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TABLE 5.2. ELECTRONIC STRUCTURE OF THE TWO OUTERMOST SHELLS OF SOME TRANSITION METALS

Sc	$3d^1 4s^2$	Ag	$4d^{10} 5s^1$
Cr	$3d^5 4s^1$	La	$5d^1 6s^2$
Mn	$3d^5 4s^2$	Os	$5d^6 6s^2$
Fe	$3d^6 4s^2$	Ir	$5d^7 6s^2$
Co	$3d^7 4s^2$	Pt	$5d^9 6s^2$
Cu	$3d^{10} 4s^1$	Au	$5d^{10} 6s^1$

Most of the transition metals have one or two outer-shell electrons and they form monovalent or bivalent positive ions. But because some of the *d* electrons are close in energy to the outermost electrons, these can also participate in chemical bond formation. Thus transition metals can form ions with variable valence. For example, copper can form Cu^{1+} and Cu^{2+} ions and iron can form Fe^{2+} and Fe^{3+} ions.

The complete electronic configuration of an iron atom is

$$Fe = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$$

It can form Fe^{2+} by losing two 4*s* electrons,

$$Fe^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$$

When iron loses two 4*s* electrons and one of the three 3*d* electrons, if forms Fe^{3+} ion

$$Fe^{3+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$$

Copper form Cu^{1+} and Cu^{2+} ions by losing one 4*s* electron, and one 4*s* and 3*d* electron respectively

$$Cu = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$$

$$Cu^{1+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$$

$$Cu^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$$

It may be noted that the structures of Fe^{2+}, Fe^{3+}, Cu^{1+}, Cu^{2+}, Cr^{3+}, etc., are not isoelectronic with any of the noble gases, and hence the *d* electrons being unstable are available for bond formation. (The atoms and ions that have the same number of electrons are said to be **Isoelectronic**).

METALLIC BONDING

The valence bonds that hold the atoms in a metal crystal together are not ionic, nor are they simply covalent in nature. Ionic bonding is obviously impossible here since all the atoms would tend to give electrons but none are willing to accept them. Ordinary covalent bonding is also ruled out as, for example, sodium atom with only one outer-shell electron could not be expected to form covalent bonds with 8 nearest neighbouring atoms in its crystal. **The peculiar type of bonding which holds the atoms together in metal crystal is called the Metallic Bonding.**

Many theories have been proposed to explain the metallic bonding. Here we will discuss the simplest of these : The Electron Sea Model.

THE ELECTRON SEA MODEL

Metal atoms are characterised by :

(1) **Low ionization energies** which imply that the valence electrons in metal atoms can easily be separated.

(2) **A number of vacant electron orbitals in their outermost shell.** For example, the magnesium atom with the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^0$ has three vacant 3*p* orbitals in its outer electron shell.

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There is considerable overlapping of vacant orbitals on one atom with similar orbitals of adjacent atoms, throughout the metal crystal. Thus it is possible for an electron to be delocalized and move freely in the vacant molecular orbital encompassing the entire metal crystal. The delocalized electrons no longer belong to individual metal atoms but rather to the crystal as a whole.

As a result of the delocalization of valence electrons, the positive metal ions that are produced, remain fixed in the crystal lattice while the delocalized electrons are free to move about in the vacant space in between. The metal is thus pictured as a network or lattice of positive ions of the metal immersed in a 'sea of electrons' or 'gas of electrons'. This relatively simple model of metallic bonding is referred to as the **Electron Sea model** or the **Electron Gas model** (Fig. 5.10.)

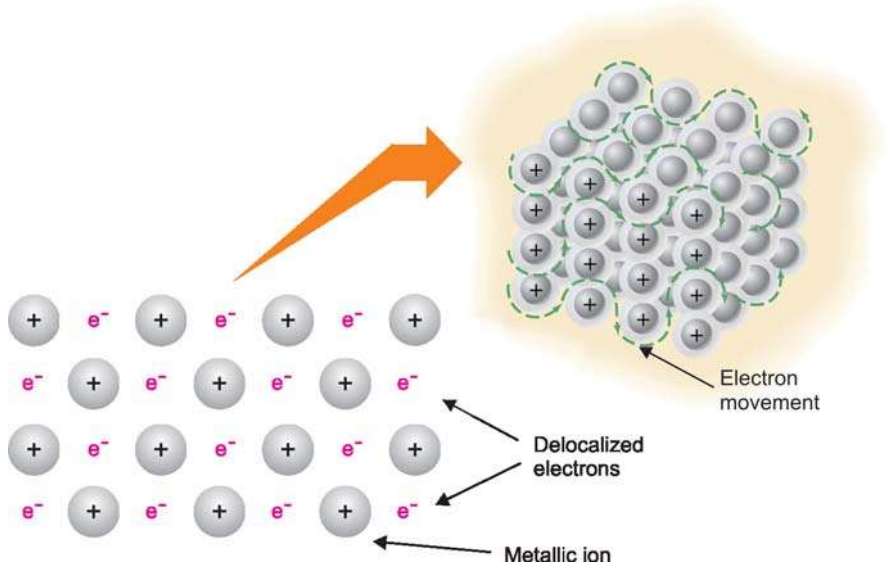
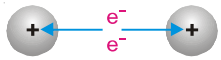


Figure 5.10
The Electron Sea model of metallic bonding.

