CHEM60001: Advanced Chemistry Topics 1 – Pericyclic Reactions

LECTURE 4

The Frontier Molecular Orbital (FMO) Approach

Alan C. Spivey
a.c.spivey@imperial.ac.uk

Imperial College London

Format & scope of lecture 4

- ***Frontier Molecular Orbital (FMO) Theory***
  - FMOs – nomenclature (HOMO, LUMO, SOMO)
  - FMOs – energies and phases
- ***Applications of FMO analysis to selected pericyclic reactions***
  - Diels-Alder reactions
  - [3,3]- and [2,3]-sigmatropic rearrangements
  - Electrocyclic ring-opening reactions
  - Electrocyclic ring-closure reactions

Key further reading:

- BOOK: Clayden, Greeves & Warren, *Organic Chemistry*, 2nd Ed.,
  - *Chapter 34 – pericyclic reactions 1*

- WEB: Pericyclic Reactions - https://www.stereoelectronics.org/webPR/PR_home.html
  - *Chapter 1 – introduction to pericyclic reactions*

Frontier Molecular Orbital (FMO) Theory

Kenichi Fukui

The 1981 Nobel Prize in Chemistry was awarded to Roald Hoffmann and **Kenichi Fukui**, the former for his orbital symmetry approach and the latter for his FMO approach to understanding 'chemical dynamics' (including pericyclic reactions).

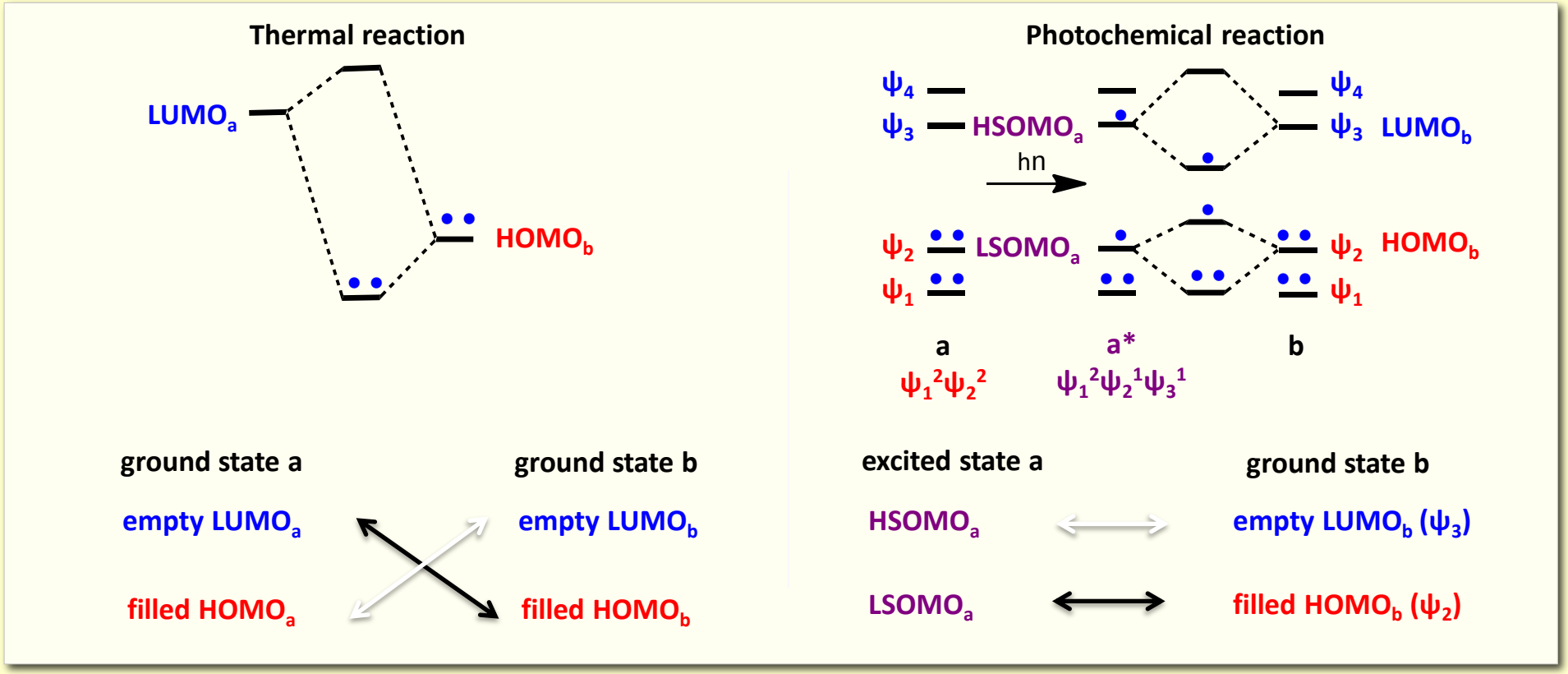
The name "Woodward–Hoffmann rules" has led some to the misconception that Woodward and Hoffmann shared a Nobel Prize. Woodward did win a Nobel Prize in 1965 for "outstanding achievements in the art of organic synthesis" in 1965 but his untimely death in 1979 made him ineligible for a second Prize in 1981. Hoffmann noted that all the award nominations prior to Woodward's death were for the two of them together and that he was certain that had Woodward lived, he would have won a share of the 1981 Prize, thereby becoming only the second person to win two chemistry Nobel Prizes (after Frederick Sanger – 1958 & 1980).

