

CHEM60001:
Advanced Chemistry Topics 1 – Pericyclic
Reactions

LECTURE 1
Molecular Orbitals

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

IMPERIAL

Format of Lecture Course

- *L1 – Molecular Orbitals*
- *L2 – Introduction to Pericyclic Reactions and Orbital Symmetry*
- *L3 – The Woodward-Hoffmann Rules & Approach*
- *L4 – The Frontier Molecular Orbital (FMO) Approach*
- *L5 – Cycloaddition Reactions*
- *L6 – Cycloaddition, Cheletropic and Group Transfer Reactions*
- *L7 – Sigmatropic Rearrangements*
- *L8 – Electrocyclic Reactions*

Format & scope of lecture 1

- ***Molecular orbitals – shapes***
 - Classification of orbitals and bonds – terminology
- ***Molecular orbitals – energies & overlap***
 - Natural Bond Orbitals (NBOs)
 - Interactions between orbitals
 - Estimating interaction energies
- ***Hückel MO theory - conjugated π -systems***
 - Orbital characteristics of conjugated π -systems
 - Frontier Molecular Orbitals (FMOs)

Key further reading:

- **BOOK:** Clayden, Greeves & Warren, *Organic Chemistry*, 2nd Ed.,
 - *Chapter 4* – structure of molecules
 - *Chapter 7* – delocalisation & conjugation
- **WEB:** Pericyclic Reactions - https://www.stereolectronics.org/webPR/PR_home.html
 - *Chapter 1* – introduction to pericyclic reactions

Molecular orbitals – *shapes*



Computer model of a mixture of molecular orbitals

Classification of orbitals & bonds - terminology

- **Orbital shapes**

- recall the following nomenclature from hybridisation and MO theory:

n = non-bonding orbital; lone pair of electrons;
can be sp^3 , sp^2 , sp or p type atomic orbital:

ω = atomic orbital

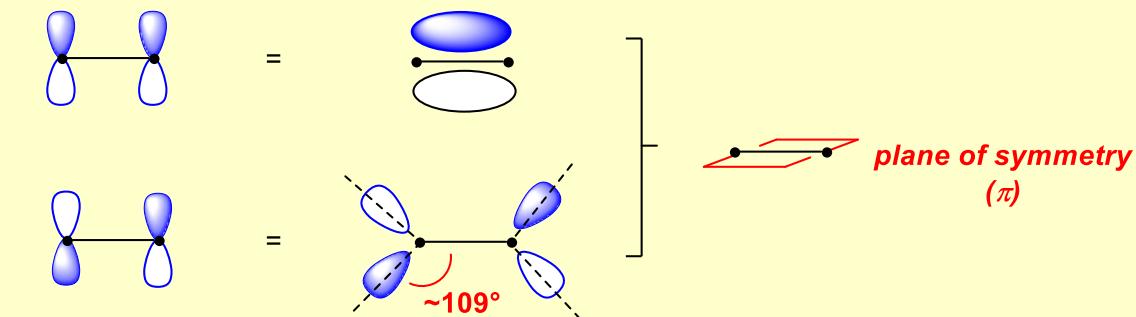
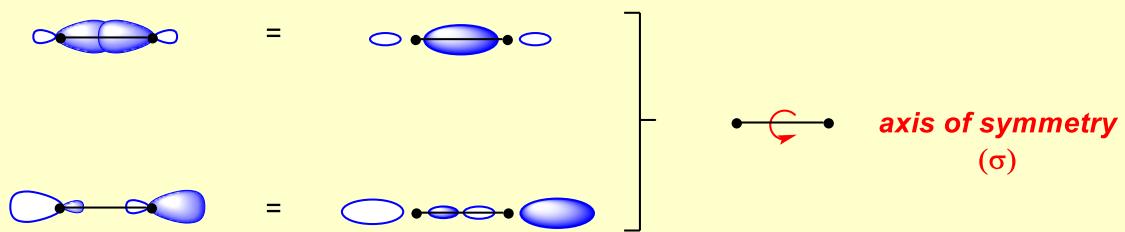
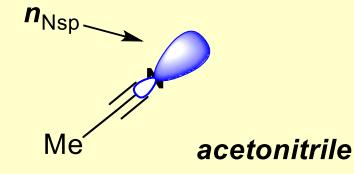
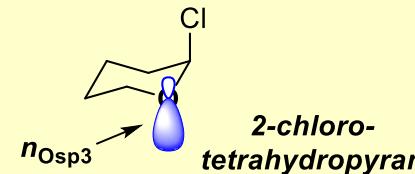
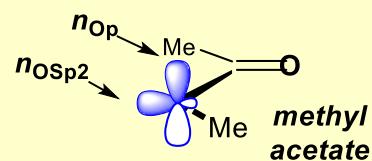
σ = sigma orbital;
bonding orbital of standard single bond
comprised of two sp^3 , sp^2 or sp hybrid atomic orbitals
has rotational symmetry along bond axis

