

Pericyclic Reactions

II M. Sc. Chemistry (Organic Chemistry)

Semester-III

Paper – I ORGANIC REACTION MECHANISMS-I

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PERICYCLIC REACTIONS

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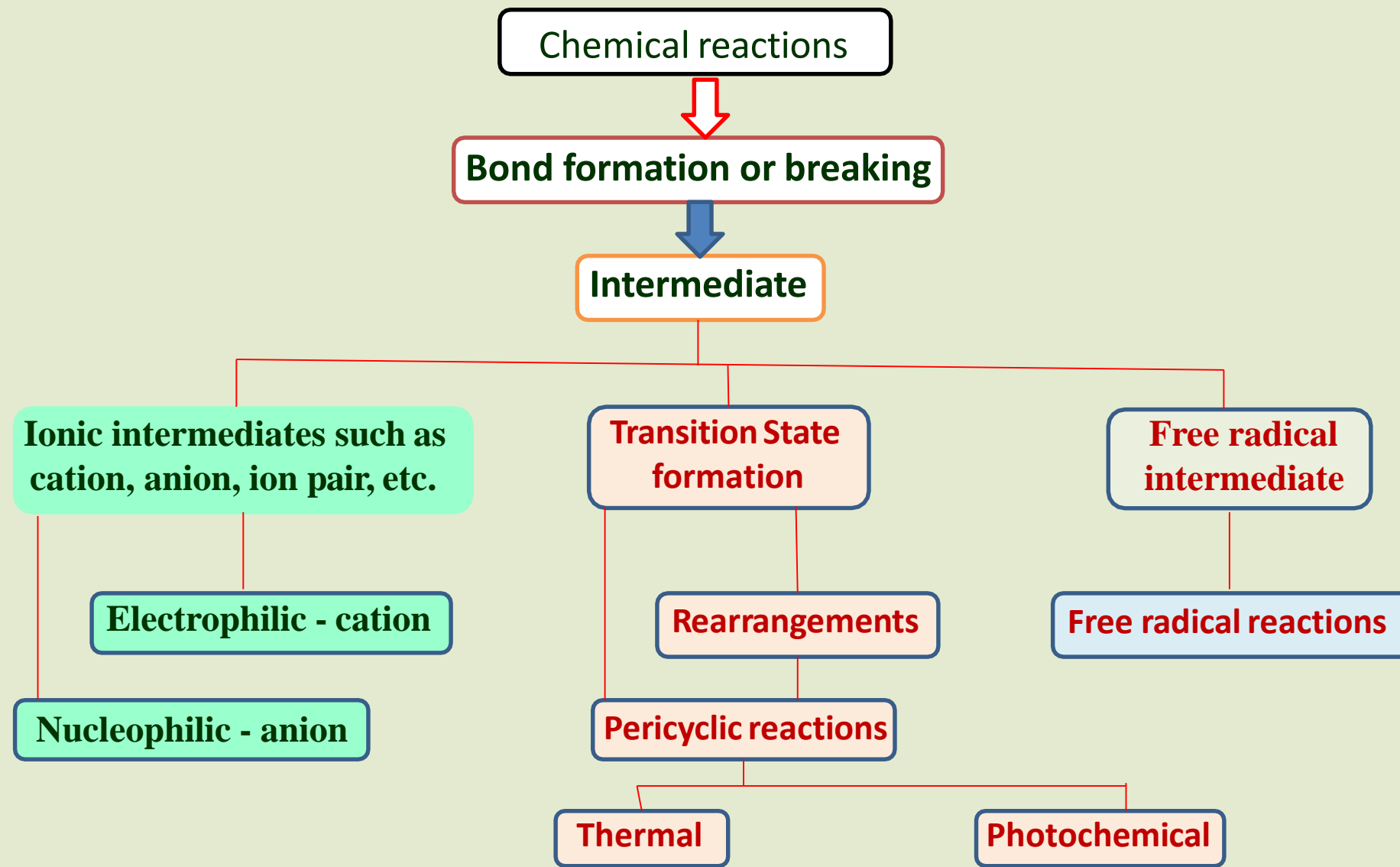
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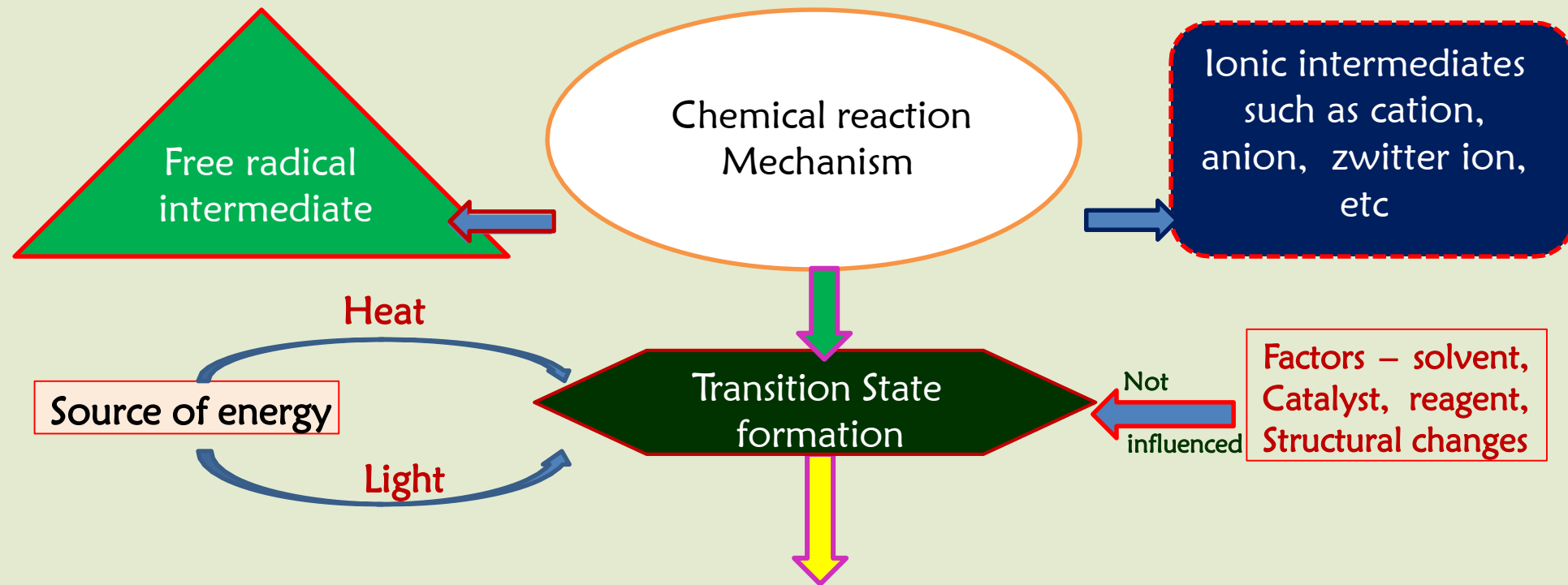
Pericyclic Reactions-I

(A) Molecular orbital symmetry, frontier orbitals of ethylene, 1,3 Butadiene, 1,3,5-Hexatriene, allyl system, classification of pericyclic reactions FMO approach, Woodward-Hoffman correlation diagram method and perturbation of molecular (PMO) approach for the explanation of pericyclic reactions under thermal and photochemical conditions.

(B) **Electrocyclic Reactions:** Con-rotatory and dis-rotatory motions ($4n$) and ($4n+2$), allyl systems

Introduction





1. Proceeds in *single cyclic transition state*.
 2. Reactions **not** influenced by any solvent, reagent, structural changes, catalysts, etc.
 3. These are **highly stereospecific** in nature.
 4. These reactions are initiated either by **heat** or **light**. Such class of reactions are called as **pericyclic reactions**.
- Reactions are either carried out **thermally** or **photochemically**.

The chemical reaction in which starting material is converted into a single stereo-isomeric product is called as stereospecific or regiospecific reaction.

STEREOSPECIFIC REACTIONS

VERSUS

STEREOSELECTIVE REACTIONS

A stereospecific reaction is a reaction in which the stereochemistry of the reactant completely determines the stereochemistry of the product without any other option

Gives a specific product from a certain reactant

Final product depends on the stereochemistry of the reactant

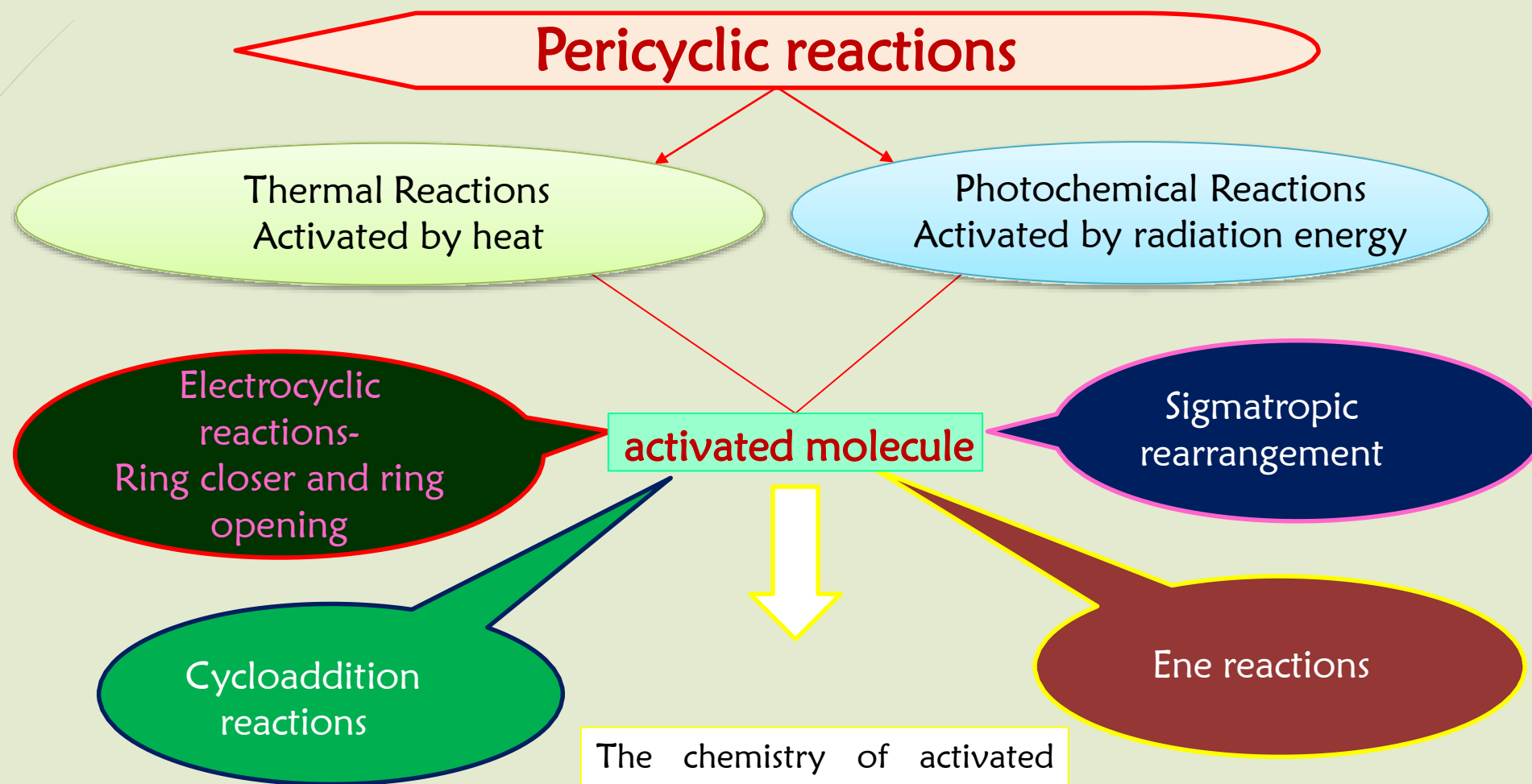
A stereoselective reaction is a reaction in which there is a choice of pathway, but the product stereoisomer is formed due to its reaction pathway being more favorable than the others available

Can result in multiple products

Selectivity of the reaction pathway depends on differences in steric effects and electronic effects

Pericyclic Reactions

Pericyclic reactions (pericyclic means shifting of electrons around the circle) are first explained by the scientist Hoffman and Woodward in 1965.



The chemistry of activated molecule in thermal and photochemical reactions is totally different. - different products are obtained.

Pericyclic Reactions

activated molecule

From mixture – one

Electrons and molecular orbitals takes part in reaction

Bonding molecular orbitals

Anti-Bonding molecular orbitals

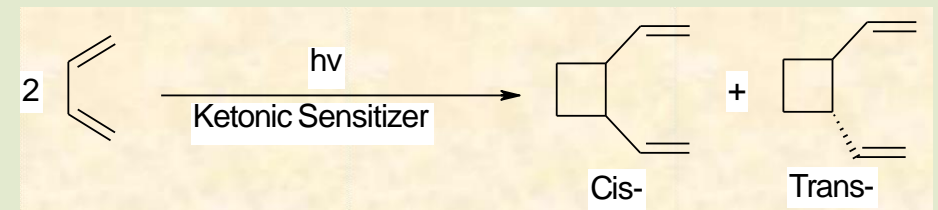
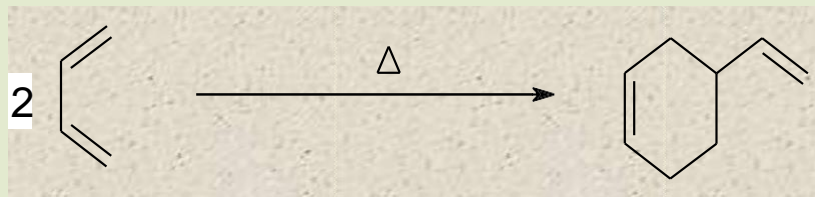
HOMO

