

Symmetry and Group Theory
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Lecture - 60
Naphthalene - II

Let us say this ψ_i is some linear combination of, now I think I need to use this, ψ_i is equal to sum over j $a_{ij} \phi_j$, okay? But I can make it a little more interesting by writing, maybe I will write it afresh.

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

$$\hat{P}_j(\psi_i) = \sum_j a_{ij} \hat{P}_j \phi_j \rightarrow \sum_j \dots$$

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

$$\phi_j = \sum_i b_{ji} \psi_i$$

ψ_i equal to sum over j $a_{ij} \phi_j$. a_{ij} is the coefficient for the j th atomic orbital in the i th molecular orbital. I think this is the most compact way of writing it. So what I am saying is this. I can understand if you make projection operator operate on ψ_i and generate some symmetry. But what I am now saying is that I am going to take this ϕ_j , make the projection operator I should write in some other way, I will write capital J operate on this and I am going to generate this linear combination itself. How is that possible?

It is possible because see if I write, this linear combination I will write it again. $\psi_i = \sum_j a_{ij} \phi_j$. Will you agree with me that I can write another system of equations where each ϕ_j can be written as a linear combination, maybe I will write b_{ji} now of the molecular orbitals. Is that right? Let us see if it is right or not.

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$$\begin{pmatrix} \cdot \\ \cdot \\ \cdot \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_n \end{pmatrix} = A^{-1} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_m \end{pmatrix}$$
$$\boxed{A^{-1}A} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_n \end{pmatrix} = \begin{pmatrix} A^{-1} \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_m \end{pmatrix}$$

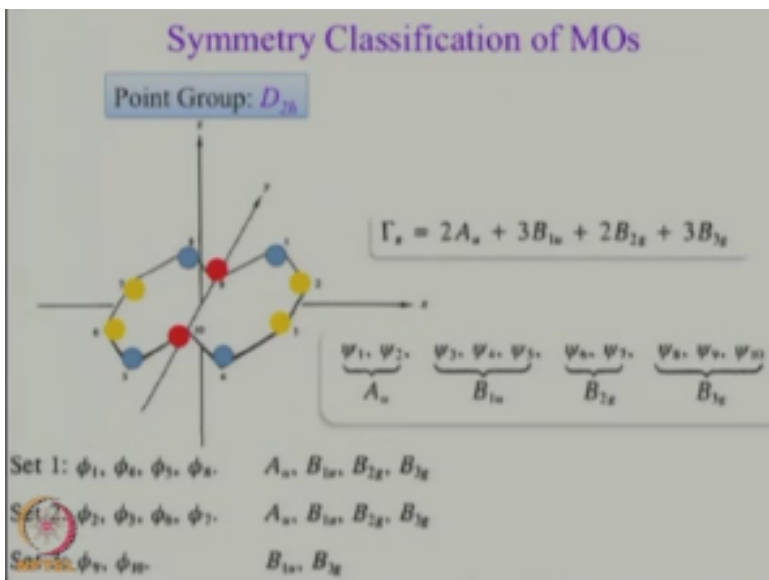
Let me try to write a matrix equation. I will not write all the coefficients of course. But this is what it is going to look like. Say phi 1, phi 2 so on and so forth up to phi n = psi , psi 2 so on and so forth up to psi n. Are you comfortable if I write like this? These are the atomic orbitals. This is the matrix containing all the coefficients. And on the right hand side I have this matrix containing all the molecular orbitals, okay?

Let me write this as say A. This matrix is A, alright? Now see, if I left multiply by A inverse, square matrix should have an inverse. Then on the right hand side also I have to multiply it by A inverse. What does A inverse A give you? Unit matrix, right? So what does the equation now become? Phi 1, phi 2 so on and so forth up to phi n is given by some square matrix A inverse multiplied by psi 1, psi 2 so on and so forth up to psi n. Do you agree?

I am just left multiplying by the inverse, okay? So that is what I mean when I say that if you can write psi i as a sum of phi j's you should also be able to write each phi j as a sum of all the phi i's, alright? Now, the argument for using projection operator on the atomic orbitals starts making sense, okay. So each atomic orbital is really a linear sum of the molecular orbitals of different symmetries.