σ^* = sigma 'star' orbital;
anti-bonding orbital of a single bond
same symmetry properties as σ orbital

π = pi orbital;
bonding orbital of a double bond
comprised of two p atomic orbitals
has plane of symmetry perpendicular to bond axis

π^* = pi 'star' orbital;
anti-bonding orbital of a double bond
same symmetry properties as π orbital

e.g.



- We will be referring to these 'bond-localised' molecular orbitals as Natural Bond Orbitals (NBOs)...

Molecular orbitals – *energies & overlap*



Prof. Gilles Klopman (b.1933, d.2015)



Prof. Lionel Salem (b.1937)

Orbital-orbital overlap

INTRAMOLECULAR ORBITAL-ORBITAL OVERLAP:

- **Valence bonds**
 - Valence bond MOs result from overlap between atomic (e.g. hybridised) orbitals (AOs) on adjacent atoms within a molecule.
 - We will refer to these as 'Natural Bond Orbitals' (NBOs).
 - These interactions can be modelled using Linear Combination of Atomic Orbital (LCAO) theory.
- **Stereoelectronic interactions & intra-molecular reactions**
 - Stereoelectronic effects result from interactions between NBOs on adjacent atoms (*i.e.* vicinal NBOs).
 - *Intra*-molecular reactions (e.g. cyclisations) result from interactions between NBOs on non-adjacent atoms.
 - These interactions can be modelled using Linear Combination of Bond Orbital (LCBO) theory.
 - Brunck and Weinhold *J. Am. Chem. Soc.* **1979**, 101, 1700 ([DOI](#))

INTERMOLECULAR ORBITAL-ORBITAL OVERLAP:

- **Inter-molecular reactions:**
 - 'Perturbation theory' and Frontier Molecular Orbital (FMO) theory use similar principles to extrapolate LCAO and LCBO to inter-molecular reactions.
 - The resulting **Klopman-Salem equation** relates the energy gained or lost when orbitals overlap.
 - Klopman *J. Am. Chem. Soc.* **1968**, 90, 223 ([DOI](#)); Salem *J. Am. Chem. Soc.* **1968**, 90, 543 & 553 ([DOI](#))
- **We will use a simplified form of this equation for both intra and inter-molecular NBO overlap**

Klopman-Salem equation

AN EQUATION FOR ESTIMATING CHEMICAL REACTIVITY

The energy (ΔE) gained and lost when the orbitals of one reactant overlap with those of another can be expressed in the following equation, developed by Klopman and Salem using Perturbation Theory:

$$\Delta E = - \sum (q_a + q_b) \beta_{ab} S_{ab} + \sum_{k < l} \frac{Q_k Q_l}{\epsilon R_{kl}} + \sum_r \sum_s^{\text{occ.}} - \sum_s^{\text{occ.}} \sum_r^{\text{unocc.}} \frac{2(\sum_{ab} c_{ra} c_{sb} \beta_{ab})^2}{E_r - E_s}$$

where q_a and q_b are the electron populations in the atomic orbitals **a** and **b**

β and S are resonance and overlap integrals

Q_k and Q_l are the total charges on atoms **k** and **l**

ϵ is the local dielectric constant

R_{kl} is the distance between the atoms **k** and **l**

c_{ra} is the coefficient of atomic orbital **a** in molecular orbital **r**, where **r** refers to the molecular orbitals on one molecule

and **s** refers to those on the other

E_r is the energy of molecular orbital **r**

A SIMPLIFIED EQUATION FOR CHEMICAL REACTIVITY

Since the interactions of all other orbitals have much larger ($E_r - E_s$) values, we can simplify the above equation by using only the **HOMO** of a nucleophile and the **LUMO** of an electrophile:

