They are the attractive or repulsive forces between molecules. These forces are much weaker than the chemical bonds that hold atoms together within a molecule, but they can still have a significant impact on the properties of a substance. For example, intermolecular forces can affect the melting and boiling points of a substance, as well as its solubility and viscosity. There are several different types of intermolecular forces, including London dispersion forces, Van Der Waals forces (interactions), ion-dipole, dipole-dipole interactions, and hydrogen bonding. The strength of these forces depends on the type of molecules involved and the distance between them. Understanding intermolecular forces can help us predict and explain many of the physical properties of substances.

The term is usually used to refer only to attractive interactions, which hold molecules and ions together in condensed phases (liquid and solid). These forces govern many of the bulk physical properties of substances and mixtures, such as melting point, boiling point, and surface tension.

#### Types of intermolecular forces

##### 1- Van Der Waals forces

**Van der Waals forces, aka Van der Waals interactions,** are the weakest intermolecular force and consist of weak dipole-dipole forces and stronger London dispersion forces. They are

names after the Dutch chemist Johannes van der Waals (1837-1923). The Van Der Waals equation, for non-ideal gases, takes into consideration these intermolecular forces. These forces determine whether a substance is a solid, liquid or gas at a given temperature.

There are two types of Van der Waals forces which we will discuss below – London dispersion forces, and dipole-dipole forces (interactions).

### Ion-dipole forces

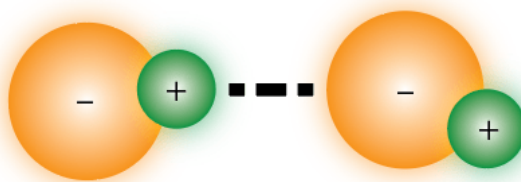
Ion-dipole forces result from the interaction of a charged species with a polar molecule. They are very similar to ionic bonds, but tend to be weaker because polar molecules only possess *partial* electric charge, which generate less electrostatic attraction. Because of these forces, polar solvents are better able to dissolve ionic solids such as NaCl, compared with nonpolar solvents.

### Ion-induced dipole interactions

Closely related to ion-dipole forces are ion-induced dipole forces. In this case, there is no permanent dipole on the molecule. Instead, the ion generates a transient dipole from a nonpolar molecule by attracting or repelling its electrons. An attraction then forms between the ion and transient partial charge.

### Dipole-dipole forces

Dipole-dipole force are a type of **Van Der Waals force**. When two polar molecules interact, opposite partial charges attract, similarly to ionic bonding, but generally weaker, because of the smaller charge magnitude. Because of these dipole-dipole forces, polar compounds tend to have higher melting and boiling points than nonpolar compounds.

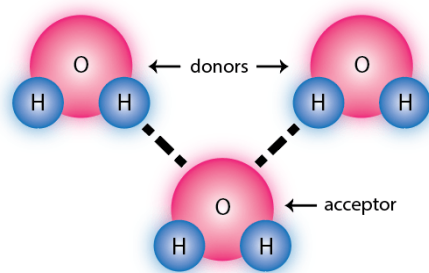


Two simple polar molecules with a dipole-dipole interaction shown as a dotted line. Note that the molecules do not need to be oriented in any special way, as long as the positive (green) end of one is interacting with the negative (orange) end of another.

## 2- Hydrogen bonding

Hydrogen bonding is a special type of dipole-dipole interaction. It can only occur when the molecules in question have a highly electronegative atom directly bonded to a hydrogen atom, leading to an unusually extreme dipole. For most purposes, these highly electronegative atoms are limited to only nitrogen, oxygen and fluorine.

Hydrogen bonding involves a “donor” molecule and an “acceptor” molecule. The donor provides the hydrogen atom for the bond, while the acceptor provides the electronegative atom. In the image below, the top two water molecules are both acting as donors, while the bottom molecule is acting as an acceptor. Some molecules can only act as acceptors.



Water molecules participate in hydrogen bonding. This gives water its characteristic high boiling point as well as low density in the solid state, which is why ice floats on liquid water.

Hydrogen bonding is also directional – a bond can only qualify as a hydrogen bond if the three participating atoms are in roughly a straight line (180-degree angle). This sets it apart further from ordinary dipole-dipole bonding, which has no directionality.

