

❖ 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.

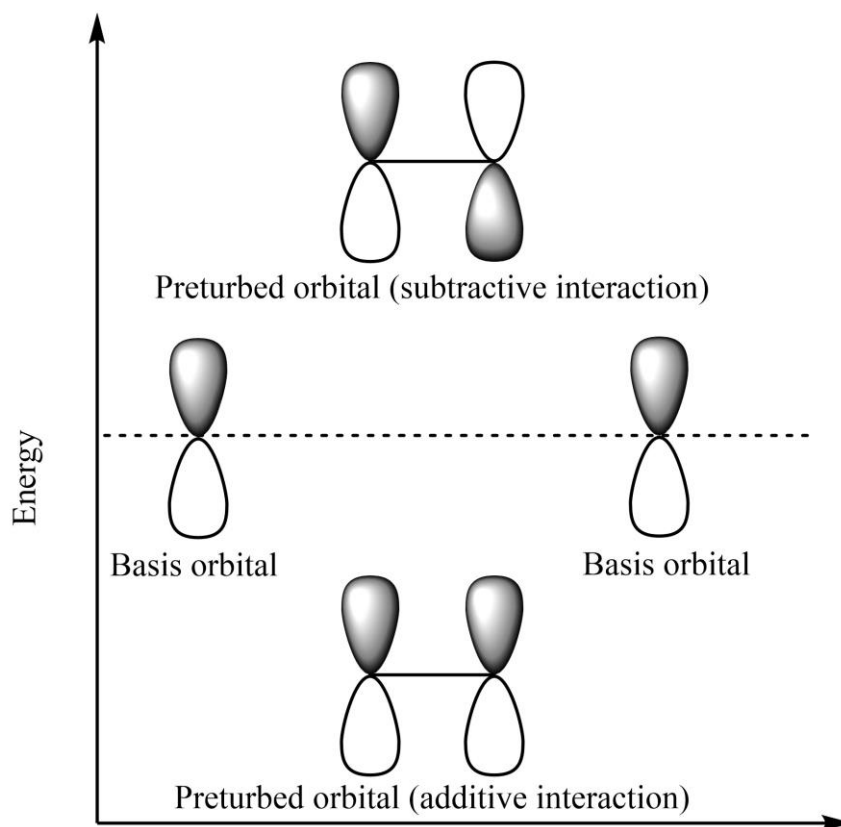


Figure 21. The perturbed molecular orbitals from degenerate basis orbitals.

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 ψ_1 and ψ_2 with different energies.

$$\psi_+ = \psi_1 + \lambda\psi_2 \quad (1)$$

$$\psi_- = \psi_2 - \lambda\psi_1 \quad (2)$$

Where the symbol λ whose value varies from 0 to 1. As the energy difference between ψ_1 and ψ_2 increases, the magnitude of λ approaches to zero.

