Symmetry and Group theory
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Lecture – 22
Reducible and Irreducible Representations

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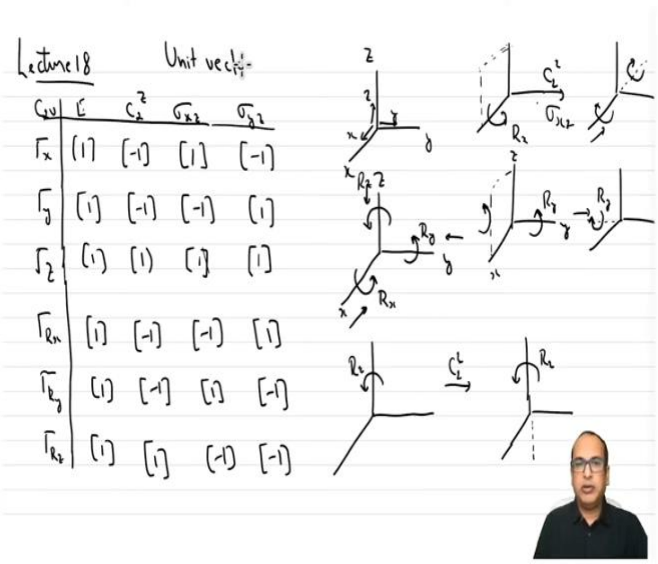

Welcome back to lecture 18. In the last lecture, we were looking at unit vector transformations. So, we saw an example of water molecule and there we saw how under C2v point group we can operate different operations on to unit vectors that is the linear vectors along x y z direction in an orthogonal coordinate system and saw what are the matrices corresponding to that and how those matrices are 1dimensional matrices because there is only 1 basis set in that. So, just to remind you again.

So, let me just write it again. So, C2v point group, so, we had E, C2z, sigma-xz, sigma-yz and under this if we had tau-x, so, E operating on x will give you x so, that takes the character or the matrix as 1, then C2z takes it as -1 because x goes to – x, then sigma-xz x remains as x so, we have +1, and for sigma-yz it will be -1. So, writing this should be fairly simple. So, for y again will be 1, C2z again will be - 1.

Now, this will be -1 and this will be +1, and for tau z all the characters or matrix elements will be just +1. So, that should be very clear. So, this was when we considered unit vectors, which are linear vectors along x, y, and z. So, linear vectors of unit length. So, this is my x vector, this is my y vector and this is my z vector. These are the unit vectors and we saw how the transformation gives us the matrix representations.

So, why are we worried about unit vector transformations, we will come back to it a little later. But let us first see how to do it. Now, as I mentioned in the last lecture, there is also a vector which is called as rotational vector. Now, rotational vectors are defined as the sense of rotation of x axis and is represented by Rx. Sense of rotation is taken as anti-clockwise when I am looking from positive side of x axis towards origin.

Similarly, sense of rotation of y axis is taken as Ry vector and again, it is anti-clockwise when I am looking from positive side of y axis towards origin and similarly, for z. So, I am looking from this side, so it appears as anti-clockwise. So, these are also vectors, which will be needed later on. So, we will see how various transformations look like under Rx, Ry, and Rz as the basis set. This is Rz.

So, let us try what happened? So, E will be the simple case, I am not going to discuss that because E will not going to change anything. So, all the characters under E for Rx, Ry, Rz will be one just like for tau x, tau y, tau z. So, let us extend this table and tau-Rx, tau-Ry, tau-Rz and as it is a single basis set, so the order of the matrix, or the dimension of the matrix will be 1 cross 1.

So, there will be just only one element in the matrix. So, we can write down for all 3 cases, it will be 1 that is very simple to see. Now for C2z, so we have to be very careful in visualizing these rotation matrices. So, if I do C2z operation on Rx vector, so Rx vector, so let me draw it here again, only for Rx. So, if I do, this is my Rx and if I do a C2z operation, what do I get? This is my - x axis and this is how it looks.