A metallic bond is the electrostatic force of attraction that the neighbour positive metallic ions have for the delocalized electrons.



The electron sea model of metallic bonding explains fairly well the most characteristic physical properties of metals.

(1) **Luster or Reflectivity.** The delocalized mobile electrons of the 'electron sea' account for this property. Light energy is absorbed by these electrons which jump into higher energy levels and return immediately to the ground level. In doing so, the electrons emit electromagnetic radiation (light) of the same frequency. Since the radiated energy is of same frequency as the incident light, we see it as a reflection of the original light.

(2) **Electric Conductivity.** Another characteristic of metals is that they are good conductors of electricity. According to the electron sea model, the mobile electrons are free to move through the vacant space between metal ions. When electric voltage is applied at the two ends of a metal wire, it causes the electrons to be displaced in a given direction. The best conductors are the metals which attract their outer electrons the least (low ionization energy) and thus allow them the greatest freedom of movement.

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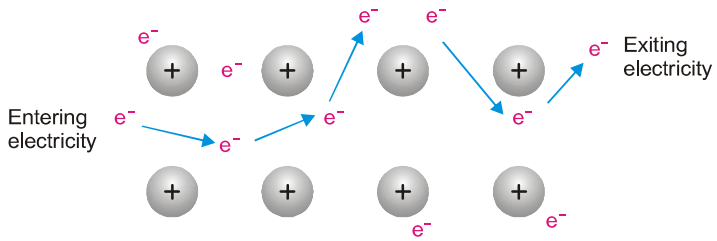

Figure 5.11
Electrical conductivity by flow of electrons based on Electron Sea model.

(3) **Heat Conductivity.** If a metal is heated at one end, the heat is carried to the other end. The mobile electrons in the area of the 'electron sea' around one end of the metal easily absorb heat energy and increase their vibrational motion. They collide with adjacent electrons and transfer the added energy to them. Thus the mobility of the electrons allows heat transfer to the other end (Fig. 5.12).

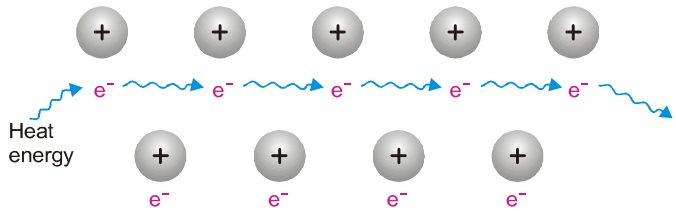

Figure 5.12
Heat conduction through a metal.

(4) **Ductility and Malleability.** The ductility and malleability of metals can also be explained by the electron sea model. In metals the positive ions are surrounded by the sea of electrons that 'flows' around them. If one layer of metal ions is forced across another, say by hammering, the internal structure remains essentially unchanged (Fig. 5.13). The sea of electrons adjusts positions rapidly and the crystal lattice is restored. This allows metals to be ductile and malleable. However, in ionic crystals of salts *e.g.*, sodium chloride, displacement of one layer of ions with respect to another brings like charged ions near to each other. The strong repulsive forces set up between them can cause the ionic crystals to cleave or shatter. **Thus ionic crystals are brittle.**

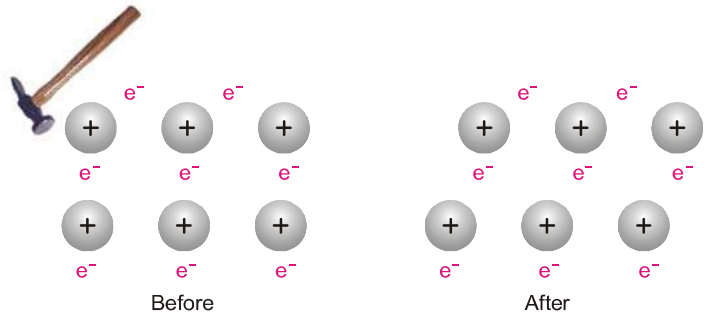

Figure 5.13
When force is applied to the upper layer of cations it slips to the right without changing the environments. illustration of malleability and ductility.

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electronic rearrangements. Out of the three factors determining the potential energy, the first two are 'repulsive' in nature and, therefore, cannot lower the potential energy in any manner. As the atoms approach each other, the electron-nucleus attractions contribute to the lowering of the potential energy, since each electron is now attracted towards the two positive nuclei at the same time, as compared to one nucleus in the isolated atoms.

BOND FORMATION (VALENCE BOND THEORY)

Bond formation between atoms to give chemical compounds can be interpreted admirably in terms of the orbital theory of atomic structure. Heitler and London believed that electron cloud of the valence orbital on one atom 'overlaps' the electron cloud of the other bonding atom to form a covalent linkage. On the contrary, the electrovalent bond formation involves a physical transfer of the electron and the orbital concept is not very useful for their explanation. The theory of '*maximum overlap*', affords an excellent interpretation of covalent bond formation. The essential conditions for the overlap of electron waves of orbitals are :

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

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

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

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

The new arrangement has lesser energy than the isolated atoms and, is therefore, more stable. The amount of energy given off or released per mole at the time of overlapping of atomic orbitals to form a bond is termed as **Bond Energy** or **Stabilisation Energy**. It also implies that this much energy must be put in to separate the atoms in a molecule.

