CHAPTER

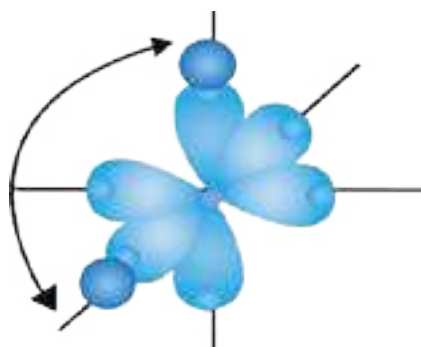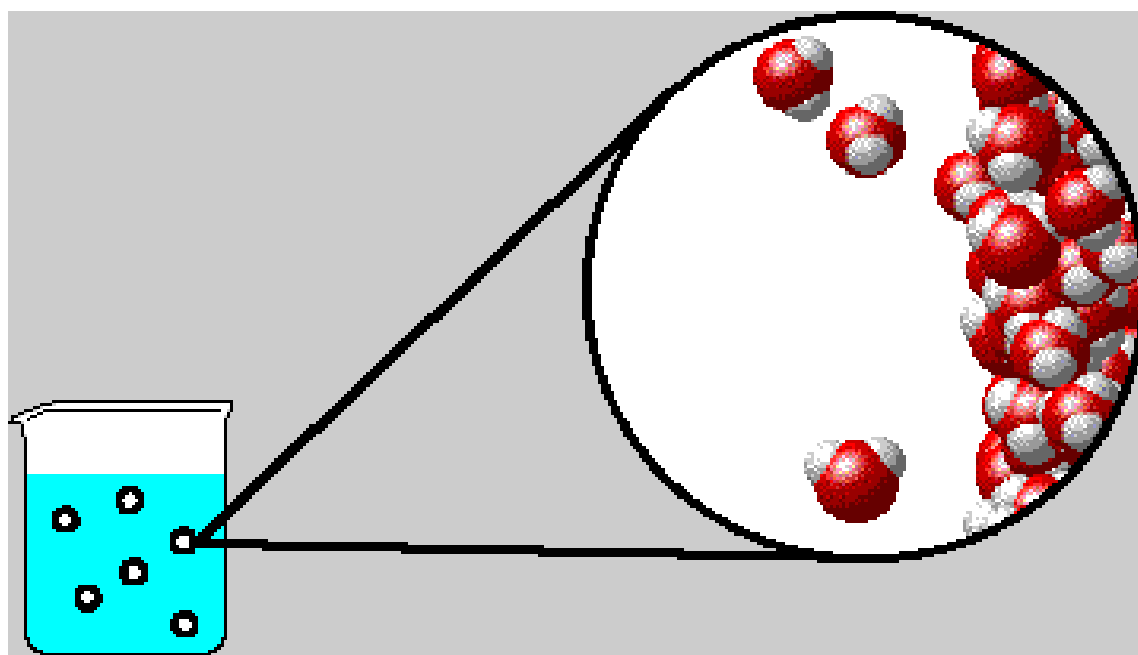## 6

CHEMICAL BONDING

Animation 6.1: Chemical Bonding
Source & Credit: chemistry.elmhurst

6.1.0 INTRODUCTION

     A chemical bond is the force, which holds together two or more atoms or ions to form a large variety of compounds. The forces which are responsible for such bonding and the shapes of the molecules formed are as a result of chemical combination.

The theory of chemical bonding has been a major problem of modern chemistry. In this chapter, we shall look into the nature of the chemical bonds formed between the atoms.

Animation 6.2: Chemical Bond
Source & Credit : geo.arizona
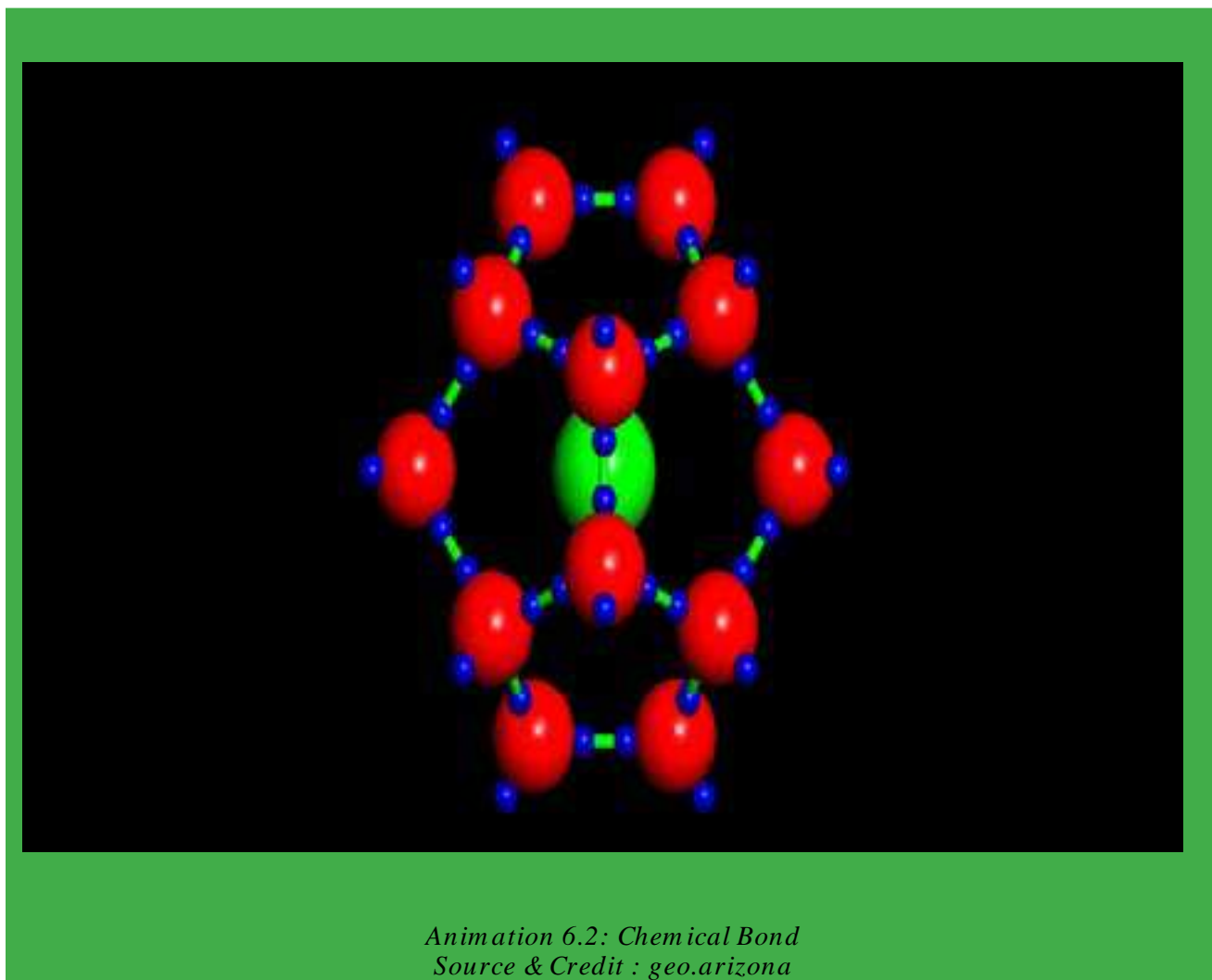
6.1.1 Cause of Chemical Combination

It has been observed that the chemical reactivities of elements, depend upon their characteristic electronic configurations. The noble gases with electronic configuration of valence shell Is^2 (He) or ns^2 np^6 (Ne, Ar, Kr, Xe, etc.) show little tendency to react chemically. There are just only a few stable compounds, formed by these elements like XeF_2, XeF_4, $XeOF_2$, XeO_3, etc. A noble gas does not react with another noble gas. Thus, these gases are the most stable of all the elements. Let us, see why noble gases are most stable. This can be explained on the basis of their special electronic configuration. Their outermost s and p orbitals are completely filled.

↑↓

↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

$_2$He =   Is $_{10}$Ne = Is   2s $2p_x$ $2p_y$ $2p_y$ $2p_z$
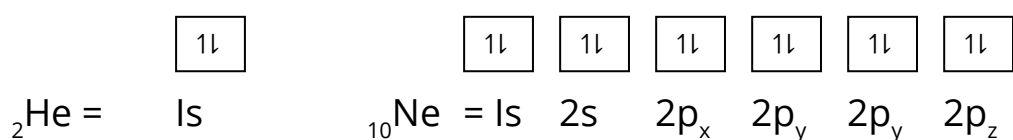
All other elements, combine with one another, due to an inherent tendency to stabilize themselves. They get their stabilization by losing, gaining or sharing electrons to attain the nearest noble gas configuration. The tendency of atoms to attain a maximum of eight electrons in the valence shell is known as the 'octet rule'. A few examples are given in Table (6.1).

In certain cases, both tendencies i.e. to lose or gain electrons have been observed. But the system will go by the conditions in which the chemical combination takes place. For example, in the chemical combination between sodium and hydrogen to form NaH, hydrogen atom gains an electron. In the formation of HF the hydrogen atom donates the major share of its electron to fluorine atom.

Any how, the 'octet' rule could not be made universal as the formation of compounds PF_5, SF_6, BCl_3 are not according to this rule.

Animation 6.3: bonding
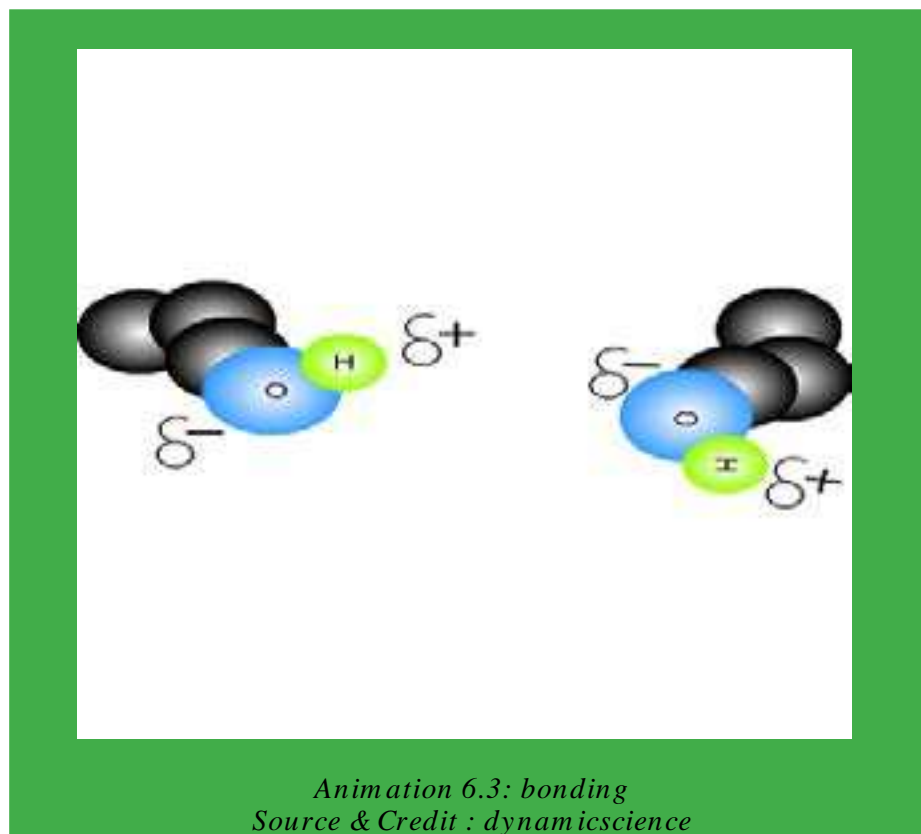*Source & Credit : dynamicscience*

Table (6.1) Change in the electronic configurations of some elements after losing or gaining electrons

Element	Tendency	Electronic configuration		Nearest nobel gas
		Befor electron loss or gain	After electron loss or gain	
$_3$Li	Electron loss	$1s^2\ 2s^1$	$1s^2$	He (2)
$_{12}$Mg	Electron loss	$1s^2\ 2s^2\ 2p^6\ 3s^2$	$1s^2\ 2s^2\ 2p^6$	Ne (10)
$_9$F	Electron gain	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$	$1s^2\ 2s^2\ 2p^6$	Ne (10)
$_{16}$S	Electron gain	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$	Ar (18)

6.1.2 ENERGETICS OF BOND FORMATION

According to the modern theory of chemical bonding, atoms form bonds as it leads to a decrease in energy. For example, when two hydrogen atoms approach each other, forces of attraction and repulsion operate simultaneously.

The attractive forces tend to bring the two atoms close to each other and the potential energy of the system is decreased. On the other hand, the repulsive forces tend to push the atoms apart and potential energy of the system is increased. It has been found that the magnitude of potential energy for attractive forces is more than for repulsive forces. Therefore, potential energy decreases as the two hydrogen atoms approach each other Fig(6.1).
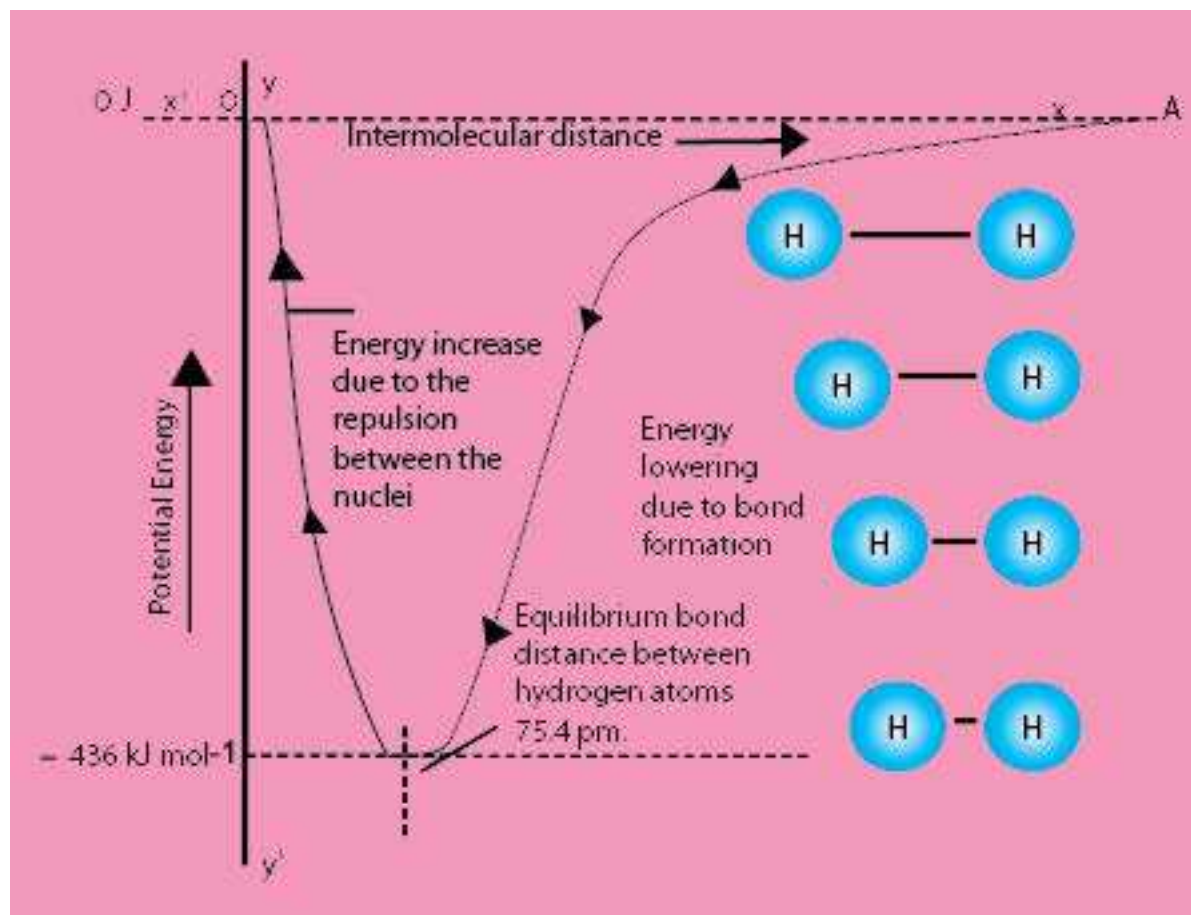

Fig: (6.1) Potential energy curve for the formation of H_2 molecule.

Eventually, a state corresponding to the distance of 75.4pm is reached, where the attractive forces dominate the repulsive forces. Here,the potential energy of the system is minimum and the hydrogen atoms are said to be bonded to form a stable molecule. So,this distance of 75.4 pm is called bond distance or bond length or compromise distance of two hydrogen atoms. When the atoms approach the distance of minimum energy, then the system of two hydrogen atoms is stabilized to maximum extent. The amount of energy evolved is 436.45k.Jmol^{-1} and is called bond formation energy. In order to break the bond, the same amount of energy has to be provided.

Animation 6.4: ENERGETICS OF BOND FORMATION
Source & Credit : 800mainstreet
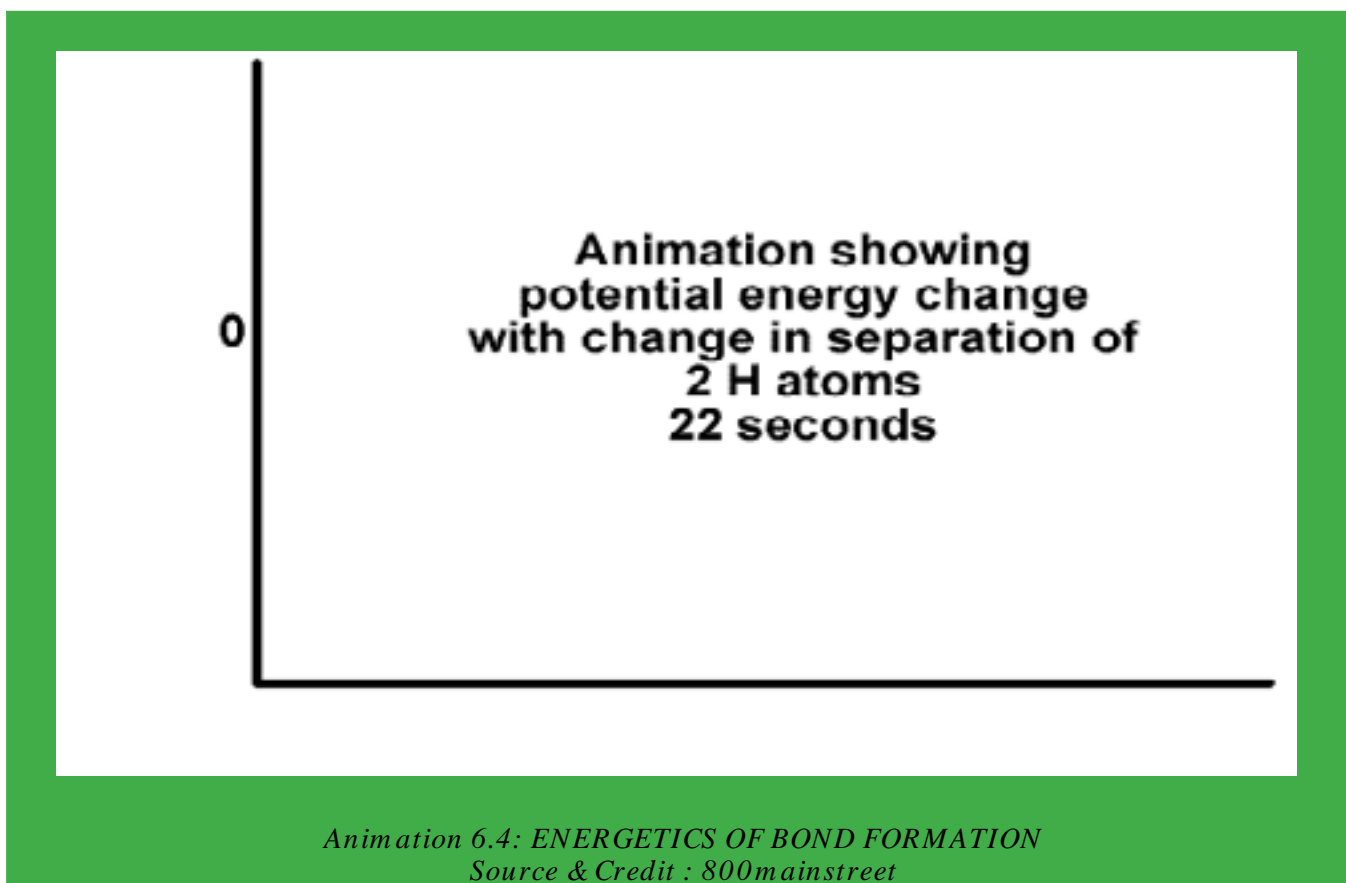
For the case, where repulsive forces are dominant than the attractive forces, the energy of the system increases and it leads to instability. Consequently, a bond is not formed. In order to understand bonding, the relative sizes of atoms should be known.

6.2. ATOMIC SIZES

ATOMIC RADII, IONIC RADII AND COVALENT RADII.

The size of an atom is very important because many physical and chemical properties are related to it. Atoms are assumed to be spherical. That is why, we report the various types of radii to guess their sizes For this reason, the sizes of atoms are expressed in terms of atomic radii, ionic radii and covalent radii, etc,. depending upon the type of the compound used for its measurement.

The atomic radius means the average distance between the nucleus of the atom and its outermost electronic shell.

The radius of an atom cannot be determined precisely due to the following reasons.

(i) There is no sharp boundary of an atom. The probability of finding an electron never becomes exactly zero even at large distances from the nucleus.

(ii) The electronic probability distribution is affected by neighbouring atoms. For this reason,the size of an atom may change from one compound to another.

Atomic radii can be determined, by measuring the distances between the centres of adjacent atoms with the help of X-rays or by spectroscopic measurements. Atomic radii of elements of the periodic table in pm are shown in Table (6.2).

atoms:
1

diameter:
0.1 nm

Animation 6.5: ATOMIC SIZES
Source & Credit : sustainable-nano
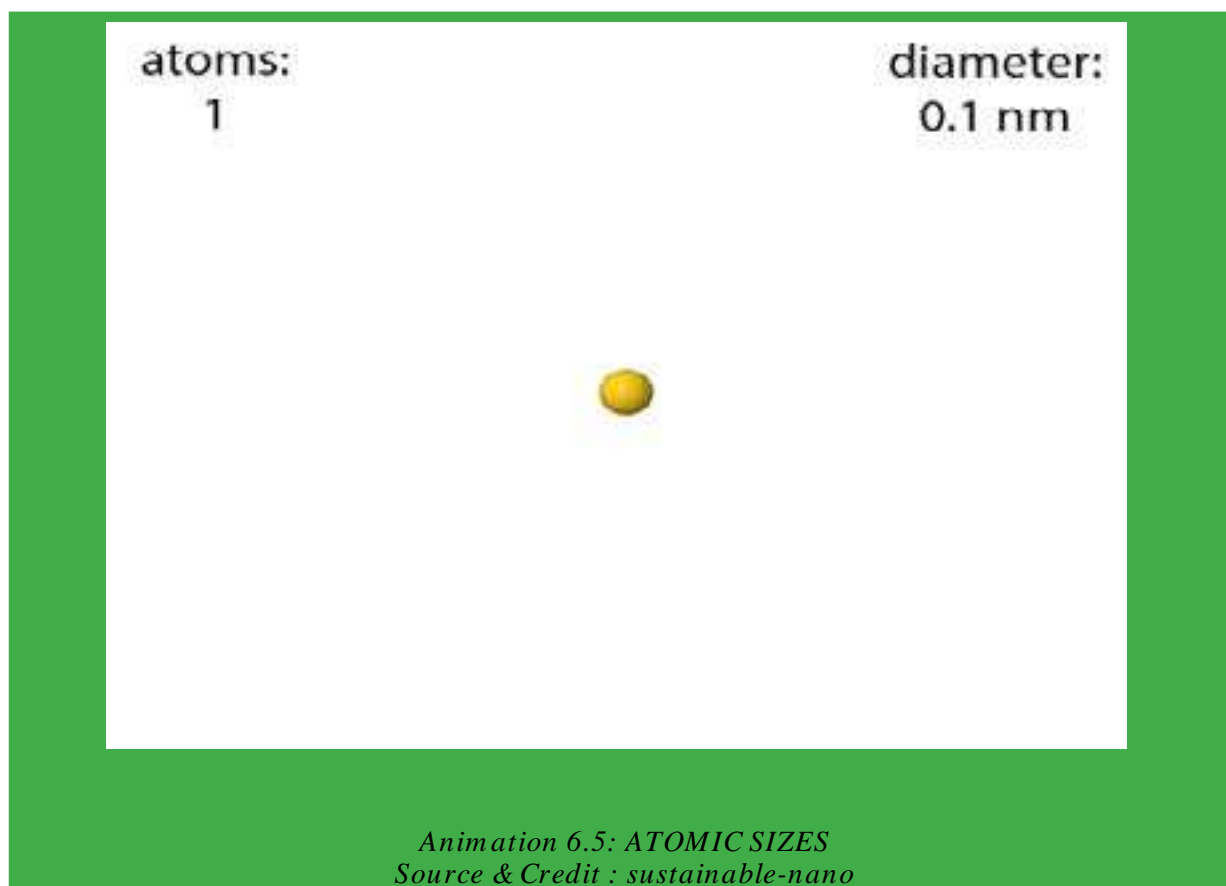
Variation of Atomic Radii in the Periodic Table

In general, the atomic radii decrease from left to the right in a period and increase from top to bottom in a group of the periodic table. The decreasing trend in a period is due to the increase in the nuclear charge. As the nuclear charge increases, the pull on the electrons is increased and size of an atom decreases. Moreover, the shielding effect remains the same from left to right in a period.

Animation 6.6: Periodic trends
Source & Credit : kaiserscience.wordpress

The increase in atomic radii in a group is due to increase in the number of shells and the screening effect. The decrease of atomic radii is very prominent in second period, but less in higher periods. Moreover, the decrease is small, when we travel from left to right in transition elements Sc(21) -Zn(30), Y(39) -Cd(48) due to the intervening electrons. The screening effect is also called shielding effect. This is responsible for the decrease in force of attraction of the nucleus for the electrons present in the valence shell.

Table (6.2) Radii of atoms and ions in the periodic table.

6.2.1 Ionic Radii and Covalent Radii

Ionic Radic

The ionic radius of an ion is the radius of the ion while considering it to be spherical in shape. The ionic radii of some ions in pm are given in Table (6.2). The ionic radius of a cation is smaller than the atomic radius of the element from which it is derived. The ionic radius of an anion is greater than the atomic radius of the corresponding atom. The radius of Na atom, for example, reduces from 186 pm to 95 pm after conversion into Na^+ ion. The ionic radius of Cl^- ion increases from 99 pm to 181 pm. The cationic radius decreases with the increase in the effective nuclear charge on the ion. The decrease in radius is larger for divalent ions (Mg^{2+}) and still larger for trivalent ions (Al^{3+}). This is due to the reason that with the successive loss of electrons, the nuclear charge attracts the remaining electrons with a greater force.

The increase in the size of the anion is due to the increase in the electron-elenctron repulsion because of the increase in the valence shell electrons. Greater the amount of negative charge on an atom, greater the size of ion.

The variation of ionic radii in groups and periods have the same trend as for atomic radii. But keep in mind that ionic radius for metals is for positive ions and for elements of group number VA to VIIA are for negative ions.

Let us consider, the positive and negative ions, which are held together by electrostatic forces of attraction in a crystal lattice. Fig. (6.2), r_+ and r_- are the values of radii of cation and anion, respectively.

The interionic distance 'R' in a crystal lattice is equal to the sum of the cationic radius r_+ and the anionic radius r.

$$R = r_+ + r_-$$

Pauling was able to determine the distance between K^+ and Cl^- ions in potassium chloride crystal and found that it was equal to the sum of the radii of the two ions.

$$R = 133pm + 181\ pm = 314\ pm$$

Thus, the ionic radius appeared to be an additive property. Pauling extended this concept to other K^+ salts and calculated the radii of other ions from the relationship:

$$r_- = R - r_+$$

Similarly, the ionic radii of different cations can also be determined.
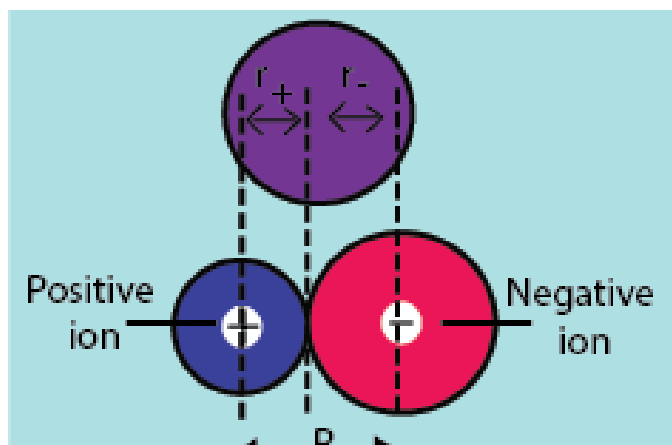
F. ig (6.2) The relationaship of interionic distance R and ionic. radii (r_+ and r_-)

Animation 6.7: Ionic Radii and Covalent Radii Ionic Radii
Source & Credit : chemwiki.ucdavis
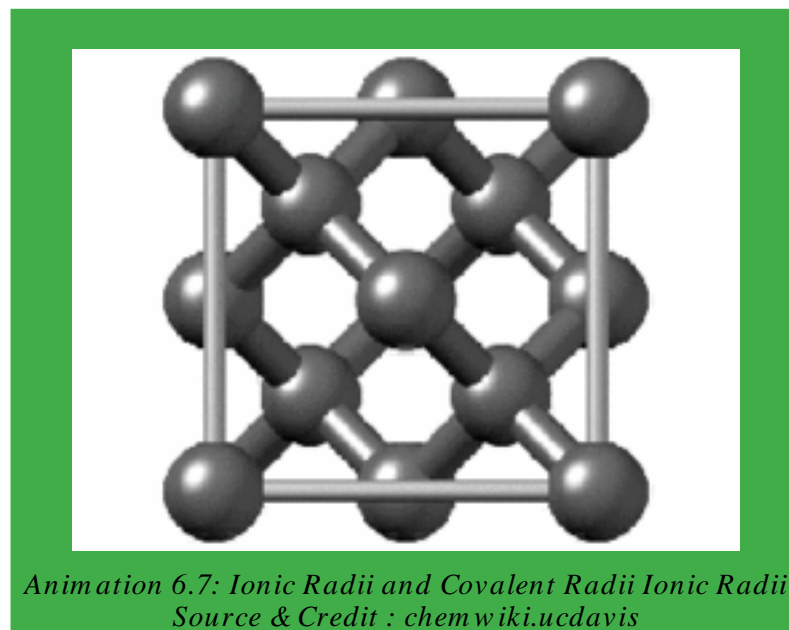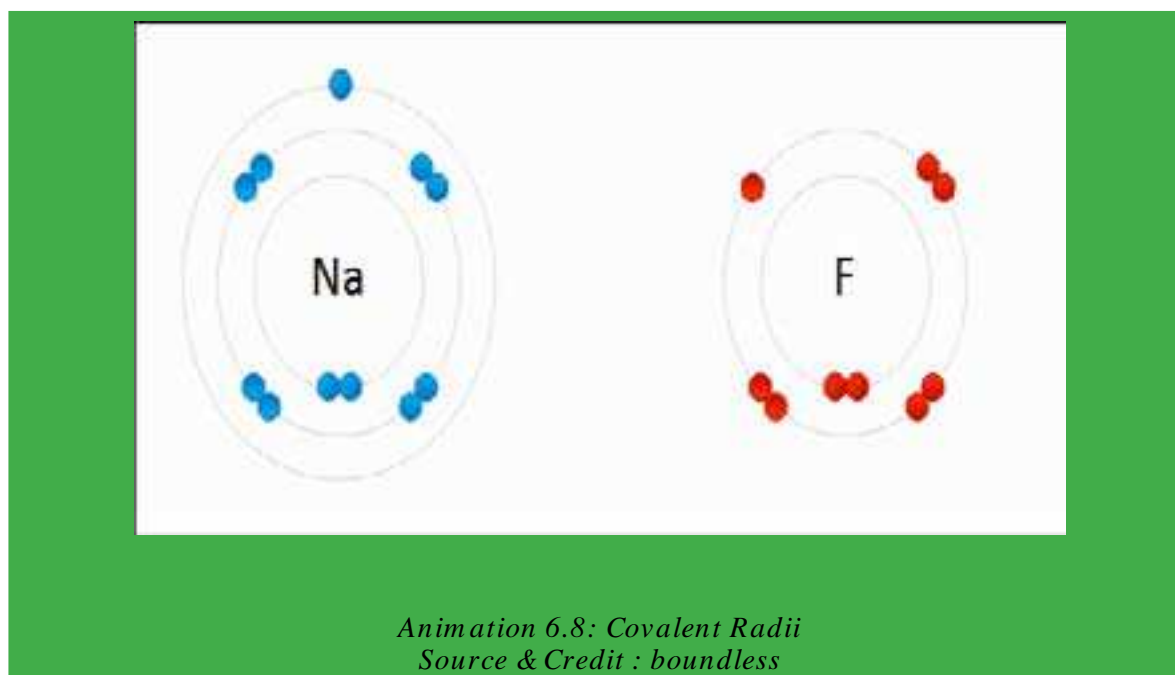
Covalent Radii

The covalent radius of an element is defined as half of the single bond length between two similar atoms covalently bonded in a molecule.

