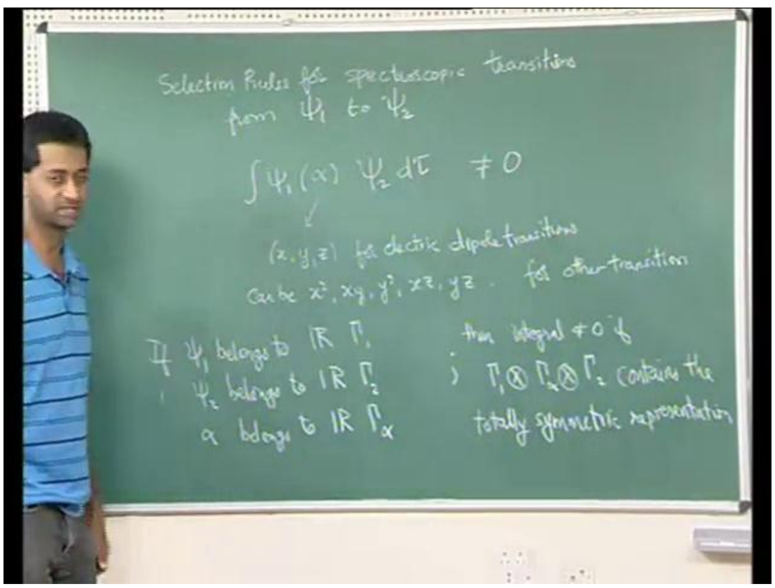
Mathematics for Chemistry
Prof. Dr. M. Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 37

So, we just saw how to get the selection rules for spectroscopy. Let us just summarize what we have seen so far.

(Refer Slide Time: 00:40)

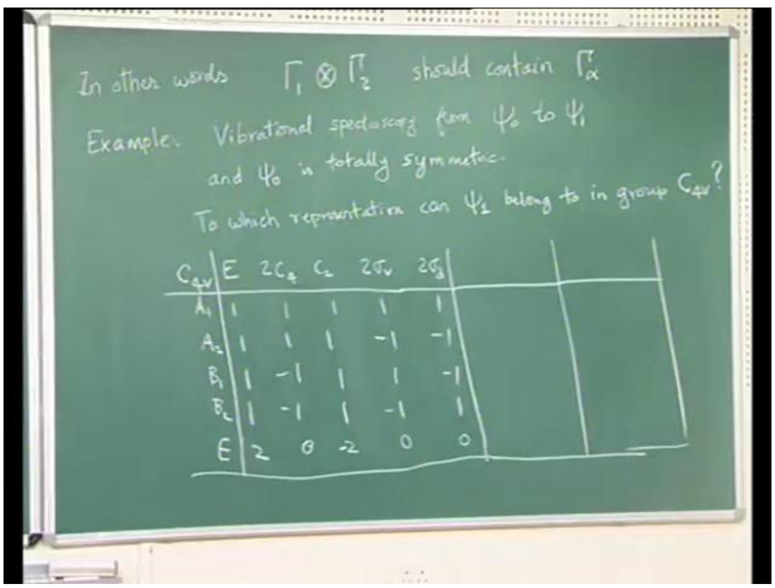


So, suppose you want a spectroscopic transition from one state is denoted by psi 1 and to another state is denoted by psi 2, then this spectroscopic transition, the intensity of this transitions is proportional to a quantity called psi 1 and I will just say alpha here and I will say psi 2 beta, where alpha can be x, y or z for electric dipole transitions. So, for electric dipole transitions alpha is either x, y or z and for other transitions, it can be x square, x y, y square, etcetera. If you look at Raman Spectroscopic, then the transitions is related to the polarizability.

So, you might have terms like x square, x y, y square, x z and so on. But essentially you have integrals of the forms psi alpha psi 2, where alpha is typically one of these quantities. Now, this quantity, if this is not equal to 0, then the transitions is allowed. The transitions from 1 to 2 is allowed, so now how do you find out whether this should be equal to or not equal to 0? Simple rules you can just look at is this integrals and you can use what we learnt in the last class about integrals.

