Symmetry and Group Theory
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Lecture – 25
Tutorial - 5

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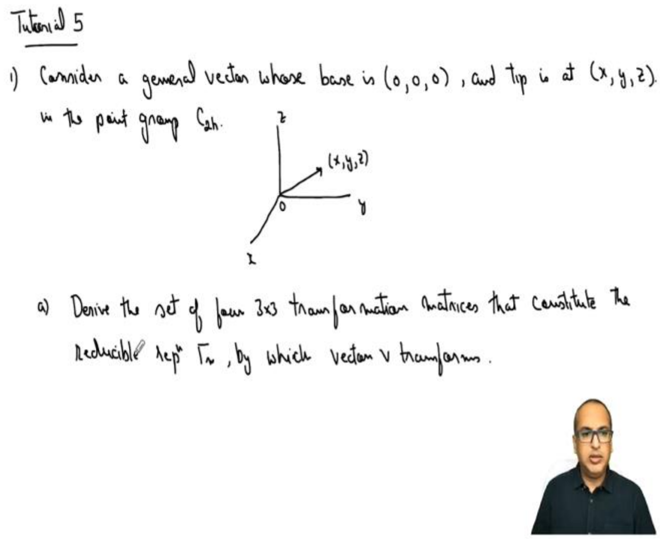

So, welcome to this week's tutorial, tutorial 5. So, let us see what we have is, try to solve a couple of questions which are of relevance with respect to this week's lectures. So, question number first is let us consider a general vector whose base is 0, 0, 0 that is origin and tip is at any general given point x, y, z in the point group so the overall environment of the molecule is in or of vector is in the point group C2h.

I am picking up a relatively easy system, but you can work out similar problems in different point groups. So, how does it look? So, you have right-handed coordinate system, so you have x, y, z and any given vector the origin is 0 and its tip is x, y, z and you know how to calculate the length of this vector and so on. So, now let us start with the parts of this question, so this is what you have been given.

Now what you have to do is, derive the set of four 3 cross 3 transformation matrices that constitute the reducible representation by which, let us call this representation as tau m by which, the vector v transforms. So, what you have to do is? you have to derive a set of four 3 cross 3 transformation matrices that constitute the reducible representation tau m by which this vector v transforms. So, this vector v transforms what do you mean by that? So, origin is supposed to be not changing. So, it is supposed to fix and only the vector tip supposed to be moving under different symmetry operations. So, what are the different symmetry operations under C2h point group?

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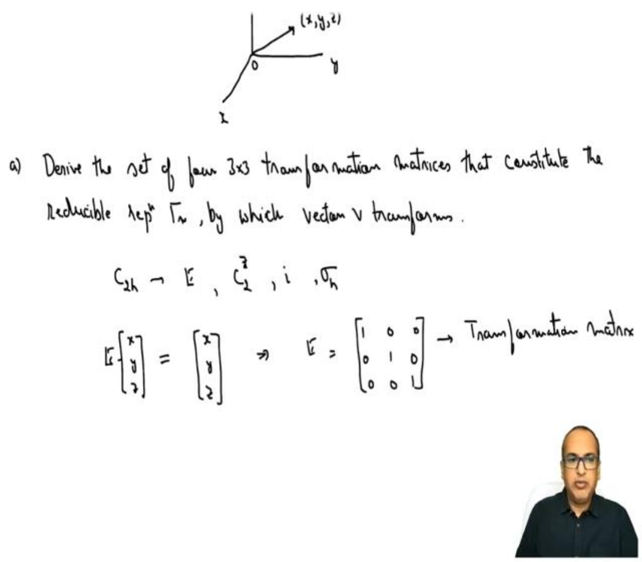

So, under C2h we have E, C2, i and sigma-h. So, the C2 is along z axis, C2z so now under each of this symmetry operation you have to see what will be the transformation matrix. So that it will define how vector v will transform. So, how do we do that? So, this is nothing but the unit vector transformation problem which we have already learned. So, basically what the question is asking is that what happens if you what will be the E matrix.

If I transform x, y, z so this vector v can be written in terms of a column matrix x, y, z where x, y, z are the coordinates of the tip of this vector, and what happens to this after I transform it using E. So, E does not do anything. So, x, y, z remain as x, y, z this implies that E is a unit matrix of order 3. So, what I have is 1, 0, 0, 0, 1, 0, 0, 0, 1. So, this is my transformation matrix. This can also be called as transformation matrix.