The vector changes its direction. So, if I am looking from this side, it now I did not draw it correctly. Let me just draw it again. So, if I now draw it correctly, it would appear clockwise this is the direction it will take if I do a C2z rotation. So, consider this the head part of this vector will go to the left side and the tail part will come here. So, that is how it will appear like this, it will appear like this.

It is not straightforward to see, but like if you try and practice it with rotation, do it by hand and then see for yourself, it will be simple enough. So, in that case, this will become a -1 element. Now, let us look at for again for C2z but for Ry. So, this is the original Ry. This is my x y z. Now, if I do a C2z operation, this vector will move over here. This will come over here. So again, it will appear like this and if I am visualizing from this side, because my visualization does not change.

So, if I am visualizing from this side, it will appear as clockwise. So, it should, the vector becomes like this. Ry. So that also gives me a character as negative 1, in this case. So, I hope it is I am making it clear. So, let me just draw for now, Rz operations as it is anti-clockwise from here. This is my Rz. So, I am looking from this side and I am drawing it anti-clockwise. So, it is the sense of rotation of this particular axis. So, this is it is curving like this from behind and coming ahead.

So, it is going behind the line and then coming up again. So that is how the anti-clockwise rotation of vector would look like if I am looking from the top right. So, now, again, if I do a C2z on this, what do I get? So, I do get is no-change. So that means I will get because this axis is collinear with z axis, C2z, so there would not be any change and Rz will as Rz or character will be 1 of the matrix will be 1.

So that should be clarified. So now, let us look at what happens if we do sigma-xz operation on to Rx. So here is your Rx, if I am doing sigma-xz operation, xz is this plane, which is bisecting this particular vector. So, if I am reflecting anything, which is crossing this plane, the let us say if I am doing sigma-xz now, the vector will turn its direction. If we do sigma-xz Rx will change its direction and it will now appear to us moving clockwise.

So, that would mean that it takes negative 1 as the matrix here. Now, if I do sigma-xz again, this plane reflect Ry by sigma-xz this vector would be just represented as a mirror image. So, this vector would come to the set and then if I am still looking from this side, it will still appear as anti-clockwise. So, sigma-yz on Rx will give me Rx. So, there is no change in sign. So, it will remain as +1.

So, similarly, again, if I do sigma Rz on Ry, so sigma Ry would remain as 1 whereas if I do sigma-yz on Ry, it will turn out to be negative. So, you have to do it yourself and try to see if you cannot understand this. I would say that what you can do is you can take a paper strip arrow and take a cut out in an anti-clockwise direction and then do the rotation by hand and then see for yourself if the direction changes or not we can discuss that more in the interactive session. If this is not clear, this operation is not clear.

So, for Rz again, because both planes are containing z axes in both the cases it will be negative. So, try to visualize this and see if you can do this unit vector transformations for any other point group also.

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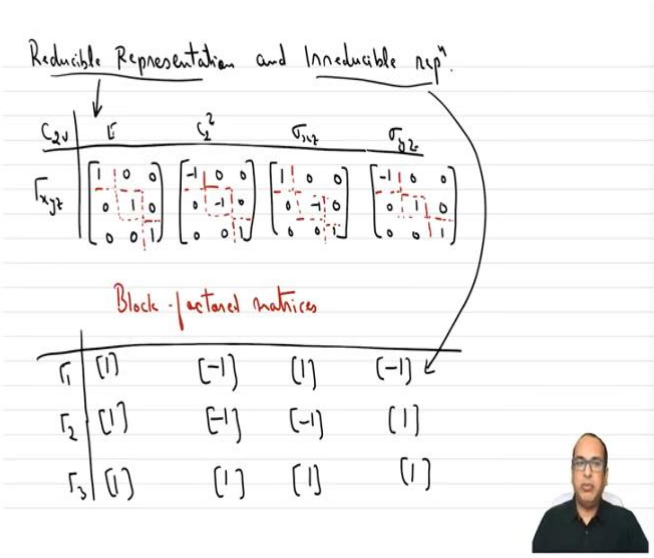

So, now, why we are doing this unit vector transformations. We earlier did with x y z together as the basis set and now we are doing x y z for linear vectors and for rotation vectors. So, let us see. There is something called as reducible representation and something called as irreducible representation. So, let us see one by one both of them. What does it mean? So, I will be writing representation as rep n. So that it is I do not have to write the full thing every time.

