Symmetry and Group Theory
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Lecture - 53
SALCs as Pi-MO and Cyclopropenyl Group

Of course by now, you have learnt where the name sigma pi etc. came from, is it not? They came from these D infinity h kind of point groups where sigma is a kind of a symmetry species, pi is another kind of symmetry species and pi is always 2-dimensional. Pi, delta these are 2-dimensional symmetry species. Sigma is one-dimensional symmetry species. So sigma would be the equivalent of A, B etc. Pi is equivalent of E, right?

So that is where your sigma ones and pi ones get their names from, okay. Now, when we talk about MOs we are going to come back to that in a little greater detail but there are many approaches by which you can construct molecular orbitals. What is the simplest of these approaches? What is the simplest approach of constructing molecular orbitals? Yes? No, even before Huckel. Huckel is an approximation that comes later. LCAO. So we are going to restrict our discussion to LCAO molecular orbitals.

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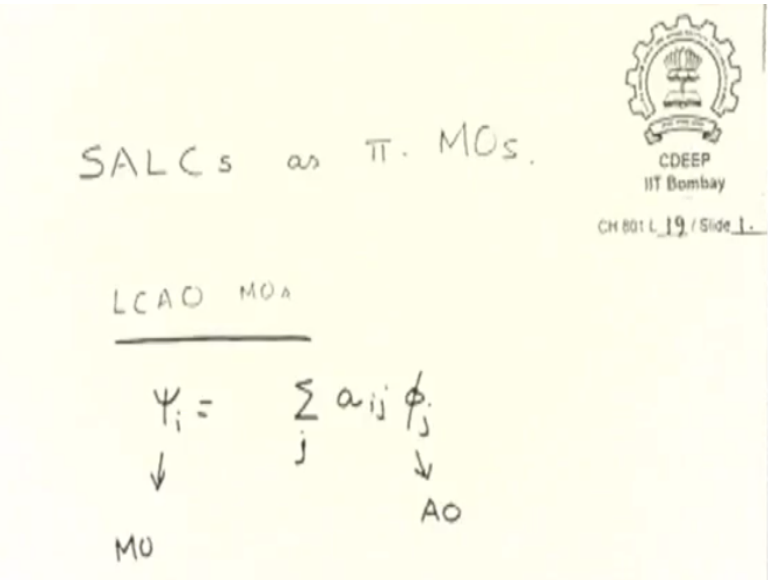

SALCs as π. MOs.

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LCAO MOs

$$\underset{\text{MO}}{\Psi_i} = \sum_j a_{ij} \underset{\text{AO}}{\phi_j}$$

What are LCAO molecular orbitals? Right. You write the molecular orbital psi as sum over i, okay let us say this is psi i, the ith molecular orbital; sum over j, a ij phi j. Where this psi i is the ith molecular orbital and phi j is the jth atomic orbital. So this linear combination of atomic orbitals is somewhat like the extension of what you do in multi-electron atoms. What is the simplest approach of handling multi-electron atoms? Okay, what is an orbital.

So let us go back to that fundamental question. One electron wave function. Everybody knows that by now. So then how is it that you write electron configuration of say lithium as 1s2 2s1. Because 1s 2s these are all correct only for hydrogenic systems. Lithium is not a hydrogenic system. So how do you write 1s2 2s1 then? What is it that allows it, what approximation? Orbital approximation, right where you write the wave function of a multi-electron system, multi-electron atom as a product of hydrogenic wave functions or orbitals, right?

That is why we can still retain 1s, 2s etc. Is it an approximation? Yes, it is an approximation. But why do we use it? Because the thing is we have developed this concept of orbitals so it makes sense to retain them to the maximum extent possible. Of course, that is only the beginning, not the end. So what we are discussing here is also only the beginning, not the end but then what happens more often than not is that even if you construct molecular orbitals by some other way, what is the modern method of constructing molecular orbital?

Suppose you are using something like Gaussian, okay what is that basis set? Some functions, right? Lot of Gaussian functions, Lorentzian functions, exponential functions, we just keep on mixing them until you get the lowest energy. That is what you do nowadays. Nobody uses LCAO-MO anymore unless in very special cases. But then if you look at these so called what is called Kohn-Sham pictures which kind of represent the molecular orbitals.