Thermal

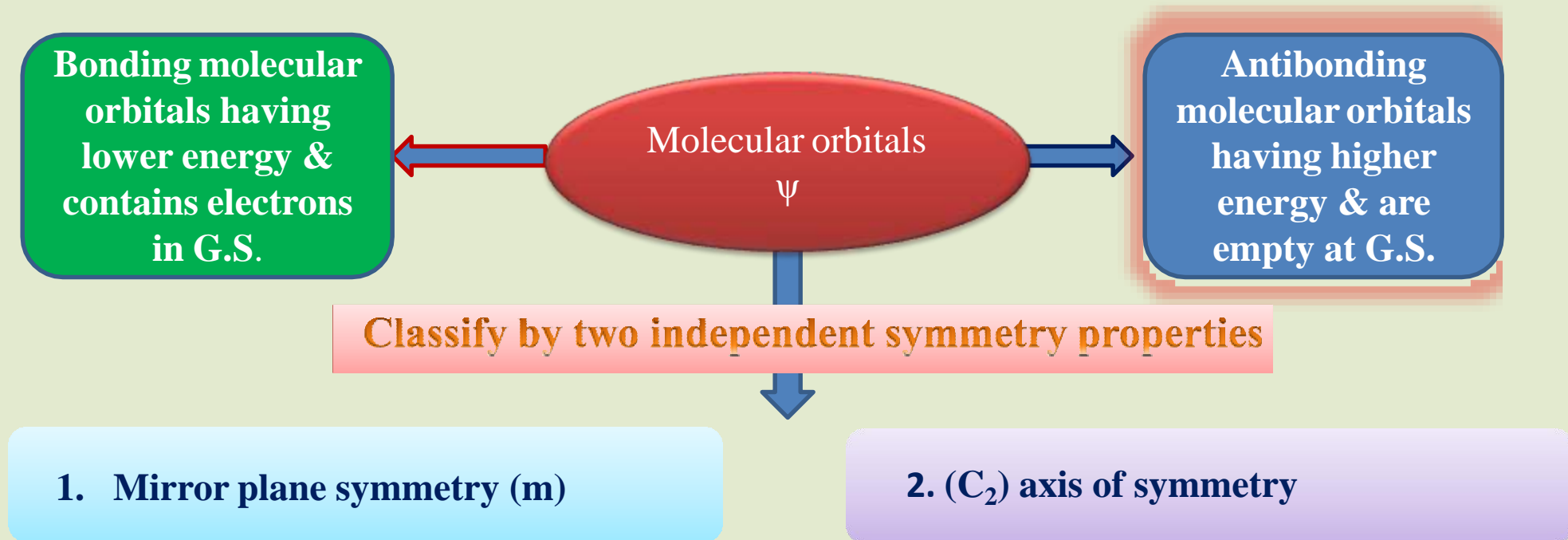
Process

Photochemical

LUMO

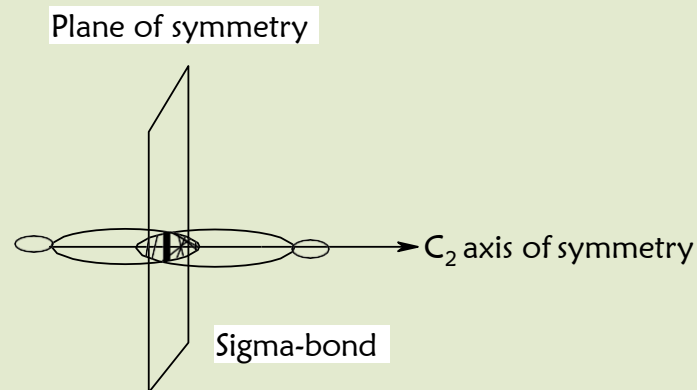
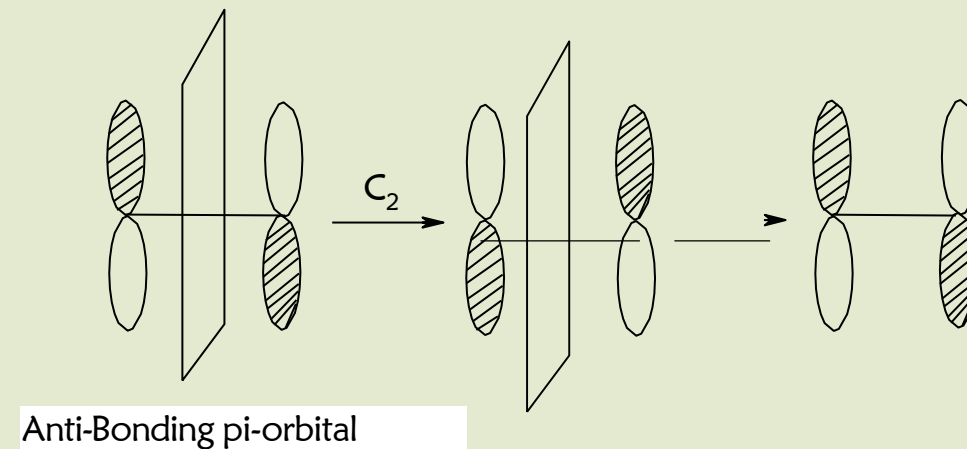
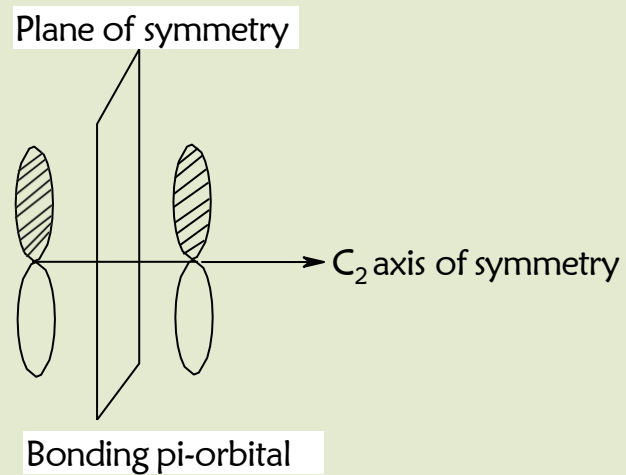


Molecular orbital symmetry



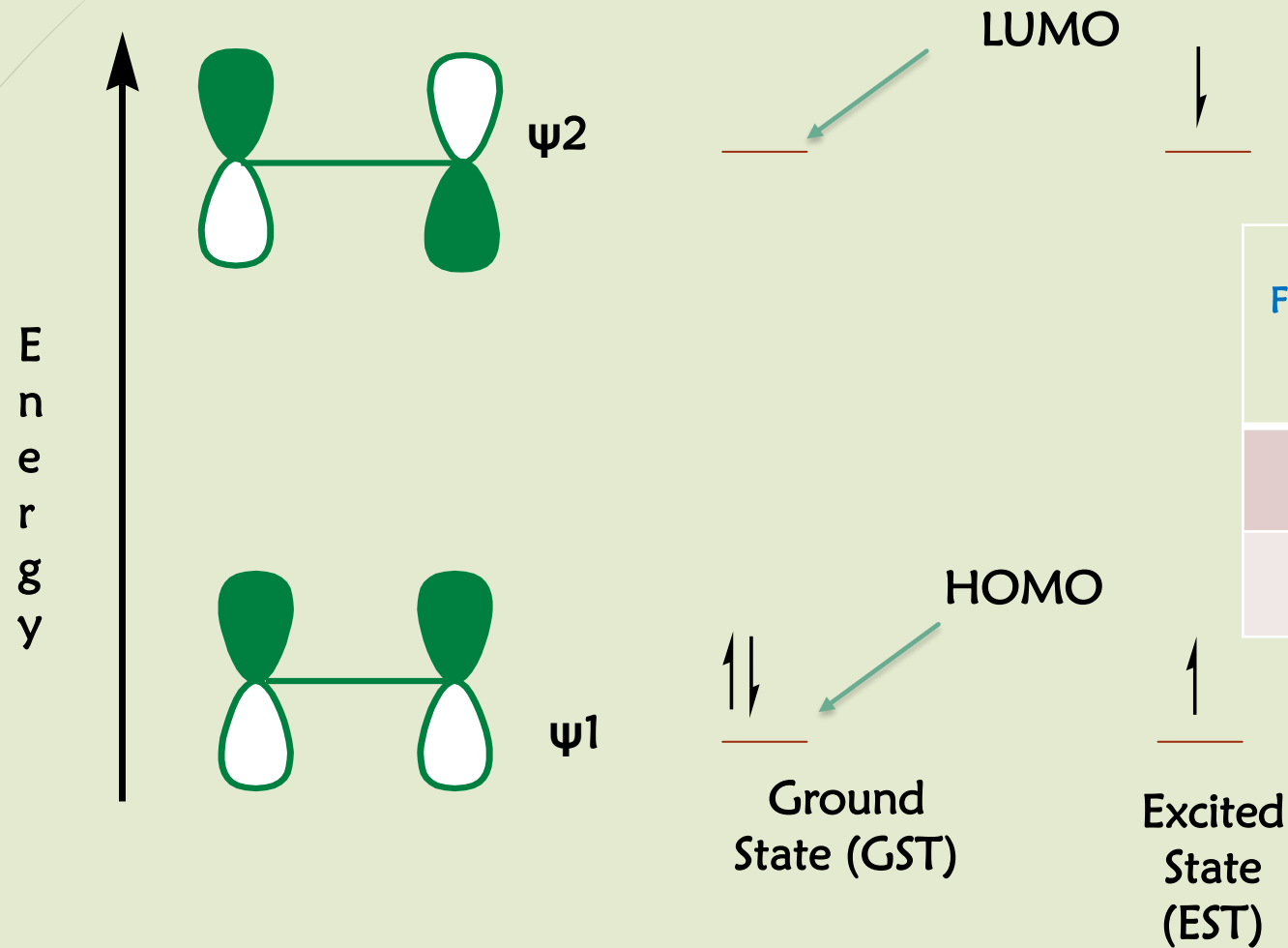
1. **Mirror plane symmetry (m)** is a plane passing through the *center of the molecular orbital and perpendicular to the molecular orbital axis*, it bisect the molecular orbital in two parts, one part is mirror image of other part. It is maintained by **Dis rotatory** process.

2. **(C₂) axis of symmetry** is assume to present if the rotation of the molecular orbital around the axis by 180° (360/2) gives raise to another orbital, then reflect it across a plane perpendicular to the axis. It is maintain by **con rotatory** process.



Ethylene

In ethylene there only two π -electrons, therefore, it has only two molecular orbitals π -bonding and π^* -anti-bonding . Symmetry properties of both the orbitals are different.



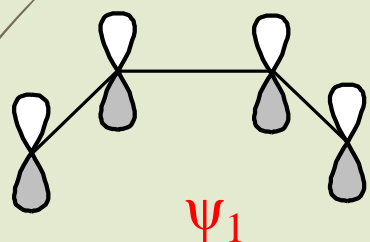
| Wave Function | No. of Nodes | Mirror plane symmetry (m) | Axis of symmetry (C2) |
|---------------|--------------|---------------------------|-----------------------|
| ψ_1 | 0 | S | A |
| ψ_2 | 1 | A | S |

Node

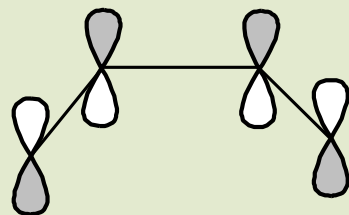
When we move in molecular orbital, the sign of the orbital change (above the plane or consider all orbitals below the plane) is called as node.

For a linear conjugated π -system the wave function ψ_n will possess $(n-1)$ nodes.

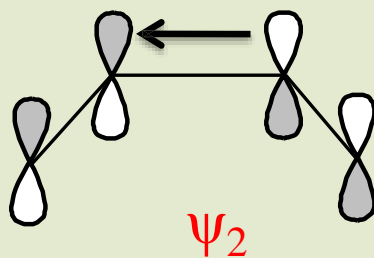
- If $(n-1)$ is zero or even integer, ψ_n will be said to be symmetric with respect to m and antisymmetric with respect to C_2 .
- If $(n-1)$ is an odd integer ψ_n will possess the C_2 axis of symmetry and antisymmetric with respect to m .



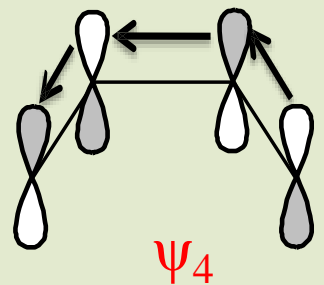
Node = 0



Node = 2



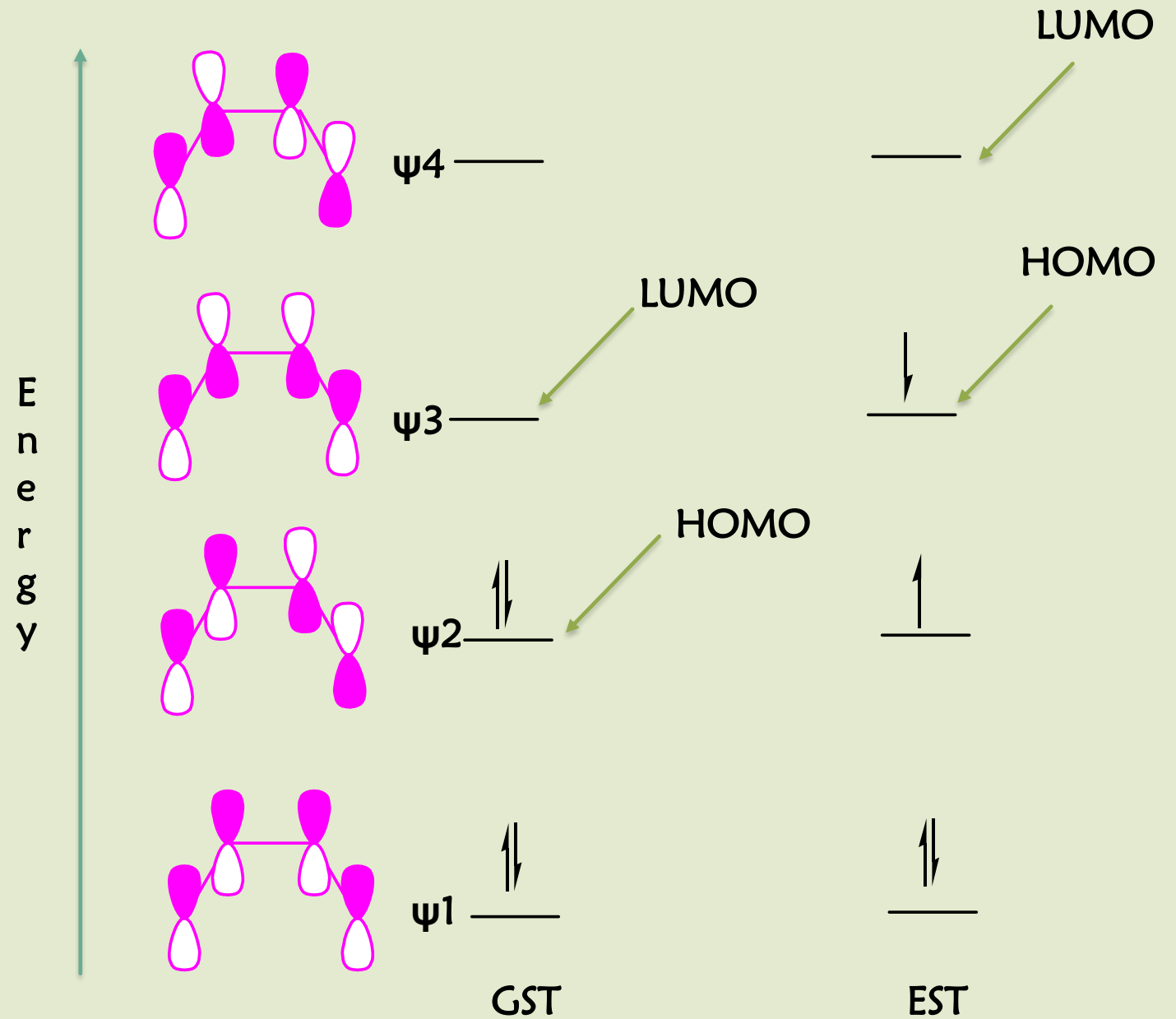
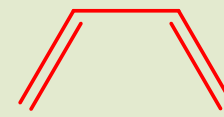
Node = 1



Node = 3

| $n-1$ | Mirror plane symmetry (m) | Axis of symmetry (C_2) |
|----------------------|-------------------------------|----------------------------|
| Zero or even integer | S | A |
| Odd integer | A | S |

1,3-Butadiene



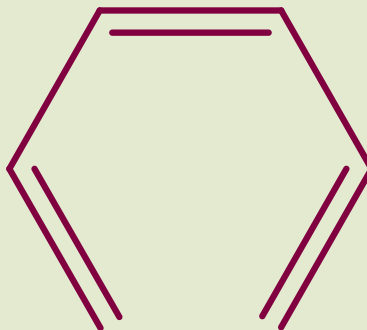
1,3-butadiene, total number of molecular orbitals are 4- π_1 , π_2 , π_2^* , π_1^* where π_1 and π_2 are bonding and π_2^* and π_1^* are antibonding molecular orbitals. They are also denoted as- (ψ_1 , ψ_2 , ψ_3 and ψ_4).

| Wave Function | No. of Nodes | Mirror plane symmetry (m) | Axis of symmetry (C2) |
|---------------|--------------|---------------------------|-----------------------|
| ψ_1 | 0 | S | A |
| ψ_2 | 1 | A | S |
| ψ_3 | 2 | S | A |
| ψ_4 | 3 | A | S |

