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. – 36
Mulliken Nomenclature, 2D Irreducible Representations and Bases

Fine, so this is what we've done so far.
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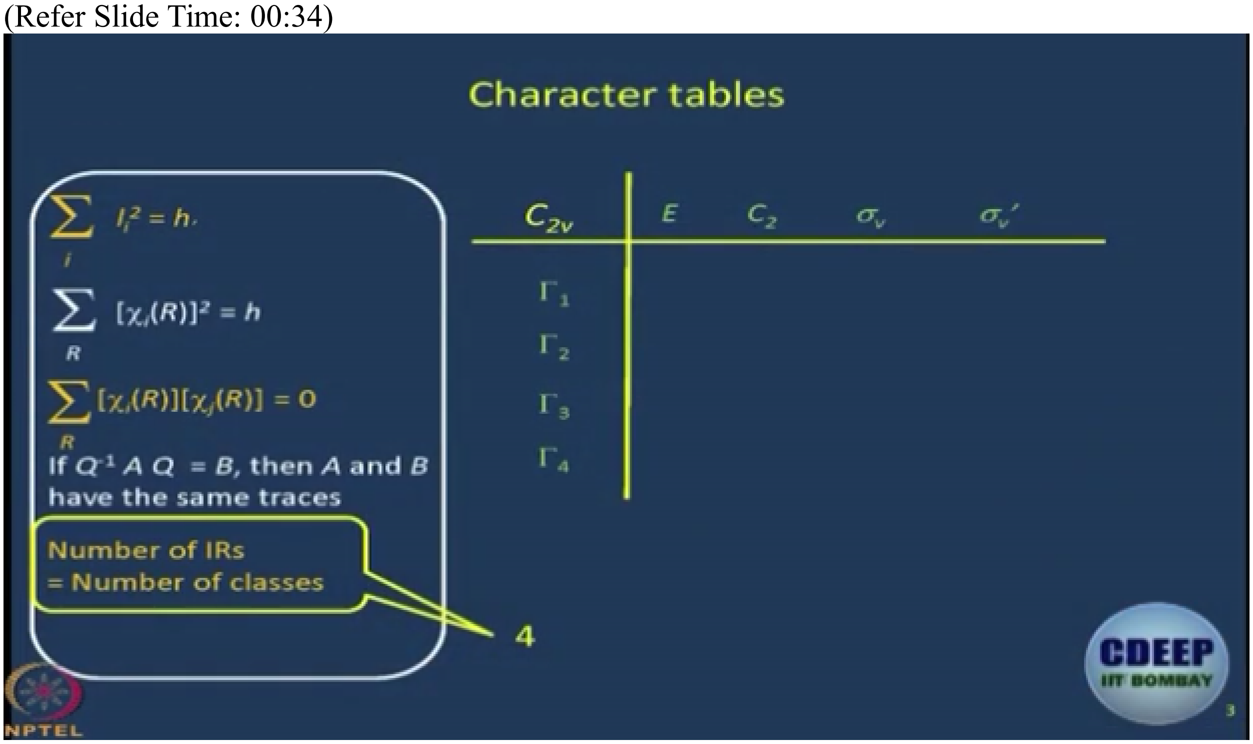

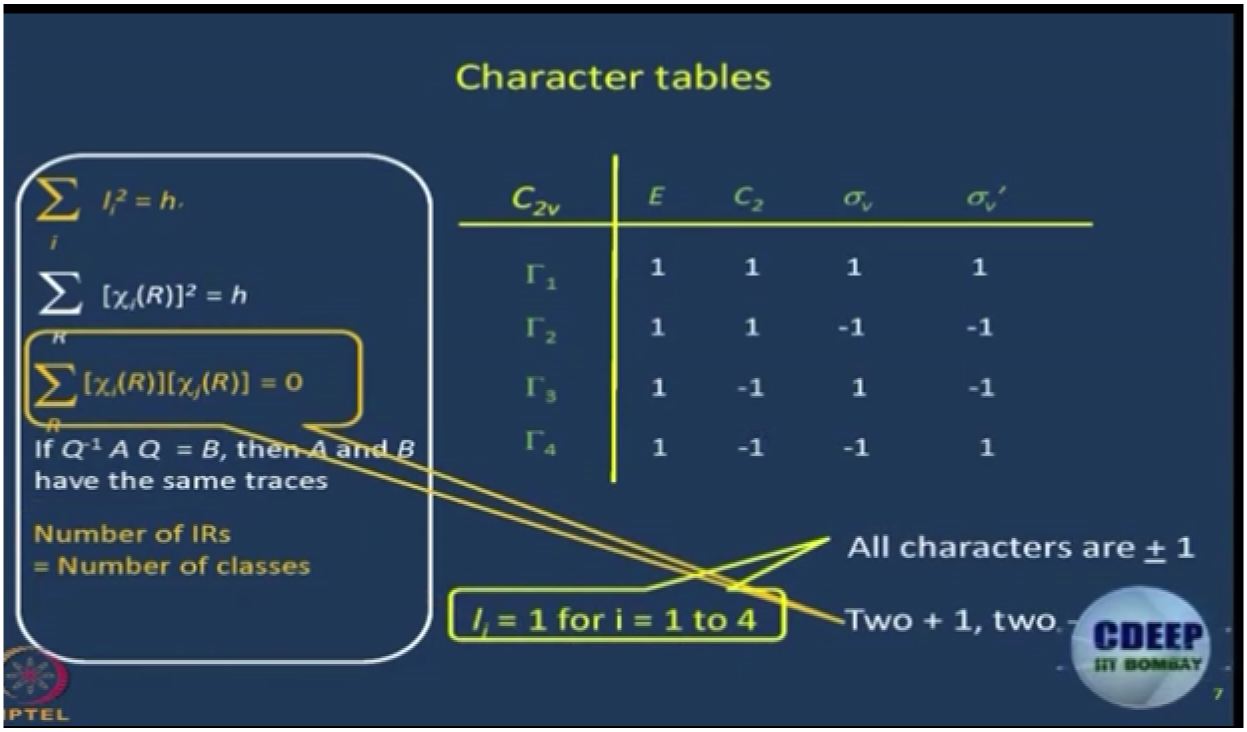

This is where we have reached in the discussion so far, now we'll start talking about character tables of little more complicated groups as well, and we also talk about the nomenclature. So what we are going to discuss now is Mulliken nomenclature, 2D irreducible representations and we will also discuss the bases.

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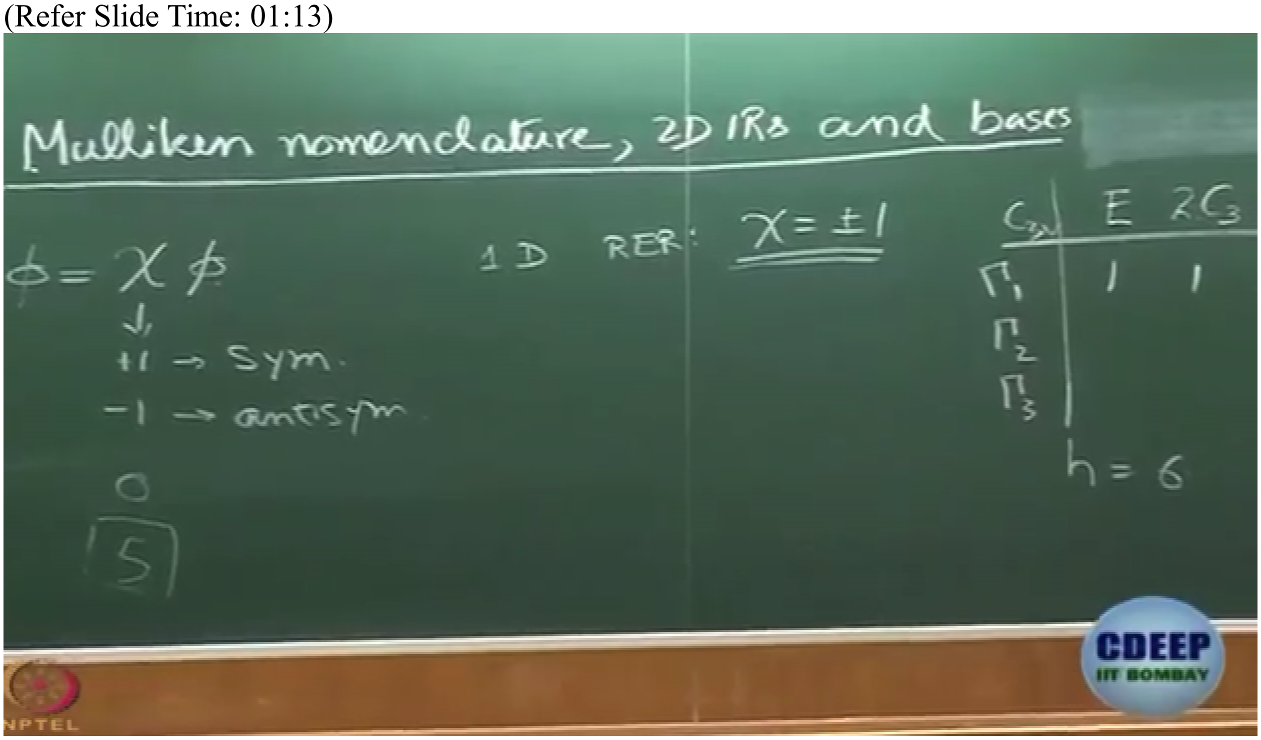

So the question is which one do we want to do first, let us finish the story of C3V and then come back to it, okay, exactly the same thing for C3V, H = 6,

