

CHAPTER 1

MOLECULAR ORBITALS AND THEIR SYMMETRY

1.1 Molecular Orbitals:

Molecular orbitals are formed by the interaction of atomic orbitals. Using the method of the linear combination of atomic orbitals (LCAO method) one can generate a set of molecular orbitals from a given set of atomic orbitals.^[1] The interaction of two atomic orbitals leads to the formation of two molecular orbitals, namely the bonding molecular orbital, which is of lower energy than the individual atomic orbital, and the antibonding molecular orbital, which is of higher energy than the individual atomic orbital. The former is formed by symmetric combination and the latter by anti-symmetric combination of the atomic orbitals. These two combinations are represented in Figure 1.1.

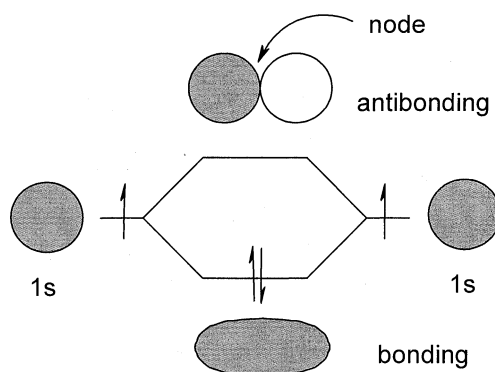


Figure 1.1 Formation of molecular orbitals of H_2 from the atomic orbitals of hydrogen atoms.

In the case of a bonding molecular orbital the electron density in the internuclear region is enhanced and hence it is more stable (lower in energy) whereas in an antibonding molecular orbital the electron density in the internuclear region is reduced and hence less stable (higher in energy). The plane which bisects the antibonding orbital is known as the nodal plane since it is characterized by zero probability of finding an electron at the center of the bond (Figure 1.1).

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In pericyclic reactions we often deal with the formation and breaking of C-C σ and π bonds and C-H σ bonds. A clear understanding of the formation and symmetry properties of these orbitals is important in order to understand pericyclic reactions.

C-H sigma bond: The C-H sigma bond is formed by the interaction of either the p orbital or one of the hybridized orbitals of carbon with the 1s orbital of hydrogen. The interaction leads to the formation of a bonding and an antibonding molecular orbital, as shown in Figure 1.2.

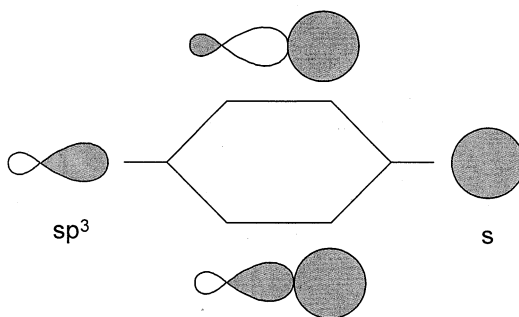


Figure 1.2 Formation of a C-H bond by the overlap of a sp^3 orbital of carbon and a 1s orbital of hydrogen.

C-C sigma bond: The C-C sigma bond is formed by the interaction of either the p orbital or one of the hybridized orbitals on each of the carbon atoms. The interaction takes place along the axis of the orbital, as shown in Figure 1.3, and leads to a bonding and an antibonding sigma molecular orbital.

C-C π bond: A C-C π bond is formed by the interaction of the p orbital on each of the carbon atoms, not along the axis of the orbital (p_z), but laterally, as shown in Figure 1.4. The interaction of p orbitals in this mode generates a π bonding and a π^* antibonding MO. Pictorially these orbitals can be represented either in the delocalized form or in the localized form. Throughout the text we shall be using the latter format, as it is much easier to represent. The nodal points are also clearly seen (Figure 1.4).

In summary, it is important to remember the following points about the LCAO method:

1. In general atomic orbitals lead to bonding molecular orbitals and stability only if the overlap integral is positive, i.e. $S > 0$.
2. Interaction of $2n$ atomic orbitals leads to the formation of $2n$ MOs, n bonding and n antibonding orbitals.
3. The bonding MO is more stable than the lower energy orbital of the starting atomic orbitals.

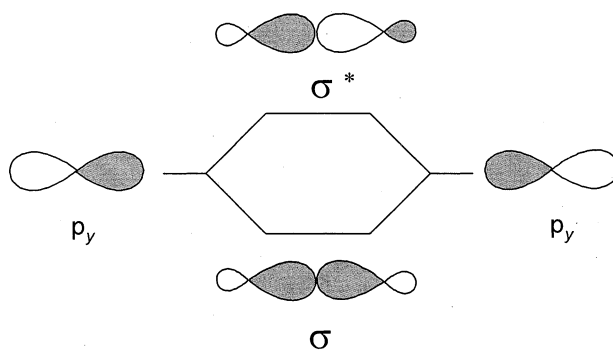


Figure 1.3 Formation of C-C sigma bond MOs by the overlap of p_y orbitals of carbon.

