Concepts of Chemistry for Engineering
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Lecture No. 21
Hückel's MOT for Butadiene-I

We are now discussing bimolecular systems. We have completed our discussion of polyatomic molecules with sigma bonds only like methane and we have discussed a first molecule which has pi bonds, that is ethylene. Today, we extend that discussion to butadiene.

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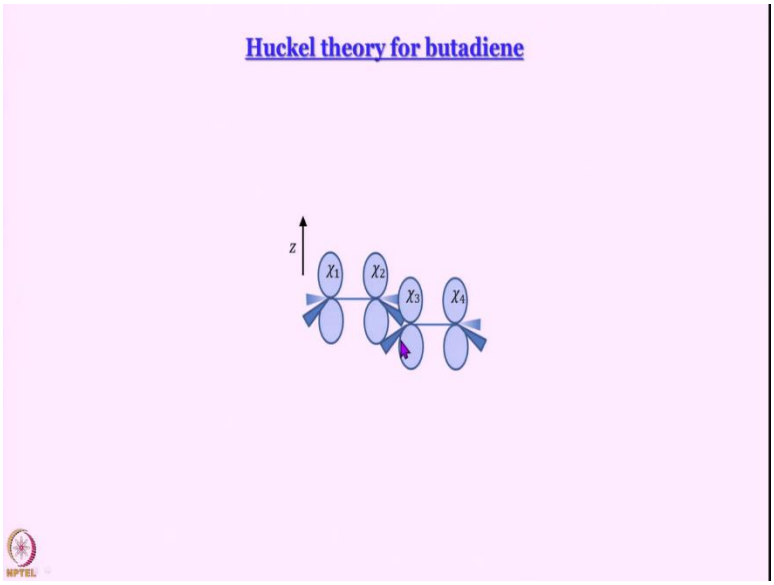

So, butadiene, of course, is a little more complicated than ethylene. You can think it is like two ethylene moieties that are joined together. So, we will see how we get there, and how we can build a Huckel theoretical description of a molecule like this. So, before that, just a small recap.

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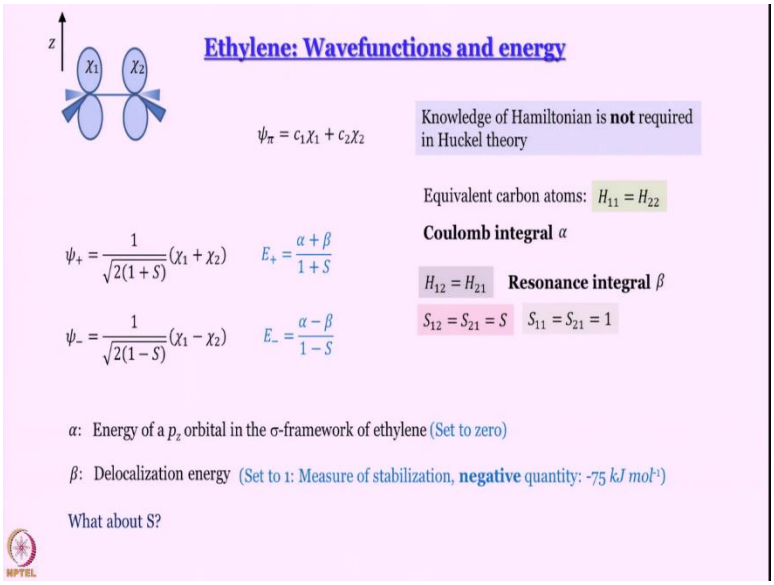

In ethylene, we have worked out wave functions and energy. We had expressed the molecular orbital, pi molecular orbital as a linear combination of the two p orbitals on the two carbon atoms and we had obtained this kind of expressions, $\psi_+ = \frac{1}{\sqrt{2(1+s)}}\chi_1 + \chi_2$, and $\psi_- = \frac{1}{\sqrt{2(1-s)}}\chi_1 - \chi_2$and the associated energies were $E_+ = \frac{\alpha+\beta}{1+S}$ and $E_- = \frac{\alpha-\beta}{1-S}$.

