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. – 33
Matrix Representation of Symmetry Point Group

We'll begin we have started our discussion of a symmetry. And once again let me remind you that the reason why we were studying symmetry in this course is that a systematic study of symmetry of molecules simplifies many of the problems in spectroscopy in particular and quantum mechanics in general. And then in spectroscopy we can tell which transitions takes place, which transitions don't take place for more complicated molecules and diatomics using symmetry, without considering symmetry it becomes rather TDS, that is why we are suddenly studying symmetry in this course, but what we'll do here is that we'll only develop a functional approach towards symmetry.

What we have discussed so far is that take any symmetry operation capital R, in the previous class we've shown that you should be able to write a transformation matrix corresponding to it. Are we clear about that part? Symmetry operation represented by a transformation matrix, right? If the basis, well we'll come to what our basis is,
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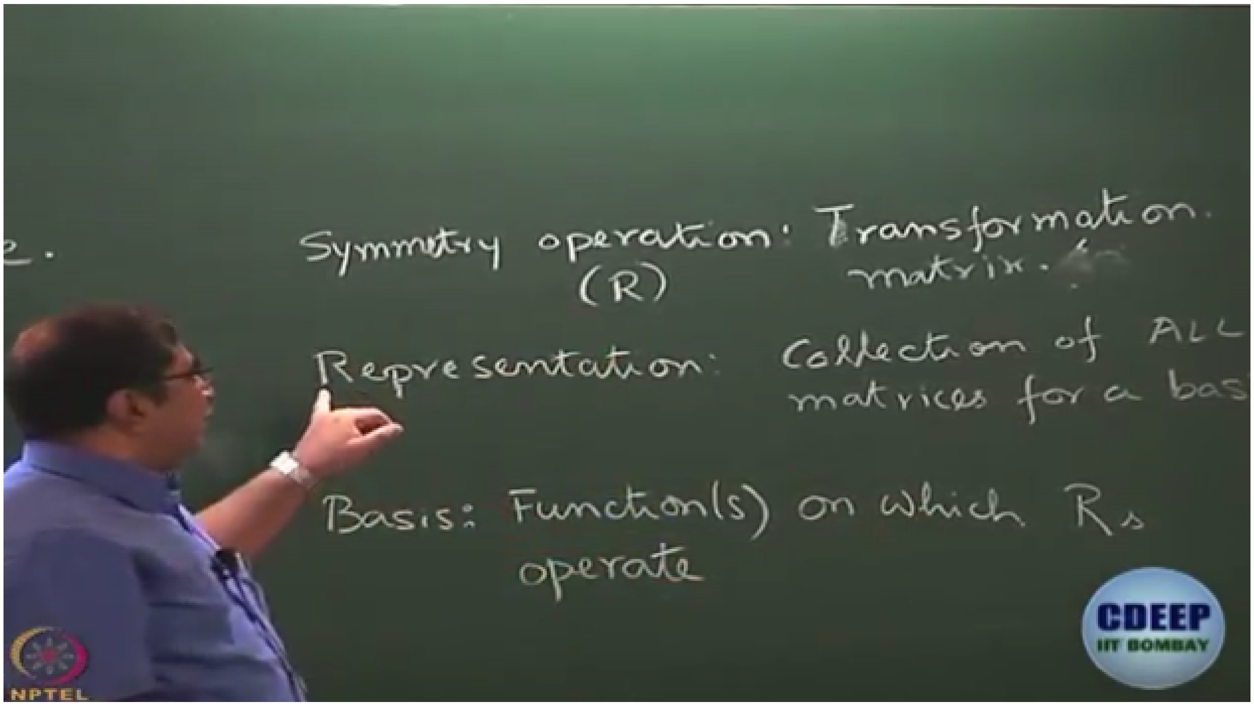

but before that let us say or maybe let us say what basis is, what is basis? Basis is the set of functions, function or functions on which the symmetry operations actually operate, for example we have started discussing this problem here water, which is a C2V molecule and there we said we’re taken X, Y, Z as basis, and we saw what kind of matrices we get for each symmetry operation, okay.

Collection of all these matrices for a particular basis is called a representation, alright, and as we have discussed towards the end of the last class, representations can be reducible or they can be irreducible. What is the meaning of reducible representation?

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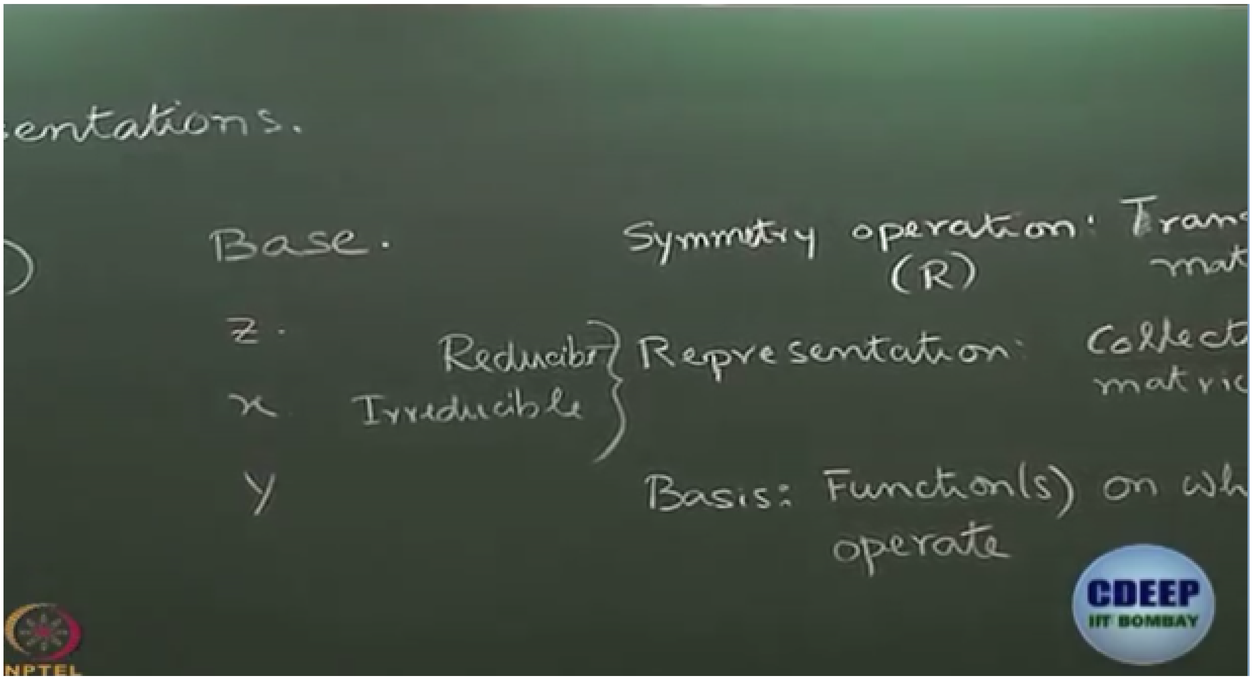

A representation in which you have larger matrices that can be blocked factorize in the same way to give you smaller representations. For example when we work with X,Y, Z the matrices we got were all 3 x 3, right, but all of them for, when we use X, Y, Z coordinates in C2V, all of this matrices turn out to be diagonal.

