Chemistry Atomic Structure and Chemical Bonding

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Lecture – 53

Huckel Molecular Orbital Theory II

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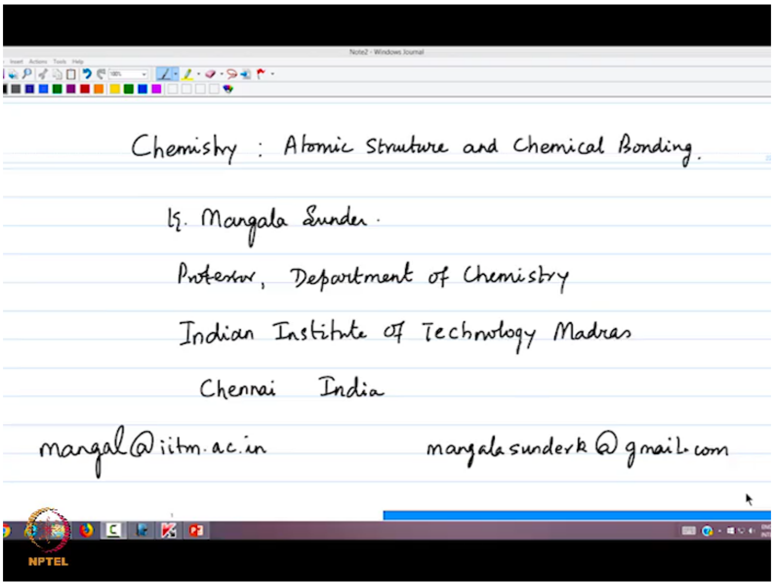

Chemistry : Atomic Structure and Chemical Bonding.

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Welcome back to the lectures in Chemistry and are the topic of Atomic Structure and Chemical Bonding. My name is Mangala Sunder and I am in the department of Chemistry, Indian Institute of Technology, Madras. In the last lecture, we began looking at the conjugated systems and an approximate method of chemical bonding, a quantum mechanical method that was proposed by Eric Huckel. And we were looking at the linear conjugated systems, starting with of course ethylene, where there is only a single double bond that is one double bond. And this was extended to the butadiene 1, 3 Butadiene, where there are two double bonds, alternate single bond and a double bond.

And a comparison was made on the energies of the butadiene electron with electrons with the hypothetical system of two ethylenes coupled to each other or connected to each other without any delocalization of the electron cloud. And we found out that the delocalization of electrons in the butadiene results in this additional stability and it is up to the order of about minus 30 kilo joules per mole or so.

The process is the process of calculating these things in order to account for what we measure experimentally is what this the approximation method is all about. We shall continue that in today's lecture by extending this to one slightly longer carbon chain a six carbon chain 1, 3, 5 Hexatriene. And also look at the more important and more often studied local system, namely the cyclic systems of conjugated aromatic hydrocarbons and extension of that multiple rings few strings, such as naphthalene, anthracene etcetera. I would not do all of that, but I shall introduce the Huckel method for benzene as part of today's lecture and then probably leave a number of problems for you to attempt along similar lines ok.

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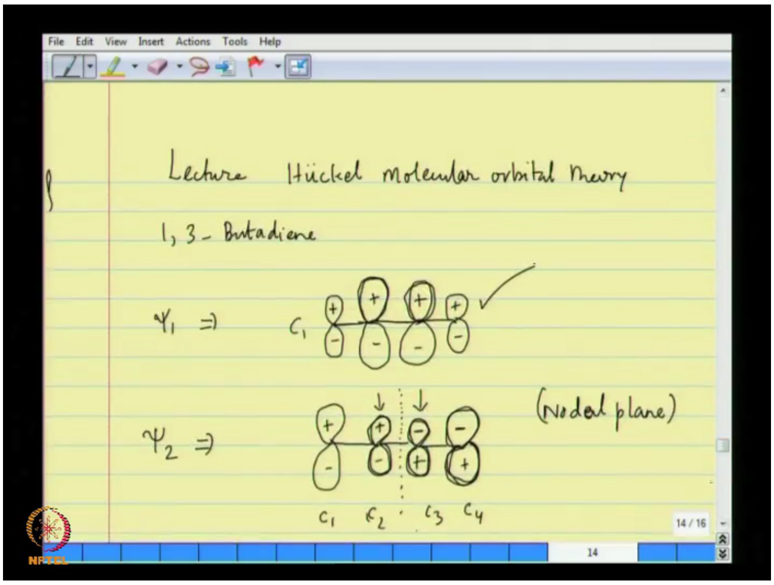

Lecture Hückel molecular orbital theory

1, 3 - Butadiene

$\Psi_1 \Rightarrow$ C_1

$\Psi_2 \Rightarrow$

(Nodal plane)

So, today's lecture we start with the we continue with the Huckel molecular orbital theory. And before we proceed with a new system, let us look at 1, 3-Butadiene a little bit more.

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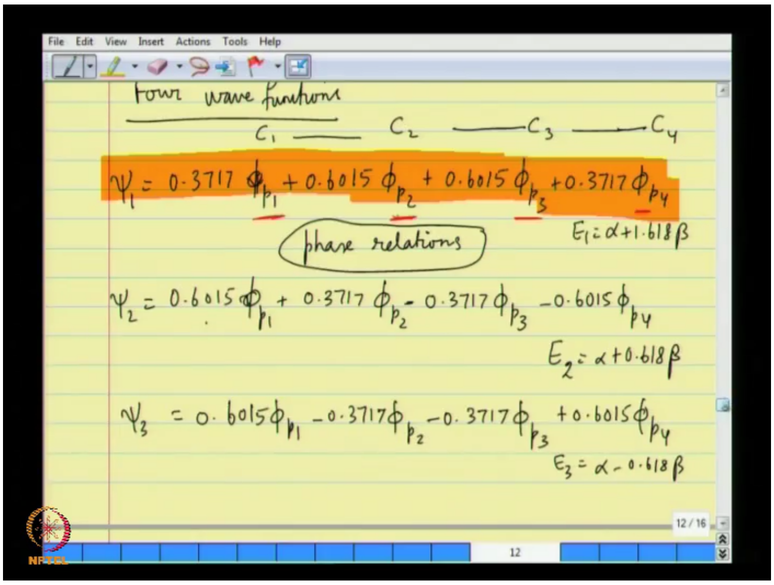

Four wave functions

C_1 —— C_2 —— C_3 —— C_4

$$\psi_1 = 0.3717\,\phi_{p_1} + 0.6015\,\phi_{p_2} + 0.6015\,\phi_{p_3} + 0.3717\,\phi_{p_4}$$

$E_1 = \alpha + 1.618\beta$

phase relations

$$\psi_2 = 0.6015\,\phi_{p_1} + 0.3717\,\phi_{p_2} - 0.3717\,\phi_{p_3} - 0.6015\,\phi_{p_4}$$

$E_2 = \alpha + 0.618\beta$

$$\psi_3 = 0.6015\,\phi_{p_1} - 0.3717\,\phi_{p_2} - 0.3717\,\phi_{p_3} + 0.6015\,\phi_{p_4}$$

$E_3 = \alpha - 0.618\beta$

Please remember from the last lecture that we wrote down the wave functions or the 1-3-Butadiene in this form, namely the four p orbitals associated with carbon 1, carbon 2 carbon 3 and carbon 4, the 4 p orbitals. And the numerical coefficients in front of them representing in a sense the amplitude of this wave function, the square of this number is the contribution to this molecular orbital from carbon 1 p orbital, 0.6015 square is the contribution to this molecular orbital from the carbon 2 p orbital and so on.

However, there are signs, which tell you that the orbital combinations are done with very specific phase relations between them phase relations between them sorry. And if you look at the second orbital, the phase relations are peculiar in the sense the 3rd phi p 3 and the 4th one phi p 4 come with a minus sign and therefore the molecular orbital is such that the phi p 1, phi p 2, they are both positive and this is negative.

Therefore, somewhere along that there is a node right in between p 2 and p 3, there is a node. And psi 3 has the phase convention phase relation as given here. And psi 4 has the phases of 2nd and the 4th p orbital inverted. So, let us plot these things to get an idea of what is meant by the nodal plane and if there is 1. So, let us see psi 1, it is 0.37, so the phi p 1 has a smaller contribution, p 2 and p 3 have larger contributions, p 4 the same as p 1. So, let us plot that.

