

CHEMICAL BONDING

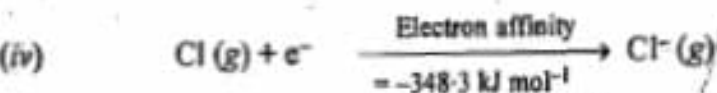
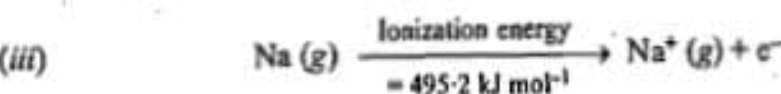
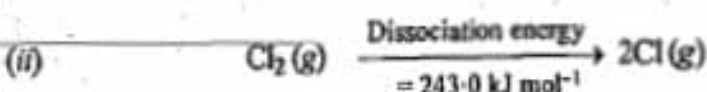
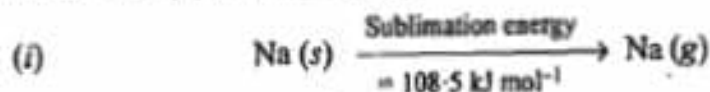
Atoms, except those of noble gases, do not have free existence. They readily combine with one another to form molecules. According to the classical view, the phenomenon of combination, called **chemical bonding**, involves the union of two or more atoms through redistribution of electrons in their outer most shells involving either transference of electrons from one atom to another or sharing of electrons amongst themselves so that all the atoms acquire the stable noble gas configurations of minimum energy. If the union takes place by the transference of electrons from one atom to another, the bonding is said to be ionic and if it takes place by the mutual sharing of electrons between the atoms concerned, the bonding is said to be covalent. There is yet another type of bonding called **coordinate covalent bonding** in which both the electrons shared between the atoms are contributed by one atom only.

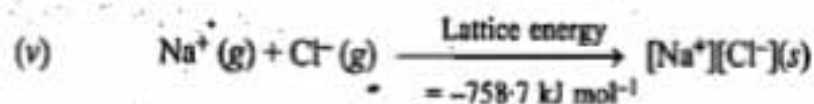
In addition to the above, some other types of chemical bonds such as *metallic bond* and *hydrogen bond* are also known.

IONIC BOND

An ionic bond results from complete transference of one or more electrons from the outermost energy shell (valency shell) of one atom to the outermost energy shell of the other atom. In this way, both the atoms acquire electronic configurations of the nearest noble gases. The atom from which the electrons are transferred, i.e., the atom which loses the electrons, acquires a positive charge and becomes, what is called, a **positive ion**. The atom which gains the electrons, acquires a negative charge and becomes, what is called, a **negative ion**. The electrostatic attraction between the oppositely charged ions results in the formation of a bond between them. This is called an **ionic bond**. The number of electrons transferred from or to the atom of an element in order to acquire the stable s^2p^6 configuration in the outer most shell is called the **electrovalency of the element**.

The formation of ionic bond (in fact, of any type of chemical bond) is invariably accompanied by decrease in energy. As an example, we may consider the decrease in energy in the formation of sodium chloride. The essential processes which occur in the formation of sodium chloride (*solid*) from sodium (*solid*) and chlorine (*gas*) are as follows:





The net change of energy involved in all the five steps put together amounts to $108.5 + \frac{1}{2}(243.0) + 495.2 - 348.3 - 758.7 = -381.8 \text{ kJ mol}^{-1}$. This is the decrease in energy in the formation of ionic bond between sodium (s) and chlorine (g) to form sodium chloride (s).

The net energy change obtained by adding all the energy terms, as in the above example, is denoted by ΔH and is referred to as the *enthalpy of formation of the ionic bond*. Evidently, if ΔH is negative, the formation of ionic bond is feasible.

Factors Influencing the Formation of Ionic Bond. The following factors facilitate the formation of an ionic bond between a metal and a non-metal.

1. Ionization Energy. It is defined as *the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom of an element*. The lesser the ionization energy, the greater is the ease of the formation of a cation. Alkali metals and alkaline earth metals have low ionization energies and, therefore, they form metal cations very easily.

2. Electron Affinity. It is defined as *the amount of energy released when an electron is added to an isolated gaseous atom of an element*. The formation of an anion occurs with the addition of one or more electrons to an atom, generally a non-metal atom. The greater the energy released during this process, the easier will be the formation of an anion, evidently. Thus, high electron affinity of a non-metal favours the formation of an anion.

Thus, low ionization energy of an atom (generally a metal atom) and a high electron affinity of another atom (generally a non-metal atom) facilitate the formation of an ionic bond between them.

3. Lattice Energy. It is defined as *the amount of energy released when cations and anions are brought from infinity to their respective equilibrium sites in the crystal lattice to form one mole of the ionic compound*. The higher the magnitude of the lattice energy, the greater is the tendency of the formation of an ionic bond.

For lattice energy to be high, the force of electrostatic attraction between the constituent ions should be high. The force of attraction between two oppositely charged ions in air (vacuum) is given by the well known Coulomb's law as $F = q_1 q_2 / r^2$ where q_1 and q_2 are the respective charges on the ions and r is the distance between them. This distance is obtained by adding the radii of the positive and negative ions.

The higher the charges on the ions and the smaller the distance between them, the greater is the force of attraction between the ions. Thus, the third factor mentioned above stipulates that *the cation and anion should be small in size and should have high electric charge so that the electrostatic attraction between them is high*.

To take an example, Na^+ ion is smaller than Cs^+ ion. Hence, the force of attraction between Na^+ ion and Cl^- ion in Na^+Cl^- is more than that between Cs^+ and Cl^- ions in Cs^+Cl^- . The lattice energy of Na^+Cl^- is, therefore, more than that of Cs^+Cl^- . The lattice energies of various alkali metal halides are given in Table 1.

TABLE 1

Lattice Energies of Various Alkali Metal Halides (kJ mol^{-1})

Halide ion	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	-994.5	-894.5	-790.2	-756.7	-719.0
Cl^-	-802.6	-758.7	-681.4	-660.6	-618.7
Br^-	-760.8	-714.8	-656.3	-631.3	-593.6
I^-	-710.6	-668.8	-618.7	-597.7	-564.3

It can be easily visualised that for a given anion, the smaller the radius of the cation, the greater is the strength of the ionic bond. Similarly, for a given cation, the smaller the radius of the anion, the greater is the strength of the ionic bond.

Tendency of Elements to form Ionic Bonds in Relation to their Position in the Periodic Table

As is well known, the elements on the left of the periodic table have low ionisation energies while those on the right have high electron affinities. Hence, ionic bonds are possible between the elements on the left (metals) and those on the right of the periodic table (non-metals). The elements of Group 1 (alkali metals), for example, react readily with elements of Group 17 (the halogens) to form ionic compounds. The elements of Group 2 (alkaline earth metals) also react with elements of Group 17, but not so readily. The reason is that these metals have two electrons in the valency shells and they have to lose both of them to acquire the stable s^2p^6 configuration in their outermost shells. The elimination of two electrons from a metal M may be represented as below :



$(IE)_1$ represents the first ionisation energy while $(IE)_2$ represents the second ionisation energy of the metal. When the first electron is taken out of an atom, it becomes increasingly difficult to remove the second electron from the resulting positively charged ion. Thus, $(IE)_2$ is very much higher than $(IE)_1$. In order to remove two electrons, evidently, the energy needed is $(IE)_1 + (IE)_2$. Hence, elements of Group 2 do not have as strong a tendency to form ions as the elements of Group 1 have.

Amongst the non-metals, elements of Groups 16 and 17 change into negatively charged ions (anions) readily. However, the non-metals of Group 16 (oxygen, sulphur, etc.) do so less readily compared to the non-metals of Group 17. The reason is that their outer configuration is s^2p^4 and thus there are two vacancies in their valency shell. The addition of one electron is accompanied by release of energy giving rise to an ion with a single negative charge but the addition of the second electron takes place with difficulty because of repulsion from its own negative ion. Hence, energy has to be supplied to add the second electron. For example, $140.9 \text{ kJ mol}^{-1}$ of energy is released when oxygen is converted to O^- ion but $769.9 \text{ kJ mol}^{-1}$ of energy has to be supplied to convert O^- to O^{2-} ion. Thus,



$$\text{Energy released, } \Delta H_1 = -140.9 \text{ kJ mol}^{-1}$$



$$\text{Energy required, } \Delta H_2 = +769.9 \text{ kJ mol}^{-1}$$

Hence, formation of oxides or sulphides is not so easy as the formation of fluorides or chlorides.

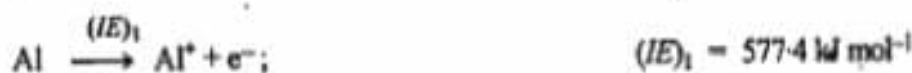
Tendency to form Cations. The larger the size of an atom, the greater is the ease with which the valency electrons can be eliminated from it. Since the atomic volume (atomic mass/density) and hence the atomic radius increases on moving down the group of alkali metals from $Li \rightarrow Na \rightarrow K \rightarrow Rb \rightarrow Cs$, the tendency of alkali metals to change into cations increases in the same order. Thus, Na changes into Na^+ ion more easily than Li. Similarly, K changes into K^+ ion more easily than Na and so on. Cesium, the last element of the group which has the largest atomic size, ionises most readily while lithium, the first element which has the smallest atomic size, ionises least readily.

Similarly, amongst the alkaline earth metals (Group 2), Ba, which is the heaviest element with the largest atomic radius, ionises most readily while Be, with the smallest atomic radius in this group, ionises least readily.

Tendency to form Anions. The smaller the atom, the greater will be its tendency to accept extra electron (or electrons) to change into an anion. For example, amongst the halogens, fluorine, with the smallest atomic size, forms an anion most readily. It is for this reason that fluorides of mercury, bismuth and tin are ionic compounds while the chlorides of these metals are largely covalent in character.

Formation of Ions of Higher Charges. As mentioned before, the formation of ions with two positive charges or two negative charges is not so easy as the formation of ions with one positive or one negative charge. The formation of simple ions with three positive or three negative charges is extremely

difficult and, therefore, highly unlikely. Consider, for example, aluminium of Group 13. Its outer electronic configuration is $3s^2p^1$. The successive ionisation energies of aluminium are as follows :



Thus, a total of $5143.9 \text{ kJ mol}^{-1}$ of energy is needed to remove all the three valency electrons to form the trivalent Al^{3+} ion. This is not a feasible proposition since rarely more than 1500 kJ mol^{-1} of energy is available when chemical reactions take place. It is, therefore, easy to understand why the elements of Groups 13 and 14 do not form ionic compounds ordinarily. Instead, they form covalent compounds by the process of sharing of electrons which we shall consider shortly.