As we said that diagonal elements stand for the contribution of a coordinate in its transform form of diagonal elements correspond to the contribution of a particular element to the transform form of another element, okay, when we talked about rotation by some angle theta you saw that the matrix turns out to be something like cos theta sin theta – sin theta cos theta, okay, so this sin theta that you get that is the contribution of Y in transformed X or X in transformed Y then it is – sin theta, that is the significance of diagonal and of diagonal elements, okay.

Since all the matrices where diagonal in the representation we got using X, Y, Z coordinates as basis, what we did is we block factorize them, we drew those vertical and horizontal lines living out all the 0 matrix elements which were of diagonal and we retained only the diagonal elements to develop 3 different representations. The first is 1, 1, 1, 1 and we said this is your totally symmetric representation, alright,

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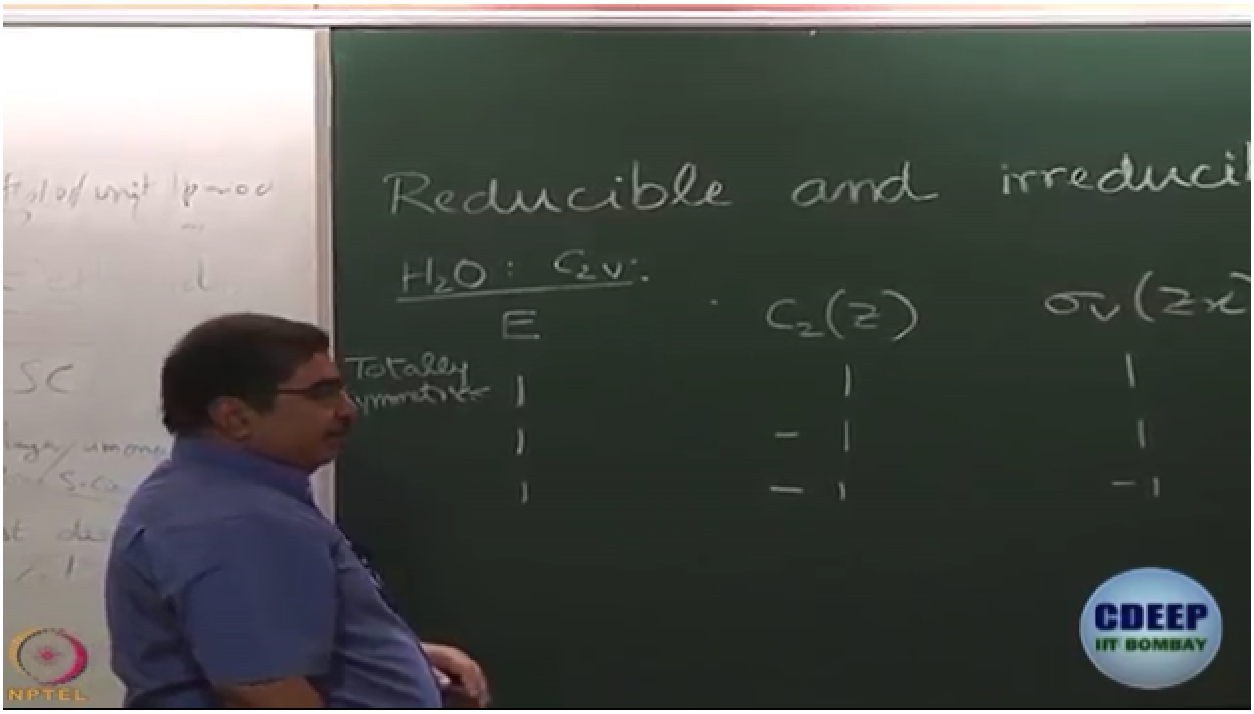

and what forms a basis for it? Z, in this case 1, -1, 1, -1 that is another representation, X forms a basis of it, 1, -1, -1, 1 is another representation for which Y is the basis, so what we did is we took this reducible representation that we got using X, Y, Z altogether as the basis and we could break it down or you could reduce it into 3 different representations.

Now what I'm saying is, this is the representation and this, and this, right.

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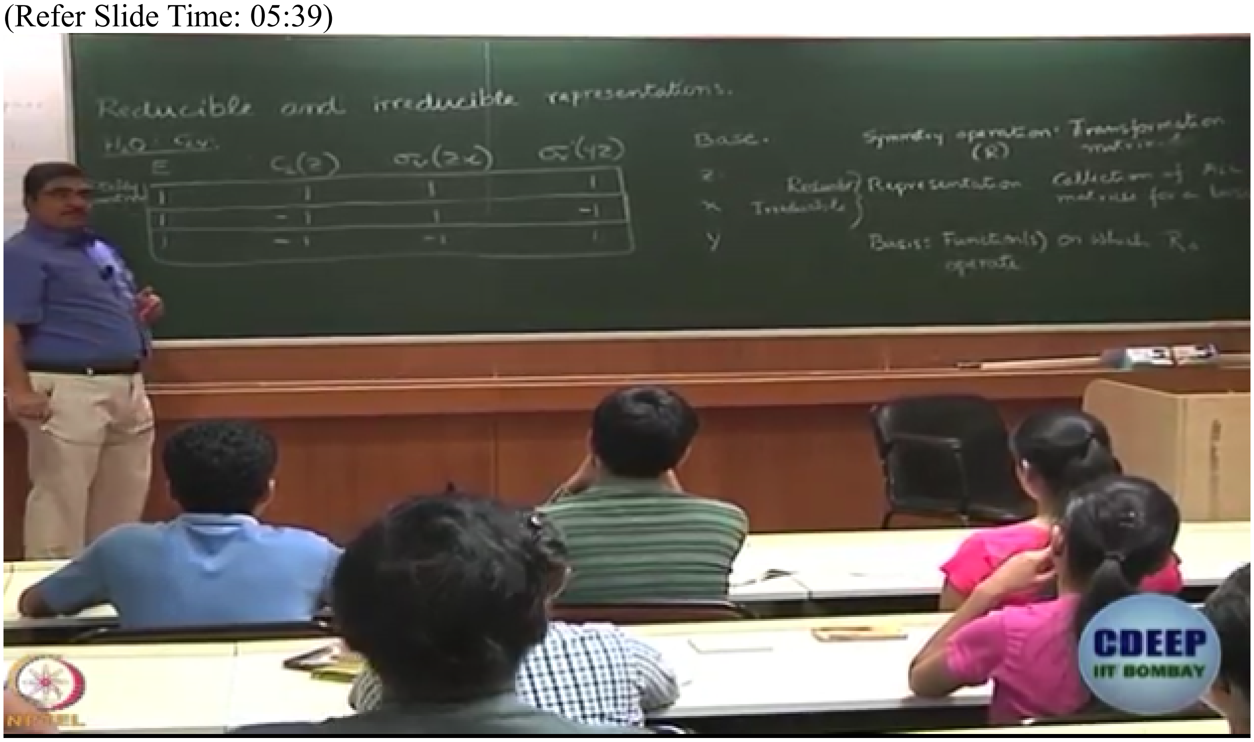