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

Bond	Covalent Bond Energy (kcal/mole)	Covalent Bond Length r_c (Å)
H – H	103.2	0.74
C – H	98.7	1.10
C – C	83	1.54
C = C	146	1.34
C ≡ C	200	1.20
C – N	70.3	1.52
C – N	148	1.29
C ≡ N	213	1.15
C – O	84	1.43
C = O	177	1.24

In the bond formation, greater the overlap greater is the energy set free, *i.e.*, the higher will be the bond strength. This implies that for a bond to be stronger, greater should be the overlap which in

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turn shortens the distance between the nuclei. **A stronger bond has, therefore, a shorter bond length.**

Formation of H_2 molecule

Let us consider the formation of hydrogen molecule (H_2) from two isolated H atoms each having an electron in its 1*s* orbital. When two H atoms approach each other, their 1*s* orbitals overlap, resulting in the formation of a bigger electron cloud known as *molecular orbital*. This new molecular orbital contains both the electrons. As a result, the two H atoms are held together in the form of Hydrogen molecule (H–H). This overlapping of atomic orbitals of hydrogen atoms is shown in Fig. 6.2.

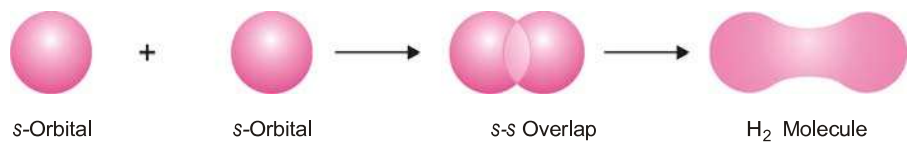

Figure 6.2
Formation of H_2 molecules (*s-s* overlap).

As the two atoms approach closer and closer for the overlap of half-filled 1*s* orbitals on them, the energy of the system goes on decreasing till it registers a minimum. At this point the overlapping halts, since the positive cores (nuclei) of the two atoms are apart by a certain equilibrium distance, the stabilizing effect of overlapping is completely balanced by the repulsion between the positive nuclei. Beyond this point the energy of repulsion predominates and there is a steep rise in the energy curve with a further decrease of internuclear distance. The point *A* in the diagram below represents a large value of internuclear distance corresponding to the two isolated atoms. By convention, the energy corresponding to this point is taken to be zero and for stabler systems, the energy of the system is negative. The energy values go on falling as the internuclear distance decreases. At point *X* on the curve, the internuclear distance decreases and so does the energy value. The minima 'B' represents the point of maximum overlap. The energy value and the internuclear distance corresponding to this point are respectively the bond energy and bond length. For the H_2 molecule, the bond length is 0.74 Å and bond energy is 103.2 kcal/mole.

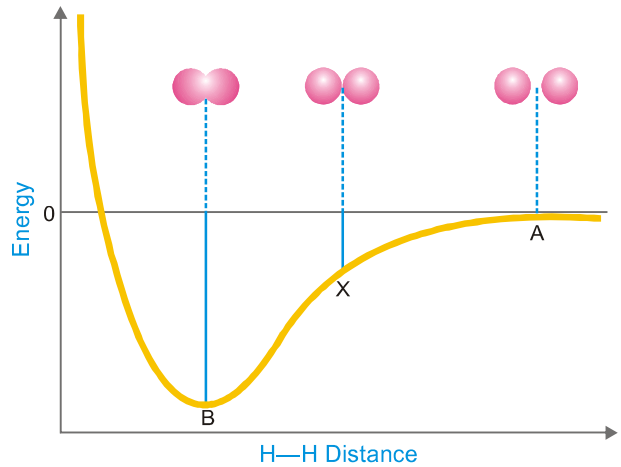

Figure 6.3
Energy diagram of *s-s* overlap.

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Types of overlapping and Nature of Covalent Bond

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

(1) Sigma (σ) bond

(2) Pi (π) Bond

(1) Sigma (σ) Bond

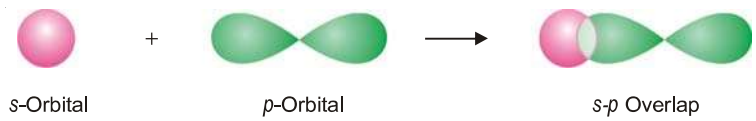
When there is end to end overlapping of atomic orbitals along the internuclear axis, the bond resulted is called sigma (σ) bond. This type of overlapping between the atomic orbitals is also called "head-on" overlapping or "axial" overlapping. It results when one of the following types of overlapping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

(*a*) ***s – s* overlapping**

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

(*b*) ***s – p* overlapping**

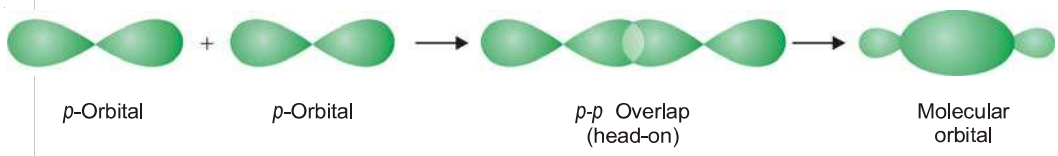
In this type of overlap *s*-orbital of one atom overlaps with the half filled *p*-orbital of the other atom as shown below :



Examples : HF, HCl etc.