#### 4- Linear Combination of Atomic Orbitals (LCAO) :

According to wave mechanics, the atomic orbitals can be expressed by wave functions ( $\psi$ 's) which represent the amplitude of the electron waves. These are obtained from the solution of Schrodinger wave equation. However, since it cannot be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtained directly from the solution of Schrodinger wave equation. To overcome this problem, an approximate method known as **linear combination of atomic orbitals (LCAO)** has been adopted.

Let us apply this method to the homonuclear diatomic hydrogen molecule. Consider the hydrogen molecule consisting of two atoms A and B. each hydrogen atom in the ground state has one electron in 1s orbital. The atomic orbitals of these atoms may be represented by the wave functions  $\psi_A$  and  $\psi_B$ . Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below:

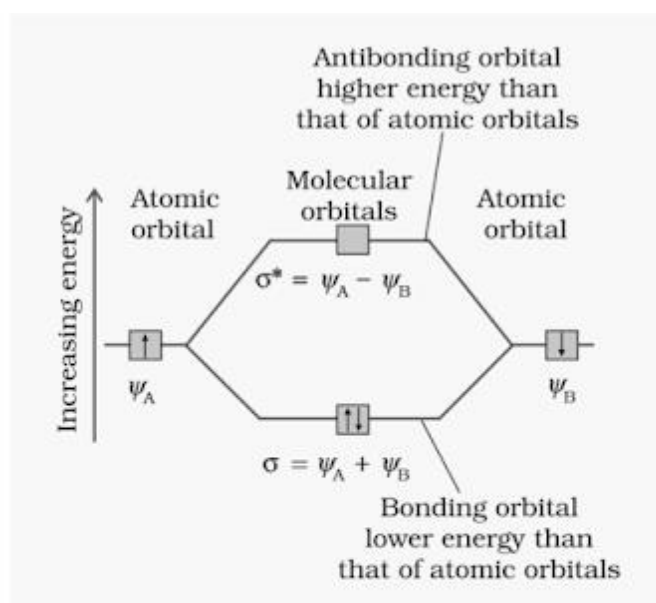
$$\psi_{\text{MO}} = \psi_{\text{A}} \pm \psi_{\text{B}}$$

Therefore, the two molecular orbitals  $\sigma$  and  $\sigma^*$  are formed as :

$$\sigma = \psi_{\text{A}} + \psi_{\text{B}}$$

$$\sigma^* = \psi_{\text{A}} - \psi_{\text{B}}$$

The molecular orbital  $\sigma$  formed by the addition of atomic orbitals is called the bonding molecular orbital while the molecular orbital  $\sigma^*$  formed by the subtraction of atomic orbital is called antibonding molecular orbital as depicted in below figure:



**Fig.4.19** Formation of bonding ( $\sigma$ ) and antibonding ( $\sigma^*$ ) molecular orbitals by the linear combination of atomic orbitals  $\psi_A$  and  $\psi_B$  centered on two atoms A and B respectively.

Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other due to constructive interference while in the formation of antibonding molecular orbital, the electron waves cancel each other due to destructive interference. As a result, the electron density

in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of the atomic orbitals that have combined to form it. In contrast, the electrons placed in the antibonding molecular orbital destabilize the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons and the nuclei, which causes a net increase in energy.

It may be noted that the energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy of the bonding orbital has been lowered than the parent orbitals. The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

- **MO diagram**

A **molecular orbital diagram** or **MO diagram** for short is a qualitative descriptive tool explaining chemical bonding in molecules in terms of molecular orbital theory in general and the Linear combination of atomic orbitals molecular orbital method (LCAO method) in particular. This tool is very well suited for simple diatomic molecules such as dihydrogen, dioxygen and carbon monoxide but becomes more complex when discussing polynuclear molecules such as methane. It explains why some molecules exist and not others, how strong bonds are, and what electronic transitions take place.

- **Dihydrogen MO diagram**

The smallest atom, hydrogen exists as dihydrogen (H-H) with a single covalent bond between two hydrogen atoms. As each hydrogen atom has a single 1s atomic orbital for its electron, the bond forms by overlap of these two atomic orbitals. In figure 1 the two atomic orbitals are depicted on the left and on the right. The vertical axis always represents the orbital energies. The atomic orbital energy correlates with electronegativity as a more electronegative atom holds an electron more tightly thus lowering its energy. MO treatment is only valid when the atomic orbitals have comparable energy; when they differ greatly the mode of bonding becomes ionic. Each orbital is singly occupied with the up and down arrows representing an electron.