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And here the interesting thing is that you do not need to know the Hamiltonian for Huckel theory. You actually work it out in terms of the integrals where Hamiltonian is just written as H. What do we do there? For equivalent carbon atoms, we remember that H_{11} has to be equal to H_{22}. We call this the coulomb integral alpha and then we set it to 0, because all measurements are with respect to alpha.

And H_{12} and H_{21}, we said they are equal to each other and they are called the resonance integral. This is what gives us the stabilization because of pi bond formation. Of course, S_{12} and S_{21} are all familiar overlap integral and S_{11} and S_{21} are just 1, because their atomic orbitals are normalized.

So, we have set α to be equal to 0, because that essentially is the energy of a p_z orbital in the sigma framework of the ethylene, so that is your starting point. And β, as we said, is delocalization energy and we had told you the value is - 75 kilojoules per mole. No need to remember this value. What

is important to remember is beta is a negative quantity. And we discussed very briefly what we do with S.

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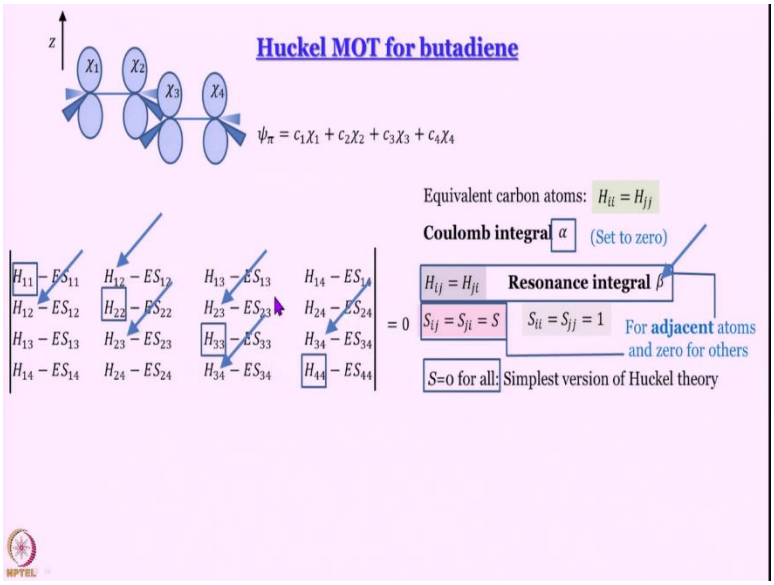

With that background, let us go over to butadiene. We have just added two carbon atoms and we have brought in two more p orbitals perpendicular to this molecular plane. What happens now is that everything remains the same, is just that the secular determinant becomes larger. Earlier, you had a 2 by 2 determinant, now you have a 4 by 4 determinant. So, since the problem is a little more complicated, it would help if we could bring in some more simplifying factors. And that is provided by Huckel theory.

We have said already that we set coulomb integral to 0. What we now say is that this H_{ij} equal to H_{ji}, we said that to be resonance integral β only for adjacent atoms and we consider them to be 0 for others, because resonance integral basically gives us the energy for delocalization of the electron over two atoms, while the electrons are actually delocalized over the entire atom. But remember, these integrals have a two wave functions, $\int \psi_i H \psi_j$, that kind of an integral. What we are saying is that if i and j are adjacent to each other, then that integral has some value beta.

If you take 1 and 3, for example, then the value is as good as 0. We are neglecting it, because after all these integrals are all worked out numerically. So, in locations, where say χ_1 has not too much value, it does not matter what the value of H χ_3 is, you are going to get 0 and vice versa. So, only for adjacent atoms, we said that this H_{ij} and H_{ji} are equal to beta, for everything else is just 0. It is

an approximation, but it is an approximation that works to a very large extent and there is some logic to it.