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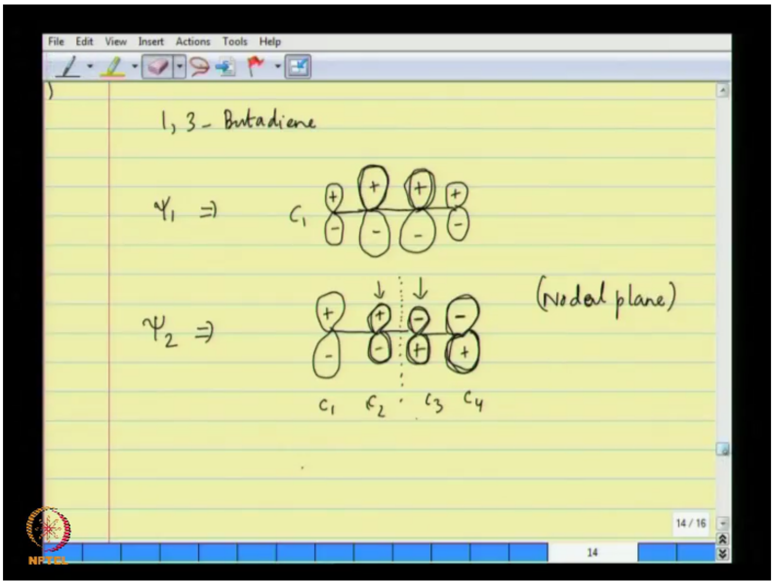

Psi 1 I would say p 1 with a plus minus a carbon 1 smaller contribution and p 2 is a larger contribution, they have to be symmetric. Let us do that and get rid of this part,coupling. It is larger because of the numerical coefficient in front of this is bigger. So, it is also with the plus sign. And the third carbon has exactly the same numerical coefficient as in the second carbon, so this is also plus minus. And the fourth carbon has the same numerical coefficient as in the first carbon, so it is plus minus. So, this wave function all the p orbitals or in the same phase and that therefore the electron density, when you square this coefficient and plot the electron density, it is a sort of a an oval shaped.

Now, psi 2; if you look at the contribution of the individual p orbitals, psi 2 has larger p 1, larger p 4, but p 3 and p 4 are negative. So, let us keep that in mind. Psi 2 is larger p 1 plus minus smaller p 2 smaller p 3 and larger p 4. Well, these are 1 and 4 have the same contribution, 2 and 3 have the same contribution, of course reduced. And let us see the signs again, the signs are plus plus minus minus.

So, what we need to do plus plus minus minus and this of course is plus. Therefore, you see that the wave function changes sign from this p 2 orbital to this p 3 orbital carbon 3 p orbital carbon 2 p orbital, therefore the wave function goes through N node. And the plane that separates carbon 1, carbon 2, from carbon 3 and carbon 4 is called a nodal plane ok. What about psi 3, psi 3 has again 1 and 4 larger, so it is a same picture, but 2 and 3 negative.

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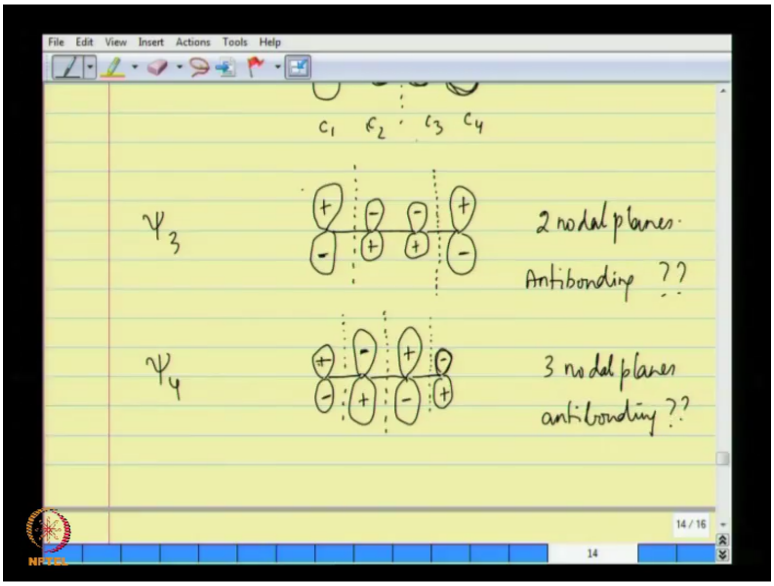

2 nodal planes.
Antibonding ??

3 nodal planes
antibonding ??

So, all that we need to do for psi 3, 1 and 4 larger, 2 and 3 smaller.

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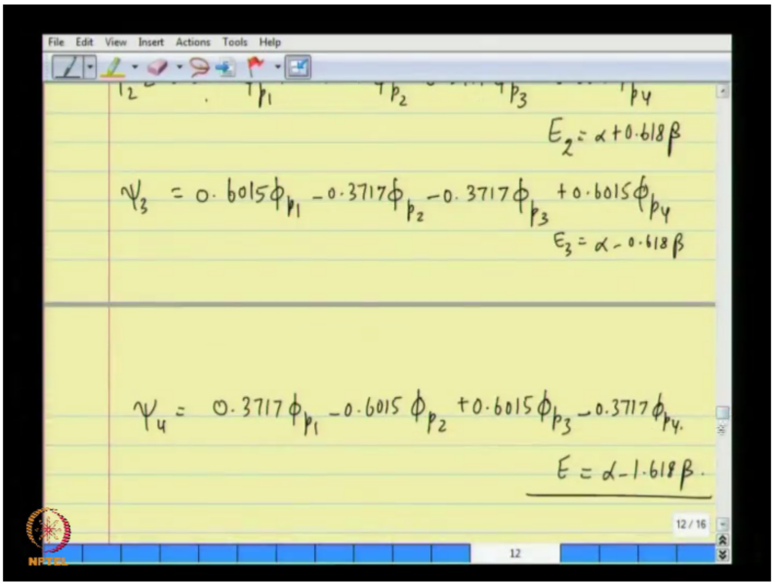

$$E_2 = \alpha + 0.618\beta$$

$$\Psi_3 = 0.6015\phi_{p_1} - 0.3717\phi_{p_2} - 0.3717\phi_{p_3} + 0.6015\phi_{p_4}$$

$$E_3 = \alpha - 0.618\beta$$

$$\Psi_4 = 0.3717\phi_{p_1} - 0.6015\phi_{p_2} + 0.6015\phi_{p_3} - 0.3717\phi_{p_4}.$$

$$\underline{E = \alpha - 1.618\beta.}$$

But, 2 and 3 the way we looked at it what was the negative sign, the sign was 2 and 3 were negative minus and minus. So, if you are looking at the signs here, so if it is minus, 2 is minus, 3 is minus, 1st one is plus, 1st one is plus, 4th one is plus minus of course, minus plus plus. So, you see that there are two nodal planes here, because the orbital is negative throughout between 2 and 3. The probabilities are of course, the squares of them, so we do not need to worry about the probabilities, probabilities will never become negative. So, you have 2 nodal planes ok, psi 3. This is psi 3, psi 4.

So, it sort of tells you that this is clearly bonding, this is less bonding. There is a nodal plane, but still the carbon density is or such that there is symmetric between I mean there is a symmetry of the electron density right reflected from the middle of the c 1, c 2, c 3, c 4 chain, but, what about psi 4.

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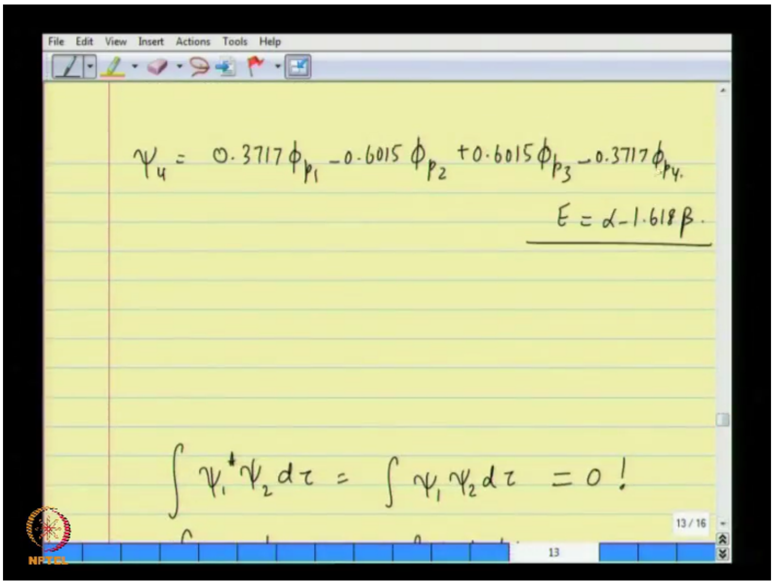

$$\psi_4 = 0.3717\phi_{p_1} - 0.6015\phi_{p_2} + 0.6015\phi_{p_3} - 0.3717\phi_{p_4}.$$

$$\underline{E = \alpha - 1.618\beta.}$$

$$\int \psi_1^* \psi_2 \, d\tau = \int \psi_1 \psi_2 \, d\tau = 0 \, !$$

If you look at psi 4 that has also 2 nodal planes, you see it is 1 smaller, 2 and 3 larger. So, first let us capture that picture 2 and 3 larger, 1 and 4 are smaller. So, 1 let me just draw that 2 and 3 are larger, 1 and 4 are smaller of the same size. And if we look at to the signs, 1, 4 small; 2, 3 large; 2 is negative, 4 is negative.