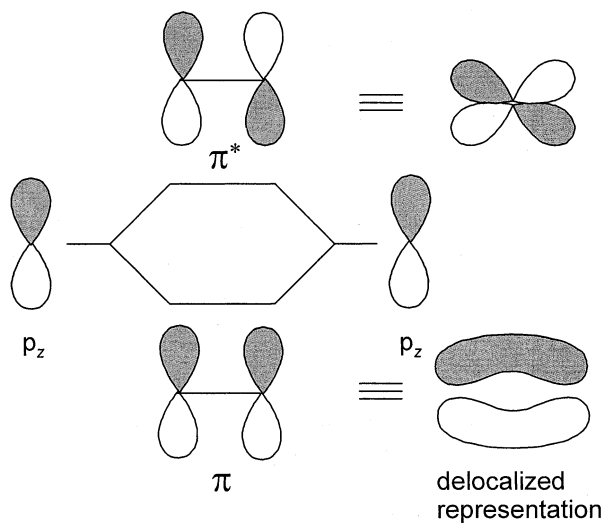


Figure 1.4 The π molecular orbitals of ethylene formed by the interaction of carbon p_z orbitals.

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4. The antibonding MO is less stable than the higher energy orbital of the starting atomic orbital.
5. The bonding orbital is stabilized less than the antibonding orbital is destabilized.

1.2 Molecular Orbitals of Conjugated Polyene Systems:^[2]

In pericyclic reactions we often encounter reactions of conjugated polyene systems. Depending upon the number of electrons the polyenes can be classified as $4n$ or $4n+2$ electron systems. Molecular orbitals of polyene systems are easy to construct and their symmetry properties easy to identify by following some simple rules. For example, if we know how to construct the MOs of ethylene from the p orbitals of two carbons, then we know how to use the linear combination of the ethylene MOs to construct the MOs of butadiene as shown in Figure 1.5.

While constructing the MO diagram of any conjugated polyene system the following points need to be considered.

1. Although there are C-C and C-H sigma bonds present in the molecule, the π MOs can be constructed independently of them. Although there may be a change in the hybridization of carbon atoms during the course of a pericyclic reaction, the MO levels of the sigma framework are relatively unaffected.
2. For a conjugated polyene system containing n ($n = \text{even}$) π electrons, there will be $n/2$ π bonding molecular orbitals that are filled MOs and $n/2$ antibonding MOs that are empty in the ground state electronic configuration of the molecule (Figure 1.6).
3. The lowest energy MO has zero nodes, the next higher one has one node and the second higher has two nodes and so on. The n th MO will have $(n-1)$ nodes.
4. The nodal points are found at the most symmetric points in a MO. In other words, no MO can be symmetric as well as antisymmetric at the same time with respect to any existing molecular symmetry element. For example the π_2 MO of butadiene has a node at the center of the bond connecting C2 and C3. It

is incorrect to assign this node to the center of the bond connecting C1 and C2 (Figure 1.7).