Experience shows that simple ions carrying more than two positive charges are rare. However, complex ions carrying more than two positive charges are well known. We shall consider here only one example. Aluminium chloride, AlCl_3 , is largely a covalent compound. When it is dissolved in water, it undergoes hydration as represented below :



The hydrated aluminium chloride contains the trivalent complex ion, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. The question arises : How does Al atom now lose three electrons to change into hydrated Al^{3+} ion ? The answer is that the hydration of aluminium chloride is an exothermic process and, therefore, a lot amount of energy is released in the reaction. This energy becomes available to accomplish the release of three electrons from aluminium atom to form hydrated Al^{3+} ion.

Now let us consider why it is not possible, ordinarily, to have anions carrying more than two negative charges. The formation of anions carrying one negative charge, e.g., halides (Group 17) and two negative charges, e.g., sulphides (Group 16) have already been considered. The question arises : Can we have easily anions carrying three negative charges, e.g., nitrides, N^{3-} and phosphides, P^{3-} (Group 15) ? The answer is : No. The reason is that the outer configuration of these atoms is s^2p^3 . The addition of three electrons to nitrogen or phosphorus atom requires much more energy than is ordinarily available in chemical reactions. The same is true for other elements of Group 15.

Thus, while formation of simple positive ions is limited, generally, to the atoms of metals of Groups 1 and 2, the formation of simple negative ions is limited, generally, to the atoms of non-metals of Groups 16 and 17. The atoms of elements of middle Groups 13, 14 and 15 do not form ionic compounds ordinarily. As we shall see, they form covalent bonds more readily by sharing their electrons with other atoms.

Variable Valency of Cations. Alkali metals and alkaline earth metals show only one valency which is 1 in the case of the former and 2 in the case of the latter. This is because the monovalent cations of alkali metals (such as Na^+ , K^+ , Rb^+) and divalent cations of alkaline earth metals (such as Mg^{2+} , Ca^{2+} , Ba^{2+}) have most stable noble gas configurations (s^2p^6) in their valency shells.

Several other cations, particularly those of the transition metals, do not have the stable s^2p^6 configuration in their valency shells. In such cases, the outermost shell of the cations is not stable. It further loses one or more electrons giving rise to metal ions of higher valencies. The transition metals thus show variable valency. Iron, cobalt and nickel, for example, form divalent as well as trivalent ions with the loss of 2 or

3 electrons from their valence $3d4s$ orbitals. In fact, most of the transition metals show variable valency by the loss of one or more electrons from their $(n-1)d$ or ns orbitals.

COVALENT BOND

Lewis Concept of Covalent Bond. G. N. Lewis was the first to suggest, in 1916, that atoms may combine with one another by *sharing of electrons* in their valency shells so that the combining atoms attain the nearest noble gas configurations in their valency shells. The shared electrons contribute towards the stability of both the atoms. This type of linkage is called **covalent linkage** or **covalent bond**. The compounds formed by this mechanism are called **covalent compounds**.

For example, hydrogen and chlorine atoms share one electron each to form HCl.



In this process, while hydrogen atom acquires electronic configuration of helium, chlorine atom acquires electronic configuration of the nearest noble gas argon.

In the formation of oxygen molecule, each oxygen atom has six electrons in the valence shell and, therefore, they contribute two electrons each for sharing. Thus, two electron pairs are shared and there is a **double bond** between the two oxygen atoms.



According to Lewis concept, the number of electrons which an atom contributes for sharing in a covalent bond is called its **covalency**. Thus, covalency of hydrogen, chlorine and oxygen is 1, 1 and 2, respectively.

Decrease of Energy in the Formation of Hydrogen Molecule. The formation of a chemical bond of any type is possible only if the approach of the atoms towards one another is accompanied by decrease in energy. When any two atoms approach each other, new forces of attraction and repulsion are set in. The forces of attraction are between the nucleus of one atom and the electrons of the other. The forces of repulsion are between two nuclei amongst themselves as well as between the electrons of the two atoms amongst themselves. The net result of these forces may be attraction or repulsion.

If the net result is attraction, the total energy of the system decreases and a chemical bond results.

If the net result is repulsion, the total energy of the system increases and no chemical bonding is possible.

Let us see how the approach of two hydrogen atoms towards each other results in decrease of energy of the system and thus results in the formation of a covalent bond to give hydrogen molecule.

Consider two hydrogen atoms A and B with nuclei H_A and H_B and corresponding electrons e_A and e_B respectively. When the two atoms approach each other, the following additional attractive and repulsive forces start operating :

a. Attractive forces between electron of atom A and nucleus of atom B (H_B) and electron of atom B and nucleus of atom A (H_A). These forces decrease the energy of the system.

b. Repulsive forces between two nuclei (H_A and H_B) and two electrons (e_A and e_B) of the two atoms. These forces increase the energy of the system.

The attractive and repulsive forces are pictorially shown in Fig. 1.

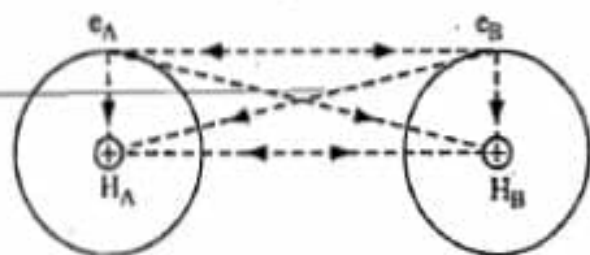


Fig. 1. Attractive and repulsive forces between H atoms in H_2 molecule.

The manner in which the potential energy of the system changes as the hydrogen atoms are brought closer to each other is represented graphically in Fig. 2.

Initially, when the hydrogen atoms lie far away, say, at infinite distance from each other, the electrostatic potential energy of one atom is independent of the presence of the other atom. By convention, this energy is taken arbitrarily as zero. This fact is represented at the far end towards the right of the graph. As the two atoms are brought closer and closer, the electrostatic potential energy goes on decreasing because attractive forces go on becoming more and more dominant. The decrease of potential energy continues till a certain minimum value is attained. If the atoms are brought still closer, the potential energy shows a *sharp rise*. This is due to the fact that the repulsive forces at such small internuclear distances become dominant. Since repulsion always causes increase in energy, the energy of the system increases, as shown in the figure. The formation of a covalent bond between two hydrogen atoms takes place at the point which corresponds to the *minimum* in the potential energy curve.

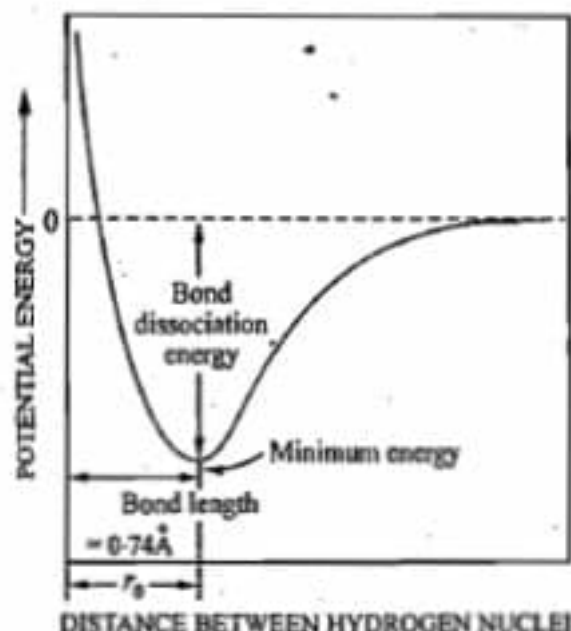


Fig. 2. Variation of potential energy with nuclear distance in the formation of hydrogen molecule.

The position of minimum energy also corresponds to the minimum distance upto which the two nuclei can be brought together before the force of repulsion between them becomes dominant. In other words, this distance corresponds to the bond length. **Bond length** is, thus, defined as the distance between the nuclei of the two atoms constituting a chemical bond. In the case of hydrogen molecule, the distance between the two hydrogen atoms corresponding to minimum energy is 0.74 \AA . The decrease in potential energy in the formation of H_2 molecule has been found to be 458 kJ mol^{-1} . Evidently, because of decrease of energy, H_2 molecule would be much more stable than H atoms.

*ATOMIC ORBITAL OVERLAP CONCEPT OF COVALENCY

It may be recalled that an orbital can accommodate a maximum of two electrons having opposite spins. As long as such electron pairs are present in orbitals, they are not available for chemical combination. If, however, only a single electron is present in an orbital of the outer shell, it will have a tendency to combine with a similar electron present in the orbital of the outer shell of another atom. This results in the formation of a covalent chemical bond between the two atoms. Thus, according to the **orbital overlap concept**, formation of a covalent bond between two atoms results from the coupling of electrons with opposite spins belonging to orbitals of outermost shells of the two atoms. The orbitals containing such unpaired electrons are said to *overlap with each other* so that the electron pair now belongs to both the orbitals. This may be illustrated by considering a few examples.

Formation of hydrogen molecule. Hydrogen atom has only one electron in its valency shell. It needs one electron more to complete this shell. In the formation of a stable hydrogen molecule, H_2 , the two hydrogen atoms having unpaired electrons approach each other and their $1s$ atomic orbitals overlap when the two approaching atoms reach a point at which the potential energy is minimum. The electrons shared between the two atoms are located in the region of space between the nuclei of the atoms concerned, as represented in Fig. 3. The $1s$ orbitals of

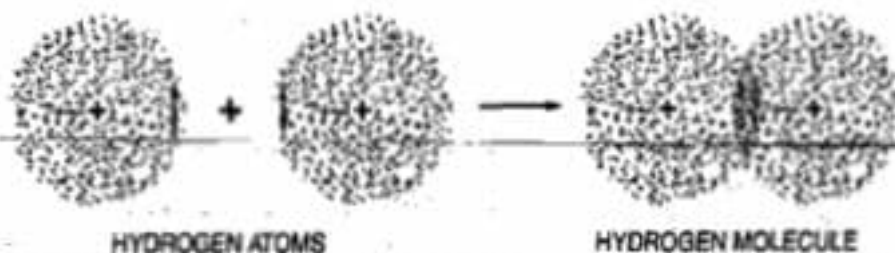


Fig. 3. Formation of hydrogen molecule by overlapping of $1s$ orbitals of both the atoms. The paired electrons have opposite spins.

*The atomic orbital overlap concept of covalency, in fact, forms the basis of the modern theories of covalent bonding (specially the valence bond theory). These theories would be discussed in details a little later in this chapter.

both the atoms, thus, get fully occupied. The bond formed between two hydrogen atoms in this manner is called an $s-s$ bond since it involves overlapping of s orbitals of the two hydrogen atoms. The overlapping of the orbitals takes place along the same axis, as shown. When a bond is formed by overlapping of the orbitals along the same axis, it is known as a **sigma bond**. This type of overlapping takes place to a substantial extent and, therefore, the resulting bond is very strong. The greater the extent of the overlapping of orbitals, the stronger is the covalent bond.