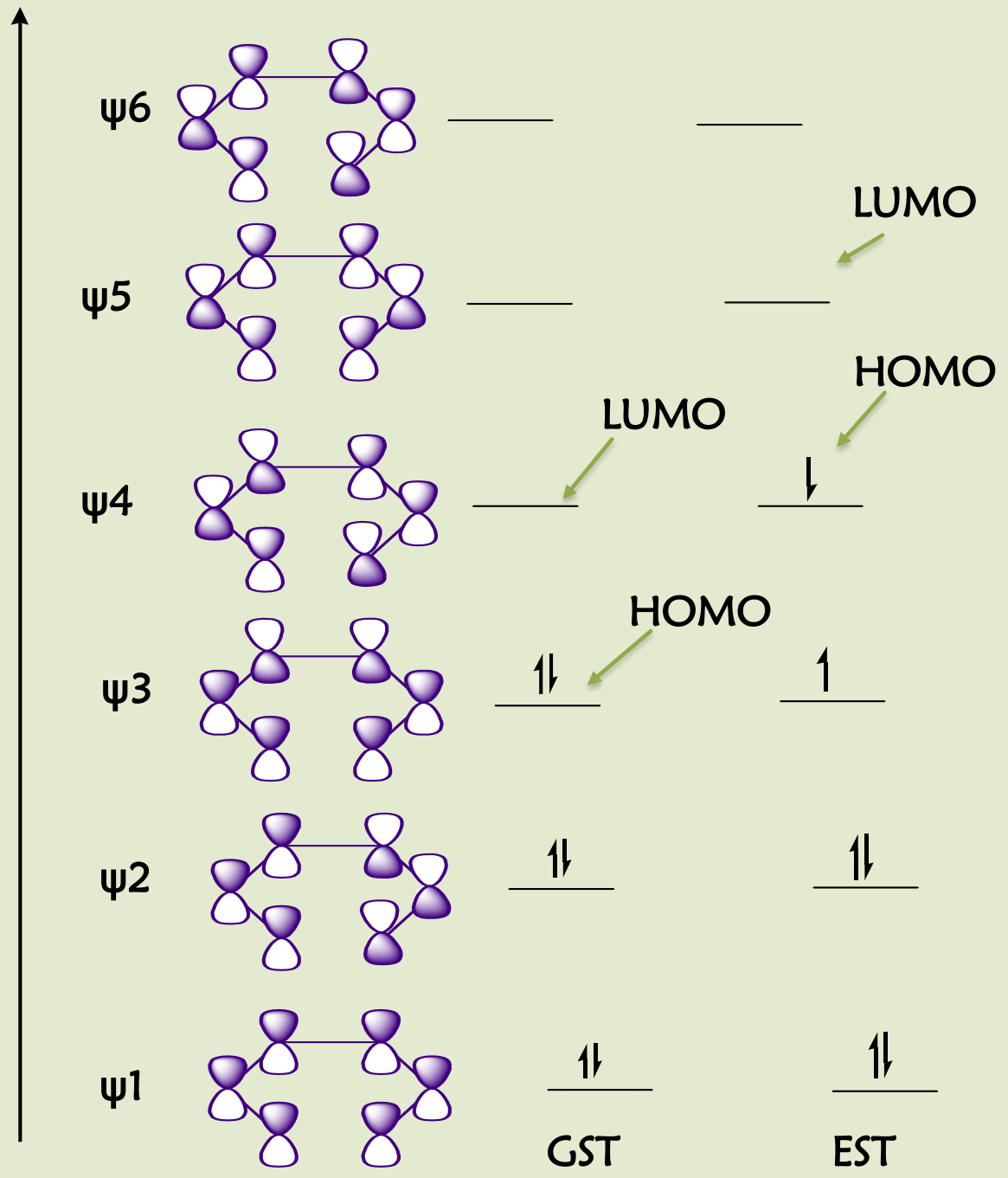
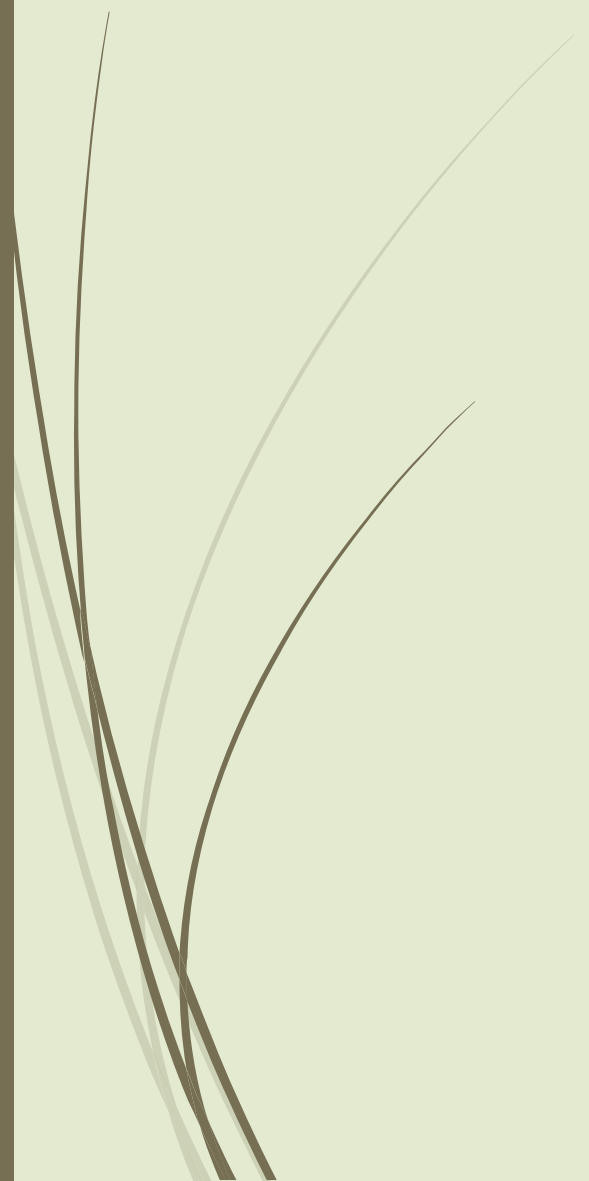
ψ_1 , ψ_2 - Bonding Mo's


ψ_3 , ψ_4 - Anti-Bonding Mo's

1,3,5- Hexatriene



1,3,5-hexatriene, total number of molecular orbitals are six i.e. π_1 , π_2 , π_3 , π_3^* , π_2^* , π_1^* where π_1 , π_2 and π_3 are bonding and π_3^* , π_2^* and π_1^* are antibonding molecular orbitals. They are also denoted as- (ψ_1 , ψ_2 , ψ_3 , ψ_4 , ψ_5 and ψ_6)





| Wave Function | No. of Nodes | Mirror plane symmetry (m) | Axis of symmetry (C2) |
|---------------|--------------|---------------------------|-----------------------|
| ψ_1 | 0 | S | A |
| ψ_2 | 1 | A | S |
| ψ_3 | 2 | S | A |
| ψ_4 | 3 | A | S |
| ψ_5 | 4 | S | A |
| ψ_6 | 5 | A | S |

Allylic Systems



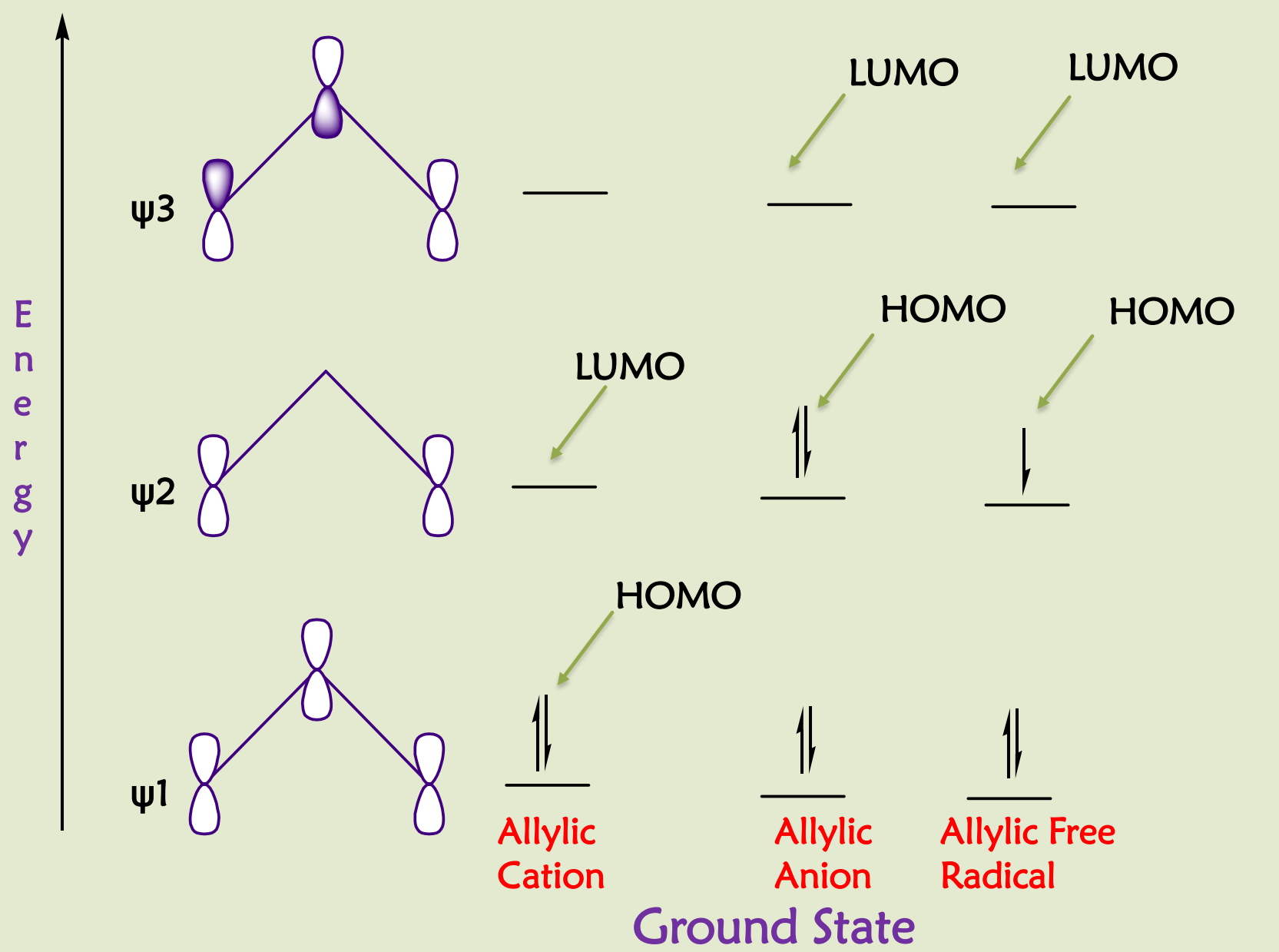
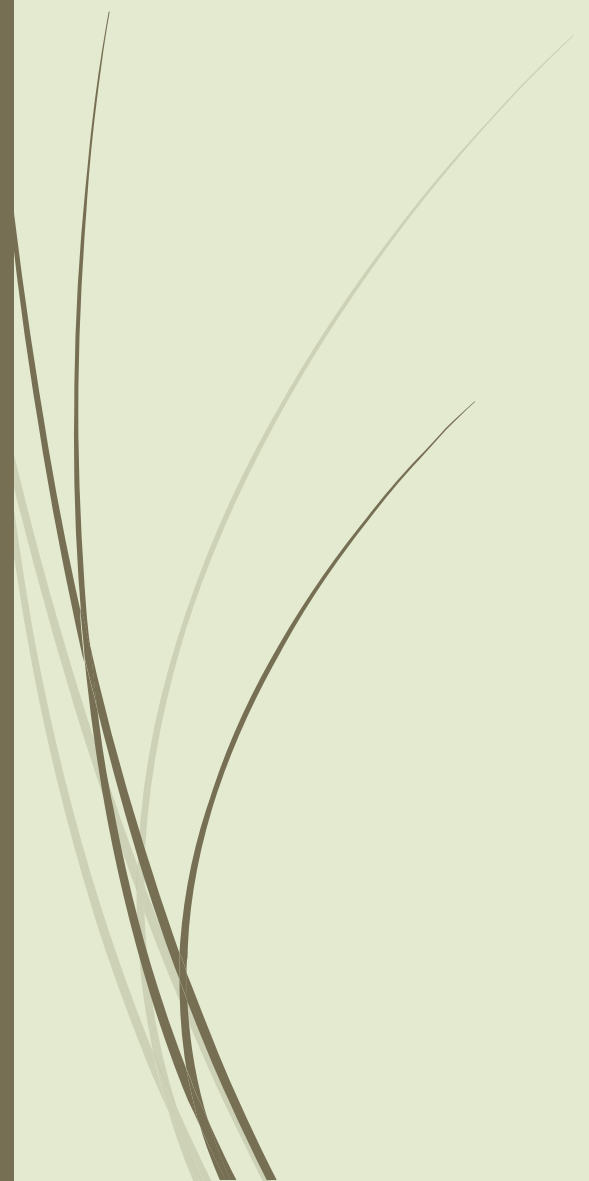
Allylic
Cation



Allylic
Anion



Allylic Free
Radical



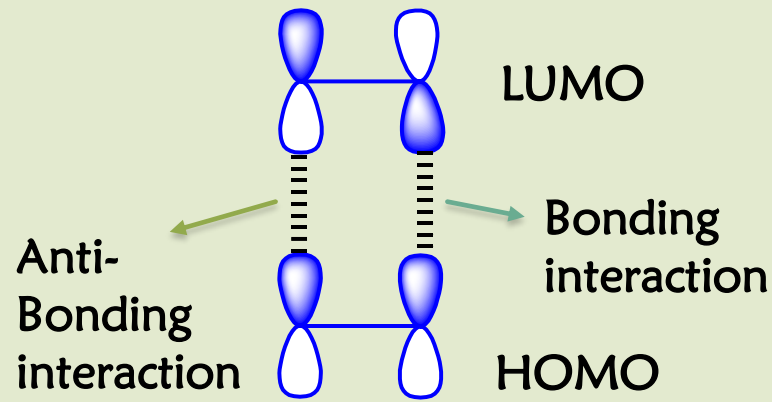
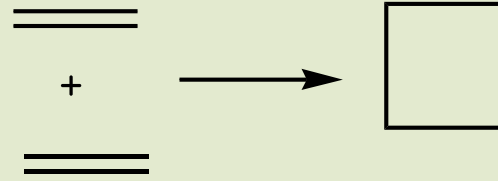


Classification of Pericyclic reactions FMO approach, Woodward-Hoffman Correlation diagram method and perturbation of molecular (PMO) approach for the explanation of Pericyclic reactions under thermal and Photochemical Conditions.

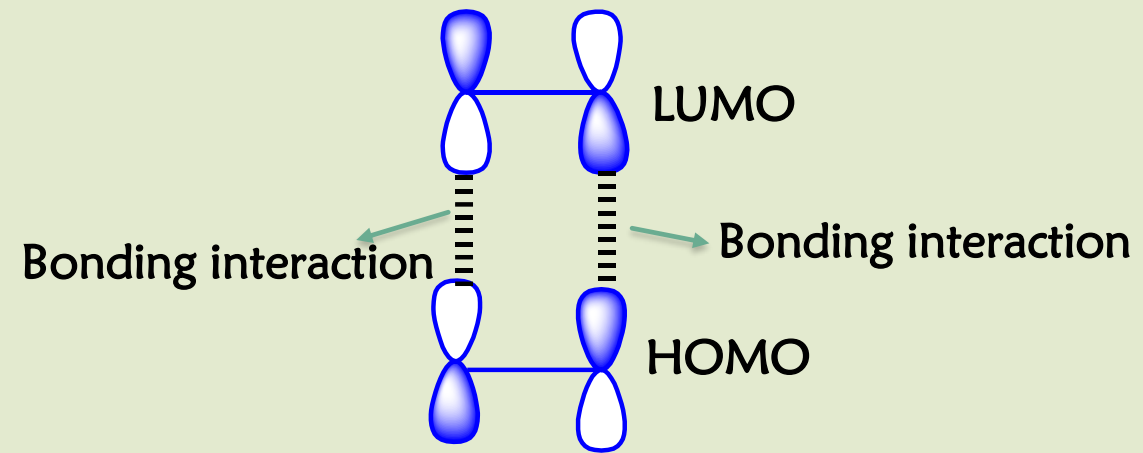
Classification of Pericyclic reactions FMO approach

- This Theory Developed in the 1960s by Kenichi Fukui who recognized that chemical reactivity can often be explained in terms of interacting HOMO, LUMO.
- The Frontier Molecular Orbital (FMO) theory is a simpler way to look at the molecular orbitals of a conjugate system based on highest occupied molecular orbital (HOMO) of one component and lowest unoccupied molecular orbital (LUMO) of the second component in a pericyclic reaction. These are the closest MO in terms of energy and make a significant contribution to lowering of transition state energy as they interact. HOMO and LUMO of any given compound have opposite symmetries. HOMO and LUMO are referred to as frontier molecular orbitals. Thus bonding takes place when lobes of equal phase on two different molecules overlap with each other.

Example:



**Ground State-
Thermally Forbidden**



**Excited State-
Photochemically allowed**

Principle:

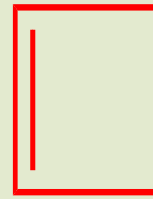
- I. Since the ground state of almost all molecules has a pair of electrons in the HOMO,
 - II. bonding interaction between two molecules or between two atoms in the same molecule cannot involve only the HOMO of each because this would lead to an orbital occupancy greater than two which is contrary to Pauli's principle.
 - III. The HOMO of one reactant needs to interact with an unoccupied molecular orbital (LUMO) of the second.
 - IV. Now since the bonding interaction between two orbitals increases as the energies of the two become more nearly equal, it is expected that the HOMO of one reactant would interact efficiently with the lowest unoccupied molecular orbital (LUMO) of the second.
- The shaded (positive) lobe overlaps only with the shaded (positive) lobe of another orbital,
 - An unshaded (negative) lobe only with the unshaded (negative) lobe of another orbital. Overlap of orbitals of unlike phase results in repulsion.