So, now, let us take again the case of water molecule because we have been discussing that and we have already solved all of it. So, let us say for C2v point group, when we took x y z as the basis what did we have? What were the matrices the matrices came out to be 1,0,0. This will be now a 3 cross 3 matrix because we have 3 vectors as the basis set of 3 basis sets, not 3 basis sets 3 elements in the basis set.

So, now, if I do C2z, I will get negative 1 for x, negative 1 for y, and positive for z similarly, if I am doing sigma-xz I will get 1,0,0 y will be negative 0,0,1 x and z will be positive. in this case it will be x will be negative y and z will be positive. That we have already worked out. So, this element got wrong here this will be 0 and 1. So, now, if you see that we can reduce this representation is to its lower basis.

So, what do I mean by that, if you carefully see, this matrix has elements only along the diagonals these elements are only along the diagonals and all the off-diagonal elements of the matrix are 0. So, this kind of matrix where the elements can be actually written only along diagonal or along the square diagonals, we will also see that example. So, only along the diagonal or along the square diagonals, these kind of matrices are called as block-factored matrices.

What is advantage and disadvantage? We will see not disadvantage when we will see the advantage of it. So, all 4 matrices in this case can be block-factored with similar dimensions. So, now, I can actually write down this representation as a linear combination, if I just write down this 1, -1, the first element first corresponding element of all 4 matrices, -1, this is my tau 1, and tau 2 will be this 1, central element -1, -1, 1, and tau 3 will be 1, 1, 1, 1.

So, this matrix can now be block factored into 3 matrices and then can be written as a linear combination of these 3 matrices. So, you can write in terms of matrix. So, what we have shown is that, when I take x y z as the basis all together as a basis, I get a representation, which can be reduced further by doing block-factorization of the matrix and converting them into simpler matrices, which individually have a basis set as x y z.

So, those were the unit vector transformations which we did, and we saw that one of this for example, this one I think is the tau z representation. One of them will be tau-x, I think this one will be tau-x and this one will be tau-y. So, we can see that upon doing block factorization of this these matrices we can convert this into one of the basic sets of the matrix representations, which cannot be reduced further.

So, you cannot reduce 1 dimensional matrix further down. So, this type of representation is called as reducible representation and these types of representations are called as irreducible representations, which cannot be reduced further. Now, what is the advantage of this. The advantage is that there can be many reducible representations for a particular point group given that we can have as many number of basis sets as possible.

So, you can have n number of reducible representations and n dimensions. there is no count on dimensions also, you can have for water also you can have 6 cross 6 matrix, 3 cross 3 matrix depending on what is the basis set. But there can be only certain number of irreducible representations for a given molecule or for a given point group.