Now take any of this representations, is it possible to decrease the dimensionality of this representations anymore, dimensionality means how many by how many elements the transformation matrices are, these are all numbers, right? Number means one by one matrix you can call it that, right, one dimensional matrix, is it possible to go down to half dimensional or something? No, right, doesn't make sense, so these are your irreducible representations.

So each of these is an irreducible representation, so if a representation is one dimensional then it goes without saying that it is an irreducible representation, however that does not mean that an irreducible representation is necessarily one dimensional, as we'll see in the course of our discussion you can have irreducible representations that are 2 dimensional or 3 dimensional, generally we don't have to deal with more than 3 dimensions but even that is actually possible.

What is the physical significance over representation that does not have a basis associated with it, and he is asking this question, because he's actually had a look at character tables, and there are in character tables you will find representations which don't have any basis associated with that, right, so what we are trying to say is in such cases we'll see how we get those representations in the first place without knowing the basis first, and the physical significance is these representations are also called symmetry species, so what we will say is that this is one kind of symmetry behavior it can be 1, 1, 1, 1 symmetric to everything, another kind of symmetric behavior 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, okay, so there are certain combinations that we'll be allowed that is certain combinations that will not be allowed, so the character table only shows you representations that come from things like X, Y, Z or their products, there can be more complicated combinations that you might have to encounter which will become part of that basis, so when we discuss say vibration of polyatomic molecules after mid-sem we'll encounter such a situation where we'll get a vibration which belongs to a representation for which there is no basis in the character table, okay.

Right now what we are trying to do is we are trying to find a way in which you can just figure out what are the different kinds of irreducible representations that are possible for a particular symmetric group.

Are we clear so far? Yes, in character table as I said what you use is X, Y, Z, X square, Y square, Z square, XY, YZ, ZX, RX, RY, RZ, rotation with respect to X, Y, Z, that is what your character table has, but then what we are going to work with, we are going to work with functions like say 3X square – 4Y + 3Z, and even those will have some kind of symmetry, so character table gives us the collection of the irreducible representations, what we try to do is we try to see the function that we are interested in does it fit somewhere, alright.

Now let us do something, let us use the different basis and see if we get any new irreducible representation, C2V is what we are dealing with, right, the simplex C2V molecule that we know is water, so let us use water.

Now I want to use O, HA, HB as basis, what am I saying? This is what I am saying, this is water, I've labeled the two hydrogen atoms A and B, alright,
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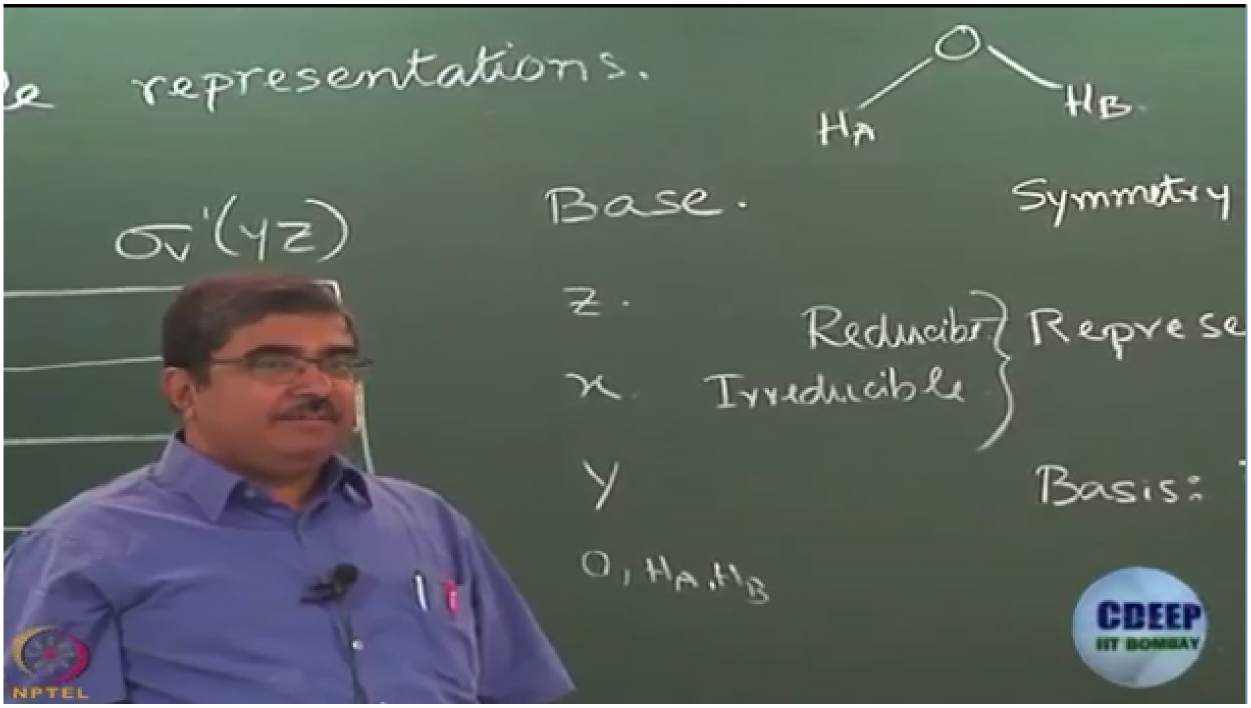

I'm calling them HA and HB and just to remind us this one is C2 which is aligned with the Z axis, this is the molecular plane ZX which means X axis is along this direction, this is your sigma V dash which is YZ, so this we call sigma V, alright,

