

MOLECULAR ORBITAL THEORY (MOT)

The wave mechanical treatment of a covalent bond based on the valence bond theory has been discussed above. The second approach to the problem is through another theory known as the **molecular orbital theory**. The two theories reflect distinctly different conceptual approaches to the basic structural model of a molecule. For instance, according to VBT, the two atoms in a diatomic molecule lie close to each other with their **completely filled atomic orbitals** remaining intact. *Only the half-filled orbital of one atom overlaps with the half-filled orbital of the same symmetry of the other atom* resulting in the formation of a covalent bond. According to MOT, on the other hand, the nuclei of the two atoms lie at appropriate distance and *all the atomic orbitals of one atom overlap with all the atomic orbitals of the other atom provided the overlapping orbitals are of the same symmetry and of similar energy*. The resulting polynuclear molecular orbitals contain all the electrons of the molecule.

The molecular orbital theory was put forth by F. Hund and R.S. Mulliken in 1930s and later further developed by I.E. Lennard-Jones and Charles Coulson.

The basic principles of molecular orbital theory are as follows :

1. When nuclei of two atoms come close to each other, *their atomic orbitals interact leading to the formation of molecular orbitals*. The atomic orbitals of the atoms in a molecule completely lose their identity after the formation of molecular orbitals.
2. Each molecular orbital is described by a wave function ψ , known as molecular orbital wave function.
3. The molecular orbital wave function ψ is such that ψ^2 represents the probability density or electron charge density.
4. Each molecular orbital wave function (ψ) is associated with a set of quantum numbers which determine the energy and the shape of the molecular orbital.
5. Each ψ is associated with a definite energy value and the total energy of the molecule is the sum of the energies of occupied molecular orbitals.
6. Electrons fill the molecular orbitals in the same way as they fill the atomic orbitals following the aufbau principle, Pauli's exclusion principle and the Hund's rule of maximum multiplicity.
7. Each electron in a molecular orbital belongs to all the nuclei present in the molecule.
8. Each electron moving in a molecular orbital has a spin of $+\frac{1}{2}$ or $-\frac{1}{2}$.

The basic difference between an atomic orbital and a molecular orbital is that while an electron in an atomic orbital is influenced by one positive nucleus only, an electron in a molecular orbital is influenced by all the nuclei of atoms contained in a molecule.

If we have a simple molecular system comprising of two electrons described by two one-electron molecular orbital wave functions ψ_1 and ψ_2 , then the combined configurational wave function for the system, i.e., the molecule, would be given by

$$\Psi = \psi_1 \psi_2 \quad \dots(21)$$

If, in general, there are n electrons, then the configurational wave function for the system would be given by

$$\Psi = \psi_1 \psi_2 \psi_3 \dots \psi_n \quad \dots(22)$$

where ψ_1, ψ_2, ψ_3 , etc., are one-electron molecular orbital wave functions*.

The individual one-electron molecular orbital wave functions such as $\psi_1, \psi_2, \psi_3, \dots$ can be determined with the application of the wave mechanical principles, especially the Ritz method of linear combination of atomic orbitals.

Linear Combination of Atomic Orbitals (LCAO). Molecular Orbital Treatment of Hydrogen Molecule Ion, H_2^+ . Linear combination of atomic orbitals which has been described earlier in this chapter, is also employed in the treatment of molecular orbital theory. We shall apply this principle in the molecular orbital treatment of a simple species, viz., H_2^+ ion, containing only one electron and then extend the treatment to more complicated systems.

Consider a H_2^+ ion consisting of two H nuclei designated as A and B (Fig. 14). The single electron is supposed to be moving in a molecular orbital formed by the interaction of atomic orbitals of the two hydrogen atoms, H_A and H_B . The potential energy of the H_2^+ system would evidently, be given by

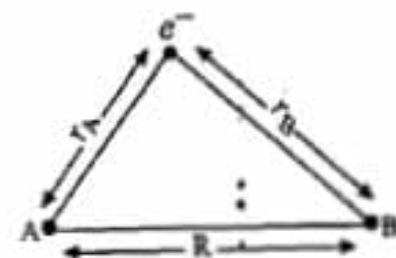


Fig. 14. Representation of H_2^+ ion.

$$V = -\frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \quad \dots(23)$$

where r_A, r_B and R are the appropriate distances, as shown in Fig. 14.

As shown in Chapter I, the energy operator (i.e., the Hamiltonian operator) \hat{H} for H_2^+ ion is represented as

$$\hat{H} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2 + V \quad \dots(24)$$

$$= -\frac{\hbar^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \quad \dots(25)$$

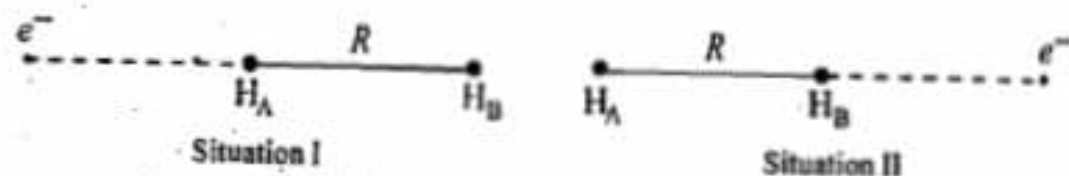
*Strictly speaking, expressions (21) and (22) are true only if we assume ψ_1, ψ_2 , and ψ_3 , etc., to be totally independent of one another. This is not exactly true since the electrons in the molecular orbitals of a multi-electron system repel one another and, therefore, ψ_1, ψ_2, ψ_3 , etc., are dependent on one another to some extent. Hence, the expressions (21) and (22) are only approximations.

Accordingly, the wave equation $\hat{H}\psi = E\psi$ becomes

$$\left(-\frac{\hbar^2}{8\pi^2m} \nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \right) \psi = E\psi \quad \dots(26)$$

If we know ψ , we can find the energy E of the molecular orbital with the help of Eq. 26. But, it is not possible to ascertain the true ψ for such a system due to reasons already discussed in Chapter 1. However, we can find a wave function which is close to the true ψ , as discussed below.

The electron in H_2^+ ion is moving in molecular orbital under the influence of both the nuclei A and B. When, at some instant, it comes nearer to nucleus A (situation I), the electron would behave as if it was moving in the atomic orbital of H_A . The motion of the electron would then be described by ψ_A (the unmixed atomic orbital of H_A). Similarly, when the electron is nearer to nucleus B (situation II), its motion would be described by ψ_B (the unmixed atomic orbital of H_B).



In between these two situations, the electron would be under the influence of both the nuclei and its motion would be described by a wave function which is a linear combination of ψ_A and ψ_B . Thus,

$$\psi = c_A\psi_A + c_B\psi_B \quad \dots(27)$$

where c_A and c_B are the coefficients of the atomic orbital wave functions ψ_A and ψ_B , respectively. The squares of the coefficients, viz., c_A^2 and c_B^2 , give, respectively, the contributions of ψ_A and ψ_B to the wave function ψ .

The energy function ϵ corresponding to this wave function is given by

$$\epsilon = \frac{\int_{-\infty}^{+\infty} \psi \hat{H} \psi d\tau}{\int_{-\infty}^{+\infty} \psi^2 d\tau} \quad (\text{cf. Eq. 8.}) \quad \dots(28)$$

$$= \frac{\int_{-\infty}^{+\infty} (c_A\psi_A + c_B\psi_B) \hat{H} (c_A\psi_A + c_B\psi_B) d\tau}{\int_{-\infty}^{+\infty} (c_A\psi_A + c_B\psi_B)^2 d\tau} \quad \dots(29)$$

Differentiating Eq. 29 with respect to c_A only and then with respect to c_B only and applying the conditions of minimisation of energy, viz., $\partial\epsilon/\partial c_A = 0$, and $\partial\epsilon/\partial c_B = 0$, we get a quadratic equation in ϵ whose solution gives two values of energy function ϵ . Since these energy functions being of minimum energy, are closest approximations of energy E , we may designate these two values of ϵ as E_+ and E_- .

Since the probability of occurrence of situation I and situation II, described above, is the same, therefore, the weightages of ψ_A and ψ_B in overall ψ would be the same. Thus, $c_A^2 = c_B^2$.

In order that ψ is an acceptable wave function, it must be normalised, i.e., it must satisfy the condition that $\int_{-\infty}^{+\infty} \psi^2 d\tau = 1$. The atomic orbital wave functions taken for the combination are already normalised, i.e.,

$$\int_{-\infty}^{+\infty} \psi_A^2 d\tau = 1 \quad \text{and} \quad \int_{-\infty}^{+\infty} \psi_B^2 d\tau = 1$$

The above conditions give the relation

$$c_A^2 + c_B^2 = 1$$

But, as shown above, $c_A^2 = c_B^2$

$$c_A = \pm c_B = \pm(1/\sqrt{2}) \quad \dots(30)$$

Thus, we get two sets of values for c_A and c_B , viz., $(+1/\sqrt{2})$, $+1/\sqrt{2}$ and $(+1/\sqrt{2})$, $-1/\sqrt{2}$ and hence two linear combinations of ψ_A and ψ_B corresponding to each set of the values of c_A and c_B . Accordingly, we have

$$\psi_+ = + (1/\sqrt{2})\psi_A + (1/\sqrt{2})\psi_B = (1/\sqrt{2})(\psi_A + \psi_B) \quad \dots(31)$$

$$\psi_- = + (1/\sqrt{2})\psi_A - (1/\sqrt{2})\psi_B = (1/\sqrt{2})(\psi_A - \psi_B) \quad \dots(32)$$

In the above equations, ψ_+ corresponds to energy E_+ and ψ_- corresponds to energy E_- . The lower value of energy E_+ is lower than either of E_A and E_B (viz., the energies of isolated H_A and H_B). The higher value of energy E_- is higher than either of E_A and E_B . Thus, we see that in the case of H_2^+ ion:

1. A linear combination of two atomic orbitals ψ_A and ψ_B leads to the formation of two molecular orbitals ψ_+ and ψ_- .

2. The energy E_+ of molecular orbital ψ_+ is lower than either of E_A and E_B . It is, therefore, designated as **bonding molecular orbital (BMO)**.

