



Module 1: Chemical Bonding

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Module outline:

Molecular orbital theory (MOT)

Applications of MOT in diatomic molecules

Band theory of solids

1.1 INTRODUCTION

The attractive force which holds various constituents (atoms, ions etc.) together in different chemical species is called a chemical bond. Since the formation of chemical compounds takes place as a result of combination of atoms of various elements in different ways.

Three different types of bond may be formed, depending on the electropositive or electronegative character of the atoms involved.

Electropositive elements + Electronegative elements \longrightarrow Ionic bond e.g. NaCl

Electronegative element + Electronegative elements \longrightarrow Covalent bond e.g. HCl

Electropositive elements + Electropositive elements \longrightarrow Metallic bond e.g. Li metal

There are theories of chemical bonding to explain geometry, energy and other molecular parameters. Kossel, Lewis, Sidwick and other have given electronic theory of valency to explain ionic, covalent and coordinate bonds. Two other theories are valence bond theory (VBT) and molecular orbital theory (MOT). Valence bond theory was given by Heitler, London, Slater and Pauling. According to this theory, atoms retain their identities after formation of chemical bond. Also the theory was unable to explain paramagnetic nature of oxygen molecule, bonding in metals and polar nature in covalent molecules.

Molecular orbital theory (MOT) is good for understanding bonding in general. It is more difficult to learn, but predicts the actual properties of molecules better than valence bond theory (VBT). Molecular orbital theory actually predicts electron transitions because of the differences in the energy levels of orbitals in the molecule. Molecular orbital theory has been more correct in numerous instances and for this reason it is preferred.

1.2 MOLECULAR ORBITAL THEORY

Molecular orbital (MO) theory was developed by F. Hund and R. S. Mulliken in 1932. The salient features of this theory are:

1. The electrons in the molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
2. The atomic orbitals are of comparable energies and proper symmetry combines to form molecular orbitals.
3. While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.
4. The number of molecular orbitals formed is equal to number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbitals (BMO) and other is called antibonding molecular orbital (ABMO).
5. The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
6. Just as electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecular is given by a molecular orbital.

7. The molecular orbitals like atomic orbitals are filled in accordance with the Aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.

1.3 LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

According to wave mechanics, the atomic orbital can be expressed by wave functions (ψ 's) which represent the amplitude of electron waves. These are obtained from the solution of Schrodinger wave equation.

However, since it can be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecular are difficult to obtain directly from the solution of Schrodinger wave equation. To overcome this problem, an approximate method known as 'linear combination of atomic orbitals' (LCAO) has been adopted.

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

$$\psi_{MO} = \psi_A \pm \psi_B$$

Therefore, the two molecular orbitals σ and σ^* are formed as:

$$\sigma = \psi_A + \psi_B$$

$$\sigma^* = \psi_A - \psi_B$$

The molecular orbital σ formed by the addition of atomic orbitals is called the bonding molecular orbital while the molecular orbital σ^* formed by the subtraction of atomic orbital is called antibonding molecular orbital as depicted in Fig. 1.1.

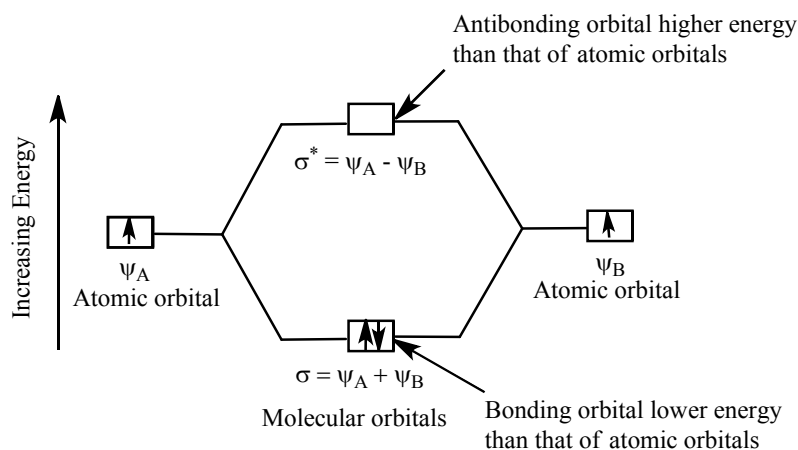


Fig. 1.1: Formation of bonding (σ) and antibonding (σ^*) molecular orbitals by the linear combination of atomic orbitals ψ_A and ψ_B centered on two atoms A and B respectively.

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

As a result, the electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei. In fact there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of the atomic orbitals that have

combined to form it. In contrast, the electrons placed in the antibonding molecular orbitals destabilize the molecule. This is because, the mutual repulsion of the electrons in these orbitals is more than the attraction between the electrons and the nuclei, which causes a net increase in energy.

It may be noted that the energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy of the bonding orbital has been lowered than the parent orbitals.

1.4 CONDITIONS FOR THE COMBINATION OF ATOMIC ORBITALS

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied.

- The combining atomic orbitals must have the same or nearly the same energy.** This means 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. This is not true if the atoms are very different.
- The combining atomic orbitals must have the same symmetry about the molecular axis.** By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, $2p_z$ orbital of one atom can combine with $2p_z$ orbital of the other atom but not with the $2p_x$ or $2p_y$ orbitals because of their different symmetries.
- The combining atomic orbitals must overlap to the maximum extent.** Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

1.5 TYPES OF MOLECULAR ORBITALS

Molecular orbitals of diatomic molecular are designated as σ (sigma), π (pi) and δ (delta) etc. In this nomenclature, the sigma (σ) molecular orbitals are symmetrical around the bond axis while pi (π) molecular orbitals are not symmetrical.

For example: The linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond axis. Such molecular orbitals are of the sigma (σ) type and are designated as $\sigma 1s$ and $\sigma^* 1s$. If internuclear axis is taken to be in the z-direction it can be seen that a linear combination of $2p_z$ orbitals of two atoms also produces two sigma molecular orbitals designated as $\sigma 2p_z$ and $\sigma^* 2p_z$. Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane. Such molecular orbitals are labeled as π and π^* . A π bonding MO has larger electron density above and below the internuclear axis. The π^* anti-bonding MO has a node between the nuclei. Following molecular orbitals are formed when atomic orbitals combine.

