Quantum Chemistry of Atoms and Molecules
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Lecture-65
Huckel MOT-1

We are about to begin the discussion of the very last topic of this course of ours and that is Huckel Molecular Orbital Theory for conjugated molecules. We are all familiar with this kind of depiction of benzene for example in which these P orbitals participate in linear combination to form Molecular Orbital.

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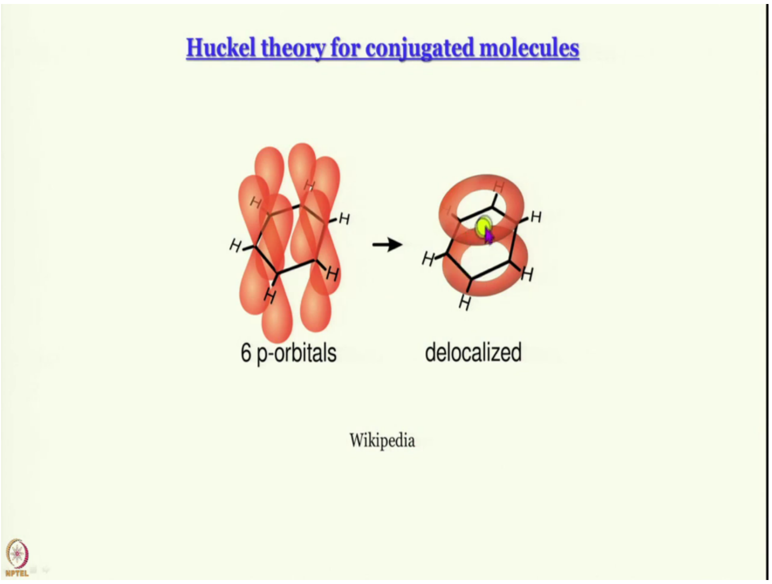

Huckel theory for conjugated molecules

Wikipedia

The lowest energy of it looks like the 1 that is depicted here. This is very common places as you see I have taken this picture from Wikipedia.

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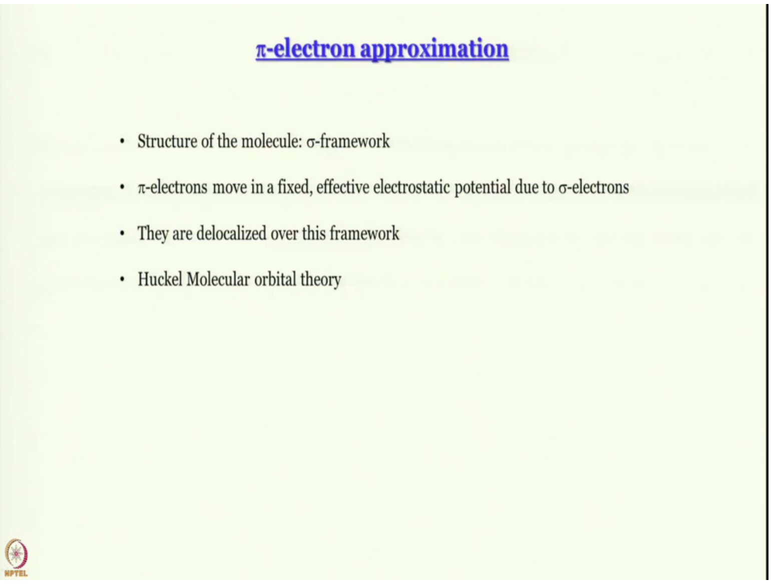

π-electron approximation

- Structure of the molecule: σ-framework
- π-electrons move in a fixed, effective electrostatic potential due to σ-electrons
- They are delocalized over this framework
- Huckel Molecular orbital theory

So, this kind of a system where we have conjugation alternate single and double bonds by valence bond theory description the most common way of dealing with it is to use the PI electron approximation or to generate what is called the Sigma Pi picture. In this approximation what we say is that the structure of the molecule is determined by the Sigma Framework common sense makes perfect sense.