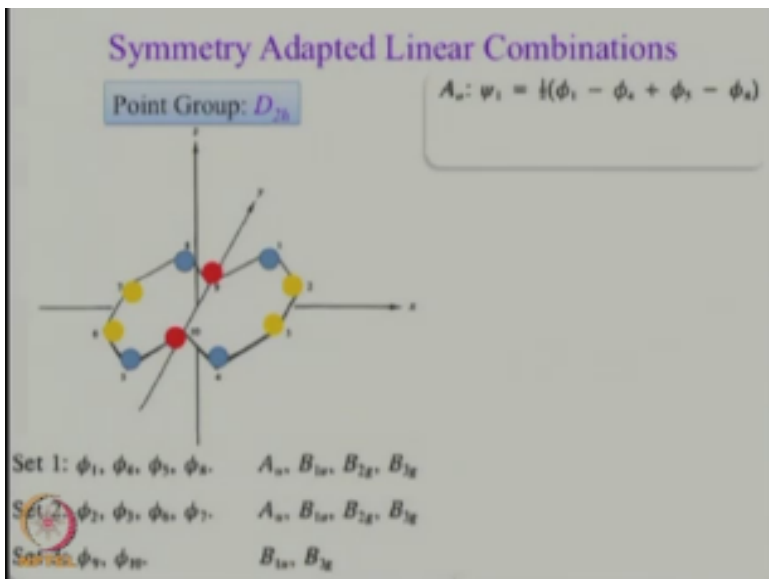
So if I use projection operator of the right symmetry on the atomic orbital I am going to get the molecular orbital of that symmetry. Yes, well of course this is a matrix element, do not forget. B_{ji} is matrix element. So those are elements of the inverse matrix, yes, alright? So that is the trick. Once you understand that everything else is just very simple. Okay, here we are.

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Now our problem is well set. Now let us see how far we can get in the next 15, 20 minutes.

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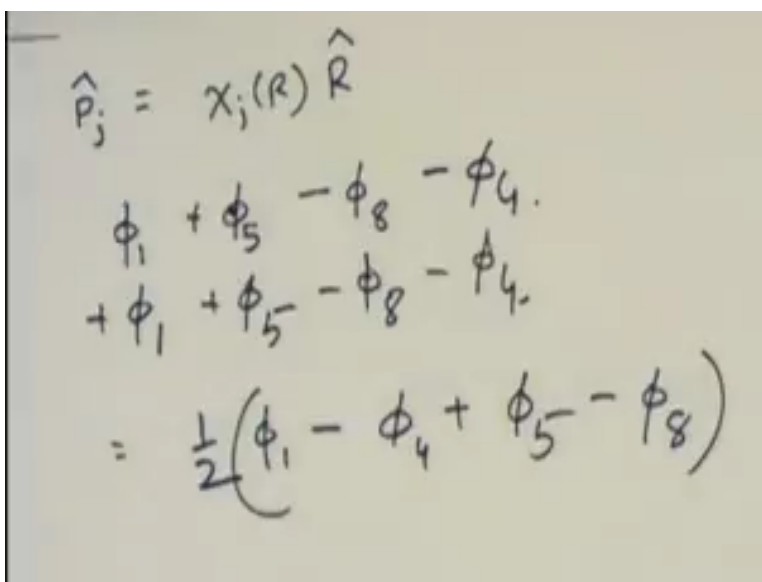


This is what I want. I want to generate the symmetry adapted linear combinations of the phi's. What are the phi's? What is phi 1, phi 4, phi 5 etc.? These are the wave functions of the p orbitals

on the carbon atoms. What are the size? They are, for now let us say they are these symmetry adapted linear combinations. So we have to go one by one, okay?

Let us start with A u. Oh, I have given you the answer unfortunately. So but you have the character table. Try doing it yourself. Take phi 1 and make the projection operator of A u operate on phi 1 and tell me if you get phi 1 - phi 4 + phi 5 - phi 8 or not? So let us see. What are we trying to do? Projection operator of A u. Why are we doing A u all of a sudden? Because we know that A u symmetry is there right for set 1. So let us try and work out projection operator.

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$$\hat{P}_j = \chi_j(R) \hat{R}$$

