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. – 35
Character Table: Compendium of Irreducible Representations

So today we'll proceed with our discussion of representations, and hopefully today we are going to learn what is the meaning of the character tables that some of us have already used in some other courses.

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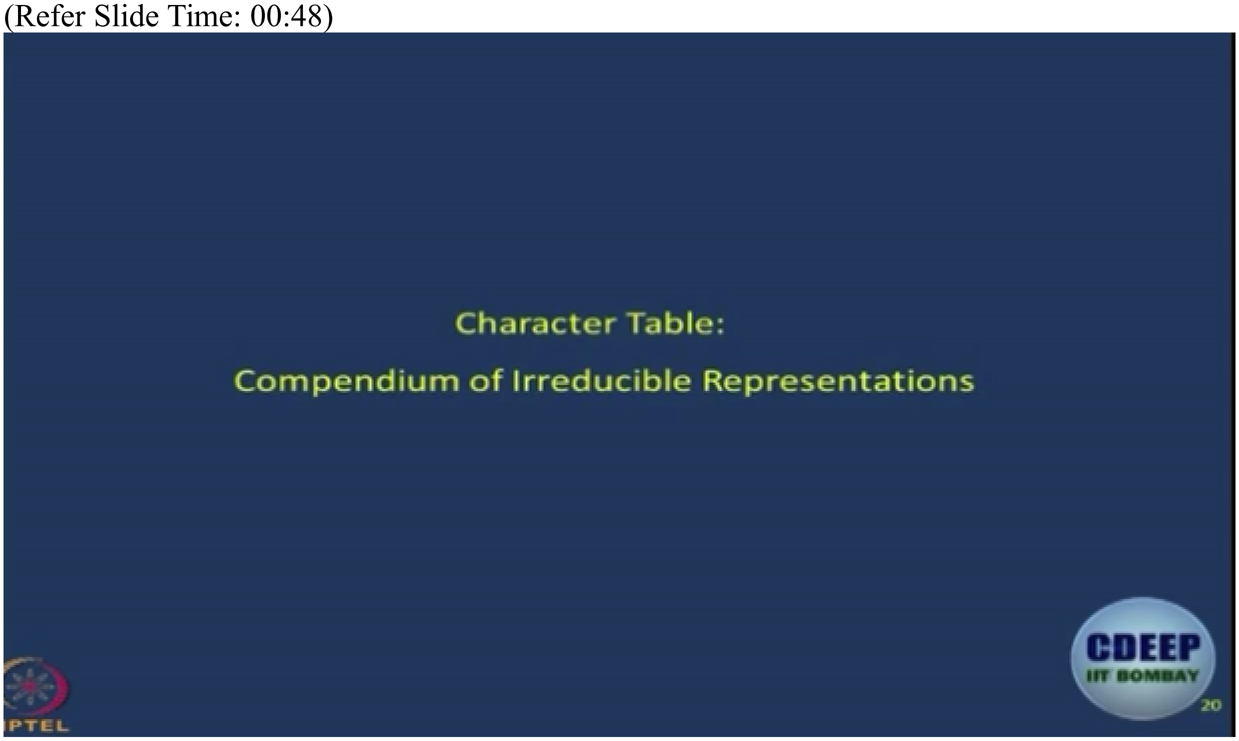

To put it in one sentence character tables are really compendia of irreducible representations.

In the discussion so far we've encountered representation, right? What are representations? You need to tell me now, what is the representation? As far as symmetry is concern, representation can be other things, yeah, representation can define character no that is a very round about answer, I want the straight forward, simple, easy answer, who will tell me? Yes, excellent, a representation is a collection of matrices, which matrices? No, one by one, transformation matrices, one dimensional or what we'll see that later.

So what we have done is we've used basis, what is the basis? Yes, basis is a set of functions on which the symmetry operations are performed, when we do that we get a set of matrices, we get one matrix for every symmetry operation, the collection of the or the entire set of transformation matrices for a given basis is a representation, and as we saw representations can be reducible, we're started working with X, Y, Z for C2V, and we got a representation that was 3 dimensional, what is the meaning of dimensionality of the matrix, sorry, I give away the answer, the meaning of dimensionality of representation is, what is the dimensionality of the matrix, okay, each matrix in a particular representation is transformation matrix has a particular dimension, same dimension, that is the dimensionality of the matrix, so when you work with X, Y, Z or with OHA, HB for water the dimensionality is 3.

What we saw further is that when we work with X, Y, Z the matrices were all diagonal, so we could block factorize them conveniently to get 3 one dimensional matrices, so the initial 3 dimensional representation was a reducible representation, one dimensional representation of course cannot be reducible, so it is an irreducible representation.

Next we work with the atoms of water, oxygen, hydrogen A, hydrogen B, and we got another 3 dimensional representation, right, does it ring a bell, was that reducible or was that irreducible? It was reducible, and it broke down into what kind of representations, how many representations? 2? 2, so one of them was one dimensional and that was the totally symmetric representation 1 1 1 1 1 and the other was 2 dimensional, okay.

Then we ended with the question, no actually we ended with something else then we asked the question that we are using different basis and getting different representation, so is that the good way of doing it? You keep on changing the basis, keep on getting representation, keep on trying to understand whether it's reducible or not, that cannot be a good method, right, representations depend on the basis we choose. And then we don't even know whether the representation we got using HA and HB are actually reducible, whether that representation was actually reducible or was it un-irreducible 2 dimensional representation, there is no way of knowing that, so the way of knowing that is to use group theory which we are not going to do here, but we have shown you the consequence of group theory, consequence of using group theory to this problem is that
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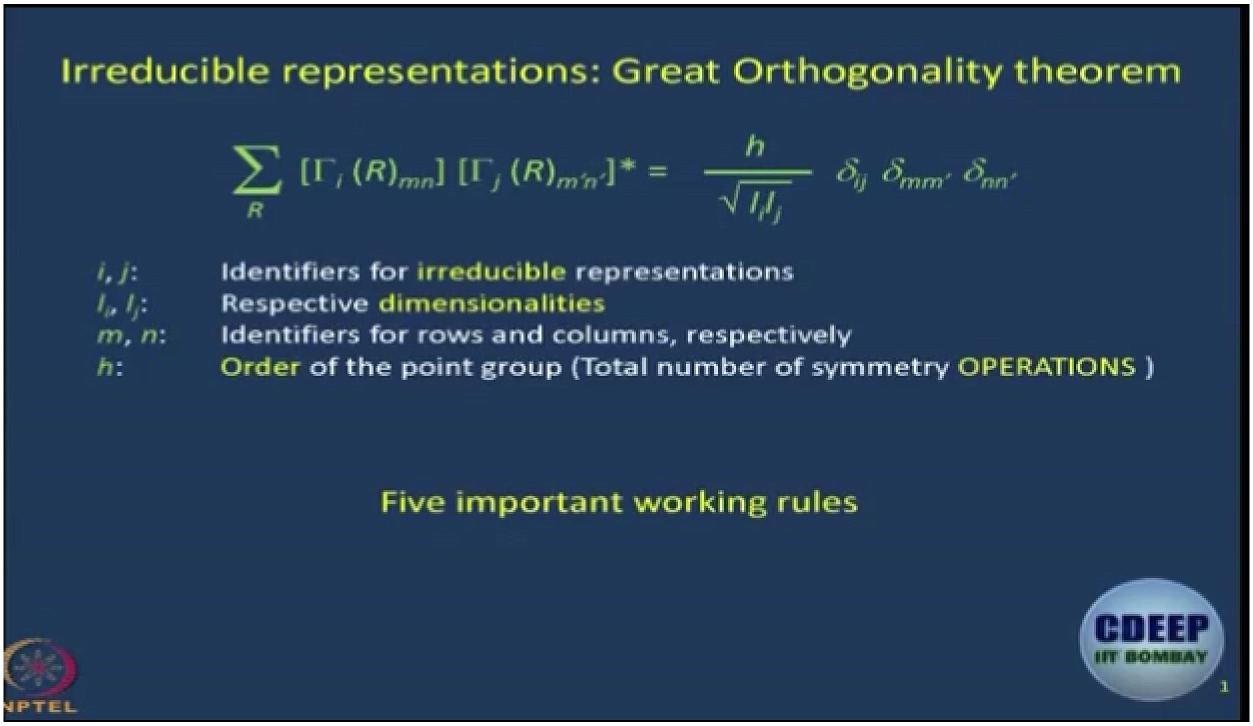

we have this great orthogonality theorem which essentially tells us that if you work with the matrix elements of irreducible representations then they behave like orthonormal vectors. Are we clear up to this point? This is where we ended yesterday I believe, right.