(c) ***p – p* overlapping**

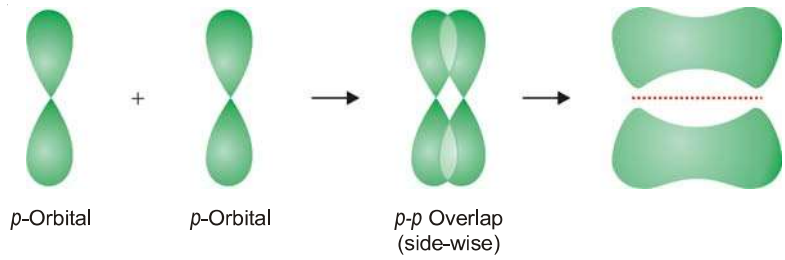
Here *p*-orbital of one atom overlaps with the *p*-orbital of the other atom on internuclear axis. It is shown below :



Examples : F_2, Cl_2, Br_2 etc.

(2) Pi (π) Bond

This type of covalent bond is formed by the sidewise overlap of the half filled atomic orbitals. It is also called **lateral** or **sidewise** overlap. This type of overlapping takes place perpendicular to the internuclear axis as shown below :



Strength of σ and π bonds

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

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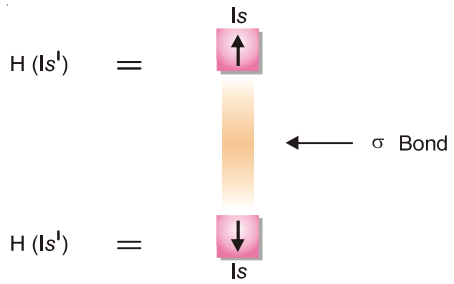
Differences Between Sigma and Pi bonds

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

ORBITAL REPRESENTATION OF MOLECULES

(*a*) Formation of H_2 molecule

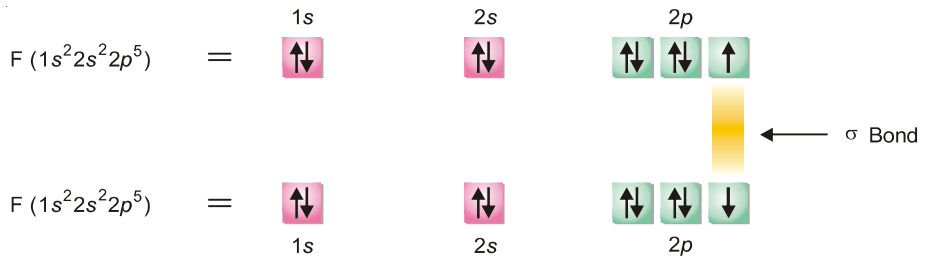
Each hydrogen atom has one electron in 1*s*-orbital. Two such atoms join to form a molecule of hydrogen. In this case *s*–*s* overlapping between two 1*s*-orbitals of hydrogen atoms taken place resulting in the formation of hydrogen molecule. There exists a sigma bond between two H-atoms. The situation is represented below :



(*b*) Formation of F_2 molecule

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

It is represented as follows :



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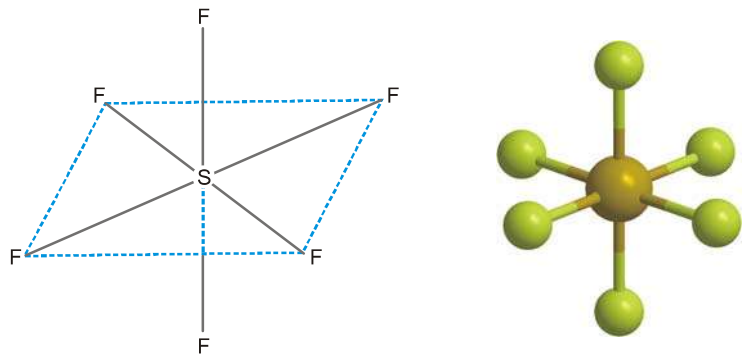

Figure 6.28
Formation of SF_6 molecule by sp^3d^2 hybridization.

the participating atoms. This results if the overlapping between the half filled atomic orbitals takes place and the strength of the bond formed depends upon the extent of overlapping between the atomic orbitals of two atoms. Though the valence bond theory explains the geometry of many molecules and ions yet it has following limitations :

(1) The presence of other nuclei should affect the electronic arrangement of all the atoms in the molecule

(2) Sometimes a single electronic structure does not explain all known properties of that molecule or ion and we have the many electronic structures called resonating structures.

(3) Valence Bond theory fails to explain the bonding in electron deficient compounds.

(4) It fails to explain the paramagnetic character of oxygen molecule.

MOLECULAR ORBITAL THEORY

Molecular orbital theory proposed by Hund and Mulliken in 1932 explains the formation of a covalent bond in a better way. According to molecular orbital theory all atomic orbitals of the atoms participating in molecule formation get disturbed when the concerned nuclei approach nearer. They all get mixed up to give rise to an equivalent number of new orbitals that belong to the molecule now. These are called *molecular orbitals*. Thus every molecule is supposed to have molecular orbitals associated with it in much the same way as a single isolated atom has. The main features of molecular orbital theory can be summed up as follows :

(1) A molecule is quite different from its constituent atoms. All the electrons belongs to the constituent atom and are considered to be moving under the influence of all nuclei.

(2) Atomic orbitals of individual atoms combine to form molecular orbitals and these MOs are filled up in the same way as atomic orbitals are formed. In other words, Pauli's exclusion principle, Aufbau principle and Hund's rule of maximum multiplicity are followed.