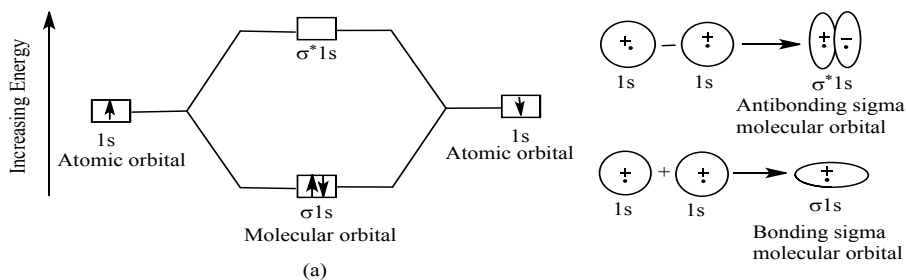
Table 1.1

Atomic Orbitals	Molecular orbitals	
	Bonding	Antibonding
1s + 1s	$\sigma 1s$	$\sigma^* 1s$
2s + 2s	$\sigma 2s$	$\sigma^* 2s$
$2p_z + 2p_z$	$\sigma 2p_z$	$\sigma^* 2p_z$
$2p_x + 2p_x$	$\pi 2p_x$	$\pi^* 2p_x$
$2p_y + 2p_y$	$\pi 2p_y$	$\pi^* 2p_y$

1.6 ENERGY LEVEL DIAGRAM OF MOLECULAR ORBITALS

We have seen that 1s atomic orbitals on two atoms form two molecular orbitals designated as $\sigma 1s$ and $\sigma^* 1s$. In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals:

Antibonding MOs $\sigma^* 2s$ $\sigma^* 2p_z$ $\pi^* 2p_x$ $\pi^* 2p_y$
 Bonding MOs $\sigma 2s$ $\sigma 2p_z$ $\pi 2p_x$ $\pi 2p_y$



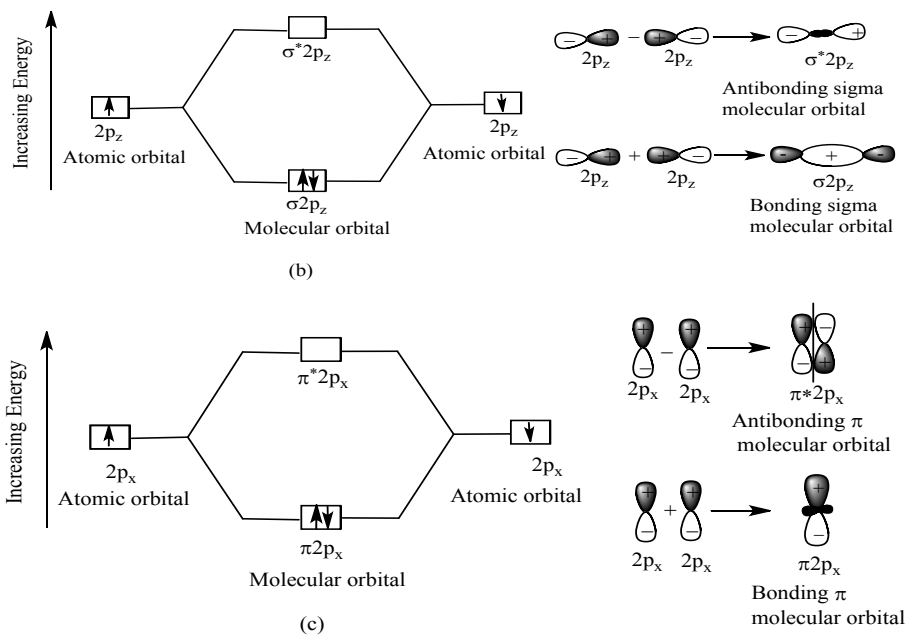
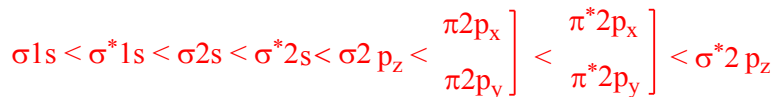
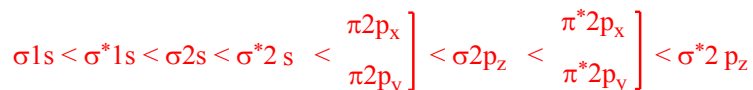


Fig. 1.2: Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) $1s$ atomic orbitals (b) $2p_z$ atomic orbital (c) $2p_x$ atomic orbital

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals of O_2 and F_2 is given below:



However, this sequence of energies levels of MO is not correct for the remaining molecules Li_2 , Be_2 , B_2 , C_2 , N_2 for instance, it has been observed experimentally that for molecules such as B_2 , C_2 , N_2 etc. The increasing order of energies of various molecular orbitals is:



The important characteristics feature of this order is that the energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals. The energy of $\pi(2p_x)$, $\pi(2p_y)$ and $\pi^*(2p_x)$, $\pi^*(2p_y)$ molecular orbitals are same, that is why they are placed at same level.

In case of small size molecules, the energy difference between $\sigma^*(2s)$ and $\sigma(2p_z)$ becomes small, because of this, repulsion occurs between these two molecular orbitals. Therefore, in small size molecules $\sigma(2p_z)$ moves away from $\sigma^*(2s)$ and $\pi(2p_x)$ and $\pi(2p_y)$ molecular orbital exist near the $\sigma^*(2s)$.

1.7 DIFFERENCE BETWEEN BONDING MOLECULAR ORBITALS AND ANTI BONDING MOLECULAR ORBITALS

BMO (Bonding Molecular Orbitals)	ABMO (Antibonding Molecular Orbitals)
1. BMO is formed by addition overlap of atomic orbitals	1. ABMO is formed by the subtraction overlap of atomic orbitals.
2. $\psi_b = \psi_1 + \psi_2$	2. $\psi_a = \psi_1 - \psi_2$
3. It may or may not have a node.	3. It always has a node in between the nuclei of bonded atoms.

4. It has higher probability density. $\psi_b^2 = \psi_1^2 + \psi_2^2 + 2\psi_1\psi_2$	4. It has lower probability density; $\psi_a^2 = \psi_1^2 + \psi_2^2 - 2\psi_1\psi_2$
5. Electrons in this orbital lead to attraction between atoms.	5. Electrons in this orbital lead to repulsion between the atoms.
6. Its energy is less than the energy of combining atomic orbitals.	6. Its energy is more than the energy of combining atomic orbitals.
7. It stabilizes the molecule.	7. It destabilizes the molecule.
8. It is denoted by Greek letter σ , π , δ etc.	8. It is denoted by Greek letter σ^* , π^* , δ^* etc.

1.8 BOND ORDER

Bond order is a parameter that determines the stability of a molecule. It may be defined as half the difference between number of electrons in bonding molecular orbitals (N_b) and the number of electrons in antibonding molecular orbitals (N_a) i.e.

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

1.9 SIGNIFICANCE OF BOND ORDER

1. Bond order \propto stability of a molecule.

Bond order of a molecule is equal to the number of covalent bonds between the atoms in a molecule

- a. If the value of bond order is positive, molecule exists and is stable.
 - b. If the value of bond order is zero, molecule does not exist.
 - c. If the value of bond order is fractional ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$), molecule or species exists but is unstable.
2. Bond order \propto bond dissociation energy. Greater the bond order more is the number of bonds and the strength of a molecule increases.
 3. Bond order $\propto \frac{1}{\text{Bond length}}$
 4. Greater the bond order, shorter will be the bond length.
 5. The magnetic behavior of a molecule can also be predicted, i.e. if all electrons in a molecule are paired, the substance is diamagnetic and in case there are unpaired electrons in a molecule, the substance is paramagnetic. It may be noted that if the bond order is fractional, the molecule will definitely be paramagnetic. However, if the bond order is whole number the molecule may or may not be paramagnetic.