The two AO's can overlap in two ways depending on their phase relationship. The phase of an orbital is a direct consequence of the wave-like properties of electrons. In graphical representations, the orbital phase is depicted either by a plus or minus sign (confusing because there is no relationship to electrical charge) or simply by shading. The sign of the phase itself does not have physical meaning except when mixing orbitals to form molecular orbitals.

Then two same-sign orbitals have a constructive overlap forming a molecular orbital with the bulk of electron density located between the two nuclei. This MO is called the bonding orbital and its energy is lower than that of the original atomic orbitals. The orbital is symmetrical with respect to rotation around the molecular axis (no change) and therefore also called a sigma bond ( $\sigma$ -bond).

The two hydrogen atoms can also interact with each other with their 1s orbitals out-of-phase which leads to destructive cancellation and no electron density between the two nuclei depicted by the so-called nodal plane as the vertical dashed line. In this anti-bonding MO with energy much higher than the original AO's the electrons are located in lobes pointing away from the central axis. Like the bonding orbital this orbital is symmetrical but differentiated from it by an asterisk  $\sigma^*$  bond

The next step in constructing a MO diagram is filling the molecular orbitals with electrons. With the case of dihydrogen at hand two electrons have to be distributed over a bonding orbital and an anti-bonding orbital. Three general rules apply:

- The Aufbau principle states that orbitals are filled starting with the lowest energy
- The Pauli exclusion principle states that the maximum number of electrons occupying an orbital is two having opposite spins
- Hund's rule states that when there are several MO's with equal energy the electrons fill one MO at a time.

Application of these rules for dihydrogen results in having both electrons in the bonding MO. This MO is called the Highest Occupied Molecular Orbital or HOMO which makes the other orbital the Lowest Unoccupied Molecular Orbital or LUMO. The electrons in the bond MO are called bonding electrons and any electrons in the antibonding orbital would be called antibonding electrons. The reduction in energy of these electrons is the driving force for chemical bond formation. For bonding to exist the bond order defined as:

$$\text{Bond Order} = \frac{(\text{Number of electrons in bonding MOs}) - (\text{number of electrons in antibonding MOs})}{2}$$

must have a value larger than 0. The bond order for dihydrogen is  $(2-0)/2 = 1$ .

This MO diagram also helps explain how a bond breaks. When applying energy to dihydrogen, a molecular electronic transition takes place when one electron in the bonding MO is promoted to the antibonding MO. The result is that there is no longer a net gain in energy.

## 5- Geometric forms of molecules :

To determine the shapes of molecules, we must become acquainted with the Lewis electron dot structure. Although the Lewis theory does not determine the shapes of molecules, it is the first step in predicting shapes of molecules. The Lewis structure helps us identify the bond pairs and the lone pairs. Then, with the Lewis structure, we apply the valence-shell electron-pair repulsion (VSEPR) theory to determine the molecular geometry and the electron-group geometry.

To identify and have a complete description of the three-dimensional shape of a molecule, we need to know also learn about state the bond angle as well. Lewis Electron Dot Structures play crucial role in determining the geometry of molecules because it helps us identify the valence electrons. To learn how to draw a Lewis electron dot structure click the link above.

### 5-1- Valence-Shell Electron-Pair Repulsion Theory :

Now that we have a background in the Lewis electron dot structure we can use it to locate the the valence electrons of the center atom. The **valence-shell electron-pair repulsion (VSEPR) theory** states that electron pairs repel each other whether or not they are in bond pairs or in lone pairs. Thus, electron pairs will spread themselves as far from each other as possible to minimize repulsion. VSEPR focuses not only on electron pairs, but it also focus on electron groups as a whole. An **electron group** can be an electron pair, a lone pair, a single unpaired electron, a double bond or a triple bond on the center atom. Using the VSEPR theory, the electron bond pairs and lone pairs on the center atom will help us predict the shape of a molecule.

The shape of a molecule is determined by the location of the nuclei and its electrons. The electrons and the nuclei settle into positions that minimize repulsion and maximize attraction. Thus, the molecule's shape reflects its equilibrium state in which it has the lowest possible energy in the system. Although VSEPR theory predicts the distribution of the electrons, we have to take in consideration of the actual determinant of the molecular shape. We separate this into two categories, the **electron-group geometry** and the **molecular geometry**.