As you said the structure is given by how the Sigma bonds are disposed with respect to each other. So the Sigma Framework decides the structure of the molecule. And the PI electrons are supposed to move in a fixed effective electrostatic potential due to Sigma electrons. What is the meaning of effective electrostatic potential that takes us back what we have learn from many electron atoms and diatomic molecules and so on and so forth.

So here what we have is your number of nuclei is your poly nuclear system anyway, if you think of benzene or even ethylene the 1 that we are going to discuss in some detail. Now; so first of all we have said that is Sigma Framework is in place and then only we start discussion about the Pi electrons. So the Pi electrons and when we start talking about them would experience a joint field of all the nuclei but that feel will be shielded by the Sigma electrons are already present.

So, the potential that these electrons feel is going to be a fixed effective electrostatic potential that is what we mean by the sentence. The electrons are supposed to be the delocalized over this

Framework. In our earlier discussion of ammonia, for example we have said that delocalization is the biggest strong point of Molecular orbital theory. So there is no reason why we should give up on this unique advantage that this theory precursors, right and even in the valance bond picture extended valance bond picture when we try to draw the structure of conjugated system we end up drawing resonance structures in which the double bond in 1 structure it is between say 1 and 2 carbon in the other structure it is between 2 and 3 and so on and so forth.

So delocalization of the Framework is a very logical common sense kind of point to start from. With all these considerations the simplest approach to Pi electron systems is provided by Huckal Molecular Orbital Theory. Remember Huckel theory is all about Pi electrons. I do not even talk about Sigma electrons here, all you know, you might have treated the Sigma electrons using valence bond theory using SP2 hybrid orbitals something like that ok.

It does not matter because we are starting from the point when the Sigma Framework is already there. But Huckel treatment is essentially in molecular orbital treatment which is all about Pi electrons delocalized Pi electrons in conjugated systems

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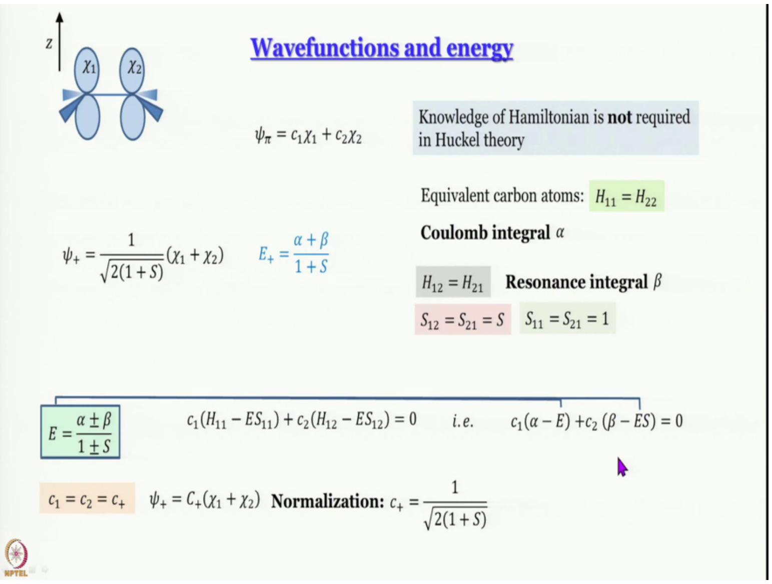

Wavefunctions and energy

$\psi_\pi = c_1\chi_1 + c_2\chi_2$

Knowledge of Hamiltonian is **not** required in Huckel theory

Equivalent carbon atoms: $H_{11} = H_{22}$

Coulomb integral α

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}(\chi_1 + \chi_2) \qquad E_+ = \frac{\alpha+\beta}{1+S}$$

$H_{12} = H_{21}$ **Resonance integral** β

$S_{12} = S_{21} = S$ $S_{11} = S_{21} = 1$

$$\boxed{E = \frac{\alpha \pm \beta}{1 \pm S}} \qquad c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \quad i.e. \quad c_1(\alpha - E) + c_2(\beta - ES) = 0$$

$c_1 = c_2 = c_+$ $\psi_+ = C_+(\chi_1 + \chi_2)$ **Normalization:** $c_+ = \frac{1}{\sqrt{2(1+S)}}$

So, the first such system the easiest 1 that we can think of is ethylene and you might notice here that I really draw a cartoon. You set time and again that this kind of Orbital and all that is not orbital this is something else this is a surface that contains certain amount to probability and so on and so forth. But you still using it. Because that is what is done in all pictorial depiction of Huckel MOT and so you better be familiar with that as well.