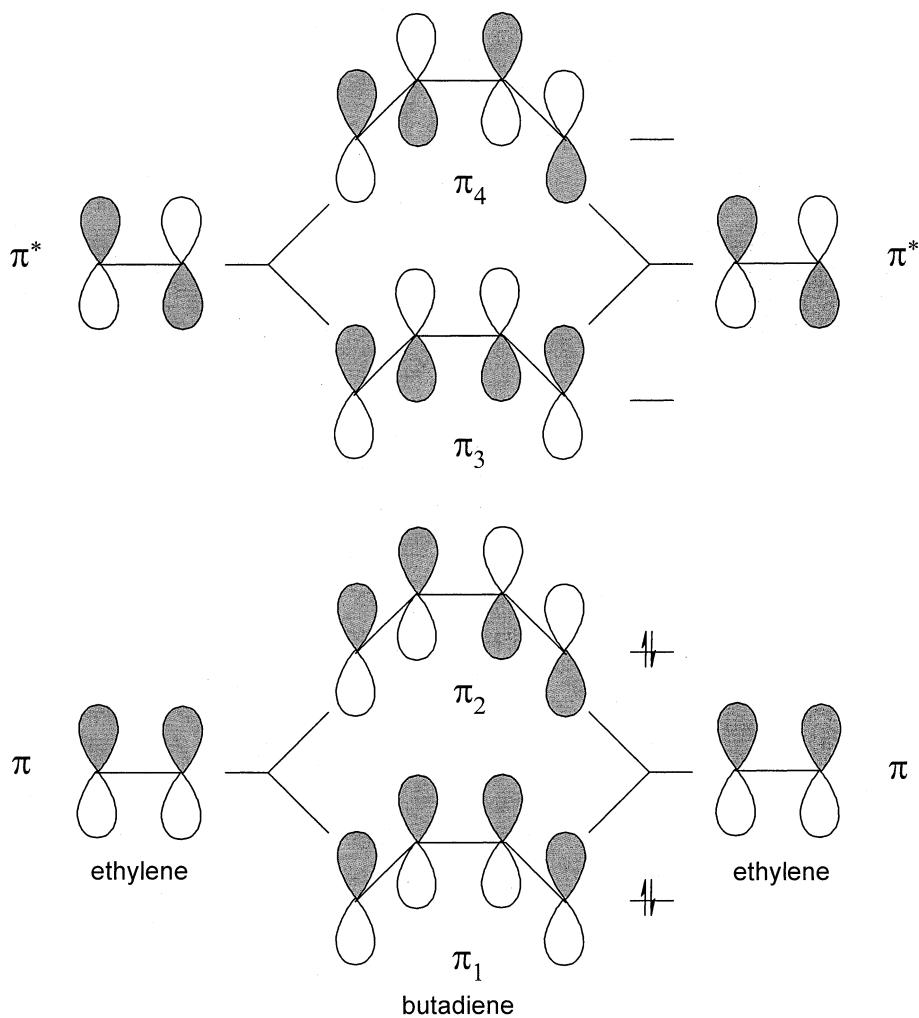


Figure 1.5 Formation of the MOs of butadiene by the combination of the MOs of two ethylene MOs.

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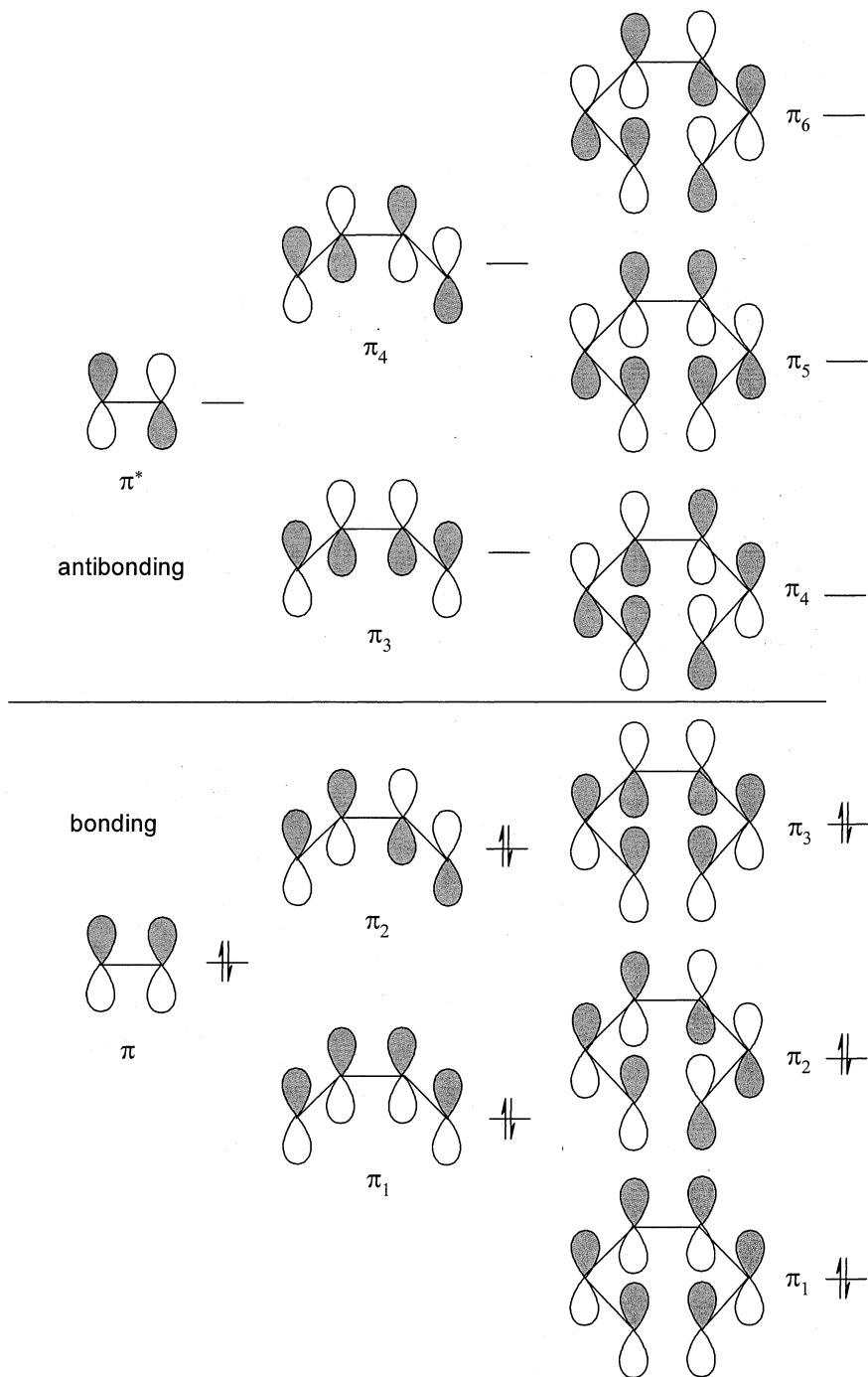