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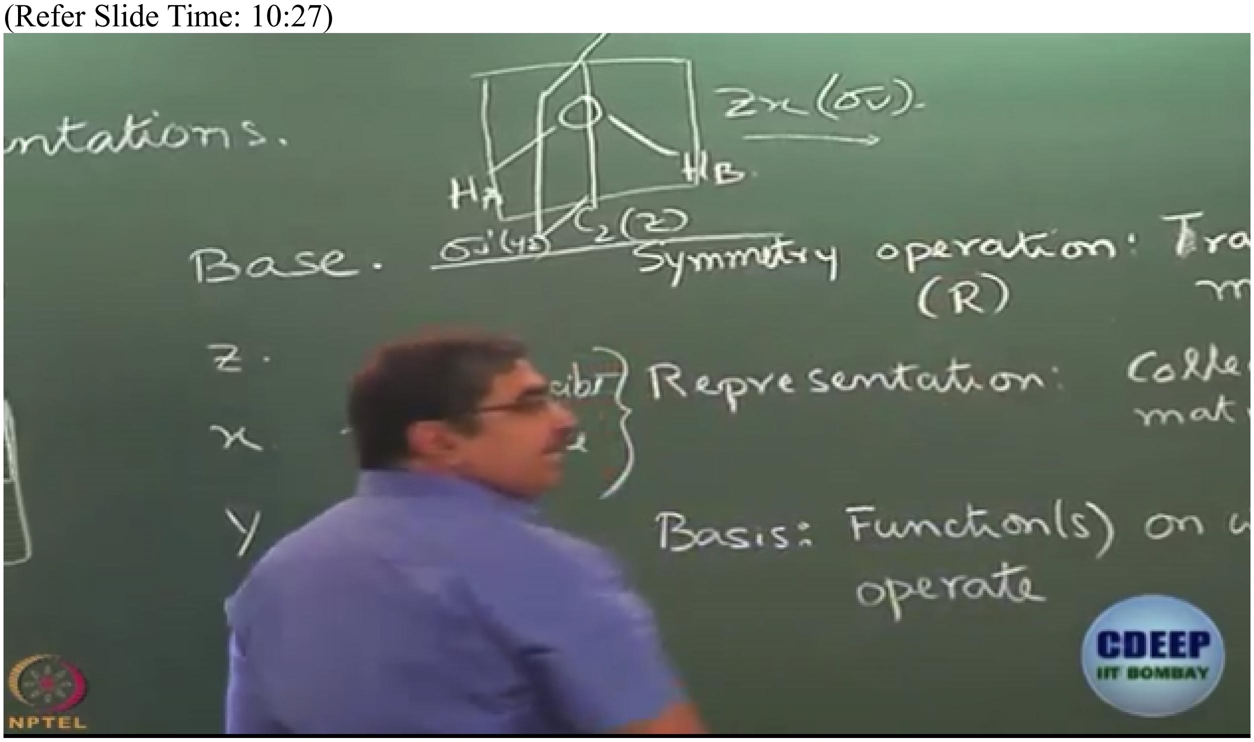

I've used X, Y, Z coordinates of some arbitrary point in space and I've got 3 different irreducible representations, now I want to use the atoms, I want to see what kind of representation I get, okay, as usual as what we did last time we had started with X, Y, Z together right, here also we are going to take this O, HA, HB together

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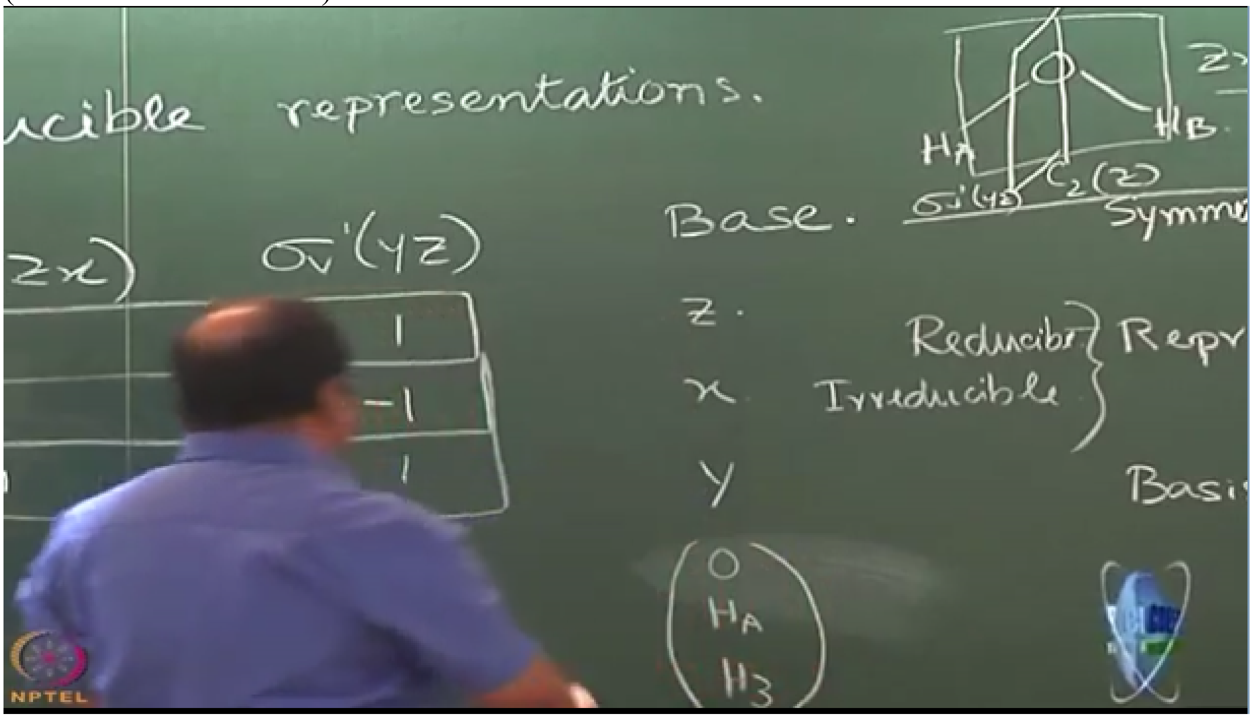

and we will try to see what kind of matrices we get, E is very easy to write, what will E be? Yeah, 1 0 0 then 0 1 0, 0 0 1 that is easy right,