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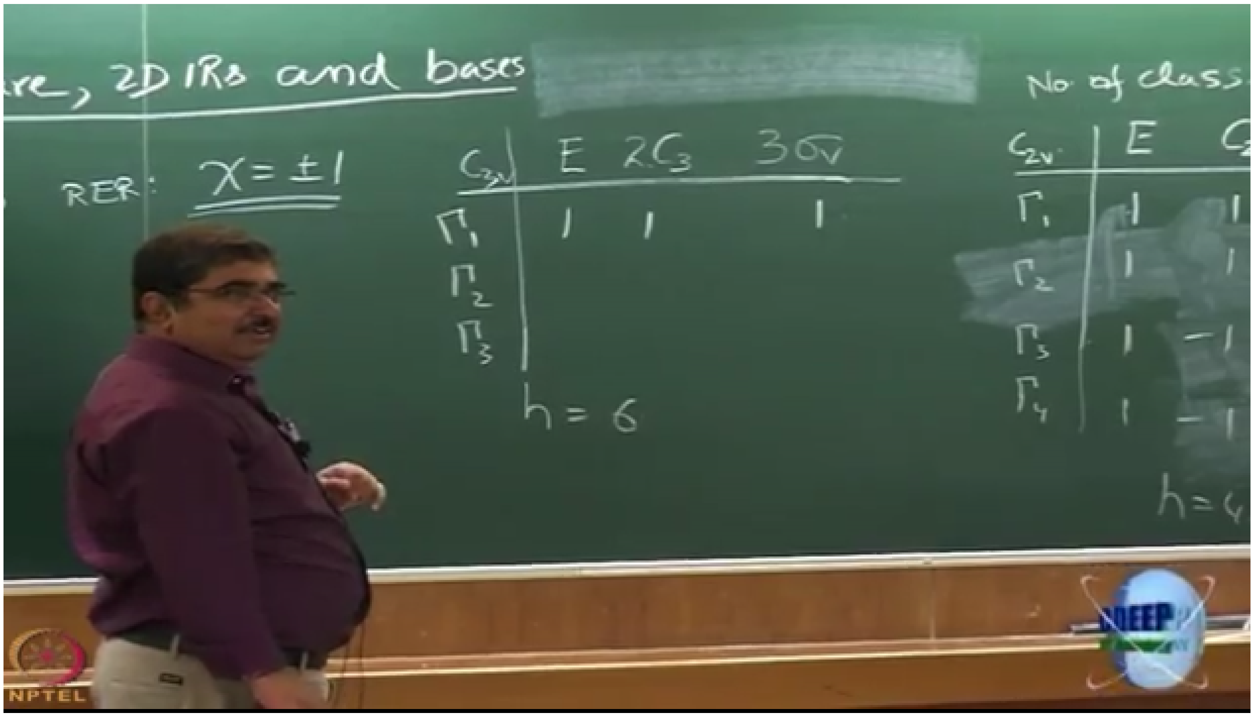

okay, number of classes = 3, so 3 irreducible representations, so what do I write? L1 square + L2 square + L3 square is equal to how much? 6,

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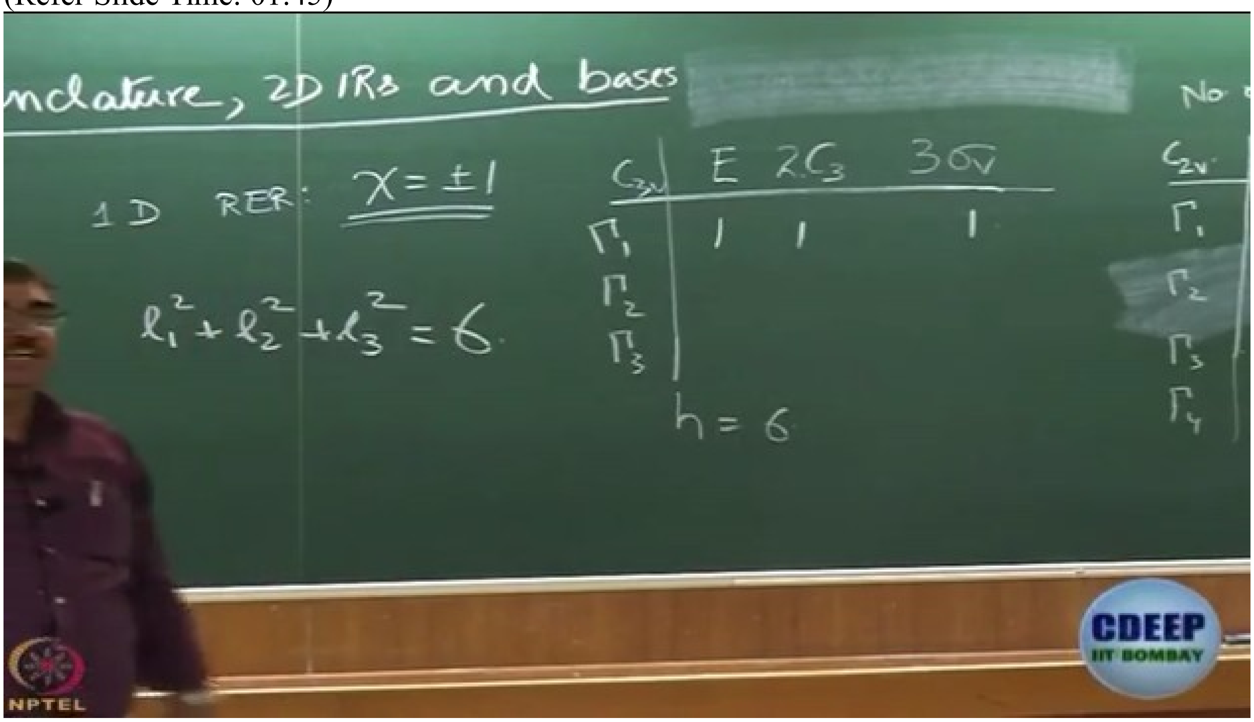

what are the possible values of L1, L2, L3? 1 1 2, it can be 1 2 1, it can be 2 1 1 doesn't matter? But conventionally we write the 1 dimensional irreducible representation first then 2 dimensional representations, then 3 dimensional representations, okay, 1 1 2, so L1 is 1, L2 is 1, L3 is 2, so here we encounter a 2 dimensional irreducible representation, I can write the characters now, characters of the identity operation, what will it be here? 1, what will it be here? 2, excellent.

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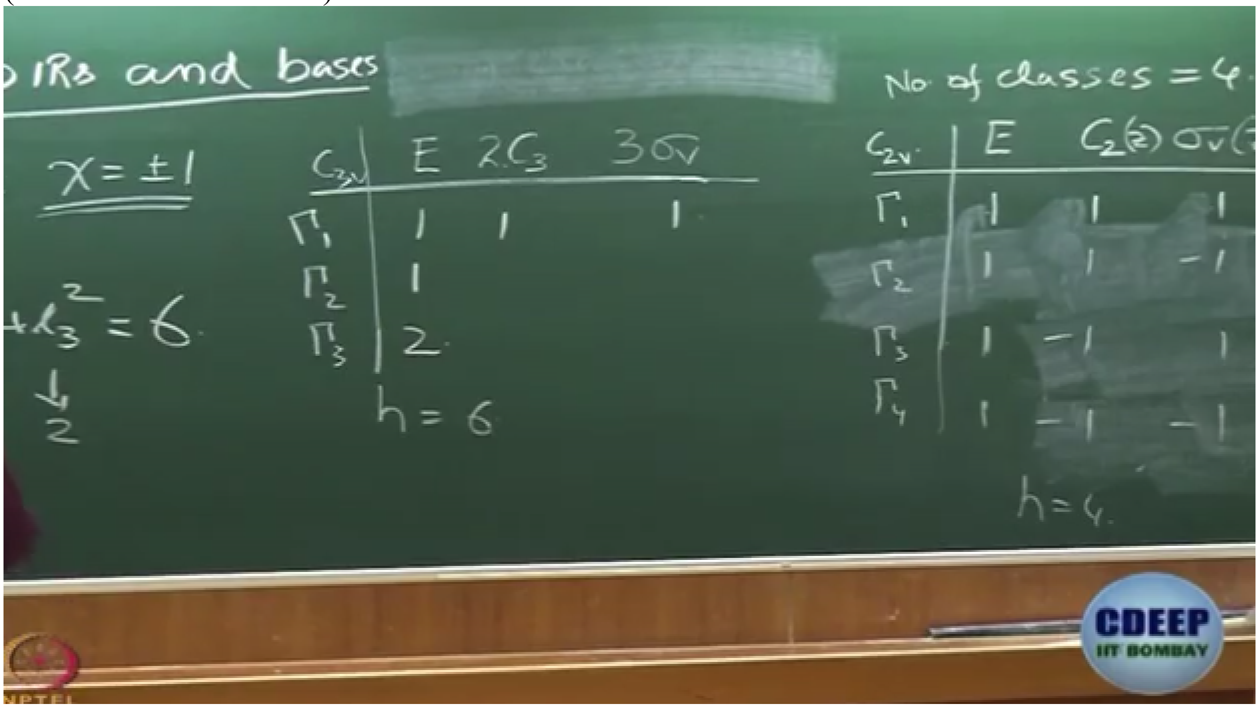

Now what I need to find is chi 2(C3), chi 2(sigma V), is this way of writing clear?

