INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

CDEEP IIT BOMBAY

MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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LECTURE NO. – 37
Character tables for Different Symmetry Point Groups

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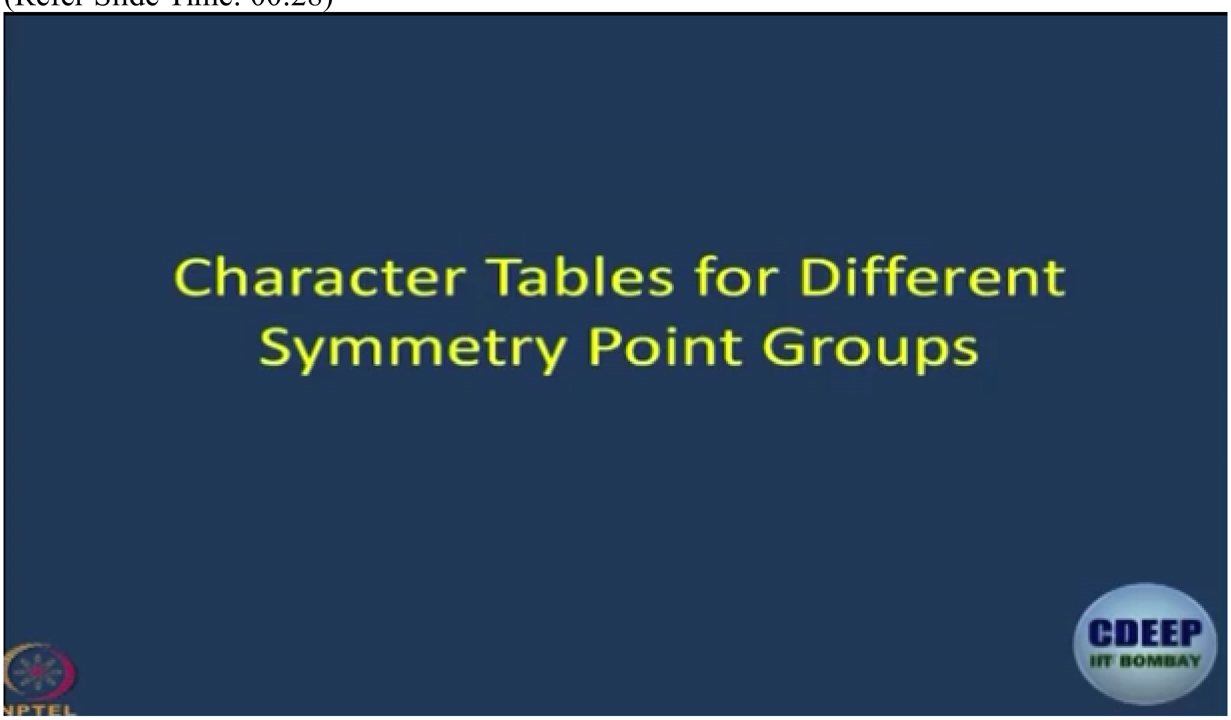

We'll continue on our discussion of character tables. So we've started from this great orthogonality theorem which we have not derived,

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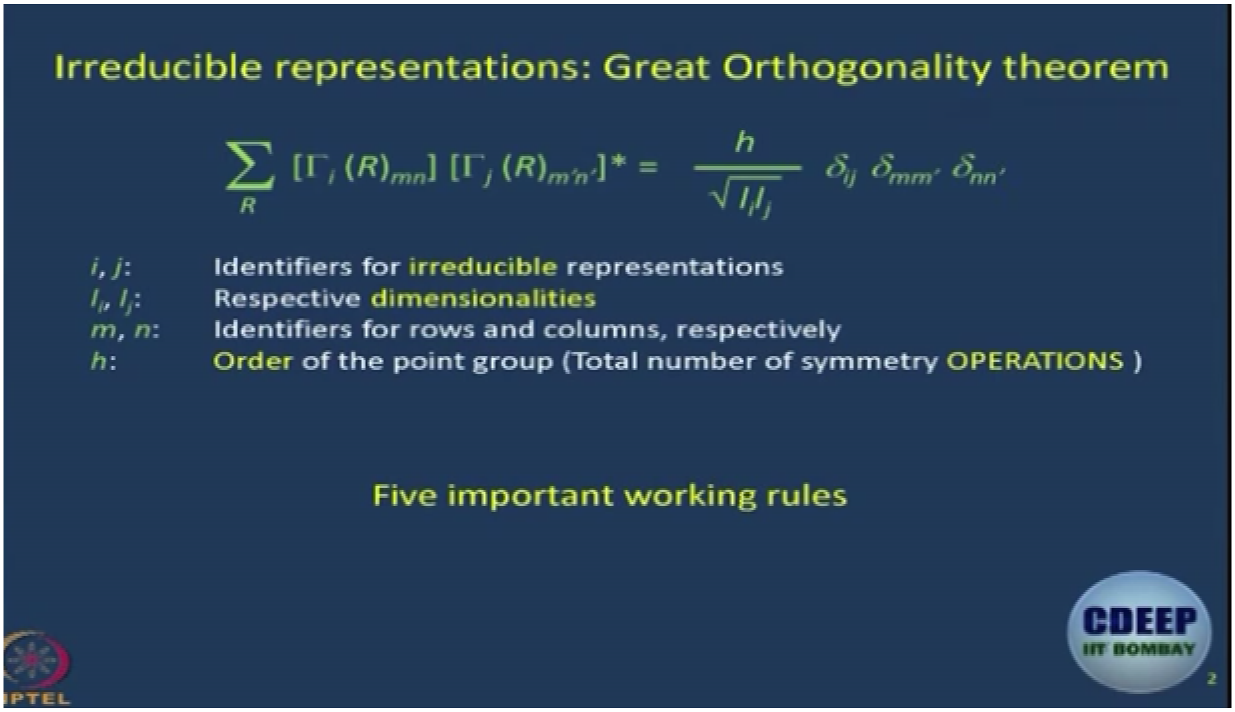

but we explain that for irreducible representations the elements of the transformation matrices behave like a set of orthonormal vectors, okay, that is what orthogonal, the great orthogonality theorem translates too, and what is really useful for us and something that we'll need to remember if you want to derive character tables and also otherwise is,

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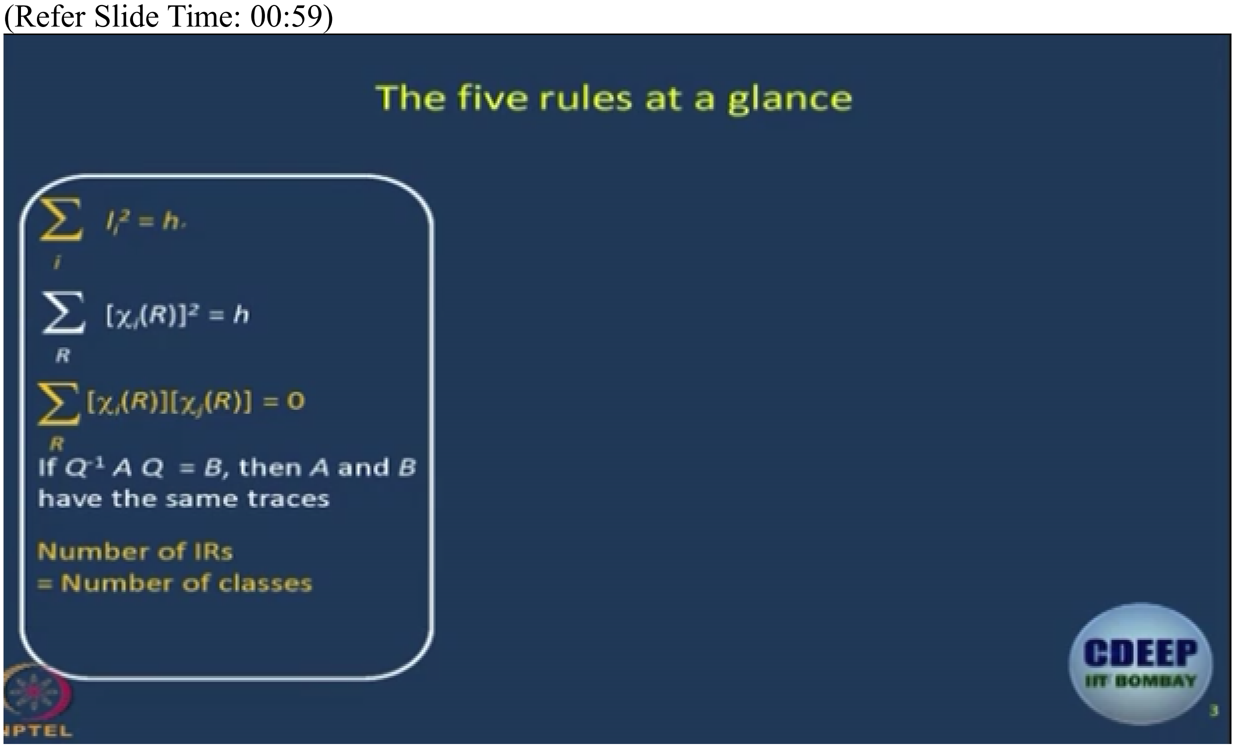

we need to remember that there are 5 important rules that come out as a result of great orthogonality theorem.

And these rules actually answer some of the questions that we've been asking, how many irreducible representations are there for a given point group. The answer is number of irreducible representations is equal to number of classes, what is the class? If I bypass group theory the answer is a class is, well symmetry operations in a class are equivalent to each other, like the three sigma V's in C3V they belong the same class. Like C3 and C3 square operation again in C3V they belong to the same class.
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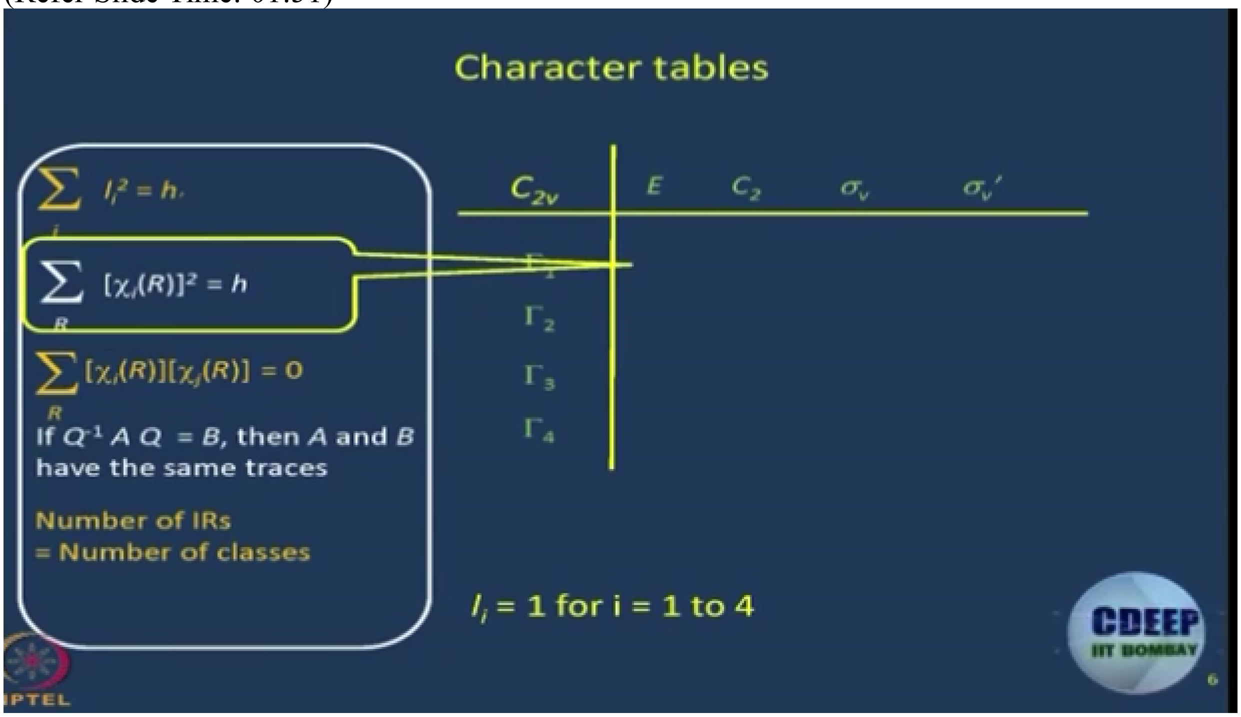

