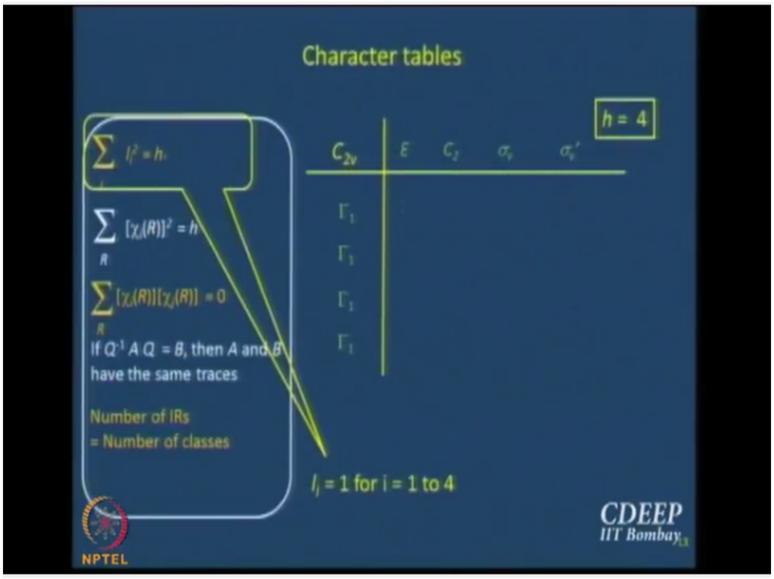
Symmetry and Group Theory
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 29
Character Tables: C2v

(Refer Slide Time: 00:16)

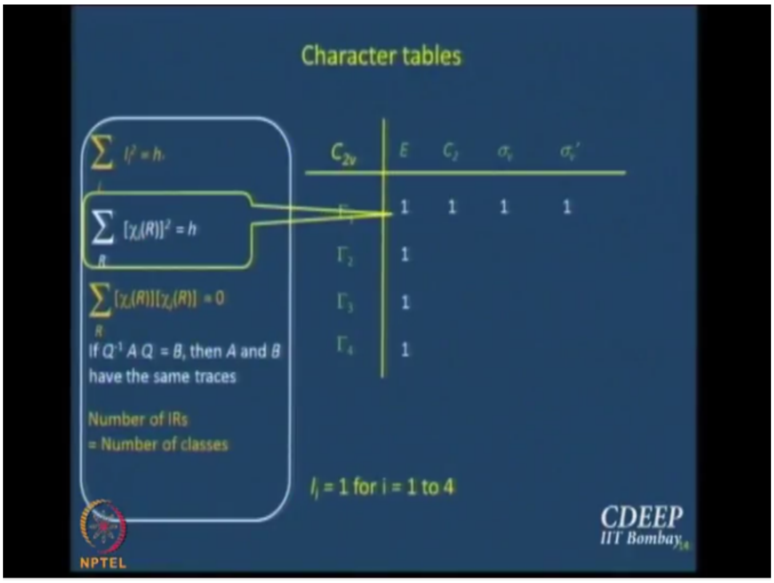


So let us start working, first question we ask is this what is the number of classes. Why three? There are four classes right E, C2, sigma v, sigma v dashed, 4 classes. So there are going to be 4 irreducible representations. So all this time the question that we have been asking that is answered in a second, you are going to do have 4 irreducible representations for C2v fine. So to start with let us name them gamma 1, gamma 2, gamma 3, gamma 4 okay.

Four classes this gamma 1, gamma 2, gamma 3, gamma 4 okay, lines are just guides to the eye, what next, the next question to be asked is what are the dimensionalities of these 4 irreducible representations and this is what will give me the answer. Sum over i li square=h what is h, h is 4 right So l1 square+l2 square+l3 square+l4 square=4, can l be a fraction, can you have C fifth by C fifth matrix okay.

Can you have -20x-20 matrix, no. So li has to be a positive integer right, it has to be a positive integer. So now see l1 square+l2 square+l3 square+l4 square=4. What will be the values of l1, l2, l3, l4? All have to be=1 right. So li=1 for i=1 to 4 that means for C2v you have a total of 4 one dimensional irreducible representations right.

