Symmetry and Group Theory
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Lecture - 29
How to Write a Complete Character Table

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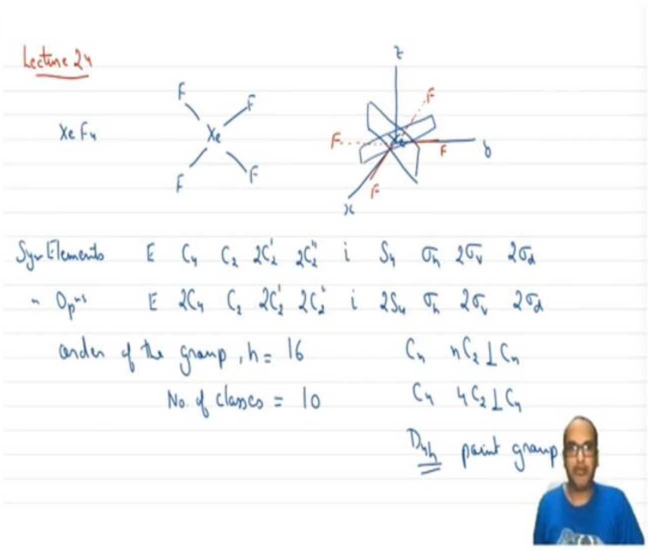

So in this lecture, we will use all the rules and whatever we have learned so far, to take an example and see if we can write a character table from scratch. So let us take an example XeF4 and see what all we know so far, whatever we have learnt in this course and can we write a character table for this particular molecule. So, I am not telling you as of now, what is the point group? What are the symmetry elements or symmetry operations present?

So let us do it from scratch. So, the structure of the molecule is square planner. So, if I try to write down, so it looks like this, now we have learned how to orient this molecule along the axis. So let us, because for unit vector transformations it will be important to orient the molecules along the axis. So, you have x, y, z and you have Xe along the center with, let me use different color, two Xe-F bonds along x axis and two Xe-F bond along y axis.

That is y and -y, Xe F. So now, we should be able to comfortably tell where all the symmetry elements are present, so let us see. So now, let us try to list down all the symmetry elements and then corresponding operations. So, we will first write down the elements here. So, this particular example will revise everything what we have learnt and we will be able to write down the character table.

So, I am taking this example because this is highly symmetric. So, we can also take octahedral example which will be more symmetric than this but then that will take a lot of time in calculation. So, I have picked up a reasonable example, where the order of the group is high, so that we know a lot of elements here. So let us start with E, then you have C4 axis which is lying along z, collinear 2 axis which is also along z then you have let us call it as C 2 prime which will be lying along F-Xe-F which is long x axis.

So this is basically a C2 prime which is lying along the x axis then you have C 2 double prime let us call it as which is lying along x and y axis. Now what else do we have in this? We have inversion center is there. So you have F Xe F everything is getting inverted here, if i will be lying along Xe. Then what else do we have? We will have S4, so S4 will be collinear with C4 and we have a sigma-h over here.

We also have S2 but S2 is basically i, so we do not write S2 here and there is no S3 or C3 because this is containing 4 atoms of fluorine which are separated by 90 degree each. So there is no C3 in this. Then what else we have, sigma-h is the molecular plane which is lying along the xy plane then we have sigma-V which will be lying along, there will be 2 sigma-Vs which will be lying along xz plane and yz plane.

Then we have 2 sigma-Ds which will be bisecting the xy axis and containing the z axis. So it will be something like this. And similarly, we have another sigma-D which will be bisecting x and -y, so something like this. So now that we have listed all the symmetry elements, I am not calling it as group elements. Now let us look at the symmetry operations present in this.

So, E will give you 1 operation, C 4 will give you 2 operations, C4 and C4 cube because C4 square will be C2, C2 will generate only 1 operation because C2 power 2 will be E. So, this C2 prime there are actually two C2 primes and two C2 double primes. This two C2 primes will be one along x axis, one along y axis and the C2 double primes will be in between xy axis and in between xy axis like this.

So along the sigma-D is basically, this will be along the sigma d s. So this will be generating the similar number of operations C 2 prime, 2C 2 double prime, i generates only 1 operation S 4 will generate how many operations? Now so, S 4 will generate 2 operations. Sigma will generate 1, each sigma v will generate 1, so there are 2 sigma v's, so 2 sigma v operations and 2 sigma d operations.