(3) The molecular orbitals have definite energy levels.

(4) The shapes of MOs formed depend upon the shape of combining atomic orbitals.

Linear Combination of Atomic orbitals (LCAO method)

According to wave mechanics the atomic orbitals can be expressed as wave functions (ψ_s) which represent the amplitude of electron waves. Their values can be calculated from the solutions of Schrödinger's wave equation. In a similar way, Schrödinger's wave equation can be applied to molecules but with slight difficulty. To cope with the difficulty an approximate method known as Linear Combination of atomic orbitals is applied.

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According to this method, the molecular orbitals are formed by the linear combination (addition or subtraction) of atomic orbitals of the constituent atoms of the molecule. Let us consider the simplest case of H_2 molecule consisting of two hydrogen atoms represented by H_A and H_B. The atomic orbitals of these atoms are represented by the wave functions ψ_A and ψ_B. When these atoms approach each other there come two possibilities.

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

$$\psi_{(MO)} = \psi_A + \psi_B \qquad ...(i)$$

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

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

$$\psi^*_{(MO)} = \psi_A - \psi_B \qquad ...(ii)$$

The MO formed is called **antibonding molecular orbital.** This type of MO corresponds to higher energy state. It has net disruptive effect. That is why this MO is termed as antibonding molecular orbital, distinguished by attaching an asterisk (*) mark with the symbolic name of the molecular orbital. The molecular orbitals formed by the combination of 1*s* orbitals of two hydrogen atoms is shown below :

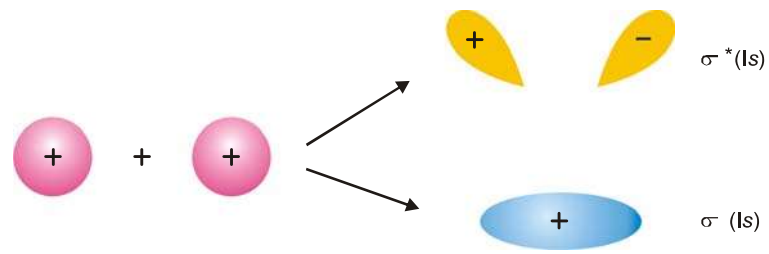

Figure 6.29
Formation of molecular orbitals from two Is orbitals of hydrogen atoms.

The wave functions either have (+) or (–) sign. The positive sign shown on 1*s* orbitals of hydrogen atoms shows that these orbitals are spherically symmetrical and their wave functions are associated with +ve sign in all directions. In case of *p*-orbitals one lobe has +ve sign while other has –ve sign. The overlapping of atomic orbitals takes place if they have similar signs on their lobes.

The probability density in bonding and antibonding molecular orbitals is given by the square of the wave functions shown in the equations (*i*) and (*ii*)

$$\psi^2_{(MO)} = (\psi_A + \psi_B)^2$$

$$= \psi^2_A + \psi^2_B + 2\psi_A\psi_B \qquad ...(iii)$$

and

$$\psi^{*2}_{(MO)} = (\psi_A - \psi_B)^2$$

$$= \psi^2_A + \psi^2_B - 2\psi_A\psi_B \qquad ...(iv)$$

From equation (*iii*) it is clear that probability density of bonding molecular orbital is greater than the sum of the probability densities of isolated atoms by the factor $2\psi_A\,\psi_B$. Thus the probability density of electrons in bonding MO is greater than that in either of atomic orbitals (ψ_A^2 or ψ_B^2).

From equation (*iv*) it is clear that probability density of antibonding MO is lesser than the sum of probability densities of isolated atoms by a factor $2\psi_A\,\psi_B$. Thus the probability density of electrons in antibonding MO is less than that in either of atomic orbitals (ψ_A^2 or ψ_B^2). In a similar way, the combination of two 2*s* orbitals produces a bonding σ (2*s*) and antibonding σ* (2*s*) molecular orbitals.

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Relative Energies of bonding and antibonding MOs

We have seen above that when atomic orbitals combine, an equivalent number of new orbitals is formed. For example, when two 1*s* orbitals combine two new molecular orbitals are formed. One of these pertains to the bonding molecular orbital with lower energy while the other corresponds to higher energy as compared to both the atomic orbitals concerned in the process. Thus we find that the number of molecular orbitals formed from atomic orbitals is equal to the number of atomic orbitals responsible for their formation and are of two types as shown below. (Fig. 6.30)

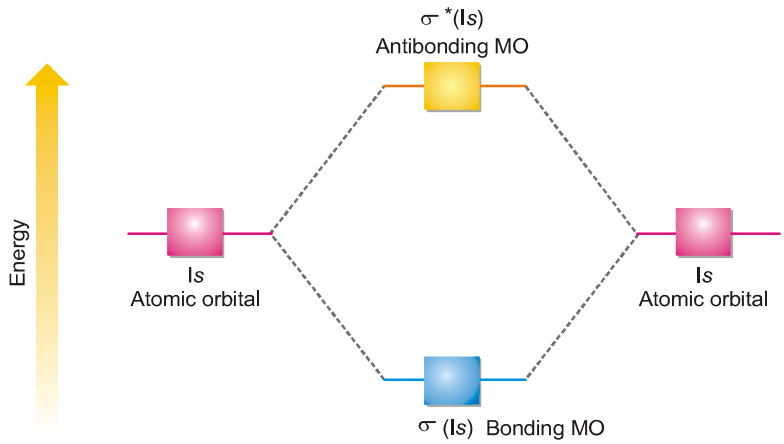

Figure 6.30
Energy level diagram for bonding and antibonding molecular orbitals arising from Is atomic orbital.