So let us just say we can construct molecular orbitals by just mixing different functions. But then if you look at those molecular orbitals, the output you will see more often than not, you can visualize them in terms of linear combination of atomic orbitals as well with a grain of with a bit of salt. The pi molecular orbitals still are above and below the plane of the molecule, okay? So they are qualitatively similar to what you get from LCAO-MO.

So learning LCAO-MO in great detail is not a bad idea after all. Okay, that is what we will do. And the good thing about LCAO-MO is that it allows us to perform a very detailed discussion because we know everything about the atomic orbitals. We know the equation, we know the shape, we know everything. So it is very easy for us to develop a rigorous treatment using this simplistic method. And then you can make further approximations and you can extend okay.

And then somebody was talking about Huckel's approximation. What is Huckel approximation? Huckel approximation is that this H ij, S ij these are nonzero only when i and j are adjacent to each other. It does not consider 1, 3; 1, 4; 1, 5 whatever. Well 1, 5 of course it has to in the case of benzene because 1 and 5 are adjacent to each other, no 1 and 6 are adjacent to each other. So we will come back to that later. But before that let us finish some unfinished agenda.

Let us start with a simple system. What we will do is we will first discuss the pi molecular orbitals generated by SALCs of this cyclopropenyl group and then once you are familiar with the method we will get into a molecule that is very near and dear to us and that is benzene. So today we will discuss benzene. We will see how the energy ordering can come qualitatively and then we will talk a little bit about Huckel approximation.

On Tuesday we come back and we discuss in detail the big brother of benzene that is naphthalene. And when we discuss naphthalene, by the way when we talk about LCAO-MOs and all you are familiar with the term secular equation are you not? Secular equation. We have actually encountered secular equations already. We will review it towards the end of today's class.

So we will see how symmetry can be used to factorize secular equations into smaller parts that are easier to handle okay and all that will be discussed in the context of naphthalene in the next class. And after that what I will do is I will ask you to do things on your own and then we can move on to inorganic chemistry. So to start with let us talk about the cyclopropenyl group.

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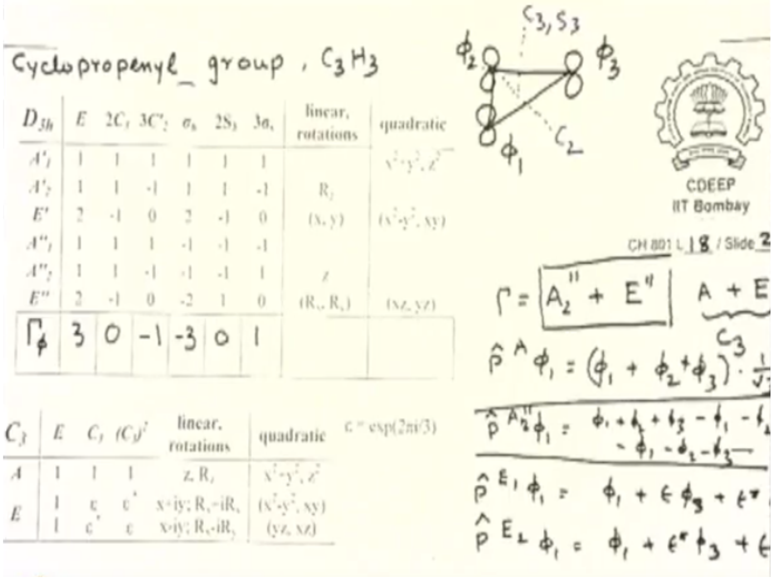

Cyclopropenyl group, C_3H_3

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 1	ε ε^*	ε^* ε	$x+iy; R_x+iR_y$ $x-iy; R_x-iR_y$	(x^2-y^2, xy) (yz, xz)

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

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

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

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

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

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

Does anybody have a glue stick? I planned to bring it, I forgot; a glue stick or a stapler. You got? Please, thanks. Thank you for joining us today. Okay, what does cyclopropenyl group like? We have become a little wiser. Instead of drawing lines I have brought this character tables as chits and we are just going to paste them. What is the formula, chemical formula? Let me just write C 3 H 3. Is there a plus sign or not? Plus sign or not, what is the structure? Triangle. Right. What?

