Symmetry and Group Theory
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Lecture - 55
SALCs as Pi-MO, Benzene

What is the point group? And where is my character table? Now, I am at a loss. I better not lose that character table. Do not tell me I did this. Oh man. It just means that you have to spend a few minutes in copying the thing and me too. Okay, benzene. Anyway, so what we will need is the basics, H character table and right now I have no option but to write it. I want to talk about pi bonding of benzene. What is my basis? The 6 p orbitals, one on each carbon, right?

So what will be the dimensionality of the representation that I get? 6, right? Now, when I break that down, I will just give you that answer.

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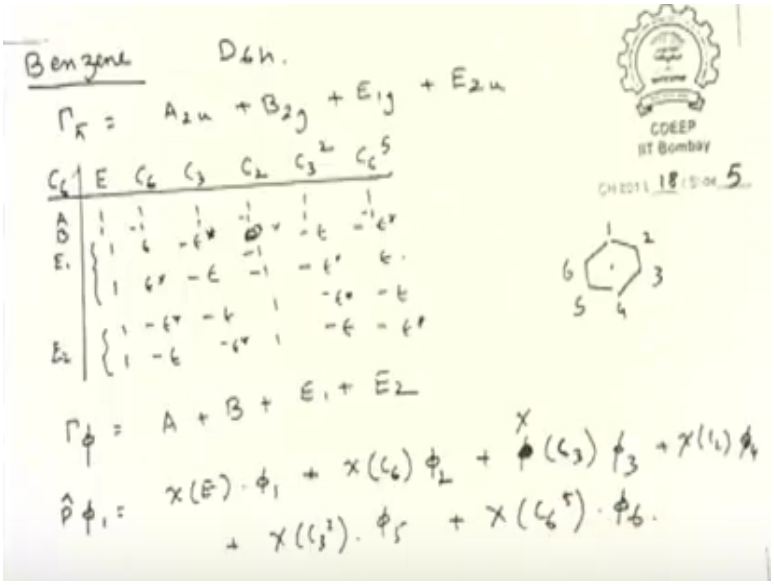

This is D 6h. Gamma pi turns out to be A 2u + B 2g + E 1g + E 2u. I strongly recommend that you work this out yourself, okay. It will be good practice. Now, what I want to do of course is that I do not want to work with D 6h, it is too big. What is the subgroup that I want to use? C 6. So that will be a smaller character table, I can write it. C 6. What do you have in C 6? We have E, C 6, C 6 square is C 3. Then C 3 square. Well the way it is written is C 2. What is C 2?

How do I get C 2? C 6 cube, right? C 6 cube is C 2, then C 3 square and finally C 6 to the power 5. So C 6 to the power 1, C 6 to the power 2, C 6 to the power 3, C 6 to the power 4, C 6 to the power 5, C 6 to the power 6, right? So A is 1 1 1 1 1 1. Then you have E 1 which is a combination of 1, epsilon, epsilon square, epsilon square *, what am I doing? 1, epsilon, - epsilon *. This is -1. This is why we did not want to do this; - epsilon, - epsilon *.

And this is 1, epsilon *, - epsilon. What is the relationship between epsilon and epsilon * other than the fact that they conjugate? They add up to give -1. You just worked it out. 1, epsilon *, - epsilon, -1, - epsilon *, epsilon, okay and then you have E 2. I will write like this. - epsilon *, - epsilon, - epsilon, - epsilon *, 1, 1, - epsilon *, - epsilon, - epsilon, - epsilon *, okay.

So what is gamma phi in C 6? What will gamma phi be in C 6? See that is why I needed the character table. Anyway, please work out the correlation yourself. You need to have the 2 character tables in front of yourself. Just believe me when I write this. A + B + E 1 + E 2. What do you mean B is not there? That is because I have not written it. 1, -1, 1, -1, 1, -1. But you should have noticed that something is missing, right? Because only 5 are there. There has to be 6.

So 1, -1, 1, -1, 1, -1. Not very difficult to remember. , -1, 1, -1, 1, -1, okay? Let me just turn the page. This is very confusing for me. So many 1s and so many epsilons. Fine. Okay, now what should I do? First thing let us recall what we said for that 3 atom system, 3 phi system. What is the only role of these C 3 operations. Okay, what happens when C 6 operation here. C 6 operates on phi 1, what will you get? Phi 2. C 6 square on phi, phi 3.