3. The energy E_- of molecular orbital ψ_- is higher than either of E_A and E_B . It is, therefore, designated as **antibonding molecular orbital (ABMO)**.

4. The extent of lowering of energy of the bonding molecular orbital is equal to the extent of increase of energy of the antibonding molecular orbital, as shown in Fig. 15.

5. Detailed LCAO calculations show that the greater the overlap of the two combining atomic orbitals ψ_A and ψ_B , the lower would be the energy of the bonding molecular orbital (ψ_+) formed.

6. The combining atomic orbitals ψ_A and ψ_B are completely used up during the formation of the molecular orbitals ψ_+ and ψ_- . The electron occupying originally the $1s$ atomic orbital of H_A or H_B , now occupies the lower level molecular orbital ψ_+ , losing energy = OM and thus gaining in stability.

The molecular orbital treatment for H_2^+ ion, discussed above, can be extended to other homonuclear and heteronuclear systems. In general, whenever atomic orbitals ψ_A and ψ_B , of the same symmetry and of similar energies, of two atoms A and B, overlap, two molecular orbitals ψ_+ and ψ_- would be formed by the linear combination of these atomic orbitals so that the equations for molecular orbitals would be

$$\psi_+ = N_+(\psi_A + \lambda\psi_B) \quad \dots(33)$$

$$\psi_- = N_-(\lambda\psi_A - \psi_B) \quad \dots(34)$$

where λ is called the **mixing coefficient** and N_+ and N_- are called **normalising constants**. The values of these constants are adjusted in such a way that the normalising conditions, viz., $\int_{-\infty}^{+\infty} \psi_+^2 d\tau = 1$ and

$\int_{-\infty}^{+\infty} \psi_-^2 d\tau = 1$ are satisfied.

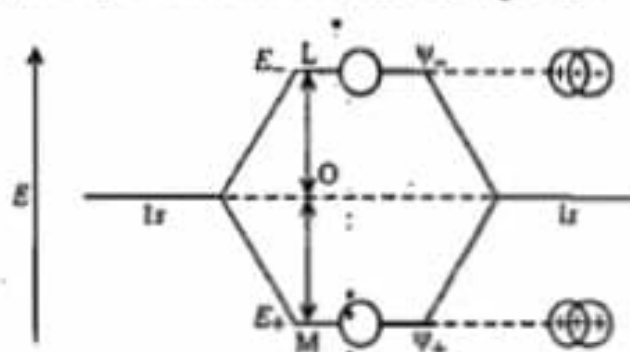


Fig. 15. Energies of bonding and antibonding molecular orbitals.

If the molecule AB is homonuclear, the weightages of ψ_A and ψ_B in both ψ_+ and ψ_- would be the same, i.e., $N_+^2 = \lambda^2 N_-^2$ and $N_-^2 \lambda^2 = N_+^2$ (weightage or contribution of a wave function is related to square of its coefficient). It readily follows from above that $\lambda^2 = 1$ so that $\lambda = \pm 1$. In such a case, Eqs. 33 and 34 for molecular orbitals would reduce to Eqs. 31 and 32, respectively because $N_+ = N_- = 1/\sqrt{2}$ and $\lambda = \pm 1$.

If, however, the molecule AB is heteronuclear, the weightages of ψ_A and ψ_B would not be the same, i.e., $N_+^2 \lambda^2 \neq N_-^2$ and $N_+^2 \neq \lambda^2 N_-^2$ so that $\lambda^2 \neq 1$ and the equations for molecular orbitals would remain as Eqs. 33 and 34.

Construction of Molecular Orbital Wave Functions and Valence Bond Wave Functions

In the preceding pages, the wave mechanical treatment of covalent bond has been discussed on the basis of valence bond and molecular orbital theories. The following typical solved examples illustrate how the above theories can be made use of for constructing molecular orbital wave functions and valence bond wave functions.

Example 1. Construct a molecular orbital wave function for the bond between H and Cl in HCl assuming that the bond is formed from the 1s electron of H atom and a 3p electron of Cl atom.

Solution : Let H atom be designated by A and Cl atom by B. Let the 1s electron of H atom be labelled as electron 1 and 3p electron of Cl atom be labelled as electron 2.

According to Eq. 21, $\psi_{MO} = \psi_1 \psi_2$ where

$$\psi_1 = c_1 \psi_A(1) + c_2 \psi_B(1)$$

and

$$\psi_2 = c_1 \psi_A(2) + c_2 \psi_B(2)$$

$$\begin{aligned} \therefore \psi_{MO} &= [c_1 \psi_A(1) + c_2 \psi_B(1)][c_1 \psi_A(2) + c_2 \psi_B(2)] \\ &= c_1^2 [\psi_A(1)\psi_A(2)] + c_1 c_2 [\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)] + c_2^2 [\psi_B(1)\psi_B(2)] \end{aligned}$$

As can be seen, the first and the last terms are ionic whereas the middle terms are covalent. Also, the covalent terms have equal weightage but the ionic terms have different weightage from the covalent terms and also from each other.

Example 2. Write down the molecular orbital wave function for H_2^- molecule anion.

Solution : H_2^- molecule anion contains three electrons which may be labelled as 1, 2 and 3. It contains two nuclei which may be designated as A and B. According to Eq. 22,

$$\psi_{MO} = \psi_1 \psi_2 \psi_3$$

where

$$\psi_1 = c_1 \psi_A(1) + c_2 \psi_B(1)$$

$$\psi_2 = c_3 \psi_A(2) + c_4 \psi_B(2)$$

$$\psi_3 = c_5 \psi_A(3) + c_6 \psi_B(3)$$

Example 3. Using the principle of LCAO for the wave function for H_2^+ ion, obtain the normalised wave functions for the BMO and the ABMO.

Solution : Using the principle of LCAO, the wave function for H_2^+ ion is written as

$$\psi = N(c_1 \psi_A + c_2 \psi_B) \quad \dots (i)$$

where N is the normalisation constant.

According to the normalization condition, for real ψ

$$\int_{-\infty}^{+\infty} \psi^2 d\tau = \langle \psi | \psi \rangle^{**} = 1 \quad \dots(ii)$$

Incorporating the value of ψ from Eq. (i) in Eq. (ii), we have

$$N^2 \langle (c_1 \psi_A + c_2 \psi_B) | (c_1 \psi_A + c_2 \psi_B) \rangle = 1$$

$$\text{or } c_1^2 \langle \psi_A | \psi_A \rangle + c_2^2 \langle \psi_B | \psi_B \rangle + 2c_1 c_2 \langle \psi_A | \psi_B \rangle = 1/N^2 \quad \dots(iii)$$

It can be shown that $\langle \psi_A | \psi_B \rangle = \langle \psi_B | \psi_A \rangle$

Assuming that ψ_A and ψ_B are normalised, i.e.,

$$\langle \psi_A | \psi_A \rangle = \int \psi_A^2 d\tau \quad \text{and} \quad \langle \psi_B | \psi_B \rangle = \int \psi_B^2 d\tau = 1, \text{ we have} \quad \dots(iv)$$

$$c_1^2 + c_2^2 + 2c_1 c_2 S = 1/N^2$$

where S is the overlap integral defined as

$$S = \langle \psi_A | \psi_B \rangle = \int \psi_A \psi_B d\tau \quad \dots(v)$$

From Eq. (iv),

$$N = (c_1^2 + c_2^2 + 2c_1 c_2 S)^{-1/2} \quad \dots(vi)$$

Hence, from Eq. (i),

$$\psi = (c_1^2 + c_2^2 + 2c_1 c_2 S)^{-1/2} (c_1 \psi_A + c_2 \psi_B) \quad \dots(vii)$$

We know that for BMO of H_2^+ ion, $c_1 = c_2$ and for ABMO, $c_1 = -c_2$.

Hence, from Eq. (vii), $\psi_{BMO} = (1/\sqrt{2(1+S)}) (\psi_A + \psi_B)$

and $\psi_{ABMO} = (1/\sqrt{2(1-S)}) (\psi_A - \psi_B)$

Example 4. Write down the normalised VB wave functions and normalised MO wave functions for H_2 molecule and comment on the expressions obtained.

Solution : H_2 molecule contains two electrons (labelled 1 and 2) and two hydrogen nuclei (labelled A and B). The pairing of electrons leads to the formation of a covalent bond. In the VB approach, if electron 1 is on nucleus A, then electron 2 would be on nucleus B and vice-versa. Since, however, the two electrons are indistinguishable, therefore, the VB wave function for H_2 molecule can be written as

$$\psi_{VB} = (1/\sqrt{2}) [\psi_{A(1)} \psi_{B(2)} + \psi_{A(2)} \psi_{B(1)}] \quad \dots(i)$$

where $1/\sqrt{2}$ is the normalization constant obtained by normalizing ψ_{VB} .

In the MO theory, the MO wave function for H_2 molecule is given by

$$\psi_{MO} = \psi_1 \psi_2 \quad \dots(ii)$$

where ψ_1 and ψ_2 are the normalised wave functions for MOs of H_2 given by

$$\psi_1 = (1/\sqrt{2}) (\psi_A(1) + \psi_B(1)) \quad \dots(iii)$$

and

$$\psi_2 = (1/\sqrt{2}) (\psi_A(2) + \psi_B(2)) \quad \dots(iv)$$

Multiplying ψ_1 and ψ_2 , we get the ψ_{MO} as

$$\psi_{MO} = (1/2) [\psi_A(1) + \psi_B(1)] [\psi_A(2) + \psi_B(2)] \quad \dots(v)$$

$$= (1/2) [\psi_A(1) \psi_A(2) + \psi_B(1) \psi_B(2)] + 1/2 [\psi_A(1) \psi_B(2) + \psi_A(2) \psi_B(1)] \quad \dots(vi)$$

**This type of notation is known as 'bra' and 'ket' notation. In this notation, $\int_{-\infty}^{+\infty} \psi_1 \psi_2 d\tau$ and $\int_{-\infty}^{+\infty} \psi_1 \hat{H} \psi_2 d\tau$ are written as $\langle \psi_1 | \psi_2 \rangle$ and $\langle \psi_1 | \hat{H} | \psi_2 \rangle$, respectively.

