# Symmetry and Group Theory
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## Lecture - 57
## Huckel Approximation: Naphthalene

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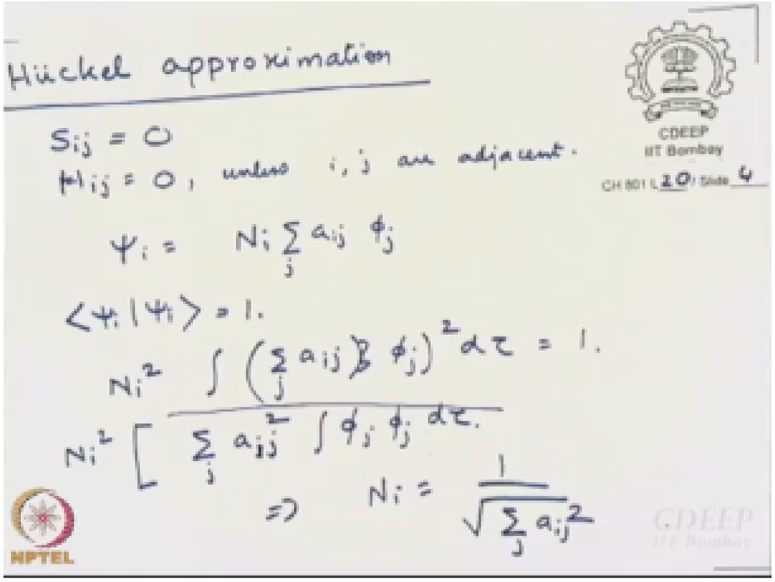

Hückel approximation

$S_{ij} = 0$

$H_{ij} = 0$, unless i, j are adjacent.

$\psi_i = N_i \sum_j a_{ij} \phi_j$

$\langle \psi_i | \psi_i \rangle = 1.$

$N_i^2 \int \left( \sum_j a_{ij} \phi_j \right)^2 d\tau = 1.$

$N_i^2 \left[ \sum_j a_{ij}^2 \int \phi_j \phi_j d\tau. \right.$

$\Rightarrow N_i = \frac{1}{\sqrt{\sum_j a_{ij}^2}}$

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Okay, since you know this already tell me what kind of systems does Huckel approximation apply to, planar and what kind of bonding? Pi bonding, right? Huckel approximation is all about pi bonding. If you are going to sigma bonding then you got a problem. Why, because Huckel approximation sets the overlap integral to be 0, okay which sounds a rather strange thing to say is it not?

Because if there is no overlap, then at least in the valence bond concept there is no bond, right? Why are we justified in using a value of 0 for the overlap integral? Because we are restricting ourselves to pi bonds, right? Pi interaction is weak is it not, okay? The internuclear distance has already been set by the sigma bond you can think.

It is a side-on overlap okay which is weak fortunately because I had a pi interaction with a cow few months ago right in front of chemistry kiosk. Fortunately pi interaction is weak that is why I was not hurt but Professor V.K. Singh had almost a sigma interaction. So he fell, he cut his forehead. We had to take him to the hospital, no joke. So that is the difference between pi and sigma interaction, okay? So pi interaction is weak.

So overlap integral can be set to 0 if you keep one eye closed. You do not have to shut the other. But keeping one eye a little bit closed we can agree with Huckel that S ij = 0 okay but. **“Professor - student conversation starts”** Yes sir. Sir, is this valid for neighboring atoms as well? I am coming to that. It is valid for neighboring atoms also, yes. **“Professor - student conversation ends”.**

And the other thing that Huckel said is that he said that H ij is also equal to 0. So of course then that is the valid question that then what are we talking about. But then there is a you know that joke that somebody was asked to testify some hen was stolen and this witness was asked how big is the hen. He said this big and then the judge of course blew his top and said how can you have a hen that is this big. He said no it is this big. I have not brought out the other hen yet.

