Symmetry and Group Theory
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture - 54
SALCs as Pi-MO, Cyclopropenyl Group

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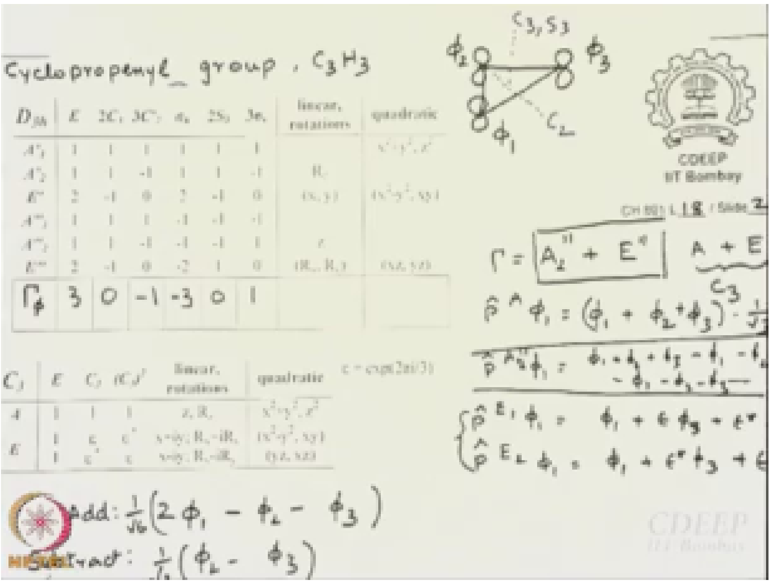

Cyclopropenyl group, C_3H_3

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$	linear, rotations	quadratic
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)
Γ_ϕ	3	0	-1	-3	0	1		

C_3	E	C_3	$(C_3)^2$	linear, rotations	quadratic
A	1	1	1	z, R_z	x^2+y^2, z^2
E	1	ε	ε^*	$x+iy; R_x+iR_y$	(x^2-y^2, xy)
	1	ε^*	ε	$x-iy; R_x-iR_y$	(yz, xz)

$\varepsilon = \exp(2\pi i/3)$

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$$\Gamma = \boxed{A_2'' + E''} \quad \underbrace{A + E}_{C_3}$$

$$\hat{P}^A\phi_1 = (\phi_1 + \phi_2 + \phi_3)\cdot\frac{1}{\sqrt{3}}$$

$$\hat{P}^{A_2''}\phi_1 = \phi_1 + \phi_2 + \phi_3 - \phi_1 - \phi_2 - \phi_3 - \phi_1 - \phi_2 - \phi_3$$

$$\hat{P}^{E_1}\phi_1 = \phi_1 + \varepsilon\phi_3 + \varepsilon^*$$

$$\hat{P}^{E_2}\phi_1 = \phi_1 + \varepsilon^*\phi_3 + \varepsilon$$

Add: $\frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)$

Subtract: $\frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$

Phi 1, no. So when you add these two you get 2 phi 1 then - phi 2 - phi 3 and when you subtract what do you get? Because something multiplied by i, but you just divide by i. Subtract and divide by i. What do you get? You got the same wrong, Anu? Root 3 is common, phi 2 - phi 3, okay? So these are the SALCs. If they are to be molecular orbitals they should be normalized right? What is the normalization constant for this. Phi 2 – phi 3? 1 by root 2.

What is the normalization constant for the first one? 1 by root 6. Do not forget the 2 in the beginning. I think there are questions, please ask.

"Professor - student conversation starts" Sir, after subtracting the i's then it shows. That is why I am dividing by i. Then divide it by phi? Ya. See our whole purpose is to just convert to something that is real. I have to divide by i. I can do whatever I want. I can add, subtract, multiply, divide by constant; i is a constant. Any other question? **"Professor - student conversation ends".**

Are you convinced, what happens if you add. What do you get? Phi 1 + phi 1 is 2 phi 1. Then you get epsilon + epsilon * phi 2 + epsilon + epsilon * phi 3 is it not? And epsilon + epsilon * is -1. That you worked out a little while earlier. That is why you write -1 here -1 here. And when you subtract what happens? Phi 1 – phi 1 is gone. Then you have epsilon - epsilon * multiplied by phi 2 and - epsilon - epsilon * multiplied by phi 3.