Using these rules you might remember we derive the character table first for C2V, okay, I'll just go through it quickly,
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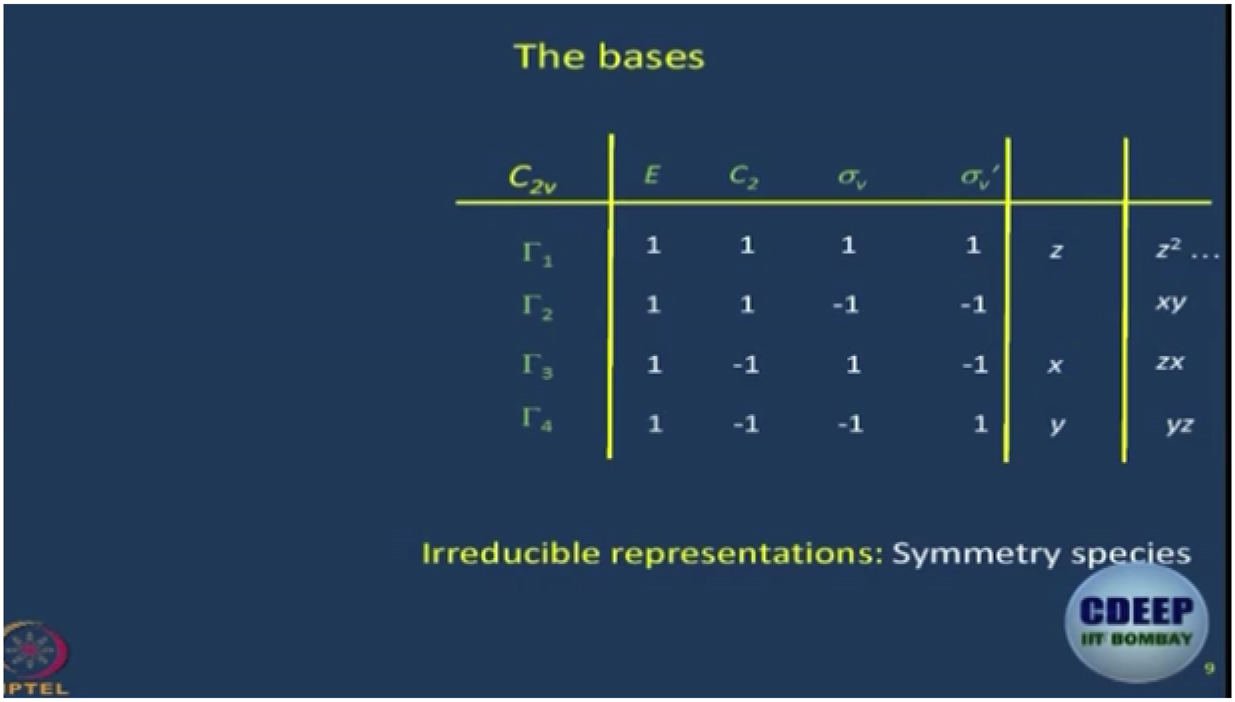

and for C2V what we found was that we are going to have only one dimensional representations and so the characters can be only either +1 or -1, cannot be anything else because if it is a one dimensional representation then in response to any symmetry operation a function can either remain itself or it can change sign, it cannot become 5 times itself, it cannot become 0, so other than 1 and -1 you cannot get anything else, alright.

And then we worked out the basis as well, and what is not written here is RX, RY, RZ did we work out RX, RY, RZ on the board? We did not do it, right, we can do it now. Or maybe we'll do it when we show you the entire character table, and then we said that these irreducible representations essentially tell you how this functions behave as a consequence of each of the symmetry operations, so if you take Z it is totally symmetric in C2V, no matter which symmetry operation you use Z remains Z it does not change.

If you take X it is symmetric with respect to E, anti-symmetric with respect to C2, symmetric with respect to sigma V, anti-symmetric with respect to sigma V dash, so if you want to know the overall behavior of a function in response to symmetry operations you have to look at the entire collection of characters which is the representation, so another name of representation is also symmetry species, so symmetry species denotes how the functions behave as a function of the symmetry operations, repeating ourselves.

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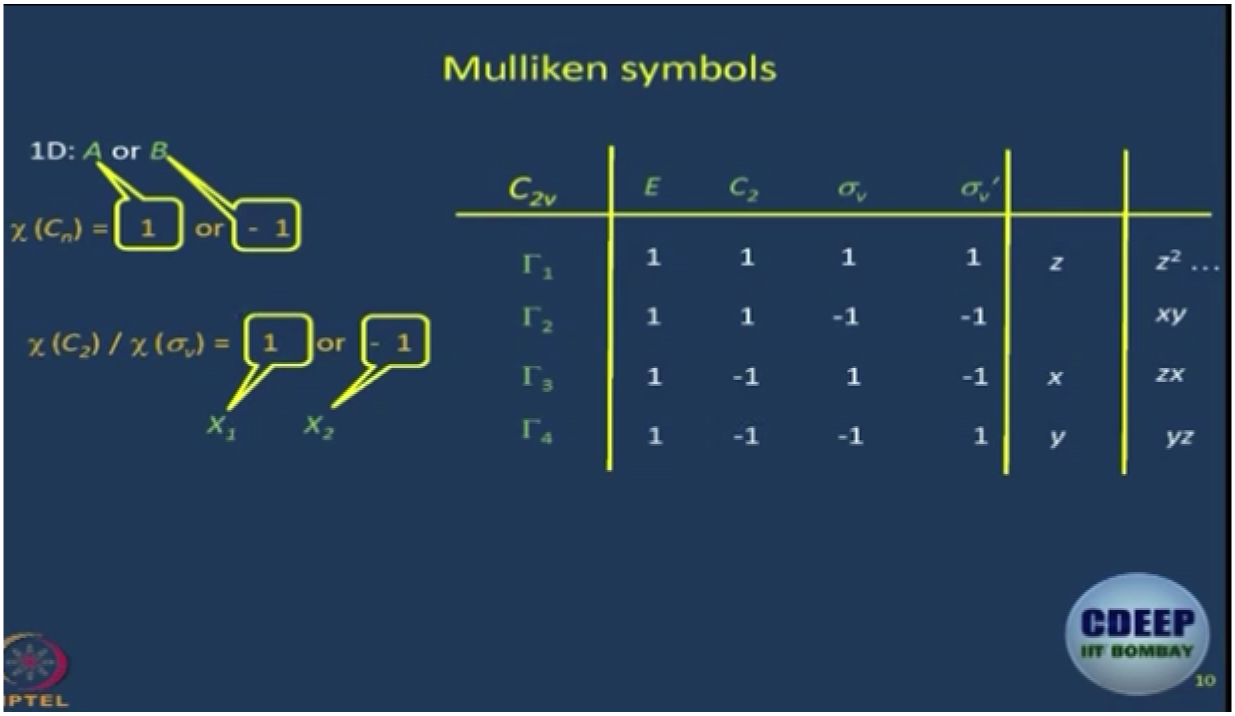

And then we talked briefly about Mulliken symbols and there we said that if it is one dimensional then we either call it A or call it B, A if the character for the principal axis of symmetry is 1, B if it is -1, and then we said that if you now take perpendicular C2s or sigma V's and if the character is + or -1 that tells you which subscript to use, 1 or 2. And so that way we arrived at the names of the symmetry species A1 A2, B1 and B2.

Now what we have not talked about so far is sigma H, we are going to show you some examples wherever there is a horizontal plane of symmetry if you've one dimensional representation which is symmetric with respect to sigma H then you use a dash, if the character is +1. And if it is anti-symmetric, character is -1 then you use a double dash, we'll show you examples shortly.

And if I is there then it is very simple, what do you call functions that are symmetric with respect to inversion? This is something we've not discussed so far, what do you call, yeah Raksha symmetric with respect to inversion? Another name, even function, okay, another name, simple name something that we have used many many times, gerade, that's right gerade functions G, remember that G functions, U functions, bonding orbital, anti-bonding orbital, right, so if it is +1 then you call it, then you use the subscript G, if it is anti-symmetric then you use a subscript U, okay.

And as you'll see in groups of high symmetry, sometimes it is not necessary to use that dash, double dash, many times we omit designations that are not required, okay, and this is something I told you already, if it is two dimensional representation you use the letter E, three dimensional representation you use the letter T.

Now see if I have a two dimensional representation which is anti-symmetric with respect to say perpendicular T, what should I call it? A two dimensional representation E anti-symmetric with respect to sigma V or a perpendicular C2, what should the name be? Yeah, so what it should be completely? I heard the right answer, but the whole thing, it is E anyway and you have to sue the subscript 2, so which symmetry specie is it? E2, right.

Now let us say that a center of inversion is also there, and this two dimensional representation we are talking about is symmetric with respect to inversion, it is E2 already, over and above, it is symmetric with respect to inversion, what will the name be? E2G, does that ring a bell? Have you heard this term E2G anywhere? Where? Octahedral, octahedral yeah, so in octahedral complexes you say that D orbital split into two groups, one is EG, the other is E2G,
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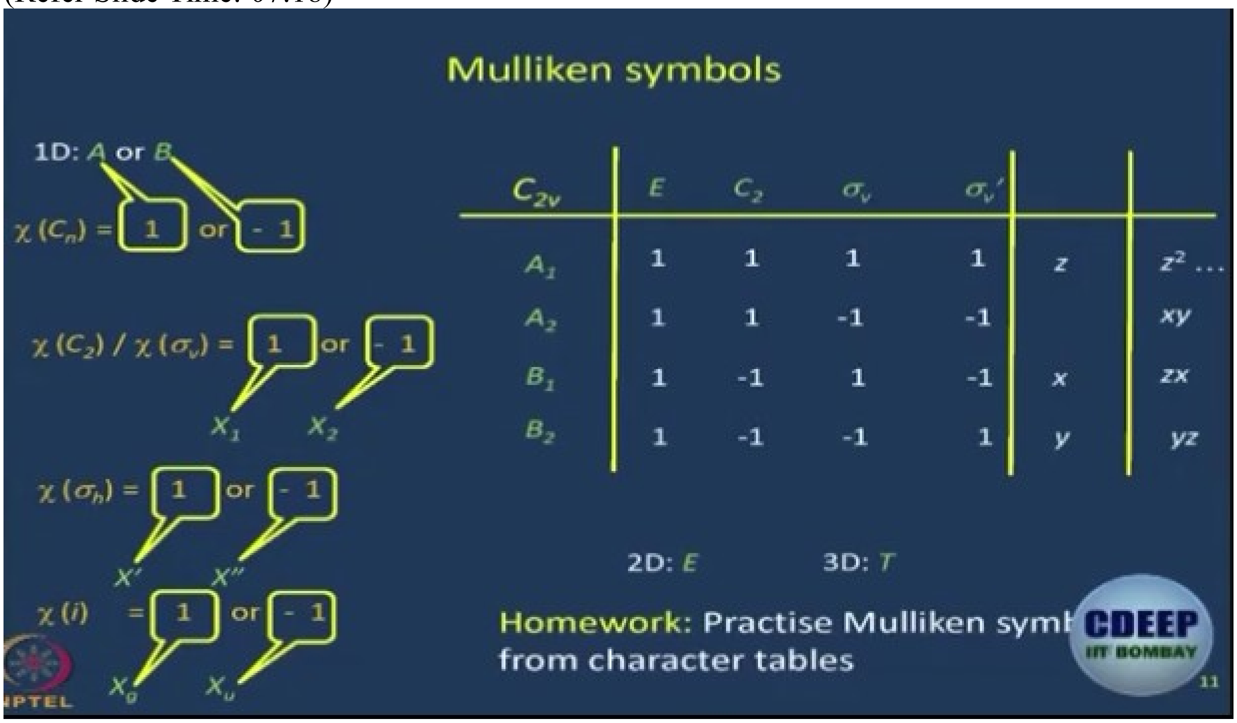