We don't even have to remember this, what we'll need to remember is the fall out of great orthogonality theorem with 5 rules that come out of great orthogonality theorem,

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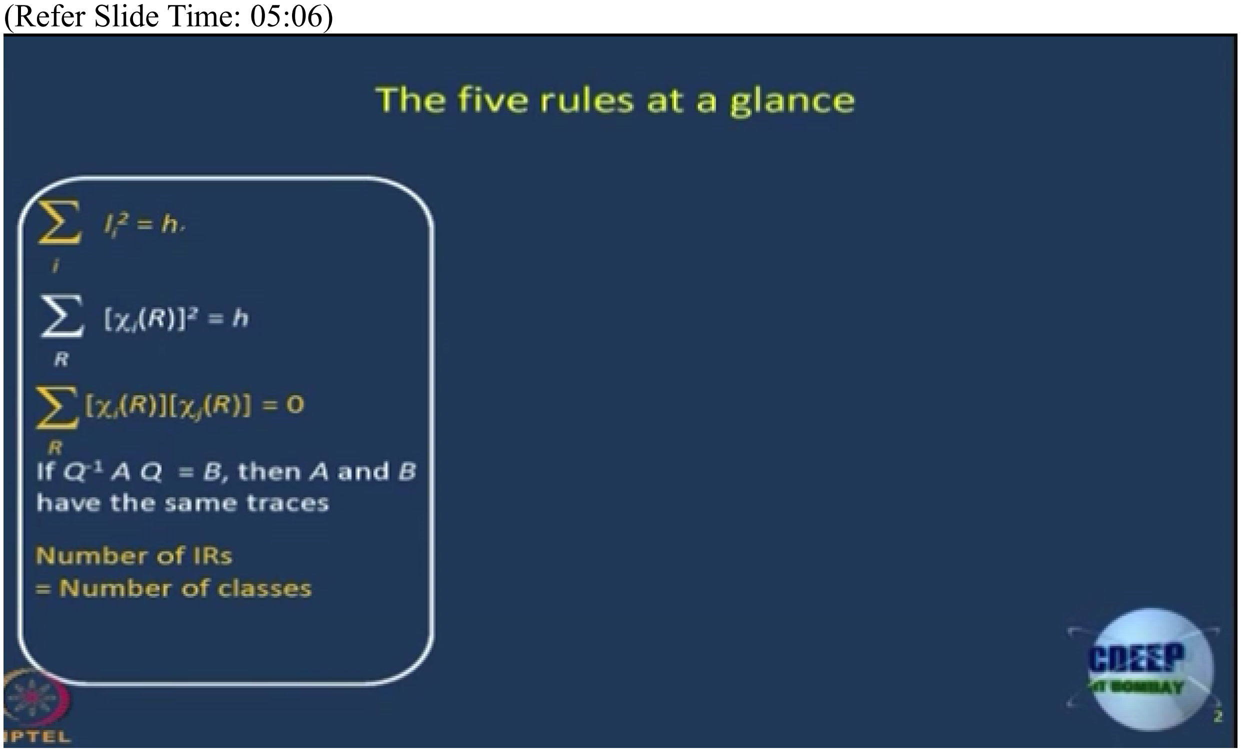

today we are going to use them and we are initially going to try and see whether we can work out the character table of C2V as usual, okay.

Before we start doing that one more point, in C2V when we had this characters of +1 and -1 what was the significance of that? What is the significance of +1? What is the significance of -1? What is the meaning of +1? What is the meaning of -1 character? Yes, yeah I heard some voice from here, symmetric, anti-symmetric, right, if the character is +1 then it is, then that basis element is symmetric with respect to that operation, if it is -1 then upon the symmetry operation it changes sign, so for one dimensional representation is very straight forward, okay, you perform a symmetry operation any function that you take is either symmetric or anti-symmetric, if it is a one dimensional representation, okay. So +1 means no change, -1 means change in sign.
As we'll see for representations of higher dimensionality +1 and -1 can have some different meaning, let's wait for that.

Let me ask you another question, is it possible that I have a one dimensional representation and the character is something other than +1 or -1, remember the eigenvalue equation we wrote, R operates on some function phi to give you, now I'll write chi as the eigenvalue multiplied by the same function phi, so what we have seen is chi = +1 means symmetric, -1 means anti-symmetric. My question is, can it be equal to 0? Can it be equal to 5?
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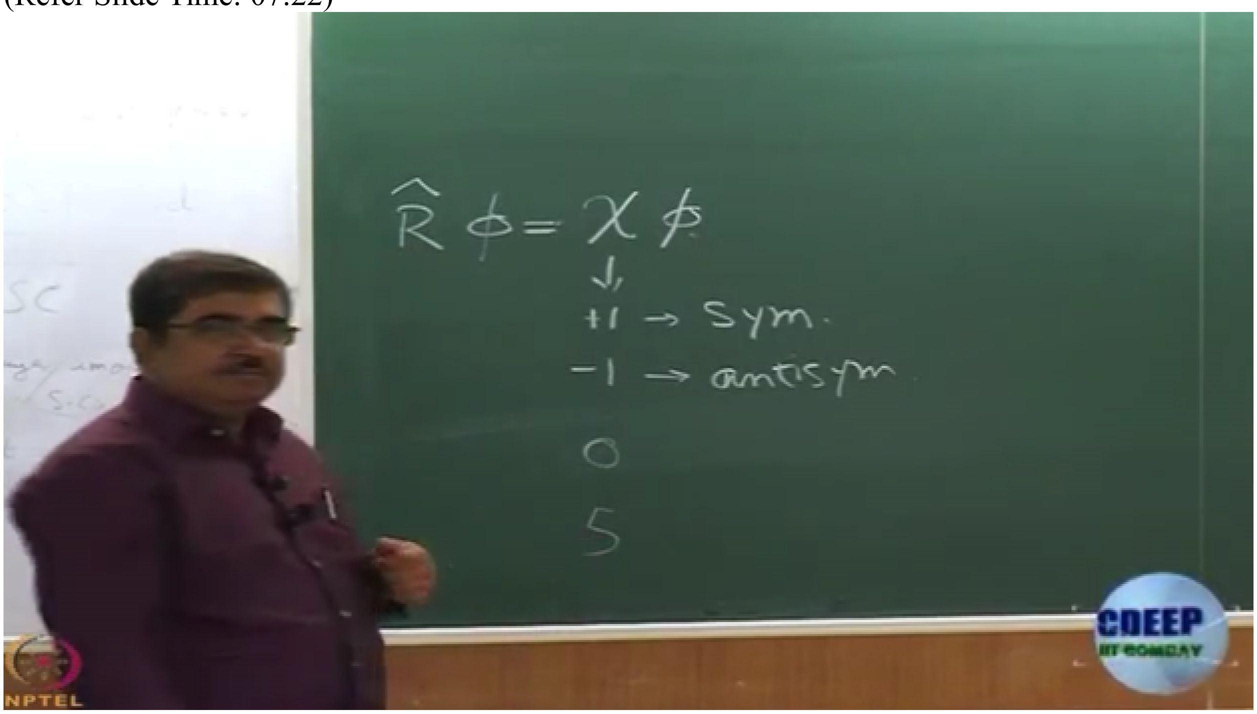

Let's start with 0, what would it mean if I had chi = 0, if I had character = 0? Why? Look at the eigenvalue equation, if chi = 0 then what is the effect of the symmetric operation on this function? Annihilation is the word, function vanishes you're right, annihilation, so a symmetry operation cannot be an annihilation operation, right, you perform a symmetry operation and the function dies, it is not even there because it is multiplied by 0, if that is the case then, there can be operations like that, annihilation operator is used in quantum mechanics, but then that cannot be a symmetry operation, okay. If the function vanishes, then where is the symmetry?

Similarly if the character is 5 then what does it mean? You have some functions some vector like this, you perform a symmetry operation, deduction does not change, the factor becomes 5 times longer, what is that? What is that called? What is this phenomenon? Something becoming longer or shorter, yeah, so I have a word for it, it is called distortion, it is distortion right? So a symmetry operation cannot lead to distortion, so the point we are trying to make is that for one dimensional representations, chi has to be + -1 and nothing else. Is the point made?