So this tells me that the order of the group h, let us count all the symmetry operations we have 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16. So h is 16 here and I am not going to do all the class calculations but we will just see here number of classes. So we have 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 classes. So we have order of the group, we have number of classes. Now let us also see what will be the point group here?

So point group will be because there is one C4 axis which is principle axis and we have 4C2 axis, so there is a Cn axis and nC 2 is perpendicular to Cn. So, we have C4 and 4C2's perpendicular to C4. This will be falling into D4 point group and because there is a sigma-h present that takes us to D4h. So point group is calculation is very simple, so D4h point group. So now that we have determined what are the symmetry operations present, order of the group, number of classes D4h point group, let us see if we can write down the character table using this information. Let us go to writing character table.

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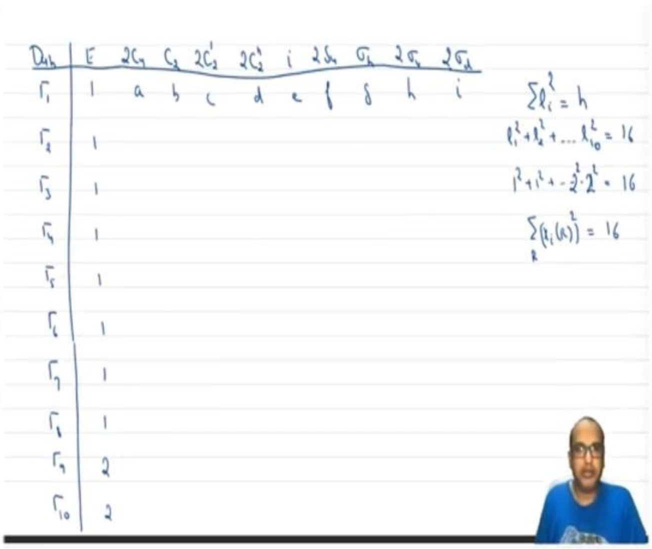

So we have listed all of them 1, 2, 3, 4, 5, 6, 7, 8, 9, 10. So since there are 10 classes, so there has to be 10 irreducible representations. So, we have tau 3, tau 4, tau 5, tau 6, tau 7, tau 8, tau 9, tau 10. Now the first rule which says that the summation li square is equal to h. So that tells you that l 1 square + l 2 square + l 10 square should be equal to 16. So because these are dimensions, so character under E will take the value as l 1. So this cannot be negative or fraction it has to be a real number.

Or it has to be a natural number. So, 0 is also not an option, so starting from 1 and above. So now, if we take all 1, let us say, so we will get 1 square + 1 square, so that gives me 10. So that does not give me 16, so that means, at least one of this will have a 2-dimensional representation. So, if I take 2 here that gives me 9 + 4 which will be 13. So, if I do this then I get 13. So, if I add 1 more to them then I have 8 + 8 which gives me 16.

So, I can say that there are 8 one dimensional representations and two 2-dimensional representations. So, very clearly, I can write one characters for, character under E. So this is 2 and 2. Now also I know that summation over all R i R square is also equal to h which is 16. So that means, for any given representation if I take the sum of squares under characters of different symmetry operations, I should get 16 and this would also be multiplied with the class sizes. So this would mean that if I say this let us say this is a, b, c, d, e, f, g, h, i. Let us go to second page, next page.

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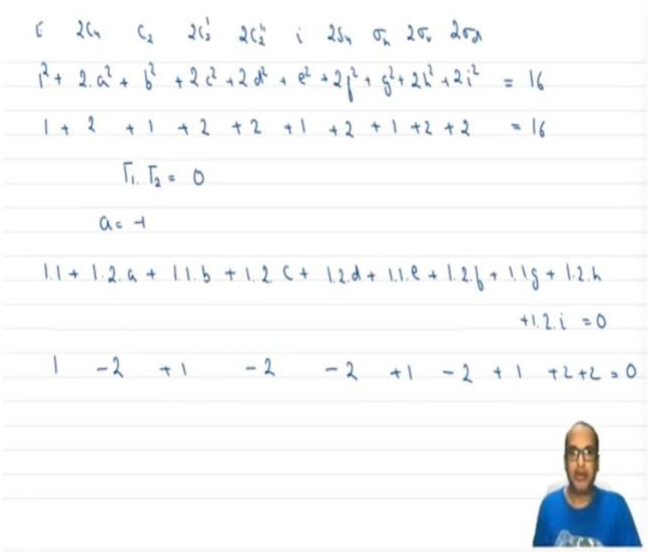

