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. – 34
Group Theory: Character Table

So we have arrived at more questions than answers by using different bases sets, right? That's what we have got so far, okay. But have we at least understood what we've written? Now we'll try to not prove, but at least know the answers to the questions that have come to our mind, okay, to do that one needs to use group theory, using group theory you arrive at what is called the great orthogonality theorem.
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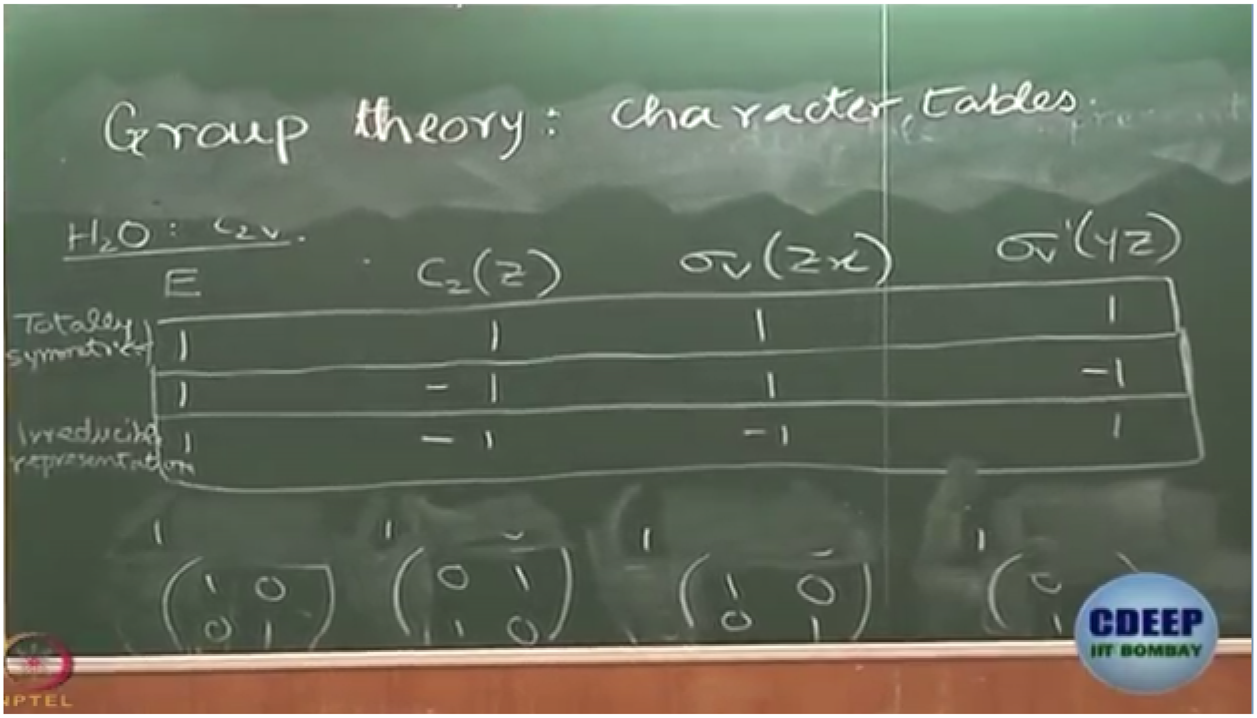

So as you've understood by now anything that has words like great or golden, they are bound to be very useful right, great orthogonality theorem is also called great for a good reason, okay. And using great orthogonality theorem we arrive at what are called character tables, things that you've already used in this inorganic course in the last semester I believe, okay, so what we are trying to do is we are, in this course we don't have the scope to derive great orthogonality theorem, but what we'll do is we'll show you 5 consequences of it and from there will at least learn how to derive character tables.

And I'll not ask you to derive character tables in the exam. But unless we do the derivation of one or two character tables we don't understand anything, we don't understand what they mean, okay, that's why we are even discussing this. Okay, so far so good we go ahead.