Figure 1.6 π -Molecular orbitals of ethylene, butadiene and hexatriene.

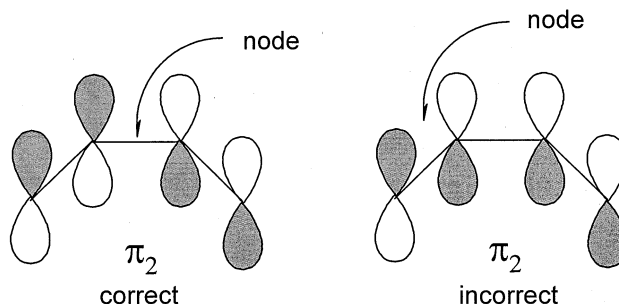


Figure 1.7 Assigning the nodal point to the π_2 orbital of butadiene.

5. In the case of π systems having an odd number of carbon atoms on the π framework such as propenyl, pentadienyl or heptatrienyl systems MOs can be constructed in a similar fashion. In these systems there are n MOs of which $(n-1)/2$ are bonding orbitals and the same number are antibonding orbitals. The $(n+1)/2$ th orbital is a nonbonding molecular orbital. Depending upon whether it is a radical, cation or anion, the electrons can be filled as shown in Figure 1.8.

1.3 Symmetry Elements and Symmetry Operations:^[3]

A symmetry operation is defined as an operation, which, when performed on an object, results in a new orientation of the object that is indistinguishable from the original. The most commonly encountered symmetry operations are rotation about an axis, reflection in a plane, inversion and rotation reflection. The axis, plane or inversion point is called the symmetry element or the symmetry operator. Consider the π and π^* MOs of ethylene. With respect to the plane bisecting the C-C bond the π MO is symmetrical because the reflections on either side of the plane are identical and lobes of the same algebraic sign are reflected. The π^* MO is antisymmetrical because reflection with respect to the plane gives lobes of opposite algebraic sign. Consider the C_2 axis of symmetry lying in the plane of the molecule and passing through the center of the C-C bond. It is perpendicular to the π orbitals. With respect to this axis of symmetry the π MO is antisymmetrical and the π^* MO is symmetrical (Figure 1.9).

1.4 Definition and Classification of Pericyclic Reactions:^[4]

Pericyclic reactions are concerted reactions that proceed through cyclic transition states. There are no distinct intermediates involved in these reactions. The bond

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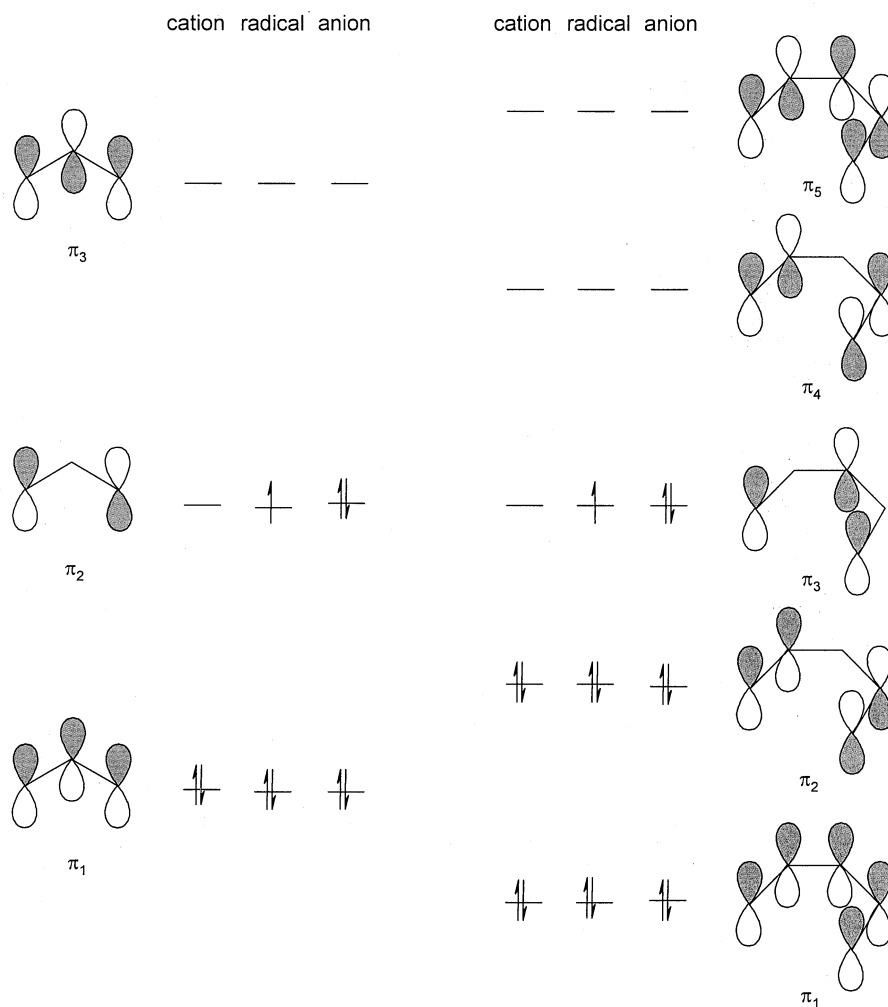