Molecular Orbitals from p-Atomic Orbitals

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

(1) Combination of $2p_z$ atomic orbitals

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

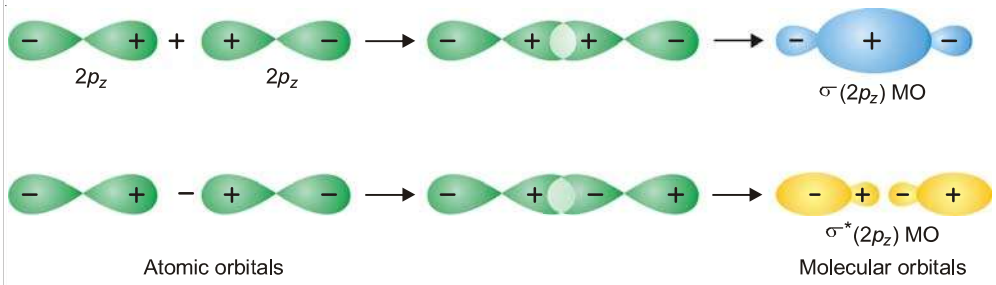

Figure 6.31
Combination of $2p_z$ orbitals to form bonding σ ($2p_z$) and antibonding σ*($2p_z$) molecular orbitals.

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(2) Combination of $2p_y$ and $2p_x$ atomic orbitals

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

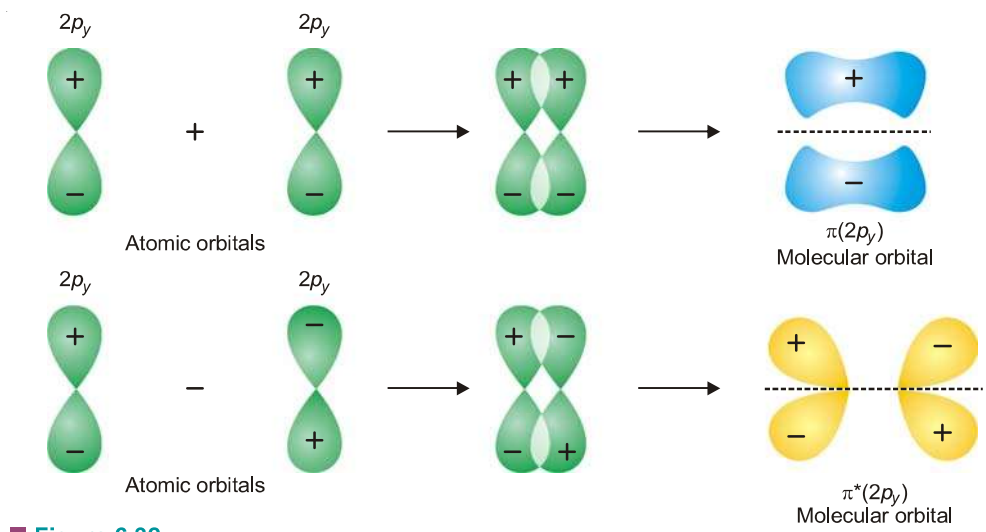

Figure 6.32
Formation of bonding and antibonding molecular orbitals by side-wise overlap of $2p_y$ atomic orbitals. $2p_x$ Orbitals also combine in the similar way.

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

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

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

They are arranged in their increasing order of energy as determined by spectroscopic measurements. It is clear from Fig. 6.33 that the three $2p$ atomic orbitals of isolated atoms are all degenerate but this degeneracy splits in the molecular orbitals. The $\sigma(2p_z)$ bonding molecular orbital has a lower energy than either of the remaining two degenerate π bonding molecular orbitals –$\pi(2p_y)$ and $\pi(2p_x)$. For diatomic molecules obtained from atom having more than one electronic shell, the inner shells do not appreciably affect the bonding and may be omitted. Such inner electrons are called Non-bonding electrons. Electronic structures of simple molecules can be worked out by feeding electrons in the molecular orbitals in the order of increasing energy. Here also Aufbau principle–feeding electrons in the increasing order of energy of orbitals repeats itself. This order shown in Fig. 6.33 may be written as :