So, what we have in this picture is 2 we have to mark negative, 4 we have to mark negative and 1 and 4 positive, positive, positive ok. Let us look at that. You see the difference between 3 and 4, there are still 2 nodal planes here, because the orbital changes sign between the carbon 1 and carbon 2, the molecular orbital has the 2 p orbitals with different signs. And there is also a change in sign. I guess there is also a change in sign here plus minus, plus minus, plus minus, 3 nodal planes.

So, clearly this is also anti bonding for this group of four electrons, anti bonding I mean you have to be careful about these phrases. But, the point is that the electrons the four electrons are likely to be in orbital psi 1 and psi 2, or the other reason that psi 1 and psi 2 have the lowest energies. Please remember, alpha and beta are negative.

If alpha and beta are negative, obviously the sum of alpha plus 1.618 beta is negative. And the second orbital is also negative, therefore the two electrons in orbitals being the wave function with the wave function psi 1 and two electrons with the wave function psi 2, so you have all the four electrons in that orbital. So, it is clear that the four electrons are placed accordingly and we also looked at this by way of looking at the Homo-Lumo gap and so on ok. So, you can see that the four psi 1, psi 2, psi 3 are I think I have already done that before, so let me not repeat that here.

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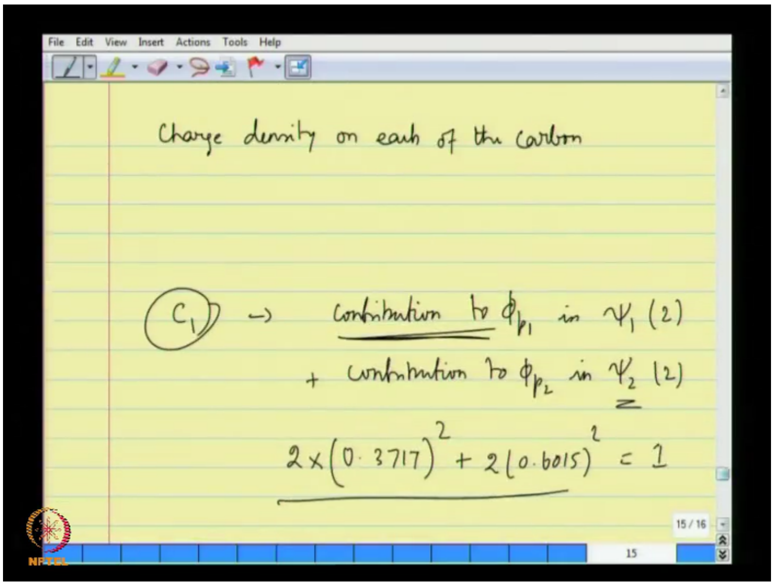

Charge density on each of the carbon

$\boxed{C_1} \rightarrow$ $\underline{\text{contribution to}}\ \phi_{p_1}$ in $\psi_1\ (2)$

$+$ contribution to ϕ_{p_2} in $\underline{\psi_2}\ (2)$

$\underline{2 \times (0.3717)^2 + 2(0.6015)^2 = 1}$

Now, there is one other thing before we move on to the cyclic system, namely what is a charge density on each of the carbon, mean we should have some reason to believe that the electron density all each of the carbon should be the same, otherwise there is going to be differences between the bonding capabilities and the bond lengths perhaps. And in 1, 3-Butadiene, we have only one carbon bond.

So, the charge density the way we calculate the charge density is you look at the wave functions here, these four wave functions. Since, the electrons are there in the first orbital psi 1 and psi 2, but not in the orbital psi 3 and psi 4, the orbital psi 3 and psi 4 would not contribute to the electron density, they are empty orbitals. The orbitals 1 and 2 molecular orbital psi 1 and psi 2 would contribute to the total electron density calculation by how much. If you look at carbon 1 in psi 1, it is 0.3717. So, therefore, the square of this represents the probability that the electron is in phi p 1.

The 0.6015 the square of that represents the probability that the electron inside two molecular orbital is found in phi p 1. Therefore, if you think about carbon 1, the total electron density is the sum of these squares, because these two represent the probabilities of finding the electrons in orbital p 1 corresponding to carbon 1. Due to the fact, that the electrons are either in psi 1 or in psi 2; in this case, both in psi 1 and both in psi 2.

How many electrons, there are two electrons in psi 1, there are two electrons in psi 2. Therefore, the total charge density that you have to calculate, would turn out to being for carbon 1, the contribution to phi p 1 in psi 1 plus the contribution to phi p 1 in psi 2 ok. There are two electrons here, there are two electrons here, the contribution to phi p 1 is the probability square, which is point what was that psi 1 was 0.3717 square, so 0.3717 square.

And since it is to be multiplied by the total number of electrons, which is 2 in this case. And the other for phi psi 2 if you look at it, psi 2 it is 0.6015 square and again two electrons in psi p 2, so it is 2 times 0.6015 square. So, this is the total charge density on each of the carbon in this case carbon 1 is the sum of this. And this is of course, equal to 1. Please remember this is how we got the normalization constant, any one of these square, square, square, square, add them all of it is 1 and that is what you have.

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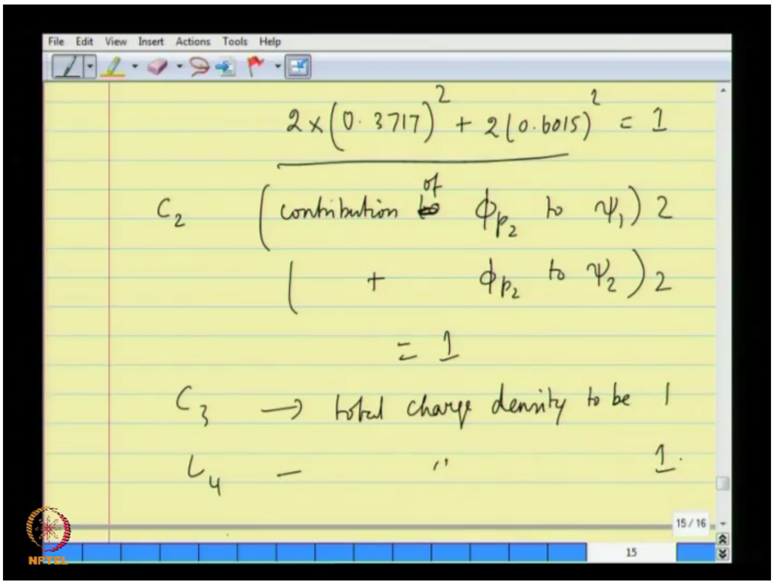

$$2\times(0.3717)^2 + 2(0.6015)^2 = 1$$

C_2 (contribution ~~to~~ of ϕ_{p_2} to ψ_1) 2

(+ ϕ_{p_2} to ψ_2) 2

= 1

$C_3 \rightarrow$ total charge density to be 1

C_4 — " 1.

Likewise, if you calculate the charge density on c 2, it is a contribution. Contribution to phi p 2 contribution of phi p 2 to psi 1 plus contribution of phi p 2 to psi 2 and each of this contribution is multiplied by the total number of electrons in each of these molecular orbital which is 2 and you will find that to be exactly 1. And likewise, for c 3, you will get the total charge density to be 1. And for c 4 also, the total charge density to be 1, which means that on each of the carbon, the total charge density of the electron density if you look at it on each of the carbon is 1, for both these molecular orbitals, which means that there is a homogenization ok.

So, this is another way of understanding what is called the delocalization in terms of the electron charge densities, in terms of placing the orbitals. The orbitals of course, come with the plus minus signs to tell you that these orbitals are orthogonal to each other and they represent the node or anti node character or bonding and anti bonding character, similar to what we did in the case of the hydrogen molecule ion and hydrogen molecule. So, these pictures are very useful. But, to a limited extent and Huckel Huckel molecular orbital theory gives you this very nice way of pictorial pictorially representing the molecular orbital and the electron charge densities. And at a time when of course, computers were not available, at a time when computational power was non-existent and so on.

Today we like to teach Huckel molecular orbital theory for some of the concepts that are introduced in the process. It is not probably as useful as doing a brute force many CPU calculations; it does not matter that is it is important to understand the basic principles of computational chemistry. And Huckel molecular orbital theory is a cornerstone in that sense ok.

