Pericyclic Reactions and Organic Photochemistry

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Module No. #01
Lecture No. #02
Pericyclic reactions – MOs of Polyene and their Symmetry properties

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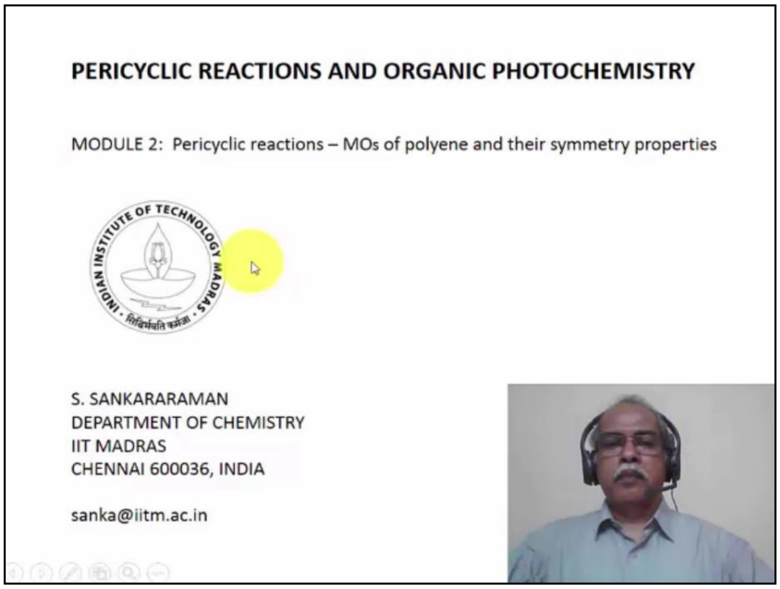

PERICYCLIC REACTIONS AND ORGANIC PHOTOCHEMISTRY

MODULE 2: Pericyclic reactions – MOs of polyene and their symmetry properties

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Hello, welcome to module two of the course on, pericyclic reactions and organic photochemistry. In this particular module, we will talk about, the molecular orbitals of polyene system and their symmetry properties. Then, we will also consider, the various methods of analyzing the pericyclic reactions.

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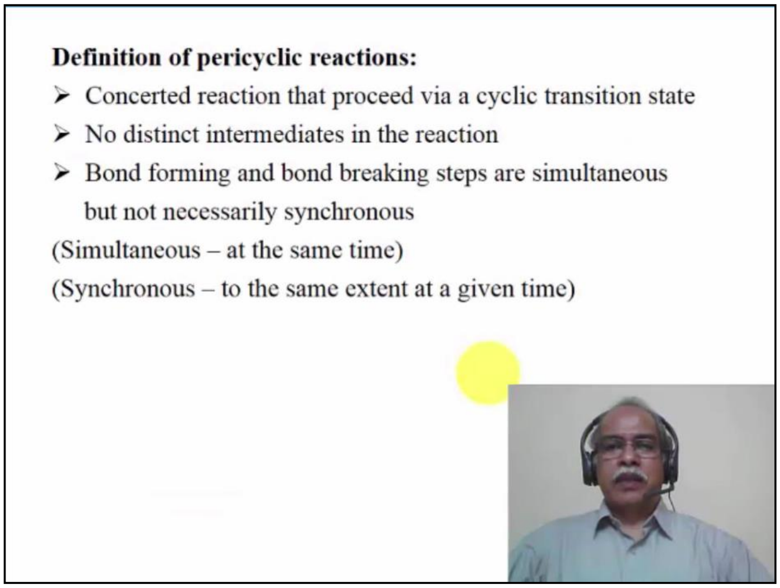

Definition of pericyclic reactions:

- Concerted reaction that proceed via a cyclic transition state
- No distinct intermediates in the reaction
- Bond forming and bond breaking steps are simultaneous but not necessarily synchronous

(Simultaneous – at the same time)

(Synchronous – to the same extent at a given time)

Now, let us first define, what are pericyclic reactions. Pericyclic reactions are concerted reaction, that proceed via a cyclic transition state. The cyclic transition state is a must. Otherwise, it could be a concerted reaction, but not a pericyclic reaction. There are no distinct intermediates formed in this reaction. That means, they are concerted. They are starting material, transition state, and it goes through a product.

The bond forming and bond breaking steps are simultaneous. But, they are not necessarily synchronous. Now, the word simultaneous, as well as synchronous, essentially means, the timing of the events. Simultaneous means, it occurs at the same time. But, synchronous precisely tells, to what extent, it is happening. In other words, the extent to which, a bond forming step, and the bond breaking steps, need not be equal in a pericyclic reaction.

They could occur at different extent, and a given time. So, pericyclic reactions are essentially reactions, proceeding through a cyclic transition state, without the formation of any kind of an intermediate. In the sense that, the bond forming as well as the bond breaking steps, are taking place simultaneously, but not necessarily, synchronously. So, this is the broad definition of any pericyclic reaction.

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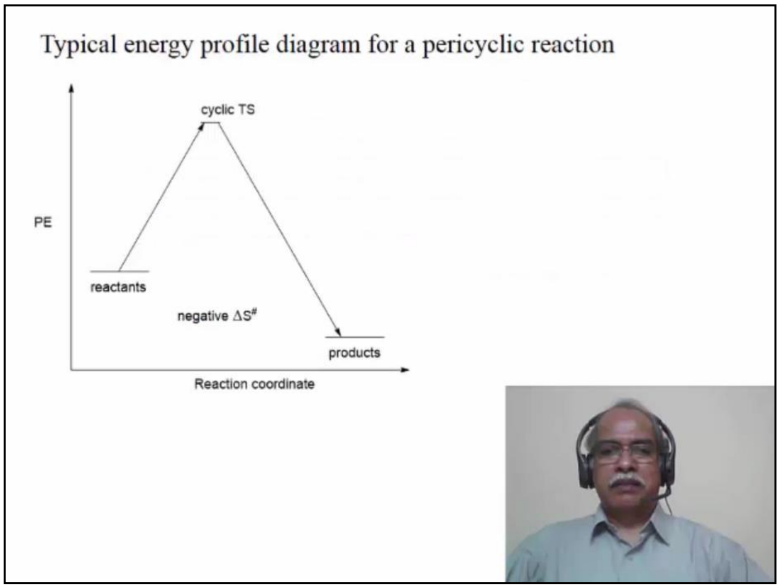

Typical energy profile diagram for a pericyclic reaction

From the potential energy point of view, one can define the pericyclic reaction as, the one going from the reactants site, to the products site, through a cyclic transition state. And, you see here, it is written Negative Delta S Double Dagger. In other words, the entropy change in a pericyclic reaction, is always negative, or the entropy of activation, is always negative, because of a very organized cyclic transition state, that through which, the reactions proceed.

So, therefore it costs some amount of entropy factor. Entropy of activation being negative, for a highly-organized system, like a cyclic transition state, in this particular instance. So, there is some significance associated with the Negative Delta S Double Dagger, and the pericyclic reaction transition state, being very organized.

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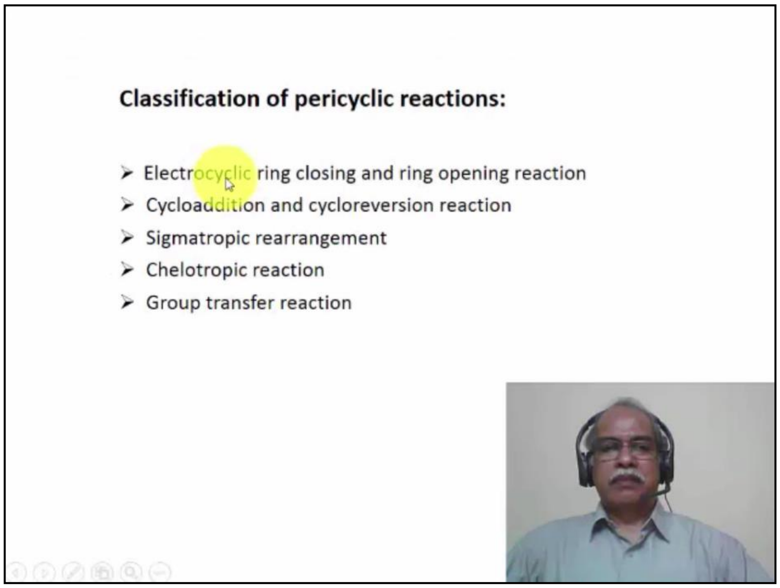

Classification of pericyclic reactions:

- Electrocyclic ring closing and ring opening reaction
- Cycloaddition and cycloreversion reaction
- Sigmatropic rearrangement
- Chelotropic reaction
- Group transfer reaction

Now, pericyclic reactions can be very broadly classified into, five different categories. These are called electrocyclic reactions. They could be a ring closing reaction, or ring opening reaction, depending upon, whether ring is formed, or a compound, which has a cyclic structure, undergoes the opening of the ring reaction. Second class of reactions are the cycloaddition reaction. Cycloaddition reactions are reactions, where two components add, to form a cyclic compound.

The reverse of that process would be, the cyclo-reversion process. Diels-alder reaction is a good example of a cycloaddition reaction. The retro diels-alder reaction would be a cyclo-reversion reaction. Then comes, the sigmatropic rearrangement, where a sigma bond is broken. And then, subsequently, the molecular rearrangement takes place, during the course of the pericyclic step.

