Chemistry Atomic Structure and Chemical Bonding
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Lecture - 52
Huckel Molecular Orbital Theory 1

Welcome back to the lectures in Chemistry and 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 this and probably part of next lecture, we would look at one of the successful approximate theories for chemical bonding and particularly for the for accounting for the pi electrons in conjugated systems. We shall look at simple aromatic and aliphatic systems, but systems with alternate single and double bonds.

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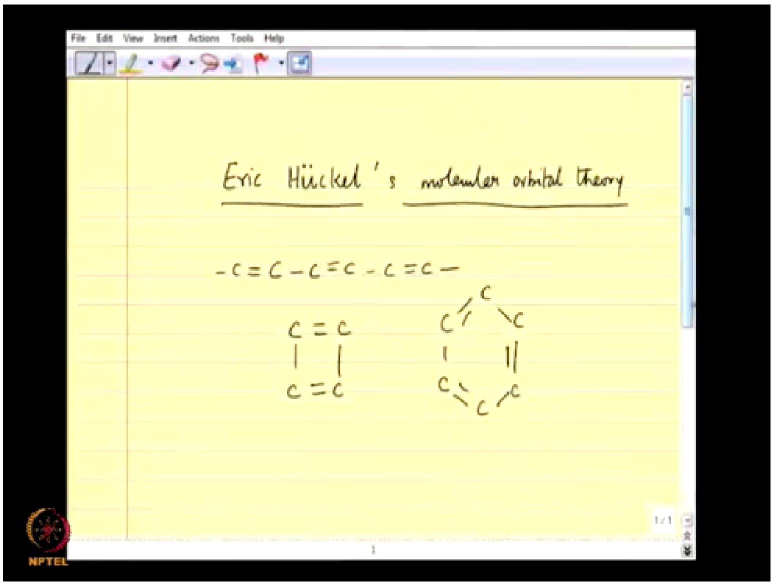

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And how an approximation method first put forward by Prof. Eric Huckel in the yearly 1930s explains the basic concepts of aromaticity and the stabilization due to the delocalization of the electron, cloud and so on. So, we shall look at the Huckel's molecular orbital theory. The systems that we want to study or systems which are either acyclic, but alternate singled and the double bonds this type or ring types such as cyclobutadiene or benzene with alternate bonds.

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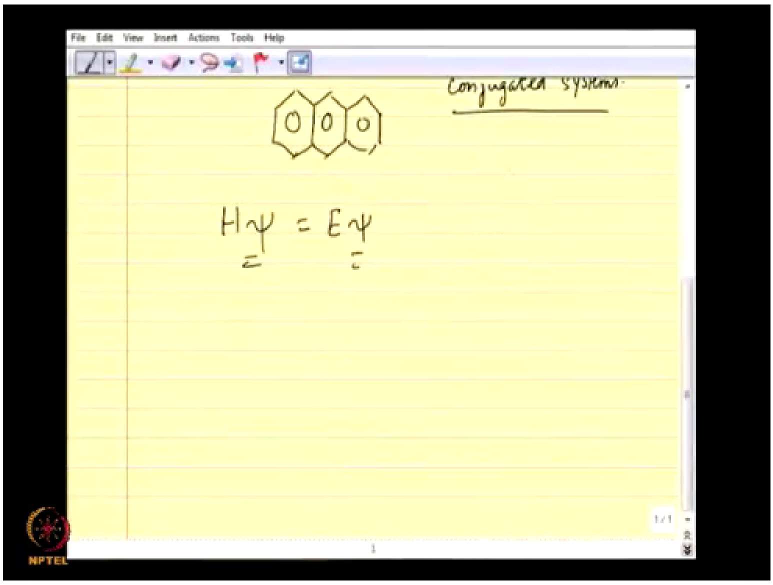

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And the whole family of aromatic hydro carbons phenolphthalein anthracene, of course this is what we are used to writing, but we will see how the pi electron concept is used to understand some of the bonding particularly the pi bonding that we see in these alternate in conjugate alternate double bond single bond systems mainly conjugated systems. Of course, one would try to solve the same equation like the Schrodinger equation for such large system h psi is equal to E psi. But, we since we are looking at only the resonance energy and the concept of pi bonds and the molecular orbital is formed from the pi bonds. We are sort of localizing our picture to the pi orbitals or the p orbitals associated with the conjugated systems.

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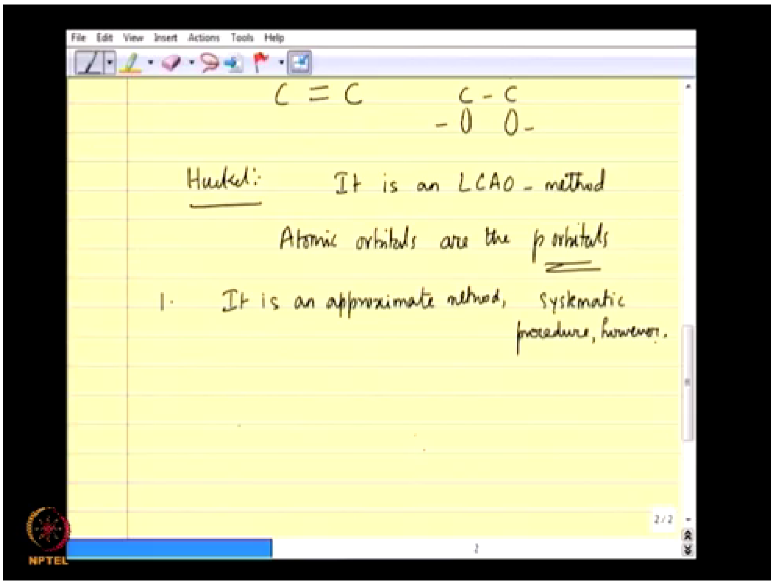

$C = C$ $C - C$

Huckel: It is an LCAO - method

Atomic orbitals are the p orbitals

1. It is an approximate method, systematic procedure, however.

So, if you start with for example two carbons there is no conjugation here, but there is a pi bond, of course but we can think about is the carbon with one of a p orbital plus minus and another p orbital plus minus or minus plus we will find out that there two possible states. And the bonding here the pi orbital bonding can be understood in a very simple manner by certain approximation first put forward by Huckel.

The atomic orbitals it is essentially linear combination of a atomic orbitals approach. It is an LCAO method. And the atomic orbitals that we use for this purpose are the p orbitals. The linear combination is the appropriate linear combination and if we involve 2 p orbitals, it is possible for us to get two linear combinations which are orthogonal to each other. If we use 3 p orbitals for a cyclic system or a linear system, then what we have is 3 orthogonal molecular orbitals. And likewise n atomic orbitals will give you n orthogonal molecular orbitals ok.

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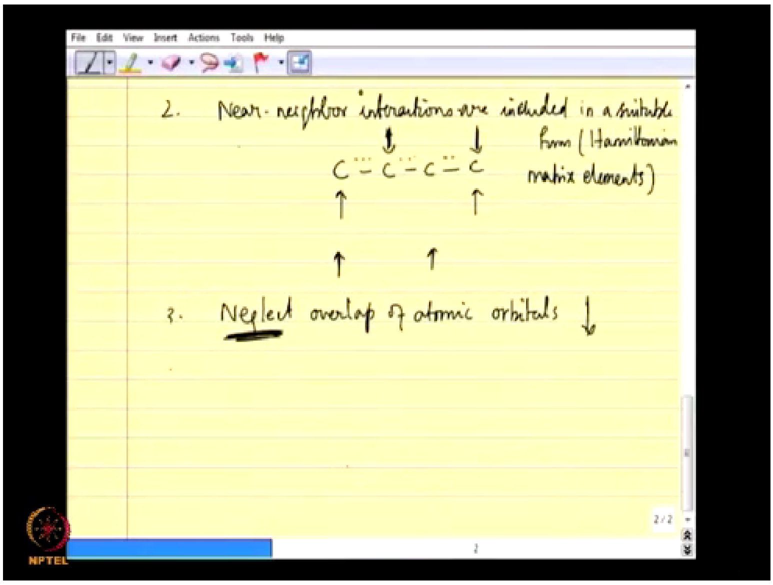

2. Near-neighbor interactions are included in a suitable form (Hamiltonian matrix elements)

3. Neglect overlap of atomic orbitals

So, let us start with the basic picture namely it is an approximate method, but a systematic procedure we worry only about near neighbor interactions that is if you are looking at systems like this for the partial bonds, the interactions between carbons which are separated by more than 1 carbon in between we do not worry about them we neglect to them. And how we do that is we will see that in the Hamiltonian matrix that we setup, we make some of the Hamiltonian matrix elements 0 and we retain only some other Hamiltonian matrix elements. And not only 1 3, but also 1 4 either this or this both we neglect as well as the interactions between this carbon and this carbon for example, ok.

So, near neighbor interaction alone are included in a suitable form basically Hamiltonian matrix elements, neglect overlap of atomic orbitals neglect. The magnitude of the overlap is sufficiently small that we do not need to consider the overlap in the calculation for the energies. We assume that the overlap is actually 0 then there is a problem with chemical bonding, because we do think that the chemical bonding is due to the overlap between these orbitals and the due to the exchange of the electron density between these different orbitals.

Therefore, strictly stating that the overlap integral is assumed to be zero is incorrect ok. What we say is that the overlap integrals are sufficiently small that we do not have to consider that in the calculation stating something is 0 is different from stating something is close to 0 and that will be neglect. So, we have to be very careful about that here ok. And the rest is we will do the algebra now ok.