So this gives me 1 square + 2 into a square + b square, let me just write down the corresponding symmetry operation, so that we know what are the class sizes here C 2, 2C 2 prime, 2C 2 double prime, i, 2S 4, sigma h, 2sigma v, 2sigma d, plus 2c square + 2d square + e square + 2f square + g square + 2h square + 2i square this should be equal to 16. So now, if you see that if I put all of them as 1, so do I get the value 16, let us see that. So, this gives me

1 + 2 + 1 + 2 + 2 + 1 + 2 + 1 + 2 + 2. So, I get 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16. So I do get 16. So that means one of the solutions is all of them can be one.

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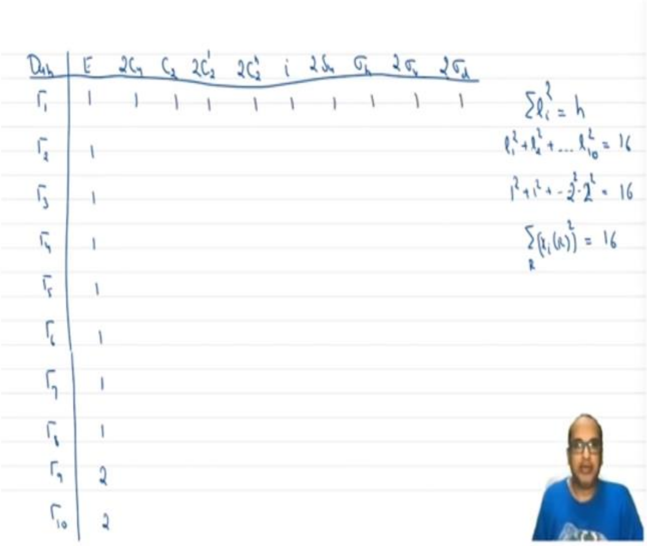

So, I will just erase this and I will substitute it with 1, all 1s is one of the solution. Now let us go to next solution. So, the values here can be positive or negative 1 because negative 1 would also give me 16. Now what all negatives it can take? It can take half of them should be negative, half of them should be positive. Why I say that? Because I can say that tau 1, tau 2 would go to 0. If half of the products will be positive, half of the products will be negative. And then we also have to factor in the class sizes here.

So for example, if I am making a as negative, so that would mean my this 2 is becoming, so I have to have 2 other values as negative. So if I, for example, if I have a as -1 then I have to have at least 2 positives to counter the negative of a, as positive values. So for example then b and e has to be positive, so that the overall tau 1 dot tau 2 = 0, so if I, let us take the tau 1 dot tau 2 = 0 condition and see how does, what do I mean?

Now again, let us see tau 1 dot tau 2 condition is 1 dot 1 + 1 dot 2 dot a + 1 dot 1 dot b + 1 dot 2 dot c + 1 dot 2 dot d + 1 dot 1 dot e + 1 dot 2 dot f + 1 dot 1 dot g + 1 dot 2 dot h + 1 dot 2 dot i should be equal to 0. So, this means, if I am taking a as negative, so I have created -2 here and then I have to take 2 positives to cancel this. And similarly, I have to cancel all of them together, so that half of them are positive and half of them are negative.

So that would mean, let us take a as negative, if I take a as negative then might be, because it is 16, this overall sum is 16, so I should have at least 8 negatives, 8 positives. So let us see that, how does it come? So 1 - 2 + 1 - 2 - 2 + 1 - 2 + 1 + 2 + 2, so if I do this, you see that I have deliberately chosen a, c, b and f as negatives. So that gives me 2, 2, 2, 2 negatives then 1, 1, 1, 1, +2, +2, so 8 positives and 8 negatives giving rise to 0, overall 0. So we have to consider all such solutions where total of 4 terms are positive and 4 terms are negative or total of +8 is coming and -8 is coming.