In Eq. (vi), the first two terms represent the probability of finding both the electrons on the same atom at the same time. In other words, these terms represent the ionic structures of H_2 molecule which may be written as $\bar{H}_A\bar{H}_B$ and $H_A H_B$.

The last two terms in Eq. (vi) represent the covalent structure of the H_2 molecule.

Comparing ψ_{VB} and ψ_{MO} , we observe that while the wave function in VBT does not give any weightage to ionic structures, the MOT gives equal weightage to covalent and ionic structures.

Example 5. Write down the wave function for the BMO for a hetero-nuclear diatomic molecule AB assuming that the electron on an average spends 90% of its time on nucleus A and 10% of its time on nucleus B.

Solution : In the LCAO-MO scheme, $\psi_{MO} = c_A\psi_A + c_B\psi_B$

where the coefficients c_A and c_B are such that $[c_A]^2$ and $[c_B]^2$ determine the probability of finding the electron in atomic orbitals ψ_A and ψ_B , respectively. Then, clearly,

$$[c_A]^2 = 90\% = 0.9 \text{ and}$$

$$[c_B]^2 = 10\% = 0.1$$

Hence,

$$c_A = \pm\sqrt{0.9} = \pm 0.95$$

and

$$c_B = \pm\sqrt{0.1} = \pm 0.32$$

Thus,

$$\psi_{MO} = 0.95\psi_A + 0.32\psi_B$$

Example 6. Write down the valence bond wave function for the HF molecule (assuming that it is formed from $1s$ orbital of H and $2p_z$ orbital of F) in the following three cases: (a) HF is purely covalent (b) HF is purely ionic and (c) HF is 80% covalent and 20% ionic.

Solution : Let the H atom be represented by A and F atom by B. Let the electron numbered 1 be the $1s$ electron of H atom and the electron numbered 2 be the $2p_z$ electron of F atom.

(a) For purely covalent structure of HF, the wave function is written as

$$\psi_{\text{covalent}} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$$

(b) For the purely ionic structure H^+F^- , both the electrons are on the F atom so that

$$\psi_{\text{ionic}} = \psi_B(1)\psi_B(2)$$

(c) HF is a resonance hybrid shown as



$$\therefore \psi_{VB} = c_1\psi_{\text{covalent}} + c_2\psi_{\text{ionic}} \text{ with } c_1^2 + c_2^2 = 1$$

Since

$$c_1^2 = 0.80 \text{ and } c_2^2 = 0.20 \text{ (given), hence,}$$

$$c_1 = \sqrt{0.80} = 0.89$$

and

$$c_2 = \sqrt{0.20} = 0.45$$

\therefore

$$\psi_{VB} = 0.89 [\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)] + 0.45 [\psi_B(1)\psi_B(2)]$$

Electron Charge Densities in Molecular Orbitals of H_2^+ Ion

Consider once again a H_2^+ ion. The square of the wave function, viz., ψ^2 , is a measure of the probability density, i.e., the probability of finding an electron in a given volume of space. Since probability density is directly related to electron charge density, hence, ψ_+^2 and ψ_-^2 give electron charge densities in the two molecular orbitals ψ_+ and ψ_- of H_2^+ ion formed in accordance with Eqs. 31 and 32. According to these equations

$$\psi_+^2 = [1/\sqrt{2}(\psi_A + \psi_B)]^2 = 1/2(\psi_A^2 + \psi_B^2 + 2\psi_A\psi_B) \quad \dots(35)$$

and

$$\psi_-^2 = [1/\sqrt{2}(\psi_A - \psi_B)]^2 = 1/2(\psi_A^2 + \psi_B^2 - 2\psi_A\psi_B) \quad \dots(36)$$

If the atomic orbitals ψ_A and ψ_B had not combined, there would have been no overlap between ψ_A and ψ_B . In that case, the overlap density, given by $\psi_A\psi_B$, would have been zero and ψ_+^2 would have been equal to $1/2(\psi_A^2 + \psi_B^2)$. This means that $1/2(\psi_A^2 + \psi_B^2)$ gives the electron charge density in between the nuclei A and B in the *uncombined atomic orbitals* ψ_A and ψ_B . When the two atomic orbitals *combine to form the molecular orbital* ψ_+ , the overlap density $\psi_A\psi_B$ between the two atomic orbitals is non-zero and the electron charge density ψ_+^2 in between the two nuclei is given by $1/2\psi_A^2 + 1/2\psi_B^2 + \psi_A\psi_B$ (Eq. 35). This means that the electron charge density in between the nuclei A and B in the molecular orbital ψ_+ *increases by $\psi_A\psi_B$* .

The increased electron charge density shields the two similarly charged nuclei very effectively and decreases the energy of the molecular orbital in the event of its being occupied by electrons. In other words, the molecular orbital ψ_+ has *lower energy* than the energy of either of the uncombined atomic orbitals ψ_A and ψ_B . This orbital, therefore, leads to the formation of a stable chemical bond and is called **bonding molecular orbital**.

The electron charge density in between the nuclei A and B in molecular orbital ψ_- is given by $1/2\psi_A^2 + 1/2\psi_B^2 - \psi_A\psi_B$ (Eq. 36). Evidently, the electron charge density in between the two nuclei in the molecular orbital ψ_- *now decreases by $\psi_A\psi_B$* . Because of the decrease in the electron charge density, the two similarly charged nuclei in this molecular orbital would be screened to a much smaller extent. As a result, the two nuclei would repel each other to a greater extent. This would lead to an increase of energy of the molecular orbital in the event of its being occupied by electrons. In other words, the molecular orbital ψ_- has *higher energy* than the energy of either of the uncombined atomic orbitals ψ_A and ψ_B . Such an orbital, evidently, opposes the formation of a chemical bond and is called **antibonding molecular orbital**.

It is evident that a filled BMO has high electron charge density in the overlap region whereas a filled ABMO has no electron charge density in between the nuclei. This may be illustrated by plotting ψ^2 for the bonding as well as the antibonding molecular orbitals against the internuclear distance of H_2^+ ion. When the electron probability density (ψ_+)² of the BMO, i.e., $1/2(\psi_A + \psi_B)^2$, is plotted against the internuclear distance, a curve represented by the *solid line* in Fig. 16. is obtained. The plots for the electron charge densities in between the two nuclei in the uncombined atomic orbitals of H atoms for the same internuclear distance are also shown in the figure *by dotted lines*. As mentioned above, the electron charge density in between the nuclei in the uncombined atomic orbitals ψ_A and ψ_B is $1/2\psi_A^2 + 1/2\psi_B^2$. It is clear from the figure that there is greater probability of finding electron between the two nuclei in BMO than in the uncombined AOs.

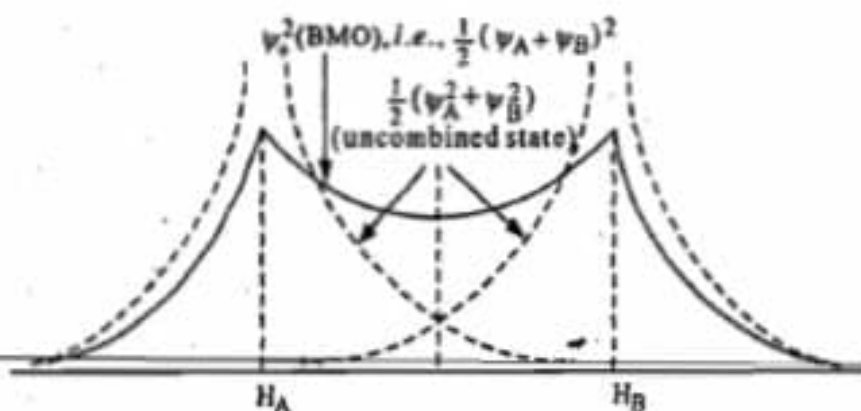


Fig. 16. The plot of electron probability density vs internuclear distance for a BMO shown by a solid line and for the separate uncombined atomic orbitals of hydrogen atoms shown by the dotted lines.

For an ABMO, the picture is quite different. When the electron probability density (ψ_-)² of an ABMO, i.e., $1/2(\psi_A - \psi_B)^2$, is plotted against the internuclear distance, a curve represented by the *solid line* in Fig. 17 is obtained. This curve indicates that the electron charge density in the middle of

internuclear distance becomes almost zero. As a result, the two nuclei repel each other more effectively than the nuclei of the uncombined atoms A and B at that internuclear distance.

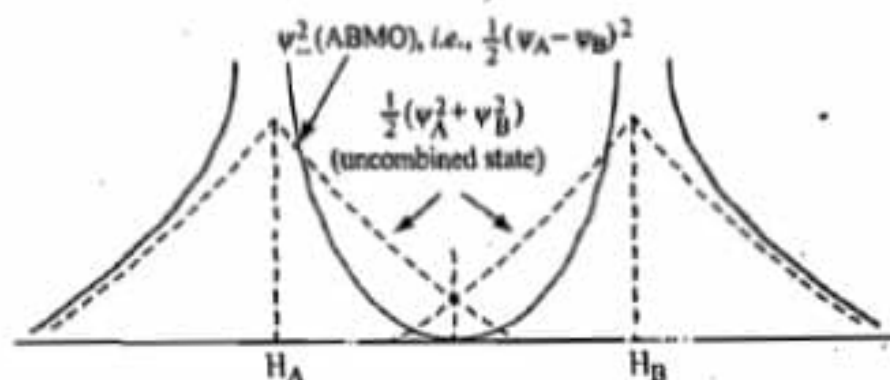
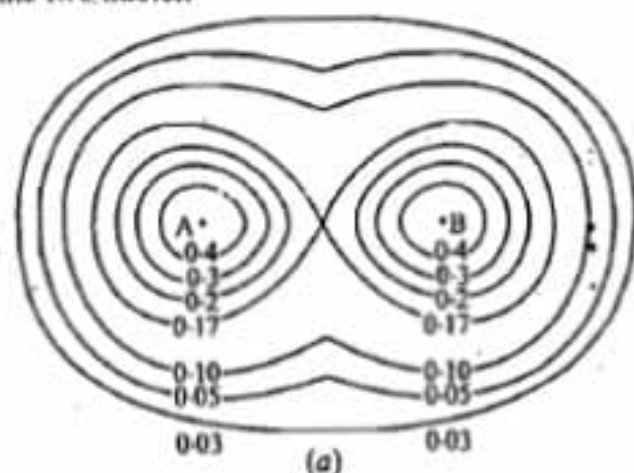


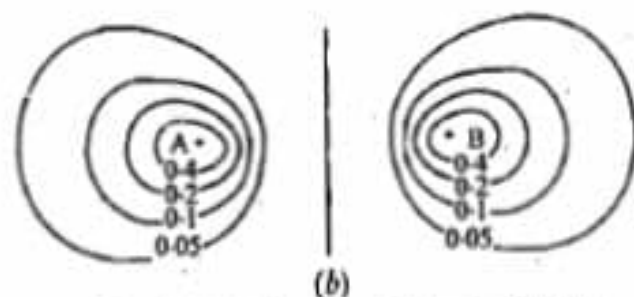
Fig. 17. The plot of electron probability density vs internuclear distance for an ABMO shown by solid line and for separate uncombined atomic orbitals of hydrogen atoms shown by dotted lines.