　　　　The covalent radius of hydrogen, for example, is 37.7 pm. It is half of the single bond length (75.4 pm) between the two H atoms in H-H molecule, as shown in Fig (6.3).

The covalent radius of an atom can be used to determine the covalent radius of another atom. For example, the experimentally determined bond length of C-Cl in CH_3Cl is 176.7 pm. The covalent radius of Cl-atom being known as 99.4 pm, that of C-atom can be calculated by subtracting this value from C-Cl bond length. So, the covalent radius of C-atom = 176.7- 99.4 = 77.3 pm.
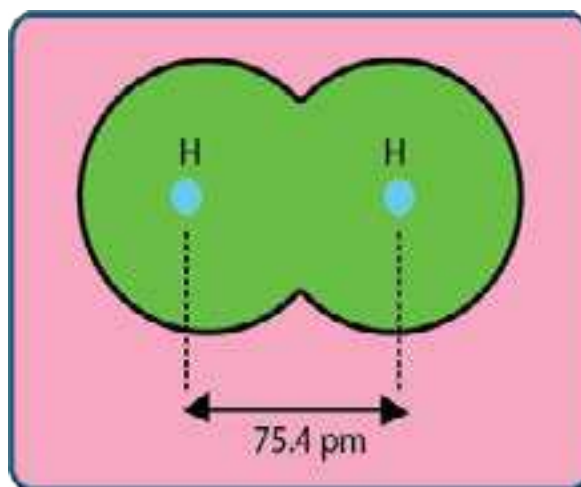
Fig (6.3) Covalent radius of H atom, (75.4/2=37.7 pm)

Animation 6.8: Covalent Radii
Source & Credit : boundless

The variation of covalent radii in groups and periods is almost the same as of atomic radii. Since energy changes are involved in the bond formation, so thermodynamic properties of elements need to be discussed before understanding the chemical bond.

6.3 IONIZATION ENERGY, ELECTRON AFFINITY AND ELECTRONEGATIVITY

6.3.1 Ionization Energy

The ionization energy of an element is the minimum energy required to remove an electron from its gaseous atom to form an ion. The process is called ionization, e.g.

$$Mg \rightarrow Mg^+ + e^- \qquad \Delta H = 738 \, kJmol^{-1}$$

Table (6.3) First ionization energies, electron affinities and electronegativities values of elements

In the gaseous phase, the atoms and ions are isolated and are free from all external influences. Thus, the ionization energy is the qualitative measure of the stability of an isolated atom. The first ionization energies of elements are given in Table (6.3).

Animation 6.9: Ionization Energy
Source & Credit : kaiserscience.wordpress
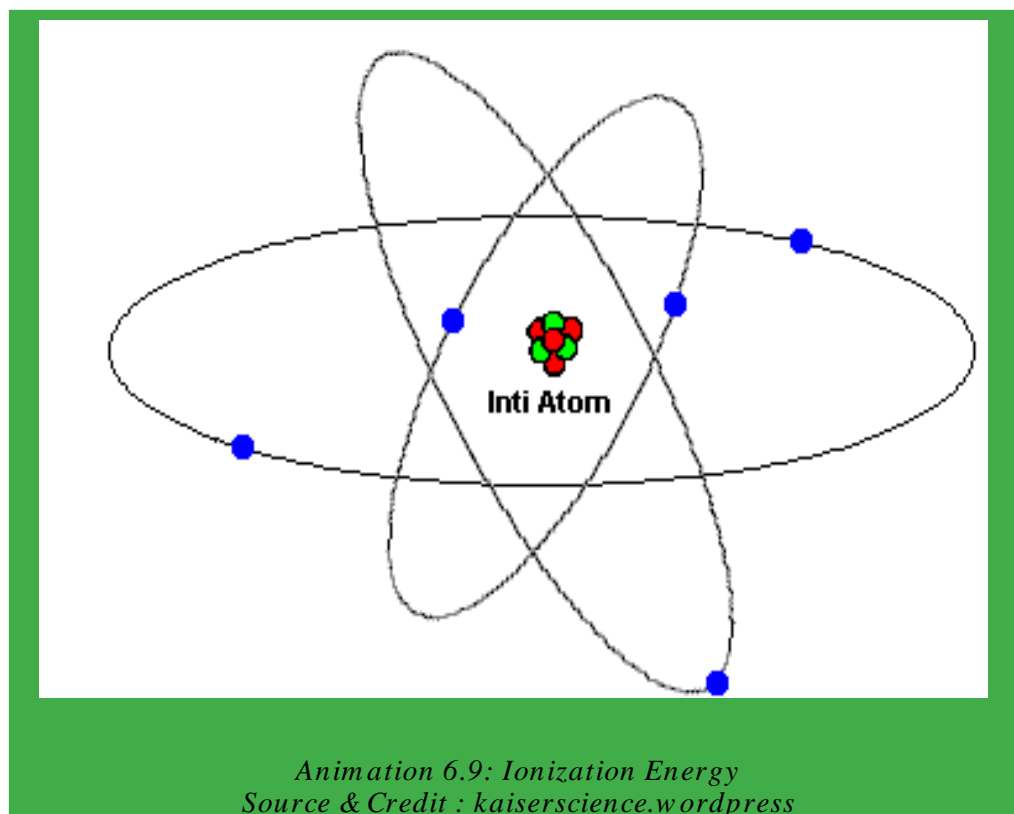
Factors Influencing the Ionization Energies

It is observed that the ionization energies of atoms depend upon the following factors.
(i)   Atomic radius of atom
(ii)   Nuclear charge or proton number of the atom
(iii)   Shielding effect of inner electrons
(iv)   Nature of orbital

Animation 6.10: Factors Influencing the Ionization Energies
*Source & Credit : kaiserscience.wordpress*
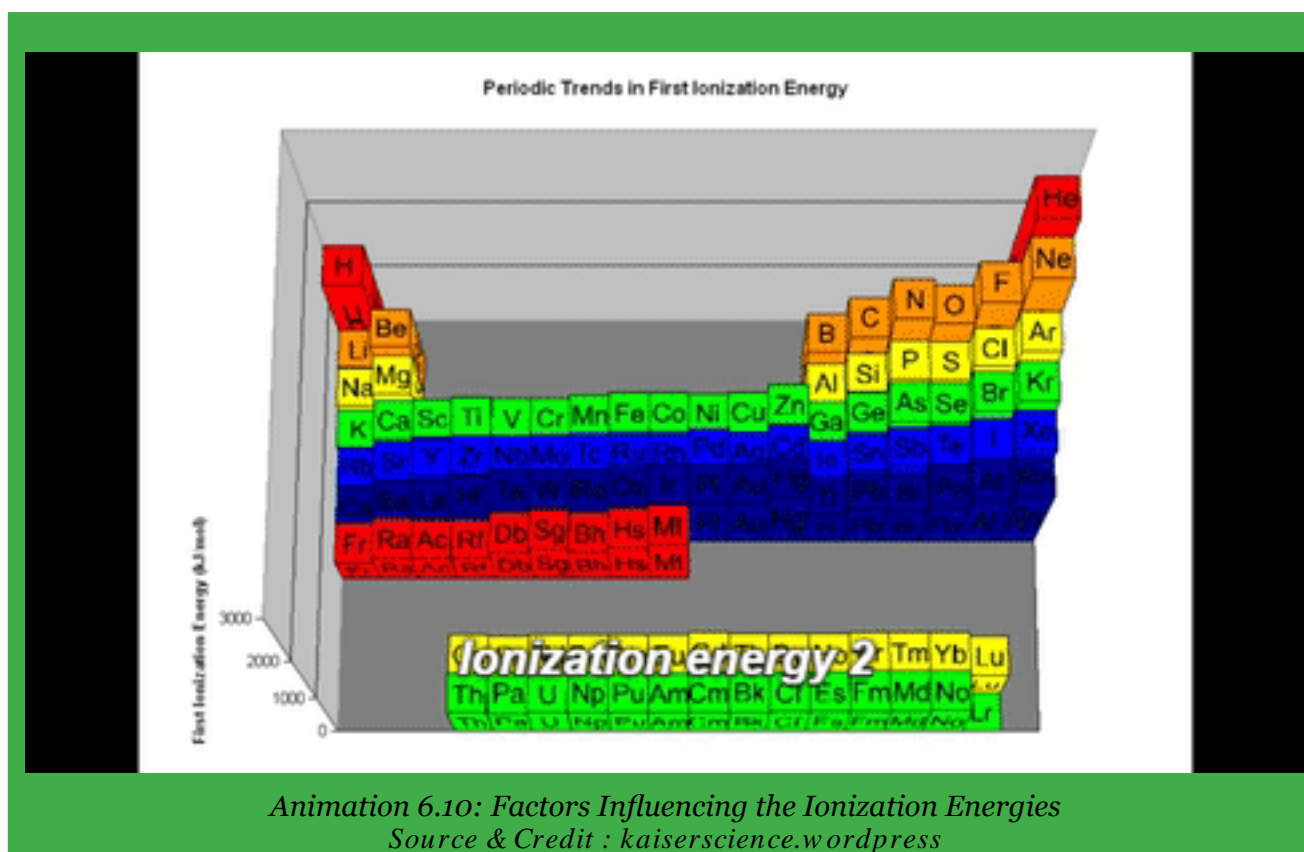
Variation of Ionization Energy in the Periodic Table

In the periodic table, the ionization energies increase from left to right in a period with the increase in the proton number, until a maximum value is reached at the end of the period. This may be explained in terms of the periodicity of the electronic configuration of elements. Each period begins with an element which has one electron in its valence shell and ends with the completion of an electronic shell. The increase in the atomic number is associated with the increase in nuclear charge which leads to a stronger force of attraction between the nucleus and the increasing number of electrons. The stronger force of attraction, ultimately results in difficult removal of electrons.

In groups, the ionization energy decrease in spite of the increase in proton number or nuclear charge. This is due to successive addition of electronic shells as a result of which the valence electrons are placed at a larger distance from the nucleus. As the force of attraction between the nucleus and the outer electron decreases with the increase in distance, the electron can be removed more easily or with less energy. Moreover, the force of attraction also decreases due to increasing shielding effect of the intervening electrons.

The ionization energies of group III-A and VI-A show abnormal trend. This can be understood from the distribution of the electrons.

Animation 6.11: Variation of Atomic Radii in the Periodic Table
Source & Credit : dynamicscience

Higher Ionization Energies

So far, we have explained the first ionization energy. The energy required to remove an electron after the removal of first electron is called second ionization energy.

$$Mg \rightarrow Mg^{++} + e^- \qquad \Delta H = 1450 \text{kJmol}^{-1}$$

Similarly, the energy required to remove third electron after the removal of second one is called the third ionization energy, and it is 7730kJ for Mg. It means that the ionization energy values undergo an increase with the increase in the number of electrons to be removed. This is due to the reason that second electron is removed from a positively charged ion rather than a neutral atom. The dominant positive charge holds the electrons more tightly and thus further removal of electrons becomes more difficult.
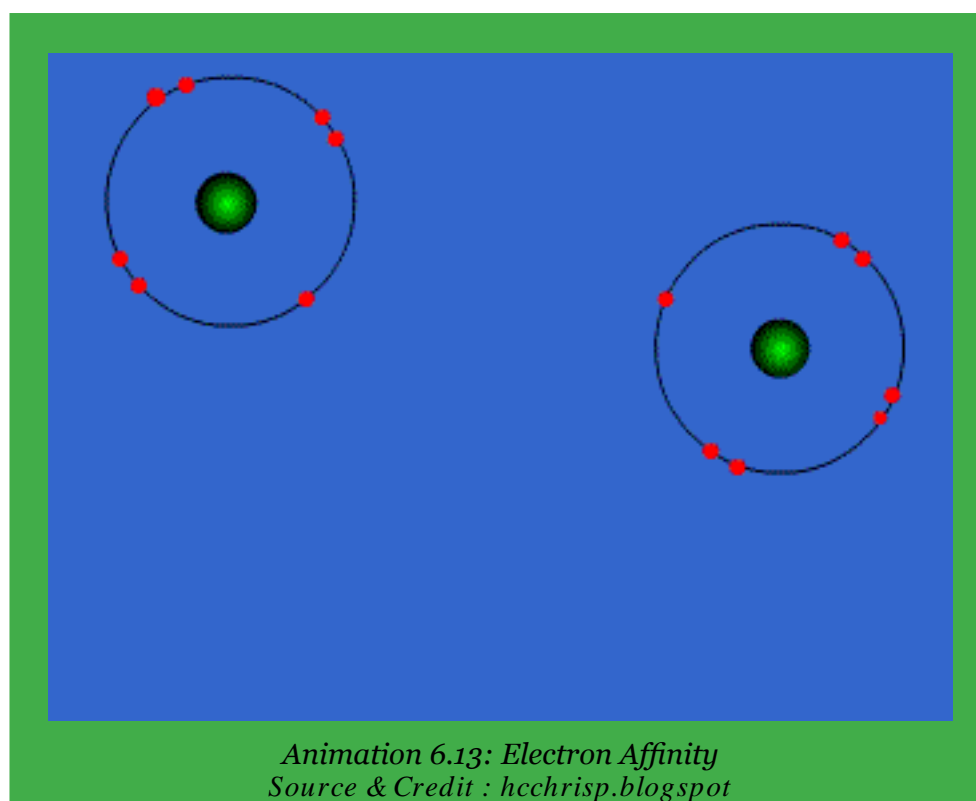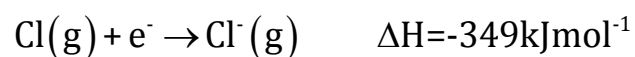
Ionization energy is an index to the metallic character. The elements having low ionization energies are metals and those having high ionization energies are non-metals. Those with intermediate values are mostly metalloids.

The gaps in the first, second, third and higher ionization energies help us to guess the valency of an element. If, there is sufficient gap between first ionization energy and second one, then the element shows valency of one.

Animation 6.12: Higher Ionization Energies
Source & Credit : 800mainstreet
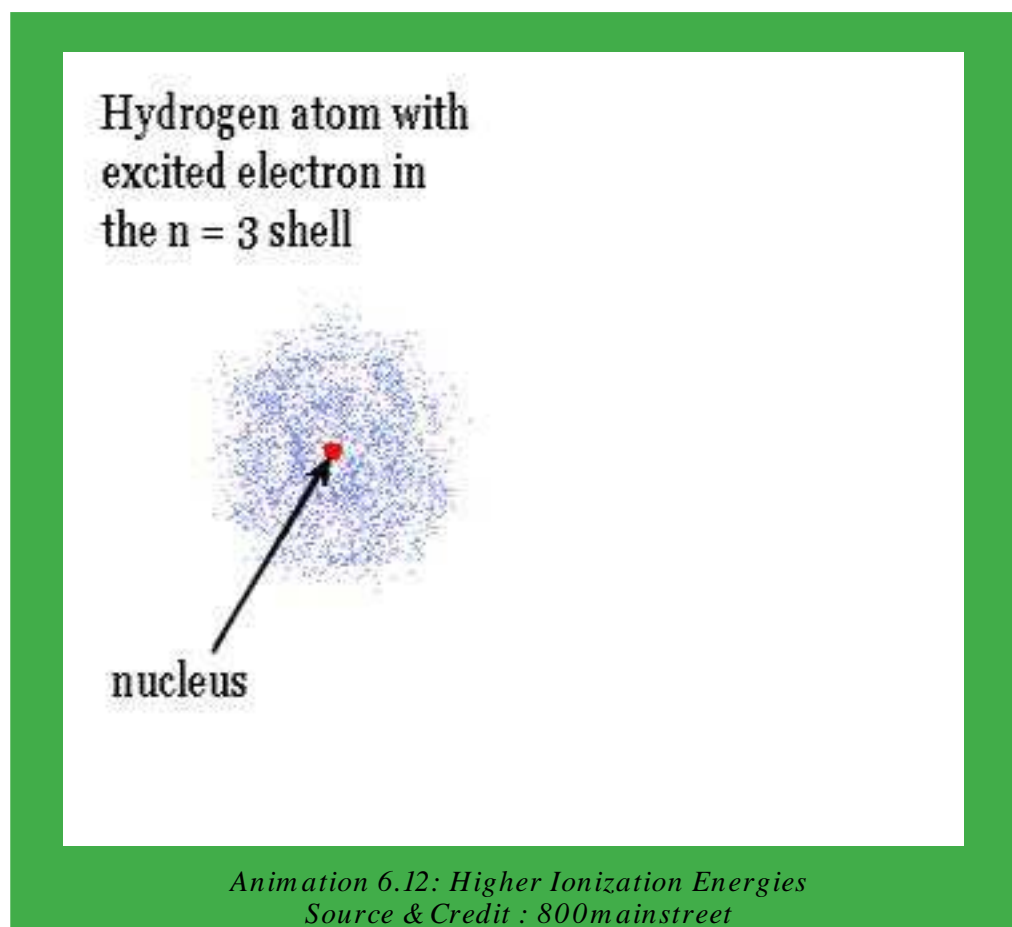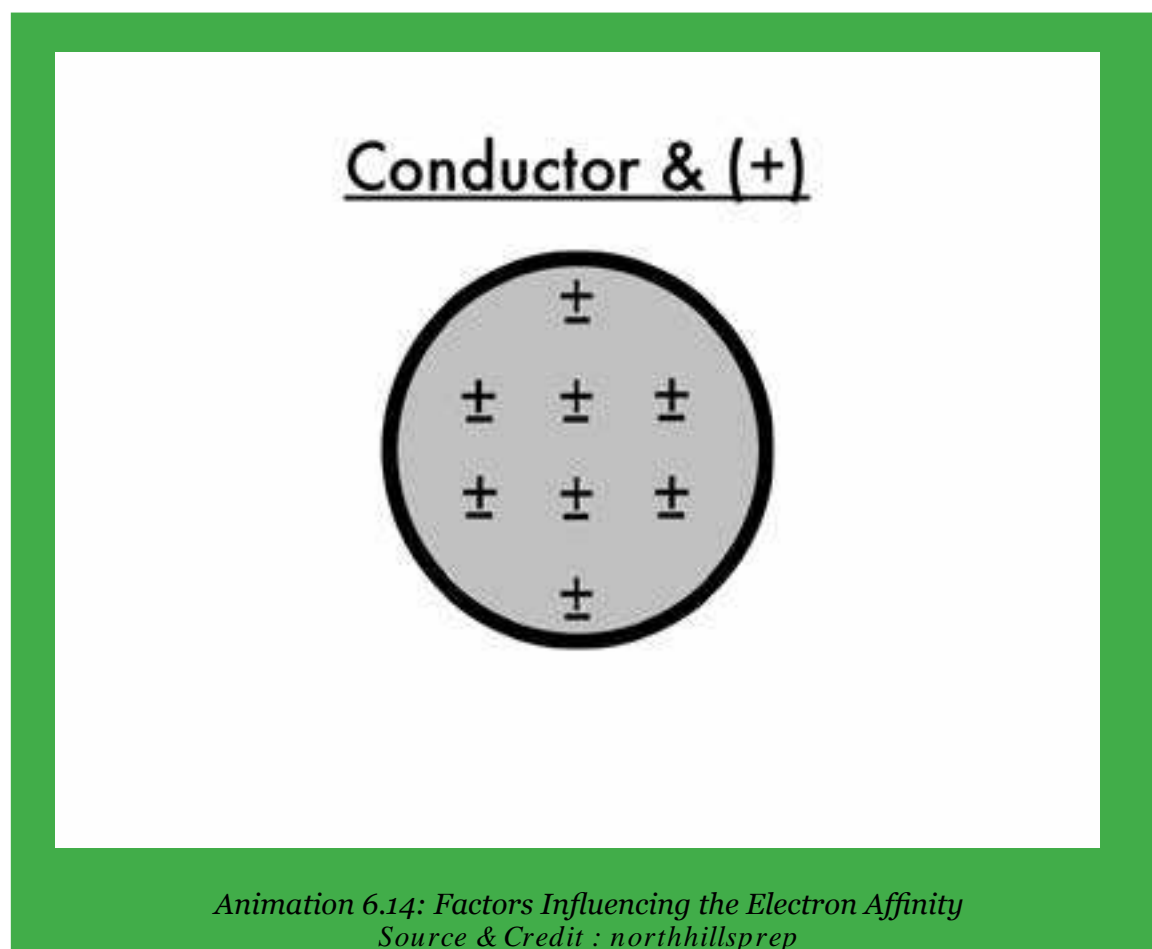
6.3.2 Electron Affinity

The electron affinity of an atom is the energy released when an electron adds to an empty or partially filled orbital of an isolated gaseous atom in its valence energy level to form an anion having a unit negative charge, e.g.

$$Cl(g) + e^- \rightarrow Cl^-(g) \qquad \Delta H = -349 kJmol^{-1}$$

Animation 6.13: Electron Affinity
Source & Credit : hcchrisp.blogspot

Since, energy is released, so electron affinity is given the negative sign. Electron affinity is the measure of the attraction of the nucleus of an atom for the extra electron. The electron affinities of elements of the periodic table are given in Table (6.3).

Factors Influencing the Electron Affinity

The electron affinities, like ionization energies, are influenced by the factors such as atomic radius, the nuclear charge and the shielding effect of inner electrons.

Animation 6.14: Factors Influencing the Electron Affinity
*Source & Credit : northhillsprep*

As the force of attraction between the valence electrons and the nucleus decrease with the increase in the atomic radius, the electron affinities usually decrease.

Variation in the Periodic Table

In a period, the atomic radius decreases due to increase in the nuclear charge. Thus, the electron affinities of elements increase from left to right in the periodic table. That is why, the alkali metals have the lowest and the halogens have the highest electron affinities. In groups, on the other hand, the atomic radii increase with the increase in the proton number due to successive increase of electronic shells.

This also exerts a shielding effect on the force of attraction between the nucleus and the valence electrons. Thus, the electron affinities usually decrease from top to bottom.

Animation 6.15: Variation in the Periodic Table
Source & Credit : vocativ
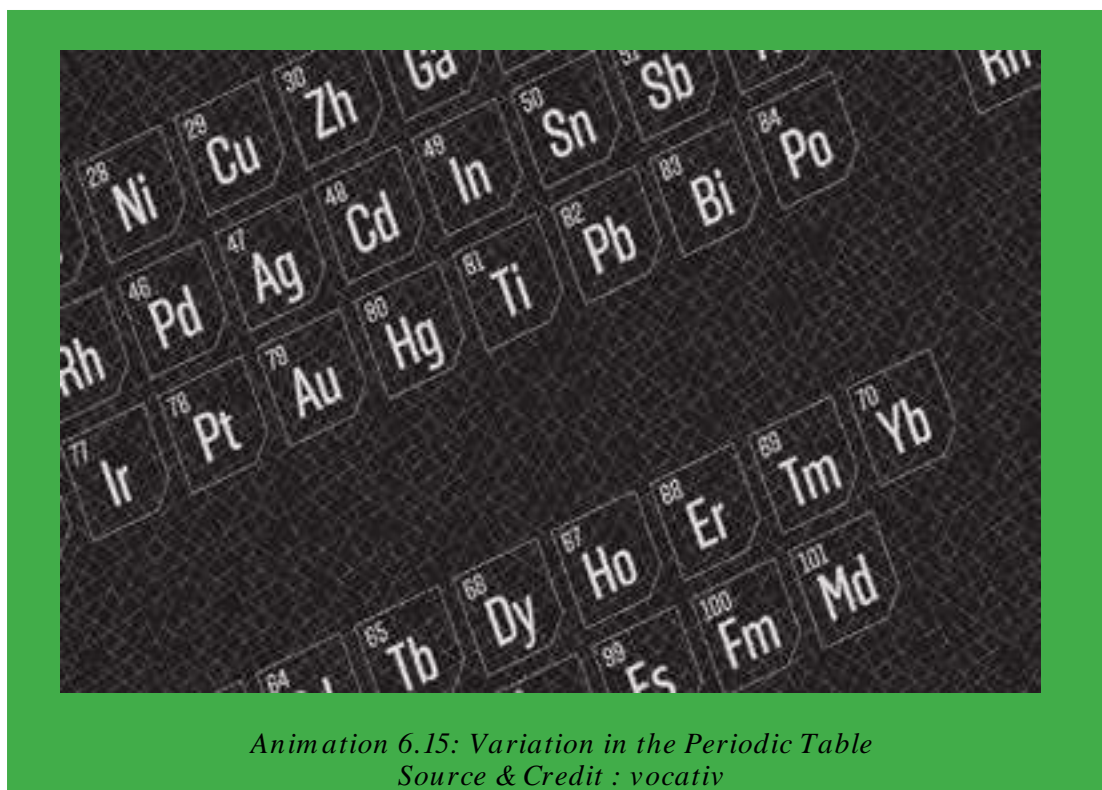
There are, of course, exceptions to this generalization e.g. fluorine has electron affinity less than that of chlorine, Table (6.3). Actually, fluorine has very small size and seven electrons in 2s and 2p subshells have thick electronic cloud. This thick cloud repels the incoming electron.

The elements of group IIA, VA and VIII show abnormally low values in every period of the periodic table. This can be understood from their electronic configurations.

6.3.3 Electronegativity

For a homonuclear diatomic molecule e.g. H_2, the bonding pair of electrons is equally shared between the atoms. On the other hand, in a bond between dissimilar atoms such as in HF the electron density of the bonding electrons lies more towards the fluorine atom than towards the hydrogen atom. The tendency of an atom to attract a shared electron pair towards itself is called its electronegativity.

It is related to the ionization energy and the electron affinity of the element. Thus, fluorine atom is more electronegative than hydrogen atom. Pauling calculated the electronegativity values of elements from the difference between the expected bond energies for their normal covalent bond and the experimentally determined values.

He devised an electronegativity scale on which fluorine is given an arbitrary standard value 4.0. It is the most electronegative element. The electronegativity values of other elements are compared with fluorine, and are given in Table (6.3). Electronegativity has no units.

Animation 6.16: Electronegativity
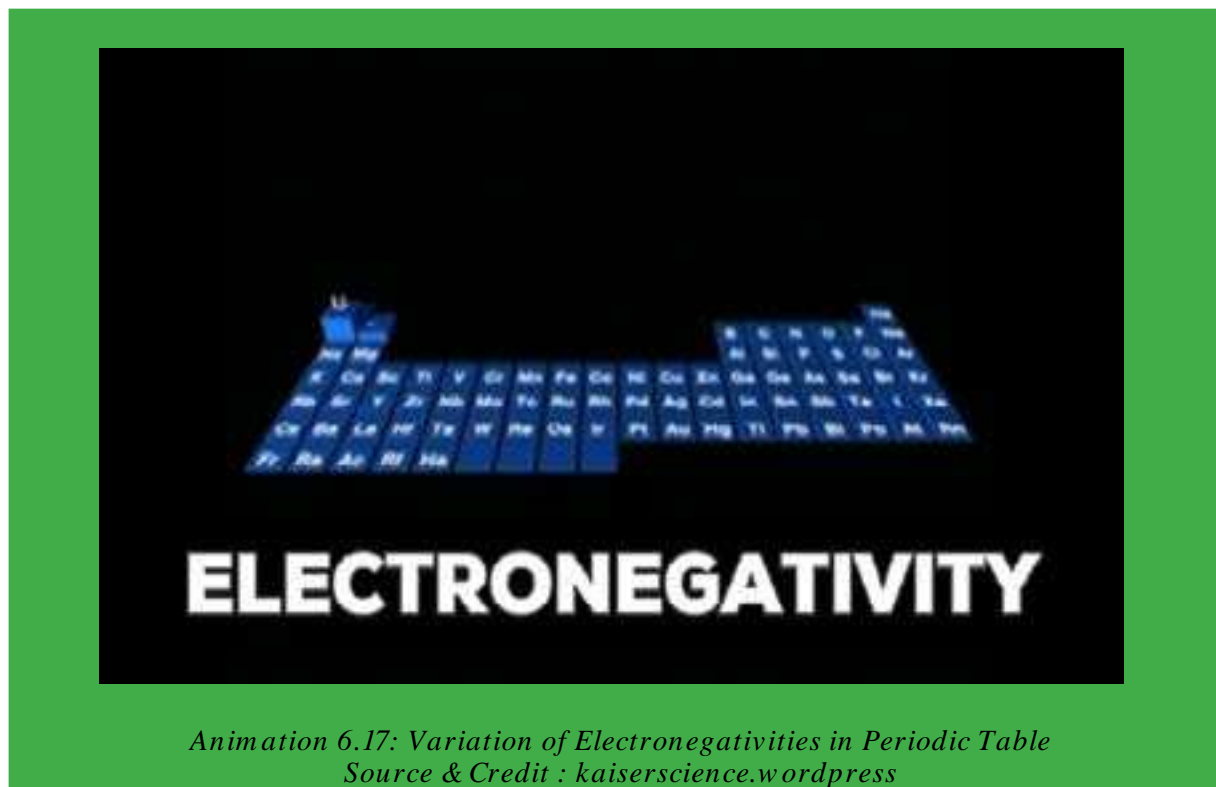*Source & Credit : makeagif*
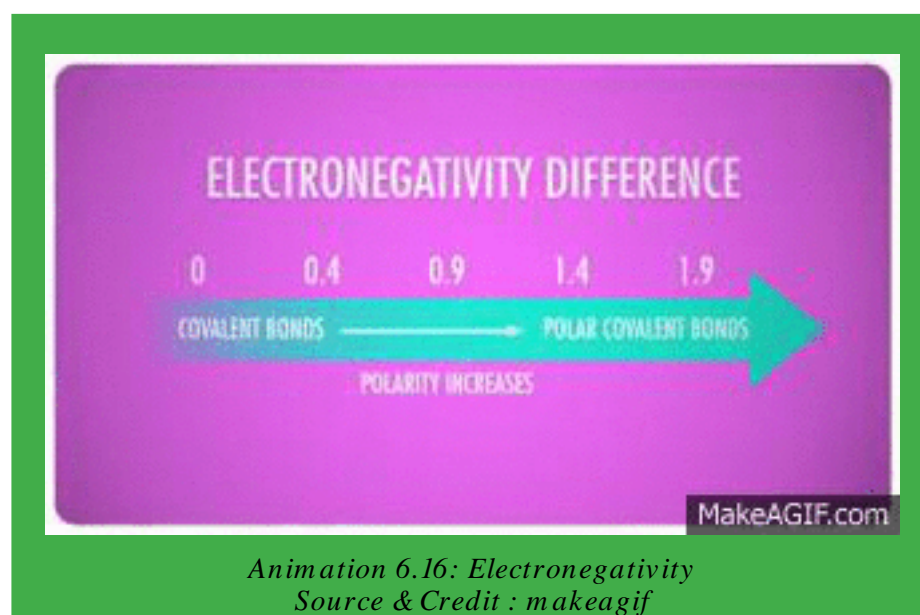
Variation of Electronegativities in Periodic Table

A comparison of electronegativities shows that the values increase in a period with the decrease in atomic size. These values decrease in a group as the size of the atoms increase. The electronegativity differences of the elements can be related to the properties of bonds such as dipole moments and bond energies.