IMAGE: https://pubs.acs.org/doi/pdf/10.1021/ed079p667

Frontier molecular orbital (FMO) approach

- FMO theory can also be applied to pericyclic reactions to predict whether reactions are thermally or photochemically allowed – it is a *complementary* approach to using the W-H rules.

- The web pages of Tim Wallace (Manchester University) are an excellent resource for FMO analysis of pericyclic reactions: ***https://www.stereoelectronics.org/webPR/PR_home.html***.

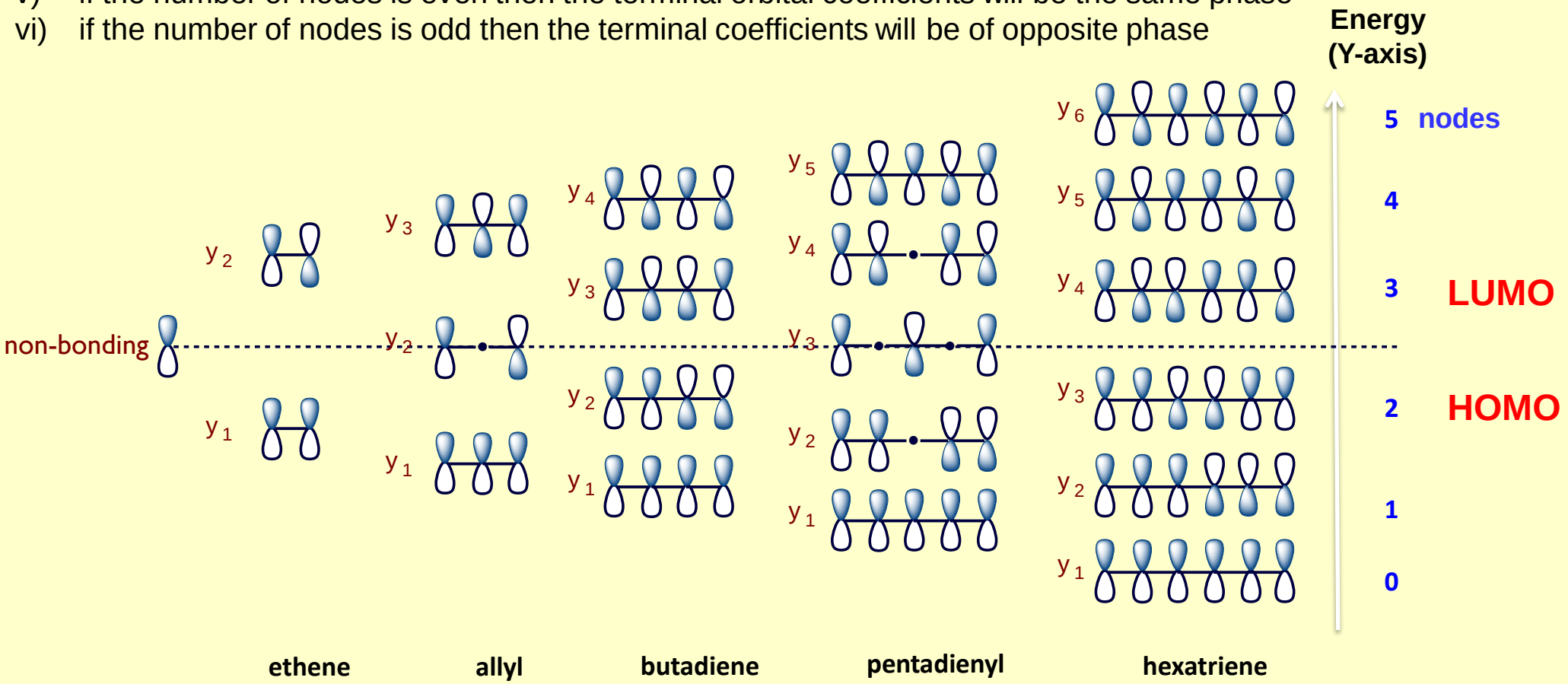


- FMO Analysis using *either* the H(S)OMO ↔ LUMO *or* the L(S)OMO ↔ HOMO pairings will give the same result - the pair that are closest in energy are the ones that will in reality dominate reactivity.