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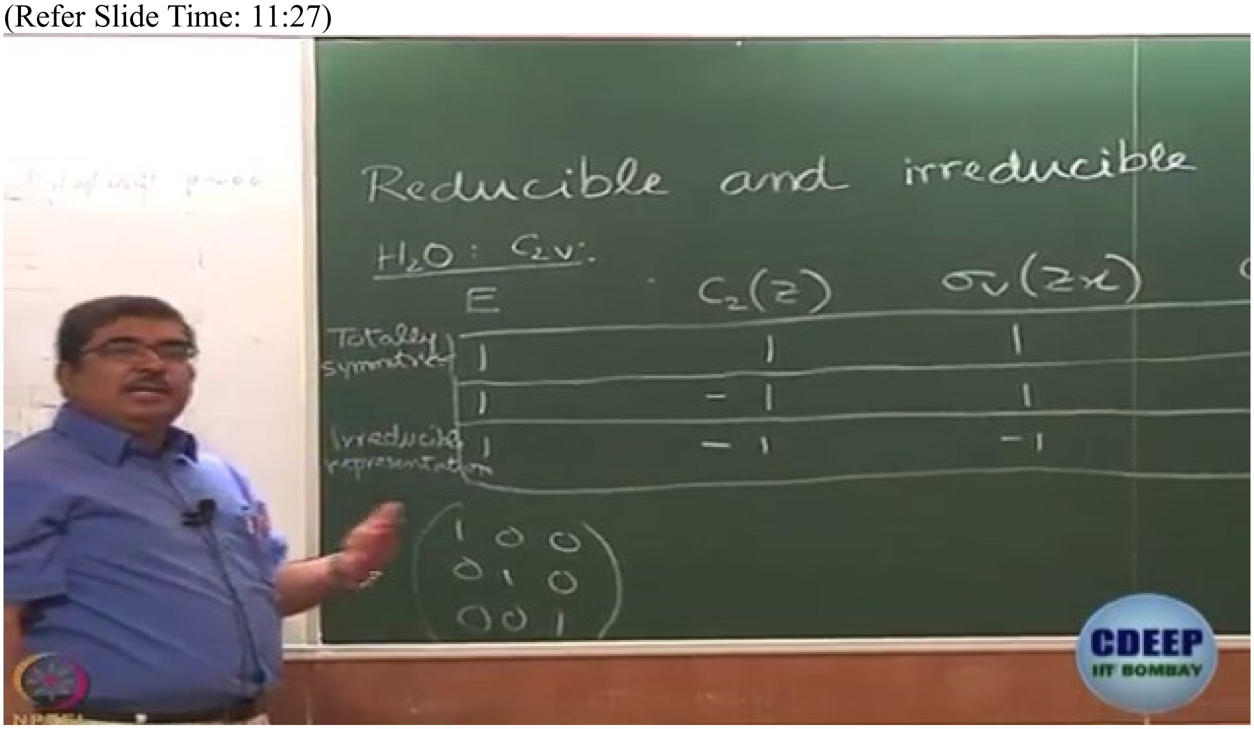

E is identity, doing nothing that means multiplication by unit matrix of whatever be the order of this representation, of the basis.

Now what about C2Z? When C2Z operates on the water molecule O remains O, HA becomes HB, HB becomes HA, is that right? Right, AB turn by 180 degrees, A becomes B, B becomes A, are we clear? What will the matrix be in that case? 1 0 0 no problem with that, then 0 0 1, then 0 1 0, now you see you don't have a diagonal matrix anymore, okay,

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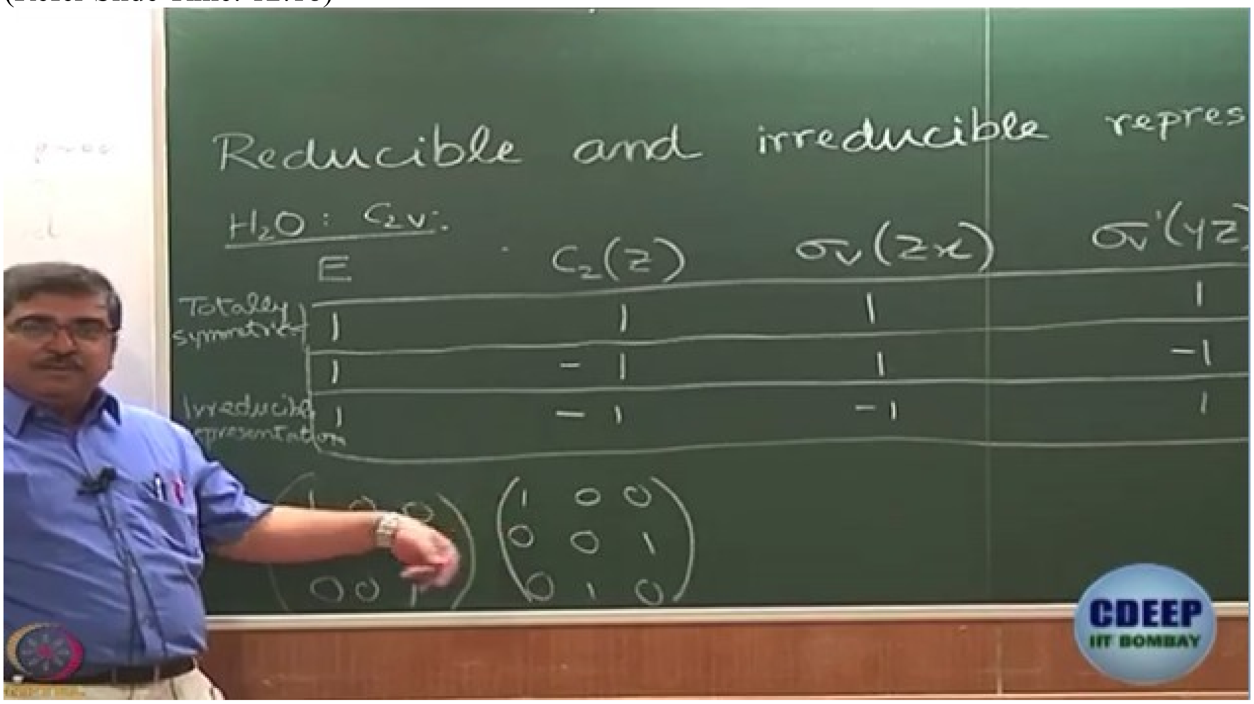

nonzero elements have gone off diagonal, why? Because A becomes B, and B becomes A there is an interchange, whenever there is an interchange or whenever there is a contribution of one original coordinate in a transform coordinate or one original element, basis element in a transform basis element you are going to have nonzero of diagonal elements, are we clear? Are you okay with this matrix? Sure, can we go to the next one?

ZX, what happens when ZX operates? ZX don't forget, it's a molecular plane, what happens to O? What happens to HA? What happens to HB? Same, what is the transformation matrix? O remains O, HA remains HA, HB remains HB, what is the transformation matrix? It's same as identity matrix, and finally sigma V dash, YZ, so O remains O, HA becomes HB, HB becomes HA. First look it seems that the operation is exactly the same as C2, right, but if you are picky then it is not, and matrix is the same, let me write the matrix first, 1 0 0, 0 0 1, 0 1 0, okay.

