

Symmetry and Group Theory
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Lecture - 59
Naphthalene - I

Right. Good afternoon. Thanks for coming on a short notice. What we will do today, we will try to understand the energy levels, electronic energy levels of naphthalene and we will try to see what we can learn about electronic spectra of naphthalene as well. Now to do this let us remind ourselves about two, three things that we are going to use here. So first thing that we write, let us say is Schrodinger equation.

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$H\Psi = E\Psi$
 $(H-E)\Psi = 0$
 LCAO-MO: $\Psi = \sum_i a_i \phi_i$
 $(H-E)(a_1 \phi_1 + a_2 \phi_2 + \dots + a_n \phi_n) = 0$
 $a_1 [\langle \phi_1 | H | \phi_1 \rangle - E \langle \phi_1 | \phi_1 \rangle] + a_2 [\langle \phi_1 | H | \phi_2 \rangle - E \langle \phi_1 | \phi_2 \rangle] + \dots + a_n [\langle \phi_1 | H | \phi_n \rangle - E \langle \phi_1 | \phi_n \rangle] = 0$
 $\langle \phi_i | H | \phi_j \rangle = H_{ij}$
 $\langle \phi_i | \phi_j \rangle = S_{ij}$
 $(i=j)$
 $a_1 (H_{11} - E S_{11}) + a_2 (H_{12} - E S_{12}) + \dots + a_n (H_{1n} - E S_{1n}) = 0$
 \vdots
 $a_1 (H_{i1} - E S_{i1}) + a_2 (H_{i2} - E S_{i2}) + \dots + a_n (H_{in} - E S_{in}) = 0$

I can rewrite this as say $H - E$ operating on $\psi = 0$, right? Now when I say ψ what I really mean in the discussion of today is molecular orbitals. How do we write molecular orbital in the level that we are dealing with right now? What is the model that we use for molecular orbitals? What approximation do you use for molecular orbitals? Ya, louder please. Linear combination of atomic orbitals. So LCAO MO.

So when you use LCAO MO, you write it as something like sum over i say $a_i \phi_i$. Well the convention is to write ψ with subscript of i and ϕ with subscript of j but then I will just write it in terms of one ψ for the moment and then let us see what comes out of it. So ψ here is

molecular orbital? The ϕ 's are atomic orbitals. So you write the molecular orbital as linear sums of atomic orbitals, right?

Why do we do this because it is not so easy to solve Schrodinger equation. Actually it is impossible for anything that has too many electrons or is too big or just like that, okay. Now the question is since we cannot really write Schrodinger equation so well, how do I know the energies? How do I know the energies? So the work we are trying to do is this. We write here say $H - E$, I will write like this $a_i \phi_i$ no, maybe I will write $a_1 \phi_1 + a_2 \phi_2$ plus so on and so forth. Let us say I am using n number of atomic orbitals in ϕ_n , that is equal to 0 okay.

What I will try to do is, I will try to arrive at a set of secular equations so that I can solve this. Of course there is no way in which I can know all these coefficients from just one equation. So the common technique that we use in quantum mechanics is left multiply by say ϕ_1 . Let us consider orbitals to be real for now. Left multiply by ϕ_1 and integrate. What do you get in that case?

You get something like $\int \phi_1 H \phi_1 - E \int \phi_1 \phi_1$ over all space plus, have I missed something here? a_1 ; plus I have a_2 . What am I doing? I am multiplying the whole thing by ϕ_1 or ϕ_1^* and integrating over all space. $a_2 \int \phi_1 H \phi_2 - E \int \phi_1 \phi_2$ and so on and so forth until the n th term $a_n \int \phi_1 H \phi_n - E \int \phi_1 \phi_n$ over all space. That will be equal to 0. Yeah, what was that? Right. Is this okay?

Now let us see if we can simplify this a little bit. So this wherever we have something like say $\phi_i H \phi_i$, we will write that as H_{ii} . Wherever we have something like $\phi_i H \phi_j$ integrated over all space, we will write H_{ij} . What is this? $\int \phi_1 \phi_1$ over all space; that is 0? That is 1, right because we are dealing with orthonormal set of orbitals, orthonormal set of wave functions. That is one.

But what is this? $\int \phi_i \phi_j$ over all space where i is not equal to j . What is that equal to? That is not 0. Why? Because do not forget the orbitals are on different atoms. We are taking linear combination of atomic orbitals from different atoms. So my 1s orbital and your 1s orbital

they are not mutually orthogonal, okay? So and in fact we have encountered this when we studied chemical bonding.