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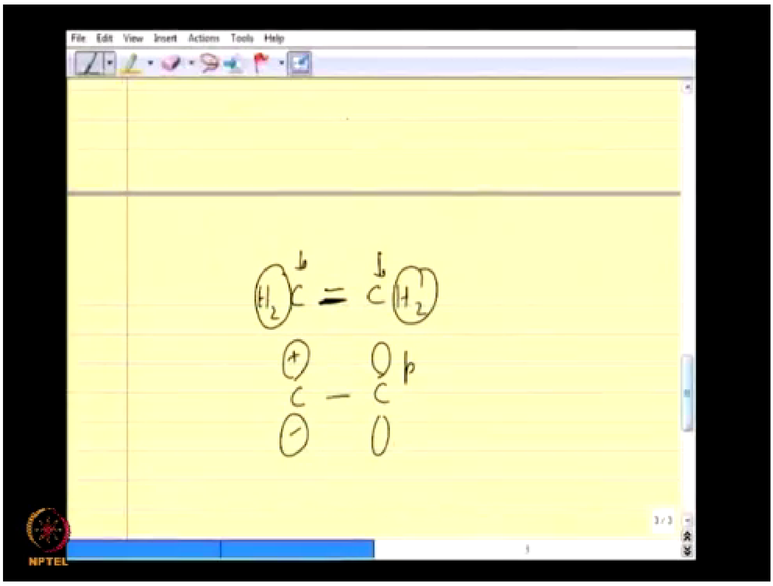

So, let us start with a simple bonding system like the ethylene C double bond C. And for the time being I will not worry about the strong bond that we have it is through the hybridization we have already seen that. What we need to worry about of course there are 2 hydrogens here, 2 hydrogens here. We also neglect the influence of these hydrogens on this carbon. And what we do is to start with a p orbital on this carbon a p orbital on this carbon I would not write the plus minus at this point of time, but in 1 it is enough to identify the direction.

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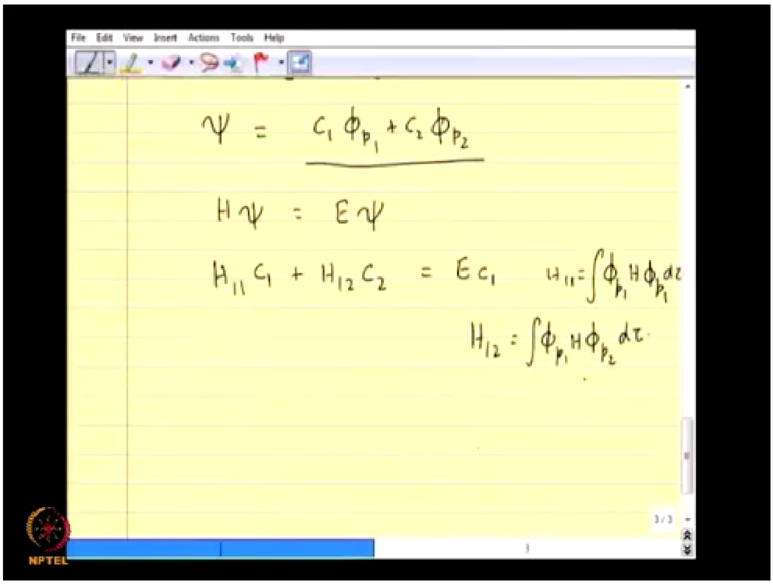

$$\psi = \underline{C_1\phi_{p_1} + C_2\phi_{p_2}}$$

$$H\psi = E\psi$$

$$H_{11}C_1 + H_{12}C_2 = EC_1 \qquad H_{11} = \int \phi_{p_1} H \phi_{p_1} d\tau$$

$$H_{12} = \int \phi_{p_1} H \phi_{p_2} d\tau$$

Now, the combination that we proposed for solving this system using the approximate procedure is that we write psi is equal to C 1 phi p 1 this is carbon 1 and this is carbon 2 plus C 2 phi p 2 ok. So, this is the molecular orbital proposed with the co efficient C 1 and C 2 and we solve this equation h psi is equal to E psi ok. If we want to solve this as matrix form, we have to setup the co efficient matrices namely H 11 C 1 plus H 1 2 C 2 is equal to E C 1, where H 11 is integral phi p 1 the Hamiltonian phi p 1 d tau and h 1 2 is the integral phi p 1 h phi p 2 d tau.

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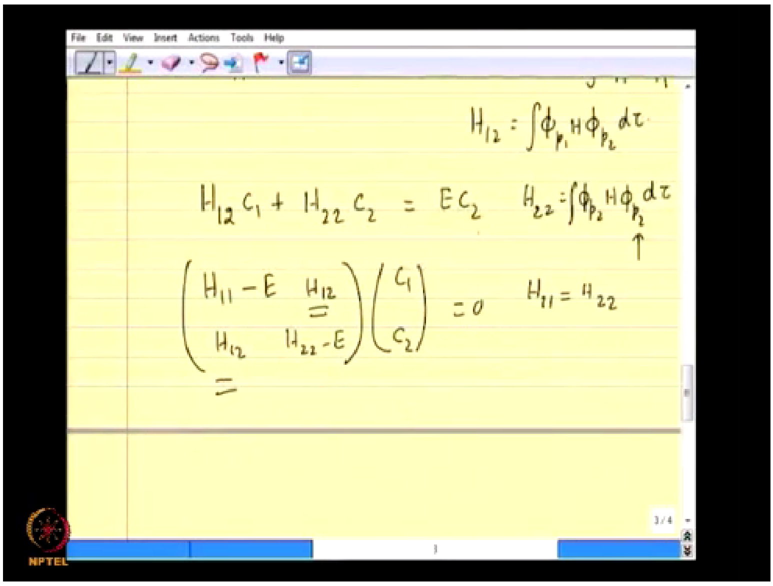

$$H_{12} = \int \phi_{p_1} H \phi_{p_2} d\tau$$

$$H_{12}C_1 + H_{22}C_2 = EC_2 \qquad H_{22} = \int \phi_{p_2} H \phi_{p_2} d\tau \uparrow$$

$$\begin{pmatrix} H_{11} - E & \underline{\underline{H_{12}}} \\ \underline{\underline{H_{12}}} & H_{22} - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0 \qquad H_{11} = H_{22}$$

So, in general H i j will involve the phi p i and H i p j, but here we are talking about 2 carbons. And the other equation is, of course H 12 C 1 plus H 2 2 C 2 is equal to E C 2 ok. So, this is easily derived from whatever you have studied so far. Therefore, the Hamiltonian matrix that we are looking at is H 11 minus E H 1 2, H 1 2 H 2 2 minus E times C 1 C 2 is 0 ok. Now, it is also easy to see that the p orbitals are associated with carbon 1 and carbon 2 are identical for that atom.

And therefore the Hamiltonian matrix elements between the p orbital the Hamiltonian and the same p orbital is going to be the same whether it is carbon 1 or carbon 2. So, H 1 1 and H 2 2 which is written as phi p 2 H phi p 2 d tau integral of over the coordinates of phi p 2 of the electron of phi 2, if you do that you see H 11 is equal to H 2 2 ok. And since the Hamiltonian is Hermitian and this we are only worried about real coefficients, it is also symmetric.

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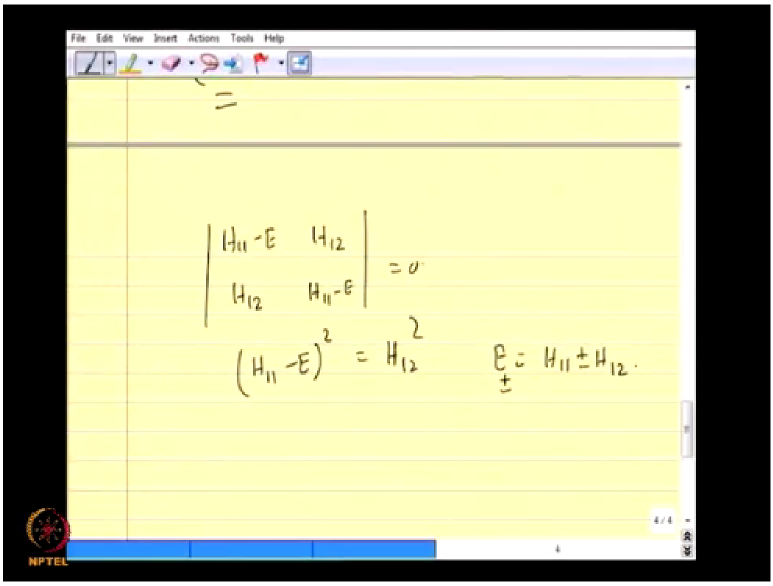

$=$

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{12} & H_{11}-E \end{vmatrix} = 0$$

$$(H_{11}-E)^2 = H_{12}^2 \qquad E_{\pm} = H_{11} \pm H_{12}.$$

So, the matrix is H 11 minus E H 1 2 H 1 2 H 11 minus E determinant is equal to 0 which tells you that H 11 minus E whole square is equal to H 12 square or E is equal to H 11 plus or minus plus or minus H 12 ok.

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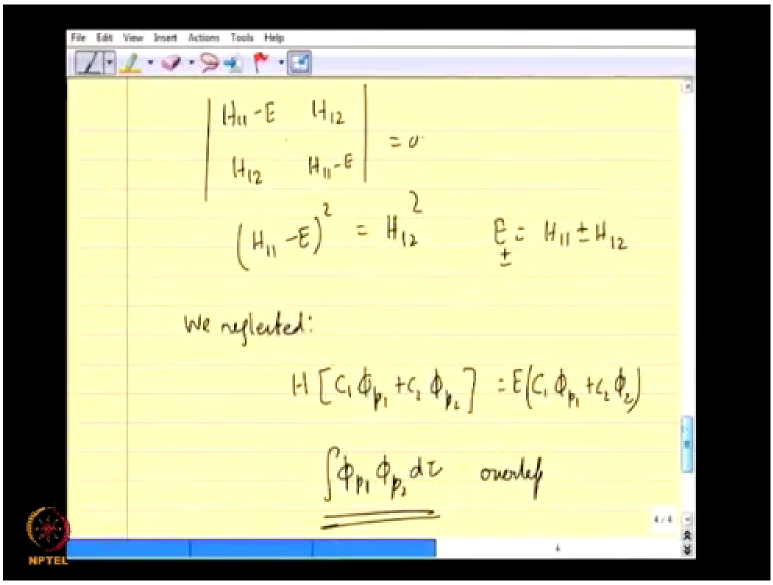

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{12} & H_{11}-E \end{vmatrix} = 0$$

$$(H_{11}-E)^2 = H_{12}^2 \qquad E_{\pm} = H_{11} \pm H_{12}$$

We neglected:

$$H\left[C_1\phi_{p_1} + C_2\phi_{p_2}\right] = E(C_1\phi_{p_1} + C_2\phi_{p_2})$$

$$\underline{\underline{\int \phi_{p_1}\phi_{p_2}\,d\tau}} \quad \text{overlap}$$

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What did we neglect in this here, we neglected something here. Please remember that when we did this h psi is equal to E psi C 1 phi p 1 plus C 2 phi p 2 is equal to E C 1 phi p 1 plus C 2 phi p 2. This is the equation we try to solve and get the Hamiltonian matrix. We have obviously neglected the quantities integral phi p 1 phi p 2 d tau. And please remember this is the overlap of the 2 p orbitals associated with the 2 carbon items, because the absented on 2 carbon items ok.