So, similarly we have to calculate all the transformation matrices all 4 transformation matrices which will be 3 cross 3 order. So, because we are in x, y, z system so that is why this will be 3 cross 3 order. So, basically the dimension of the space in which we are it is a 3-dimensional space. So that is why this will be 3 cross 3, but this can be multi dimensional this can be lower dimensional than 3. So, depending on in what dimension we are working the order of the matrix will change.

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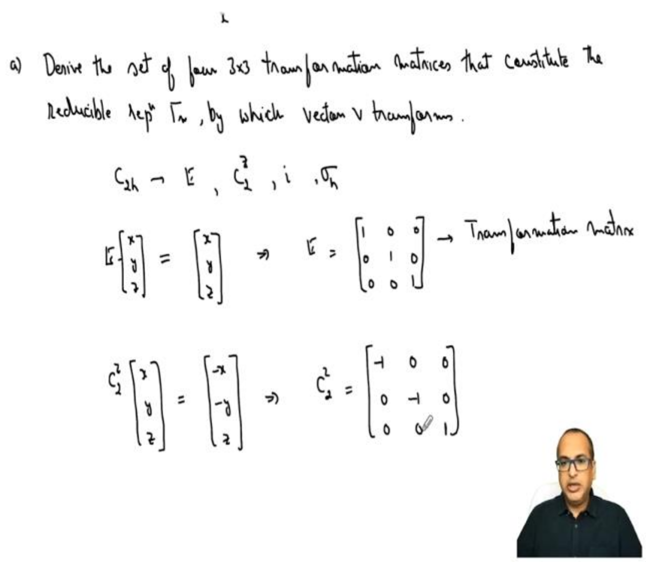

So, now let us do the same thing for C2z. For C2z, if I operate C2z on to the tip of the vector that is my x, y, z now understand that what happens to x so if I go back to the picture here so if I do a C2z operation so my C2 is lying along that axis my x axis moves to -x, my y is moved to – y, and z remains and z. So that means this vector will change its coordinates as -x, - y, z. So, now let us write it down here. So, this is the resultant vector -x, - y, and z.

So, this implies C2z can be written as so now you have to imagine a matrix which would multiply with x, y, z to give you this. So, you must be very thorough with the matrix multiplication. So, now I understand that if I multiply -1 with x, I will get - x. So that means it will be -1 here and since x is remaining as x, there is no other component in place of y and z. So, it will be 0 and 0.

Similarly, y is multiplying with -1 to give you y suppose if there is an x component or y component or z component then I will have some numbers here also but since there is no x and z here only y so that means I will have -1 here and 0 and 0 here. Now for z again this will be 0 and 0 and 1. So, this is my transformation matrix for C2z.

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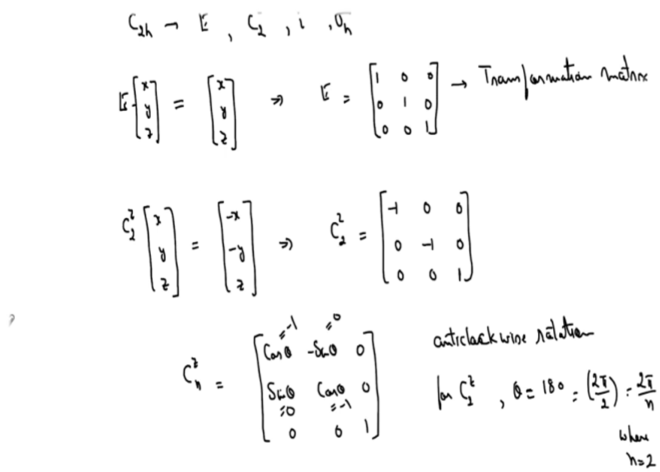

So, you can also write the similar thing for a general. So, in general we can say let us write the general one Cnz. So, any Cnz matrix can also be written as that we have already calculated. So, mind you that the rotation here will be anti-clockwise rotation because if you are using clockwise rotation the result will be different. So, this you have to keep in mind that all the rotations that we are doing in this class are anti-clockwise so cos theta, -sin theta, 0 then I have sin theta, cos theta, 0, 0, 0, 1. So, z does not change, so that is why +1.