Formation of fluorine molecule. Fluorine atom with electronic configuration $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ has one half-filled p orbital. It needs one more electron to fill this orbital. In the formation of fluorine molecule, this half-filled p orbital of one atom overlaps with a similar p orbital of another atom to form a molecule of fluorine, F_2 . This is shown in Fig. 4. In the figure, only p orbitals are shown. The completely filled s orbitals are omitted for the sake of clarity.

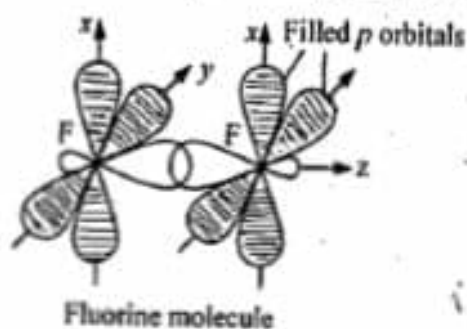


Fig. 4. Formation of fluorine molecule by overlapping of $2p$ orbitals of both the fluorine atoms.

Formation of hydrogen fluoride molecule. As has been shown earlier, the $1s$ orbital of hydrogen can accommodate one electron more. Also one of the $2p$ orbitals of fluorine is only half-filled and, therefore, there is room for one electron more. Hence, $1s$ orbital of hydrogen and the half-filled $2p$ orbital of fluorine overlap and form a covalent bond. This is shown in Fig. 5.

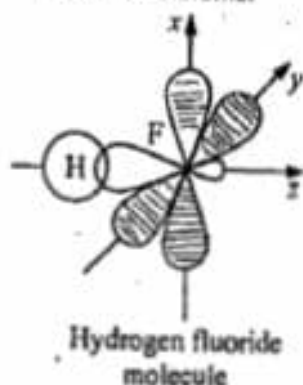


Fig. 5. Formation of hydrogen fluoride molecule by overlapping of $1s$ orbital of hydrogen atom and $2p$ orbital of fluorine atom.

Pi (π) Bonds. As discussed above, the overlapping of atomic orbitals along the same axis results in the formation of sigma bond. There is also another type of bond known as **pi (π) bond**. This type of bond is formed by the sidewise overlapping (also called lateral overlapping) of the two half-filled orbitals. The formation of pi bonds may be illustrated by reference to the formation of oxygen and nitrogen molecules.

Formation of oxygen molecule. The electronic configuration of oxygen ($Z = 8$) is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. Oxygen atom has two half-filled p orbitals. When two oxygen atoms approach each other, one of the two half-filled p orbitals of each atom overlaps along the molecular axis forming a $p-p$ sigma bond. The second half-filled p orbital of each atom overlaps sidewise to form a pi bond. This is shown in Fig. 6.

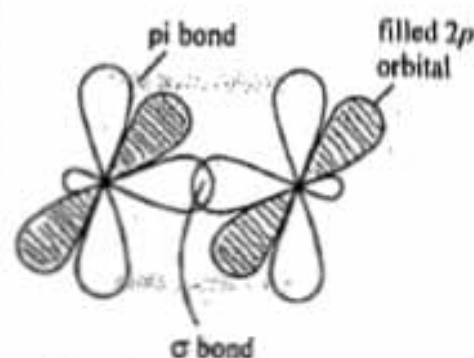


Fig. 6. Formation of oxygen molecule by overlapping of the two half-filled p orbitals of each oxygen atom.

Thus, in oxygen molecule, the two oxygen atoms are held together by a **double bond** comprising of one sigma bond and one pi bond.

Formation of nitrogen molecule. The electronic configuration of nitrogen is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. All the three p orbitals are only half-filled in accordance with Hund's rule. Hence, the three half-filled p orbitals of one nitrogen atom overlap with the three corresponding half-filled p orbitals of another nitrogen atom to form N_2 molecule. This is represented in Fig. 7.

Thus, in nitrogen molecule the two nitrogen atoms are held together by a **triple bond** made up of one sigma bond and two pi bonds.

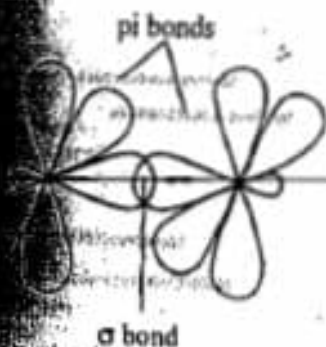


Fig. 7. Formation of nitrogen molecule by overlapping of the three half-filled p orbitals of each nitrogen atom.

Relative Strengths of sigma and pi bonds. The strength of a covalent bond depends upon the extent of overlapping of half-filled atomic orbitals. The extent of overlapping between two atoms is always greater when there is end to end overlapping of orbitals than when there is lateral overlapping of orbitals. Hence, a sigma bond is always stronger than a pi bond.

Variable Covalency. Maximum Covalency

Ordinarily, the covalency of an element is equal to the number of unpaired s or p electrons present in the outermost shell of its atom in the ground state. Thus, hydrogen (electronic configuration : $1s^1$) has its solitary s electron unpaired and hence its covalency is one. Fluorine (electronic configuration : $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$) has only one unpaired p electron and its covalency is also 1. Oxygen (electronic configuration : $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$) has two unpaired p electrons and its covalency is 2. Nitrogen (electronic configuration : $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$) has three unpaired p electrons and its covalency is 3. None of these atoms contains d orbitals in its electronic configuration.

The outer electronic configuration of sulphur atom in the ground state, i.e., the lowest energy state is $3s^2 3p_x^2 3p_y^1 3p_z^1$. Like oxygen, it has two unpaired electrons and exhibits a covalency of 2 (in compounds such as H_2S , SF_2 , etc.). Sulphur atom belongs to the third period ($n = 3$). Hence, it has d orbitals also which, however, are vacant. When sulphur combines with more electronegative elements such as fluorine, oxygen, chlorine or bromine, sufficient amount of energy is released to cause unpairing of s and p electrons which get promoted to the vacant d orbitals. This unpairing of electrons increases the covalency of sulphur. Thus, if only the p electrons are unpaired, the total number of unpaired electrons will be four and if both p and s electrons get unpaired, the total number of unpaired electrons will be six. The covalency of sulphur in the former case will be 4 and in the latter case 6. This is illustrated in Fig. 8.

Sulphur atom in ground state	$3s$ $\uparrow\downarrow$ $3p$ $\uparrow\downarrow$ \uparrow \uparrow $3d$ \circ \circ \circ \circ \circ	Two unpaired electrons account for a covalency of 2.
Sulphur atom in first excited state	$3s$ $\uparrow\downarrow$ $3p$ \uparrow \uparrow \uparrow $3d$ \uparrow \circ \circ \circ \circ	Four unpaired electrons account for a covalency of 4.
Sulphur atom in second excited state	$3s$ \uparrow $3p$ \uparrow \uparrow \uparrow $3d$ \uparrow \uparrow \circ \circ \circ	Six unpaired electrons account for a covalency of 6.

Fig. 8. Variable covalency exhibited by sulphur.

Thus, sulphur exhibits tetravalency in the formation of compounds like SF_4 and SOF_2 and hexavalency in the formation of compounds such as SF_6 .

The halogens (excepting fluorine) also contain vacant d orbitals in their valency shells. These vacant d orbitals allow for easy excitation of p as well as of p and s electrons and account for higher covalencies of 3, 5 and 7 in the case of the halogens (other than fluorine). This is illustrated in Fig. 9.

Halogen atom (other than F) in ground state	s $\uparrow\downarrow$ p $\uparrow\downarrow$ \uparrow d \circ \circ \circ \circ \circ	One unpaired electron accounts for a covalency of 1.
Atom in first excited state	s $\uparrow\downarrow$ p $\uparrow\downarrow$ \uparrow d \uparrow \circ \circ \circ \circ	Three unpaired electrons account for a covalency of 3.
Atom in second excited state	s \uparrow p \uparrow \uparrow \uparrow d \uparrow \uparrow \circ \circ \circ	Five unpaired electrons account for a covalency of 5.
Atom in third excited state	s \uparrow p \uparrow \uparrow \uparrow d \uparrow \uparrow \uparrow \circ \circ	Seven unpaired electrons account for a covalency of 7.

Fig. 9. Variable covalency exhibited by the halogens other than fluorine.

In the ground state, there is only one unpaired electron in the outer electronic configuration of each halogen. Hence, the halogens exhibit covalency of 1, as in the formation of HF , HCl , HBr and HI . In the first excited state, of halogens other than fluorine, one pair of p electrons gets unpaired providing three

unpaired electrons. This accounts for covalency of 3. Thus, in the interhalogen compounds such as ClF_3 , BrF_3 and IF_3 , chlorine, bromine and iodine exhibit covalency of 3. In the *second excited state*, both the pairs of p electrons get unpaired providing five unpaired electrons which account for covalency of 5. Thus, in HClO_3 , HBrO_3 and HIO_3 , all the three halogens exhibit covalency of 5. Similarly, in BrF_5 and IF_5 , bromine and iodine exhibit covalency of 5. In the *third excited state*, all the pairs of p as well as s electrons get unpaired, providing seven unpaired electrons which account for covalency of 7. Thus, in HClO_4 and Cl_2O_7 , chlorine exhibits covalency of 7.

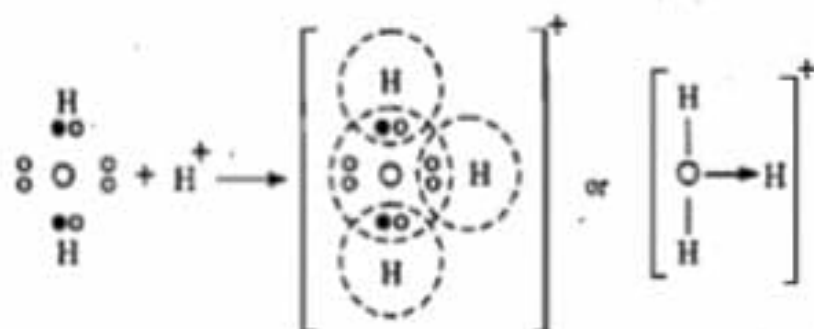
It is evident from the above discussion that elements whose atoms contain vacant d orbitals in their valency shells, can, on account of unpairing of s and p electrons, exhibit variable covalency in forming covalent bonds with more electronegative elements. The maximum covalency is generally equal to the total number of s and p electrons present in the valency shell. Thus, sulphur having six s and p electrons (s^2p^4 configuration) exhibits a maximum covalency of 6. The halogens (Cl , Br , I) having seven s and p electrons (s^2p^5 configuration) exhibit maximum covalency of 7. Phosphorus having five s and p electrons (s^2p^3 configuration) exhibits maximum covalency of 5, and so on.

COORDINATE COVALENT BOND OR DATIVE BOND

Lewis proposed that a different type of covalent bond can be formed when both the electrons for sharing between the atoms are contributed by one atom only. This type of bond is known as **coordinate covalent bond** or **dative bond**.