So Huckel is now going to bring out the other hen, right. He says H ij = 0 and then sets us off completely and then he says unless i and j are adjacent, okay? So it is important to understand what is the physical meaning of this assumption. What he is saying is that pi interaction you can say you can consider that the interaction is only between adjacent atoms first of all. Secondly, since it is pi interaction overlap is not that much, okay? So as you will see it works.

But if you try to use this in sigma interaction, then you are completely lost. So an approximation that holds in some system need not necessarily hold in another system. This is very important to understand. Science is all about at least to start with, making intelligent guesses. But the guess has to be intelligent. Approximation cannot be such that it is completely bizarre, okay, fine. So first thing that normalization becomes very easy.

So how will I write the molecular orbital wave function? Psi i = sum over j a ij phi j and let me multiply this by a normalization constant Ni okay. What is the normalization condition? That integral psi i psi i * d tau = 1. So that is N i square integral okay sum over j a ij square, let me put phi also, phi j square d tau = 1. So what I will do is let me write it in as two terms.

N i square multiplied by first let me say sum over j a j a j square, there are 2 cases right where i = j and i not equal to j okay. So first say a j a j square integral phi j phi j d tau. **“Professor - student conversation starts”** This will not be a summation on j when pi is not a variable. Right**.** It will be a summation on j, right? Why not? When you are equating i = j that is only 1 k, not a double sum over. That is right. **“Professor - student conversation ends”.**

Okay, evaluate this, see what you get. Evaluate this. Evaluate this sum, see what you get. It should be sum over j a ij square integral phi j phi j d tau no? Sum over j a ij square then integral phi j phi j d tau is it not? Now you evaluate, see what you get. What do you get? What is the value of N that you get if you evaluate this? The second one of course will be sum over jk a ij a jk integral phi j phi k d tau. Right.

So you work this out you get N i = 1 over square root of sigma j a ij square. So normalization constant becomes very easy, okay. **“Professor - student conversation starts”** Yes, sir. How do you write Phi by 2. Work it out, write the two terms, which one? This? Break it up into two sums. Break it up into two terms. One in which you are going to get phi j phi j; another one in which you are going to get phi j phi k where k is not equal to j. work it out. Okay. **“Professor - student conversation ends”.**

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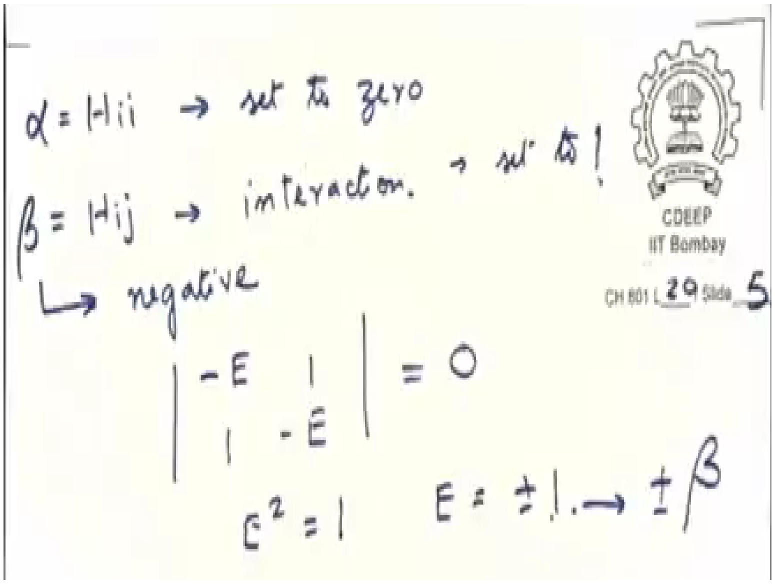

$\alpha = H_{ii} \rightarrow$ set to zero

$\beta = H_{ij} \rightarrow$ interaction. $\rightarrow$ set to 1

↳ negative

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

$E^2 = 1 \qquad E = \pm 1 \rightarrow \pm\beta$

The second thing that happens is, what is H ii what is H ij tell me. What is H ii? So phi ih phi i integrated over all space. So it means it does not stand for interaction between adjacent atoms or any such thing right. So you call this alpha. And this value is set to 0. That might sound as a rather drastic thing to do is it not. Why is alpha set to 0? Alpha will have some value, that is not a problem. But it is set to 0 because tell me this, will alpha be different for different carbon.