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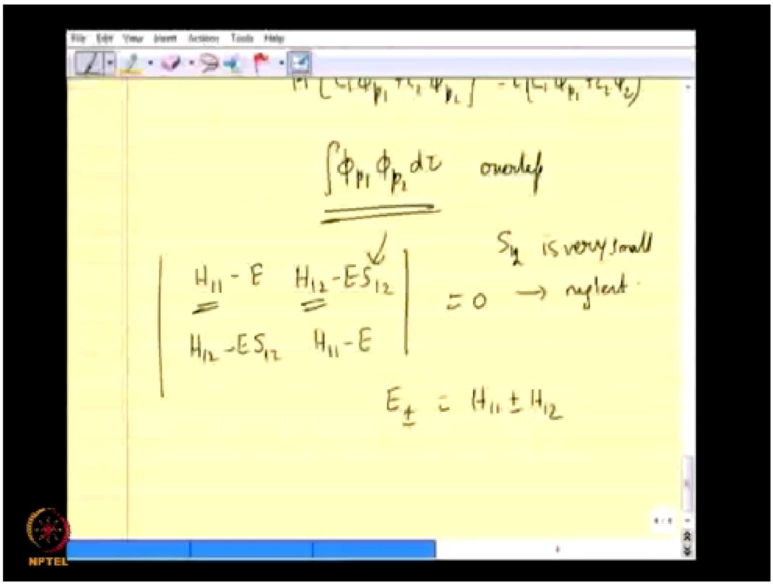

$$H\left[C_1\phi_{p_1} + C_2\phi_{p_2}\right] = E(C_1\phi_{p_1} + C_2\phi_2)$$

$$\underline{\underline{\int \phi_{p_1}\phi_{p_2}\,d\tau}} \quad \text{overlap}$$

$$\begin{vmatrix} \underline{\underline{H_{11}-E}} & \underline{\underline{H_{12}}}-ES_{12} \\ H_{12}-ES_{12} & H_{11}-E \end{vmatrix} = 0 \qquad S_{12} \text{ is very small} \rightarrow \text{neglect}$$

$$E_{\pm} = H_{11} \pm H_{12}$$

.

Therefore, we have inherently neglected this. Otherwise what would have been our results, our results would have been H11 minus E S 11, but S 1 1 is the normalization of the p orbital 1. So, we do not need to worry about that H1 2 minus e s 1 2 H 1 2 minus E S 1 2 H 1 1 minus E. This is what we should have solved, but we assumed that S1 2 is very small compare to what compare to all the other things which are here H 11 H12 and the energy that we are computing. So, S 1 2 is very small neglect only then we can get this energy E plus minus is equal to H 1 1 plus or minus H 1 2 ok.

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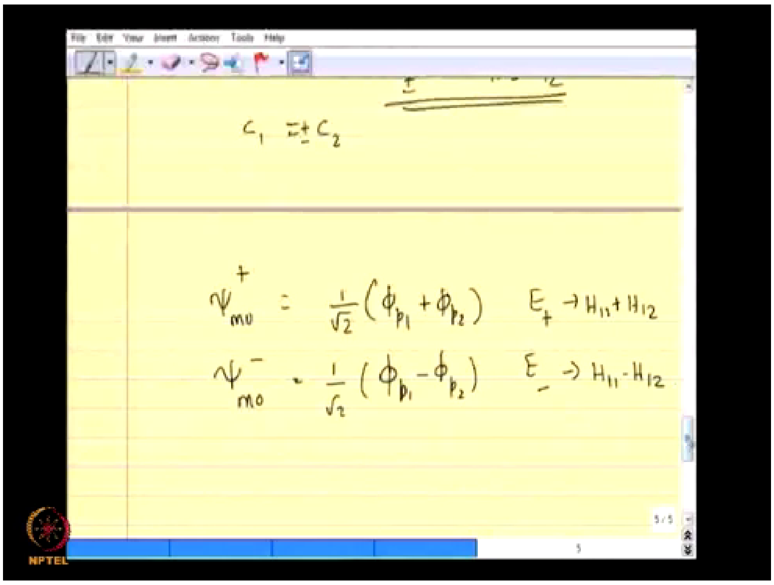

$c_1 = \pm c_2$

$\psi_{mo}^{+} = \frac{1}{\sqrt{2}}(\phi_{p_1} + \phi_{p_2}) \quad E_{+} \rightarrow H_{11} + H_{12}$

$\psi_{mo}^{-} = \frac{1}{\sqrt{2}}(\phi_{p_1} - \phi_{p_2}) \quad E_{-} \rightarrow H_{11} - H_{12}$

Therefore, the difference between the 2 p i electrons in the bonding orbital, you can also say C 1 is equal to C 2 we will get the 2 values plus minus C 1 plus minus C 2 and that is depended on which energy that you should take if you take the plus combination, you will get the plus. You take the minus combination you will get the minus ok. So, there are 2 molecular orbital wave functions namely psi m o plus as 1 by root 2, because we are neglecting the overlap it is phi p 1 plus phi p 2 and E plus is H 1 1 plus H 1 2 and psi m o minus is 1 by root 2 phi p 1 minus phi p 2 and E minus is H 1 1 minus H 1 2.

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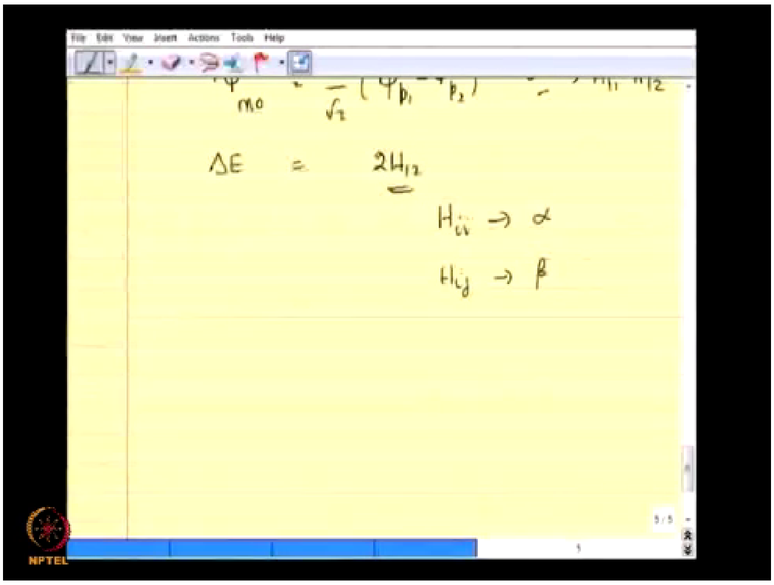

$\Delta E = \underline{2H_{12}}$

$H_{ii} \rightarrow \alpha$

$H_{ij} \rightarrow \beta$

Therefore, you see the difference between the 2 is delta E as 2 H 1 2. The usual location is that H i i which is 1 1 or 2 2 is denoted by alpha H i j is denoted by beta ok.

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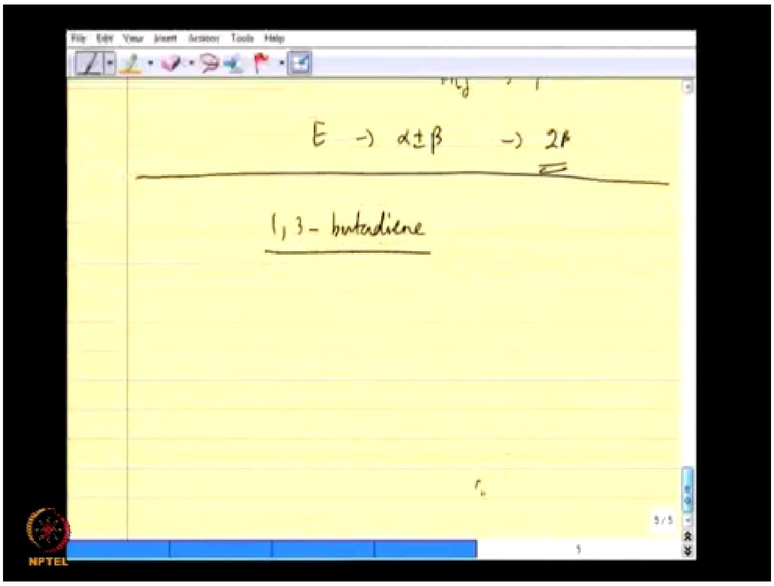

$E \rightarrow \alpha \pm \beta \rightarrow \underline{2\beta}$

1, 3- butadiene

Therefore, you can see that the energy is alpha plus or minus beta and the difference between the two is 2 beta ok. So, this is very simple way of doing things you have the bonding orbital you have the anti-bonding orbital you have the two energies you calculated it. And therefore, the rest of it is to find out the value of beta by substituting in the Hamiltonian for the system what interactions that you want to keep and the wave functions in terms of the p orbitals. Now, what about the next step let us take the next item that is slightly bigger conjugated poly conjugated poly nuclear systems like C double bonds C single bonds C single bonds etcetera. So, let us consider a simple example of a butadiene 1 3. And see how we can push this idea further.

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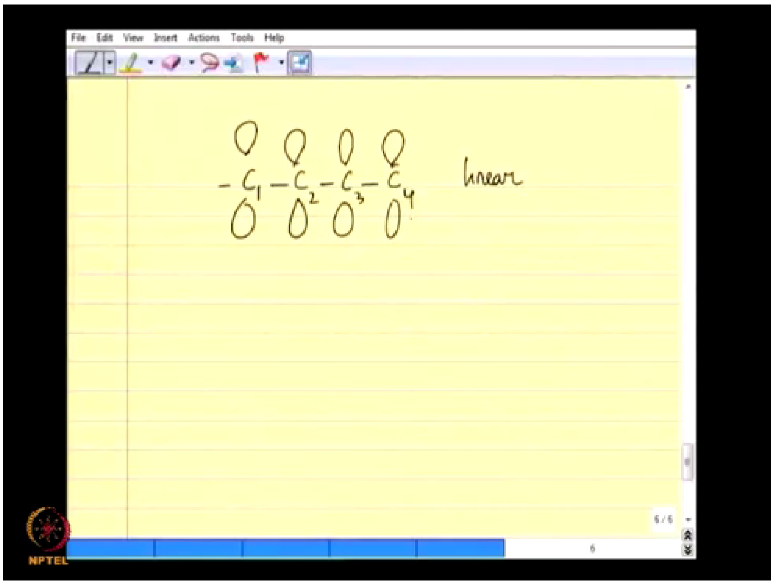

$-C_1-C_2-C_3-C_4$ linear

Butadiene if we are neglecting the hydrogens for the moment and we have the 4 carbon chain linear chain with 4 p orbitals and call them 1, 2, 3, 4 or a, b, c, d whatever that you wish to.