Now if I put 180-degree cos 180 degree will be -1. So, for C2z, I can said theta = 180 degree. So, this will be 2pi / 2. So, if it is 2pi / 2 you will have 180 degree, or I can said 2pi / n where n = 2. So, because theta is 180 degree my cos theta = -1, sin theta = 0, sin theta = 0, cos theta = -1. So, I get the same matrix here. So, either you use the general formula or you actually do the transformation on x, y, z and see where they are going, either way you should get the same result. So, this is my transformation matrix for C2z.

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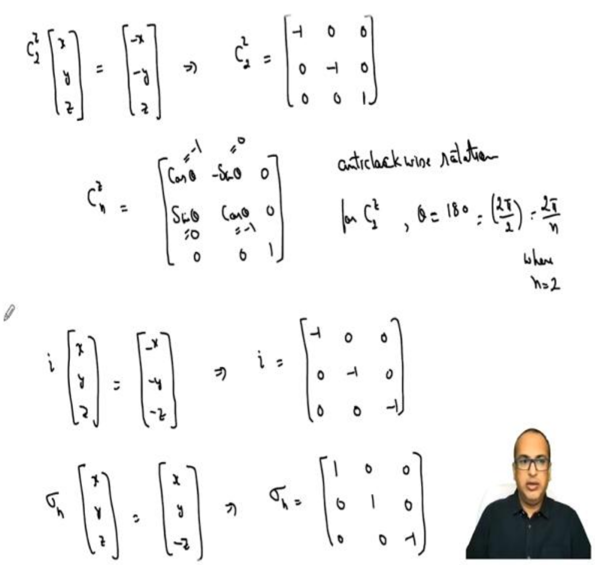

Now let us write down for i and sigma-h. Now if I do i operation on x, y, z by definition i should flip all the coordinates. So, i should get -x, -y, -z. So, now the vector basically is moved to the opposite quadrant in the 3-dimensional space. So, x goes to -x, y goes to -y, z goes to - z. So that means i is again a unit vector but with all 1s as -1, 0, 0, -1. Now for sigma-h if I do sigma-h on what will be the orientation of sigma-h that is important to understand.

So, by definition it is a horizontal plane a horizontal plane has to be perpendicular to the principal axis, principal axis C2z here. So, if perpendicular if C2z or principal axis is lying along z axis so that means my sigma-h will be lying along xy. So, if sigma is lying along xy or xy axis are lying on to the sigma plane they will not change their sign. So, x remains as x, y remains as y and z changes its sign to - z.

So, if we go back again here so if this is my sigma my x, y will not change the z actually goes down to -z. So that is how it changes to -z. So, once you have identified the final result all you have to do is now identify what will be the matrix which will multiply with x, y, z to give you x, y, -z. So, now that is simple to find out because x is multiplying with 1. So, there is no y component there is no z component in this column in this row. So, again you have 0, 1, 0, 0, 0, -1.

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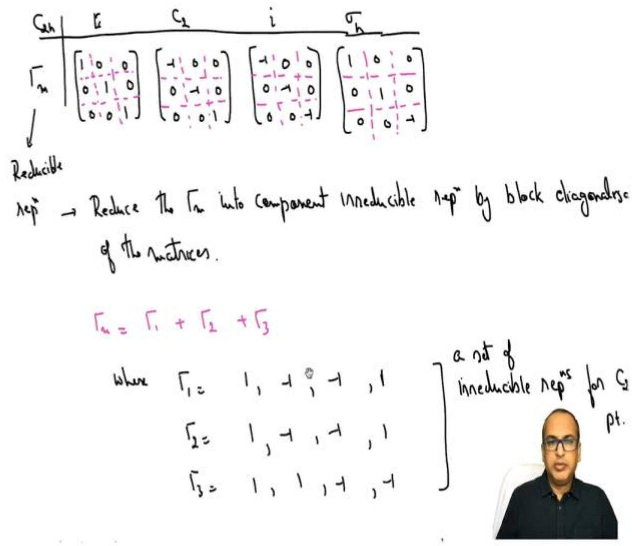

Now, so my set of transformation matrices or my reducible representation I can write as C2h, E, C2 , i, sigma-h now this is my tau-m which is the irreducible representation. So, I will say this is my which the question asked reducible representation consisting of 3 cross 3 matrices. So, this is my for C2 I have -1, 0, 0, 0, -1, 0, 0, 0, 1. For i I have -1, 0, 0, 0, -1, 0, 0, 0, -1. For sigma-h I have 1, 0, 0, 0, 1, 0, 0, 0, -1. So, this is my tau-m which is reducible representation. So that is how so you can also call it as set of transformation matrices under which vector V will transform in C2h point group.