The logic is that we have to consider, we do not have to consider atoms that are too far apart from each other when we build these pairwise terms like this, where we have two orbitals, two atomic orbitals from two atoms and the Hamiltonian operator operating on one of them. So, that is the justification put in very, very simple terms.

Now, let us see what we have. Another thing that we need to worry about is overlap integral. Even overlap integral, in Huckel theory, it is considered that by similar logic overlap integral can have some non-zero value only for adjacent items. χ_1 and χ_3 is not going to have too much of overlap anyway, because the distance is already fixed by the sigma bonding network. They cannot come any closer.

So, as we have studied for say H_2 or H_2^+, when they come close together, then only the overlap integral increases from 0 to some determinable value. So, since 1 and 3 are far apart from each other anyway, we can set that overlap integral to be equal to 0. In fact, in the simplest version of Huckel theory that we are going to use, we are going to set all overlap integrals to be equal to 0. This might sound to be very arbitrary.

But then let us think what kind of overlap we are talking about. We are talking about pi overlap like this, not sigma overlap like this. So, the distances between the two centers is already fixed. They cannot come closer than this. And p orbital sort of held like this. So, how much will overlap? Not much. That is why it is approximately set to be equal to 0. Of course, if you want more precise results, you cannot set them to be equal to 0, at least for nearest neighbors, but for our purpose, it is okay if we go with the simplest version of Huckel theory, set overlap integral to be 0 as well. Coulomb integral, of course, is set to 0 as we said earlier.

So, now this determinant becomes very simple. So, for all these H_{11}, H_{22}, H_{33}, H_{44}, I can write alpha and then I can happily set them to equal to 0. S_{11}, S_{12} all that is happily equal to 0. You do not have to worry about them. So, what am I left with? I am left with wherever we have beta. So, H_{12} would be equal to beta and H_{12} occurs in two places H_{21} is equal to H_{21}, as we said earlier.

What about H_{13}? H_{13} is going to be 0, because 1 and 3 are not adjacent to each other, do not have to bother about it. Similarly, H_{14} the distances even bigger. There is no way we can, we have to

worry about those. But what about say H_{23}. H_{23} is not equal to 0. H_{23} actually is equal to beta, because 2 and 3 are adjacent to each other and H_{23} appears in two terms. Similarly, H_{34} also appears in two terms and they can be replaced as beta.

So, what do we have now? What is the first term here, 0 minus 0, second term is beta, then 0, 0, then we have beta, well, this is beta – ES_{12}, so that is equal to 0, ES_{11}, remember, this is not equal to 0, I think I made a mistake there. S_{11} is just S that is equal to 1. So, here I have -E, then I have, this is beta. So, this way, we can keep on writing.

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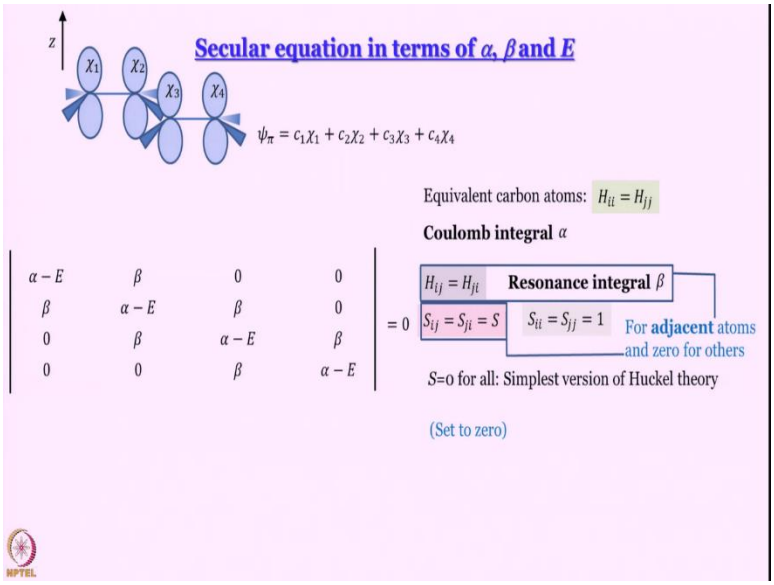