What do we call this? Integral over $\phi_i \phi_j$ over all space where i and j are different atoms actually. Overlap integral is it not? So I call this S_{ij} , alright? So in terms of that we can write this expression. We get a 1 multiplied by $H_{11} - E$. then you have plus, okay I should put a bracket, a 2, what will this be $\phi_1 H \phi_2$ yeah integral $\phi_1 H \phi_2$ this one what will it be? $H_{12} - E S_{12}$ right plus so on and so forth. Okay, I goofed up a little bit.

Plus a $n H_{1n} - E S_{1n}$. That is equal to 0. S is not a subscript, I am sorry $S_{1n} = 0$, right? So I have one equation, but then I have n unknowns. How will I find this? I need n equations. How do I generate n equations like this? How did I get these equations in the first place? I have left multiplied by ϕ_1 and integrated over all space. So I can do that for ϕ_2 , I can do that for ϕ_3 ϕ_4 ϕ_5 so on and so forth up to ϕ_n . So when I do that, what do I get?

I get a system of equation and in each one let me just write the general term here. I will get a 1 multiplied by what will this be, I am left multiplying by say the i th coefficient, sorry i th wave function, ϕ_i . Then this will be $H_{i1} - E + a_2$ into $H_{i2} - E$ sorry $E S_{i2}$ plus so on and so forth plus a n multiplied by $H_{in} - E S_{in}$ that is equal to 0, okay. So this is the general form of equation where i ranges from 1 to n , alright?

And what is common in this family of equations? What are the unknowns? The unknowns are the coefficients, right? a_1 , a_2 , a_3 etc. So we have n unknowns and n equation. So if you have a way of knowing H_{ii} and if you have a way of knowing E then I should be able to find what these are. Yes. What did I say? S_{i1} did I write oh I am sorry. No that was a mistake. It is not equal to 1 you are right.

So this is the peril of copying. I copied from the previous line. There it was S_{11} , that is why I wrote it. That was a mistake. Of course, it is not. So S_{ii} is going to be 1, alright. So was that your question as well? Okay. So this is the system of equations and then if you have studied the

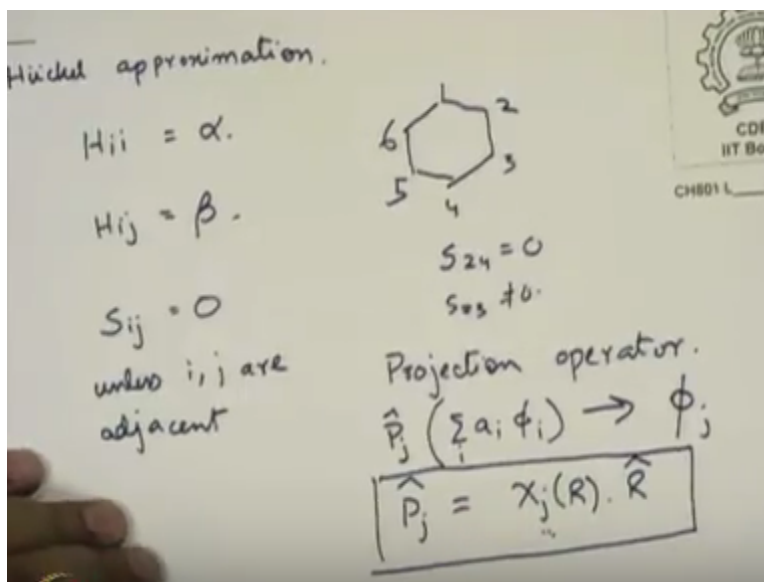
systems of equation you know that these are going to have solutions when the secular determinant is equal to 0, right? What is the secular determinant.

You do not write this a 1, a 2 etc. You take this $H_{i1} - ES_{i1}$ $H_{i2} - ES_{i2}$ etc., make a determinant out of that, equate to 0. That is the condition. So that is called the secular determinant. Now, when you do this and if you expand the determinant you will get a kind of an expression in i , sorry you will get an expression in E is it not? Understand what I am saying?

You have a determinant like that, expand it, equate to 0, you have an expression in a polynomial of E . What is, which order polynomial is it? N . So in principle you should be able to solve that and you should be able to find out what it is, alright? Now, of course we do not want to do that. So what we are discussing today is we are talking about naphthalene and naphthalene is an example of an organic molecule, annular organic molecule which has a pi electron system.

