Symmetry and Group Theory

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Lecture -34

1) **Degenerate Eigen Functions**
2) **Direct Product**

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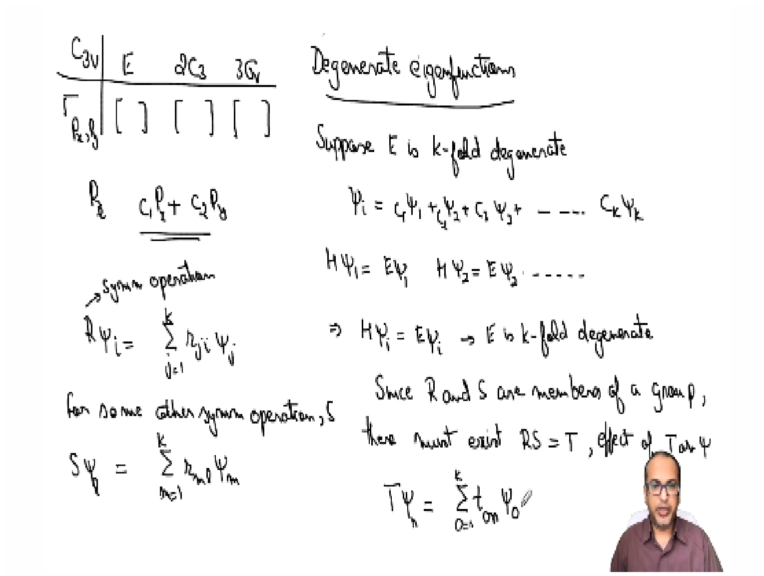

So, in the previous lecture we have looked at when we were developing the representation using wave functions as the basis for C3v point group. So, we saw that for C3v point group when we took wave functions as basis that is Px and Py what we got is a 2 cross 2 matrix. So, here for all 3 of them and that was a irreducible representation. So, that means although we started with Px as the basis we ended up getting a representation, which is a linear combination of Px and Py.

So, we started with Px but we ended up with some coefficients with Px + Py. So, this was what we were getting for example, when we were doing C3 rotation, we got minus half Px + or minus root 3 by 2 into Py. So, that means eigen function can also have degenerate eigenvalues. So, what does it mean? So, let us say that if we have degenerate eigen functions. So, let us look at this example in more details, degenerate eigen functions.

So, suppose E is our energy of a particle or a system is k-fold degenerate. What does it mean when I say k-fold degenerate? I will tell. So that means that if my psi i can be expressed as a linear combination of psi 1 psi 2, of course with coefficients C1, C2, C3 psi 3 + Ck psi k and if H psi 1 is equal to E psi 1, H psi 2 is equal to E psi 2 and so on. So, then I can say that H psi i is equal to E psi i. So, all of them will give you same energy and then there if let us say there are multiple eigen functions which give me same energy.

Then if I take a linear combination of those eigen functions that would also give me the same eigen value. So, this would be, so in this particular equation I would say that my E is k-fold degenerate. Like in this case we found that our representation is two-fold degenerate where Px and Py were giving me same eigenvalues. So, similarly now we are considering the case of k-fold degenerate.

So, let us further look at this let us say if we have R Psi i, I can express this as a linear combination. So, this can be written as r ji and psi j where j goes from 1 to k. Because my E is k-fold degenerate, so I can express my psi a into k linear combinations of different eigen functions and r is any particular symmetry operation. So, this is a symmetry operation, so now similarly for any other symmetry operation I can again write, so for some other symmetry operation.

Let us call it as S. I can write S psi, now let us call it as some other index psi l this can be written as summation m goes from 1 to k, so I am just using different index just to keep it different from the previous one, Psi m. So, now R is a symmetry operation which is acting on a linear combination of eigen functions which are degenerate and then S is some other symmetry operation which is acting on same linear combination going from 1 to k. And these are the corresponding coefficients of linear combinations.

Not the coefficients here, so these are the corresponding characters actually upon doing when R is operated whatever character you get corresponding to each eigen function, this is the corresponding character. So, now we can say that since R and S are members of a group, there must exist, as per group definition there must exist product of R and S equal to P which should also follow the similar behavior.

So, that means effect of T on psi should also be similar. So, let us try to write down T let us call it as psi n is equal to summation t and let us give it as a index o, o goes from 1 to k and this would be psi o.

