## ❖ PMO Approach

The PMO (perturbation molecular orbital) theory is nothing but an extension of the general molecular orbital theory. In this approach, the participating atomic orbitals are considered as the initial state, which in turn, is actually perturbed by the interaction to give the final state i.e. molecular orbitals. Furthermore, the PMO approach can also be applied to molecular orbitals to give new molecular orbitals. Now, depending upon the energy of basis orbitals i.e. unperturbed orbitals, the perturbed molecular orbitals can take two routes as discussed below.

### ➢ *Perturbed Molecular Orbitals from Degenerate Basis*

The perturbed molecular orbitals are formed by the additive and subtractive interaction of the basis orbitals; and if the unperturbed basis orbitals are degenerate, they equally contribute toward the additive and subtractive interaction.

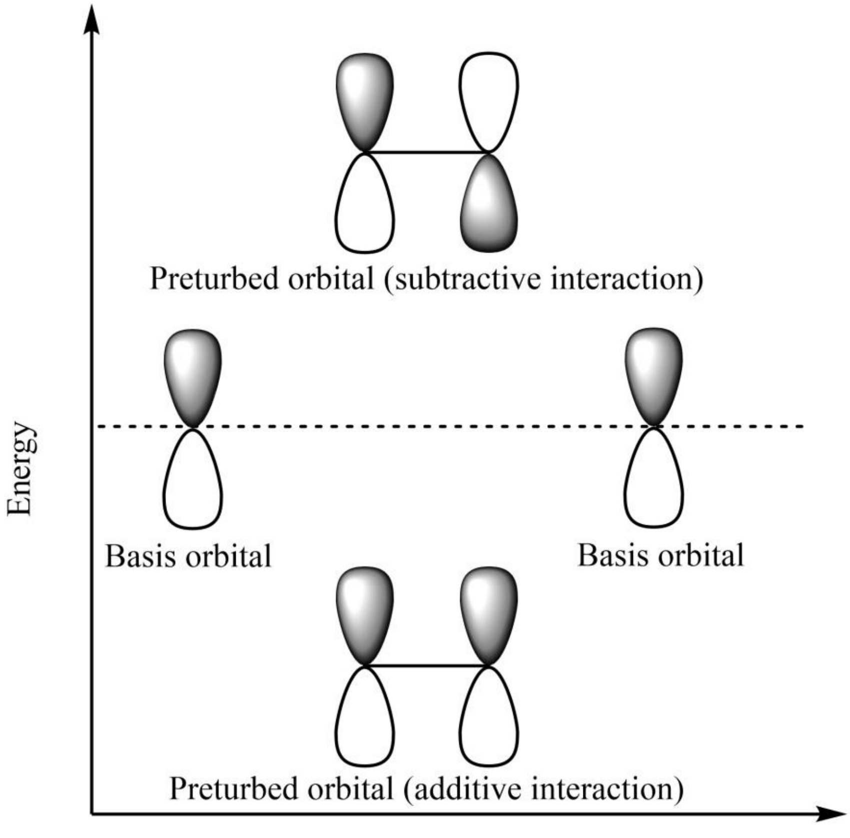


Figure 21. The perturbed molecular orbitals from degenerate basis orbitals.

In other words, the subtractive perturbation increases the energy whereas the additive interaction decreases the total energy of the molecular orbital formed.

### ➢ *Perturbed Molecular Orbitals from Non-Degenerate Basis*

The perturbed molecular orbitals are formed by the additive and subtractive interaction of the basis orbitals; and if the unperturbed basis orbitals are not degenerate, they do not equally contribute toward the additive and subtractive interaction. Consider the two unperturbed basis orbitals $\psi_1$ and $\psi_2$ with different energies.

$$\psi_+ = \psi_1 + \lambda\psi_2 \tag{1}$$

$$\psi_- = \psi_2 - \lambda\psi_1 \tag{2}$$

Where the symbol λ whose value varies from 0 to 1. As the energy difference between $\psi_1$ and $\psi_2$ increases, the magnitude of λ approaches to zero.