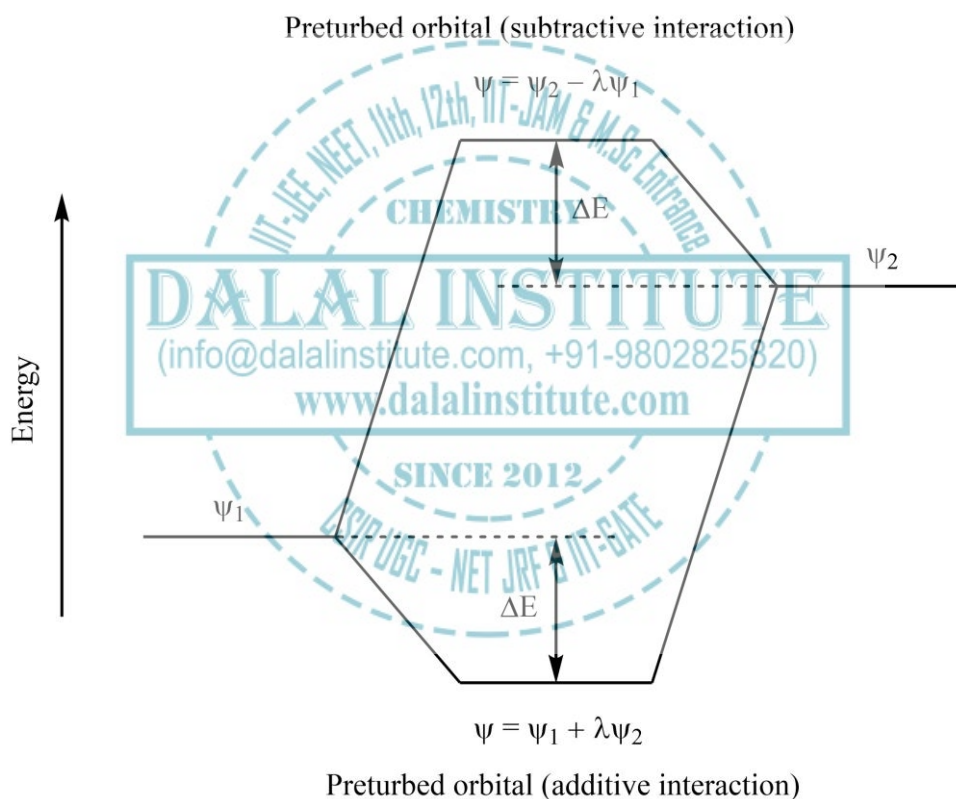


Figure 22. The perturbed molecular orbitals from non-degenerate basis orbitals.

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.

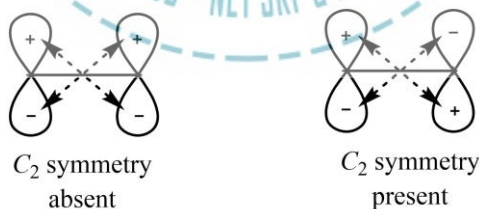
1. Depiction of perturbed molecular orbitals: Unlike conventional MO theory, the molecular orbitals in the PMO approach are portrayed as in terms of basis orbitals rather than the actual shapes. Therefore, every shape with more than one atomic orbital is actually a molecular orbital.



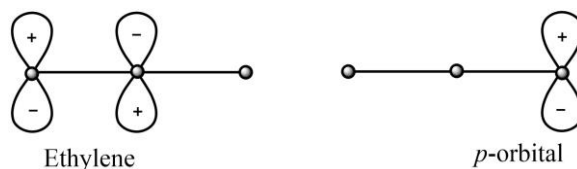
2. Symmetry of perturbed molecular orbitals: If a molecular orbital can be divided into two equal halves, the MO will be said to possess mirror or 'm' symmetry.



Similarly, a molecular orbital has a two-fold symmetry axis, the MO will be said to possess inversion or 'C₂' symmetry.



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.



➤ **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 $n-1$.

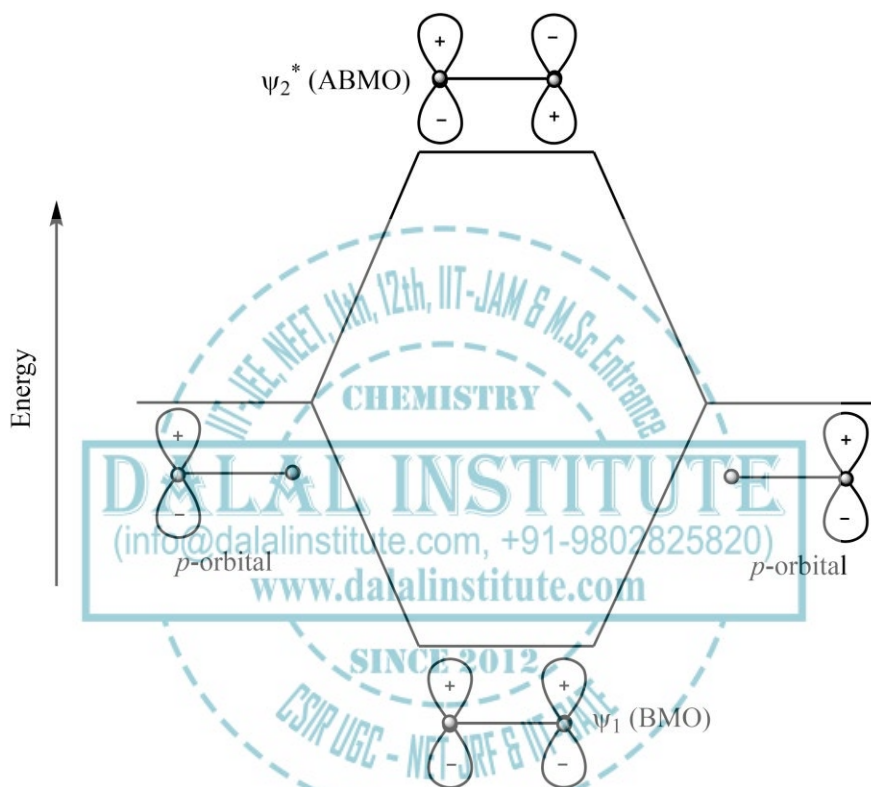


Figure 23. The perturbed molecular orbitals of ethylene.