The difference in the electronegativity values of the bonded atoms is an index to the polar nature of the covalent bond. When the difference is zero, the bond between the two atoms is non-polar. Thus, all the bonds which are formed between similar atoms are nonpolar in character, while those formed between different elements are mostly polar. Elements of widely different electronegativities form ionic bonds.

A difference of 1.7 units shows roughly equal contributions of ionic and covalent bonds. Some examples of polar and non-polar bonds are discussed under covalent bond in section 6.4.1.

Having understood the periodic properties of elements, let us discuss types of bonds.


Animation 6.17: Variation of Electronegativities in Periodic Table
Source & Credit : kaiserscience.wordpress

## 6.4 TYPES OF BONDS

Chemical bonds can be classified as :
(i)   Ionic bond
(ii)   Covalent bond
(iii)   Coordinate covalent bond
We shall explain these bonds with the help of different theories of chemical bonding. First of all let us discuss the Lewis concept of bond formation.

Animation 6.18: TYPES OF BONDS
Source & Credit : employees.csbsju
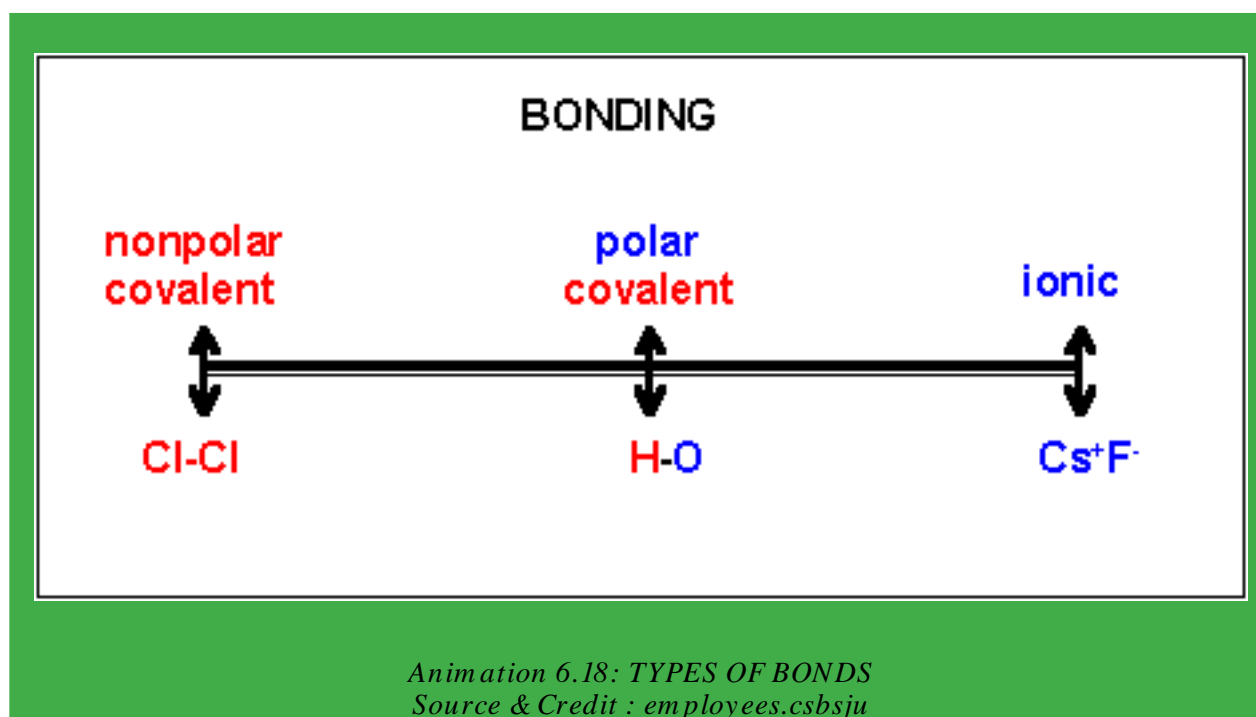
6.4.1 LEWIS CONCEPT

With the help of this concept, we can understand the tendencies of elements to have relation with each other.

Animation 6.19: LEWIS CONCEPT
Source & Credit : nku
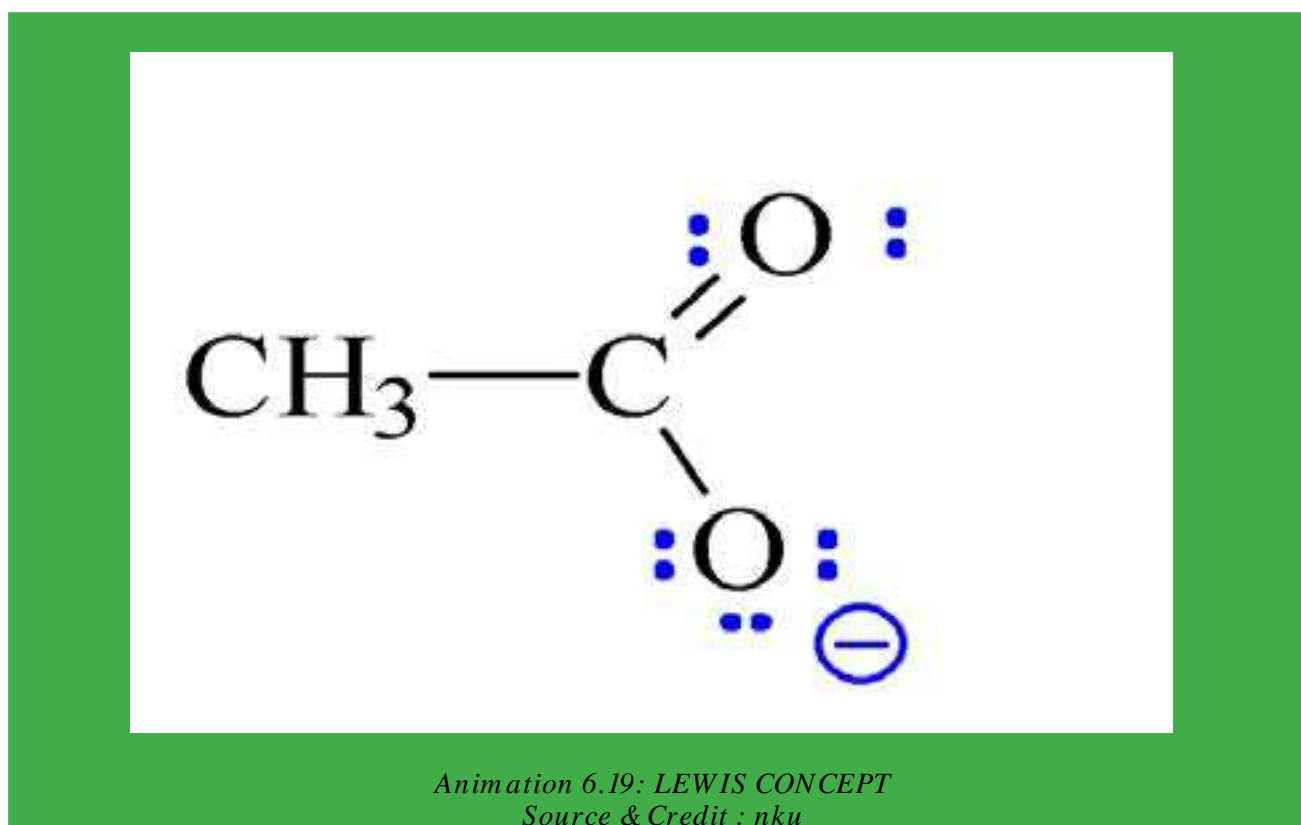
(i) Ionic Bond

According to the Lewis theory, ionic bond is formed by the complete transfer of electron or electrons from an atom with low ionization energy to another atom with high electron affinity. In energy terms, the electropositive elements are at a higher energy state than the electronegative elements. The energy difference will be responsible for the transfer of electrons from a higher energy state to a lower energy state.

Let us consider, the example of the formation of potassium chloride. The electronic configuration of potassium is $Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$. It may be represented as K (2,8,8,1). It tends to lose the outermost electron and to form K^+ ion. The energy needed to detach an electron from potassium atom is equal to its first ionization energy. So

$$K(2,8,8,1) \rightarrow K^+(2,8,8) + e^- \qquad \Delta H = 419.0 kJmol^{-1}$$
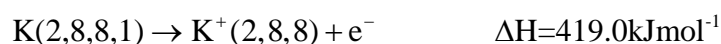
The oppositely charged K^+ and Cl^- ions are held together by strong electrostatic force of attraction. K^+ and Cl^- ions arrange themselves to form a crystal lattice where proportionate number of cations and anions are packed together. The energy released during the formation of crystal lattice is 690 $kJmol^{-1}$. It is called lattice energy of KCl.
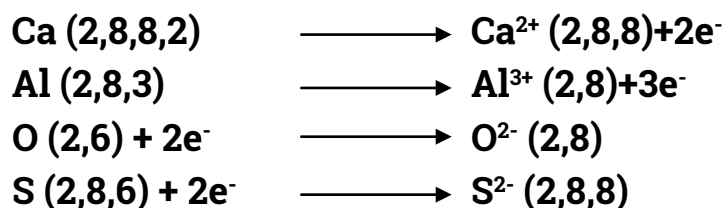
After the loss of an electron, potassium attains the nearest inert gas configuration of Ar (2,8,8). Chlorine atom has the electronic configuration $Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ or Cl (2,8,7). It tends to gain electron lost from potassium atom to attain the nearest inert gas configuration of Ar (2,8,8) releasing 348.6 $kJmol^{-1}$ energy. This energy corresponds to the electron affinity of chlorine.

$$:\ddot{C}l\cdot + e^- \rightarrow :\ddot{C}l^-: \qquad \Delta H = -349 kJmol^{-1}$$

Similarly, the elements of I-A Li, Na, K, Rb, Cs are good losers of electron. The elements of VII-A, F, Cl, Br, I are good gainers. So, ionic bonds are there in these atoms. A similar type of bond is expected between elements of group II-A and VI-A.

Animation 6.20: Ionic Bond
Source & Credit : gcsechemistryhelp.tumblr
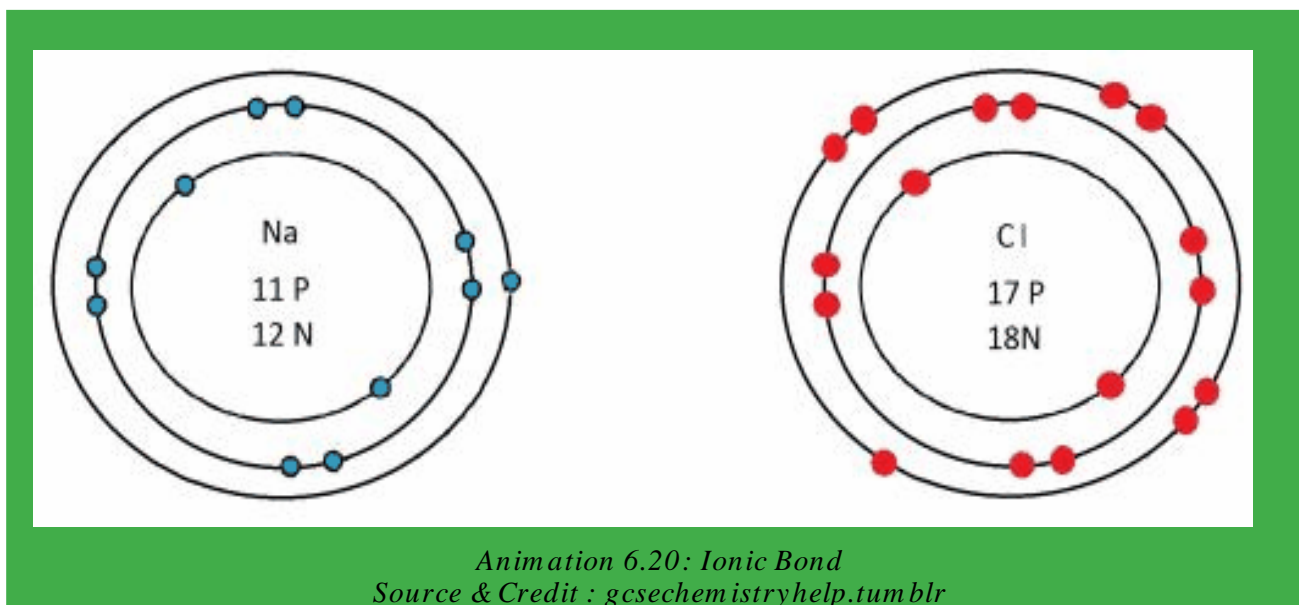
In most of the cases the formation of dipositive, tripositive and dinegative ions takes place as follows:

$$Ca\ (2,8,8,2) \longrightarrow Ca^{2+}\ (2,8,8)+2e^-$$
$$Al\ (2,8,3) \longrightarrow Al^{3+}\ (2,8)+3e^-$$
$$O\ (2,6) + 2e^- \longrightarrow O^{2-}\ (2,8)$$
$$S\ (2,8,6) + 2e^- \longrightarrow S^{2-}\ (2,8,8)$$

Calcium oxide contains ions in the ratio of $Ca^{2+} : O^{2-}$ and its formula is CaO, while in aluminium oxide, Al^{3+} and O^{2-} ions are present in the ratio 2 :3. Its formula is $Al_2 O_3$. Similarly, CaS and Al_2S_3, are also ionic compounds to some extent.

The compounds formed by the cations and anions are called ionic or electrovalent compounds. There exists a strong electrostatic force of attraction between cations and anions in these compounds.

Criteria of electronegativity also helps us to understand the nature of bond. So, in order to decide the % of ionic nature in a compound, it is better to note the difference of electronegativity between the bonded atoms. If the difference is 1.7 or more than that, then the bond is said to be ionic. Keeping this aspect in view, NaCl has 72% ionic character. CsF has 92% ionic character and calculations tell us that there is no bond with 100% ionic character.

(ii)　Covalent Bond (electron pair bond)

According to Lewis and Kossel, a covalent bond is formed by the mutual sharing of electrons between two atoms. While sharing, each atom completes its valence shell and attains the nearest inert gas configuration. A covalent bond may be non-polar or polar in character.
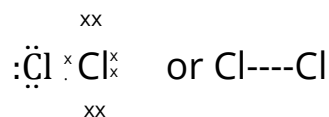

Animation 6.21: Covalent Bond (electron pair bond)
Source & Credit : edcoogle
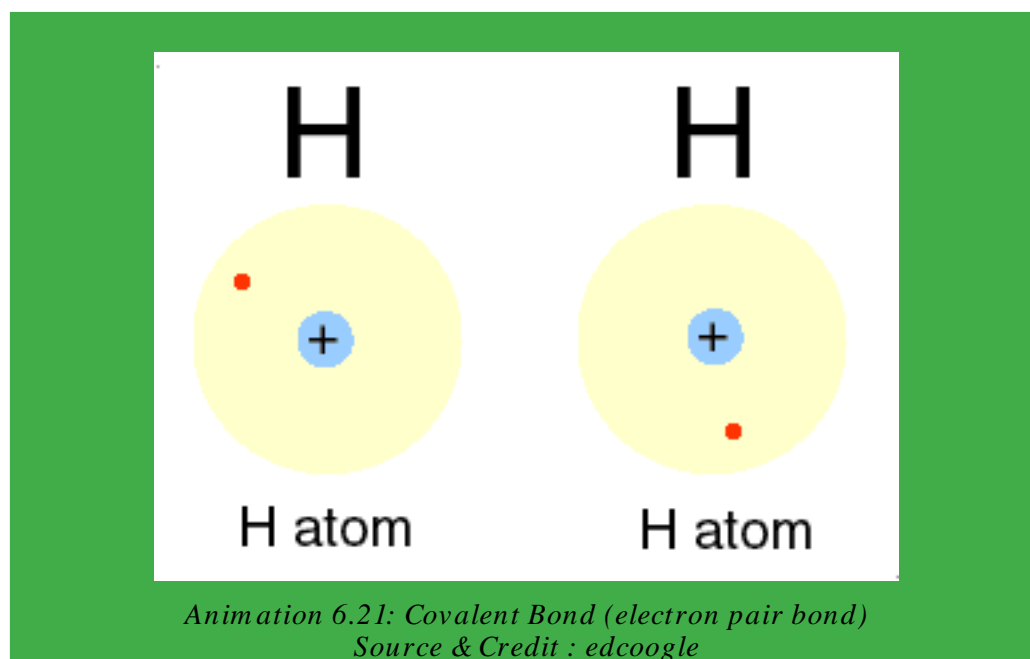
Non-Polar Covalent Bonds

In such bonds, the bonding electron pairs are equally shared. For example, in H_2 or Cl_2 molecules, the two electrons forming the covalent bond are equally shared by the two identical atoms having same electronegativities.
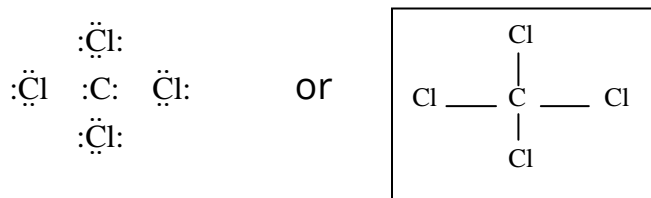
Hydrogen

H : H　　or　　H - H

Chlorine

:C̈l ×Cl×　　or　Cl----Cl

Due to an even distribution of charge, the bonded atoms remain electrically neutral.The other such molecules are F_2, Br_2 and I_2.Similarly, CCl_4 is a non-polar compound. This is due to cancellation of all the dipoles of this molecules due to its symmetry. Actually, all the C-Cl bonds are polar, but molecule is non-polar overall.

Animation 6.22: Non-Polar Covalent Bonds
Source & Credit : bsc2.ehb-schweiz2
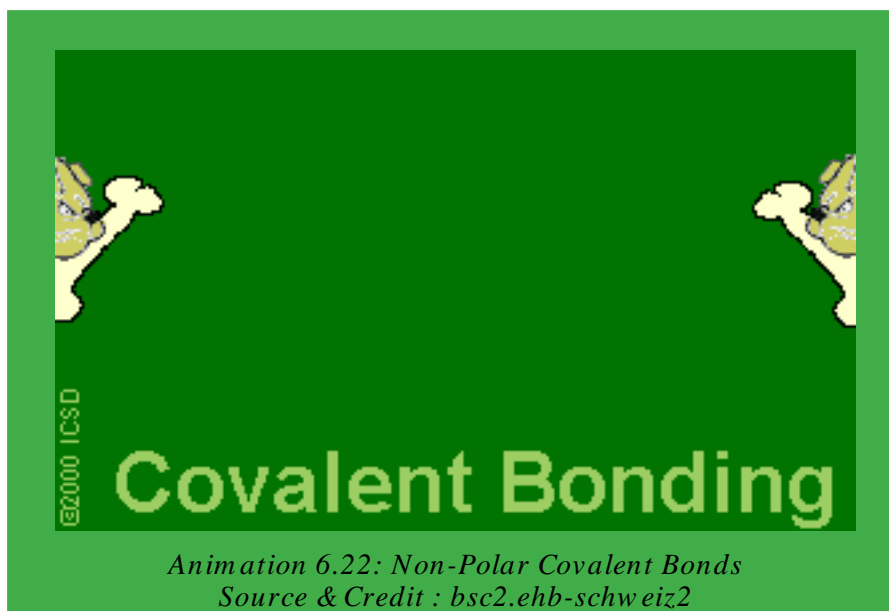
Tetrachloromethane

:Cl:
:Cl :C: Cl: or
:Cl:

Cl
|
Cl — C — Cl
|
Cl

The molecules like CH_4, SiH_4, and $SiCl_4$ also follow the same attitude of non-polarity due to symmetry of structure.
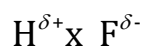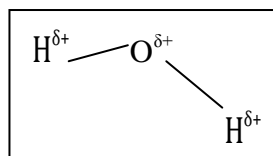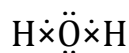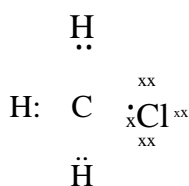
Polar Covalent Bonds

When two different atoms are joined by a covalent bond, the electron pair is not equally shared between the bonded atoms. The bonding pair of electrons will be displaced towards the more electronegative atom
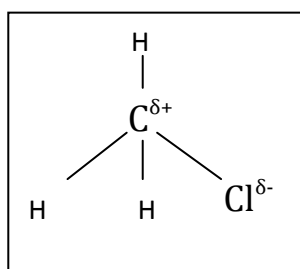
This would make one end of the molecule partially positive and the other partially negative as shown by the following examples.
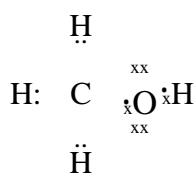
Hydrogen fluoride		Water

$$H \overset{\times}{\cdot} \overset{\cdot\cdot}{\underset{\cdot\cdot}{F}} : \qquad \text{or} \qquad H^{\delta+} \times F^{\delta-} \qquad\qquad H \overset{\times}{\cdot} \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \overset{\times}{\cdot} H$$

$$H^{\delta+} \!\!-\!\! O^{\delta+}$$
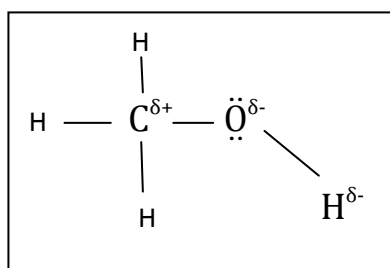$$H^{\delta+}$$

Methyl chloride

Methanol is an other best example of a polar covalent molecule, because it contains a polar bond.
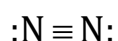
Methanol

An atom can share more than one electrons to form what is called a double or triple bond. The examples are O_2, N_2, CO_2, CS_2, etc.
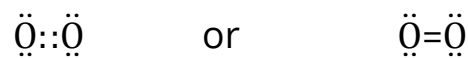
N_2 is an inert gas having a strong triple bond.

Nitrogen

$$:N:::N: \qquad \text{or} \qquad :N \equiv N:$$

The molecule: of O_2 makes a double bond.

Oxygen

$$\ddot{O}::\ddot{O} \qquad \text{or} \qquad \ddot{O}=\ddot{O}$$

Here, carbon dioxide is a non-polar covalent compound, although it is formed from heteroatoms. The linear structure balances the polar character on both sides of the carbon atom.
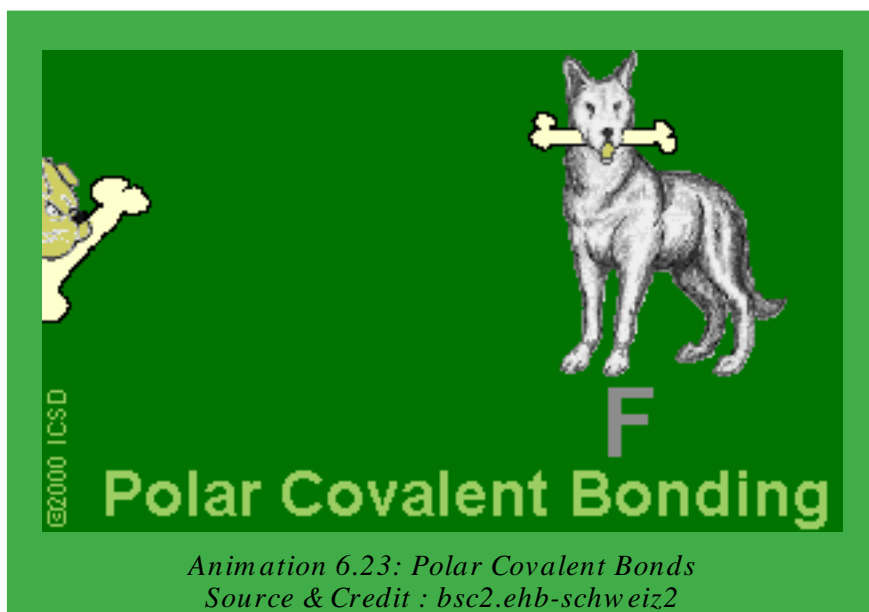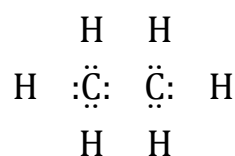
Carbon dioxide

$$:\ddot{O}::C::\ddot{O}: \qquad \text{or} \qquad \ddot{O}=C=\ddot{O}$$

Here, each bond represents a pair of electrons. Thus, in the formation of a double bond (=), two shared pairs and in that of a triple bond (≡), three shared pairs of electrons are involved.

Some of the non-metallic atoms, particularly carbon atoms mutually share their electrons with each other. This leads to the formation of extended chains which is the basis of the formation of large sized molecules called macromolecules. Diamond, graphite and SiC are the best examples of such molecules.
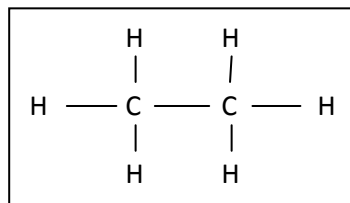
Carbon can make single, double and triple covalent bonds in alkanes, alkenes and alkynes.

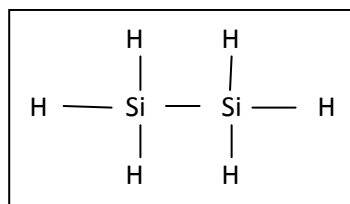*Animation 6.23: Polar Covalent Bonds*
Source & Credit : bsc2.ehb-schweiz2

Ethan

$$H \quad H$$
$$H \; :\ddot{C}: \; \ddot{C}: \; H$$
$$H \quad H$$

or

$$H - C - C - H$$
(with H above and below each C)

Silicon also gives similar type of hydrides, called silanes. The formula of disilane is like that of ethane.

Disilane

$$H \quad H$$
$$H \; :\ddot{S}i: \; \ddot{S}i: \; H$$
$$H \quad H$$
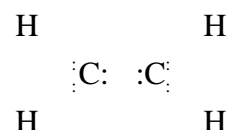
or
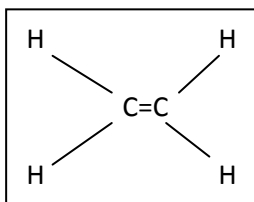
$$H - Si - Si - H$$
(with H above and below each Si)
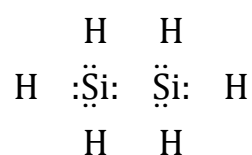
The compounds of carbon and hydrogen showing double and triple bonds are called alkenes and alkynes. Let us, take the examples of ethene and ethyne.

Ethan

$$H \qquad H$$
$$:C: \; :C:$$
$$H \qquad H$$

or

$$\begin{array}{c} H \qquad\quad H \\ \diagdown \qquad \diagup \\ C=C \\ \diagup \qquad \diagdown \\ H \qquad\quad H \end{array}$$

Ethan

$$H:C::C:H \quad \text{or} \quad H-C \equiv C-H$$

(iii) Coordinate Covalent Bond

A coordinate covalent bond is formed between two atoms when the shared pair of electrons is donated by one of the bonded atoms. Let us consider, the example of bond formation between NH_3 and BF_3. NH, has three covalent bonds and there is a lone pair of electrons on nitrogen atom. On the other hand, boron atom in BF_3 is deficient in electrons. Actually, the octet of B is not complete in BF_3. Therefore, nitrogen can donate the pair of electrons to the acceptor BF_3 and this results in the formation of a coordinate covalent bond.

The complex so produced is overall neutral, and charges are indicated on N and B atoms. In some of the compounds, after the formation of a coordinate covalent bond, the distinction between covalent bond and coordinate bond vanishes.
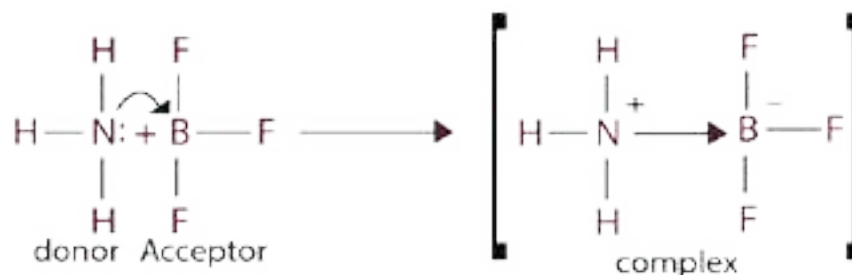
Water donates its electron pair to H^+ ion to give H_3O^+ ion. All the three bonds between oxygen and hydrogen have equal status. Every bond is 33% coordinate covalent and 66% covalent.
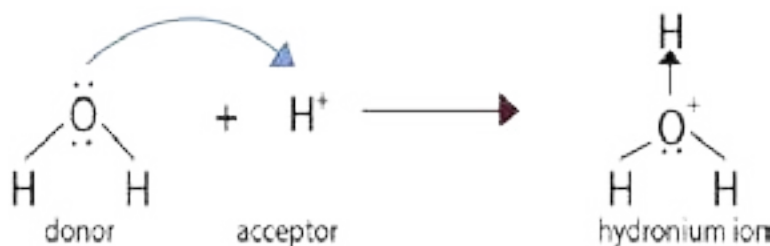
Similarly, all the alcohols and ethers offer their lone pairs to H^+, just like water to give coordinate covalent bonds. The ions so produced are called oxonium ions.
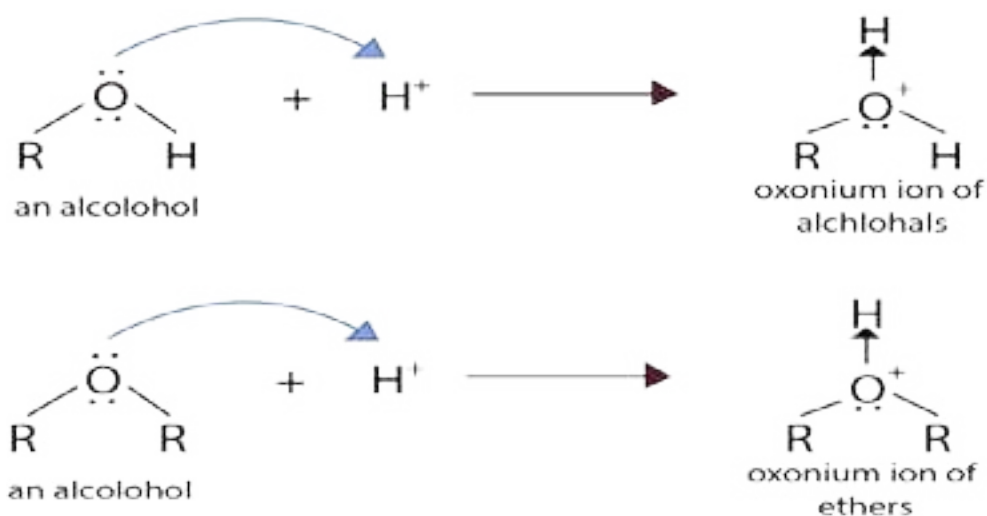
Ammonia donates its electron pair to H^+ ion to give NH_4^+ ion. All the four bonds behave alike, in NH_4^+ ion.