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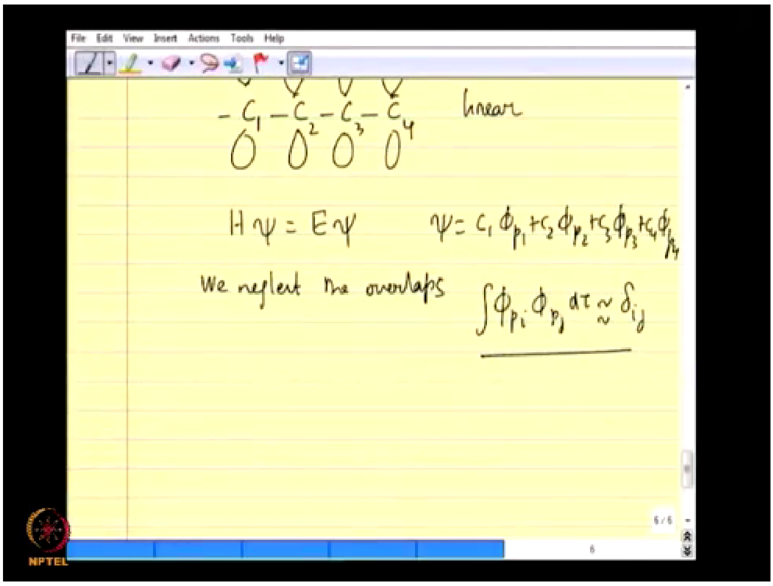

$-C_1-C_2-C_3-C_4$ linear

$H\psi = E\psi \qquad \psi = c_1\phi_{p_1}+c_2\phi_{p_2}+c_3\phi_{p_3}+c_4\phi_{p_4}$

We neglect the overlaps $\int \phi_{p_i}\phi_{p_j}\,d\tau \approx \delta_{ij}$

And look at the H psi is equal to E psi to see what is meant by delocalization or what is meant by the stabilization due to the what you call as the homogenization of electronic cloud across the molecule ok. So, you have H psi is equal to E psi, a psi will be a linear combination of all the4p orbitals. So, we can write this as C 1 phi p 1 plus C 2 phi p 2 plus C 3 phi p 3 plus C 4 phi p 4 and again because we neglect the overlap overlaps here the many phi p I, phi p j d tau is assumed to be delta i j which is 1 if i is equal to j or 0, when i is not equal to j. So, this is approximately this is our approximate well this is delta i j if i is not equal to j, but it is exactly 1 when phi p i is equal to phi p j, because it is a normalized p orbital

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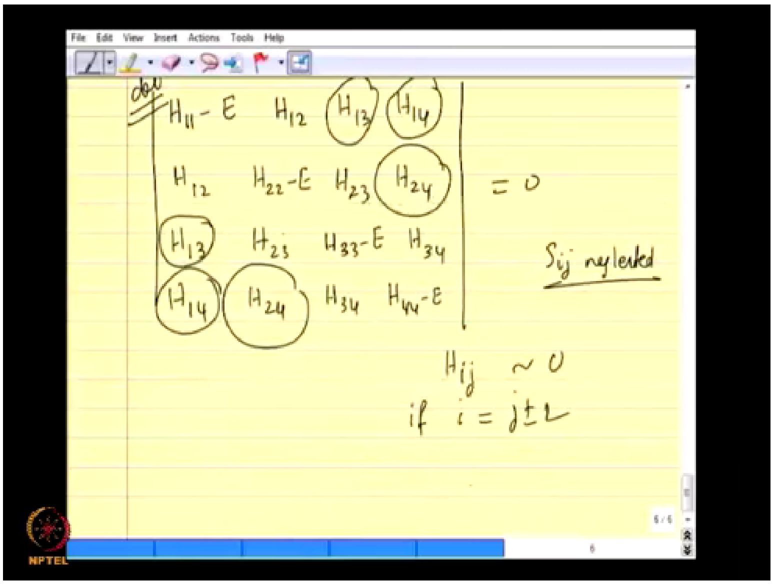

det
$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} & H_{14} \\ H_{12} & H_{22}-E & H_{23} & H_{24} \\ H_{13} & H_{23} & H_{33}-E & H_{34} \\ H_{14} & H_{24} & H_{34} & H_{44}-E \end{vmatrix} = 0$$

S_{ij} neglected

$H_{ij} \sim 0$
if $i = j \pm 1$

.

So, given that you know that the Hamiltonian matrixes going to be immediately H 11 minus E H 1 2 H 13 H 14 H 2 2 sorry 1 2 H 2 2 minus E H 2 3 H 2 4 and H instead of 3 1 I will write again 1 3, because the Hamiltonian in symmetric. In this case, H 2 3 symmetric here, H 3 3 minus E H 3 4 H 14 H 2 4 H 3 4 and H 4 4 minus E ok; this determinant should be 0 in order for the Hamiltonian matrix to be solved, obviously they have neglected s i j s ok.

Now, the Huckel approximation is clearly seen here as supposed to the ethylene case the simple 2 atomic 2 carbon case, because here now we see that there are carbons which are further way from each other 1 3, 1 4, 2 4, if you look at, these are the corresponding Hamiltonian matrix elements 1 3 here 1 4, 2 4 and they are all also on this of the (Refer

Time: 20:37). If you look at these are assumed to be again small due to the factors the orbits are quite far from each other this is 1 carbon away from each other. And these are set to 0, H i j is set 0 if i is equal to j plus or minus 2 not plus or minus 1 near by the interaction H 1 2 is kept H 2 3 is important H 34 is important.

So, 1 2, 2 3, 3 4, or 2 1, 3 2, 4 3, that is important, but they further away neighbors who are further away are not included in the Hamiltonian matrix. And if you do that the Hamiltonian, now becomes an approximate for H 1 1 minus E ok, before I write it 1 more thing we need to that. The H 1 1 corresponds to the Hamiltonian of the molecule with the matrix element being calculated between the pi orbitals the p orbitals of the carbon C 1. H 2 2 is the Hamiltonian with the p orbitals of the carbon 2, H 3 3 is with that of carbon 3 and that of carbon 4 for H 4 4.

Though there are two hydrogen atoms here and 2 hydrogen atoms here, terminals carbon do have a chemical environment slightly different from the carbons entering in the chain. For the time being we will also not worried too much about their effect. And if we neglect to the terminal carbon effect, you see that the quantity that we calculate the Hamiltonian with the p orbital for carbon 1 or the p orbital for carbon 2 or for 3 or 4 they all should be the same. Therefore, you have also this term H 1 1 let me make sure that we do not circle it, but I highlight it H 1 1, H 1 1, H 2 2, H 3 3, H 4 4 they are all equal and therefore now we call that as alpha.

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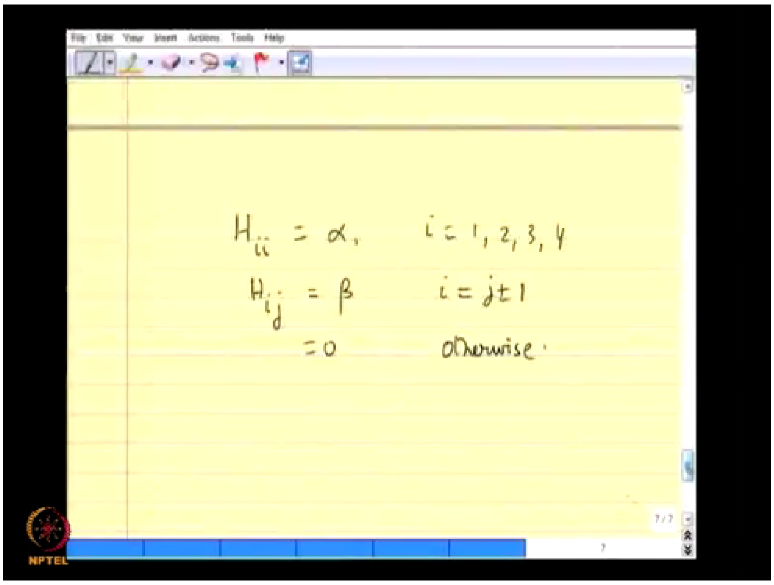

$H_{ii} = \alpha, \quad i = 1, 2, 3, 4$

$H_{ij} = \beta \quad i = j \pm 1$

$= 0 \quad$ otherwise.

We will we will erase this and set our definitions namely H i i is equal to alpha i is equal to 1, 2,3,4 and let us call H i j is equal to beta if i is equal to j plus or minus 1 and is equal to 0 otherwise. There is i is j plus or minus 2 or plus or minus 3 does not matter ok.

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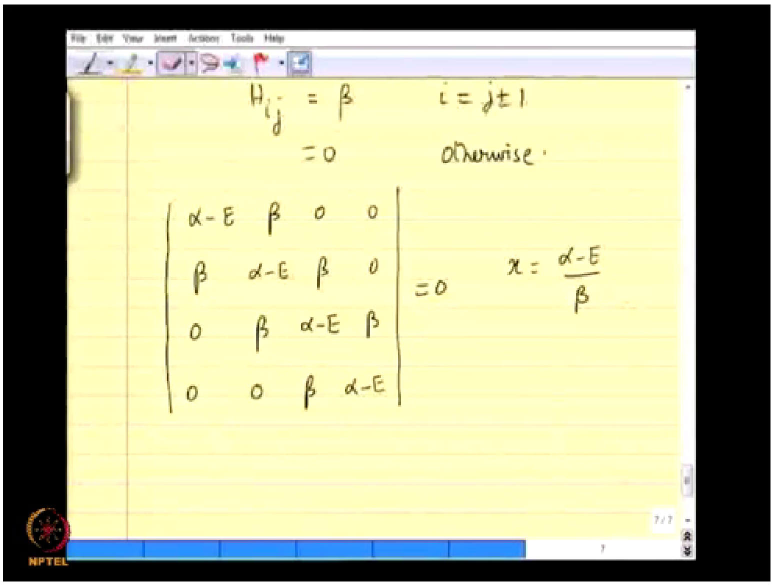

$$H_{ij} = \beta \qquad i = j \pm 1$$
$$= 0 \qquad \text{otherwise.}$$

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \qquad x = \frac{\alpha - E}{\beta}$$

Then it is easy to write the matrix as alpha minus E beta 0 0. Then this is beta alpha minus E beta 0, this is 0 beta alpha minus E beta and 0 0 beta alpha minus E this should be 0. And since it is a determinant we can probably do a simple definition one more definition namely x is equal to alpha minus E by beta ok. And we will take the beta out.