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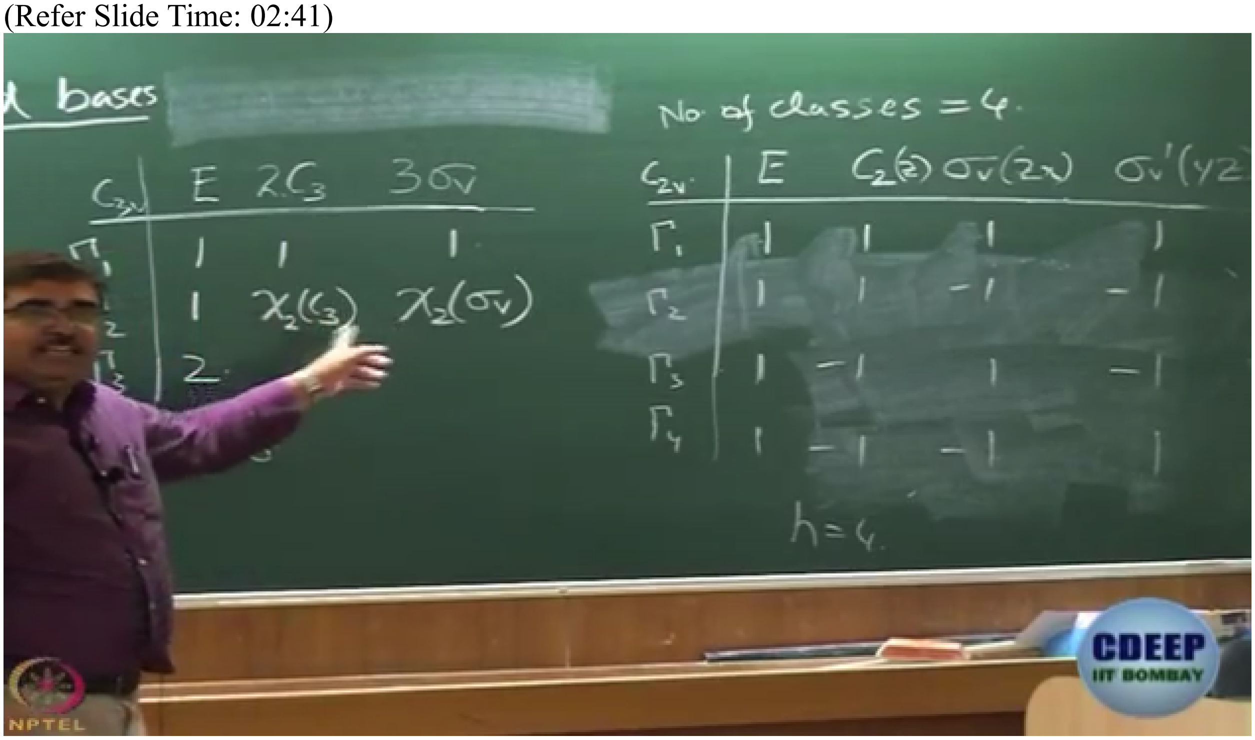

You understand what I mean by chi 2(C3) and chi 2(sigma V)? See earlier when I talked about C2V, it was enough to talk about chi I, because I knew that the chi I's would be only +1 and -1, all where 1 dimensional representations, here one is 1 dimensional the other is 2 dimensional, so it's going to be little different, so I have to write 2 and 3 specifically.

This one is chi 3(C3), chi 3(sigma V), okay,
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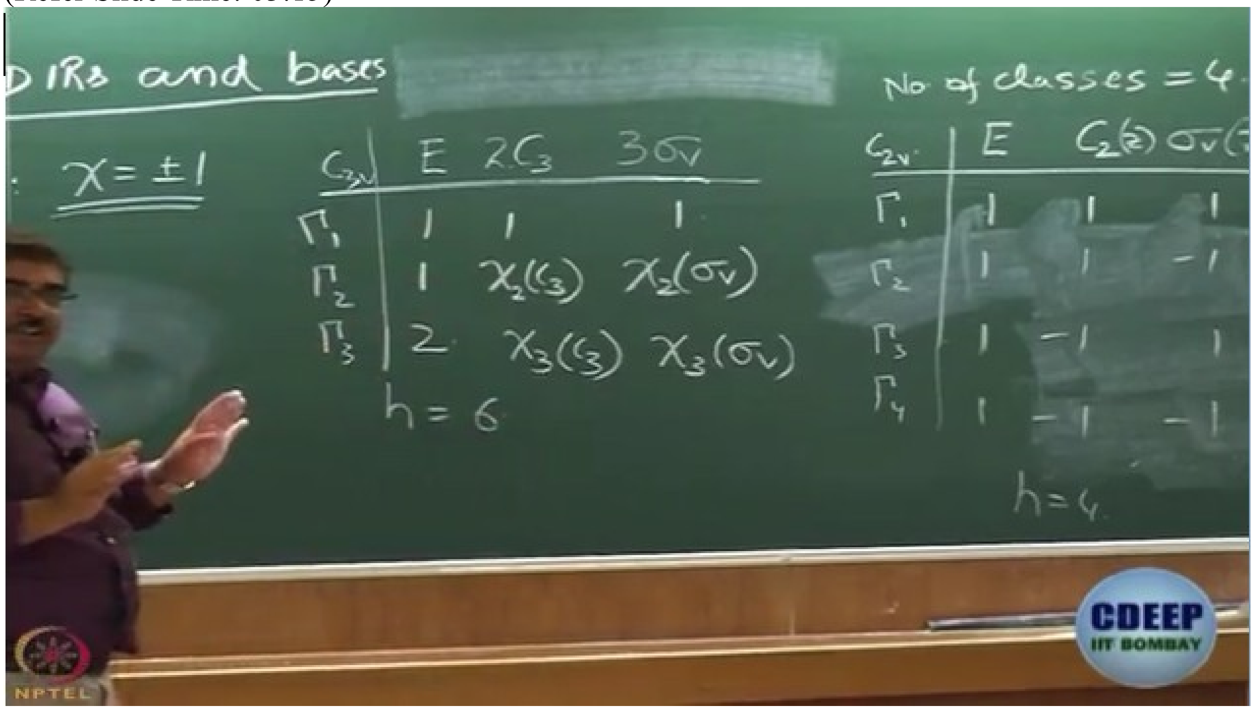

what is the next thing to do?
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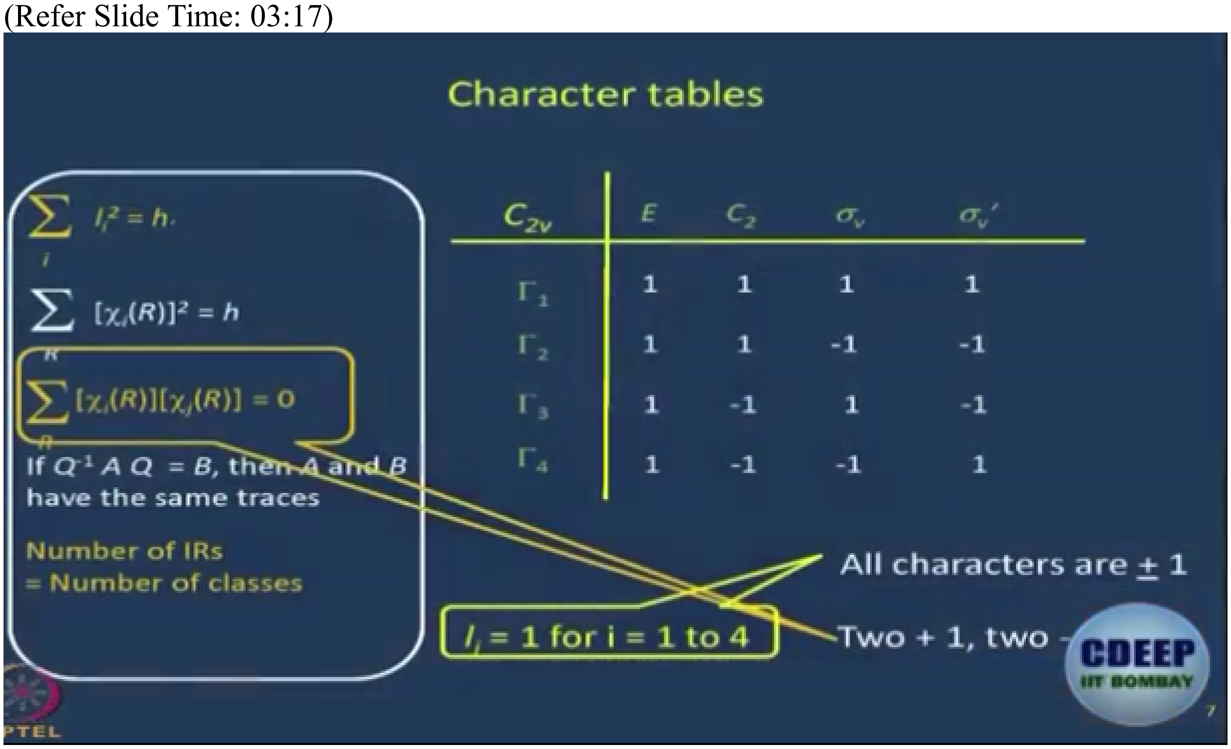

We can use the orthogonal thing, right, you can use the rule of orthogonality so what will it be? First take the combination of these two, remember chi 2(C3) and chi 2(sigma V) have to be either +1 or -1 we know that already, that's one good thing, okay. So I'm using the rule sum over R chi I(R) chi J(R) = 0 orthogonality,

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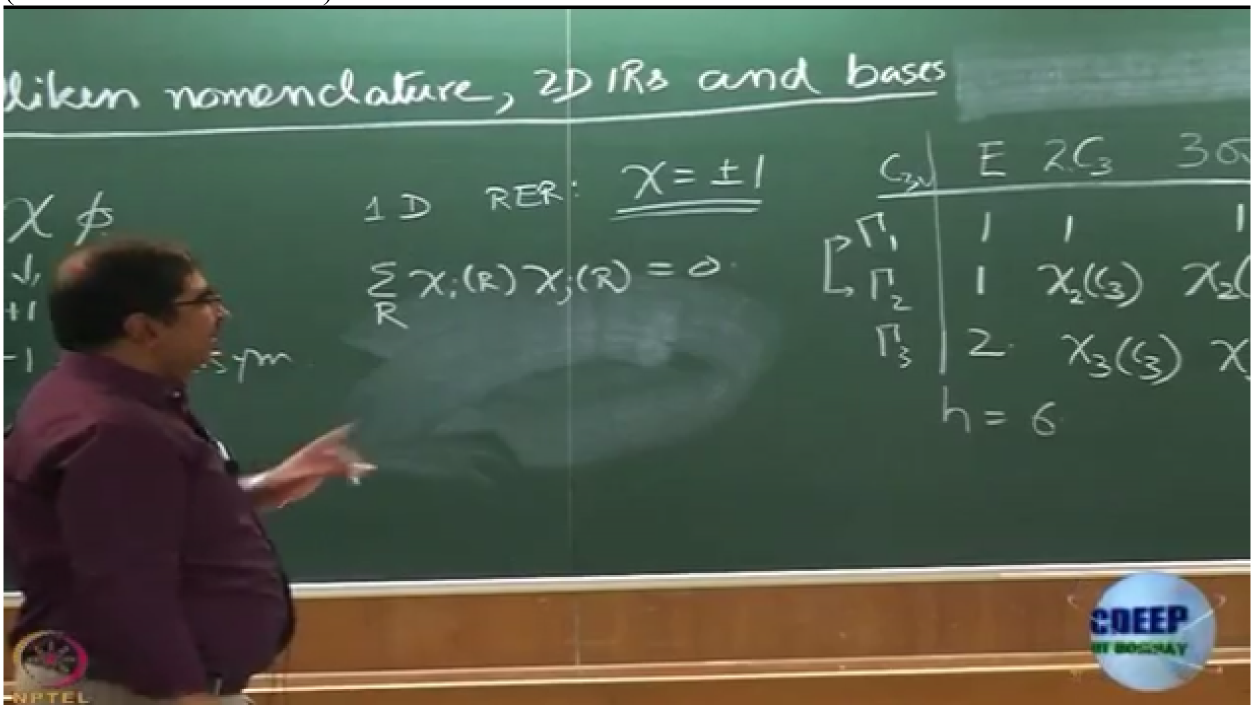