C 6 cube, C 6 to the power 4, C 6 to the power 5 and C 6 to the power 6. So it does not matter which projection operator I use. I can write it like this. Any projection operator operating on phi 1 should give me something like this. Chi * phi 1 + chi C 6 into phi 2 + chi why not? C 6. C 6 means one rotation. One rotation, right. One rotation by, by what? 360 degrees by 6 that is 60 degrees. One rotation by 60 degrees should take me from phi 1 to phi 2. Right or wrong?

This is C 6. If you rotate once you go from 1 to 2. Rotate twice, you go from 1 to 3. Rotate thrice, you go from 1 to 4. Rotate four times, go to 5. Rotate 5 times, go to 6. Rotate 6 times

come back to one. Shubanghi is this okay? Are you all okay with this? So chi into phi 1 + chi C 6 into phi 2 + chi C 3 into phi 3 + chi C 2 into phi 4 + chi C 3 square into phi 5 + chi C 6 to the power 5 into phi 6, okay?

So once again what we have generated is a linear combination of atomic orbitals. That is going to happen for cyclic systems. Okay, I hope you have taken down the character table? So may I go to a fresh page. I myself do not like the sight of this ugly character table that I have written, alright. So if you do that what do you get? Work out the 6 what is it called SALCs that you get this way. What will be the symmetries? A, B then for E 1 you will get 2, for E 2 you will get 2.

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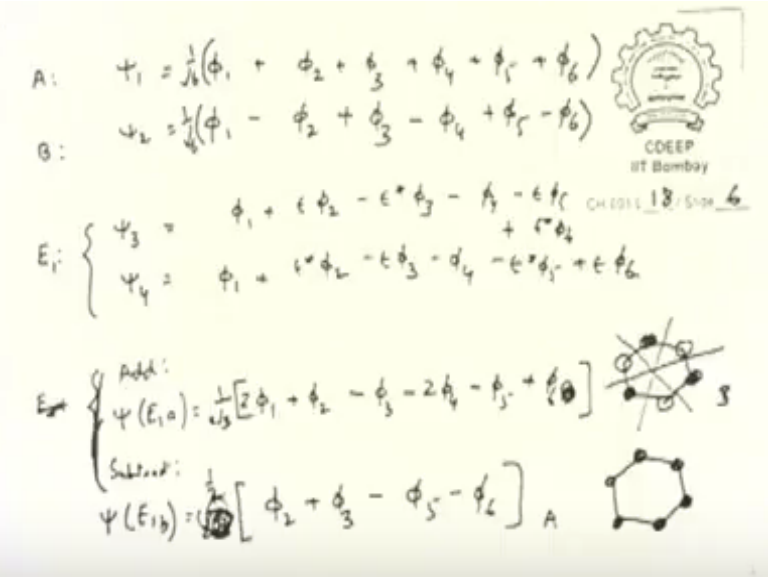

So A, B, E 1 you should get 2 and for E 2 also you should get 2. What do you get? A even I will write. That is very easy right? Especially since you have written that chi E * phi 1 + chi C 6 * phi 2 and so on and so forth A is very easy. All chi's are 1, right? So that is what it is. What about B? That is also easy. Just have to multiply by chi's now. What will it be? Phi 1 – phi 2 then + phi 3 – phi 4 then + phi 5 – phi 6.

Even before writing the other two, I want to see if I can draw the nodes, okay. So this is for A, this is for B. So here everything is possible, everything is positive rather; everything is positive. So how many nodes for A? 0. And what about this? Phi 1 is +, phi 2 is -. Phi 3 is +, phi 4 is -. Phi

5 is +, + 6 is -. So it is full of nodes. How will I draw the nodes? See this is one node, this is one node, this is another node. Three nodes is it not?

Does that remind you of the pi orbitals of benzene or not? You have drawn it in some way or the other, right? So this is the lowest energy pi orbital of benzene. This is actually the highest energy pi orbital of benzene. No node and 3 nodes is it not? So what will be the normalization constant, both cases? Now, what about E 1? What are the two? What is psi 3? Remember you just had to multiply by the corresponding characters; phi 1, phi 2, phi 3, phi 4, phi 5, phi6 are there.

You just have to multiply by the corresponding characters. It is not difficult. Two phi? No. I am taking that separately, right? These are one-dimensional IRs. Which group am I working with? Am I working with D 6h? No. I am working with C 6, right? So if I can get back to my ugly character table, that is later. First you use the IRs, okay. So this is one IR, this is one IR. It is just that we have combined them and given the name like that.