For this we use another approximation. I think chemistry students know it. What is the approximation that is commonly used for this pi electronic systems? Huckel approximation. Can you tell me what Huckel approximation is? What is Huckel approximation?

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See H_{ii} is one thing, then you have H_{ij} and then you have S_{ij} . Now can you tell me? What is the value of H_{ii} ? H_{ii} ; what do we call H_{ii} , what do we call H_{ij} ? Alpha? Which one is alpha? H

α_{ij} is called α and in fact α is said to be 0 in our calculation. What about H_{ij} ? That is called β . And what about S_{ij} ? $S_{ij} = 0$. Is it always 0? When is it not 0? Let us draw our old friend, benzene okay. Let me label the carbons, 1, 2, 3, 4, 5, 6.

So what we are saying is $S_{24} = 0$ but S_{23} is not equal to 0. So $S_{ij} = 0$ unless i and j are adjacent to each other, okay? Does that recall? Does that ring a bell? We recall this? Now, so this is the quantum mechanics that we are trying to develop and we are trying to do it using symmetry. And when you try to use symmetry, again we have to use a kind of an operator. The operator that we are going to use in our discussion of naphthalene is called a projection operator.

We write it as P_j . So what does the projection operator do? What does an annihilation operator do? What is the meaning of annihilation? Yeah, it will annihilate, you are right. But how will it annihilate in the language of quantum mechanics? It gives you an Eigenvalue of 0 is it not? The function gets multiplied by 0. Similarly, a projection operator what it does is, if an annihilation operator annihilates, a projection operator would better project.

The question is what does it project? So what it does is, you take a projection operator and make it operate on some kind of a linear sum, say $\sum_i \phi_i$ it is going to give you, it is going to project the wave function that has the symmetry j , alright and what is the projection operator that we have learnt. How do we write? What is the form of projection operator? P_j is χ_j of R multiplied by \hat{R} where \hat{R} is a symmetry operation.

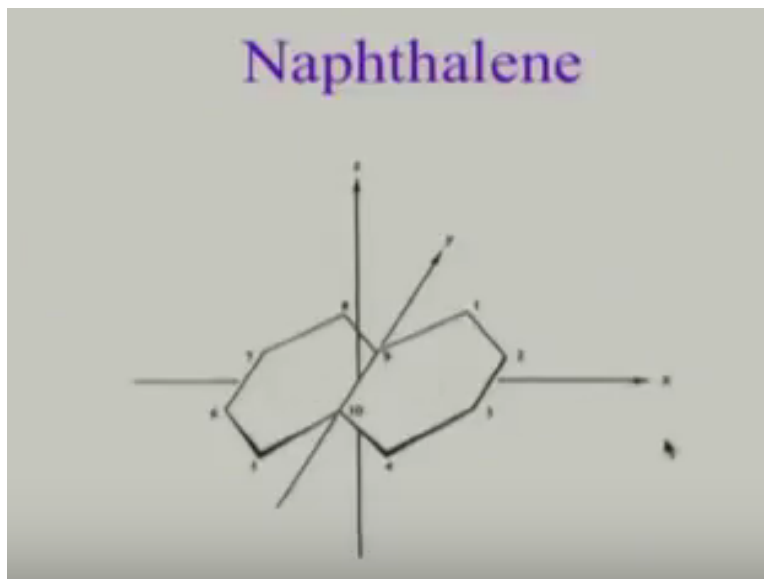
χ_j of R is the character for that same symmetry operation in the j th irreducible representation, alright? So that is what we are going to do today and the system that we are going to study is naphthalene where your Huckel approximation is going to be applicable and then if you are going to study naphthalene and we are going to use projection operator, first thing we need to know is what is the symmetry point group of naphthalene.

What is the point group of naphthalene? Yeah, D_{2h} , right? So naphthalene has a planar structure. The C_2 axis perpendicular to it, we usually call z and there are 2 other axis x and y . They are in the molecular plane. They are also C_2 axis but they are not the principle axis. Which other

symmetry operations are there? Sigma H, sigma H is there. Anything else? Okay. So what we will need is, we are going to need the D_{2d} character table, okay?

Sorry, D_{2h} character table I am sorry. So D_{2h} character table. Of course everybody has a smartphone. Please bring up the character table. Since I am a little more old fashioned than you I will bring out a book. D_{2h}. This is your naphthalene, a D_{2h} molecule.