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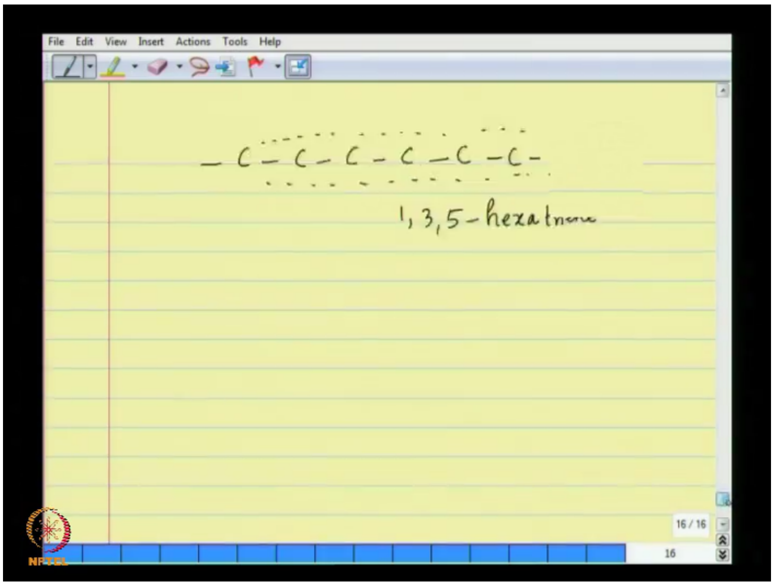

Now, the since we are running out of time, I am going to write the linear chain 1, 3, 5 what is this 1, 3, 5-hexatriene. Very quickly and leave you with the electron density sort of homogenized ok, there is nothing called the plus or minus for the electron density both up and down are the same.

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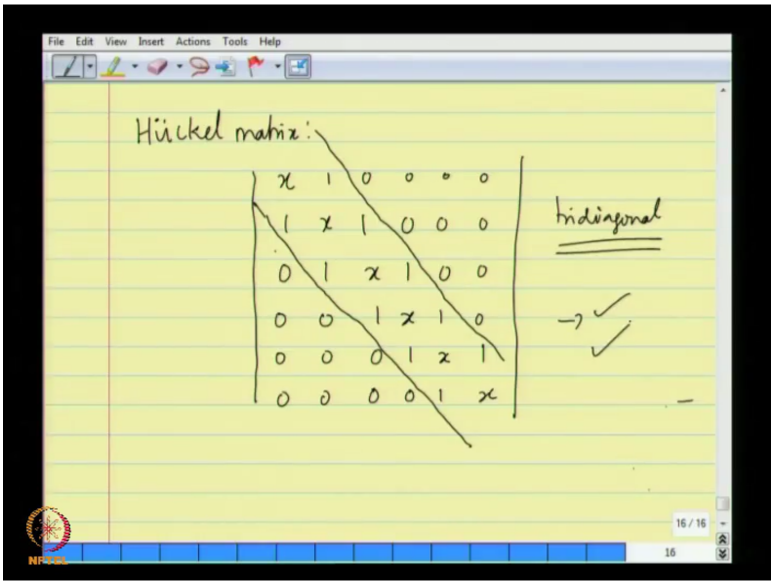

Hückel matrix:

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

tridiagonal

→ ✓

✓

So, if you do that the Huckel matrix as an exercise, I would want you to derive that and let me write the Huckel matrix very quickly, it is x 1 sorry let us go back, it is x 1 0 0 0 0, it is 1 x 1 0 0 0, 0 1 x 1 0 0, 0 0 1 x 1 0, 0 0 0 1 x 1, 0 0 0 0 1 x ok. All these matrices are tridiagonal. Let me just get rid of that. All these matrices are tridiagonal. Let me see if I can draw that line, you can see that one of diagonal here and one of diagonal here ok, tridiagonal matrices eigenvalues can be easily obtained.

There is a general expression for this in textbooks, maybe in the assignment I will give you that expression for you to calculate. But, the energies are known, the eigenvalues are known and you can calculate the charge densities, the same way that we did a few minutes ago, you can also write the wave functions that appear with the plus minus sign depending on how you solve the eigenvectors and so on. Therefore, I leave this problem to you to study the all these aspects as an assignment.

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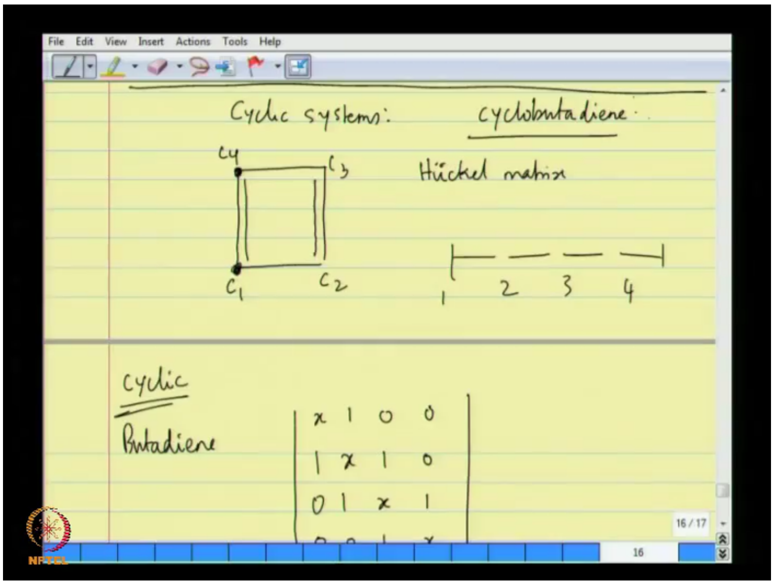
Cyclic systems: cyclobutadiene

Hückel matrix

cyclic Butadiene

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

Now, let us get to the other important aspect, namely the cyclic systems. And we will start with the aromatic sorry, we will start with the first system, namely cyclobutadiene cyclic systems cyclobutadiene. Picture, 4 carbons and now you cannot tell which is 1, which is 2, which is 3, which is 4. In a linear chain, you had terminal carbons and you had carbons in the middle. So, a numbering makes made sense, here my 1, 2, 3 can be your 2, 3, 4, 1 and so on. The point is that with one label, we will see that the Hamiltonian matrix, the Huckel matrix has just a small variation from the butadiene matrix.

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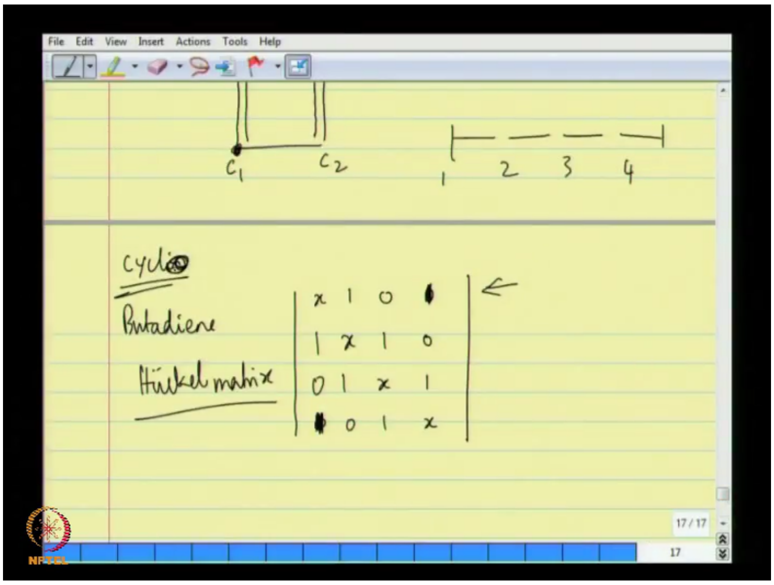

cycl Butadiene

Hückel matrix

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

The butadiene matrix if you remember is x 1 0 0, 1 x 1 0, 0 1 x 1, 0 0 1 x, this is for butadiene. Now, cyclic butadiene you see that the atom 1 carbon 1 p orbital and carbon 4 p orbitals are adjacent and therefore the 1, 4 which was not there in the linear chain, because they were far away this is 1, 2, 3, 4. The 1, 4 linear chain, now since it is a cyclic chain, you have 1, 4 which also contributes a beta term and therefore this is 1 for cyclic butadiene. And likewise, for 4 atom 4, it is 1 that is all there is a difference the Huckel matrix.

So, from any linear chain through a cyclic chain cyclic system when you go in, the end to end bonding we will ensure that the terminal carbons what you called as a terminal carbons in a linear chain, now we will have a hij matrix element, h1n, hn1 matrix element. Inside nothing else changes, all the other things are exactly what you had in the linear chain. Therefore, this is the only difference between the butadiene and cyclic butadiene and cyclobutadiene sorry cyclobutadiene. (Refer Time: 25:15) what I said here, I have said that yes.