A coordinate covalent bond is established between two atoms one of which has a complete octet and at the same time possesses at least one pair of unshared electrons while the other is short of the two electrons. The former atom contributes one such pair of electrons for mutual sharing between the two atoms as a result of which the second atom also completes its octet and acquires a stable noble gas configuration. The atom which contributes the pair of electrons is known as the **donor** and the atom which accepts these electrons is called the **acceptor**. The unshared pair of electrons is known as the **lone pair**.

In the formation of hydronium ion, for example, the oxygen atom in water molecule is the donor whereas the hydrogen ion is the acceptor. The coordinate covalent bond is conventionally represented by an arrow pointing from the donor to the acceptor, as shown below in the formation of hydronium ion.



It is important to note that the coordinate covalent bond once formed is indistinguishable from a covalent bond.

According to the atomic orbital overlap concept of covalency, a coordinate covalent bond results when an orbital containing a lone pair of electrons in one atom overlaps with an empty orbital present in the other atom. The central atom, oxygen, in water molecule has four orbitals. Two of these orbitals contain bond pairs of electrons while the other two (shaded ones) contain lone pairs of electrons, as shown in Fig. 10. The H^+ ion has an empty s orbital which overlaps with one of the orbitals of oxygen atom containing a lone pair of electrons forming hydronium ion, H_3O^+ , as illustrated in Fig. 10.

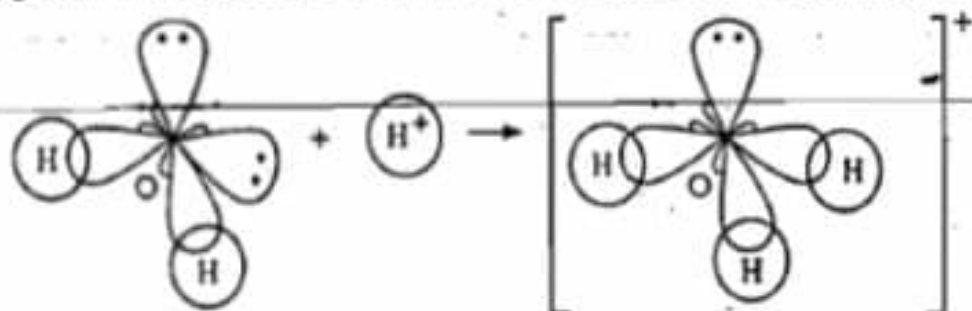
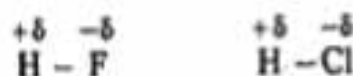


Fig. 10. Formation of hydronium ion.

Polarity in Covalent Bonds. A covalent bond formed between two *identical* or *similar* atoms is said to be a **non-polar covalent bond** but if formed between two *dissimilar* atoms, the bond formed is said to be a **polar covalent bond**. The reason is that in the former case the shared electron pair is attracted equally by both atoms and lies exactly midway between them, as in hydrogen molecule, $\text{H}:\text{H}$. The molecule formed is said to be a **non-polar molecule**.

In the case of a covalent bond formed between two dissimilar atoms, one of the atoms generally has a greater tendency to attract the electrons towards itself (*i.e.*, it is more electronegative). The electron pair is, therefore, pulled closer to that atom, as in hydrogen fluoride molecule, $(\text{H}:\ddot{\text{F}}:)$ in which the electron pair shared between hydrogen and fluorine atoms remains closer to the fluorine atom. This unsymmetric distribution of electrons leads to partial charge separation, *i.e.*, development of partial negative charge near fluorine end and partial positive charge near hydrogen end. This is represented in HF and HCl molecules as follows :



The molecules formed are said to be **polar molecules**. The polar covalent bond, therefore, has **partial ionic character**. The two opposite charges at the ends are called **electrical poles** and the molecules are called **dipoles**.

Covalent Character of Ionic Bond. Polarisation of Ions. It is a common experience that many times an ionic bond has some covalent character and a covalent bond has some ionic character. The formation of a bond intermediate between an ionic and a covalent bond occurs through a phenomenon known as **polarisation of ions**. When oppositely charged ions approach each other, the attraction between the positive charge of cation and negative charge of anion and also the simultaneous repulsion between their nuclei and between their electrons results in the **distortion, deformation or polarisation of the electron charge cloud of the anion**. The electron charge cloud of the anion no longer remains spherical but gets distorted, *i.e.*, polarised towards the cation, as shown in Fig. 11. The electron charge cloud of the cation also gets distorted, *i.e.*, polarised by the anion through a similar process but the polarisation of the cation is far less pronounced because of its small size. The polarisation of ions results in a high electron charge concentration between the two nuclei. This results in the formation of a bond which is intermediate between an ionic and a covalent bond. This type of bond is called **polar covalent bond**. A polar covalent bond is more stable than a pure covalent bond. The higher the degree of polarisation, the greater is the stability of the polar covalent bond. The extent of polarisation depends, evidently, on the polarising power of the cation and the polarisability of the anion.



Fig. 11. Polarisation of electron charge cloud of an anion by a cation.

The rules regarding polarisation are known as **Fajan's rules**. These are given below.

Fajan's Rules. 1. The cations with smaller size have higher polarising power, *i.e.*, they cause polarisation of electron charge cloud of an anion to a greater extent. Such cations have positive charge concentrated over a small surface area, *i.e.*, they have a **high charge density** and thus distort the electron charge cloud of the anion highly efficiently. The cations with large size have low polarizing power.

2. The anions with large size have high polarizability, *i.e.*, their electron charge cloud can be deformed easily. The grip of the nucleus on the orbital electrons in large anions will be weak and hence such anions will get polarised by a cation relatively easily.

3. For effective polarisation, there should be a high charge on the cation or the anion or both. The electrostatic forces which cause polarisation, would increase with increase in the charge on the ions.

4. Cations with pseudo inert gas configuration, viz., $ns^2p^6d^{10}$ or with inert pair configuration, viz., $d^{10}(n+1)s^2$, have high polarising power while cations with noble gas configuration, viz., ns^2p^6 , have low polarising power. This is due to greater effective nuclear charge in the former cases and smaller effective nuclear charge in the latter cases.

Effects of Polarisation. 1. Bromides and iodides have higher lattice energies (and hence higher stabilities) than expected from theoretical calculations. The extra stability is due to polarisation of the anions resulting in the formation of a polar covalent bond which is more stable than a pure ionic bond.

2. The solubility of ionic compounds in polar solvents decreases with increase in the degree of polarisation, i.e., with increase in the degree of covalent bonding.

3. The hardness of ionic compounds decreases with increase in the degree of polarisation, i.e., with increase in the covalent character.

Per cent Ionic Character of a Polar Covalent Bond. The per cent ionic character of a polar covalent bond depends upon two factors: 1. *The Electronegativity Difference of the Bonded Atoms* and 2. *Dipole Moment of the Compound Formed*.

1. **Electronegativity Difference and Per cent Ionic Character.** A pure covalent bond is formed between atoms A and B when the electronegativities of the two atoms are the same. If A and B have different electronegativities, the resulting bond would be a polar covalent bond since the bonding electron pair is pulled more towards the more electronegative atom thereby bringing some excess negative charge on the latter. As a result, some excess positive charge is developed on the less electronegative atom. If A is more electronegative than B, a polar covalent bond $A^{\delta-} - B^{\delta+}$ would be formed between A and B. The larger the difference in the electronegativities of A and B, the greater would be the magnitude of δ and the higher would be the polarity of the bond.

Several empirical equations have been proposed to calculate the per cent ionic character of a covalent bond from the electronegativities of the bonding atoms. Two of these equations are the Pauling equation and the Hannay-Smith equation.

The Pauling Equation. Pauling proposed the following empirical equation for determining the per cent ionic character of a covalent bond:

$$\text{Per cent ionic character} = 1 - e^{-\frac{1}{4}(\chi_A - \chi_B)^2} \quad \dots(1)$$

where χ_A and χ_B are the electronegativities of A and B. He established the following empirical relationship between $\chi_A - \chi_B$ and the per cent ionic character:

$\chi_A - \chi_B$	0.6	1.0	1.4	2.0	2.4	3.0
Per cent ionic character	9	22	39	63	76	89

The Hannay-Smith Equation. Hannay and Smith proposed the following equation for the purpose:

$$\text{Per cent ionic character} = 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2 \quad \dots(2)$$

Both the equations, however, give only approximate values.

2. **Dipole Moment and Per cent Ionic Character.** Consider the bond H - X where X is a halogen atom. If the bond is purely covalent, its dipole moment would be negligibly small. If the bond is ionic, H^+X^- , it implies that complete transfer of an electron has taken place from H to X and the bond would have an appreciable dipole moment which is determined by the product of the electronic charges and the internuclear distance between H and X. For a polar covalent bond which is intermediate between pure covalent and a pure ionic bond, the dipole moment would be given by the product of the charge separated due to polarisation and the internuclear distance. The magnitude of δ will depend upon the

extent of the ionic character developed in the bond. Thus,

$$\text{Per cent ionic character} = \frac{\text{Actual dipole moment of the bond}}{\text{Dipole moment of pure ionic bond}} \times 100$$

For example, in HF molecule, the internuclear distance is 0.92 Å and the dipole moment for the ionic structure H^+F^- when an electron is completely transferred from hydrogen atom to fluorine atom is given by $4.8 \times 10^{-10} \text{ esu} \times 0.92 \times 10^{-8} \text{ cm}$, i.e., 4.42 D. The actual dipole moment of HF molecule is found to be 1.98 D. (1 Debye = $1 \times 10^{-18} \text{ esu cm}$)

$$\therefore \text{Per cent ionic character} = \frac{1.98 \text{ D} \times 100}{4.42 \text{ D}} = 44.8 \approx 45$$

Similarly, for HCl molecule, using SI units,

$$\text{Internuclear distance} = 127 \text{ pm} = 127 \times 10^{-12} \text{ m}$$

$$\text{Actual dipole moment} = 3.44 \times 10^{-30} \text{ coulomb metre}$$

$$\left. \begin{array}{l} \text{Dipole moment when an electron is} \\ \text{completely transferred from H to Cl} \end{array} \right\} = 1.6 \times 10^{-19} \text{ C} \times 127 \times 10^{-12} \text{ m}$$

$$= 2.03 \times 10^{-29} \text{ C m}$$

$$\therefore \text{Per cent ionic character} = \frac{3.44 \times 10^{-30} \text{ C m}}{2.03 \times 10^{-29} \text{ C m}} \times 100 = 16.9 \approx 17$$

It may be mentioned, however, that dipole moment calculated from the ionic structure of the compound alone contributes only partly towards the total molecular dipole moment. Other factors such as the differences in the sizes of the two atoms, the hybridisation of orbitals involved and the directions of the lone pairs of electrons with respect to the nucleus also contribute towards the total molecular dipole moment. Hence, the per cent ionic character calculated on the basis of dipole moment obtained from the ionic structure of the compound alone, without considering other factors, is only *approximate*.