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
ψ_1	0	Present	Absent
ψ_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.

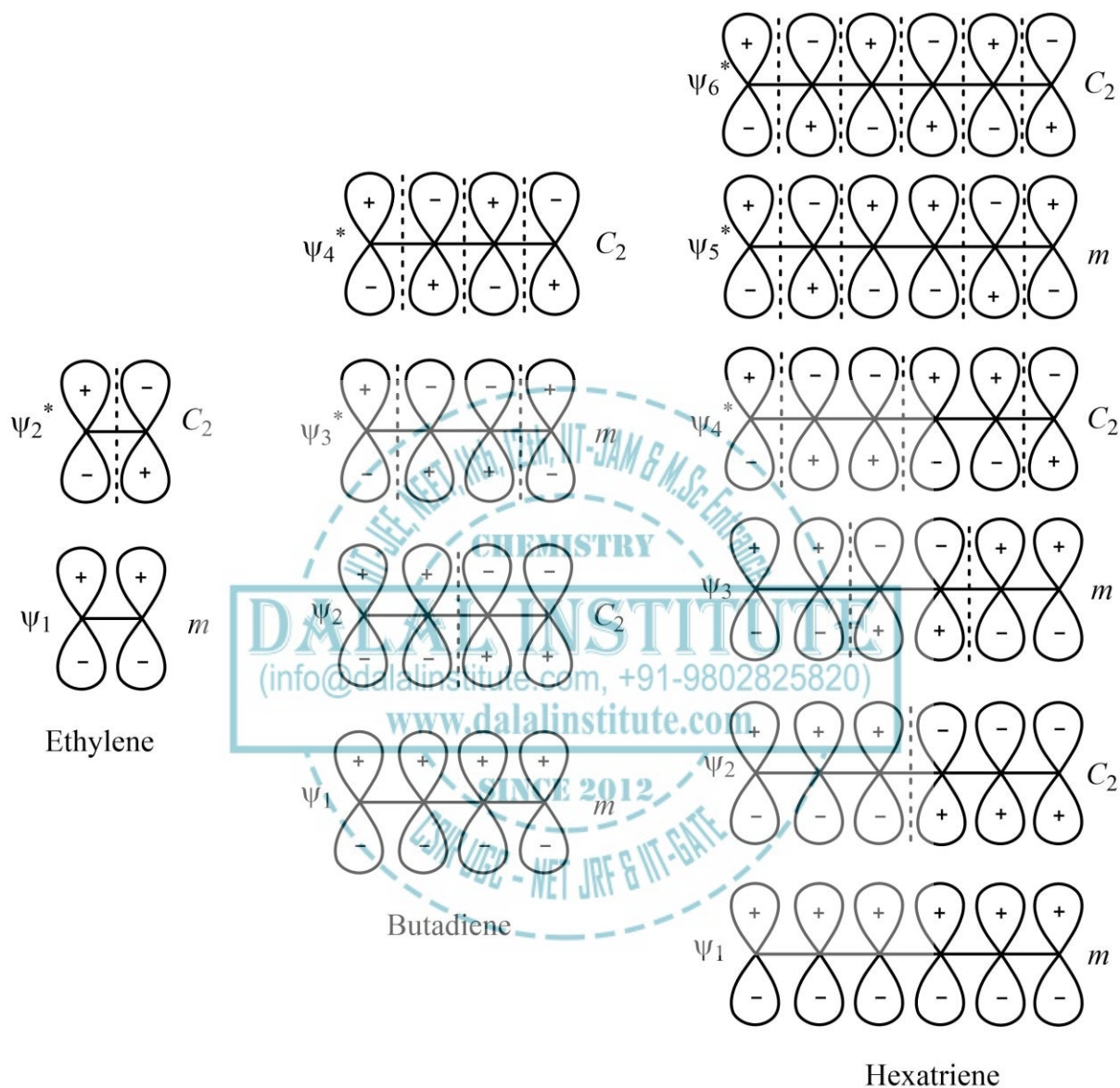


Figure 24. The perturbed molecular orbitals (along with the symmetry) of ethylene, butadiene, and hexatriene.