Classification of Pericyclic reactions

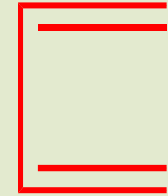
Woodward- Hoffman Correlation diagram method:

- Most important observation about pericyclic reactions is that, in them molecular orbital symmetry is conserved, i.e., symmetrical orbitals are converted into symmetrical orbitals; whereas asymmetric orbitals are transformed to antisymmetric orbitals.
- We can predict whether a reaction is feasible thermally or photochemically by constructing correlation diagram in which molecular orbitals of similar symmetry of reactants and products are matched.
- If they are matched in ground state, the reaction is feasible thermally. On the other hand if molecular orbitals of reactants in G.S.T. are matched to excited state of products or vice-versa the reaction is allowed under photochemical conditions.
- For constructing correlation diagram first step in writing the symmetry properties of reactants as well as products with respect to mirror plane (m) or C_2 -axis, keeping in view which symmetry is being conserved during the reaction.

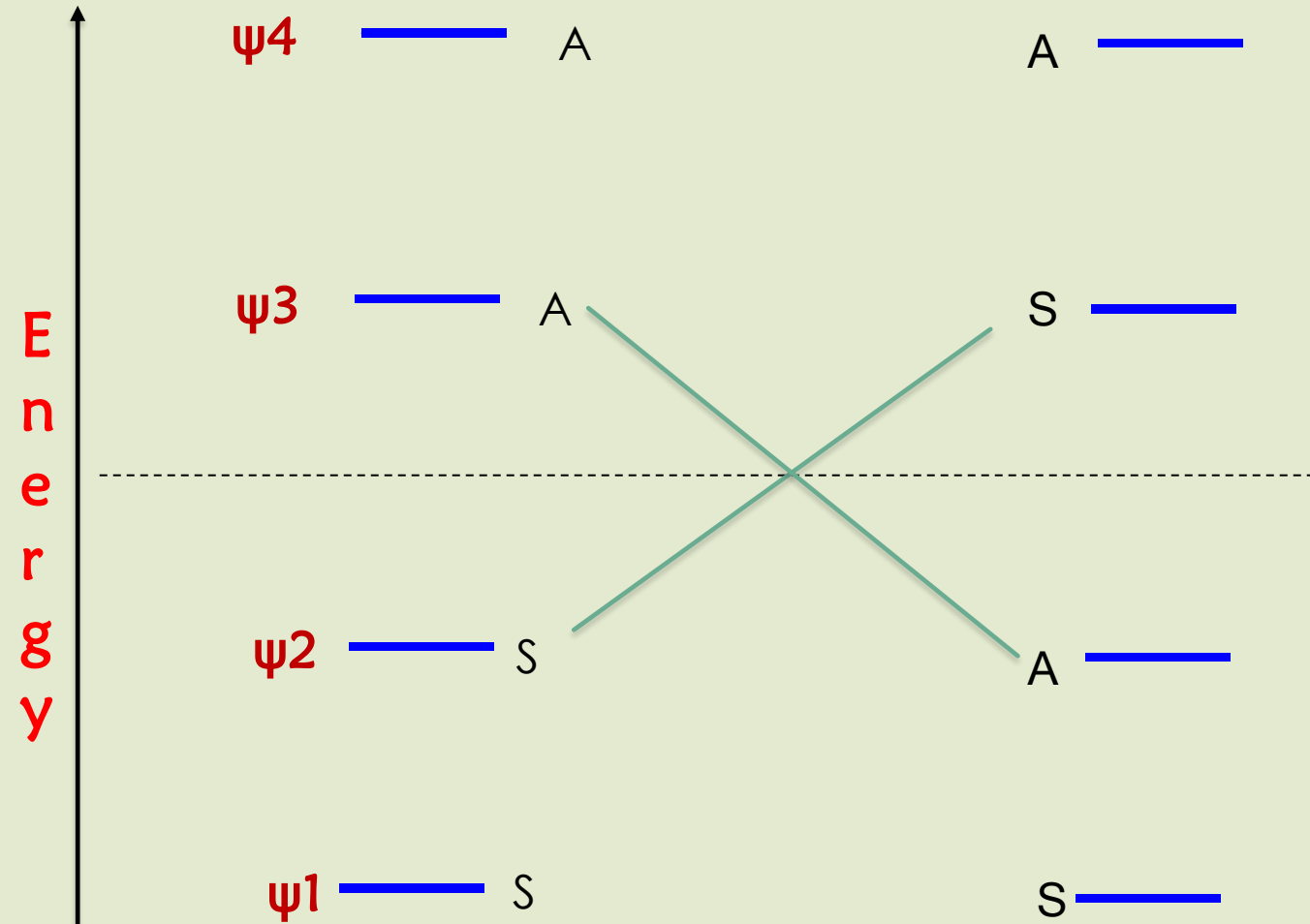
Example:



DIS ROTATION

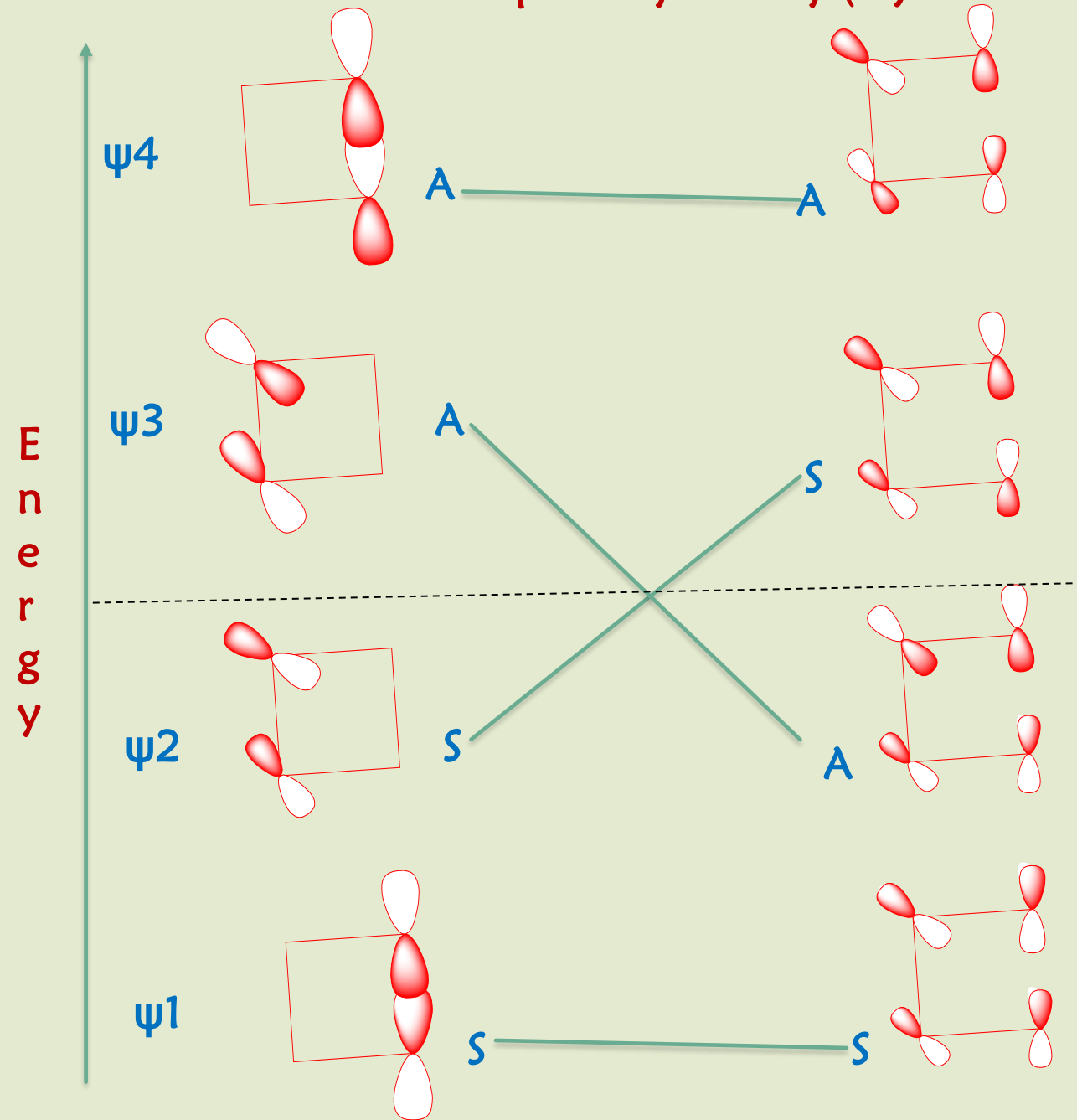


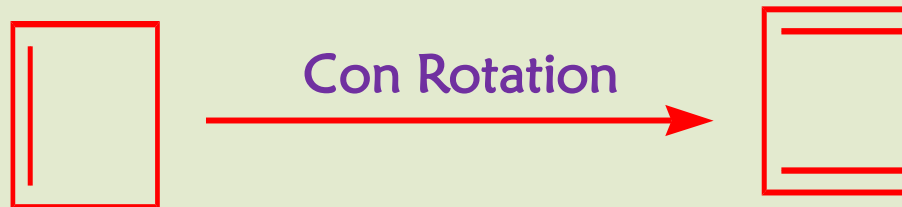
Mirror plane symmetry (m)



Dis Rotation hv Allowed .

Mirror plane symmetry (m)



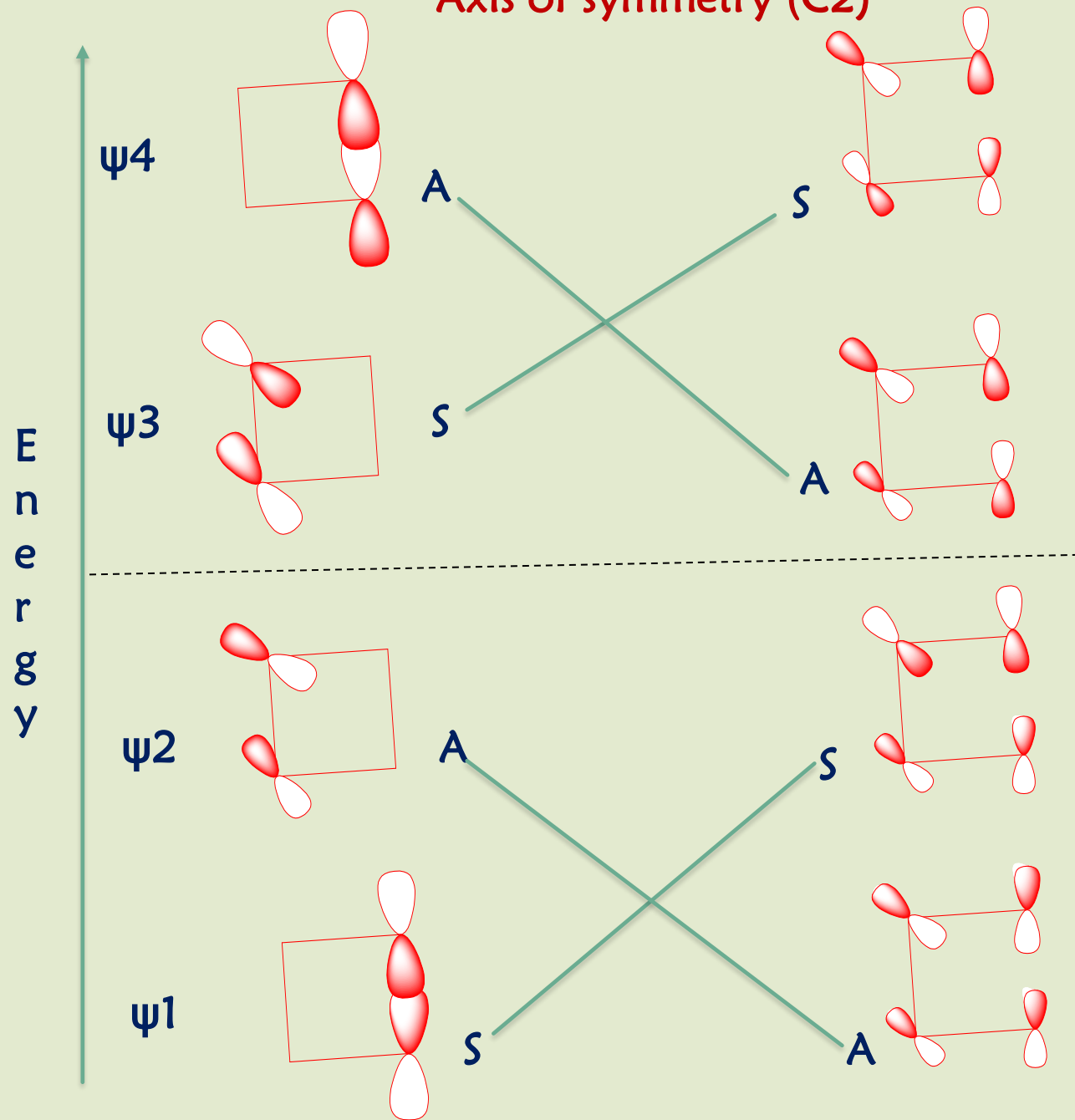


Dis Rotation \longrightarrow Mirror plane symmetry (m)

Con Rotation \longrightarrow Axis of symmetry (C_2)

- During conrotation two fold axis of symmetry (C_2) is conserved through out the process.
- For dis rotatory ring closure mirror plane (m) symmetry is conserved.

Axis of symmetry (C2)



Con Rotation
thermally allowed.

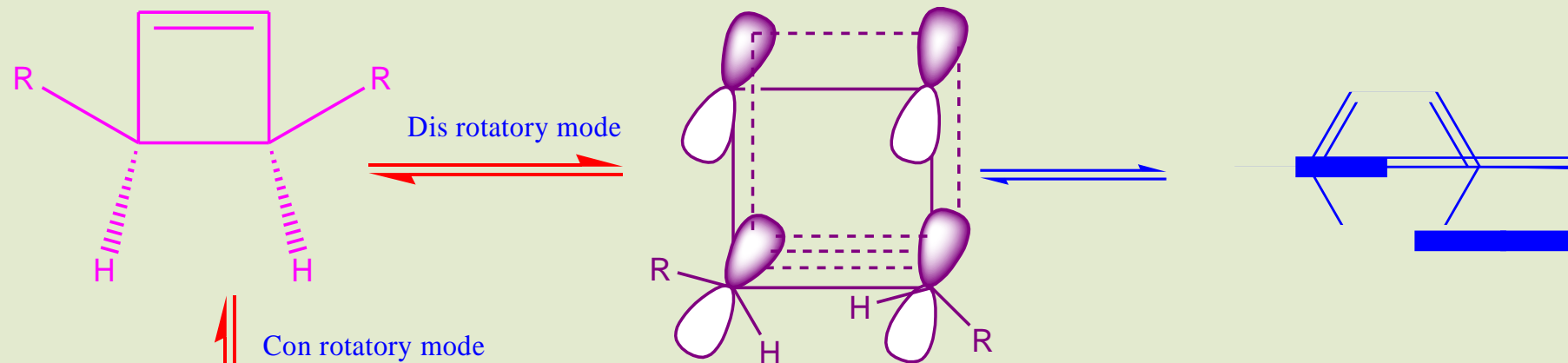
Classification of Pericyclic reactions

Perturbation of molecular (PMO) approach

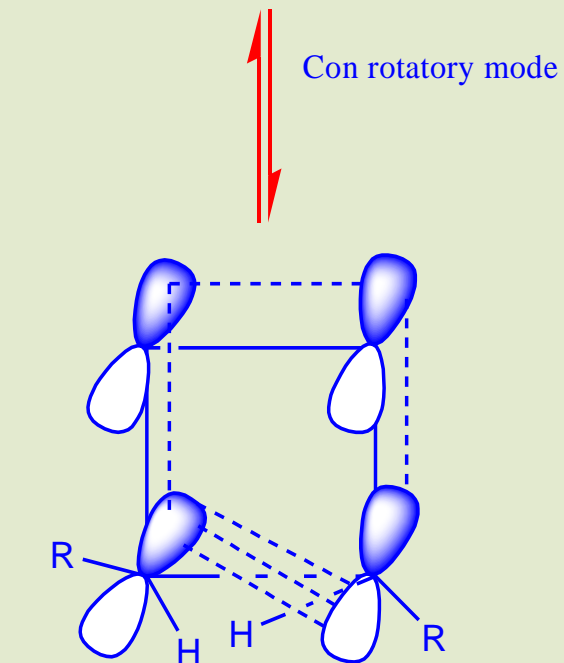
This approach was developed by M.J.S. Dewar and too leads to similar conclusion about pericyclic reactions as above two methods without taking into account symmetry of molecular orbitals.