$$\phi_1 + \phi_5 - \phi_8 - \phi_4$$

$$+ \phi_1 + \phi_5 - \phi_8 - \phi_4$$

$$= \frac{1}{2}(\phi_1 - \phi_4 + \phi_5 - \phi_8)$$

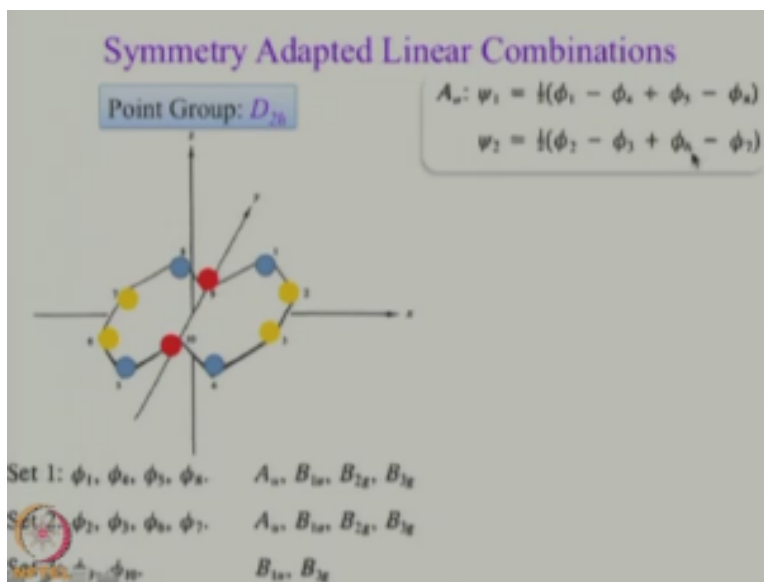
What is projection operator just to remind you once again. That is your chi jR R, is that all? Is that all or is there a sum somewhere? You have sum after all right? So let us do that. So A u. So tell me E operating on phi 1, what do u get? You get phi 1 and then what is the character of phi 1? 1 multiply by that you get the same thing. What is the next one? C 2z. C 2z operating on phi 1, what do you get? C 2z operating on phi 1, what?

C 2z yeah that gives you phi 5 and what is the character of C 2z, 1. Actually, the first 4 characters are +1. The last 4 characters are -1. So it is simple, phi 5. Next operation is C 2y. What happens when C 2y operates on phi 1? You get phi 8 but do you get a +phi 8 or do you get a -phi 8? - phi 8. Then C 2x operating on phi 1; - phi 4, alright. Now, the next four remember we have to multiply by - 1 always. So again, i operating on phi 1 gives you what?

Does it give you ϕ_5 or $-\phi_5$? And then there is a -1 that is multiplied. So you get $+\phi_5$. Then σ_{xy} . σ_{xy} operating on ϕ_1 gives you, ϕ_1 or $-\phi_1$? $-\phi_1$ but then it is multiplied by -1 . So that gives you $+\phi_1$. Then we have σ_{xz} . σ_{xz} operating on ϕ_1 what do you get? ϕ_4 , $+\phi_4$ or $-\phi_4$? $+\phi_4$ multiplied by -1 is $-\phi_4$. So it is important not to get these wrong.

And finally σ_{yz} , σ_{yz} on ϕ_1 gives you ϕ_8 but that is multiplied by -1 so $-\phi_8$. So what do you have? You have, there is no need of writing 2 here because in any case we have to normalize right? So basically we have $\phi_1 - \phi_4 + \phi_5 - \phi_8$. And what will the normalization constant be? Half. So this is your normalized symmetry adapted linear combination that I get right arising out of ϕ_1 A u, okay.

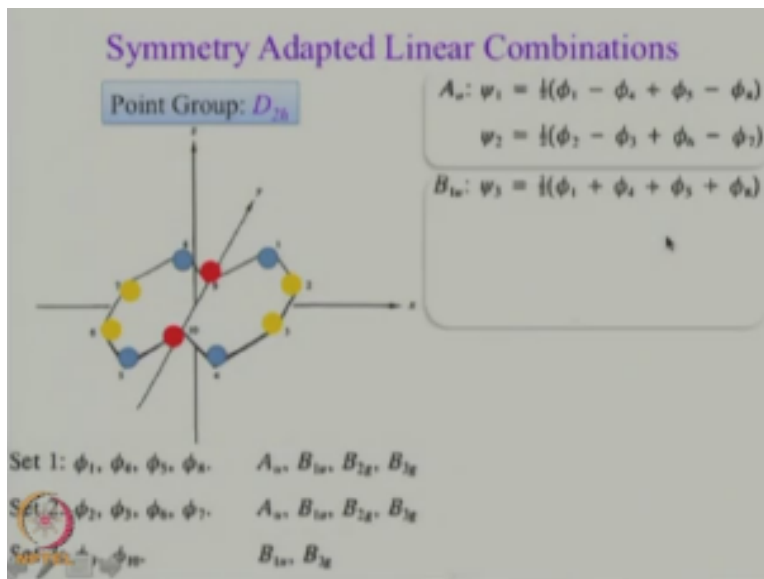
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Now let us try the next one then. What is the next symmetry? B_{1u} , right? Can you do it for me? Projection operator of B_{1u} operating on ϕ_1 , what do I get? B_{1u} . The characters this time are 1, 1, -1, -1, -1, -1, 1, 1. You are allowed to discuss with your neighbor, no problem. What you are close, most of you have done this course. Jolandhar, unveil the treasure man. Okay, forget I ever said that. Let us come back. Do you have an answer. B_{1u} . Yeah, what is the answer Vaishaghi?

I have to understand what you are saying. $\phi_1 + \phi_4 + \phi_5 + \phi_8$, this is the answer. Actually I am showing you a different answer. I am showing you A_u . Sorry, hold on to that answer. So what I have shown you here is sorry this ψ_2 is different. ψ_2 is the same symmetry but the different set, set 2 right and you can understand that all that will happen is that 1 will be replaced by 2, 4 by 3, 5 by 6, and 8 by 7. So that is done. But now, the answer Vaishaghi is giving is this one.