The distinction between bonding and antibonding molecular orbitals can be made more clear by showing the contours of electron charge densities or probability densities around the two nuclei A and B for these orbitals, as illustrated in Figs. 18 (a) and (b).

In a **bonding MO**, the high probability density contours are localised on the two nuclei but tend to polarise towards the space located in between the two nuclei. The low probability density contours are, however, spread over both the nuclei. This implies enhancement of electronic charge in the space in between the two nuclei.



(a) $\sigma(1s)$ Bonding Molecular Orbital



(b) $\sigma^*(1s)$ Antibonding Molecular Orbital

Fig. 18. Contours of electron charge densities in bonding and antibonding molecular orbitals.

In an **antibonding MO**, the high as well as low probability density contours are localised on two nuclei and tend to polarise away from the space falling in between the two nuclei. This implies depletion of electronic charge from the space in between the two nuclei.

Pictorial Representation of Combination of Atomic Orbitals to form Molecular Orbitals

1. Combination of s atomic orbitals. To begin with, we consider a simple case of combination of $1s$ atomic orbital of one hydrogen atom with $1s$ atomic orbital of another hydrogen atom to give two MOs. As discussed earlier, there are two ways of linearly combining AOs. One is by the *additive combination* while the second is by the *subtractive combination* of atomic orbitals. The overlapping of two $1s$ atomic orbitals by linear additive combination to form a bonding molecular orbital is shown in Fig. 19. In such a combination, the region between the two nuclei has a $(+) \times (+)$, i.e., algebraic $+$ sign. This implies that the electron charge density in the region between the two nuclei would get intensified.

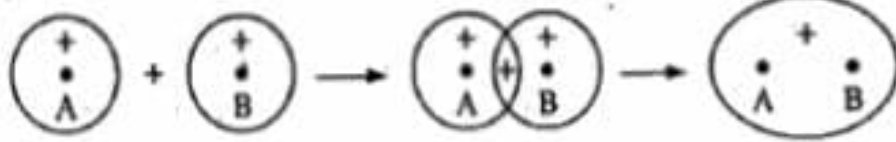


Fig. 19. Formation of a bonding molecular orbital by overlapping of two $1s$ atomic orbitals by linear additive combination.

The high electron charge density in between the two positive nuclei shields them from mutual repulsion and holds them together at the observed distance from each other. Such a linear additive combination gives a BMO. It is designated as $\sigma(1s)$ orbital. The sign σ signifies that the molecular orbital is symmetrical about the molecular axis and the script ($1s$) indicates that it is formed by the combination of $1s$ atomic orbitals.

The overlapping of two $1s$ atomic orbitals by linear subtractive combination is shown in Fig. 20. The region of overlap between the two nuclei has $(+) \times (-)$, i.e., algebraic - sign. This implies that the electron charge density would get removed from the middle of the two nuclei. It may be noted that a negative overlap means removal of electron charge from the region in between the nuclei. Thus, there will be no shielding of the nuclei. The repulsion between the two nuclei would, therefore, increase thereby increasing the energy of the molecular orbital formed (Fig. 20). Such a molecular orbital is termed as ABMO and is designated as $\sigma^*(1s)$.

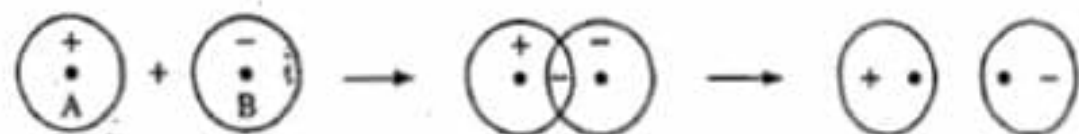


Fig. 20. Formation of antibonding molecular orbital by overlapping of two $1s$ atomic orbitals by linear subtractive combination. The thick dots represent the nuclei.

It may be noted that the positive and negative signs shown above in atomic and molecular orbitals are only algebraic signs of wave functions and should not be confused with charges.

Just like the combination of $1s$ atomic orbitals, $2s$ atomic orbitals also combine to form bonding and antibonding molecular orbitals. These are designated as $\sigma(2s)$ and $\sigma^*(2s)$, respectively. They differ from $\sigma(1s)$ and $\sigma^*(1s)$ MOs with regard to their size only.

2. Combination of p_z atomic orbitals. There are three p atomic orbitals designated as p_x , p_y and p_z . As a convention, the Z -axis is taken as the internuclear axis. The X and Y axes would then be perpendicular to the nuclear line. The combination of two p_z atomic orbitals belonging to different nuclei would, evidently, give a sigma BMO represented as $\sigma(2p_z)$ and a sigma ABMO represented as $\sigma^*(2p_z)$.

The formation of a $\sigma(2p_z)$ BMO by the linear additive combination of two p_z atomic orbitals is represented in Fig. 21. The thick dots represent the nuclei. In this combination, the positive lobes of the two AOs overlap so that the electron charge density between the two nuclei is enhanced. The nuclei are thus well shielded from each other. Since the repulsion between the nuclei in such a case is minimum, the energy of this MO is lower than the energy of the atomic orbitals which have gone into its formation.

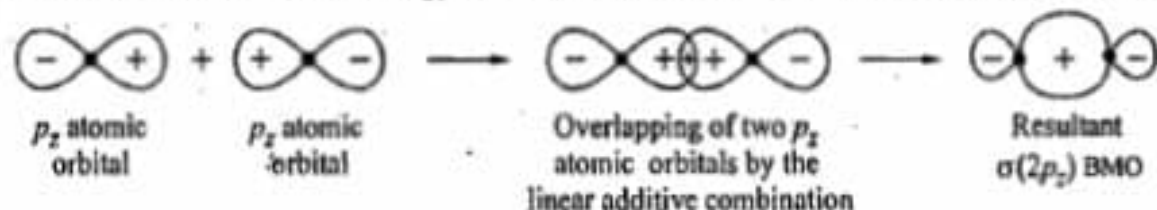


Fig. 21. Formation of a $\sigma(2p_z)$ BMO by the linear additive combination of two p_z atomic orbitals.

The corresponding ABMO is obtained by the linear subtractive combination of two p_z atomic orbitals, as represented in Fig. 22.

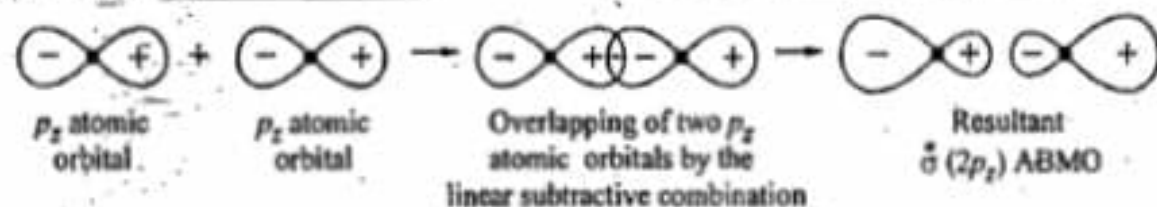


Fig. 22. Formation of a $\sigma^*(2p_z)$ ABMO by the linear subtractive combination of two p_z atomic orbitals.

The positive lobe of one p_z AO overlaps with the negative lobe of the other p_z AO resulting in the negative overlapping region. The electron charge density between the nuclei, therefore, gets depleted. The similarly charged nuclei are, thus, exposed to each other and hence tend to repel each other. This orbital, being antibonding, is designated as $\sigma^*(2p_z)$. The energy of this ABMO is higher than the energy of either of the AOs which have gone into its formation.

3. Combination of p_x and p_y atomic orbitals. Suppose a p_x orbital of an atom overlaps with a p_x orbital of another atom. The overlap would be positive but it would be side to side and not end to end as in the case of p_z orbitals. The resulting molecular orbitals will, thus, be called π molecular orbitals. The formation of the BMO, designated as $\pi(2p_x)$, is shown in Fig. 23.

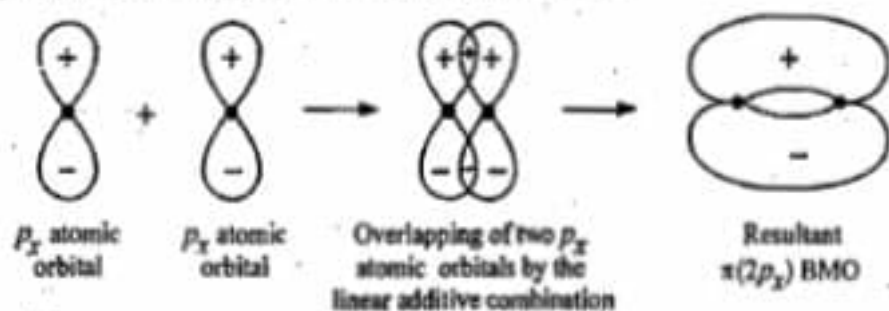


Fig. 23. Overlapping of two p_x atomic orbitals by linear additive combination to give $\pi(2p_x)$ BMO orbital.