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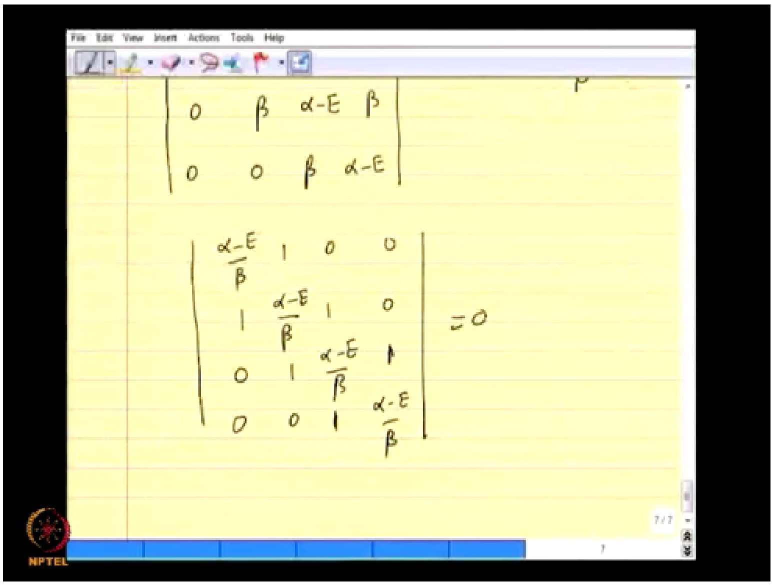

$$\begin{matrix} 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{matrix}$$

$$\begin{vmatrix} \frac{\alpha - E}{\beta} & 1 & 0 & 0 \\ 1 & \frac{\alpha - E}{\beta} & 1 & 0 \\ 0 & 1 & \frac{\alpha - E}{\beta} & 1 \\ 0 & 0 & 1 & \frac{\alpha - E}{\beta} \end{vmatrix} = 0$$

So, if we do that this is given by alpha minus E by beta 1 0 0 1 alpha minus E by beta 10 0 1 alpha minus E by beta 0 0 0 sorry this is 1 and this is 1 alpha minus E by beta ok, this is equal to 0.

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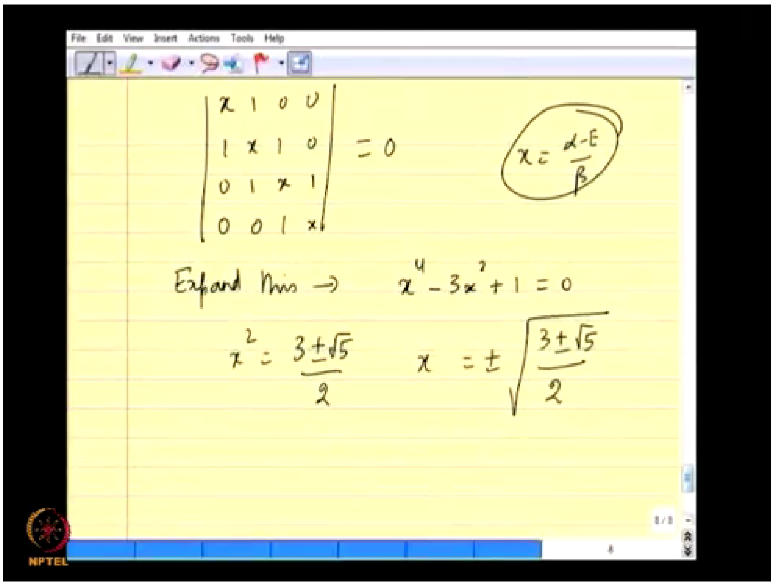

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \qquad \boxed{x = \frac{\alpha - E}{\beta}}$$

Expand this $\rightarrow$ $x^4 - 3x^2 + 1 = 0$

$$x^2 = \frac{3 \pm \sqrt{5}}{2} \qquad x = \pm\sqrt{\frac{3 \pm \sqrt{5}}{2}}$$

So, the matrix are the determinant becomes simply x 1 0 0 1 x 1 0 0 1 x 1 0 0 1 x is equal to 0 ok. This is very easy to expand this and I want to tell you what the process is when you do the expansion the equation that you get is x raise to 4 minus 3 x square plus 1 is equal to 0 that is the secular equation. And remember x is equal to alpha minus E by beta, so E is here in the x the solution of this is of course x square is minus this b square plus or minus 4 a c that you can do the discriminant formula and so the answer turns out to be 3 plus or minus root 5 by 2. And therefore x is equal to plus or minus square root of 3 plus or minus root 5 by 2 ok.

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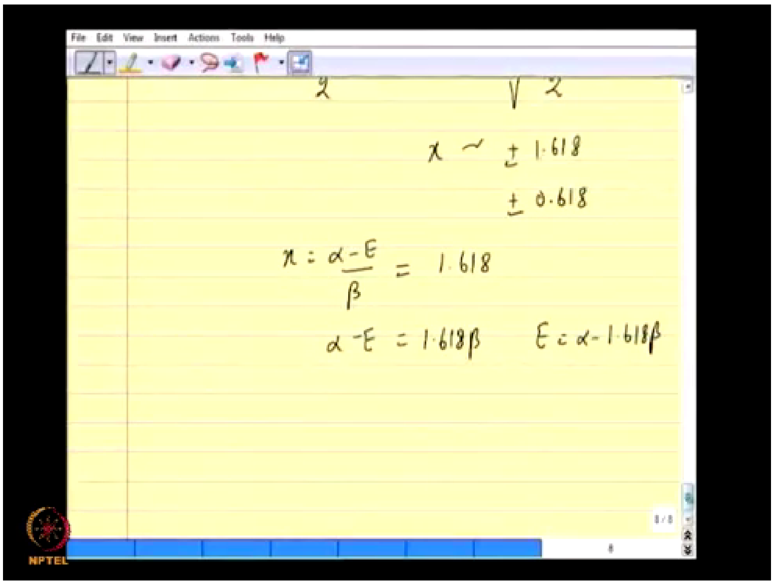

$x \sim \pm 1.618$

± 0.618

$$x = \frac{\alpha - E}{\beta} = 1.618$$

$\alpha - E = 1.618\beta \qquad E = \alpha - 1.618\beta$

So, the answer is when you actually do the numbers x turns out to be plus or minus 1.618 and plus or minus 0.618. So, there are 4 energies. And remember x is equal to alpha minus E by beta and that is equals say if we take 1 of them 1.618, then alpha minus E is 1.618 beta or E is equal to alpha minus 1.618 beta.

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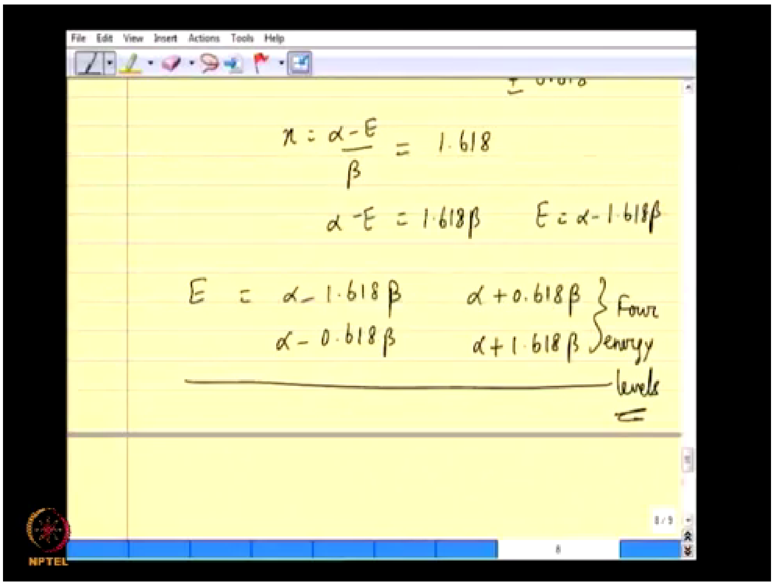

$$x = \frac{\alpha - E}{\beta} = 1.618$$

$\alpha - E = 1.618\beta \qquad E = \alpha - 1.618\beta$

$$\left.\begin{matrix} E = \alpha - 1.618\beta & \alpha + 0.618\beta \\ \alpha - 0.618\beta & \alpha + 1.618\beta \end{matrix}\right\} \text{Four energy levels}$$

So, there are obviously 4 energies namely E is equal to alpha minus 1.618 beta alpha minus 0.618 beta then you have alpha plus 0.618 beta and alpha plus 1.618 beta 4 of them 4 energy levels.

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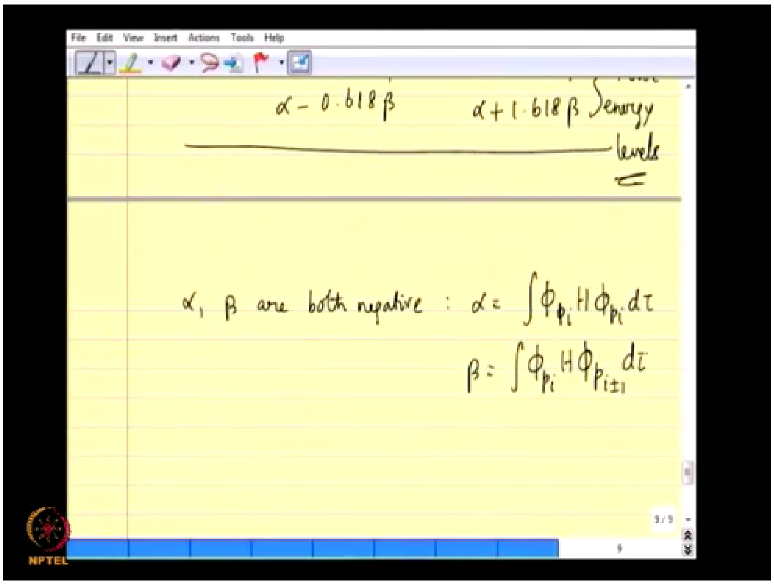

$\alpha - 0.618\beta$ $\quad$ $\alpha + 1.618\beta$ } energy levels

α, β are both negative : $\alpha = \int \phi_{p_i} H \phi_{p_i} d\tau$

$\beta = \int \phi_{p_i} H \phi_{p_{i\pm 1}} d\tau$

So, the quantities alpha and beta are both negative. When we calculate, the integrals are both negative. Again recall that alpha is the wave function phi p i H phi p i d tau and beta is phi p i H phi p i plus or minus 1 d tau both are negative.