1.10 MOLECULAR ORBITAL DIAGRAM OF SOME HOMONUCLEAR, DIATOMIC MOLECULES/ IONS

1.10.1 Hydrogen molecule (H_2)

It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1s atomic orbital. Therefore, in hydrogen molecule total electrons are two which are present in $\sigma 1s$ molecular orbital.

Electronic configuration of H_2 molecule is $\sigma 1s^2$

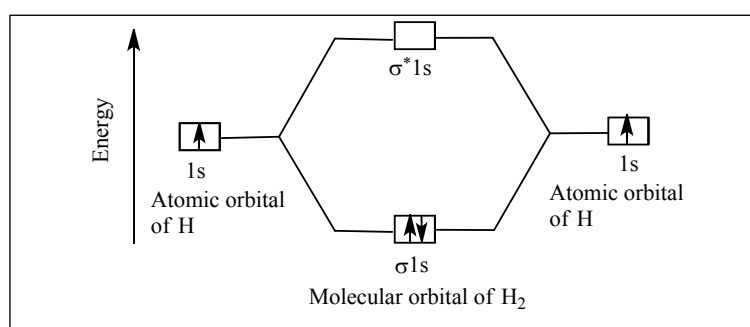


Fig. 1.3: MO energy level diagram of Hydrogen molecule

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

Thus, two hydrogen atoms are bonded together by a single covalent bond [H-H]. Since no unpaired electron is present in hydrogen molecule, therefore it is diamagnetic.

1.10.2 Helium Molecule (He₂)

Atomic electronic configuration of Helium: ${}_2\text{He} = 1s^2$

Total number of electrons in He₂ molecule is $(2+2) = 4$.

Molecular orbital configuration of He₂ molecule is $\sigma 1s^2 \sigma^* 1s^2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 2}{2} = 0$$

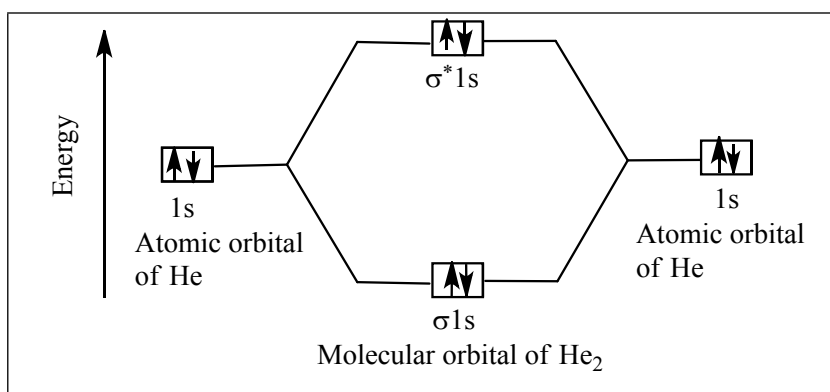


Fig. 1.4: MO energy level diagram of Helium molecule

Since in this case bond order is zero, therefore, Helium molecule does not exist.

Table 1.2

Atomic Electronic Configuration	Molecule	Total no. of electron in Molecule	Molecular orbital configuration	Bond order	No. of unpaired electrons	Magnetic character
${}_3\text{Li} : 1s^2 2s^1$	Li ₂	6	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^0$	$\frac{4-2}{2} = 1$	Zero	Diamagnetic
${}_4\text{Be} : 1s^2 2s^2$	Be ₂	8	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2$	$\frac{4-4}{2} = 0$	Zero	Diamagnetic
${}_5\text{B} : 1s^2 2s^2 2p_x^1$	B ₂	10	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \begin{matrix} \pi 2p_x^1 \\ \pi 2p_y^1 \end{matrix}$	$\frac{6-4}{2} = 1$	Two	Paramagnetic
${}_6\text{C} : 1s^2 2s^2 2p_x^1 2p_y^1$	C ₂	12	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \begin{matrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{matrix}$	$\frac{8-4}{2} = 2$	Zero	Diamagnetic

1.10.3 Nitrogen Molecule (N₂)

Atomic electronic configuration of nitrogen:

$${}_7\text{N} = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$$

Total number of electrons in N₂ molecule is $(7+7) = 14$

Molecular orbital configuration of N₂ molecule is,

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \begin{matrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{matrix} < \sigma 2p_z^2$$

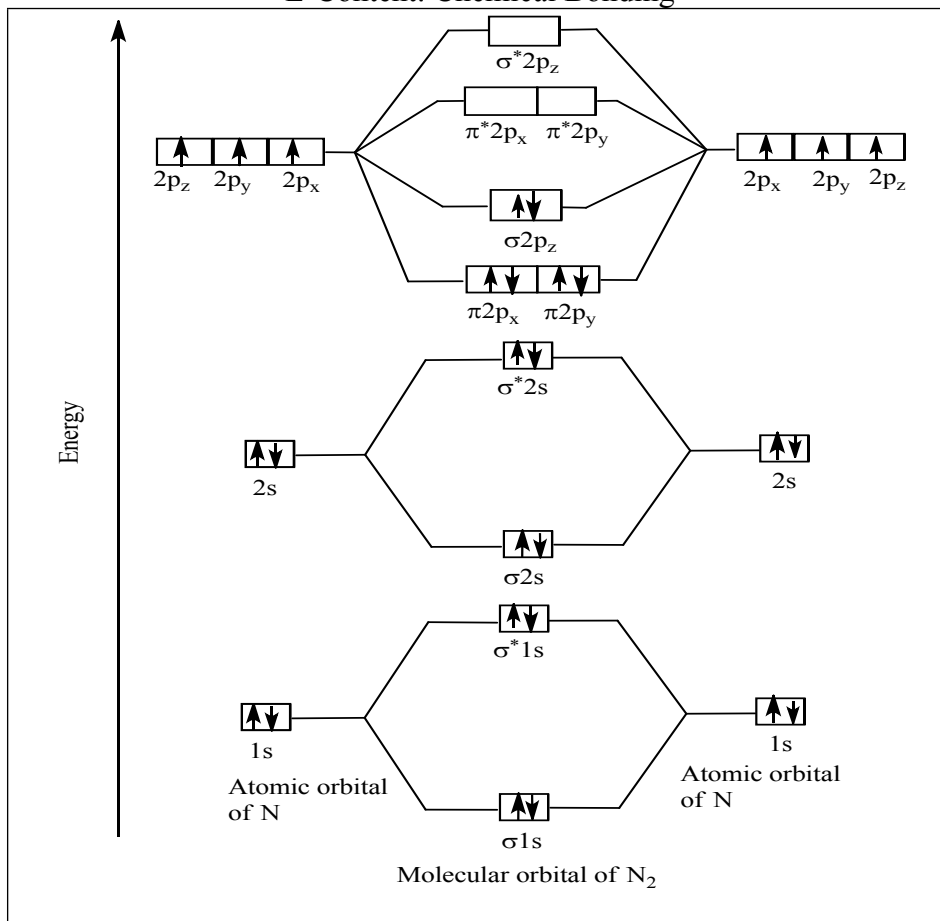


Fig. 1.5: MO energy level diagram of Nitrogen molecule

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

The two nitrogen atoms are strongly bonded by triple bond. As it has no unpaired electron, so nitrogen molecule is diamagnetic.