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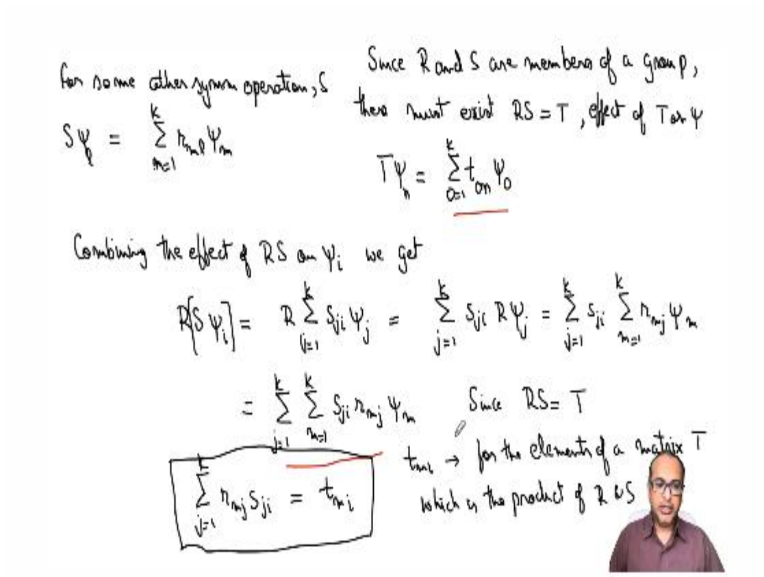

So, now if we have this so because R and S are members of a group there must exist R S equal to T. So, if we say that the effect of t on the linear combination of eigen functions should be this then if we calculate the effect of R and S, on to a given linear combination the coefficients should match or the characters should match. So, let us see if we combine the effect of R and S, what do we get?

Combining the effect of RS on psi i, we get psi i is equal to so let us first operate s and then we will operate R, so if we operate S, we will get summation j equal to 1 to k and we will get small s ji and we will get psi j, the same way. So, what we have done is we have just operated s onto psi. Now next we will operate R onto psi j, so that will give us or I will just write it here that I can take the summation out j equal to 1 to k and s ji and I will now bring R into picture psi j.

So, that R can operate on to this and what do I have now? So, then now I can write summation j equal to 1 to k and I have s ji and now I can write this as another summation. Let us call it as m equal to 1 to k and this will be r m j and psi m. Now if I take those summation out I have got j equal to 1 to k summation, so this is nothing fancy about it, this is just whatever we have shown in C3v point group, we are just doing it for a general k-fold degenerate case.

Now this will be s ji and this will be r mj and psi m. Now since we can say that R S is equal to T so we have chosen this that if R S are members of a group R S must be equal to T, there must have a T as a member of the group which should be equal to product of the two group elements. So, that would define that this particular part over here should be equal to this part over here. So, let us equate these two, what do we get?

So, we get and we see that one of the summations is not required, because we will see. So, we will say is summation over j equal to 1 to k, so I will write r mj and s ji and this should be equal to only this part t in the index we can of course we can take this as mi. So, do not get confused about the index, so indices I am just choosing that one it is showing that all the linear combinations should go from 1 to k for different values.

So, indices do not have really any meaning over here in terms that the what they are representing that they are representing it is a k-fold degenerate case. So, now if we look at this particular case, what do we have what can be say about this? So, t mi, what do we think what is t mi? So, t mi is nothing but it is a form of a matrix or this expression is for the elements of a matrix T which is the product of R and S.

So, if I want to write a general matrix element T which is the product of the matrix R and matrix S then I would get this expression.