Now next is, the next part is reduce the tau-m into component irreducible representations. So, we now know what is reducible and what is the irreducible representation by block-diagonalization of the matrices. So, now what you have to do is you have to block-diagonalize these matrices so what do you mean by block-diagonalize? So, what we have to do is we have to see if I can find out only diagonal elements.

So, block-diagonalized means that only diagonal elements matter and rest where the elements are 0 it does not matter. So, I can see that this is my first element and this is my second. So, rest other elements are 0 so this is the diagonal which is already block-diagonal. So, similarly and it has to follow in all 4 matrices. So, suppose if there is a number here let us say if there is a number 1 here.

In that case I would not be able to consider this -1 and this -1 as blocked diagonals. In fact, I will have to consider this 2 cross 2 matrix and if that happens I have to consider the 2 cross 2 matrix in all 4 cases. So, because it is 0 in all the cases I can consider 1 cross 1 matrix in all of them as block matrices. So, I will just write 0 back again. So, we have already discussed what is block-diagonalization? So once you do this.

Now I can say that this matrix representation or this reducible representation tau-m can be written as tau 1 + tau 2 + tau 3. So, what do you mean by that, where tau 1 is nothing but I will write first component here 1, -1, -1, 1. So, this 1 coming from here this -1 coming from here -1 coming from here. So, respective elements of all the matrices basically, tau 2 again 1, -1, -1, 1. So these 2 are same so there is no dot here.

So, for tau 3 this is the third element which is 1, 1, -1, -1. So, now if you notice let us not discuss that because we have not discussed Mulliken symbols yet, so we will do that later. So, these are the set of irreducible representations for C2h point group.

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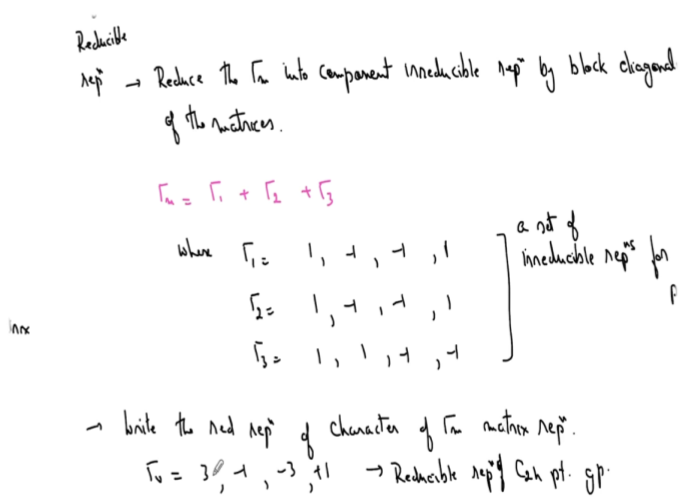

Now what is the next part of this question? So, this is, so write down write the reducible representation of characters of tau-m matrix representation. So, what do you mean by writing tau-m writing the characters of tau-m matrix representation. So characters means nothing but the sum of the diagonal elements. Now these some of the diagonal elements are nothing but called a trace or character, trace of the matrix or character.

So, how do I write? So, let me just look at this is matrices. So, what I will have is tau let us call it as tau v tau v is so if I sum all the diagonal elements here what do I get? 3, this will be -1, this will be -3, this will be +1. So, I have 3, -1, -3, +1. So, these are the set of characters which are obtained from summation of the diagonal elements of the matrices. Now this is also called as a reducible representation because this can be reduced into these ones, reducible representation of C2h point group.

As we know that there can be in finite different numbers of reducible representations. So, this is 1 of the infinite possibilities of reducible representation under C2h point group. So that should be clear.

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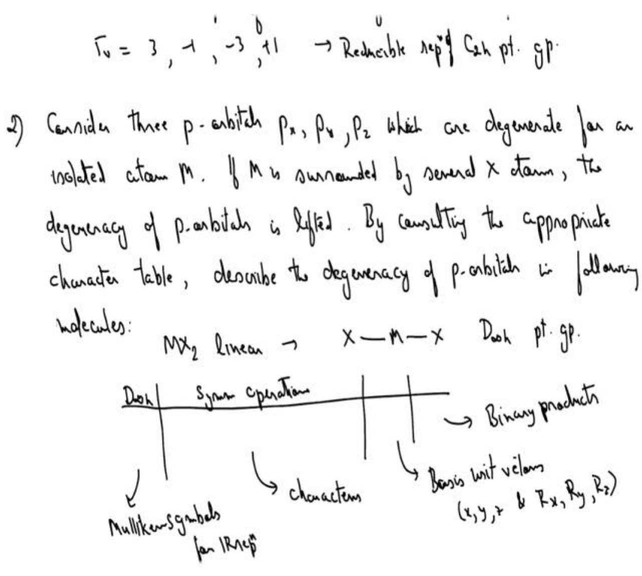