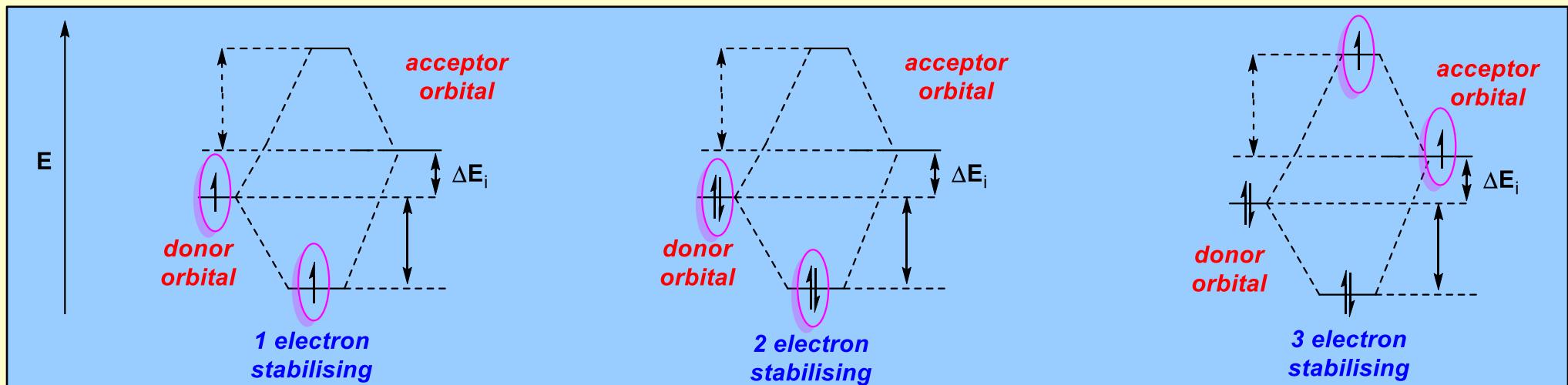
$$\Delta E = - \frac{Q_{nuc} Q_{elec}}{\epsilon R} + \frac{2(c_{nuc} c_{elec} \beta)^2}{E_{HOMO(nuc)} - E_{LUMO(elec)}}$$

Coulombic term **frontier orbital term**

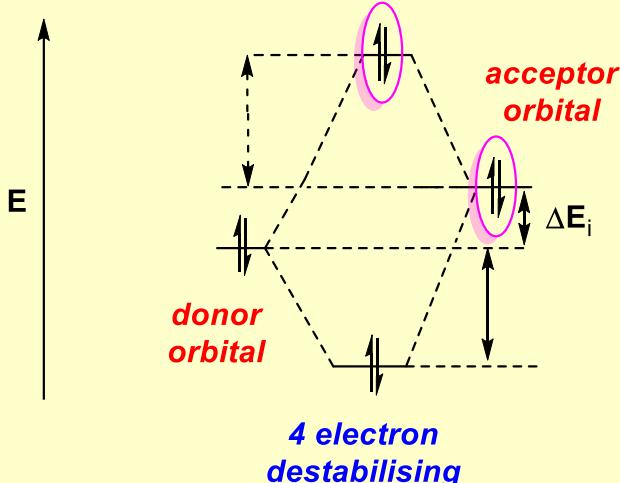
N.B. The Klopman-Salem equation is described here for *inter-molecular* reactivity (as originally formulated). We will use it in a simplified form lacking the colulombic (=electrostatic) term (see next slides).