Whatever you put the minus in front of anyone, it does not matter. So this is how we generate the MOs. And why am I calling this MOs because in this stage they are actually linear combinations of all the atomic orbitals, alright? So this is a simple example by which what we have learnt is we have learnt how to handle a little big molecules. Is only a 3-atom molecule I agree but 3 is more than 2 is it not?

"Professor - student conversation starts" So you are saying these are the 2 MOs. Yes. So yesterday we talked about something like orthogonality. Work out if they are orthogonal or not. **"Professor - student conversation ends".** Multiply them together and add. What do you get? Phi 1 of course would not even come. Are they orthogonal or not? Please multiply. The answer is not written anywhere. You have to work it out and see.

Please multiply 1 by root 2 * 2 phi 1 - phi 2 - phi 3 by 1 by root 2 phi 2 - phi 3 and see whether you get 0 or not. Remember that phi 1 phi 2 phi 3 in themselves are orthogonal. Do you get 0 or not? Are you getting 0? Then what about phi 1 + phi 2 + phi 3 and 2 phi 1 – phi 2 – phi 3. Are they orthogonal? Rishit?

"Professor - student conversation starts" Is it just coincidental that we added and subtracted then we got orthogonal. It is not coincidental. It is a result of experience, right. We see further because we stand on the shoulders of giants remember. So giants have worked it out for us. **"Professor - student conversation ends".**

And the logic is that you are going to get E double dash. When you combine these 2 irreducible representations corresponding to E, right and there are only 2 ways to combine, add and subtract.

So what this does is this saves us a lot of trouble. That if you generate by actual symmetry operation and all what will happen is you are going to end up with not the actual LCAOs but their linear combinations. I skip that part. Please go through Cotton's book.

They have done it that way. By using the full D 6h group they have worked out. They have seen what they get. They do not get these two. They get linear combinations. Well they get first one. They do not get the second one. And then you have to do it by Brute Force Method, trial and error and find the last one. That is not such a happy situation, okay? So this is something that saves us a lot of trouble, okay? So let me, this page is a little cluttered. Let me write this on a little fresh page.

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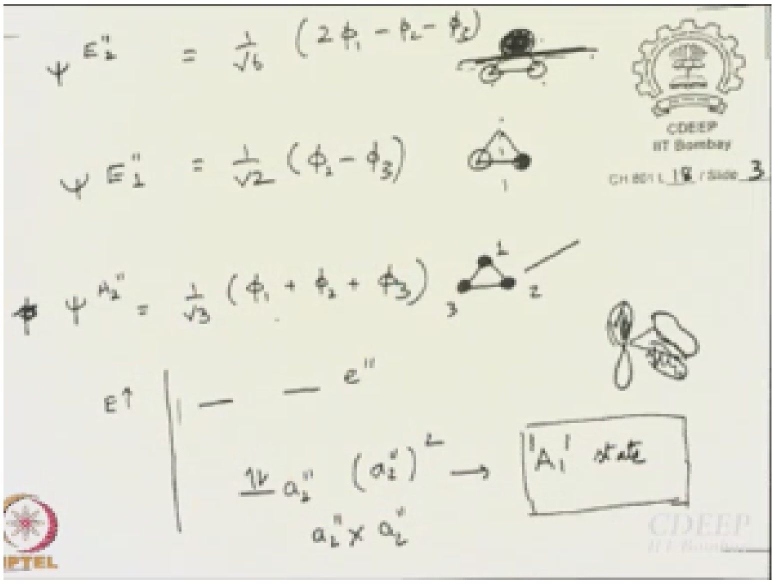

$\psi^{E_2''} = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)$

$\psi^{E_1''} = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$

$\psi^{A_2''} = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)$

$E\uparrow$ — — e''

$\uparrow\downarrow\ a_2''$ $(a_2'')^2 \rightarrow$ $\boxed{{}^1A_1' \text{ state}}$

$a_2'' \times a_2''$

What are the orbitals we said? I will write it like this, maybe psi, I will write psi. Psi A 2 double dash is 1 by root 3 phi 1 + phi 2 + phi 3. If I want to sketch it and instead of drawing it in such a weird manner I like to draw it like this, okay? The plane of the paper is the molecular plane. The circles are p orbitals. You are looking down upon them. Not in the figurative sense. Do not look down upon orbitals, they are extremely useful, right. So you are looking down from the top.

