CHEMISTRY

Paper 9; Organic Chemistry-III

Module 26; Molecular orbital symmetry and Frontier molecular orbitals
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1. Learning Outcomes

After studying this module, you shall be able to

- Know what are frontier molecular orbitals
- Learn about molecular orbital symmetry
- Identify HOMO/LUMO in various conjugated systems
- Evaluate the symmetry operations on molecular orbitals
- Analyze practical applications of Frontier molecular orbital theory

2. Introduction

Electrons in an atom are associated with wave-like and particle-like character. As a wave, the electrons are defined by a wave function ($\psi$). Square of $\psi$ gives the probability of finding electron in a given space which is close to the definition of an atomic orbital. Comparing the motion of electrons with standing waves, the atomic orbitals (AO) are defined by parameters such as amplitude, phase of wave and a nodal plane.

The diagram shows the first three possible mode of vibration for particle in a box. As can be seen, in the first mode $\psi_1$, the amplitude of wave increases from zero to a maximum and then comes back to zero again. For $\psi_2$, the amplitude increases to a maximum, decreases through zero (a node) to a minimum and then back to zero again. Thus here a change in phase of the wave occurs as it passes through the node, goes to minimum and then comes back to zero again. In $\psi_3$, there are two nodes and the phase of the wave changes twice. The displacement above the nodal plane are conventionally designated as ‘+’ and those below the nodal plane are designated as ‘−’. Since plus and minus signs are associated with charges, for the sake of avoiding confusion the relative phase differences are shown by shading of lobes on a p-orbital.
Thus for p atomic orbitals, the lobes are shown as:

![Nodal Plane](image)

Linear combination of atomic orbitals of comparable energy gives molecular orbitals (MO). Before proceeding further, let us first revise the principles of molecular orbital theory (MOT). Qualitative MO theory was introduced in 1928 by Robert S. Mulliken and Friedrich Hund. According to MOT:

- Total number of molecular orbitals is equal to the total number of atomic orbitals from combining atoms.
- Anti-bonding molecular orbitals have more energy than the constituent atomic orbitals before bonding.
- Following both the Pauli Exclusion Principle and Hund’s rule, electrons fill in orbitals of increasing energy.
- Molecular orbitals have maximum bonding interactions when the atomic orbitals of comparable energy combine together.

Similar to atomic orbitals, molecular orbitals are wave functions giving the probability of finding electrons in certain regions of a molecule. Each MO can accommodate maximum of 2 electrons of opposite spins. The simple hydrogen molecule (H₂) has two molecular orbitals, an anti-bonding orbital and a bonding orbital. Compared to the original atomic orbitals, a bonding molecular orbital has lower energy and is therefore more stable. A bonding orbital can only be formed if the orbitals of the constituent atoms have the same phase. This is because, the wave functions of electrons of the same phase interfere constructively which leads to bonding. Thus for ethylene two MO (\(\pi\) and \(\pi^*\)) arises from combination of two p atomic orbitals.

![LUMO and HOMO](image)

MOs of ethylene arising from overlap of two p atomic orbitals

In the bonding orbital of ethylene, there is overlap of similar signs in the bonding region between the nuclei. In the anti-bonding orbital there is cancelling of opposite signs in the bonding region.
This cancelling of the wave function is called destructive overlap. Only wave functions with same sign combine together to give constructive overlap.

The two \( \pi \) bonds of 1, 3-butadiene are formed by overlap of four \( p \) orbitals on four adjacent carbons. The four \( p \) orbitals can combine in four different ways to form four molecular orbitals designated by \( \psi_1-\psi_4 \). Out of these four orbitals, two are bonding molecular orbitals (\( \psi_1 \) and \( \psi_2 \)), and two are anti bonding molecular orbitals (\( \psi_3^* \) and \( \psi_4^* \)). The \( p \)-orbitals from which they are formed are at higher energy than the two bonding MOs, whereas the two anti-bonding MOs are higher in energy than the \( p \) orbitals from which they are formed.

Here, the MOs are arranged in increasing order of energy. As can be seen, as the number of nodes increases in a MO, its corresponding energy increases. Thus the MO \( \psi_1 \) has the minimum energy and is without a node.

\[
\begin{align*}
\psi_1 & \quad 0 \text{ nodes} \\
\psi_2 & \quad \text{HOMO - 1 node} \\
\psi_3^* & \quad \text{LUMO - 2 nodes} \\
\psi_4^* & \quad 3 \text{ nodes}
\end{align*}
\]
This is because the electrons in the bonding orbitals are more delocalized than they were in the AO. This leads in a decrease in the kinetic energy of the electron. Thus when the orbital contains a node its kinetic energy is greater than in the AOs.