The corresponding ABMO formed by linear subtractive combination of p_x AOs, designated as $\pi^*(2p_x)$, is shown in Fig. 24.

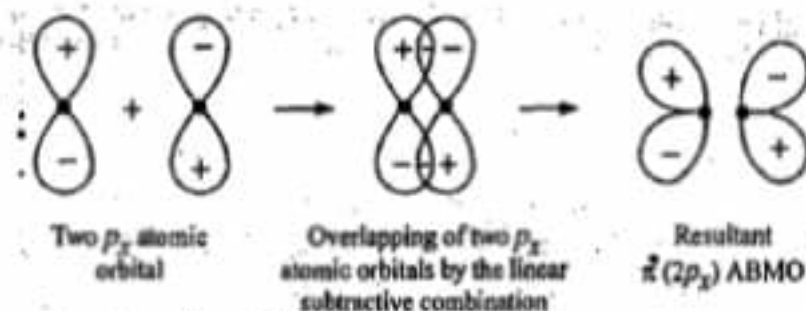


Fig. 24. Overlapping of two p_x atomic orbitals by the linear subtractive combination to form $\pi^*(2p_x)$ ABMO.

The energy of the antibonding molecular orbital would be high because the similarly charged nuclei are not effectively screened by the electronic charge and, therefore, repel each other considerably.

The formation of $\pi(2p_x)$ and $\pi^*(2p_x)$ MOs is similar to the formation of $\pi(2p_y)$ and $\pi^*(2p_y)$ MOs discussed above. The only difference is that the AOs which combine and MOs which are formed now lie perpendicular to the plane of the paper.

Difference Between Bonding and Antibonding Molecular Orbitals. The difference between bonding and antibonding molecular orbitals has been summed up in Table 5.

TABLE 5
Difference Between Bonding and Antibonding Molecular Orbitals

BMO	ABMO
1. A BMO is formed by the addition overlap of atomic orbitals.	An ABMO is formed by the subtraction overlap of atomic orbitals.
2. It has lower energy than the AOs from which it is formed.	It has higher energy than the AOs from which it is formed.
3. The electron charge density in between the nuclei is high and hence the repulsion between the nuclei is very low. This results in stabilisation of the BMO. In other words, the electrons in the BMO favour stable bond formation.	The electron charge density in between the nuclei is low and hence the repulsion between the nuclei is high. This results in de-stabilisation of the ABMO. In other words, the electrons in the ABMO oppose bond formation.

Conditions for the Combination of Atomic Orbitals. It should be noted that any two atomic orbitals will not essentially combine to form molecular orbitals. There are, in fact, certain limitations to the combination of atomic orbitals. These are discussed below :

1. *The energy of the AOs involved should not differ much from one another.* Thus, in the formation of a homonuclear diatomic molecule of the type A_2 , $1s$ orbital of one atom does not combine with $2s$ orbital of another atom of the same element as the energy difference between them is quite high. Likewise, $2s$ orbital of one atom does not combine with $2p$ orbital of another atom of the same element as the energy difference between them is very high.

In the case of heteronuclear diatomic molecules of the type AB, however, such combinations may be possible.

2. *The AOs combine only if they overlap to a considerable extent.* This overlap increases the electron charge density in between the two nuclei thereby minimising their mutual repulsion.

3. *The AOs should have the same symmetry about the molecular axis.* Thus, a p_x (or p_y) orbital of one atom does not combine with an s orbital of another atom. This is illustrated in Fig. 25. The s orbital of an atom A is shown to overlap with the p_x orbital of another atom B. But, since the molecular axis is in the Z-direction and the p_x orbital is oriented at right angles to this axis, no combination is possible. Thus, no molecular orbital can result in spite of the overlap. In fact, the + overlap is cancelled by the - overlap, as shown in the figure.

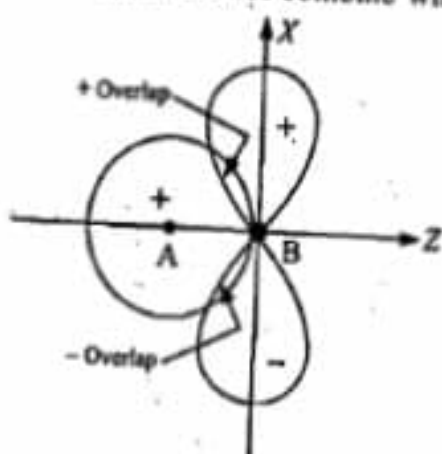


Fig. 25. Limitation of a p_x atomic orbital to combine with an s atomic orbital due to lack of symmetry about the molecular axis.

Similarly, a p_y orbital does not combine with an s orbital as they have different symmetry.

A p_z orbital, however, is able to combine with an s orbital since they have the same symmetry, as shown in Fig. 26.

The s and p atomic orbitals which can combine with each other to form molecular orbitals (assuming Z-axis as the internuclear axis) are as shown below :

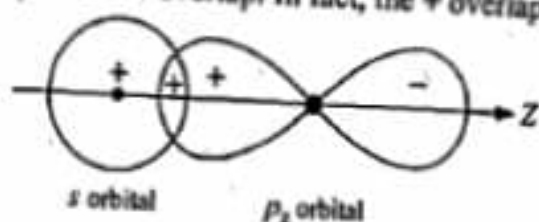


Fig. 26. Freedom of p_z atomic orbital to combine with an s orbital because of the same symmetry about the axial line.

First orbital	Second orbital	Type of molecular orbital formed
s	s, p_z	σ
p_z	s, p_z	σ
p_x	p_x	π
p_y	p_y	π

Energy Level Diagram for Molecular Orbitals. We have seen that $1s$ atomic orbitals of two atoms give rise to two MOs designated as $\sigma(1s)$ and $\sigma^*(1s)$. The $2s$ and $2p$ atomic orbitals (eight AOs on two atoms) give rise to the following eight MOs :

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

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data. The energy generally increases as we move from left to right in the following list :

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

— Energy increases —>

The energy levels of different molecular orbitals are shown diagrammatically in Fig. 27*. In this diagram, the molecular orbitals are shown in the centre and the atomic orbitals which combine are shown on the two extremes. The atomic orbitals of same energy are shown at the same level while the BMOs are shown lower and the ABMOs are shown higher than the corresponding atomic orbitals. This indicates that while the BMOs are more stable, the ABMOs are less stable than the AOs from which they are formed. It is clear from the figure that the extent of stabilization for a BMO is always equal to the extent of destabilization of the corresponding ABMO.

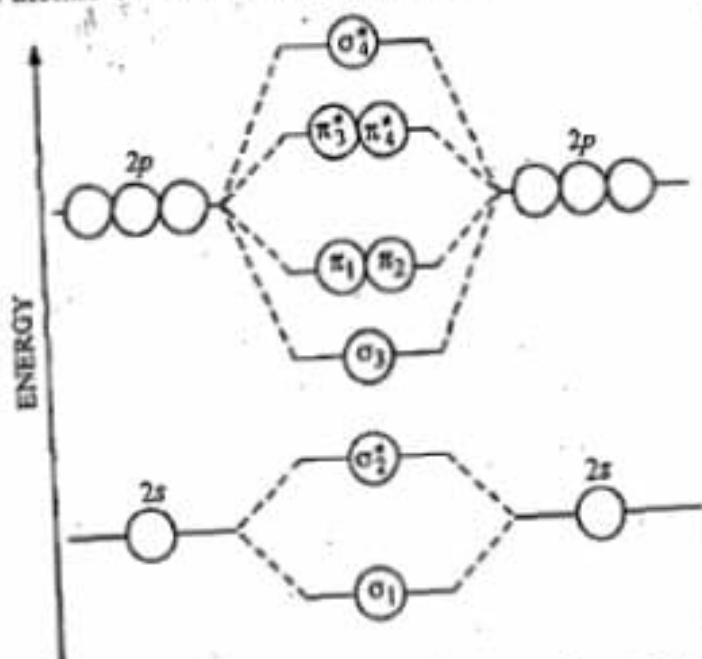


Fig. 27*. Energy levels of different molecular orbitals.

Spectroscopic studies have revealed that the above sequence of energy levels of MOs is not correct for all molecules. It has been observed that in the case of homonuclear diatomic molecules of Second row elements of the periodic table upto N_2 (viz., Li_2 , Be_2 , B_2 , C_2 , N_2), the $\sigma(2p_z)$ MO is higher in energy than the $\pi(2p_x)$ and $\pi(2p_y)$ MOs. The reversal in the sequence of energy levels of MOs is due to the mixing of $2s$ and $2p_z$ orbitals, as discussed below.