And also brings out the fact that this is an approximate theory. It is semi empirical theory as you are going to mention once again, unless I forget about it. This is your ethylene; carbon 1 carbon 2 we are considering the Sigma framework to be in xy plane. So if you talk about SP2 hybrid orbitals. Then the SP2 hybrid orbitals are made up of S Px and Py orbital if you want to talk about MOT to describe the sigma bonding also then 2S 2Px and 2Py will be the orbitals involved in sigma bonding.

The z orbitals in the way I have drawn this molecule the Pz orbitals Chi 1 and Chi 2 for account number 1 number 2 are available for Pi bonding. So, we are going to work only with Chi 1 and Chi 2, remember Sigma Framework is already there we are right now worried only about the PI molecular system. So what is the first step write the MO, how do you write the MO? As a linear combination of the participating P orbitals participating atomic orbitals in this case Pz orbitals so it is very straight forward.

Psi Pi is equal to C 1 Chi 1 + C 2 Chi 2 nothing to explain it is very, very simple here. What do I do next? Next what I should do is, I should Schrodinger equation I have not written it here I will write it erase again. So essentially I write Schrodinger equation H C 1 Chi 1 + C 2 Chi 2 is equal to E C 1 Chi 1+ C 2 Chi 2 then what do you do first left multiply by Chi 1 remember so what do you get integral; so you should write inside that even; when I want to write Chi I end up writing on the other side.

So this is something like C 1 square Chi 1 H Chi 1+ C 1 C 2 integral Chi 1 H Chi 2 is equal to E multiplied by C 1 integral Chi 1 and I do not need to say Chi 1 star here because I know Pz orbital is a real 1 + C 2 integral Chi 1 Chi 2 over all space. So, this is essentially what I get this is C 1 square and then I go ahead and I develop this treatment of linear; I develop this system of linear equations and from there we get or by now familiar to us the secular equation and secular determinant is equal to 0.

And whatever integral I wrote here all get written once again in an abbreviated form. So this is what we have the secular equation H 11 - ES1 H 12 - ES2 H 12 - ES12 H 22 - ES2 we evaluate that again H 11 - ES1 H 12 – ES12 - H 22 - ES 22 that determinant is equal to 0 and we know that this comes from the requirement that we have the strong nontrivial routes. Non trivial roots means roots in what coefficient C 1 and C 2. So, what we have written here is something that is already shown you when I wrote this thing by hand H ij is integral Chi i H Chi j is equal to H ij.

S ij is integral Chi I Chi j is equal to S ij, second one is very easy to understand. It is a product of two functions integrated overall space sequence does not matter. First one would be very easy to understand it is Hamiltonian of was for the particular atom. But you can be confused little bit because I want and Chi i and Chi j are the atomic orbitals and atomic orbitals belong to different atoms do not forget the Hamiltonian is of the entire molecule.

And interestingly knowledge of Hamiltonian is not required in Huckel theory. So, far we have been at the first thing I have been trying to do is to write Hamiltonian in the analytical form. We do not have to do it. I do not need it in Huckel theory. Because Huckel theory is a semi empirical theory Hamiltonian is required to find energy. Energy is determined from known experimental results So, I do not need to know what the Hamiltonian looks like.

That is what makes Huckel theory very advantages, but it was a little dangerous because starting this point one might start for getting all that we have learned because we then get some integral even if you do not know anything before will actually be able to get the right answers. So that is the danger of things that are easy one needs to be careful about that right. Now H 11 has to be equal to H 22 because we are talking about two equivalent carbon atoms.