Think of benzene. For the 6 carbon atoms, will alpha have different value or will it have the same value? So how will it contribute to the energy of the system? It will just give it an offset, right? So all I am saying is that whatever that value has gone to that is because of the atoms themselves. Even in absence of bonding interaction that value of energy is there. See if I set that to 0 then what will happen is that anything that goes above or below that is going to be because of bonding purely. That is why alpha is set to 0.

More often than not it is written in terms of alpha, okay if you want to get the absolute energy. But then many times it is set to 0. So are you all clear why alpha can be set to 0? It is just the offset. Alpha rises out of the atoms themselves. Not because of bonding or anti-bonding interaction. What is H ij? H ij stands for interatomic interactions, right? That is set, that is called beta. So the moment I call it beta, what is it that I am assuming? When is H ij not equal to 0?

When they are adjacent to each other. So if I set the value of that to beta irrespective of what is i what is j, that means what I am saying is that the unit interaction is the same everywhere is it not? Right? So this is often set to 1. So in terms like say H by 2 pi is often set to 1 in many cases right? You write in terms of, you just write square root of S into S + 1 or square root of L into L + 1. What is the angular momentum? You say square root of L into L + 1 right?

You do not worry about that H plus term. Because you write it in terms of that. You call it the atomic unit, right? So here also you are doing the same thing. You write it in terms of beta. Beta would have some value. Does anybody know the value of beta? You have to say which unit it is also. 18 point something joule or calorie or kilojoule or what? So first of all it is set to 1. Another thing that is very important to understand is that, is beta positive or negative.

It is a negative quantity please do not forget that. Why is it negative? Because, so once again it is a matter of convention. In thermodynamics what is the convention that we follow, what is the modern convention? Anything that flows into the system is positive. Anything that flows out of the system is negative, right? If you want to be a little more dramatic you say anything that enriches the system is positive, anything that impoverishes the system is negative, right?

So it is the same thing. Energy is going out. Stability means energy is going out. So system is impoverished. That is why it is negative. So it is an inherently negative quantity, okay. So we set that to if you write like this then in terms of alpha and beta what does the secular determinant become. This is a secular determinant for a 2-electron system, for a 2-atom system rather.

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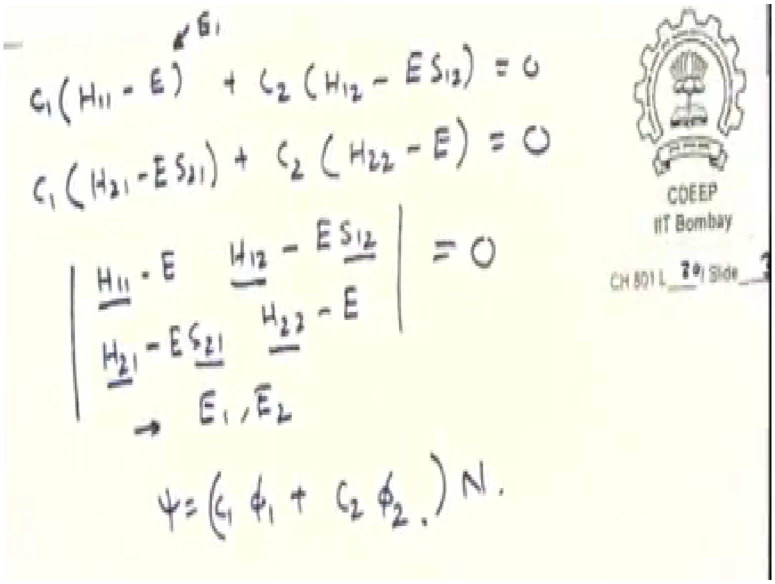