Mixing of Orbitals. We have seen that $\sigma(2s)$ and $\sigma^*(2s)$ MOs are formed by the combination of $2s$ atomic orbitals of two atoms while $\sigma(2p_z)$ and $\sigma^*(2p_z)$ MOs are formed by the combination of $2p_z$ atomic orbitals of the two atoms. However, if the energy differences between $2s$ and $2p$ atomic orbitals are small, there is a possibility of mixing of molecular orbitals $\sigma(2s)$ with $\sigma(2p_z)$ as they are of the same symmetry and $\sigma^*(2s)$ with $\sigma^*(2p_z)$ as they are also of the same symmetry with the result that the $\sigma(2s)$ and $\sigma^*(2s)$ MOs do not retain the pure s character and the $\sigma(2p_z)$ and $\sigma^*(2p_z)$ MOs do not retain the pure p character. In fact, all the four MOs acquire a mixed sp character. Due to this $s-p$ mixing,

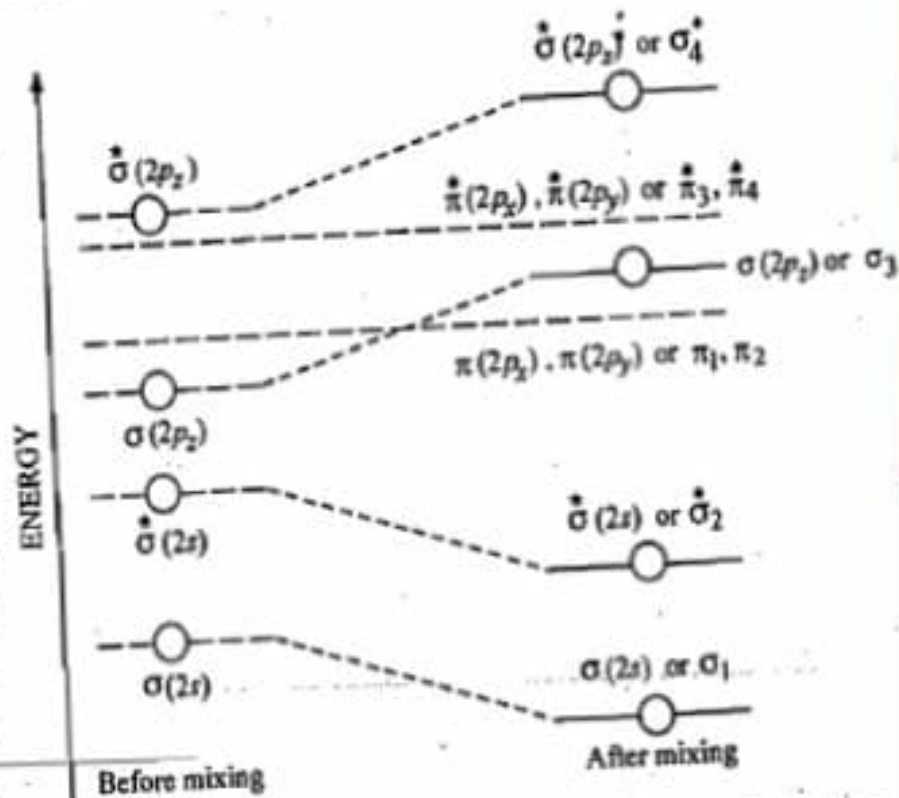


Fig. 28. The change in energies of MOs due to mixing of molecular orbitals of the same symmetry.

*The d orbitals are not included in the present discussion since the purpose is to consider the formation of simple diatomic molecules only.

the energies of all the four orbitals change in such a way that the resulting MOs $\sigma(2s)$ and $\dot{\sigma}(2s)$, which also contain some p character, become more stable and are thus lowered in energy whereas the MOs $\sigma(2p_z)$ and $\dot{\sigma}(2p_z)$ which contain some s character also now become less stable and are thus raised in energy, as illustrated in Fig. 28.

Since $\pi(2p)$ orbitals are not involved in mixing, the energies of $\pi(2p_x)$ and $\pi(2p_y)$ MOs remain unchanged, as shown in the figure.

As can be seen from Fig. 28, $\sigma(2p_z)$ MO is raised to such an extent that it becomes higher in energy than $\pi(2p_x)$ and $\pi(2p_y)$ MOs. The new sequence of energy of MOs, therefore, becomes

$$\sigma(1s), \dot{\sigma}(1s), \sigma(2s), \dot{\sigma}(2s), \pi(2p_x) = \pi(2p_y), \sigma(2p_z), \pi(2p_x) = \pi(2p_y), \dot{\sigma}(2p_z)$$

— Energy increases —>

or

$$\sigma_1, \dot{\sigma}_2, \sigma_3, \pi_1 = \pi_2, \pi_3 = \pi_4, \dot{\sigma}_5$$

— Energy increases —>

Now, a question arises: How is it that the mixing of $\sigma(2s)$ with $\sigma(2p_z)$ and of $\dot{\sigma}(2s)$ with $\dot{\sigma}(2p_z)$ occurs in the case of second row elements upto nitrogen only and not in the case of oxygen and fluorine. The answer lies in the differences in energies of $2s$ and $2p$ atomic orbitals of atoms of second row elements, as shown in Table 9.

TABLE 9

Differences in the Energies of $2s$ and $2p_z$ AOs of Atoms of Second Row Elements

Atoms	Li	Be	B	C	N	O	F
Difference in energies of $2s$ and $2p_z$ AOs (kJ mol^{-1})	178	262	449	510	570	1430	1970

It is clear from the above table that the differences in energies of $2s$ and $2p_z$ atomic orbitals of atoms up to nitrogen are small. Therefore, the energy differences between BMOs $\sigma(2s)$ and $\sigma(2p_z)$ [and between ABMOs $\dot{\sigma}(2s)$ and $\dot{\sigma}(2p_z)$] is also small upto N_2 . Since $\sigma(2s)$ and $\sigma(2p_z)$ are of the same symmetry, these would mix effectively with each other and energies of the resulting mixed molecular orbitals would be considerably different from the energies of pure $\sigma(2s)$ and pure $\sigma(2p_z)$ molecular orbitals. A similar situation occurs in the case of molecular orbitals obtained by mixing of $\dot{\sigma}(2s)$ with $\dot{\sigma}(2p_z)$ molecular orbitals of molecules upto N_2 .

In the case of O_2 and F_2 , however, the energy differences between $2s$ and $2p$ atomic orbitals are quite large. Consequently, the energy differences between $\sigma(2s)$ and $\sigma(2p_z)$ or between $\dot{\sigma}(2s)$ and $\dot{\sigma}(2p_z)$ molecular orbitals in case of O_2 and F_2 are also quite large with the result that neither $\sigma(2s)$ and $\sigma(2p_z)$ nor $\dot{\sigma}(2s)$ and $\dot{\sigma}(2p_z)$ can mix to any significant extent in these molecules. Hence the energies of $\sigma(2s)$, $\dot{\sigma}(2s)$, $\sigma(2p_z)$ and $\dot{\sigma}(2p_z)$ molecular orbitals practically remain unaltered so that the energy of $\sigma(2p_z)$ molecular orbital continues to remain lower than the energies of $\pi(2p_x)$ and $\pi(2p_y)$ molecular orbitals.

Mixing of Orbitals. An Alternative Explanation. The $2s$ and $2p_z$ atomic orbitals of each atom are of the same symmetry and if the energy difference between the $2s$ and $2p$ orbitals of each atom is small, there is a possibility of mixing of these atomic orbitals to produce two mixed sp_z atomic orbitals on each atom. The two mixed orbitals, viz., $\psi_{sp_z} = \frac{1}{\sqrt{1+\lambda^2}} (\psi_{2s} + \lambda\psi_{2p_z})$ and $\psi_{sp_z} = \frac{1}{\sqrt{1+\lambda^2}} (\lambda\psi_{2s} - \psi_{2p_z})$ ($\lambda^2 \neq 1$), on each atom will be of unequal energy. Since the $2s$ atomic orbital was of lower

energy than the $2p_z$ atomic orbital of the atom, the lower energy mixed sp_z atomic orbital thus formed on each atom will have more contribution from $2s$ atomic orbital and less contribution from the $2p_z$ atomic orbital. Similarly, the higher energy mixed sp_z atomic orbital will have more contribution from the $2p_z$ atomic orbital and less contribution from the $2s$ atomic orbital of the atom. Since all the four mixed sp_z atomic orbitals of both the atoms are of the same symmetry, they linearly combine with one another to give four σ MOs. (The number of molecular orbitals obtained is always equal to the number of atomic orbitals combined). Each such σ MO contains contributions from all the four sp_z atomic orbitals. But, the greater the contribution of an sp_z atomic orbital, the closer to it will be the resulting molecular orbital. Because of the formation of molecular orbitals (σ type) having contributions from s as well as p_z orbitals, it has been calculated that the energy of σ_1 is lower than the energy of $\sigma(2s)$ orbital of Fig. 27 and the energy of σ_3 orbital is higher than the energy of pure $\sigma(2p_z)$ orbital of Fig. 27. While drawing Fig. 27, it was assumed that $\sigma(2s)$ and $\sigma^*(2s)$ molecular orbitals are formed from $2s$ atomic orbitals of the atoms whereas $\sigma(2p_z)$ and $\sigma^*(2p_z)$ molecular orbitals are formed from $2p_z$ atomic orbitals of the atoms.

The modified molecular orbital energy levels for homonuclear diatomic molecules, where $2s$ and $2p$ atomic orbitals are comparable in energy, are shown in Fig. 29. This order of energy levels has been confirmed spectroscopically.