And this is what we are left with,

$$\begin{vmatrix} \alpha\text{-}E & \beta & 0 & 0 \\ \beta & \alpha\text{-}E & \beta & 0 \\ 0 & \beta & \alpha\text{-}E & \beta \\ 0 & 0 & \beta & \alpha\text{-}E \end{vmatrix}$$

This is where we started from. We said that we are going to set H_{11}, H_{22}, H_{33}, H_{44} those who are actually alpha, we are going to set it to 0 later on. Then we said S_{11}, S_{22}, S_{33}, S_{44} these are all equal to 1.

So, the first diagonal terms become something like α-E everywhere. Then, H_{12} is β and this minus ES_{12} that becomes 0, because S_{12} is equal to 0, so here H_{13} – ES_{13} that is 0 anyway.

So, we get ,

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix}$$

So, this determinant is equal to 0.

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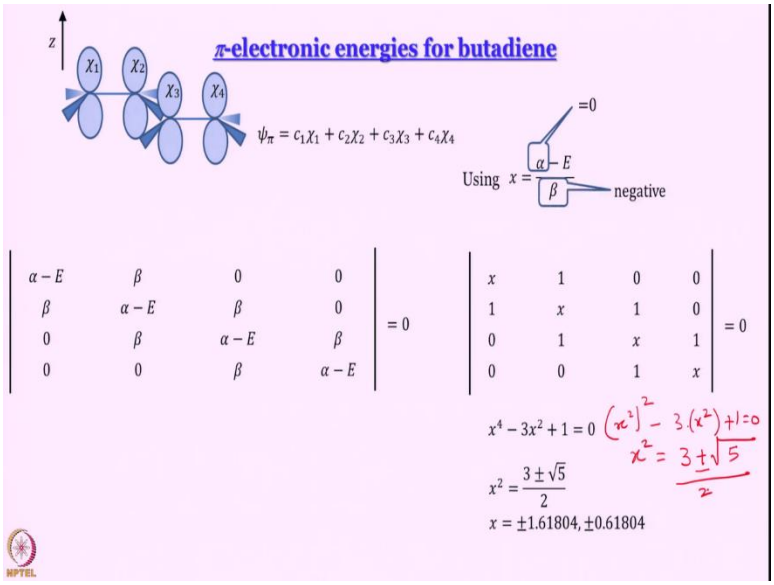

Now, we will simplify this a little further before going ahead. So, how can I simplify. What happens if I divide say (α-E)/b? If I take some quantity x, where x is (α-E)/β not b, I keep on saying b for β inadvertently, please do not get confused. When I say b in this context, I actually mean beta. So, (α-E)/β, I put it as x. And now we have a nice determinant here,

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix}$$

that determinant equal to 0.

What is the next step? We should expand it. When we expand, I leave it to you to do the expansion by yourself. It is not difficult. I just show you the answer, $x^4-3x^2+1=0$. Now, please do not get daunted seeing x^4. x^4 is just x^2. So, this is really a quadratic equation in x^2, is not it? So, we know how to solve quadratic equations. We are going to proceed in the same way.

We are just going to write this as $(x^2)^2 -3(x^2) +1= 0$. So, what is x^2 going to be then. $x^2 = \frac{-b\pm\sqrt{b^2-4ac}}{2a}$ where b^2 is 9, -4ac is 5. $\frac{\pm\sqrt{b^2-4ac}}{2a}$ is 2. This is your answer. $X^2 = \frac{3\pm\sqrt{5}}{2}$ And fortunately, root over 5 is less than 3. So, we get all positive numbers here. It does not matter whether you take the plus combination or a minus combination, you get all positive numbers. And that is good, because if x^2 is negative, then we end up getting something that is imaginary that is unphysical.

So, if you take square root of this now, you are going to get four roots for x. And they are, I leave it to you to calculate it, $\pm$1.61804, $\pm$0.61804. I find this to be particularly amusing because the characteristic is the only thing that changes 1 and 0. After the decimal point, it is 61804 in both the, in all four terms actually. That is what it is. We have found the values of x.