Types of Natural Bond Orbital (NBO) overlap

- **Stabilising** (attractive) interactions result from 1, 2 & 3 electron interactions

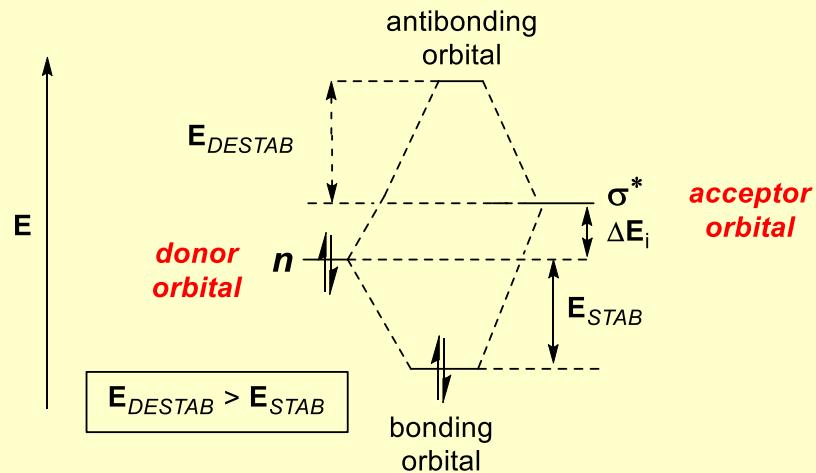


- **Destabilising** (repulsive) interactions result from 4 electron interactions



The energetics of NBO overlap

- *The Klopman-Salem equation allows us to estimate the energy gained or lost when orbitals overlap – we will ignore the electrostatic term*
- *Consider an attractive, 2 electron interaction between a filled donor orbital and an empty acceptor orbital:*



Klopman-Salem

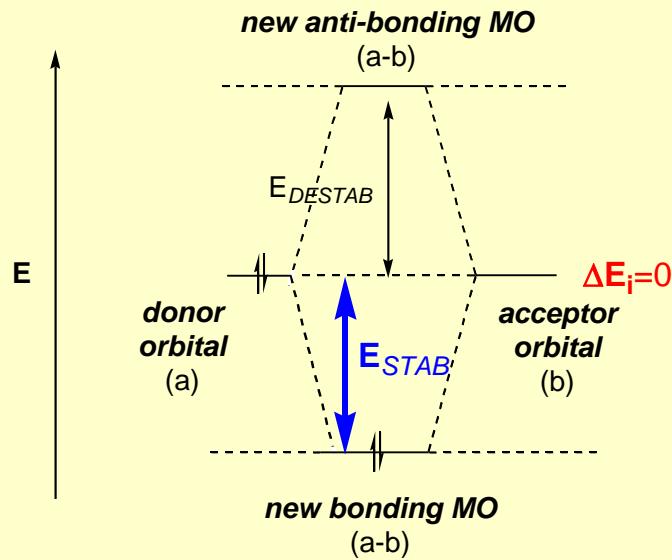
$$E_{STAB} \propto \frac{S^2}{\Delta E_i}$$

E_{STAB} = stabilisation energy
 S^2 = overlap integral
 ΔE_i = interaction energy

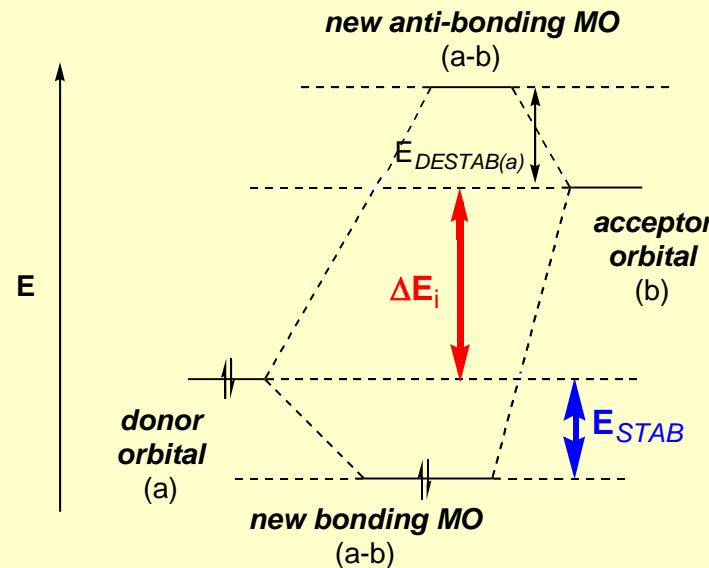
- *For maximum E_{STAB} (i.e. large ‘effect’) we need:*
 - INTERACTION ENERGY, ΔE_i (i.e. difference in energy between orbitals) = **Small**
 - OVERLAP INTEGRAL, S = **Large**