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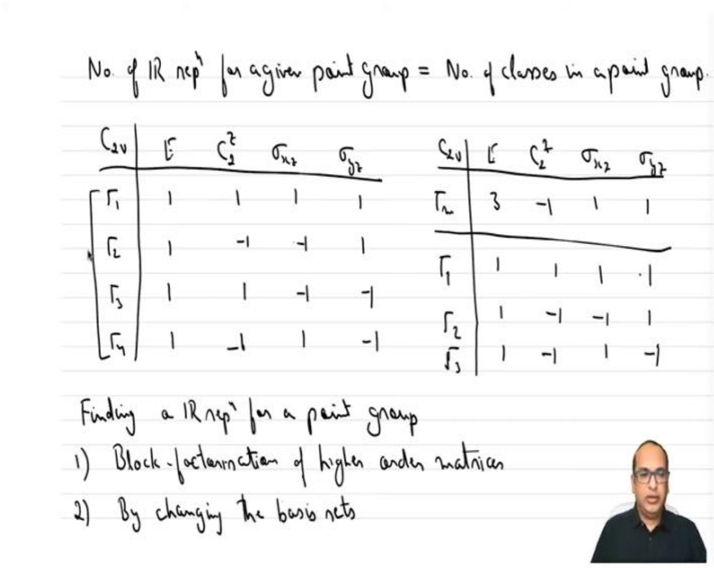

What is that number? So, number of irreducible, so, I will write IR for irreducible and rep n for representation. So, number of irreducible representations for a given point group is equal to number of classes. So, that means, let us say again if we consider the C2v point group, we have how many classes we have 4 classes there. Each element is a class in itself, because it is a cyclic group.

So, you should have tau 1, tau 2, tau 3, tau 4 and then we have seen earlier that you can have these ones as your representations let us not worry about what is the basis set in this but it will be the x y z or Rx Ry Rz or one of these basically, so, you have -1, 1, -1 and then you can also arbitrarily write down for this particular point group, it is easy to write down by just assuming these characters and seeing if they follow the rules of GMT whether the product of these characters give rise to the product which should come out as per GMT.

So, we can see that we can arbitrarily also fill this table by writing this irreducible representation by just writing the characters or you can write down a reducible representation and reduce it by block-factorization by writing just characters. There is another way if you actually do, let us also calculate the trace here. So, trace here will be 3, -1, +1, and +1. so, let us write down the trace over here.

So, tau-m, let us call it as tau-m, so, 3, -1, +1, +1 and then you can see by doing a simple trial and error method, you can divide this into sums of 3 irreducible representations. So, 1, 1, 1 and this will be -1, -1, 1, this will be 1, -1, 1 and 1, 1, -1. I think this will not follow the rules of GMT. So, because there is only 1 negative, so, this will amount to be the correct thing because 2 needs to be positive and 2 characters needs to be negative.

So, now, we have tau-1, tau-2, tau-3 and we can also get the fourth one by using unit vector transformation, but these are the ways to actually reduce irreducible representation into something called as irreducible representations which are these. So, once you have the irreducible representation, you can do many more things, which we will see down the line, but the important part is that how do we arrive at irreducible representation, what is the best way to write irreducible representation?

So, let us see different ways of writing, finding an irreducible representation for a point group. So, the first thing which we saw was to write down the complete matrices using a given basis set and then block factorization of the matrix that was the first way. The second way is to do it by changing the basis sets. So, like we went from instead of taking x, y, z together, we went to a unit vector transformations and we saw that a single unit vector gave us the irreducible representations. So, by changing so, what we did we changed the basis sets.

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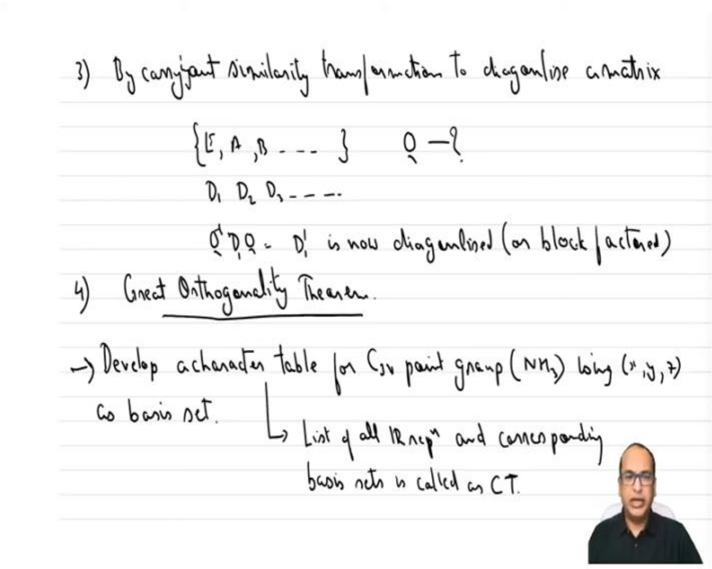