Table 1.3

Ion	N_2^+	N_2^-	N_2^{2+}
Total Number of Electrons	$(14-1) = 13$	$(14 + 1) = 15$	$(14 - 2) = 12$
Molecular Orbital Configuration	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_x^2 < \pi 2p_y^2 < \sigma 2p_z^1$	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_x^2 < \pi 2p_y^2 < \sigma 2p_z^2 < \pi^* 2p_x^1 < \pi^* 2p_y^1$	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_x^2 < \pi 2p_y^2$
Bond Order	$\frac{9-4}{2} = 2.5$	$\frac{10-5}{2} = 2.5$	$\frac{8-4}{2} = 2$
No. of Unpaired Electrons	One	One	Zero
Magnetic Character	Paramagnetic	Paramagnetic	Diamagnetic
Stability Order*	$N_2^+ > N_2^- > N_2^{2+}$		
Bond dissociation energy order	$N_2^+ > N_2^- > N_2^{2+}$		
Bond length order	$N_2^{2+} > N_2^- > N_2^+$		

Note

1. Bond order of both N_2^+ and N_2^- is 2.5 but N_2^- ion is less stable than N_2^+ ion. This is attributable to the presence of one electron in the antibonding molecular orbital due to which the destabilizing effect is more and hence the stability is less.
2. The electronic configuration of derivative ions like $N_2^+ > N_2^- > N_2^{2+}$ will be depend on the electronic configuration of parent neutral molecule (N_2).

1.10.4 Oxygen Molecule (O_2)

Atomic orbital configuration of oxygen atom is ${}_8O = 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

Total number of electrons in O_2 molecule is $(8+8) = 16$.

Molecular orbital configuration of O_2 molecule is :

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \left[\begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right] < \left[\begin{array}{l} \pi^* 2p_x^1 \\ \pi^* 2p_y^1 \end{array} \right]$$

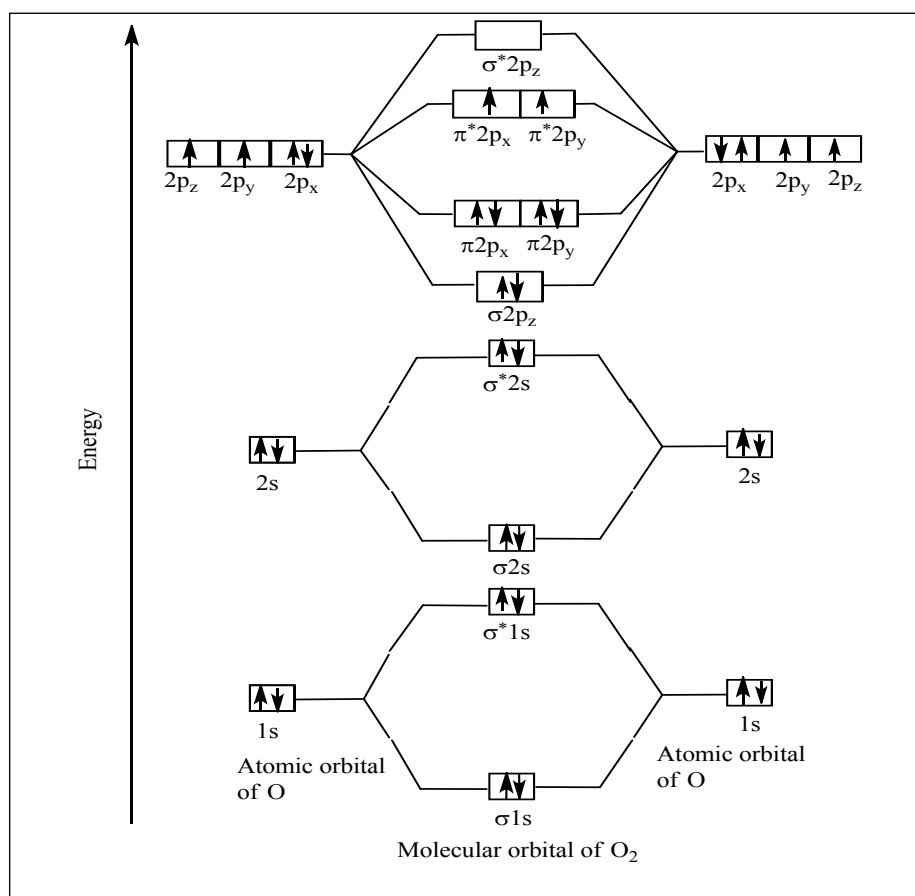


Fig. 1.6: MO energy level diagram of Oxygen molecule

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$$

So in oxygen molecule, two oxygen atom are held by a double bond. From the MO diagram of oxygen molecule, it has two unpaired electrons, so oxygen molecule is paramagnetic.

Table 1.4

Ion	O_2^+	O_2^-	O_2^{2-}
Total Number of Electrons	$(16 - 1) = 15$	$(16 + 1) = 17$	$(16 + 2) = 18$

Molecular Orbital Configuration	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2$ $< \sigma 2p_z^2 < \begin{matrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{matrix} < \begin{matrix} \pi^* 2p_x^1 \\ \pi^* 2p_y^1 \end{matrix}$	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2$ $< \sigma 2p_z^2 < \begin{matrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{matrix} < \begin{matrix} \pi^* 2p_x^2 \\ \pi^* 2p_y^1 \end{matrix}$	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2$ $< \sigma 2p_z^2 < \begin{matrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{matrix} < \begin{matrix} \pi^* 2p_x^2 \\ \pi^* 2p_y^2 \end{matrix}$
Bond Order	$\frac{10-5}{2} = 2.5$	$\frac{10-7}{2} = 1.5$	$\frac{10-8}{2} = 1$
No. of Unpaired Electrons	One	One	Zero
Magnetic Character	Paramagnetic	Paramagnetic	Diamagnetic
Stability Order*	$O_2^+ > O_2^- > O_2^{2-}$		
Bond dissociation energy order	$O_2^+ > O_2^- > O_2^{2-}$		
Bond length Order	$O_2^{2-} > O_2^- > O_2^+$		

1.10.5 Fluorine Molecule (F₂)

Atomic electronic configuration of fluorine is

$${}_9F = 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$$

Total number of electrons in F₂ molecule is (9+9) = 18

Molecular orbital configuration of F₂ molecule is

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \begin{matrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{matrix} < \begin{matrix} \pi^* 2p_x^2 \\ \pi^* 2p_y^2 \end{matrix}$$