Dependence on the interaction energy (ΔE_i)

- The closer in energy the two interacting NBOs the more significant the energy gain*



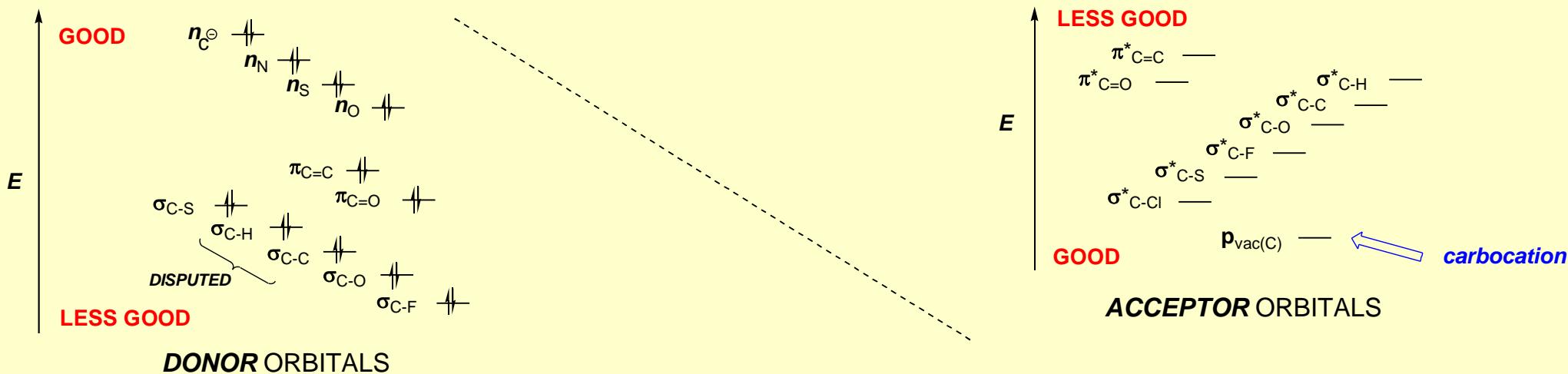
Most favourable case -
both orbitals have ~ the same energy
 $\Delta E_i = \text{small} \rightarrow E_{STAB} = \text{big}$



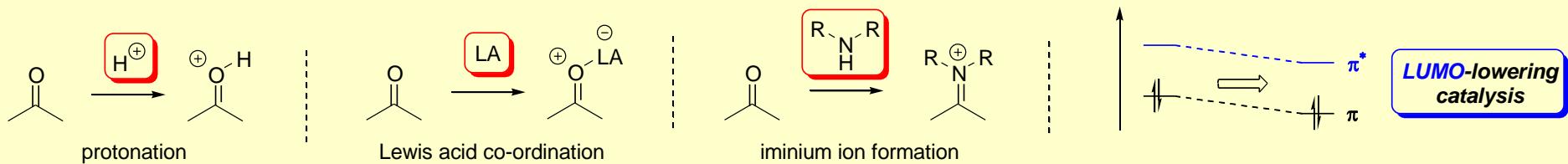
Less favourable case -
orbitals are of significantly different energy
 $\Delta E_i = \text{big} \rightarrow E_{STAB} = \text{small}$

Estimating the interaction energy (ΔE_i)