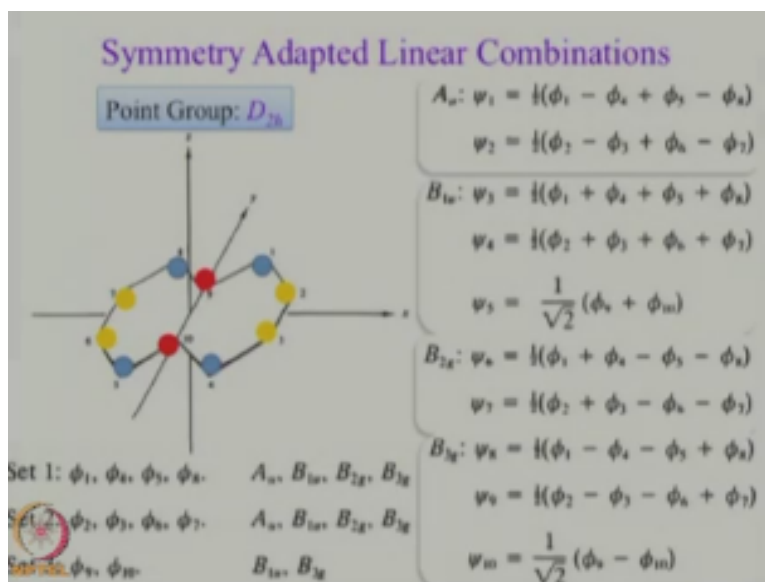
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But you, but this is not the answer you got, okay? So B_{1u} the first answer I get is $\phi_1 + \phi_4 + \phi_5 + \phi_8$. Please work it out yourself and satisfy yourself that this is what is going to come. But you can tell me what the second B_{1u} will be is it not? What will the second B_{1u} be? Second B_{1u} comes from set 2. Same kind of thing. $\phi_2 + \phi_3 + \phi_6 + \phi_7$ multiplied by half.

What will the third one be? Beyond u remember there are 3 and the third one comes from set 3. So it will only have ϕ_9 and ϕ_{10} . What will it be? So I think we got it figured. We can even guess the answer now. Once you know 1 or 2, since it is a symmetry course answers are also symmetric. So you can kind of guess but do not try to guess because sometimes the guess might be wrong, alright. Similarly, you can work out B_{2g} .

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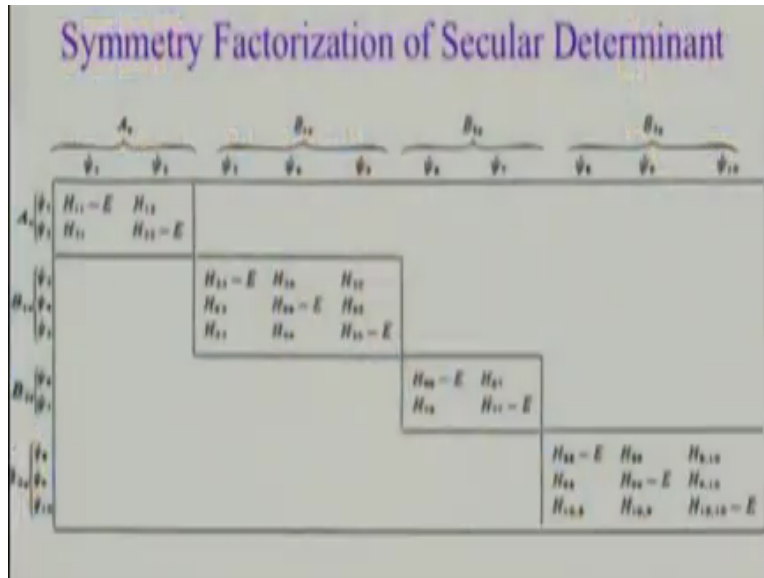


That is going to be half multiplied by $\phi_1 + \phi_4 - \phi_3 - \phi_2$ and half multiplied by $\phi_2 + \phi_3 - \phi_4 - \phi_1$. And finally B_{3g} these are the answers. So what we can do as we have seen is that using projection operators we can generate some symmetry adapted linear combinations, right, which give us the right symmetries. Now, if I come back to the question Jolandhar had asked, are these the MOs? They are definitely not the MOs, right.

Because you know molecular orbitals are actually delocalized over the entire molecule. What we have done is that in every set we have restricted our discussion to 4 or 2 p orbitals. So these are definitely not the molecular orbitals, not the full MOs. But they are constituents. So if you can combine 2 A_u 's, 2 A_u SALCs you are going to get the A_u molecular orbitals. And again you can combine them in 2 ways, plus or minus and coefficients can be different.