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 $n-1$.

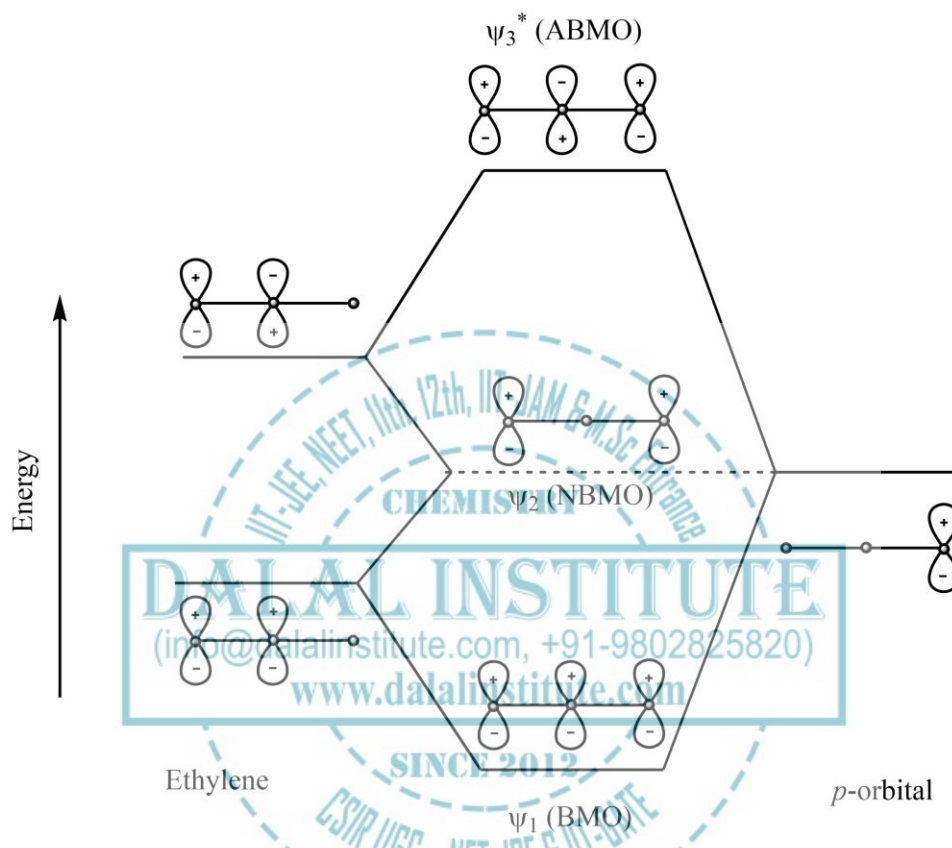


Figure 25. The perturbed molecular orbitals of allyl.

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
ψ_1	0	Present	Absent
ψ_2	1	Absent	Present
ψ_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.