Carbon, carbon, carbon. So if you insist on drawing your comfortable valence bond theory picture then you are going to draw a double one somewhere and then you are going to write a plus sign somewhere because it is CH CH CH right? So if you draw a double bond then these 2 CH groups are happy. This CH group is not happy. So to make it happy yes, you have to give it a positive charge is it not? And then you can do your favorite arrow pushing game, right?

And you say that resonance almighty is taking place and this is how delocalization takes place, is that right? Of course we will do no such thing. So this is, you understand what I say right, CH CH CH, there is a plus charge somewhere and what I am more concerned about is that this P orbitals are there perpendicular to the plane of the ray okay. So let me call this phi 1. Let me call this phi 2. Let me call this phi 3.

These are the 3 p orbitals that are going to be used to construct the SALCs which will turn out to be the molecular orbitals, the pi molecular orbitals okay. So far so good. Which point group is it?

D 3h. So let us have a look at the D 3h character table. This here is your D 3h character table and I can cover this D 3h without a prick of my conscience because in any case D 3h is written here, alright. This is the character table of D 3h group.

What are the symmetry operations you have? E, 2C 3. This I do not know why there is a dash. There is no reason why there should be a dash on C 2. 3C 2. 3 perpendicular C 2s. Sigma h, 2S 3, 3 sigma v. where is C 3. This is C 3 as well as S 3. Where are the C 2s? Connecting an edge to the midpoint of the other side and there are 3 such. These are C 2s. Where is sigma h, the molecular plane. No problem with that.

What about sigma v's? Along the C 2s right, perpendicular to sigma h containing C 2 and C 3, alright? So you understand what is what, okay? So what is the next step? The next step is to construct this reducible representation using these phi orbitals. Can you do that? How many pi orbitals are there? How many p orbitals are there? 3. So this character is 3 without any problem. What happens when you apply C 3? 0. They interchange, they move, so 0.

What about C 2? 1 or -1? This is a p orbital. This is plus, this is minus. This is C 2 right. So apply C 2 what happens? Plus becomes minus. What about the other 2? They interchange. So they do not contribute. Only one contributes. The one on the C 2 axis and it becomes minus. So this character is -1. What about sigma h? No, -3. It is good that we are all very positive but some things are negative in life what can you do? This is sigma h right?

So it is true that the p orbital do not change places, right? But then because of reflection they are going to change direction. So this is -3. S 3, 0. They all move and sigma v, 1 or -1? 1 right because this is sigma v, no change. What about these 2? They change places. So 1. If you now break this up what do you get? What is gamma equal to? Gamma is equal to, break this up. Okay, I will give you the answer. You have done this. What was that. Yeah, tell me.

You gave me the answer, the right answer. What is the problem of saying it again? Yes. (()) (15:06) is called A 2 double dash + E double dash. E double dash not E dash, E double dash, okay. So now what am I supposed to do? What I am saying then the symmetries are A 2 double dash and E double dashed. So I have to use the projection operator of A 2 double dash and E double dash and I am going to generate the SALCs, right?

But before that I know something that will simplify my life a little bit. What is that something that we learnt yesterday? What did we learn yesterday, descent of symmetry. So what I am going to do is instead of using this full D 3h group, I am going to use a subgroup. Which subgroup should I use? C 3. Just C 3 is enough. Nothing else is required. Because see, the point is only axis of rotation C n with n greater than equal to 3 are going to cause mixing of orbitals, is it not?

What does C 2 do? C 2 is (()) (16:29) rotation. So its orbital remains just itself or becomes minus. Or sometimes x and y mix if there are no x and y. but if it is more than 2, if it is 3 or 4 then definitely orbitals are going to mix, okay? So that is the subgroup that we should work with. So what we do is we focus on the pure rotational subgroup C 3. We are going to work with C 3.

That is the rule of thumb. Work with the pure rotational subgroup because it is the rotation with respect to C n with n greater than 2 that is going to really cause the mixing of orbitals and it is the easiest to approach the problem by using a rotational subgroup, okay? So here we use C 3 and you see life has become so simple, right? What do you have? You only have C 3, C 3 square and C 3 cube that is all, right?

The only problem is that life has become simple but in that process life has become a little complex also, you have complex quantities here. But then we know how to handle complex quantities. Is that a question Nishit?