All the primary, secondary and tertiary amines like ammonia make such bonds with H^+. PH_3 combines with H^+ to give PH_4^+ ion called phosphonium ion. Coordinate covalent bonds are present in HNO_3. Many oxyacids of halogens, like ($HClO_2$, $HClO_3$, $HClO_4$) have coordinate covalent bonds between chlorine and oxygen.

6.4.2 MODERN THEORIES OF COVALENT BOND

Limitations of Lewis Model

Classical Lewis model does explain, that how atoms are bonded to one another. It also tells, how the electron pairs are shared between the bonded atoms. But a logical question arises:
Are these explanations just enough to justify the diversified world of molecules and how do the electrons avoid each other inspite of their repulsions?
The answer simply lies in the fact, that the Lewis model seems to be an over simplification. Shapes of molecules are very important because many physical and chemical properties depend upon three dimensional arrangement of their atoms.

Animation 6.24: MODERN THEORIES OF COVALENT BOND
*Source & Credit : chem.umass*

A true model should be able to justify molecular shapes and geometries of molecules, bond polarities, bond distances and various energy transitions as evident by spectroscopic techniques. This model should also make clear the unique behaviouria! features of molecules during chemical reactions.

Following are the modern theories, which explain satisfactorily the above requirements for covalent bond formation, based on wave-mechanical structure of atoms:
1.   Valence shell electron pair repulsion theory (VSEPR Theory)
2.   Valence bond theory (VBT)
3.   Molecular orbital theory (MOT)

In addition to above, crystal field theory and ligand field theory explain the formation of coordination complex compounds formed by transition metals.

Animation 6.25: Limitations of Lewis Model
*Source & Credit : en.wikipedia*
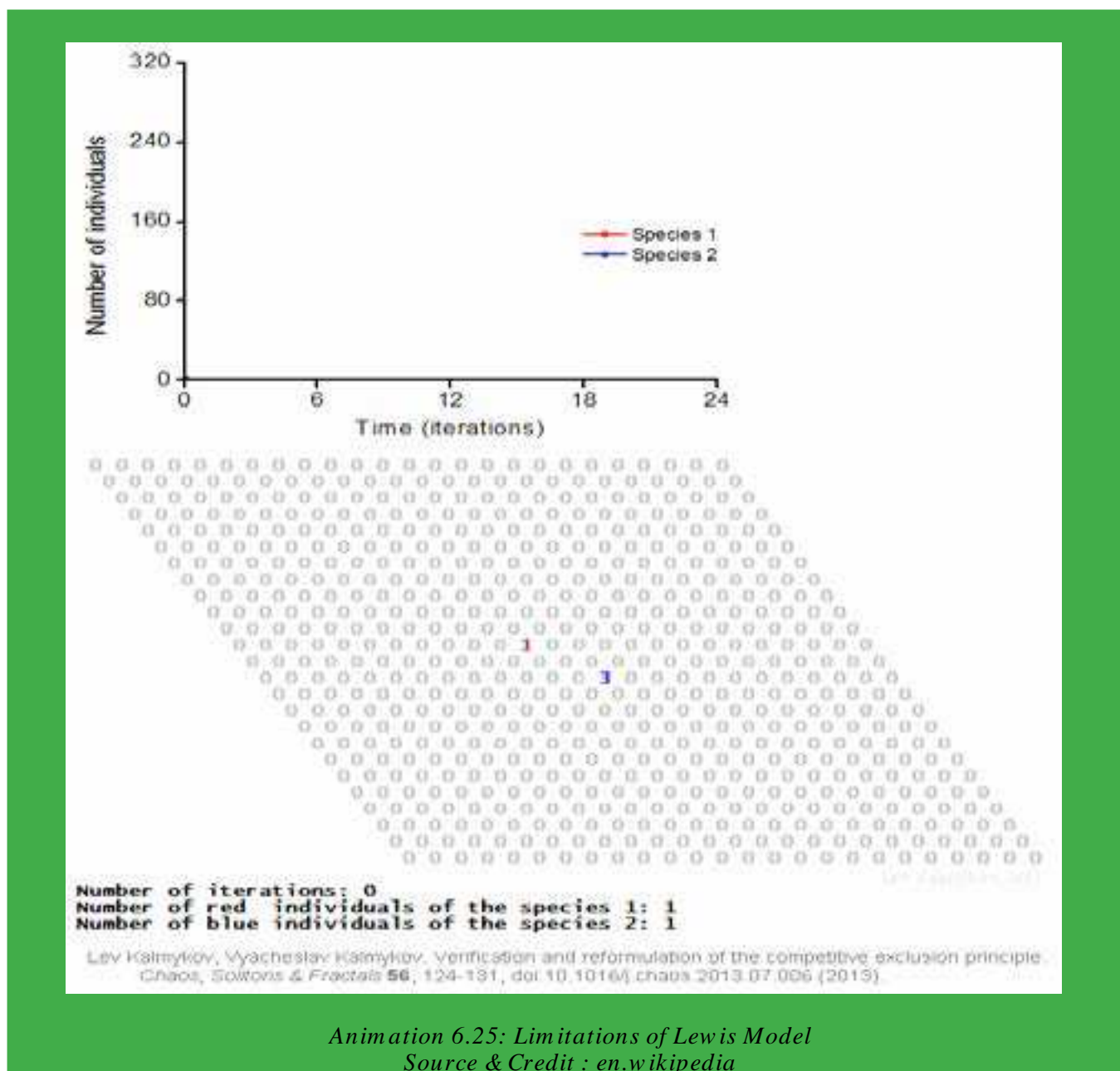
6.4.3 VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Sidgwick and Powell (1940) pointed out that the shapes of molecules could be interpreted in terms of electron pairs in the outer orbit of the central atom. Recently, Nylholm and Gillespie developed VSEPR theory, which explains the shapes of molecules for non- transition elements.

Basic Assumption

The valence electron pairs (lone pairs and the bond pairs) are arranged around the central atom to remain at a maximum distance apart to keep repulsions at a minimum.

Animation 6.26: VALENCE SHELL ELECTRON PAIR REPULSION THEORY
Source & Credit : barmaton.info
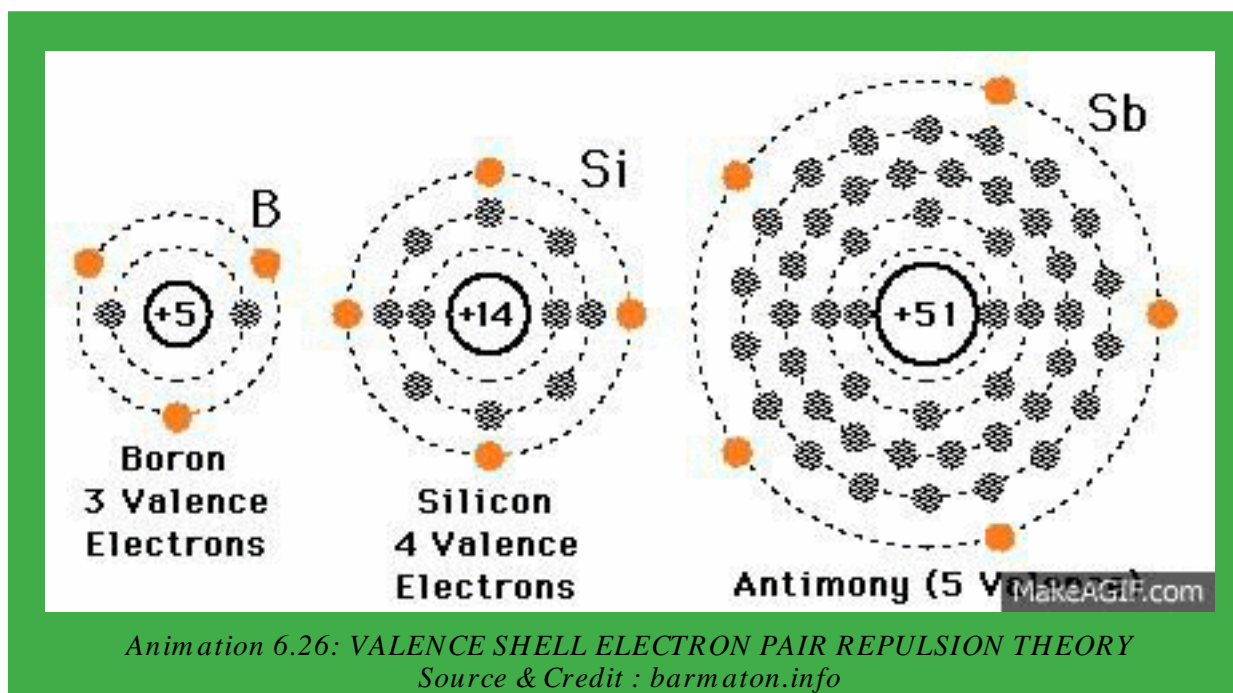
Postulates of VSEPR Theory

(i)   Both the lone pairs as well as the bond pairs participate in determining the geometry of the molecules.

(ii)   The electron pairs are arranged around the central polyvalent atom so as to remain at a maximum distance apart to avoid repulsions.

(iii)   The electron pairs of lone pairs occupy more space than the bond pairs.

A bonding electron pair is attracted by both nuclei of atoms while non- bonding by only one nucleus. Because a lone pair experiences less nuclear attraction, its electronic charge is spread out more in space than that for bonding pair. As a result, the non- bonding electron pairs exert greater repulsive forces on bonding electron pairs and thus tend to compress the bond pairs.

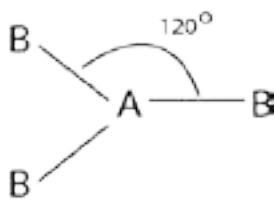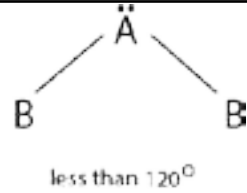The magnitude of repulsions between the electron pairs in a given molecule decreases in the following order:
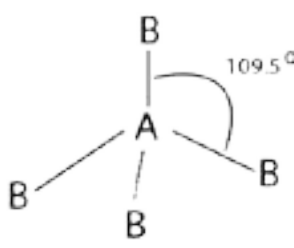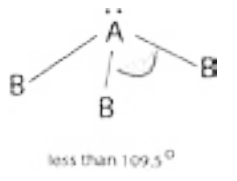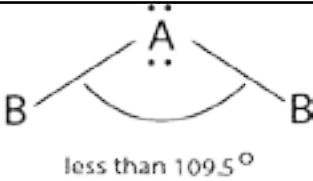
Lone pair- lone pair > lone pair -bond pair > bond pair - bond pair

These repulsions are called van der Waals repulsions

(iv)   The two electron pairs of a double bond and three electron pairs of a triple bond, contain a higher electronic charge density. Therefore, they occupy more space than one electron pair of a single bond, but behave like a single electron pair in determining the geometry of the molecule. This is because, they tend to occupy the same region between the two nuclei like a single bond.

In order to illustrate this theory, let us consider, that the central atom is 'A' and this atom is polyvalent. More than one 'B' type atoms are linked with 'A' to give AB_2, AB_3, AB_4, etc. type molecules. It depends upon the valency of A, that how many B are attached with that. Following Table (6.4) gives the shapes of different types of molecules.

Table (6.4) Shapes of molecules according to VSPER Theory

Type	Electron Pairs			Arrangement of pairs	Molecular geometry	Shape	Example
	Total	Bonding	Lone				
AB_2	2	2	0	Linear	Linear	B-A-B	$BeCl_2$ $HgCl_2$
AB_3	3	3	0	Trigonal planar	Trignol planar		BH_3, BF_3 $AlCl_3$
		2	1		Bent (or angular)		$SnCl_2$, SO_2
AB_4	4	4	0	Tetrahedral	Tetrahedral		CH_4, $SiCl_4$, CCl_4, BF_4, NH_4^+, SO_4^{2-}
		3	1		Trignol pyramidal		NH_3, NF_3, PH_3
		2	2		Bent (or angular		H_2O, H_2S

1   Molecules Containing Two Electron Pairs (AB$_2$ type)

In such, molecules two electrons, pairs around the central atom are arranged at farther distance apart at an angle of 180°, in order to minimize repulsions between them. Thus, they form a linear geometry.

Beryllium chloride is a typical linear molecule, which contains two electrons pairs. $MgCl_2$, $CaCl_2$, $SrCl_2$. $CdCL_2$ and $HgCl_2$ are also linear molecules. The central atoms have two electrons in outer most orbitals.
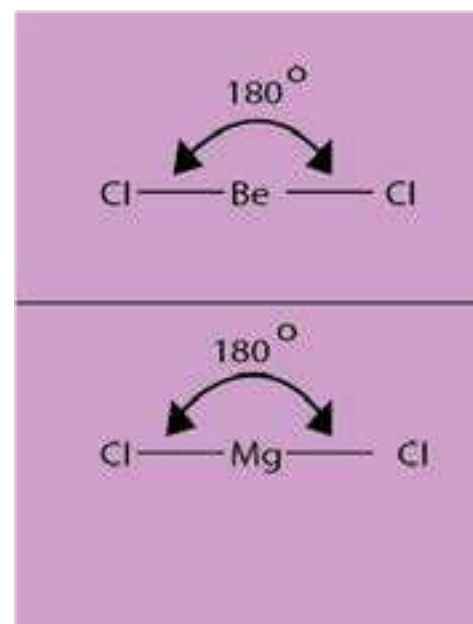
2.   Molecules Containing Three Electron Pairs — (AB$_3$ type:)

(a)   AB$_3$ Type with no Lone Pairs

In such molecules, central atom contains three bonding electron pairs, which are arranged at maximum distance apart at a mutual angle of 120°, giving a triangular planar geometry. The boron atom in BH_3 is surrounded by three charge clouds, which remain farthest apart in one plane, each pointing towards the corners of an equilateral triangle. Thus, BH_3, molecules has a trigonal planar geometry, with each H- B-H bond angles of 120°.

We expect similar geometries in hydrides of group III-A (AlH_3, GaH_3, InH_3 and TlH_3)and their halides (BF_3, $AlCl_3$,etc.)

### (b)   AB$_3$-Type with One Lone Pair and Two Bond Pairs

In $SnCl_2$, one of the corner of the triangle is occupied by a lone pair, giving rise to a distorted triangular structure in vapour phase.

(c)   AB$_3$-Type with Multiple Bonds

In SO$_2$, one corner of triangle is occupied by a lone pair and two corners each by S=O double bond, while in SO$_3$ all three regions, each are occupied by S = O bonds. This structure of SO$_3$ is perfectly triangular.
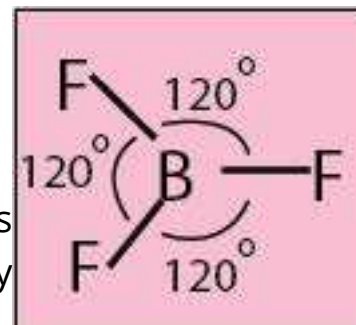
(iii) Molecules Containing Four Electron Pairs (AB$_4$- Type:)
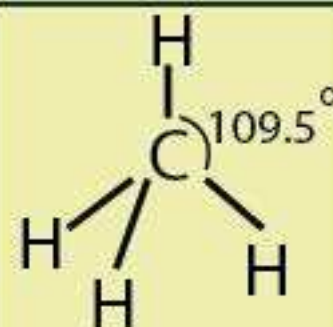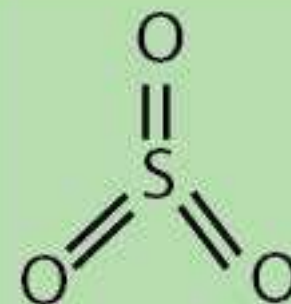
(a)   AB$_4$ Type with no Lone Pairs

The charge clouds due to four electron pairs avoid their electrostatic repulsions by drifting apart, so as to maintain a mutual bond angle of 109.5 °. Such geometry enables to a form a shape of regular tetrahedron.
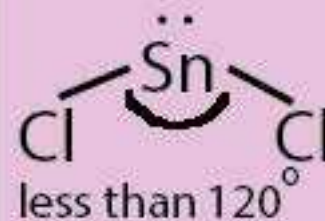
Examples:

Each of the four valence electrons of carbon pair up with sole electron of hydrogen in methane.

$$_6C = 1s^2, 2s^1, 2px^1, 2py^1, 2py^1$$
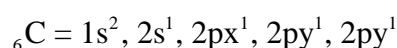
The four electron pairs are directed from the center towards the corners of a regular tetrahedron, with each apex representing a hydrogen nucleus. The arrangement permits a non-planar arrangement of electron pairs. Each H-C-H bond is perfectly 109.5 °. On the same grounds, SiH$_4$, GeH$_4$, CCl$_4$ form similar geometries. This structure has four corners, four faces, six edges and six bond angles.
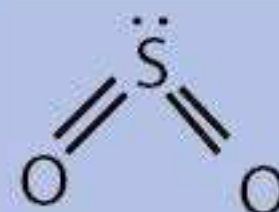
(b)   AB$_4$ - Type with One Lone Pair and Three Bond Pairs

In such cases, the charge cloud of lone pair electrons (nonbonding electrons) spreads out more than that of bonding electrons.

Animation 6.27: Molecules Containing Two Electron Pairs (AB2 type)
Source & Credit : employees.csbsju
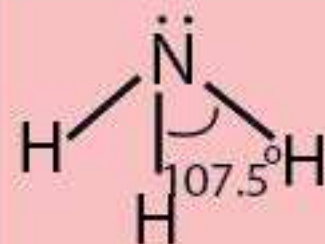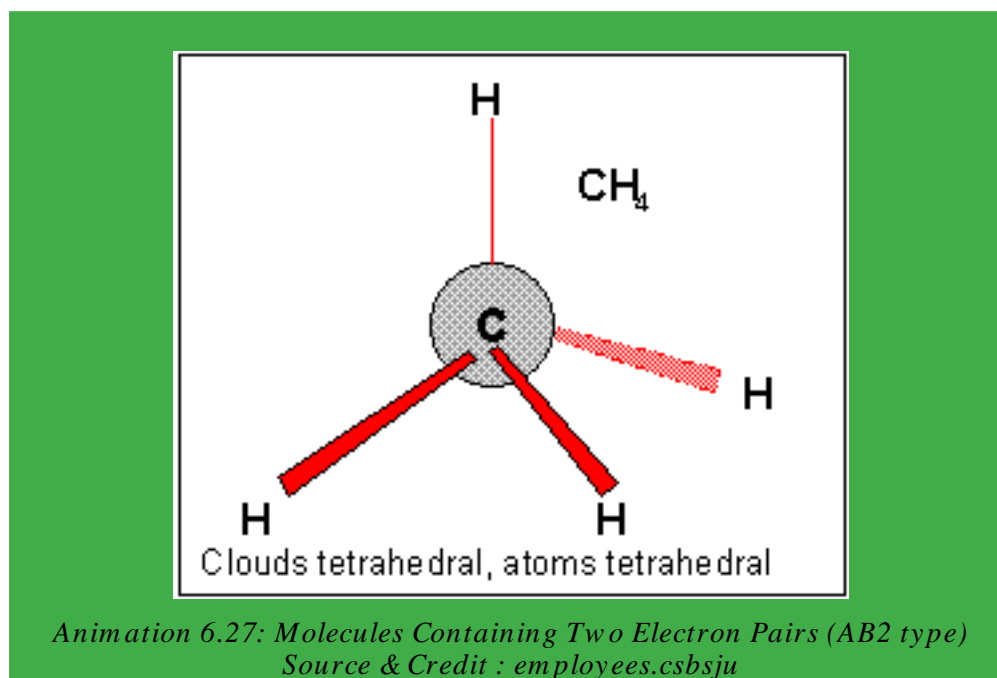
As a result, some what large lone pair charge cloud tend to compress the bond angles in rest of the molecules.

Ammonia, $\ddot{N}H_3$ is a typical example.

$$_7N = 1s^2, 2s^2, 2p_x^{\,1}, 2p_y^{\,1}, 2p_z^{\,1}$$

The non-bonding electron in 2s orbital takes up more space and exerts a strong repulsive force on the bonding electron pairs. Consequently, to avoid a larger repulsion, the bonding electron pairs move closer that reduces the ideal bond angle from 109.5^0 to $107.5°$. This effect compels ammonia to assume a triangular pyramidal geometry instead of tetrahedral, as in methane.
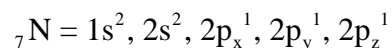
Similar, affects are evident in the geometries of molecules like $\ddot{P}H_3, \ddot{A}sH_3, \ddot{S}bH_3$ and $\ddot{B}iH_3$. Substitution of hydrogen with electronegative atoms like F or Cl further reduces the bond angle. In NF_3, the strong polarity of N-F bond pulls the lone pair of N atom closer to its nucleus, which in turn exerts a stronger repulsion over bonding electrons. Thus, the angle further shrinks to $102°$. Moreover, the bond pairs N-F bonds are more close to F atoms than N atoms. The increased distances in these bond pairs makes their repulsions less operative.

Animation 6.28: Molecules Containing Three Electron Pairs — (AB;i type:)
Source & Credit : nano-ou
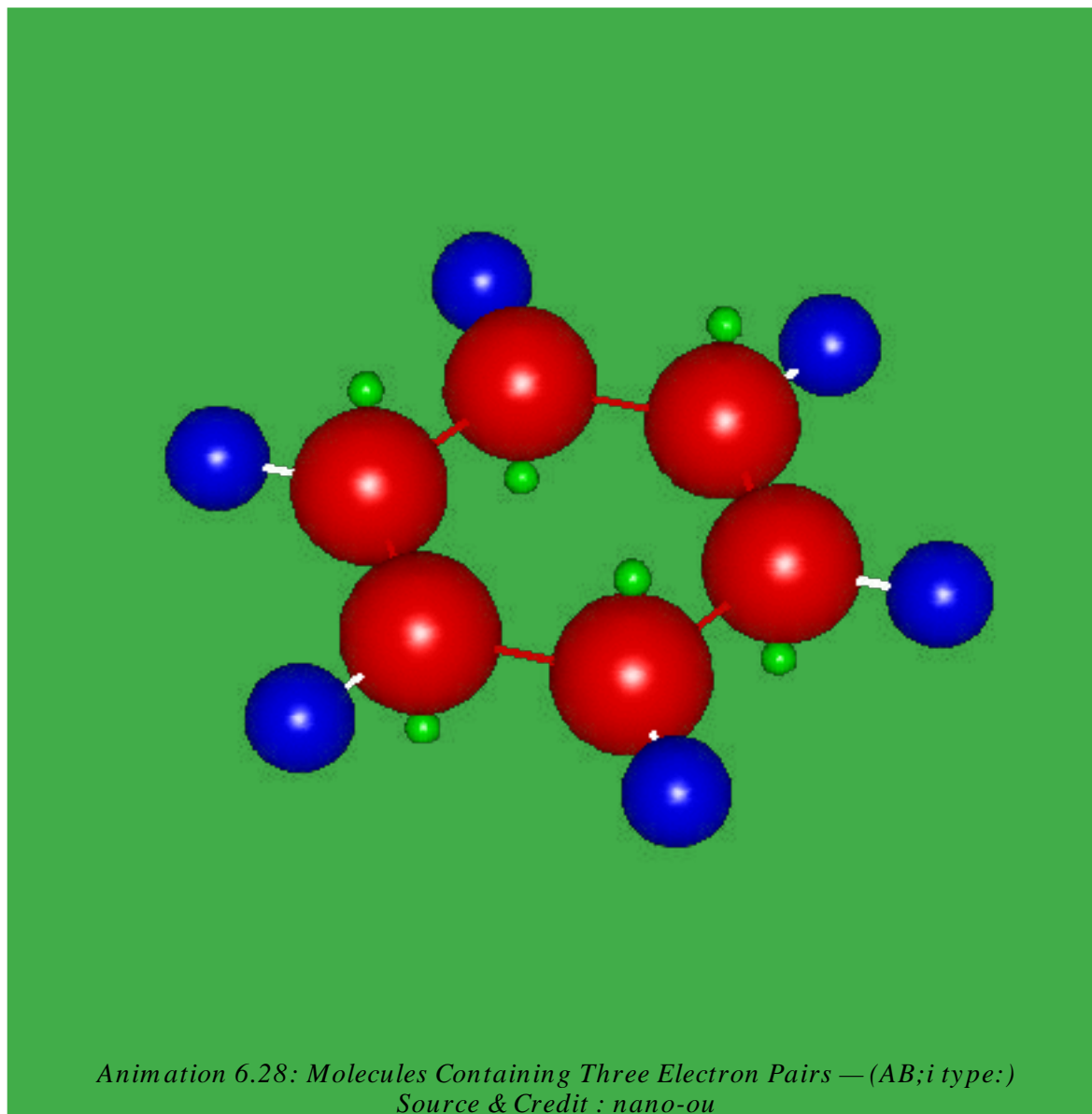
(c)   AB$_4$-Type with Two lone Pairs and Two Bond Pairs:

Presence of two lone pairs, introduces three types of repulsion i.e. lone pair-lone pair, lone pair-bond pair and bond pair-bond pair repulsion. For example: water (H_2O), a triatomic molecule is expected to be an AB$_2$ type linear molecule like $BeCl_2$ and CO_2. But, experimental evidences confirm a bent or angular geometry. VSEPR theory, successfully justifies the experimental results by arguing the participation of lone pairs, in addition to bond pairs in determining overall geometry of water molecule.

$$_8O = 1s^2, 2s^2, 2p^2_x, 2p^1_y, 2p^1_z$$
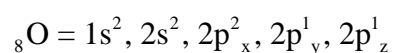
Two of the corners of a tetrahedron are occupied by each of the two lone pairs and remaining by bond pairs. But owing to spatial arrangement of lone pairs and their repulsive action among themselves and on bond pairs, the bond angle is further reduced to 104.5°. H_2S, H_2Se, H_2Te form similar geometries.

6.4.4 Valence Bond Theory (VBT)

VSERP theory predicts and explains the shapes of molecules but does not give reasons for the formation of bonds. VBT is concerned with both the formation of bonds and the shapes of molecules. This method of describing a covalent bond considers the molecule as a combination of atoms. According to the quantum mechanical approach, a covalent bond is formed when half-filled orbitals in the outer or valence shells of two atoms overlap, so that a pair of electrons, one electron from each atom, occupies the overlapped orbital, As a result of this overlap, the electrons with opposite spins become paired to stabilized themselves.

Larger the overlap, the stronger is the bond. The essential condition for chemical bonding, is that the orbitals of atoms participating in bond formation must overlap and the direction of the bond is determined by the direction of the two overlapping orbitals.

The formation of few molecules as a result of s and s orbital overlap, s and p orbital overlap and p and p orbital overlap are discussed below.

The formation of a hydrogen molecules according to VB theory is shown in Fig. (6.4). As the two atoms approach each other, their 1s orbitals overlap, thereby giving the H-H bond.

Seperated H atoms   Overlapping of orbitlas   Covelent bond H

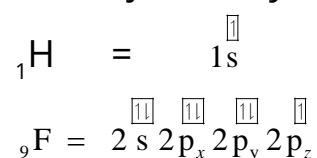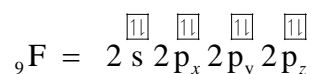Fig. (6.4) s and s orbital overlap in H_2

The electron density becomes concentrated between the two nuclei. The bond is called a sigma (σ) bond and it is defined as follows:

A single bond is formed when two partially filled atomic orbitals overlap in such a way that the probability of finding the electron is maximum around the line joining the two nuclei.

Let's look at a molecule hydrogen fluoride, HF. The H-F bond is fomed by the pairing of electrons - one from hydrogen and one from fluorine. According to VB theory, we must have two half-filled orbitals - one from each atom that can be joined by overlap.

$$_1H \; = \; \overset{\uparrow}{\boxed{\;}} \atop 1s$$

$$_9F \; = \; \overset{\uparrow\downarrow}{\boxed{\;}}\,\overset{\uparrow\downarrow}{\boxed{\;}}\,\overset{\uparrow\downarrow}{\boxed{\;}}\,\overset{\uparrow}{\boxed{\;}} \atop 2s\;2p_x\;2p_y\;2p_z$$

The overlap of orbitals provides a means for sharing electrons, thereby allowing each atom to complete its valence shell. The fluorine atom completes its 2p subshell by acquiring a share of an electron from hydrogen as shown below.