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Are we ready? Are you ready with the D_{2h} character table? You (()) (17:37). What are the symmetry species in D_{2h}? What is the totally symmetric symmetry species? A_g right and then you have b_{1g}, b_{2g}, b_{3g}. Then you have A_u, B_{1u}, B_{2u}, B_{3u}, okay? So what is the good thing about D_{2h}? If you look at the character table there is something nice about it, yes? All irreducible representations are one-dimensional. So all characters are either +1 or -1.

So if you look at your projection operator you have to make the symmetry operation operate on the function and then multiply by the character. That becomes very easy. You always multiply by either +1 or -1. It does not get easier than that, right? So let us proceed with naphthalene. So this is the convention we are going to use. We are going to use z axis perpendicular to the molecular plane. X axis is taken. So x axis is also called the long axis.

Because if you look at the molecule, of course all axis are from plus infinity to minus infinity. But then it is called a long axis because if you look at the molecule, the molecule has a greater length along x axis and a smaller length along y axis. So x is called conventionally the long axis and y is called the short axis, okay and I think numbering everybody knows.

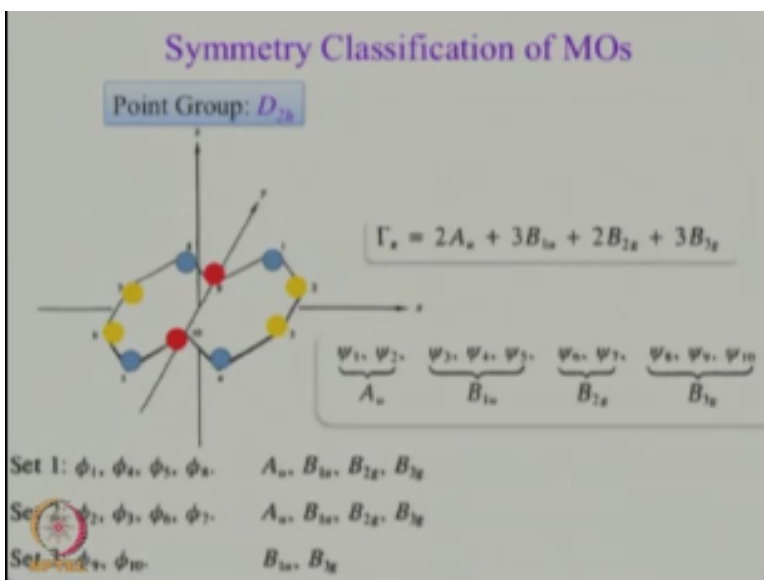
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The Secular Equations

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} & H_{13} - ES_{13} & \dots & H_{1,10} - ES_{1,10} \\ H_{21} - ES_{21} & H_{22} - E & & & \\ & & H_{33} - E & & \\ & & & \ddots & \\ & & & & H_{10,10} - E \end{vmatrix} = 0$$

This is the secular determinant for your naphthalene. What is n here? What is the order? 10, right? 10 atoms. You want to solve this determinant, you are going to get an equation in E to the power 10. Of course, it is solvable, you can do it. But what we will see is we do not have to do it. We can use symmetry to break it down into smaller equations, right. So here we are.

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Let us begin. And while we begin, we will make our problem even easier by recognizing that p orbitals of naphthalene can actually be classified into 3 groups. But well even before that I have spared you some trouble by giving you the answer here. So ideally when we work out problems like this what we do is we start with all the 10 p orbitals, make a reducible representation out of it and try and break it down into its components. So I have done that for you. This is the answer.

The answer is this $\Gamma_{pi} = 2 A_u + 3 B_{1u} + 2 B_{2g} + 3 B_{3g}$. So how many in all? $2 + 3, 5 + 2 + 3 = 10$, total 10 irreducible representations and that is how it has to be, right? because there are 10 orbitals after all. So what we will say is just for the matter of for the sake of convenience we will say that ψ_1 and ψ_2 have A_u symmetry, ψ_3, ψ_4, ψ_5 have B_{1u} symmetry, ψ_6, ψ_7 have B_{2g} symmetry, $\psi_8, \psi_9, \psi_{10}$ have B_{3g} symmetry, right?