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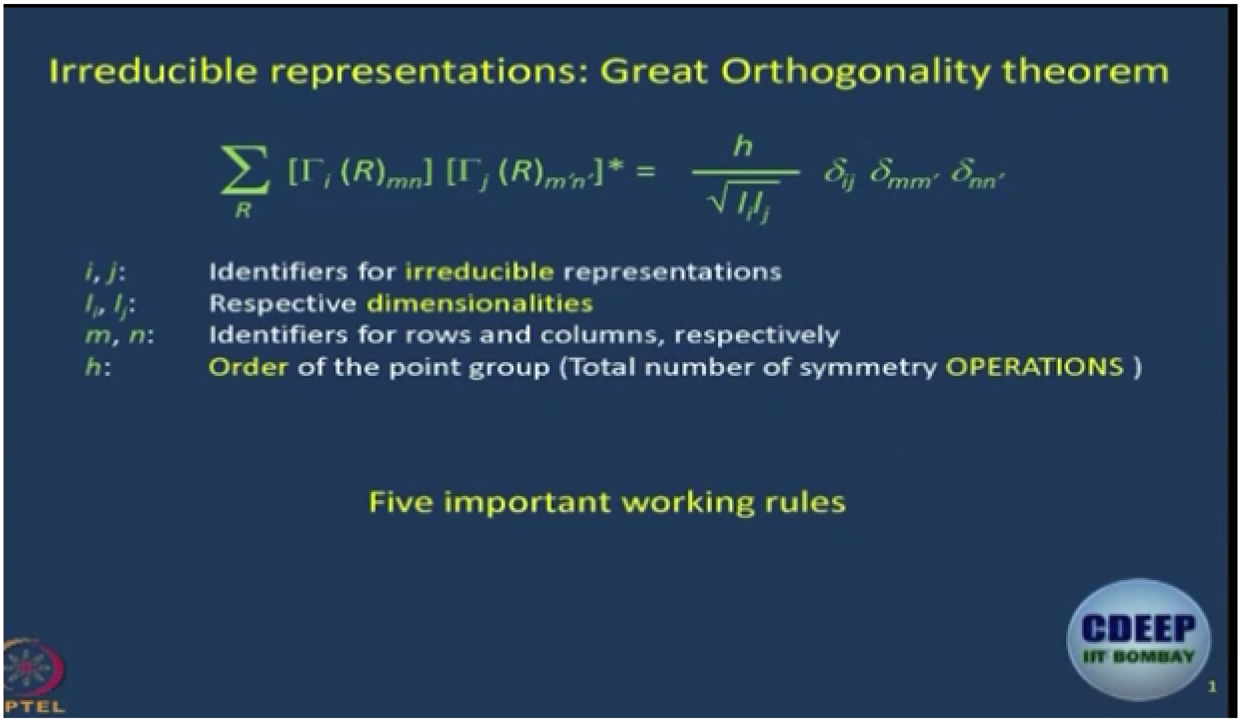

Now if you look at this great orthogonality theorem of course I should paraphrase it a little bit for you, what this gammas mean, this capital gamma, this is not tau, some people call it tau by mistake, it's not tau, it's capital gamma, gamma I(R) MN, what does this mean? It means the MN element of the transformation matrix corresponding to symmetry operation R in the ith irreducible representation, ith means let us say I have five irreducible representation, I can be 1, 2, 3, 4, 5, okay, I'll say it once again, look at this, gamma I(R) MN what it means is the MN element of the transformation matrix of symmetry operation R in the ith representation, have you understood what this means? Have we understood what it means?

Let us say I have some representation, say E will be there anyway, R1, R2, so on and so forth something R, no I'll not write, I'll just leave it at that,

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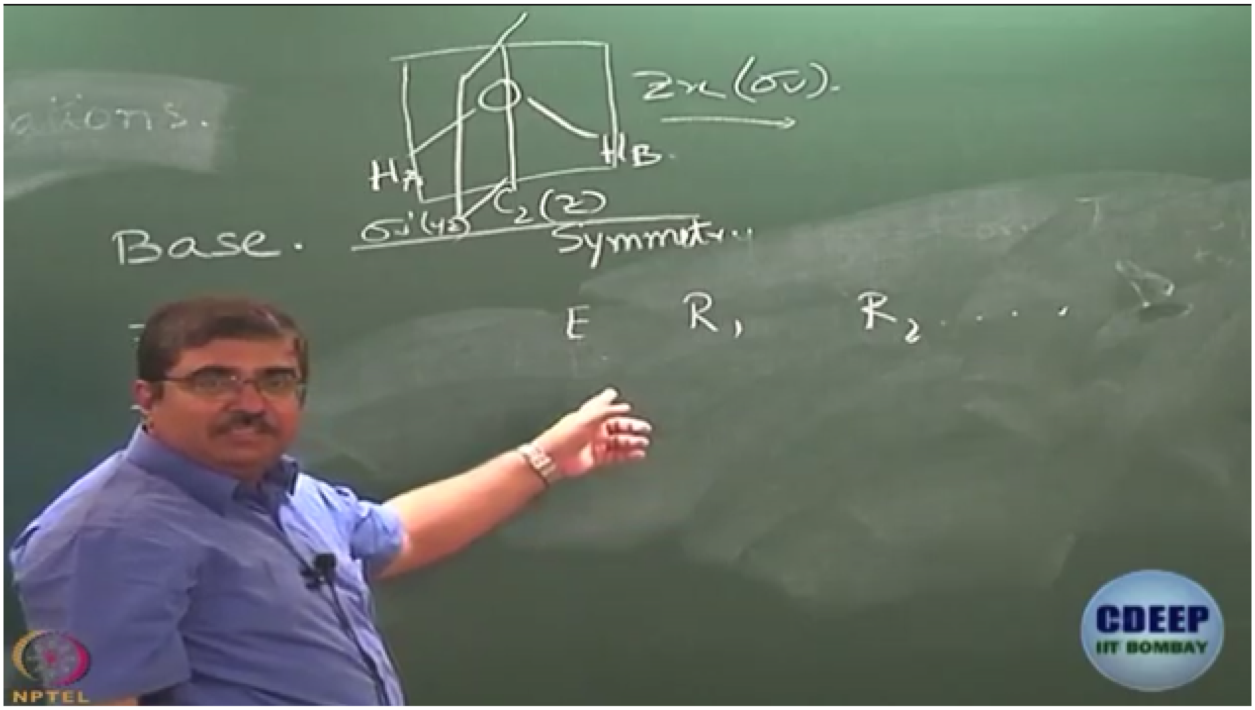