Figure 1.8 Molecular orbitals of propenyl and pentadienyl systems.

breaking and bond making take place simultaneously but not necessarily synchronously. They are distinctly different from reactions that proceed in a stepwise manner with the involvement of intermediates. Pericyclic reactions can be classified into five categories as follows.

1.4.1 Electrocyclic Ring Closure and Ring Opening Reactions:

Electrocyclic ring closure reactions occur by the reorganization of π electrons of an acyclic conjugated polyene system due to the interaction between the terminal carbons forming a sigma bond to a cyclic system. The reversal of the reaction, namely ring opening, also occurs in a concerted manner.

1.4.2 Cycloaddition and Cycloreversion Reactions:

Cycloaddition reactions involve the interaction of two or more π systems forming a cyclic structure. Reorganization of the π electrons leading to the formation of sigma bonds takes place during a cycloaddition reaction. When the interacting π systems are part of the same molecule we have intramolecular cycloaddition reactions. The reversal of cycloaddition reactions known as cycloreversion, also occurs in a concerted manner. Although the above definition is very general it must be emphasized that not all cycloaddition reactions proceed in a concerted manner. There are many examples of cycloaddition reactions that proceed by a stepwise ionic or radical mechanism. These are not considered under the pericyclic type.

1.4.3 Sigmatropic Rearrangements:

Reactions involving the breaking and migration of a sigma bond (a group connected by a sigma bond) through a π framework with concomitant reorganization of the π framework and formation of a new sigma bond are known as sigmatropic rearrangements.

1.4.4 Chelotropic Reactions:

These are cycloaddition reactions involving a single atom center as one of the cycloaddition components. The reverse reaction is also included in this category.

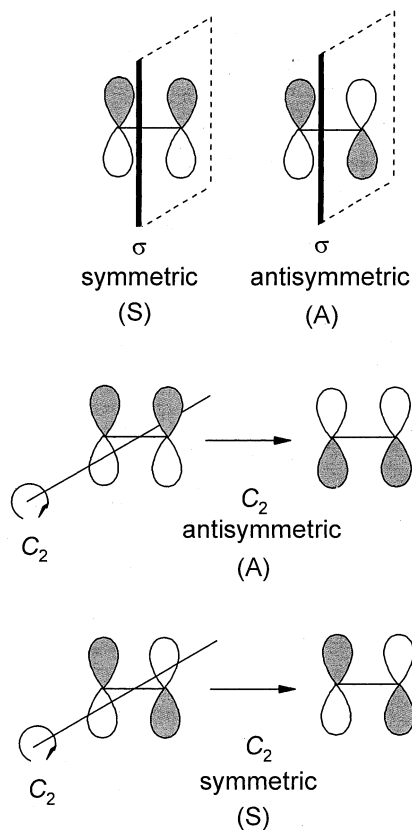


Figure 1.9 Symmetry properties of the MOs of ethylene.

1.4.5 Group Transfer Reactions:

These reactions are characterized by the transfer of a group or groups from one molecule to another molecule in a concerted manner.

All of the above types of pericyclic reactions can be considered in the broad category of cycloaddition reactions. However, it is advantageous to consider them individually for the sake of clarity.

1.5 Methods of Analyzing Pericyclic Reactions:

There are three common methods used for the analysis of pericyclic reactions.

1. The Orbital symmetry correlation method (developed by Woodward and Hoffmann and also by Longuet-Higgins and Abrahamson).