So, there is no reason why the integration with different if I write Chi 1 H Chi 1 and Chi 1 Chi 2 or Chi 2 H Chi 2 So H 11 and H 22 are same H 11 and H 22 are one and the same these are called coulomb integral alpha. And what is the meaning of coulomb integral. We can say it now, but this sweat little bit and we say it in a little while. Next thing is H 12 and H 21. H 12 and H 21 are equal to each other something that you already discussed this is called resonance integral beta again we are going to discuss the physical meaning of beta what does beta stand for and why it is important?

So S 12 equal to S 21 not very difficult to understand that we just call S. So how does the simplified instead of H 11 and H 22 and I will write Alpha instead of H 12 in these 2 places I will write beta. S 11 is equal to 1 is not it, S 11 and sorry, this is S 22 not S 21 peril of copy paste as usual this is S 22, so S 11 and S 22 they are equal to 1 is not it because this Pz orbitals are normalized after all. So, what will I get instead of the first one H 11 is equals to Alpha – E into 1 so Alpha – E.

Second element here 12 element will be beta - ES, same thing here and this 22 element will be Alpha – E, alpha – E, beta minus ES, beta - ES Alpha - E that determinant is equal to 0 and the rest is very simple expanded and you get an expression for it. And just in order to ensure that you all know how to explain determinants it is even though we have still handle determinants many determinants already and expand this one.

What does this mean? It means Alpha - E whole Square - beta - ES why I started writing so low whole square is equal to 0 this is x square - y square kind of situation on the left hand side. So I Know we know you know what it means. It means x + y into x - y equal to 0. So, setting the first factor to be equal to 0 what do you get? You get E multiplied by 1 + S is equal to alpha + beta, or E is equal to alpha + beta divided by 1 + S and if you set this factor to be equal to 0 then what do you get? You get E Into 1 - S is equal to Alpha – beta E is equal to Alpha - beta divided by 1 – S.

I you write them together you get E is equal to alpha +- beta divided by 1 + - S and so these are the two energy that you get. See how many linear combinations will be there? There 2 atomic orbital sides. I should be able to combine them into ways and even before going to the coefficients. I know that one will be plus and one will be minus one will have higher energy than the other. So, which one has higher energy which one is lower energy Alpha +- beta divided by 1 + - S that is what we will see.

Before that is find the coefficient, so do that let go back to one of the equations recorded in the first place C 1 multiplied by H 11 – S 11 + C 2 multiplied by H 12 – S 12 is equal to 0 this is what we have. So C 1 multiplied by H 11 is alpha, S 11 is alpha H 12 is beta and S 12 is S we can write like this C 1 multiplied by Alpha - C + C 2 multiplied by beta - ES is equal to 0. So, if you put the value of E in both the terms it occurs and well; see your choice side.

You can put either the plus combination or you can put the minus combination. So let us start with the plus combination E+ will we call it E+ since we are using the plus combination using alpha + beta by 1 + S you substitute that, that is 1 is for you do it yourself. It turns out that C + is equal to C 2 sorry C 1 equal to C 2 recall both to C plus. Since; we got them by this plus combination. So the wave function we call Psi + equal to C + into Chi 1 + Chi 2 and sorry about the typo here. I do not capital C here in the next one. I wrote small c so but they are actually the same please do not get confused.

By normalizing this wave functions E+ knowing that Chi and Chi 2 are actually normalized you get a value of C + 2 to be 1 divided by root 2 into 1 + S remember what you got for H2 + and all see this is invalid but they are varied by 1 divided by root 2 into 1 + S. So I have got an expression of the wave function we got the corresponding energy, of course you have another value of energy where your minus sign between alpha and beta minus sign between 1 and S substitute that in this same equation.

By the way with another equation remember you get the same result if you substituting that in the same equation also.

