
1.10 FORMATION OF BONDING AND ANTIBONDING MOLECULAR ORBITALS (LCAO METHOD)

An electron in an atom is described by a wave function, ψ , called an *atomic orbital*. Similarly, the behaviour of an electron in a molecule is described by a molecular wave function called the *molecular orbital*. The most convenient way of working out the wave functions for molecular orbitals is to adopt the method of *linear combination of atomic orbital* (LCAO).

Quantum mechanics show that linear combination of two functions gives not one but two combinations and hence two molecular orbitals, a bonding orbital and an antibonding orbital.

1. **Addition when two waves are in phase:** If ψ_A and ψ_B are the atomic wave functions of the combining atoms A and B, then the wave functions of orbitals can be obtained by the *addition* or *subtraction* of the wave functions of the two atomic orbitals. The additive effect of the electron waves as a result of the addition combination of atomic orbital wave functions when the two waves are in phase is shown in Fig. 1.15(a).

2. **Subtraction when two waves are not in phase:** Similarly, the subtractive effect of the electron waves as a result of the subtraction combination of atomic orbital wave functions when the two waves are out of phase is shown in Fig. 1.15(b).

Thus the wave function of bonding orbital is given as:

$$\psi_b = \psi_A + \psi_B \text{ (Bonding orbital stabilizes molecule)} \quad (1.1)$$

The wave function of antibonding orbital is given as:

$$\psi_a = \psi_A - \psi_B \text{ (Antibonding orbital destabilizes molecule)} \quad (1.2)$$

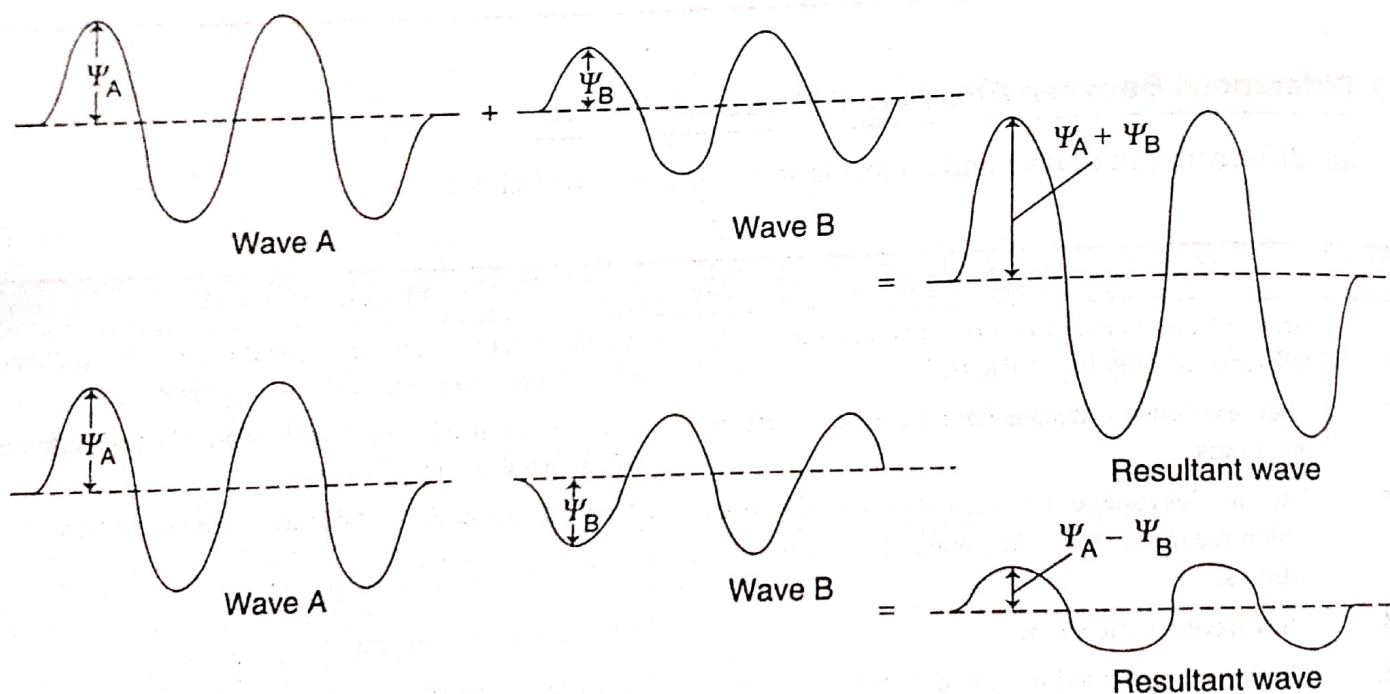


Figure 1.15 (a) Additive combination of waves. **(b)** Subtractive combination of waves.

ψ_b is called *bonding molecular orbital* and ψ_a is called *antibonding molecular orbital*.

Squaring Equation 1.1, we get the expression for the electron density (probability) of the bonding molecular orbital:

$$\psi_b^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A \psi_B \quad (1.3)$$

It is evident that probability ψ_b^2 is greater than the sum of the probabilities $\psi_A^2 + \psi_B^2$ by an amount $2\psi_A \psi_B$, i.e. in the molecular orbital, there is greater electron density in the region between the nuclei than the two isolated atoms. In this molecular orbital, both the nuclei for the electrons is increased. As a result, the energy of the molecule is lowered and this accounts for the stability of bond A–B. The orbital ψ_b is therefore termed as *bonding molecular orbital*.