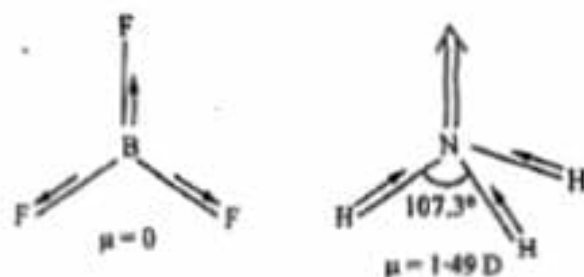
Dipole Moment and Structure of Molecules. A diatomic molecule is polar if the bond formed between the atoms is polar. In such a molecule, the dipole moment of the bond gives the dipole moment of the molecule. For example, the dipole moment of HCl molecule is the same as the dipole moment of HCl bond and is known to be 1.03 D. However, in the case of molecules containing more than two atoms, the dipole moment not only depends upon the individual dipole moments of the bonds but also on the spatial arrangement of various bonds in the molecule. In such cases, the dipole moment of the molecule is the vector sum of the dipole moments of the various bonds. Obviously, the polar or non-polar nature of molecule will depend upon the spatial arrangement of atoms in the molecule. The bonds may be polar yet the molecule may be non-polar.

For example, carbon dioxide (CO_2) and water (H_2O) molecules are both triatomic molecules but the dipole moment of carbon dioxide is zero while that of water is 1.84 D. This can be easily explained on the basis of their structures as illustrated below :

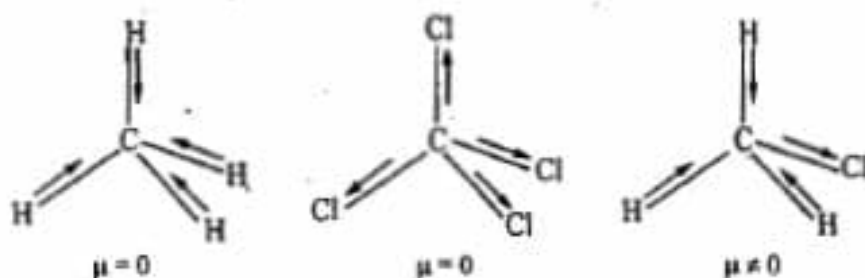
In carbon dioxide molecule, both the carbon-oxygen bonds are polar. But since the molecule is linear, the dipole moment of C = O bond (2.3 D) on one side of the molecule is cancelled by that on the other side of the molecule giving net zero dipole moment. On the other hand, water molecule is not linear but has a *bent structure* as shown. Therefore, the dipole moment of water molecule is not zero. It is the resultant of the dipole moments of the two O - H bonds inclined at an angle of 104.5° and the contribution of the two lone pairs of electrons on oxygen atom. It has been found to be 1.84 D.



Likewise, the dipole moment of BF_3 is zero while that of NH_3 is 1.49 D, although both the molecules are tetra-atomic. This is because BF_3 has symmetrical structure in which the three B-F bonds are oriented at an angle of 120° to one another. The three bonds lie in one plane and the dipole moments of these bonds cancel one another giving net dipole moment equal to zero. On the other hand, the ammonia molecule has *pyramidal structure*. The individual dipole moments of three N-H bonds and the contribution of the lone pair of electrons on nitrogen atom to dipole moment give the resultant dipole moment of NH_3 molecule as 1.49 D, as shown.



CH_4 and CCl_4 molecules have symmetrical tetrahedral structures and their resultant dipole moments are zero. CH_3Cl molecule has also tetrahedral structure but its dipole moment is not zero because its structure is not symmetrical and the dipole moments of C-Cl and H-C bonds are not equal. This is illustrated below :



Some Important Characteristics of Covalent Bond. The important characteristics of a covalent bond are its bond length, bond angle and bond energy. These are discussed below.

Bond Length. Let us consider a diatomic molecule. The atoms in this molecule are always vibrating with respect to each other. The question of any *fixed* distance between them, therefore, does not arise. We can, however, think of an average distance between the nuclei of the two atoms bonded to each other. This is called bond length or bond distance. Thus, **bond length** is defined as the average distance between the nuclei of two bonded atoms in a molecule. We have already seen that in the formation of hydrogen molecule, when two hydrogen atoms approach each other, a stage is reached when there is maximum electrostatic attraction and minimum repulsion between the two atoms. At this point the potential energy of the system becomes minimum and the atoms get bonded together. The distance between the nuclei of the bonded hydrogen atoms is called the length of the H-H bond. For hydrogen molecule, this length has been found to be 0.74 \AA .

The bond lengths have been determined, fairly accurately, in the case of crystals by X-ray diffraction and in the case of gases by spectroscopy. The values obtained for some common diatomic molecules are given in Table 2.

It may be noted that bond length decreases with multiplicity of the bond formed between the two atoms. Thus, $\text{C} \equiv \text{C}$ bond is shorter than $\text{C} = \text{C}$ bond which, in turn, is shorter than $\text{C}-\text{C}$ bond.

TABLE 2
Bond Lengths (\AA) of Some Common Bonds

Bond	Bond length	Bond	Bond length
H-H	0.74	H-F	0.92
C-H	1.00	H-Cl	1.27
O-H	0.96	H-Br	1.41
F-F	1.42	H-I	1.61
Cl-Cl	1.99	C-C	1.54
Br-Br	2.28	C=C	1.34
I-I	2.67	C \equiv C	1.20

Bond Angle. Bond angle may be defined as the angle between two bonds of the atom in a molecule or the internal angle between the orbitals containing bonding electron pairs in the valency shell of the atom in a molecule. For example, the bond angles in H_2O , NH_3 and CH_4 molecules are 104.5° , 107.3° and 109.5° , respectively.

The bond angle gives an idea of the distribution of the orbitals in three-dimensional space around the central atom in the molecule and thus gives an idea of the shape of the molecule.

Bond Strength or Bond Energy. Energy is required invariably to break a chemical bond. For instance, in the breaking of one mole of hydrogen gas into atoms, 458 kJ of energy is required. The bond strength in this case is said to be 458 kJ per mole, i.e., per Avogadro's number of bonds. **Bond strength or bond energy** of a particular type of bond is defined as the energy required to break one mole of bonds of that type in a substance in gaseous state. The bond energies of some common bonds are given in Table 3.

TABLE 3

Bond Energies of Some Common Bonds

Bond	Bond energy (kJ mol ⁻¹)	Bond	Bond energy (kJ mol ⁻¹)
H-H	458.0	O=O	494.6
F-F	154.8	N=N	945.6
Cl-Cl	242.7	C-C	347.0
H-Cl	430.0	C=C	619.0
I-Cl	209.2	C≡C	836.8

The strength of the bond indicates the stability of the bond. Thus, $\text{N}=\text{N}$ bond is more stable than $\text{O}=\text{O}$ bond. Hence, nitrogen molecule is more stable than oxygen molecule. Consequently, nitrogen is much less reactive than oxygen. The strength of $\text{F}-\text{F}$ bond is lower than that of $\text{Cl}-\text{Cl}$ bond. Hence, fluorine is more reactive than chlorine. Similarly, ICl is more reactive than Cl_2 .

WAVE MECHANICAL TREATMENT OF COVALENT BOND

The Lewis concept of covalent bond based on sharing of electrons satisfactorily explains the bonding between atoms all of which have a tendency to gain electrons in order to acquire the stable noble gas configurations. It also explains adequately the polarity of molecules. However, the concept remains purely qualitative and it cannot answer a number of questions such as

1. Why a covalent bond is formed at all?
2. How do the electrons distribute themselves in space around the central atom in a molecule?
3. What are the forces of attractive interaction in a covalent molecule?
4. What is the concept of bond energy in a covalent bond?
5. How are the compounds such as PF_5 , IF_7 , SF_6 , BF_3 , with central atoms having more than or less than 8 valence shell electrons so stable?

Wave mechanics has provided satisfactory answers to most of these questions and has led ultimately to the development of more comprehensive theories of covalent bonding. These theories are : 1. *The Valence Bond Theory*. 2. *The Molecular Orbital Theory*.

But, before we discuss the two theories, it would be worthwhile to elucidate the wave mechanical principles which are involved in their treatment. These principles are :

1. If ψ_1 is a solution of the wave equation $\hat{H}\psi = E\psi$, then $c_1\psi_1$ is also the solution of the same wave equation where c_1 is a constant known as *coefficient of the wave function*. This means that ψ_1 and $c_1\psi_1$ give the same value of energy E .
2. If ψ_1 and ψ_2 are separately the solutions of the wave equation $\hat{H}\psi = E\psi$, then $c_1\psi_1$, $c_2\psi_2$ and $c_1\psi_1 \pm c_2\psi_2$ are also the solutions of the same wave equation. This means that ψ_1 , ψ_2 , $c_1\psi_1$, $c_2\psi_2$ and $c_1\psi_1 \pm c_2\psi_2$ would give the same value of energy E . The squares of the coefficients, viz., c_1^2 and c_2^2 give the contributions of ψ_1 and ψ_2 , respectively, to the total wave function.

Approximate Solution of Schrodinger Wave Equation. We have already discussed in the first chapter that the Schrodinger wave equation can be solved only for hydrogen and hydrogen-like systems, such as He^+ in which a single electron moves under the influence of a single nucleus. The wave equation cannot be solved for systems containing more than one electron or more than one nucleus. Nevertheless, methods have been devised for finding out approximate ψ closest to the true ψ and the corresponding approximate energy closest to the true energy of multi-electron and multi-nucleus systems. One such method is based on the *variation principle*.

The Variation Principle. Consider the wave equation $\hat{H}\psi = E\psi$. Multiplying each side of the wave equation by ψ and integrating it throughout the space, we get

$$\int_{-\infty}^{+\infty} \psi \hat{H} \psi d\tau = \int_{-\infty}^{+\infty} \psi E \psi d\tau \quad \dots(3)$$

$$= E \int_{-\infty}^{+\infty} \psi^2 d\tau \quad (\because E \text{ is constant}) \quad \dots(4)$$

where $d\tau$ is a small space element.

$$\text{From Eqs. 3 and 4,} \quad E = \int_{-\infty}^{+\infty} \psi \hat{H} \psi d\tau / \int_{-\infty}^{+\infty} \psi^2 d\tau \quad \dots(5)$$

We can, thus, calculate energy E of the system if we know true ψ . If we do not know true ψ , even then we can guess a wave function which is close to the true wave function ψ by using our chemical intuition. If this approximate wave function is ψ_1 , then Eq. 5 takes the form

$$\epsilon = \int_{-\infty}^{+\infty} \psi_1 \hat{H} \psi_1 d\tau / \int_{-\infty}^{+\infty} \psi_1^2 d\tau \quad \dots(6)$$

where ϵ , known as **energy function**, will have the dimensions of energy but will *not be equal* to the true energy of the system.