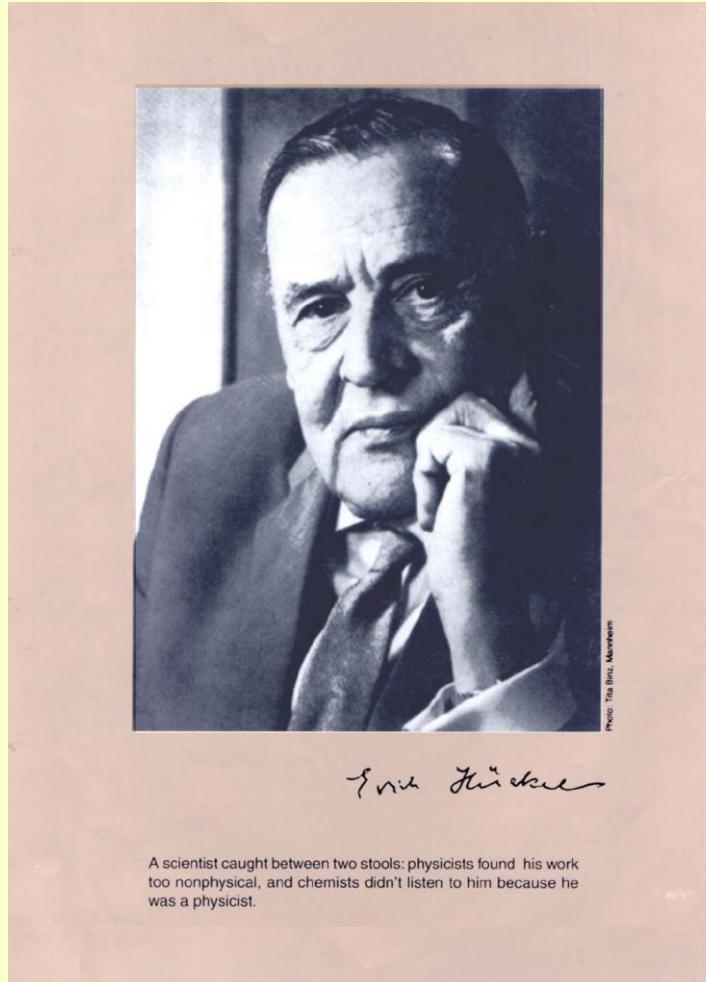
- **Assessment of the INTERACTION ENERGY (ΔE_i):**
 - **Filled orbitals (donors) will be lower in energy than the empty orbitals (acceptors)** (~Aufbau principle)
 - **The smallest ΔE_i will be between the HOMO (donor) & the LUMO (acceptor)**
 - **For n_x , σ_{C-X} & $\pi_{C=X}$ orbitals:**
 - $X = \text{EWG}$ (electronegative) $\rightarrow \text{LOWERS}$ the energy of $n/\sigma/\pi$ & σ^*/π^*
 - $X = \text{EDG}$ (electropositive) $\rightarrow \text{RAISES}$ the energy of $n/\sigma/\pi$ & σ^*/π^*



- I.V. Alabugin and T.A. Zeidan *J. Am. Chem. Soc.* **2002**, 124, 3175 ([DOI](#))
- **Protonation & Lewis Acid co-ordination to X & iminium ion formation** $\rightarrow \text{LOWERS}$ the energy of σ/π & σ^*/π^*



Hückel MO theory for conjugated π -systems



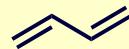
Hückel MO theory - conjugated π -systems

- **Hückel theory allows us to calculate the orbital characteristics of π -systems:**

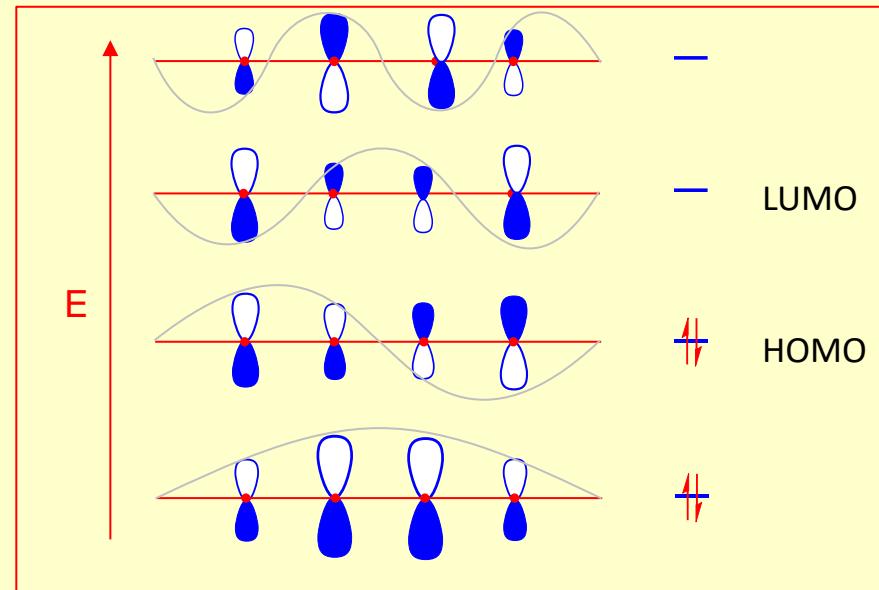
We can approximate each orbital using the 'particle in a box' model