so these are the symmetry operations and I have these irreducible representations gamma 1, gamma 2, so on and so forth, let us say gamma I, understood?

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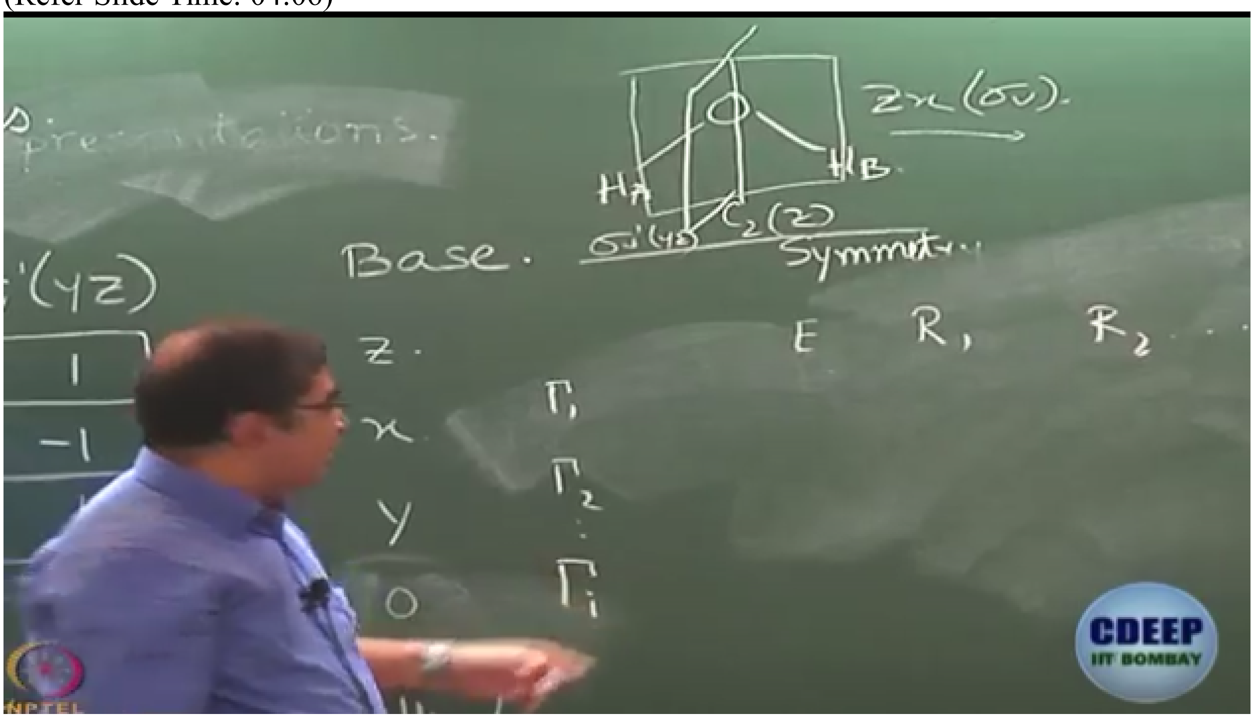

What is this? What is this matrix? It will be 1 0 0 something like that, 0 1 0 so on and so forth, and finally you'll have 0 0 1,