(Refer Slide Time: 02:18)

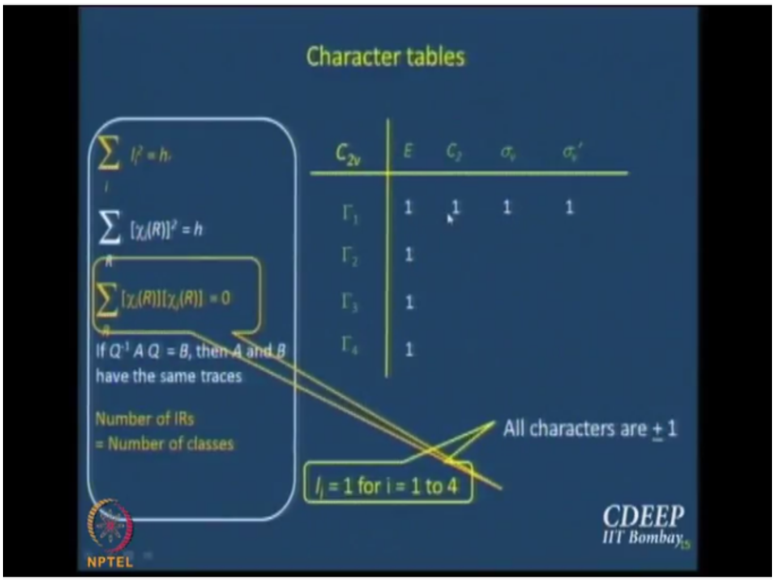


What is the next job? I want to fill in, I want to know what the characters are and to do that we are going to start with we are going to use this. Chi i R square=h, in fact we do not even have to go that far to start with, can you fill in one of the columns, the first column is not very difficult to fill right. If you remember chi i E=li, li is 1 in all these cases, so I can write the first column very easily 1 1 1 1 okay.

And I can write the first row also, the first row is always 1 1 1 1 as many number of 1s that we have to write because that would stand for something that is totally symmetric. What is the meaning of 1 here, no matter which symmetry operation you perform your basis remains unchanged, that is the meaning of character of 1 right. Yes "**Professor - student conversation starts.**"

How come you notice it from there, I did not notice it from one foot away okay. **"Professor - student conversation ends."** So first row is always all 1s that is called the totally symmetric representation. No matter what you do there is no change that will be there for all symmetric point groups. Now we have to fill in the rest. How we are filling the rest? Okay to start with sum over R chi i R square=h.

(Refer Slide Time: 04:09)



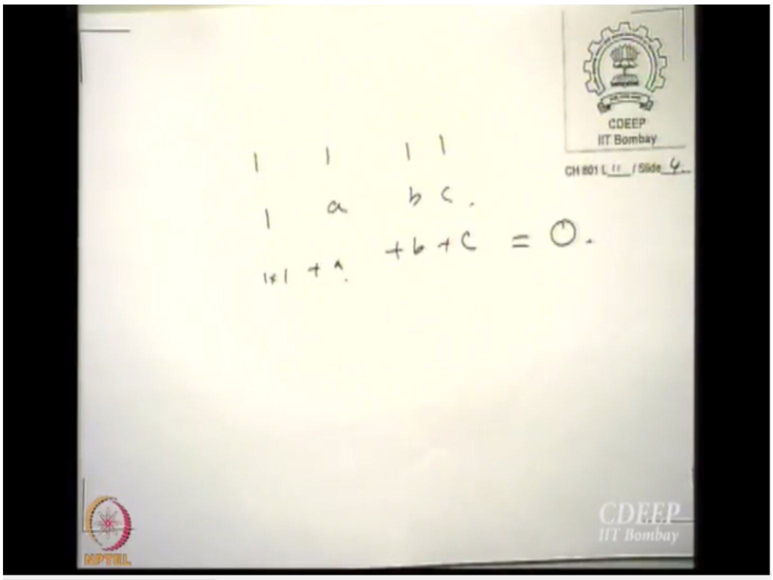
What is h? So the thing is this. They are all one dimensional representations you told me right, so will you agree with me that all characters have to be either +1 or -1, why, what is the meaning of +1? It does not change symmetric right. What is the meaning of -1? Antisymmetric, changes sign. What will be the meaning of 0? Suppose one dimensional representation with character 0 what would it mean? One dimensional representation, one dimensional representation character 0 would mean annihilation right.