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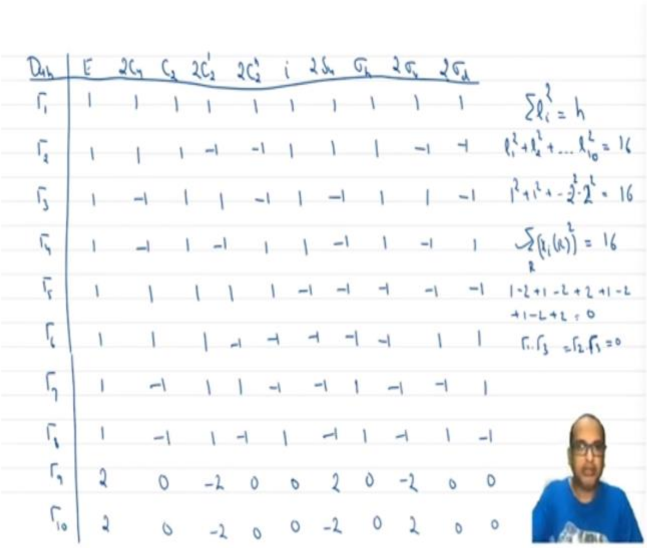

And if I keep doing that I can find all the solutions, because this is the orthogonality condition which will follow. So let us write down the solution. So, I am just now going to write down all the solutions, I will just read out from my notes. So, we have 1, 1, -1, -1, so I take 2 2's as negative and you have 1, 1, 1 over here and -1, -1. So, this gives tau 1 dot tau 2 = 0. This satisfies that condition and also it satisfied the summation over all R, sum of squares will give you 16.

So if both the conditions it has to satisfy, it does satisfy that. Also each of this should follow the orthogonality condition. So if tau 2 is orthogonal to tau 1, it should also follow that tau 2 dot tau 3 is also equal to 0, tau 2 dot tau 4 is also equal to 0 and so on. So that means, as we keep on solving, we increase our chances of solving to a perfect number. So that means, less of hit and trial as we move forward.

So, for example, now for tau 3, we will have 3 conditions, 1 condition comes from here and 2 more conditions will come, tau 1 dot tau 3 = 0, tau 2 dot tau 3 = 0. So both these conditions you can form the equation, the equation is now simple as we have seen and we can, I will just read out the answers directly. So you have -1, the concept is same, so I am not going to do all the calculation otherwise it will take forever to just show the calculations which is now trivial because we have already seen that, -1 then we have 1 and 1 and -1.

So again, what I have done here is I have taken negatives in front of those symmetry operations, where the class sizes are 2. So here 2, here 2, here 2 and here 2. But I also have to take care of that. So, using this tau 1 dot tau 3 will be equal to 0 but I also have to see if tau 2 dot tau 3 = 0 or not. So, we should be, whenever we are writing next IR representation, we should always be testing whether it satisfies all the conditions or not.

So let us see if this satisfies tau 2 dot tau 3 equal to 0 because I have not used it. So 1, -2, +1 so let us just quickly write down, so 1, -2, +1, -2, +2, +1, -2, +1 we have -2, we have +2. So we have 2, 2, 2 so 4 2s are negative and the rest are positive. So that means this will be 0. So it does satisfy tau 1 dot tau 3 which we have used and we have tested now the tau 2 dot tau 3 is also equal to 0. So, using the same principle, let us keep on writing for tau 4.

So, tau 4 will now be, I am not doing this calculation again, I will just read out from my notes which I have done before, so 1, -1, 1, -1, 1. Now for tau 5, again this will be 1, 1, 1, 1 up to here all of them are negatives here. So, at each point, I am not doing it explicitly but when I am writing tau 5 that means, I also tested it for all 4 about that, product of tau 5 to tau 4 will be equal to 0, tau 5 to tau 3 = 0, tau 5 to tau 2 = 0.

So, all these are orthogonal to each other, so I should be testing each and every IR representation whether it is following the orthogonality condition or not. Even if one of them is not followed that means your IR representation is not correct. So, you have to make sure that your IR representation whatever you are writing, it should follow all the rules of GOT. So let us write down for tau 6. First here positive then you have negatives up to and then you have two positives.

For tau 7. Tau 7 will be -1, 1, 1, -1, -1 here just one mistake can actually screw the whole calculation. And the last one-D representation is tau 8 which is 1, -1, 1, -1, 1, -1, 1, -1, 1, -1 and for 2D again using the same rules you can find out the characters for 2D also. So, you have 2, 0, -2, 0, 0, 2, 0, -2, 0, 0 for this one, 2, 0, -2, 0, 0, -2, 0, 2, 0, 0. So you must also appreciate the fact that all the irreducible representations are uniquely defined by different characters.