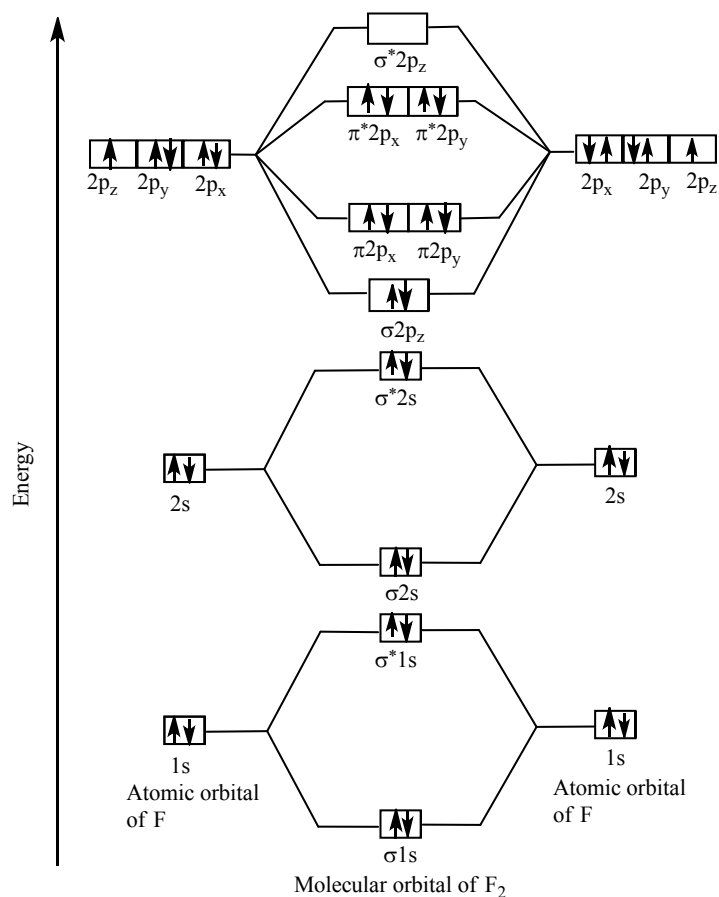


Fig. 1.7: MO energy level diagram of Fluorine molecule

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 8}{2} = 1$$

Fluorine molecule exists and stable. It is a diamagnetic due to absence of unpaired electrons as shown in the molecular orbital diagram.

1.11 MOLECULAR ORBITAL DIAGRAM OF SOME HETERONUCLEAR DIATOMIC MOLECULES/ IONS

The molecular orbitals of heteronuclear diatomic species of AB type (e.g. HF, HCl, CO, NO, CN etc.) differ from those of homonuclear diatomic molecules. Since the two combining atoms are of different electronegativities, the electron distribution is not symmetrical.

The Atomic Orbitals of Heteronuclear molecules are present in two different energy levels whereas in Homonuclear, they are present at same level in M.O. energy level diagram:

1.11.1 Hydrogen Fluoride (HF) Molecule

The hydrogen atom (atomic number = 1) and fluorine atom (atomic number = 9) have one and nine electron respectively. Their electronic configurations are:

$${}_1\text{H} = 1s^1$$

$${}_9\text{F} = 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$$

Thus, in HF molecule, there are ten electrons which need to be accommodated in the molecular orbital of HF molecule. The formation of HF molecule occurs by linear combination of 1s atomic orbital of hydrogen atom with $2p_x$ orbital of fluorine atom. Combination with 1s and 2s atomic orbitals of F can be ruled out because their energies are too low. If overlap occurred between the fluorine $2p_y$ and $2p_x$ orbitals it would be non-bonding. This is because the positive lobe of hydrogen will overlap equally with the positive and negative lobes of the $2p_y$ and $2p_z$ atomic orbitals of F atom. Thus, the only effective overlap is with the fluorine $2p_x$ orbital.

Thus combination of H ($1s^1$) and F ($2p_x^1$) gives both bonding (σ_{sp_z}) and antibonding ($\sigma^*_{sp_z}$) orbitals. Moreover, the two electrons occupy the bonding molecular orbitals leaving the antibonding molecular orbital ($\sigma^*_{sp_z}$) empty. The F ($2p_z$) atomic orbital contributes more than the H ($1s$) atomic orbital to the bonding (σ_{sp_z}) molecular orbital.

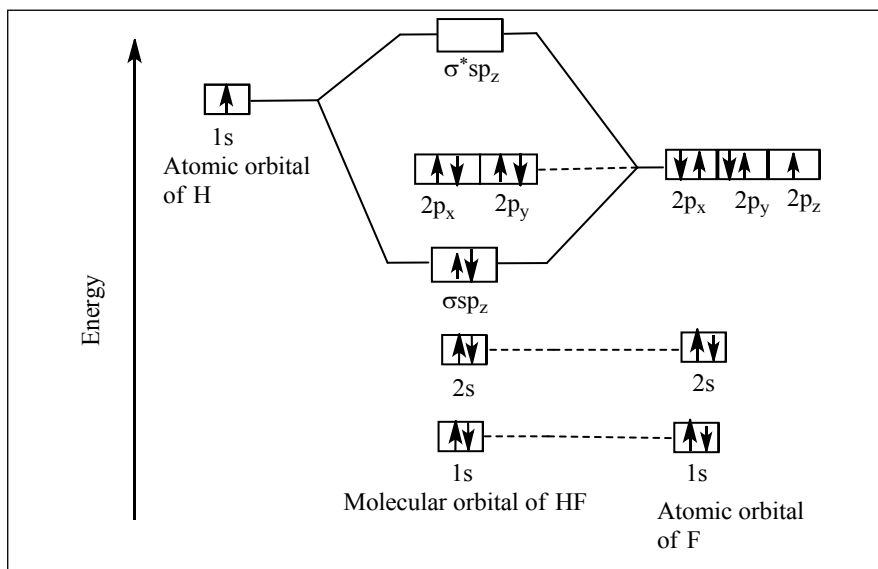


Fig 1.8: Molecular orbital energy level diagram for HF molecule.

The over-simplification ignores any ionic contribution such as can be shown with the valence bond resonance structures $\text{H}^+ \text{F}^-$ and $\text{H}^- \text{F}^+$. The former would be expected to contribute significantly (As fluorine is more electronegative than hydrogen), resulting in a strong bond.

The molecular orbital electronic configuration of HF molecule is:

$$1s^2 < 2s^2 < \sigma sp_z^2 < \begin{matrix} 2p_x^2 \\ 2p_y^2 \end{matrix} < \sigma^* sp_z$$

Magnetic energy: Since all the molecular orbitals, (where nonbonding or bonding molecular orbital) are completely filled, so HF molecule is diamagnetic.