Animation 6.29: Valence Bond Theory (VBT)
Source & Credit : chem.umass

$$_9F \; = \; \overset{\uparrow\downarrow}{\boxed{\;}}\,\overset{\uparrow\downarrow}{\boxed{\;}}\,\overset{\uparrow\downarrow}{\boxed{\;}}\,\overset{\uparrow\downarrow}{\boxed{\;}} \atop 2s\;2p_x\;2p_y\;2p_z$$

The requirements for bond formation are met by overlapping the half-filled Is orbital of hydrogen with the half-filled 2p orbital of fluorine. There are then two orbitals plus two electrons whose spins can adjust so they are paired. The formation of the bond is illustrated in Fig.(6.5)

The bond in the fluorine molecule, F_2 is formed by the overlap of half-filled $2p_z$ orbital on each fluorine atom,Fig (6.6).
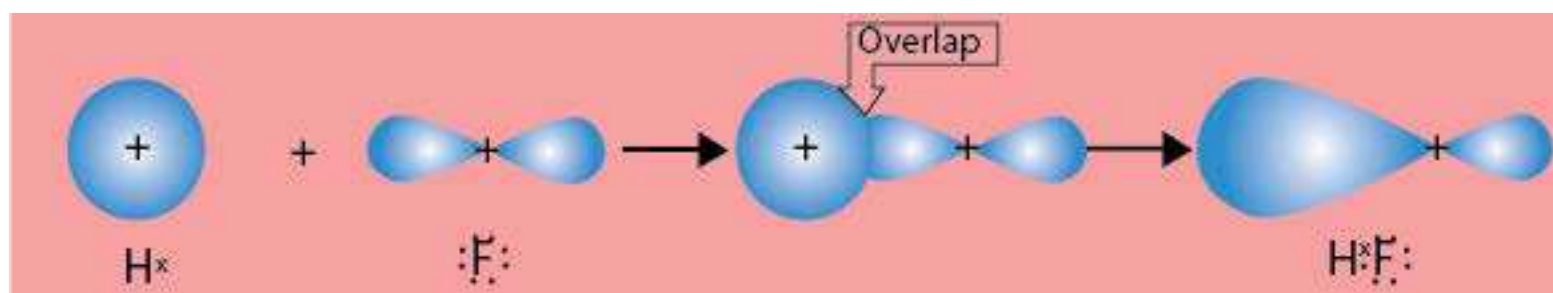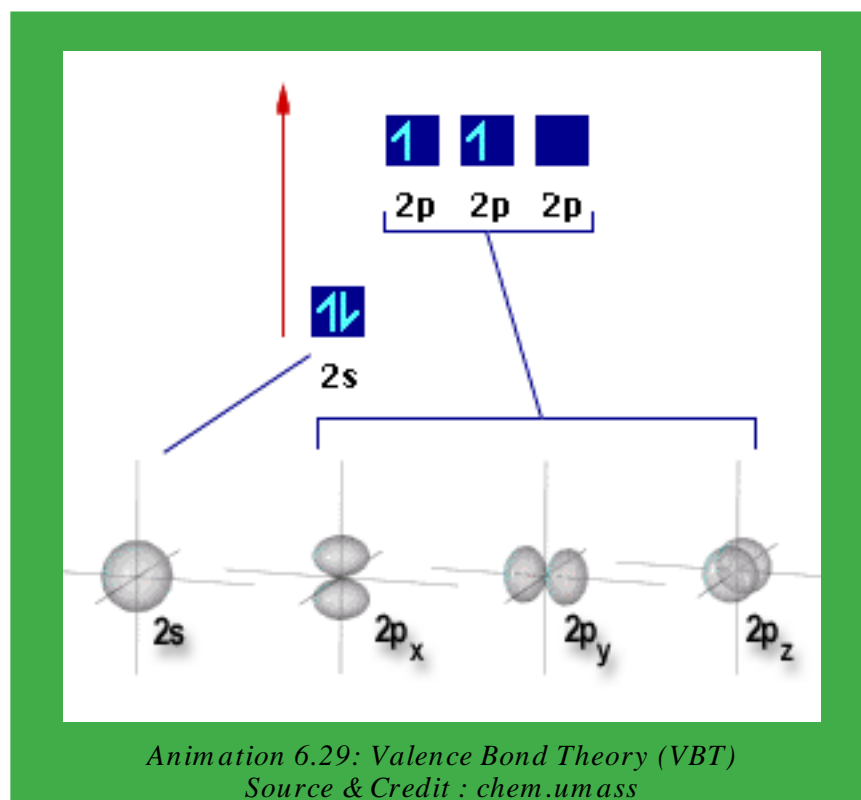

Fig. (6.5) The formation of the hydrogen fluoride molecules.
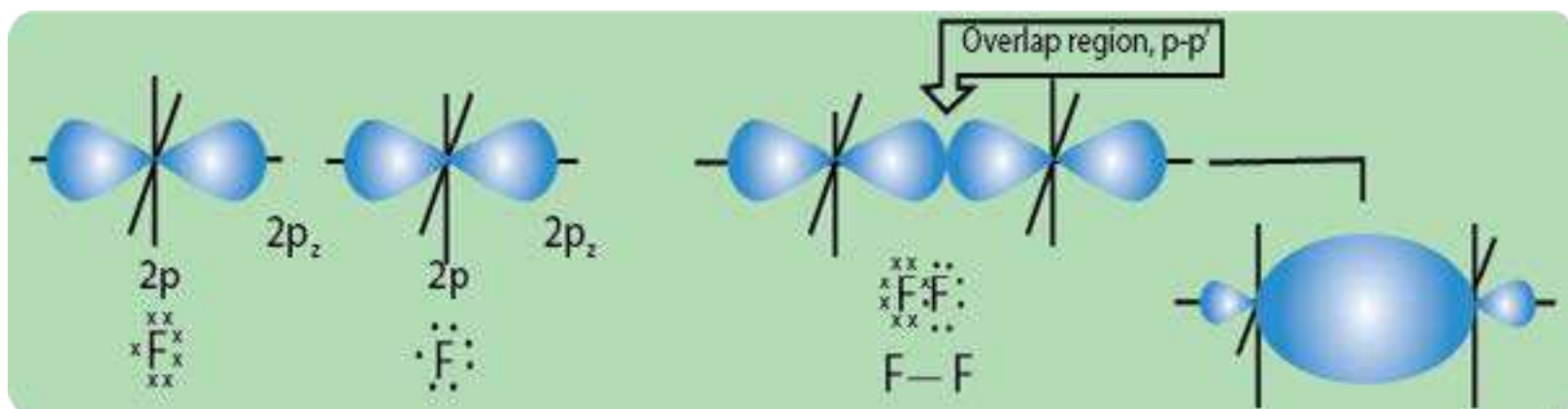
Fig.(6.6)The formation of the fluorine molecule.

Covalent bonds can also form by side-to-side overlap of p orbitals, as shown in Fig.(6.7). The result is a pi (π) bond, in which the greatest electron density lies above and below the internuclear axis.

Consider, the bonding between nitrogen atoms having the electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. The three unpaired electrons on each atom are located in perpendicular p orbitals, which are oriented so that if one end-to-end p orbital overlap occurs (resulting in a sigma bond), the other two p orbital cannot overlap in the same fashion. Rather, they are aligned parallel to the corresponding orbital in the other atom Fig(6.8).
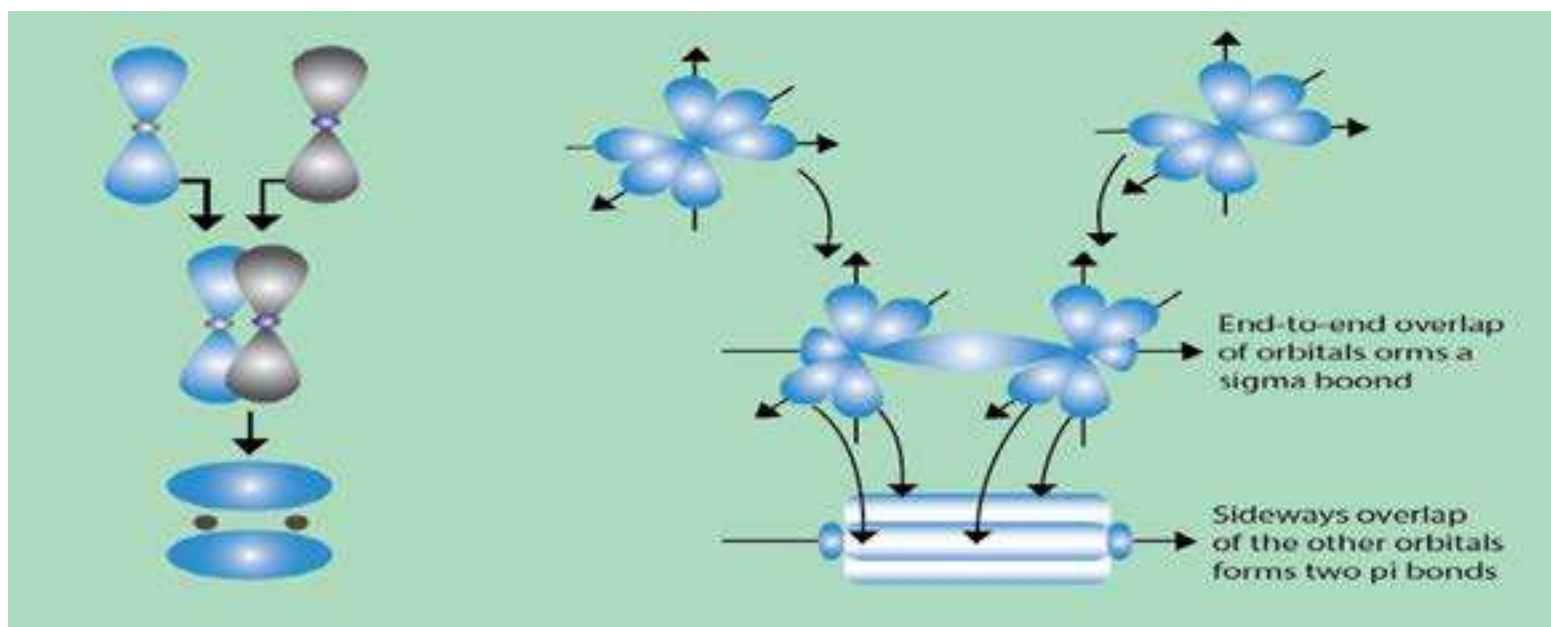
Fig. (6.7) The sideway overlap of two atomic p orbitals to give a n bond.

End-to-end overlap of orbitals orms a sigma boond

Sideways overlap of the other orbitals forms two pi bonds

Fig.(6.8)The two nitrogen atoms showing one sigma bond and two n bonds

Now, let us look at the molecule of H_2S. This is a non-linear molecule, and the bond angle between the two H-S bonds is about 92°.

Each two 3p orbitals of sulphur containing one electron can overlap with the 1s orbitals of hydrogen atoms.

$$S = \quad \underset{3\,s}{\boxed{\uparrow\downarrow}} \ \underset{3p_x}{\boxed{\uparrow\downarrow}} \ \underset{3p_y}{\boxed{\uparrow\downarrow}} \ \underset{3p_z}{\boxed{\uparrow\downarrow}}$$
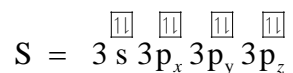
Thus, the VBT requires the idea of overlap to explain the geometry of the hydrogen sulphide molecule, Fig. (6.9).

Fig.(6.9)Bonding in H_2S showing overlap of orbitals

6.4.5 Atomic Orbital Hybridization and Shapes of Molecules

So far we have regarded overlap taking place between unmodified atomic orbitals. Formation of some molecules present problems.

We face the problem of explaining equivalent tetra-valency of carbon and the bond angles in H_2O and NH_3 molecules. In order to explain the formation of bonds and shapes or geometry of molecules, the idea of hybridization has been introduced.
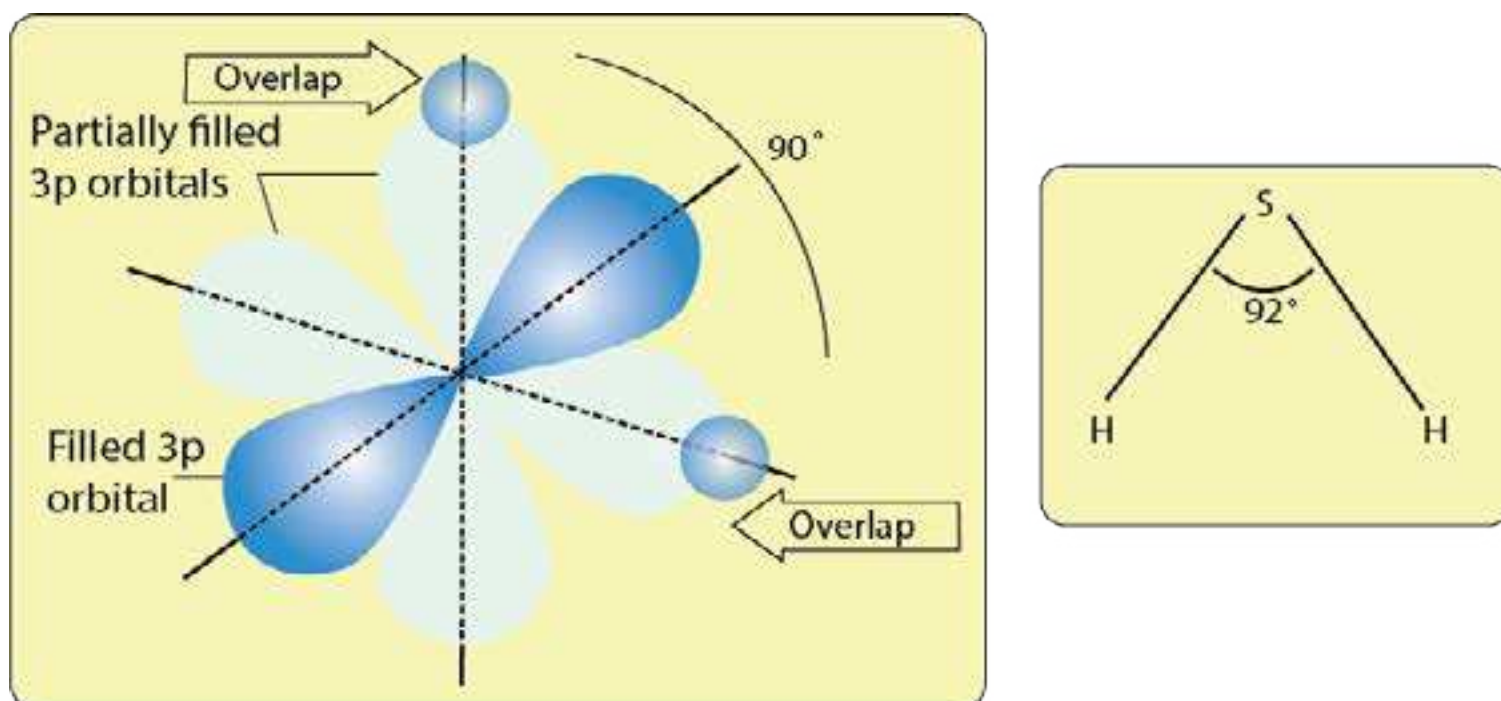
According to this, atomic orbitals differing slightly in energy intermix to form new orbitals, which are called hybrid atomic orbitals. They differ from the parent atomic orbitals in shape and possess specific geometry.
The atomic orbital hybridization gives a satisfactory explanation for the valency of the elements. In some cases, the electrons belonging to the ground state are promoted to the excited state as a result of which there is an increase in the number of unpaired electrons.

These excited orbitals undergo hybridization simultaneously, because promotion of electrons and hybridization is a simultaneous process. The energy required for the excitation is compensated by the energy released during hybridization and the process of bond formation with other atoms. Hybridization leads to entirely new shape and orientation of the valence orbitals of an atom. It holds significant importance in determining the shape and geometry of molecules.

Depending upon the number and nature of the orbitals participating in hybridization, different types of hybridization take place. For example, s and p orbitals of simple atoms are hybridized to give sp^3, sp^2 and sp hybridized orbitals.

(i) sp^3 Hybridization

In sp^3 hybridization, one s and three p atomic orbitals intermix to form four equivalent orbitals called sp^3 hybrid atomic orbitals. Let us discuss the structures of CH_4, NH_3 and H_2O by understanding the sp^3 hybridization of carbon, nitrogen and oxygen-atoms.

Animation 6.30: Atomic Orbital Hybridization and Shapes of Molecules
Source & Credit : web.clark
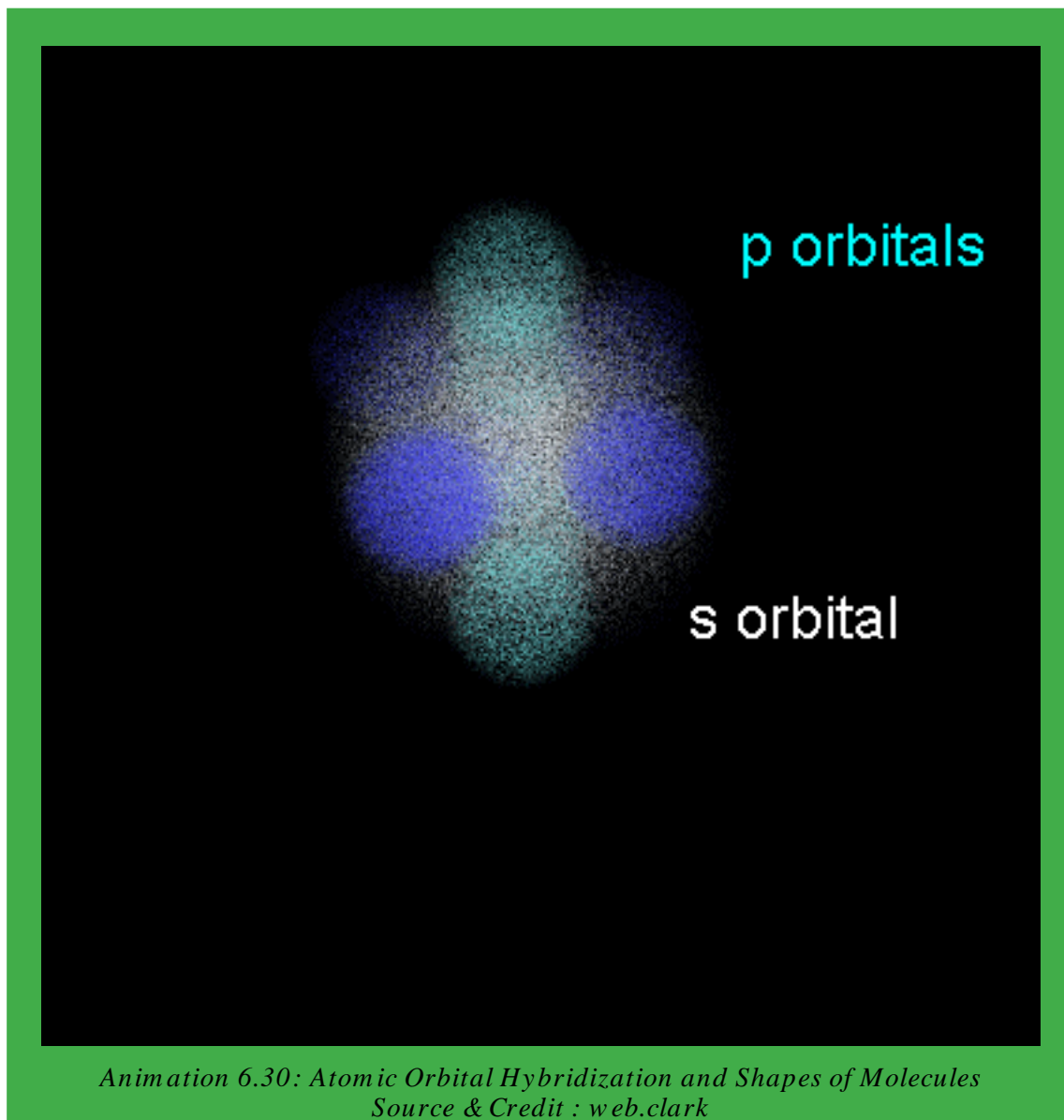
Bonding and Structure of Methane, Ammonia and Water

The electronic distribution of carbon atom should be kept in mind to understand intermixing of orbitals.Electronic configuration of $_6C$, its electronic excitation and hybrization is giyen as follows.

C_6=(ground state) $= 1s\ 2s\ 2p_x\ 2p_y\ 2p_z^0$

C_6=(excited state) $= 1s\ 2s\ 2p_x\ 2p_y\ 2p_z$

C_6=(hybridized state) $= 1s\ sp^3\ sp^3\ sp^3\ sp^3$
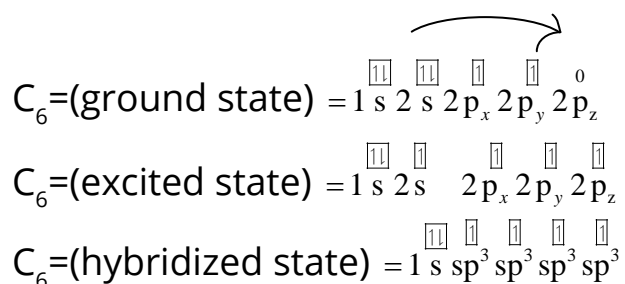
The e nergies of hybrid orbitals are lower than unhybridized orbitals. Following diagram Fig. (6.10) shows, howoutermostfouratomicorbitalsofcarbonmixuptogivefourhybridorbitalsofequalenergyandshape. hen 90°.

The four new hybrid orbitals of equal energy have a tetrahedral geometry with carbon at the centre. The four equivalent hybrid orbitals are directed towards the four corners of a regular tetrahedron. Each sp^3 hybrid orbital consists of two lobes, one larger and the other smaller. For the
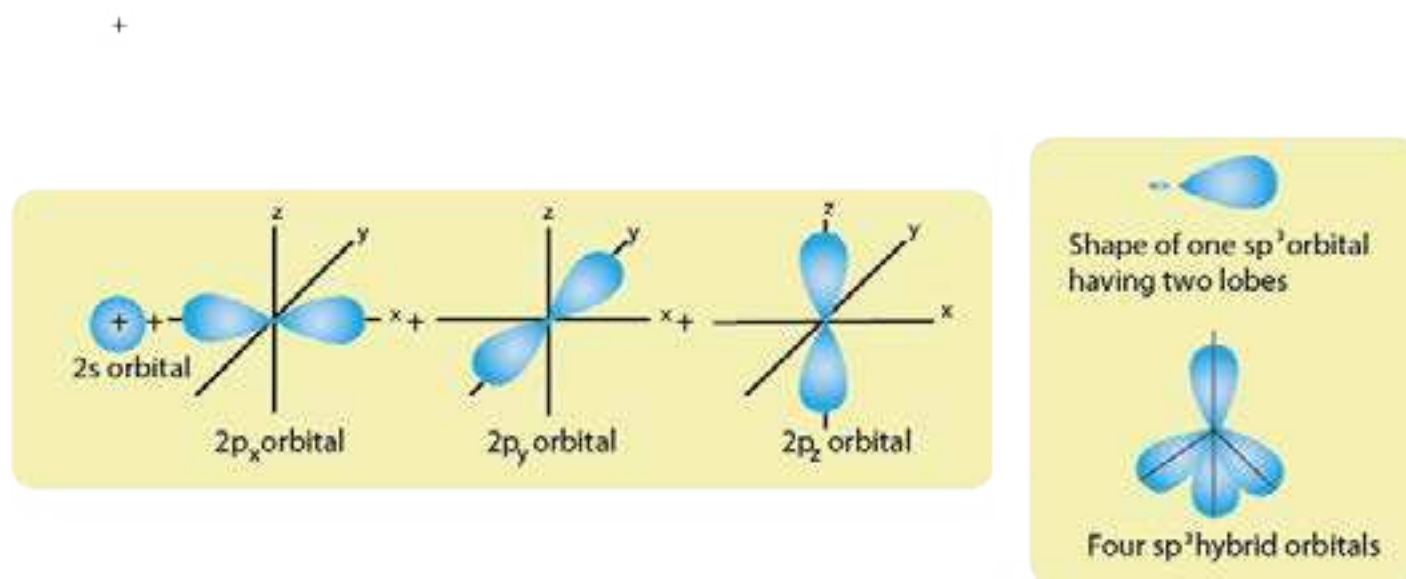
Fig (6.10) sp^3 hybridization of carbon atom
to give four sp^3-hybrid orbitals

sake of simplicity, the small lobe is usually not shown while representing sp^3 hybrid orbitals.

The hybrid orbitals are oriented in space in such a manner that the angle between them is 109.5° as shown in Fig(6.11a,b). Methane molecule is formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms separately to form four sigma bonds. The molecule, thus formed, possesses a tetrahedral geometry. The four C-H bonds which result from sp^3 -s overlaps are directed towards the corners of a regular tetrahedron. There are six bond angles each 109.5°. The tetrahedral structure of CH_4 has four faces, four corners and six edges.
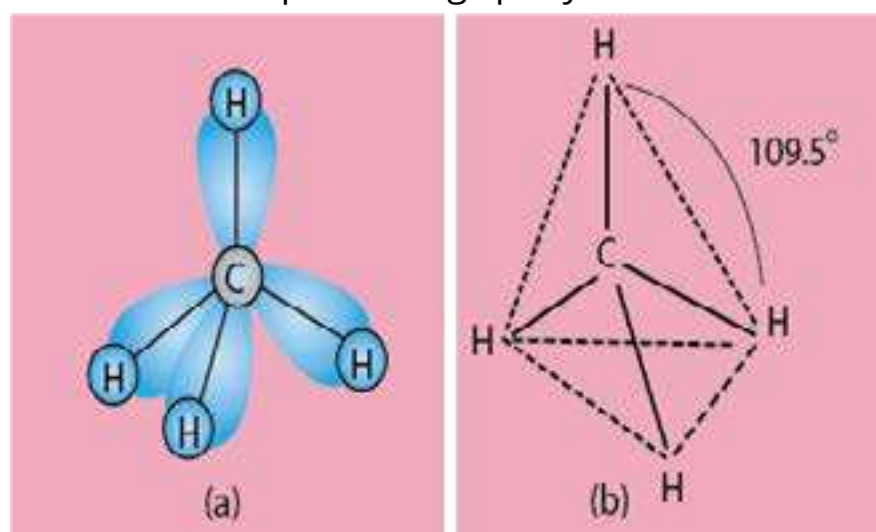
Fig(6.11) Four sp^3-s overlaps in tetrahedral structure of CH_4 molecule.

(b) Ammonia

To understand the sp³ hybridization of nitrogen-atom in NH³, we should know electronic configuration of $_7$N.

$_7$N (ground state) $= 1\,s\ 2\,s\ 2p_x\ 2p_y\ 2p_z$

$_7$N (hybridized state) $= 1\,s\ sp^3\ sp^3\ sp^3\ sp^3$
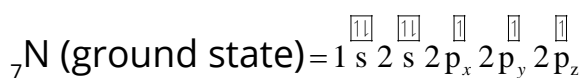
One s and three p orbitals of nitrogen atom hybridize to form four sp³ hybrid atomic orbitals. They are directed towards the four corners of a tetrahedron. One of the hybrid orbitals is completely filled with electrons and the remaining three orbitals are half filled. The nitrogen atom undergoes three sp³-s overlaps with three s-orbitals of hydrogen atoms. The three hydrogen atoms are located at three corners whereas the lone pair of electrons is at the fourth corner of the tetrahedron. The result is a pyramidal molecule in which the three hydrogen atoms form the base and the lone pair of electrons the apex Fig(6.12).

The experimentally determined angle in ammonia is 107.5°. The deviation from the tetrahedral angle (109.5°) is explained on the basis of repulsion between the lone pair and the bond pairs of electrons. The lone pair is closer to the nucleus of nitrogen, then the bond pair and bond angles are decreased.
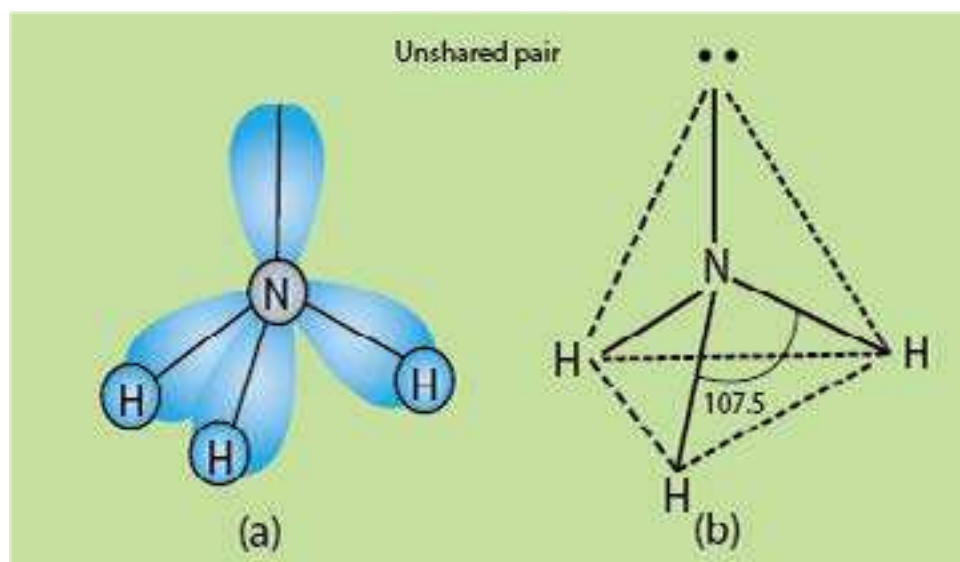

Fig (6.12) Three sp³- s overlaps in NH₃ molecule to form a pyramidal structure.

(c) Water, H_2O

To know the structure of water write down the electronic configuration of $_8O$:

$_8O$ (ground state) $= 1s\ 2s\ 2p_x\ 2p_y\ 2p_z$

$_8O$ (hybridized state) $= 1s\quad sp^3\ sp^3\ sp^3\ sp^3$
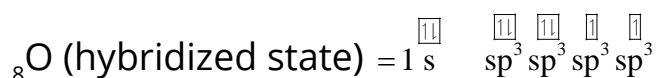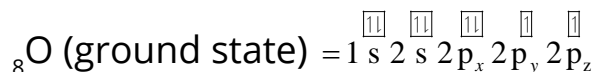
Here, 2s and three 2p orbitals of oxygen hybridize to form four sp³ hybrid orbitals which will have a tetrahedral arrangement. Two hybrid orbitals are completely filled by the two available lone pairs of electrons. The remaining two half filled hybrid orbitals undergo sp³-s overlaps with H atoms to form two sigma bonds. The two H atoms occupy two corners of the tetrahedron and the remaining two are occupied by two lone pairs of electrons, Fig(6.13).

Fig (6.13) sp³-s overlaps in H_2O to form an angular structure

The bond angle in water is 104.5°. The deviation from the tetrahedral angle (109.5°) is explained on the basis of repulsion between the two lone pairs of electrons, with bond pairs. The lone pairs are closer to the nucleus 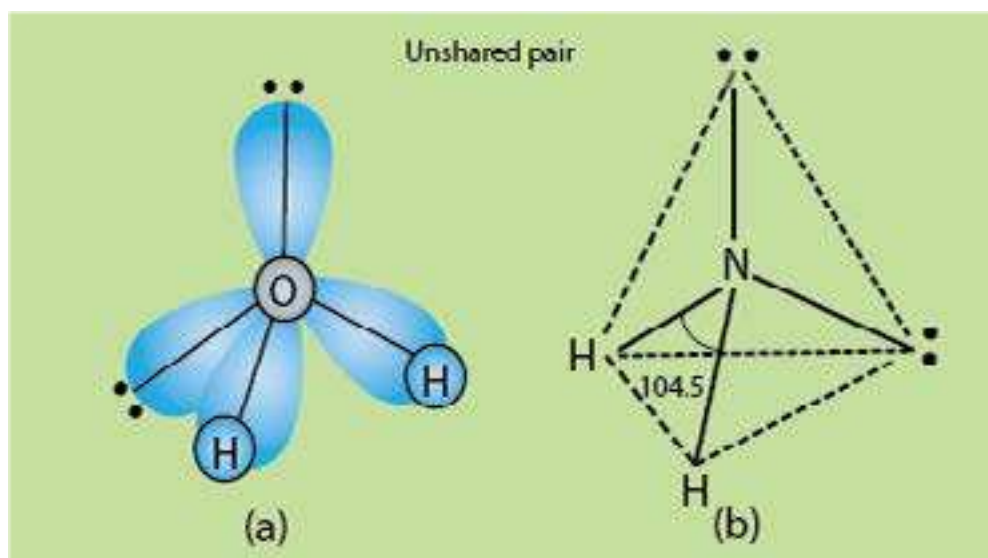of oxygen. They repel bond pairs and the bond angle decreases from 109.5° to 104.5°. So, the molecule of water has bent or angular structure.

(ii) sp²- Hybridization

In sp² hybridization, one 's' and two 'p' atomic orbitals of an atom intermix three orbitals called sp² hybrid orbitals.