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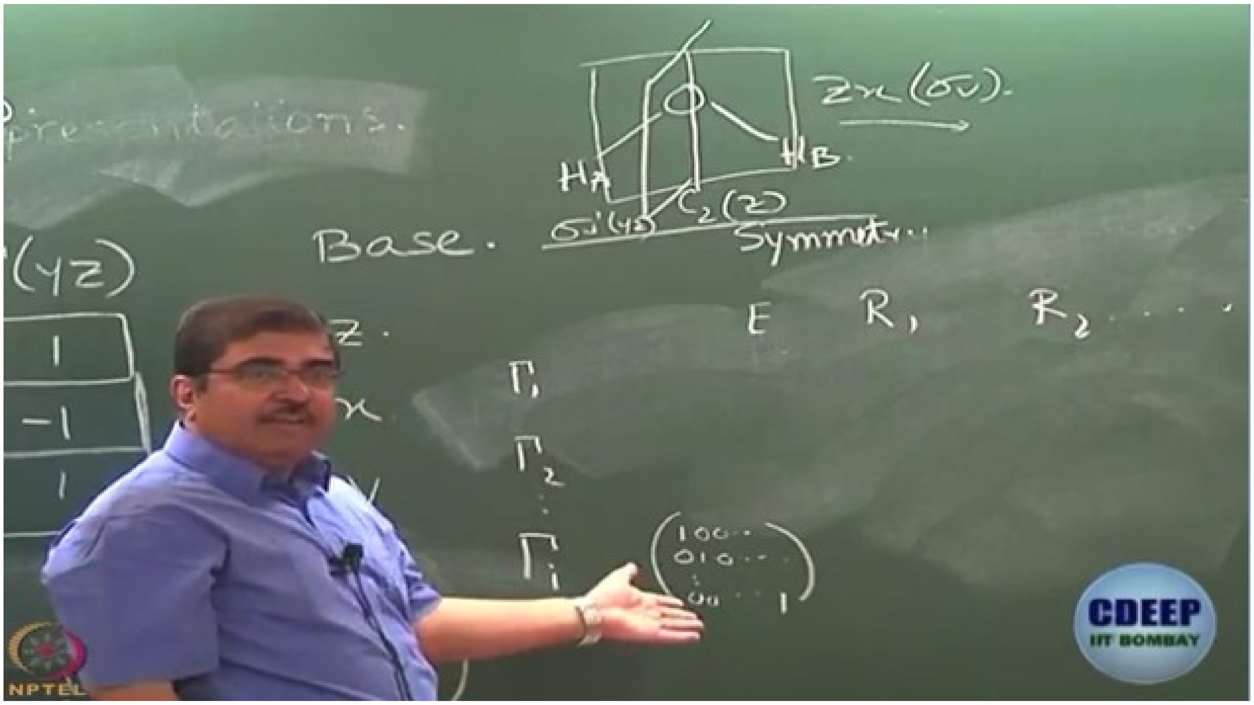

I’ve not defined what the dimensionality of this matrix is. Dimensionality of the matrices in a representation is the dimensionality of the representation itself, so dimensionality of these matrices is 1, so 1, 2, 3,

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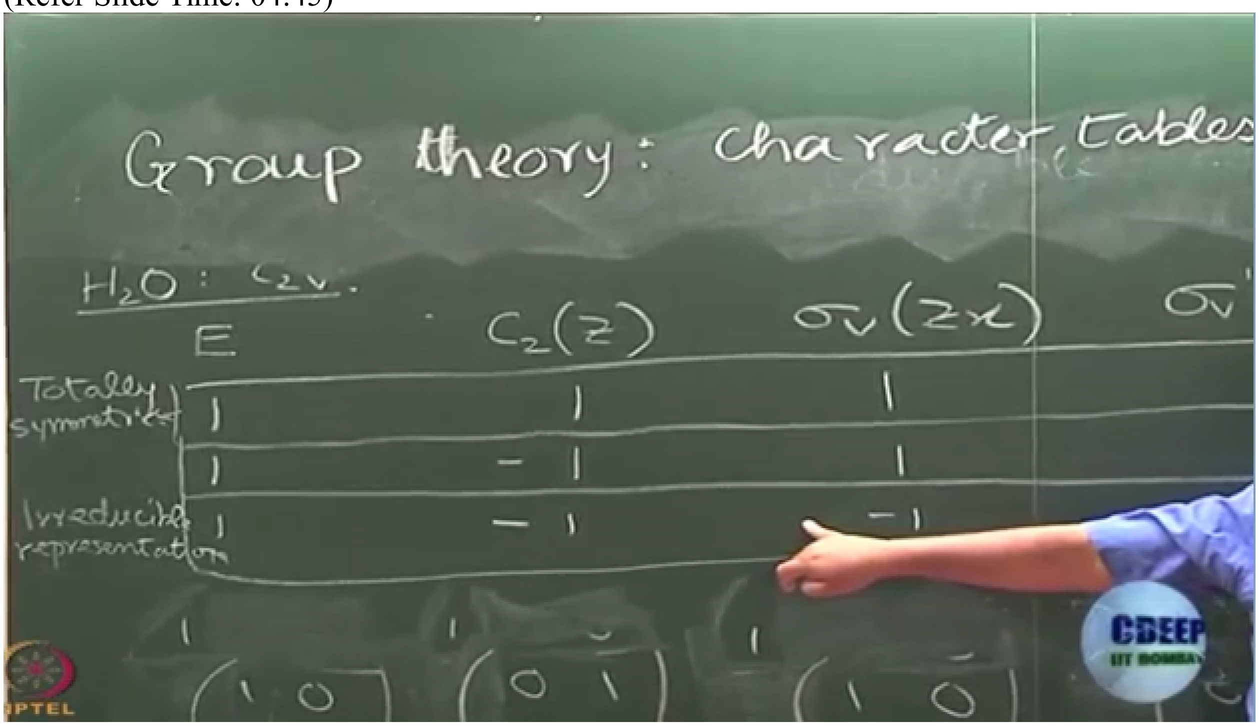

these representations are 1 dimensional representation.