and I want to work with gamma 1 and gamma 2, help me, first one is for E, 1 x 1 is 1, what do I get for C3? Yes, 1 x chi 2(C3) is that right? Yes, I heard something very faintly, into 2 right, don't forget into 2, do not forget and this is where, well this is where we can make mistakes, so let's be very clear about this, you cannot neglect this,

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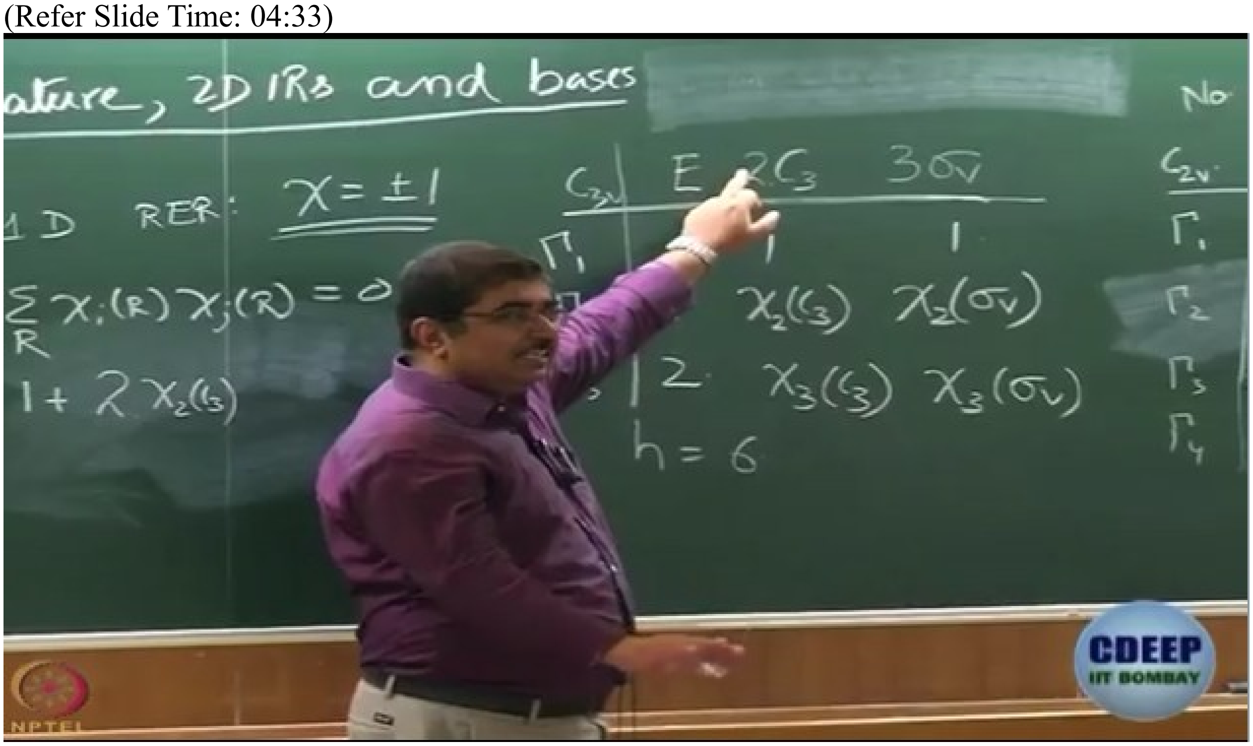

don’t forget as we have discussed a little earlier there are 2C3 operations, C3+ and C3-, it is just that the characters are same that’s why we have written them together, does not mean you can neglect them while taking the summation, you’ll get the wrong result if you neglect them while taking with summation, okay, so don’t forget the 2, very good.

What is the next one, next term? +3 chi 2(sigma V) = 0
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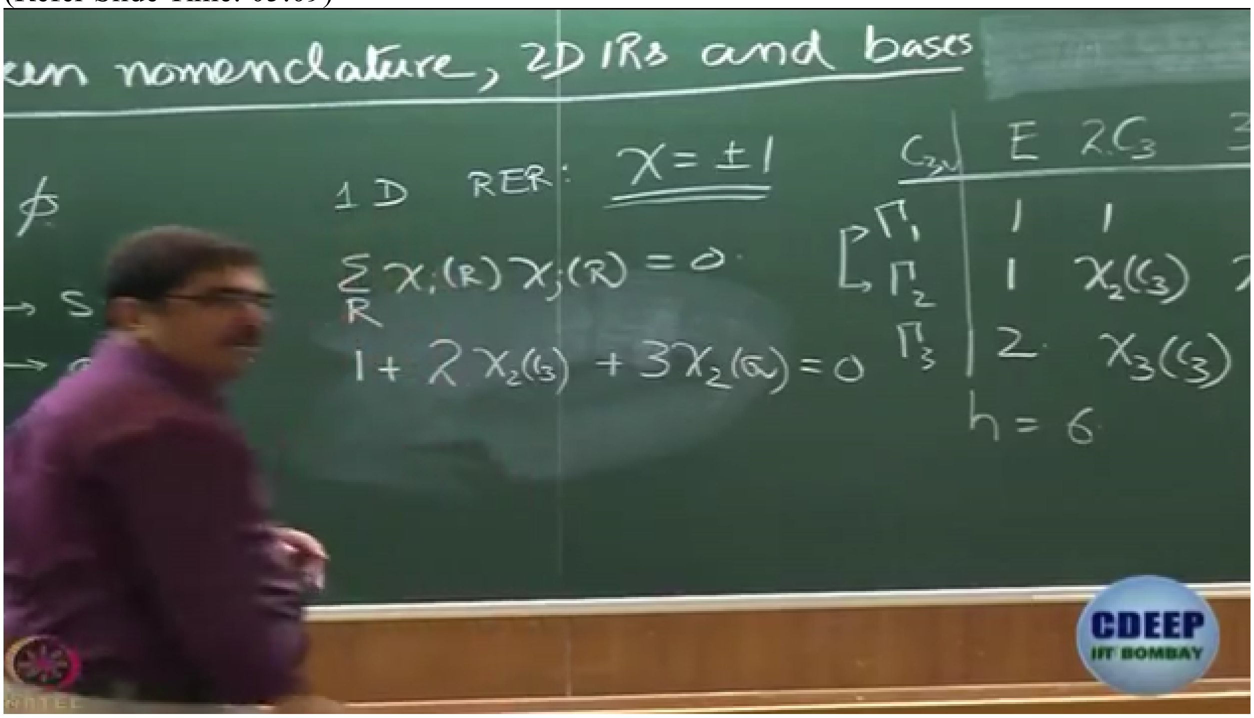

and let us not forget that gamma 2 is 1 dimensional so the chi had to be either +1 or -1, which one is +1, which one is -1? Very simple, this is -1, this is +1,
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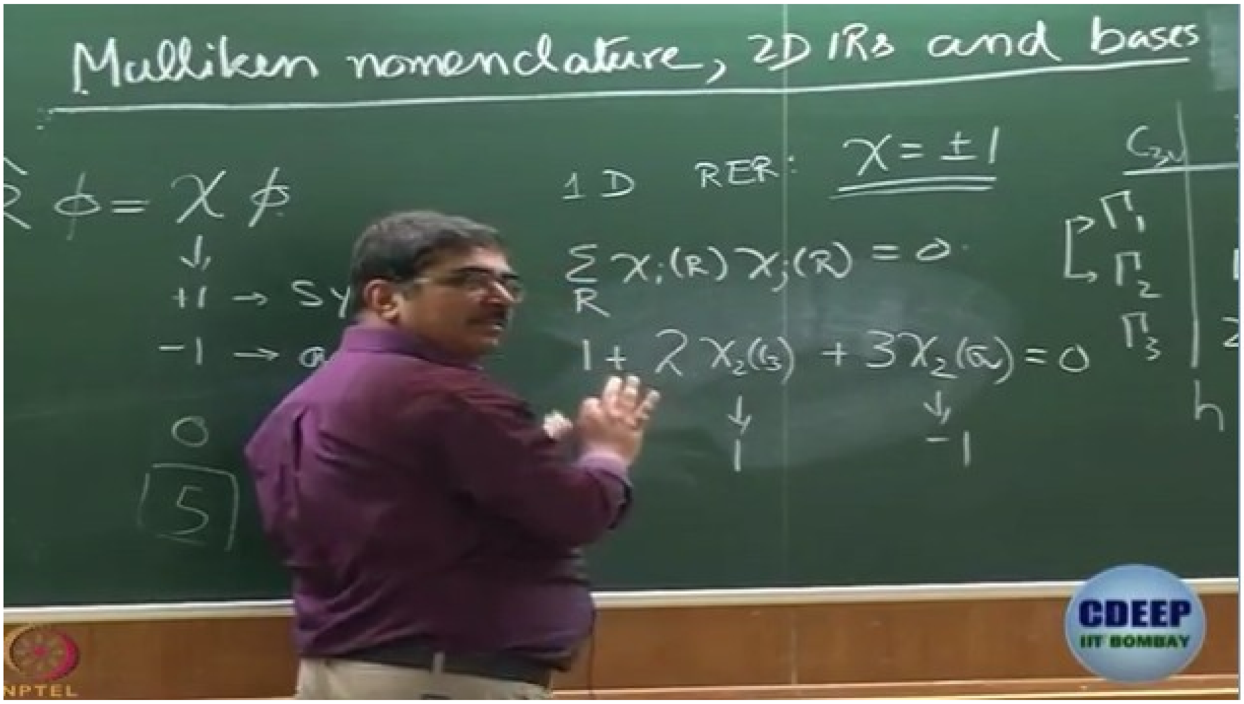

simple, any doubts? Any question? Sure? Can I substitute that?