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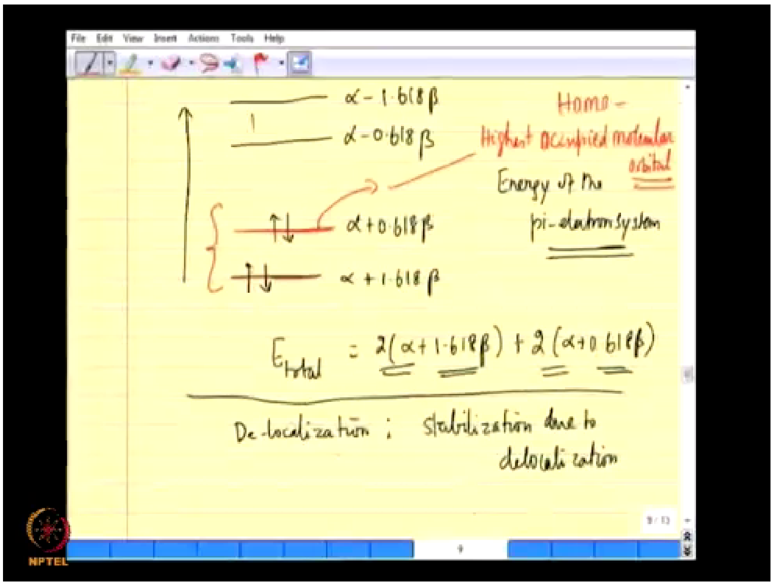

$E_{total} = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$

De-localization ; stabilization due to delocalization

Therefore, if we arrange the energy levels in the increasing order we can say well they are not exactly the distance let us this is alpha plus 1.618 beta, this will be the lowest. The next one will be alpha plus 0.618 beta and then the other energy will be alpha minus 0. 618 beta and this will be alpha minus 1. 618 beta ok. So, since there are 4 electrons and we have 4 molecular orbitals. If we put a 2 electrons paired in each of them essentially what you have is the 4 electrons having this energy.

So, what is the energy, therefore of the pi electrons system in this case. The pi electron system in this case has 4 electrons 2 of which have this energy alpha plus 1.618 beta and then 2 of them have the energy alpha plus 0. 618 beta. And if we neglect for the time being the hiring energy of the electron repulsion energy between the paired electrons if we neglect that, the total energy E total is 2 times alpha plus 1.618 beta plus 2 times alpha plus 0.618 beta, where we worried about this, because we want to know what is meant by delocalization.

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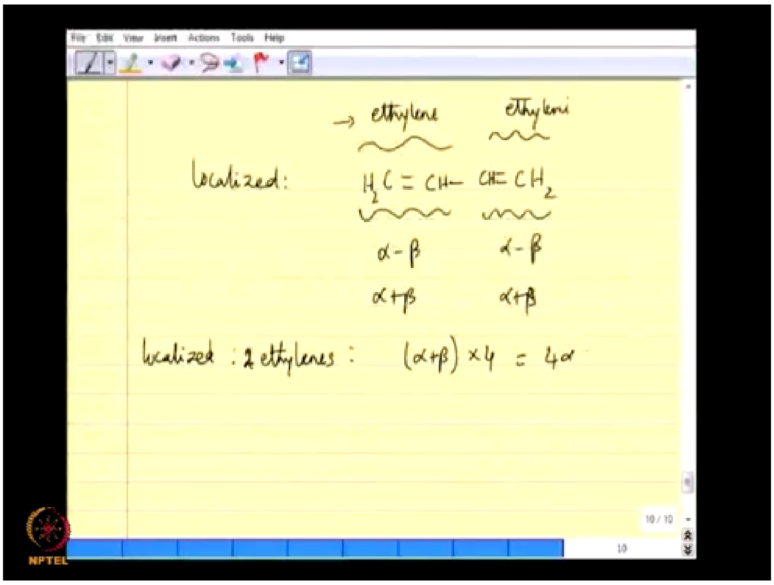

→ ethylene ethylene

localized: $H_2C=CH-CH=CH_2$

$\alpha-\beta$ $\alpha-\beta$

$\alpha+\beta$ $\alpha+\beta$

localized : 2 ethylenes : $(\alpha+\beta)\times 4 = 4\alpha$

And what is meant by stabilization of the electron cloud due to the delocalization. To do that the best would be to consider what is not delocalized or what is localized. So, suppose we have the butadiene as 2 ethylenic bonds each of which C H CH this has a local pi electron cloud and this is a local pi electron cloud. Then the energy of the system is similar to that of the ethylene this is another ethylene, if they do not interact with each other.

And in the case of ethylene we have seen that the energy are alpha plus beta alpha plus beta for the lower energy and alpha minus beta alpha minus beta for the higher energy, because this will be, so let me just write it in the correct order sorry. So, let us write the lower energy as alpha plus beta alpha plus beta and the higher energy is alpha minus beta alpha minus beta.

Therefore, if we had butadiene as the some of the 2 ethylene systems, then there are for electrons each of which will occupy an energy level with energy alpha plus beta. Therefore, the total energy of that system will be localized localized 2 ethylenes would be alpha plus beta times 4 electrons. So, it will give you for alpha plus 4 beta ok.

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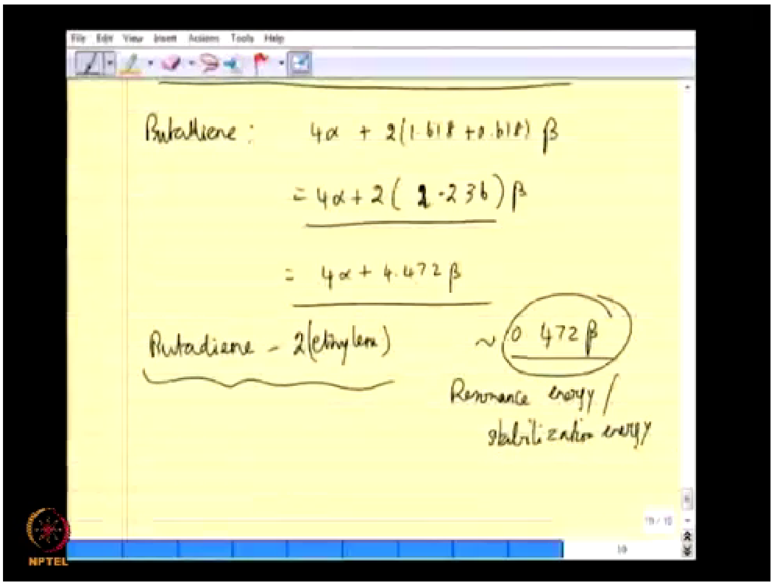

Butadiene : $4\alpha + 2(1.618 + 0.618)\beta$

$= 4\alpha + 2(2.236)\beta$

$= 4\alpha + 4.472\beta$

Butadiene - 2(ethylene) $\sim 0.472\beta$

Resonance energy / stabilization energy

However, for butadiene we just calculated the total energy of the electrons by placing them in this order 2 in the lowest energy level and 2 in the next higher energy level. This is what we call as the ground stay for the pi electron system. Here the total energies 4 alpha plus 2 times 1.618 and 2 times 0.618. So, butadiene energy is 4 alpha plus 2 into 1.618 plus 0.618 beta which turns out to be 4 alpha plus 4 alpha plus 2 times, this is what 36, 6 plus 6; 12, I do this very fast in my own language in Tamil. So, I should say local language helps here much better than adding things in a language which is not your mother tongue is beta here.

So, what you have is 4 alpha sorry this is 1 point, so this should be 2.236. So, the answer is 4 alpha plus 4 times what, 0.472 ok, 4.472 beta compare this with that of the ethylene. So, butadiene minus ethylene minus 2 ethylene sorry minus 2 ethylene in terms of the energy, if you are looking at the difference is 0.472 beta. Since, beta is negative you see that 0.472 times beta seems to be the stabilization energy due to the electrons being placed in these 4 the 2 orbitals which are obtained by the linear combination of all the 4 pi electron p electrons the p orbital of the 4 carbons.

In ethylene if we have to do it locally there are 2 ethylenes, so p 1 plus p 2 and p3 plus p4, they would be independent of each other. So, compared to that the linear combination in which the electron cloud is started delocalized over all the 4 orbitals seem to be give here stability of 0.472 beta. And this is what is called the resonance energy or the stabilization energy for larger systems stabilization energy.

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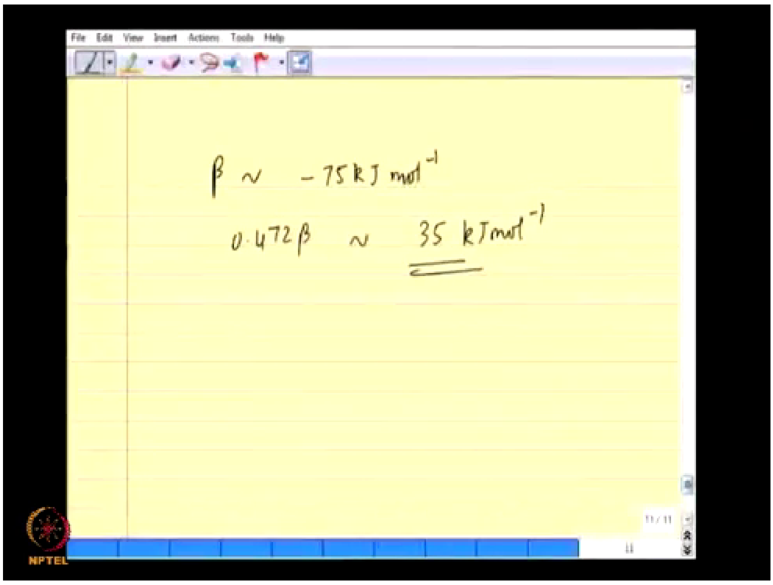

$\beta \sim -75\ \text{kJ mol}^{-1}$

$0.472\beta \sim \underline{\underline{35}}\ \text{kJ mol}^{-1}$

So, Huckel was after this to find out to what extend these systems are more stable than the sum total of the individual the individual unsaturated systems. So, here you look at it the typical calculation of beta from numerical works appears to be minus 75 kilo joules per mole and therefore you see that the 0.472 beta is about 35 kilo joules per mole ok, so this the stabilization.