now look at this thing. T, T is the three dimensional representation, right, so in 3 dimensional representation if it is anti-symmetric with respect to sigma V or perpendicular C2 it becomes T2, and if it is symmetric with respect to inversion then it becomes T2G, so this EG and T2G, these names that you’ve learnt from maybe class 11 or class 12 they actually come from this symmetry of wave functions. So in the second part of our discussion today we are going to talk about symmetries of wave functions as well.

Okay, so this is your homework,
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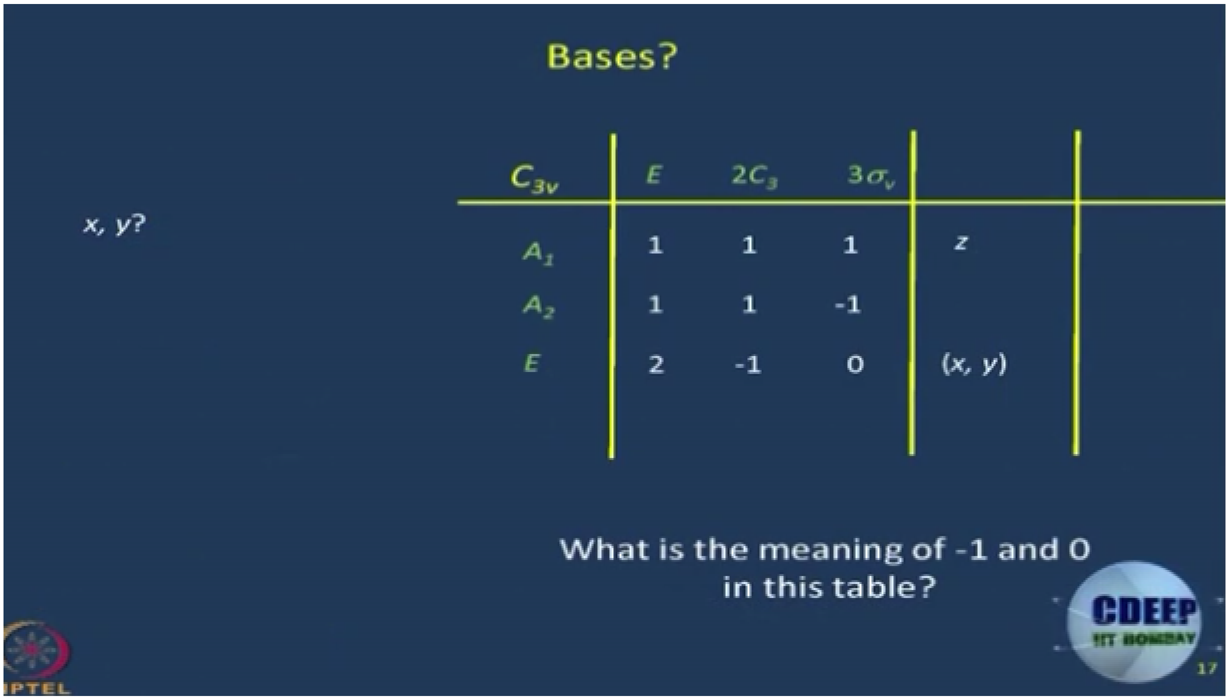

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	
A_2	1	1	-1		
E	2	-1	0	(x, y)	

then C3V we have, and here for the first time we encountered a two dimensional irreducible representation E in this case, now the question that we want to ask is what is the meaning of -1, what is the meaning of 0? Okay, I think we asked that question but we did not answer earlier. To do that let us look at the basis, I'm telling you that X and Y jointly form the basis for E, right, so to understand the meaning of -1 and 0 here, what we should do is we should work out the transformation matrices for E, well E, as in E irreducible representation, what is the transformation matrix for the identity operation? E, yeah, 1 0 0 1 that's very simple.

What is it for, okay let us do sigma V first. What will it be for sigma V? Of course I can take sigma V anywhere, right, and what is the basis we are using? We are using the basis X, Y, so let us take I mean any sigma V, it doesn't matter, the only thing that we have to remember that your C3 axis is Z, so the plane that you take sigma V must contain Z in it, right, so our discussion becomes simpler if you take XZ or YZ plane, or you can take anything in between, but the point is your Z must be contained in that plane, are we clear about that? The sigma V it must contain the principal axis of symmetry which by definition here is along Z.

Let us use sigma V(ZX), so if I use sigma V(ZX) what happens to X? What happens to Y? What is X dash? What is Y dash? ZX, maybe I'll draw it, this is X, this is Y, what happens when I apply sigma ZX to on X, does it change, does it? So it remains X right? Remains X, what happens to Y? Y becomes –Y very simple, what is the matrix? Yeah, 1 0 0 -1,
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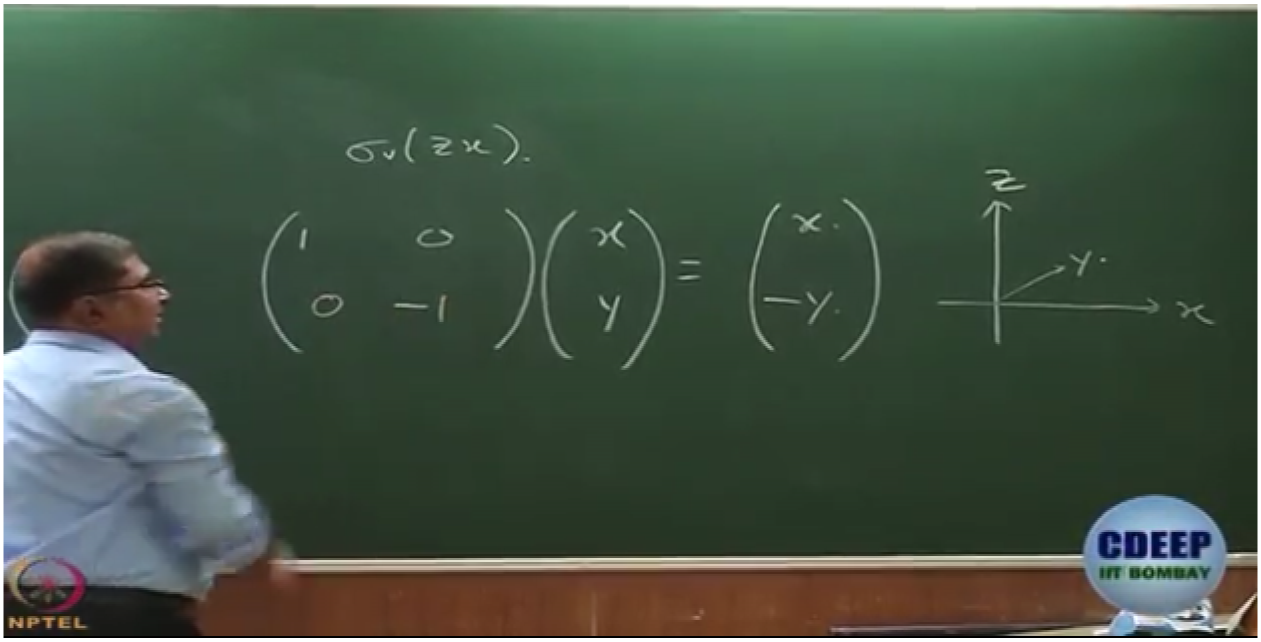

it's not very difficult to see that the same thing will happen if I use sigma YZ, right, okay.

Suppose I use something like this, now I'll take a different perspective, this is X, this is Y, of course Z is pointing towards you right. What happens if I take this plane?

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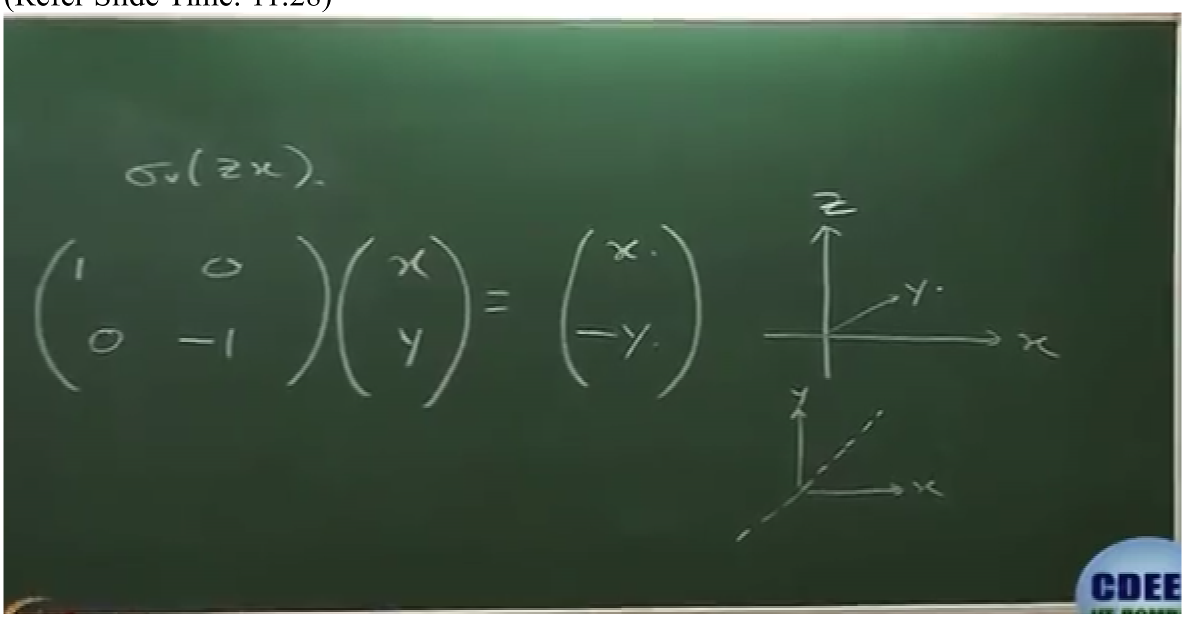

Right, so what will X be? –Y, -X, X will become Y, right, X will become Y and what will Y become?