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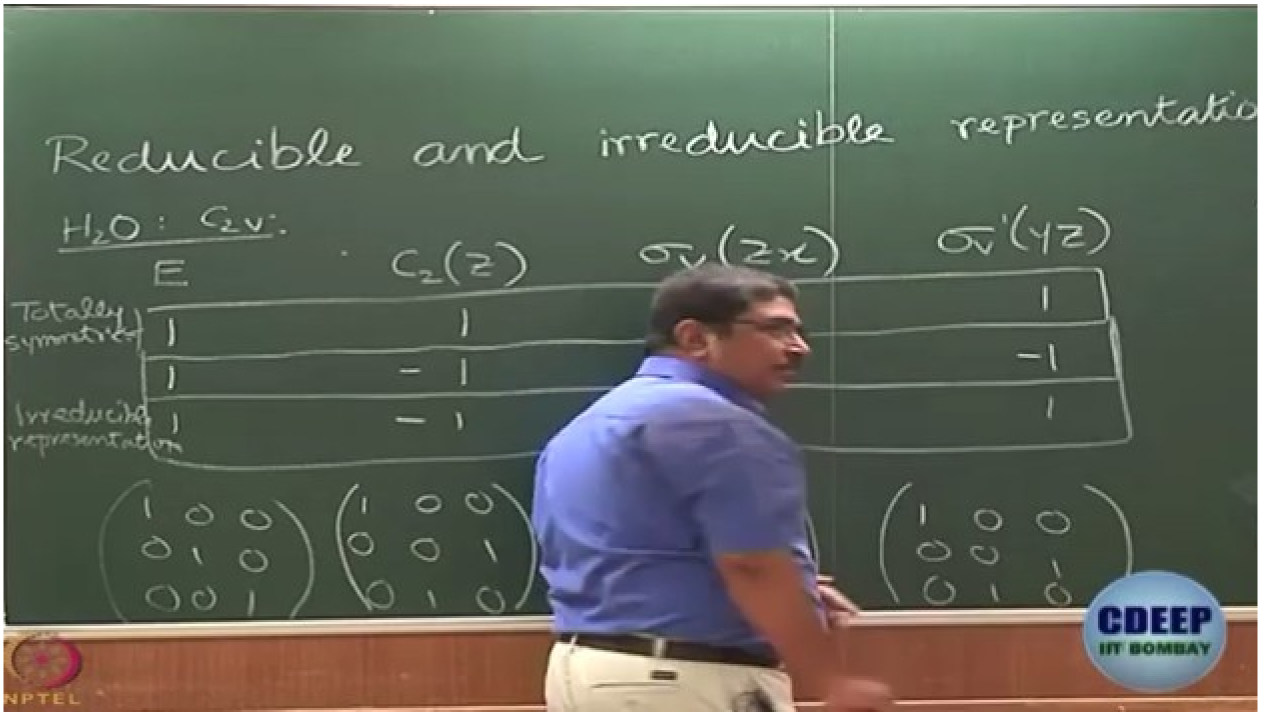

Now let us comeback to what we were saying. HA, HB this is what happens when we turn it, right? Instead of doing it with my hands, this is better to do it like this, HA, HB, O, when I turn this is what happens, when I reflect then what happens? This is what happens, do you see the difference? When you turn this is what happens, when you reflect, this is what happens, so look at the clips now, maybe I'll put it like this then you see better, look at the clips, the way I've held it that both the clips point towards you, when I turn the clips go behind, they point away from you, but when I do a reflection the clips still point towards you, right.

Now think of atoms, atoms we can model simply as pairs, right, when they turn then what happens? The hemisphere that was facing you, now faces away, when you reflect then the hemisphere that was facing you still faces you, okay, it is like the face of the moon that we always see, are we clear? So even though the matrices are the same the action has some settle difference depending on what we are doing, okay, if may or may not be imported for us in this course, but it's worth noting. Are we okay with the matrices? If there is any unhappiness over the matrices or if you've not understood something, you want me to repeat please say that.

Now may I go ahead? What is the next step? Block factorize right? Have a look at this matrices and tell me how I can do block factorization? And don't forget then when I do block factorization I cannot draw the lines in different ways in different matrices, I've to draw the lines in exactly the same way, so what is the best way of block factorizing this matrices so that you leave out the maximum number of 0 of diagonal elements. How should I draw the line? And to do that it is better to look at this matrix or that one, how do I block factorize this one? This one is completely block factorizable actually, I can do it like this,

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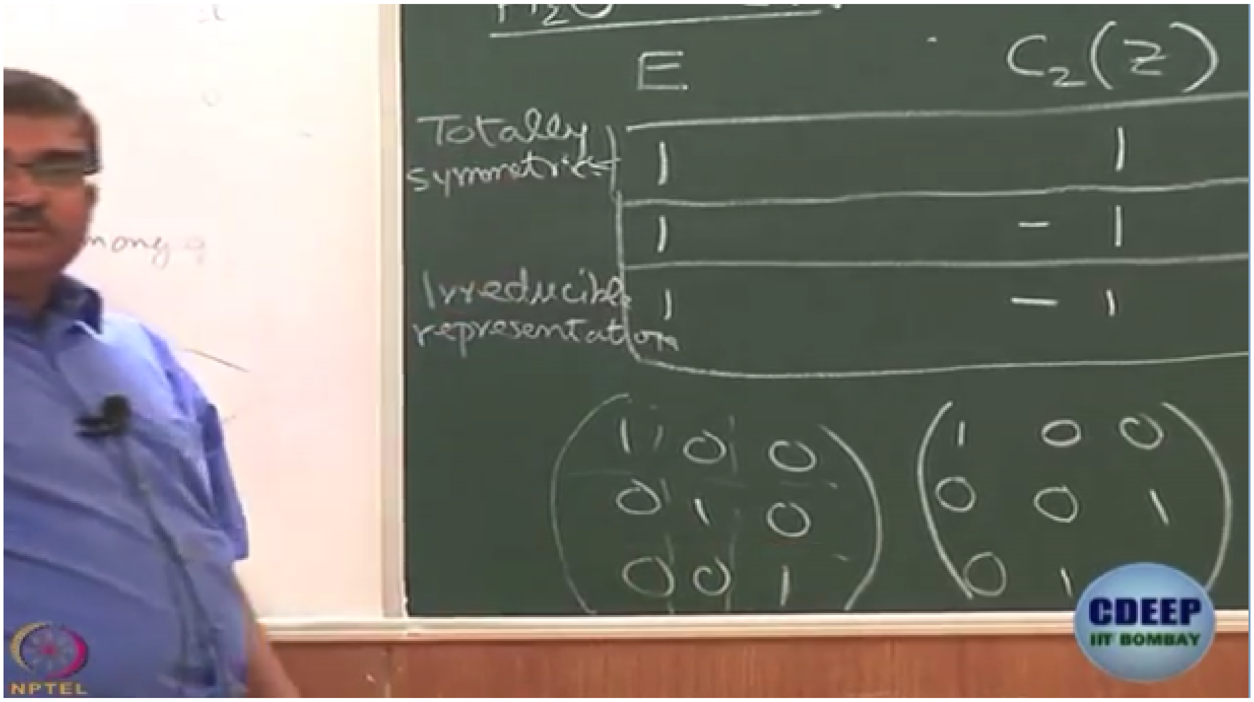