The fourth kind of pericyclic reactions are, the chelotropic reactions. Here, small molecules like carbon monoxide, carbon dioxide, nitrogen, and so on, are eliminated, during the course of the pericyclic reaction. And, finally comes the group transfer reaction. These are reactions, where, for example, a pair of hydrogen atoms are transferred in a pericyclic manner, or in a concerted manner, to undergo hydrogenation reaction. We will see, some examples of the group transfer reaction, towards the end of the session.

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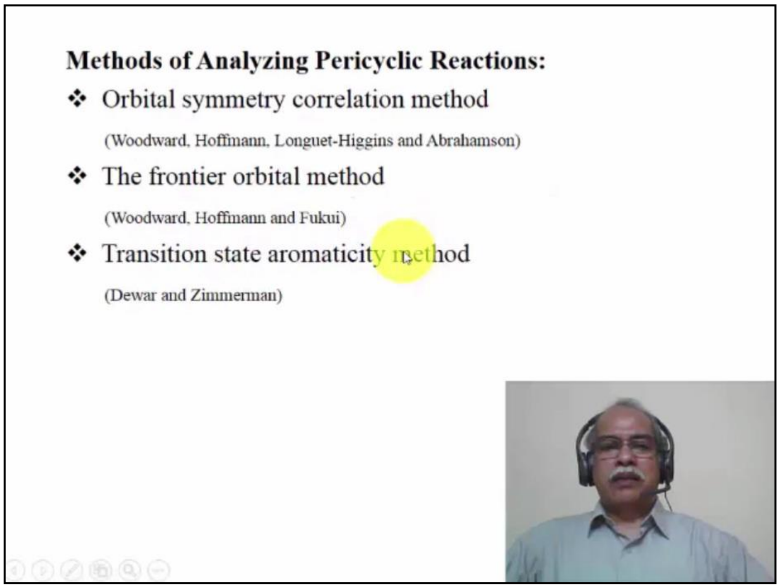

Methods of Analyzing Pericyclic Reactions:

- Orbital symmetry correlation method
  (Woodward, Hoffmann, Longuet-Higgins and Abrahamson)
- The frontier orbital method
  (Woodward, Hoffmann and Fukui)
- Transition state aromaticity method
  (Dewar and Zimmerman)

We will start with, the methods of analyzing pericyclic reaction. Now, the pericyclic reaction, as we define, it is a reaction, which proceeds through a cyclic transition state, without the involvement of any kind of an intermediate stage. So, there was a time that, people, scientist, thought that, the pericyclic reactions are no mechanism reactions. But, on the contrary, over a period of the last 30, 40 years, the theoretical development, as well as the practical aspects of pericyclic reactions, have given a wealth of information, regarding the mechanism of pericyclic reactions.

Now, pericyclic reactions are very strong foundation, in theoretical organic chemistry, in quantum mechanics. Now, these are the various methods, by which the pericyclic reactions can be analyzed. The first methodology is called the Orbital Symmetry Correlation Methodology, largely developed by Hoffman, Longuet-Higgins, and Abrahamson. In this particular methodology, the symmetry properties of the starting molecular orbitals, are correlated to the symmetry properties of the product molecular orbital. We will see more details of, how this methodology works, as we proceed with the modules.

The second methodology is called the Frontier Molecular Orbital Methodology. In the Frontier Molecular Orbital Methodology, we consider, interaction between frontier molecular orbitals. What are frontier molecular orbitals? You have a set of occupied molecular orbital, and unoccupied anti-burning molecular orbital, in any molecular orbital picture of a molecule. Now, the highest occupied molecular orbital, and the lowest unoccupied molecular orbital, which could be an antibonding molecular orbital, are called the frontier molecular orbitals.

So, this interaction between, let us say, compound A and B. The interaction between, the HOMO of highest occupied molecular orbital, which is abbreviated as HOMO, H O M O, is the interaction between this particular molecular orbital, and the lowest unoccupied molecular orbital, L U M O, LUMO. This interaction is what, is being considered, in the frontier molecular orbital picture.

This is largely developed by Hoffman and Fukui. Fukui is a Japanese scientist. Hoffman is an American scientist. They are largely responsible, for the development of this particular theory. Then, comes the Transition State Aromaticity Method. Because, all pericyclic reactions go through a cyclic transition state, depending upon, how many electrons are involved, and how the electrons are being overlapping, with respect to each other, one can define the transition state as an aromatic transition state, or an antiaromatic transition state.

And, based on this transition state aromaticity, one can predict, or one can propose a mechanism, for the pericyclic reaction. This is largely developed by M J S Dewar and Zimmerman. Now the Woodward-Hoffmann rules are essentially the rules, that are derived by applying anyone of this methodology.

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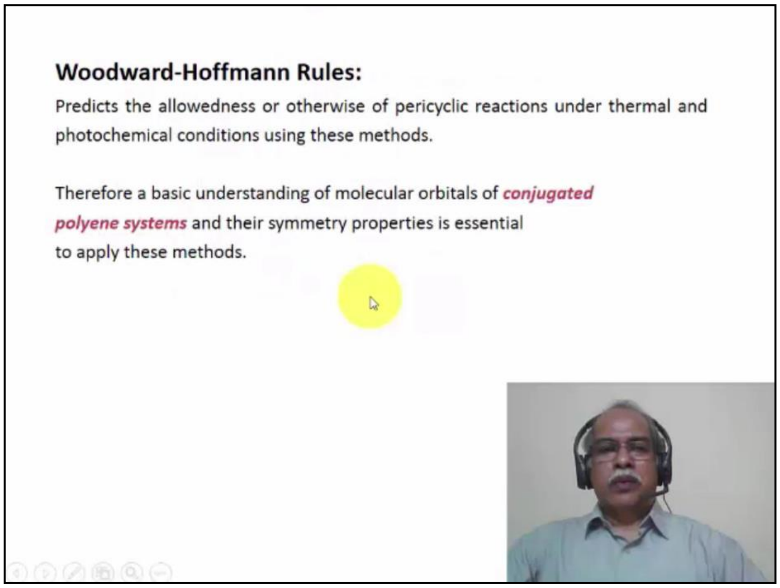

Woodward-Hoffmann Rules:

Predicts the allowedness or otherwise of pericyclic reactions under thermal and photochemical conditions using these methods.

Therefore a basic understanding of molecular orbitals of ***conjugated polyene systems*** and their symmetry properties is essential to apply these methods.

To predict the allowedness, or the dis-allowedness of pericyclic reaction, under the conditions of thermal excitation, or photochemical excitation, as the case may be. So, Woodward-Hoffmann rule essentially govern the, not only governs, it predicts the possibility of a pericyclic reaction taking place, either under thermal condition, or photochemical condition. It can also very precisely predict, whether the reaction is allowed or disallowed, under the reaction condition.

So, in order to understand the Woodward-Hoffmann rule, which are derived from the methods of analyzing the pericyclic reaction, by these three methodologies, it is necessary to have a very good understanding of the molecular orbital pictures of conjugated polyene system, and also identify the symmetry property, with respect to certain symmetry elements. And, this is essential, in order to apply these methods, or in order to understand these methods and their application, in the analysis of pericyclic reaction.

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R. B. Woodward

R. Hoffmann

So, let us have a look at, one by one. Before that, let us see the scientist, who are behind the development of this theory. R B Woodward was a professor at Harvard university. And, he is largely responsible, for the synthesis part of the pericyclic reaction. In other words, using pericyclic reaction is synthesized, a lot of molecules. In the process, he also showed, the allowedness and dis-allowedness, experimentally, for many of the pericyclic reaction. Hoffmann is from the Karnal University.

He is a theoretical chemist. And, he is responsible for the development of the frontier molecular orbital theory, and many other theories, related to the pericyclic reaction.

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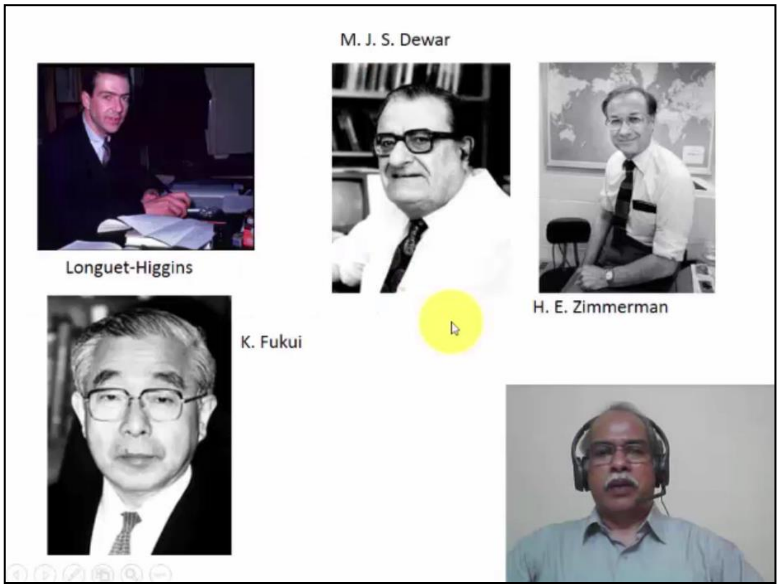

Longuet-Higgins is the person, who is involved in the development of the Orbital Correlation Method, Symmetry Correlation Method. M J S Dewar and Zimmerman are responsible for the development of the Transition State Aromaticity Model. Finally, Fukui in combination with Professor Hoffman, were responsible for the development of the Frontier Molecular Orbital Methodology.