Bond order of HF molecule

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

1.11.2 Hydrogen Chloride (HCl) Molecule

The hydrogen atom (atomic number = 1) and fluorine atom (atomic number = 17) have one and nine electron respectively. Their electronic configurations are:

$${}_1\text{H} = 1s^1$$

$${}_{17}\text{Cl} = 1s^2 2s^2 2p^6 3s^2 2p_x^2 2p_y^2 2p_z^1$$

The molecular orbital electronic configuration of HCl molecule is:

$$1s^2 < 2s^2 < 2p^6 < 3s^2 < \sigma sp_z^2 < \begin{matrix} 3p_x^2 \\ 3p_y^2 \end{matrix} < \sigma^* sp_z$$

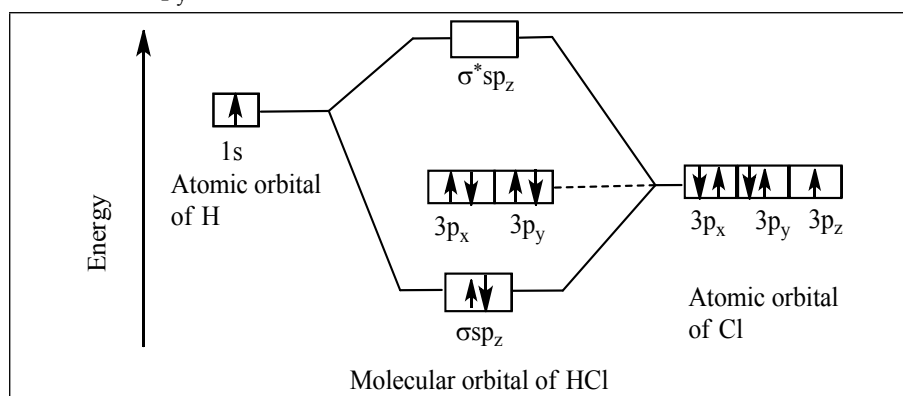


Fig 1.9: Molecular orbital energy level diagram for HCl molecule.

Magnetic energy: Since all the molecular orbitals, (where nonbonding or bonding molecular orbital) are completely filled, so HCl molecule is diamagnetic.

Bond order of HCl molecule

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

1.11.3 Carbon monoxide molecule (CO)

Electronic configurations of carbon and oxygen atoms are:

$${}_6\text{C} = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$$

$${}_8\text{O} = 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$$

Thus, in CO total (6+8) = 14 electrons are to be accommodated in the molecular orbitals of CO molecule. Molecular orbital configuration of CO is,

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \left. \begin{matrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{matrix} \right\} < \sigma 2p_z^2$$

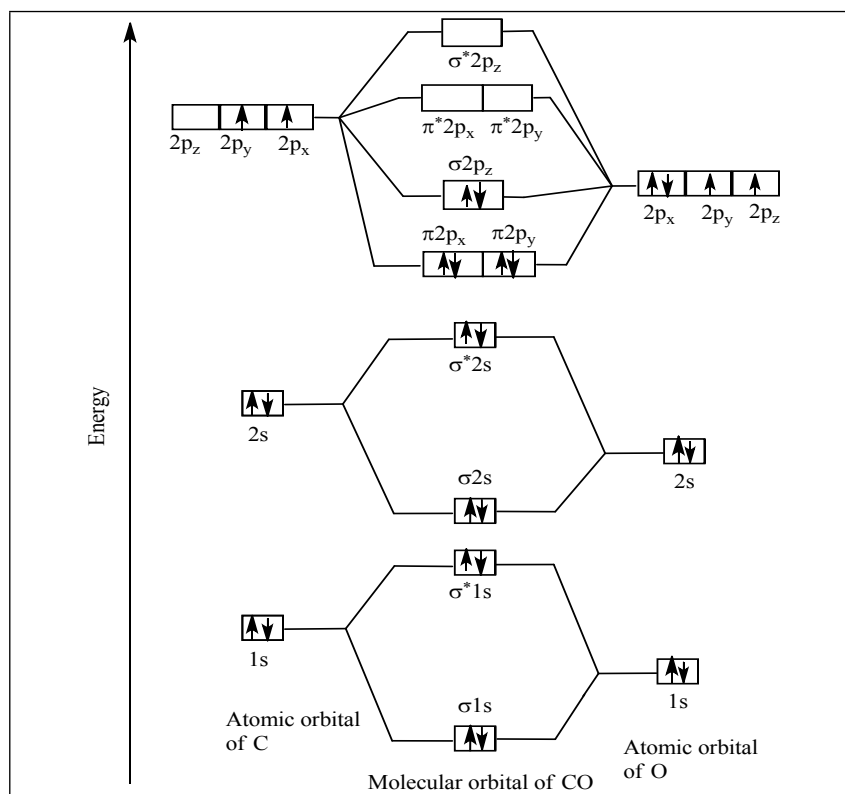


Fig 1.10: MO energy level diagram of carbon monoxide (CO)

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

Thus CO molecule has a triple bond. As it has no unpaired electrons, the molecule is diamagnetic.

Explanation of CO and CO⁺

The bond order may be calculated using the formula $(N_b - N_a)/2$, and is $(10 - 4)/2 = 3$. The simple picture is not adequate, since if CO is ionised to give CO⁺ by removal of one electron from the $\sigma 2p_z$ orbital then the bond order should be reduced to 2.5 and the bond length increased. In fact the bond length in CO is 1.128 Å and in CO⁺ it is 1.115 Å. Thus, the bond length decreases when we expected it to increase, and it indicates that the electron must have been removed from an antibonding orbital. The problem remains if we assume the order of energy for the MOs is the same as for atom heavier than carbon since this only reverse the position of the $\sigma 2p_z$ and the ($\pi 2p_x$ and $\pi 2p_y$) MOs. The most likely explanation of the bond shortening when CO is changed to CO⁺ is that the $\sigma 2s$ and $\sigma^* 2s$ molecular orbitals differ in energy more than as shown in the Fig. 1.10. This means that they are wider apart, and the $\sigma^* 2s$ MO is higher in energy than the $\sigma 2p_z$, $\pi 2p_x$ and $\pi 2p_y$ MOs. This illustrates very plainly that the order of MO energy levels for simple homonuclear diatomic molecules used above is not automatically applicable when two different types of atoms are bonded together, and it is certainly incorrect in this particular heteronuclear case.

The MO electronic configuration of CO molecule is:

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \left[\begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right] < \sigma 2p_z^2 < \sigma^* 2s^2$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = \frac{6}{2} = 3$$

Magnetic character: diamagnetic molecule

Note: CO⁺ molecular ion is more stable than CO molecule. Formation of CO⁺ from CO requires removal of one electron from an antibonding molecular orbital $\sigma^* 2s$.