So, this integral, if psi 1 belongs to irreducible representation gamma 1 and psi 2 belongs to irreducible representation gamma 2 and let us say alpha belongs to irreducible representation gamma alpha, if each of these belong to the irreducible representation, then this integral will be non-zero. Then integral is not equal to 0 only if, gamma 1 direct product with gamma alpha direct product with gamma 2 contains the total symmetric representation. So, this direct product, this integrand should be totally symmetric and should contain the totally symmetric representation.

(Refer Slide Time: 04:26)



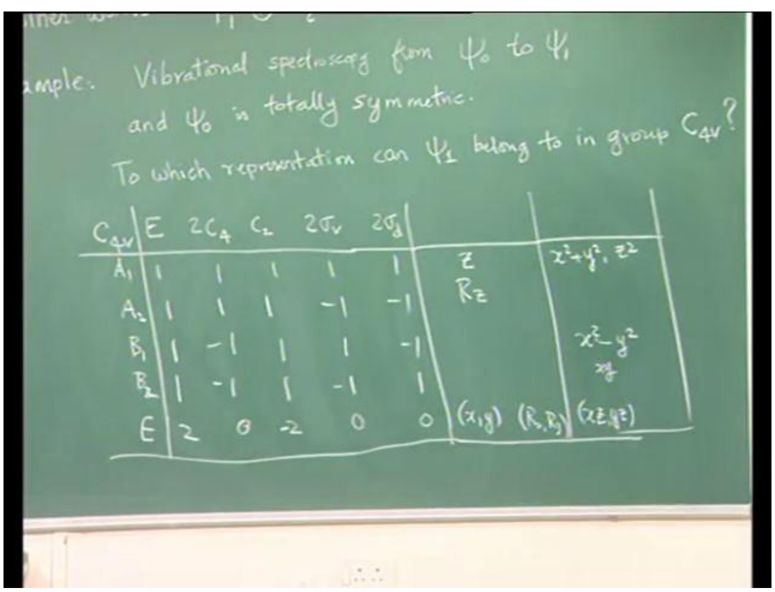
So, that is a simple condition and also in other words using that again we go back to the theorem we had about direct product, in other words your gamma 1 cross gamma 2. So, this representation, this direct product should contain gamma alpha. So, the representation, the direct product representation of one and two should contain the representation of alpha. So, these are the general rules and if this is satisfied, then this integral will not be equal to 0 and the spectroscopic transition will be allowed.

So, now let us see a simple application of this. Let us look at vibrational spectroscopy. So, for example, the vibrational spectroscopy from psi 0 to psi 1. So, you are looking at a transition that goes from psi 0 to psi 1. These are the two vibrational states and psi 0 is totally symmetric. So, psi 0 is totally symmetric and psi 0 belongs to the totally symmetric representation. So, that means psi 0 belongs to the totally symmetric representation.

Now, the next question is, to which representation can psi 1 belong to in group C 4 V? To which representation can psi 1 belong to in group C 4 V? So, the question is you want to look for transition from psi 0 to psi 1. You are told that when psi 0 is totally symmetric, then in which representation can psi 1 can belong, if you are in this group C 4 V. Now, this can be answered very easily if you look at the character tables. So, if you look at the character tables of C 4 V, C 4 V has E as the identity and then it has 2 C 4, C 2 , 2 sigma v and 2 sigma d. So, the order of the group is 8. The order of irreducible representation is 1.