a tic tac toe kind of picture, but this I can draw this line, no problem, I can draw this line, no problem, can I draw this? No, because then one gets left out, okay, so the only way I can block factorize this is this, so I'll draw the same lines here as well, and here, and here.

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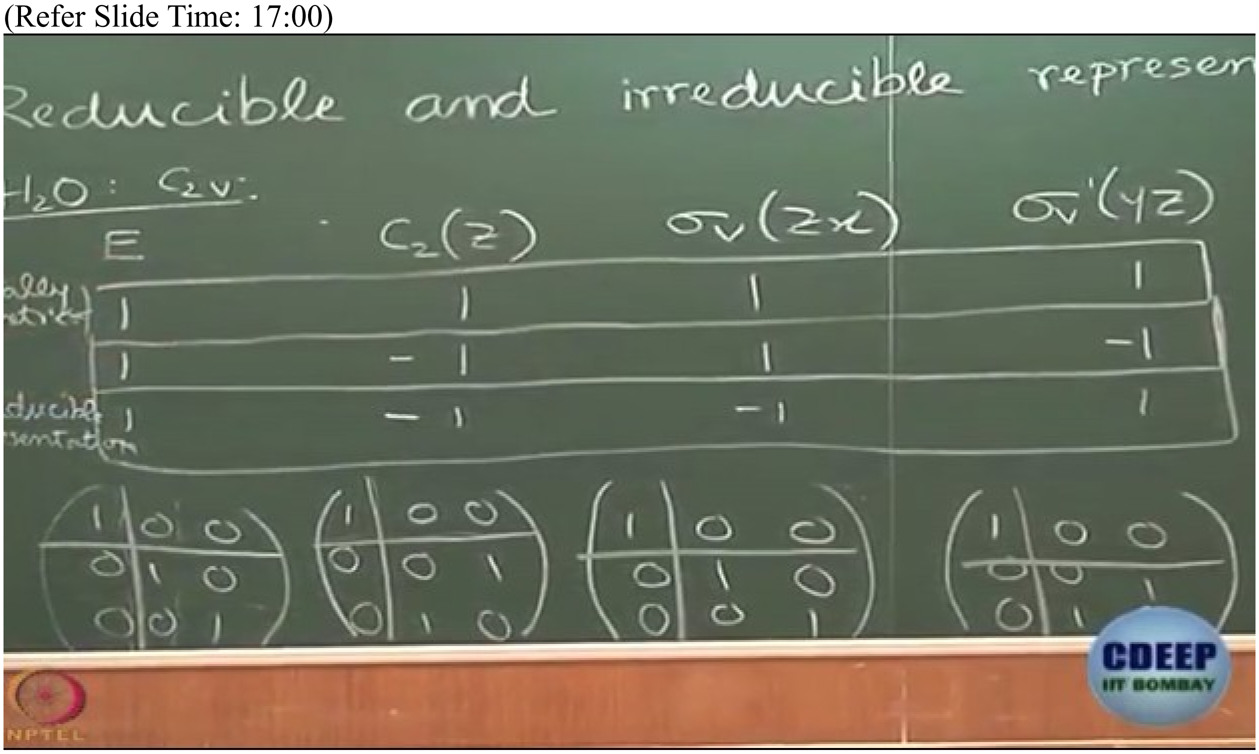

If you remember what we did last day, we erased all the zeros that were left outside this lines, okay, let us do that. Yeah, so when I do block factorization what I do is, I try to retain the elements of the transformation matrices that completely describe the transformation of some basis elements.

See, so even before I erase, what happens in all this transformations? No matter what you do, E C2, sigma V, sigma V dash, O remains O, O cannot become H, right? Symmetry operation is not capable of doing a nuclear transformation, so O cannot suddenly become H, just because you've to _17:54_ round or you've reflected or you've done nothing, so O remains O. However in two of the symmetry operations that we have used here the hydrogen atoms have interchanged, right? Okay, so that tells us that our basis contains two different kinds of elements, one O is unique, it remains the same no matter what you do, and the other kind of elements are HA and HB which sometimes remain what they are, sometimes interchange.

By block factorization what I do is, I separate O from HA and HB, and let me erase, this is gone, this is gone, this is gone, this is also gone, this and this, and this, and this,
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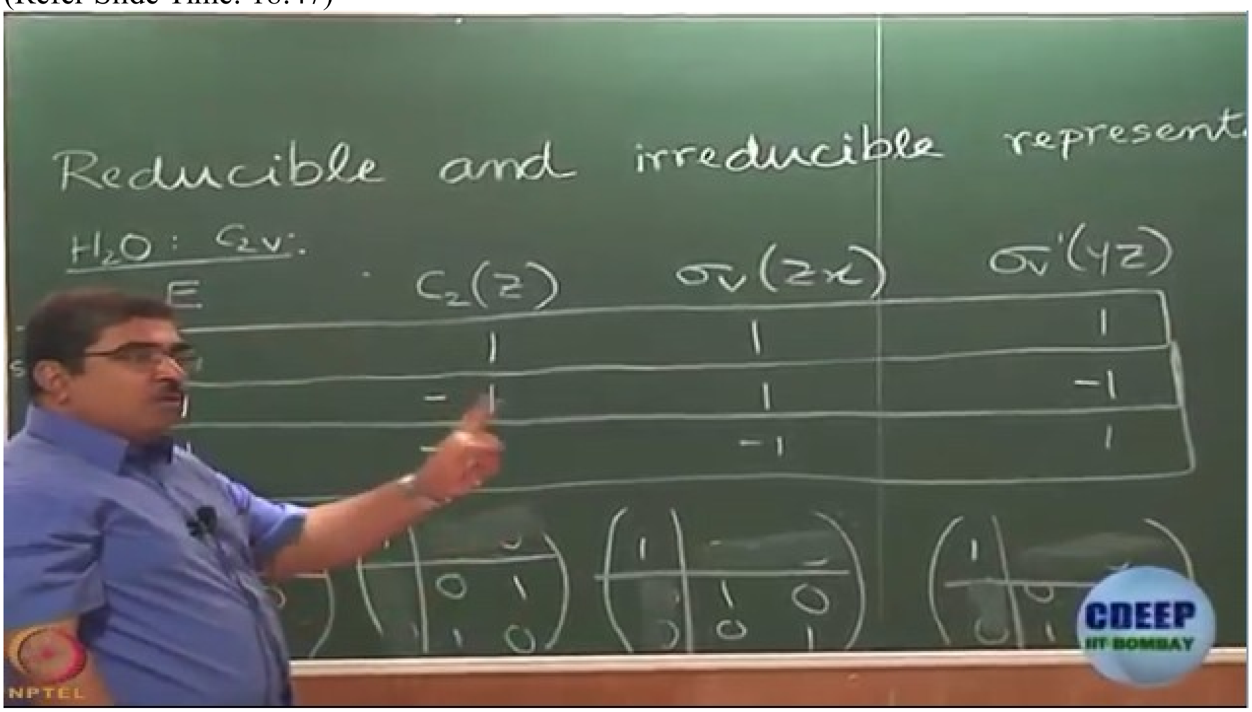