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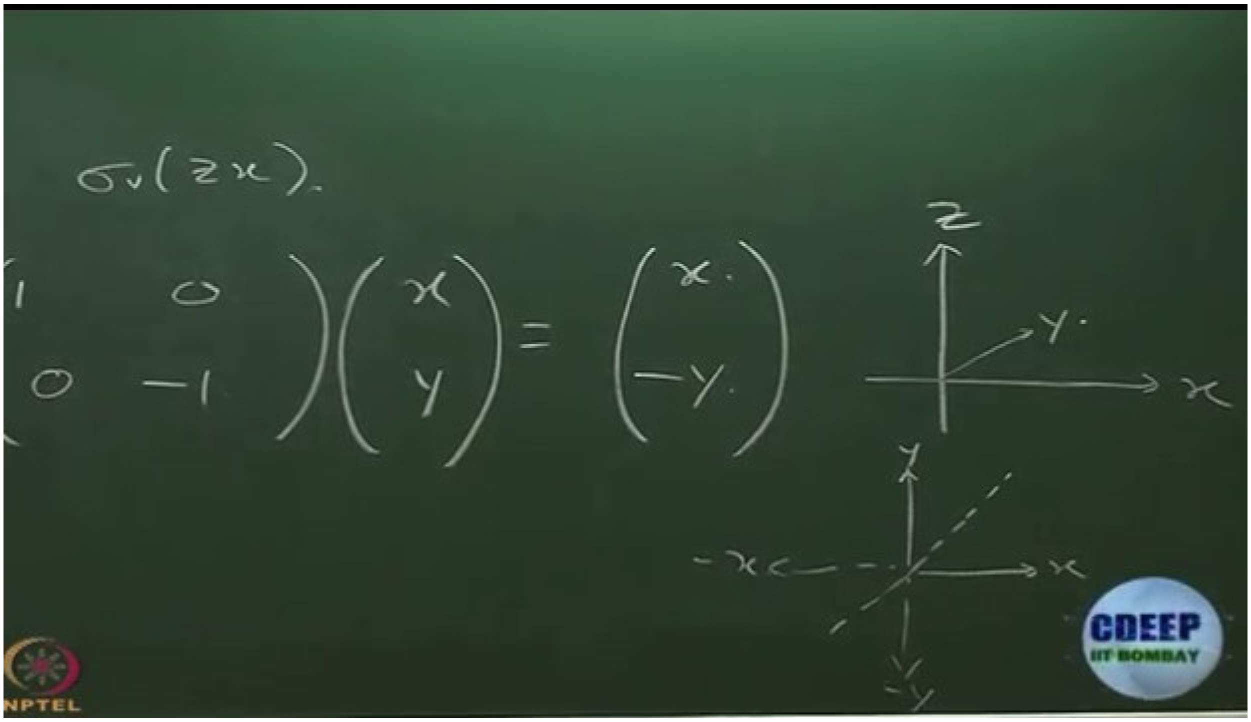

Of course Y will become X, in that case what is the matrix? If this becomes something like this YX, what is the matrix then? 0 1, what is the character? 0, what is the character here? Still 0 right, so that is the meaning of this 0 here.

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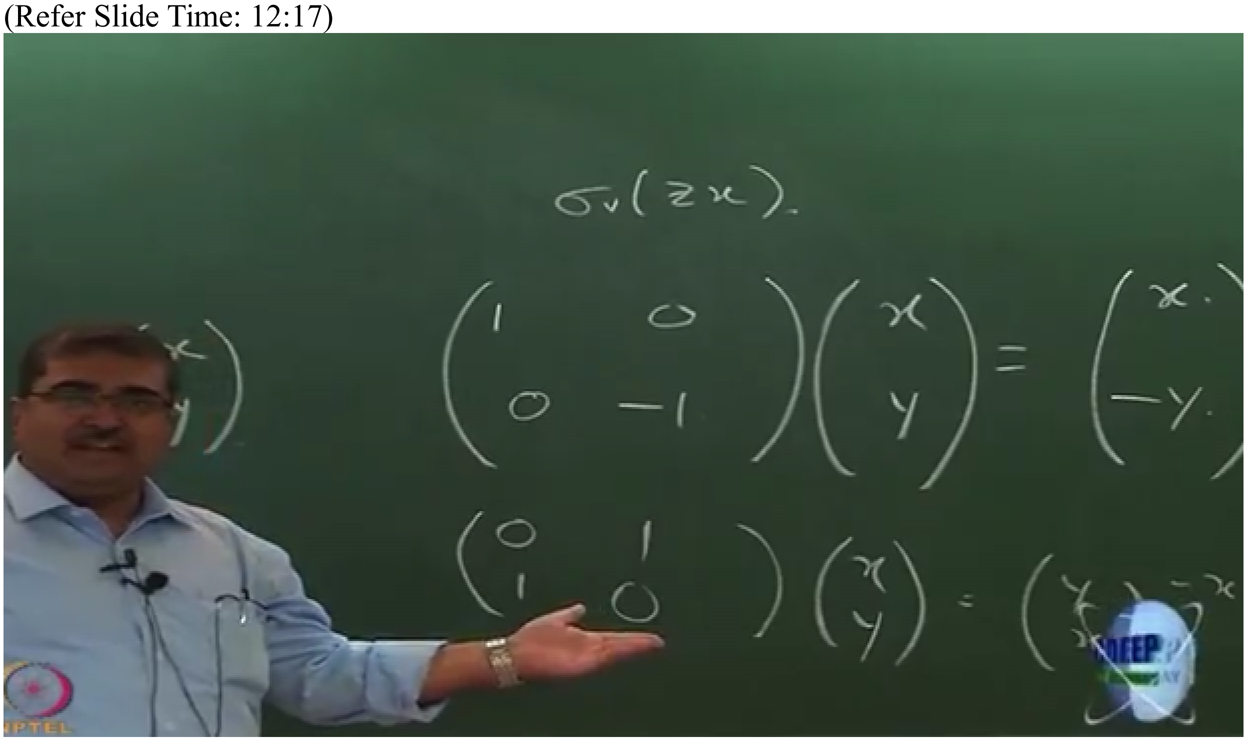

If it was one dimensional representation it could not never have been 0 with the question, how it is 0? Do you agree on the matrices? Right, what is the character? Character is sum of the diagonal elements, isn't it? So here 1 – 1 is 0, and here 0 + 0 is 0, okay,

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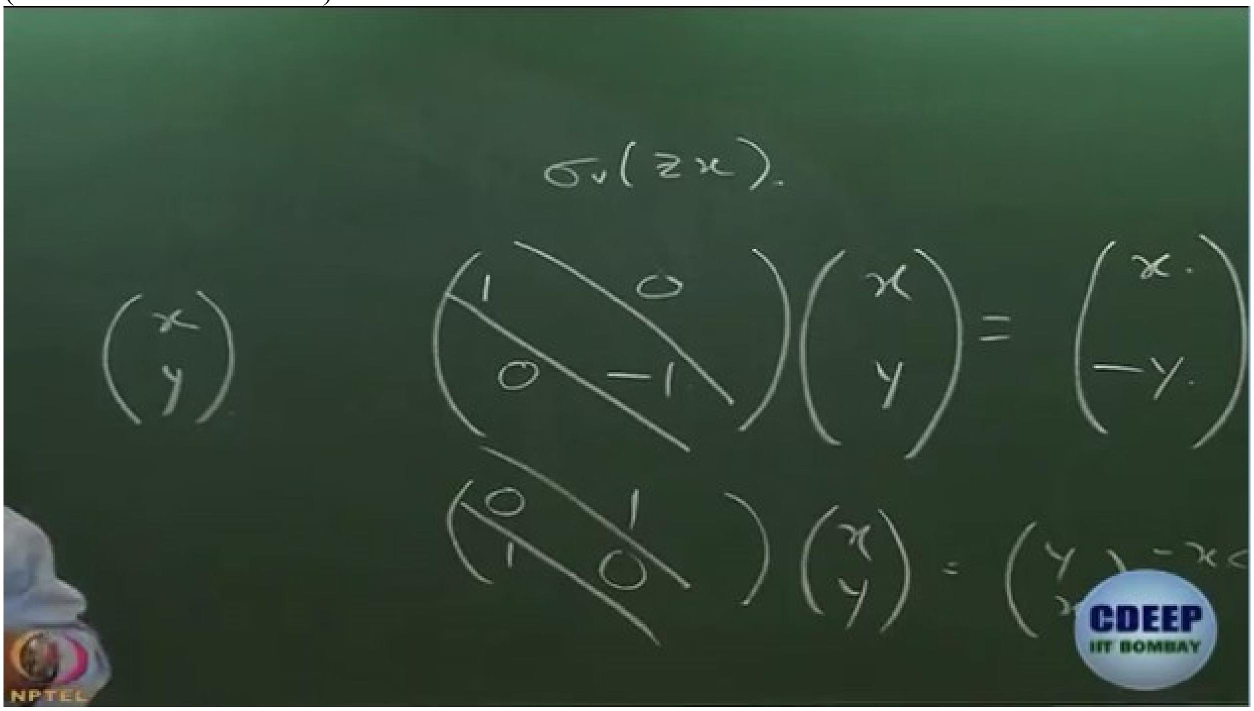

remember this trace not the other one, okay, so see if it was one dimensional representation you could never have a character of 0 right, as you said it had to be either +1 or -1, but now we see 0 is possible if you have two dimensional representations, why? Because this two dimensions are actually being mixed by the symmetry operation, okay, if you cannot take them by themselves, so depending on which plane you choose either one remains the same, the other remain same or they interchange that is how you get 0, that is the meaning of 0 here, okay.

Now another point to remember here, this is going to come very handy in our subsequent discussion is that when two coordinates interchange, their contribution to the character is 0, do you see that here? X and Y got interchanged here right in the second case, so the moment they get interchange what happens is that, the nonzero elements go off diagonal, and that is why the character is 0, we'll come back to this in a subsequent discussion later on, so character here is 0, so sigma V you can write any of this two matrices it does not matter, 0 1 1 0 or you could write 1 0 0 1, 1 0 0 -1,