In case ψ and ψ_1 are complex wave functions, then Eq. 3 is written as

$$\int_{-\infty}^{+\infty} \psi^* \hat{H} \psi d\tau = \int_{-\infty}^{+\infty} \psi^* E \psi d\tau$$

and Eq. 6 is written as

$$\epsilon = \int_{-\infty}^{+\infty} \psi_1^* \hat{H} \psi_1 d\tau / \int_{-\infty}^{+\infty} \psi_1^* \psi_1 d\tau$$

where ψ_1^* is the complex component of ψ_1 . In case ψ and ψ_1 are real, then ψ^* is the same as ψ and ψ_1^* is the same as ψ_1 . *For the sake of simplicity we have assumed ψ to be real.*

According to the variation principle, if we are able to guess at a number of wave functions ψ_1, ψ_2, ψ_3 , etc., which are thought to be close approximations of the true wave function ψ , then we can calculate the energy functions, $\epsilon_1, \epsilon_2, \epsilon_3$, etc., with the help of Eq. 6. In such a case

1. All the energy functions calculated as above would have *higher values* than the true energy of the system.
2. Out of $\epsilon_1, \epsilon_2, \epsilon_3$, etc., the energy function with the *minimum value* would be closest to the true energy E .
3. The wave function which gives the minimum value of energy function is the closest approximation of the true wave function ψ .

One may question, why we cannot calculate E directly from the relation

$$E = \hat{H}\psi/\psi \quad \dots(7)$$

The answer is as follows: Eq. 7 can be employed for calculating E only if ψ is a true wave function. If ψ is an approximate wave function (as is usually the case in multi-electron systems), then, $\hat{H}\psi/\psi$ would be a function of x, y, z and would vary from place to place in a three-dimensional space. The value of E would also vary accordingly. In other words, if E is calculated with the help of Eq. 7, it would not be a constant parameter.

The approximate ψ can also be calculated with the help of Ritz linear combination method which too is based on the variation principle. Suppose we have reasons to believe that the wave function ψ has some characteristics of a known wave function ψ_1 and some characteristics of another known wave function ψ_2 . The wave function ψ can then be written as a linear combination of ψ_1 and ψ_2 , i.e., as $\psi = c_1\psi_1 + c_2\psi_2$. Accordingly,

$$\text{Energy function, } \epsilon = \int_{-\infty}^{+\infty} \psi \hat{H} \psi dt / \int_{-\infty}^{+\infty} \psi^2 dt \quad \dots(8)$$

$$= \int_{-\infty}^{+\infty} (c_1\psi_1 + c_2\psi_2) \hat{H} (c_1\psi_1 + c_2\psi_2) dt / \int_{-\infty}^{+\infty} (c_1\psi_1 + c_2\psi_2)^2 dt \quad \dots(9)$$

The coefficients c_1 and c_2 are so adjusted in the total wave function ψ as to yield a minimum value of ϵ . This is done by differentiating Eq. 9 with respect to c_1 and also with respect to c_2 and then putting $\partial\epsilon/\partial c_1$ and also $\partial\epsilon/\partial c_2 = 0$ as these are the conditions for minimization of ϵ . By doing so we get two equations containing ϵ , c_1 and c_2 . From these equations, we can derive a quadratic equation in ϵ . The solution of this quadratic equation gives ϵ , c_1 and c_2 . Similarly, if we have reasons to believe that the true wave function ψ has characteristics of known wave functions ψ_1, ψ_2, ψ_3 , etc., the actual ψ can then be written as $\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \dots$. The coefficients c_1, c_2, c_3 , etc., are so adjusted as to yield minimum value of the energy function.

This method has an advantage that if we guess at a wrong wave function (ψ_i), its coefficient (c_i) would automatically come out to be zero.

With the help of the wave mechanical principles elucidated above, it is possible to discuss at length the Valence Bond and the Molecular Orbital theories of covalent bonding.

VALENCE BOND THEORY

The valence bond theory was first put forward by W. Heitler and F. London, in 1927, to explain the stability of a covalently bonded hydrogen molecule. It was extended further by J. C. Slater and L. Pauling. The theory utilises the following wave mechanical principles:

1. If ψ_A and ψ_B are the wave functions for any two completely independent (non-interacting) systems A and B, then the total wave function ψ for these independent systems, taken together, would be given by

$$\psi = \psi_A \psi_B \quad \dots(10)$$

and the total energy E of these non-interacting systems would be equal to the sum of the energies of systems A and B. The total hamiltonian is also equal to the sum of the hamiltonians for the systems A and B, i.e.,

$$E = E_A + E_B \text{ and } \hat{H} = \hat{H}_A + \hat{H}_B$$

2. If the wave function for a many-electron system has characteristics of several wave functions $\psi_1, \psi_2, \psi_3, \dots, \psi_n$, then according to the Ritz principle of linear combination, the wave function ψ closest to the true wave function of the system is given by

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \dots + c_n\psi_n \quad \dots(11)$$

where $c_1, c_2 \dots c_n$ are the various coefficients. As already mentioned, the square of the coefficient of a particular wave function gives the contribution of that wave function, generally called the *weightage* of that wave function, to the total wave function. The coefficients c_1, c_2 , etc., are so adjusted as to give a state of lowest energy, i.e., a state of maximum stability. Further, the wave function ψ should be normalised (cf. Chapter 1) so that

$$c_1^2 + c_2^2 + c_3^2 + \dots = 1 \quad \dots(12)$$

We will elucidate the Valence Bond theory by taking into consideration the formation of H_2 molecule.

Formation of Hydrogen Molecule. Consider two hydrogen atoms lying far apart from each other so that no interaction between them is possible. Let A and B represent the nuclei and e_1 and e_2 the two electrons. The two atoms of hydrogen may thus be represented as $H_A(e_1)$ and $H_B(e_2)$.

Let the wave functions for the electrons in separated atoms be represented by $\psi_A(1)$ and $\psi_B(2)$. The wave function $\psi_A(1)$ is also called the wave function of the atomic orbital containing electron (1) and the wave function $\psi_B(2)$ is called the wave function of the atomic orbital containing electron (2). According to Eq. 10, the combined wave function ψ for the two separated atoms of hydrogen can be written as

$$\psi = \psi_A(1)\psi_B(2) \quad \dots(13)$$

When the two atoms are brought closer together, their energy changes and, consequently, the energy operator \hat{H} also changes. Assuming that the combined wave function ψ , as represented by Eq. 13, still describes the wave function for H_2 molecule, the energy of the hydrogen molecule, following Eqs. 3 and 4, would be given by

$$E = \frac{\int_{-\infty}^{+\infty} \psi_A(1) \psi_B(2) \hat{H} \psi_A(1) \psi_B(2) d\tau}{\int_{-\infty}^{+\infty} [\psi_A(1) \psi_B(2)]^2 d\tau} \quad \dots(14)$$

The energy changes that take place as the two H atoms are gradually brought closer to each other are shown graphically in Fig. 12.

When the two atoms are far removed from each other, i.e., when the internuclear distance r_{AB} is infinity, the total energy of the system is taken as zero*. As the atoms are brought closer in a region in which the electric field due to one can influence that of the other, the energy of the system starts decreasing till a certain minimum value is reached. This stage corresponds to the formation of H_2 molecule. The internuclear distance at this stage is designated as r_0 .

When we calculate the energy of the system of the two hydrogen atoms by using Eq. 14 and plot these energies as a function of internuclear distance, the curve *a* is obtained. The bonding energy given by the minimum in potential energy curve *a* is only 24 kJ mol^{-1} . This is too far below the experimental value of 458 kJ mol^{-1} (represented by the minimum in the experimental curve). Moreover, the minimum is found at an internuclear distance of about 0.90 \AA (curve *a*) whereas the experimental bond distance in hydrogen molecule is 0.74 \AA . Evidently, the wave function $\psi_A(1)\psi_B(2)$, as applied to H_2 system, is not a good approximation. Apparently, some other interactions between the two hydrogen atoms are required to be

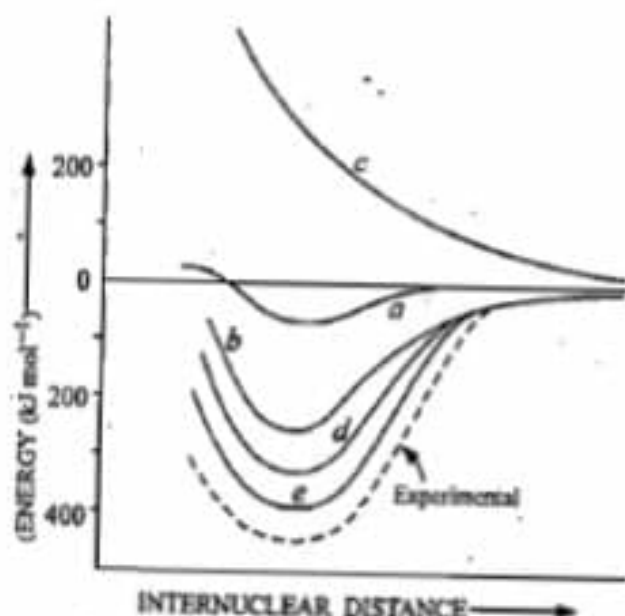


Fig. 12. Variation of energy with internuclear distance in the formation of hydrogen molecule.

*Since we are interested in finding out only the change in energy when the two atoms A and B come close to each other from infinite distance to form a bond, the sum of energies of the two isolated atoms A and B, when they are at infinite distance from each other, is taken as zero.

taken into consideration to arrive at the correct wave function for the combined H_2 system. Some of these interactions are as follows.

1. Exchange of Electrons. In arriving at Eq. 14, we had assumed that the electrons of the two hydrogen atoms could be distinguished from each other and, therefore, the electron around nucleus A was labelled as e_1 and that around nucleus B was labelled as e_2 . This assumption, however, is not correct because when a bond is formed, *the two atomic orbitals overlap* and the two electrons become *indistinguishable* from each other. We can no longer be sure that electron 1 will always be near the nucleus A and electron 2 will always be near the nucleus B. The system of two hydrogen atoms may then be represented by two different states, I and II, as shown below :



(I)



(II)

In state I, nucleus A is associated with electron 1 and nucleus B is associated with electron 2. In state II, nucleus A is associated with electron 2 and nucleus B is associated with electron 1. Both the states I and II are equally probable.

If ψ_I and ψ_{II} are the wave functions representing states I and II, respectively, then, according to Eq. 10, we can write

$$\psi_I = \psi_A(1) \psi_B(2) \quad \text{and} \quad \psi_{II} = \psi_A(2) \psi_B(1)$$

A linear combination of ψ_I and ψ_{II} (and not ψ_I or ψ_{II} alone) should be employed for calculating the energy of H_2 molecule. There are evidently two possible modes of linear combination, viz., additive and subtractive according to which there are two wave functions, viz., ψ_+ and ψ_- , given by

$$\psi_+ = \psi_I + \psi_{II} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) \quad \dots(15)$$

$$\text{and} \quad \psi_- = \psi_I - \psi_{II} = \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1) \quad \dots(16)$$

The actual normalised ψ_+ and ψ_- are $1/\sqrt{2}(\psi_I + \psi_{II})$ and $1/\sqrt{2}(\psi_I - \psi_{II})$, respectively. However, since the normalising constant $1/\sqrt{2}$ does not enter into the calculation of energy, it is not written in the expression for ψ_+ and ψ_- .