$$c_1(H_{11} - \overset{S_1}{E}) + c_2(H_{12} - ES_{12}) = 0$$

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - E) = 0$$

$$\begin{vmatrix} \underline{H_{11}} - E & \underline{H_{12}} - E\underline{S_{12}} \\ \underline{H_{21}} - E\underline{S_{21}} & \underline{H_{22}} - E \end{vmatrix} = 0$$

$$\rightarrow E_1, E_2$$

$$\psi = (c_1\phi_1 + c_2\phi_2.)N.$$

What is H 11, alpha. Alpha – E right and this is, this is beta minus nothing. S 12 is 0 do not forget. So this is beta. This is beta – 0 and this is alpha. Alpha – E. So if I set alpha to be equal to 0 and beta to be equal to 1 what will the determinant be? This is what. Alpha – E right and alpha is set to 0. So what does it become? – E. Then what was the next one, beta? Beta is set to 1. What do you write then? 1. What about this? This is also beta, 1. What does this become? – E.

Now you have very simple equation. What is it? E square = 1 so E is plus minus 1, right? Plus minus 1 means plus minus beta. Which one is bonding, which is anti-bonding? Is plus bonding or is minus bonding? Plus is bonding because you are writing it in terms of beta, do not forget; beta is negative. Very good. Okay. Now, without working out all this, can you tell me what will be the secular determinant of naphthalene? There are 10 p orbitals.

What will the secular determinant look like? It will be an extension of this, right? So 2 p orbitals is what you get. 10 p orbitals what will it be? So, what will the determinant look like? You will have E in the diagonal, right and adjacent to E you are going to have these bonds. What was that? Other terms? Other terms will be 0. So this is what it is.

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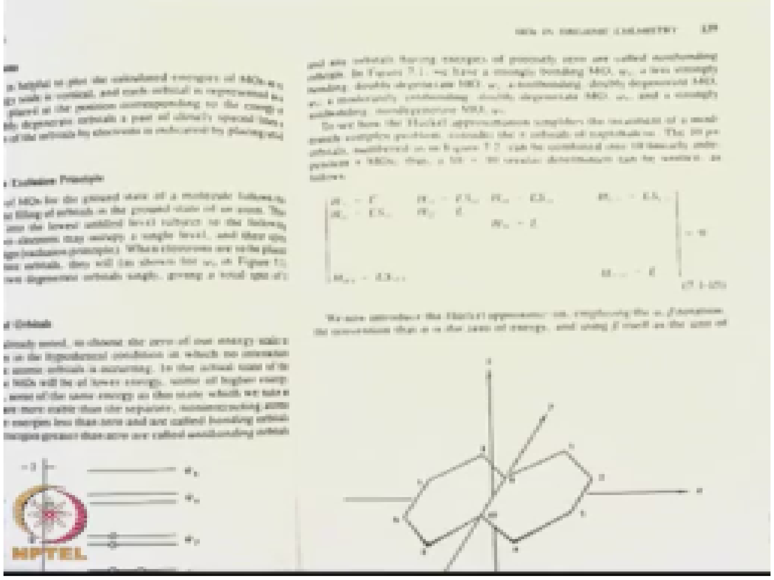

For naphthalene this is what it is. Now you put in alpha and beta and satisfy yourselves. What will it look like? This is what it will look like in terms of alpha and beta, okay?