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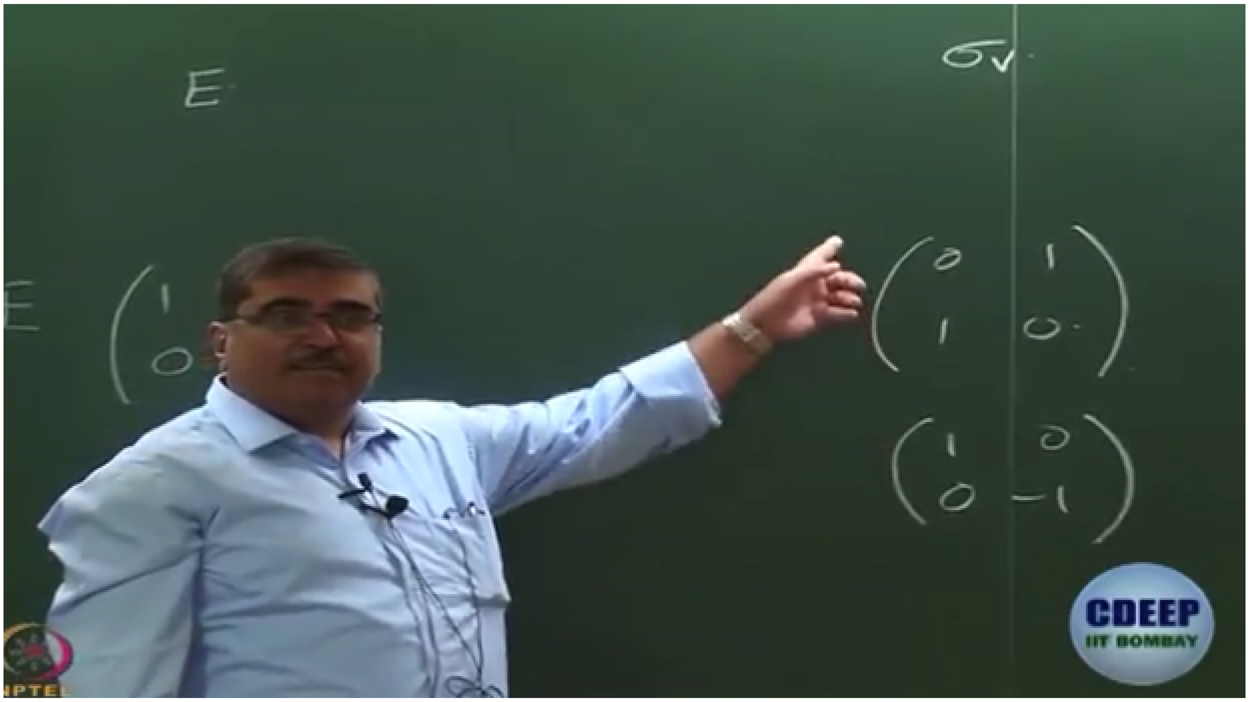

and this is something that should make us appreciate the character table a little more, see if you had to write the matrices then I'd have to write both the matrices here, right, in fact I might have had to write more matrices, because if I took this plane for example then what would it be, then why would interchange with –X, X would interchange with –Y, so another matrix is possible, even there the character is the same, this is the advantage of working with characters, it does not, you don't have to think any more of what the matrix looks like, you don't have to think anymore of the basis, okay, the character is given and that is good enough.

Okay, now let's work out C3. The C3 is something that we should be able to do because we know the matrix for rotation by theta, remember the matrix for rotation by theta, what was it? Cos theta –sin theta, sin theta cos theta, isn't it? So what is cos theta here? What is theta for C3? 120 degrees, so what is cos theta? -1/2, what is –sin theta? – root 3/2, what is sin theta? + root 3/2, and what is cos theta again? -1/2, this is the transformation matrix.
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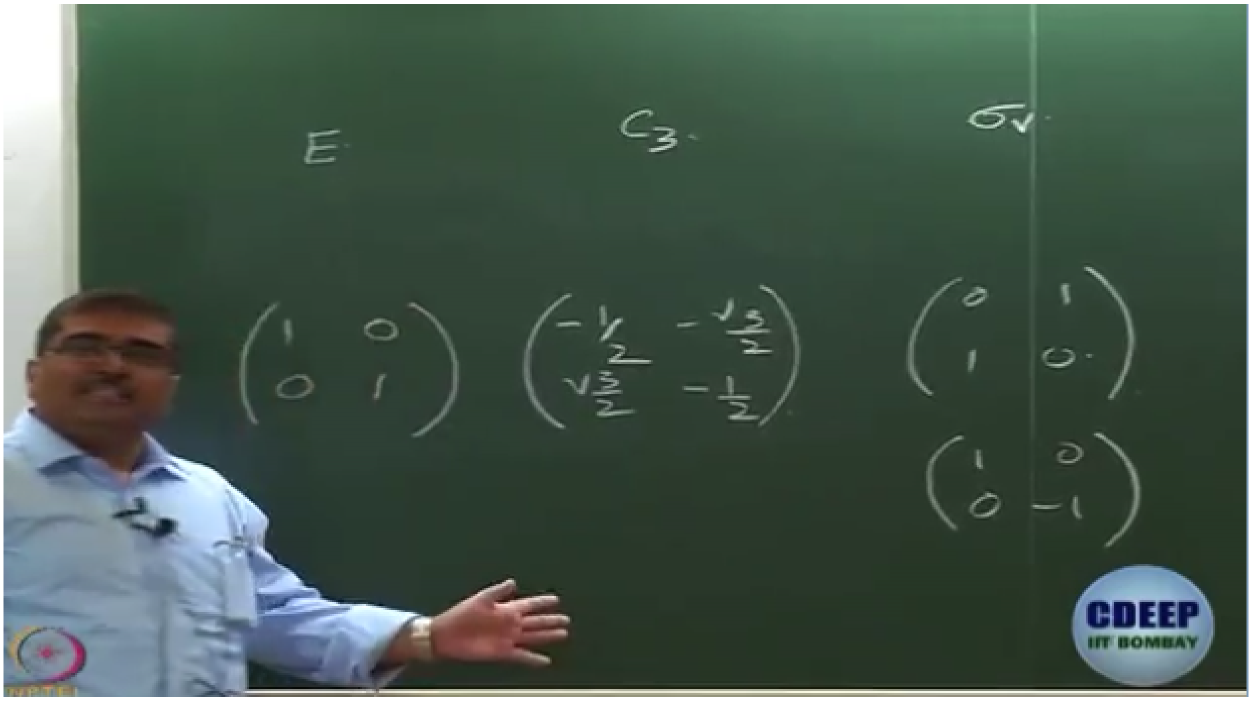

What is the character? This plus this, -1/2 -1/2 that gives you -1,
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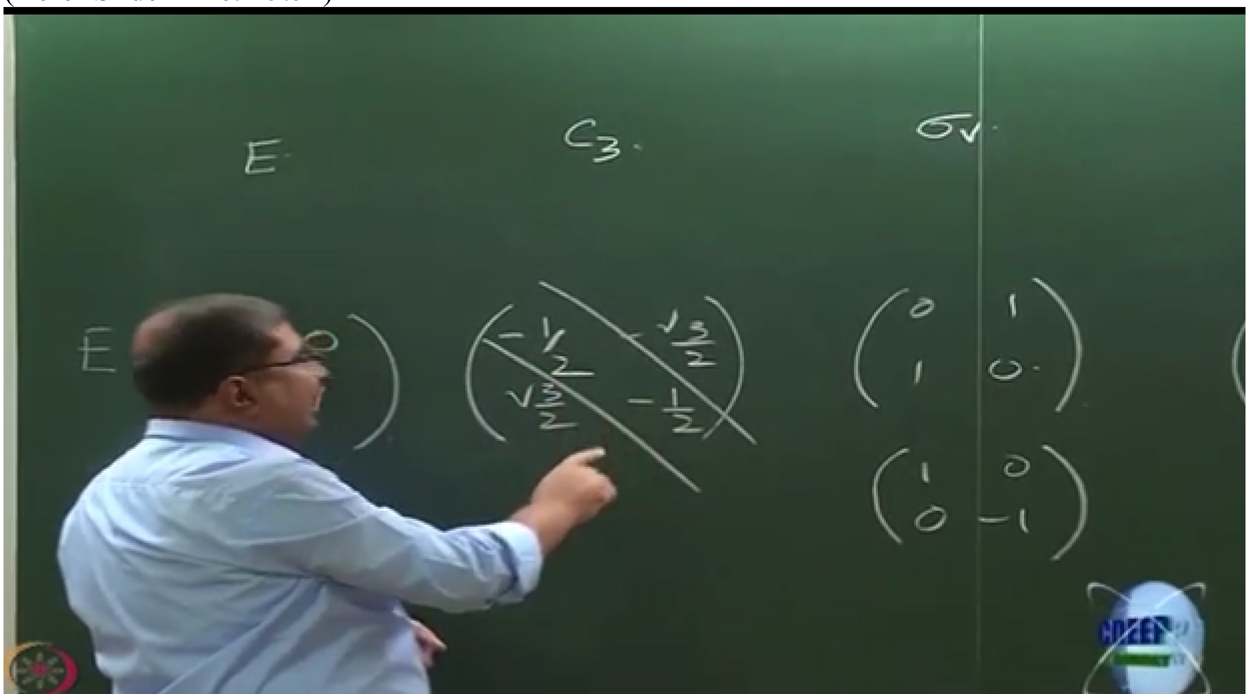

so this -1 that we see does not really have the same implication as the -1 that we see here,
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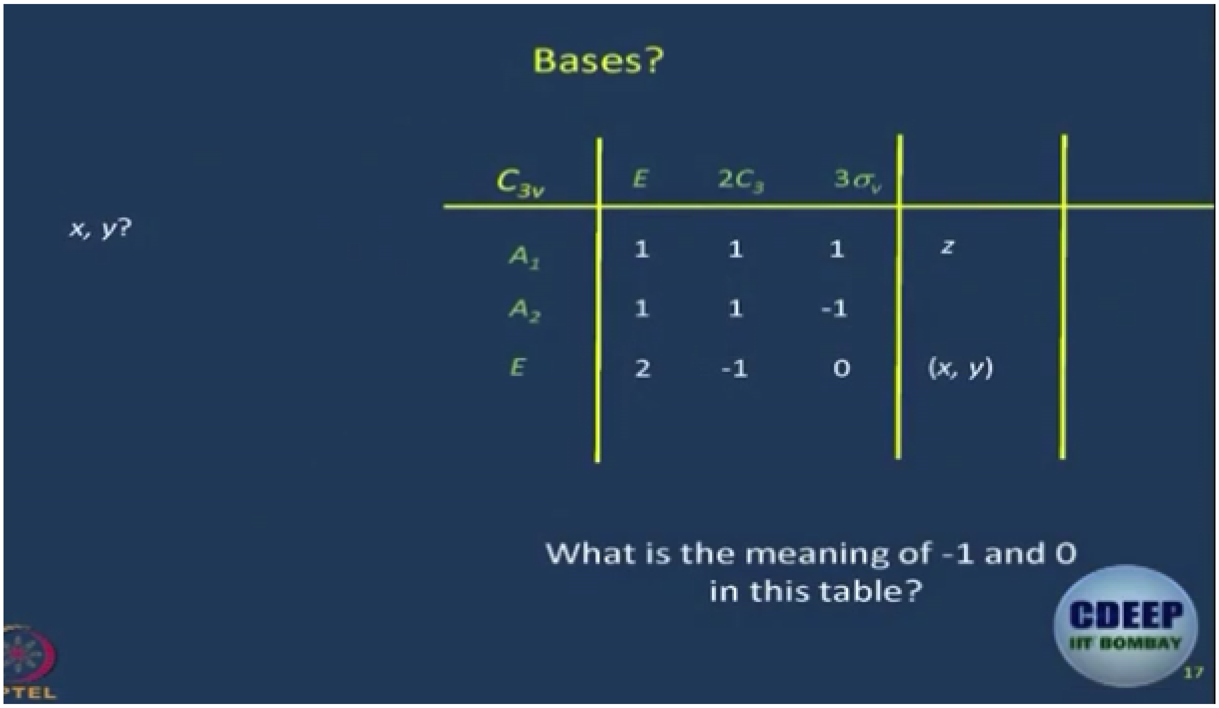

even though numbers are the same, the implications can be different depending on the dimensionality of the matrix, so that is something that is important to understand, numbers are same right this -1 just means that a function becomes minus of itself, that's not what it means here, okay, so when it's two dimensional this -1 means a little, has a little more complicated meaning and the meaning becomes apparent if you look at the matrix, alright.