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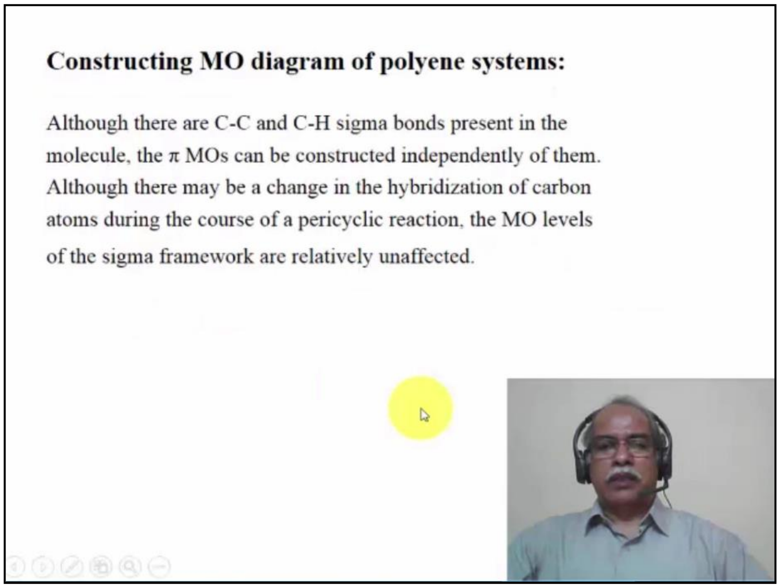

Constructing MO diagram of polyene systems:

Although there are C-C and C-H sigma bonds present in the molecule, the π MOs can be constructed independently of them. Although there may be a change in the hybridization of carbon atoms during the course of a pericyclic reaction, the MO levels of the sigma framework are relatively unaffected.

Now, how does one construct, a molecular orbital picture of a polyene system. This is what, i am trying to explain, in the next few slides. Now, although, there are Sigma framework and CH bonds being present in every organic molecule, it is a PI framework, that are important in the pericyclic reaction. So, the construction of the PI molecular orbital, can be taken independent of the Sigma, or the sigma bonds, namely the CC sigma bond and the CH sigma bonds.

Although, there may be hybridization changes, during the course of the pericyclic reaction, the molecular orbital levels of the sigma framework, are relatively unaffected. So, one can independently treat the PI molecular orbital, just like you would do by huckel molecular orbital theory, for example, without bothering much about the carbon-carbon sigma bonds, or the carbon hydrogen sigma bonds, which may be present in the molecular system.

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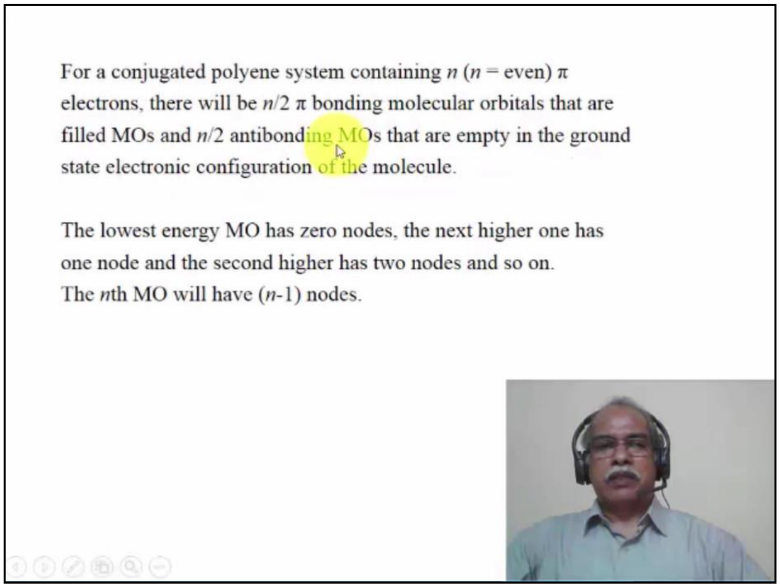

For a conjugated polyene system containing n (n = even) π electrons, there will be $n/2$ π bonding molecular orbitals that are filled MOs and $n/2$ antibonding MOs that are empty in the ground state electronic configuration of the molecule.

The lowest energy MO has zero nodes, the next higher one has one node and the second higher has two nodes and so on.
The nth MO will have (n-1) nodes.

Now, for a conjugated polyene system, let us take butadiene. There are two double bonds in butadiene. That means, there are four PI molecular orbitals. So, if there are four PI molecular orbitals, then there must be four electrons. Four PI electrons should be occupied in, four PI molecular orbital, out of which, half of it will be, bonding molecular orbital. So, four by two will be two.

So, two bonding molecular orbitals, and two antibonding molecular orbitals, will be present. If you take hexatriene, 135 hexatriene, there are six PI electrons. That means, there should be six molecular orbitals. The six PI electrons, are occupied in three bonding molecular orbitals, to each of the bonding molecular orbital. And, three antibonding molecular orbitals, which are empty, are antibody molecular orbitals, in the ground state electronic configurations of the molecule.

So, this is fundamentally important for the construction of the molecular orbital pictures of the polyenes. Now, in addition to that, one need to observe the science, algebraic science of the lobes of the molecular orbital properly. This is easily done, by identifying the number of nodes, that will be present in the system.

The lowest energy molecular orbital has, zero nodes. The next higher molecular orbital will have, one node. The second molecular orbital will have, one node. And, the third molecular orbital will have, two nodes. In other words, the nth molecular orbital will have, n-1 nodes. We will see, what this means, essentially. The node is essentially a point, in a molecular orbital, where the probability of finding electron, essentially is zero. In other words, the electron density at that particular point, is close to zero.

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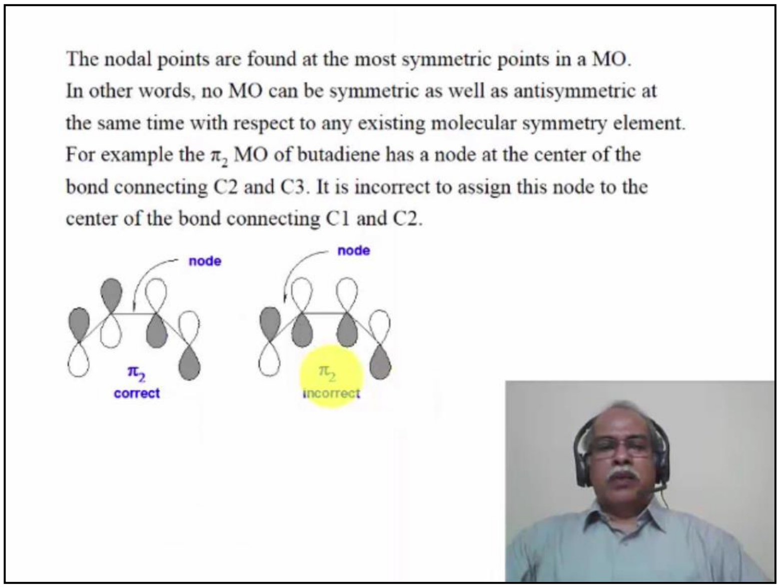

The nodal points are found at the most symmetric points in a MO.
In other words, no MO can be symmetric as well as antisymmetric at the same time with respect to any existing molecular symmetry element.
For example the π_2 MO of butadiene has a node at the center of the bond connecting C2 and C3. It is incorrect to assign this node to the center of the bond connecting C1 and C2.

Now, the nodal points are generally placed, at the most symmetric place of the molecular orbital. If you consider, the PI two molecular orbitals of butadiene, take it from me, that this is a PI two molecular orbitals of the butadiene. In a few minutes, we will see, how we arrive at the PI two molecular orbitals of butadiene. Now, the butadiene PI molecular orbital has one node. And, that node has to be placed, at the most symmetrical point in the molecular picture of the molecule, not at an unsymmetrical point, with respect to the node being placed here.

In this particular picture, the nodal point is here, where there is a change in the algebraic sign, passing through the node. In other words, change in the algebraic sign, from the grey shaded area, with a positive algebraic sign. And, the empty lobe here, with a negative algebraic sign, for example. So, it is important to place the node, in the most symmetrical point of the molecular orbital, in any molecular orbital construction.