That is how you are going to generate the A_u MOs, alright? That is what it is going to be.

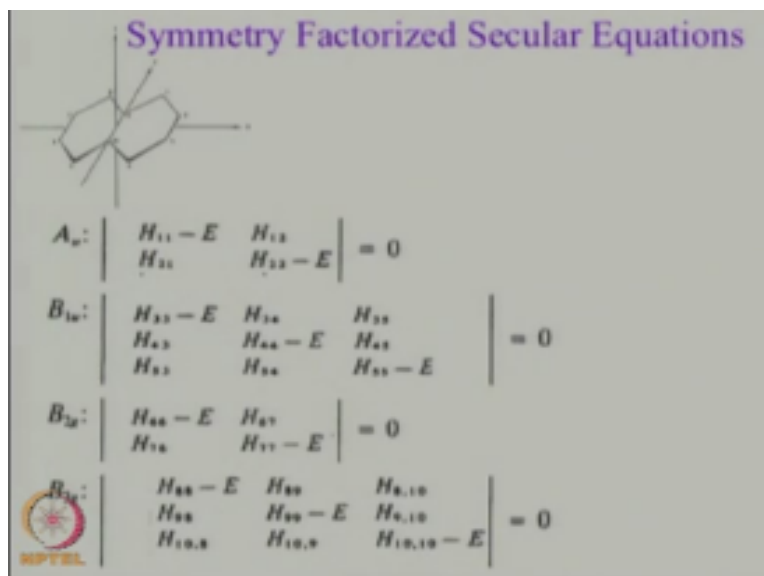
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But even before we get there, now see we had this huge determinant, right 10 by 10. I hope it is not very difficult to see that now instead of writing that 10 by 10 determinant we might as well work with 4 different determinants, two 2 by 2 and two 3 by 3 because since you have done symmetry factorization the functions of one symmetry do not really talk to another. Do not talk to functions or another symmetry.

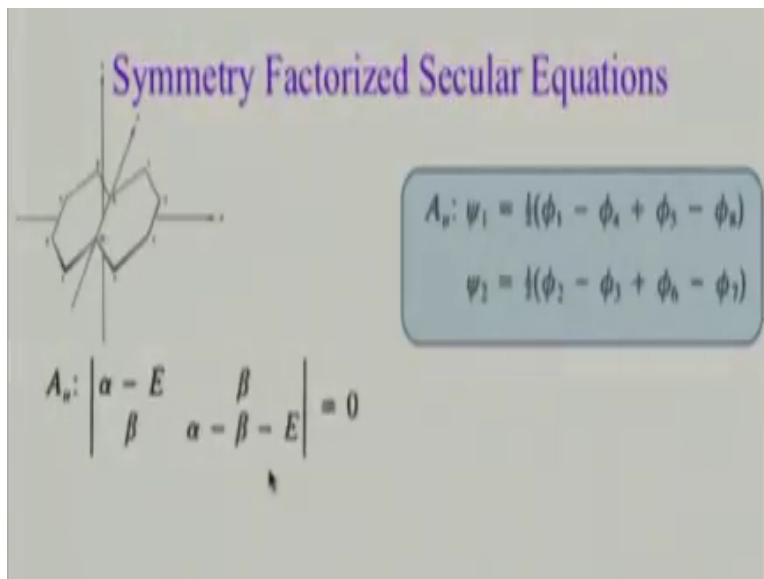
So what you can do is you can just block factorize this determinant using symmetry and now you are going to have 4 different much smaller determinants, equate each to 1 and now you have much smaller equations. What are those equations? These are the equations, alright?

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For A u the equation is $H_{11} - E$. Just one word of caution. This H_{11} here, is this the Huckel H_{11} ? No, because the wave functions that you are using here are really the linear combinations. As we are going to see we will be able to reduce H_{11} and we will be able to express H_{11} in terms of the Huckel alpha beta, okay? But it is important to understand that H_{11} by itself is not really Huckel alpha. Okay, so these are the 4 equations that we get. So let us try to solve them one by one.

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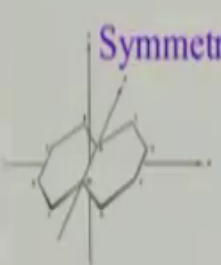
This is the easiest equation. How do I solve? I solve by using the wave functions ψ_1 and ψ_2 , okay? Now we actually have to work out what is H_{11} , okay? Are you ready for that? Alright, so I want you to tell me what is H_{11} ? It is $\int \psi_1 H \psi_1$ over all space. So what will it be? Of course, there is one half from this ψ_1 , another half from this ψ_1 , they are multiplied together. So I am going to get one-fourth outside and inside what do I get?