It would be annihilation, you perform a symmetry operation and your bases vanishes, not going from one bases to another bases, going from bases to no bases, annihilation. Annihilation is definitely not a symmetry operation right. Annihilation is non-symmetry as it gets, so 0 cannot be there. What about 5? Can I have a character of say 5 in a one-dimensional representation?

Let us see, let us say I have some bases x and I have some symmetry operation R whose character in the one-dimensional representation is 5. Now when the symmetry operation operates on x what does it become? Five times x, 5x right, what is that? If I hold you and somehow stretch you, then you are not going to call it scaling anymore you are going to call it distortion right, so this is distortion.

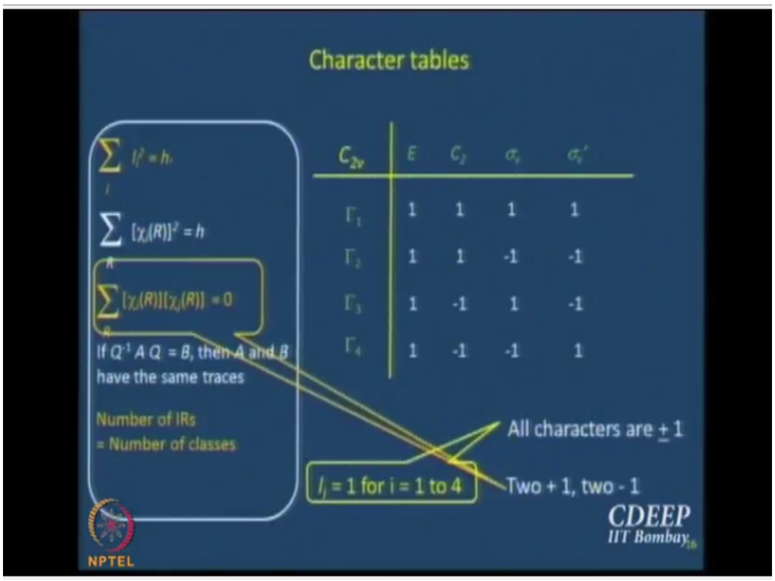
If it is just multiplied by some number that is not 1 then it is distortion. Distortion once again is not a symmetry operation. So it cannot be anything other than +1 or -1. Since all the representations are one-dimensional the only characters you can have are +1 and -1 right. How many +1s, how many -1s? The answer comes from here. Sum over R chi i R chi j R=0 what does that mean? I know one representation anyway 1 1 1 1, now let us say this is a, this is b, this is c.

(Refer Slide Time: 07:05)



So now 1*1+better write here 1 1 1 1, first one is 1 anyway I call this a, b and c. So 1*1+a+b+c that should be=0 and all are either +1s or -1s, what does that mean? Out of a, b and c, two have to be -1, one has to be +1 okay.

(Refer Slide Time: 07:44)