Bonding and Structure of Boron Trifluoride and Ethene

(a) Boron Trifluoride (BF₃)

The three half filled sp² hybrid orbitals are planar and are oriented at an angle of 120°, Fig(6.14). The sp² hybridization explains the geometry of planar molecules such as BF_3. Electronic configuration of $_5B$ is,

$_5B$ (ground state) $= 1\overset{1\downarrow}{s} 2\overset{1\downarrow}{s} \quad 2\overset{1}{p_x} 2\overset{0}{p_x} 2\overset{0}{p_z}$

$_5B$ (excited state) $= 1\overset{1\downarrow}{s} 2\overset{1}{s} 2\overset{1}{p_x} 2\overset{1}{p_y} 2\overset{0}{p_z}$

$_5B$ (hybridized state) $= 1\overset{1\downarrow}{s} \quad \overset{\boxed{1}}{sp^2} \overset{\boxed{1}}{sp^2} \overset{\boxed{1}}{sp^2}$
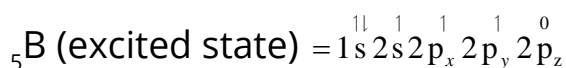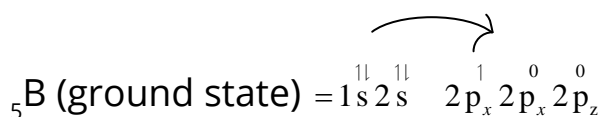
In sp² hybridization, one s and two p atomic orbitals of an atom intermix to form three orbital called sp² hybrid orbitals.
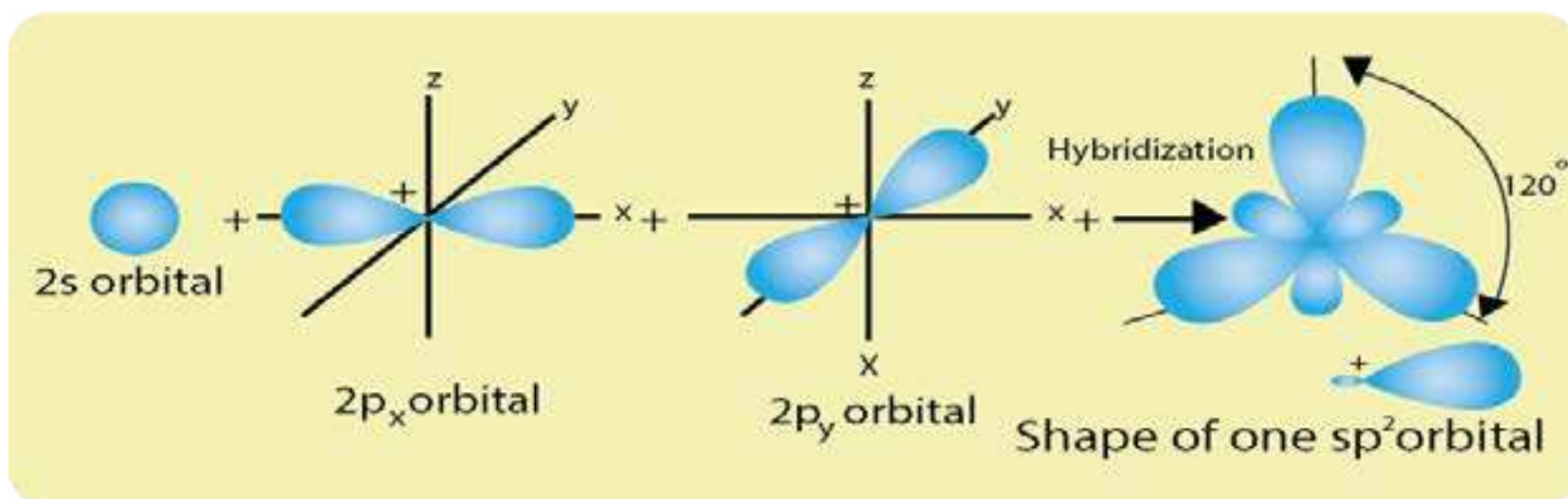
Fig (6.14) Three sp² hybridized orbitals in one plane and at 120° to each other.

One of the p orbitals of fluorine is half filled i.e. $2p_z$. This p-orbital of F is in the form of a lobe. BF_3 is formed by the overlap of three half filled sp^2 hybrid orbitals of boron with lobe shaped p-orbitals of three fluorine atoms Fig.(6.15). The structure is triangular planer.

(b) Ethene ($CH_2=CH_2$)

Electronic configuration of $_6C$ is

$_6$C (ground state) $= 1s^{\uparrow\downarrow}\ 2s^{\uparrow\downarrow}\ 2p_x^{\uparrow}\ 2p_y^{\uparrow}\ 2p_z^{0}$

$_6$C (excited state) $= 1s^{\uparrow\downarrow}\ 2s^{\uparrow}\ 2p_x^{\uparrow}\ 2p_y^{\uparrow}\ 2p_z^{\uparrow}$

$_6$C (hybridized state) $= 1s^{\uparrow\downarrow}\quad sp^2{}^{\uparrow}\, sp^2{}^{\uparrow}\, sp^2{}^{\uparrow}\quad 2p_z^{\uparrow}$
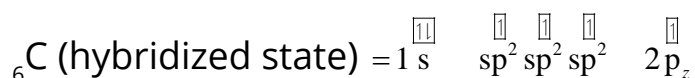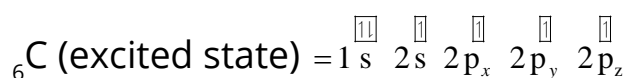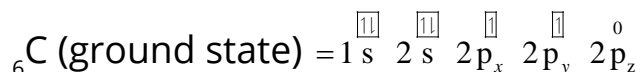
In the formation of ethene molecule, each carbon atom undergoes sp^2 hybridization to form three hybrid orbitals which are co-planar and are oriented at an angle of 120°. Each atom is left with one half filled p-orbital perpendicular to the planar sp^2 hybrid orbitals.
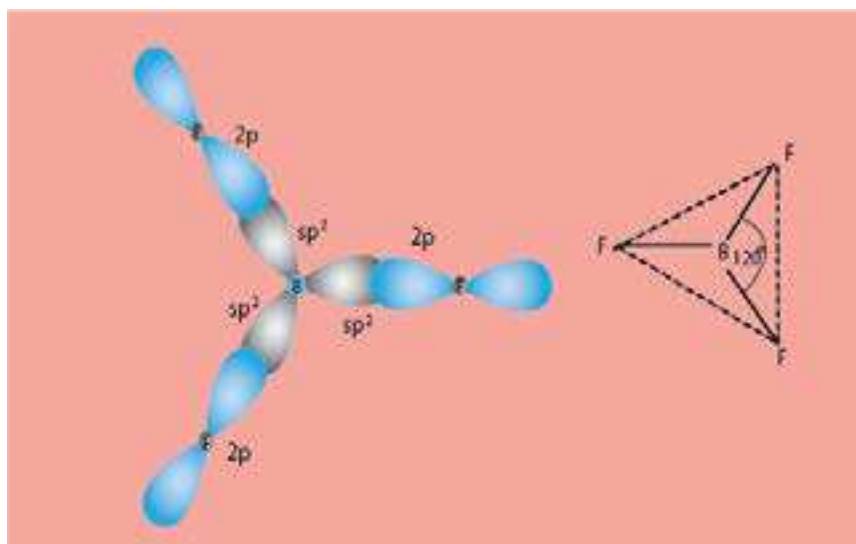
Fig. (6.15) sp^2-p overlaps in BF_3 to form triangular planar structure.

One of the p-orbitals does not take part in hybridization. Each carbon atom undergoes sp^2-s overlaps with two hydrogen atoms and sp^2-sp^2 overlap between themselves to form sigma bonds. These overlaps lead to the shapes shown in Fig.(6.16a). The partially filled p-orbitals undergo sidwrays overlap to form a π–bond.

So, a π-bond is formed by the sideways overlap of two half filled co-planar p-orbitals in such a way that the probability of finding the electron is maximum perpendicular to the line joining the two nuclei. It should be made clear that a π-bond is formed between two atoms only when they are already bonded with a sigma bond.

The two clouds of the π-bond are perpendicular to the plane in which five π-bonds are lying. Just like σ-bond, π -bond can be represented by a line as in Fig (6.16 b). The final shape of C_2H_4 is shown in Fig. (6.16 c).
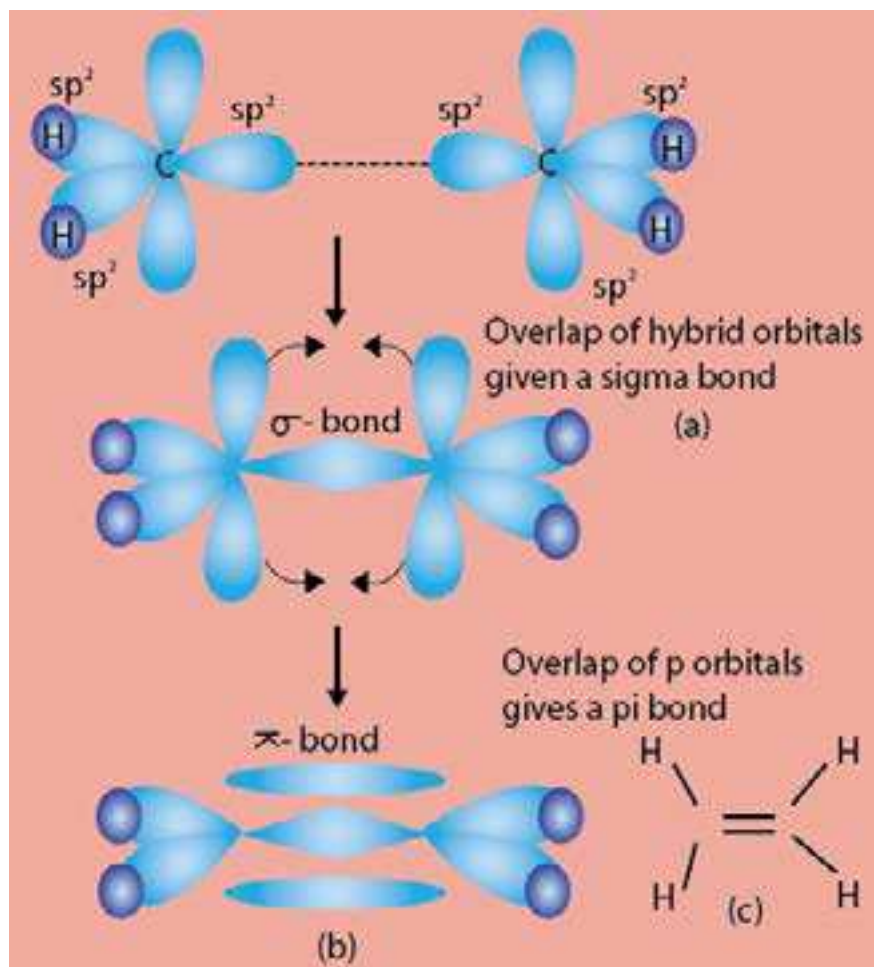
Fig. (6.16) Formation of one sigma between
two carbon atoms and one π-bond in C_2H_4.

(iii) sp-Hybridization

In sp hybridization, one 's' and one 'p' orbitals.intermix to form two sp-hybrid orbital called sp hybrid orbitals.

Bonding and Structure of Beryllium Dichloride and Ethyne
(a)   Beryllium Bichloride

Electronic configuration of $_4$Be is

$_4$Be (ground state) $= 1s^{\uparrow\downarrow}\ 2s^{\uparrow\downarrow}\ 2p_x^{0}\ 2p_y^{0}\ 2p_z^{0}$

$_4$Be (excited state) $= 1s^{\uparrow\downarrow}\ 2s^{\uparrow}\ 2p_x^{\uparrow}\ 2p_y^{0}\ 2p_z^{0}$

$_4$Be (hybridized state) $= 1s^{\uparrow\downarrow}\ \underset{sp\,sp}{\uparrow\ \uparrow}$
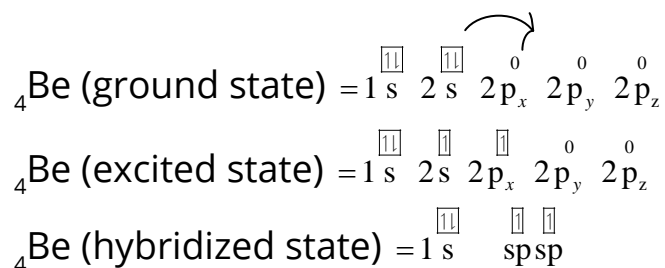
The two sp hybrid orbitals lie in linear way, Fig (6.17). The sp hybridization explains the geometry of linear molecules such as beryllium chloride, $BeCl_2$. It is formed when two sp hybrid orbitals of Be atom overlap with the half filled p-orbitals of chlorine atoms. The outermost half filled $3p_z$ orbital of Cl has lobe shape.
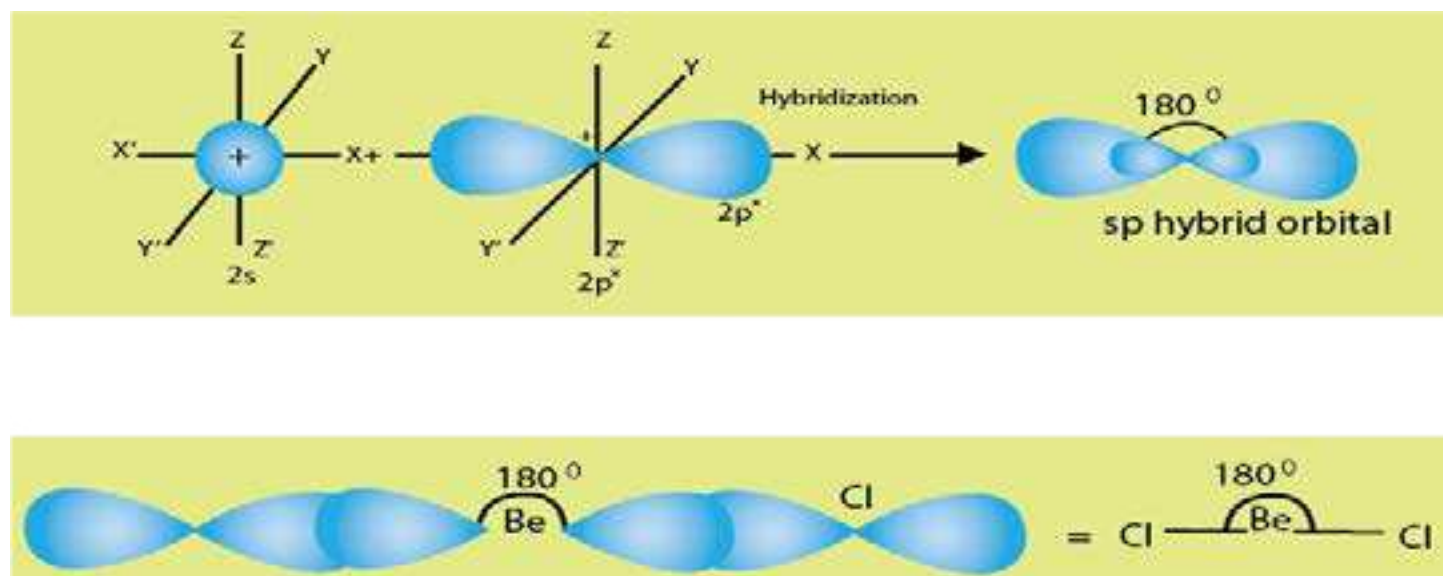
Fig. (6.17) sp-hybridization to form a linear structure

Be atom lies at the center and two Cl atoms on either side so that the Cl-Be-Cl angle is 180°.

(b) Ethyne (CH≡CH)

The electronic configuration of

$_6$C (ground state) $= 1s^{\uparrow\downarrow}\ 2s^{\uparrow\downarrow}\ 2p_x^{\uparrow}\ 2p_y^{\uparrow}\ 2p_z^{0}$

$_6$C (excited state) $= 1s^{\uparrow\downarrow}\ 2s^{\uparrow}\ 2p_x^{\uparrow}\ 2p_y^{\uparrow}\ 2p_z^{\uparrow}$

$_6$C (hybridized state) $= 1s^{\uparrow\downarrow}\ \underset{sp^2\ sp^2}{\uparrow\ \uparrow}\ 2p_y^{\uparrow}\ 2p_z^{\uparrow}$
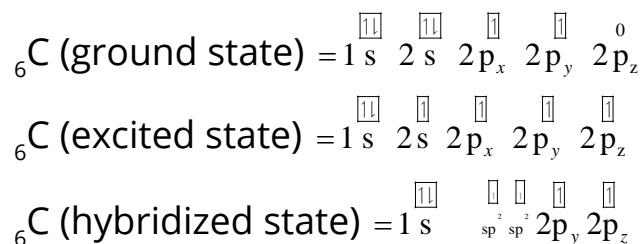
Ethyne is formed as a result of sp hybridization of carbon atoms and subsequent formation of σ and π bonds. Each carbon atom undergoes sp-s overlap with one hydrogen atom and sp-sp overlap with other carbon atom. Each carbon atom is left with two unhybridized p orbitals perpendicular to the plane of sp hybrid orbitals. The two half filled p orbitals (on separate carbon atoms) are parallel to each other in one plane while the other two p orbitals are parallel to each other in another plane. The sideways π overlap between the p-orbitals in two planes results in the formation of two π bonds as shown in Fig.(6.18).

Ethyne molecule contains one σ and two π bonds between the two carbon atoms and each carbon atom is bonded with, one H atom through σ bond. Actually, four electronic clouds of two π-bonds intermix and they surround the sigma bond in the shape of a drum.

Overlap of hybrid orbitals gives a sigma bond

σ-bond

Overlap of p orbitals gives a pi bond

π-bond

π-bond
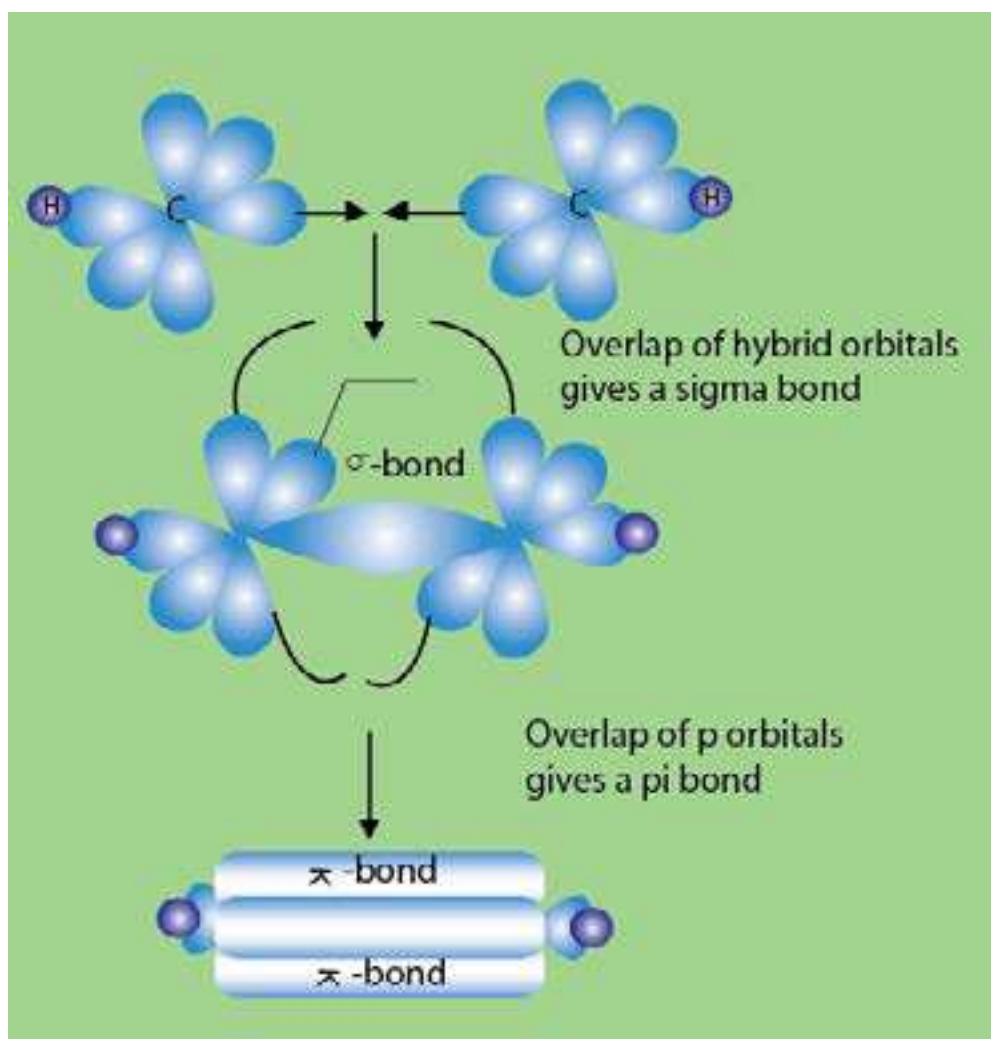
Fig. (6.18) Formation of one sigma and two pi-bonds in C_2H_2 (ethyne)

6.4.6. Molecular Orbital Theory

The molecular orbital approach considers the whole molecule as a single unit. It assumes that the atomic orbitals of the combining atoms overlap to form new orbitals called molecular orbitals which are characteristic of the whole molecule. The molecular orbital surrounds two or more nuclei of the bonded atoms. Two atomic orbitals, after overlapping, form two molecular orbitals which differ in energy. One of them, having lower energy, is called bonding molecular orbital while the other having higher energy is called anti-bonding molecular orbital.

The bonding molecular orbital is symmetrical about the axis joining the nuclei of the bonded atoms (molecular axis). It is designated as sigma (σ) bonding molecular orbital while the antibonding molecular orbital, is called σ^*. The process of formation of molecular orbitals from 1s atomic orbitals of hydrogen is shown in Fig (6.19).

The filling of electrons into the molecular orbitals takes place according to the Aufbau principle, Pauli's exclusion principle and Hund's rule. The two electrons (one from each hydrogen atom), thus fill the low energy σ_{1s}-orbital and have paired spin ($\overline{1\downarrow}$), while the high energy σ^*_{1s} orbital remains empty.
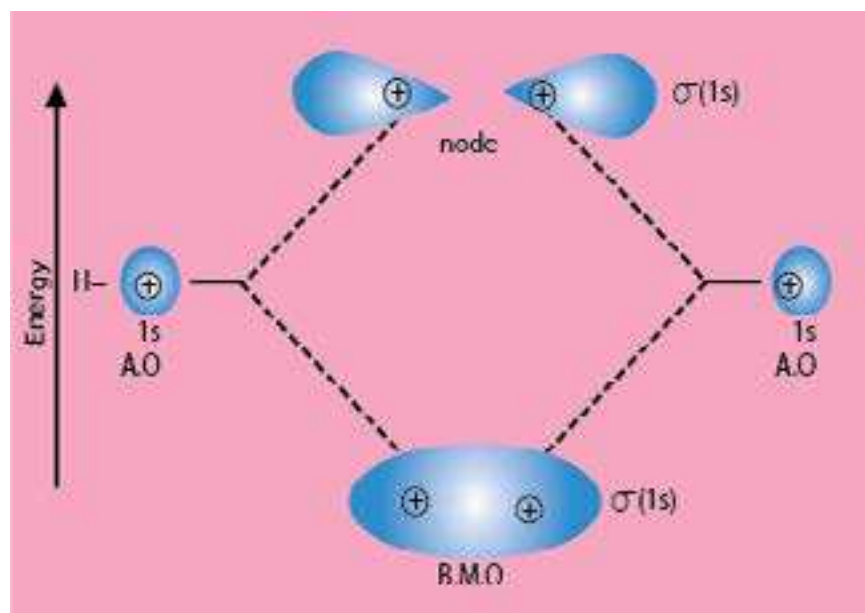
Fig (6.19). Formation of bonding and anti-bonding molecular orbitals for hydrogen molecule (H_2)

Animation 6.31: Molecular Orbital Theory
Source & Credit : andrew.cmu
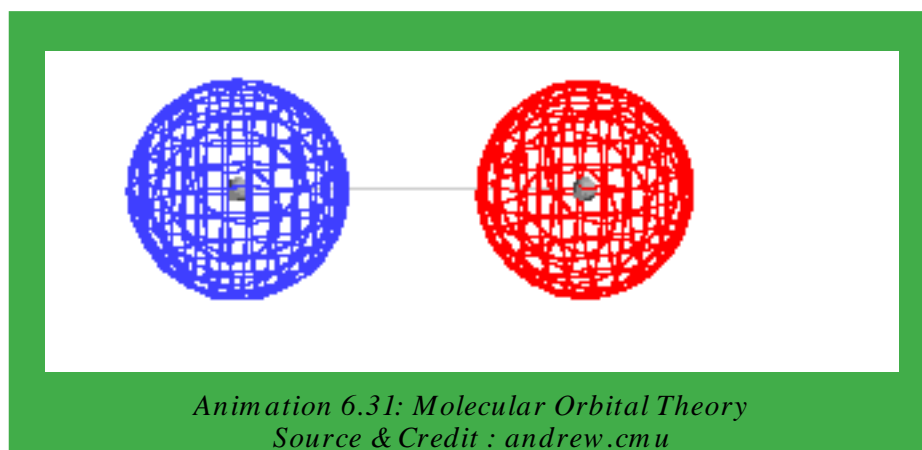
So far, we have considered s and s orbital overlap for the formation of molecular orbitals of hydrogen molecule. Other types of overlaps occurring between p and p atomic orbitals to form molecular orbitals are described below. There are three 2p atomic orbitals directed along the three perpendicular x, y and z coordinates. For the formation of molecular orbitals from p- orbitals, two cases arise:

(a) Head on Approach

Here, the p-orbitals of the two atoms approach along the same axis (i.e. p_x axis) as shown in Fig. (6.20).

This combination of the atomic orbitals gives rise to $\sigma(2p_x)$ bonding and $\sigma^*(2p_x)$ antibonding molecular orbitals. Both are symmetrical about the nuclear axis.

Fig. (6.20) Head on overlap of two p-orbitals

(b) Sideways Approach

When the axes of two p-orbitals (i.e p_y or p_z orbitals) are parallel to each other, they interact to form molecular orbitals as shown in Fig.(6.21).

Fig. (6.21) Sideways overlap of two p-orbitals

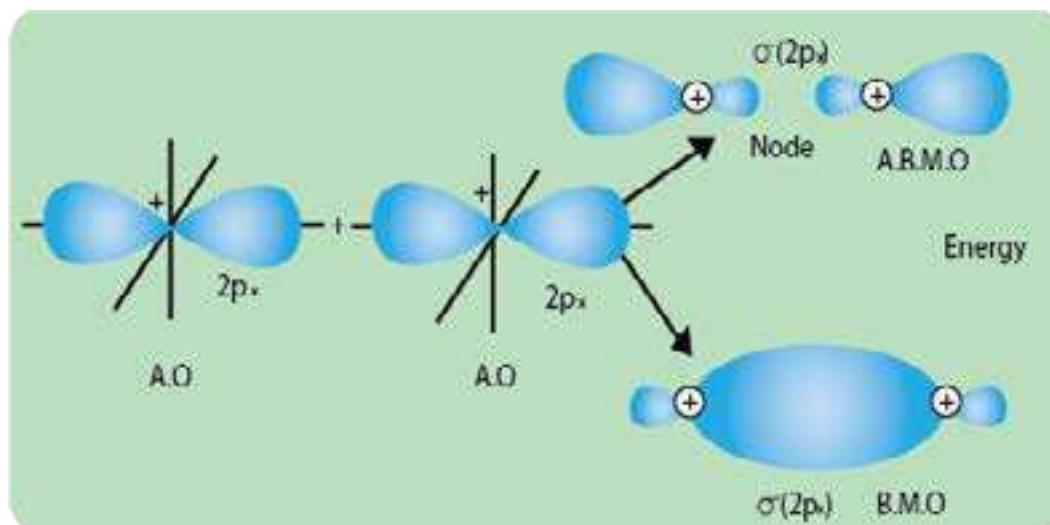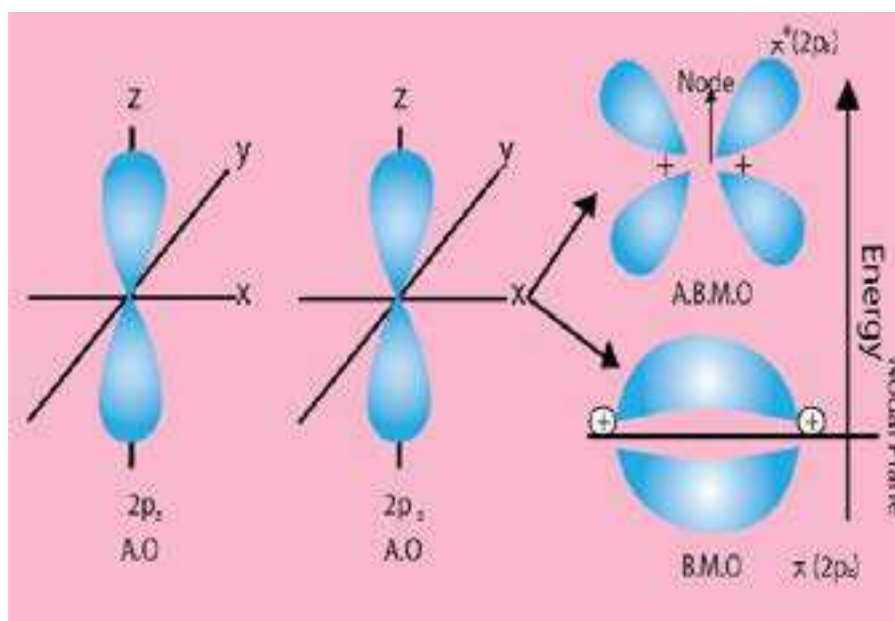The bonding molecular orbitals $\pi(2p_y)$ or $\pi(2p_z)$ have zero electron density on the nuclear axis (called the nodal plane). The electron density is uniformly distributed above and below the nodal plane.

On the other hand, anti-bonding molecular orbitals $\pi^*(2p_y)$ and $\pi^*(2p_z)$ have the least electron density in the π inter-nuclear region. Since the $2p_y$ and $2p_z$ atomic orbitals are degenerate (having the same energy), the π - molecular orbitals i.e. $\pi(2p_y)$ and $\pi(2p_z)$ are also degenerate. So,are also the $\pi^*(2p_y)$ and $\pi^*(2p_z)$ molecular orbitals.

Overall six molecular orbitals (three bonding and three anti-bonding) are formed from two sets of 2p atomic orbitals. The bond formed as a result of linear overlap is ó bond, while that formed as a result of sideways overlap is called a π (pi) bond. As there are three bonding molecular orbitals, the p-orbitals overlap can lead to the formation of at the most three bonds: one sigma and two π -bonds.

Relative Energies of the Molecular Orbitals

The relative energies of the molecular orbitals formed from 2s and 2p atomic orbitals in the case of homonuclear di-atomic molecules are shown in Fig. (6.22).