Drawing MO diagrams and identifying FMOs

- To draw a molecular orbital diagram for a ***conjugated array of p-orbitals***:

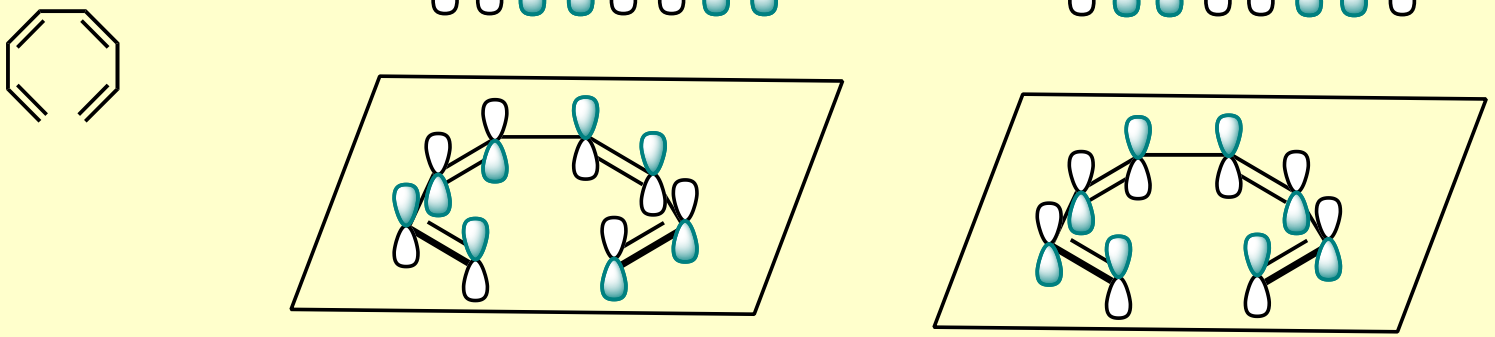
i) count the number of p-orbitals: n
ii) count the number of electrons: π-bond = 2, unpaired electron = 1, carbanion = 2, carbocation = 0
iii) draw n horizontal lines stacked on top of one another to represent the MOs
iv) draw the MOs as the combination of p-orbitals with an increasing number of **nodes** from 0 for ψ_1 to n-1 for ψ_n such that *each MO is symmetric or antisymmetric with respect to any symmetry operation of the array.*
v) if the number of nodes is even then the terminal orbital coefficients will be the same phase
vi) if the number of nodes is odd then the terminal coefficients will be of opposite phase



‘Frontier Molecular Orbitals’ - *the HOMO & LUMO*

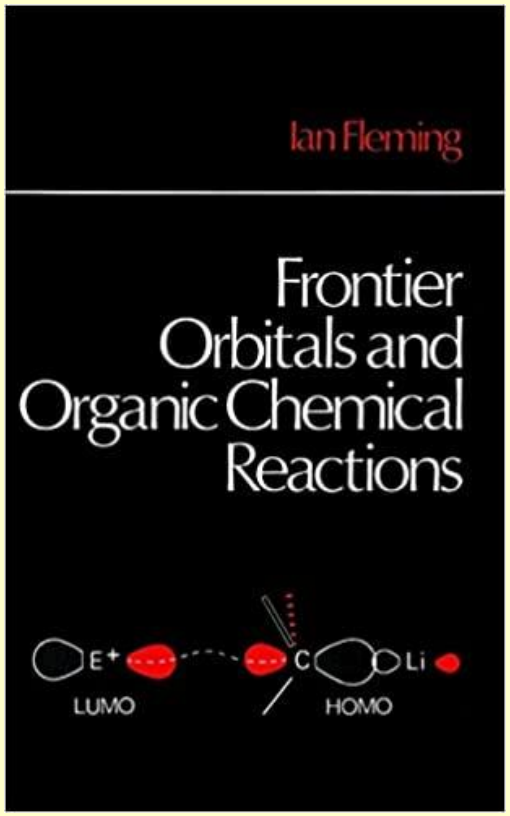
The **HOMO** of (neutral) polyenes can be readily constructed by putting nodes on the single bonds; hence the HOMO appears to be alternating isolated π-bonding pairs.

The **LUMO** of (neutral) polyenes can be constructed by beginning with an ‘isolated’ p-orbital and then alternating ‘isolated’ π-bonding pairs and ending with an ‘isolated’ p-orbital.