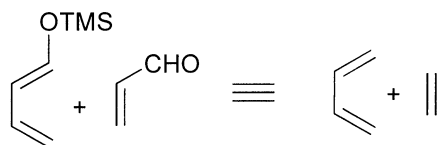
2. The frontier orbital method (developed initially by Woodward and Hoffmann and later by Fukui).
3. The transition state aromaticity method (developed by Dewar and Zimmerman).

1.5.1 Orbital Symmetry Correlation Method:^[5]

In this method the MOs corresponding to the bonds being formed and broken during the reaction are considered. Their symmetry properties with respect to the elements of symmetry that are present throughout the course of the reaction are identified. Then a correlation diagram is drawn by matching the symmetry of the MOs of the starting material to that of the product MOs. While doing so attention is paid to the fact that the non-crossing rule is not violated, i.e., orbitals of the same symmetry must not cross in the correlation diagram. If the symmetry of the MOs of the starting material in the ground state electronic configuration is correlated with that of the product in the ground state, then the reaction is thermally symmetry allowed. On the other hand if the symmetry of the MOs of the starting material in the excited electronic state is correlated with that of the product, then the reaction is photochemically symmetry allowed. While constructing an orbital correlation diagram the following points need to be considered.

1. *Each reacting system must be reduced to its highest inherent symmetry by the removal of all substituents.*

For example, while analyzing the cycloaddition reaction between 1-trimethylsilyloxybuta-1,3-diene and acrolein, the system is reduced to butadiene and ethylene (Scheme 1.1). Substituents affect only the electronic energy levels and coefficients of MOs and not the symmetry properties of the MOs.

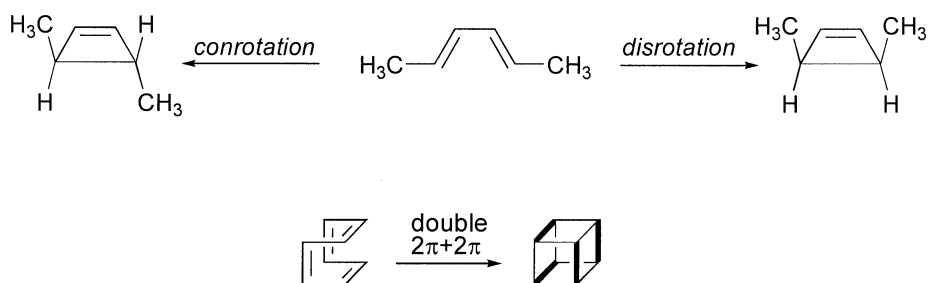


Scheme 1.1 Reactant molecules reduced to their highest symmetry for a cycloaddition reaction.

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- Processes that are independent must be considered separately even if they occur in the same molecule.

For example hexa-2,4-diene is capable of undergoing electrocyclic ring closure in two modes, namely the conrotatory and the disrotatory modes (Scheme 1.2). These two processes need to be considered as independent from the point of view of symmetry correlation. Similarly, consider the hypothetical double $2\pi+2\pi$ cycloaddition of cyclooctatetraene to cubane (the newly formed sigma bonds are indicated by thick lines). Each of the two cycloaddition processes has to be considered separately for the construction of the orbital correlation diagram. *If two independent processes are considered together for the construction of the orbital correlation diagram the outcome can be erroneous.*



Scheme 1.2 Processes that are independent occurring in the same molecule.

- The symmetry element used for the analysis must bisect the bonds that are made or broken during the reaction.

For the $2\pi+2\pi$ cycloaddition of ethylene to cyclobutane in the suprafacial-suprafacial mode only the planes that bisect the π bonds and the newly formed sigma bonds in cyclobutene constitute symmetry planes (Figure 1.10). The two planes containing the ethylene units are not to be considered as symmetry elements for the cycloaddition process. Similarly, for the Diels-Alder reaction of butadiene with ethylene in the suprafacial-suprafacial mode the plane bisecting the two π systems alone is the symmetry element (Figure 1.10).

4. *The chosen symmetry element(s) should be present throughout the reaction i.e., through the entire process of starting material going to product through the transition state.*
5. *Orbitals of the same symmetry do not cross, as required by the non-crossing rule.*