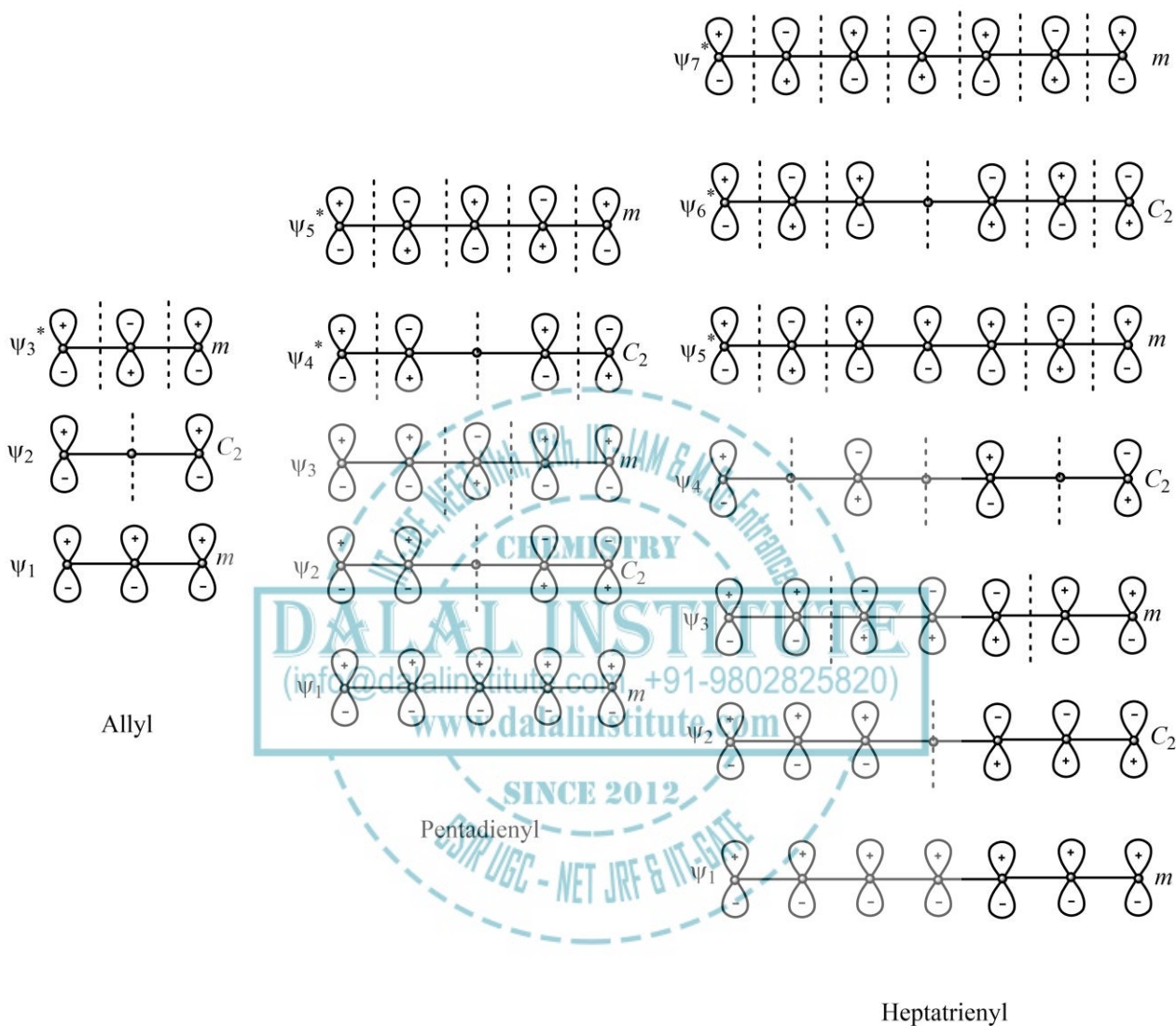


Figure 26. The perturbed molecular orbitals (along with the symmetry) of allyl, pentadienyl, and heptatrienyl.

It is obvious from the above diagram that all the nodes in ψ_{odd} pass through in-between the carbon nuclei whereas all nodes in ψ_{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 π -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).