Electron-group geometry is determined by the number of electron groups.


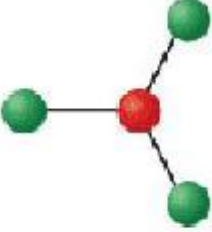


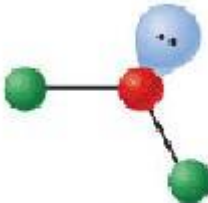
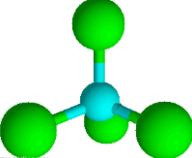
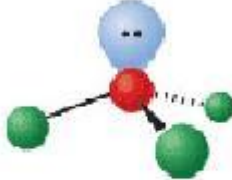
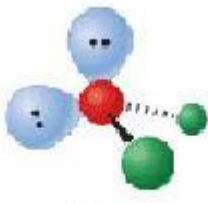
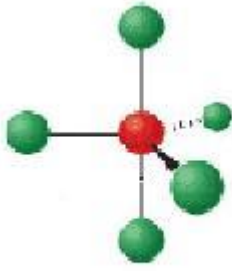
Number of electron groups	Name of electron group geometry
2	linear
3	trigonal-planar
4	tetrahedral
5	trigonal-bipyramidal
6	octahedral

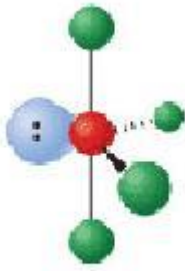
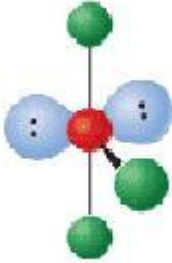
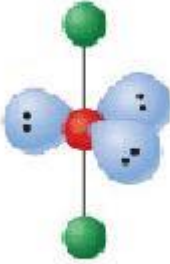
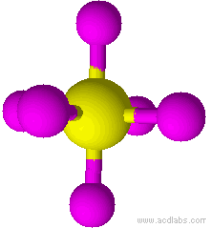
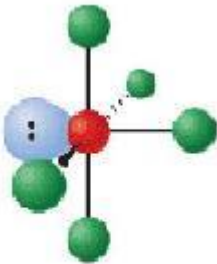
Molecular geometry, on the other hand, depends on not only on the number of electron groups, but also on the number of lone pairs. When the electron groups are all bond pairs, they are named exactly like the electron-group geometry. See the chart below for more information on how they are named depending on the number of lone pairs the molecule has.

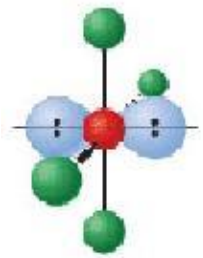
### VSEPR Notation

As stated above, molecular geometry and electron-group geometry are the same when there are no lone pairs. The VSEPR notation for these molecules are  $AX_n$ . "A" represents the central atom and n represents the number of bonds with the central atom. When lone pairs are present, the letter  $E_x$  is added. The x represents the number of lone pairs present in the molecule. For example, a molecule with two bond pairs and two lone pairs would have this notation:  $AX_2E_2$ .

Geometry of Molecules Chart						
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Examples
2	Linear	1	$AX_2$	 Linear	$180^\circ$	$BeH_2$
3	trigonal-planar	0	$AX_3$	 Trigonal planer	$120^\circ$	$CO_3^{2-}$

		1	$AX_2E$	 <p>Bent</p>	$120^\circ$	$O_3$
4	Tetrahedral	0	$AX_4$	 <p>Tetrahedral</p>	$109.5^\circ$	$SO_4^{2-}$
		1	$AX_3E$	 <p>Trigonal Pyramidal</p>	$109.5^\circ$	$H_3O^+$
		2	$AX_2E_2$	 <p>Bent</p>	$109.5^\circ$	$H_2O$
5	trigonal-bipyramidal	0	$AX_5$	 <p>Trigonal-bipyramidal</p>	$90^\circ, 120^\circ$	$PF_5$

		1	$AX_4E^b$	 <p>Seesaw</p>	$90^\circ, 120^\circ$	$TeCl_4$
		2	$AX_3E_2$	 <p>T-shaped</p>	$90^\circ$	$ClF_3$
		3	$AX_2E_3$	 <p>Linear</p>	$180^\circ$	$I_3^-$
6	Octahedral	0	$AX_6$	 <p>octahedral</p>	$90^\circ$	$PF_6^-$
		1	$AX_5E$	 <p>Square Pyramidal</p>	$90^\circ$	$SbCl_5^{2-}$

		2	AX <sub>4</sub> E <sub>2</sub>	 <p>Square Planer</p>	90°	ICl <sub>4</sub> <sup>-</sup>
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### 5-2- Hybridization :

There are various types of hybridization involving s, p, and d orbitals. The different types of hybridization are as under.