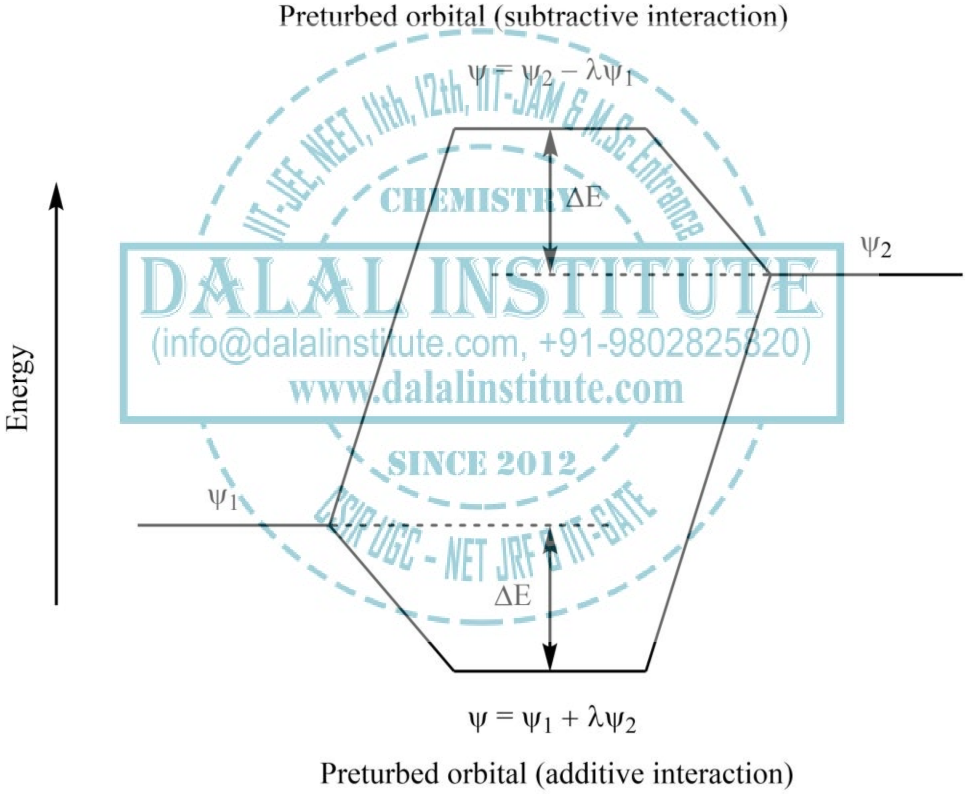


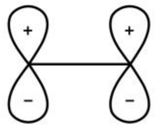
Figure 22. The perturbed molecular orbitals from non-degenerate basis orbitals.

In other words, the subtractive perturbation increases the energy whereas the additive interaction decreases the total energy of the molecular orbital formed. It is obvious from the above energy level diagram that the perturbation made the lower-energy basis orbital to lowered down and higher energy-orbital to rise above in energy further.

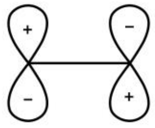
### ➢ *Characteristic Features of PMO Approach*

Before we apply the PMO method to draw all the molecular orbitals of different linear and cyclic systems, it is very important to discuss some characteristic features of perturbed molecular orbitals first as given below.

**1. Depiction of perturbed molecular orbitals:** Unlike conventional MO theory, the molecular orbitals in the PMO approach are portrayed as in terms of basis orbitals rather than the actual shapes. Therefore, every shape with more than one atomic orbital is actually a molecular orbital.

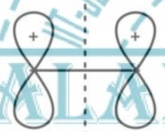


Bonding molecular orbital (BMO)

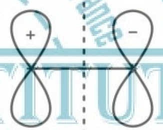


Antibonding molecular orbital (BMO)

**2. Symmetry of perturbed molecular orbitals:** If a molecular orbital can be divided into two equal halves, the MO will be said to possess mirror or '*m*' symmetry.