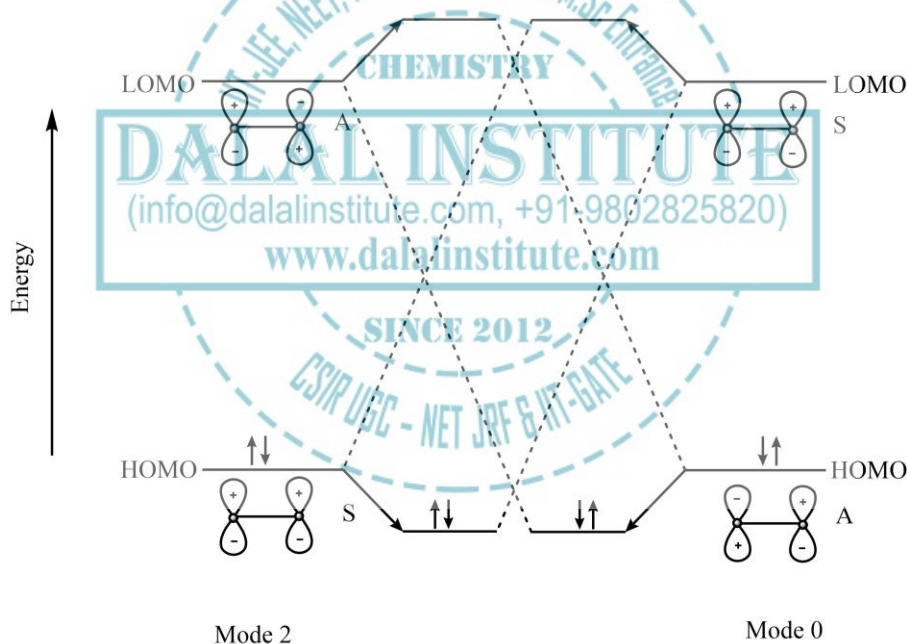


Figure 27. The pictorial depiction of Mode 2 overlap with Mode 0.

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 $4n$ π -electrons respectively; the combination of Mode 2 and Mode 0 will create a total of $4n + 2$ π -electrons (aromatic), whereas Mode-2–Mode-2 or Mode-0–Mode-0 will create a total of $4n$ π -electrons (antiaromatic).

LEGAL NOTICE

This document is an excerpt from the book entitled “A Textbook of Organic Chemistry – Volume 1 by Mandeep Dalal”, and is the intellectual property of the Author/Publisher. The content of this document is protected by international copyright law and is valid only for the personal preview of the user who has originally downloaded it from the publisher’s website (www.dalalinstitute.com). Any act of copying (including plagiarizing its language) or sharing this document will result in severe civil and criminal prosecution to the maximum extent possible under law.



This is a low resolution version only for preview purpose. If you want to read the full book, please consider buying.

Buy the complete book with TOC navigation, high resolution images and no watermark.

Home

CLASSES

CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, IIT-JEE, NEET, 11th and 12th

Want to study chemistry for CSIR UGC – NET JRF + IIT-GATE; IIT-JAM + M.Sc Entrance; IIT-JEE + NEET + 11th +12th; and all other postgraduate, undergraduate & senior-secondary level examinations where chemistry is a paper?
[READ MORE](#)

BOOKS

Publications

Are you interested in books (Print and Ebook) published by Dalal Institute?
[READ MORE](#)

VIDEOS

Video Lectures

Want video lectures in chemistry for CSIR UGC – NET JRF + IIT-GATE; IIT-JAM + M.Sc Entrance; IIT-JEE + NEET + 11th +12th; and all other postgraduate, undergraduate & senior-secondary level examinations where chemistry is a paper?
[READ MORE](#)

Postgraduate Level

Senior-Secondary Level

Undergraduate Level

CSIR UGC – NET JRF & IIT-GATE

First Chemistry Batch
(1st January – 31st May)

Second Chemistry Batch
(1st July – 30th November)

11TH, 12TH, NEET & IIT-JEE

First Chemistry Batch
(1st April – 31st August)

Second Chemistry Batch
(1st October – 28th February)

M.SC ENTRANCE & IIT-JAM

First Chemistry Batch
(1st February – 30th June)

Second Chemistry Batch
(1st August – 31st December)

Regular Program

Online Course

Result

Regular Program

Online Course

Result

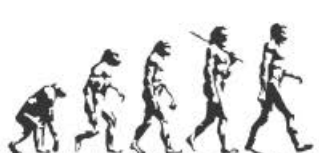
Regular Program

Online Course

Result

Join the revolution by becoming a part of our community and get all of the member benefits like downloading any PDF document for your personal preview.

[Sign Up](#)



JOIN THE REVOLUTION FROM BEAST TO

BUDDHA

D DALAL INSTITUTE

.....Chemical Science Demystified.....

Main Market, Sector 14, Rohtak, Haryana 124001, India
(+91-9802825820, info@dalalinstitute.com)
www.dalalinstitute.com

..... India's Best Coaching Center for Academic and Competitive Chemistry Exams
(CSIR UGC – NET JRF + IIT-GATE; IIT-JAM + M.Sc Entrance; IIT-JEE + NEET + 11th +12th; and all other postgraduate, undergraduate & senior-secondary level examinations where chemistry is a paper)