What is x by the way? x, essentially is this. If I set α to be equal to 0, x is what, -E divided by beta. So, can I say that x is E in units of β. So, if it is 1.61804, that is the energy in units of beta, keeping in mind that beta is a negative quantity.

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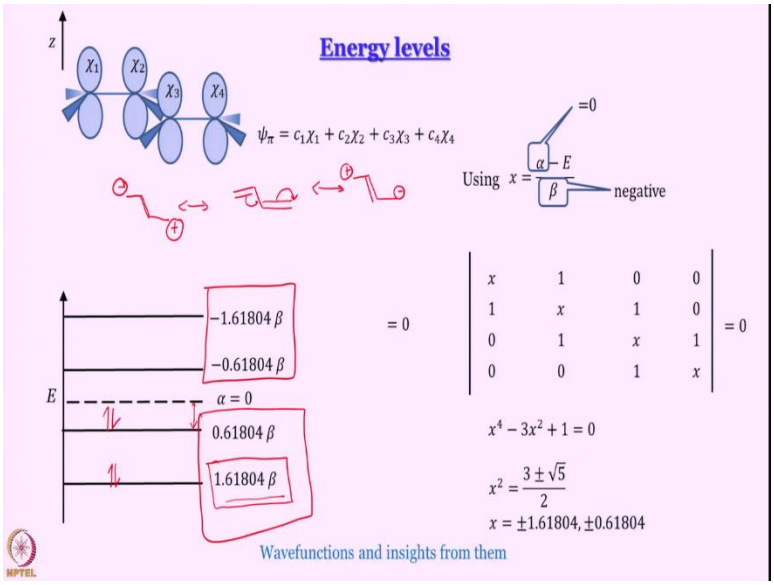

Now, with that understanding, we can draw the energy levels. We have not drawn the wave functions yet, we will get there, but we have drawn the energy levels. The center here is alpha equal to 0. We start calculations from here. 0.61804 is really this separation. Do not forget, because after all, the expression does have alpha minus E kind of thing. So, and then this is 1.61804. Even though I said it several times, please remember, plus 1.61804 beta actually means a negative quantity, because beta is negative. That is why it is lower.

Now, these are the energy levels. What can I do now? I can fill in the electrons like we always do. How many pi electrons are there in butadiene, 4. So, I can just put in like this. I will draw in the conventional manner, not worrying too much about those spin wave functions, just draw like this. This is the configuration.

See, for these two orbitals, lower energy orbitals, the energy is actually negative. These are bonding orbitals. For the higher two, these are the anti-bonding orbitals. Their energies are positive. So, what we see here is that for butadiene the pi electrons reside in bonding orbitals only and you can calculate what the bond order, pi order is 2. And if this was a valence bond theoretical treatment, you would be able to draw these resonating structures very easily. I will draw one, because it is easy.

One resonating structure is something like this. And this is a structure that I can draw without much hassle. Let us see if I can draw the second one. I think this is how you push the arrows. So, this is your second picture here. The double bond is between atoms 2 and 3, carbon atoms 2 and 3. Here I have minus sign, here I have plus sign. And if you go exactly the same way, then the other thing that you could draw is just push the arrows in the opposite direction, you can have minus, plus.

Please do not get confused. We are discussing molecular orbital theory. And now what I am drawing is really a valence bond description with resonance built in. I am just trying to do a comparison. We are going to come to this very soon from the molecular orbital picture. So, see, which one of these three is going to contribute more. Naturally, whenever there is charge separation, we know that contribution is less.

So, these two structures where you have the double bond in the middle, they are going to contribute less, and the central one where your double bond between one and two and two and three, that is

going to be the major contributor. Remember this and let us see whether we get something similar, at least qualitatively, from the molecular orbital picture. But before we do that, we need to talk about wave functions, then only can we think about insights that we can get from the wave functions.