The energies of the molecular orbitals are determined by spectroscopic measurements. The molecular orbitals of diatomic molecules such as O_2, F_2 and their positive and negative ions can be arranged in the following-increasing order of energy (Fig 6.22a).
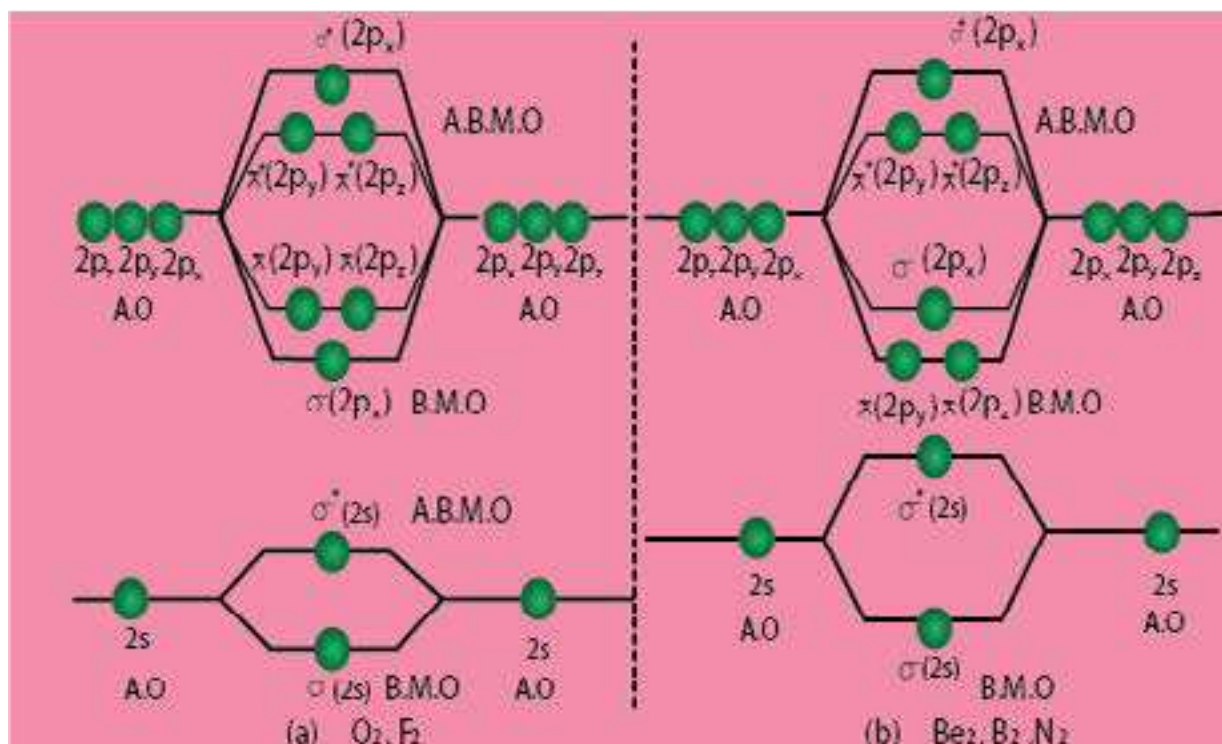
Fig(6.22)(a)Molecular orbital energy diagram for O_2, F_2 and their positive and negative ions
(b) Molecular orbital energy diagram for Li_2, Be_2, B_2 and N_2.

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

The diatomic molecules, such as N_2 and other -lighter molecules like B_2, C_2 show slightly different energy order. See Fig. (6.22 b):

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

Reason

It has been observed that in case of B_2, C_2 and N_2 ,$\sigma 2p_x$ is higher in energy than $\pi 2p_y=\pi 2p_x$. MOs. This reversal is due to mixing of 2s and $2p_x$ atomic orbitals.

Actually, the energy difference of 2s and 2p atomic orbitals is small. There is a possibility of mixing of these orbitals (i.e. hybridization of A.O.) as a result of which $\sigma 2s$ and σ^*2s MOs do not retain pure s-character. Similarly, $\sigma 2p_x$ and σ^*2p_x MOs do not have pure p-character. All the four MOs acquire sp-character. Due to this mixing, their energies change'in such a way that MOs $\sigma 2s$ and σ^*2s become more stable and are lowered in energy MOs as $\sigma 2p_x$ and σ^*2p_x become less stable and are raised in energy. Since, πp-orbitals are not involved in mixing, so energy of $\pi 2p_y=\pi 2p_z$ remains unchanged.$\sigma 2p_x$ is raised to such an extend that it becomes higher in energy than π-bondings.

Anyhow, O_2 and F_2 do not do so. The re ason is high energy difference of their 2s and 2p i.e. 1595 and 2078 kJmol^{-1}, for O_2 and F_2 , respectively. These values are 554kJmol^{-1} for boron, 846kJmol^{-1} for carbon, and 1195kJmol^{-1} for nitrogen. These energy differences have been calculated by spectroscopic techniques.

Bond Order

The number of bonds formed between two atoms after the atomic orbitals overlap, is called the bond order and is taken as half of the difference between the number of bonding electrons and anti-bonding electrons. The number of bonds formed between H-atoms in hydrogen molecule may be calculated as follows:

Number of electrons in the bonding orbitals   = 2
Number of electrons in the anti-bonding orbitals   = 0

Bond order $= \dfrac{2-0}{2}$ = 1

It is a common practice that only MOs formed from valence orbital are considered in bond order calculations.

Molecular Orbital Structures of Some Diatomic Molecules

(i)   Helium, He$_2$

The electronic configuration of He is 1s^2. The 1s orbitals of He-atoms combine to form one bonding σ (1s) and one anti-bonding σ* (1s) orbitals as shown in Fig (6.23).

Each He-atom contributes two electrons. Two electrons enter bonding molecular orbital σ (ls) and the remaining two go to antibonding σ* (Is) molecular orbital.

The bond order for He$_2$ is zero i.e. $\dfrac{2-0}{2}$ picture of He$_2$ molecule is not formed.
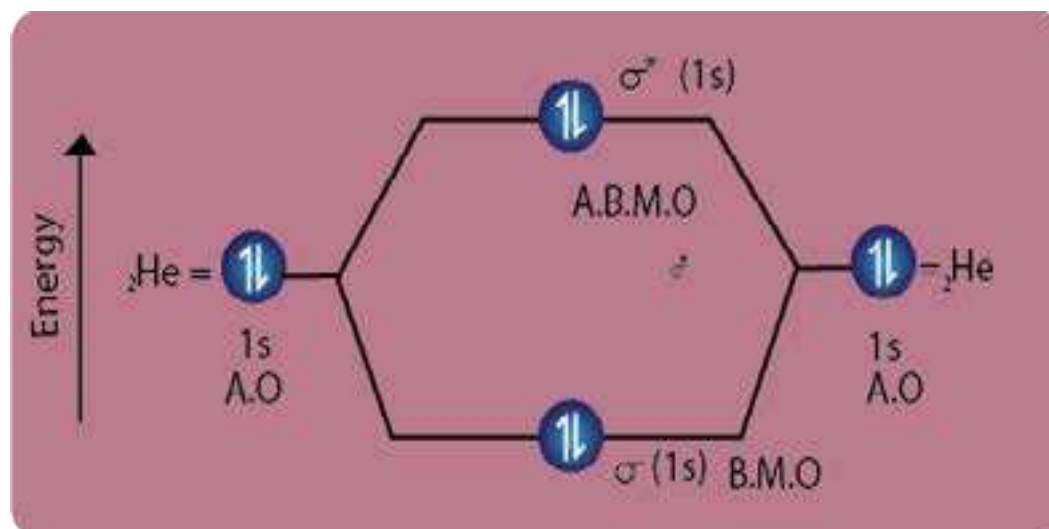
Fig Fig. (6.23) Hypothetical orbital
picture of He$_2$ molecule.

(ii)   Nitrogen, N$_2$

The molecular orbital structure of N$_2$ molecule is shown in Fig (6.24). Electronic configuration of N$_2$ molecule is

$$\sigma\left(1s^2\right)<\sigma^*\left(1s^2\right)<\sigma\left(2s^2\right)<\sigma^*\left(2s^2\right)<\pi\left(2p^2_{\ y}\right)=\pi\left(2p^2_{\ z}\right)<\sigma\left(2p^2_{\ x}\right)<\pi^*\left(2p_y\right)=\pi^*\left(2p_z\right)<\sigma^*\left(2p_x\right)$$
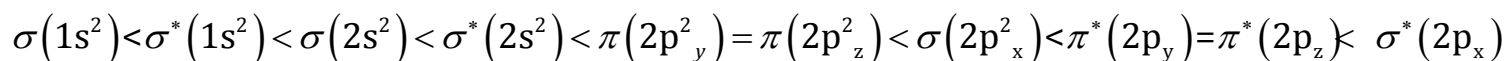
From the electronic configuration of N$_2$, it is clear that six electrons enter into three outermost bonding orbitals while no electrons enter into anti-bonding orbitals.

Thus, the bond order in N$_2$ molecule is $\dfrac{6-0}{2}=\dfrac{6}{2}=3$, which corresponds

to the triple bond consisting of one sigma and two π bonds. The bond dissociation energy of N$_2$ is very high, i.e. 941kJmol^{-1}.
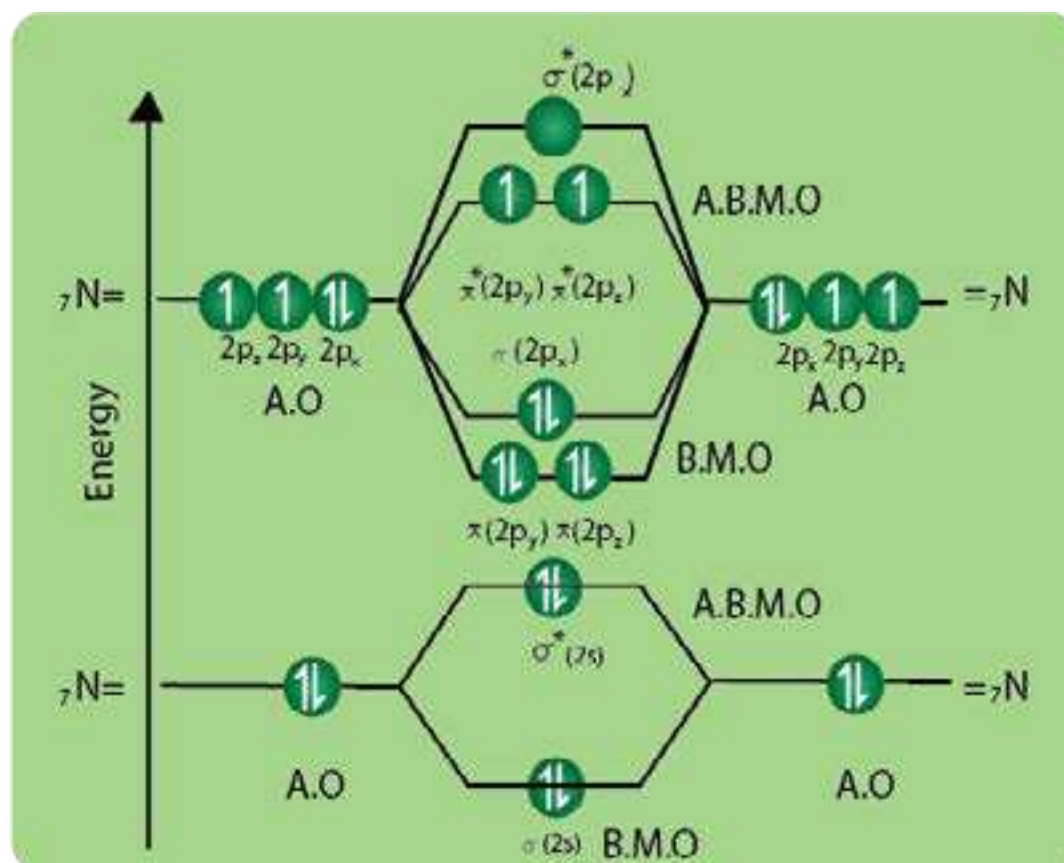
Fig. (6.24) Molecular orbitals picture of N₂ molecule.

(iii) Oxygen, O_2

The formation of molecular orbitals in oxygen molecule is shown in Fig. (6.25). The electronic configuration of O_2 is

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

The bond order in O_2, is $\dfrac{6-2}{2}$ =2, which corresponds to a double bond.

This is consistent with the large bond energy of 496kJ mol^{-1} of oxygen molecule. Fig(6.25) shows that the filling of molecular orbitals leaves two unpaired electrons in each of the $\pi^*(2p_y)$ and $\pi^*(2p_z)$ orbitals. Thus, the | electronic configuration of the molecular orbitals accounts admirably for the paramagnetic properties of oxygen. This is one of the greatest successes of the molecular orbital theory. Liquid O_2 is attracted towards the magnet.

Anyhow, when two more electrons are given to O_2, it becomes O_2^{2-}. The paragmanetism vanishes. Similarly, in O_2^{2+} the unpaired electrons are removed and paragmagnetic property is no more there. Bond order of O_2^{2-} are also different from O_2 and are one and three, respectively.

Similarly, M.O.T justifies that F_2 has bond order of one and Ne does not make a bond with Ne.
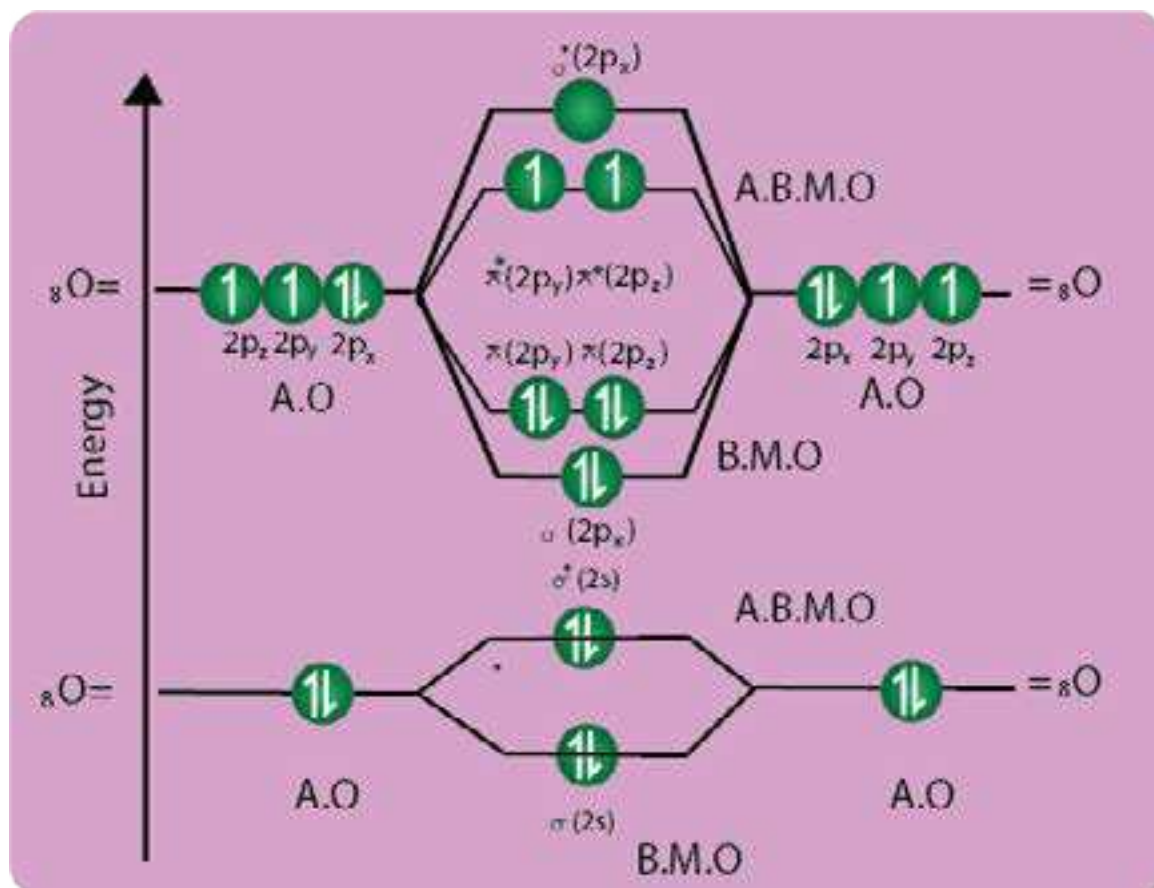

Fig. (6.25) Molecular orbitals in 0, molecule.

6.5 BOND ENERGY, BOND LENGTH AND DIPOLE MOMEN

6.5.1 Bond Energy (bond enthalpy)

When a bond is formed between two atoms, energy is released. The same amount of energy is absorbed when the bond is broken to form neutral atoms. So, the bond energy is the average amount of energy required to break all bonds of a particular type in one mole of the substance. It is determined experimentally, by measuring the heat involved in a chemical reaction. It is also called bond enthalpy, as it is a measure of enthalpy change at 298 K. The enthalpy change in splitting a molecule into its component atoms is called, enthalpy of atomization.

The bond energy is given in kJ mol^{-1} which is the energy required to break an Avogadro's number (6.02 x 10^{23}) of bonds. It is also released when an Avogadro's number of bonds are formed. Table (6.5).
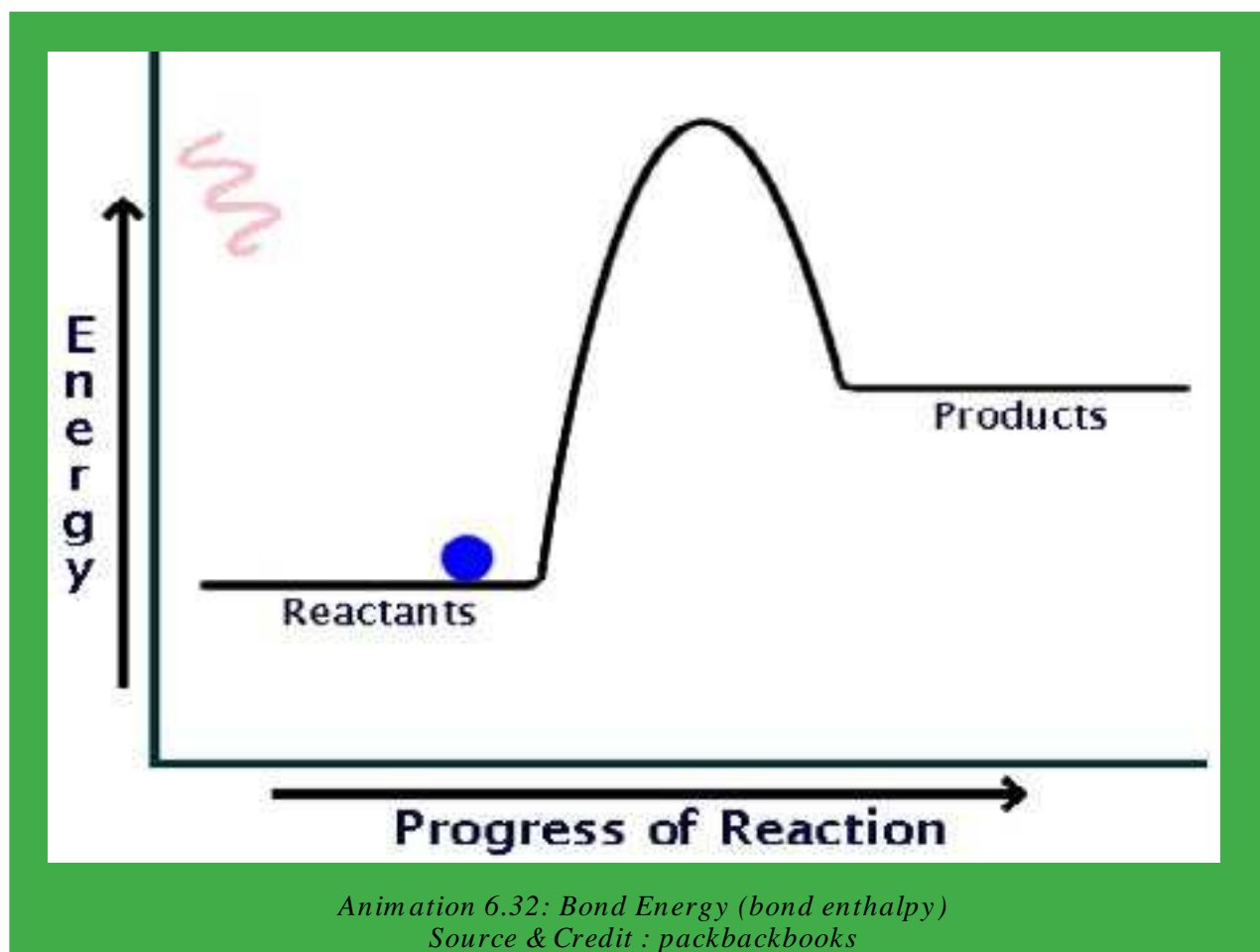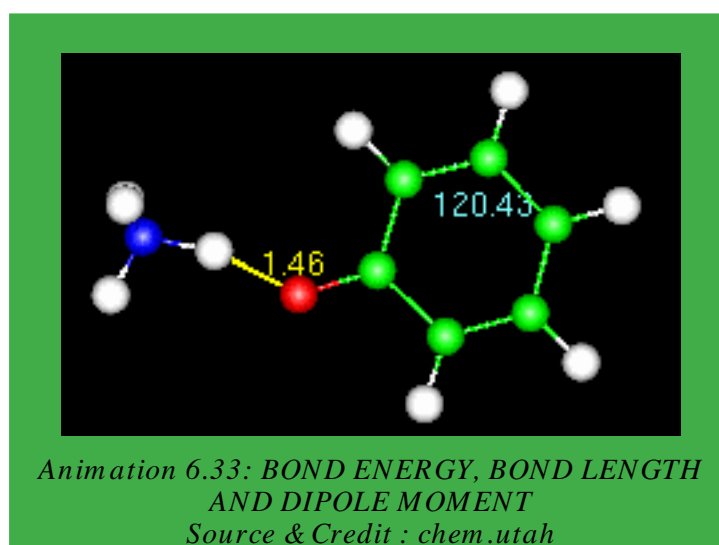

Animation 6.32: Bond Energy (bond enthalpy)
Source & Credit : packbackbooks

Table (6.5) Average bond enthalpies of some important bonds (kjmol^{-1}).

Bond	Bond energy (kJmol^{-1})	Bond	Bond energy (kJmol^{-1})	Bond	Bond energy (kJmol^{-1})	Bond	Bond energy (kJmol^{-1})
C-C	348	H-H	436	O-O	146	Si-H	323
C=C	614	H-F	567	O=O	495	Si-Si	226
C≡C	839	H-Cl	431	O-H	463	Si-C	301
C-H	413	H-Br	366	O-F	190	Si-O	368
C-N	293	H-I	299	O-Cl	203	F-H	155
C=N	615	N-N	163	O-I	234	Cl-F	253
C≡N	891	N=N	418	S-S	266	Cl-Cl	242
C-O	358	N≡N	941	S=S	418	Br-F	237
C=O	799	N-H	391	S=O	523	Br-Cl	218
C≡O	1072	N-O	201	S-H	339	Br-Br	193
C-F	485	N-F	272	S-F	327	I-Cl	208
C-Cl	328	N-Cl	200	S-Cl	253	I-Br	175
C-Br	276	N-Br	243	S-Br	218	I-I	151
C-I	240						
C-S	259						

It may be noted that energies of multiple bonds are greater than those of single bonds. But a double bond is not twice as a strong as a single bond or a triple bond is not thrice as strong as a single bond. It means that σ- bond is stronger than a π-bond. Similarly, a polar covalent bond is stronger than a non-polar covalent bond.

Animation 6.33: BOND ENERGY, BOND LENGTH AND DIPOLE MOMENT
Source & Credit : chem.utah
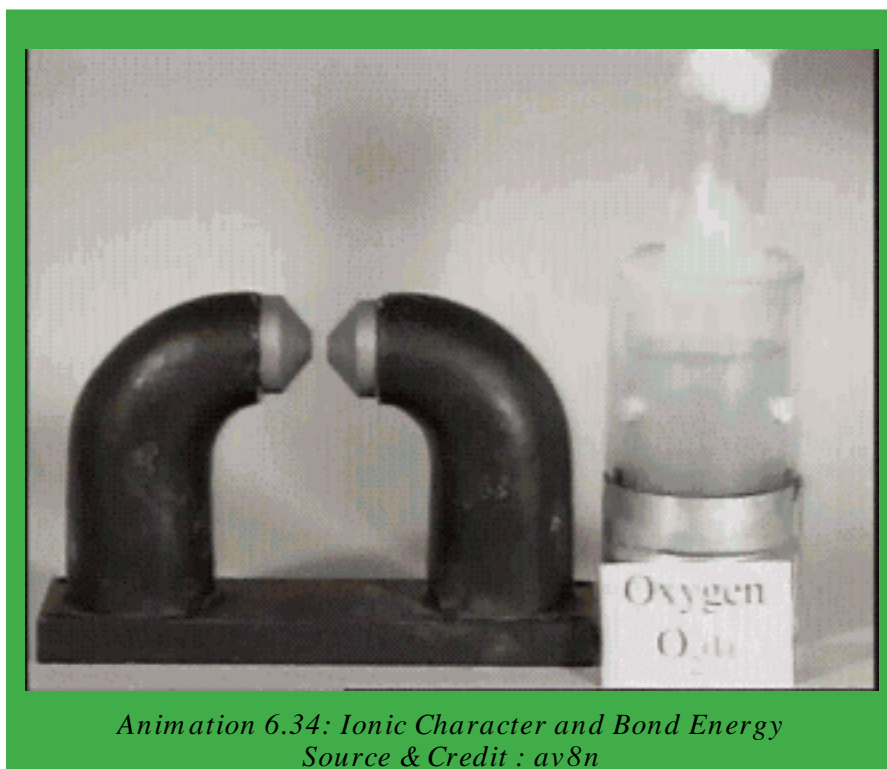
6.5.2 Ionic Character and Bond Energy

Bond energy is a measure of the strength of a bond. The strength of a bond depends upon the following factors.

(i) Electronegativity difference of bonded atoms   (ii) Sizes of the atoms (iii)Bond length Let us consider, first the part played by electronegativity difference. Look at the bond energies of H-X type of compounds, where X=F, Cl, Br, I, Table (6.6).This data show that electrons are not equally shared between the bonded atoms i.e. HX. As halogen atom is more electronegative, the bonded pair is more attracted towards X atom and thereby polarity develops. This gives rise to additional attractive force for binding.

From the difference between experimental bond energies and those calculated by assuming equal sharing, it is possible to estimate relative electronegativities. The comparison of these values shows that the discrepancy is the greatest for HF and the least for HI, Table (6.9).

Let us calculate, the increase in the strength of H-Cl bond,due to the ionic character present in it.The H-H bond energy is 436 kJ mol^{-1}

It means 436 kJ of heat is required to break the Avogadro's number of H_2 molecules into individual atoms. Thus, bond energy per bond is 72.42 x 10^{-23}kJ. This is obtained by dividing 436 by 6.02 x 10^{23}. As the bonding electron pair is equally shared between the two H atoms, we can assume that each bonded H-atom contributes half of the bond energy i.e., 36.21x10^{-23}kJ.

Similarly, the bond energy for Cl_2 is 240 kJ mol^{-1}. Therefore, each Cl-atom should contribute 19.93 x 10^{-23} kJ to any bond, where sharing of an electron pair is equal.

$$H+H \rightarrow H_2 \qquad \Delta H = -436 kJmol^{-1}$$

Animation 6.34: Ionic Character and Bond Energy
Source & Credit : av8n

Table (6.6) Comparison of experimental and theoretical bond energies

Bond	Bond energies (kJmol^{-1})			
	X=F	X=Cl	X=Br	X=I
X-X	155	242	193	151
H-X (calculated)	293	336	311	291
H-X (observed)	567	431	366	299
difference	274	95	55	8

Let us, now consider, the bond in HCl. This bond is polar, but we consider the electron pair to be equally shared. On adding up the bond energy contributions of H-atom and Cl-atom, we expect the bond energy of H-Cl to be 56.14 x 10^{-23}kJ per molecule which is the sum of 36.21xl0^{-23}kJ and 19.93x10^{-23}kJ. For Avogadro's number of HCl molecules, the calculated bond energy is 337.96 kJmol^{-1} which is obtained by multiplying 56.14 x 10^{-23} with 6.02 x 10^{-23} The experimentally found bond energy for HCl is 431 kJmol^{-1}.The observed bond energy is significantly greater than the calculated value and that means a more stable H-Cl bond. This stability is due to the ionic character present in the molecule.The decreasing polarity from HF to HI shows a trend toward equal sharing of electrons which is consistent with decreasing electronegativity from F to I.

The bonds with higher bond energy values have shorter bond lengths. The bond energies of C to C bonds being in the order C $\equiv$ C >C=C>C-C. Their bond lengths are in the reverse order i.e. C -C > C=C > C $\equiv$ C.

6.5.3 Bond Length

The distance between the nuclei of two atoms forming a covalent bond is called the bond length. The bond lengths are experimentally determined by physical techniques. The techniques may be electron diffraction, X-ray diffraction or spectral studies.

The covalent bond length between two atoms is often but not always independent of the nature of the molecules. For instance, in most of the aliphatic hydrocarbons, the C-C bond length is very close to 154 pm. The C-C bond length is also found to be the same in diamond.

The covalent radii for different elements are almost additive in nature. The single bond covalent radius of carbon is 77 pm which is half of the C-C bond length (154 pm). Similarly, the covalent radius of Cl is 99 pm i.e. one half of the Cl-Cl bond length (198 pm). So the bond length of C-Cl bond will be 77 + 99= 176 pm. Some selected bond lengths are given in Table (6.7).

Table (6.7) Some selected bond lengths alongwith and hybridization of central atom.

Compound	Hybridization	Bond	Bond length (pm)
BF_3 (Boron trifluoride)	sp^2	B-F	130
BCl_3 (Boron trifluoride)	sp^2	B-Cl	175
SiH_4 (Monosilane)	sp^3	Si-H	148
SiF_4 (silicon tetrafluoride)	sp^3	Si-F	155
C_2H_6 (Ethene)	sp^3	C-C	154
C_2H_4 (Ethene)	sp^2	C=C	133
C_2H_2 (Ethene)	sp	$C \equiv C$	120
$(CH_3)_2$ C=O (Acetone)	sp^2	C=O	122

Animation 6.35: Bond Length
Source & Credit : ch.ic.ac

With an increase in electronegativity difference between the bonded atoms, the bond becomes shortened. For example, Si-F bond length in SiF_4 is found to be 154-159 pm, whereas the addition of their covalent radii (Si=117 pm and F=64 pm) give Si-F bond length to be equal to 181 pm, Table (6.7). The calculated values are almost always higher due to electronegativity differences. The ionic character results in shortening of the bond length due to force of attraction between the polar ends.

Moreover, hybridization scheme involved, also explains the shortening of bonds due to the predominant participation of s-orbitals. Since, the 2s-orbital of carbon has smaller mean radius than the 2p-orbitals, it would be expected that greater the s character in the hybrid orbitals used, the shorter will be the bond distance. Thus, the C-C bond lengths are 154,133 and 120 pm for ethane, ethene and ethyne, respectively where s orbital contribution increases from sp^3 to sp. Further, p-bonding also reduces the internucleft bond distance.

The bond length increases, as we move from top to bottom in group IV-A of the periodic table. Thus, Si-Si bond length is more than C-C bond length in group IV-A and P-P bond length is much more than N-N bond length in group V-A. As the atomic radii increase in a group (N to P or C to Si), the effect of the effective nuclear charge decreases on electrons. As a result the bond length will increase. In the periodic table, shortening of bond lengths occurs from left to right in, a period. This can be attributed to the pull by nuclear charge with the same value of principal quantum number. Therefore, C-C bond length is greater than N-N bond length.

6.5.4 Dipole Moment

In heteronuclear molecules, e.g. HCl where the bonded atoms are of different elements, the molecule becomes polar due to the electronegativity difference. Partial positive and negative charges become separated on the bonded atoms. The se paration of these charges on the molecule is called a dipole and the molecule is said to have a dipole moment.