International
Edition



A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

Table of Contents

CHAPTER 1	11
Nature of Bonding in Organic Molecules	11
❖ Delocalized Chemical Bonding	11
❖ Conjugation	14
❖ Cross Conjugation	16
❖ Resonance.....	18
❖ Hyperconjugation	27
❖ Tautomerism.....	31
❖ Aromaticity in Benzenoid and Nonbenzenoid Compounds	33
❖ Alternant and Non-Alternant Hydrocarbons	35
❖ Huckel's Rule: Energy Level of π -Molecular Orbitals	37
❖ Annulenes.....	44
❖ Antiaromaticity.....	46
❖ Homoaromaticity.....	48
❖ PMO Approach.....	50
❖ Bonds Weaker Than Covalent	58
❖ Addition Compounds: Crown Ether Complexes and Cryptands, Inclusion Compounds, Cyclodextrins	65
❖ Catenanes and Rotaxanes	75
❖ Problems.....	79
❖ Bibliography.....	80
CHAPTER 2	81
Stereochemistry	81
❖ Chirality.....	81
❖ Elements of Symmetry	86
❖ Molecules with More Than One Chiral Centre: Diastereomerism	90
❖ Determination of Relative and Absolute Configuration (Octant Rule Excluded) with Special Reference to Lactic Acid, Alanine & Mandelic Acid	92
❖ Methods of Resolution.....	102
❖ Optical Purity	104
❖ Prochirality	105
❖ Enantiotopic and Diastereotopic Atoms, Groups and Faces	107
❖ Asymmetric Synthesis: Cram's Rule and Its Modifications, Prelog's Rule	113
❖ Conformational Analysis of Cycloalkanes (Upto Six Membered Rings).....	116
❖ Decalins.....	122
❖ Conformations of Sugars	126
❖ Optical Activity in Absence of Chiral Carbon (Biphenyls, Allenes and Spiranes)	132
❖ Chirality Due to Helical Shape	137
❖ Geometrical Isomerism in Alkenes and Oximes	140
❖ Methods of Determining the Configuration	146

❖ Problems.....	151
❖ Bibliography.....	152
CHAPTER 3.....	153
Reaction Mechanism: Structure and Reactivity	153
❖ Types of Mechanisms.....	153
❖ Types of Reactions	156
❖ Thermodynamic and Kinetic Requirements.....	159
❖ Kinetic and Thermodynamic Control	161
❖ Hammond's Postulate.....	163
❖ Curtin-Hammett Principle	164
❖ Potential Energy Diagrams: Transition States and Intermediates	166
❖ Methods of Determining Mechanisms.....	168
❖ Isotope Effects	172
❖ Hard and Soft Acids and Bases.....	174
❖ Generation, Structure, Stability and Reactivity of Carbocations, Carbanions, Free Radicals, Carbenes and Nitrenes.....	176
❖ Effect of Structure on Reactivity	200
❖ The Hammett Equation and Linear Free Energy Relationship.....	203
❖ Substituent and Reaction Constants.....	209
❖ Taft Equation.....	215
❖ Problems.....	219
❖ Bibliography.....	220
CHAPTER 4.....	221
Carbohydrates	221
❖ Types of Naturally Occurring Sugars	221
❖ Deoxy Sugars	227
❖ Amino Sugars.....	229
❖ Branch Chain Sugars	230
❖ General Methods of Determination of Structure and Ring Size of Sugars with Particular Reference to Maltose, Lactose, Sucrose, Starch and Cellulose.....	231
❖ Problems.....	239
❖ Bibliography.....	240
CHAPTER 5.....	241
Natural and Synthetic Dyes	241
❖ Various Classes of Synthetic Dyes Including Heterocyclic Dyes	241
❖ Interaction Between Dyes and Fibers	245
❖ Structure Elucidation of Indigo and Alizarin	247
❖ Problems.....	252
❖ Bibliography.....	253
CHAPTER 6.....	254
Aliphatic Nucleophilic Substitution	254
❖ The S_N2 , S_N1 , Mixed S_N1 and S_N2 , S_Ni , S_N1' , S_N2' , S_N1'' and SET Mechanisms.....	254