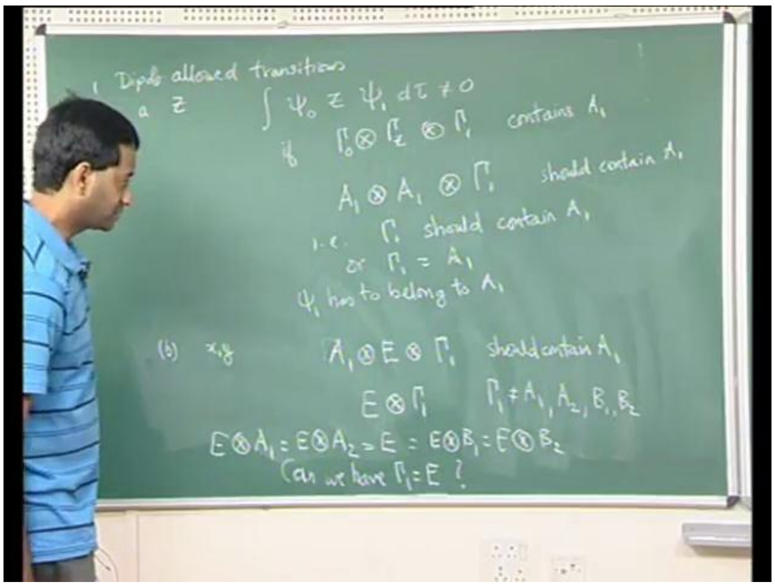
These A 1 and A 2 are one dimensional representations, as are B 1 and B 2 and E is a two dimensional representation. The characters of A 1 are 1 1 1 1 1 and is a totally symmetric representation, the characters of A 2 are 1 1 1 minus1 minus1, characters of B 1 should be 1 1. Two of these can be minus1. I will just check minus1 minus1. It should be minus1 minus 1 1, B 2 will be 1 1 minus1 minus 1 1 and E is 2 0 minus 2 0 0. So, these are the characters of the various representations. You can just start from this and you can quickly see. You can immediately see that in this column z belongs to the totally symmetric representation.

(Refer Slide Time: 09:34)



R z belongs to A 2 and x, y belong to E, that is x, y or R x, R y. So, x and y together form basis for this representation as 2 R x and R y. As far as a product, you have x square plus y square and z square, then x square minus y square, then you have x y, x z and y z. So, these are the products. So x z and y z together form a basis for this two dimensional representation and x y forms a basis for B 2, x square minus y square forms a basis for B 1. So, now using this table you can very quickly answer this question. So, now first let us look at the dipole transitions. Let us look at dipole allowed transitions.

(Refer Slide Time: 11:03)



So, first dipole allowed transitions. In this we look at z. Now, z belongs to A 1. So, then the integral psi 0 z psi 1 d tau is not equal 0, if gamma 0, gamma z, gamma 1 contains A 1. Now, I have already told that gamma 0 is a totally symmetric representation. So, in other words A 1 cross and gamma z belongs to A 1. So, A 1 direct product with gamma 1 should contain A 1. Now, you can immediately see that if I take a direct product of A 1 and A 1, I will get back A 1. Both, these are one dimensional representation. So, the direct products will just give me A 1.

So, A 1 direct product with gamma 1 will just give me gamma 1. So, in other words gamma 1 should contain A 1. Since, A 1 is a totally symmetric representation, direct product of A 1 with gamma will just give me whatever representation gamma 1. So, in other words gamma 1 should contain A 1 or gamma 1 is equal to A 1. So, if gamma 1 is irreducible, if you say irreducible representation, the only irreducible representation to which psi 1 can belong is A 1. So, if you want to see vibrational transitions polarized by z, then psi 1 has to belong to A 1.