HOMO LUMO

Applications of FMO analysis to selected pericyclic reactions



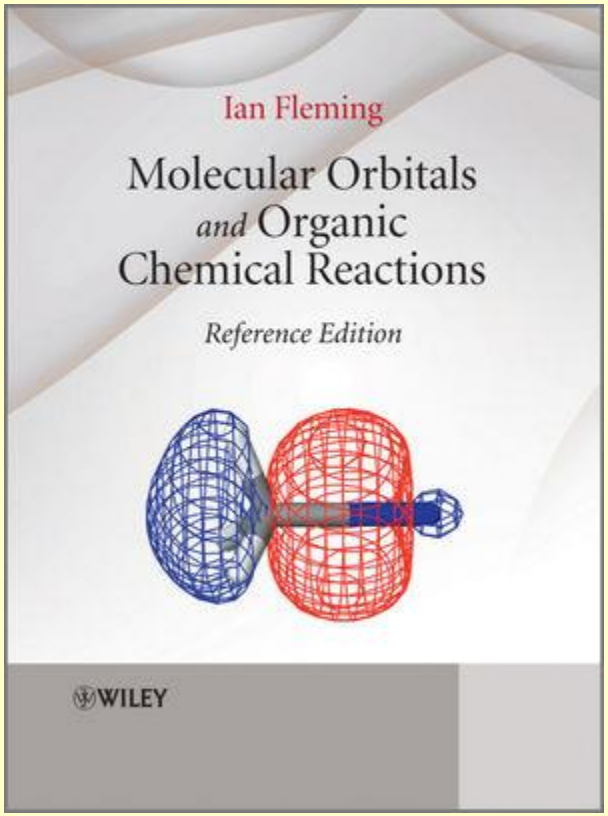
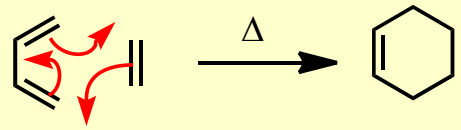


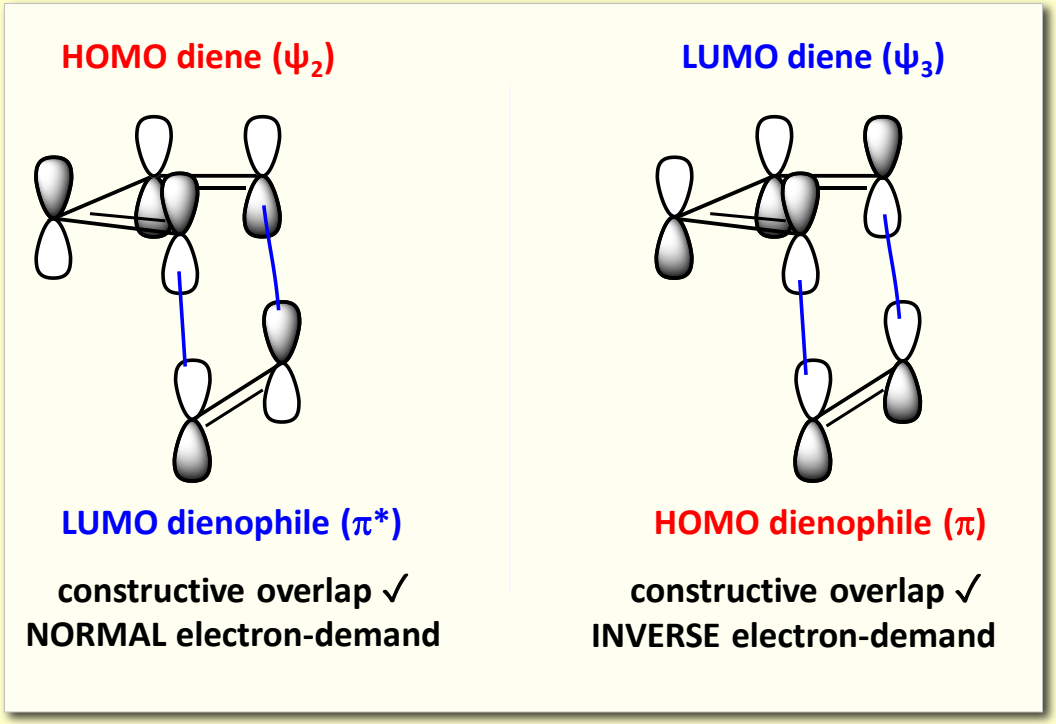
IMAGE: https://www.wiley.com/en-us/Molecular+Orbitals+and+Organic+Chemical+Reactions%2C+Reference+Edition-p-9780470746585

FMO approach: *a Diels-Alder reaction*

- 1. draw 3D orbital diagram to show approach and overlap of the FMOs
- 2. assign a HOMO and a LUMO for the reaction
- 3. check for constructive overlap between the orbitals