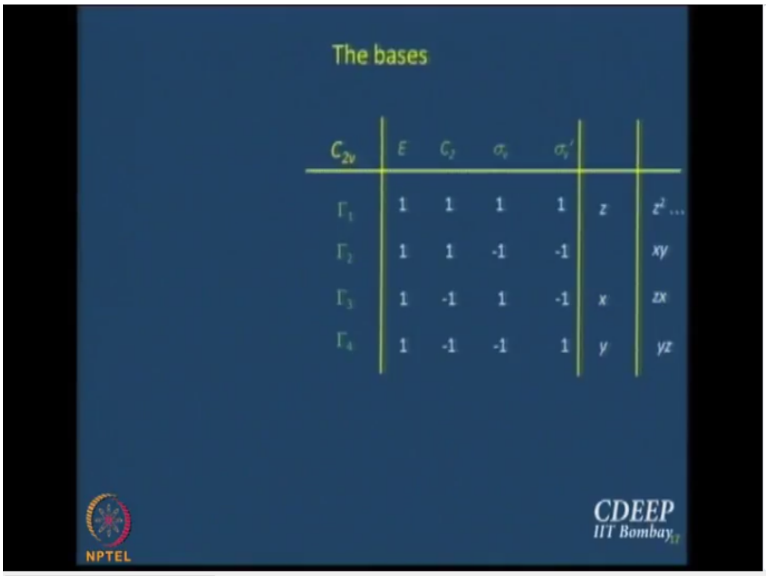


Now knowing that what you do is you fill in the different places by the -1s and +1s right. There are 3 places, 3 places and two -1s, 3 places are to be filled with two -1 and one +1. How many possible combinations are there? Three and how many vacancies are there? 1, 2, 3 right, so it is good LHS=RHS as you always want it to be, no problem with that, you fill in two -1 and one +1.

So in all every representation you should have two +1s and two -1s. So this is what you get, 1 1 -1 -1 1 -1 1 -1 1 -1 -1 1 question. Yes “**Professor - student conversation starts**.” We do not to start with at this point we do not. **“Professor - student conversation ends.”** You will be perfectly right to write 1 -1 -1 1 first but as we see we are not going to leave these representations named so generically gamma 1, gamma 2, gamma 3, gamma 4.

You are going to give them some names and when you give them some names we like to arrange them by those names as well that is why as always I have the benefit of hindsight but to start with if you work this out and if you write it in a scrambled order I am fine okay. Are you okay? Can we go ahead? Okay good.

(Refer Slide Time: 09:26)



So now let us see the bases. What fits in where, let us start with x, y and z. Let us start with z. Where will z fit? If you perform E on z character is 1, if you perform C2 and you consider C2 to be in the z axis, character is 1. Sigma v, what is sigma v is that x, character is 1. What is sigma v dashed, yz, character is 1 alright 1 1 1 1. So that is where z belongs to gamma 1. Z is totally symmetric with respect to all the symmetry operations of C2v.

Now do you think that is the case everywhere, can I have some symmetry species, no can I have some point group where z is not going to be totally symmetric, anything that has a sigma h right. This is z axis. This is usually where sigma h would be. So for reflection with respect to sigma h +z would become –z, -z would become +z. So whenever there is horizontal plane of symmetry, z would definitely not be total asymmetry okay fine.

What about x and what about y? Consider sigma v to be zx and sigma v dashed to be zy. This is this conversion taken to be zx, first one is x after all x comes before y in the alphabet. So sigma v is zx, sigma v dashed is yz right, symmetric with respect to sigma v so x is in the zx plane, it has to be symmetric with respect to sigma v whereas y is perpendicular to it so it has to be antisymmetric with respect to sigma v.

And the same logic holds for sigma v dashed. The behaviour of x and y are just opposite because the plane is now yz instead of zx fine simple okay. Now what about x square where it will belong? X square, suppose I take x square, where will x square belong? X square is always positive right. It has to belong here gamma 1. It cannot change sign is not it? X square cannot change sign, y square will also belong there and z square will of course belong there.

That is not the case everywhere, it is a guess here but that is not the case everywhere okay. So all the square terms will belong here. What about xy? Okay what we could do is you could just multiply the characters and see what symmetry species you get okay, xy that means this and this, you multiply gamma 3 with gamma 4 what do you get? 1*1 is 1, -1*-1 is +1 good, just checking if everyone is awake and attending, 1*-1 is -1, -1*+1 is -1.