$$\text{Bond order of CO}^+ = (10 - 3)/2 = 3.5$$

1.11.4 Nitric oxide molecule (NO)

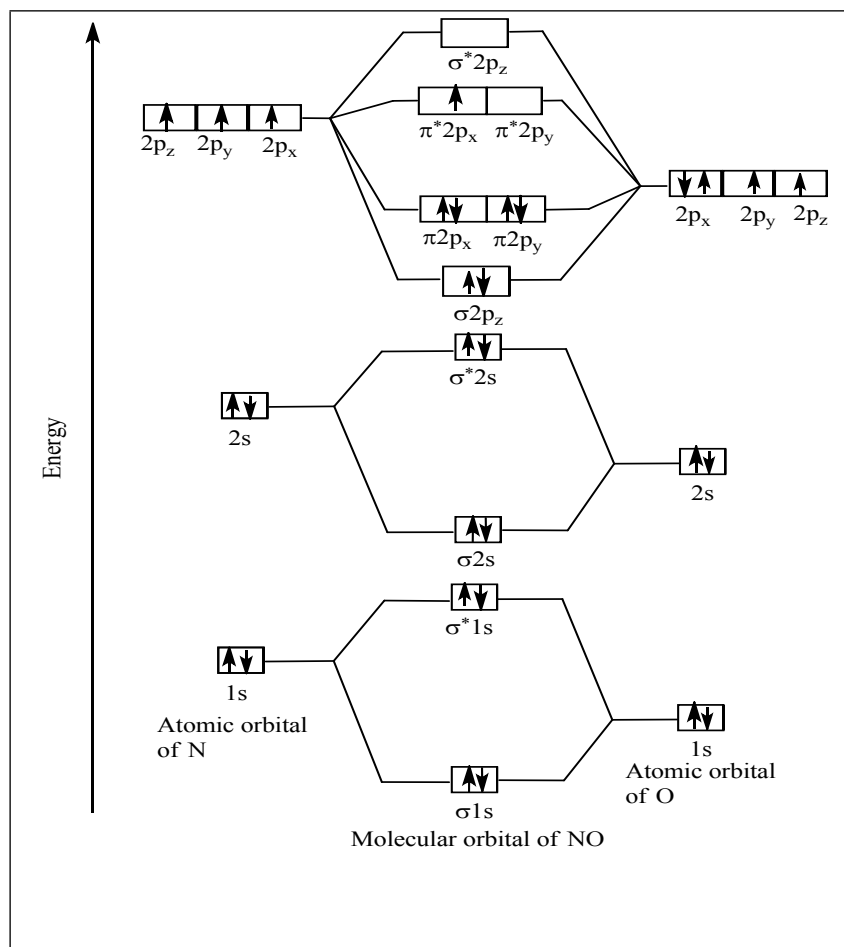
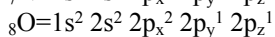
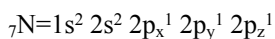


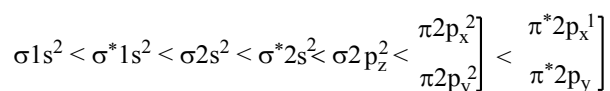
Fig. 1.12: M.O. energy level diagram of nitric oxide molecular (NO)

The electronic configurations of Nitrogen and Oxygen atoms are:



Thus total (7+8) 15 electrons are to be accommodated in the molecular orbital of NO molecule.

Molecular orbital configuration of NO is:



$$\text{Bond Order} = \frac{\text{Nb} - \text{Na}}{2} = \frac{10 - 5}{2} = 2.5$$

Nitric Oxide molecule exists. It is paramagnetic due to presence of one unpaired electron in $\pi^* 2p_x$ orbital.

Note: The molecular orbital configuration of CO is similar to isoelectronic CN^- , N_2 and O_2^{2+} .

Table: 1.5

Molecule or Ion	CN	NO^+	NO^-
Total no. of electrons	(6+7)=13	(7+7)=14	(7+9)=16
Molecular orbital configuration	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \left[\begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right] < \sigma 2p_z^1$	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \left[\begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right]$	$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \left[\begin{array}{l} \pi 2p_x^2 \\ \pi 2p_y^2 \end{array} \right] < \left[\begin{array}{l} \pi^* 2p_x^1 \\ \pi^* 2p_y^1 \end{array} \right]$

Bond order	$\frac{9-4}{2} = 2.5$	$\frac{10-4}{2} = 3$	$\frac{10-6}{2} = 2$
Number of unpaired electrons	One	Zero	Two
Magnetic character	Paramagnetic	Diamagnetic	Paramagnetic
Stability Order	$\text{NO}^+ > \text{CN} > \text{NO}^-$		
Bond Dissociation energy order	$\text{NO}^+ > \text{CN} > \text{NO}^-$		
Bond length order	$\text{NO}^- > \text{CN} > \text{NO}^+$		

1.12 COMPARISON OF VALENCE BOND AND MOLECULAR ORBITAL THEORIES

Valance Bond Theory (VBT)	Molecular Orbital Theory (MOT)
1. After the bond formation, the combining atoms in a molecule retain their identity. Bonding is explained with the help of atomic orbitals	1. After the bond formation, the combining atoms in a molecule lose their identity. Bonding is explained with the help of molecular orbitals.
2. Only the help filled atomic orbitals of the valency shell take part in bond formation.	2. It considers all the electrons in the given atoms for the prediction of number of bonds per atom.
3. The concept of resonance is applicable only to valance bond theory.	3. Resonance has no role in molecular orbital.
4. It fails to explain the paramagnetic character of O_2 molecule.	4. It explains the paramagnetic character of O_2 molecule.
5. This theory finds difficulty in explaining the stability of one and three electron bonds having unpaired electrons.	5. The formation of one electron bond and three electron bonds can be easily explained by MOT.
6. VBT fails to explain the formation of O_2^+ and O_2^- ions from O_2 , if O_2 has the stable octet.	6. MOT can explain the formation of O_2^+ and O_2^- ions from O_2 .

1.13 METALLIC BOND

Metals are characterized by the following facts:

1. They crystallize with close packing forming body centered cubic or face centered cubic lattice or hexagonal close packed lattice.
2. They are good conductors electricity and electrical conductivity decreases with temperature.
3. They can be drawn into thin wires (or metals are ductile) and can be hammered into sheets (or metals are malleable).
4. They form alloys with other metals easily and these alloys (solid solutions) also have the above listed properties.
5. Most metallic properties remain even when the metal is in the liquid state.

"Metallic bond is the electrostatic force of attraction that bind together the metallic cation and the mobile electrons and this force holds the metal atoms firmly together in the metallic crystal."

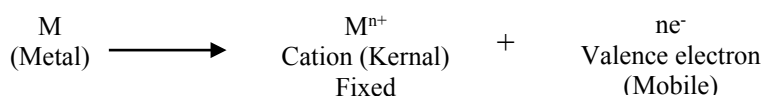
Theories to explain the nature of metallic bond

Electron sea theory.

Molecular orbital theory or band theory.

1.13.1 Electron Sea Theory

This theory is also called as electron-gas theory or electron cloud theory and was given by Lorentz. According to this theory, due to low ionization energies, metals readily lose their valence electrons and formation of positive metal ions, called Kernal.



1.13.2 Molecular Orbital Theory of Solid or Band Theory

Molecular orbital theory extended to solids is also called as band theory. Since the smallest perceptible piece of metal would contain $\sim 10^{23}$ atoms, a large number of molecular orbitals are formed from a large number of atomic orbitals.