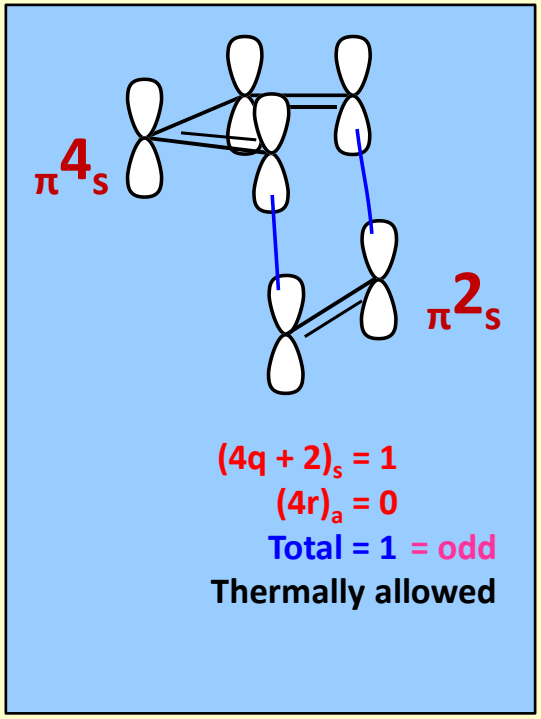


Diels-Alder [$_{\pi}4_s$+$_{\pi}2_s$]-cycloaddition



FMO approach

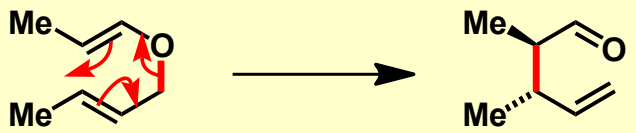
cf.



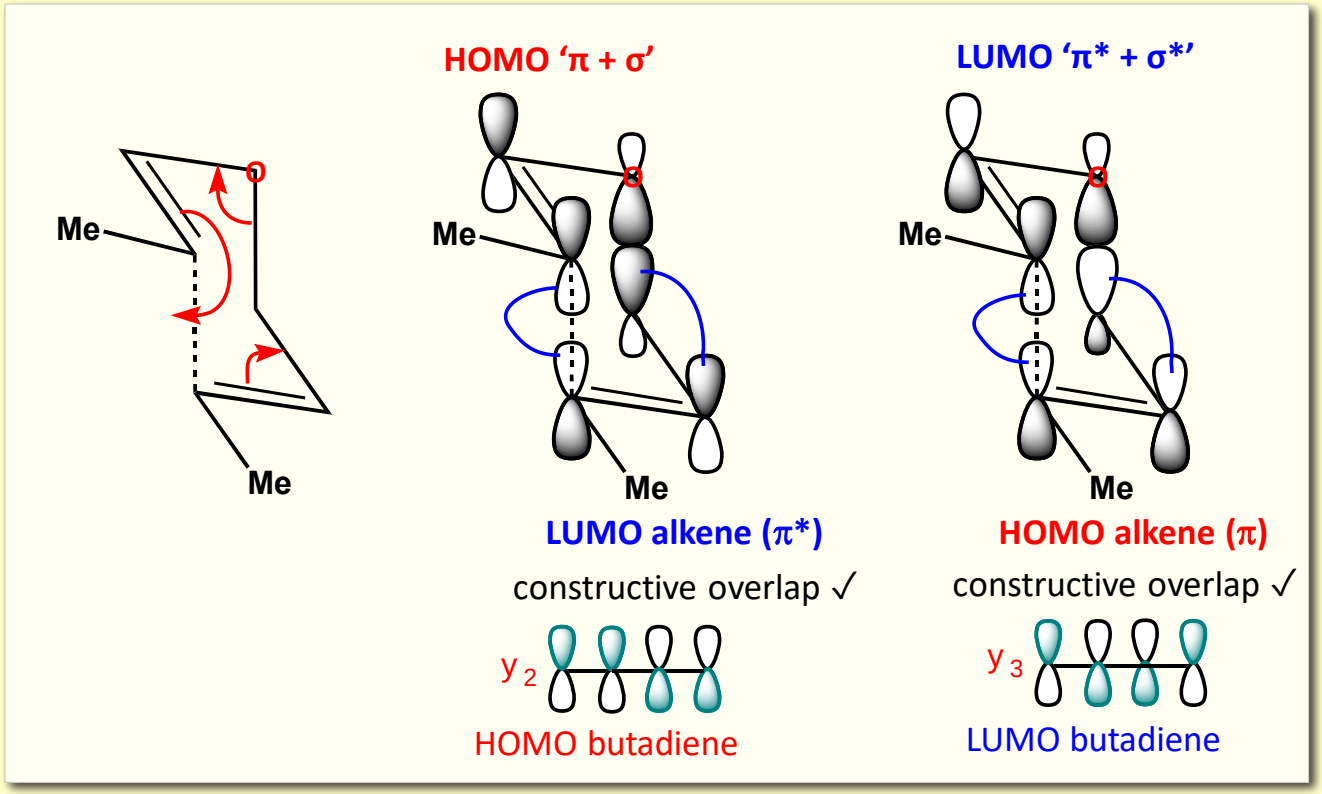
W-H approach (lecture 3)