Dimensionality of the matrices here is 2, so it is called a 2 dimensional representation, whether it is reducible or irreducible that will come later, okay, but here what we are saying is that suppose we know all the reducible representations, and I make a chart of that, then I can write these matrices for all of them.

Now let us say, there is something like this, X1, X2 so on and so forth, Y1, Y2, so on and so forth,
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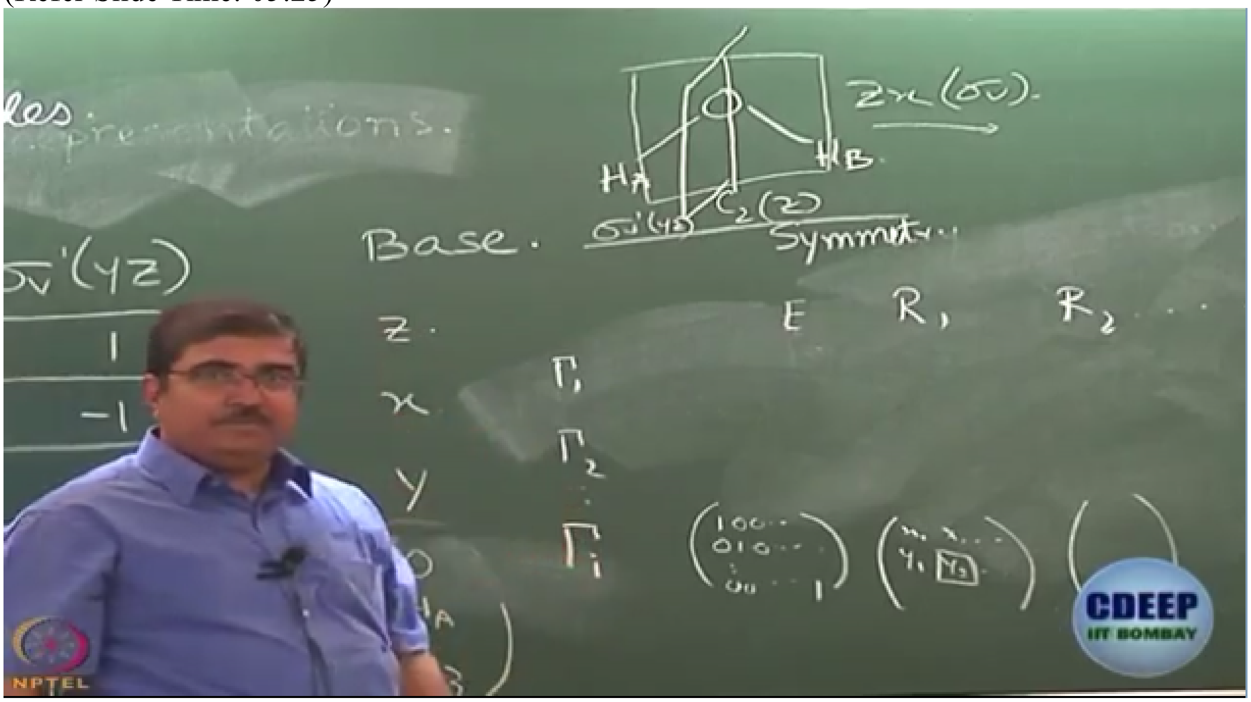