so what do you have? O is unique right, so what I'll do is I'll not write O in these brackets anymore, so for O the representation that I get is, for O the representation that I get is 1 1 1 1,
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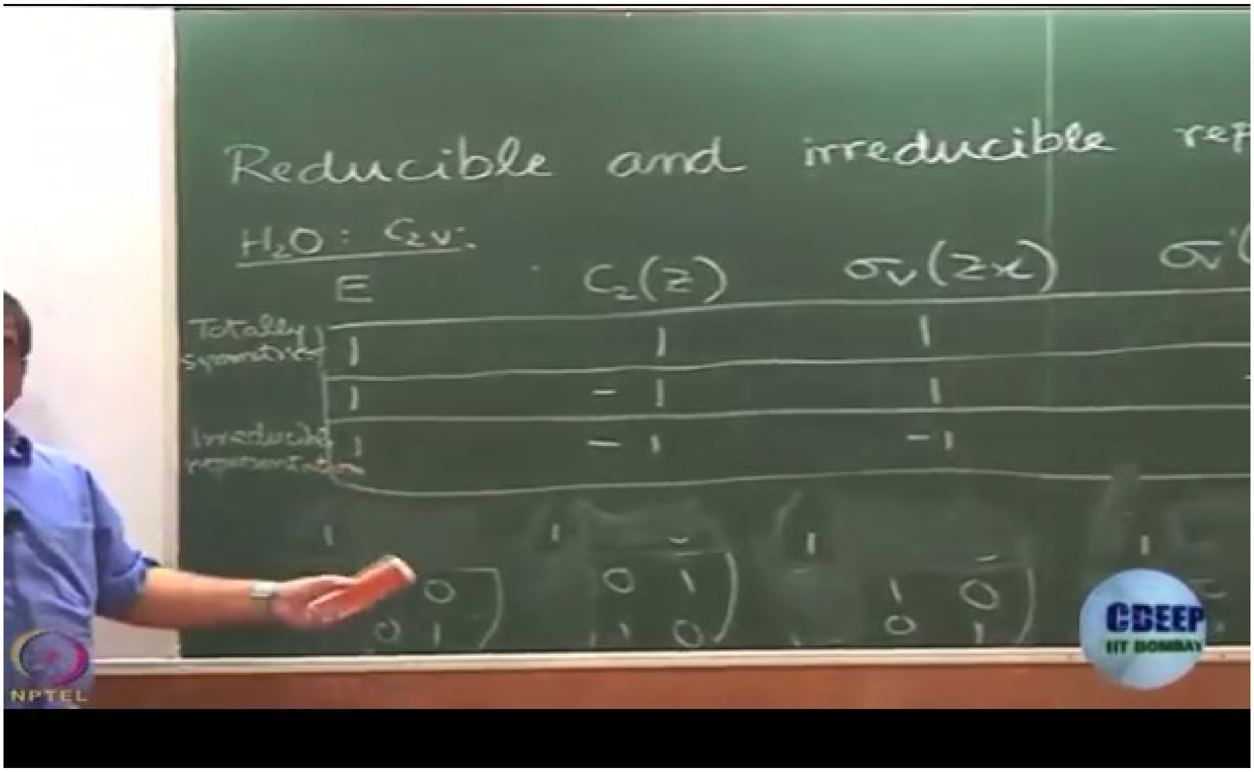

have we encountered this somewhere else? Here, when we use Z we got the same representation, and it is as we said the totally symmetric representation.

What about X and Y? In X and Y the representation that you get is 1 0 0 1, 0 1 1 0, 1 0 0 1, 0 1 1 0, okay, so what we see is the treatment that we have done, in that treatment HA and HB jointly formed a two dimensional basis that gives me a two dimensional representation, are we clear with that?

Now what we have got is, what are things we have understood? We have understood first of all that the representations you get depend on basis that you use, right, when we use X, Y, Z we get some nicely reducible representation which breaks down into three reducible representation, but when I use O, HA, and HB I get one irreducible representation for sure, but I get another representation that is two dimensional, at this stage I've no idea whether this two dimensional representation is reducible or irreducible, from the look of it, it is irreducible right, but that just doesn't sound right isn't it? I mean you can understand that if I use a different basis I would get a different representation, how would I know? How would I know in a given point group how many representations are there, how would I know what are the dimensionalities? I've given a two dimensional representation, or a three dimensional representation, how do I know whether it is reducible or whether it is irreducible, I hope I have been able to state all the questions that are in your mind right now.

What I have done essentially is that instead of saying I'm using the atoms OA, OHA, HB, I might well I've said I'm using the two ways orbital and the one way orbitals of these atoms, I would have got the same representation, right, but suppose I use say PZ are vitals, I would get the same representation.

Suppose I use PX orbitals, I would get a different representation, right, so all are valid basis, you might want to work with all of them, the question is the representation that we end up using all of those, are they reducible, are they irreducible, that is what we need to, that is what we are trying to get at.

Is there any other question? So are the questions clear? Answers are definitely not clear at this stage, are the questions clear? The only answer that is clear is that depending on which basis are use I can get different representations, this is something that we hopefully have understood. Questions that should be on our mind right now is, how do I know whether a particular representation, if it is more than one dimensional whether a particular representation is reducible or irreducible. Another question that should be on our mind right now is that, how do I know is the number of irreducible representations infinite or is it finite? Okay, so essentially our questions can be roughly block factorized into these three questions, or these two questions, right? That is what we try to answer using group theory.

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