The third way is by carrying out similarity transformations to diagonalize a matrix. So, this is a tedious method. It is not straightforward, because here we need to find out matrix which can be used for similarity transformation to actually diagonalize a matrix. So, sometimes when we take a higher-order basis set, we get the matrices which are not in block-factored or diagonalized form.

So, in that case, we need to do is carry out a similarity transformation, which is equivalent of changing the basis set as we have learned. So, we need to carry out a similarity transformation. So, for example, if we have let us say, if we have E, A, B and certain set of elements and the corresponding matrix representations are D1, D2, D3 and so on. So, what we need to do is we need to find a matrix Q such that we can do Q inverse D Q, to find the D1 prime so that D1 prime is now diagonalized or block-factored.

Once you block-factored you have block-factored matrix, you can now write it as a linear combination and then you have are you arrive at irreducible representation, but this is not a very straightforward method, finding Q is a big challenge. Because it is not apparently intuitive. What will you use to multiply here to find a new matrix which is now diagonalized matrix, it is not straightforward?

So, we will not be discussing this, but this is a way to do it. Let us now look at another way which is much more easier and more mathematical, which is called as which is by using great orthogonality theorem. Let us discuss great orthogonality theorem in the next class and meanwhile, we have few minutes left. So, what we can do is we can actually look at let us, I was planning to do it as a home exercise but let us do it for here.

So, let us try to develop a character table. So, I have also not introduced what is a character table. So, develop a character table for C3v point group, NH3 molecule example, using x y z as the basis set. Let us work it out over here. So, let us first define what is a character table, so, character table is a list of all irreducible representations and corresponding basis sets is called as character table.

So, we will see it has multiple uses, a lot of applications, and let us see how to write one for C3v point group. We will only write the basic character table without worrying about what are the basis sets for now and then later on when we actually look at the great orthogonality theorem. Then we will see how to write for complete character table. Let us start with writing a incomplete character table. We have already written one character table for C2v point group. Now, let us see how to write one for and this was fairly easy, because this one was actually by simply using the unit vector and linear and rotation vectors.

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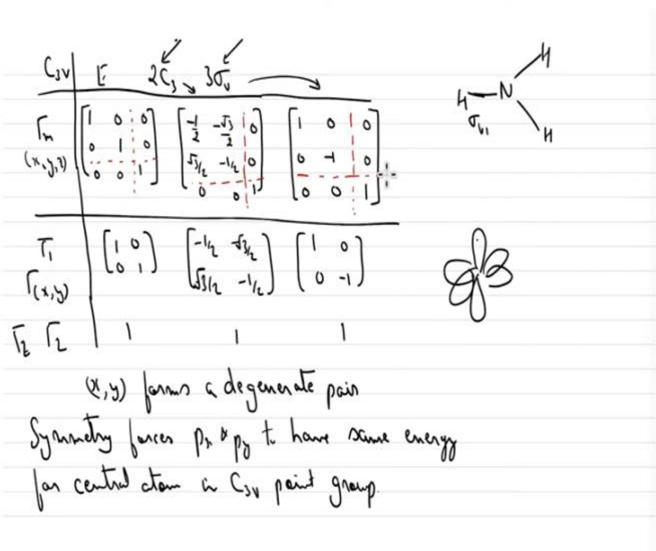

So, now, let us see how to write one for C3v point group. So, C3v point group the elements are group elements are the operations are 2 C3, 3 sigma-V. So, now you notice one thing here that I have clubbed C3 and C 3 square here into one class here, and then I have written 2 in front of because there are 2 elements in that particular class. So, I have written 2 over here. So, this is called as order of the class and then 3 sigma.