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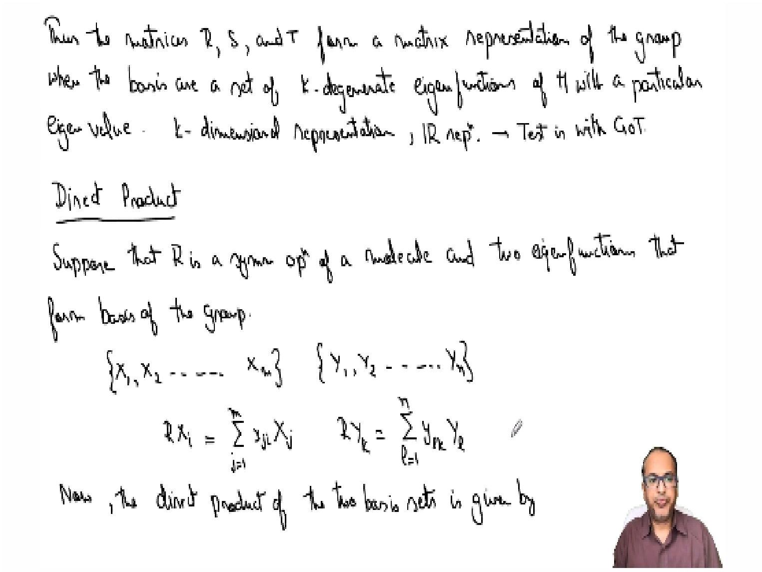

Thus we can say that, thus the matrices R, S, and T, together they form a matrix representation of the group. When the basis are a set of k-fold degenerate eigen functions of H Hamiltonian with a particular eigen value. So, that will be a k-dimensional representation, this will be a k-dimensional representation and it would also be a irreducible representation. We have seen again that in the case of C3v point group that when we started with Px we got a two-fold degenerate representation, which was an irreducible representation and we can always test it with the GoT.

So, that should be clear now. So, what we have shown so we started with an example of two folded degenerate case and we have shown that the same thing can happen for k-fold degenerate representation. So, whenever your eigen functions give a k-fold degenerate eigen value the IR representation that you will get using those wave functions or eigen functions as the basis set that will be k-dimensional representation and it will be a irreducible representation.

So, this covers the wave functions as the basis set subtopic of group theory and quantum mechanics. Next topic in this quantum mechanics is the direct product, we will see what the direct product is. Well we would have all seen what is the direct product of matrices. It is very similar here exactly same actually. So, we will see what is the direct product and we will see what is the application of this in group theory.

So, let us start with understanding what the direct product is. So, suppose that R is a symmetry operation of a molecule and there are two sets of eigen functions that form basis of the group. So, let us write down one set as X1, X2 going all the way to X let us say Xm. The second set is let us say Y1, Y2 and this one is going all the way to n. So, now if we want to write in the short hand notations we can write it as RX i can be written as summation the character obtained can be written as x ji and Xj where j goes from 1 to m. So, this was up to m.

And similarly, here we can write R operating on Y let us call it as k. This can be now written as summation y lk where l goes from 1 to n and I have Yl. So, now how do we write the direct product of this?

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Now, the direct product of the two basis sets is given by

$$DP = \{X_1Y_1, X_1Y_2, X_1Y_3 \cdots X_1Y_n, X_2Y_1, X_2Y_2 \cdots X_2Y_n, \cdots X_mY_n\}$$

→ Functions (perhaps eigenfunctions) in the direct product also form a basis for the repn

$$R X_iY_k = \sum_{j=1}^{m}\sum_{l=1}^{n} x_{ji} X_j \, y_{lk} Y_l = \sum_{j=1}^{m}\sum_{l=1}^{n} x_{ji} y_{lk} X_j Y_l$$

Substitute $x_{ji} y_{lk} = z_{jl,ik}$

$$\Rightarrow \underline{R X_iY_k} = \sum_j \sum_l \underline{z_{jl,ik}} X_j Y_l$$

This is a standard expression relating Symm opn & eigen fn

The direct product of the two basis sets is given by so direct product we can write it as let us say direct product has so what you have to do is basically multiply each element of the basis set with the other each element. So, that is X1Y1, X1Y2, X1Y3 going all the way to X1Yn. Similarly, we have X2Y1, X2Y2, going all the way to X2Yn, again similarly we have XmYn.

So, each element of the basis set is multiplied with each element of the other basis set of that gives you the direct product of the two basis sets. So, now what we will show here is functions maybe call them as perhaps Eigen functions in the direct product also form a basis for the representation. So, what do I mean, so what I am saying is that if the set of representation that is or set of eigen functions X1, X2, X3 form a basis and Y1, Y2, Y3 etcetera form a basis, then their direct product will also form the basis of the representation?