look at this element in this matrix what would we call it? This is the 1 1 element, this is the 2 2 element right, what is this? And this? 2 1 and 1 2, right, and in fact in different books actually use different notations as well, but let’s agree on one what is this 2 1 or 1 2? 1 2, and this is 2 1, okay, so this 2 is M, 1 is N, in this case what is M? What is N? M is 1, N is 2, so understood then?
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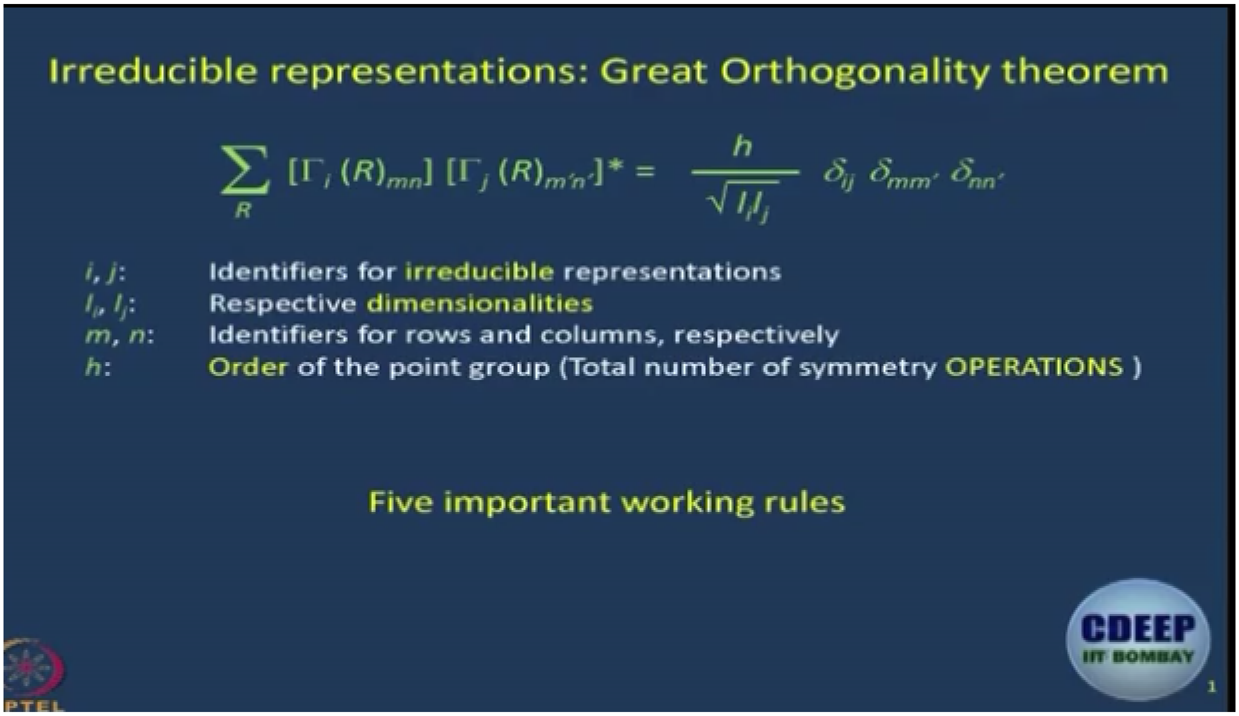

Now does this make a little more sense? Gamma I R MN means the MN element of the transformation matrix of the symmetry operation are in the ith, remember irreducible representation, now have you understood what this means? Not the entire thing only this, understood? What have I done here or what has been done here? Take this, multiply it by the complex conjugate of another matrix element of another representation, alright, M dash, N dash element of symmetry operation are in the jth irreducible representation, so you multiply it one matrix element of a irreducible representation by the complex conjugate of another matrix element of another irreducible representation and you have summed over all values of R, okay, so you have done this operation for E, you have done it for C2V, you've done it for sigma V, you've done it for sigma V dash, if we are talking about C2V. Understood left hand side? If you've not understood the left hand side, please raise your hand now. Can I go ahead? You understand what have I done, on the left hand side I had just multiplied a matrix element, some matrix element of the ith irreducible representation by the complex conjugate of another matrix element of the same symmetry operation R from a different irreducible representation and if summed over all values of R.

Right hand side is H divided by square root of LI, LJ, where LI and LJ are the dimensionalities of gamma I and gamma J, dimensionalities of the ith and jth irreducible representations respectively, okay, so H/root over LIJ, what is H by there? What is H? H is called the order of the group, for our purpose order of the group means total number of symmetry operations, very important to remember this, total number of symmetry operations, not total number of symmetry elements, it's going to make a difference later on.

In case of C2V, what is the total number of symmetry operations? 3 or 4? How many say 3? Okay, how many say 2? This is becoming like a bidding what is the total number of symmetry operations in C2V? The correct answer is 4, E, C2, sigma V, sigma V dash these are all symmetry operations right, okay, 4. For C2 I can rotate once or I can rotate twice, right, once, twice, is that one operation or two operations? Actually one associated with C2, because C2 square is equal to E that is the different symmetry operations let us not forget that, okay.

Another quick ways, C3V we have done ammonia C3V, what are the symmetry elements? Symmetry elements, what are the symmetry operations? E of course has to be there, C3 is there, and 3 sigma V's are there, is there anything else? C3 square is also there, isn't it? C3 square, these are the 3 bonds, the problem is, yeah, right, C3V, so this is C3, this is ammonia, turn once start with, what is this colour? Green, green on the top right, I turn it once, blue comes on the top, this is blue, this is not green even I can see that, yeah, blue on the top, right, I turn once again it is white on the top, so how many symmetry operations would that be, leaving out E? When white comes on the top that is 1, right, but this C3 and C3 square or we start it from here, we are supposed to start from here, right, this is C3, this is C3 square, what else can we do? I can started with this, I can do this as well, right minus, so how many symmetry operations associated with C3? Not 1 but 2.

Yes, we are doing the same process of rotating so, no we cannot, that's what I am saying, because that's why I've used chalks of three different colours. Yeah, so C2 is with respect to an axis, sigma V with respect to a plane, so there is no confusion in your mind that they are different, but C3 and C3 square are performed with respect to the same axis, not only axis same axis that is why you are confused whether they are two or whether they are one, have I got the problem right? They are two, because they leak to different configurations, when we talk about configurations you would have studied in stereochemistry something, so this is called is A, well W, B, and G, this is the configuration you start with, you rotate it is G, W, B, rotate the other way, it is B, G, W all different configurations, okay. So C3+ C3- or what you can call C3 and C3 square are different symmetry operations, this part is important to understand, otherwise we'll get all our calculations wrong later on, okay, are we clear?