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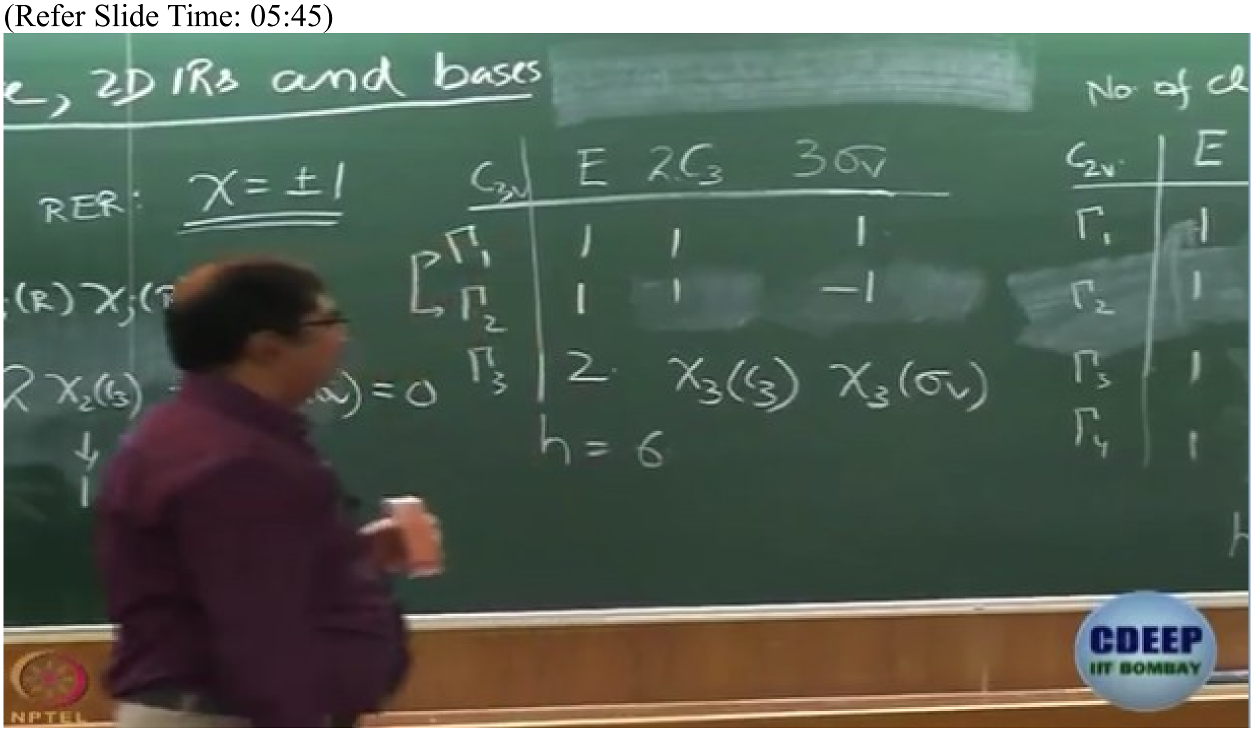

+1, -1, are we okay? Now we'll go ahead and we'll try to find out chi 3(C3) and chi 3(sigma V), now these promise to be a little more interesting because now we are not dealing with, for the first time we are not dealing with one dimensional irreducible representation anymore, so characters can be something other than +1 and -1, and even if there are +1 and -1 the implication is not the same as what it is for the one dimensional irreducible representation.

Let's proceed, so we'll use the same thing, we'll use the same rule here, first let us, I'll get rid of this, right, first let us take gamma 1 and gamma 2, okay, help me, what is the left hand side for this, using gamma 1 and gamma 2? 1 into, gamma 1 and gamma 2, I'm not doing gamma 1 and gamma 3 yet, so 1 then + 2 x, 2 x 1 x chi 3(C3), right, let's write chi 3(C3) right now, oops, oops, oops, why I am using gamma 1 and gamma 2, sorry, sorry, my mistake, Vishwaroop you are right, we have done gamma 1 and gamma 2 already, sorry, this is a manifestation of another very well-known physical principal, it is called inertia.

So we'll use gamma 1 and gamma 2, gamma 3 once and just to help my poor memory, next time we are going to use gamma 2 and gamma 3, you're right Vishal so why don't we say it once again, what is it? 1 x 2, 2 this time, right, + 2 x chi 3(C3) + 3 x chi 3(sigma V) = 0 and this time you'll not be able to figure out the values of the characters only from this equation because there
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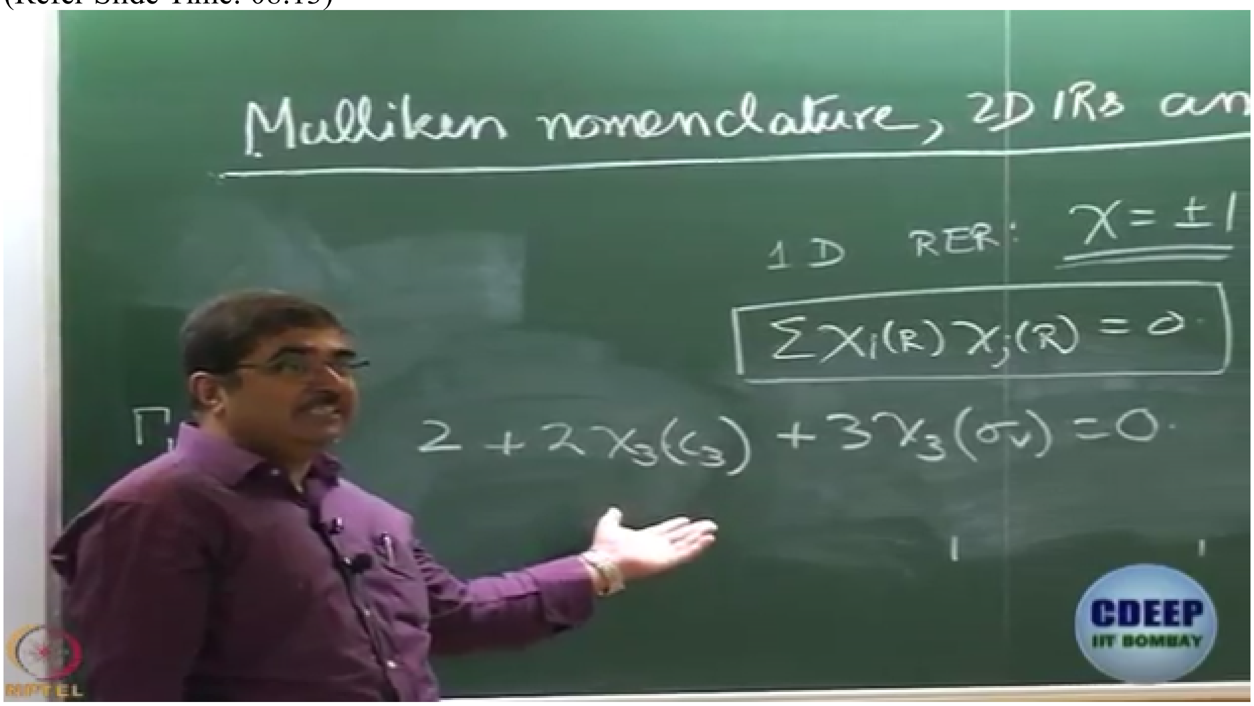

is no condition that they have to be +1 or -1, you need another equation, 2 unknowns, 2 equations.

What is the equation you get when you use gamma 2 and gamma 3? This one, yeah, help me, 1, 1 x 2 = 2 + 2 x chi 3(C3) then – 3 x chi 3(sigma V) = 0, excellent,
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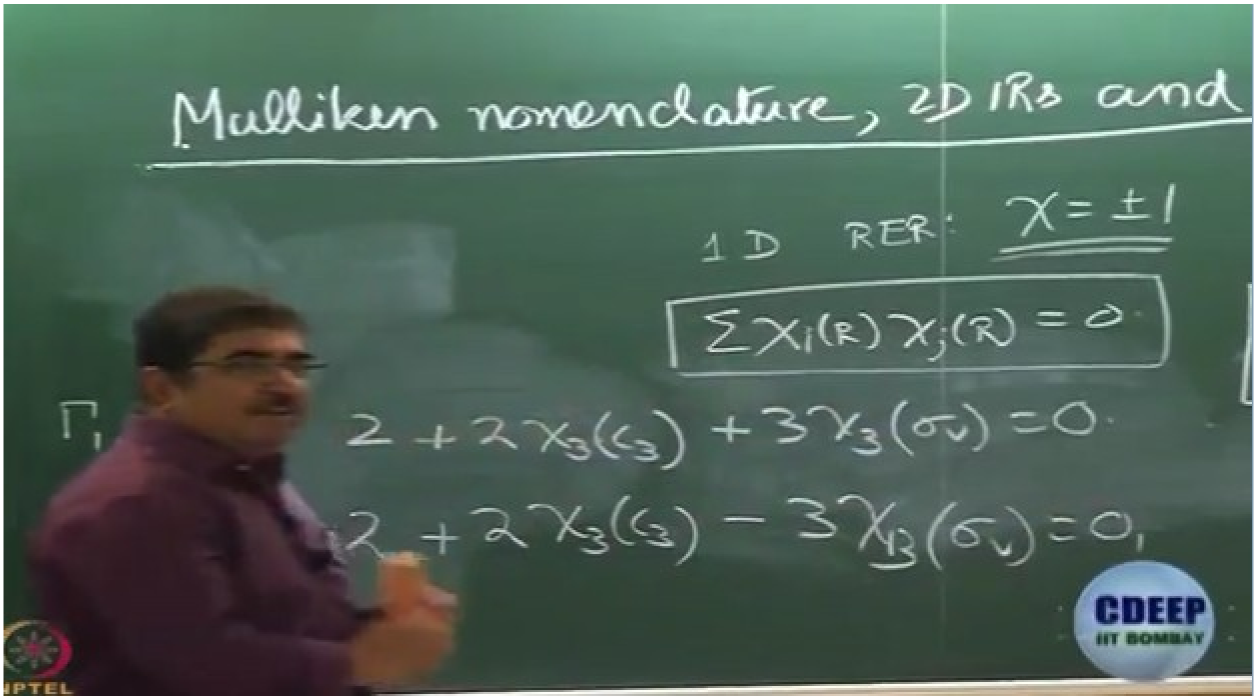