On the other hand, squaring Equation 1.2 gives the expression for the probability of the antibonding molecular orbital:

$$\psi_b^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B \quad (1.4)$$

Evidently, probability is ψ_b^2 less than $\psi_A^2 + \psi_B^2$ by an amount $2\psi_A\psi_B$, i.e. in this molecular orbital, there is *less electron density in the region between the nuclei* than the two isolated atoms. This results in *greater repulsion* between the nuclei and hence the orbital ψ_a represents the state of *higher energy* as compared to the energy of the individual atoms. Such an orbital obviously cannot lead to the formation of a chemical bond and is, therefore, termed as an *antibonding molecular orbital*.

We have seen above that the combination of the two atomic orbitals forms two molecular orbitals, one bonding (ψ_b) and the other antibonding (ψ_a). The bonding molecular orbital has lower energy than that of atomic orbitals whereas the antibonding molecular orbital has higher energy than that of atomic orbitals from which it is formed as shown in Fig. 1.16.

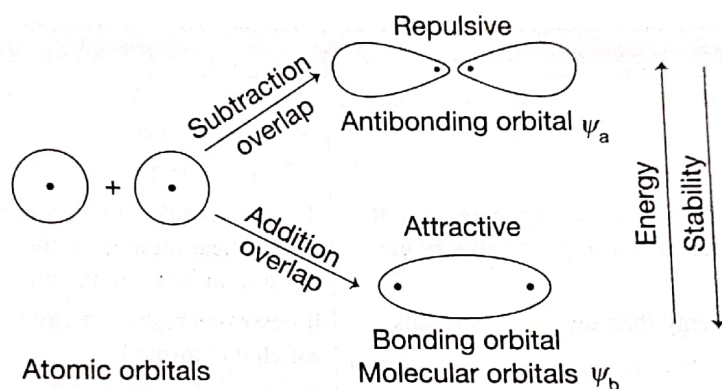


Figure 1.16 Molecular orbitals formed by the combinations of two 1s atomic orbitals.

1.10.1 Bonding and Antibonding Molecular Orbitals in Terms of Wave Functions

We can interpret bonding and antibonding molecular orbitals by considering the interacting AOs as each being a stationary wave, having a crest (+ sign) and a trough (– sign) as shown in Fig. 1.17. *It may be mentioned here that signs (+) and (–) simply determine the symmetry of the wave functions and have nothing to do with the electrical charges.*

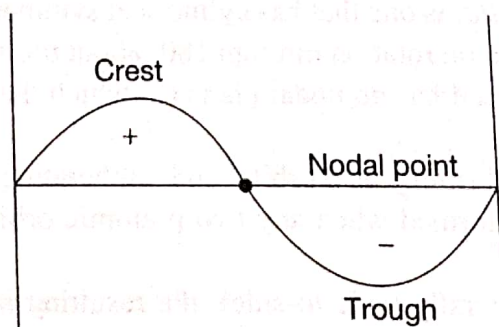


Figure 1.17 Stationary wave showing crest (+) and trough (–).

When the two functions interact in such a way that crest (+ sign) of one coincides with the crest (+ sign) of the other, i.e. when the wave functions of the combining atomic orbitals are in phase and reinforce each other, we get a resultant wave corresponding to a bonding molecular orbital. In other words, bonding molecular orbitals is formed by the overlap of atomic orbitals with the same sign.

On the other hand, when the two wave functions interact so that the crest (+ sign) of one coincides with the trough (– sign) of the other, i.e. when the wave functions of the combining atomic orbitals are out of phase and cancel each other, we get a resultant wave corresponding to an antibonding molecular orbital is formed by the combination of atomic orbitals with opposite signs.

1.10.2 Differences between Bonding and Antibonding Molecular Orbitals

The main characteristics and difference between bonding and antibonding molecular orbitals are as follows:

S. no.	Bonding molecular orbital	Antibonding molecular orbitals
1.	It is formed by the addition overlap of wave functions of atomic orbitals: $\psi_b^2 = (\psi_A + \psi_B)^2$	It is formed by the subtraction overlap of wave functions of atomic orbitals: $\psi_a^2 = (\psi_A - \psi_B)^2$
2.	It has high electron density in the region between the two nuclei and this accounts for the stability of the bond.	The electron density is concentrated away from the internuclear region, i.e. the probability of finding the electron in between the nuclei is negligible.
3.	It possesses lower energy than the atomic orbitals from which it is formed.	It possesses higher energy than the atomic orbitals from which it is formed.
4.	It is formed when the lobes of combining atomic orbitals have the same sign.	It is formed when the lobes of combining atomic orbitals have opposite sign.
5.	Electron presents in bonding MO contributes to attraction and bonding MO is represented by σ or π .	Electron present in antibonding MO contributes to repulsion and antibonding MO is represented by σ^* or π^* .

1.11 COMBINATION OF ATOMIC ORBITALS—SIGMA (σ) AND PI (π) MOLECULAR ORBITALS

In the MO theory, orbitals are identified σ or π depending on the type of the *symmetry* of the molecular orbital. A *sigma (σ) molecular orbital* is one that has cylindrical symmetry around the internuclear axis, i.e. it does not show any change of sign on rotation through 180° about the axis (Fig. 1.18). Alternatively, it can be said that a sigma molecular orbital has no nodal plane (in which the electron density is zero) along the internuclear axis.

The bonding orbital is designated simply as σ orbital and antibonding as σ^* .

Such a sigma (σ) orbital is also formed when any two p-atomic orbitals overlap in end-on (along their axis) position (Fig. 1.19).

When atomic orbitals overlap laterally (side-to-side), the resulting molecular orbital is called a *pi (π) orbital*. A π -type orbital does not possess cylindrical symmetry about the internuclear axis, i.e. if we rotate this molecular orbitals through 180° , it will change sign. In contrast to σ -orbital, π -MO has a nodal plane (zero electron density) along the internuclear axis as shown in Fig. 1.20.