Now some more character tables,
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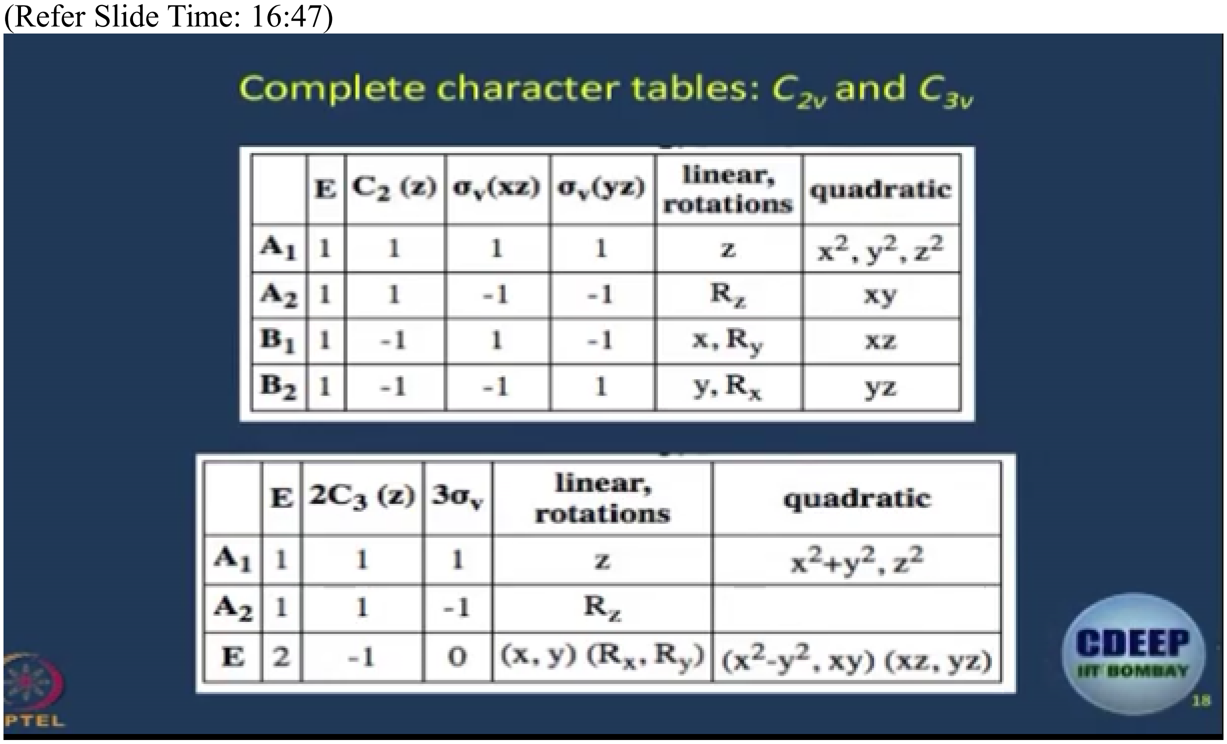

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

this is before that this is your C2V character table, this is C3V, some other terms that you see are RX, RY, RZ, what is the meaning of RX, RY, RZ? Rotation with respect to X, rotation with respect to Y, rotation with respect to Z, okay, let us try and see if we can figure this out, why RX, RY, RZ belong, where they belong here? To do this let me denote this or at least let's do one, then we'll understand, we'll just do one, you can do the rest, if I write this as X, write this as Y, in which direction will Z be? Which one is +Z, this or this? XY + Z points towards you, I keep forgetting this, I've never been able to overcome this short coming, so I'll draw RX as A circle, circular arrow, do you understand what this means? This is what it means, okay? Okay.

Now let us see where it should belong. When E operates on RX, what do you get? You get RX itself, no problem with that, so character is 1. What is the next symmetry operation? Next symmetry operation is C2Z this, now we have to be careful. What happens, this is RX like this, this is your symmetry operation, or maybe let us do sigma V first, okay, let us do sigma V and sigma V dash first, that's easier.

Let's apply sigma V, if we apply sigma V which is along the plane of the board, does RX remain RX or does it become –RX? This is the mirror plane, this is the direction of motion, what will the, I'll do it like this, this is the mirror plane, this is the direction of rotation, what will the image be? Like this, is that plus or minus? Minus, are we clear about this? This is the mirror plane, this is the direction of rotation, reflection of that will be like this, I can draw it, this is my mirror plane, which plane is this? The way we have formulated the problem so far it is ZX, right, ZX, so X axis is somewhere here, pointing out like this, this is the direction of rotation, what is the reflection? This, okay, and this if this is RX this of course is -RX. Are we clear?
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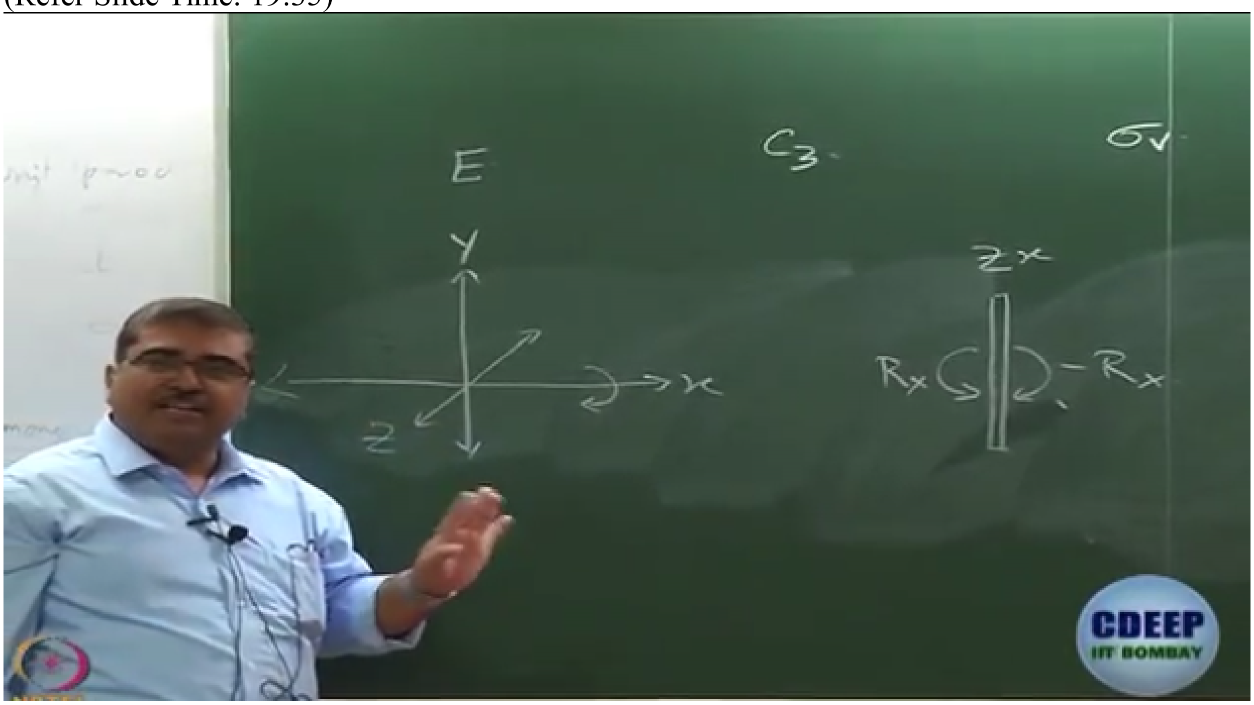

So far sigma V the character is -1.

What about sigma V dash? What is sigma V dash remember?
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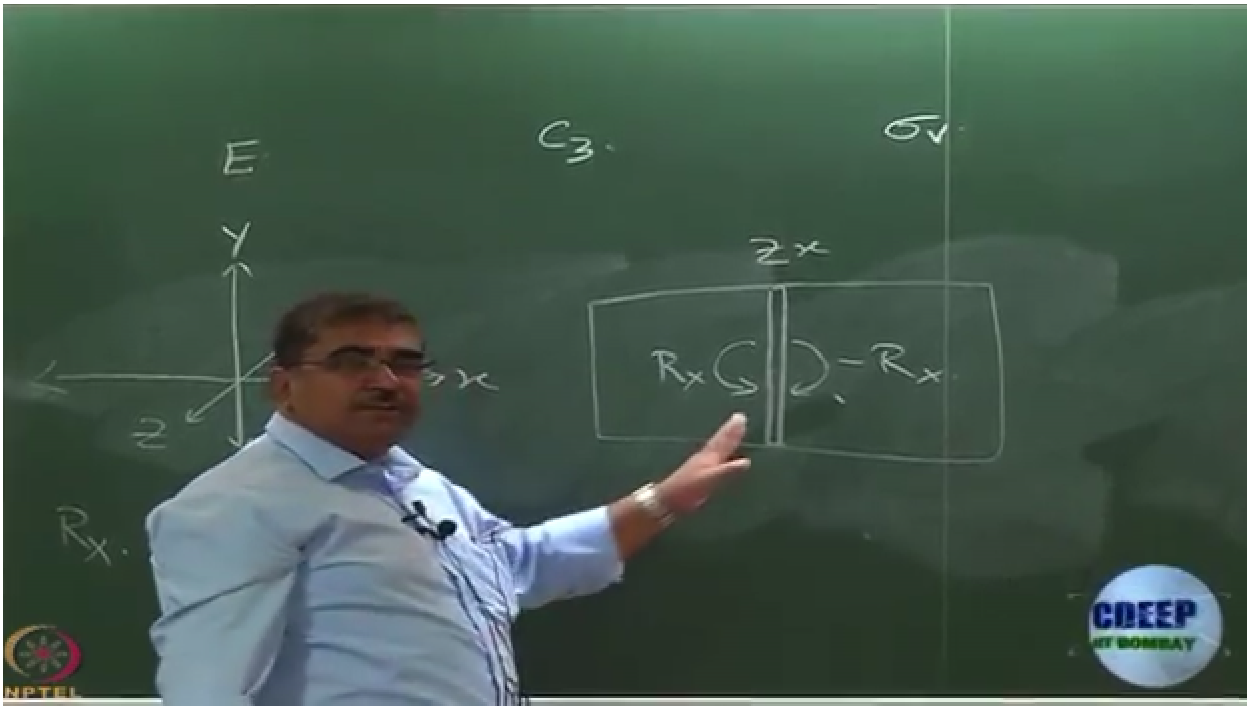

It is this plane, please don't get confused, now I've interchange the directions of the two planes, now this here is the molecular plane, okay, this plane of the board right now is your perpendicular plane. Now what happens when this perpendicular plane, plane of the board operates on RX? You get back the same thing, so character is +1, what I'm trying to say is this, you understood what RX is? This is X, this is RX.

Now of course character of E is going to be 1, no issue with that, but if I know apply sigma V, sigma V is ZX, okay this time I'll try another orientation, this is Z, this is X, this plane of the board now is your sigma VX,

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okay, what is RX? How did we draw it? Something like this, what will be the reflection on the plane of the board? Something like this, the important thing to understand is that the plane containing this two segments of circles is perpendicular to the board, okay, is that not RX? This was going like this and the reflection is going like this, the sense is reversed so character is -1, okay.

Are we okay with sigma V now? What about sigma V dash? Now if I draw sigma V dash like this, what will happen?