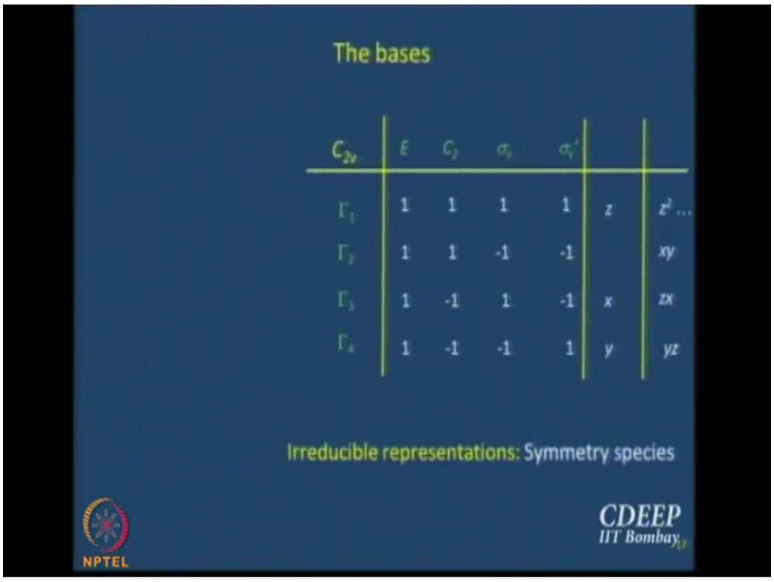
So we have 1 1 -1 -1 gamma 2 so that is where xy should belong. So then tell me where yz should belong? See the nice thing about z is that all characters are 1. What is easier than multiplying by 1s, so yz will belong in this case to the same irreducible representation as y and zx will also belong to the same symmetry species as x right okay. So we have now more or less completely constructed what is called the character table for C2v.

There is something else that you will see in character tables that is Rx, Ry, Rz. For now, I am leaving that aside because we would not really use that too much in this course, that Rx, Ry, Rz just means rotation with respect to x or y or z. "**Professor - student conversation starts**." Not here, that will come later. You will see z square i square will not go there directly. So here z square-x square will belong to the same place.

But here we do not need to invoke that because x square and z square directly belong to some irreducible representation fine. **"Professor - student conversation ends."** So almost done almost but not quite, we better give names to these irreducible representations. We do not want to leave them as gamma 1, gamma 2 and all that and the thing is we do not have to make of our own nomenclature, somebody much bigger has already done it.

But even before you go there, I want to make this point. The another name for irreducible representation is symmetry species and I would like you to understand the meaning of the terms symmetry species. See if we look at this character table what is the information that you get? You get the information of how each of these bases behave with respect to each of the symmetry operations right.

(Refer Slide Time: 15:30)

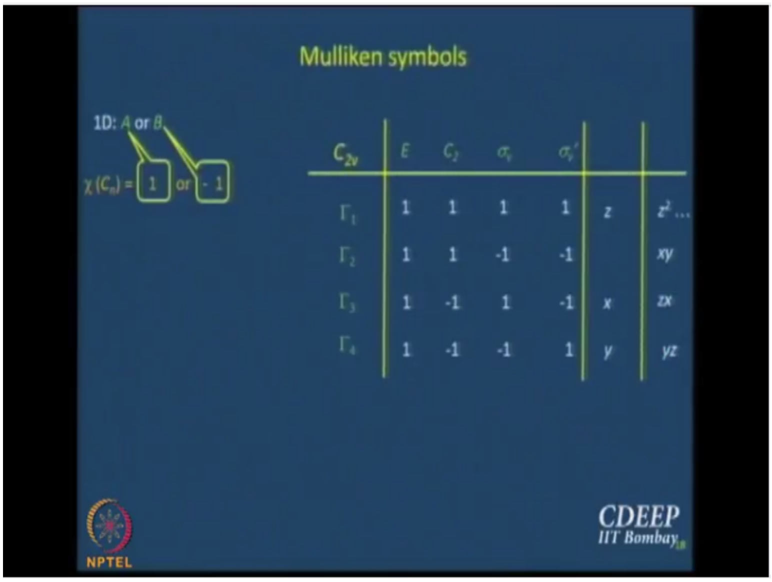


So take x, it is symmetric with respect to E, antisymmetric with respect to C2, symmetric with respect to sigma v, antisymmetric with respect to sigma v dashed. Is there any other symmetry operation left? E, C2, sigma v, sigma v dashed is any other symmetry operation left for this point group? No right. So what we have done essentially is that if you just look at this line the irreducible representation, you will know exactly the complete behaviour of each of the bases with respect to each and every symmetry operation okay.