Inside I get $\int \phi_1 H \phi_1$ then, then what? How many terms will I get, first tell me that? How many terms am I going to get? 16 terms. But do I need to write all 16 terms? Because this ψ_1 , ψ_1 that I write, will you agree with me that, that is Huckel alpha, right? Because ϕ_1 is p right? So if it is Huckel alpha then I know very well what to write and what not to write. If it is s we do not even bother, okay? So can you simplify that for me and tell me what you are going to get?

Okay, I think now you can work it out. I will show you the answer. This is the answer you get. It turns out to be $\alpha - E$ which you could have actually got by mistake thinking H_{11} is just α but then you can make no mistake about this. This one turns out to be $\alpha - \beta - E$. that = 0.

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Symmetry Factorized Secular Equations



$$B_{1u}: \psi_3 = \frac{1}{2}(\phi_1 + \phi_4 + \phi_5 + \phi_6)$$

$$\psi_4 = \frac{1}{2}(\phi_2 + \phi_3 + \phi_6 + \phi_7)$$

$$\psi_5 = \frac{1}{\sqrt{2}}(\phi_5 + \phi_m)$$

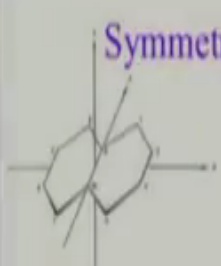
$$A_g: \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - \beta - E \end{vmatrix} = 0$$

$$B_{1u}: \begin{vmatrix} H_{11} - E & H_{12} & H_{13} \\ H_{21} & H_{22} - E & H_{23} \\ H_{31} & H_{32} & H_{33} - E \end{vmatrix} = 0$$

Second one, this is the secular determinant for B_{1u} . so I request you to please work this out yourselves. Right now, I will only show you the answer because otherwise it gets kind of boring. But then please work this out yourselves and convince yourself that this is correct. So this is B_{1u} , this is the secular determinant for B_{1u} and these are the linear combinations that I have.

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Symmetry Factorized Secular Equations



$$B_{1u}: \psi_3 = \frac{1}{2}(\phi_1 + \phi_4 + \phi_5 + \phi_6)$$

$$\psi_4 = \frac{1}{2}(\phi_2 + \phi_3 + \phi_6 + \phi_7)$$

$$\psi_5 = \frac{1}{\sqrt{2}}(\phi_5 + \phi_m)$$

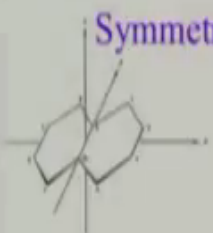
$$A_g: \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - \beta - E \end{vmatrix} = 0$$

$$B_{1u}: \begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha + \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha + \beta - E \end{vmatrix} = 0$$

If I substitute and simplify this is what I am going to get, another determinant in terms of alpha beta and E.

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Symmetry Factorized Secular Equations



$$B_{1g}: \psi_6 = \frac{1}{2}(\phi_1 + \phi_4 - \phi_3 - \phi_6)$$

$$\psi_7 = \frac{1}{2}(\phi_2 + \phi_5 - \phi_6 - \phi_1)$$

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

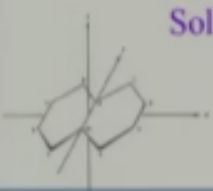
$$B_{1u}: \begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha + \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha + \beta - E \end{vmatrix} = 0$$

$$B_{2g}: \begin{vmatrix} H_{66} - E & H_{67} \\ H_{76} & H_{77} - E \end{vmatrix} = 0$$

Similarly, you can do the same thing for B 2g and for B 3g. Alright, you got the determinant.

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Solution of Secular Equations



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

$$B_{1u}: \begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha + \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha + \beta - E \end{vmatrix} = 0$$

$$B_{2g}: \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + \beta - E \end{vmatrix} = 0$$

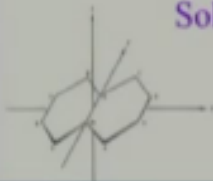
$$B_{3g}: \begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha - \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha - \beta - E \end{vmatrix} = 0$$

What is the next step? Solve the equation and get the values of E. So see what have we got so far? Have we got the MOs? We have not got the MOs. But we have got an idea of the constituents of MOs of particular symmetries. But even without knowing what the MOs are really like, what they really look like what we are able to do is we now see by solving these

equations we will be able to get expressions for energies for the different symmetries for molecular orbitals of different symmetries.