But you must work with the individual IRs okay? So first we are going to generate the complex LCAOs, okay and then from there we are going to generate the real ones. So now tell me, what is psi 3? Phi 5 + epsilon phi 2 - epsilon * phi 3 - phi 4 very good epsilon phi 5 minus or plus, wait. I think it is my mistake translated to you. Hold on. Let me check. I think it is plus. Yeah, plus. These are plus. That is why I took the printout. Plus epsilon * phi 6.

And what about psi 4? Phi 1 + epsilon * phi 2 - epsilon phi 3 - phi 4 - epsilon * phi 5 + epsilon phi 6, okay? So I have generated the SALCs. What is the next step? Add and subtract. See what we will do is we will worry about E 2 later in the next page maybe. Let us worry about this first. Add and subtract, what do you get? What do you get when you add? Hold on. 2 phi 1 + phi 2, right? Do not tell me there is another mistake somewhere. Okay, what have we got?

2 phi 1 – phi 2 then? Okay then? For some reason all your plus minuses are interchanged. I do not know why. It is 2 pi i by 6 that is why. It is 2 pi i by 6. Remember we had discussed that once, 2 pi i by 6. That is why you are getting a different result. Because I will spare you the

trouble and write the answer. 2 phi 1 + phi 2 - phi 3 - 2 phi 4 - phi 5 + phi 6. What is the normalization constant? 1 by okay what is this? 1 by 2 root 3 will be common.

Now can you work out? When you subtract and divide by i what you get? - phi 2, - phi 3 then + phi 5 + phi 6 that is right. It is just that? I am justified in writing the -1 also. If you write that you are fine. There is no problem. But generally we write to, I see it is not 1 by root 2. What am I doing? I write it like phi 2 + phi 3 - phi 5 - phi 6. Normalization constant 1 by 2. So now let me, you had this written down in your notebook anyway, right? So let me just draw the diagram once again.

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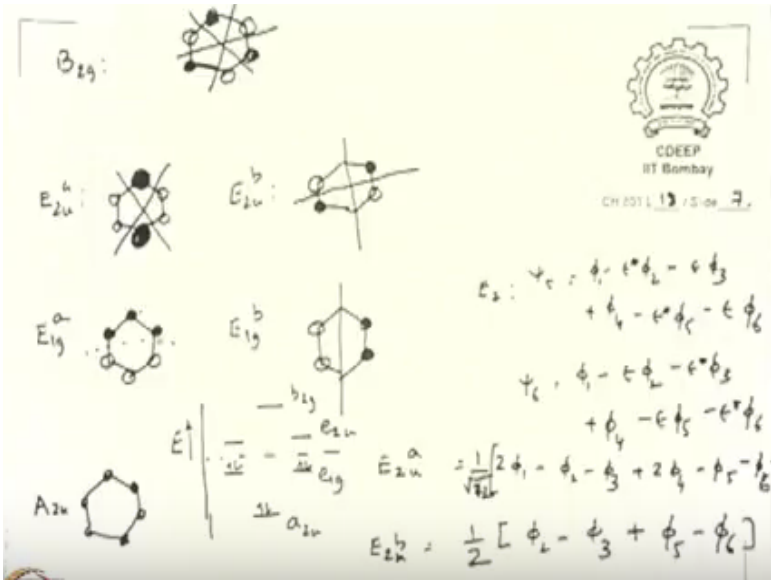

Maybe I can write the others here. So first you have A. Should I call it A? When I go back to D 6h what will it become? It is not A anymore right? What is it in D 6h? D 6h, what is it? A 1g is it not? A 1g, is it A 1 g. I do not have A 1g. What were the symmetries that we got from D 6h? A 2u + B 2g + E 1g + E 2u right? So this is A 2u. See this is what I told you is it not? That in D 6h gamma pi is A 2u + B 2g + E 1g + E 2u. Then we went from D 6h to C 6.

Then we said that by that correlation diagram A 2u becomes A, B 2g becomes B, E 1g becomes E 1, E 2u becomes E 2, right? Now jumping steps here, but you can work it out yourself. You can work out the correlation diagram, okay? So now what we did is after that we worked out what is the linear combination of A symmetry, okay? And that is just plus plus plus plus.

“Professor - student conversation starts” Yes? Sir, when you tell about the coefficients, last one. Which one? In the next slide. 1 by 2 root 3 and, wait we will come to that. Let us first finish this. **“Professor - student conversation ends”.** So if it is A in C 6 which symmetry species is it in D 6h? Has to be A 2u, right? We do not have A 1g or anything. The only A kind of symmetry species we have is A 2u, right? So it is A 2u.