On the other hand $\psi_4$ the highest MO has three nodes, leading to three anti bonding interactions.

$\psi_4$ orbital has three nodes and all non bonding interactions

Thus with three nodes, $\psi_4$ orbital has the maximum energy.

Based on frontier molecular orbital (FMO) theory, the highest energy orbital that contains electrons is called the highest occupied molecular orbital (HOMO). In the ground state of 1, 3-butadiene, $\psi_2$ is the HOMO. The lowest energy orbital that contains no electrons is called the lowest unoccupied molecular orbital (LUMO). In the ground state of 1, 3-butadiene, $\psi_3^*$ is the LUMO.

The three $\pi$ bonds of 1, 3, 5-hexatriene are formed by overlap of six p orbitals on six adjacent carbons. The six p orbitals can combine in six different ways to form six molecular orbitals designated by $\psi_1$-$\psi_6$. 
MOs of 1, 3,5-hexatriene arising from overlap of atomic overlap of six p orbitals

Out of the six MOs, three are bonding molecular orbitals (ψ₁-ψ₃), and three are anti bonding molecular orbitals (ψ₄*-ψ₆*). In the ground state electronic configuration, the six π electrons occupy the three bonding MOs, ψ₃ is the HOMO, and ψ₁* is the LUMO. In the excited state, which results from electron promotion from ψ₃ to ψ₄*, ψ₄* is the HOMO and ψ₃* is the LUMO.

The allyl system (cation, anion or radical) has three carbons and three p orbitals, hence three molecular orbitals are involved. For allyl system three new molecular orbitals are obtained by linear combination of one molecular orbital of ethylene and one isolated p orbital. This means that we need to look at the results of the π ± p and π* ± p interactions.
MOs of allyl system arising from overlap of MO of ethylene and one isolated p orbital

For the allyl system the unique features are:

1. The allyl system has odd number of orbitals i.e. three p orbitals.
2. The system has one non-bonding molecular orbital whose energy is always equal to the unhybridized p orbital. The non-bonding molecular orbital is central molecular orbital of the system.
3. In non-bonding molecular orbital the nodal plane passes through the carbon nucleus.

The MOs of the allyl system apply equally well to the allyl cation, allyl radical and allyl carbanion because all the three species contain the same p orbitals. These species differ only in the number of π electrons.

3. Orbital symmetry and Frontier molecular orbital theory

The Frontier Molecular Orbital (FMO) theory is a simpler way to look at the molecular orbitals of a conjugate system based on highest occupied molecular orbital (HOMO) of one component and lowest unoccupied molecular orbital (LUMO) of the second component in a pericyclic reaction. The electrons in the HOMO of a molecule are like the outer shell electrons of an atom. They can be removed most easily with the least expenditure of energy because they are already in a highest energy level than any of the other electrons in the molecule. The LUMO of a molecule is the orbital to which electrons can be transformed with the least expenditure of energy. The higher is the energy of HOMO of a molecule, the more easily electrons can be removed from it. The lower is the energy of the LUMO of the molecule, the more easily electrons can be transferred into it. HOMO and LUMO are referred to as frontier molecular orbitals. Also HOMO/LUMO becomes the most important orbitals for consideration since they are closest in energy and make a significant contribution to lowering of transition state energy as they interact. For a given molecule, HOMO and LUMO have opposite symmetries.
Orbital symmetry: There are various symmetry operations that can be performed on orbitals to determine their symmetry characteristics. The symmetry operations allow classifying the molecular energy states and molecular orbitals with respect to the symmetry transformations of the molecule i.e. can predict the reactions a molecule can undergo. The most important symmetry elements are,

Mirror plane: A π molecular orbital possesses either a mirror plane symmetry or a centre of symmetry. Both symmetries are not present together in a given π molecular orbital. Some molecular orbitals have the symmetry about the mirror plane (m) which bisects the molecular orbitals and is perpendicular to the plane of the molecule.

![Mirror plane diagram](image1)

Both the orbitals have a plane of symmetry

![No mirror plane diagram](image2)

There is no plane of symmetry

C₂-symmetry: The centre of symmetry is a point in the molecular axis from which if lines are drawn on one side and extended an equal distance on the other side, will meet the same phases of the orbitals.

![Centre of molecular axis diagram](image3)

Both orbitals are symmetrical with respect to centre of the molecular axis.