What is the use of that we will see? But let us first see that this is the case, so let us try to do this mathematically. So, Xi a general product here can be written as Yk and now if you apply R on to this what do we get, we will get 2 summations and we will get 2 characters over here. R will up we applied on X as well as onto Y, so we can say that this x ji and Xj. So, that means there will be summation of j equal to 1 to m. And then we will have y lk Y l, so this summation will be going from l to n.

Now I can combine these two numbers and write summation j goes from 1 to m summation l goes from 1 to n x ji, y lk, X j and Y l. Now we can substitute this these two are numbers so we can make a product and substitute this. So, substitute x ji, y lk with z and we will combine the two indices jl and ik. I can always do that because these are numbers. So, this means that I can write R Xi Yk as double summation z jl, ik Xj Yl. This is summation over j this is summation over l.

But what do we have now this is a general expression; this is a standard expression relating symmetry operation and eigenfunction. So, we are applying so as if we are taking this as an eigen function we are getting one value as a character. So, when we apply symmetry operation onto a product of eigen functions, we are getting the same product back along with some character. So, this is standard expression so now that means if X forms the basis separately.

And Xi or linear combination of X forms the basis separately and linear combination of Y forms the basis separately what we have shown here is that product of XY will also be of the same form and does this will also form basis for the symmetry operations or for the particular representation given any symmetry operation.

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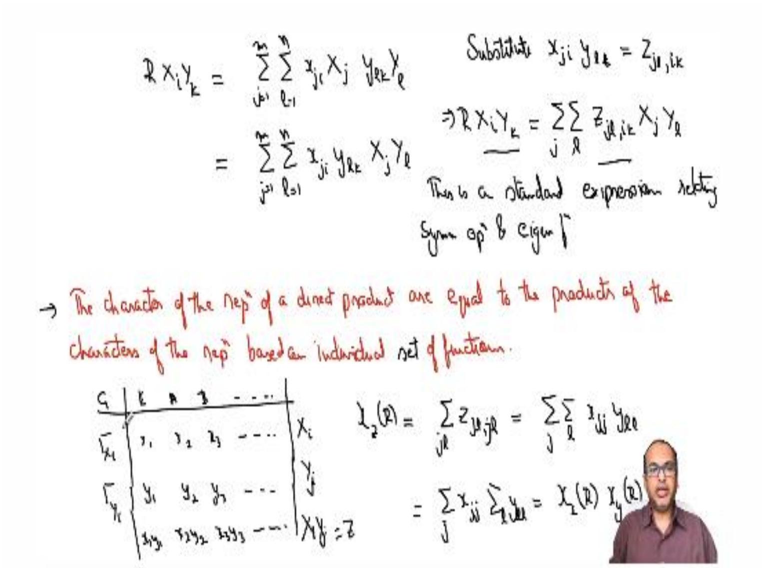

So, one more point over here to discuss, now we can say from this we will see that we can reduce that the character of the representation of a direct product. So, now from direct product we get a separate representation and that representation has some character. So, we are talking about the character of that representation. So, character of the representation of a direct product are equal to the products of the characters of the representation based on individual set of functions.

So, that means what I intend to say here is that let us say we have a general group E, A, B and so on and Xi that is X1, X2, X3. All of them are forming a basis set in general and then their characters are let us say x1, x2, x3 and so on. Similarly, Y i is also forming a basis that will give you IR representation as Tau Yi. So, this will give you y1, y2, y3 and so on. So, if X and Y are forming the basis separately the direct product of that let us call it as j j, X i Y j will also form the basis and their characters will be given by x1y1, x2y2, x3y3 and so on.

So, this can be seen from here, so let us say we want character of x z. Let us say if X and Y are individual sets of functions that form the basis then the direct product is called YZ. So, we can call it as Z. So, Xz under any symmetry operation, which is this one, let us say any symmetry operation E, A, B, C and so on is given by summation over small z that is j l j l and now this can be written as summation. So, I am just using this equality, I am expanding this.

So, this can be written as summation j summation l and I can say that this can be x jj and y ll. Now and then I can separate this out as summation over j, x jj summation over l, y ll and now this can be written as character of X under that i R and character of Y under the R. So, the product of the two characters will give you the product of the character under the representation which is formed by the direct product of the set of functions.

So, I hope this is clear we will take examples of this and we will solve those examples in next class. Meanwhile you can practice through the maths and then look at the indices carefully that if you got this thing correctly, think that is all will discuss examples in the next class.