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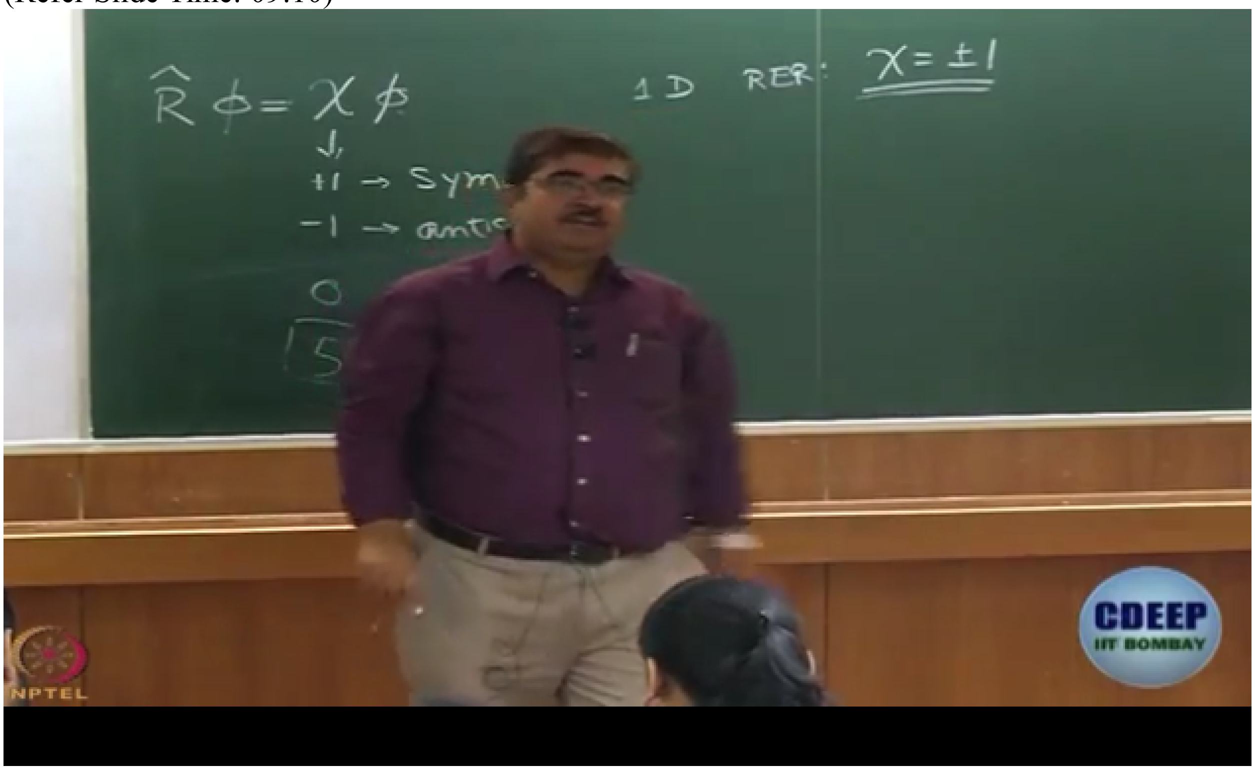

Right now we are discussing only one dimensional representations, we are not talking about multidimensional representations as of now. Will you agree with me that for one dimensional representation, one dimensional representation means what? It means that the functions don’t mix with each other, okay, so any symmetry operation can either leave the function intact or utmost it can change sign, if it say turns by some angle then this vector cannot be represented by itself, it requires two components, that means it cannot be one dimensional, okay, right.

So with this knowledge we can try to work out the character table, but before that let us take a look at the 5 rules,

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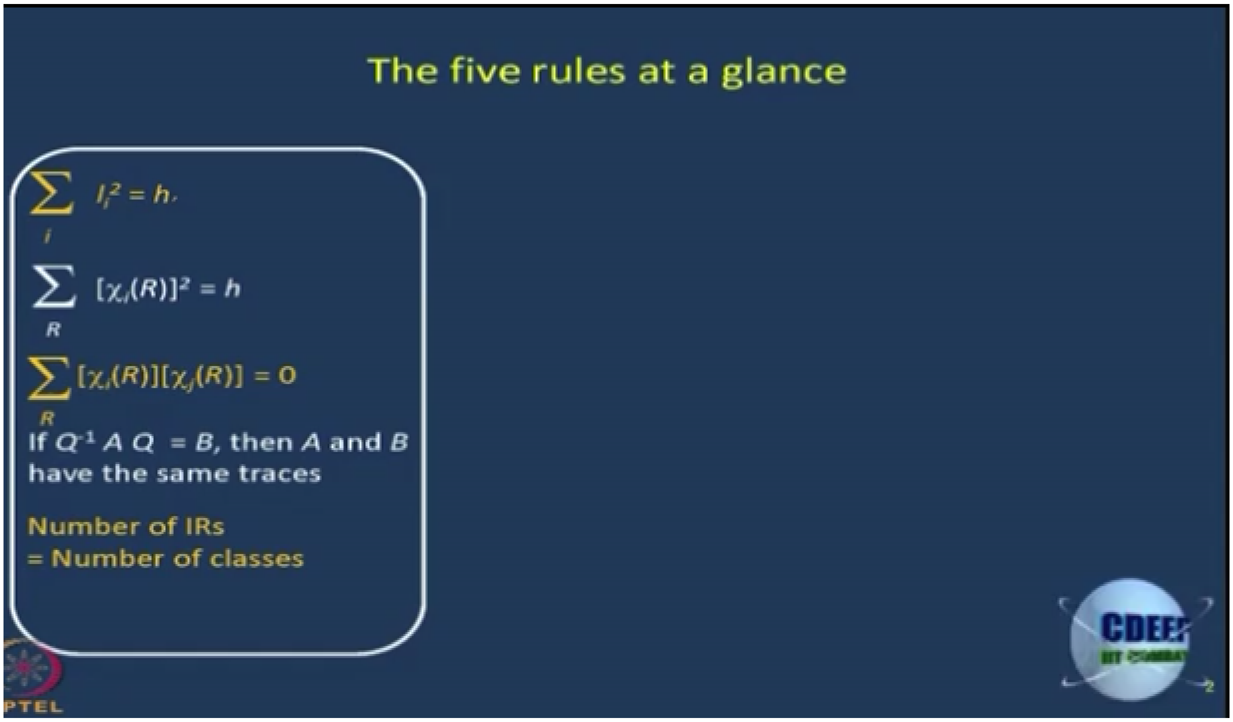

if you want you can read up the derivation of these rules from Cotton's book. First tool actually is written at the bottom, I should have written at the top but then I forgot and then you can still read that bottom one first.

First is one of the questions we have asked so far is how many irreducible representations are there? And this is the answer, it can be derived using group theory, number of irreducible representations IR in this context means irreducible representation is equal to number of classes, okay, that is the first rule, number of irreducible representation is equal to number of classes, how it counts we are not deriving, okay, in this course we take it axiomatically unfortunately.

So these are the 5 rules we need to know, number of irreducible representations equal to number of classes. So let us take our familiar example C2V, what are the symmetry operations? E, C2, sigma V, will write it as ZX, I'll write this as Z, and sigma V dash which is YZ, how many symmetry operations?

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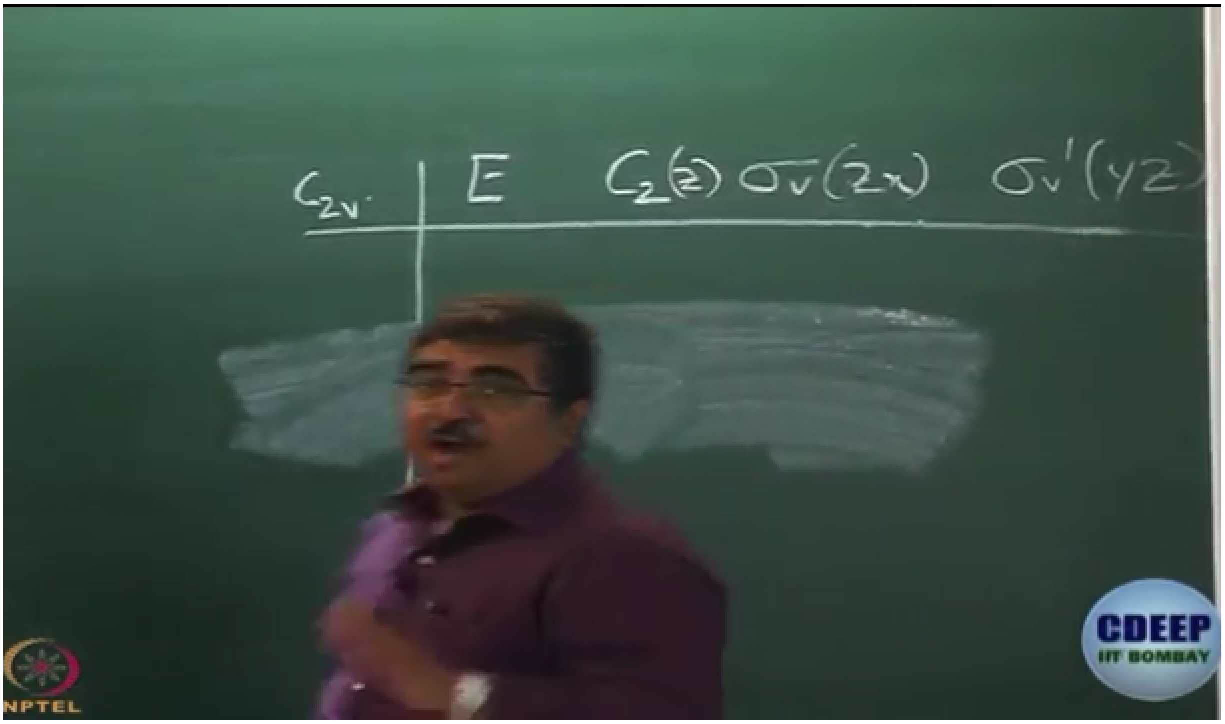