If it is plus then it will be filled. If it is minus then it will be hollow, okay? So do you agree that this is a depiction of phi 1 + phi 2 + phi 3? Now, next one. Psi E double dash. I will put the subscript here 1. What is it? Let me write the simpler one first. 1 by root 2 phi 2 - phi 3. Now if I want to draw it, maybe let me put the number here 1, 2, and 3. It can be anything it does not matter; 1, 2 and 3. So if it is phi 2 – phi 3 what should it be? In 1 I do not draw anything, right?

Phi 2 is plus this is minus. The third one psi E double dashed 2 that is equal to 1 by root 6 2 phi 1 - phi 2 - phi 3. What will it look like? Let me write the minuses first. - phi 2 – phi 3 and maybe I will draw a bigger circle. Remember it is not, so this is easier to depict if you look from side. You just draw a p orbital that is double the size. Double the size in length, not width, okay? So what have I done? I have generated the molecular orbitals.

How many nodes are there in each? 0, 1, why 2? 1; 0, 1, 1 is it not? This is one node, this is one node. Where is the node here? There is no node. Here node means wave function changes sign, right? And here there is nothing. So there is no question of changing sign. So wave function changes sign from between here and here. And here also wave function changes sign between here and here. See from here to here there is no change in sign.

From here to here there is a change; from here to here there is a change. But then that is depicted by this one plane, one nodal plane. That same nodal plane served to separate the thing. Or you might want to draw it like this. If you now look from that side okay what do you see? You see one big p orbital okay and let me draw it like this. These 2 are of the same sign is it not? So I can mix them and I can draw it this way. This is above the plane. This is below the plane.

Now do you see there is only one plane? This is one, this is one, this is one, right? This is your 2 phi 1 – phi 2 – phi 3. It is just that this should have been really long, double the size. So see from here to here there is no sign change. This is the nodal plane is it not? There is only nodal plane. It is not here to here and here to here. These 2 have mixed right. So there is only one nodal plane. Got it? You see only one nodal plane. How will I put my hand there, ya like this.

Do you see only 1 nodal plane. This is your 2 phi 1. This is - phi 2 - phi 3. This is the nodal plane, right? Are you all okay with this? Only one nodal plane. And what was the other one? The other one is like this. Phi 2 – phi 3. Where is the nodal plane? Here. Right? So now we have reached something that we must have studied at some stage or the other, right? What we do as a rule of thumb is that we correlate energy with the number of nodes.

So see this one psi A 2 double dash that has no nodal plane, no node. So if you plot energy qualitatively this is where it is going to come, right? And I will even drop psi, I will call it the A 2 double dashed molecular orbital. And then will you agree with me that psi E 1, psi E double dash 1 and psi E double dash 2 they would have the same energy? Both have one node each. So they will occur together.

Let me draw it like this and I will call them the E double dashed degenerate set of wave functions. **"Professor - student conversation starts"** We have same node but their configurations are different. It does not matter. Will the energy be same? **"Professor - student conversation ends".**

So to answer that question, what do we need to do? We need to perform a full Huckel treatment. We have to get to the secular equations, solve the secular equations and see. But qualitatively, this is what I have to say. We know from our very basic studies that symmetry, not symmetry, degeneracy and symmetry go hand in hand, right. We have studied particle in a box, 2-dimensional box. For a square box, 1, 2 and 2, 1 states are of same energy.

For rectangular box 1, 2 and 2, 1 states are of different energies, right? Degeneracy and symmetry go hand in hand. In a free metal iron all the 5 d orbitals have the exactly the same energy, they are degenerate. You put it in an octahedral field, they will separate into T 2g and D g sets, right? So E g sets are still, the orbitals in E g set are still degenerate between each other, they will have one kind of energy. The 3 orbitals in T 2 g will have one kind of energy, right?