Sigma-V1, sigma-V2, sigma-V3. I have combined because these 3 form class and then have combined and then I have written it as 3 sigma-Vs. So, this is just to highlight that I am combining the class elements over here. Now, let us try to write down the matrix representation using so, using x y z as the basis set that was given in that question. So, that means, if we are using x y z as the basis of our matrix will be 3 cross 3 order, and E will be just an identity matrix or the unitary matrix.

Unit matrix of order 3. Now, for C3 we know for C3 we can write as cos theta - sine theta 0 sine theta cos theta, which will take the value as 120, theta will take the value as 120 degrees, so, we will have cos 120, which will be - half, then we will have - root 3 / 2 which is - of sine 120 and then 0 and then we have root 3 / 2, - half, 0, 0, 0, and then we will have one over here. This is for C3, one of the matrix on we have to write.

Because the other operation although it will have a different matrix representation, but the trace will be same. For C3 square so, this is for C3 and for C3 square, I do not need to write because I am interested in trace and trace will be same for C3 and C3 square because the both elements belong to same class. Now for sigma-V again, so we do not need to write for all 3 sigma we can write only for sigma-V1, remember that we discuss if we have one of the sigma-V1 actually lies along yz plane.

So, it will be easier to write for this one, than for the other sigma. So, we will just write for sigma-V1 and then we will work with trace. So now this will be 1, 0, 0, 0, -1, 0 and 0, 0, 1. So, I am not writing for the other 2 sigmas, because the trace is going to be same for those 2 sigmas. So, now, if you notice here, this matrix can be block-factored as, 1 cross 1 1 cross 1 1 cross 1, but this one can be block factored only as 2 cross 2, and 1 cross 1. So, if you notice here, I cannot because there are off-diagonal elements present.

So, I have a 2 cross 2 matrix and 1 cross 1 matrix. Similarly, here, I have a 2 cross 2 matrix and a 1 cross 1 matrix. So, then I have to divide this also in the same fashion, so that the dimension of the matrices become equal. So now, if I divide this what I get, two different representations, so tau-1 will be 1, 0, 0, 1, - half, - root 3 / 2, root 3 / 2, - half and 1, 0, 0, -1 and then tau-2 will be 1, 1, 1. So now, as it turns out, the basis for this one is actually z.

You can actually do the unit vector transformation to see which one gives you 1, 1, 1 as the matrix element or the character and this one, we will see that later, how to find the basis sets, but this one we have this is a 2 dimensional matrix and you cannot reduce it further and the combined basis for this is x comma y. So, I am writing x comma y because in this particular case xy forms a degenerate pair.

Why this happens? Because x and y cannot be separated in this particular point group. So, what does it mean? So, any property which lie along x axis and y axis, you will not be able to separate. For example, let us say if on the central metal atom there is there is pz orbital, px orbital, and py orbital. So, for this particular case, tau-z has a different property. So, that means, pz has a different property as compared to px and py orbital and because you cannot separate out x and y.

So, px and py orbitals are actually degenerate and they have same energy. So, we can see that the symmetry. So, these are the purely symmetry rules there is no chemistry here. So, these are the pure symmetry rows. So, symmetry forces px and py to have the same energy for central atom in C3v point group. So, this is a direct relevance or direct application of symmetry into the orbital diagram.

So, we have shown that symmetry forces px and py, because x and y cannot be separated. So, that means px and py also cannot be separated because px and py lie along the coordinate system x and y. And because now, px and py cannot be separated that means you do not know which one is px and which one is py that means they both have same energy. So, with this we can stop here and then in the next lecture we will discuss a great orthogonality theorem. And how do we use this theorem to actually obtain irreducible representations. Thank you.