- According to Huckel's rule of aromaticity a planer conjugated system with $(4n + 2)\pi$ -electrons is aromatic; therefore, stable in ground state. On the other hand, a system with $(4n)\pi$ -electrons is antiaromatic and hence, unstable in ground state.
- Calculations have shown that these rules are reversed in presence of a node or odd number of nodes in arrangement of atomic orbitals. Therefore, a system with $(4n+2)\pi$ -electrons and one node is antiaromatic in G.S. Conversely, $(4n)\pi$ system with one node is aromatic is G.S.
- Thermal reactions proceed through aromatic transition state and photochemical reactions involve antiaromatic transition states.

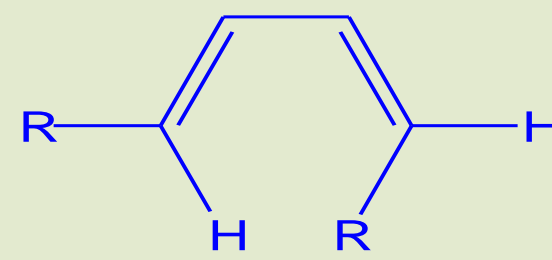
Example



0 node, 4 electrons
antiaromatic hv allowed



1 node, 4 electrons aromatic,
thermally allowed





Electrocyclic Reactions

Electrocyclic reactions- Process in which two π bonds convert into one π & one σ bond and vice versa.

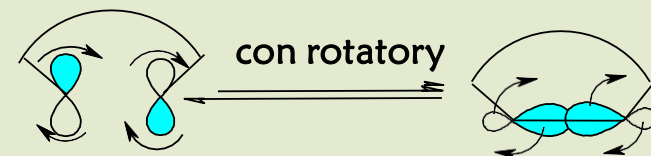
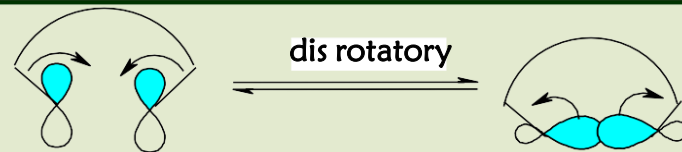
Ring opening-one π & one σ - bond into two π bonds
Ring opening-

Ring closer-two π bonds into one σ and π bond
Ring closer-

If the substitutions are present on the rotating carbons also rotate in same direction

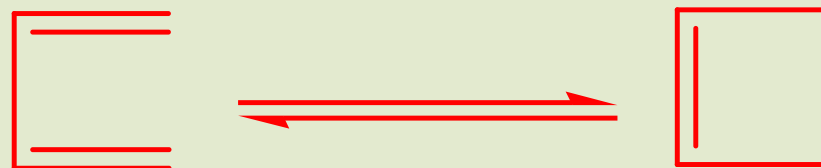
Two atomic orbitals forming a σ -bond may be rotating in opposite directions, one in clockwise and other in anticlockwise manner is called as *dis-rotatory process*

Two atomic orbitals forming a σ -bond may be rotating in same direction either in clockwise or anticlockwise manner is called as *con-rotatory process*.

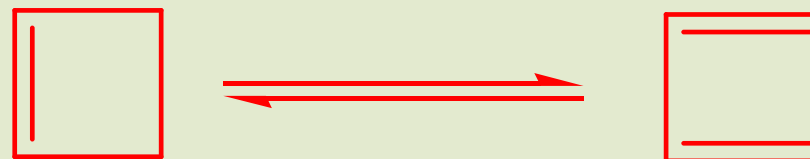


Electrocyclic Reactions

- An electrocyclic reaction is a reversible reaction that involves ring closure of a conjugated polyene to a cycloalkene, or ring opening of a cycloalkene to a conjugated polyene.
- σ - (sigma) Bond Formation across the conjugated polyene.
- Electrocyclic ring closing Reaction



- Electrocyclic ring opening Reaction



Stereochemistry

- ✓ Electrocyclic reactions are completely stereo specific.

Note:

If two double bonds present in the one molecule or compound the over all geometry of the compound designated as:

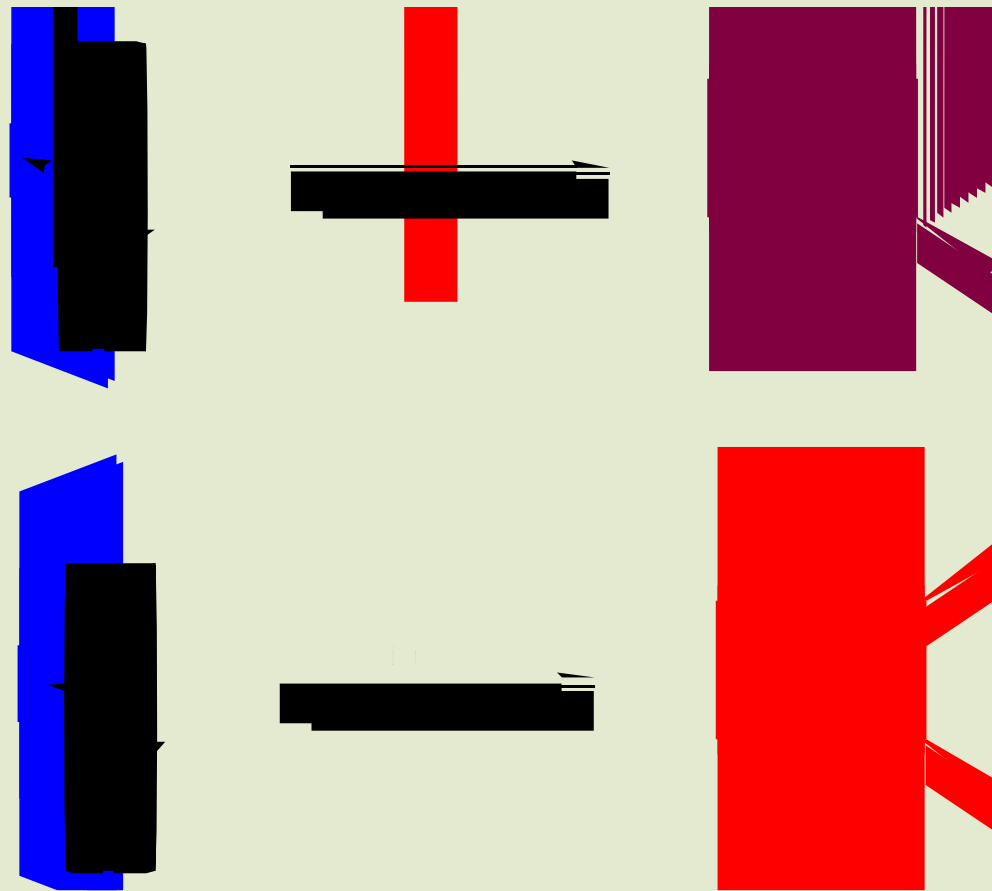
Cis \times Cis = Cis

Trans \times Trans = Cis

Cis \times Trans = Trans

Trans \times Cis = Trans

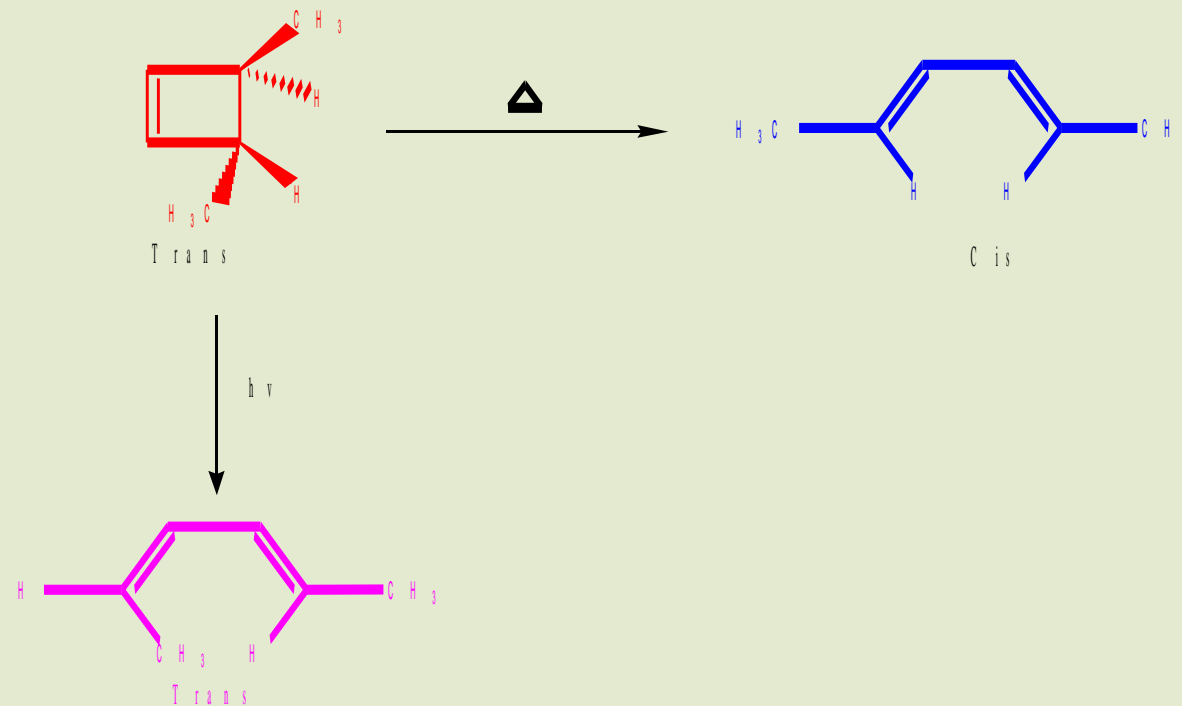
- ✓ For example Cyclization of Cis-2,4-hexadiene with heat forms a cyclobutene with trans methyl groups, whereas cyclization with light forms a cyclobutene with cis methyl groups.



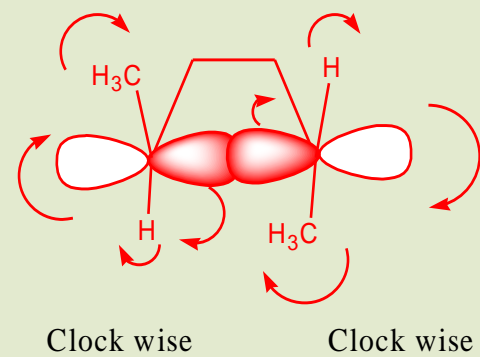
- ✓ The stereochemistry of the product of an electrocyclic reaction also depends on reaction condition, i.e., Thermal or photochemical reaction conditions.

4n π Electrons System:

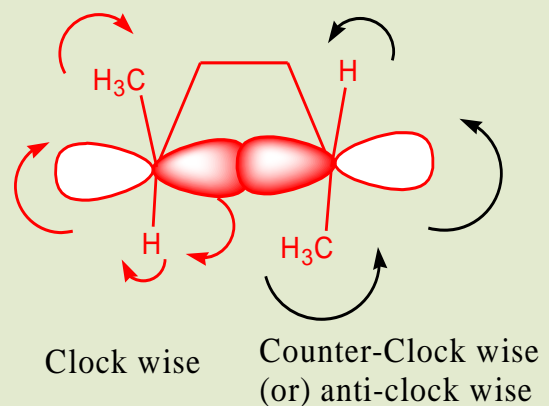
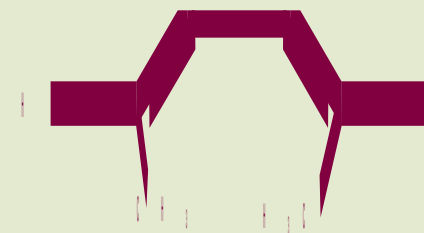
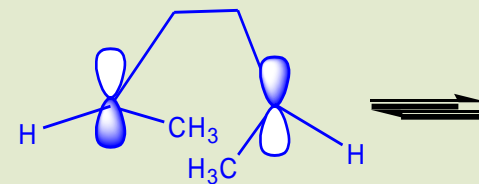
- Let us consider the simplest example in which a cyclobutene derivative opens to a 1, 3-butadiene derivative, i.e., open-chain conjugated system has 4n conjugated π electrons.
- In thermal condition trans-3, 4-dimethylcyclobutene gives cis-2, 4-hexadiene. Thus, this reaction is completely stereospecific.
- In the photochemical condition the same substrate gives Trans-2, 4-hexadiene. In this case too, the reaction is completely stereospecific. Thus the reaction can be performed thermally or photochemically, and under either condition the reaction is completely stereospecific.



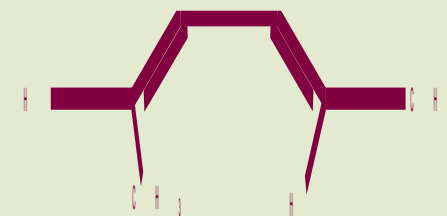
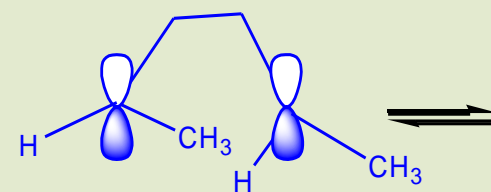
Stereochemistry of the thermal reaction can only be explained if process should be conrotatory.



Conrotatory



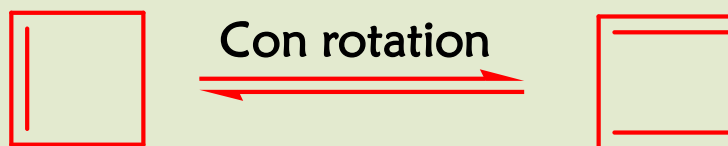
Disrotatory



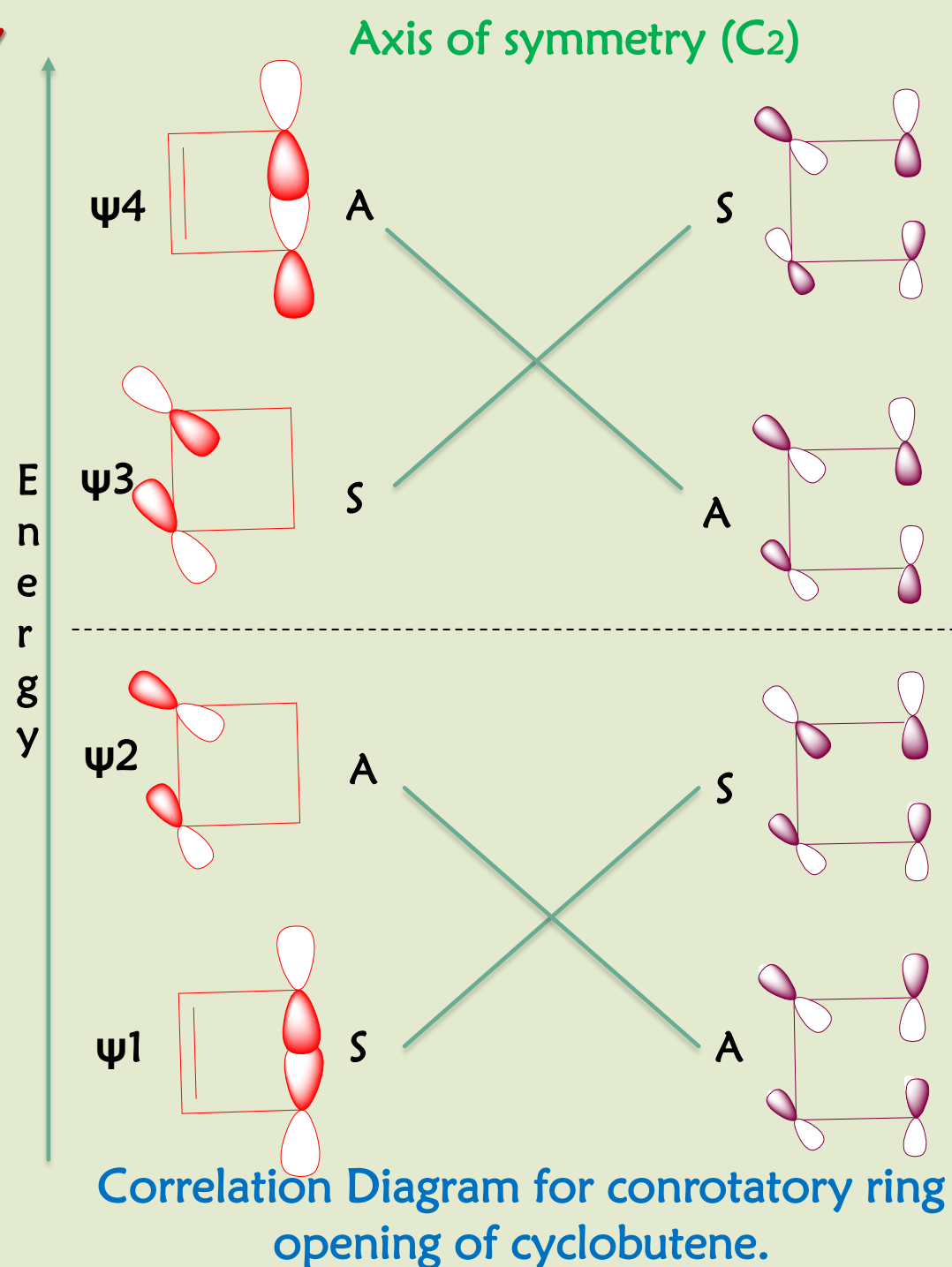
PREDICTIONS OF FEASIBILITY

4n π - Electron System

Example:

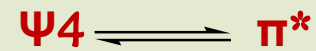
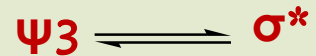
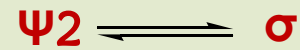
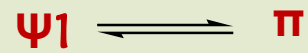


- According to Woodward's rules, during conrotatory ring opening or ring closing electrocyclicization, the axis of symmetry (C_2) will be conserved.