Now, you bring in Jahn-Teller distortion. Now what will happen? What happens in Jahn-Teller distortion? Degeneracy is lifted further is it not? So that is something that we know from very basic studies. So, so far let us be happy with that. But let us keep this. We are going to discuss your secular equations also. We should work this out and satisfy ourselves that these 2 orbitals indeed have the same energy, alright? Okay. How many pi electrons are there? 2.

Where will they go? So what will the configuration be if I now want to write electron configuration. Yes. A 2 double dash 2. So this is the situation where occupied molecular orbitals are completely occupied. Whatever molecular orbital is occupied, is occupied completely, right? So this is a state right? Electron configuration defined state, alright? So this state is called a totally symmetry state.

When occupied orbitals are completely occupied then the state is a totally symmetric state. For D 3h what is the totally symmetric state? D 3h, what is the totally symmetric state? A 1 dash. Here, A 1 dash. So this state, this whole thing, this configuration, it is called an A 1 dashed state. State of what? A 1 dash state of what? The molecule, not the electron. Understand what I am saying? **"Professor - student conversation starts"** Sir, how you planated that? That is rule of thumb. **"Professor - student conversation ends".**

This is something that is discussed in very great detail in Harrison (()) (16:57) book. Rule no. 1, rule no.2, rule no. 3. They have up to 6 rules. The first rule is that when all the occupied orbitals are occupied fully then the state is a totally symmetric state. So you call it an A 1 dash state. To answer your question. It is not exactly a rule of thumb. You can work it out. Now what do you have. We have A 2 double dashed square, right?

So one is A 2 double dash, second is also A 2 double dashed, right. Do not add, multiply. If you take a direct product, you cannot add, you have to multiply. What is A 2 double dash cross A 2 double dashed, without looking at the character table? It has to be the totally symmetric one because you are multiplying it with itself right. So wherever you have +1 you will have +1, wherever you have -1 you will have -1. +1 * +1 is +1; -1 * -1 is also +1.

So when you multiply something with itself you get the totally symmetric state. That is why we call the state the totally symmetric state, alright? What happens when an electron is here? Let us say now you have got in some light. And you have promoted an electron from A 2 double dash molecular orbital to one of these E double dash orbitals. What should it be? It should be, no forget about singlet, triplet that comes later. It should be A 2 double dashed cross E double dashed.

Work it out. A 2 double dashed cross E double dashed. A 2 double dashed cross, are you getting E dash, everyone is convinced? I have worked it out myself. But if you are getting E dashed then we are little lucky. Generally, it does not work out like that. Generally, what you get is a reducible representation which breaks down into multiple terms. But if you are getting it, it is fine. Work it out. You are getting E dash? So we are lucky. What will we call that state?

E dash state, right? And then depending on what is the electron, what is the spin wave function it can be a singular state or a triplet state, okay. So what is the, what is it that you get? Is it a singular state or a triplet state? Why is it a singular state? No, do not work like that. Work like this. You know Pauli principle? What is Pauli principle? No, that is Pauli exclusion principle. And they have also watered down Pauli exclusion principle simplified for high school kids.

What is Pauli principle, ya. Pauli principle states that the total wave function for a fermion, say the whole thing. Total wave function for a fermion like electron, what is a fermion? A spin half particle. Fermion is not anti-symmetric. Fermion is a spin half particle that total wave function of a fermion has to be anti-symmetric, right? Anti-symmetric. Anti-symmetric with respect to what? Exchange of particles. So what are the spin wave functions possible, alpha and beta, right?

How many wave functions can we write out of them if there are 2 electrons, electron number 1, electron number 2. Electron number 1 is in alpha spin. Electron number 2 is in beta spin. It is okay. First is both are alpha, alpha 1, alpha 2. That is possible. Is it symmetric or anti-symmetric? Symmetric. Can I use that here? Because your spatial part is symmetric, right? So if you multiply that by a symmetric spin part then you get a symmetric total wave function, you cannot use that. So alpha, alpha is not allowed.

Alpha beta is not, beta beta is also not allowed. What about alpha beta, alpha 1 beta 2? Alpha 1 beta 2 is also not allowed because electron do not have numbers written on them. They are indistinguishable. So you have to write alpha 1 beta 2 + beta 1 alpha 2 or alpha 1 beta 2 minus you are all clear about this right? Alpha 1 beta 2 + beta 1 alpha 2 or alpha 1 beta 2 - beta 1 alpha 2. Which one of these is anti-symmetric?