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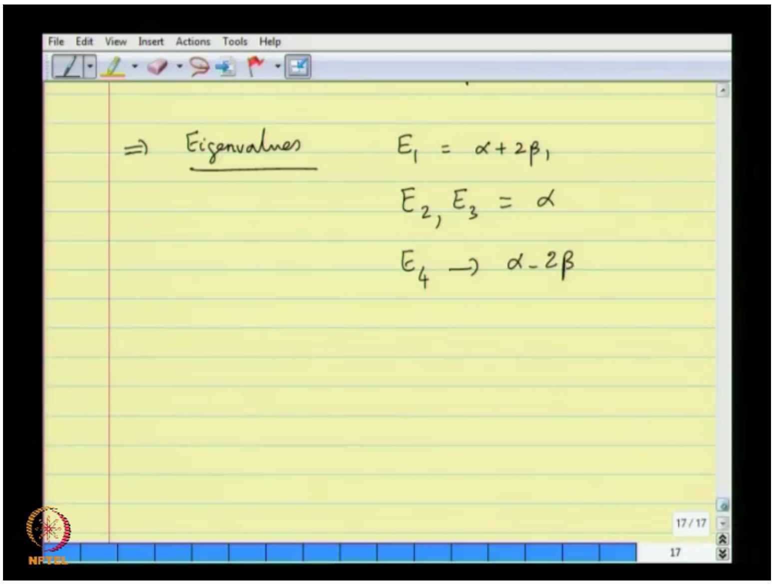

⇒ Eigenvalues

$E_1 = \alpha + 2\beta,$

$E_2, E_3 = \alpha$

$E_4 \rightarrow \alpha - 2\beta$

So, in the cyclic system you have that and its eigenvalues can be written down. So, the eigenvalues for cyclobutadiene when you solve this, basically you are going to expand to this determinant and get the values, the eigenvalues will turn out to be E 1 is alpha plus 2 beta. E 2 and E 3 will be alpha, it is a degenerate system. And E 4 will be alpha minus 2 beta ok.

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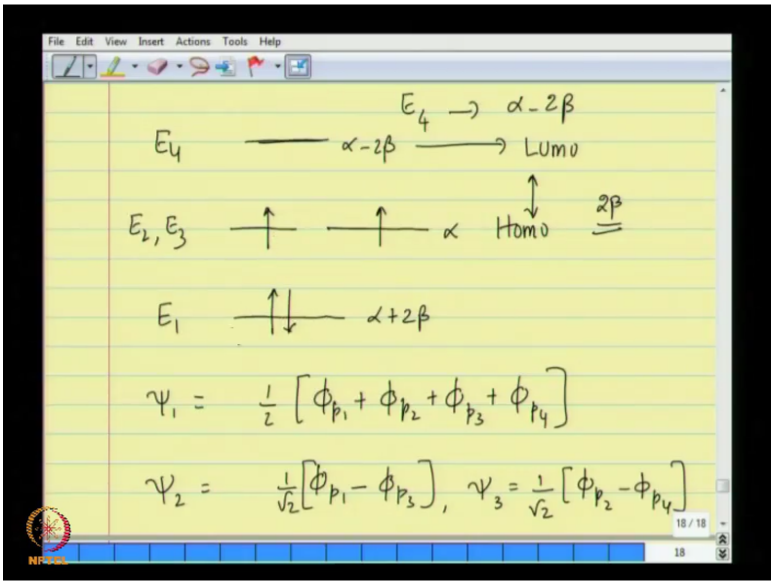

$E_4 \rightarrow \alpha - 2\beta$

E_4 ——— $\alpha - 2\beta \longrightarrow$ Lumo

$\updownarrow$ $\underline{\underline{2\beta}}$

E_2, E_3 $\uparrow$ $\uparrow$ α Homo

E_1 $\uparrow\downarrow$ $\alpha + 2\beta$

$$\psi_1 = \frac{1}{2}\left[\phi_{p_1} + \phi_{p_2} + \phi_{p_3} + \phi_{p_4}\right]$$

$$\psi_2 = \frac{1}{\sqrt{2}}\left[\phi_{p_1} - \phi_{p_3}\right], \quad \psi_3 = \frac{1}{\sqrt{2}}\left[\phi_{p_2} - \phi_{p_4}\right]$$

So, if you draw the molecular orbitals for the energies E 1, this is alpha plus 2 beta and then you have alpha, which is doubly degenerate. So, it is E 2, E 3, this is alpha. And the number of electrons that we can assign as for the ground state alpha plus 2 beta two electrons and because it is degenerate, the spin is supposed to be such that they are unpaired. And then we have E 4, which is given by alpha minus 2 beta.

And therefore, you see that the Homo-Lumo gap, this is the highest occupied molecular orbital and this is the lowest unoccupied molecular orbital. The Homo-Lumo gap is obviously, 2 beta ok. What are the wave functions the Eigen functions for this system, psi 1 is 1 by 2 phi p 1 plus phi p 2 plus phi p 3 plus phi p 4 ok.

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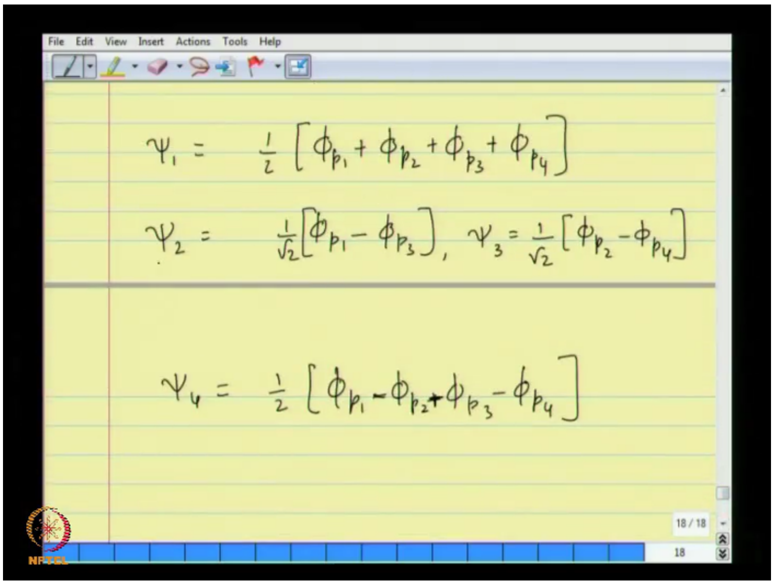

$$\psi_1 = \frac{1}{2}\left[\phi_{p_1} + \phi_{p_2} + \phi_{p_3} + \phi_{p_4}\right]$$

$$\psi_2 = \frac{1}{\sqrt{2}}\left[\phi_{p_1} - \phi_{p_3}\right], \quad \psi_3 = \frac{1}{\sqrt{2}}\left[\phi_{p_2} - \phi_{p_4}\right]$$

$$\psi_4 = \frac{1}{2}\left[\phi_{p_1} - \phi_{p_2} + \phi_{p_3} - \phi_{p_4}\right]$$

Then psi 2, there are two ways of doing it psi 2 and psi 3. In principle if we do a symmetry group analysis, we will end up getting the 1 by 2 with the two positive signs and two negative signs and there are four such combinations that is one way. But, let me do the other way around, which is right to the psi 2 as 1 by root 2 phi p 1 minus phi p 3, and psi 3 which is degenerate to psi 2 will have the other 1 by root 2 phi p 2 minus phi p 4. I will tell you in a minute, what this leads to. And psi 4 is of course, you have 1 by 2 times phi p 1 minus phi p 2 minus phi p 3 and by plus phi p 4 I think sorry minus plus minus sorry, it is minus phi p 4.

Well, the reason why we chose this instead of taking the four linear combinations all the four orbitals is pedantic in this case of course, because you see that psi 2 and psi 3 correspond to regenerate orbitals. And if you are talking about degenerate systems the two wave functions corresponding to degenerate systems, any linear combination of those two wave functions is also an Eigen function of the same Hamiltonian.