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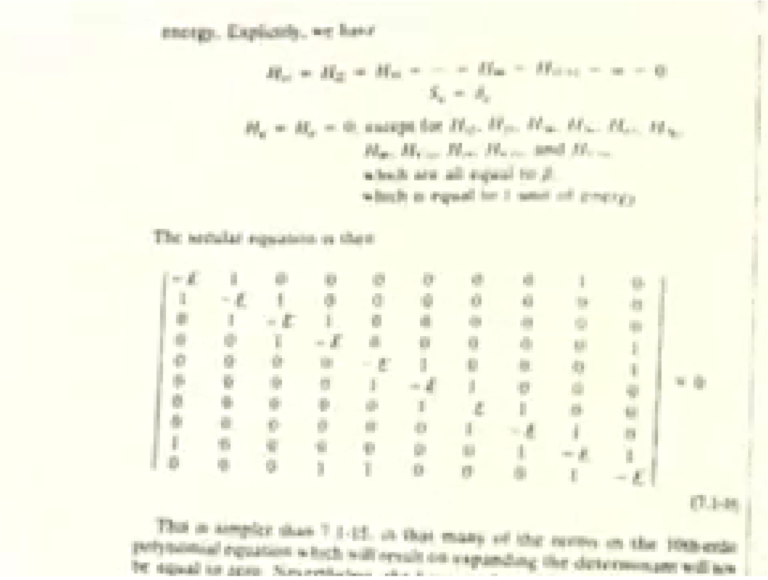
energy. Explicitly, we have

The secular equation is then

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

Simple determinant, you can solve it. Yes, but then if I set this in the end sem, then I have to set only this question. Because you have to solve an equation where you have E to the power 10, right? So what we want to do is now we want to use symmetry. So, so far we had been talking about Huckel approximation, quantum chemistry only. Now we want to use symmetry, okay? If you use symmetry and we are going to see tomorrow how it works, tomorrow when is the class?

5 o'clock do not forget. Where is it? Room 5350, seminar room chemistry. So if I use symmetry then what happens? So what we will do tomorrow is this. We are going to take those 10 p orbitals, right and we will do what we are experts at. We are going to construct that reducible representation and we are going to break it down. In fact to make our job a little easier, I request you to do it tonight, okay and when you do it you see you are going to get this.

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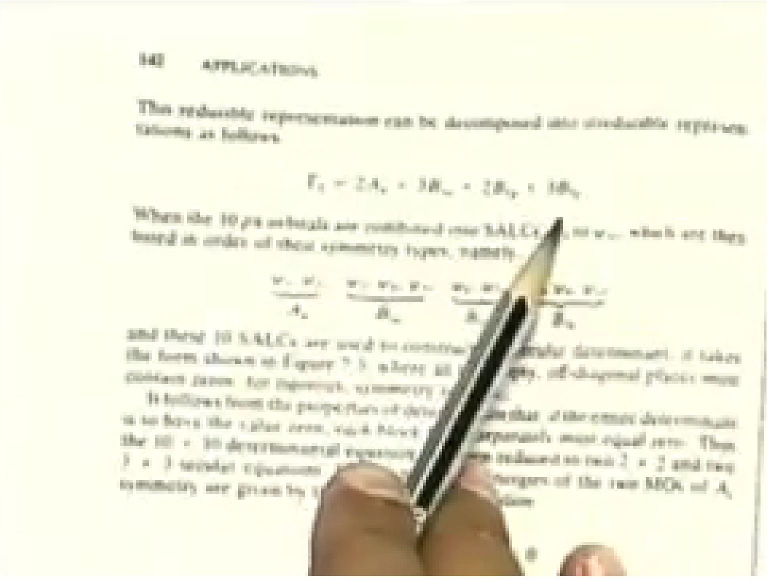

Where is the pencil? 2A u + 3B 1u + 2B 2g + 3B 3g okay? Then what we are going to do is this. We are going to combine them to form SALCs. SALCs will have the same symmetry, right. SALCs will also have the similar kind of symmetry. Two of the SALCs psi 1 psi 2 will have symmetry A you; 3 of them will have symmetry B 1u, 2 will have symmetry B 2g, 3 will have symmetry B 3g, okay? Then what we are going to do is this that, what happens in this SALCs?