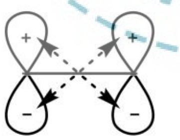


Mirror symmetry present

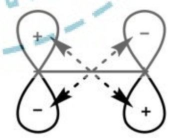


Mirror symmetry absent

Similarly, a molecular orbital has a two-fold symmetry axis, the MO will be said to possess inversion or '$C_2$' symmetry.

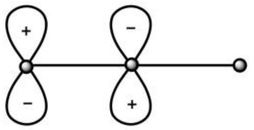


$C_2$ symmetry absent

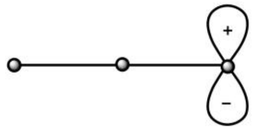


$C_2$ symmetry present

**3. Representation of basis orbitals:** The basis orbitals in PMO approach are portrayed combined number of participating atoms. For instance, if the molecular orbital of ethylene and a *p*-orbital are basis orbital, both should be depicted three carbon centres.



Ethylene



*p*-orbital

### ➢ *Construction of Perturbed Molecular Orbitals of Linear Conjugated Systems*

The π-molecular orbitals of linear conjugated systems can primarily be classified into two categories, even-numbered systems, and odd-numbered conjugated systems.

**1. Molecular orbitals of even-numbered linear conjugated systems:** If the number of carbon atoms in the conjugated system is even, half of the molecular orbitals will be bonding and half of the molecular orbitals will be antibonding in nature. The number of vertical nodes in the *n*th molecular orbital will be *n*–1.

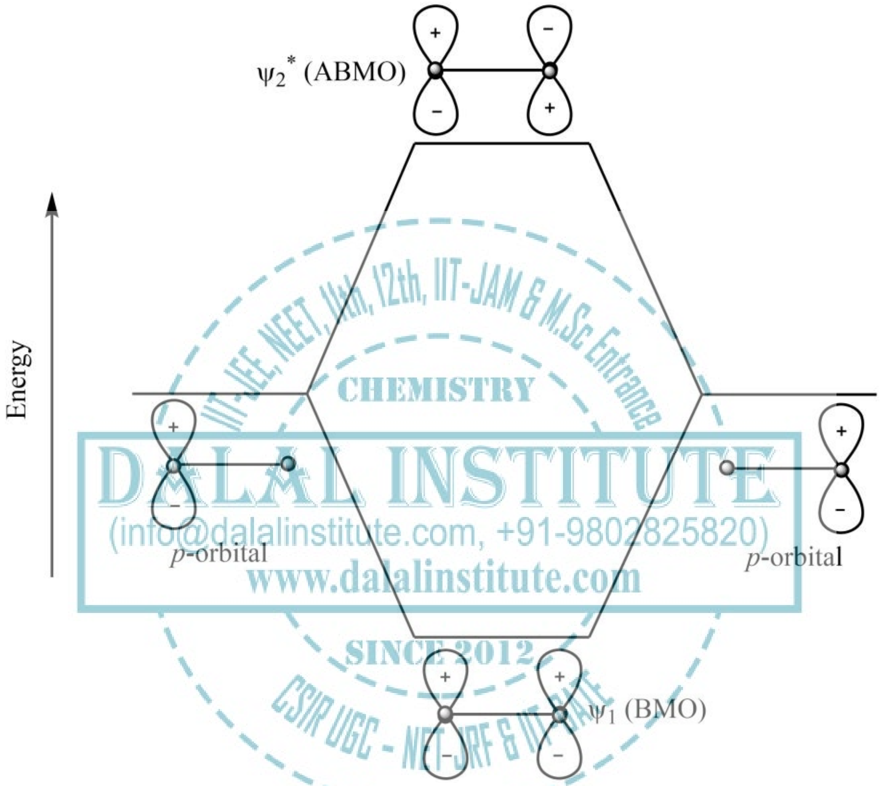


Figure 23. The perturbed molecular orbitals of ethylene.

The nature of the symmetry and number of nodes in the perturbed molecular orbitals (PMO) of ethylene are given below.

Table 1. Symmetry and nodes in different PMOs of ethylene.

| PMO | Number of nodes | Mirror symmetry | $C_2$-symmetry |
|---|---|---|---|
| $\psi_1$ | 0 | Present | Absent |
| $\psi_2$ | 1 | Absent | Present |

The nature of the symmetry and number of nodes in the perturbed molecular orbitals (PMO) of other even-numbered π-bonding systems are given below.