#### Types of Hybridization :

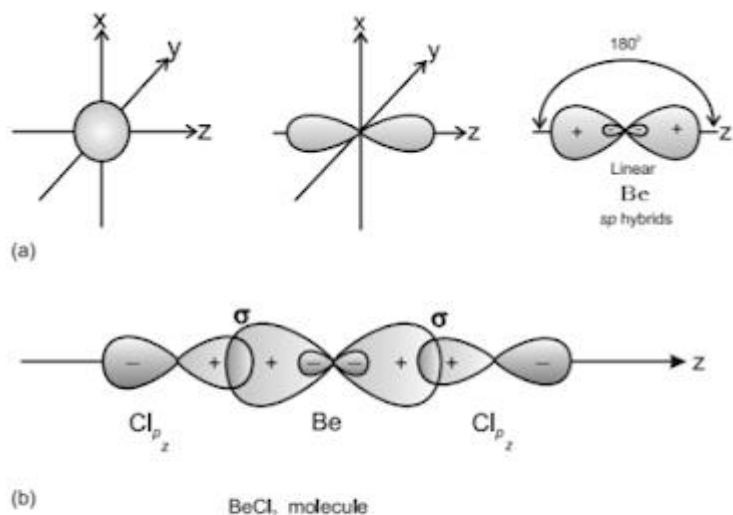
- **sp hybridization:**

This type of hybridization involves the mixing of one *s* and one *p* orbital resulting in the formation of two equivalent *sp* hybrid orbitals. The suitable orbitals for *sp* hybridization are *s* and *p<sub>z</sub>*, if the hybrid orbitals are to lie along the *z*-axis. Each *sp* hybrid orbital has 50% *s*-character and 50% *p*-character. Such a molecule in which the central atom is *sp*-hybridized and linked directly to two other central atoms possesses linear geometry. This type of hybridization is also known as diagonal hybridization.

The two *sp* hybrids point in the opposite direction along the *z*-axis with projecting positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

#### **Example of molecule having sp hybridization**

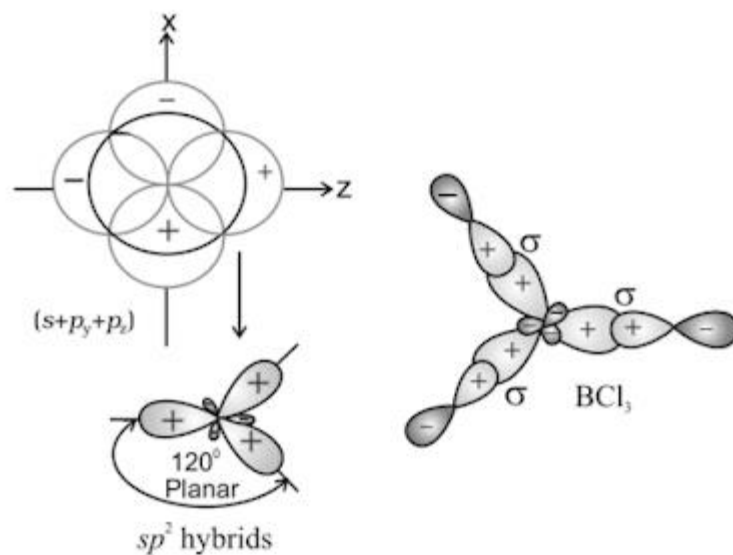
BeCl<sub>2</sub>: The ground state electronic configuration of Be is 1s<sup>2</sup>2s<sup>2</sup>. In the excited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its divalency. One 2s and one 2p-orbitals get hybridized to form two *sp* hybridized orbitals. These two *sp* hybrid orbitals are oriented in opposite direction forming an angle of 180. Each of the *sp* hybridized orbital overlaps with the 2p-orbital of chlorine axially and form two Be-Cl sigma bonds. This is shown below figure.