The dipole moment is a vector quantity, which has a magnitude as well as a direction. Fig . (6.26) illustrates the dipole and its vecrtor representation. The dipole moment (m) is be defined as the product of the electric charge (q) and the distance between the positive and negative centres (r):
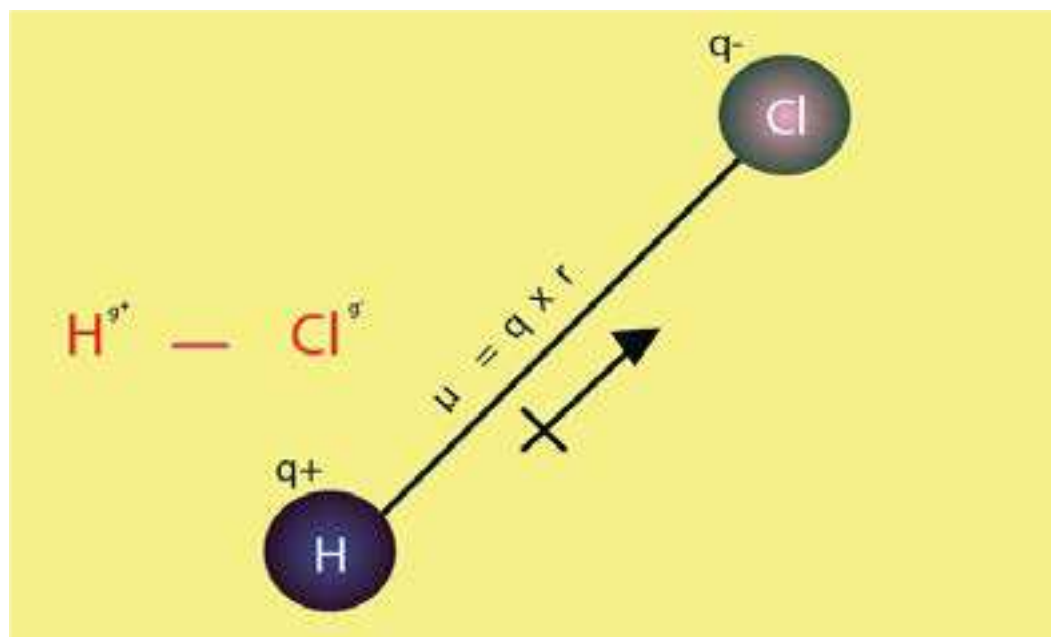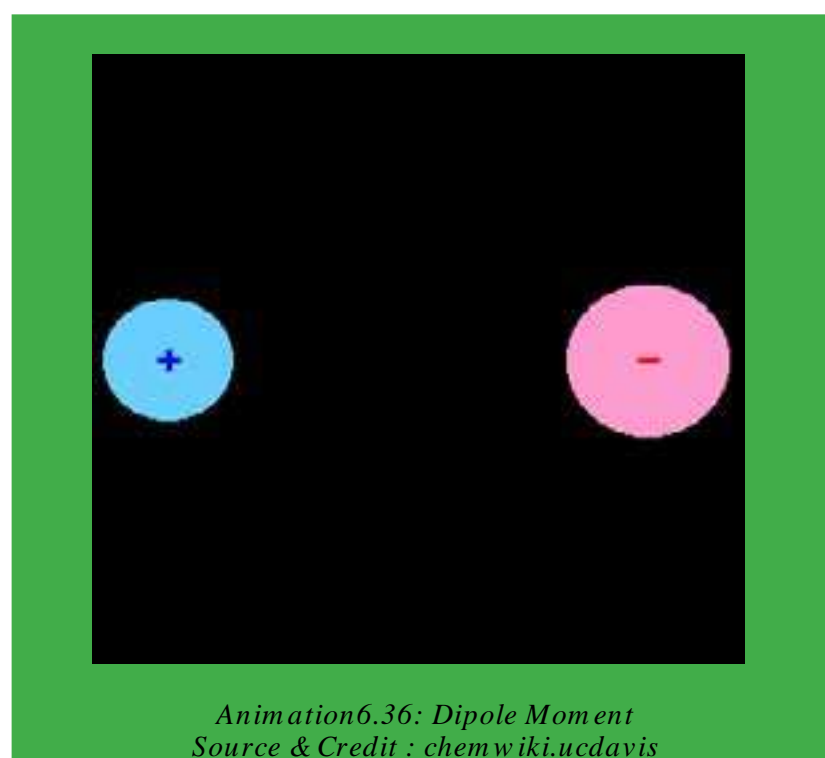
$$\mu = q \ x \ r$$

Fig. (6.26) Dipole moment and its vector representation

The dipole moments of simple heteronuclear diatomic molecules like HF, HCl, HBr. HI, CO, NO, etc. are directed from electropositive ends to electronegative ends.

The dipole moments are measured in Debye (D) units. Let us consider a hypothetical molecule (A^{*}—B^{-}), or a unit negative charge separated from a unit positive charge by distance r = 100 pm (1 Å)The dipole moment of such a molecule can be calculated by multiplying the distance 100pm to charge of one electron or proton is 1.6 $orx10^{-19}$C $\mu=(1.6022x10^{-19}C)x(100x10^{-12}m) = 1.6022x10^{-29}$ mC

Animation6.36: Dipole Moment
Source & Credit : chemwiki.ucdavis

Another unit of dipole moment is Debye. The equivalence of Debye and mC is 1 D = 3.336x10^{-30}mC. So, the dipole moment of the, above system in Debye units is

$$= \frac{1.6022 \times 10^{-29}\,mC}{3.336 \times 10^{-30}\,mC} = 4.8\ D$$

The dipole moments of some substances in Debye units are given in Table (6.8). If the molecule is polyatomic and contains two or more dipoles, then the net dipole moment is the resultant of the vector addition of the individual bond moments. Examples of CO_2 and H_2O are shown in Fig (6.26).

Table (6.8) Dipole moments of some substances in Debyes

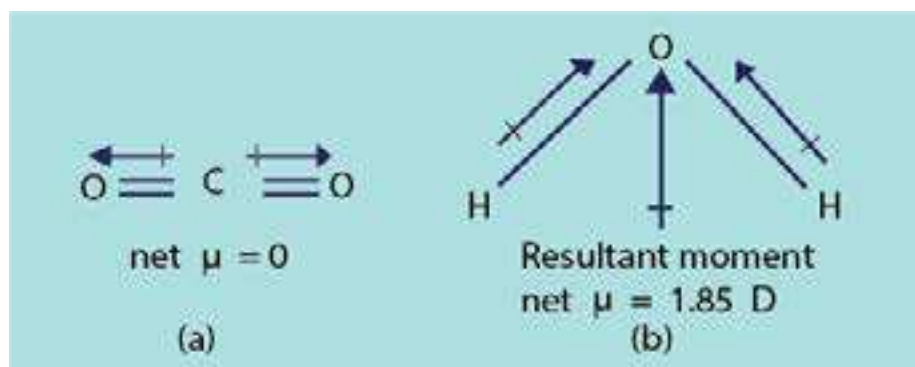| Compound	Dipole moment (D)
H_2	0.00
HCl	1.03
HBr	0.78
HI	0.38
H_2O	1.85
H_2S	0.95
NH_3	1.49
SO_2	1.61
CO_2	0.00
CO	0.12
NO	0.16
H_2O_2	2.20
CH_4	0.00
CH_3F	1.81
CH_3Cl	1.45
CH_3Br	1.85
CH_3I	1.35
C_2H_5OH	1.69

Fig (6.26) Vector addition of bond moments in
(a) linear CO_2 molecule and (b) angular H_2O molecular

6.5.5 Dipole Moments and Molecular Structure

Dipole moment provides two types of information about the molecular structure:
    (i) Percentage ionic character of a bond
    (ii) Angles between the bonds or the geometry of molecules

Animation 6.37: Dipole Moments and Molecular Structure
Source & Credit : uni-marburg
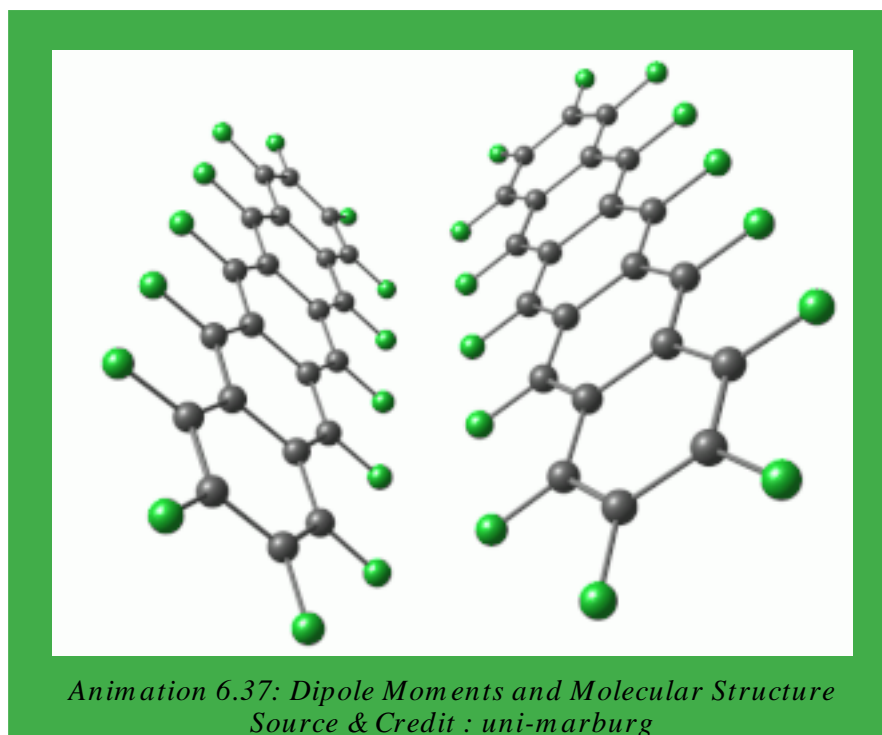
(1)   Percentage Ionic Character

From the experimentally determined dipole moments, the percentage ionic character in a bond can be calculated. For this purpose, we should know the actual dipole moment μ_{obs} of the molecule and actual bond, length. The dipole moment of 100% ionic compound is represented as μ_{ionic}.

$$\text{\%age of ionic character} = \frac{\mu_{obs}}{\mu_{ionic}} \times 100$$

Example 1:

The observed dipole moment of HF is 1.90 D. Find the percentage ionic character in H-F bond. The distance between the charges is 0.917×10^{-10} m.
(Unit positive charge= 1.6022×10^{-19} C).

Solution:

Let us suppose that HF molecules is 100% ionic. It means that H has full positive charge and F has full negative charge.

To calculate its dipole moment multiply the bond length with full charge of electron or proton i.e. 1.6022×10^{-19} C. This dipole moment is called μ_{ionic}.

So,

$$\mu_{ionic} = qxr$$
$$= (1.6022 \times 10^{-19} C)(0.917 \times 10^{-10} m)$$
$$= 1.469 \times 10^{-29} \; mC$$

Scince 1 D
$$= 3.336 \times 10^{-30} \; mC$$

So,
$$= \mu_{ionic} = \frac{1.469 \times 10^{-29} m_c}{3.336 \times 10^{-30} m_c} = 4.4D$$

The actual dipole moment is given as it is observed.
$$\mu_{observed} = 1.90 \; D$$

$$\%ionic \; character = \frac{\mu_{observed} \times 100}{\mu_{ionic}}$$

$$= \frac{1.90 \, D \times 100}{4.4 D} = \boxed{43.2\%} Answer$$

Hence, 43% of HF bond is ionic in nature and 57% covalent. The bond is predominantly covalent.

(ii)   Bond Angles or the Geometry of Molecules

We can understand this aspect by taking some important examples.

The dipole moment of water is 1.85 D which ruled out its linear structure. The calculations show that water has an angular structure with a bond angle 104.5° between the two O-H bonds. A linear H_2O molecule (H-O-H) would have zero dipole moment.

Similarly, the triatomic molecules H_2S or SO_2 etc. are also bent like H_2O.

$$\mu = 0.95\ D \qquad \mu = 1.61\ D$$
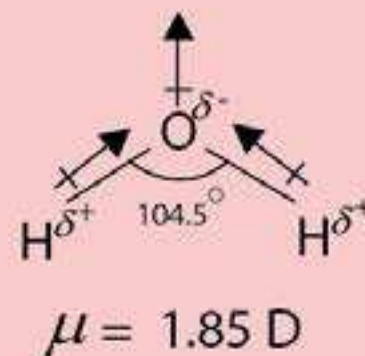
CO has a dipole moment while CO_2 does not have any. The reason is that CO_2 has a linear structure, where the dipoles being equal and opposite, cancel out each other's effect. Similarly, CS_2 has zero dipole moment.

$$\mu = 0.12\ D \qquad \mu = 0 \qquad \mu = 0$$
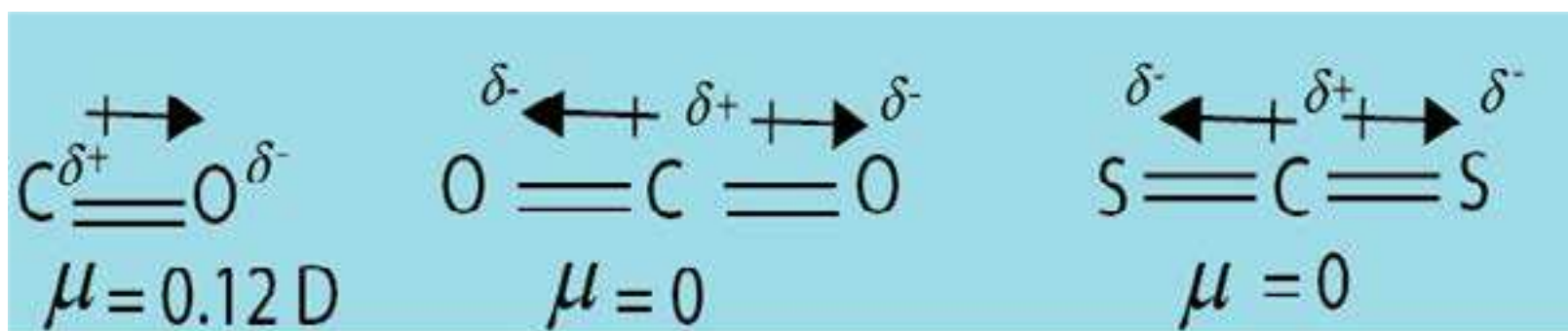
Symmetrical triangular planar molecules of BF_3, $AlCl_3$ and perfectly tetrahedral molecules like CH_4, SiH_4, CCl_4 also have zero dipole moments. This is all due to the cancellation of individual bond moments.

$$\mu = 0 \qquad \mu = 0$$
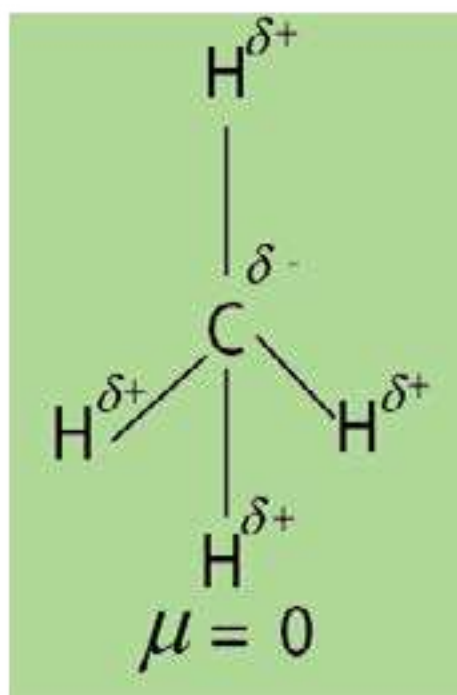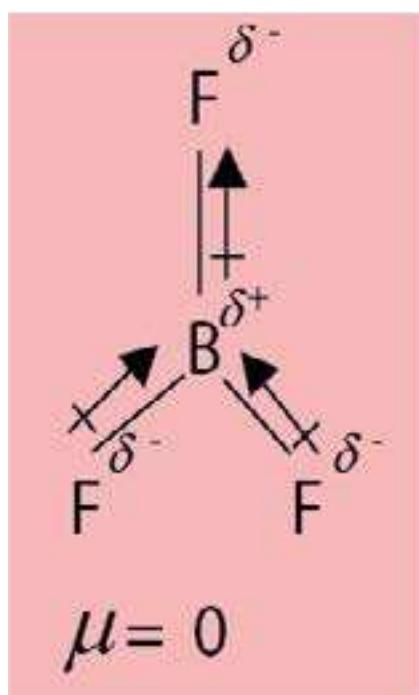
6.6 THE EFFECT OF BONDING ON THE PROPERTIES OF COMPOUNDS

The properties of substances are characterized by the types of bonding present in them. Here, we shall consider the effects of the type of bond on physical and chemical properties of compounds.

(1) Solubility

(a) Solubility of Ionic Compounds

Mostly, ionic compounds are soluble in water but insoluble in non-aqueous solvents. When a crystal of an ionic substance is placed in water, the polar water molecules detach the cations and anions from the crystal lattice by their electrostatic attraction. Thus, the ions are freed from the crystal lattice by hydration. This happens when the hydration energy is greater than the lattice energy and the ions are freed from their positions in the crystal. Many ionic compounds do not dissolve in water, as the attraction of water molecules cannot overcome the attraction between the ions. For the same reason, non-polar solvents like benzene and hexane do not dissolve, ionic compounds.

(b) Solubility of Covalent Compounds

In general, covalent compounds dissolve easily in non-polar organic solvent (benzene, ether, etc.)

Here, the attractive forces of solvent molecules are enough for overcoming the intermolecular forces of attraction. Mostly, covalent compounds are insoluble in water. However, some of them dissolve in water due to hydrogen bonding.

Animation 6.38: THE EFFECT OF BONDING ON THE PROPERTIES OF COMPOUNDS
Source & Credit : ausetute
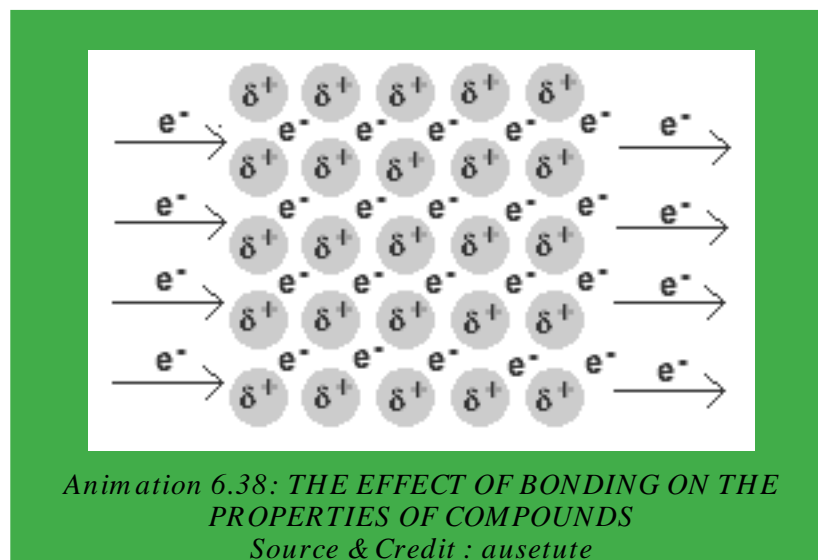
(2) Isomerism

(a) Non-Directional Nature of Ionic Bonds

The ionic compounds involve electrostatic lines of forces between oppositely charged ions. Therefore, such bonds are non-rigid and non-directional. Because of this, ionic compounds do not exhibit the phenomenon of isomerism.

(b) Directional Nature of Covalent Bonds

Covalent compounds are rigid and directional. This leads to the possibility of a variety of isomerism. For example, the compounds, C_2H_6O, shows structural isomerism.
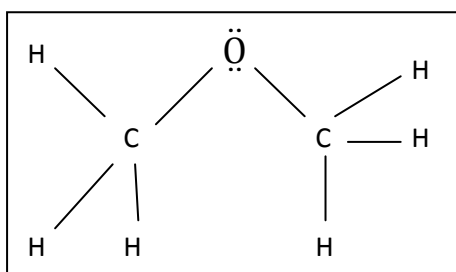
Dimethyl ether
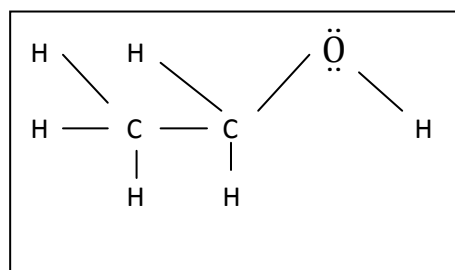
Ethanol

(3)　Reaction Kinetics:

(a)　Speed of Reaction of Ionic Compounds

The ionic compounds exist in the form of ions in an aqueous solution. The chemical reaction between ions occur rapidly.

For example, addition of silver nitrate solution to sodium chloride solution produces a white precipitate of silver chloride instantaneously. The reaction is rapid because on mixing the solutions, no bonds have to be broken, only a new bond is formed. The ionic compounds have already been broken while forming their aqueous solutions.

(b)　Speed of Reactions of Covalent Compounds

Since, there is no strong electrical force to speed up a chemical reaction (like in ionic reaction), the covalent bonds are generally much slower to react as they involve bond breaking and making of bonds. The molecules undergo a chemical change as a whole. Covalent bonds react in a variety of ways and their reactivity depends upon the way a reaction proceeds and the kind of a reaction.

KEY POINTS

1. Atoms combine together due to their inherent tendency to attain the nearest noble gas electronic configurations and the formation of a chemical bond always results in a decrease of energy.

2. The size of an atom is expressed in terms of atomic radius, ionic radius and covalent radius and van der Waals radius.

3. It is necessary to understand thermodynamic properties of elements. The minimum amount of energy required to remove an electron from an atom in gaseous state is called ionization energy. It depends upon the atomic size, nuclear charge and shielding effect of electrons. The electron affinity of an atom is the energy given out when an electron is added to a gaseous atom. The tendency of an atom to attract a shared pair of electrons to itself is called electronegativity. Fluorine, is the most electronegative atom and it has arbitrarily been given a value of 4.0.

4. The ionic bonds are formed by transfer of electron from one atom to another. Covalent bonds are formed by mutual sharing of electrons between combining atoms. After the formation of a coordinate covalent bond, there is no distinction between a covalent bond and a coordinate covalent bond.

5. A polar covalent bond is formed when atoms having different electronegativity values mutually share their electrons. Due to polarity, bonds become shorter and stronger and dipole moment may develop.

6. According to valence bond theory, the atomic orbitals overlap to form bonds but the individual character of the atomic orbitals are retained. The greater the overlap, the stronger will be the bond formed.

7. The VSEPR theory gives information about the general shapes and bond angles of molecules. It is based upon repulsion between bonding and lone pairs of electrons, which tend to remain at maximum distance apart so that interaction between them is minimum. The concept provides an alternate way to explain various geometrical shapes of molecules.

8. The geometrical shapes and bond angles are better explained by different hybridization schemes, where different atomic orbitals are mixed to form hybrid orbitals.

9. According to molecular orbital theory, atomic orbitals overlap to form molecular orbitals, n atomic orbitals combine to form n molecular orbitals. Half of them are bonding molecular orbitals and half antibonding molecular orbitals. In this combination, the individual atomic orbital character is lost in order to form an entirely new orbital that belongs to the whole molecule. The theory successfully explains bond order and paramagnetic property of O_2.

10. The bond energy in defined as the average amount of energy required to break all bonds of a particular type in one mole of the substance. It is a measure of the strength of the bond. Stronger the dipole of a bond, greater will be the bond energy.

11. The distance between the nuclei of two atoms forming a covalent bond is called bond length. In general, it is the sum of the covaleht radii of the combined atoms.

12. The dipole moment may be defined as the product of electric charge (q) and the distance (r) between the two oppositely charged centres. It is a vector quantity as it has magnitude and direction. It plays a major role, in determining the % age ionic character of a covalent bond and the shapes of molecules. It has magnitude and direction.

13. Properties of substances are characterized by the type of bonds present in them.

EXERCISE

Q.1   Select the correct statement

(i)   An ionic compound A^+B^- is most likely to be formed when
   (a)   the ionization energy of A is high and electron affinity of B is low.
   (b)   the ionization energy of A is low and electron affinity of B is high.
   (c)   both the ionization energy of A andelectron affinity of B are high.
   (d)   both the ionization energy of A and electron affinity of B are low.

(ii)   The number of bonds in nitrogen molecule is
   (a)   one ó and one π
   (b)   one ó and two π
   (c)   three sigma only
   (d)   two ó and one π

(iii)   Which of the following statement is not correct regarding bonding molecular orbitals?
   (a)   Bonding molecular orbitals possess less energy than atomic orbitals from which they are formed.
   (b)   Bonding molecular orbitals have low electron density between the two nuclei.
   (c)   Every electron in the bonding molecular orbitals contributes to the attraction between atoms.
   (d)   Bonding molecular orbitals are formed when the electron waves undergo constructive interference.

(iv)   Which of the following molecules has zero dipole moment?
   (a) NH_3 (b) $CHCl_3$ (c)H_2O (d) BF_3

(v)   Which of the hydrogen halides has the highest percentage of ionic character?
   (a) HCl   (b) HBr   (c)HF   (d)Hl

(vi)   Which of the following species has unpaired electrons in antibonding molecular orbitals.

(a) O_2^{2+} (b) N_2^{2-} (c) B_2 (d) F_2
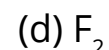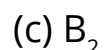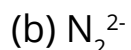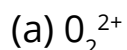
Q.2   Fill in the blanks

(i)   The tendency of atoms to attain maximum _____ of electrons in the valence shell is called completion of octet.

(ii)   The geometrical shape of $SiCl_4$ and PCl_3 can be explained on the basis of _____ and _____ hybridizations.

(iii)   The VSEPR theory stands for_____ .

(iv)   For N_2 molecule, the energy of σ $(2p)_x$ orbital is_____ than $\pi(2p_y)$ orbital.

(v)   The paramagnetic property of O_2 is well explained on the basis of MO theory in terms of the presence of_____ electrons in two MO orbitals.

(vi)   The values of dipole moment for CS_2 is _____while for SO_2 is _____

(vii) The bond order of N_2 is_____ while that of Ne_2 is _____ .

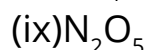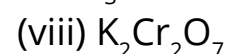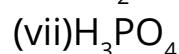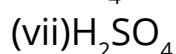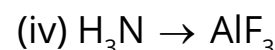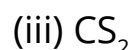Q.3   Classify the statements as true or false. Explain with reasons.

(i)   The core of an atom is the atom minus its valence shell.

(ii)   The molecules of nitrogen ($N \equiv N$) and acetylene ($HC \equiv CH$) are not isoelectronic.

(iii)   There are four coordinate covalent bonds in NH_4^+ ion.

(iv)   A σ-bond is stronger than a π-bond and the electrons of σ-bond are more diffused than π-bond.

(v)   The bond energy of heteroatomic diatomic molecules increases with the decrease in the electronegativities of the bonded atoms.

(vi)   With increase in bond order, bond length decreases and bond strength increases.

(vii) The first ionization energies of the elements rise steadily with the increasing atomic number from top to bottom ina group.

(viii) A double bond is stronger than a single bond and a triple bond is weaker than a double bond.

(ix)   The bonds formed between the elements having electronegativity difference more than 1.7 are said to be covalent in nature.

(x)   The re pulsive force between the two bonding pairs is less than that between the two lone pairs.

(xi)   The number of covalent bonds an atom can form is related to the number of unpaired electrons it has.

(xii) The rules which govern the filling of electrons into the atomic orbitals also govern filling of electrons into the molecular orbitals.

Q.4   What is a chemical bond? Discuss the formation of ionic and covalent bonds. How does the electronegativity differences differentiate between ionic and covalent bond?

Q.5

    (a)   Define ionization energy and electron affinity. How these quantities change in the periodic table. What factors are responsible for their variation?

    (b)   Explain, what do you understand by the term electronegativity? Discuss its variations in the periodic table. How does it affect the bond strengths?

Q.6   Write the Lewis structures for the following compounds:

    (i)HCN (ii)CCl_4 (iii) CS_2 (iv) $H_3N \rightarrow AlF_3$

    (v)NH_4OH (vii)H_2SO_4 (vii)H_3PO_4 (viii) $K_2Cr_2O_7$

    (ix)N_2O_5 (x) $Ag(NH_3)_2NO_3$

Q.7

    (a)   Explain qualitatively the valence bond theory. How does it differ from molecular orbital theory?

    (b)   How the bonding in the following molecules can be explained with respect to valence bond theory? Cl_2, O_2, N_2, HF, H_2S.

Q.8   Explain VSEPR theory. Discuss the structures of CH_4, NH_3, H_2O, $BeCl_2$, BF_3,SO_2, SO_3 with reference to this theory.

Q.9   The molecules NF_3 andBF_3 all have molecular formulae of the type XF_3. But they have different structural formulas. Keeping in view VSEPR theory sketch the shape of eachtnolecule and explain the origin of differing in shapes.

Q.10 The species NH_2^-, NH_3, NH_4^+ have bond angles of 105°, 107.5° and109.5^0 respectively. Justify these values by drawing their structures.

Q.11

    (a)   Explain atomic orbital hybridization with reference to sp^3, sp^2 and sp modes of hybridizations for PH_3, C_2H_4 and C_2H_2. Discuss geometries of CCl_4, PCl_3, and H_2S by hybridization of central atoms.

    (b)   The linear geometry of $BeCl_2$ suggests that central Be atom is sp-hybridized. What type of hybridization a central atom undergoes, when the atoms bonded to it are located at the corners of (a) an equilateral triangle (b) a regular tetrahedron and (c) triangular bipyramide?

Q.12

(a) Give the basis .of the molecular orbital theory and discuss the molecular orbital configurations of the following molecules?

(i)He_2 (ii)N_2 (iii) O_2 (iv)O_2^{2+} (v)O_2^{2-}

(b) How does molecular orbital theory explain the paramagnetic character of O_2, O_2^{2+} and O_2^{2-} species ?

Q.13

a) Sketch the molecular orbital pictures of

(i) $\pi(2p_x)$ and $\pi^*(2p_x)$ (ii) O_2, O_2^{2+} ,O_2^{2-} (iii) He_2 and Ne_2

b) Sketch the hybrid orbitals of the species, PCl_3, $SiCl_4$ and NH_4^+

Q.14

(a) Define bond energy. Explain the various parameters which determine its strength.

(b) How do you compare the bond strengths of

(i) Polar and non-polar molecules   (ii) σ-and π-bonds?

(c) Calculate the bond energy of H-Br. The bond energy of H-H is 436 kJmol^{-1} and that of Br- Br is 193 kJmol^{-1}.

(Ans : 314.5kJmol^{-1})

Q.15

(a) Define dipole moment. Give its various units. Find relationship between Debye and mc. How does it help to find out the shapes of molecules?

(b) The bond length of H-Br is 1.4 x10^{-10}m. Its observed dipole moment is 0.79D. Find the percentage ionic character of the bond. Unit positive charge = 1.6022 x 10^{-19}C and 1D = 3.336 x 10^{-30} mc.

(Ans: 11.7%)

Q.16 PF_3 is a polar molecule with dipole moment 1.02 D and thus the P-F bond is polar. Si, is in the proximity of P in the periodic table. It is expected that Si-F bond would also be polar, but SiF_4 has no dipole moment. Explain it?

Q.17 Which of the following molecules will be polar or non-polar, sketch the structures and justify your answer.

   (i) CCl_4 (ii) SO_3 (iii)NF_3 (iv)SO_2

Q.18 Explain the following with reasons:

   (i)   Bond distance is the compromise distance between two atoms.

   (ii)   The distinction between a coordinate covalent bond and a covalent bond vanishes after bond formation in NH_4^+, H_3O^+ and $CH_3NH_3^+$.

   (iii)   The   bond angles of H_2O and NH_3 are not 109.5° like that of CH_4. Although, O- and N-atoms are sp^3 hybridized.

   (vi)   π-bonds are more diffused than σ-bonds.

   (v)   The abnormality of bond length and bond strength in HI is less prominent than that of HCl.

   (vi)   The dipole moments of CO_2, and CS_2 are zero, but. that of SO_2 1.61D.

   (vii)   The melting points, boiling points, heat of vaporizations and heat of sublimations of electrovalent compounds are higher as compared with those of covalent compounds.