So, now let us move to second question. So, now let us see consider three p orbitals px, py, pz which are degenerate for an isolated atom let us call that atom m. So, if you have an isolated atom the three p orbital's would always be degenerate If there is no ligand or there is no surrounding atom to it, so p, by degenerate I mean that they will have equal energy. So, by symmetry they are forced to have equal energy they are identical.

So, px, py, pz orbitals would be identical to each other and thus they will be degenerate in energy they will have same energy but now what happens if M is surrounded by several x atoms the degeneracy of p orbitals is lifted. So, if degeneracy is lifted, can we use symmetry arguments to say in under what molecular shape the symmetry forces some of the orbitals to remain degenerate or separate from the other orbitals.

So, by consulting the appropriate character table by consulting the appropriate character table describe the degeneration of p orbitals in the following molecules. So, now you are given some molecules and you have to describe whether the p orbitals will be degenerate or not how do we do that? by looking at the character table? So, let us start looking at that. So, the first molecule is MX2 linear. So, but we should know which character table to look.

So, for MX2 linear what will be the molecular shape, molecular shape is like this. what will be the point group? point group will be D-infinity-h. Now this is my point group now what you have to do is in the character table there are several areas in the character table that we will learn maybe in the next class. So, if you see character table D-infinity-h, this area will be in the symmetry operations listed on various characters are listed, Mulliken symbols for IR representations are listed, and here is the basis unit vector rotation as well as translational.

So that is x, y, z and Rx, Ry, Rz are set are listed. And in this area binary products of the unit vectors are listed, binary products. So, now what you have to do is you have to see under this area this particular area so what are how are my x, y, z listed. So, let me just write down for one particular example and that will make it clear. So, let us go to next page.

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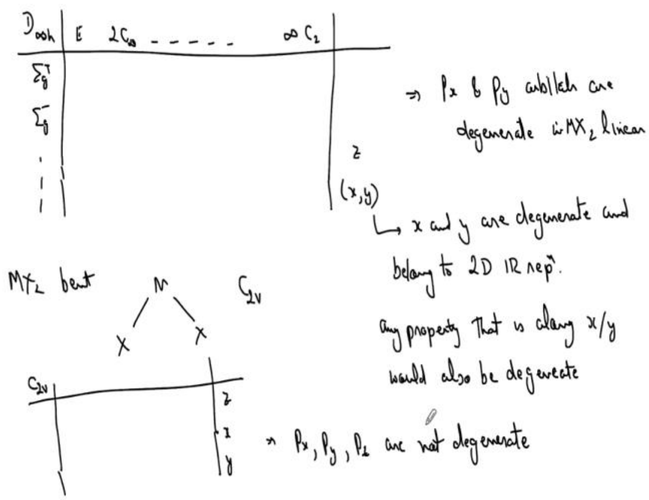

So, for D-infinity-h it looks something like this. So, there are several lines in the symmetry elements 2C-infinity and so on so forth. So, infinity C2 and so on, so here again there are several symbols written do not worry about what those symbols are we will get it clear in the next few classes sigma g- and so on so forth. So, in certain area here could be written z and it will be written here x and y.

So x comma y and within bracket means that this type of arrangement means that x and y are degenerate and belong to 2 dimensional irreducible representation. So, this would mean that any property that also lies along x and y, would also degenerate. So, any property that is along x, y would also be degenerate. So, z is separate from x y. So, suppose if z is also written as like that so that would mean that x, y, z all three are degenerate.

But that is not the case. In this case z is separated from x and y this is purely due to symmetry arguments. So, this would imply that px and py orbitals are degenerate in MX2 linear molecule. So that is very, very simple just look at the character table, find out whether x and y are written together within brackets, or separately that would define whether px, py, pz orbitals are degenerate or not now let us see few more examples.