They are symmetry adapted linear combinations, right? So when I consider psi 1 and psi 2 is there any need for me to consider psi 3, psi 4, psi 5 etc. There is not, right? Because there are 2 things. One is symmetry one is; one is energy, another is symmetry. Here, since I have done symmetry classification what I can do is I can work with psi 1, psi 2 then I can work with psi 3, psi 4, psi 5.

Then I can work with psi 5, psi 6, psi 7 and then I can work with the remaining 3 wave function separately. There is no need for me to have a 10 by 10 determinant. Rather what I need is a 2 by 2 determinant, a 3 by 3 determinant, a 2 by 2 determinant, a 3 by 3 determinant. So I am able to do what is called symmetry factorization of the determinant, okay?

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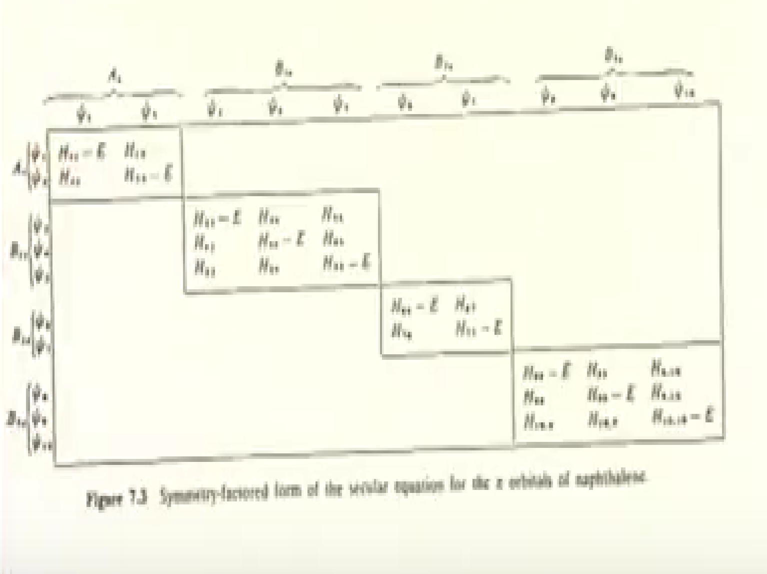

Figure 7.3 Symmetry-factored form of the secular equation for the $\pi$ orbitals of naphthalene.

Does this look more complicated or less complicated than the determinant that we just showed you earlier? I will not blame you if you say it looks more complicated. At least there are more non zero terms it seems. But actually it is less complicated because this determinant is block factorized. Hold on. I can work with the independent blocks and what are these blocks? Psi 1 psi 2, psi 1 psi 2 that is one block. Psi 3 psi 4 psi 5, psi 3 psi 4 psi 5 that is another block. Psi 6 psi 7, psi 6 psi 7 that is another block. And then the remaining 3, remaining 3 another block.

**"Professor - student conversation starts"** Yeah, Anup. In the previous determinant we had a couple of terms. Yeah, that one is 1. Yes. The last one, this one is 1. So we would not be able to block factorize. You will be able to block factorize because Yz = 1? Yz = 1? What is this one due to? It is 1 atom on this side and this is 1 atom due to the other side. That is taken care of when you consider symmetry. **"Professor - student conversation ends".**

We will do it in a little more detail tomorrow. Wait until then. But we will be able to block factorize. Because the point is SALCs will have particular symmetries, okay? We come back to this tomorrow. So this is what we do and we make, as we will see once you have small secular equations it is possible for us to actually work out the energies first. We have not done that for benzene yet, right? So what I will do?

I will do it for naphthalene, I will ask you to work it out for benzene. Benzene is easier. You do not even need such complications and then once you know the energies, we will plug in the value of energy like what we said and we are going to find the coefficients and then we will see some more complicating factor that will come in.