So how many symmetry operations are there in C3V? Yes, E, C3, C3 square then? Sigma V number 1, sigma V number 2, sigma V number 3, okay, 6, so what is, that 6 is H for your, what is it called? C3V, so what we have learnt is for C2V, H is 4, H is 4 right for C2V? For C2V H is 4, E, C2, sigma V, sigma V dash for C3V H is how much? 6, E , C3, C3 square, sigma V number one, sigma V number 2, sigma V number 3, so now are we clear what is H is? H is called the order of the group, it is equal to the total number of, please don't forget this symmetry operations, it is not the total number of symmetry elements, symmetry operations, okay.

So we are trying to understand the right hand side, I should change the title of this module, it is group theory, great orthogonality theorem GOT, it's not a goat, it is got, A is not there, great orthogonality theorem, alright, now and then so on the right hand side, left hand side we've understood, right hand side we've H divided by square root of LI, LJ, LI LJ are the dimensionalities of ith and j-th irreducible representations respectively, clear?

Now what else do we have multiplied by delta IJ, delta MM dash, delta NN dash, you know by now by virtue of having done quantum chemistry, quantum mechanics courses what is the meaning of delta? What is delta? Suppose delta IJ, what does that mean? Simple mathematical answer, when is it 1, when is it 0? So it required a collaborative effort one of them gave half the answer, the other gave half the answer at the same time, so both of you are right, very good, full marks.

So when I = J then delta IJ = 1, when I is not equal to J delta IJ = 0, okay, same is true for delta MM dash and delta NN dash, okay. Now since we've now understood all the terms, all the factors in this equation, I hope we know appreciate why it is called an orthogonality theorem, you remember what orthogonality is or rather you remember what orthonormality is? Integral over all space, product of two vectors is equal to sum value when they at the same, and 0 when they are different that is orthonormality, right, so what great orthogonality theorem leads us to is that if you are working with irreducible representations then the matrix elements of these irreducible representations behave like a set of orthonormal vectors, okay. Are we convinced that is what the great orthogonality theorem means, okay, but this also is only for the purpose of knowing where everything comes from, what we are really going to use is this five important working rules that arise out of this great orthogonality theorem, we are not going to derive the rules either, if you are interested in the derivation please look up Cotton's book, okay. Cotton's book does not give you the derivation of great orthogonality theorem as such, but it does give you derivation of this 5 working rules from great orthogonality theorem, they are pretty straight forward you can go through them, we will not ask questions from that in this course.

These are the 5 working rules, as we'll see tomorrow, using this 5 working rules we can work out the character tables of whichever point group we want, that's what we'll do tomorrow, but today before we close, that's one point that I want to make is this, what is the character of the matrix standing for E in the one dimensional representation? That might sound like an idiotic question, but please bear with me, you remember what character is? Trace, some of all the diagonal elements, what is that character for the transformation matrix of E for a one dimensional representation, has to be one cannot be anything else, there is only one number anyway, what is it for a 2 dimensional representation? 2, what is it for a 5 dimensional representation? 5, what is it for a 232 dimensional representation? Okay, that is kind of too much of an exaggeration, the point we are trying to make is this, and this is something that's not retain in those 5 rules, so I'll write it separately.
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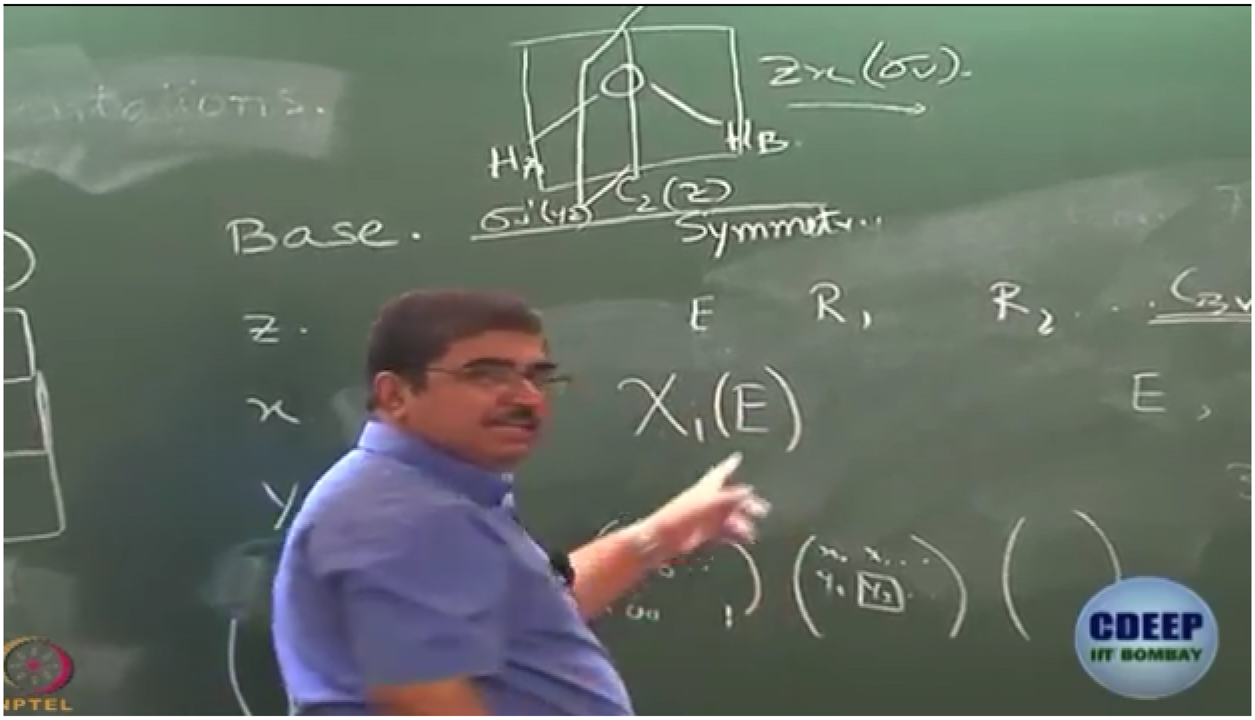