For the 1, 3-butadiene system let us classify the orbitals as symmetric and anti symmetric with respect to mirror plane and axis of symmetry.
Table 1: Classification of orbitals in 1, 3-butadiene as symmetric (S) and anti symmetric (A)

<table>
<thead>
<tr>
<th>Orbital</th>
<th>No of nodes</th>
<th>M (mirror plane)</th>
<th>C_2 (axis of symmetry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ψ_4^*</td>
<td>3</td>
<td>A</td>
<td>S</td>
</tr>
<tr>
<td>ψ_3^*</td>
<td>2</td>
<td>S</td>
<td>A</td>
</tr>
<tr>
<td>ψ_2</td>
<td>1</td>
<td>A</td>
<td>S</td>
</tr>
<tr>
<td>ψ_1</td>
<td>0</td>
<td>S</td>
<td>A</td>
</tr>
</tbody>
</table>

Correlation diagrams use elements of symmetry as a guiding rule which should be preserved throughout the reaction for a pericyclic reaction. It is assumed that an orbital in the starting material must feed into an orbital of same symmetry in the product. Therefore, if the number of orbitals of each symmetry type is not the same in the reactants as in the products, that reaction will not take place readily.


Woodward and Hoffmann established the principle of conservation of orbital symmetry, which predicts that certain pericyclic reactions are allowed and others are forbidden. It has been reported that the orbital-symmetry rules apply only to concerted reactions. Based on the rules of conservation of orbital symmetry (correlation diagrams), Woodward and Hoffmann were the first one to deduce a set of rules to define feasibility of reactions and stereochemistry of products formed in pericyclic reactions.

According to the Woodward-Hoffmann rules, the reactions in which symmetry of molecular orbital (MO) is conserved involve a relatively low energy transition state and thus are symmetry allowed. In contrast, in the reactions where symmetry of orbitals is destroyed by bringing one or more orbitals out of phase, the energy of transition state becomes too high due to an anti bonding interaction and the reaction becomes symmetry forbidden. Another important foundation of the rules is the fact that thermally allowed reactions are forbidden photochemically and vice versa. Also the products formed as a result of thermal tractions have opposite stereochemistry than...
products of a photochemical reaction. It is important to note that symmetry forbidden reaction might as well proceed if sufficient energy is provided to the reaction.

The generalized Woodward-Hoffmann rule states that,

**In a thermal pericyclic reaction the total number of \((4q + 2)\), and \((4r)\), components must be odd.**

For illustration of the rule, a component is a bond or orbital taking part in a pericyclic reaction as a single unit. A double bond is a \(\pi 2\) component. The number 2 refers to the number of electrons in the system. The prefix \(\pi\) indicates the type of electrons. A single component may have any number of electrons (a diene is a \(\pi 4\) component) but may not have mixtures of s and p electrons.

The designations \((4q + 2)\) and \((4r)\) refer to the number of electrons in the component where \(q\) and \(r\) are integers. An alkene is a \(\pi 2\) component and so it is of the \((4q + 2)\) kind. A diene is a \(\pi 4\) component and so is of the \((4r)\) kind. The suffix ‘s’ stands for suprafacial and ‘a’ for antarafacial. A suprafacial component forms new bonds on the same face at both ends while an antarafacial component forms new bonds on opposite faces at both ends.

Finally let us have a look at the application of Woodward-Hoffman rules based on FMO theory proposed by Fukui. The Diels-Alder reaction [4+2] between maleic anhydride and cyclopentadiene is a suprafacial reaction with one \((4q + 2)\), component and no \((4r)\), component, which means the reaction is allowed thermally.

The HOMO of butadiene and the LUMO of ethylene is both anti symmetric (rotationally symmetric), meaning thereby the reaction is allowed.
5. Summary

- Due to wave-like nature of electrons, atomic orbitals are defined by parameters such as amplitude, phase, and nodal plane.
- Linear combination of atomic orbitals of comparable energy gives rise to molecular orbitals.
- Presence of nodes in a molecular orbital increases its energy.
- Compared to original atomic orbitals, a bonding molecular orbital has lower energy and is therefore more stable.
- The allyl system has a bonding, a non-bonding, and an anti-bonding molecular orbital.
- The highest energy orbital that contains electrons is called the highest occupied molecular orbital (HOMO). The lowest energy orbital that contains no electrons is called the lowest unoccupied molecular orbital (LUMO).
- HOMO and LUMO are referred to as frontier molecular orbitals.
- HOMO/LUMO of two molecules are closest in energy and make a significant contribution to lowering of transition state energy as they interact. For a given molecule, HOMO and LUMO have opposite symmetries.
- The symmetry operations (mirror plane and axis of symmetry) allow classifying the molecular energy states and molecular orbitals with respect to the symmetry transformations of the molecule.
- Woodward and Hoffmann established the principle of conservation of orbital symmetry, which predicts that certain pericyclic reactions are allowed and others are forbidden.
- Woodward-Hoffmann rules are based on orbital symmetry conservation.
- Symmetry forbidden reaction might as well proceed if sufficient energy is provided to the reaction.