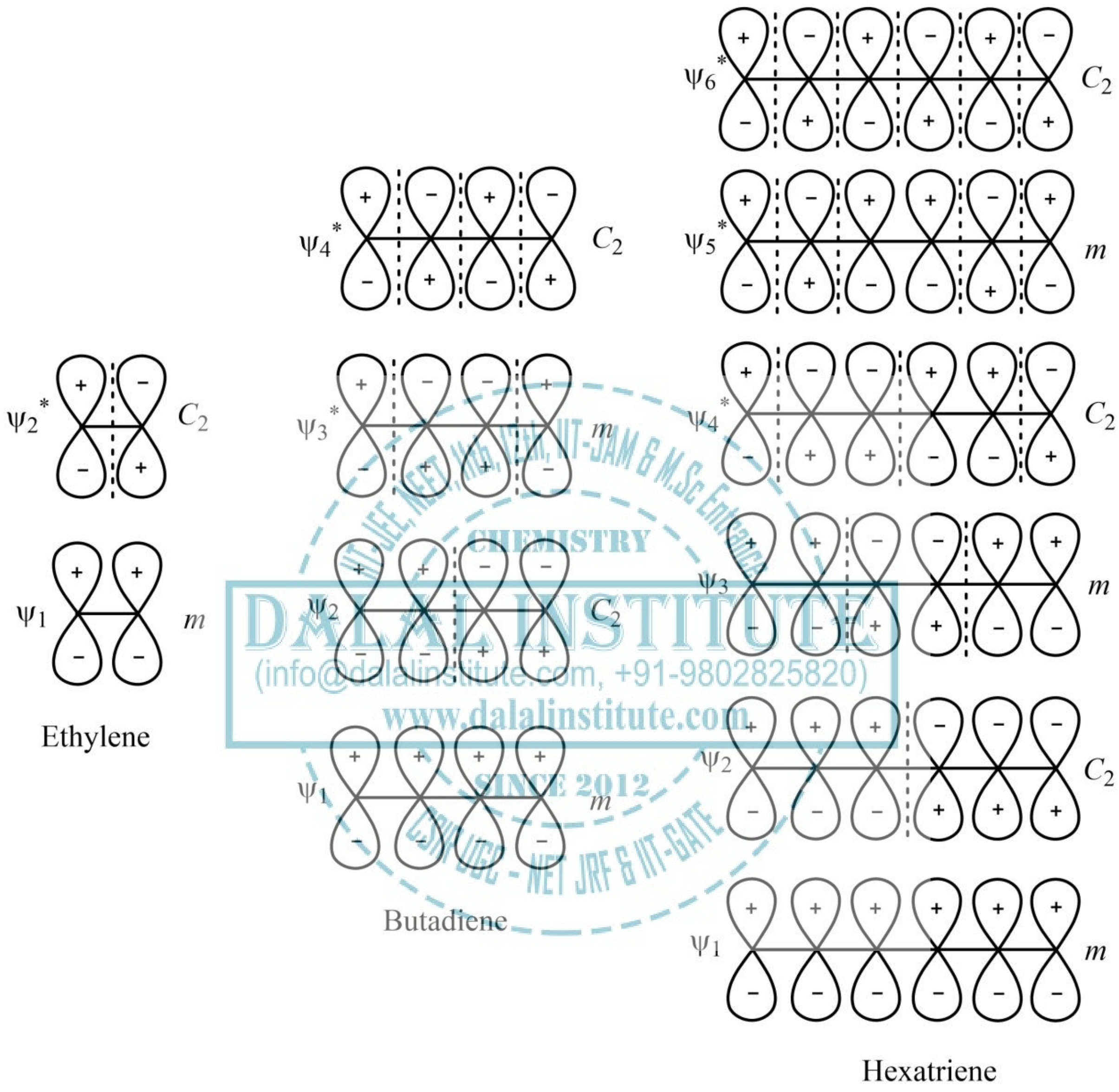


Figure 24. The perturbed molecular orbitals (along with the symmetry) of ethylene, butadiene, and hexatriene.