4, how many classes of symmetry operations? 4, remember what is the meaning of 2 symmetry operations belonging to one class? They should be, they should have the same action or they should be inter-convertible by some other symmetry operation, okay, so number of classes here is 4.

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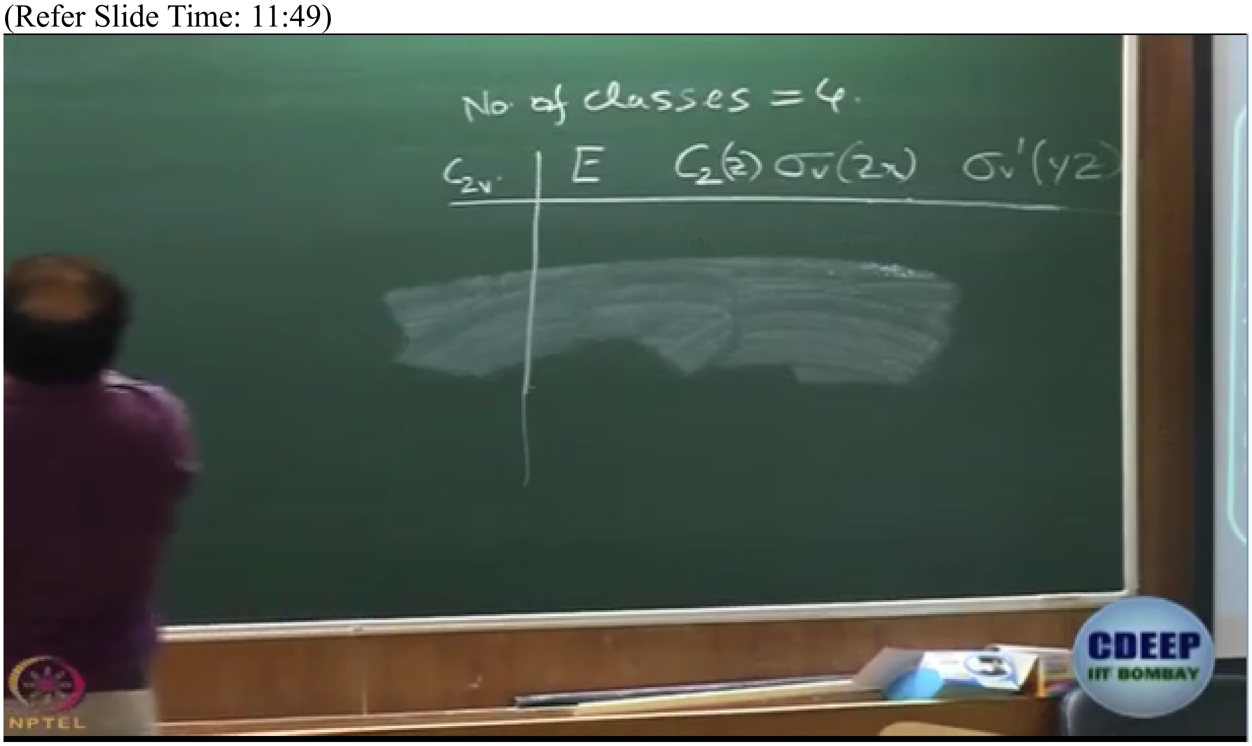

On the other hand if you want to talk about C3V, what are the symmetry operations? Ammonia C3V, of course E is there, and C3 is there,

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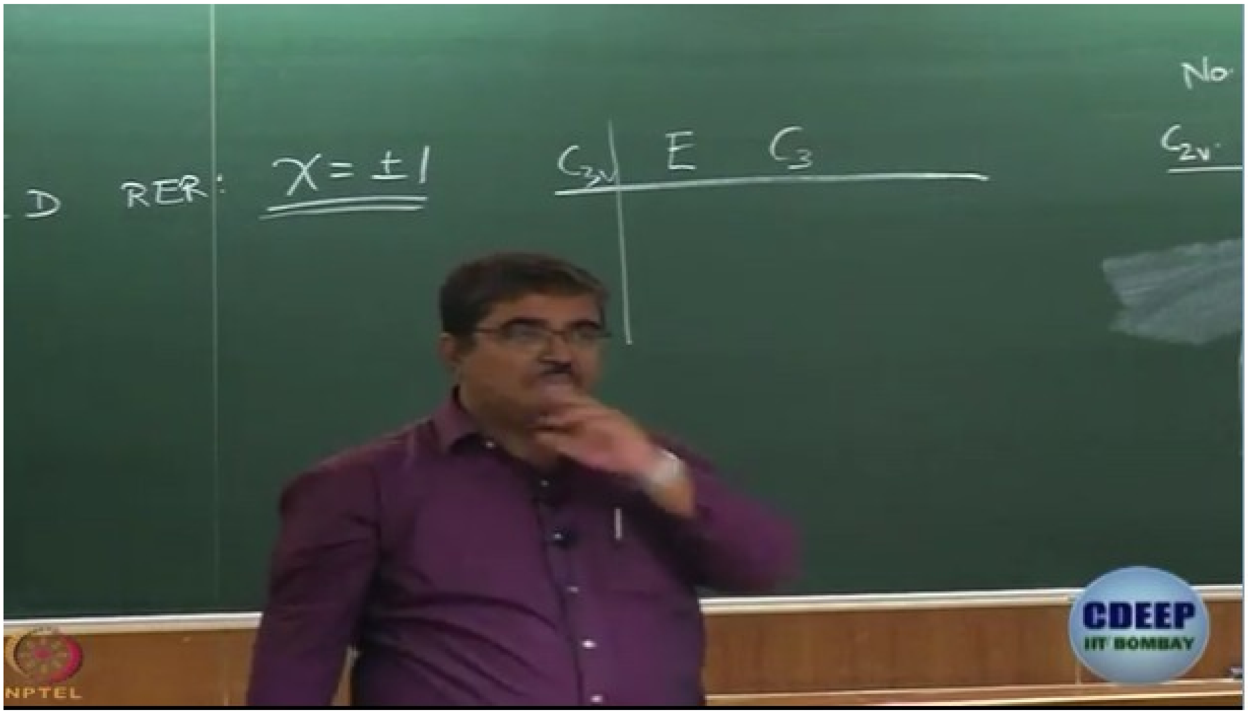

how many C3 operations are there? 2, right, C3+ and C3- or C3 and C3 square, but they belong to the same class we discussed, so they should have the same character, what we've trying to do here is that we are going to write a table with only the characters of the irreducible representations, okay, so I can write C3 and C3 square separately, but it doesn't make sense because the columns will be the same, so I write it as 2C3.