The energy of the system, calculated by using ψ_+ in the wave equation is shown by the curve *b* while that calculated from ψ_- is shown by the curve *c* in Fig. 12**. It is evident that ψ_- leads to *increase of energy*. Thus, *bonding is not possible in ψ_-* . We may, therefore, regard ψ_- as a *repulsive state*. The wave function ψ_+ , however, leads to *fall of energy*. Thus, *bonding is possible in this state*. We may, therefore, regard ψ_+ as a *bonding state*.

The wave function ψ_+ (Eq. 15) which represents the *bonding state* is also referred to as *covalent wave function*. Therefore, it may be written as ψ_{covalent} . The reason for this terminology is that in state I as well as in state II, there is equal distribution of charge on both the nuclei A and B.

As mentioned above, the bonding energy calculated from Eq. 14 is only 24 kJ mol^{-1} . The bonding energy corresponding to ψ_+ (Eq. 15) is 303 kJ mol^{-1} and the internuclear distance is 0.80 \AA . The *additional energy resulting from the exchange of electrons between the two hydrogen atoms is called the exchange energy*. Thus, $303 - 24 = 279 \text{ kJ mol}^{-1}$ is the exchange energy for H_2 molecule.

2. Screening Effect of Electrons. The wave function given by Eq. 15 is further improved by considering the screening effect of the electrons. When the two atoms come close to each other, the electron of one atom shields the electron of the other atom from the nucleus so that the electrons do not feel the full charge of the nucleus. The actual charge felt by an electron is termed as its *effective nuclear charge*. This will be, evidently, less than the actual nuclear charge. If we use the effective nuclear charge

**Since both the states I and II are equally probable, a linear combination having equal contributions from ψ_I and ψ_{II} is employed to calculate the energy of H_2 molecule.

and improve the wave function given by Eq. 15, bonding energy of 365 kJ mol^{-1} is obtained. This is depicted by the minimum in the curve *d*.

3. Ionic Character of H-H Bond. The bond energy of 365 kJ mol^{-1} is still appreciably smaller than the experimental value of 458 kJ mol^{-1} . This shows that ψ_+ still does not give the *true wave function* for H_2 molecule. Evidently, further improvement of wave function is needed. Since the calculated value of bond energy is smaller than the experimental value, it is necessary to provide in our model of H_2 molecule an additional factor which will tend to enhance the binding force between the two hydrogen atoms because increase in such a force will lead to increase in the bond energy. The additional factor that has been suggested is the possibility that *momentarily both the electrons may simultaneously be present close to one nucleus or the other. This gives rise to ionic configurations represented by states III and IV:*



(III)



(IV)

These two ionic structures may be represented as $\text{H}_A^- \text{H}_B^+$ and $\text{H}_A^+ \text{H}_B^-$, respectively. However, the coulombic repulsion between the two electrons present so close to each other would far exceed the coulombic attraction between H_A^- and H_B^+ or between H_A^+ and H_B^- . This reduces the probability of the existence of these additional structures to a bare minimum. Nevertheless, the incorporation of these structures as resonance structures does increase the stability of the hydrogen molecule and hence its bond energy.

The states III and IV are, amongst themselves, equally probable and the wave functions corresponding to state III (ψ_{III}) and state IV (ψ_{IV}) may be expressed as

$$\psi_{\text{III}} = \psi_A(1)\psi_A(2) \quad \text{and} \quad \dots(17)$$

$$\psi_{\text{IV}} = \psi_B(1)\psi_B(2) \quad \dots(18)$$

The total ionic wave function ψ_{ionic} may be expressed as a linear combination of ψ_{III} and ψ_{IV} , as

$$\psi_{\text{ionic}} = \psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2) \quad \dots(19)$$

Since both the states III and IV are equally probable, hence there is equal contribution from ψ_{III} and ψ_{IV} , towards ψ_{ionic} .

However, states III and IV are less probable than states I and II as the two electrons present on the same H atom would repel each other and make states III and IV less likely compared to states I and II.

Considering the possibilities of covalent as well as ionic structures, the combined wave function for H_2 molecule is written as

$$\begin{aligned} \psi &= \psi_{\text{covalent}} + \lambda \psi_{\text{ionic}} \\ &= [\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)] + \lambda [\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)] \quad \dots(20)^* \end{aligned}$$

where λ gives the extent to which the ionic structures contribute to the bonding. For H_2 , λ is calculated to be 0.17. Knowing λ , we can find out the extent of the contribution of the ionic structures. The fraction λ is called the **mixing coefficient**.

With all these modifications, the calculated bond energy comes out to be about 388 kJ mol^{-1} which can be considered as reasonably close to the experimental value of 458 kJ mol^{-1} . The internuclear

*The actual normalised wave function is $\frac{1}{\sqrt{1+\lambda^2}} \{(\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)) + \lambda(\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2))\}$. However,

$\left(\frac{1}{\sqrt{1+\lambda^2}}\right)$ is omitted since it does not enter into the calculation of energy.

distance between hydrogen atoms now comes out to be 0.75 Å which is quite close to the experimental value of 0.74 Å. The differences which still persist are considered to be due to some complicated electronic interactions, the discussion of which is beyond the scope of this book.

Bond energies and bond lengths for H_2 molecule corresponding to various wave functions are summed up in Table 4.

Singlet and Triplet Wave Functions. In the valence bond

treatment of H_2 molecule, the linear combination of the two appropriate wave functions yields the following two space covalent wave functions:

$$\psi_+ = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) \quad \dots(\text{Eq. 15})$$

$$\psi_- = \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1) \quad \dots(\text{Eq. 16})$$

where ψ_+ is the wave function for the bonding state and ψ_- is the wave function for the repulsive state.

If we exchange the coordinates of electron (1) with those of electron (2) in ψ_+ and ψ_- , the sign of ψ_+ does not change whereas the sign of ψ_- changes from plus to minus so that the wave function changes from ψ_- to $-\psi_-$. Therefore, while ψ_+ is designated as $\psi_{\text{symmetric}}$, ψ_- is designated as $\psi_{\text{asymmetric}}$.

The complete wave function for the system which includes both the space as well as the spin part of the wave function is written by assuming that these two parts of the wave function do not influence each other, that is, there is no 'spin-orbit' interaction. Accordingly, the complete wave functions for the two states are written as

$$\psi_{+ (\text{complete})} = \psi_{+} \times \psi_{\text{spin}} = \psi_{+} \alpha_1 \alpha_2, \psi_{+} \beta_1 \beta_2, \psi_{+} (\alpha_1 \beta_2 + \alpha_2 \beta_1), \psi_{+} (\alpha_1 \beta_2 - \alpha_2 \beta_1)$$

$$\psi_{- (\text{complete})} = \psi_{-} \times \psi_{\text{spin}} = \psi_{-} \alpha_1 \alpha_2, \psi_{-} \beta_1 \beta_2, \psi_{-} (\alpha_1 \beta_2 + \alpha_2 \beta_1), \psi_{-} (\alpha_1 \beta_2 - \alpha_2 \beta_1)$$

where α_1, α_2 are the spin wave functions representing $+\frac{1}{2}$ spin states of electrons 1 and 2, respectively and β_1, β_2 are the spin wave functions representing $-\frac{1}{2}$ spin states of electrons 1 and 2, respectively. As discussed in Chapter 1, the complete wave function of a system is acceptable if it is asymmetric with respect to the exchange of the coordinates of electrons, that is, if the sign of the complete wave function changes on changing the coordinates of electrons.

As can be seen, of the four expressions which can be written for $\psi_{+ (\text{complete})}$ there is only a single expression for $\psi_{+ (\text{complete})}$ which is asymmetric and hence acceptable. Therefore, $\psi_{+ (\text{complete})}$ is called a **singlet state**.

Thus, the single asymmetric and hence acceptable $\psi_{+ (\text{complete})}$ is $(\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1))(\alpha_1\beta_2 - \alpha_2\beta_1)$.

However, there are three asymmetric and hence acceptable wave functions for $\psi_{- (\text{complete})}$ namely, $(\psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1))\alpha_1\alpha_2$, $(\psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1))\beta_1\beta_2$ and $(\psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1))(\alpha_1\beta_2 + \alpha_2\beta_1)$ in which the exchange of coordinates of electrons yields a change of sign of ψ_- . Hence, $\psi_{- (\text{complete})}$ is called a **triplet state**.

Consider again, the singlet state, viz., $\psi_{+ (\text{complete})} = (\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1))(\alpha_1\beta_2 - \alpha_2\beta_1)$ which is responsible in forming a chemical bond according to VB theory. The spin part of the wave function is the contribution of the product $\alpha\beta$ of opposite spins of electrons 1 and 2. It does not have any contribution from the parallel spin functions $\alpha\alpha$ and $\beta\beta$ of electrons 1 and 2. It follows from the above that in a chemical bond, the two participating electrons must be of opposite spins.

Table 4

Bond Energies and Bond Lengths for H_2 Molecule
Corresponding to Various Wave Functions

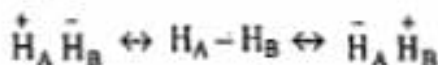
Wave Function	Bond Energy (kJ mol ⁻¹)	Bond Length (Å)
$\psi = \psi_A(1)\psi_B(2)$	24	0.90
$\psi_{\text{covalent}} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$	303	0.80
ψ_{covalent} with screening effect	365	0.76
$\psi = \psi_{\text{covalent}} + \lambda \psi_{\text{ionic}} =$ $[\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)] +$ $\lambda[\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)]$	388	0.75
Experimental values	458	0.74

CONCEPT OF RESONANCE

The physical interpretation of Eq. 20 is that H_2 molecule can neither be represented adequately by the pure covalent bond $H-H$ nor by the ionic structures $H_A^+H_B^-$ and $H_A^-H_B^+$. The true structure lies somewhere in between these three structures.

When a molecule cannot be completely represented by a single structure but its characteristic properties can be described by two or more different structures, then the true structure is said to be a resonance hybrid of these structures. In such a case we say that there is resonance between the various possible structures. The possible structures are called resonating structures. As a result of resonance, the energy of the molecule becomes lower than the energy of any of the resonating structures. The molecule with a lower energy has higher stability and also higher bond energy. Thus, resonance imparts extra stability to the molecule.

The resonance between two or more structures is represented by drawing double-headed arrows between the various structures, as shown below in the case of hydrogen :



The molecule is said to *resonate* between the three resonance structures.