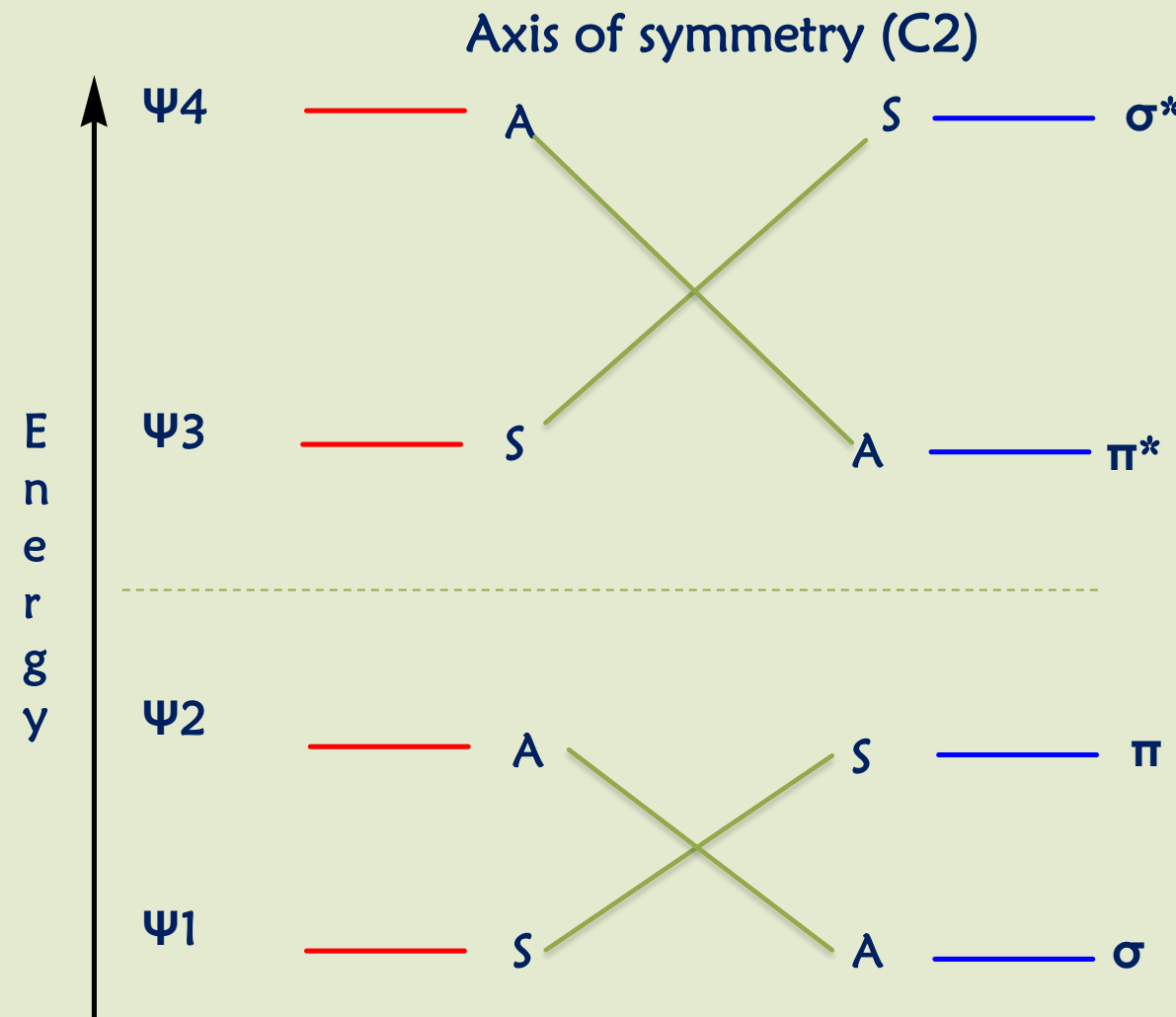


The ground state orbitals of cyclo-butene correlates with ground state orbitals of butadiene. Hence it is thermally-Symmetry allowed process.

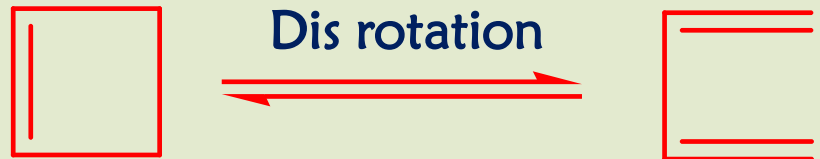
Correlations:



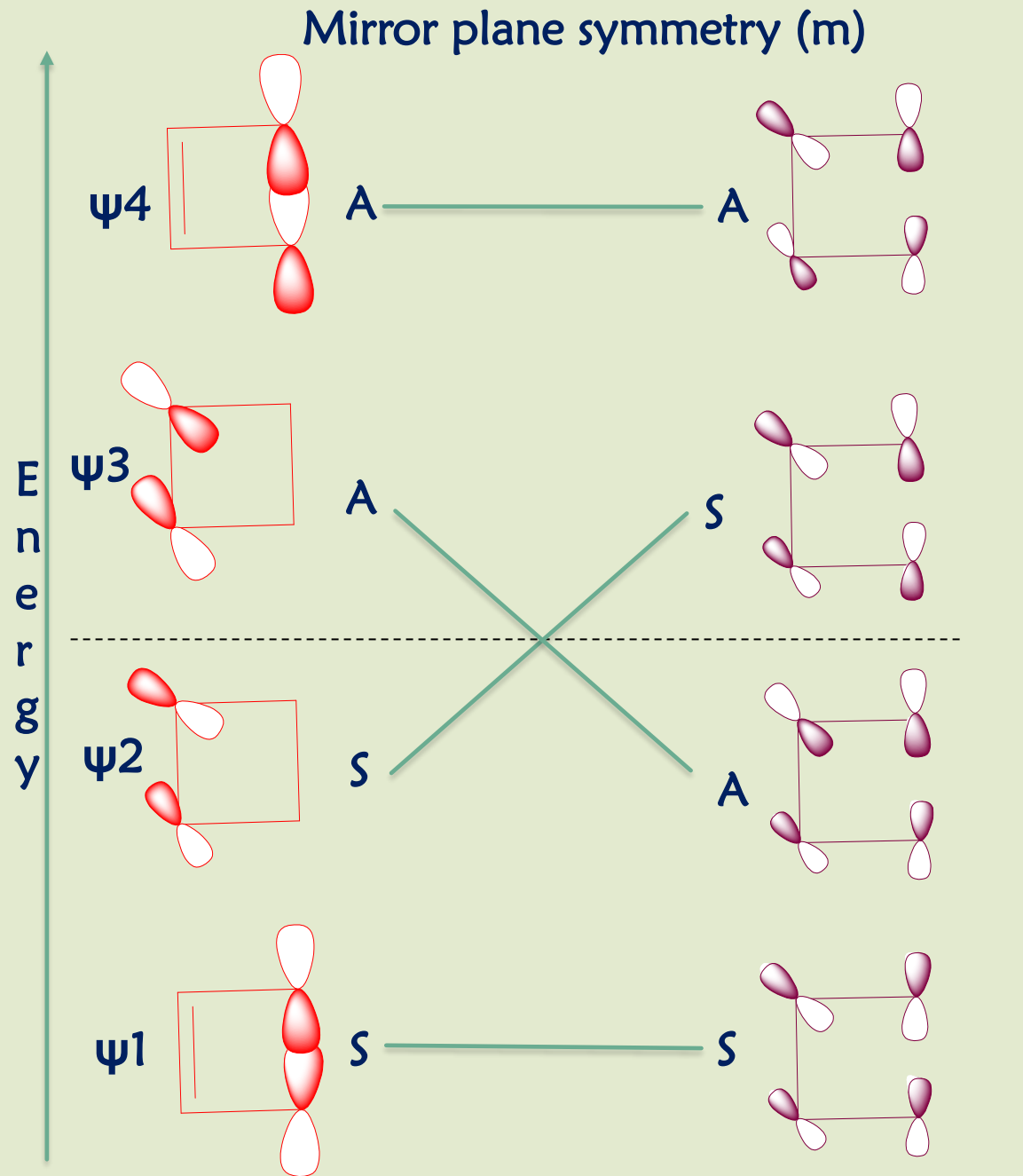
Here HOMO = ψ_2
LUMO = ψ_3



Correlation Diagram for conrotatory ring opening of cyclobutene.



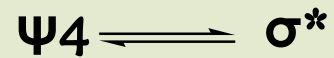
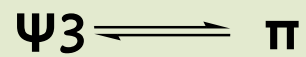
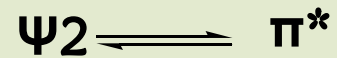
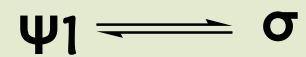
- According to wood wards rules During conrotatory ring opening or ring closing electrocyclization Mirror plane symmetry (m) will be conserved.
- On irradiation of cyclobutene precursor electron is promoted from ground state ψ_2 to Excited state ψ_3 .



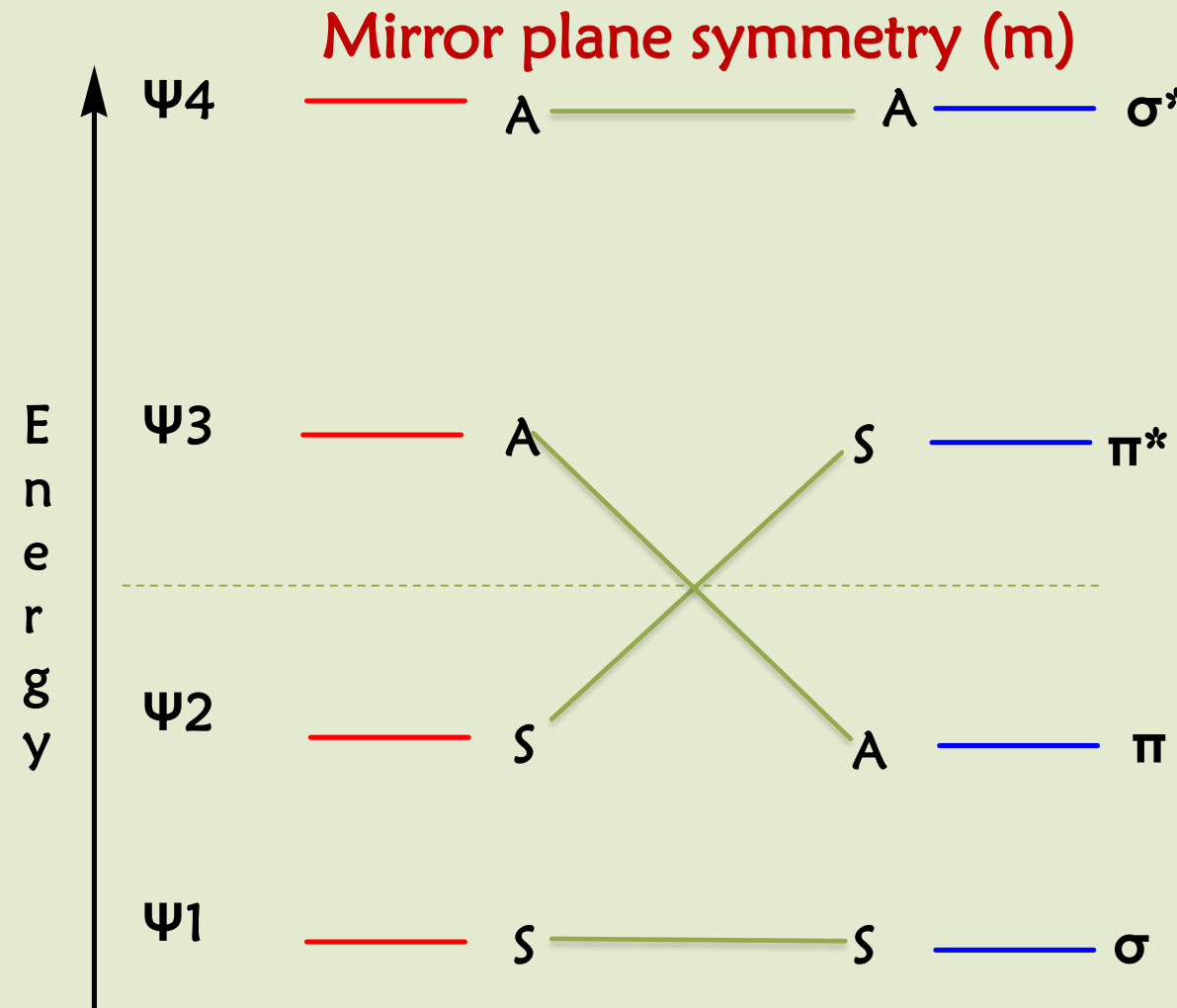
Correlation Diagram for Dis rotatory ring opening of cyclobutene.

The ground state orbitals of cyclo-butene correlates with Excited state orbitals of butadiene. Hence it is Photochemically-Symmetry allowed process.

Correlations:



On irradiation with light
electron promote from ψ_2
to ψ_3 hence HOMO= ψ_3
LUMO= ψ_4



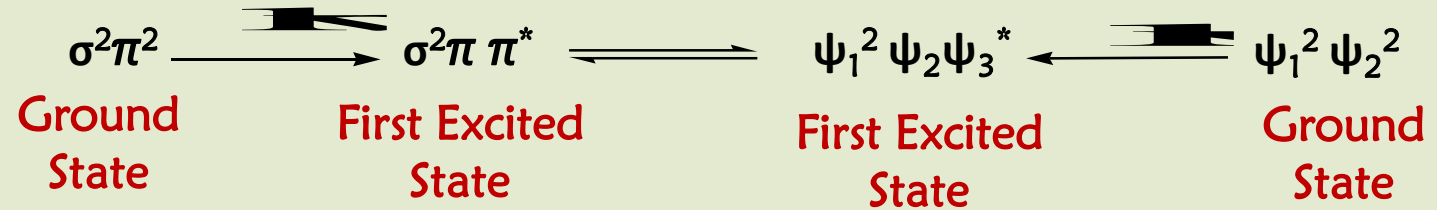
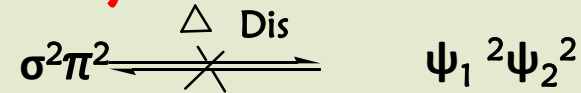
➤ This Generalization holds good for all systems with $4n \pi$ Electrons .