first that I can see from here is that this chi 3(sigma V) has to be equal to 0, right, because no matter whether you add it, I'll add three times of it or no matter whether you subtract three times of it to 2 + 2 chi 3(C3) you get 0, right, so this chi 3(sigma V) has to be equal to 0, do you agree? If you don't agree the spoke of the values, you have two equations, you have two unknowns, tell me what is the value of chi 3 or sigma V, tell me what is the chi 3(C3)? Which one is 0, which one is -1? Chi 3(sigma V) is 0, and chi 3(C3) is -1, are we in agreement over that? Right, so you've got it. -1, 0, so we've at least tabulated the characters of all irreducible representations of not only C2V but also C3V, okay, and once again if you allow me to show off my animations, that's the different sequence, we're following a different sequence, so anyway you see this right.

So what does this mean?
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This one means that no matter which function you take, if the molecule is C3V then you should be able to write it as a linear sum of functions that belong to one of these, what are called symmetry species, and irreducible representation is also called symmetry species.

What is the meaning of symmetry species? Unique types of symmetry that you can see in a point group, so what we are saying is there are only 4 kinds of symmetries you can see in C2V, one that is totally symmetric, second symmetric with respect to, well I'll not even talk about it, symmetric with respect to C2, anti-symmetric with respect to the planes that is another kind of symmetry you can get. Third is symmetric with respect to the molecular plane or well sigma V, anti-symmetric with respect to the axis as well as the perpendicular plane.

And the last one is anti-symmetric with respect to C2 and sigma V symmetric with respect to the perpendicular plane. These are the only four kinds of symmetries that you can get in C2V that is the meaning.

What about C3V? First of all, you can get 2 1, okay another important thing is that in C2V what we understand is that, there is no mixing of functions by any symmetry operation, okay, now when you took the hydrogen atoms it appear that there was mixing right, because of diagonal 1 is there, what it means is that it's an reducible representation by doing what is called a proper similarity transformation,
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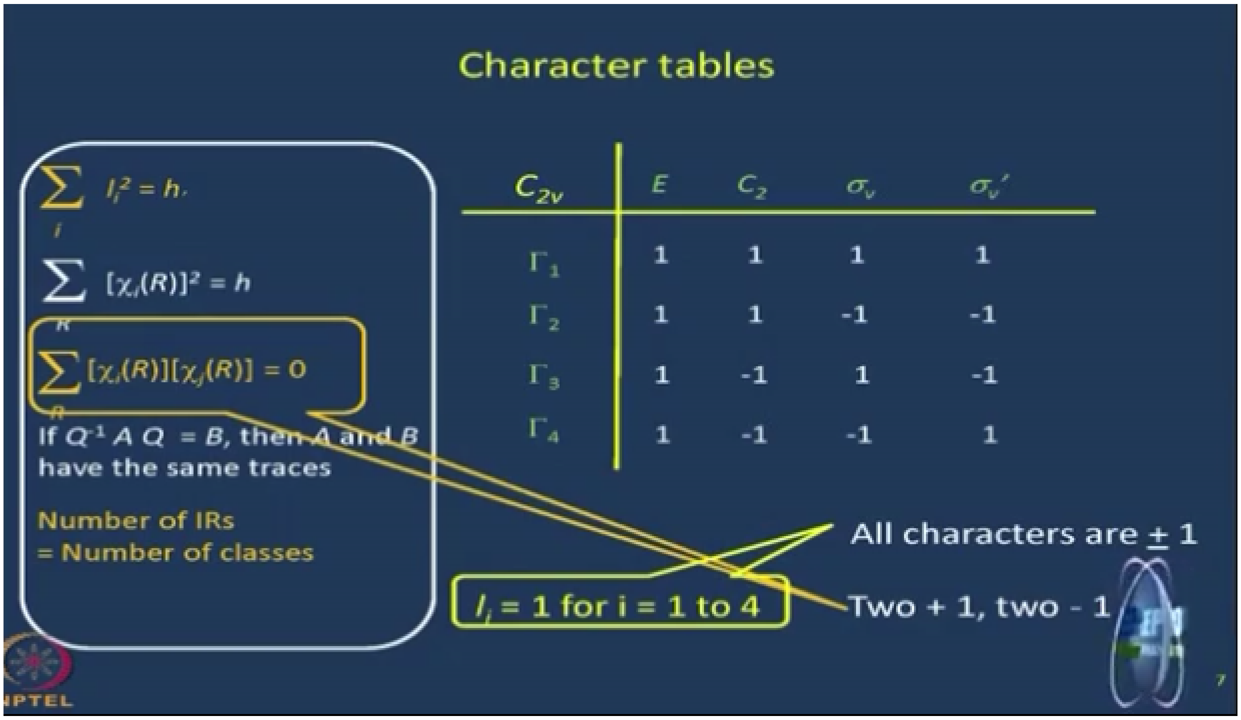

those who are acquainted with matrix algebra would know what I am talking about here, or those of you have studied little bit of group theory, this is called similarity transformation, so by an appropriate similarity transformation we should be able to reduce that 2 dimensional representation into its constituent one dimensional representations, we don't have to do it.

So now here for the first time we have a two dimensional representation, first question we want to understand is what is the meaning of this 0? What is the meaning of this -1? Is 0 annihilation operator? And those of you who have gone through the old questions would see that this is something that I've asked in the past, what is the meaning of this 0? What is the meaning of this -1? To understand that we need to go back and look at the matrices, to do that we need to know the bases, so once you've worked out the bases we're going to talk about the matrices and then we'll understand a little better what is the meaning of this -1 and 0, just bear with me for maybe 7, 8 minutes while before we come to that question, okay.

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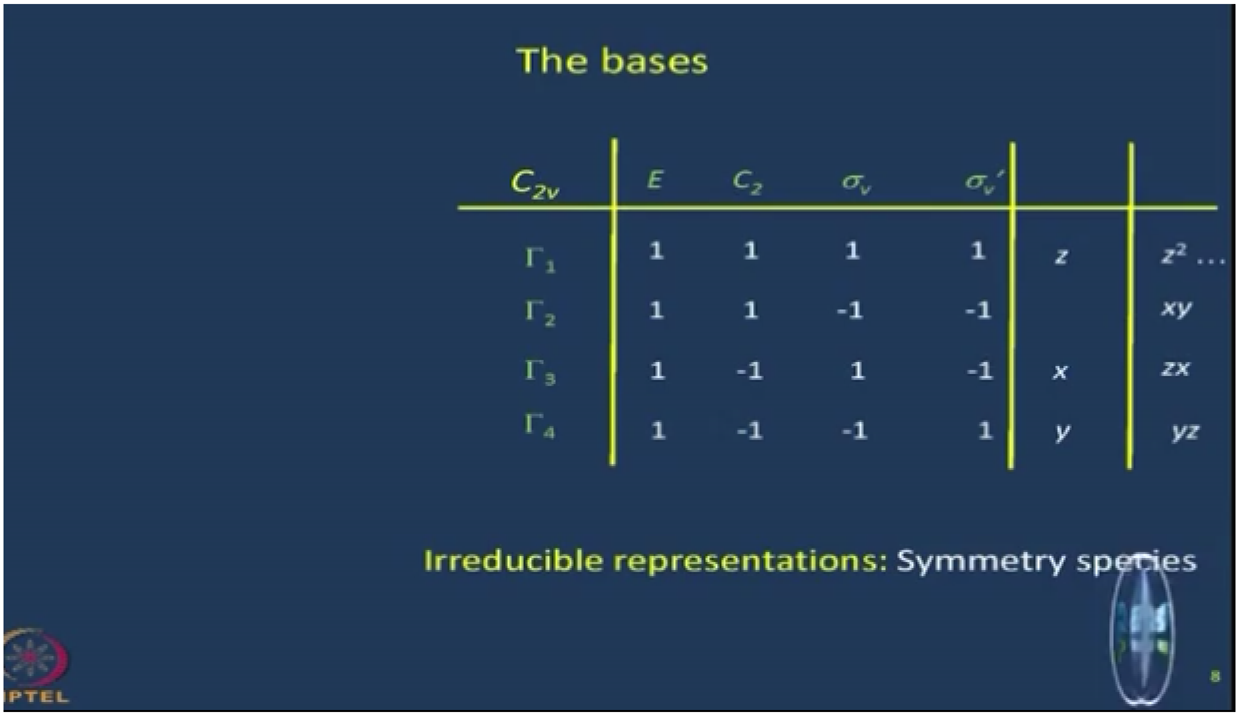

Now for C2V let us think if we think of some simple bases X, Y and Z, or XY, YZ, ZX or X square, Y square, Z square, where will this functions belong? Which symmetry will they have? Okay, we'll try and fill in the bases now. We've already done X, Y, Z right, so if you can flip your notebook you will be able to tell me where Z belongs, where X belongs, where Y belongs, and I think Jaideep has already told us that Z belongs to the top, right, totally symmetric representation, at least for the C2V it is totally symmetric, this is where Z belongs.