Our quest is for an anti-symmetric wave function. Both are linear combinations. They have linear combination with minus sign. So that is the only spin wave function that survives is it not? So what will be the total wave function then? This space part multiplied by alpha 1 beta 2 - beta 1 alpha 2. So there is only one total wave function that is possible, right? So we call this the singlet state. Singlet A 1 dashed state.

When I write a single as a superscript before the letter do not read it as 1. It is not 1 A 1 1 state. It is singlet A 1 dashed state, okay. Not from symmetry exactly. We have to invoke the Pauli exclusion principle, Pauli principle rather which says that the total wave function has to be anti-symmetric, right?

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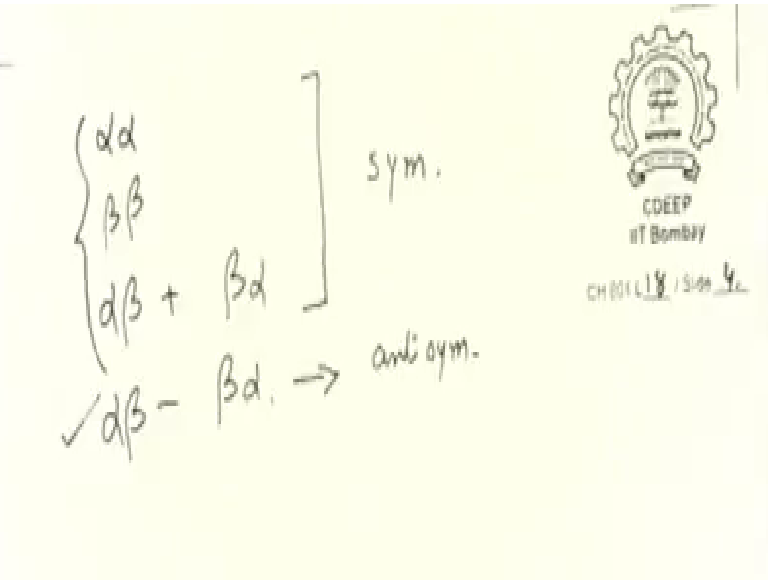

$$\left.\begin{array}{l}\alpha\alpha \\ \beta\beta \\ \alpha\beta + \beta\alpha\end{array}\right] \text{sym.}$$

$$\checkmark\ \alpha\beta - \beta\alpha \rightarrow \text{anti sym.}$$

So now, for a 2 electron system, the wave functions that are possible are alpha alpha, beta beta, alpha beta + beta alpha and alpha beta – beta alpha. See all these 3 are symmetric with respect to particle exchange. This is a unique wave function that is anti-symmetric, okay? So if you are dealing with a fermion like electron and if the space part is symmetric then this will be the only spin part that will be allowed. So you understand what I am saying?

So if you are dealing with electrons and if the space part is symmetric like what it is, then only this spin part is allowed, right? So that the total wave function is anti-symmetric. Then it is singlet. Now suppose the space part is anti-symmetric with respect to particle exchange then what will happen is that all these 3 will become allowed, right? So for one space part you will have 3 spin parts. So you will have 3 total wave functions. That is the meaning of triplet.

Singlet means one wave function, triplet means 3 wave functions. That 2s + 1 is another example of chemical jugglery with numbers to get the right answer. No, not exactly. There is a question of degeneracy but this is what it means, okay fine. We will revisit that in a later class. Let us move on to the bigger problem, benzene. **“Professor - student conversation starts”** How does higher spin states work for metals? It becomes complicated. Becomes more complicated. So do not have to go to metals. Think of oxygen. **“Professor - student conversation ends”.**

I think even from a very preliminary discussion we know that oxygen has a triplet ground state, right? Where does that triplet ground state arise from? This 3 wave functions, right? The next exited state is singlet. There are 2 singlet states. Now that excitation is just a change in the spin wave functions, okay. So you do not even have to go that far. So what I am trying to say is that the states that you get, do not think that different states arise only from the space part.

They can also arise from the spin part and there are numerous such examples in inorganic chemistry. I consider O 2 to be an inorganic molecule also starting right from oxygen, okay. If we get time, we will come to that.