Where $n = 1, 2, 3, \dots$

Correlations for Con-Rotatory



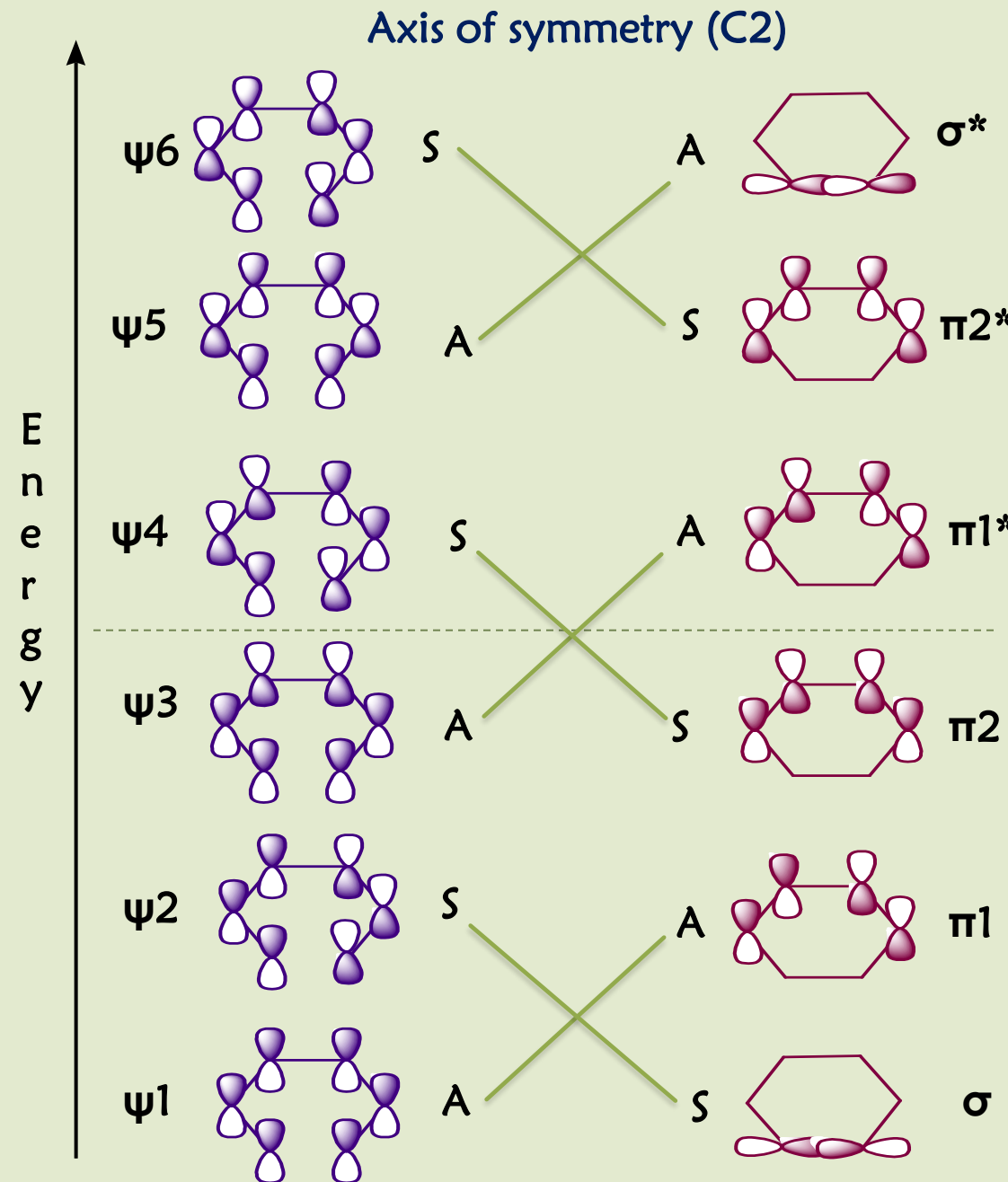
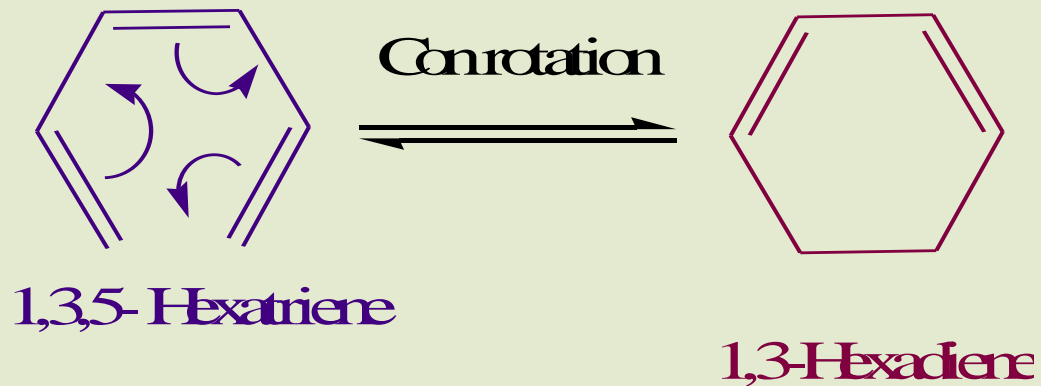
Correlations for Dis-Rotatory



| $4n$ | Thermal | Photo Chemical |
|--------------|-----------|----------------|
| Con-Rotatory | Allowed | Forbidden |
| Dis-Rotatory | Forbidden | Allowed |

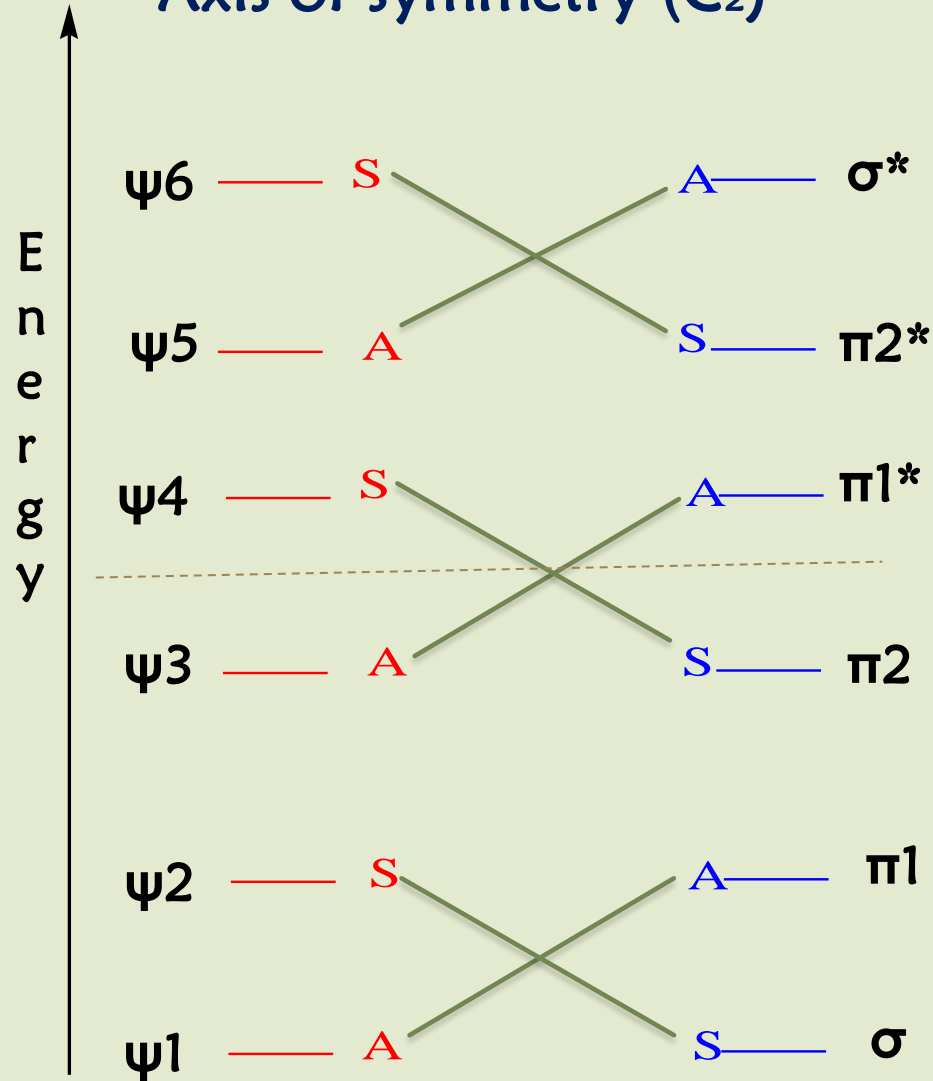
4n+2 π Electrons System:

Let us consider cyclisation of 1,3,5-hexatriene to 1,3-cyclohexadiene System. In this six molecular orbitals of 1,3,5-hexatriene and six Molecular orbitals of 1,3-cyclohexadiene are involved.

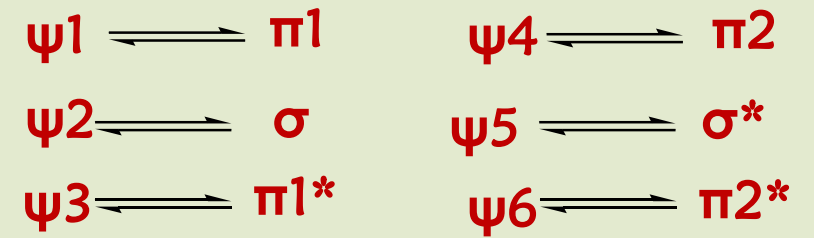


Correlation Diagram for Con Rotatory Cyclisation of 1,3,5-Hexatriene.

Axis of symmetry (C_2)




Correlations:

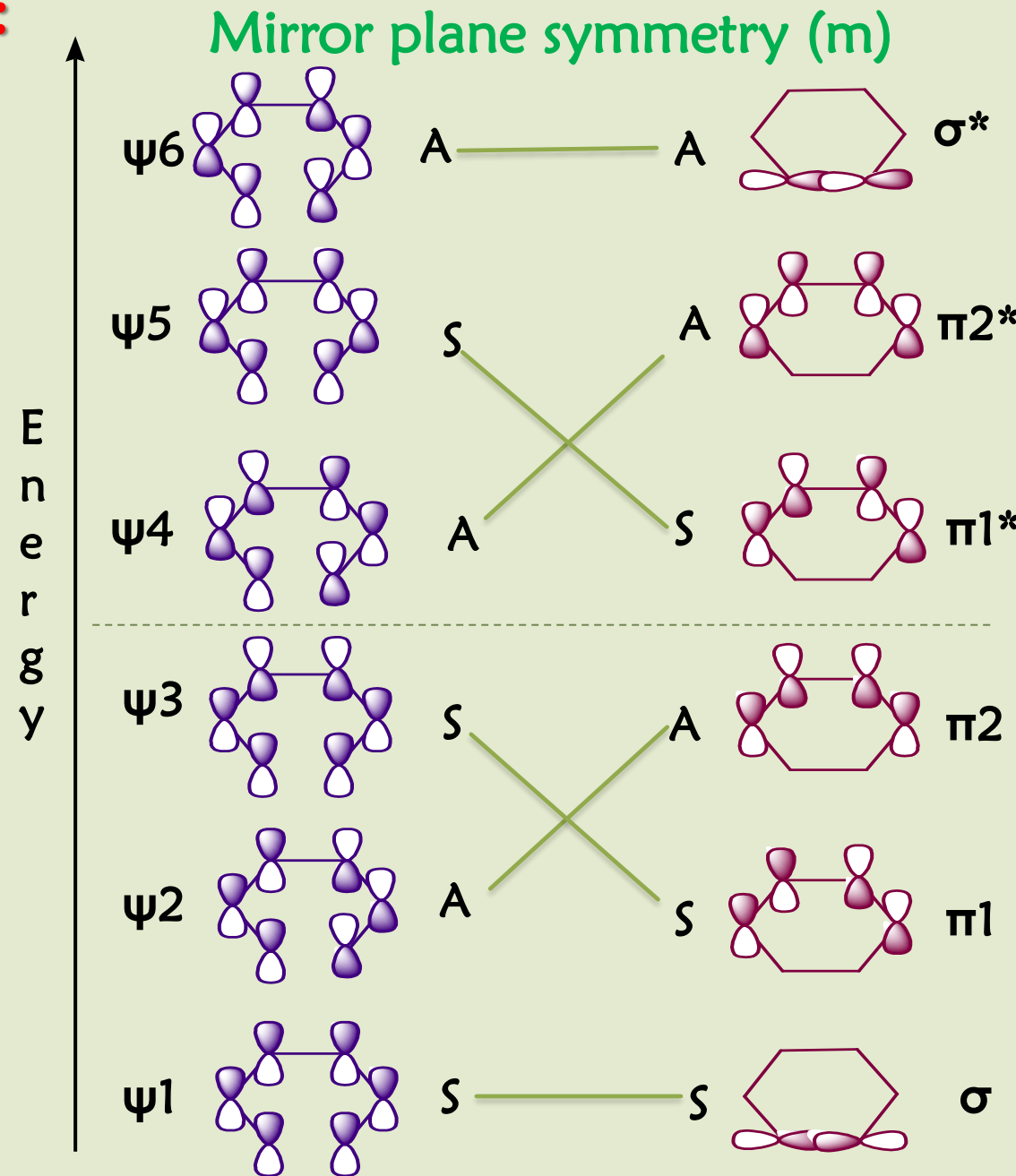
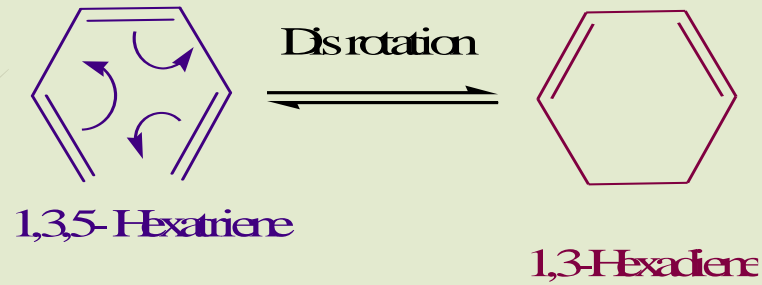


Here HOMO = ψ_3
LUMO = ψ_4

Correlation Diagram for Con Rotatory
Cyclisation of 1,3,5-Hexatriene.

- 
- According to Woodward's rules, during conrotatory ring opening or ring closing electrocyclicization, the axis of symmetry (C_2) will be conserved.
 - In this Con Rotatory mode, the ground state orbital (ψ_1) of 1,3,5-Hexatriene does not correlate with the ground state orbital (ψ_1) of 1,3-Hexadiene.
 - The Molecular Orbitals of 1,3,5-Hexatriene correlate with the first excited state molecular orbitals of 1,3-Hexadiene.
 - Hence, it is a photochemically symmetry-allowed process by conrotation.
 - This generalization holds good for all systems with $4n+2$ π electrons.
Where $n = 1, 2, 3, \dots$

4n+2 π Electrons System:



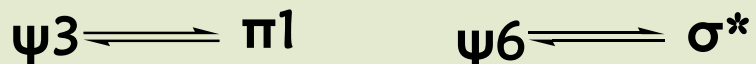
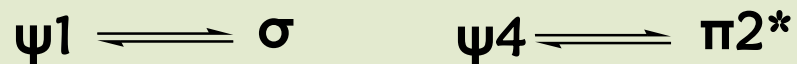
Correlation Diagram for Dis Rotatory Cyclisation of 1,3,5-Hexatriene.

- According to Woodward's rules During Disrotatory ring opening or ring closing electrocyclization Mirror plane symmetry (m) will be conserved.

- In this Dis Rotatory mode the ground state orbital (ψ_1) of 1,3,5-Hexatriene correlate with ground state orbital (ψ_1) of 1,3-Hexadiene.
- Hence it is a Thermally Symmetry allowed Process by Dis Rotation.
- This Generalization holds good for all systems with $4n+2$ π Electrons .