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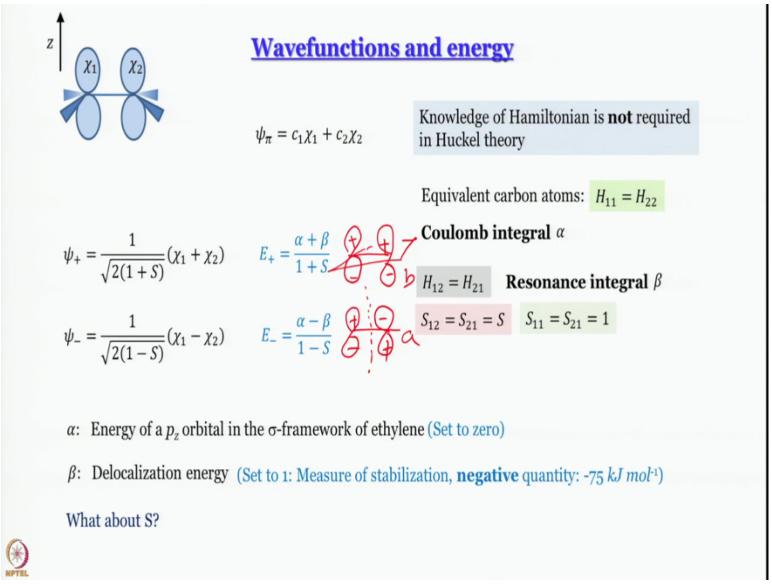

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$H_{12} = H_{21}$ **Resonance integral** β

$\psi_- = \frac{1}{\sqrt{2(1-S)}}(\chi_1 - \chi_2)$ $E_- = \frac{\alpha-\beta}{1-S}$

$S_{12} = S_{21} = S$ $S_{11} = S_{21} = 1$

α: Energy of a p_z orbital in the σ-framework of ethylene (Set to zero)

β: Delocalization energy (Set to 1: Measure of stabilization, **negative** quantity: -75 $kJ\ mol^{-1}$)

What about S?

So you get the wave function corresponding to E – we call that Psi minus is 1 by root over 2 into 1 – S Chi 1 - Chi 2, so one combinations plus one combination is minus equal contribution from both the atomic orbitals here and since I forgot to draw this diagram here I will draw it so I will draw it by hand so this Psi plus what would it be not very difficult to understand. I can draw like this, if you draw the first orbital this way then the second orbital will be like this that is plus and for Psi minus if you draw the first orbital like this second orbital has two point downwards because it is minus.

So here the only node that is there is a node that already exists in p orbital in xy-plane. Here however, you have an additional node between these two this here is the mounting of bonding orbital. This is the antibonding orbitals and energy of the second one is higher than the energy of the first. Energy of the second one is higher than the energy of the first when is that going to happen when beta is negative. We said E- is higher value than E+ it is obviously beta has to be negative and it makes perfect sense for beta to be negative will come to that.

First we will done with Alpha, so it is important to realize that Alpha is essentially is energy of a Pz orbital in the Sigma framework of ethylene. Short simple sentence quite profound what is alpha integral Chi 1 H Chi 1. What is Chi 1? This P orbital and in the integral same Chi 1 appears in bra, as well as in ket vector. What is Hamiltonian? Hamiltonian for the entire Pi molecular system and what terms would it contain even though we are not going to bother to write it is going to contain terms in internuclear repulsion is going to term contain terms in for attraction of electron with electron nucleus 1 as well as nucleus 2 and so on and so forth.

So the Hamiltonian is really a Hamiltonian of the entire molecule. So, this energy Alpha that you get is energy of Pz orbital in Sigma framework of ethylene. Even there is one Pz orbital that would be the energy. So if you remember what you studied in H2 + that 3 terms. The first 2 terms said in energy of 1s orbital and nucleus-nucleus repulsion. So, it is sort of something like that alpha. So, that is the basic line in this framework.

Even if there is no bonding that alpha energy will always be there if you place the Pz electron 1 electron in the Sigma network. So that is our starting point based value. That is why we see what it is said to be. What is beta? Beta is delocalization energy Chi 1 H Chi 2 integrated over all space that accounts for delocalization of each electron over the entire molecule all the Pi bond so it would better be negative because it that energy is not negative then why will Pi bond form, negative energy means stabilization is not it.