And now of course you can compare this with the experimental experimentally obtained or spectroscopy obtained values and do an iteration on this by taking better p orbitals or by taking other types of linear combination if possible or improving upon the Huckel's the Huckel's approximation by including terms, which you neglected and so on, but those all are details what is important is that this captures the bulk of what experimentally one observes the stabilization. And therefore this is the very successful method considering the time, when this was proposed that there were no computers and almost all the molecular orbital calculations had to be done by hand and even by hand calculators were very few at the time. Therefore, this is a very useful method in terms of quantitatively getting the first approximate sort of values ok.

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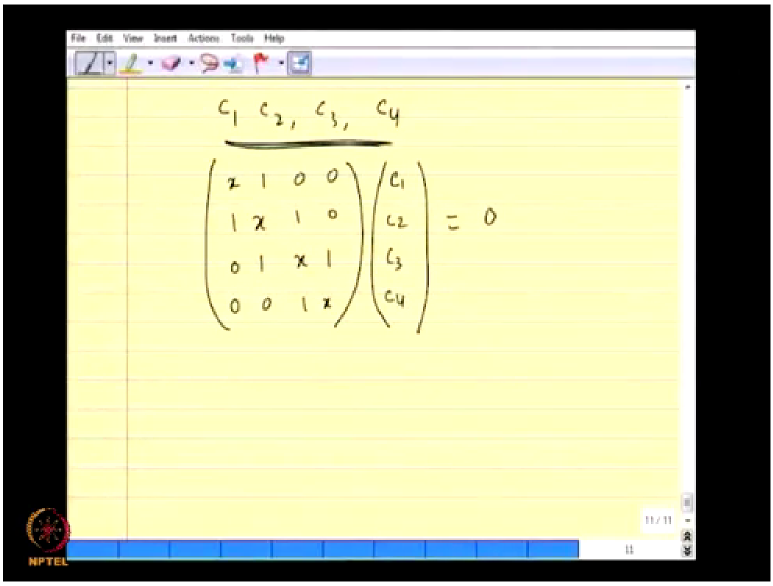

$$\underline{c_1\ c_2,\ c_3,\ c_4}$$

$$\begin{pmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

Now, the other thing that we have to do is to find out C 1, C 2, C3, C4 and we see that these 4 coefficients are not necessary all the same. You remember the Huckel matrix the Huckel matrix was x 1 0 0 1 x 1 0 0 1 x 1 0 0 1 x. It was a determinant that was set to 0, but the determinant was actually obtained by solving the matrix equation with the 4 coefficients C 1, C 2, C3, C4 is equal to 0.

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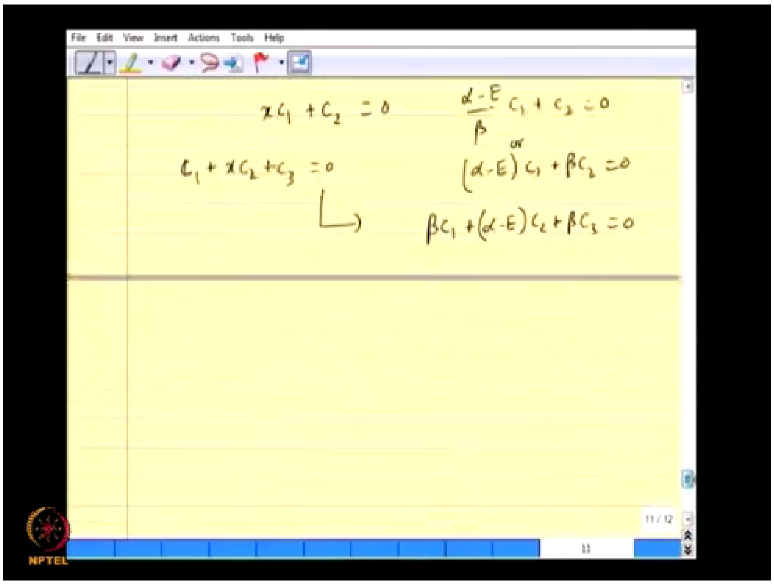

$x c_1 + c_2 = 0$ $\quad \frac{\alpha - E}{\beta} c_1 + c_2 = 0$

or

$(\alpha - E) c_1 + \beta c_2 = 0$

$c_1 + x c_2 + c_3 = 0 \quad \hookrightarrow \quad \beta c_1 + (\alpha - E) c_2 + \beta c_3 = 0$

And therefore, you see that the equation is x c 1 plus c 2 is equal to 0, which is alpha minus E by beta c 1 plus c 2 is equal to 0 or alpha minus E times c 1 plus beta c 2 is equal to 0. And likewise you write the other equations, namely 1 c 1 plus x c 2 plus c 3 is equal to 0 that will give you the equation beta c 1 plus alpha minus E c 2 plus beta c 3 is equal to 0. And one more equation we need, because this is linearly depended set of coefficients. So, only three of them needs to be solved need to be solved.

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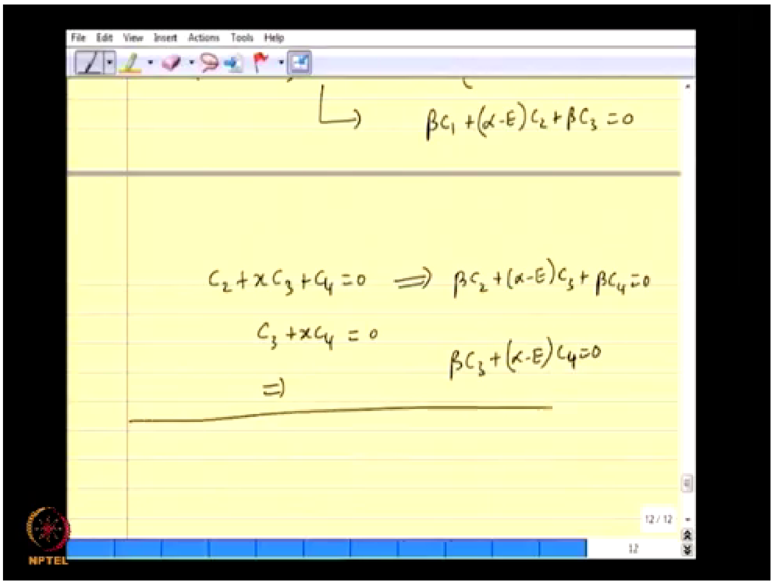

$\hookrightarrow \quad \beta c_1 + (\alpha - E) c_2 + \beta c_3 = 0$

$c_2 + x c_3 + c_4 = 0 \Rightarrow \beta c_2 + (\alpha - E) c_3 + \beta c_4 = 0$

$c_3 + x c_4 = 0 \quad \beta c_3 + (\alpha - E) c_4 = 0$

$\Rightarrow$

.

The third equation is c 2 plus x c 3 plus c 4 is equal to 0, which will be beta c 2 plus alpha minus E c 3 plus beta c 4 is equal to 0. And the last of course, you do not need it, it only verifies this, which is c 3 plus x c 4 is equal to 0, which is beta c 3 plus alpha minus E c 4 is equal to 0 ok.

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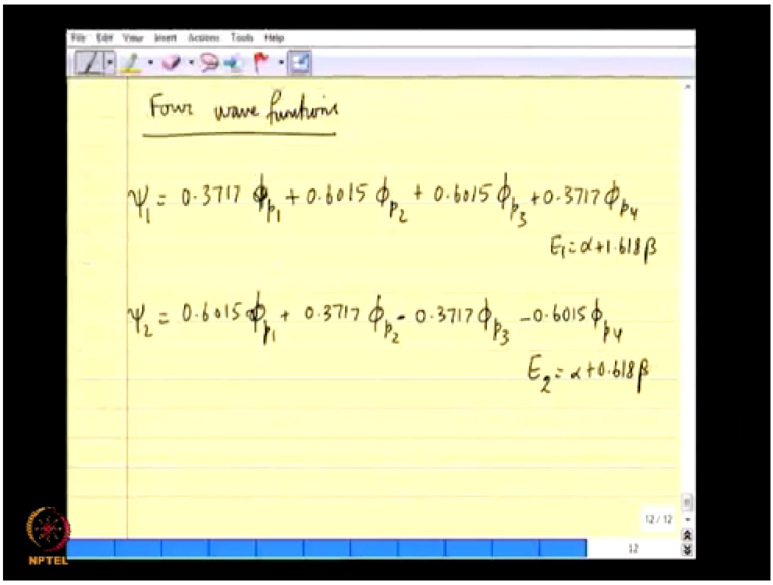

Four wave functions

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

$$E_1 = \alpha + 1.618\beta$$

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

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

.

So, if you solve this numerically with the energies that we have with the energies E 1 being 1 plus alpha plus 1.618 beta and one point alpha plus 0.618 beta and so on. There are four energies. If you do that, you get four wave functions, namely psi 1 is equal to 0.3717 psi p 1 phi p 1 plus 0.6015 phi p 2 plus 0.6015 phi p 3 plus 0.3717 phi p 4. I believe it is normalized, because you can take the squares of these and add them, I am sure you should get 1.

And we have neglected the overlap between p 1 and p 2, p 1 and p 3, p 1 and p 4; and likewise p 2 and p 3, p 2 and p 4 and p 3 and p 4 neglecting those things, we can normalize this. The second wave function, this is for I believe energy E 1, which is E 1 is alpha plus 1.618 beta ok. Now, for the energy E 2, the second wave function Eigen function is 0.6015 phi p 1 plus 0.3717 phi p 2 minus 0.3717 phi p 3 minus 0.6015 phi p 4 and the energy associated with this orbital is alpha plus 0.618 beta.