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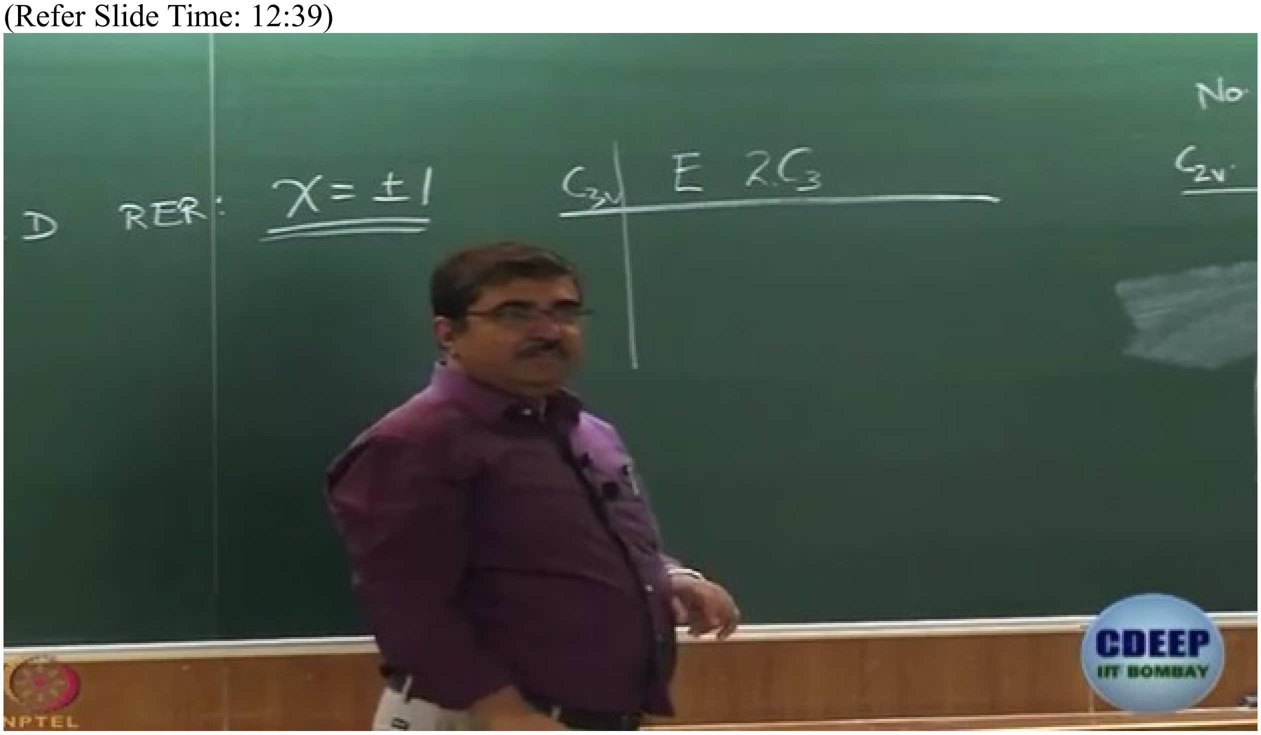

Have you understood what we are doing? It is absolutely okay if I write C3 and C3 square separately, but characters will all be the same because what this translates as is that symmetry

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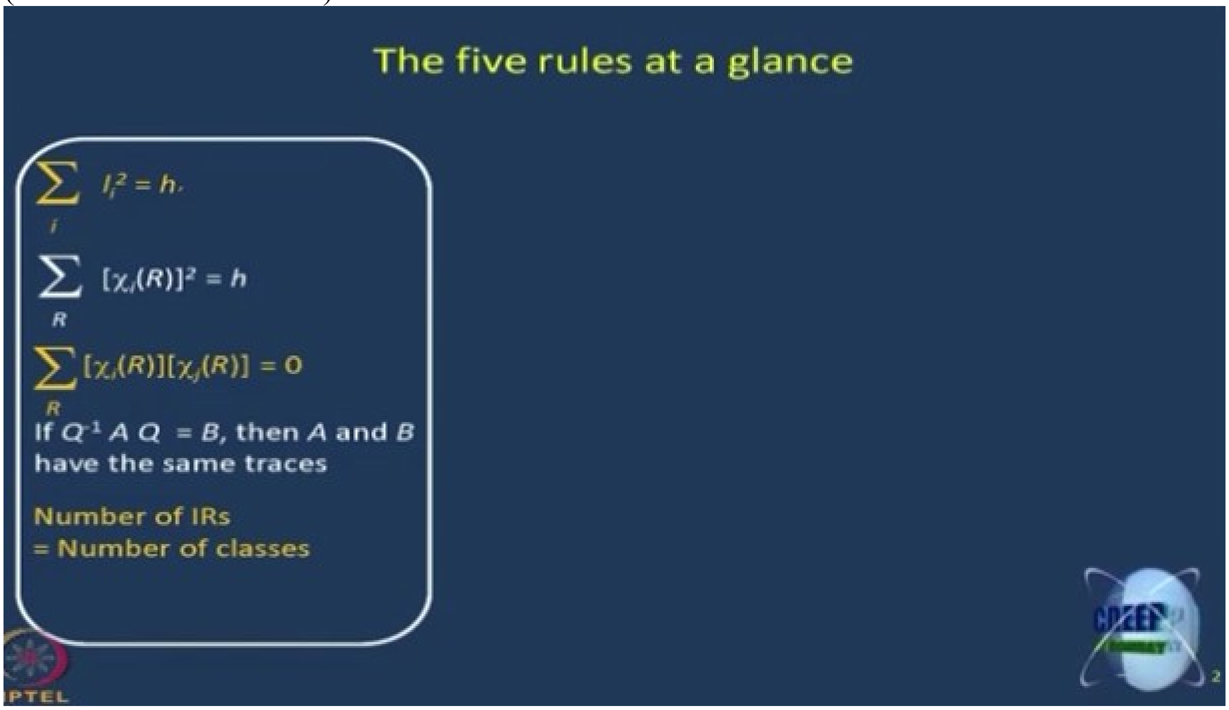

operations belonging to the same class have the same characters, this is something we have not proven but demonstrated to you using I think plus and minus rotation by theta, right, remember, cos theta sin theta, -sin theta cos theta, and cos theta –sin theta, sin theta cos theta those were two matrices when we turned by theta characters were the same, so I just write them together.

How many vertical planes were there? 3, do they belong to the same class? Are they equivalent? Yes, so again I'll write as 3 sigma V, and do not forget I'm writing it like this because they have same character, it is absolutely okay if I write sigma VA, sigma VB, sigma VC, but then they'll have the same character, okay.

So for here what is the number of classes? What is the number of symmetry operations? 6, and what is the number of classes? 3, let me write down this also, H is the order of the group which is equal to number of symmetry operations that is 6 here, and it is 4 here, okay. So in C2V, how many irreducible representations will be there? 4, for now let me call them gamma 1, gamma 2, gamma 3, gamma 4, later on we'll learn how to give them little more meaning full names, right now let us use a generic roll number kind of nomenclature, gamma 1, gamma 2, gamma 3, gamma 4, how many irreducible representations will be there in C3V? 6, 6 or 3? 6 or 3? 3 or 6? 3, so make up your mind, you're oscillating between 3 and 6. 3, 3 is global minimum, we converts to that, okay, so gamma 1, gamma 2, gamma 3, alright.

Now let us, let me write one more thing a little axiomatically, the first row is always going to be this, no matter which character table it is, totally symmetric representation always exists, there will always be functions that are totally symmetric,

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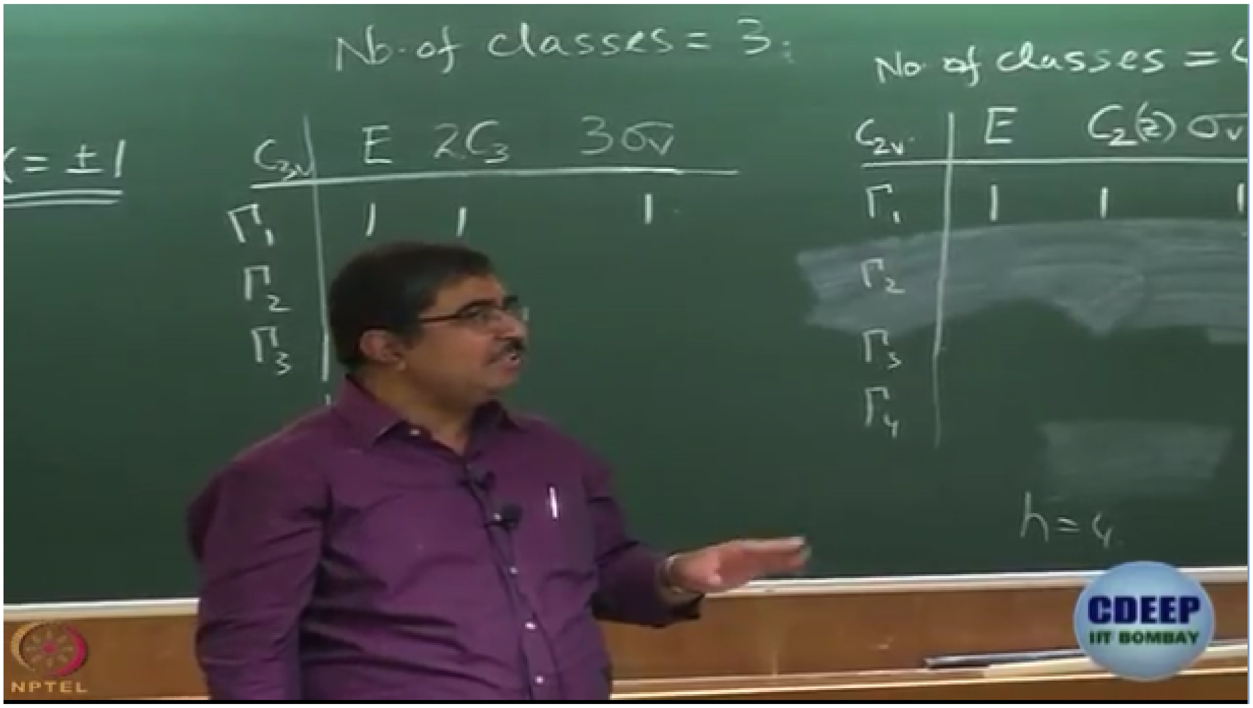