1. We only consider the π -system and ignore the σ -system
2. With n atoms in the π -system, there will be n molecular orbitals (MOs) with coefficients governed by a sine function
3. Each MO must be symmetric or antisymmetric with respect to any symmetry operation of the molecule

- For butadiene: 4 atoms & 4 MOs



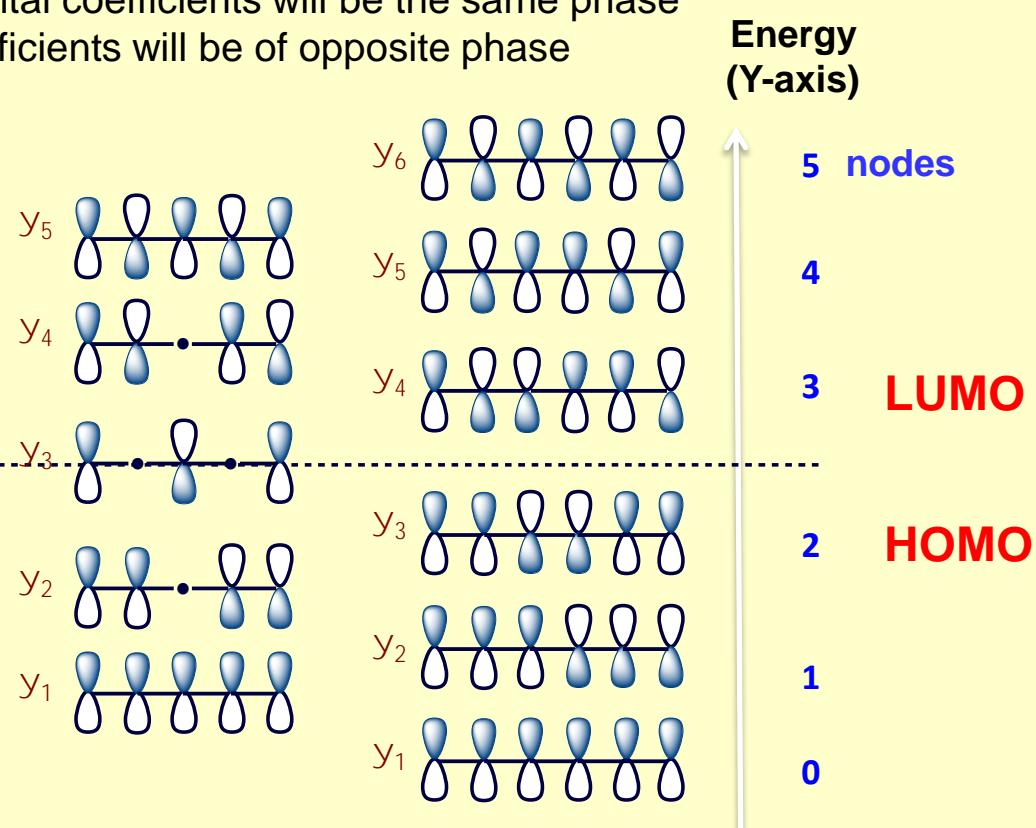
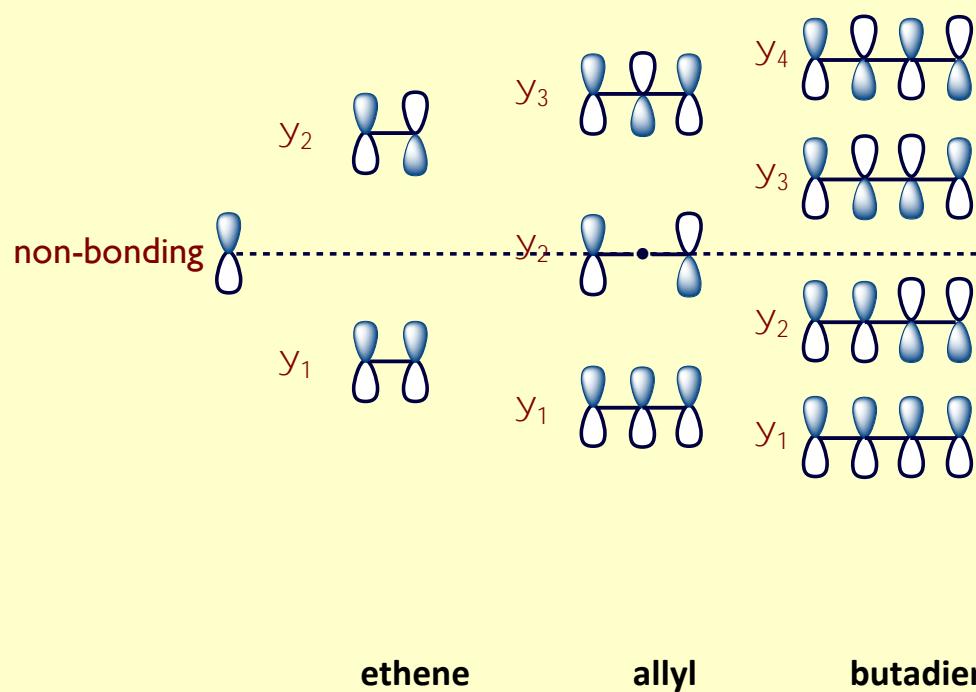
- Superimpose n sine waves onto structure (representing orbitals of increasing energy)
- Magnitude and sign of the sine wave represent phase and coefficient of orbital on that atom
- Same phase: bonding interaction
- Opposite phase: antibonding interaction