Where does X belong, gamma 2, gamma 3 or gamma 4? Gamma 3, yes, and where does Y belong? Gamma 4, okay, nothing belongs to gamma 2, there will be something that will belong to gamma 4, sorry gamma 2, now let us talk about X square, Y square, Z square, where will X square, Y square, Z square belong, Jaswinder? I want to know out of these 4 rows, or 4 symmetry species, 4 irreducible representation, where does Z square belong? Where will Z square go? If I use Z square as the bases let us see, if I apply C2, do I get Z square or do I get -Z square? C2, what do I get? We get Z square right, what?

How will Z square transform? Z square is Z x Z, I apply C2 on Z it becomes Z or rather I should say it remain Z, I apply C2 on the second Z that also remains Z, so C2 operates on Z square to give me my Z square, character is 1, alright.

What about sigma V? Sigma V operating on Z, basically you take Z x Z and then make the symmetry operation operate on the constituents, sigma V operating on Z is Z, sigma V operating on the second Z is also Z, right, so character is 1 once again. Same is true for sigma V dash, so Z square belongs to the first representation totally symmetry.

What about X square? Where does X square belong? This is X, E of course is 1, when C2 operates on X square you have to make it operate twice, right, C2 operates on X square to give you, sorry, C2 operates on X to give you what? –X, right, and then again C2 operates on the second X to give you –X, so what is –X into –X? +X square, so what is the character? 1, same will hold for sigma V dash as well, so X square also belongs here, Y square also belongs here, okay, so one thing that we have said something that we are going to use always is chi I of, how do I write two functions? I'll write F and G = chi I(F) x chi I(G), and well derivation is not even required for this, it kind of comes from commonsense.

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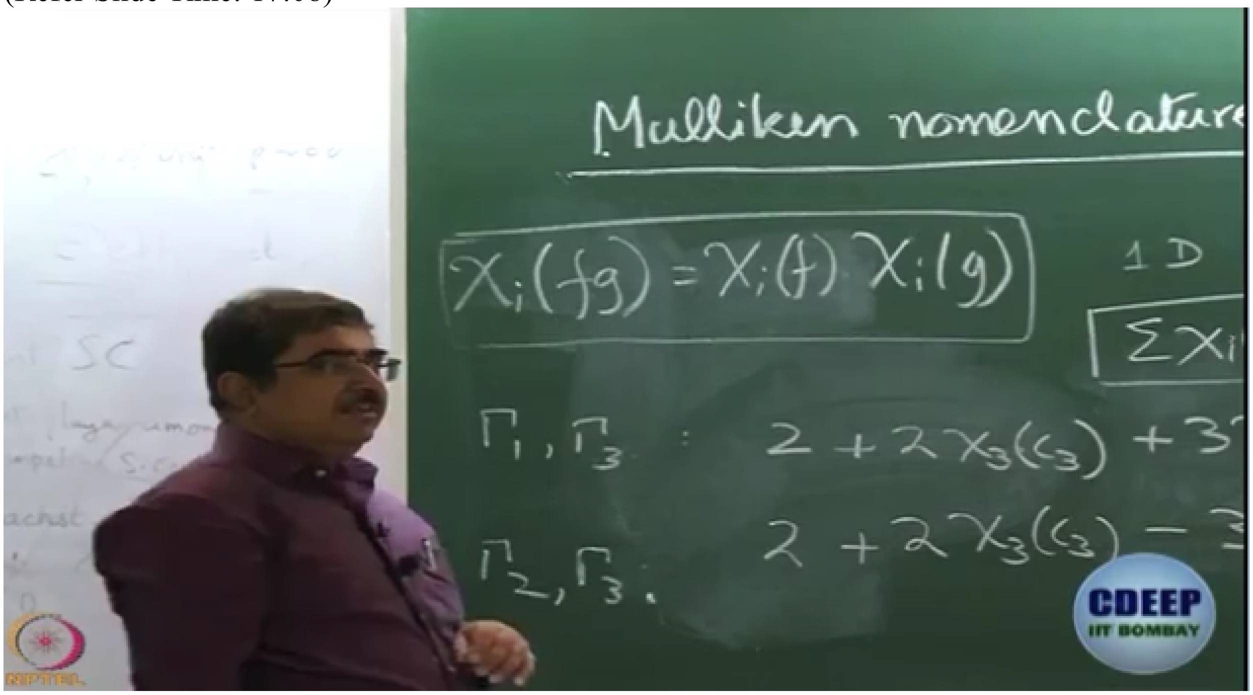

Chi I character in the ith irreducible representation or ith representation for that matter for a product of two functions, character of a product is equal to product of characters that is what we are using, okay, if that is the case tell me where XY belongs? Where YZ belongs? Where ZX belongs?

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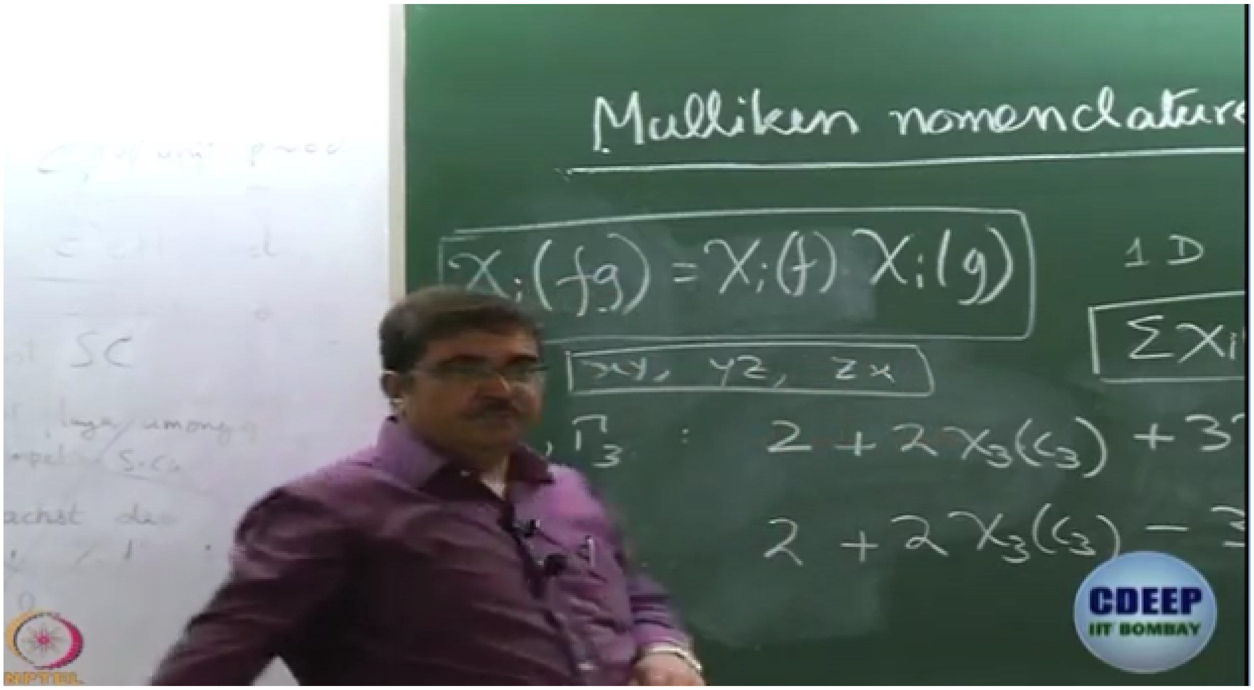

Where will XY go? Yes, gamma 2, why?
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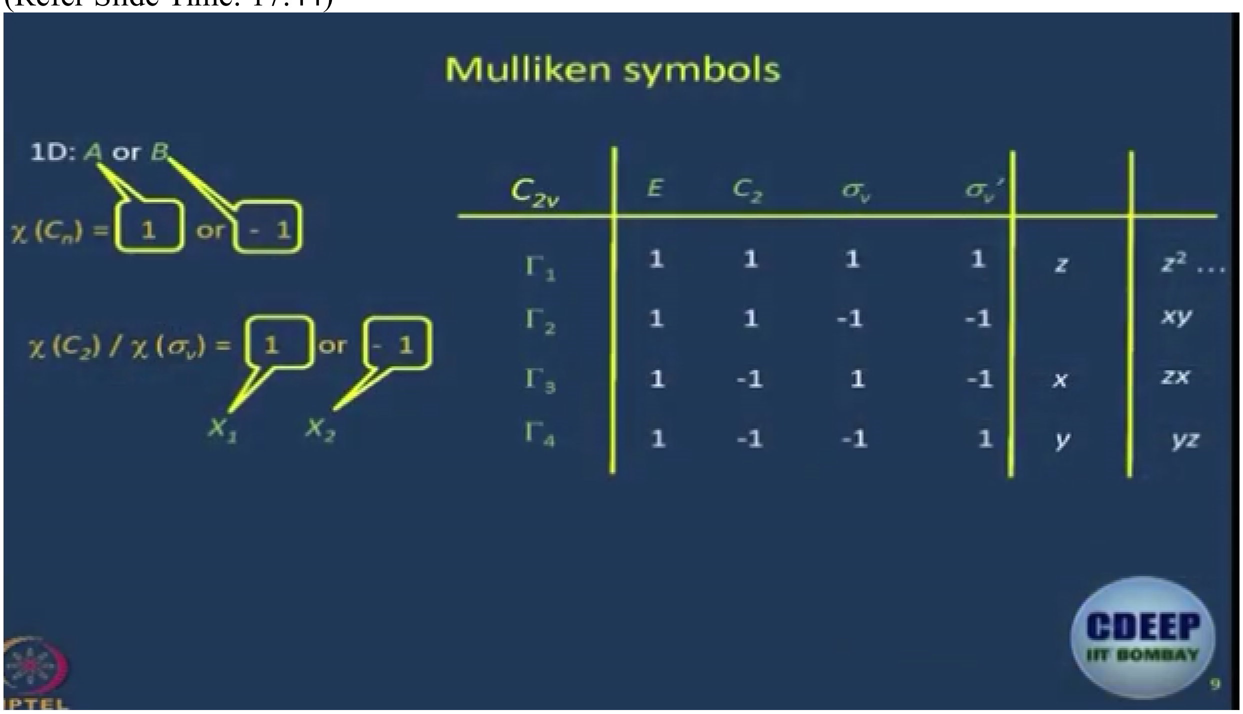

Because if I want to know the character of XY, all I have to do is I have to multiply the corresponding characters right, 1 x 1 that is 1, -1 x -1 is +1, 1 x -1 is -1, -1 x +1 is -1, so XY belongs to gamma 2 and hopefully Vandhan is now happy, okay, we've found something for his favorite irreducible representation gamma 2, so XY belongs here.