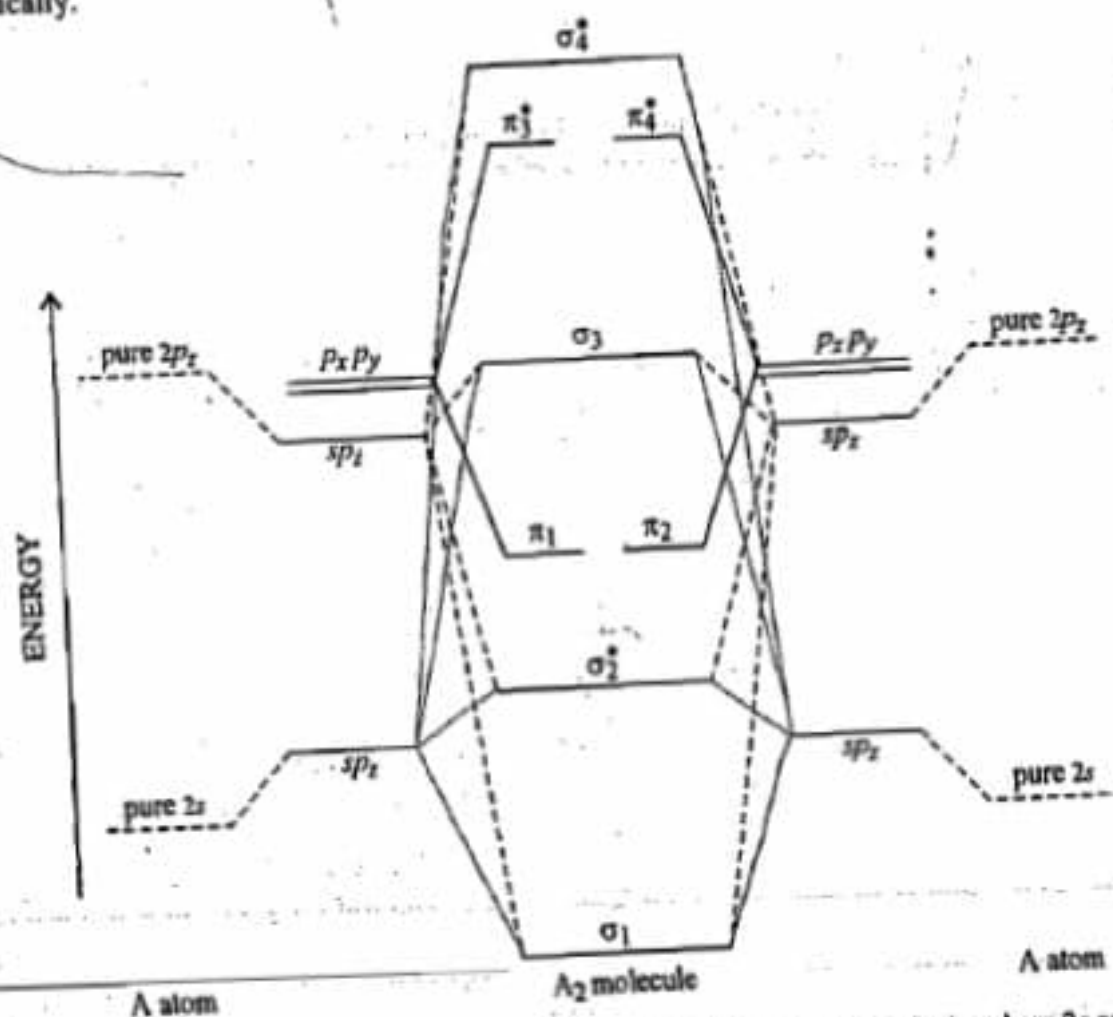


Fig. 29. Modified molecular orbital energy levels of homonuclear diatomic molecule A_2 where $2s$ and $2p$ orbitals are of comparable energy.

In the atoms where the energy difference between $2s$ and $2p$ atomic orbitals is very high, the mixing of $2s$ and $2p_z$ atomic orbitals of an atom is insignificant, even though they are of the same symmetry. Therefore, the atomic orbitals of such atoms as O and F remain almost pure $2s$ and pure $2p_z$ orbitals so that the order of energies of the resulting molecular orbitals of O_2 and F_2 remains the same as shown in Fig. 27. This order has also been confirmed from spectroscopic techniques for O_2 and F_2 .

Rules for Adding Electrons to MOs. The molecules are built up by adding electrons to molecular orbitals in the same way as the atoms are built up by adding electrons to atomic orbitals. The principles involved are the same in both cases. These may be summed up as follows :

1. The molecular orbital with lowest energy is filled first.
2. The maximum number of electrons in a molecular orbital cannot exceed two and the two electrons must be of opposite spin.
3. If there are two or more molecular orbitals at the same energy level, pairing of electrons will occur only after each orbital of the same energy has one electron.

Electronic Configurations of Molecules. While discussing the electronic configurations of molecules, we shall frequently make use of a term called **bond order**. This is calculated from the number of electrons in bonding and antibonding molecular orbitals as follows :

$$\text{Bond order} = \frac{1}{2} [\text{Number of electrons in BMOs} - \text{Number of electrons in ABMOs}]$$

If the number of electrons in bonding and antibonding MOs is the same, the bond order is zero, i.e., no bond is formed. The bond order of 1, 2 or 3 corresponds to single, double or triple bond.

The bond order of a molecule is directly proportional to its bond dissociation energy and inversely proportional to its bond length. This means that the higher the bond order, the larger is the bond dissociation energy of the molecule and the smaller is the bond length.

As would be discussed at appropriate places, the electronic configuration of a molecule helps to predict the magnetic character of the molecule. If all the electrons in a molecule are paired, the substance is *diamagnetic*. On the other hand, if some of the electrons are unpaired, the substance is *paramagnetic*.

Electronic Configurations of Homonuclear Diatomic Molecules. The electronic configurations of some simple diatomic molecules may now be considered.

Hydrogen molecule, H_2 . It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in $1s$ orbital and, therefore, there are two electrons to be accommodated in MOs. Both these electrons would be accommodated in the $\sigma(1s)$ BMO. In accordance with Pauli's exclusion principle, these two electrons should have opposite spins. The molecular orbital energy level diagram for H_2 molecule is presented in Fig. 30.

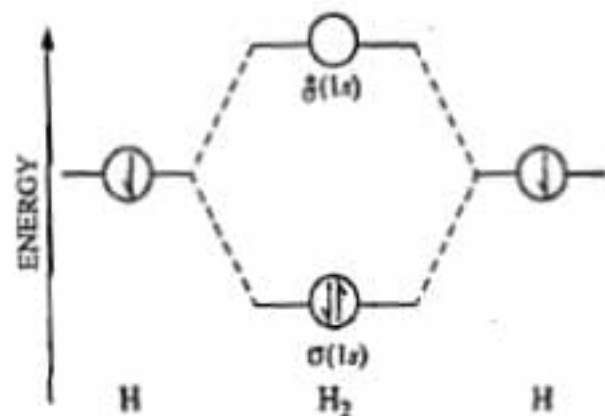


Fig. 30. Molecular orbital energy level diagram of H_2 molecule.

The electronic configuration of H_2 molecule is, thus, $H_2 : \sigma(1s)$ and its bond order $= 1/2(2 - 0) = 1$.

This means that two hydrogen atoms are bonded together by a single bond. The bond dissociation energy of H_2 molecule has been found to be 458 kJ mol^{-1} and bond length equal to 0.74 \AA .

Hydrogen molecule ion, H_2^+ . This molecule has been detected spectroscopically when electric discharge is passed through hydrogen gas under reduced pressure. The molecule has only one electron and its electronic configuration is $H_2^+ : \sigma(1s)^1$ and bond order $= 1/2(1 - 0) = 1/2$.

The positive value of bond order indicates that the bond does get formed and the molecule is stable. However, the bond in H_2^+ ion is weaker than that in H_2 molecule. The bond dissociation energy of H_2^+ ion (269 kJ mol^{-1}) is less than that of H_2 molecule (458 kJ mol^{-1}). The bond length in H_2^+ ion (1.04 \AA) is larger than that in H_2 molecule (0.74 \AA).

Helium molecule, He_2 . Each helium atom has two $1s$ electrons and thus there are four electrons to be accommodated in He_2 molecule. Since each molecular orbital, just like atomic orbital, can accommodate only two electrons of opposite spins, only one pair can be accommodated in $\sigma(1s)$ BMO. The other pair will have to be accommodated in $\sigma^*(1s)$ ABMO.

The electronic configuration of He_2 is, thus,

$$\text{He}_2: \sigma(1s)^2 \sigma^*(1s)^2 \text{ and its bond order} = \frac{1}{2}(2-2) = 0.$$

The zero bond order indicates that the molecule does not exist. Calculations have shown that the antibonding effect of a filled ABMO is slightly stronger than the bonding effect of a filled BMO. Consequently, there is no possibility whatsoever for the existence of He_2 molecule.

Diatomic Molecules of Second Row Elements. In these elements, the 1s orbitals are completely filled. In the formation of molecular orbitals, the electrons in the inner shells (i.e., 1s electrons) of each atom remain essentially unperturbed in their respective atomic orbitals and may be kept out of consideration. In the formulation of electronic configurations of these molecules, the letters *KK* are generally used for denoting the fully filled inner shells (*K*-shells) in the two atoms.

Lithium molecule, Li_2 . The electronic configuration of lithium ($Z = 3$) is $1s^2 2s^1$. There are six electrons in lithium molecule. The four electrons are present in *K*-shells and there are only two electrons to be accommodated in molecular orbitals. These two electrons go into $\sigma(2s)$ BMO which has lower energy and $\sigma^*(2s)$ ABMO remains empty.

The electronic configuration of Li_2 molecule is thus represented as

$$\text{Li}_2: KK \sigma(2s)^2 \text{ or } KK \sigma_1^2 \text{ and its bond order} = \frac{1}{2}(2-0) = 1$$

Thus, there is one Li-Li sigma bond. The bond dissociation energy of the molecule is quite low, being about 105 kJ mol^{-1} . The bond length of the molecule is 2.67 \AA .

Beryllium molecule, Be_2 . The next element beryllium ($Z = 4$) has electronic configuration $1s^2 2s^2$. In the formation of a diatomic molecule, evidently, two outer electrons of each atom, i.e., four in all, have to be accommodated in molecular orbitals. Two of these (one pair) will go into $\sigma(2s)$ BMO while the other two (the second pair) will have to go into $\sigma^*(2s)$ ABMO.

The electronic configuration of Be_2 molecule is, thus,

$$\text{Be}_2: KK \sigma(2s)^2 \sigma^*(2s)^2 \text{ or } KK \sigma_1^2 \sigma_1^{*2} \text{ and its bond order} = \frac{1}{2}(2-2) = 0.$$

The zero bond order suggests that the existence of stable Be_2 molecule is not possible.

Boron molecule, B_2 . The electronic configuration of boron ($Z = 5$) is $1s^2 2s^2 2p^1$. The outer shell (i.e., the second shell) of each atom contains 3 electrons. When two boron atoms combine to form the molecule B_2 , there are 6 electrons which need to be accommodated in the molecular orbitals of B_2 . Two of these will be accommodated in $\sigma(2s)$ molecular orbital (i.e., σ_1 MO) which has the lowest energy and the other two in $\sigma^*(2s)$ molecular orbital which comes next in the order of increasing energy. Due to the mixing of orbitals as discussed above, the energies of MOs would be as shown in Figs. 28 and 29. Accordingly, the $\pi(2p_x)$ and $\pi(2p_y)$ molecular orbitals (i.e., π_1 and π_2 orbitals) lie at lower energy level than the σ_2 molecular orbital. Since $\pi(2p_x)$ and $\pi(2p_y)$ molecular orbitals (i.e., π_1 and π_2 MOs) have equal energies, therefore, the two electrons distribute themselves between these two orbitals, one going to each orbital according to rule 3 above. As both these π molecular orbitals are bonding molecular orbitals, the B_2 molecule is expected to be stable. Further, since each bonding molecular orbital contains a single, i.e., an unpaired electron, the molecule B_2 is paramagnetic as is experimentally observed. (Had there been no mixing of orbitals, the order of energy levels should have been as shown in Fig. 27 and the configuration of B_2 would have been $KK(\sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2)$, i.e., the molecule B_2 should have been diamagnetic which is contrary to experimental observation). The electronic configuration of B_2 molecule is, thus,

$$\text{B}_2: KK \sigma(2s)^2 \sigma^*(2s)^2 \pi(2p_x)^1 \pi(2p_y)^1 \text{ or } KK \sigma_1^2 \sigma_1^{*2} \pi_1 \pi_2$$

$$\text{and its bond order} = \frac{1}{2}(4-2) = 1$$

The molecule has only one bond. The bond dissociation energy of B_2 molecule has been found to be 289 kJ mol^{-1} and bond length equal to 1.59 \AA .