“Professor - student conversation starts” Sir, in case of say an octahedral molecule we preserve the C 3i, C 4 and we only preserve the axis that are higher than 3. Yes, equal to or greater than 3. We are doing the same thing here. Where the same logic is there that you cause a mixing by using this rotation axis, okay? Fine. **“Professor - student conversation ends”.**

So but then we know already what is epsilon, what is epsilon star, right? What is epsilon? It is written here. E 2 to the power 2 pi i by 3. What is that? Square root of 1, is it not? Cube root of 1.

Square root of 1 is too simple, cube root of 1. And if I write it in the trigonometric form what would it be? E to the power 2 pi i by 3 in trigonometric form what would it be? Yes, so we are going to use that form eventually, right? So, so now rest is simple.

You can just use the projection operator of A. okay, what is the correlation? A 2 double dash becomes A, is that right? Let me cover everything other than what is relevant. I do not need this. I do not need this also. This is the only thing that is required is it not.

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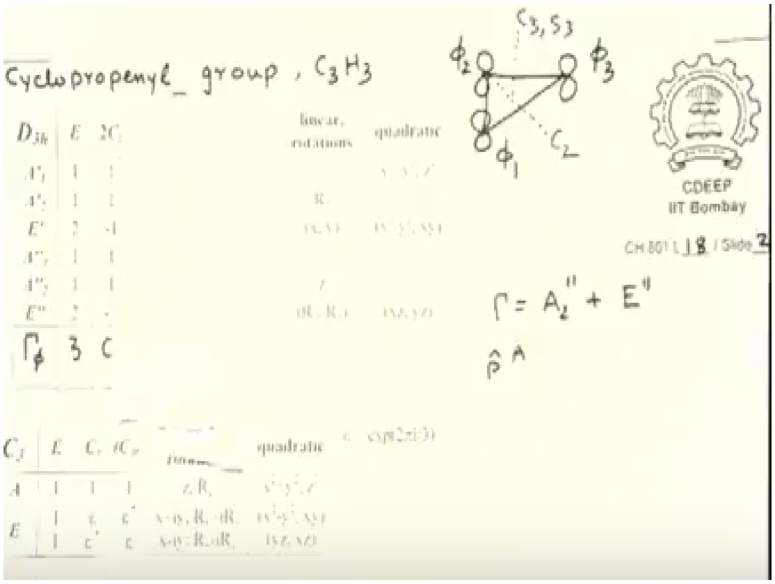

Cyclopropenyl group, C_3H_3

Γ_ϕ 3 C

$\Gamma = A_2'' + E''$

$\hat{P}^A$

Because 2C 3 is basically C 3 and C 3 square. I only wish I brought some cardboard instead of paper. Okay. So what does A 1 dash become? So you have to read the character of C 3 twice right if you want a correlation between D 3h and C 3 you have to read the character of C 3 twice because here we have written C 3 and C 3 square separately. They do not belong to the same class anymore. So A 1 dash becomes A. A 1 dash corresponds to A.

A 2 dashed corresponds to A. A 1 double dash corresponds to A. A 2 double dashed also corresponds to A right? Right or wrong? Okay, what about E dash. Oh what is epsilon + epsilon *? Can you work that out? Write in trigonometric form and work it out. What is epsilon + epsilon *? What is epsilon? Yes, it is -1. But let us work it out so that we all understand. What is the trigonometric form tell me, epsilon? Cos 2 pi/ 3 + iota sin 2 pi/ 3.

And what is epsilon *? Cos 2 pi/ 3 - iota multiplied by sin 2 pi/3 okay. So when you add them, what do you get? -1 are you all convinced that is -1? Okay, you subtract what do you get? So if I divide that by i then again it becomes a then again I can get rid of this. Does that remind you of something? You add once and you add 2 imaginary numbers, 2 complex numbers and get a real number and then you subtract one from the other, divide by i you get another real quantity. Have you done that somewhere?

P orbitals remember? P+ plus p- gives you px. P+ minus p- divided by i gives you py, right? We are using the same technique here nothing else, okay? So if you are a physicist you do not need all this. You can just work with the expressions. You do not care about figures. We chemists like to draw figures and like to work with figures that is why we have this inclination of converting all imaginary quantities into real quantities by adding and subtracting, multiplying by i wherever required, okay?