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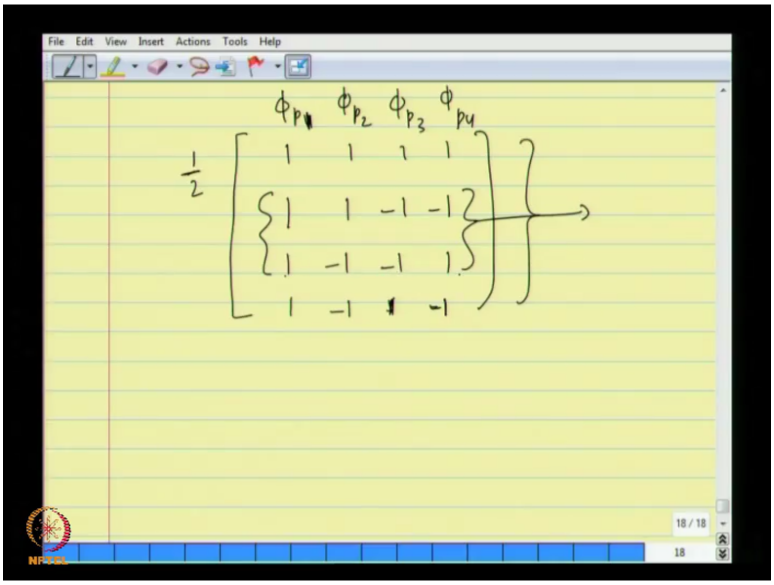

$$\frac{1}{2}\left[\begin{array}{cccc} \phi_{p1} & \phi_{p2} & \phi_{p3} & \phi_{p4} \\ 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 \end{array}\right]$$

Therefore, in principle, you can have the all the four orbitals with the plus minus signs done in such a way that if I write a coefficients of 1 by 2 outside with 1 1 1 1 and these are the weights are given to the orbitals phi p 3, phi p 4. Then in principle, I can have 1 1 minus 1 minus 1 1 minus 1 minus 1 1 1 minus 1 by 1 minus 1. Now, you saw that it is all 1 by 2 multiplied, so this is also a possible way of writing the cyclobutadiene sorry the atomic the molecular orbitals with the contributions of phi p 1, phi p 2 etcetera.

The Eigen functions in this case because of the degeneracy can be represented in multiple ways ok. And one way is that contribution phi p 1 minus phi p 3 and the contribution phi p 2 minus phi p 4 corresponding to E 2. And the other way is that the contribution like this phi p 1 plus phi p 2 minus phi p 3 minus phi p 4 multiplied by 1 by 2. And likewise, phi p 1 minus phi p 2 minus phi p 3 plus phi p 4 all multiplied by 1 by 2, it does not matter. What is important is that the Eigen functions are such that the electron densities when you calculate on each of the carbon, they will all turn out to be the same ok.

Now, the only difference that you have to keep in mind is that the electrons are now contributed the electrons contribute differently. For example, the wave function psi 1 has 2 electrons associated with that and the wave function psi 2 and psi 3 have 1 electron each associated with that. And therefore if you are looking at the carbon 1 electron density you have to multiply the coefficient of phi p 1 on psi 1 squared coefficient squared by 2, because there are 2 electrons in psi 1 and the psi 2 and psi 3 contributing 1 electron you have to multiply the corresponding coefficient squared by just 1.

So, here for example if you do that it is 1 by 4 multiplied by 2 and 1 by root 2 squared multiplied by 1. The psi 3 does not have any phi p 1. Therefore, you will have 1 by 2 plus 1 by 2, which is 1, so the electron density is still turns out to be the 1. Ultimately, it is the electron density and it is a properties which are important the wave functions are such that the square of the wave functions have the meanings of probability interpretations.

The signs of the wave functions are important in determining bonding anti bonding kind of a concept, but the coefficients themselves do not have any other interpretation it is there squares. And therefore, the signs and linear combinations can be chosen conveniently ok, so this is for cyclobutadiene. Let us, go quickly to benzene and finish this part of the lecture and leave you to study Huckel molecular orbital theory in more detail on your own ok.

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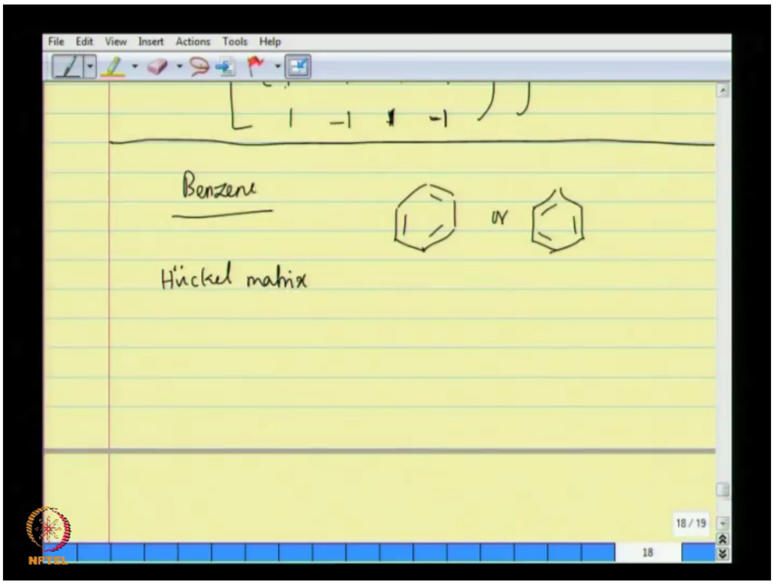

$[\ 1 \quad -1 \quad 1 \quad -1\ )\ )$

Benzene

or

Hückel matrix

Let us, do benzene 6 carbons or your original kekule structures whichever it is. We know in molecular orbital picture or in the quantum mechanics that we cannot distinguish between these carbons. The Huckel matrix now is the same. Starting matrix like what we had earlier for the tri diagonal matrix for the 1, 3, 5 cyclo sorry 1, 3, 5 hexatriene except to that we are going to add the 2 terminal proportions 1, 6 and 6, 1, 2, 1 ok.

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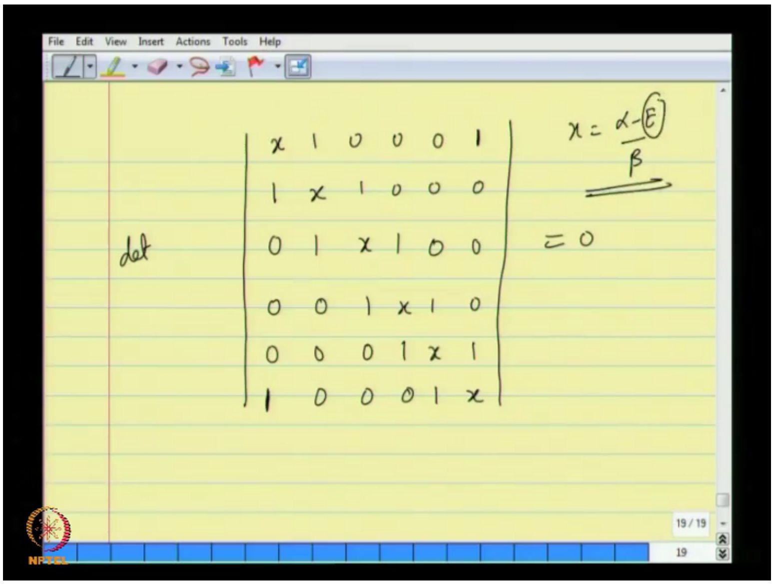

$$\det \begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

$$\underline{\underline{x = \frac{\alpha - \boxed{E}}{\beta}}}$$

So, what is the Huckel matrix, therefore for benzene it is x 1 0 0 0 1, because the 6 carbon is bonded to carbon 1. Then you have 1 x 1 0 0 0, 1 x 1 these things do not change the near neighbors are only the 2 neighbors on either side 0 1 x 1 0, 0 0 0 1 x 1 and now on the sixth row you have 1 here 0 0 0 1 x ok. This is the determinant that you want to set. And remember, x is equal to alpha minus E by beta. So, the energy E is there.

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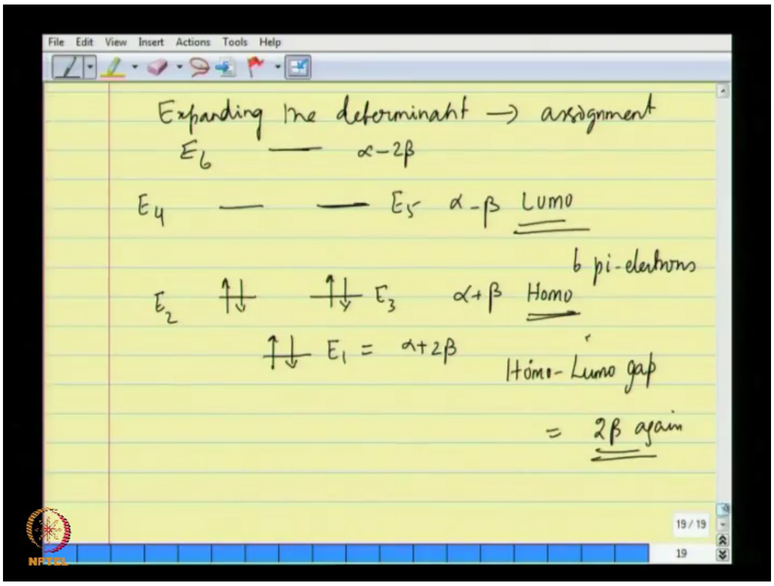

Expanding the determinant → assignment

E_6 — $\alpha - 2\beta$

E_4 — — E_5 $\alpha - \beta$ Lumo

6 pi-electrons

E_2 ↑↓ ↑↓ E_3 $\alpha + \beta$ Homo

↑↓ $E_1 = \alpha + 2\beta$

Homo-Lumo gap

= 2β again

What are the solutions ok? I expanding this determinant is your first time and obtaining the secular equation it is an assignment please do it. And the answer that we get for benzene let me write down the answers. We get again 2 degenerate states. In fact, there is a general theorem that when the molecule has a symmetry of more than a certain type on rotational axis, it will have degenerate states, but those are all things we will do when we go to group theory.