so the first row is always 1 1 1 1 1, okay.

Now what is the next rule? Second rule is sum over I, actually we have, it was the third rule because we have already used up this one, isn't it? Sum over I LI square = H, what is LI? Yes, it is the dimensionality of the ith irreducible representation, okay.

Now here H = 4, and there are 1, 2, 3, 4, for example if there is a horizontal plane of symmetry, okay and Z is the principal access of symmetry, will the character of Z be equal to 1 with respect to horizontal plane, no right? It will be -1, so Z doesn't always, Z is not always totally symmetric, okay, right now forget the basis we are, entire purpose of this exercise is that we want to be able to figure out the irreducible representations without knowing the basis, okay, so once we know the irreducible representations we will try and fit the basis there, okay, and the answer to your question is no, Z is not always totally symmetric, it is never totally symmetric if there is a horizontal plane, alright, great.

Now 1, 2, 3, 4, 4 irreducible representation, so I can write the dimensionalities as L1, L2, L3, L4, this are the dimensionalities of gamma 1, gamma 2, gamma 3, and gamma 4, okay.
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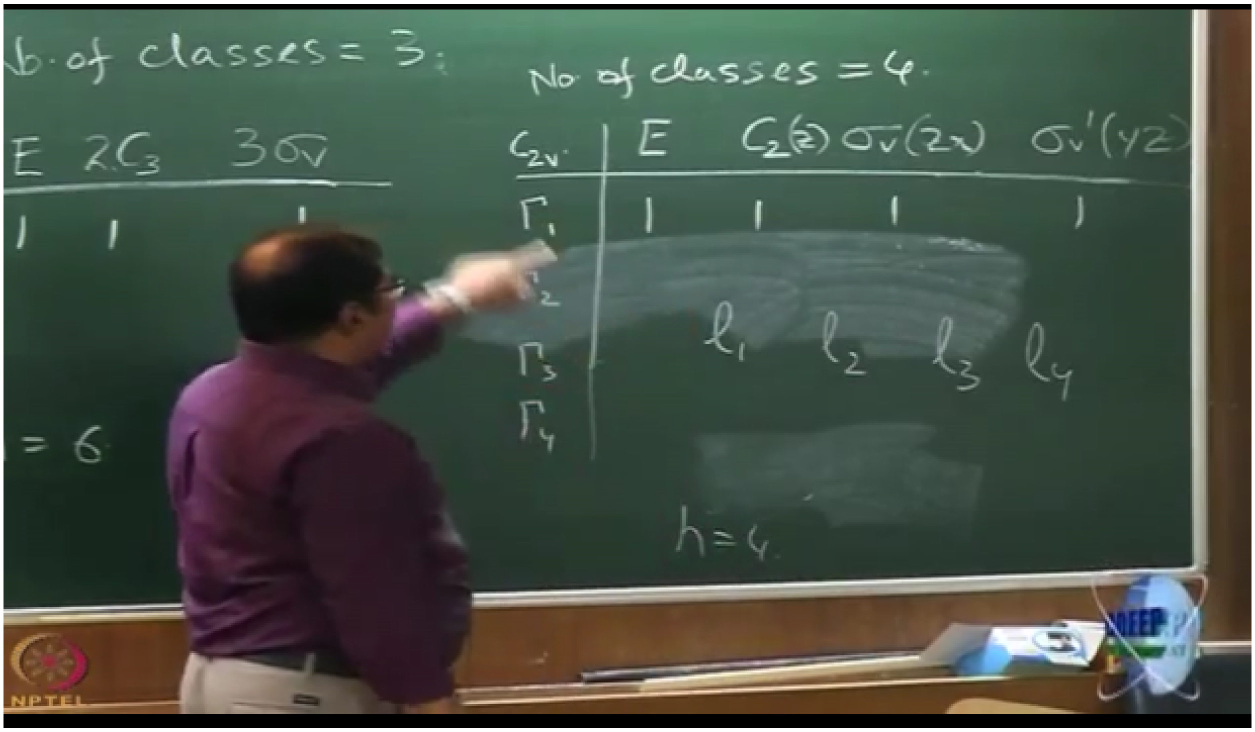

So now if I use this rule here sum over I LI square = H, what is L1 square + L2 square + L3 square + L4 square? That's equal to 4, is that right? H = 4?

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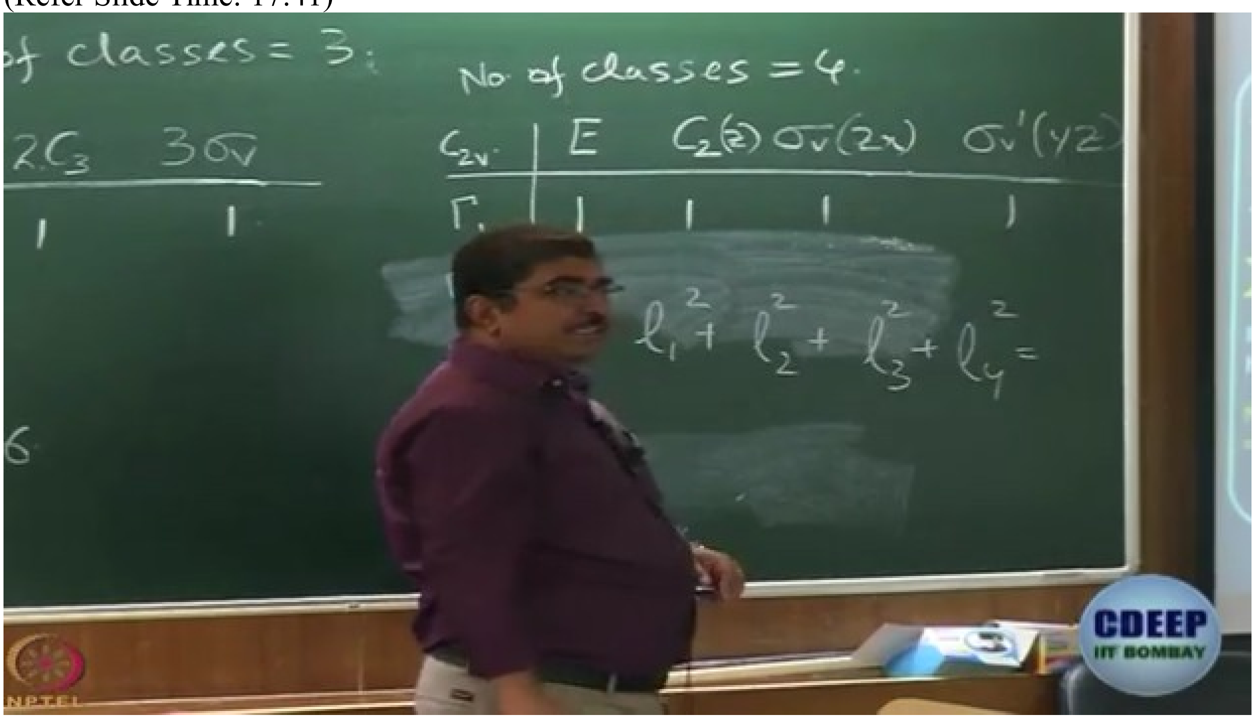

1, 2, 3, 4, understood? Total 4 symmetry operations that is equal to H, so L1 square + L2 square + L3 square + L4 square that will be equal to 4, are we clear so far? Now tell me what are the only possible values of L1, L2, L3, and L4? It has to be 1 1 1 1, right, none of them can be 2, none of them can be -1, because dimensionality has to be a positive integer, so what we learned right away is that for C2V you can only have one dimensional representations, which means that the two dimensional representation that we had obtained using hydrogen atoms A and B that is irreducible representation, it is not an irreducible representation. Are we clear? Okay.