Chi is how we denote the character, okay, chi for E identity operation for the ith irreducible representation is equal to the dimensionality of that representation,

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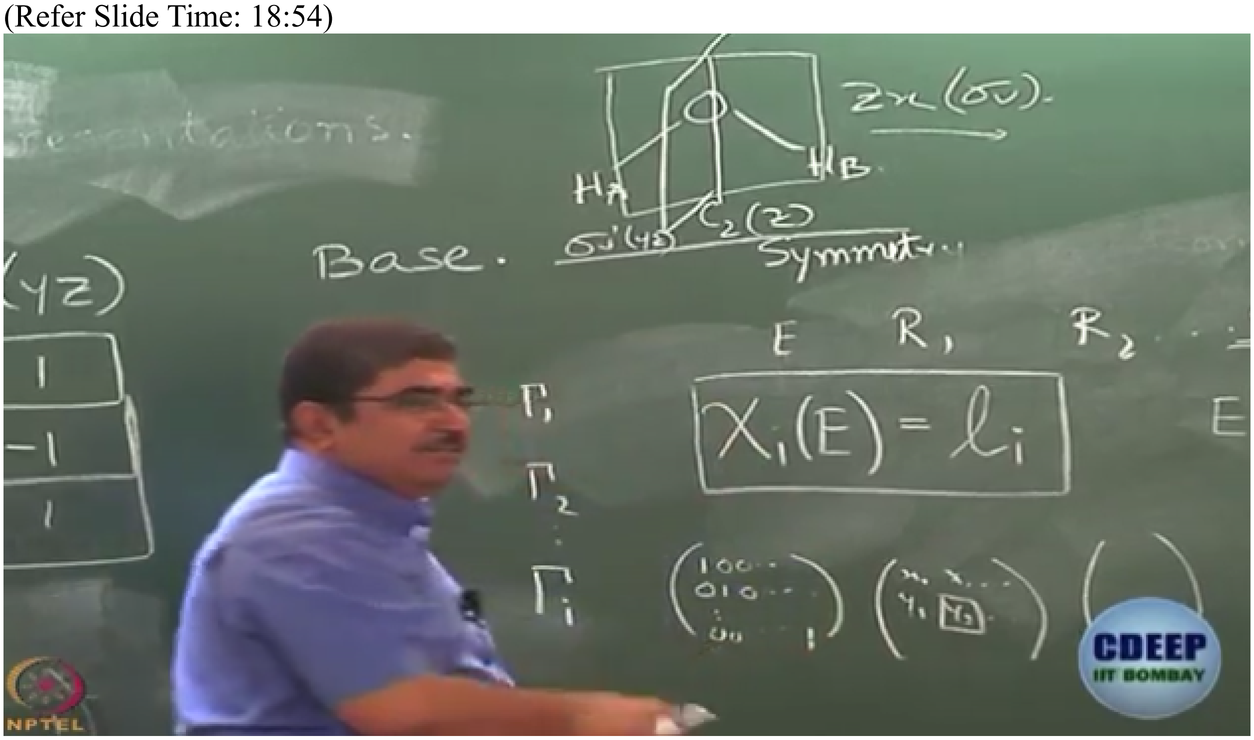

do we agree with this or do we not agree with this? Chi I(E) is equal to LI, this is a very simple rule that we can understand very easily, right, character of the unit matrix for the ith irreducible representation is equal to the dimensionality of that representation.

Let us remember this, tomorrow we are going to take this and the 5 working rules axiomatically and we'll work out character tables of C2V and then C3V.

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