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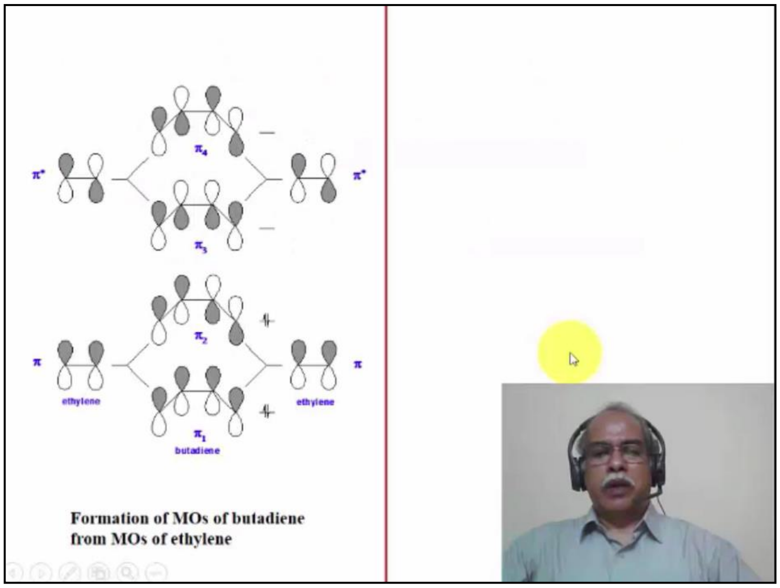

Formation of MOs of butadiene from MOs of ethylene

Now, molecular orbitals can be constructed. The PI molecular orbital of polyenes can be constructed, just as easily as the linear combination of atomic orbitals, being considered for the consideration of construction of molecular orbital pictures of simple molecules. Now, here on the left-hand side, the ethylene PI molecular orbitals are given. Ethylene has two PI electrons. That means, it should have two molecular orbitals.

The PI molecular orbital, and the PI star molecular orbital. This is the occupied molecular orbital. And, this is an empty molecular orbital. This is a bonding molecular orbital. And, this is antibonding molecular orbital, of the ethylene. Now, the molecular orbital of butadiene can be easily constructed, by the linear combination of the PI molecular orbitals of ethylene.

In other words, if you take ethylene molecular orbital, and another ethylene molecular orbital, a symmetrical combination of the bonding molecular orbital of ethylene, and the bonding molecular of the other ethylene, essentially gives you, two molecular orbitals of butadiene, one with a symmetrical combination, where all the algebraic signs, in other words, with a zero node of the molecular orbital picture here.

Then, you have a molecular orbital combination, where these two molecular orbitals combined to give the butadiene, with a node point being present, at the center of the molecular orbital here. So, the cursor is the nodal point, in this particular molecular orbital. Whereas, this molecular orbital does not possess, any kind of a nodal point, along the carbon-carbon bond. Then, take the two-antibonding molecular orbital.

You can have a symmetrical combination of the antibody molecular orbital, or the anti-symmetrical combination of the molecular orbital, of these two PI star molecular orbitals. In other words, the antibonding molecular orbitals of ethylene. Now, butadiene is supposed to have, four molecular orbitals. So, we have constructed four molecular orbitals, by the linear combination.

Symmetric and anti-symmetric combination of the bonding molecular orbitals of ethylene. Symmetric and anti-symmetric combination of the molecular orbitals of the ethylene in the higher energy level. In other words, the PI star, or the antibonding molecular orbitals of ethylene. This is SI-one, SI-two, SI-three, and SI-four. Or, you want to call it as PI-one, PI-two, PI-three, PI-four, that is also fine.

Now, this has zero nodes. There are no nodal points, along the carbon-carbon bond. This has only one node, here. In other words, there is a change in the algebraic sign, or change in the color shading of the lobes of the molecular orbitals. So, that is a nodal point. At this point, the probability density of the electron is close to zero, for example. This has two nodal points. One nodal point is kept in this carbon-carbon bond, that is carbon one and carbon two bond.

The second node is placed, between carbon three and carbon four bond. So, that is, one node here, and another node here. Now, in the case of PI four molecular orbitals, there are three nodal points. Every one of the carbon-carbon bond has a nodal point. So, this is one nodal point. This is another nodal point. And, this is the third nodal point. If you follow the cursor moment, you will be able to identify, one, two, and three nodes, are being present in the PI star molecular, PI four molecular orbitals of the butadiene.

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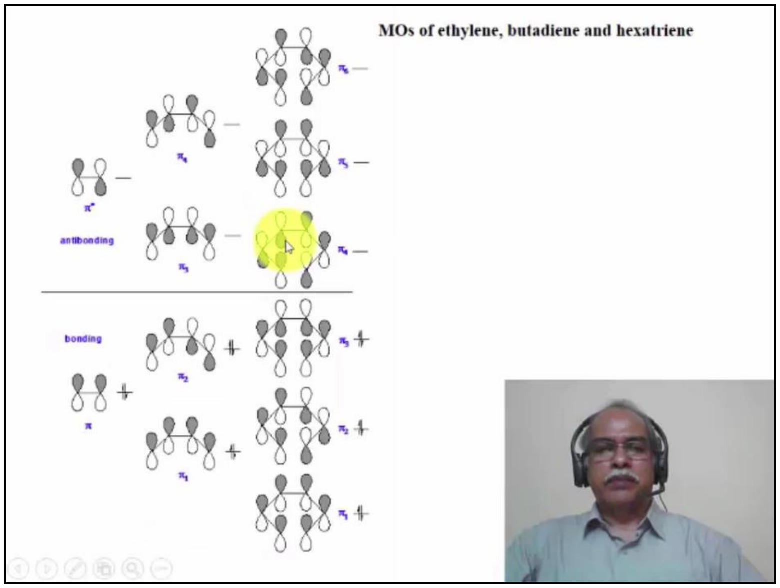
MOs of ethylene, butadiene and hexatriene

Now, this diagram essentially tells you, the molecular orbital pictures of the ethylene molecular orbital, the butadiene molecular orbital, and 135 hexatriene molecular orbital. Take the example of the 135 hexatriene molecular orbital. The PI one is the lowest energy with zero nodes, being present here. And, that has two electron occupancy. And then, the PI two with a single node, which is placed at the middle of the carbon-carbon bond.

In other words, carbon three-carbon four bond, middle portion of the, center of the carbon-carbon bond. C3 C4 bond is essentially the nodal point. And, this is also an occupied molecular orbital, with two electrons. Then, you have one nodal point here. Another nodal point here. There are two nodes present, in the third molecular orbital of the hexatriene unit. In other words, if you go from here, this is a grey shaded area.

This is a grey shaded lobe, for example. And, then comes an unshaded loop. So, there is a nodal point here. This is again, unshaded lobe. There is no nodal point here. This is, change in the color of the shading here. So, there is a nodal point here. So, this has two nodal points. This has three nodal points. One in this position. One at the center. And, one at this position here, which are indicated by the cursor movement here.

And then, the PI five molecular orbitals will have, four nodal points. The four nodal points are essentially given by, one, two, three, and four. In other words, there is one nodal point between, carbon one and two. Another nodal point between two and three. There is a third nodal point between, four and five. And, the fourth nodal point is between, carbon number five and six, in this position here, for example.

In the case of PI six molecular orbitals, there should be five nodal points. The center of every carbon-carbon bond, in this molecular orbital, is essentially a nodal point, with respect to this molecule. You can see here, this is with increasing energy, they have placed the molecular orbital. All the filled molecular orbitals have the lowest energy. And the unfilled molecular orbitals have the higher energy in the system.

Now, the frontier molecular orbitals are the, molecular orbitals, which are at the frontier of the non-bonded level. This line essentially indicates the nonbonded level. These are bonding levels. And, the top ones are antibonding levels. So, this is a non-bonded level. So, these molecular orbitals, PI three for example, of the hexatriene is the highest occupied molecular orbital. And, PI four molecular orbitals is the lowest unoccupied molecular orbital.

So, this is the HOMO of the hexatriene. And, this is the LUMO of the hexatriene. Similarly, the PI two is the HOMO of butadiene, and PI three is the LUMO of the butadiene. Here, there are only two molecular orbitals. One is occupied. The other one is unoccupied. So, this will be the HOMO, and this will be the LUMO, of the ethylene molecular orbital.

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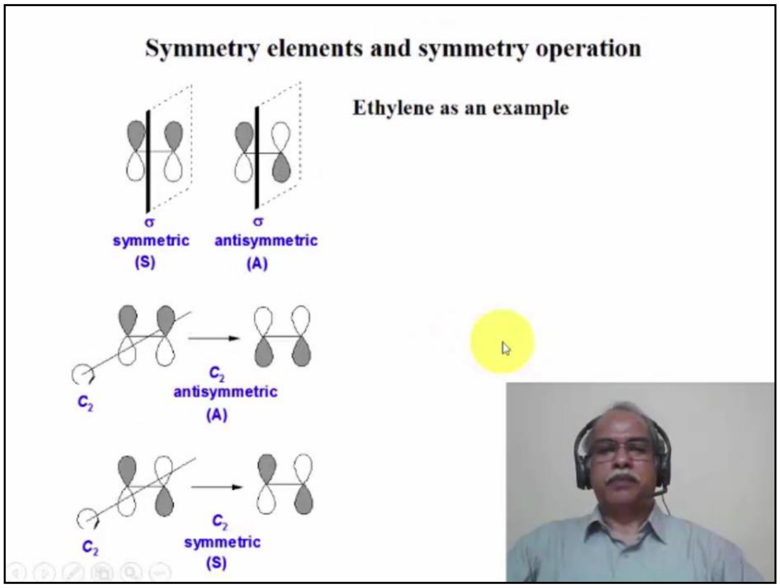

Symmetry elements and symmetry operation

Ethylene as an example

Now, let us try to identify the symmetry elements, and symmetry operation. There are two symmetry elements, that one needs to worry about. One is a mirror symmetry. Other one is a rotational axis symmetry. Mirror symmetry is essentially a plane of mirror, placed on the molecule is such that, the plane bisects the molecule, such the mirror reflections are identical, with respect to each other. Now, let us take the example of trying to identify their mirror symmetry, that may or may not be present in the ethylene molecular orbital. This is PI molecular orbital of ethylene. This is a PI star molecular orbital of ethylene.