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Solution of Secular Equations



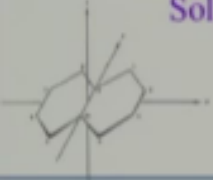
	Energy in β with $\alpha = 0$
$A_{1g}: \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - \beta - E \end{vmatrix} = 0$	
$B_{1u}: \begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha + \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha + \beta - E \end{vmatrix}$	
$B_{2u}: \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + \beta - E \end{vmatrix} = 0$	
$B_{2g}: \begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha - \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha - \beta - E \end{vmatrix}$	

What does the first one give you? Well when we do this remember that the usual practice is set alpha to be equal to 0 and write your expression in terms of beta and one more question from your previous knowledge. Is beta positive or negative? Beta is negative, do not forget. It is stabilization energy, right. Beta is negative. Can you solve this equation for me, the first one Au? Of course what you do is put 1 in place of beta and put 0 in place of alpha before you begin.

So the determinant becomes $-E$, 1 and second line is 1 and $-1 - E$ and by the way we are discussing from Cotton's book but this B_{2g} determinant is actually written wrongly in Cotton's book. They have written alpha - beta. That is not correct. It is alpha + beta - E. Any answer for the first one? Just do the first one and I will give you the rest. What have you got? This?

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Solution of Secular Equations

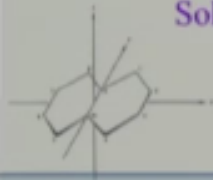


		Energy in β with $\alpha = 0$
A_g :	$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - \beta - E \end{vmatrix} = 0$	$\frac{-1 \pm \sqrt{5}}{2} = -1.618, +0.618$
B_{1u} :	$\begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha + \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha + \beta - E \end{vmatrix}$	
B_{2u} :	$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + \beta - E \end{vmatrix} = 0$	
B_{2g} :	$\begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha - \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha - \beta - E \end{vmatrix}$	

So that simplifies as -1.618 and 0.618 . can you tell me which one of this is bonding and which one of this is antibonding? -1.618 that is stabilization therefore bonding and $+0.618$ that is destabilization therefore antibonding, right? Wrong. Because it is 0.618β . β is actually negative. We have taken β to be 1 that is a different issue, alright. So we get 2, energies of 2 MOs already. From the second one, how many will we get? That would give me a third order equation in E is it not? Right, so 3 should come? And actually there are 3 B_{1u} molecular orbitals.

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Solution of Secular Equations

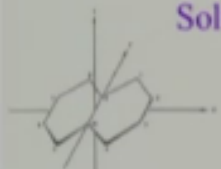


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A_g :	$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - \beta - E \end{vmatrix} = 0$	$\frac{-1 \pm \sqrt{5}}{2} = -1.618, +0.618$
B_{1u} :	$\begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha + \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha + \beta - E \end{vmatrix}$	$1, \frac{1 \pm \sqrt{13}}{2} = 2.303, -1.303$
B_{2u} :	$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + \beta - E \end{vmatrix} = 0$	
B_{2g} :	$\begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha - \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha - \beta - E \end{vmatrix}$	

So the answer you get from there is $1, 2.303, -1.303$. Work it out you will get it.

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Solution of Secular Equations

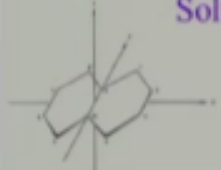


	Energy in β with $\alpha = 0$
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$B_{1g}: \begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha + \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha + \beta - E \end{vmatrix}$	$1; \frac{1 \pm \sqrt{13}}{2} = 2.303, -1.303$
$B_{2g}: \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + \beta - E \end{vmatrix} = 0$	$\frac{1 \pm \sqrt{5}}{2} = 1.618, -0.618$
$B_{3g}: \begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha - \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha - \beta - E \end{vmatrix}$	

Next one gives you 1.618 and -0.618 . So see if you look at just this A u the bonding one is 0.618 antibonding one is 1.618. I am only talking about magnitude. But if you consider A u and B 2g then it is exactly balanced, is it not, energy balanced. So finally when we look at everything together then you will get energy balance. But you will not get energy balance by looking at only one kind of symmetry by itself, it is not necessary.

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Solution of Secular Equations