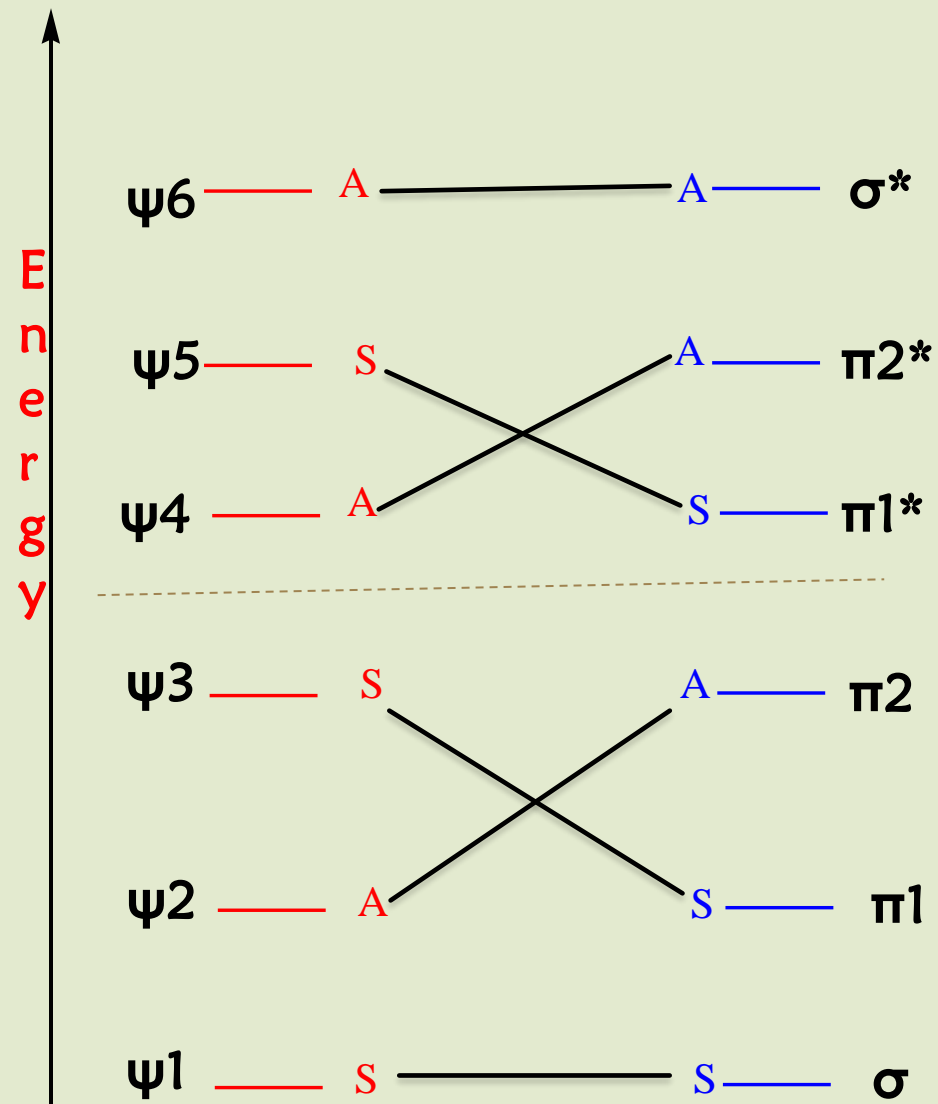
Where $n = 1, 2, 3, \dots$

Correlations:

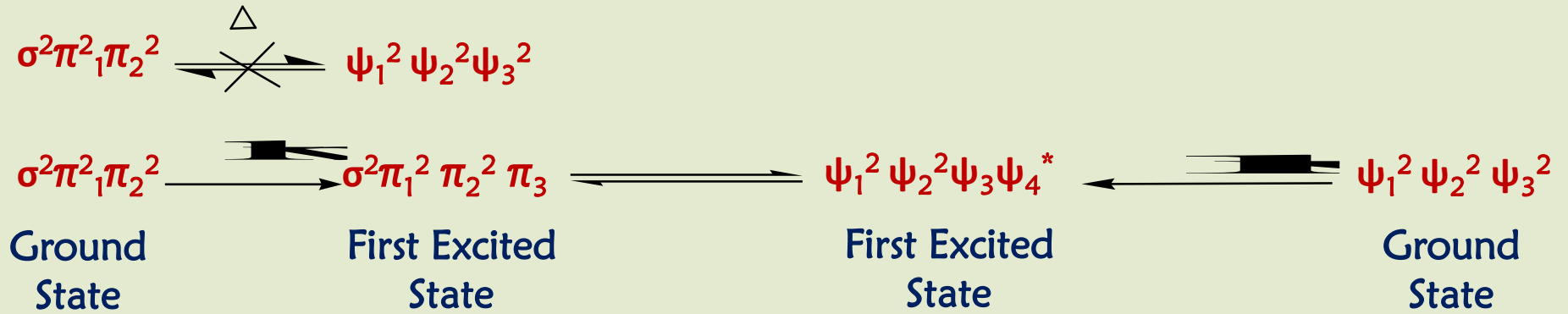


- On irradiation with light Electron promoted from ψ_3 to ψ_4 hence HOMO = ψ_4
LUMO = ψ_5

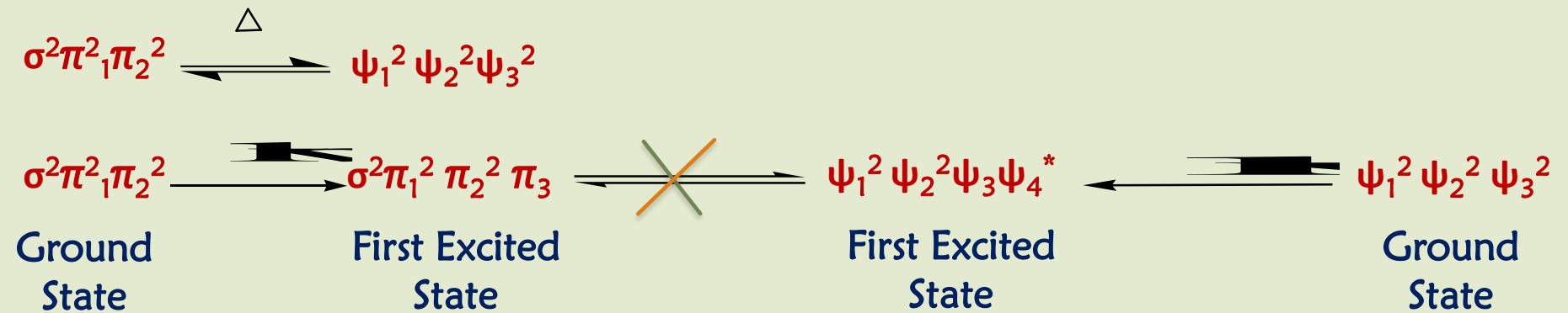
Mirror plane symmetry (m)




Correlations for Con Rotation



Correlations for Dis Rotation





| $4n+2$ π Electrons | Thermal | Photochemical |
|---|------------------|----------------------|
| Con Rotation | Forbidden | Allowed |
| Dis Rotation | Allowed | Forbidden |

| | Thermal | Photochemical |
|--------------------------|---------------------|----------------------|
| $4n$ | Con rotation | Dis rotation |
| $4n+2$ | Dis rotation | Con rotation |

Summary of Electrocyclization:

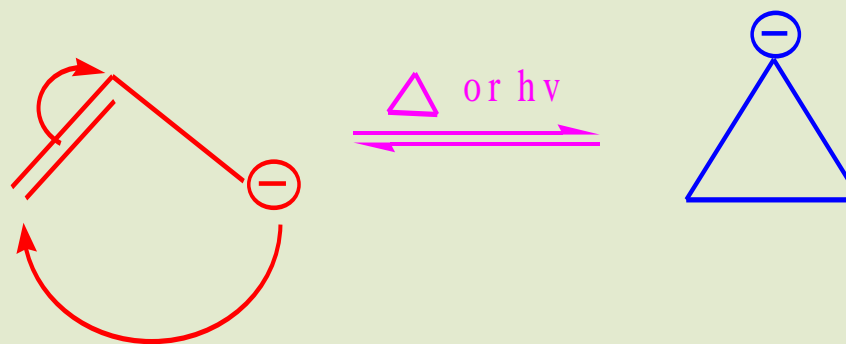
If the HOMO having C_2 -axis of symmetry (node is odd), then reaction will follow con- rotatory path.

If HOMO posses a mirror plane symmetry (node is zero or even number), a reaction will follows dis-rotatory path.

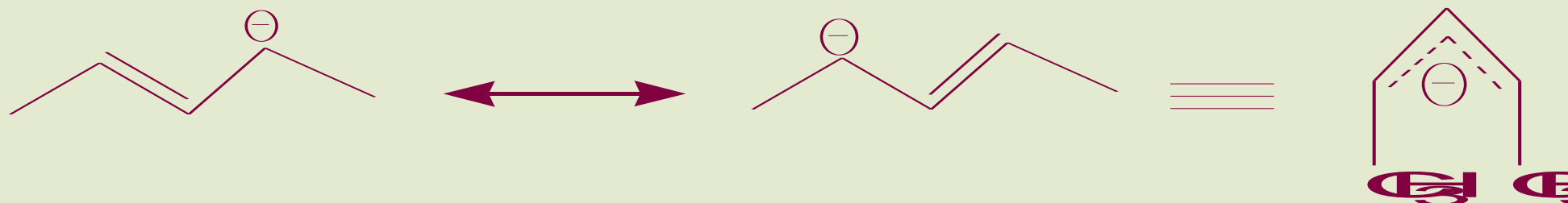
| | | |
|-------------------------|---------------------|----------------------------|
| Thermal Reactions | Transition State | Configurational Preference |
| | $4n + 2$ (aromatic) | Disrotatory |
| Photochemical Reactions | $4n$ (antiaromatic) | Conrotatory |
| | Transition State | Configurational Preference |
| | $4n + 2$ (aromatic) | Conrotatory |
| | $4n$ (antiaromatic) | Disrotatory |

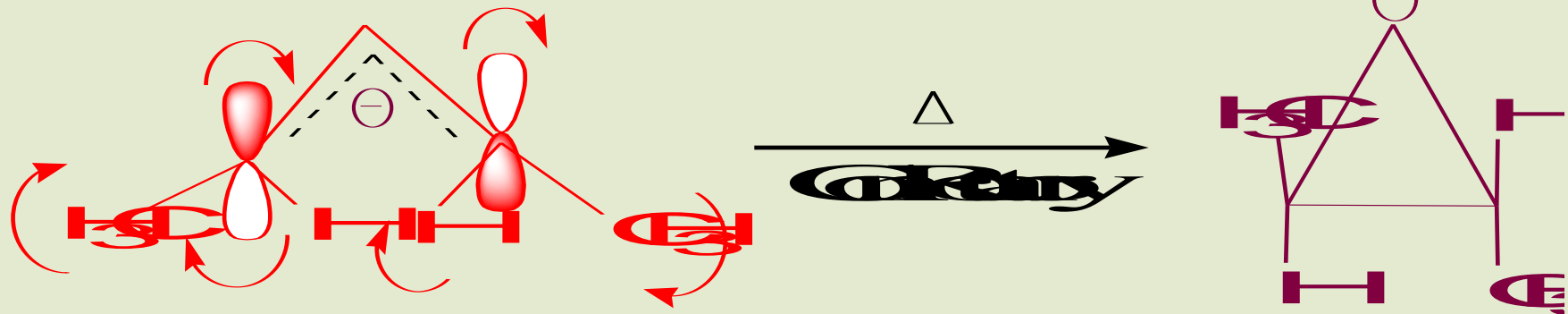
Electrocyclic ring-closure given by allyl carbanion

Allyl carbanion is also a $4n\pi$ conjugated system.

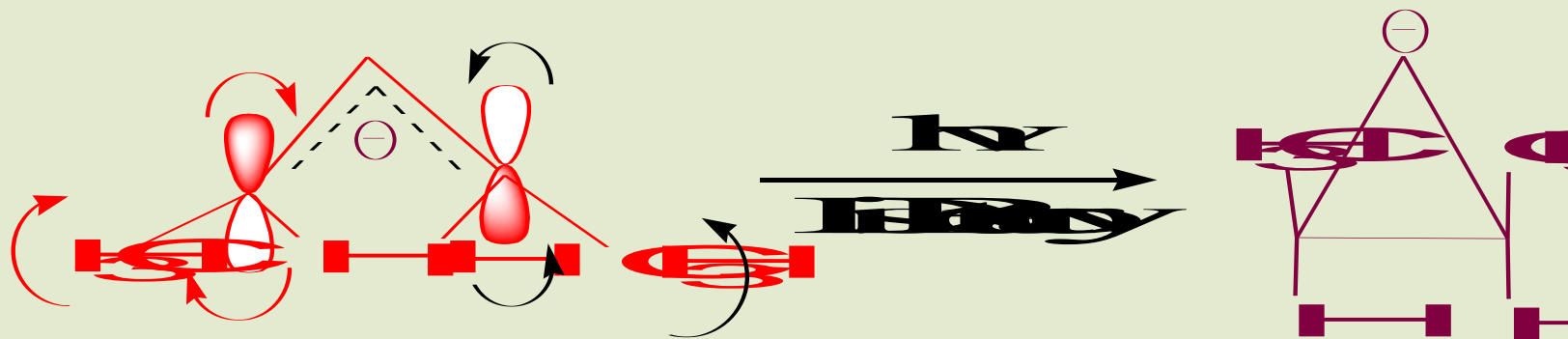


- HOMO of the allyl carbanion in the ground state is ψ_2 which has C_2 -symmetry. Therefore, conrotatory motion is the mode of cyclisation in the thermal condition.



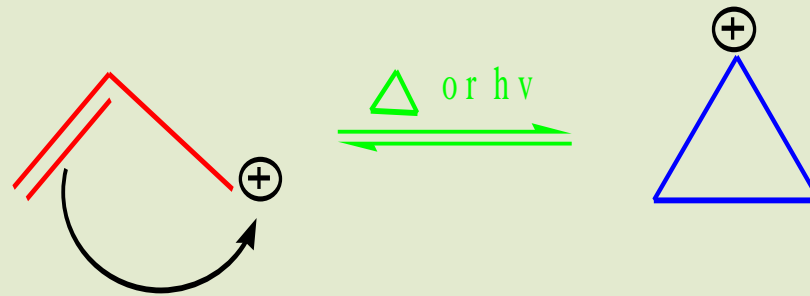
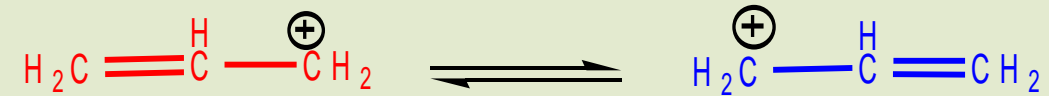


- In case of photocyclization, the excited HOMO is ψ_3^* which has m-symmetry. Thus, disrotatory motion is required for σ (sigma) bond formation.



Electrocyclic ring-closure reaction given by allyl carbocation

Allyl carbocation contains $(4n + 2)\pi$ conjugated electrons.



Thermal-induced cyclisation: HOMO of the allyl carbocation in the ground state is ψ_1 which has m-symmetry. Therefore, dis rotatory motion is the mode of cyclisation in the thermal condition.

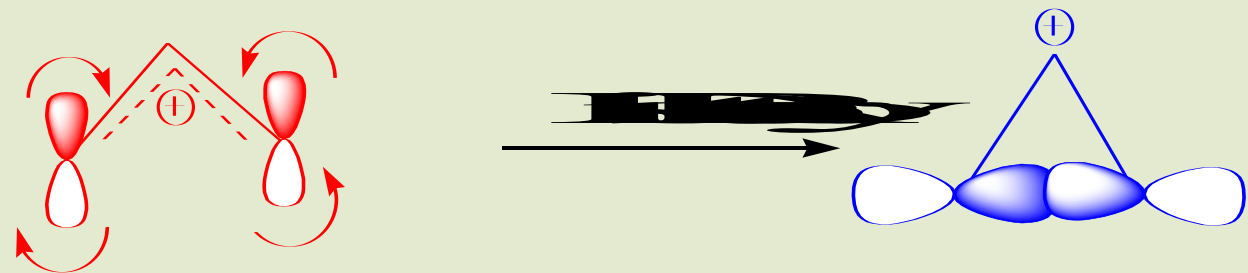
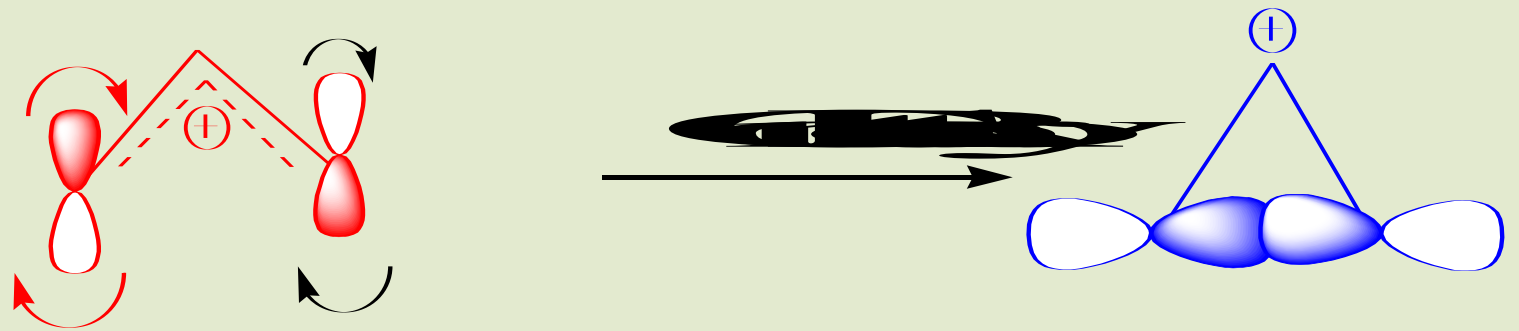


Photo-induced cyclisation: HOMO of the allyl carbocation in the excited state is ψ_2 which has C_2 -symmetry. Thus, conrotatory motion is required for σ (sigma) bond formation.





Thank You