It may be emphasised here that the various postulated resonating structures of a molecule have *no real existence*. Also, it does not mean that the actual molecule exists for a certain fraction of time in one form and for another fraction of time in another form. In fact, *the actual structure has no pictorial representation*. The resonating structures are only a convenient way of picturing a molecule to account for all the properties of a molecule.

Resonance Energy. As mentioned above, the resonance hybrid is more stable than any of the contributing structures. The extra stability of the resonance hybrid over and above the stability of the most stable of the various resonating structures is reflected through an extra decrease in the energy of the molecule. This extra decrease in energy which results from the extra stabilisation of the molecule because of resonance, is called resonance energy. *Resonance energy is thus the difference between the actual energy of the molecule and that of the most stable of the resonating structures.* For example, the resonance energy of carbon dioxide is 138 kJ mol^{-1} . This means that the molecule of CO_2 is about 138 kJ more stable than the most stable contributing structure of the molecule.

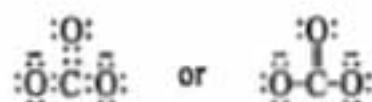
Let us assume that E_1 , E_2 and E_3 are the energies of the three resonating structures for a molecule and among these E_3 is the lowest energy corresponding to the most stable contributing structure. If E_0 is the actual energy of the molecule (determined experimentally), then, resonance energy is $E_3 - E_0$.

There are certain rules which permit the selection of the structures which contribute towards resonance. These are given below.

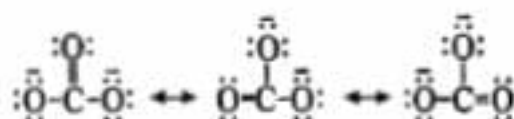
1. The contributing structures should have the same atomic positions. They should differ only in the positions of electrons.
2. The contributing structures should have the same number of unpaired electrons.
3. The contributing structures should not differ much in energy.
4. Contributing structures should be such that negative charge resides on an electronegative element and positive charge resides on an electropositive element.
5. In contributing structures, like charges should not reside on atoms close to each other and unlike charges should not be widely separated.

As an illustration, we may consider resonance structures of CO_3^{2-} ion and CO molecule.

Carbonate ion (CO_3^{2-}). According to the octet rule, the electronic structure of carbonate ion (CO_3^{2-}) carrying two negative charges (*i.e.*, with two additional electrons) may be represented as follows :

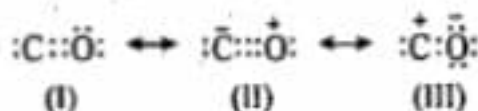


In this structure, there are three carbon-to-oxygen bonds, two of which are single bonds while the third is a double bond. Evidently, a carbon-to-oxygen double bond should be shorter than a carbon-to-oxygen single bond. But it is known from X-ray studies that all the three carbon-to-oxygen bonds in carbonate ion are of equal length which lies in between the usual single and double bond lengths. Pauling explained this observation on the basis of resonance between the three possible structures, as shown below :



This implies that the double bond resulting from the sharing of four electrons is *not localised* between carbon and any one particular oxygen atom. It is spread over all the three oxygen atoms.

Carbon monoxide molecule, CO. Carbon monoxide is a resonance hybrid of the following three resonating structures :



The carbon-oxygen bond length determined by X-ray diffraction is 1.13 Å which is close to the calculated $\text{C}\equiv\text{O}$ bond length. This suggests that the bond between carbon and oxygen atoms in CO molecule is *closer to a triple bond*. Hence, structure II predominates.

Structures II and III have dipole moments in the opposite direction. Therefore, as expected, carbon monoxide has very low dipole moment (0.12 D).

LINNET'S DOUBLE QUARTET APPROACH

The valence bond theory, however, could not explain the unexpected paramagnetic behaviour of certain molecules such as O_2 . In order to explain this behaviour, Linnet introduced the concept of **double quartet** according to which the 8 electrons (completed octet) around an atom, instead of constituting four pairs of 2 electrons each, constitute *two groups of four electrons each* (hence the name double quartet). The spins of all the electrons in a quartet are the same. But the spins of electrons in one quartet is opposite to the spin of electrons in the other quartet. Because of the effects of like charge (*charge correlation*) and same spin (*spin correlation*) of the four electrons in each quartet, each set of four electrons in a quartet has a high probability of occurring in a regular tetrahedral arrangement around the nucleus of the atom.

The charge correlation effect which tends to keep all the electrons of the two quartets apart and Pauli exclusion principle (*i.e.*, spin correlation), which tends to keep electrons of opposite spins together, oppose each other and roughly cancel each other so that the two tetrahedra are *spatially uncorrelated to each other*. This results in a spherical symmetry of electronic charge in free atoms and ions as in Ne, Na^+ , F^- , O^{2-} , etc. The most probable positions for the electrons of a double quartet of a free ion or atom, which will result in spherical symmetry of electronic charge, are shown in Fig. 13a. These tetrahedra become strongly correlated to one another because of the localisation of electron pairs which form the covalent bonds. Since the two electrons in a bond pair have to be of opposite spin, each bond pair shall bind one

corner of one tetrahedron of electrons having one type of spin with one corner of the other tetrahedron of electrons having opposite type of spin. This is shown below in the case of H_2O , NH_3 and CH_4 molecules (Figs. 13b, c and d).

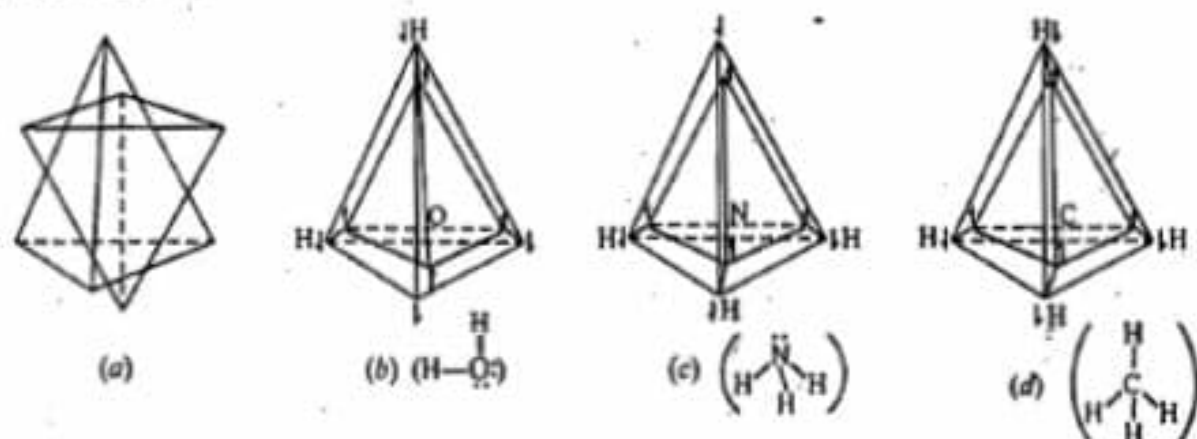
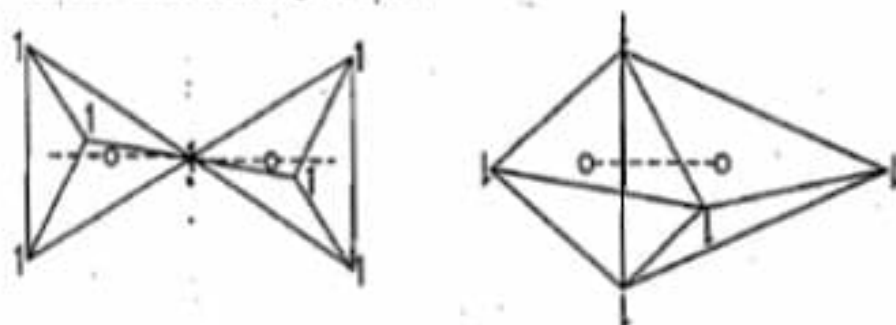


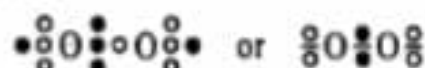
Fig. 13. (a) shows the most probable orientations of two tetrahedra of free atom or ion. Figs. (b), (c) and (d) indicate the fixation of tetrahedra around O, N and C nuclei in H_2O , NH_3 and CH_4 molecules respectively.

As is clear from the above figures, the bond pairs of electrons (as in H_2O , NH_3 and CH_4 molecules) fix the spacial orientation of the two tetrahedra of electrons with respect to each other.

In order to explain the paramagnetic behaviour of O_2 , seven electrons are assigned one type of spin and five electrons are assigned the opposite spin. Each set of electrons is arranged in two tetrahedra around the oxygen nuclei in the following manner :

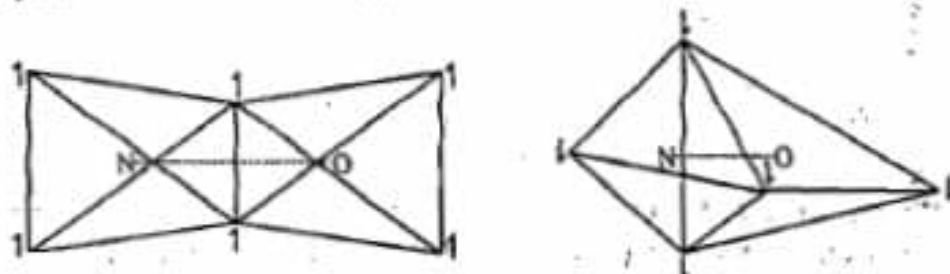


If the two figures are superimposed on each other in such a way that the O-nuclei of two figures coincide, then each O nucleus will be surrounded by eight electrons arranged in two tetrahedra. The resulting situation can be represented as :



The circles represent electrons with one type of spin and dots represent electrons with the other type of spin. The short line represents an electron pair. The molecule is obviously paramagnetic with a resultant spin equivalent to *two unpaired electrons*. (Four unpaired electrons are having one type of spin and the other two unpaired electrons are having the opposite type of spin).

The structure of NO molecule can also be explained by the double quartet approach. The IR, X-ray and thermodynamic studies of this molecule reveal that its bond order is intermediate between those of N_2 and O_2 (which contain 6 and 4 electrons, respectively, in the internuclear region). The double quartet approach explains it by means of the following two structures, each consisting of two tetrahedra of electrons one of which contains 6 electrons of one type of spin and the other contains 5 electrons of the other type of spin.



If the two figures are superimposed in such a way that N and O nuclei of the figures coincide and that each nucleus is surrounded by 8 electrons arranged in two tetrahedra, the structure obtained can be written as :



The molecule apparently contains a bond order of $2\frac{1}{2}$ (i.e., it has 5 electrons in the internuclear region). The molecule is paramagnetic because of the resultant one electron unpaired spin, as is experimentally observed.

However, the quartet approach, being entirely empirical, failed to receive any recognition.