And now let us recognize the 3 groups of p orbitals that we can think of. This is the first group. Will you agree with me if I say that 1, 4, 5 and 8, p orbitals on atoms 1, 4, 5 and 8 form a group. Why? Because no matter what you do it, C_{2z}, C_{2y}, C_{2x} or i what happens when I apply inversion to atom No. 1. Where does it go? Atom No. 5. Now if I work with say p z orbital of atom No. 1 and invert it, what do you get?

P z orbital of atom No. 1, yes it becomes and I invert it, so this is the point of inversion. What does it become, does it become the p z orbital of atom No. 5? P z orbital of atom No. 1 after inversion does it become p z orbital of atom No. 5? No? Then what does it become? It becomes minus of that, okay? It is important to realize that, we are going to use it, alright? So please remember when you do an inversion actually it changes sign as well.

It is not just 1 becoming 8 it is p 1 becoming $-p_8$ and similarly p 8 sorry p 1 becoming $-p_5$; p 8 becoming $-p_4$ and so on and so forth, alright but is it possible for any of the operation, sigmas the planes or the inversion or the C_{2s} is it possible to take 1 to 6 or 1 to 7? Never, okay. So these four 1, 4, 5 and 8 form one group. 2, 3, 6 and 7 form another group. And these 2 groups are very similar to each other, right? Both the groups have 4 p orbitals each. Is that right?

Both groups have 4 p orbitals. See so actually they are going to have very similar symmetries at the end of the game. And we are left with one more pair, 9 and 10. Will u agree with me that 9 and 10 form a group. You perform C_2 let us say C_{2z} . What happens? And let us work with p orbitals. P 9 becomes p 10, p 10 becomes p 9. What happens when you apply p x? p 9 becomes - p 10; p 10 becomes - p 9. Inversion same thing, p 9 and - p 10. P y, what happens when I do p y.

When I apply p y, what happens to p 9 and p 10? Sorry why I am saying p y, sorry. When I apply C_{2y} , C_2 with respect to y what do I get? What happens to p 9 and p 10? P 9 becomes - p 9, p 10 becomes - p 10 alright. So these 3 form three different groups. And also you can, what you could do is you could take $\phi_1, \phi_4, \phi_5, \phi_8$ together, form the reducible representation, break them down and you will see that the breakdown into $A_u + B_{1u} + B_{2g} + B_{3g}$. Well, yes and no. They are molecular orbitals.

But then when we do a classification like what we are doing now, we are not going to get molecular orbitals, we will get symmetry adapted linear combinations, combinations of which is going to give me molecular orbitals. But you see when you combine the SALCs, so the question that was asked is the ψ_1, ψ_2 are these molecular orbitals. What I am saying is they are but then what we are doing now when we consider these 3 groups separately is that we are not going to get molecular orbital straight away.

We are just going to generate SALCs and then we are going to combine SALCs of same symmetry to generate the molecular orbitals, right? So coming back to what we were saying actually there is no need to do this. With a little bit of experience if you just look at this linear sum, $2A_u + 3B_{1u} + 2B_{2g} + 3B_{3g}$ right? I can write it as 2 multiplied by $A_u + B_{1u} + B_{2g} + B_{3g} + B_{1u} + B_{3g}$. Is that right?

So actually I can tell right from there that $B_{1u} + B_{3g}$ is going to be the symmetry of ϕ_9 and ϕ_{10} . And each of these will be $A_u + B_{1u} + B_{2g} + B_{3g}$, okay? So this much is done. What is the next step? The next step is to use the appropriate projection operator to generate the symmetry adapted linear combination. That is what we will take up in the next module. Okay, welcome back after a long break.

We are discussing the electronic, we are discussing the molecular orbitals, ψ molecular orbitals of naphthalene and what we have got so far is that we have been able to determine the symmetries of the molecular orbitals that we are going to get. We have also been able to break down the constituent p orbitals into 3 different groups. Two consisting of 4 p orbitals each, one consisting of 2 p orbitals, alright and we have also said that the first two sets of p orbitals are going to have symmetry $A_u + B_{1u} + B_{2g} + B_{3g}$. The last one will have $B_{1u} + B_{3g}$.

Now what we will do is we will use projection operators on these ψ_1, ψ_4 etc. and generate the linear combinations. But let me stop here and ask you a question. Why is it that okay how what are SALCs? What are symmetry adapted linear combinations? They are linear combinations of atomic orbitals that give you some particular symmetry.

So now I am saying that I am going to generate those linear combination by using the projection operator of right symmetry on one of the constituent p orbitals. How does that happen? You understand the question? This is what I am trying to say.