It is obvious from the above diagram that all the nodes in linear conjugated systems with an even number of carbon atoms pass through in-between the carbon nuclei.

**2. Molecular orbitals of odd-numbered linear conjugated systems:** If the number of carbon atoms in the conjugated system is odd, say *N*; *N*/2 of the molecular orbitals will be bonding whereas *N*/2 of the molecular orbitals will be antibonding in nature. One perturbed molecular orbital will be non-bonding in nature. The number of vertical nodes in the *n*th molecular orbital will be *n*–1.

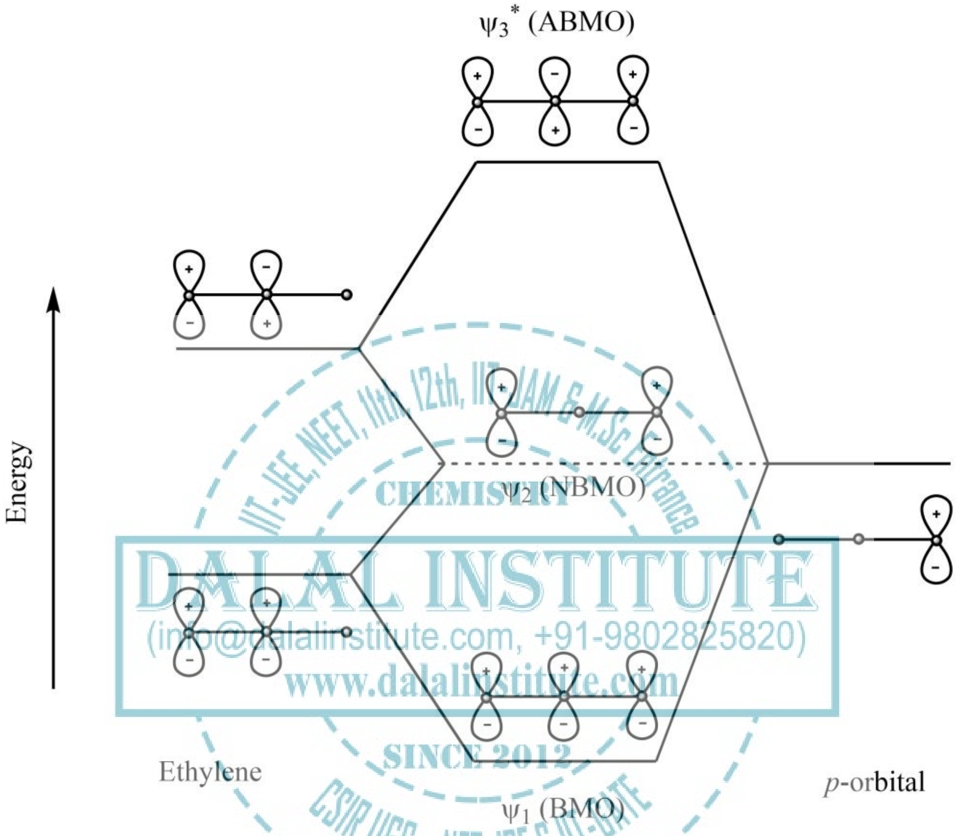


Figure 25. The perturbed molecular orbitals of allyl.

The nature of the symmetry and number of nodes in the perturbed molecular orbitals (PMO) of ethylene are given below.

Table 2. Symmetry and nodes in different PMOs of allyl.

| PMO | Number of nodes | Mirror symmetry | $C_2$-symmetry |
|---|---|---|---|
| $\psi_1$ | 0 | Present | Absent |
| $\psi_2$ | 1 | Absent | Present |
| $\psi_3$ | 2 | Present | Absent |

The nature of the symmetry and number of nodes in the perturbed molecular orbitals (PMO) of other odd-numbered π-bonding systems are given below.