So that is what tells you about the symmetry behaviour that is why these are called symmetry species. Each irreducible representation is called a symmetry species, make sense okay. In fact, I like symmetry species better than irreducible representations. If you approach it from a mathematical point of view like what we have done then irreducible representation make sense.

If you approach it more from a chemistry point of view, symmetry species is much more (()) (16:45) fine.

(Refer Slide Time: 16:50)

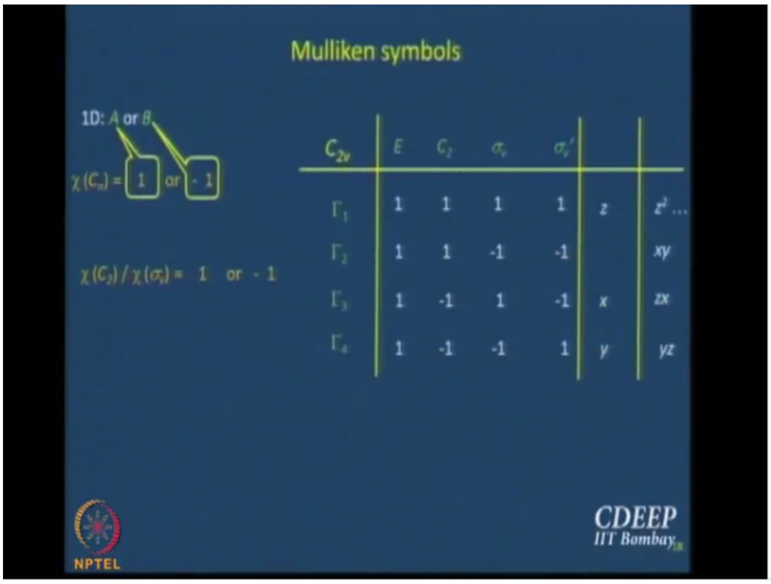


Now let us go there and give the names and the system has been worked out by Mulliken long ago and this is what it is. For one-dimensional representations, the names that are given are either A or B very systematic nomenclature okay, either A or B. When it is A and when it is B? It is not left to you, look at the characters. One-dimensional representation right so characters can be either +1 or -1 that is the advantage.

Now look at if there is a principle axis of symmetry then look at the principle axis of symmetry. What are the characters? If the character is +1 then you call the symmetry species A. If the character is -1 then you call it B alright that is why looking at the character of the principle axis of rotation. Now let us see here, so gamma 1 is it A or B? A, gamma 2 A, gamma 3 B, gamma 4 B.

So we have done some classification already but it is not enough obviously because we have two As and two Bs, how will I know which A is which, how will I know which B is which? So I need a second level of identification, Menak you with me, from where? Okay.

(Refer Slide Time: 18:24)



So believe me when I say that if it one-dimensional, we will call it either A or B, that you better believe. Now what I am saying is this to determine whether an irreducible representation is A or B what we do is will look up the character table and see what is the character for the principle axis of rotation. That is going to be either +1 or -1, see here for gamma 1 and gamma 2 the character is +1, gamma 3 and gamma 4 character is -1.

So if it is +1 you call it A, if it is -1 then you call it B. So these first two IRs are A and second, third and fourth are B but then A and B are obviously not enough, you have to call it A1, A2, B1, B2 something like that, is not it, big A, small a whatever. So we need a second level of nomenclature okay and the second level is provided by of course what is next sigma v, E is hopeless in this matter right.

There is nothing whose character is anything other than 1 in this case. Can the character of E be anything other than 1? Ever not in this case but what happens if you have a two dimensional irreducible representation? Then the character is 2 character of E, is not it. Then, you cannot call it A or B, you do not even call it C or D. You call it E okay and then what if it is 3? Then it is called T, T for three okay.

So that letter will change but in this case what we do is A and B are defined fine, you need a subscript or superscript or something. We start with the subscript, so look at what is next, suppose you have C2 axis perpendicular to the principle axis of symmetry or suppose you have vertical plane, any one of these two, if you have both then you go by the perpendicular C2 axis first that is your own priority.