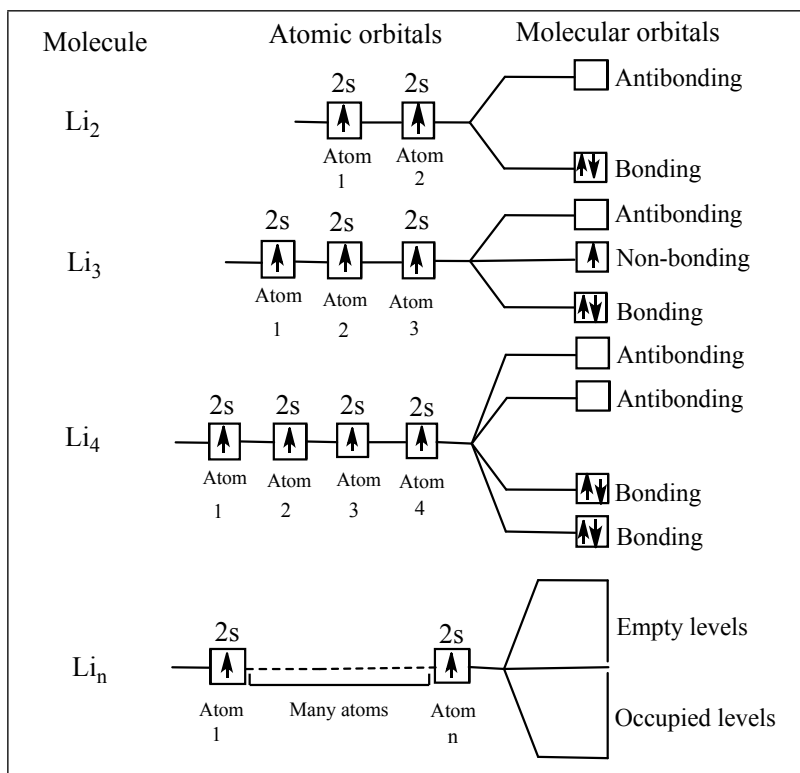


Fig 1.13: Formation of Band Theory

Let us consider an idealized one dimensional lattice. Imagine the step by step formation of a chain of Li atoms, Li-Li, Li-Li-Li and so on, until finally we have Li_n , where n is a very large number of the order of 10^{23} . Each lithium atom has electronic configuration ${}_3\text{Li} = 1s^2 2s^1$, with a single 2s electron.

In diatomic Li_2 molecule, according to molecular orbital theory when two atomic orbitals combine, two molecular orbitals are formed, one of which is bonding and the other antibonding molecular orbital. When three atomic orbitals combine, three molecular orbitals are formed, e.g. bonding, antibonding and non-bonding. When four atomic orbitals combine, four molecular orbitals, two bonding and two antibonding molecular orbitals are formed. Similarly, when n atomic orbitals combine n -molecular orbitals are formed.

1.13.3 Salient Features of Band Theory

1. The number of molecular orbitals formed is equal to the number of atomic orbitals combined.
2. As the number of atomic orbitals increases, interspacing between molecular orbitals decreases.
3. When n -energy levels of identical atoms interact, each energy level splits into n number of infinitesimal energy levels. As a result of this, each original energy level becomes a band of very closely spaced levels of extremely small energy difference and may be considered to be continuum. A band is a group of infinitesimal energy levels in a solid or crystal.
4. The outer most energy band that is completely filled or partially filled is known as valence band.
5. The energy band above valence band and is empty at 0K is known as conduction band.

6. The gap between valence band and conduction band is known as forbidden gap. No electron can exist in forbidden gap. The width of forbidden gap is called energy gap.

1.14 CLASSIFICATION OF MATERIALS BASED ON BAND THEORY

With the help of band theory, materials can be classified into three categories viz. conductor, semiconductor and insulator depending on the size of the energy gap between valence band and conduction band.

1.14.1 Conductor (A Metal)

There is no energy gap between valence band and conduction band. A significant number of electrons are thermally excited into conduction band, creating holes in the valence band. The electrons in the conduction band and the holes in the valence band can move throughout the material, allowing it to easily conduct electricity, e.g. metals.

1.14.2 Semiconductor

In semiconductors energy gap is small (of the order of 1eV) but large enough so that a fairly small number of electrons are in the conduction band due to thermal energy, and these materials conduct poorly. But the presence of small percentage of doping material (impurity atoms of group III and or V) can bridge the gap and increase conductivity dramatically, e.g. silicon and germanium.

1.14.3 Insulator

The electrons in the valence band are separated by very large energy gap (of the order of 5-10 eV) from the conduction band. So the electron are not promoted to the conduction band due to thermal energy, and these materials do not conduct electricity, e.g. rubber, plastic, wood, glass etc.

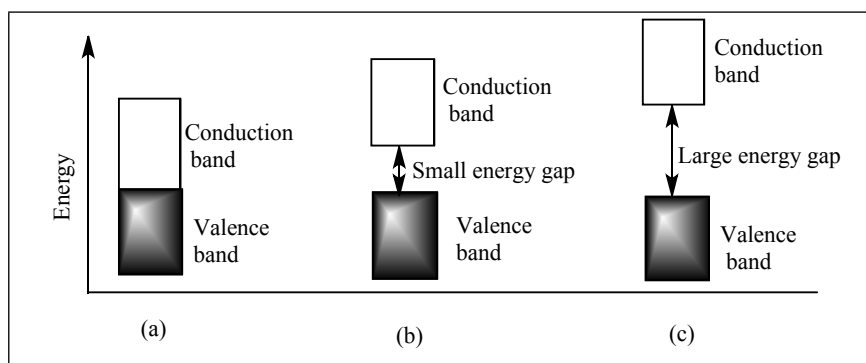


Fig. 1.14: Representation of energy band and gaps (a) conductor (b) semiconductor (c) insulator

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Short answer type questions:

1. Arrange the following molecules/ions in order of their increasing bond length: O_2 , O_2^- , O_2^{2-} .
2. How do bonding and antibonding molecular orbitals differ with respect to (a) energies (b) the spatial distribution of electron density?
3. Calculate the bond order of O_2^+ molecular ion.
4. What do you understand by bonding molecular orbital?
5. Calculate the bond order of He_2^+ molecular ion.
6. What is an antibonding molecular orbital?
7. Write the ground state electronic configurations of O_2^+ .
8. Write the ground state electronic configuration of N_2^- .
9. What is bond order?
10. How is bond order related with dissociation energies?
11. How is bond order related to the bond length of a molecule?
12. Arrange molecular species N_2 , N_2^+ , N_2^- , N_2^{2+} in increasing order of stability.
13. Calculate the bond order of the following species: O_2 , O_2^- , O_2^+ , O_2^{2-} .
14. Also provide the increasing order of stability of these ions.
15. Explain why bond energy of N_2 is greater than bond energy of CO_2 .

Long answer questions:

1. With the help of molecular orbital diagram, explain why hydrogen forms diatomic molecule while helium remains monoatomic.
2. On the basis of molecular orbital theory explain why F_2 is diamagnetic while O_2 is paramagnetic calculate their bond order.
3. Describe conductors, semiconductors and insulators in the light of band theory.
4. What are the salient features of band theory?
5. What is molecular orbital theory? With the help of M.O. diagram, calculate the bond order of the following :
6. He_2^+ , NO, N_2 and N_2^-
7. Draw molecular orbital diagram of CN and CO. Calculate the bond order, bond length and magnetic behavior.
8. Calculate the bond order of the following species and report which species has the shortest bond length: NO, NO^+ , NO^{2+} , NO^-
9. With the help of M.O. theory, explain the "paramagnetic" character of O_2 and "diamagnetic" character of N_2 .
10. Draw the molecular orbital diagram of NO molecule.
11. Draw the molecular orbital diagram of CO molecule.
12. Draw the molecular orbital energy level diagram for HF molecule.
13. With the help of molecular orbital diagram, explain why NO molecule is paramagnetic.