Now if dimensionalities are all 1 then I hope you will allow me to write 1 1 and 1 here, why?
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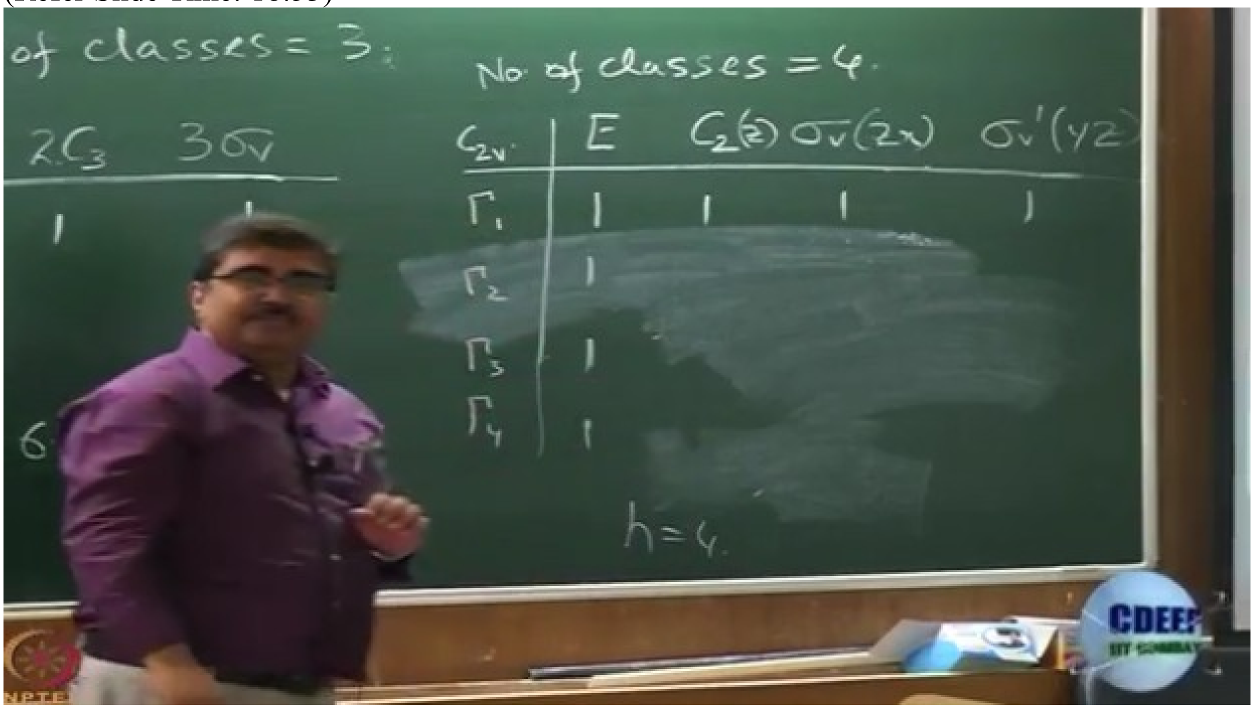

Because character of the identity operation is always equal to dimensionality of the irreducible, sorry, dimensionality of the representation that is something we have discussed earlier, are we okay with this? Right, now what would have we said? These are all one dimensional representations, so the characters can only be +1 and -1, right, do you agree? We said that about 10 minutes ago right, +1 or -1? So these 3 spaces have to be filled with +1s and -1, how many +1, how many -1 that we have to decide. To do that, come to this, what is this?
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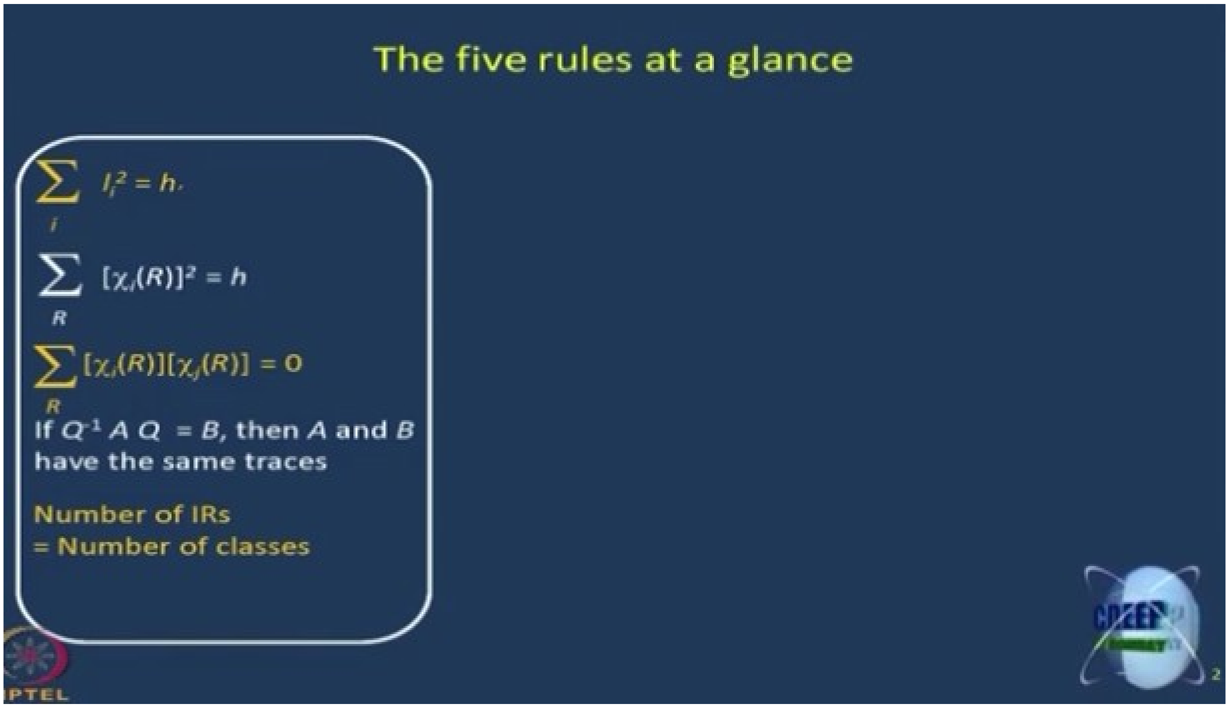

This is the orthogonality condition isn't it? Sum over R, chi I(R) multiply it by chi J(R) = 0, right, so if I write one of these as say chi I(C2), chi I(sigma V), chi I(sigma V dash) then what does it mean? 1 multiplied by 1 + 1 multiplied by chi I(C2) + 1 multiplied by chi I(sigma V) + 1 multiplied by chi I(sigma V dash) is equal to what?