Now, when you are considering a symmetry plane, the symmetry plane should bisect the carbon-carbon bond. So, this vertical plane is, what is the symmetry plane, with respect to which, we are trying to identify, whether this molecular orbital is symmetric or anti-symmetric. Now, if we place the mirror between these two carbon-carbon bonds, this passing through the center of the carbon-carbon bond.

Otherwise, the plane is passing through the center of the carbon-carbon bond, the orbital on the left-hand side is essentially reflected, on the right-hand side. In other words, with respect to this mirror symmetry, these molecular orbital reflections are identical. That means, they are symmetric, with respect to the mirror plane, that is placed here. On the other hand, if you take the antibonding molecular orbital of the ethylene, this is not reflected here.

In other words, the shaded portion is not reflected, by the bisecting mirror. That means, this is an anti-symmetric molecular orbital, with respect to that particular symmetry operation. The symmetry operation being a mirror plane, is placed between the carbon-carbon bond, and see whether the left-hand side is reflected, on the right-hand side or not. Here, it is not clearly reflected. Whereas here, this is clearly reflected.

So, this is symmetric, with respect to the sigma. Whereas, this is anti-symmetric, with respect to the sigma. So, taking ethylene as an example, we are illustrating the mirror symmetry, that is present in this PI molecular orbital, and the mirror symmetry, that is absent in the PI star molecular orbital. So, with respect to the mirror symmetry, the PI molecular orbital is symmetric, and the PI star molecular orbital is anti-symmetric. That is the conclusion, we arrive at.

What about rotational symmetry. Let us consider, a C2 axis of rotation. What is a C2 axis of rotation? It is a 180° rotation. Whether, it regenerates the original picture or not, is what we need to worry about. Here, the two shaded lobes are on the top. And, the two unshaded lobes are on the bottom. If you consider a C2 axis passing through the carbon-carbon bond, perpendicular to the carbon-carbon bond, passing through the center of the carbon-carbon bond, if you make 180° rotation, this is a picture, that you will get.

Clearly now, the shaded portion has become unshaded portion. So, the original picture is not generated, upon the C2 axis of rotation. Therefore, with respect to the C2 axis of rotation, the PI molecular orbital of ethylene is essentially, anti-symmetric. On other hand, if you consider the PI star molecular orbital of ethylene, with respect to the C2 axis of rotation, this is essentially regenerated here. In other words, this lobe here, essentially becomes this lobe here, by a C2 axis of rotation. So, this operation namely the C2 operation, regenerates the original picture.

So, with respect to the C2 axis of rotation, the PI star molecular orbital of ethylene is symmetrical, with respect to the C2 axis of rotation. So, one can identify the symmetry property of a particular molecular orbital, either using a sigma plane, or using an axis of symmetry. Depending upon the situation, we could either use the sigma plane, or C2 axis of symmetry. We will consider, which one of this symmetry operation to be performed, at a later stage, when we discuss the orbital correlation diagram methodology, with an illustrative example.

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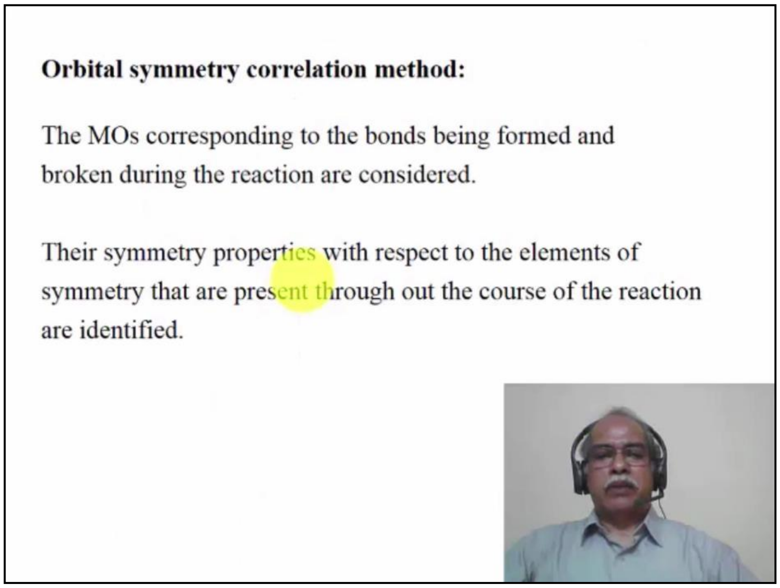

Orbital symmetry correlation method:

The MOs corresponding to the bonds being formed and broken during the reaction are considered.

Their symmetry properties with respect to the elements of symmetry that are present through out the course of the reaction are identified.

Now, in the orbital correlation method, the molecular orbitals, corresponding to the bonds being formed and broken are considered, during the course of the reaction. In other words, on the left-hand side, you write the molecular orbitals of all the starting molecular orbital, that is undergoing a reaction. And, in the right-hand side, you write the molecular orbitals of all the bonds, that are being formed during the course of the reaction of the product, that is being formed in this.

The symmetry properties of each one of the molecular orbital, with respect to a symmetry element, that is present throughout the course of the reaction is identified. In other words, you identify a symmetry element. It should be present in the starting point. It should be present at the end point. It should also be present, in the proposed transition state of the particular transformation, that is being considered.

So, we will consider illustrative examples in a minute. But, try to understand that, the symmetry property with respect to the element of symmetry, that is being present throughout the course of the reaction, are identified, is what is important for constructing the molecular orbital symmetry correlation methodology.

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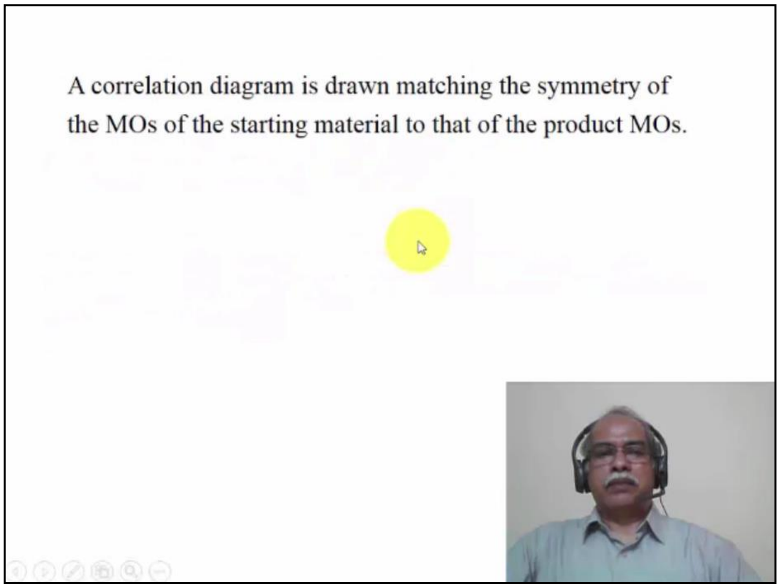

A correlation diagram is drawn matching the symmetry of the MOs of the starting material to that of the product MOs.

Then, after we construct, all the molecular orbital picture, and identify the symmetry. You correlate the diagram, by matching the symmetry of the molecular orbitals, from the starting point to the endpoint. Symmetrical molecular orbitals of the starting point, should match with the symmetrical molecular orbital of the endpoint. Similarly, the anti-symmetrical molecular orbitals of the starting point, should match with the anti-symmetric molecular orbitals of the endpoint. This is important.

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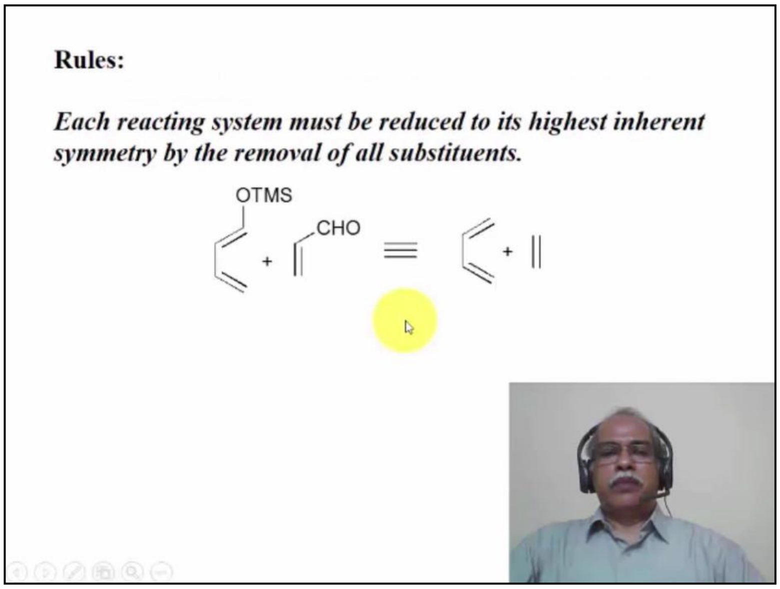

Rules:

Each reacting system must be reduced to its highest inherent symmetry by the removal of all substituents.