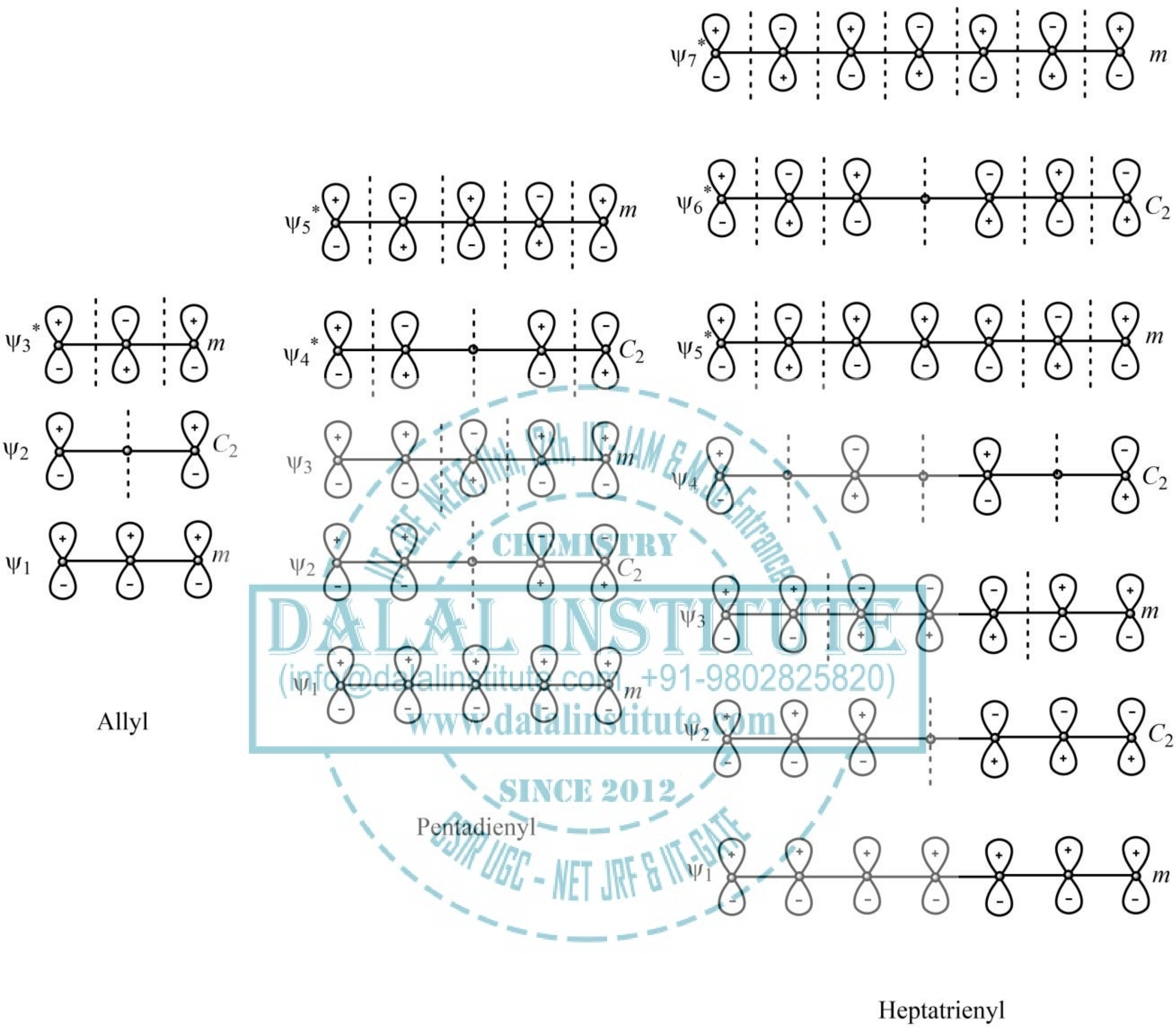


Figure 26. The perturbed molecular orbitals (along with the symmetry) of allyl, pentadienyl, and heptatrienyl.