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

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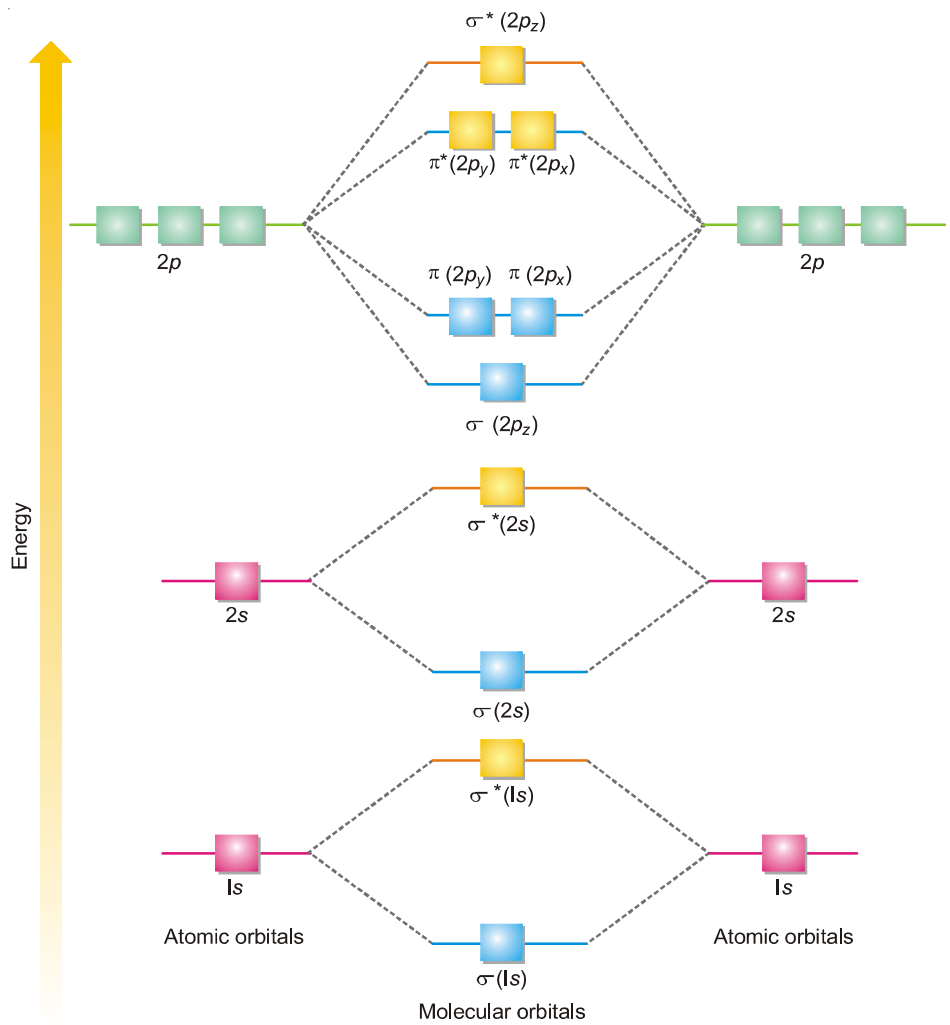

Figure 6.33
Schematic energy level representation of molecular orbitals for simple molecules of elements.

Conditions for the combination of Atomic Orbitals

The atomic orbitals may combine when certain conditions are met with. For effective combinations of atomic orbitals following are the conditions.

(1) The energies of atomic orbitals should be comparable. For homonuclear diatomic molecules of the type X_2 similar atomic orbitals combine *i.e.* 1*s* orbital of one atom combines with 1*s* orbital of another and similarly 2*s* orbital combines with 2*s* orbital of another atom and so on. This means that 1*s* orbital cannot combine with 2*s* orbital because of large energy difference between the two orbitals. In case homonuclear molecules this condition may not be valid.

(2) The extent of overlap between the atomic orbitals should be to a considerable extent. Greater the overlap between the atomic orbitals, greater is charge density between the nuclei.

(3) The symmetry of the combining atomic orbitals should be the same. The atomic orbitals should have the same symmetry about the internuclear axis. For example, 2*s* orbital of one atom can combine with 2*s* or $2p_z$ orbital of another atom but not with the $2p_y$ or $2p_x$ orbital. In other words

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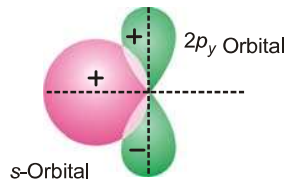
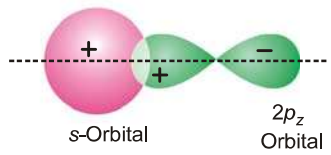
++ or – – interaction is allowed. It is made clear in the following diagram :



s-Orbital does not combine with $2p_y$ orbital because they do not have the same symmetry about the internuclear axis.



s-Orbital combines with $2p_z$ orbital as they have same symmetry about the internuclear axis.

Allowed Combinations of Atomic orbitals

Due to symmetry reasons allowed combinations of atomic orbitals are given in Table 6.1.

TABLE 6.1. ALLOWED COMBINATIONS OF ATOMIC ORBITALS

1st Orbital	2nd Orbital	Type of MO formed
s-orbital	*s*-orbital	σ (Sigma)
s-orbital	p_z-orbital	σ (Sigma)
p_z-orbital	p_z-orbital	σ (Sigma)
p_y-orbital	p_y-orbital	π (pi)
p_x-orbital	p_x-orbital	π (pi)

Energy Levels of Molecular orbitals

We have already discussed that the energy of a bonding MO is lesser than that of atomic orbital whereas the energy of an antibonding MO is higher than the atomic orbitals from which it has been formed. This was shown in Fig. 6.30 for hydrogen molecule.

The total energy of a diatomic molecule can also be plotted against the internuclear distance between its atoms. When these two atoms are brought closer the energy changes are shown in Fig. 6.34.