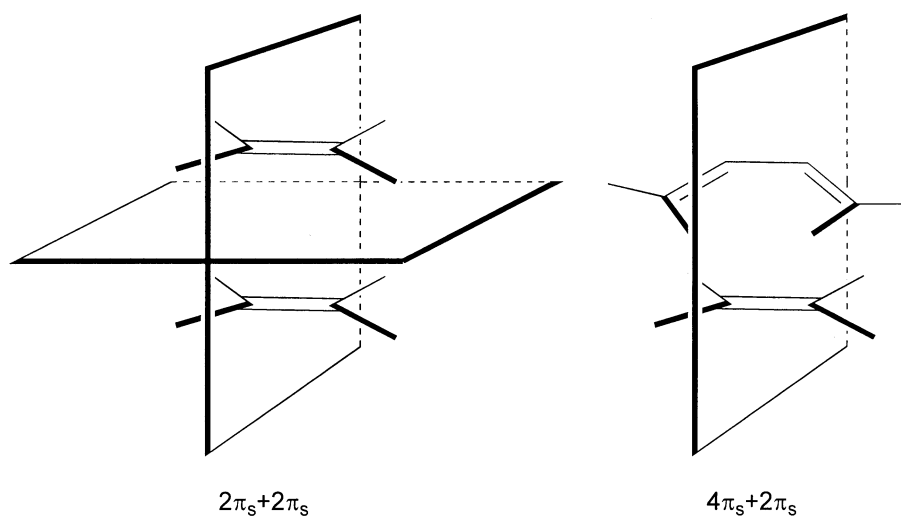


Figure 1.10 Symmetry planes for the [2+2] and [4+2] cycloaddition reactions in the suprafacial-suprafacial mode.

1.5.2 Frontier Orbital Method:^[6]

Frontier orbitals of a system are comprised of the pair of the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO). For example, the π MO of ethylene is the HOMO of ethylene and the π^* level is the LUMO in the ground state electronic configuration. In the case of the excited state of butadiene, π_3 is the HOMO and π_4 is the LUMO (Figure 1.6). Pericyclic reactions can be analyzed by the interaction of the HOMO and LUMO of the reacting systems. When two reacting systems are separated by an infinite distance their MOs are unperturbed by each other. When they approach sufficiently close to each other, their MOs begin to interact. MOs that are close in energy interact more strongly than others. The interaction of two filled MOs does not lead to any net stabilization of the system. It is the interaction of

one filled MO with an unfilled MO that leads to the net stabilization of the system. Hence it is the interaction of the HOMO of one of the reacting system with the LUMO of the other reacting system that is considered in this method of analysis. If the interaction of the two MOs is of the bonding type in the ground state electronic configuration, then we call the reaction thermally allowed. If the HOMO-LUMO interaction leads to anti-bonding interaction in the ground state electronic configuration then the reaction is thermally disallowed.

1.5.3 Transition State Aromaticity Method: ^[7]

In this method a cyclic pathway of the interacting orbitals of the reacting systems in the transition state is constructed. This is called the interaction diagram and it depicts sets of basis orbitals and not molecular orbitals. After the construction of the interaction diagram algebraic signs are assigned to the orbital lobes so as to minimize the number of phase inversions. The following examples illustrate the construction of orbital interaction diagrams for the [1,3] shift by suprafacial and antarafacial modes (Figure 1.11), for $[2\pi+2\pi]$ and $[4\pi+2\pi]$ cycloadditions by supra-supra and supra-antara modes (Figure 1.12). The star (*) indicates the phase inversion where the signs of the orbital lobes change along the interaction. (The term suprafacial implies that

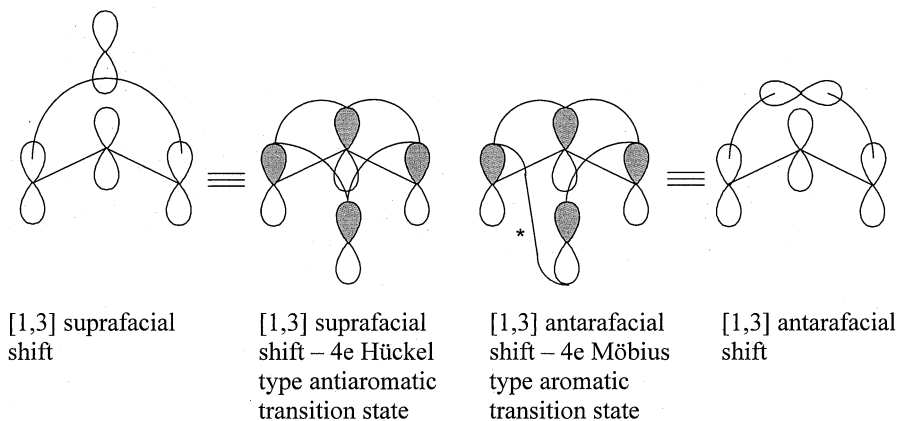


Figure 1.11 Orbital interaction diagram for [1,3] suprafacial and antarafacial shifts.