Right now, the four these four energy levels that we find with the degeneracies are E 1 is alpha plus 2 beta the lowest energy E 2 and E 3 is alpha plus beta E 4 E 5 is alpha minus beta. And E 6 is alpha minus 2 beta. And there are 6 pi electrons. So, assigning them carefully will give rise to this picture that we have 6 electrons in the first 3 orbitals and this is the highest occupied molecular orbital. And this is the lowest unoccupied molecular orbital. And therefore, you see that the delta E the Homo-Lumo gap is 2 beta again.

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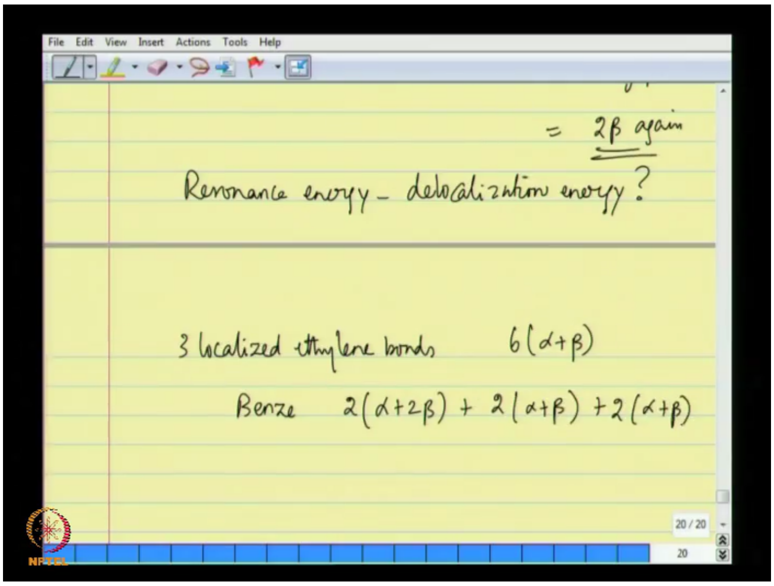

$= \underline{\underline{2\beta \text{ again}}}$

Resonance energy - delocalization energy?

3 localized ethylene bonds $6(\alpha+\beta)$

Benze $2(\alpha+2\beta) + 2(\alpha+\beta) + 2(\alpha+\beta)$

What is the resonance energy or delocalization energy? The difference between the energies of the 6 electrons minus the energies of the 6 electrons assuming that bonds are the double bonds are localized. So, if you calculate that the in the case of ethylene if you remember, the resonance energy 3 localized ethylene bonds is going to give you 6 into alpha plus beta. And benzene you have 2 electrons in alpha plus 2 beta 2 electrons in alpha minus plus beta and 2 electrons in alpha plus beta; so, alpha plus 2 beta. So, if you look at it, the difference between these two is again 4 plus 2 plus 8 beta this is 6 beta the alphas cancel out resonance energy is 2 beta.

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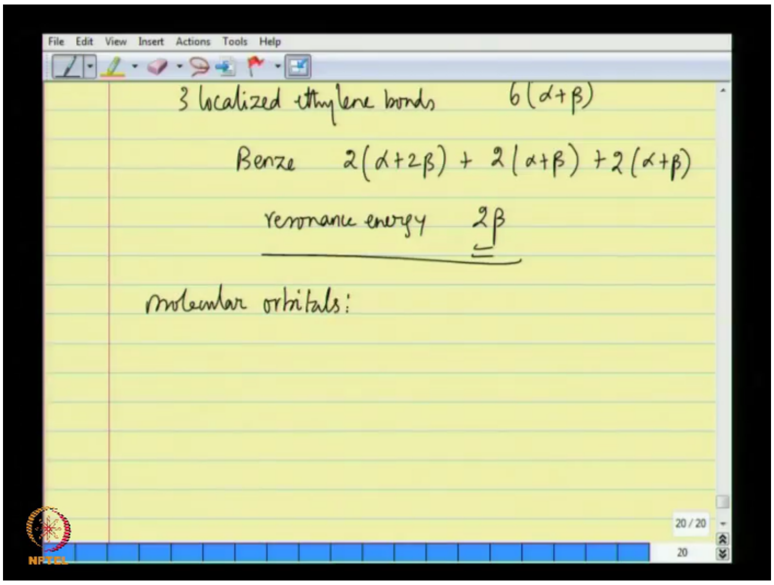

3 localized ethylene bonds $6(\alpha+\beta)$

Benze $2(\alpha+2\beta) + 2(\alpha+\beta) + 2(\alpha+\beta)$

resonance energy $\underline{\underline{2\beta}}$

molecular orbitals:

So, what about the molecular orbitals for benzene the expressions are long, but let me write them down.

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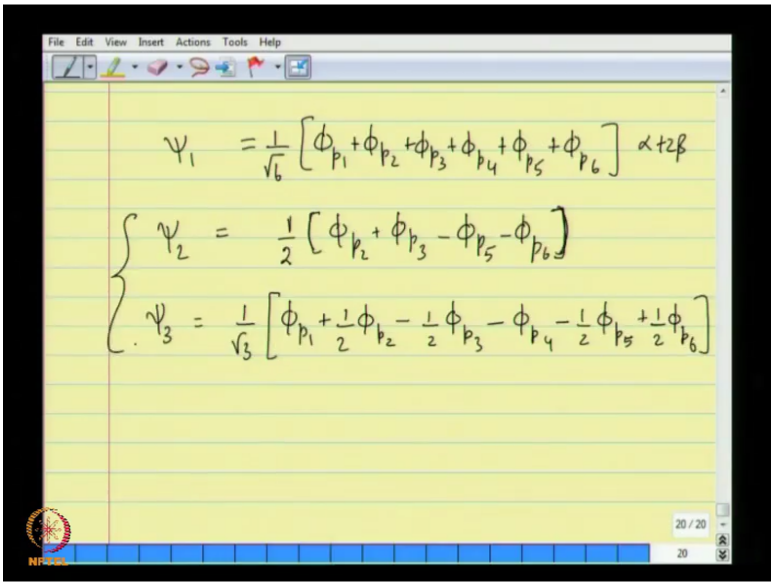

$$\psi_1 = \frac{1}{\sqrt{6}}\left[\phi_{p_1}+\phi_{p_2}+\phi_{p_3}+\phi_{p_4}+\phi_{p_5}+\phi_{p_6}\right] \quad \alpha+2\beta$$

$$\left\{\begin{array}{l} \psi_2 = \frac{1}{2}\left[\phi_{p_2}+\phi_{p_3}-\phi_{p_5}-\phi_{p_6}\right] \\ \psi_3 = \frac{1}{\sqrt{3}}\left[\phi_{p_1}+\frac{1}{2}\phi_{p_2}-\frac{1}{2}\phi_{p_3}-\phi_{p_4}-\frac{1}{2}\phi_{p_5}+\frac{1}{2}\phi_{p_6}\right] \end{array}\right.$$

Psi 1 which has the energy alpha plus 2 beta is 1 by root 6 very symmetric phi p 1 plus phi p 2 plus phi p 3 plus phi p 4 plus phi p 5 plus phi p 6. It is normalized you can see that the contributions of the individual orbitals phi p 1 square phi p 2 square each 1 is normalized. And therefore, psi 1 star psi 1 deta if you do that and neglect the overlap which we did in the Huckel molecular orbital theory it is 1 by 6 multiplied by 6 and therefore the wave function is normalized to 1. What are the other 5 orbitals let me quickly write them down and also write the pictures of some of them to give you an idea of what are the nodal planes and the and so on.

So, let us look at psi 2 it is 1 by it is 1 by 2 phi p 2 plus phi p 3 minus phi p 4 phi p 5 minus 5 p 6. Psi 3 is 1 by root 3 times phi p 1 plus 1 by 2 phi p 2 minus 1 by 2 phi p 3 minus phi p 4 minus 1 by 2 phi p 5 plus 1 by 2 phi p 6 ok. These are both are degenerate orbitals. And therefore, in principle 2 orthogonal linear combinations of these two will also form the corresponding molecular orbital.