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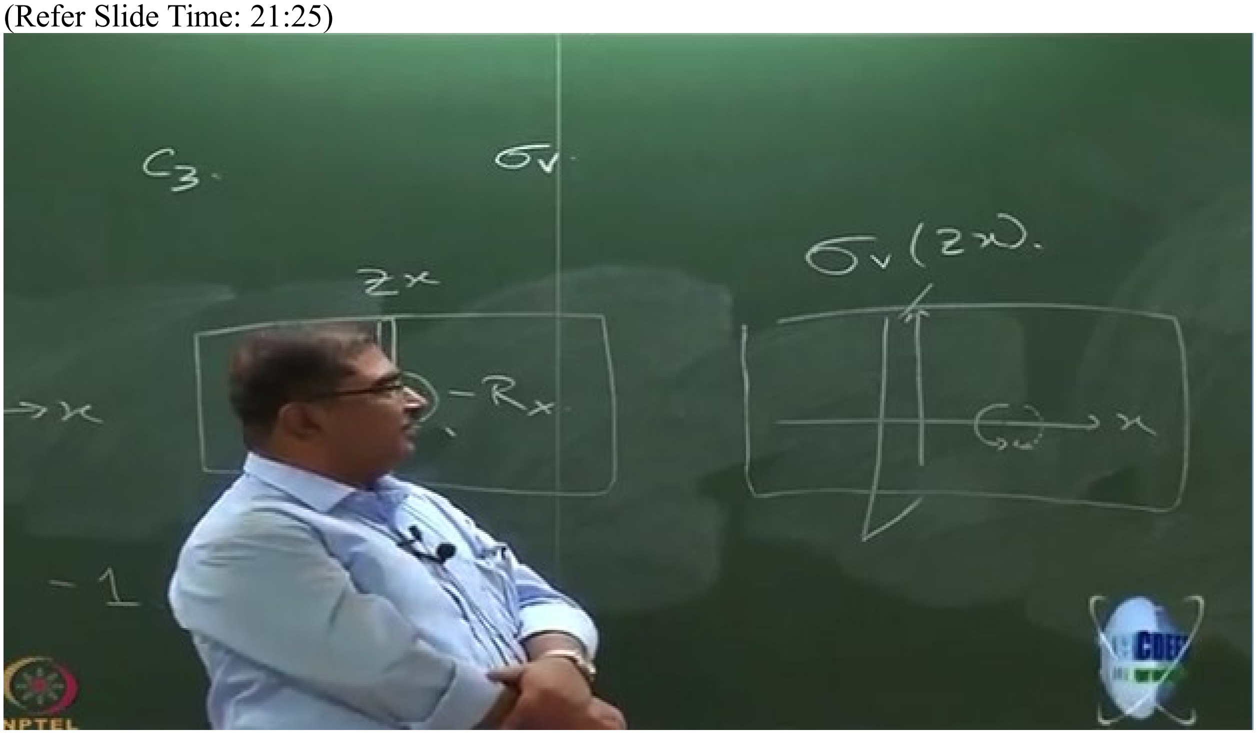

It was rotating in this direction it's still rotating in this direction, so character is +1.

What about C2? What about C2? This is your Z axis, this is C2,
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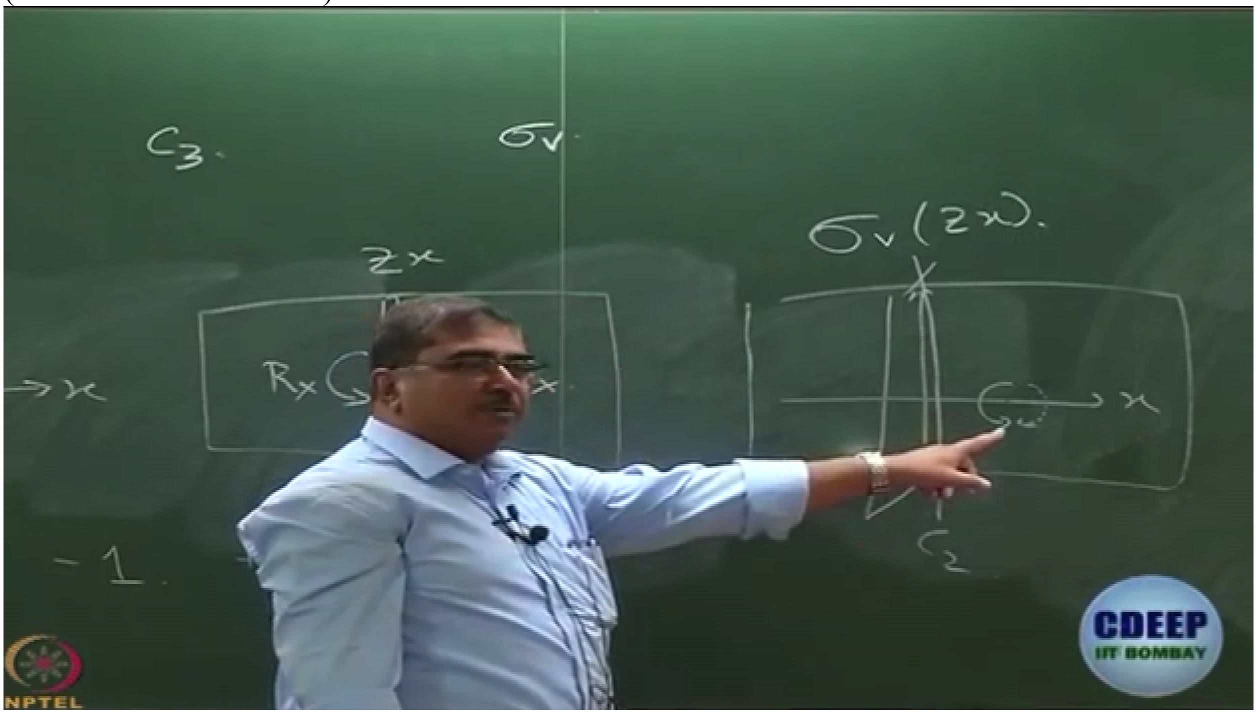

if you now think of this RX called arrow, if you turn it by 180 degrees where will it go? It'll go, first of all this one is above the board right, it's on our side of the board, when you turn it it'll go behind the board, okay, but the tail will remain at the top, the head will remain at the bottom, so it will be something like this. Isn't that –RX? Right, so character of that is -1, 1 -1, -1 1 where does it belong? 1 -1, -1 1 RX is B2, okay, this way you should try to work out RY and RZ and then this is the little more tricky, here in C3V the problem is RX and RY jointly formed the basis of a two dimensional representation,
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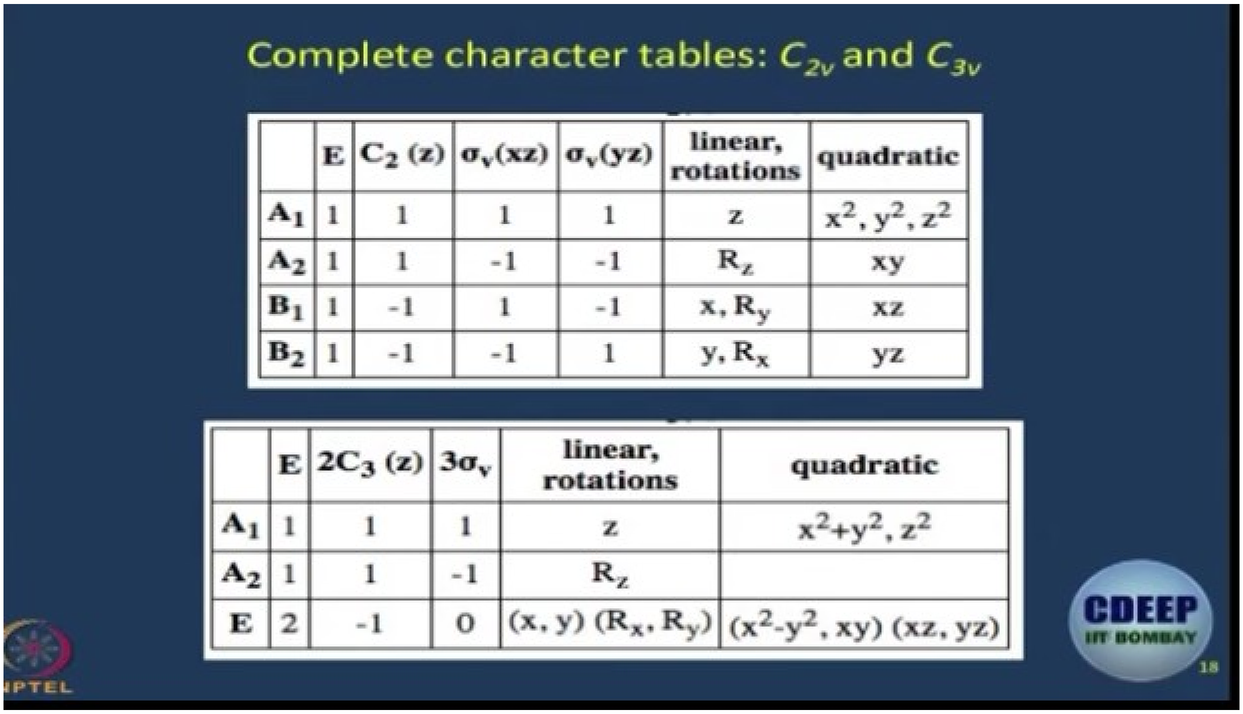

Complete character tables: C_{2v} and C_{3v}

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

see if you can work that out then you've really understood, and then you've really developed the vision that is required to understand symmetry, okay, give it a try it will work out, in any case for our purpose your character table will be given to you, you will not be required to derive it.

Okay, so much for, so now we've learned what is there in a character table right, generally here the place that I've left blank this is where we write the name of the symmetry point group, the top row contains the symmetry operations, the first column contains the Mulliken nomenclature, this segment contains all the characters and then in the last two columns, the second last column contains XYZ, RX, RY, RZ, the last column contains the quadratic terms X square, Y square, Z square, XY, YZ, ZX sometimes you can see things like X square – Y square and all that depends on the character, that depends on the symmetry point group that you are dealing with. So what I request is please have a look at D6H for example,

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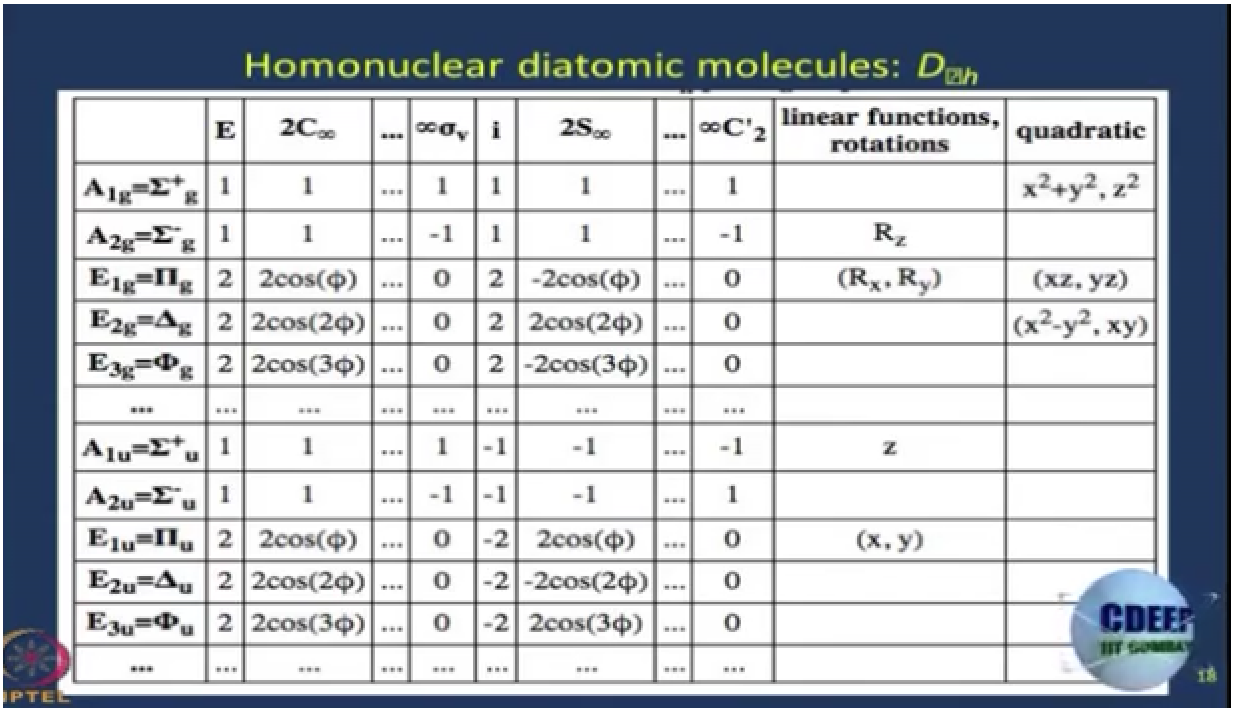