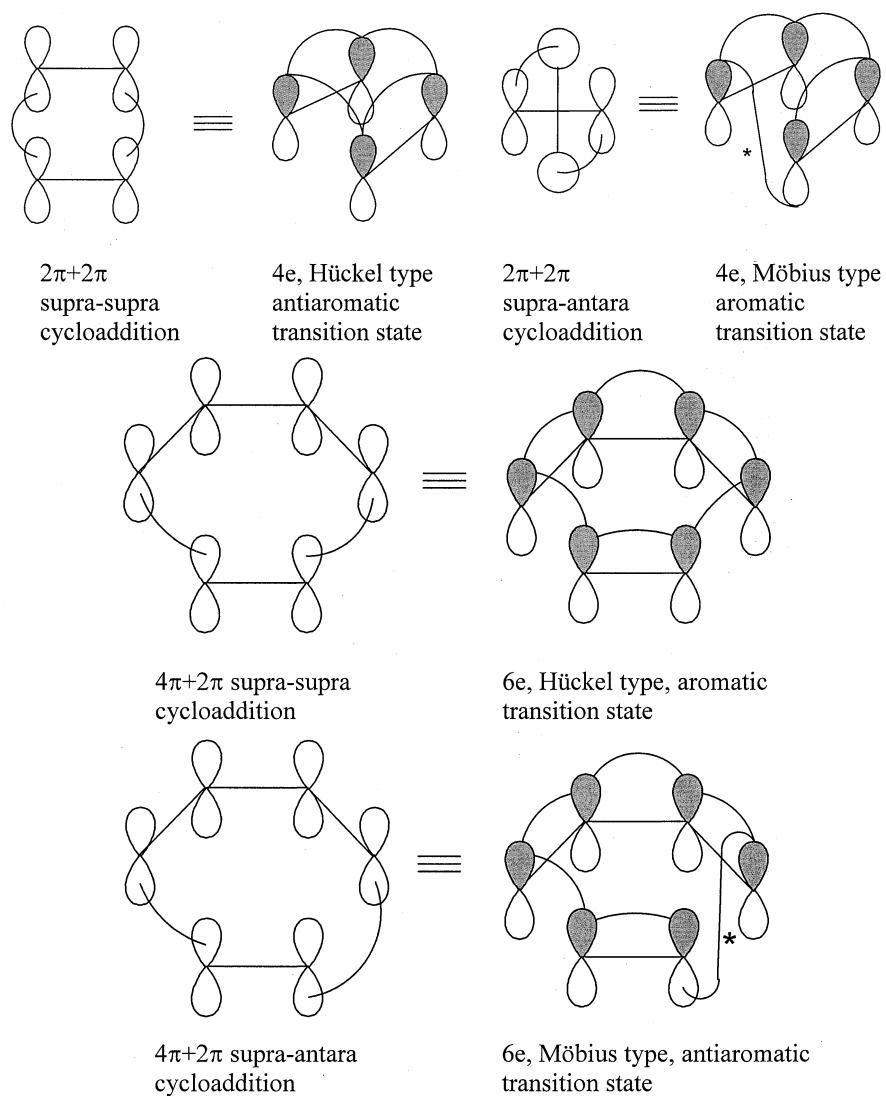


Figure 1.12 Orbital interaction diagrams for cycloaddition reactions.

with respect to a molecule the orbital lobes of that molecule interact from the same face. The term antarafacial implies that the lobes from opposite faces interact. For a detailed description of these terms, refer to Chapter 3, Sec. 3.3 for cycloaddition reactions and Chapter 4 for sigmatropic reactions). Those orbitals having zero phase inversions are classified as Hückel type rings. These have a continuous strip of a closed loop of orbitals without a twist in them. Those having one phase inversion are

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classified as anti-Hückel type and they are like the Möbius strip with a twist in the closed loop of orbitals. The allowedness or the disallowedness of the reactions is predicted as follows. For Hückel ring systems with $4n+2$ electrons in the transition state the reaction is thermally allowed in the ground state. For $4n$ electron systems the reaction is thermally forbidden in the ground state. For an anti-Hückel system containing $4n$ electrons, the reaction is thermally allowed and for the $4n+2$ electron system the reaction is thermally forbidden in the ground state.

Table 1.1 Woodward-Hoffmann rules based on the transition state aromaticity method.

No. of phase inversion	Ring type	No. of electrons	Allowedness
zero	Hückel	$4n+2$ (aromatic)	Thermally allowed
		$4n$ (antiaromatic)	Thermally forbidden
one	Möbius	$4n$ (aromatic)	Thermally allowed
		$4n+2$ (antiaromatic)	Thermally forbidden

According to Dewar and Zimmerman the basic criterion for deciding whether a given process is allowed or forbidden depends upon the stabilization or destabilization of the cyclic transition state in comparison with the open chain system. The aromatic or the anti aromatic character of the ground state decides the stabilization or the destabilization of the systems, which in turn is decided by the number of electrons in the system.^[8]

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