So, none of these 2 will have same characters at all places, so there would be some difference so that they are uniquely defined. So, now that we have written all 10 representations, let us try to find out the Mulliken symbols corresponding to each of this. So let me just copy this page. So that I can rub this off.

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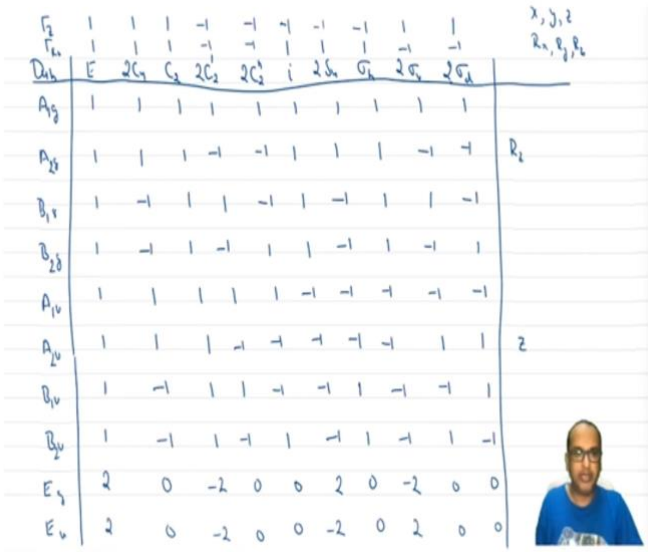

So the Mulliken symbol, let us try to work out the Mulliken symbol. So, the 1D representations as we have learned earlier, so 1D representations have to be either A or B. Now between A and B, it will be A if it is plus or symmetric with respect to principal axis which is C4 here otherwise it will be B. So, I can say that, this will be A, this will be A because it is +1 under C 4, this 2 will be B. Again, I will have 2 A's here and 2 B's here.

And then I have two 2-dimensional representation which we will be E, now doing this, so we have to go one more step forward because it does not differentiate between tau 1 and tau 2, tau 3 and tau 4 and so on. So, both of them are still A, both of them are still B. So we have to uniquely define the Mulliken symbol for each of this. So now if we go to second part, this second step, second step will be, if it is positive under the perpendicular C2 axis or negative or symmetric under the perpendicular C2 axis or negative under the perpendicular C2 axis.

And if there is no perpendicular C2 axis, we do have perpendicular C 2 axis. So if there is no perpendicular C2 axis then we have to go to sigma-v. Also, we can take symmetry under inversion which is which will give me a subscript of g or u. So let us write down, so these all 4 are positive, so I can write g here, g here, g, g and these are all negative, so negative under i. So this will be u, u, u, u, u and this will be g and u. But it still does not differentiate between A g and A g, A u and A u, B g and B g, B u and B u and so on.

Now, so to differentiate between Ag and Ag, I can see that this one is having positive character under perpendicular C2, this one is having negative character under perpendicular C2. So that means, I can say that this one is 1, this one is 2. Similarly, this is positive, this is negative, so I can say 1, 2. Again it is positive, negative I can say 1, 2 again this is positive negative, so this will be 1 and 2. So Eg and Eu are already defined. So, there is no need to further give any symbol because this is already uniquely different.

So that gives me the Mulliken symbols for all of this. Now let us also try to work out the basis sets because it is still not complete character table. So let us try to work out the basis set. So, unit vector transformations that we have to take x, y, z and Rx, Ry, Rz. So, this is a square planar molecule oriented where the molecular plane is lying along xy axis, so z axis is not going to be mixed with xy for sure, whereas because it has a C4 axis, so x and y are going to be mixed because we already have seen that there is a 2D representation.

That means x and y are going to be mixed. So let us work out the symbol for z first and then we will do it for xy. So let us see which one will give you z. So z let us say, so character for tau z, we will see which one of them is corresponding to say. So under E, it will be +1, under C 4 it will be +1, under C 2, z does not change. C 2 prime, z does change to negative because C 2 is the perpendicular C 2.

So +z goes to -z, against C 2 double prime, +z goes to -z, i it does go to -1 then we have S 4, so S 4 again z goes to -1, sigma h. Sigma h is the molecular plane, so again z goes to -1. So we have sigma v, z is positive, sigma d, z is positive. So this tells me, so if I now match these characters with one of these characters I see that just matches nicely with A2u. So, tau z and A2u are same so that means, I can write very safely here that z is following the basis for A2u.