But, in doing so, there are certain basic rules, that one needs to follow. Possible that, the molecules by themselves are inherently unsymmetrical, because of substituents, that may be present. If you take a diels-alder reaction, essentially the basic framework, that is undergoing the diels-alder reaction is the four-carbon framework of the diene, which is this particular one. And, the two-carbon framework of the dienophile, which is this one.

The substituents, of course, will have their own effect, in terms of accelerating or decelerating the reaction. But, it does not affect the analysis of the orbital correlation diagram. So, one has to strip off all the functional group, and take the bare skeleton for the highest inherent symmetry, to be considered for the orbital correlation method. You remove all the substituents, and take the basic skeleton, which is the most symmetrical with the highest inherent symmetry, that is being present in the molecular orbital picture.

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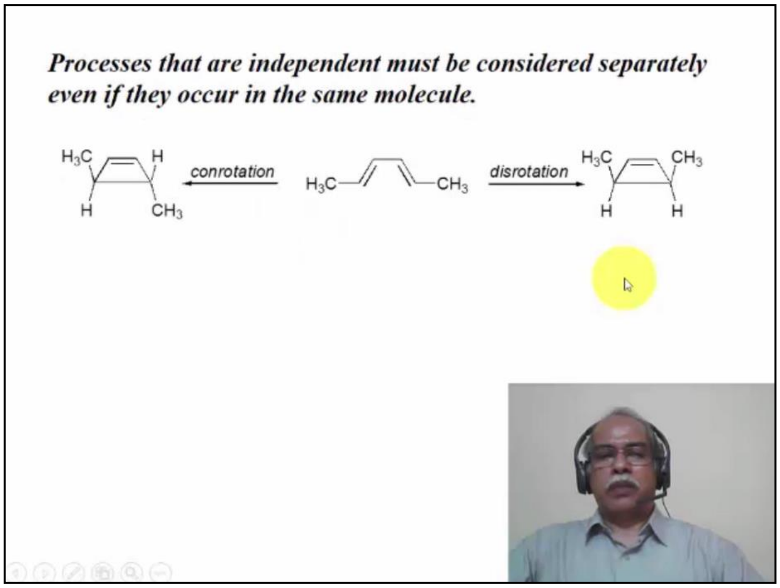

Processes that are independent must be considered separately even if they occur in the same molecule.

Now, in this case, there are two processes that is taking place, with the respect to the butadiene molecule. These are electrocyclic reaction. We will come to that, little later. Electrocyclic reaction can either take place, by a disrotatory process, or by a conrotatory process. I will define, what is dis-rotation and con-rotation, when you come to the electrocyclic reaction. These two process have to be considered independently. Although they are, both give the cyclo-butane ring, as the product.

These two processes are entirely different, from the point of view of the symmetry element, that is being present in this particular system, which is different from this particular system, over here. So, we will consider this, when we consider the electrocyclic reaction, in a detailed manner. Of the time being, you must understand that, when there are two processes, that are inherently possible in a system, the two processes have to be dealt with separately, independently, and not to be combined together.

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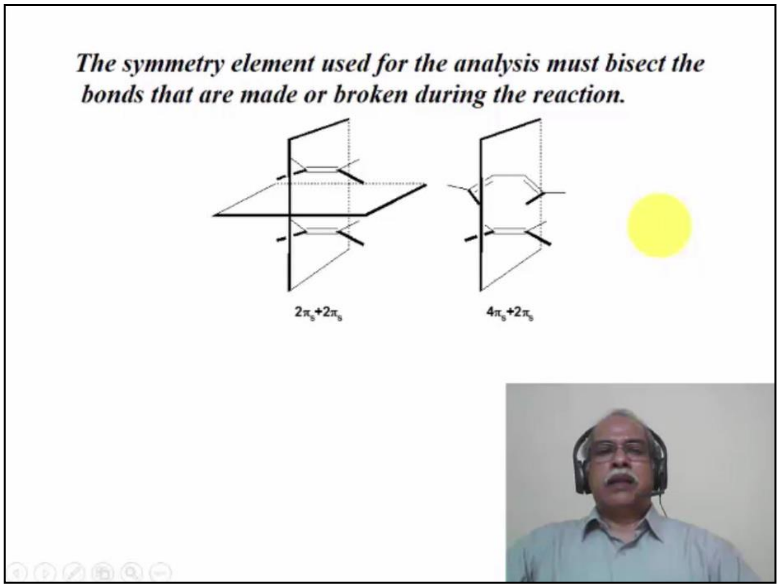

The symmetry element used for the analysis must bisect the bonds that are made or broken during the reaction.

Because, the symmetry element, or the symmetry operator, may be very different in the system. The symmetry element, that is used for the analysis, must bisect the bond, that are made and broken during the course of the reaction. If you consider, a two plus two cyclo-addition reaction between two ethylene molecules, to give a cyclo-butane, in a suprafacial, suprafacial manner, this vertical plane, mirror plane, essentially bisects a carbon-carbon PI bond, both the PI bonds.

The horizontal plane essentially bisects, the carbon-carbon sigma bond, that will be formed during the course of the reaction. So, these are the two sigma planes, that are present as symmetry elements, in this particular system. One symmetry element, which is a vertical plane of symmetry, essentially bisects the PI bonds of the starting material, and the horizontal plane of symmetry essentially, if you once, you consider cyclobutene as the product, that bisects the sigma bonds of the cyclobutene in a horizontal manner.

Now, if you consider diels-alder reaction, diels-alder action does not have a horizontal plane of symmetry. It has only one vertical plane of symmetry, bisecting, passing through the center of the dienophile, and the center of the diene, which is this point here, and this point here, respectively. So, this plane essentially bisects, the carbon two, carbon three of the butadiene, carbon one, carbon two of the ethylene molecule, in this particular instance. And, passes through the center, in terms of bisecting the molecule at the midportion.

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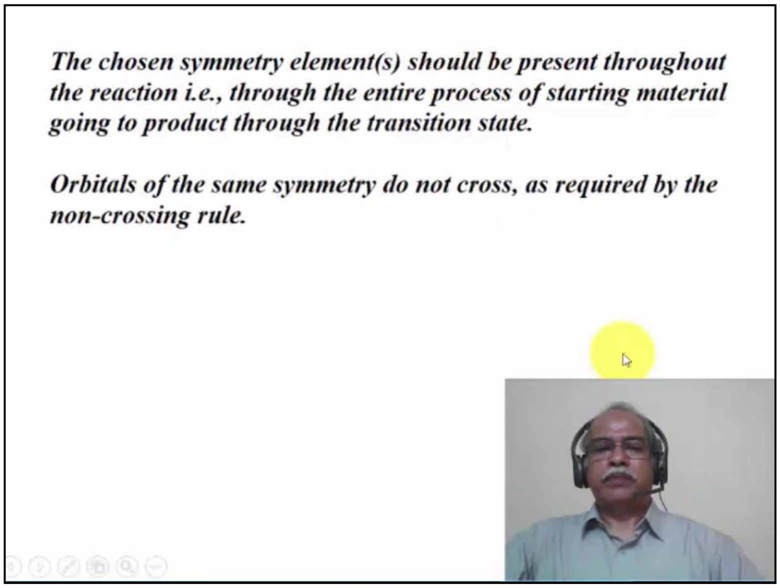

The chosen symmetry element(s) should be present throughout the reaction i.e., through the entire process of starting material going to product through the transition state.

Orbitals of the same symmetry do not cross, as required by the non-crossing rule.

The symmetry element should be present, throughout the course of the reaction. This is what, i mentioned earlier also. Through the entire process of starting material, going to the product, through a transition state. In the transition state also, the symmetry element must be present, which will be considered for the orbital correlation, symmetry correlation methodology. Orbitals of the same symmetry do not cross, as required by the non-crossing rule.

I can give a lot of explanation for this. But, i will illustrate this point with the example, when we come to the construction of the molecular symmetry, molecular orbital symmetry correlation methodology. At that time, i will explain this properly to you.

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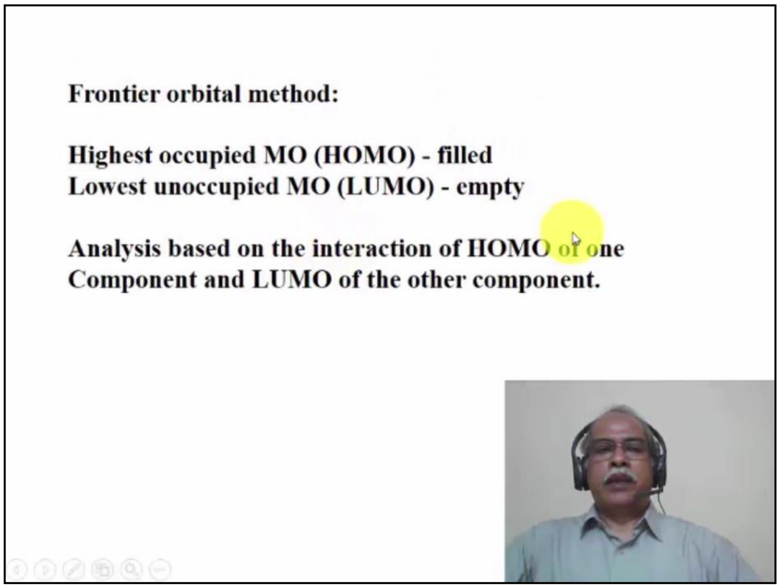

Frontier orbital method:

Highest occupied MO (HOMO) - filled
Lowest unoccupied MO (LUMO) - empty

Analysis based on the interaction of HOMO of one Component and LUMO of the other component.