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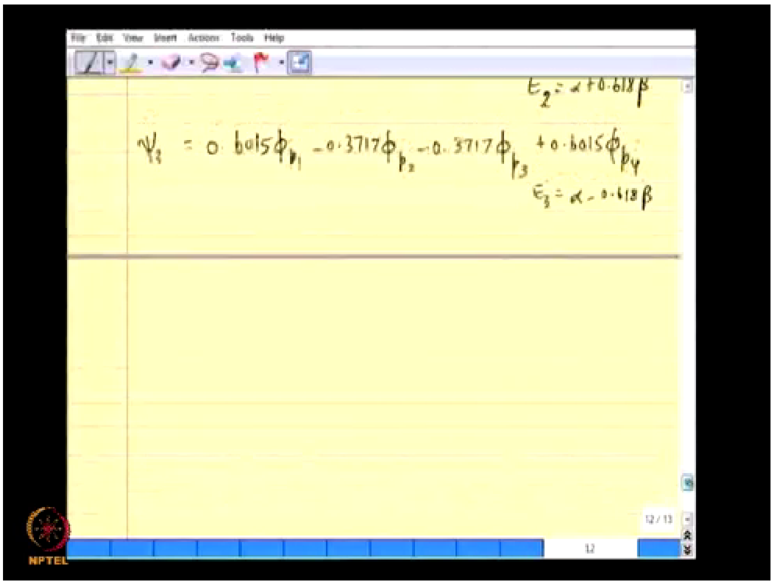

$E_2 = \alpha + 0.618\beta$

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

$E_3 = \alpha - 0.618\beta$

.

There are two other wave functions psi 3 is 0.6015 phi p 1 minus 0.3717 phi p 2 minus 0.3717 phi p 3 plus 0.6015 phi p 4 and this is associated with the energy E 3 is equal to alpha minus 0.618 beta.

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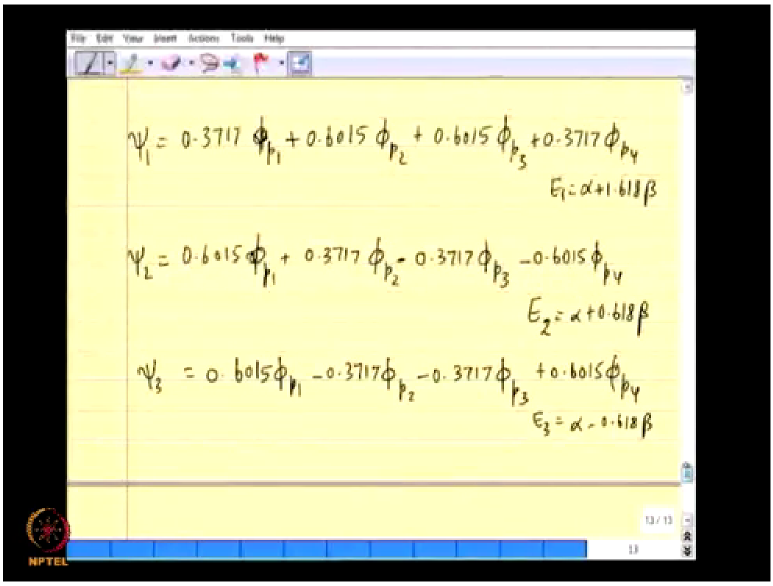

$\psi_1 = 0.3717\phi_{p_1} + 0.6015\phi_{p_2} + 0.6015\phi_{p_3} + 0.3717\phi_{p_4}$

$E_1 = \alpha + 1.618\beta$

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

$E_2 = \alpha + 0.618\beta$

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

$E_3 = \alpha - 0.618\beta$

.

And the last one E 4 the psi 4 is 0.3717 phi p 1 minus 0.6015 phi p 2 plus 0.6015 phi p 3 minus 0.3717 phi p 4 for the energy E is equal to alpha minus 1.618 beta ok. So, there are four energy levels. And if you look at them very carefully, you would see that the orbitals the molecular orbitals psi 1 and psi 2 are orthogonal to each other. Here orthogonality is very simple to verify, because we are neglecting the overlap between orbitals, which are not from the same atom, therefore, phi p 1 phi p 1 star. When you do psi 1 star psi 2, it is going to involve terms containing phi p 1 with phi p 1 star phi p 2 star p 3 star and p 4 star, they are all 0, except the phi p 1 and that is 1. Therefore, it is a numerical multiple of 0.3717 with 0.6015 the numerical multiple of 0.6015 with 0.3717.

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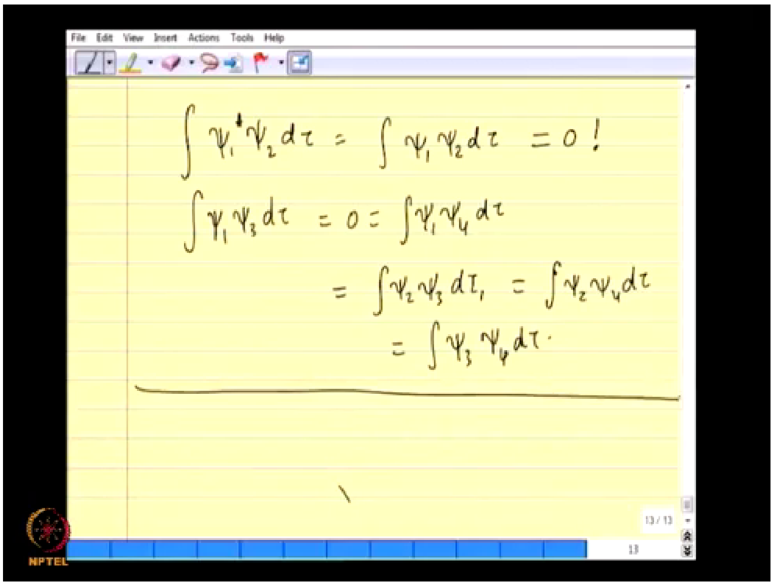

$$\int \psi_1^* \psi_2 \, d\tau = \int \psi_1 \psi_2 \, d\tau = 0\,!$$

$$\int \psi_1 \psi_3 \, d\tau = 0 = \int \psi_1 \psi_4 \, d\tau$$

$$= \int \psi_2 \psi_3 \, d\tau, = \int \psi_2 \psi_4 \, d\tau$$

$$= \int \psi_3 \psi_4 \, d\tau .$$

And two more multiples with of the same quantity with the minus signs and therefore, you see that the integral psi 1 star psi 2 d tau which is of course, because it is all real psi 1 psi 2 d tau that integral is 0. So, the orbitals are orthogonal to each other, the orbitals are normalized. And it is of course, true that you can verify that psi 1 psi 3 d tau is equal to 0 is equal to psi 1 psi 4 d tau, which is also 0, which is equal to psi 2 psi 3 d tau and is equal to psi 2 4 d tau. And this is also 0 is psi 3 psi 4 d tau. So, all the four orbitals are orthogonal to each other and all the four orbitals are normalized. And therefore, orbitals are such that two of them which are lower in energy, which are filled, if we go back to this picture.

Now, let me tell you the standard terminology the people use for this is that the filled orbitals and if you call this is the higher energy filled orbital and this is the lower energy filled orbital, the highest energy filled orbital is called in (Refer Time: 43:53) chemistry highest occupied molecular orbital. And the abbreviation or the acronym is HOMO. And the lowest unoccupied the first unoccupied orbital the first unoccupied orbitals is called to the lowest unoccupied molecular orbital. And it is called L U M O, so it is called the LUMO ok. And the gap between the two energies, which in this case is 2 times 0.618 beta, delta E its messy, but let me write the delta E is equal to 2 0.618 beta that is called let me go on right, there is not enough space there.

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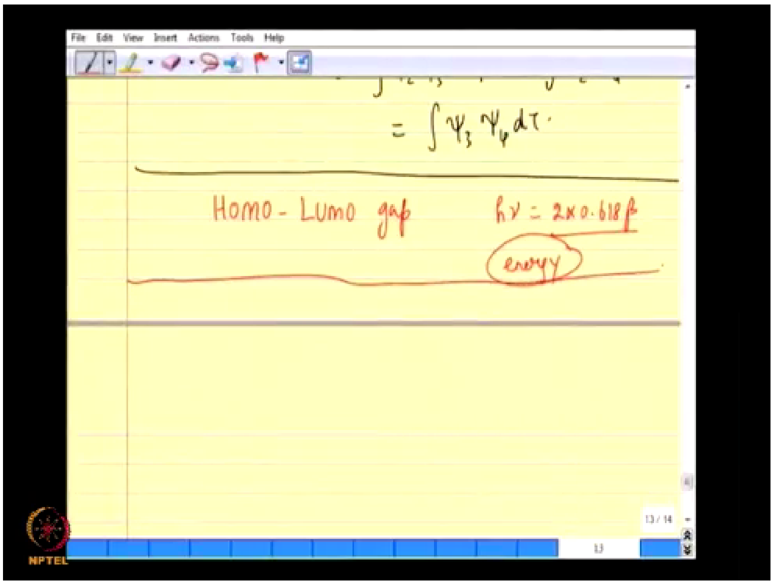

$= \int \psi_3 \psi_4 \, d\tau \cdot$

Homo - Lumo gap $h\nu = 2 \times 0.618\beta$

energy

Let us call this as it is called the HOMO-LUMO gap. Something that the spectroscopy can measured by proper tuning and the frequency corresponding to the HOMO-LUMO gap is now calculated as h nu is equal to 2 times 0.618 beta in energy ok. So, these are all the things that one usually computes, when one applies approximate models. And one fills up the atomic orbital the molecular orbitals to the point of having the electron spared and then leaving the molecular orbitals, which are empty and calculating the difference between the highest level and the lowest unoccupied level. This is this is what it is.

So, let me stop at this point the version of the Huckel theory, we have only look at the linear system. In the next lecture, what I would do is to give you an indication of how this proceeds in general and what are the general solutions for these. And then discuss also the cyclic system wave Huckel theory was very useful in predicting the resonance stabilization energy reasonably accurately for benzene and Eric Huckel. Of course, won the Nobel prize in chemistry for his contribution to the theory of electrolytes along with the famous theory known as the Debye Huckel theory.

But, this contribution to organic chemistry is forever remembered because of the simplicity and the physical picture that is associated with these orbitals. And is with which non-quantum chemist can handle molecular orbitals with simple diagrams and try and qualitatively understand these spectral features, the energetics and the resonance energies and so on. So, it is also fundamentally important method and what we have to looked at is of course part of it, namely if you choose simple systems of linear the conjugated systems, we will generalize this result we will also look at the cyclic systems in the next lecture. With that, I would leave the Huckel theory for you to look at further in the literature, until then.

Thank you very much.