Drawing MO diagrams and identifying FMOs

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

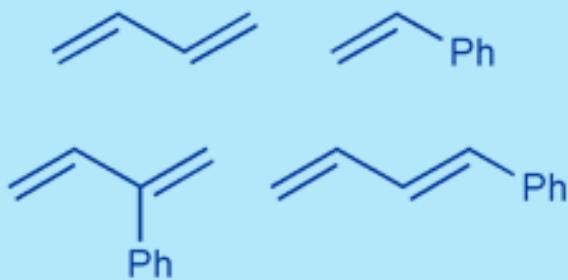
- count the number of p-orbitals: n
- count the number of electrons: π -bond = 2, unpaired electron = 1, carbanion = 2, carbocation = 0
- draw n horizontal lines stacked on top of one another to represent the MOs
- draw the MOs as the combination of p-orbitals with an increasing number of **nodes** from 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**.
- if the number of nodes is even then the terminal orbital coefficients will be the same phase
- if the number of nodes is odd then the terminal coefficients will be of opposite phase



Effect of substituents on alkene orbitals

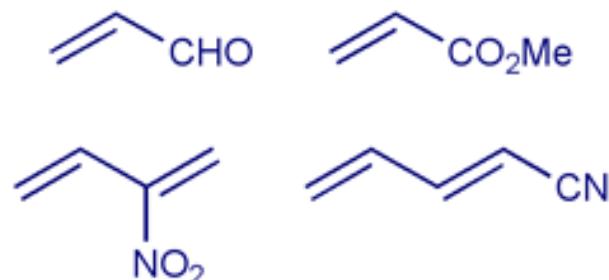
Conjugating groups

- higher HOMO energy
- lower LUMO energy



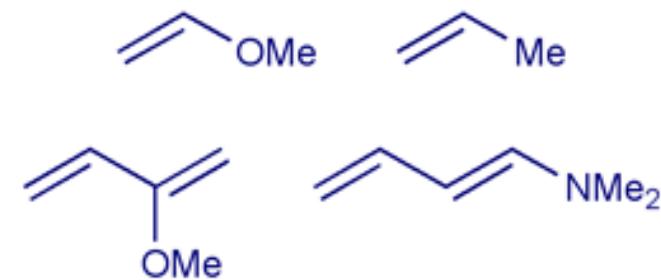
Electron-accepting groups

- lower HOMO energy
- lower LUMO energy



Electron-donating groups

- higher HOMO energy
- higher LUMO energy



The reason for the reduction in the energy gap between HOMO and LUMO with increasing conjugation follows from the Huckel model (previous slides); see also:

<https://chemistry.stackexchange.com/questions/8910/why-does-the-energy-gap-for-%CF%80-%CF%80-transitions-shrink-with-the-size-of-the-pi-co>