So instead of writing it as A if I go back to the full group, I should write it as A 2u. What is A 2u? No node, okay? What is the next one that we have worked out? B. So B is what B 2u? B 2u or g? B 2g. We will come back to that later. Now let me answer that question. So you are asking how I got 1 by 2 root 3? What did you get? I am trying to normalize, right? So if, to normalize what do I have to do? I have to multiply it by itself and get 1 right?

So what do I get? 4 +1, +1, +1, +2, +4 sorry +1, +1. What is that? Hey do not talk? 12, right? So then it becomes 1 by square root of 12. So 4 in any case you can get square root. So 2 comes out and you are left with 1 by 2 root 3. The answer given in Cotton’s book is 1 by root 12. But 1 by 2 root 3 is fine. You just neglect that because you have to finally normalize. Whatever coefficient comes out is of no consequence because eventually you have to normalize, okay?

So just neglect all coefficients. Whatever comes out common just throw. Work with only the sum and then find the coefficient from the condition of normalization, okay fine. So now next tell me, what was I writing? E 1. So E 1 a. What is the point group, what is symmetry species in D 6h, E 1g right? So let us write it as E 1g and then what will I write. Let me write A here. What is the expression? 2 phi 1. So this is plus. + phi 2 - phi 3 - 2 phi 4 minus plus.

How many nodes? And these orbitals are bigger than this. Sometimes you see that diagram also right. The orbitals are drawn bigger. One is big, one is small. This is what it means. Got it? So what is your E 1g b? Phi 2 + phi 3 – phi 5 – phi 6 right? Did you work that out or not? Phi 2 + phi 3, nothing in phi 4, - phi 5 - phi 6. How many nodes? Where is it? That is the node, not this, right? This is not a node because this is plus, this is minus. Wave function is not changing sign.

Wave function is changing sign from here to here, right? From left to right. So one node here, one node there. Should they not be degenerate, right? What is the symmetry species that belong to? E 1g which is a 2-dimensional symmetry species. So see this is another manifestation that degeneracy and symmetry go hand in hand. If the orbitals belong to a 2-dimensional symmetry species then they are going to be doubly degenerate.

If they belong to a 3-dimensional symmetry species then they are going to be triply degenerate, okay? Now, what is left, E 2? And now we are close so can you work out E 2 quickly? Psi 5, what is psi 5? Work in the C 6 point group and get me the complex wave function. What is psi 5? Phi 1 - epsilon * phi 2 – epsilon phi 3 + phi 4 – epsilon * phi 5 – epsilon phi 6 and what is psi 6? Phi 1 – epsilon phi 2 – epsilon * phi 3 + phi 4 – epsilon phi 5 – epsilon * phi 6.

Add and subtract what do you get? So when I add and subtract what should I get? E 2u a is equal to what? 2 phi 1 – phi 2 – phi 3 + 2 phi 4 – phi 5 – phi 6 very good. Coefficient, I mean 1 by root 12 or 2 root 3 whatever you want to write, but definitely not 1 by root 2. What is your E 2u b. Phi 2 – phi 3 + phi 5 – phi 6. Normalization constant 1 by 2, 1 by root 4. So 2 phi 1 big black circle. - phi 2, small hollow circle. - phi 3, hollow circle.

+ 2 phi 4, - phi 5, - phi 6. Let us finish this one also. Phi 2 – phi 3 + phi 5 – phi 6. Do you see the nodes. This is a node, this is a node. And here this is a node, this is a node, okay? Okay, and let me just draw the last one also. What is it that we had worked out already? What is the symmetry point group? Sorry, what is the symmetry species in D 6h point group? D 2g, tell me what it is? Phi 1, phi 2; phi 1 – phi 2 + phi 3 – phi 4 + phi 5 – phi 6.

How many nodes? 1, 2, 3. So see just by going by the number of nodes we can say that the energy levels of benzene would be like this. This is something that you know already, right? These 3 are bonding orbitals, those 3 are anti-bonding orbitals. How many electrons are there? How many pi electrons? 6. So this is how you generally fill in a simple manner. But what we have learnt now is that now you can write the labels, right for the orbitals.

This is a 2u, this is e 1g, this is e 2u, this is b 2g. How to get the symmetry of states or how to get the nomenclature of states comes after this.