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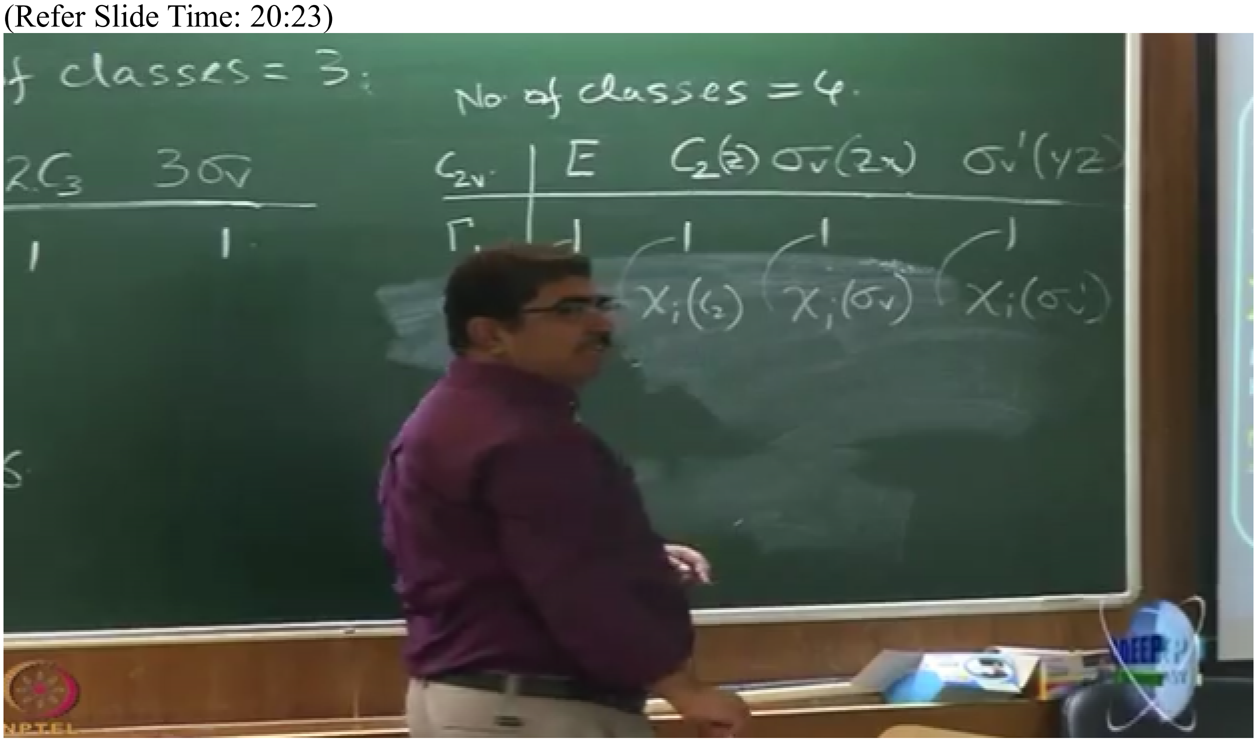

0, let me write it here then, I'm going to just write here and then erase. So maybe I'll write here itself, so I get 1 + chi I(C2) + chi I(sigma V) + chi I(sigma V dash) = 0, okay 3 unknowns one equation,

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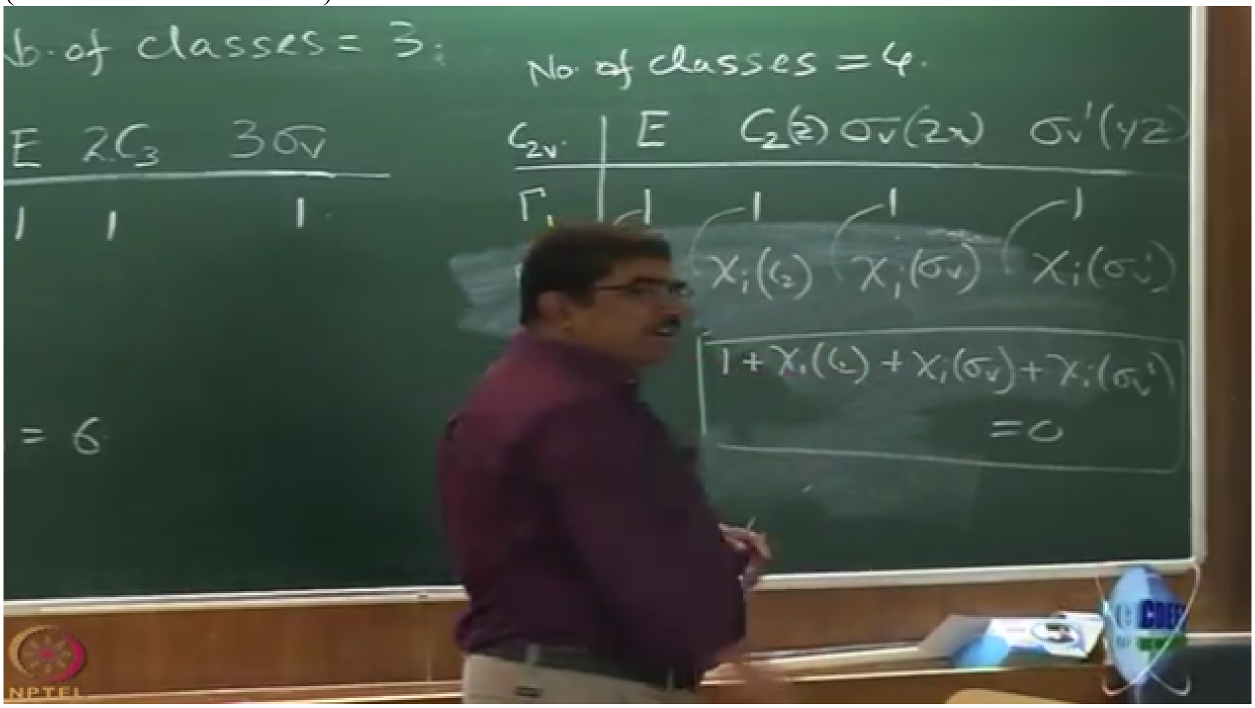

is it possible to solve this? In this case it is, because you also know that each of the unknowns can only be +1 or -1, right.

So now tell me how many +1s will be there, how many -1s will be there? There has to be two -1s and one +1, right? So now what we can do is we can just fill in, it's like playing Sudoku. To start with, let us not forget these are all +1s, one +1 and two -1s right, so I'll basically write all these 1s and play around with the minus signs, I'll first put the minus signs here, then I'll put say one minus sign here, and one minus sign here, then I'll put one minus sign here, one minus sign here, your character table is ready.

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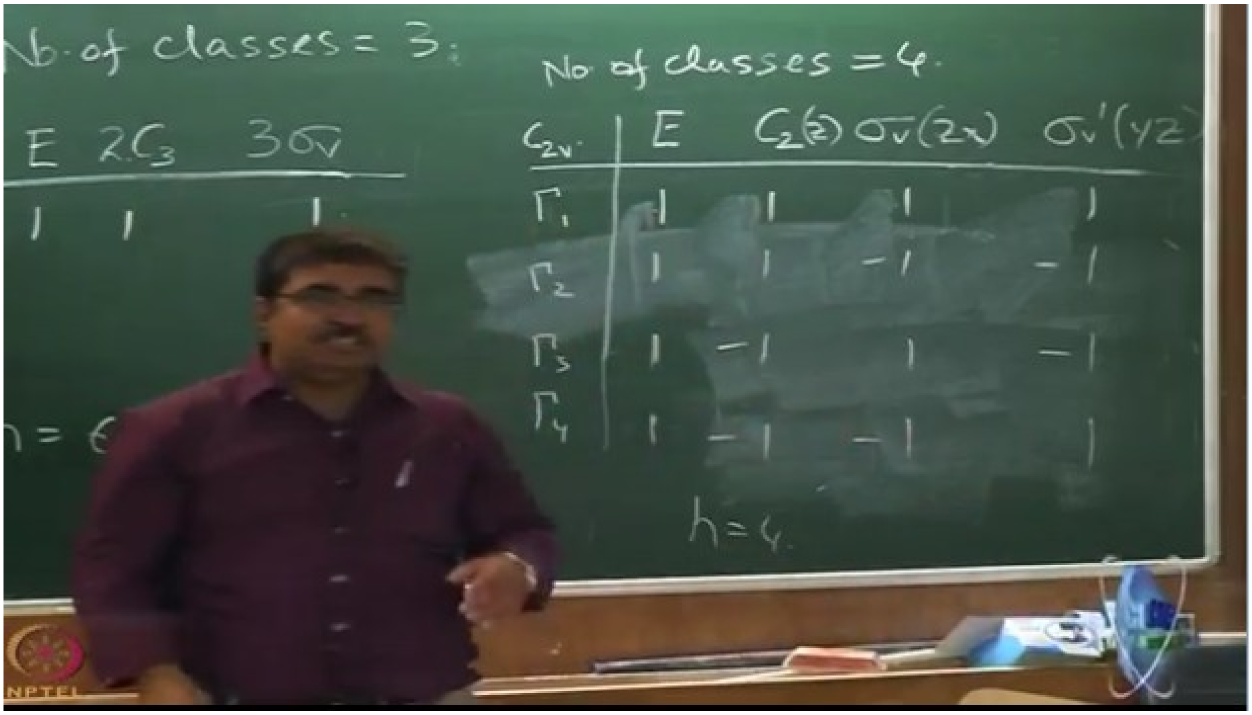

Tell me two -1s, and one +1, you can put it in any order you want, I've put it in this order because I already know how I am going to name them, okay. I already know the priority that we are going to follow for nomenclature that's why I've written it that way, you could have done anything, alright, so we'll stop here and we come back and talk about, first of all how to name this, and we'll talk a little bit about two dimensional representations.

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