So epsilon + epsilon * is -1. So now tell me what is E dashed? E dashed is just E is it not? Just add these two. Do not forget that E is not really a reducible representation. One epsilon, epsilon * is a reducible representation, one epsilon * epsilon is another reducible representation. They are taken together and they are called E that is all, okay? So E dashed here becomes E. What about E double dash? That also corresponds to E, same thing. Are we clear?

So in C 3 what will I write? This is correct in D 3h. in case of C 3 what will I write? I will write A + E when I am working with the C 3 subgroup, okay? So now see. Let us use the projection operator on phi 1, what do you get? Character tables are there in front of you. Now you should be able to work out. And also we are working with only this small character table. E operating on phi 1 is phi 1. That multiplied by 1 is how much? Phi 1. + C 3 operating on phi 1 what is it?

Phi 2, multiplied by 1 is phi 2. Then C 3 square operating on phi 1 is phi 3. That multiplied by 1 is phi 3. So this is the SALC that you get of A symmetry, belonging to symmetry species A. Because when I say of A symmetry then our organic chemistry background might interfere. It is not asymmetry. A symmetry. But just to make up a point what you could do is to check here. Can you go back to D 3h point group and use the projection operator of A 1 dashed on phi 1 and satisfy yourself that you still get phi 1 + phi 2 + phi 3.

A 2 dash sorry, A 2 double dash. When A 2 double dash separates do you still get phi 1 + phi 2 + phi 3 in D 3h not in C 3? And while doing that do not forget these coefficients. And do not forget that C 3 and C 3 square are going to give you different results. That is the easiest way of going wrong. C 3 phi 1 is phi 2, C 3 square phi 1 is phi 3. Do not forget that. Phi 1 + phi 2 + phi 3 it is coming right? Yeah, what about C 2, 3 C 2s.

This C 2 operating on phi 1 makes it - phi 1. The second C 2 operating on phi 1 what does it do? C 2. Yeah. - phi 2 - phi 3 right. Then sigma h minus then S 3 - phi 2 - phi 3. Then 3 sigma v's. I think sigma 1 sigma 2 sigma 3, okay? So finally you get the same answer. (()) (27:17) What? Yeah if minus is there, there is no problem. It is just a constant right? If -1 comes out it is fine. As long as, oh right. So please do that. Do that and see what you get.

I completely forgot to do that. So some signs will change and then see what you get. Got it? So you get something multiplied by phi 1 + phi 2 + phi 3 right? So that is what it is. Now, what will be the normalization constant? Root 3; 1 by root 3. So I hope everybody is convinced that when you, no matter whether we work in the full D 3h group or whether we work in the C 3 subgroup, at least for the first one, for the one-dimensional representation we get the right answer, okay.

Work it out, it will come. Now, the advantage of using the subgroup comes when you are working with the 2-dimensional representation. Because now what we have done is we have essentially broken down the 2-dimensional representation into E 1 and E 2 or E A and E B whatever you want to call it, okay. So next is, let us use the projection operator of E 1. What is E 1? The first line of 1 on phi 1. What do you get? What do you get tell me?

P E1, 1 epsilon, epsilon * on phi 1. Phi 1 + epsilon phi 2 epsilon phi 3 + epsilon * phi 2, does not matter what you write. What is, what do you get when you make P E 2 operate on phi 1? Because you told me. It does not matter. Actually I got it to be phi 2. Depends on whether you are rotating this way or that way, it does not matter. So phi 1 + epsilon * phi 3 + epsilon phi 2, okay.

Before going any further, I would like to draw your attention to what is going on here. By using this rotational subgroup we are actually generating a linear combination of atomic orbitals, right? Because we rotate once, you get phi 2 from phi 1. You rotate twice you get phi 3. You rotate thrice you get back phi 1. And you are doing all these rotations. So no matter what you do you are going to get a linear combination of atomic orbitals. You are going to get the MOs right?

And you can say that these are the MOs and be happy about it. But the problem is if we leave it here there are 2 issues. First of all how do we justify that these are the MOs for this cyclopropenyl group. The cyclopropenyl group there is no character that is epsilon, epsilon *. We should go back to D 3h group. And secondly we do not really want imaginary coefficients. How will I get back to D 3h group? How did I get E 1 and E 2? By splitting E double dash is it not?