Do you have perpendicular C2 axis here? No. Do you have sigma v? Yes. Which one do you go by? You go by the one that you have written first alright. You will go by the one that you have written first alright you go by the one that you have written first fine. So then next is very simple, if that character is +1 then there is no point in writing another letter, you write a number, you use a subscript of 1.

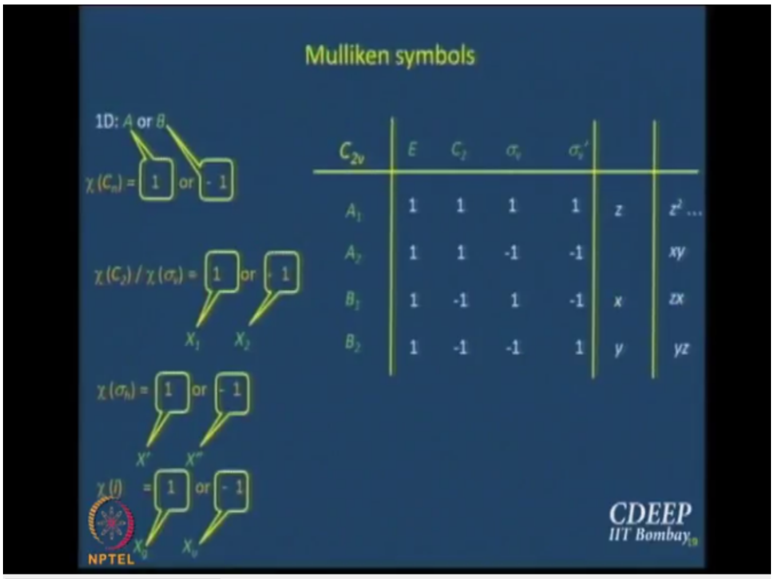
And if it is -1 then you use a subscript of 2, simple. Now see these two are A's gamma 1 is A, gamma 2 is also A. So chi of sigma v here is +1, chi of sigma v here is -1. So this is A1, this is A2 and that is why you asked right why I have written that first because it is A1. So I am writing it in some particular order that is all. Are you all okay with this? Very simple okay. "**Professor - student conversation starts**." To the principle axis of symmetry which is not there.

Then, it would have been not C2v but something like D2 something, something okay. **"Professor - student conversation ends."** So now we know what the names are A1, A2, B1, B2, now the character table is complete except for that Rx and Ry. At least, nomenclature is complete alright. Now the thing is there is no guarantee that all irreducible representations have to be one-dimensional.

We are going to see some example of two-dimensional irreducible representation today itself alright. So what happens if it is 2D it is E, what happens if it is 3D it is T, that is one point. Actually that should come later but even before that the issue is these are not the only symmetry elements right, you can have a sigma h right. If you have sigma h this is what you do. If the character of sigma h is +1 then you use now instead of subscript you use a superscript.

You use prime and if it is -1 you use double frame. These are very simple rules that we unfortunately have to remember, x double frame.

(Refer Slide Time: 23:21)



And then you could also have inversion, center of inversion. So if the symmetry species is symmetric with respect to inversion, symmetric means what is the character? We are only talking about one-dimensional representation so far. What is the character if it is symmetric? 1 then you call it g, then you use a second subscript of g. What is the meaning of g? gerade, gerade means symmetry and opposite of g is U ungerade not symmetric, antisymmetric actually okay.

So now see everybody knows about those two sets of d orbitals, T2g and Eg. Where is the names come from? The names came from here a Mulliken nomenclature, Eg one of the d orbitals in Eg, z square, h square-y square right. They belong to Eg that is because when you look at the character table right of OH octahedron you see that there is a symmetry species that is two-dimensional and the name is Eg that is where your those two d orbitals will belong.

And T2g is another three-dimensional symmetry species, three-dimensional irreducible representation in the OH group that is where the other 3d orbitals belong that is where the name has come from Eg and T2g okay. When you talk about tetrahedral complex for example, do you call them Eg and T2g anymore? What do you call them? Because the question of (()) (25:17) does not arise anymore.

There is no center of inversion okay, so those names actually come from here okay E, T what we are talking about all comes from here and we will have a chance to talk about those as well little later on.