FMO approach: *a [3,3]-sigmatropic rearrangement*

- 1. draw 3D orbital diagram to show approach and overlap of the FMOs
- 2. assign a HOMO and a LUMO for the reaction
- 3. check for constructive overlap between the orbitals

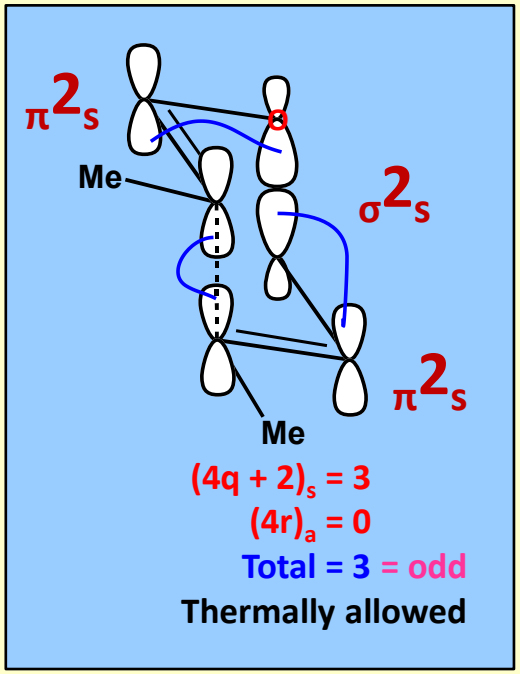


Claisen [3,3]-rearrangement



FMO approach

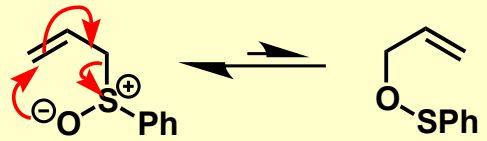
cf.



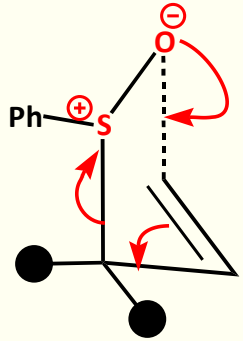
W-H approach (lecture 3)

FMO approach: *a [2,3]-sigmatropic rearrangement*

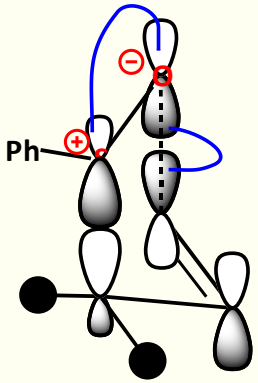
- 1. draw 3D orbital diagram to show approach and overlap of the FMOs
- 2. assign a HOMO and a LUMO for the reaction
- 3. check for constructive overlap between the orbitals



Allyl sulfoxide [2,3]-rearrangement

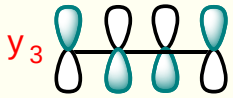


HOMO ω



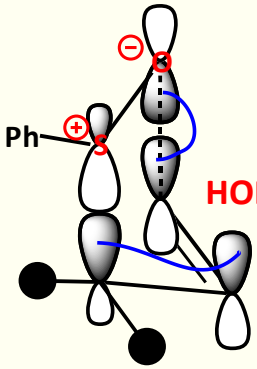
LUMO, 'π* + σ*'

constructive overlap ✓



LUMO butadiene

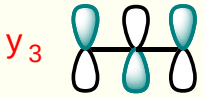
LUMO, 'σ* + ω'