Now similarly, let us do it for R z. So, tau Rz, so what will be for tau Rz? The tau Rz E will be 1, C4 principal axis the character for z and Rz will remain same. So that will be 1, 1, 1, 1 and then for C2 prime again it is rotation. So, character will be same, so you have -1, -1. So for i, it should be now +1. We have seen the thumb rules for S4, again it will be +1 because for z it takes the opposite character otherwise for sigma h, this is sigma xy.

So in that case z will go to +1, R z will go to +1 then you have sigma v, sigma v's, sigma basically it is containing the z axis. So that means, this will be -1 and this will be -1. So, this tells me that this is the representation for A2g. So, I can say Rz is forming the basis here. Now this is done, now for xy and Rx Ry, so xy will clearly be either Eg or Eu and similarly Rx, Ry will also be one of those Eg or Eu. So let us try to look for which one is forming for. So x and y together, let us say we take, so let me again go to next page.

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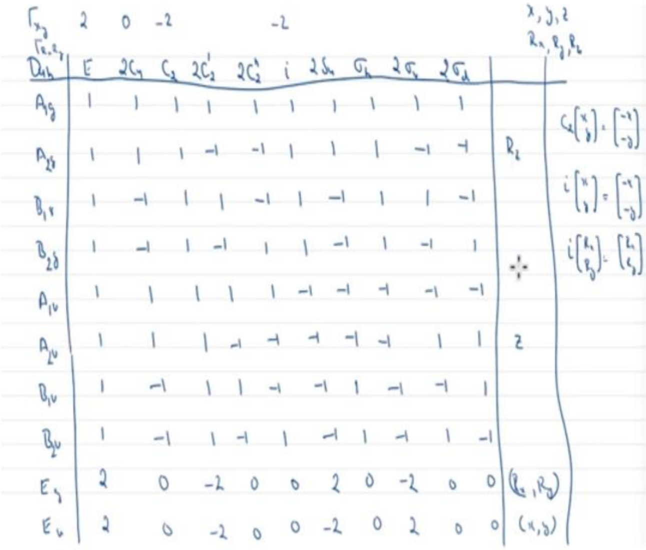

So now, let us try to write for tau xy. So for E, x remains at x, y remains y, so that means, I will get trace as 2. For C 4, x goes to y, y goes to -x that means it will be 0, 0, both of them will be 0 because x is, suppose if x goes to -x then for x it will be a -1 trace and for y it will be -1 but, in this case, x goes to y because it is a C4 and y goes to -x. So, both of them will contribute nothing to diagonal and that will be 0, for C2, it will be let us say if I do a C 2 operation here C 2 on x, y. x goes to -x, y goes to -y.

So that means both of them are at giving -1, -1, so this will be -2 over here. So that still does not differentiate between E g and E u because, so far we have seen 2, 0, -2, 2, 0, -2 and then here also it is 2, 0, -2. Actually we should directly see for i because i and sigma h are the only one which are differentiating between the 2. So let us see the character under i. So i, if it is applied to xy what happens? So x goes to -x, y goes to -y, so it should be -2.

So -2 meaning this one that means, I can already see that Eu will be the representation based on characters under i. So Eu will be the representation where xy together will be the basis. Now similarly, if I do it for tau R x R y, the only differences with i or sigma h, so we can directly see that, so if I do i Rx Ry, what I get is Rx Ry. So remember the thumb rules, the rotation vectors do not change their assignments under inversion. So that means this will be +2. So Rx and Ry will form the basis of this.

Now that is done, so that means we have almost completely written this, the only thing which is left is now the binary products which I leave it for home assignments. So, try to work it out yourself that, what will be the basis for different binary products. So, you can take example of d-orbital's as we have discussed earlier and see for yourself that what d-orbital's will form basis for which of these representations and that will go into next column, so here.

So now, we have seen clearly that how to write. So, starting from the molecule, how to list down all the symmetry elements, symmetry operations, find out the point group and then number of classes, order of the group and so on so forth. And then using all of this, write down a character table, complete character table from scratch, corresponding Mullikens symbols for each IR representation, find out the unit vector transformation as the basis for different representations.

So that finishes a great orthogonality theorem discussion with an example now. So in the next class, we will be looking at cyclic groups and how to write representations for cyclic groups. Thank you very much.