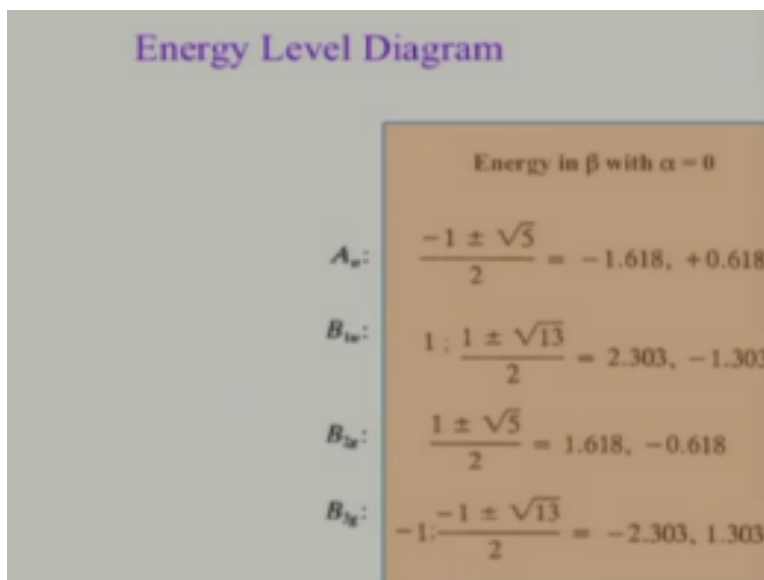


	Energy in β with $\alpha = 0$
$A_{1g}: \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - \beta - E \end{vmatrix} = 0$	$\frac{-1 \pm \sqrt{5}}{2} = -1.618, +0.618$
$B_{1g}: \begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha + \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha + \beta - E \end{vmatrix}$	$1; \frac{1 \pm \sqrt{13}}{2} = 2.303, -1.303$
$B_{2g}: \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + \beta - E \end{vmatrix} = 0$	$\frac{1 \pm \sqrt{5}}{2} = 1.618, -0.618$
$B_{3g}: \begin{vmatrix} \alpha - E & \beta & \sqrt{2}\beta \\ \beta & \alpha - \beta - E & 0 \\ \sqrt{2}\beta & 0 & \alpha - \beta - E \end{vmatrix}$	$-1; \frac{-1 \pm \sqrt{13}}{2} = -2.303, 1.303$

Finally, B 3 g. These are the answers. -1 , -2.303 and 1.303 . Okay, can you quickly count how many bonding, how many antibonding I have got? The ones with $-$ sign, are they bonding or antibonding? Antibonding. So, how many antibonding have we got? 5? How many bonding have you got? 5. So we are happy, right. So, I mean it is good to do this kind of checks when we do a

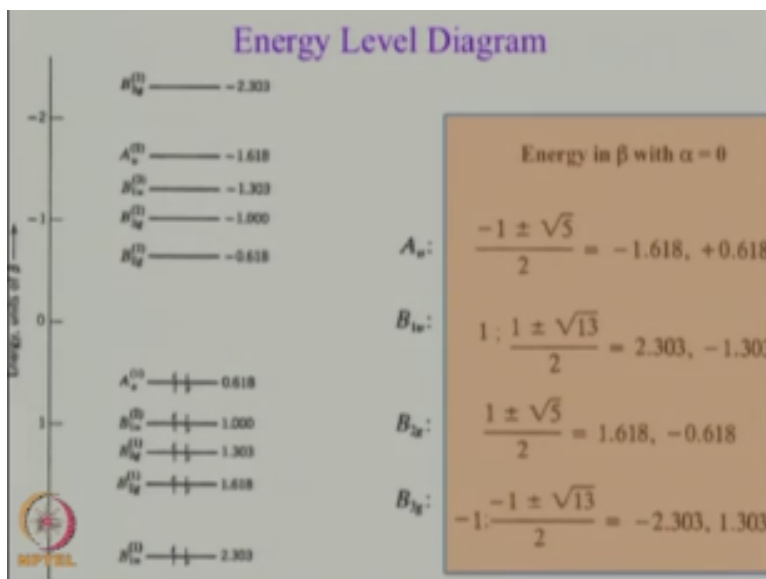
calculation like this because if something has gone wrong usually you are not going to get 5 and 5 and then you know right away that something is goofed. Alright, so this is what it is.

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Now what I can do is, I can draw the energy diagram. What will the energy diagram look like? What is the symmetry of the lowest energy bonding orbital? Yes, B₃₁. What is B₃₁? What are you saying? B₃ or B₁, u or g? B_{1u} and what is the energy, yes so 2.303; 2.303 beta is the stabilization energy. What is the next one? B_{2g}. What is the next one? A_u is 0.618 and what about B_{3g}, right do not forget that. So this is what you get.

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So lowest energy orbital is B 1u then B 2g, B 3g, B 1u, A u and then you have B 2g, B 3g, B 1u, A u, B 3g. So one very significant difference with benzene. Is there some very significant difference from benzene? There is no degeneracy here. In benzene there is degeneracy and why is it that in benzene there is degeneracy and there is no degeneracy here? Because remember it is a D_{2h} molecule.

In D_{2h} there is only one-dimensional representation, one-dimensional irreducible representation. No 2-d representation. So degeneracy does not follow automatically, right? This is one thing. Anything else? What are the symmetries of the orbitals in benzene? Okay, maybe that is asking for too much. It is fine. We will go with this. Fine. So now we take a break and we will come back and we will discuss how these energy levels can be probed experimentally and when you try to do that what kind of more interesting situation arises.