It is obvious from the above diagram that all the nodes in $\psi_{odd}$ pass through in-between the carbon nuclei whereas all nodes in $\psi_{even}$ pass through in-between the carbon nuclei excepting one that passes through the central carbon nucleus. Furthermore, all the nodes in the case of non-bonding molecular orbitals pass through the carbon nuclei.

## ➢ ***PMO Approach for Aromaticity***

One of the most important applications of the PMO approach is that it can also be used to predict the aromatic character of different organic compounds. According to this method, we need to observe the total energy of the conjugated system when it is molded into a ring. If the energy of the cyclic conjugated system becomes less than the open chain counterpart, it will be labeled as aromatic. Contrariwise, If the energy of the cyclic conjugated system becomes greater than the open chain counterpart, it will be labeled as antiaromatic. M. J. Goldstein and Roald Hoffmann wrote a very important paper in 1971 on symmetry, topology, and aromaticity. In their method, a cyclic conjugated system is considered as a derivative of two open-chain fragments that are joined at the ends, something like a donor-acceptor assembly. Now after taking mirror symmetry into consideration, we should expect a stable association if the symmetry of HOMO of one fragment matches with the symmetry of LUMO of the other fragment and vice-versa.

For simplicity, we will study conjugated systems with an even number of $\pi$-electrons only. Goldstein and Hoffmann divided these types of systems into two categories; Mode 2 (HOMO symmetric and LUMO antisymmetric) and Mode 0 (HOMO antisymmetric and LUMO symmetric).