What we do this with set Alpha to be equal to 0 because all measurement with respect to Alpha and delocalization energy we can set to 1 very often we write the energy in terms of Beta we do not even bother writing beta. Today we are going to write beta anyway, but this is the measure of stabilization it is important to understand it is a negative quantity the value of Beta is - 75 kilo joule per mole. How do I know that it is - 75 kilo joule per mole. I know it from experiment.

Because as you see we know this is all we know the expression side E+ and E- now if I know what is the energy of transition between homo and lumo of your ethylene then I can figure out what the value of Beta is? Alpha in any case will settle to 0, we will see what will do to S and then whatever is the difference that turns out to be 2 beta. Ok from there you see that it turns out to be - 75 kilo joule per mole and it is beta is used as a known constant quantity in Huckel theory.

This is the approximation and this is the semi empirical assets. Now what is S? S actually is when you talk about butadiene we will see how we handle S but S is very, very small number Let us just say that. This is really a very small number. So we do not bother about this most of the time. It is ok if you set S to 0. If you set S to 0 then what will happen E+ will be beta E- will be minus beta.

So you draw the energy level diagram like this. I will draw it here let us say this is your energy. I cannot draw it here because I will so this first I will draw it here energy goes up this is the energy level corresponding to Psi plus this is energy level corresponding to Psi minus minus this energy turns out to be what beta and this energy turns out to be minus beta. It is important to understand that minus beta is higher energy and if you want to be a little more accurate you might as well write this energy is alpha.

All measurements are with respect to Alpha anyway, so we are setting S to 0 here. We have shown you expression in which is not set to 0 but we are saying that S will be equal to 0 because it is Pi interaction anyway we will come back to that when we talk about butadiene.

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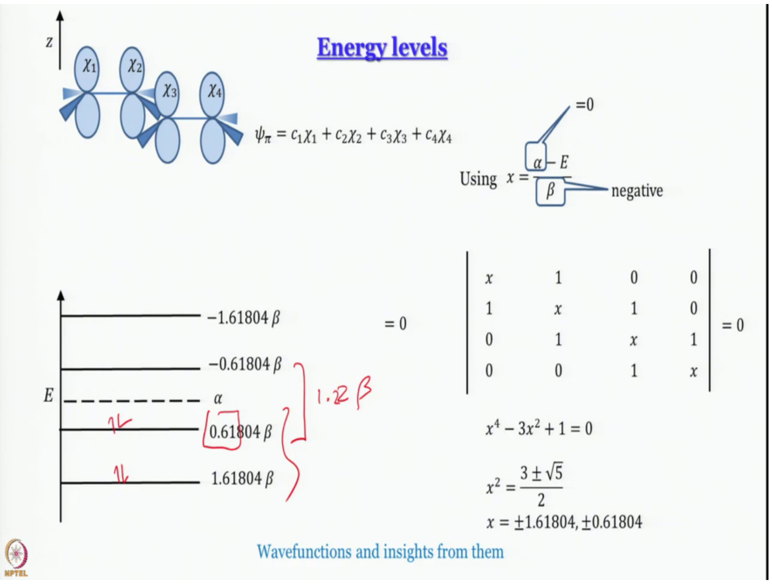

Energy levels

$$\psi_\pi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

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

$=0$

negative

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

$$x^4 - 3x^2 + 1 = 0$$

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

$$x = \pm 1.61804, \pm 0.61804$$

Wavefunctions and insights from them

Let us quickly complete the formulation of the problem for butadiene and then will come back and talked a little more about it. This is the picture for butadiene sorry for this kind of situation. This is same secular determinant and that is equal to 0 is a bigger secular determinants. If you want to work it out it require little more effort obviously but the basic formulation is the same by are calling Pz orbitals of atoms 1 2 3 and 4 carbon atoms 1 2 3 and 4 Chi 1 Chi 2 Chi 3 Chi 4 so Psi Pi will of course be C 1 Chi 1 + C 2 Chi 2 + C 3 Chi 3 + C 4 Chi 4.

WE are going to learn in the next module how to find out C 1 C 2 C 3 C 4 well we will not find out how you know already know how to do it from ethylene we just show you the values. But what we can do here is that from our previous knowledge we know that this H ii H jj coulomb integral Alpha all these diagonal elements instead of H ii I can write alpha. H ii and H ij for ethylene we said that the resonance integral beta.