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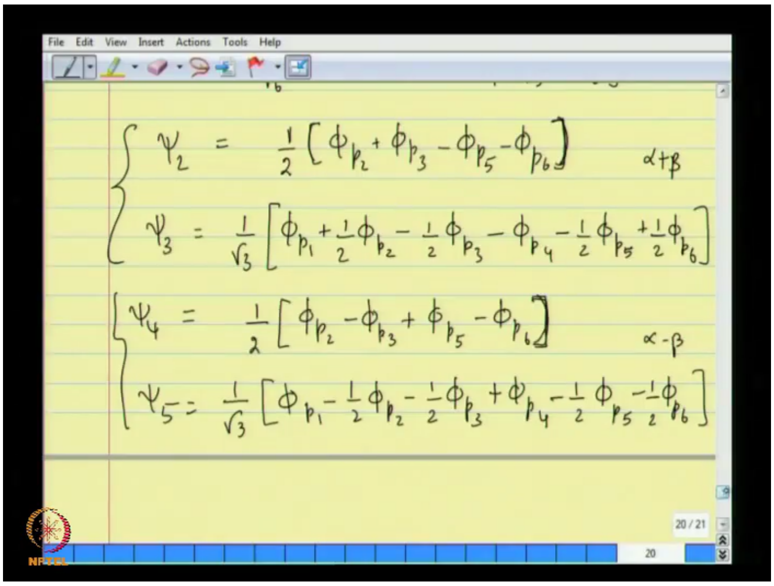

$$\psi_2 = \frac{1}{2}\left[\phi_{p_2} + \phi_{p_3} - \phi_{p_5} - \phi_{p_6}\right] \qquad \alpha+\beta$$

$$\psi_3 = \frac{1}{\sqrt{3}}\left[\phi_{p_1} + \frac{1}{2}\phi_{p_2} - \frac{1}{2}\phi_{p_3} - \phi_{p_4} - \frac{1}{2}\phi_{p_5} + \frac{1}{2}\phi_{p_6}\right]$$

$$\psi_4 = \frac{1}{2}\left[\phi_{p_2} - \phi_{p_3} + \phi_{p_5} - \phi_{p_6}\right] \qquad \alpha-\beta$$

$$\psi_5 = \frac{1}{\sqrt{3}}\left[\phi_{p_1} - \frac{1}{2}\phi_{p_2} - \frac{1}{2}\phi_{p_3} + \phi_{p_4} - \frac{1}{2}\phi_{p_5} - \frac{1}{2}\phi_{p_6}\right]$$

Psi 4 is you can write from psi 2 it is 1 by 2 times phi p 2 minus phi p 3 plus phi p 5 minus phi p 6 ok. psi 5 is also written from the orbital psi 3 1 by root 5 phi p 1 minus 1 by 2 phi p 2 minus 1 by 2 phi p 3 plus 1 by 4 1 by 2 sorry plus phi p 4 minus 1 by 2 phi p 5 minus 1 by 2 phi p 6. And these two are the degenerate orbitals with the energy alpha minus beta these are with the orbital energies alpha plus beta.

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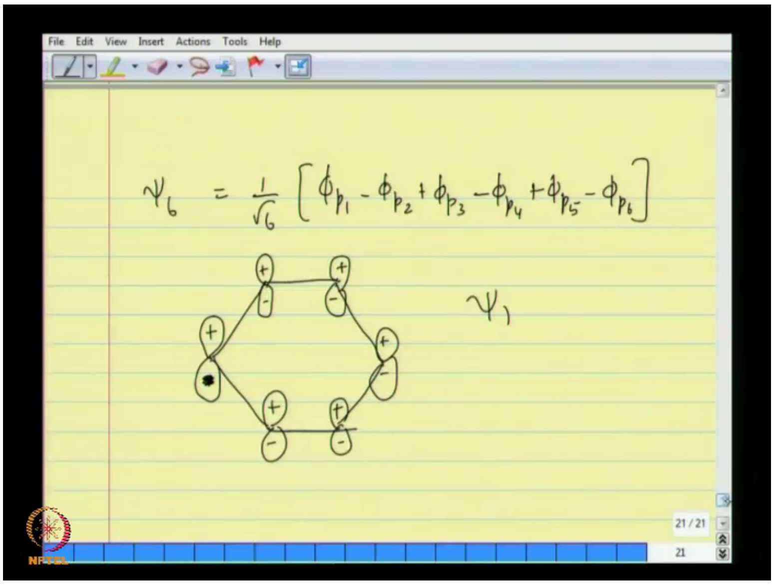

$$\psi_6 = \frac{1}{\sqrt{6}}\left[\phi_{p_1} - \phi_{p_2} + \phi_{p_3} - \phi_{p_4} + \phi_{p_5} - \phi_{p_6}\right]$$

And the last one psi 6 is obtained from psi 1 with alternate minus signs namely phi p 1 minus phi p 2 plus phi p 3 minus phi p 4 plus phi p 5 minus phi p 6. So, now, if we look at the orbitals on the ring, psi 1 essentially means all the orbitals are plus minus all of them or in the same phase plus minus plus minus, no nodal plane. The electron density is such that it does not go through any the electron wave function is such that it does not go through any 0s between the p orbitals.

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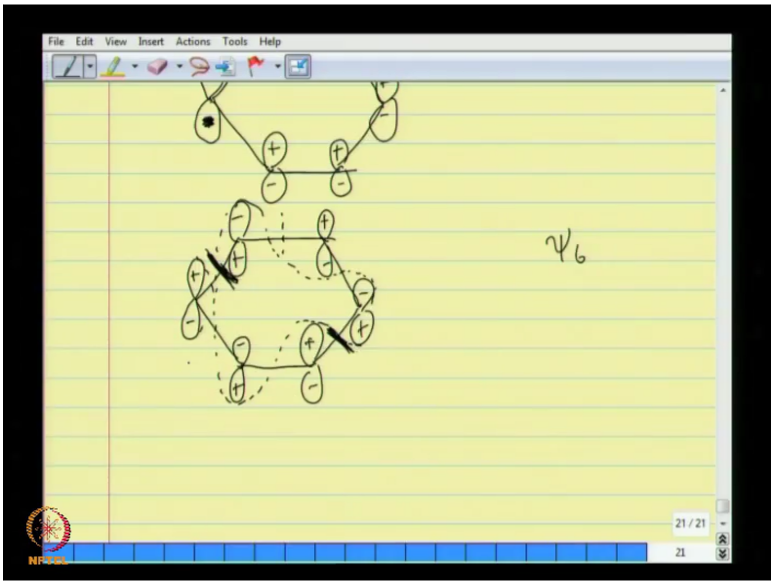

What about psi 6 which is also easy to draw, because the carbon p orbitals every alternate p orbital is of the same sign. So, you have plus minus, plus minus and plus minus. And the other three are negative combinations minus plus, minus plus, minus plus ok. Now, you can see that there is a nodal plane here the orbital sort of goes through and it goes through a nodal plane here. And again, it goes through a nodal plane, you can see that plus minus, plus plus and goes through that you can see that it sort of goes down here.

So, you see that there are plus minus there is a nodal plane that is a nodal plane, there are only three planes, because you can see that this nodal plane is exactly the in a in a symmetric system, these two this is one nodal plane, these two is another nodal plane and these two is another nodal plane. So, you have your way of looking at pictorially the 6 molecular orbitals of the benzene. And also look at the charge densities on all the 6 carbons, if you calculate it by the way I did namely take each molecular orbital determine the square of the coefficient corresponding to the carbon p orbital multiplied by the number of electrons that orbital has and add them all up for all the molecular orbitals for that single carbon atom. If you add them all up, you get answer 1.

We have done that earlier and you repeat this exercise to verify for yourself that the theory gives you uniform electron density and all the 6 carbons ok. So, Huckel molecular orbital theory is a very beautiful approximate theory. Please remember that these things were discussed I mean developed long before the computers were discovered and computers were invented and computational calculations were done.

The Linear combination of this kind of atomic orbitals to form the molecular orbital there is an entirely different approach based on the point group symmetry of these molecules where due to the irreducible representations of the fine groups or based on them we can in fact construct some of these linear combinations. You will see that the results are exactly the same that is a different way of doing it often people think that that is a more elegant way of doing it, but elegance is not a question I mean it is it is a question of one’s own viewpoint.

Ultimately, we should be able to compute the molecular orbital, we should be able to calculate the energies and compare them with the experiments in order to do this in a meaningful way that theory and experiments corroborate each other. Therefore, in that sense I would say the Huckel molecular orbital theory is a very good starting point for a large number of systems to be studied in organic chemistry. And I will not deal with this any further an extended molecular orbital approach may be given later in an advanced series of lectures until then.

Thank you very much.