❖ The Neighbouring Group Mechanisms.....	263
❖ Neighbouring Group Participation by π and σ Bonds	265
❖ Anchimeric Assistance	269
❖ Classical and Nonclassical Carbocations	272
❖ Phenonium Ions.....	283
❖ Common Carbocation Rearrangements.....	284
❖ Applications of NMR Spectroscopy in the Detection of Carbocations	286
❖ Reactivity – Effects of Substrate Structure, Attacking Nucleophile, Leaving Group and Reaction Medium	288
❖ Ambident Nucleophiles and Regioselectivity	294
❖ Phase Transfer Catalysis.....	297
❖ Problems.....	300
❖ Bibliography	301
CHAPTER 7	302
Aliphatic Electrophilic Substitution	302
❖ Bimolecular Mechanisms – SE_2 and SE_i	302
❖ The SE_1 Mechanism	305
❖ Electrophilic Substitution Accompanied by Double Bond Shifts	307
❖ Effect of Substrates, Leaving Group and the Solvent Polarity on the Reactivity	308
❖ Problems.....	310
❖ Bibliography	311
CHAPTER 8	312
Aromatic Electrophilic Substitution	312
❖ The Arenium Ion Mechanism	312
❖ Orientation and Reactivity	314
❖ Energy Profile Diagrams	316
❖ The Ortho/Para Ratio.....	317
❖ <i>ipso</i> -Attack	319
❖ Orientation in Other Ring Systems	320
❖ Quantitative Treatment of Reactivity in Substrates and Electrophiles	321
❖ Diazonium Coupling.....	325
❖ Vilsmeier Reaction	326
❖ Gattermann-Koch Reaction	327
❖ Problems.....	329
❖ Bibliography	330
CHAPTER 9	331
Aromatic Nucleophilic Substitution	331
❖ The $ArSN_1$, $ArSN_2$, Benzyne and S_RN_1 Mechanisms.....	331
❖ Reactivity – Effect of Substrate Structure, Leaving Group and Attacking Nucleophile.....	336
❖ The von Richter, Sommelet-Hauser, and Smiles Rearrangements	339
❖ Problems.....	343
❖ Bibliography	344

CHAPTER 10	345
Elimination Reactions	345
❖ The E ₂ , E ₁ and E ₁ CB Mechanisms	345
❖ Orientation of the Double Bond.....	348
❖ Reactivity – Effects of Substrate Structures, Attacking Base, the Leaving Group and The Medium	352
❖ Mechanism and Orientation in Pyrolytic Elimination.....	355
❖ Problems.....	358
❖ Bibliography.....	359
CHAPTER 11	360
Addition to Carbon-Carbon Multiple Bonds	360
❖ Mechanistic and Stereochemical Aspects of Addition Reactions Involving Electrophiles, Nucleophiles and Free Radicals.....	360
❖ Regio- and Chemoselectivity: Orientation and Reactivity	370
❖ Addition to Cyclopropane Ring	374
❖ Hydrogenation of Double and Triple Bonds	375
❖ Hydrogenation of Aromatic Rings.....	377
❖ Hydroboration	378
❖ Michael Reaction.....	379
❖ Sharpless Asymmetric Epoxidation	380
❖ Problems.....	382
❖ Bibliography	383
CHAPTER 12	384
Addition to Carbon-Hetero Multiple Bonds.....	384
❖ Mechanism of Metal Hydride Reduction of Saturated and Unsaturated Carbonyl Compounds, Acids, Esters and Nitriles	384
❖ Addition of Grignard Reagents, Organozinc and Organolithium Reagents to Carbonyl and Unsaturated Carbonyl Compounds.....	400
❖ Wittig Reaction.....	406
❖ Mechanism of Condensation Reactions Involving Enolates: Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe Reactions	411
❖ Hydrolysis of Esters and Amides.....	433
❖ Ammonolysis of Esters.....	437
❖ Problems.....	439
❖ Bibliography.....	440
INDEX.....	441



Mandeep Dalal

(M.Sc, Ph.D, CSIR UGC – NET JRF, IIT-GATE)

Founder & Educator, Dalal Institute

E-Mail: dr.mandeep.dalal@gmail.com

www.mandeepdalal.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder of "Dalal Institute" (India's best coaching centre for academic and competitive chemistry exams), the organization that is committed to revolutionize the field of school-level and higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK), and Springer (Netherlands).

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY – VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY – VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY – VOLUME I, II, III, IV

ISBN: 978-81-952427-3-3



9 788195 242733 >

MRP: Rs 800.00

**D DALAL
INSTITUTE**

..... Chemical Science Demystified

Main Market, Sector 14, Rohtak, Haryana 124001, India

(info@dalalinstitute.com, +91-9802825820)

www.dalalinstitute.com