But now what will says that it is equal to beta only for adjacent atoms. So, what we are saying is that for energy calculation we consider pair wise potential. No need to consider interaction between 1 and 3, 1 and 2, 2 and 3, 3 and 4 these interactions are enough. Ok the electrons are delocalized everything but approximation, right contribution from distant terms is going to be small enough Huckel approximation than neglected. So what is do it will set H ij equal to H ji to beta only for adjacent atom and we set them to be 0 for all others.

And similarly we set S ij to be equal to S ji to be equal to S only for adjacent atoms and in fact what will do in this simple version of Huckel theory that were discussing in this course is that we set everything to 0 why is it justified to set S to be equal to 0 is that already this structure is determined by the Sigma network right change due to Pi bonding is sort of like a correction term. So the overlap in Sigma is much more than in Pi.

So overlap integral is negligible small compared to Sigma that is the motivation for making this approximation that we can set S to be equal to 0 for all in the simplest fashion for little more advanced version of Huckel theory we cannot do that. You still have to consider the overlap integral for adjacent atoms that is good enough. Ok. So let us see where we have to write beta. Alpha we already know it H 11 H 22 H 33 H 44 these are alpha and we set them to be equal to 0.

What about beta? See one and two adjacent to each other right we set S to 0 fine. Now for beta 1 and 2 are adjacent to each other so instead H 12 we will write beta in the 12 element as well as in the 21 element then 1 and 3 are not adjacent. You do not bother 1 and 4 we do not bother 2 and 3 are adjacent to each other. So H 23 is going to be beta in the 32 as well as 23 elements and then 34 are adjacent to each other. So, H 34 is going to be beta in this two elements.

So knowing this just substitute alpha beta this is what you get. I hope that was not too fast wherever we have to write Alpha wherever we have to write beta we write that and we set all the overlap integral to be equal to 0 that gives us this kind of a nice simple matrix determinant. I am very sorry that this vertical line on the left side is not showing up something wrong some incompatibility. So it is what it is. Now, what will you do?

You have to expand the determinant and how do you explain the determinant is a little long. Alpha - E multiplied by this 3 by 3 determinant minus beta multiplied by 3 by 3 determinants in which the column are beta 00 H beta alpha - E beta 0 beta – E tedious but doable see do it, but even before you do it what you do if you set x equal to Alpha – E by beta that make it even simpler you can write in transfer x and 1 ok and then you get an equation like this x to the power 4 - 3x square + 1 equal to 0.

Do not be daunted seeing x to the power 4 this equation is really a quadratic equation not an x but in x square. So, you know how to solve quadratic equations minus B plus minus B square root over b square minus 4ac by 2a do that and you get this value for x square 3 + - root over 5 - 5 divided by 2 and now you know what exists take square root in these two cases you get 4 answers you get plus minus 1.61804 and a plus minus 0.61804 ok this 1 and 0 the digits after decimal point all the same.

What is x? If you set alpha to be equal to 0 then it is really is minus E divided by beta is it not it is an energy terms in terms of beta but in terms of negative beta also let us not forget that. Now so put in the values and this is what you get, you get this energy levels not to forget that beta is negative. The lowest point is 1.61804 beta followed by 0.61804 beta -0.61804 beta. -1.61884 beta and the very centre is at Alpha.

So measurements are with respect to Alpha. Now how many electrons are there? 4 electrons is it not 4 Pi electrons are there in butadiene so I just fill in the electrons then I can draw like this if I draw in the conventional methods. So, these turn out to be the bonding orbitals, occupied orbitals those are the anti-bonding unoccupied orbitals. So the homo lumo energy gap how much is homo lumo energy gap? That turns out to be; I will just consider two decimal places 1.22 beta.

That is the energy gap that we get between home and lumo. So if you know the energy gap you can find out beta, if you know beta you can find out energy gap. So these are the energy levels. Next we have to worry about wave functions. What do the wave functions look like and more importantly we learn what kind of information about the molecule we can get from these wave functions.