# MM Experiment 1: Frontier Orbital and Pericyclic Reaction

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## Introduction

Molecules form as a result of the overlapping of the molecular orbitals of individual atoms. The possible overlapping of orbitals around respective atoms of molecules can be described using a variety of approximation and theories. The energy and shape of molecular orbitals in a possible product can be predicted by computation using these methods.

In the molecular orbitals of ethane, the Highest Occupied Molecular Orbital (HOMO) is the π bonding molecular orbital and the Lowest Unoccupied Molecular Orbital (LUMO) is the π\* antibonding molecular orbital. The molecular orbital formed in the boding of the two carbon atoms can be described as the overlap of the two respective PZ atomic orbitals.

The interaction in a number of intermolecular bonding scenarios will be examined in this experiment. The effect of the respective reactants’ orbitals on one another will be used to estimate the most favourable reaction pathway, or indeed whether a specific product will be formed. Perturbation theory will be utilised to estimate reaction pathways.

In mathematics, Perturbation theory is a means to approximate a solution for an equation which cannot be solved directly. This is achieved by describing the complex system by adding “small” terms to the description of the solvable problem. In this way, the system which cannot be solved is approximated as a deviation from the solution of solvable problem in the form increasingly small “small” terms.

In this experiment the molecular orbitals of reactants will be examined with the aim of determining whether the reactants will react. The perturbation that the respective molecules’ molecular orbitals will have on each other can be simplified to a system similar to that of the interaction of orbitals in the formation of ethene.

Molecular orbitals in the reacting species will bond in bonding and antibonding combinations. The interactions which will be most important in the scenarios examined will be that of filled molecular orbitals (MOs) and unfilled MOs. In such an interaction, a net gain in energy will occur as the bonding combination will be filled.

The net change in energy in the interaction of two molecular orbitals can be approximately expressed using perturbation theory as follows:

$$∆E=-\sum\_{ab}^{}(q\_{a}+q\_{b})β\_{ab}S\_{ab}+\sum\_{k<1}^{}\frac{Q\_{k}Q\_{L}}{εR\_{Kl}}+\sum\_{r}^{occ.}\sum\_{s}^{unocc.}-\sum\_{r}^{occ.}\sum\_{s}^{unocc.}\frac{2(\sum\_{ab}^{}c\_{ra}c\_{sb}β\_{ab})^{2}}{E\_{r}-E\_{s}}$$

The term $-\sum\_{ab}^{}(q\_{a}+q\_{b})β\_{ab}S\_{ab}$ corresponds to the overlap of filled MOs and is a large positive energy. This term will be ignored for this experiment as it is similar for different reaction pathways between two molecules.

The term $\sum\_{k<1}^{}\frac{Q\_{k}Q\_{L}}{εR\_{Kl}}$ corresponds to the coulombic force in the molecular interaction. As this term corresponds to the net difference in charge between molecules, it has significance in ionic interactions. The bonding under scrutiny in this experiment in covalent in nature and hence this term will be ignored in calculations.

The final term describes the interaction of filled MOs with unfilled MOs. The Pauli Exclusion Principle does not allow two electrons in an interaction occupy the same quantum state. The result of this is that when a bond is formed between two respective atomic or molecular orbitals, two orbitals are formed; an anti-bonding orbital whose energy is higher than the initial orbitals which formed the bond and a bonding orbital whose energy is lower than that of the initial orbitals. The electrons occupy the bonding orbital in most bonds as this lower energy orbital stabilises the molecule and encourages bind while the anti-bonding orbital acts to destabilize the bond.

The bonding undergoing scrutiny in this experiment will be formed by HOMOs and LUMOs in respective reactants. The bonds formed will be Pi bonds and the orbitals will be adjacent to the plane of nuclei for both π and π\*  orbitals.

 The HOMO in this experiment will be the highest energy bonding orbital in one molecule and the LUMO will be the lowest energy antibonding orbital.

## The symmetry of the orbital interaction

The MOs of butadiene were calculated using PM3 wave mechanics and are displayed as follows:

LUMO



HOMO

The following data was recorded for Butadiene:

|  |  |  |
| --- | --- | --- |
| Orbital Coefficient | Orbital | energy |
| 10 | HOMO-1 | -11.994 |
| 11 | HOMO | -9.468 |
| 12 | LUMO | 0.264 |
| 13 | LUMO+1 | 2.144 |

## Questions Proposed in the Experiment:

1.

The most important atoms in the LUMO and HOMO are the central atoms, carbon 2 and 3 in the chain. The HOMO is asymmetric and will therefore be less stable at the molecule’s central point.

2.

The ethene molecule’s HOMO is symmetric between its central carbon atoms where the butadiene molecule had no point of symmetry.

3.

4.

The HOMO in ethene is symmetric and the LUMO is asymmetric. The reaction carbons in maleic anhydride have a similar symmetry and hence the reaction is unfavourable.

 The HOMO in butadiene is asymmetric and the LUMO is symmetric. This difference is symmetry of the respective reactants HOMOs and LUMOs makes the reaction favourable as there is no interaction between bonding and bonding (or antibonding and antibonding) orbitals.

## General Principles of Symmetry

The MOs of a conjugated 6 carbon chain was calculated:

LUMO

HOMO

The MOs of a conjugated 8 carbon chain was calculated:

LUMO



HOMO



Question 1:

|  |  |  |
| --- | --- | --- |
| No. Carbons  | HOMO | LUMO |
| 2 | Symmetric | Asymmetric |
| 4 | Asymmetric | Symmetric |
| 6 | Symmetric | Asymmetric |
| 8 | Asymmetric | Symmetric |

|  |  |  |  |
| --- | --- | --- | --- |
| Combining chains | HOMO | LUMO | Pericylic reaction allowed |
| 2+6 | S S | AA | NO |
| 2+8 | S A  | AS | YES |
| 4+4 | AA | SS | NO |
| 4+8 | AA | SS | NO |
| 6+6 | SS | AA | NO |
| 6+8 | SA | AS | YES |

Question 2:

A general rule for the number of Pi electrons required in a reactant for a pericyclic reaction to be favourable is that the number total number of Pi electrons available should be equal to 2n+2 where n is any whole integer.

Question 3:

The pericyclic reaction taking place can be simplified to one between ethene and butadiene. The diene can be simplified to ethene as it consists has one pi bond between two central atoms. The dieneophile can be simplified to butadiene as it consists of a conjugated carbon chain(through conjugation in the aromatic rings). When using this simplification the total number of pi electrons is 6.This is allowable by the 2n+2 law, making the reaction favourable.