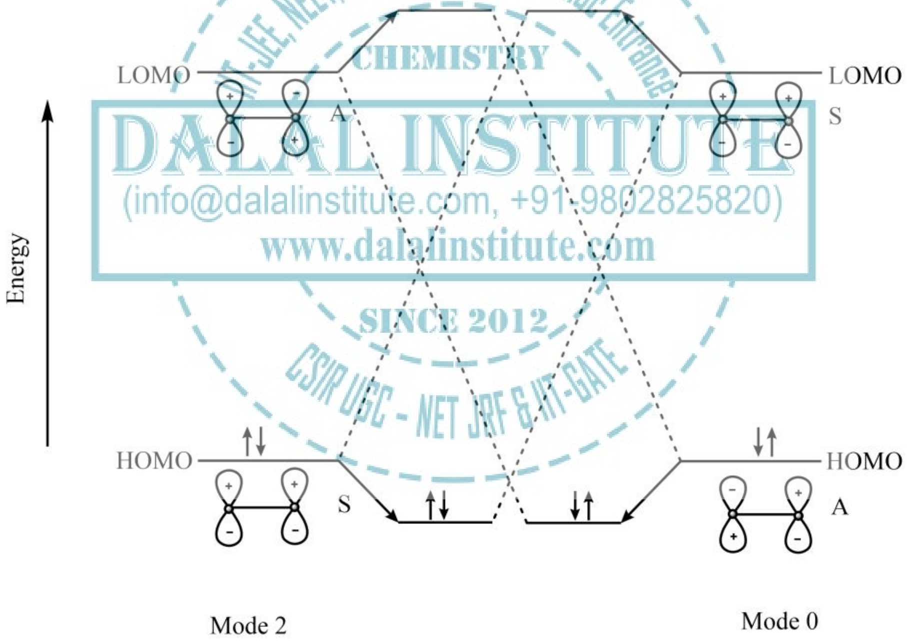
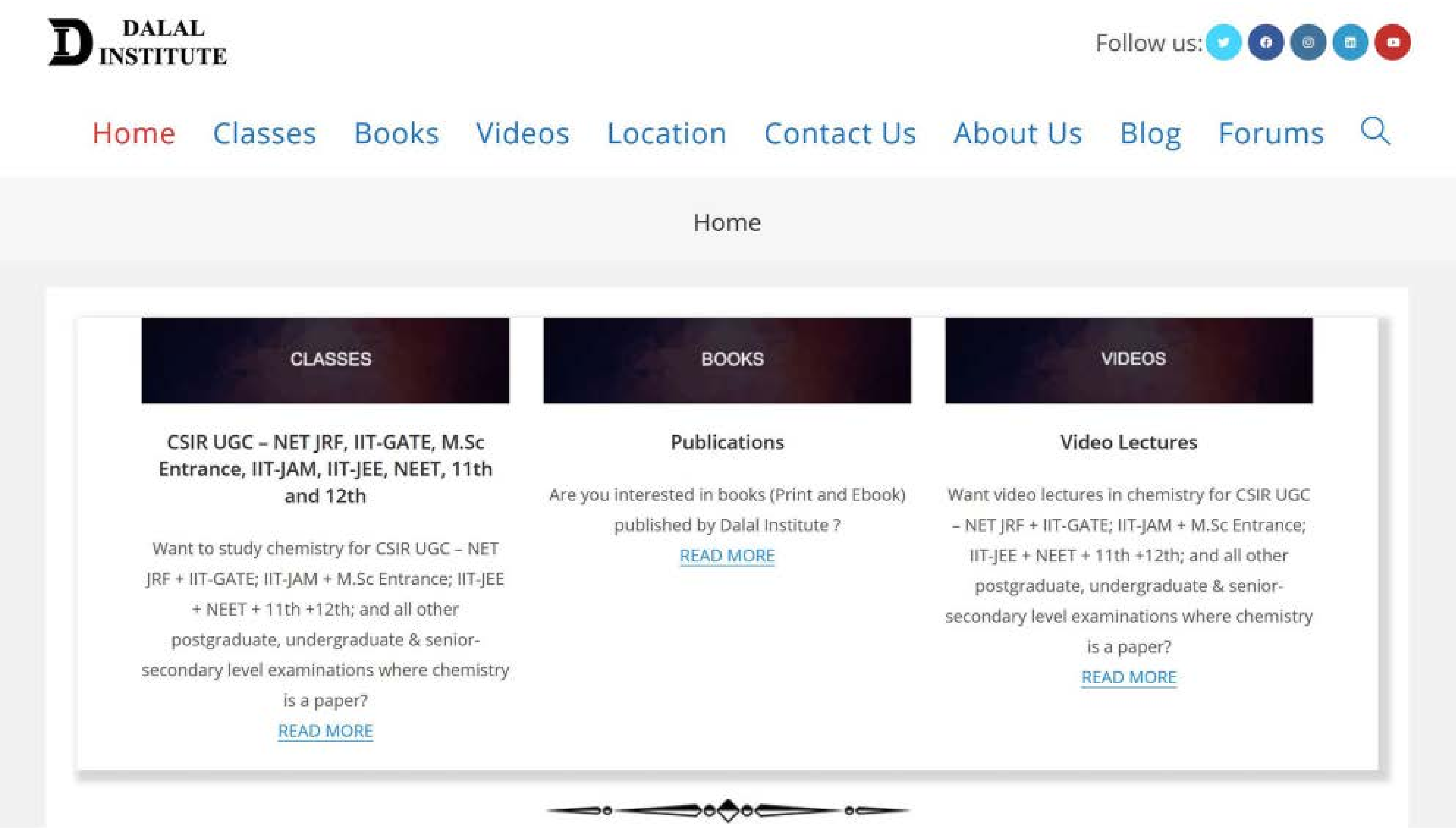


Figure 27. The pictorial depiction of Mode 2 overlap with Mode 0.

Similarly, if we consider Mode 2 interaction with Mode 2 or Mode 0 with Mode 0, we will get an unstable cyclic system owing to a symmetry disparity. Now since Mode 2 and Mode 0 fragments contain $4n + 2$ and $4n$ $\pi$-electrons respectively; the combination of Mode 2 and Mode 0 will create a total of $4n + 2$ $\pi$-electrons (aromatic), whereas Mode-2–Mode-2 or Mode-0–Mode-0 will create a total of $4n$ $\pi$-electrons (antiaromatic).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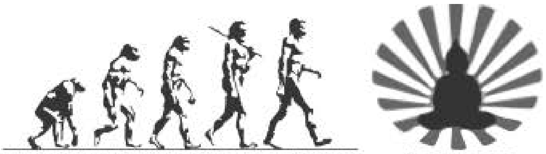

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