Now, the second methodology, which is the frontier molecular orbital methodology. We consider the highest occupied molecular orbital, which is a filled molecular orbital. The lowest unoccupied molecular orbital, which is a LUMO, or the empty molecular orbital. The analysis is based on the interaction between, the HOMO of one component, and the LUMO of the other component, of the interacting system.

If you are talking about, a diels-alder reaction between a diene and dienophile, we will consider the highest occupied molecular orbital, interacting of that, butadiene interacting with the lowest unoccupied molecular orbital of the ethylene, for example.

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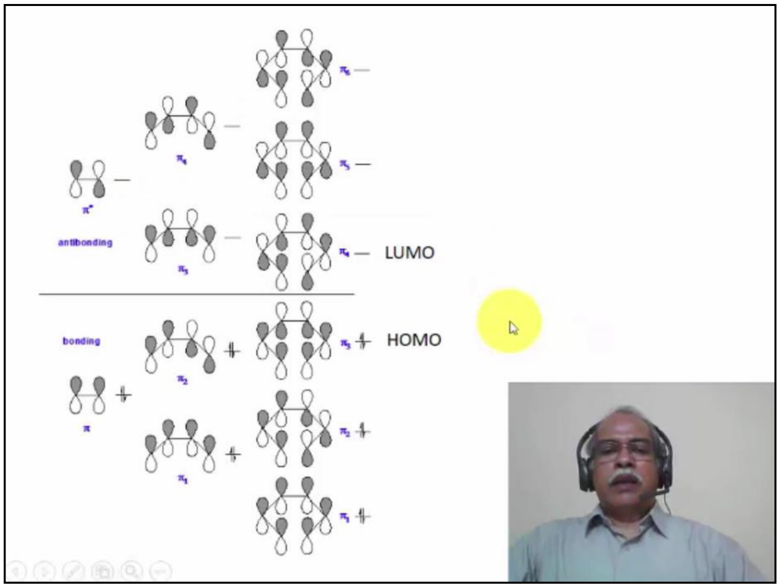

So, this is what, i defined earlier also. Let me rephrase it, once again. This is a highest occupied molecular orbital of the hexatriene, butadiene, and ethylene. This is the lowest unoccupied molecular orbital of the hexatriene, butadiene, and ethylene. Essentially, the molecular orbital, which is at the frontier of the non-bonded level, which is the horizontal line, that is shown here. These are antibonding levels. And, these are bonding levels.

I mean, the PI 1, PI 2, PI 3, are the bonding levels. The PI 4, PI 5, and PI 6, are the antibonding molecular orbitals of the hexatriene. So, this is HOMO and LUMO of the respective systems.

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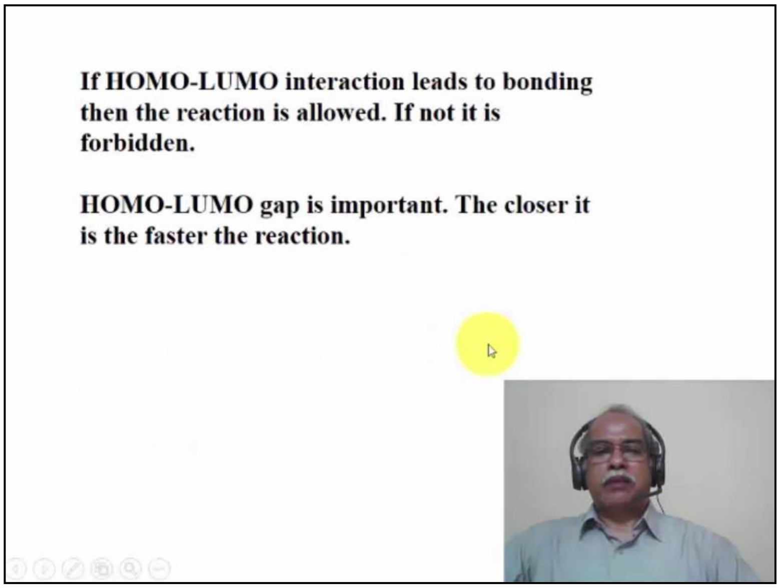

If HOMO-LUMO interaction leads to bonding then the reaction is allowed. If not it is forbidden.

HOMO-LUMO gap is important. The closer it is the faster the reaction.

If the HOMO-LUMO interaction leads to a bonding type of a situation, then we call that, the reaction is allowed. In other words, is energetically favorable. So, it is an allowed process. If the HOMO-LUMO interaction essentially leads to an antibonding kind of an interaction, then would call it as a forbidden. Because, the energy of the transition state is going to be much higher than the transition state, which goes through the bonding type of an interaction.

The HOMO-LUMO gap is important. Because, the closer the gap, the faster will be the reaction. And, that is where the substituents play very important role, in making the HOMO-LUMO gaps come closer to each other. Substituent effects will be dealt in detail, in the case of the diels-alder reaction and other reactions.

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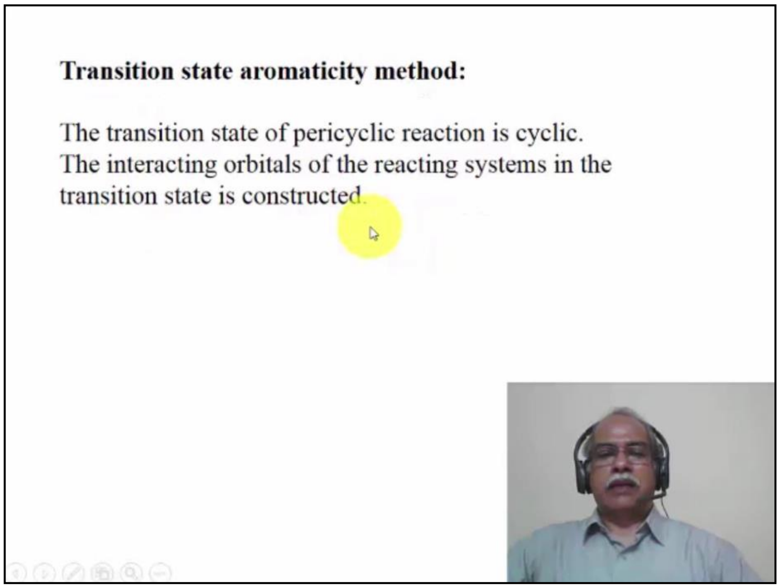

Transition state aromaticity method:

The transition state of pericyclic reaction is cyclic. The interacting orbitals of the reacting systems in the transition state is constructed.

Now, the third methodology, and the last methodology, is to deal with the transition state aromaticity method. In the transition state aromaticity method, the transition state of the pericyclic reaction, being a cyclic transition state, the aromaticity of the particular cyclic transition state, is being dealt with. In other words, the interacting orbitals of the reactant systems in the transition states, are constructed.

In other words, when you have a loop of PI electrons reacting, you can have the loop with 4N number of electrons, or 4N +2 number of electrons, which should consider to be cyclic, aromatic, or antiaromatic, as the case may be, according to the huckel molecular orbital theory.

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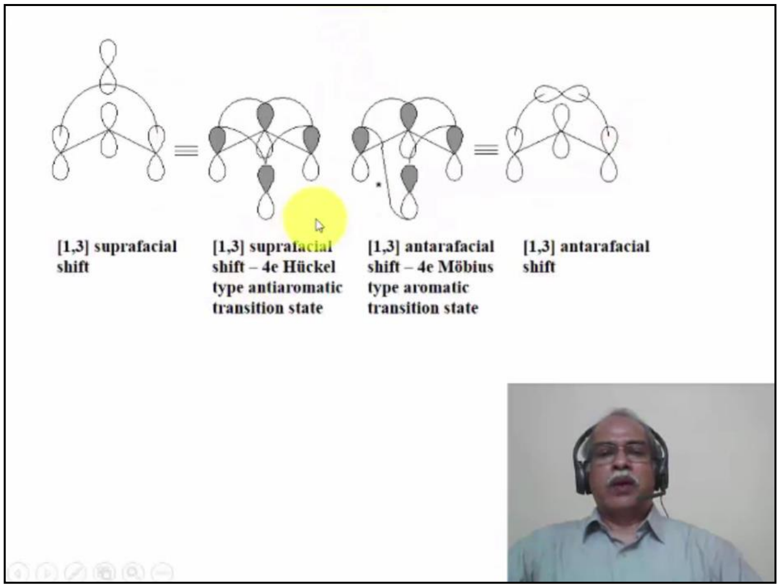

[1,3] suprafacial shift

[1,3] suprafacial shift – 4e Hückel type antiaromatic transition state

[1,3] antarafacial shift – 4e Möbius type aromatic transition state

[1,3] antarafacial shift

Now, take the example of a suprafacial migration, which is taking place. With respect to this group, which is migrating, it is suprafacial. In other words, the bond, which was originally bonded here. Now, it is getting bonded here. This group is migrating, from the one position to the third position. In doing so, it is undergoing a suprafacial migration. What is suprafacial migration.