Carbon molecule, C_2 . The next element is carbon ($Z = 6$). Its electronic configuration is $1s^2 2s^2 2p^2$. The outer shell of each atom contains 4 electrons. In the formation of C_2 molecule, there will be, evidently, 8 electrons to be accommodated in the molecular orbitals of C_2 in accordance with Figs. 28 and 29. The electronic configuration of C_2 molecule is

$$C_2 : KK(2s)^2 \bar{\sigma}(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2 \text{ or } KK\sigma_1^2 \bar{\sigma}_2^2 \pi_1^2 \pi_2^2$$

$$\text{and its bond order} = 1/2(6 - 2) = 2$$

Since, C_2 molecule does not have any unpaired electron, it is *diamagnetic*, as observed experimentally.

The bond dissociation energy of C_2 molecule has been found to be $627.9 \text{ kJ mol}^{-1}$ and bond length equal to 1.31 \AA .

It may be noted that in this case also, the $\sigma(2p_z)$ or σ_3 molecular orbital is left vacant indicating that it is at a higher energy level than the π_1 and π_2 molecular orbitals. If, in accordance with the energy level diagram shown in Fig. 27, six electrons had gone into $\sigma(2s)$, $\bar{\sigma}(2s)$ and $\sigma(2p_z)$ molecular orbitals, the remaining two electrons would have distributed themselves equally between the two $\pi(2p)$ molecular orbitals which are of equal energy. In that case, the molecule C_2 , having two unpaired electrons, would have been paramagnetic. But actually the molecule is diamagnetic. This can be explained only on the basis of the reversal of energies of $\sigma(2p_z)$, i.e., σ_3 and $\pi(2p_x)$, and $\pi(2p_y)$, i.e., π_1 and π_2 , molecular orbitals as a result of mixing of molecular orbitals, as discussed earlier.

Nitrogen molecule, N_2 . Consider, next, the formation of N_2 molecule. The electronic configuration of nitrogen ($Z = 7$) is $1s^2 2s^2 2p^3$. The outer shell in this case contains 5 electrons. Thus, there are 10 electrons to be accommodated in the molecular orbitals of N_2 . The electronic configuration of nitrogen molecule is, thus,

$$N_2 : KK \sigma(2s)^2 \bar{\sigma}(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2 \sigma(2p_z)^2 \text{ or } KK \sigma_1^2 \bar{\sigma}_2^2 \pi_1^2 \pi_2^2 \sigma_3^2$$

$$\text{and its Bond order} = \frac{1}{2}(8 - 2) = 3$$

Thus, nitrogen molecule contains a **triple bond**.

It is evident that in the formation of N_2 molecule, only one antibonding molecular orbital is involved (the remaining four being all bonding molecular orbitals). Hence, the nitrogen molecule is highly stable. This is confirmed by its high bond dissociation energy, viz., $945.6 \text{ kJ mol}^{-1}$ and small bond length equal to 1.10 \AA . Also, since there are no unpaired electrons in any orbital, N_2 molecule is *diamagnetic*.

Oxygen molecule, O_2 . As already explained, there is negligible mixing of $2s$ and $2p$ atomic orbitals on each O atom. Therefore, the order of energy levels in O_2 is as given in Fig. 27. The electronic configuration of oxygen ($Z = 8$) is $1s^2 2s^2 2p^4$. In the formation of O_2 molecule, 12 outer electrons are to be accommodated in MOs. Four of these electrons fill the $\sigma(2s)$ and $\bar{\sigma}(2s)$ molecular orbitals. Six of them (i.e., 3 pairs) go into the three bonding MOs, viz., $\sigma(2p_z)$, $\pi(2p_x)$ and $\pi(2p_y)$ and the remaining two electrons go into the antibonding MOs. The lowest ones are $\pi(2p_x)$ and $\pi(2p_y)$. Since both these orbitals are of equal energy, the electrons will distribute themselves one in each orbital. Since there are now two unpaired electrons, the oxygen molecule is *paramagnetic*.

The electronic configuration of oxygen molecule is, thus

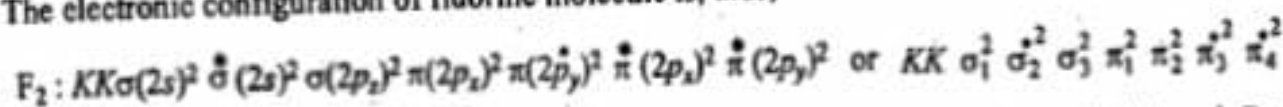
$$O_2 : KK\sigma(2s)^2 \bar{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \pi(2p_x)^1 \pi(2p_y)^1 \text{ or } KK \sigma_1^2 \bar{\sigma}_2^2 \sigma_3^2 \pi_1^2 \pi_2^2 \pi_3^1 \pi_4^1$$

Bond order in this case is $= \frac{1}{2}(8 - 4) = 2$. Oxygen molecule, thus, contains a double bond.

Because of the presence of 4 electrons in ABMOs, oxygen molecule is less stable than nitrogen molecule. Its bond dissociation energy is much less, being $494.6 \text{ kJ mol}^{-1}$ and bond length is larger being 1.21 \AA .

Fluorine molecule, F_2 . Because of large energy difference in $2s$ and $2p_z$ orbitals on each F atom, the mixing of these orbitals is negligible and the order of MO energy levels will be as shown in Fig. 27. The electronic configuration of fluorine ($Z = 9$) is $1s^2 2s^2 2p^5$. In the formation of F_2 molecule by the combination of two fluorine atoms, there would be 14 outer electrons to be accommodated in molecular orbitals.

The electronic configuration of fluorine molecule is, thus,

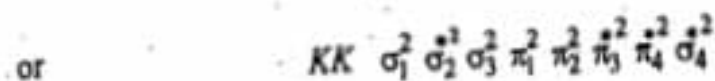
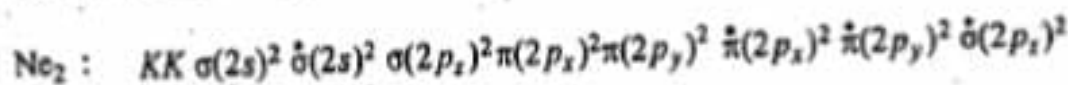


Bond order in this case is $= \frac{1}{2}(8 - 6) = 1$. The F_2 molecule, thus, contains a single bond. Because of the presence of as many as 6 electrons in ABMOs, the bonding in F_2 is weaker than that in O_2 . Therefore, bond dissociation energy of F_2 is very low being 155 kJ mol^{-1} and bond length is 1.42 \AA .

Since there are no unpaired electrons, the molecule is *diamagnetic*.

Neon molecule, Ne_2 . The order of energy levels in hypothetical Ne_2 should be as given in Fig. 27 because the energy gap between $2s$ and $2p$ orbitals on Ne is very high and the extent of their mixing will be negligible. The electronic configuration of neon ($Z = 10$), is $1s^2 2s^2 2p^6$. In the formation of Ne_2 , if possible, 16 outer electrons have to be accommodated in molecular orbitals.

The electronic configuration of hypothetical neon molecule is



Bond order in this case is equal to $= \frac{1}{2}(8 - 8) = 0$. Since antibonding MOs slightly dominate over the bonding MOs, Ne_2 molecule would be incapable of existence.

Problem 1. Write the electronic configurations of H_2 , H_2^+ and the H_2^- in terms of molecular orbital theory.

Answer. H_2 , H_2^+ and H_2^- have 2, 1 and 3 electrons, respectively. Hence, their electronic configurations would be as follows :



Problem 2. Why does He_2^+ exist whereas He_2 does not ?

Answer : Electronic configuration of He_2 is : $\sigma(1s)^2 \sigma^*(1s)^2$

$$\therefore \text{Bond order} = \frac{1}{2}(2 - 2) = 0$$

Electronic configuration of He_2^+ is : $\sigma(1s)^2 \sigma^*(1s)^1$

$$\therefore \text{Bond order} = \frac{1}{2}(2 - 1) = \frac{1}{2}$$

Thus, while the bond order of He_2 is zero, that of He_2^+ is $1/2$. Hence, He_2^+ exists while He_2 does not.

Problem 3. Of the species O_2 , O_2^+ , O_2^- , O_2^{2-} , which would have the maximum bond strength?

Answer : Higher bond orders are associated with shorter bond lengths and higher bond strengths. We will first calculate the bond orders for the various species from their electronic configurations :



$$\therefore \text{Bond order} = 1/2 (8 - 4) = 2$$

O_2^+ : One electron is removed from $\uparrow\downarrow \pi(2p_x)$ ABMO.

$$\therefore \text{Bond order} = 1/2 (8 - 3) = 2\frac{1}{2}$$

O_2^- : One electron is added to $\uparrow\downarrow \pi(2p_x)$ ABMO.

$$\therefore \text{Bond order} = 1/2 (8 - 5) = 1\frac{1}{2}$$

O_2^{2-} : Two electrons are added to the outermost ABMO.

$$\therefore \text{Bond order} = 1/2 (8 - 6) = 1$$

Since O_2^+ has the highest bond order, it has the shortest bond length and hence the maximum bond strength.