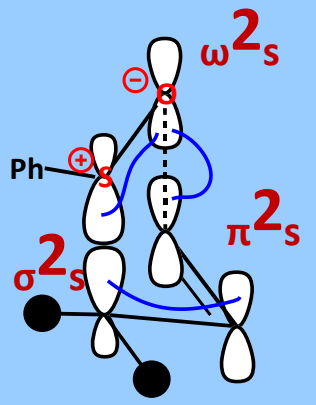
HOMO alkene

π

constructive overlap ✓



LUMO 4e⁻ allyl



$(4q + 2)_s = 3$

$(4r)_a = 0$

Total = 3

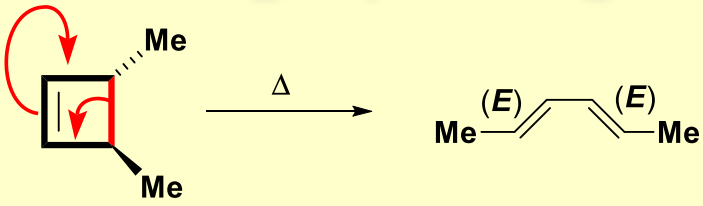
odd ✓

Thermally allowed

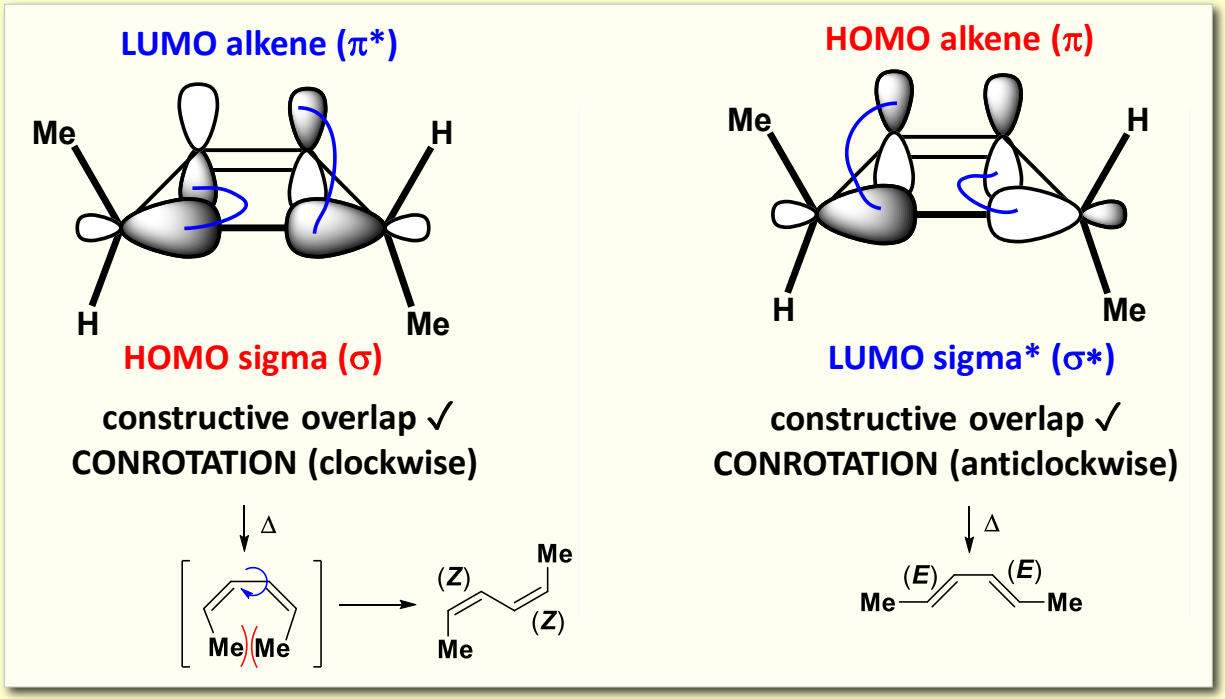
NB. 'ω' = atomic orbital (lecture 1)

FMO approach: *thermal electrocyclic ring-opening*

- 1. draw 3D orbital diagram to show approach and overlap of the FMOs
- 2. assign a HOMO and a LUMO for the reaction
- 3. check for constructive overlap between the orbitals

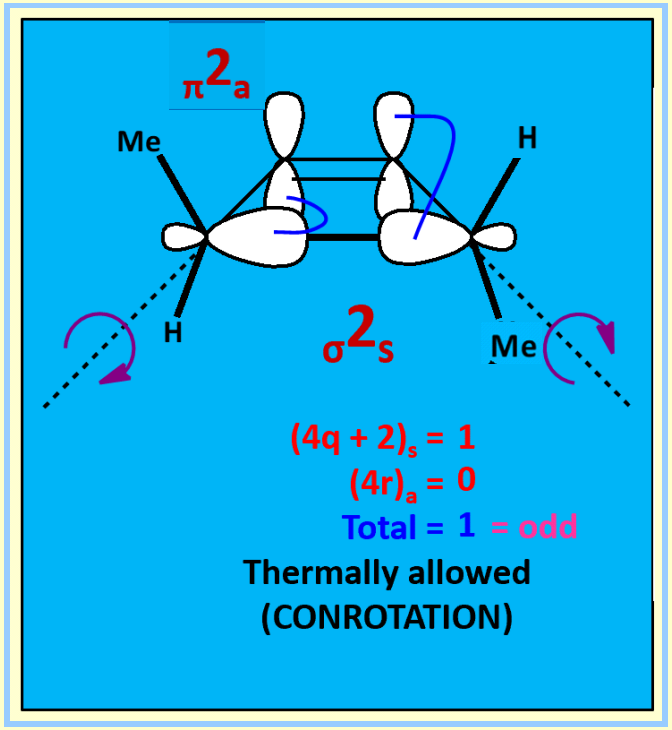


Cyclobutene ring-opening



FMO approach

cf.