What about YZ? YZ and XZ are very easy, because that is 1 1, 1 1, so YZ and XZ will belong to the same irreducible representation as, what about, do you say YZ and ZX? XZ and YZ will belong to the same irreducible representation as X and Y respectively, okay, there is something else, unfortunately for whatever reason I had not written it here but if you look at a complete character table you'll find it. Generally in character tables, so these are the different regions, you write the symmetry point group here, list the operations in the top header, okay, and when you list them you don't write operations of the same class separately, you just write it as 2 x operation of 5 x operation of, whatever it is.

In this region come the name of the irreducible representations that's what we'll do next, in this region you have the characters and here there are two sub-divisions, the first one is XYZ, RX, RY, RZ, a rotation with respect to X axis, rotation with respect to Y axis, rotation with respect to Z axis, here you have the quadratic terms, okay, so before we come to the rotations let us think whether we can give some name to these irreducible representations gamma 1, gamma 2, gamma 3, gamma 4, okay, because nobody wants to deal with gamma 1, gamma 2, gamma 3, gamma 4, right, when any new product is launched, first of all they give a very strange code name, but eventually some name that sounds good or some name that is more systematic that takes the place of the generic name, so the systematic nomenclature of this irreducible representations was done by Mulliken and they are called Mulliken's symbols, and if you've used character tables you'd already be familiar with them, so this is what it is, so what Mulliken symbol the way it works is that if it's a one dimensional representation then it will be called either A or B, alright, no good reason just convention either A or B, the good reason comes after this, when do you call it A, when do you call it B? Yes, when A, when do you call it A, when do you call it B? You're saying something, yes you are right, so just be brave and say it loudly, symmetric A and anti-symmetric B you're perfectly right, symmetric or anti-symmetric with respect to which symmetry operation. The most prominent symmetry operation, if you have A, so what is the most prominent symmetry operation? So that comes from the name nomenclature of the, what do you call point groups itself.

If there is a principal axis of symmetry C, we call it either C or D, right? So whatever is the principal axis, okay, if there is a principal axis you decide on bases of that, if it is symmetric with respect to the principal axis then you call it A, otherwise you call it B, okay.

So let us write A or B here, for C2V what will the first one be? Is it A, or is it B? A why? Because the character of C2 is 1. For gamma 2 will it be A, or will it be B? A why? Because this symmetry species, this symmetric with respect to C2 operation. For the third one will it be A, or will it be B? B, because it is -1, and the fourth one will also be B, right.
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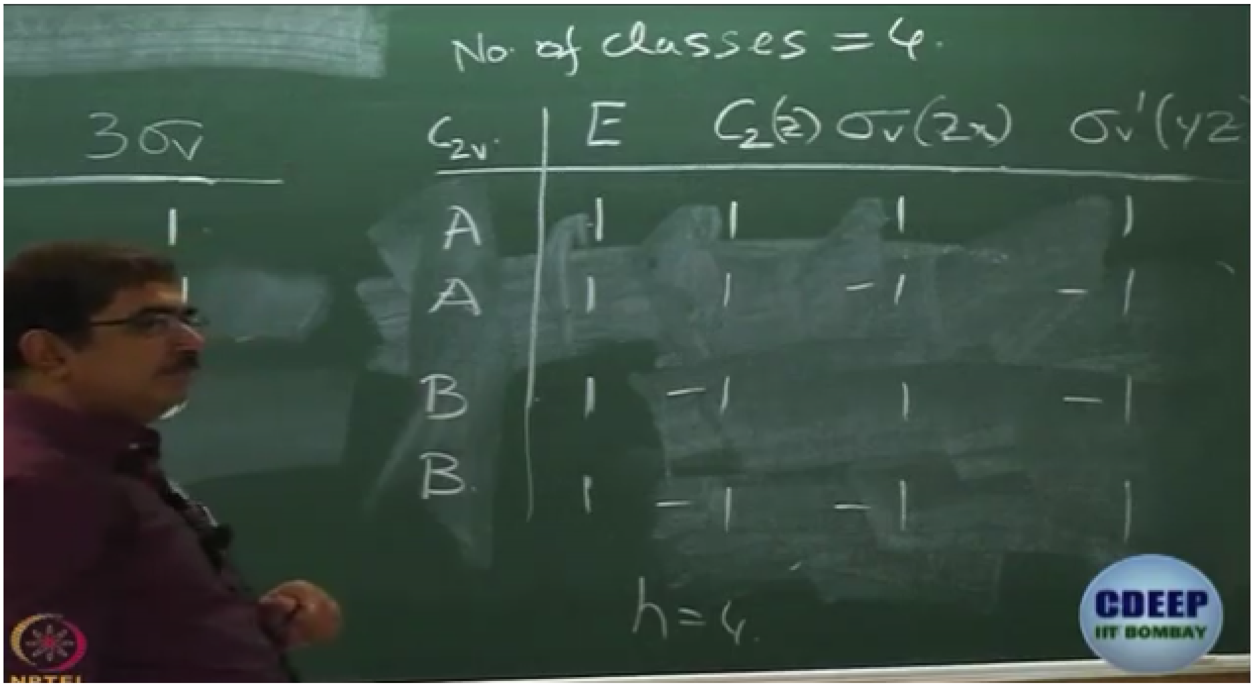

What about C3V? First one A or B? A, second one? A, third one? Cannot be B, because it is not one dimensional, so now Mulliken had to think a little more, and said okay one dimensional is over either A or B, what do we call A2 dimensional representation, C, D I have no idea whatsoever why Mulliken did not likes C or D, but he said that if it is 2 dimension you call it E,

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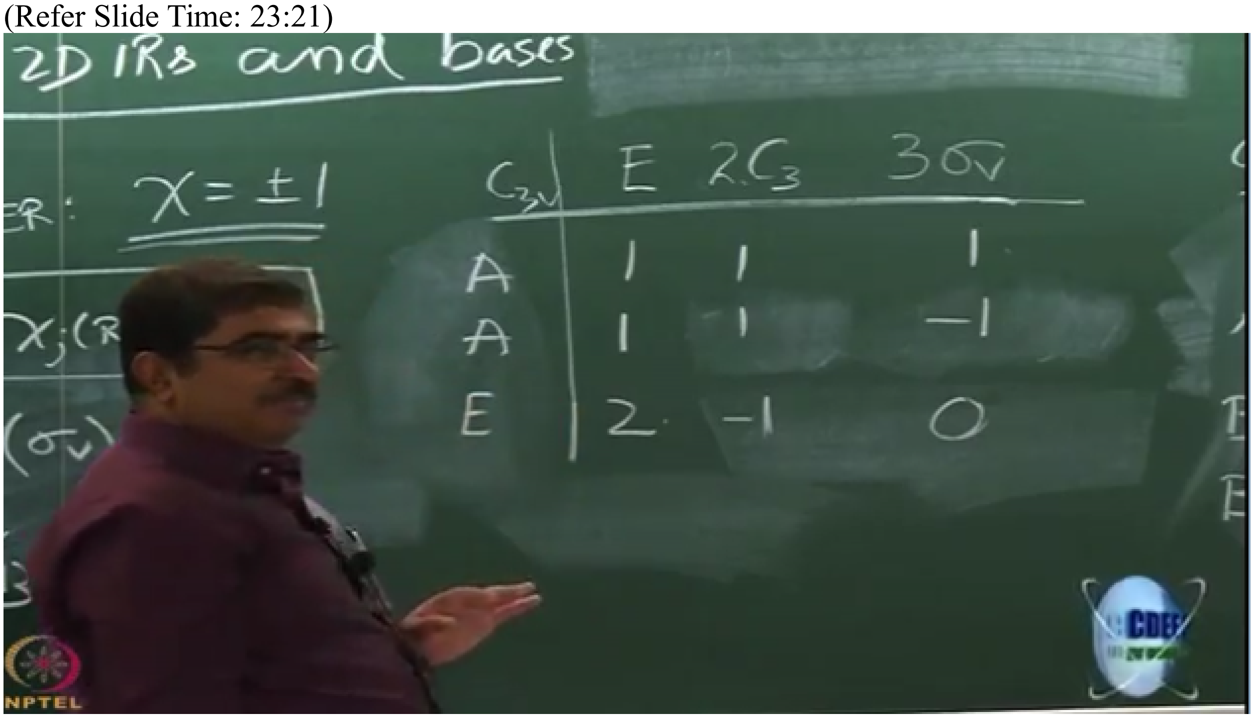

but see this is not a happy situation, I have two A's, and two B's how do I differentiate? So I call this A1 A2, B1 B2, A1 on the bases of that, the next one, the next symmetry operation that is there the plane with respect to that, if it is symmetric you call it A1, if it is anti-symmetric you call it A2, so here also this will be A1 A2, here there is no further number is required for E because there is only one E, alright, since our time is over we stop here today, we come back we talk a little bit about nomenclature after mid sem.

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