CHEM60001: Advanced Chemistry Topics 1 – Pericyclic Reactions

LECTURE 1
Molecular Orbitals

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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:**
  - Chapter 4 – structure of molecules
  - Chapter 7 – delocalisation & conjugation
- WEB: Pericyclic Reactions - [https://www.stereoelectronics.org/webPR/PR_home.html](https://www.stereoelectronics.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:

  \[ \omega = \] atomic orbital

  \[ \sigma = \] 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

  \[ \sigma^* = \] sigma 'star' orbital;
  anti-bonding orbital of a single bond
  same symmetry properties as \( \sigma \) orbital

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

  \[ \pi^* = \] pi 'star' orbital;
  anti-bonding orbital of a double bond
  same symmetry properties as \( \pi \) orbital

  \[ \text{We will be referring to these ‘bond-localised’ molecular orbitals as Natural Bond Orbitals (NBOs)...} \]
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 (LBAO) theory.

**INTERMOLECULAR ORBITAL-ORBITAL OVERLAP:**

- **Inter-molecular reactions:**
  - ‘Perturbation theory’ and Frontier Molecular Orbital (FMO) theory use similar principles to extrapolate LCAO and LBAO 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
The energy ($\Delta E$) 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:

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

where $q_a$ and $q_b$ are the electron populations in the atomic orbitals $a$ and $b$.
$\beta$ and $S$ are resonance and overlap integrals.
$Q_k$ and $Q_l$ are the total charges on atoms $k$ and $l$.
$\varepsilon$ 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:

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

**Coulombic term**
**frontier orbital term**

**NB.** 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

  ![Diagram of stabilising interactions](image)

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

  ![Diagram of destabilising interactions](image)
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:

For maximum $E_{\text{STAB}}$ (i.e. large ‘effect’) we need:

- INTERACTION ENERGY, $\Delta E_i$ (i.e. difference in energy between orbitals) = Small
- OVERLAP INTEGRAL, $S$ = Large
Dependence on the interaction energy ($\Delta E_i$)

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

Most favourable case - both orbitals have ~ the same energy

$\Delta E_i = \text{small} \rightarrow E_{\text{STAB}} = \text{big}$

Less favourable case - orbitals are of significantly different energy

$\Delta E_i = \text{big} \rightarrow E_{\text{STAB}} = \text{small}$
Estimating the interaction energy ($\Delta E_i$)

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

  - Protonation & Lewis Acid co-ordination to $X$ & iminium ion formation $\rightarrow$ **LOWERS** the energy of $\sigma/\pi$ & $\sigma^*/\pi^*$

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**DONOR ORBITALS**

**ACCEPTOR ORBITALS**

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protonation  | Lewis acid co-ordination  | iminium ion formation
Hückel MO theory for conjugated $\pi$-systems

Hückel MO theory - *conjugated* \( \pi \)-systems

- **Hückel theory allows us to calculate the orbital characteristics of \( \pi \)-systems:**

  We can approximate each orbital using the ‘particle in a box’ model
  1. We only consider the \( \pi \)-system and ignore the \( \sigma \)-system
  2. With \( n \) atoms in the \( \pi \)-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
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: \( \pi \)-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 \( \psi_1 \) to \( n-1 \) for \( \psi_n \) 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

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**Diagram**

- **Ethene**
  - 1 node
- ** Allyl**
  - 2 nodes
- **Butadiene**
  - 3 nodes
- **Pentadienyl**
  - 4 nodes
- **Hexatriene**
  - 5 nodes

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**Energy (Y-axis)**

- **HOMO**
  - 1
- **LUMO**
  - 5 nodes
The reason for the reduction in the energy gap between HOMO and LUMO with increasing conjugation follows from the Hückel 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