So, next example is MX2 bent so how would the molecular shape will be this is like a water molecule. So, you have MX2, the point group is C2v. So, now if I refer to the C2v character table it gives like so you have z here then x and y in 3 separate rows. So, z corresponds to some other some IR representation, x and y corresponds to some other IR representation. So that means x, y, and z are not equivalent to each other that would imply that px, py, pz are not degenerate. There can be accidental degeneracy which is a separate thing but because of symmetry you can argue that because of symmetry arguments px, py, pz are not degenerate. So, this is for MX2 bent.

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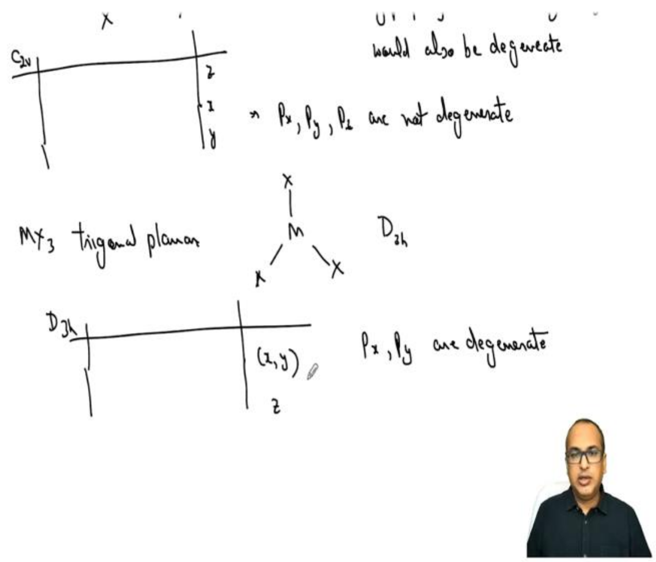

Now let us look at more examples. What is the MX3 trigonal planar? so if you screw up here in the point group determining point group of the molecule or the shape of the molecule then you will get a wrong answer. So, if it is a trigonal planar how the molecule would look like this will be like BF3 all of them are in 1 plane. So that means the point of is D3h. So, for D3h what I have here is x, y, and z are in separate rows. That means only px, py are degenerate, z is separated from px and py. So, very, very simple. But very important application? Just by looking at symmetry you are saying something about energy.

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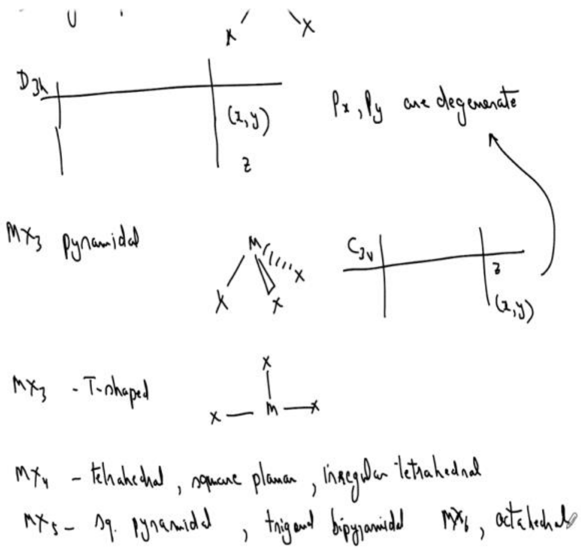

MX3 pyramidal, so MX3 pyramidal like ammonia so you have so this will be C3v point group. So, under C3v, z coming here and x, y coming here. So, this also implies px and py are degenerate. Let us look at more molecules. You have MX3 T-shaped. Now what will be the point group of this T-shaped molecule? Let us draw the molecule first you have M, X, X, X. So, try to work out this thing as a home assignment.

So, I will leave some of those examples as home assignment. So, you have MX3 T-shaped and then let us increase it MX4 tetrahedral. So, all you have to do is just look at the find out what is the point group look at the character table and look at the unit vector transformations whether it is transforming together or separately if it is together, it is degenerate, if it is not it is non degenerate so very, very simple.

So, tetrahedral MX4 can also have square planar can also have irregular tetrahedral. So, this example we have not discussed, but I would like you to find out what is irregular tetrahedral and how does it what will be the point group of that. So, MX5 squared pyramidal, then trigonal, bipyramidal and last will be MX6 which will be octahedral. Find out how the symmetry of p orbital changes whether they will be degenerate or not in all of these shapes. So, I think that will be all. Next class we will discuss more problems. Thank you very much.