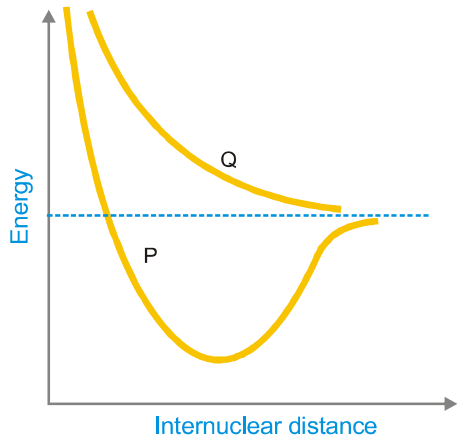


Figure 6.34
Plot of energy of diatomic molecules versus internuclear distance.

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The curve *P* represents the formation of a bonding molecular orbital and the curve *Q* represents the formation of an antibonding molecular orbital. It is clear from the curve *Q* that repulsive forces dominate during the formation of an antibonding molecular orbital. During the formation of a bonding molecular orbital the energy starts decreasing and reaches to a minimum value which corresponds to the bond length between the two atoms (r_0). At a distance less than r_0 the repulsive forces start dominating over the attractive forces and energy starts increasing.

Difference Between Bonding and Antibonding Molecular Orbitals

The difference between bonding and antibonding orbitals is summarised below :

TABLE 6.2. DIFFERENCE BETWEEN BONDING AND ANTIBONDING MOLECULAR ORBITALS

Bonding MO	Antibonding MO
1. It is formed by **addition** overlap of atomic orbitals.	1. It is formed by **subtraction** overlap of atomic orbitals.
2. The wave function of a bonding MO is given by $\psi_{(MO)} = \psi_A + \psi_B$	2. The wave function of an antibonding MO is given by $\psi^*_{(MO)} = \psi_A - \psi_B$
3. Its formation takes place when the lobes of atomic orbitals have **same** signs.	3. Its formation takes place when the lobes of atomic orbitals have **different** signs.
4. The energy of bonding MO is **lower** than that of atomic orbitals from which it is formed.	4. The energy of antibonding MO is **higher** than that of atomic orbitals from which it is formed.
5. The electron density is **high** in the region between the nuclei of bonded atoms.	5. The electron density is **low** in the region between the nuclei of bonded atoms.
6. Every electron in bonding MO contributes towards the **attractive force.**	6. Every electron in antibonding contributes towards **repulsive force.**

Combination of s and p_z-orbitals

s and p_z-orbitals can also combine in a similar way along internuclear axis to form bonding and antibonding molecular orbitals as shown in Fig. 6.35.

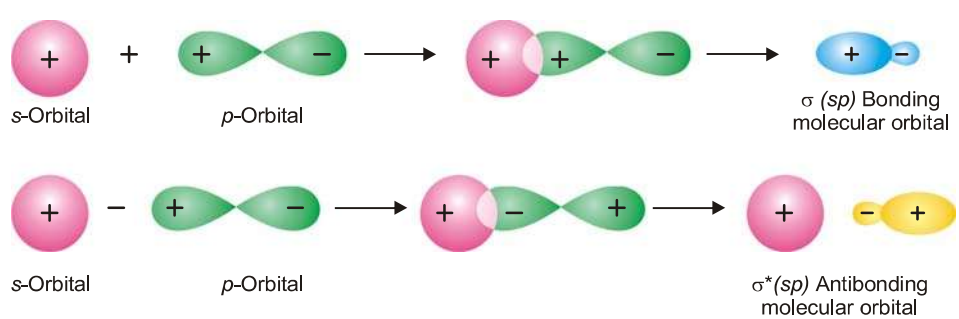

Figure 6.35
Formation of bonding and antibonding orbitals by the combination of *s* and p_z orbitals.

Difference between Sigma and Pi molecular orbitals

The main points of difference between sigma and Pi molecular orbitals can be summed up in the Table 6.3.

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TABLE 6.3. DIFFERENCE BETWEEN SIGMA AND PI MOLECULAR ORBITALS

Sigma (σ) MO	Pi (π) MO
1. It is formed by **head to head** overlapping of atomic orbitals.	1. It is formed by the **sidewise** overlapping of p_y or p_x atomic orbitals.
2. The overlap is **along internuclear axis.**	2. The overlap is **perpendicular** to **internuclear** axis.
3. As a result of this **strong** bond is formed.	3. As a result of this **weak** bond is formed.
4. This orbital is **symmetrical to rotation** about the line joining the two nuclei.	4. This orbital is **not symmetrical to rotation** about the line joining the two nuclei.
5. The region of overlap is **greater.**	5. The region of overlap is **lesser.**

BOND ORDER

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

$$\text{Bond order} = \frac{\begin{pmatrix}\text{No. of electrons in}\\ \text{bonding orbitals}\end{pmatrix} - \begin{pmatrix}\text{No. of electrons in}\\ \text{antibonding orbitals}\end{pmatrix}}{2} = \frac{N_b - N_a}{2}$$

In common practice, only MOs formed from valence orbitals are considered for determining bond order.

The predicted bond orders are found to be in conformity with other methods of determining it. Thus Molecular Orbital theory helps in establishing whether the existence of a bond is feasible or not. For instance, the formation of He_2 molecule, discussed in the following section, is completely ruled out as the bond order predicted is zero.

In general,

(*a*) A molecule is stable if $N_b > N_a$

(*b*) A molecule is unstable if $N_b < N_a$

Information given by Bond order

The bond order as determined by the above formula is very helpful as it gives us the following valuable information :

(1) Stability of the Molecule/Ion

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

(2) Bond Dissociation Energy

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

(3) Bond Length

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

(4) Magnetic Properties

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

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