This orbital essentially, which was originally bonded here, is now going to get bonded here. In other words, there is a continuous loop of electrons, without a nodal point, as opposed to an anti antarafacial migration. If you look at this picture, it is very clear. Originally, this lobe was attached here. And now, it is migrating to this particular carbon. 1, 3 shift is what is taking place in this particular case.

So, you can see here, with respect to the PI framework, it is suprafacial. But, with respect to this carbon, which is migrating is antarafacial. Because, originally, this is the bonded lobe. Whereas, now it is happening, the bonding is happening, from the opposite side of the molecule, in from the other side of the lobe of that particular molecule. So, in this particular case, the transition state is cyclic, but it has a nodal point.

You can see here, there is a change in the coefficient of the molecular orbital, of this particular algebraic sign of the coefficient of the molecular orbital. So, that is a nodal point. So, in other words, this is like a twisted system, twisted loop of PI interacting molecular orbital. See here for example. And, this would have essentially corresponded to a four-electron system of mobius type, which has an aromatic transition state.

Remember, if there is a 4 electrons system, which is a cyclic system, and if it is a continuously overlapping system like this, then you would call it as a aromatic huckel anti aromatic system. Whereas, if it is a 4 N mobius system, then it will be an aromatic kind of a transition state.

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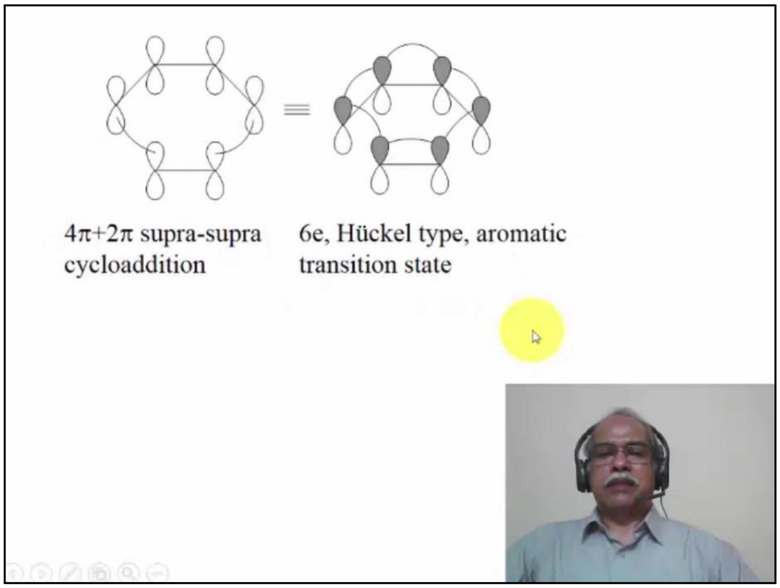

$4\pi+2\pi$ supra-supra cycloaddition

6e, Hückel type, aromatic transition state

Is more clear, when you consider the six-electron system. Because, it is very similar to the benzene transition state. Benzene molecular orbital picture, essentially has these six molecular orbitals, without any node, they are interacting with each other. And, this will be a 4 PI, 2 PI, suprafacial, suprafacial, cycloaddition transition state is represented like this. This involves six electrons. And, it is a huckel type of an overlap.

So, huckel type of an overlap with the six electrons would correspond to an aromatic transition state. So, if the reaction proceeds with this kind of a transition state, then it would be an allowed process. Because, an aromatic transition state will always have a lower energy, compared to a anti aromatic transition state. On the other hand, if the 4 plus 2 cycloaddition reaction, where to take place in a suprafacial, antarafacial manner.

With respect to this molecular orbital, it is suprafacial. With respect to this molecular orbital, it is antarafacial. You can see here, there is a nodal point here. In other words, overlap between this orbital, and this orbital, is what is taking place. So, it is a continuous loop, with a twist in this position. And, the twist is, what is responsible for making it is a mobius strip.

A six-electron system with their continuous overlap of molecular orbitals of this type, which will correspond to a huckel type, will be aromatic. With the twist, it will be a mobius strip. And, it will be an antiaromatic transition state.

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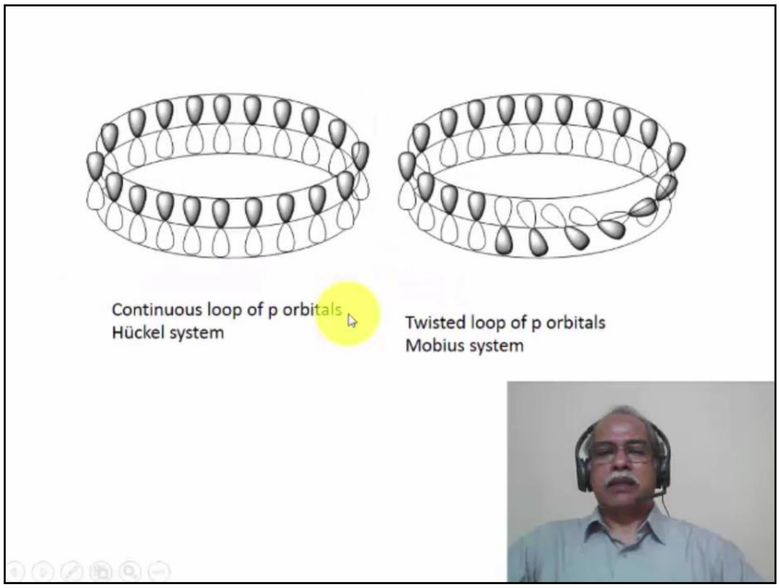

Continuous loop of p orbitals
Hückel system

Twisted loop of p orbitals
Mobius system

Now, this picture essentially tells you, what is a huckel strip of continuous loop, and what is a mobius type of a continuous loop. If you look at this loop here, this is all the shaded portion is on the top. And, it is continuous. And, if you have 4N number of electrons in this continuous loop of system, then it would correspond to huckel antiaromatic system. If it is a 4N +2 kind of an electron, just as in the case of benzene, for example, then it would correspond to the aromatic kind of a loop.

On the other hand, if you consider this loop, it is continuous up to this point here. And then, there is a twist of the loop here. And, this is what is known as the mobius loop, here. And, the mobius loop essentially, if it is a 4N electron system, it would be aromatic. And, if it is a 4N +2 electron system, it will be antiaromatic in nature.

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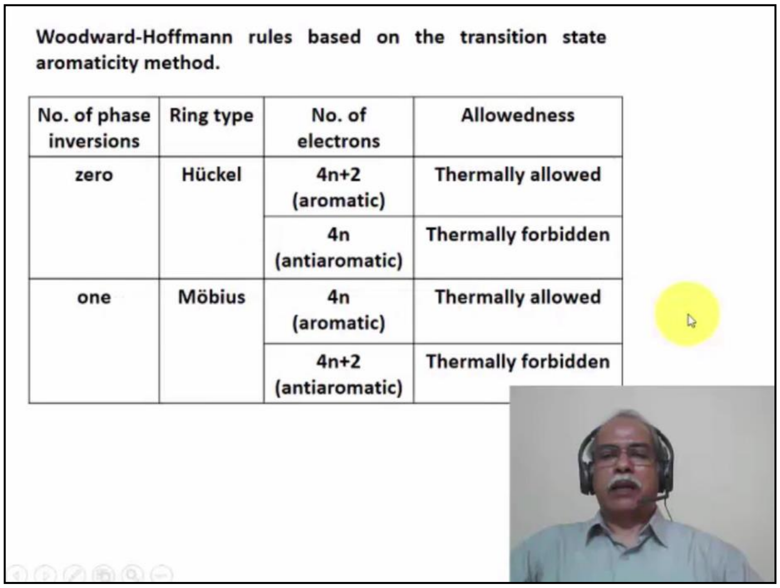

Woodward-Hoffmann rules based on the transition state aromaticity method.

No. of phase inversions	Ring type	No. of electrons	Allowedness
zero	Hückel	4n+2 (aromatic)	Thermally allowed
		4n (antiaromatic)	Thermally forbidden
one	Möbius	4n (aromatic)	Thermally allowed
		4n+2 (antiaromatic)	Thermally forbidden

So, Woodward-Hoffmann rules, based on the transition state aromaticity, can be summarized using this particular slide, here. You consider the number of face inversions, that is taking place. In this case, there is no face inversions. So, it is zero. Here, there is a face inversion. You can see here, there is a face inversions, at this particular point here. So, this will be, one phase inversion is happening here.

So, depending upon, whether there is a face inversions or not, you classify it as a huckel or the mobius thing. And, if it is a huckel, then it is 4N +2 would be aromatic transition state, that will be thermally allowed. If it is a 4N kind of an electron system, it is antiaromatic state. It is thermally forbidden. And, if it is a mobius system, 4N will be aromatic. It is thermally allowed. And, 4N +2 will be antiaromatic.

And, thermally it is a forbidden. This is essentially talking about the ground state electronic configurations. Because, we are talking about the thermally allowedness or dis-allowedness of the process, that is being considered. So, in this model, what we have seen is essentially, a molecular orbital picture construction, for simple molecules like hexatriene, butadiene, and ethylene. How to place them.

How to identify their symmetry properties, of each other molecular orbitals, that are under consideration. And then, looked at the various methodologies of analyzing the pericyclic reaction namely, the orbital symmetric correlation methodology, the frontier molecular orbital methodology, and finally the transition state aromaticity methodology. Thank you, very much for your kind attention.