**Fig.4.10** (a) Formation of  $sp$  hybrids from  $s$  and  $p$  orbitals; (b) Formation of the linear  $BeCl_2$  molecule

- **$Sp^2$  hybridization :**

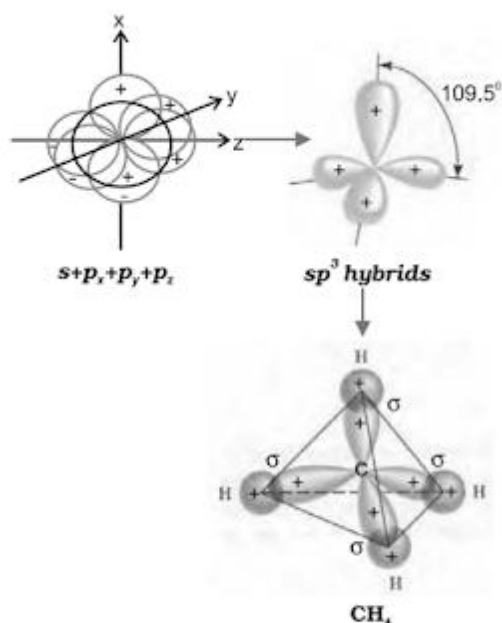
In this hybridization there is involvement of one  $s$  and two  $p$ -orbitals in order to form three equivalent  $sp^2$  hybridized orbitals. For example, in  $BCl_3$  molecule, the ground state electronic configuration of central boron atom is  $1s^2 2s^2 2p^1$ . In the excited state, one of the  $2s$  electrons is promoted to vacant  $2p$  orbitals as a result boron has three unpaired electrons. These three orbitals (one  $2s$  and two  $2p$ ) hybridise 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 ClBCl bond of  $120^\circ$ .



**Fig.4.11** Formation of  $sp^2$  hybrids and the  $BCl_3$  molecule

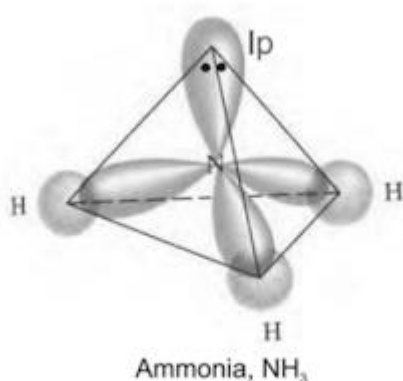
- **Sp<sup>3</sup> hybridization:**

This type of hybridization can be explained by taking the example of  $CH_4$  molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four  $sp^3$  hybrid orbitals of equivalent energies and shape. There is 25% s-character and 75% p-character in each  $sp^3$  hybrid orbital. The four  $sp^3$  hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between  $sp^3$  hybrid orbitals is  $109.5^\circ$  as shown below.



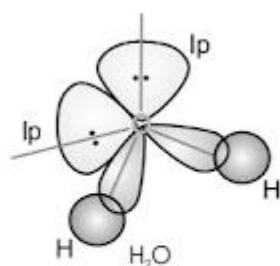
**Fig.4.12** Formation of  $sp^3$  hybrids by the combination of  $s$ ,  $p_x$ ,  $p_y$  and  $p_z$  atomic orbitals of carbon and the formation of  $CH_4$  molecule

The structure of  $NH_3$  and  $H_2O$  molecules can also be explained with the help of  $sp^3$  hybridization. In  $NH_3$ , the valence shell (outer) electronic configuration of nitrogen in the ground state is  $2s^2 2p^1_x 2p^1_y 2p^1_z$  having three unpaired electrons in the  $sp^3$  hybrid orbitals and a lone pair of electrons is present in the fourth one. These three hybrid orbitals overlap with  $1s$  orbitals of hydrogen atoms to form three N-H sigma bonds. As we know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to  $107^\circ$  from  $109.5^\circ$ . The geometry of such a molecule will be pyramidal as shown below.



**Fig.4.13** Formation of  $NH_3$  molecule

In the case of H<sub>2</sub>O molecule, the four oxygen orbitals (one 2s and three 2p) undergo  $sp^3$  hybridization forming 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 hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5 from 109.5 and the molecule thus acquires a V-shape or angular geometry.



**Fig.4.14** Formation of H<sub>2</sub>O molecule