Homonuclear diatomic molecules: $D_{\infty h}$

	E	$2C_\infty$	...	$\infty\sigma_v$	i	$2S_\infty$	...	$\infty C'_2$	linear functions, rotations	quadratic
$A_{1g}=\Sigma^+_g$	1	1	...	1	1	1	...	1		x^2+y^2, z^2
$A_{2g}=\Sigma^-_g$	1	1	...	-1	1	1	...	-1	R_z	
$E_{1g}=\Pi_g$	2	$2\cos(\phi)$	...	0	2	$-2\cos(\phi)$	...	0	(R_x, R_y)	(xz, yz)
$E_{2g}=\Delta_g$	2	$2\cos(2\phi)$	...	0	2	$2\cos(2\phi)$	...	0		(x^2-y^2, xy)
$E_{3g}=\Phi_g$	2	$2\cos(3\phi)$	...	0	2	$-2\cos(3\phi)$	...	0		
...	...	...	...	...	...	...	...	...		
$A_{1u}=\Sigma^+_u$	1	1	...	1	-1	-1	...	-1	z	
$A_{2u}=\Sigma^-_u$	1	1	...	-1	-1	-1	...	1		
$E_{1u}=\Pi_u$	2	$2\cos(\phi)$	...	0	-2	$2\cos(\phi)$	...	0	(x, y)	
$E_{2u}=\Delta_u$	2	$2\cos(2\phi)$	...	0	-2	$-2\cos(2\phi)$	...	0		
$E_{3u}=\Phi_u$	2	$2\cos(3\phi)$	...	0	-2	$2\cos(3\phi)$	...	0		
...	...	...	...	...	...	...	...	...		

D6H is the symmetry point group of which one? Benzene right? See this here is the character table for C3H.

First thing to note is you have A dash, E dash, A double dash, E double dash,

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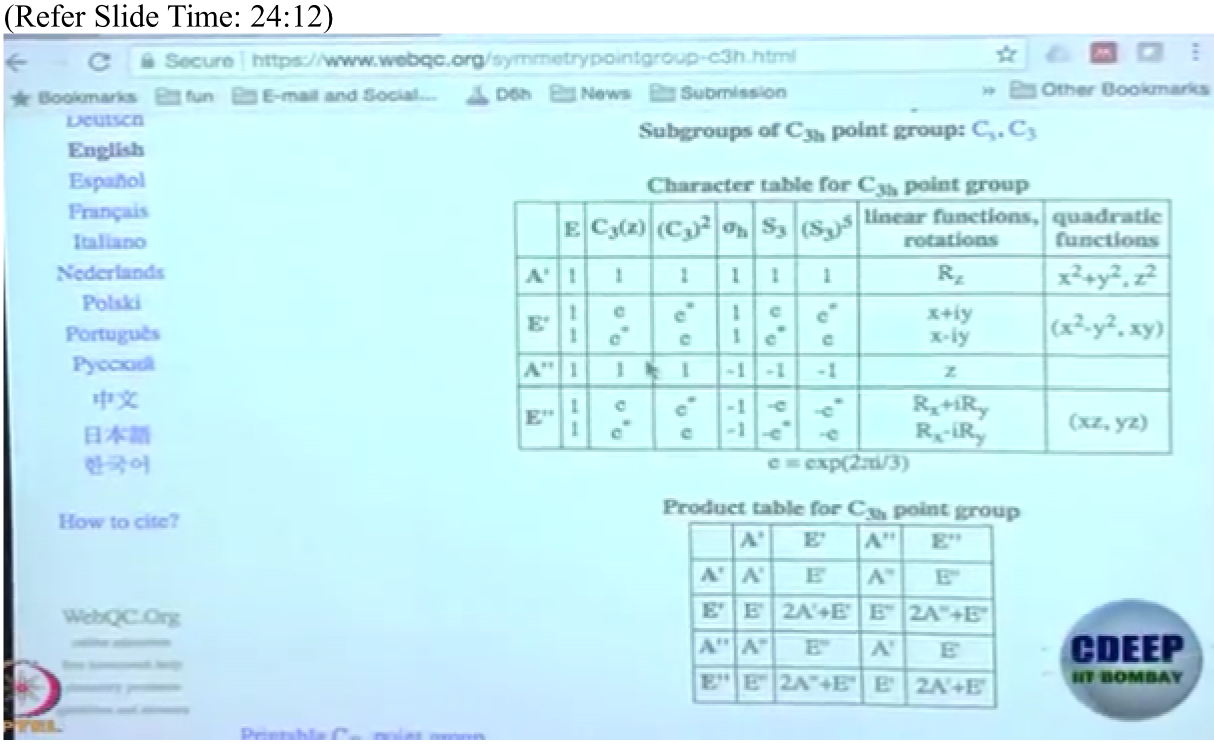


Subgroups of C_{3h} point group: C_s, C_3

Character table for C_{3h} point group

	E	$C_3(z)$	$(C_3)^2$	σ_h	S_3	$(S_3)^5$	linear functions, rotations	quadratic functions
A'	1	1	1	1	1	1	R_z	x^2+y^2, z^2
E'	1 1	ε ε*	ε* ε	1 1	ε ε*	ε* ε	x+iy x-iy	(x^2-y^2, xy)
A''	1	1	1	-1	-1	-1	z	
E''	1 1	ε ε*	ε* ε	-1 -1	-ε -ε*	-ε* -ε	R_x+iR_y R_x-iR_y	(xz, yz)

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

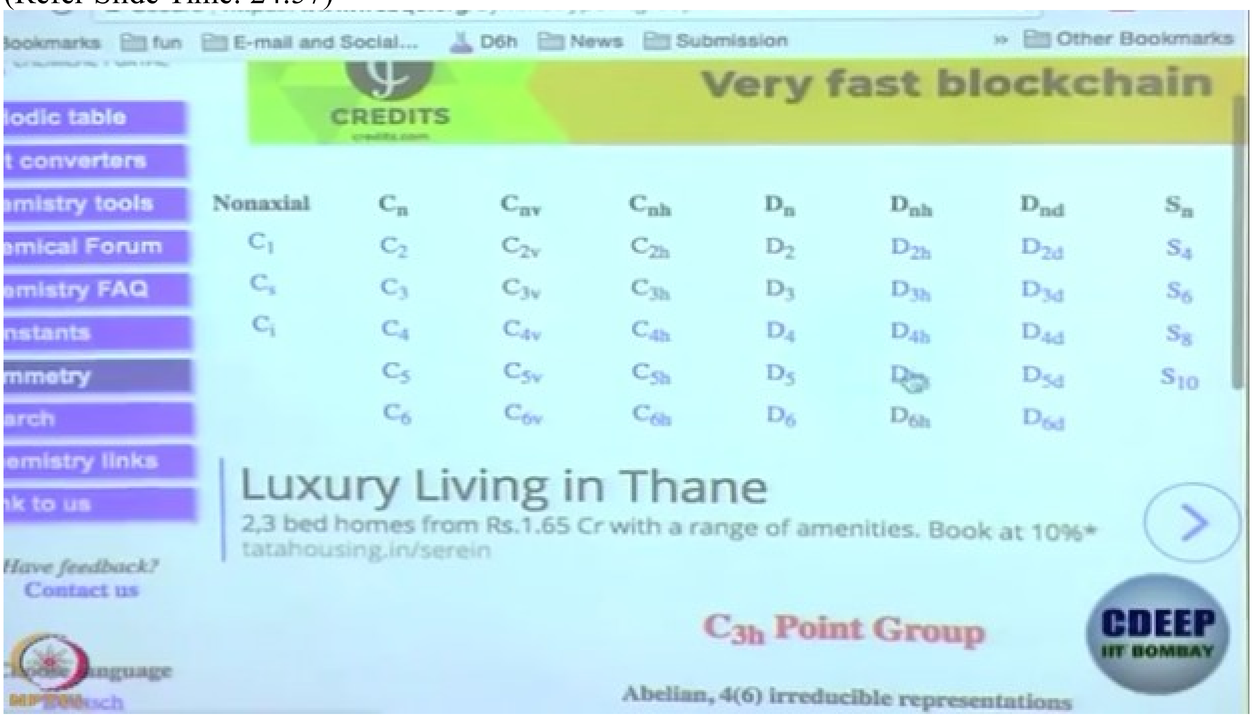
Product table for C_{3h} point group

	A'	E'	A''	E''
A'	A'	E'	A''	E''
E'	E'	2A'+E'	E''	2A''+E''
A''	A''	E''	A'	E'
E''	E''	2A''+E''	E'	2A'+E'

what do this dash and double dash denote? Symmetric and anti-symmetric with respect to the horizontal plane sigma H.

Second point to note is we have this carry E, E star, right, what is E here? Exponential 2 pi I/3, which tells you that characters can actually be complex, okay. In this course we are not going to deal with complex characters, in case you study the course on group theory later on that is where we'll talk about this at length.

Next is D6H is what I wanted to show you, D6H,
(Refer Slide Time: 24:57)



what is the claim to fame of D6H? Why are we talking about D6H all of the sudden?
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Subgroups of D_{6h} point group: C_s, C_i, C_2, C_3, C_6, D_2, D_3, D_6, C_{2v}, C_{3v}, C_{6v}, C_{2h}, C_{3h}, C_{6h}, D_{2h}, D_{3h}, D_{3d}, S_6

Character table for D_{6h} point group

	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	Linear, rotations	Quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x, y)	
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

Product table for D_{6h} point group

Because D6H is the symmetry point group of a molecule that is an all-time favorite with chemist especially organic chemist, which molecule? Benzene, right benzene is D6H, and in this course we are going to talk about electronic spectroscopy of benzene, we are going to need this character table there, now the reason why I am showing you this is that, see there is sigma H or not, there is sigma H, but you might notice that this dash and double dash have been omitted, why because if you just write this 1 2, and G U, then your symmetry species are all defined uniquely, there is no need of dash or double dash, that is why it is not written, okay, there is nothing wrong if you incorporate dash and double dash in the Mulliken nomenclature of this irreducible representations, but it is not necessary. Okay. That brings us to the end of this discussion. We'll now proceed to talk about wave functions as basis.

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