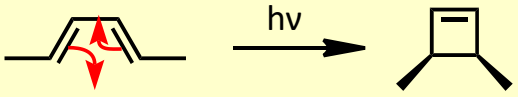


W-H approach (cf. slide 6)

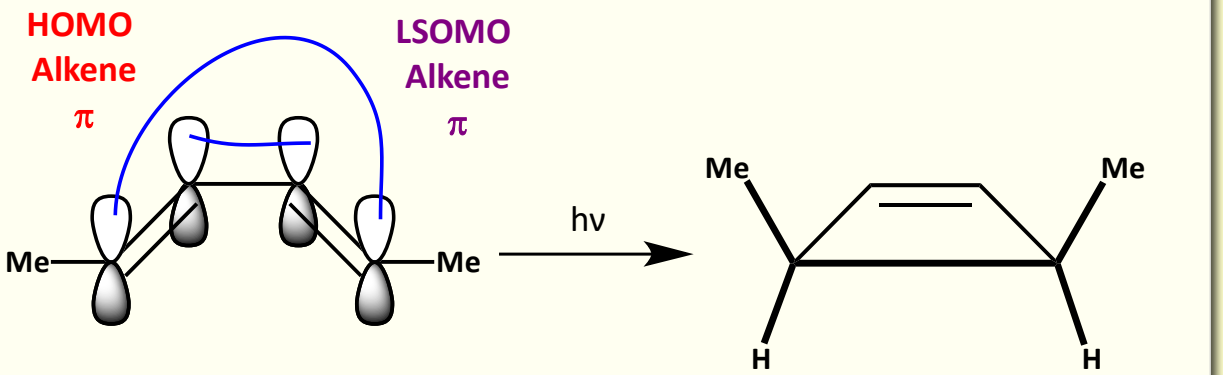
- The preference of one conrotatory mode (*i.e.* clockwise *vs*. anticlockwise) is termed ***torqueoselectivity***.
- Similarly for disrotatory modes – *i.e.* 'inside-out' *vs*. 'outside-in' is also ***torquoselectivity***.

FMO approach: *photochemical electrocyclic ring-closure*

- 1. draw 3D orbital diagram to show approach and overlap of the FMOs
- 2. assign *EITHER* a HSOMO and a LUMO *OR* a LSOMO and a HOMO to the reaction.*
- 3. check for constructive overlap between the orbitals

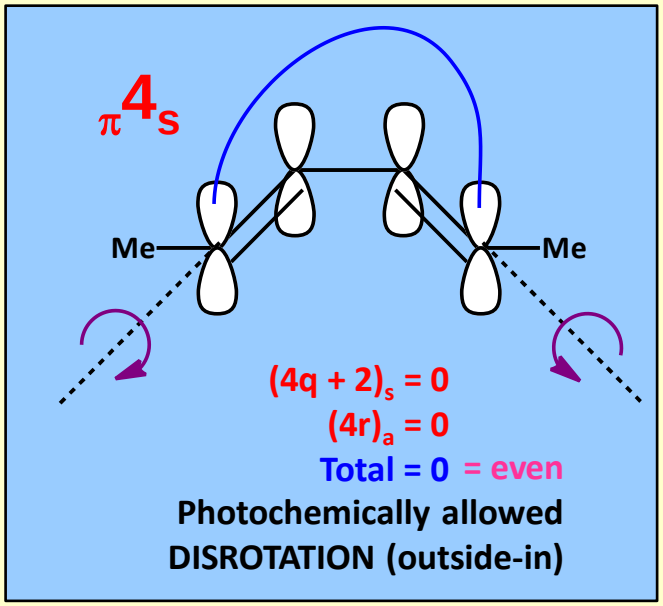


Butadiene ring-closure



constructive overlap ✓
DISROTATION - 'outside-in', as drawn, gives *cis*-product.
('inside-out' also gives *cis*-product)

cf.



FMO approach ***W-H approach***

* *NB*. The HSOMO has the same phases as the LUMO & the LSOMO has the same phases as the HOMO