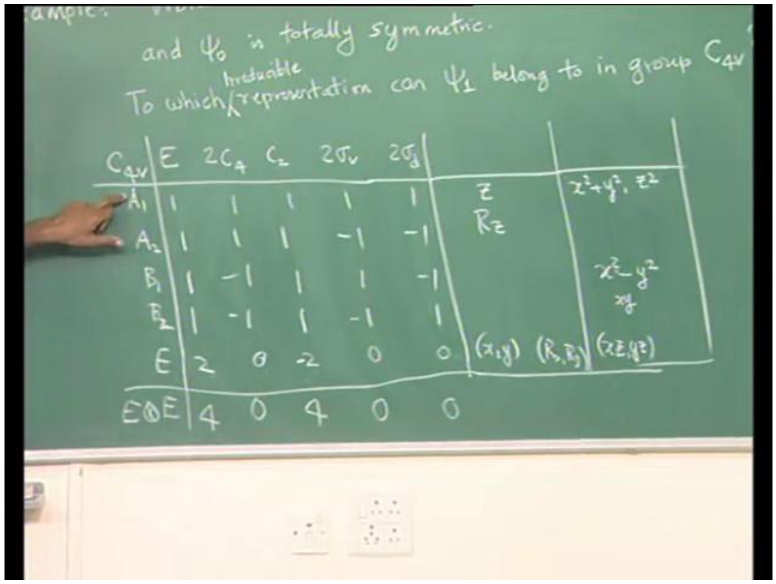
So, psi 1 has to belong to A 1. Now, the other case is you have x y polarized. You can have transitions, that is x y polarized and in this case x y forms a basis for E. So, you do the same thing. Then, you say that A 1, instead of gamma z you have gamma x y, gamma x y is nothing but E times gamma 1. This should contain A 1. Now, you can look at this and you can immediately identify the following, that suppose I take 1 times E, I will just get E cross gamma 1. Now, you have a direct product of E and gamma 1.

Now, you look at the characters of E. They are 0. These two terms are 0. It is only these two terms are non zero. So, these three terms are 0 and only these two terms are non zero. Only these two character are non zero. So, if I take a direct product of E with any of these representations, if I take a direct product with A 1, I will just get E. So, therefore gamma 1 is not equal to A 1, because clearly if I take a direct product of E with gamma 1, I will just get E. E does not contain A 1, because E itself is irreducible.

Then, what happens if I take a direct product with A 2? So, E direct product to A 2, so the characters will be 2 into 1 0 minus 2 into 1 0 0. So, you will get back E. So, E into gamma E into A 2 is also identity. So E direct product A 1is equal to E direct product A 2 equal to E. That is why gamma 1 cannot be equal to A 1 or A 2. What about B? Similarly, you can see that E direct product of E with B 1 is equal to direct product of E with B 2.

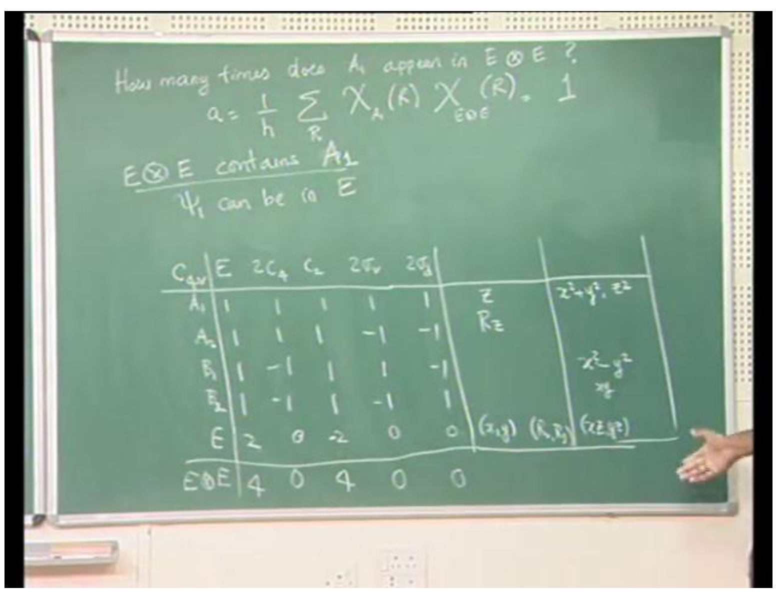
In all the cases you will just get back E. So, if I take E B 2 for example, so I just get 2 0 minus 2 0 0. So, essentially E cannot be A 1, A 2, B 1, B 2. So, the only possibility E is gamma 1 is equal to E. So, gamma 1 cannot be equal to A 1, A 2, B 1 or B 2. So, now can we have gamma 1 equal to E? So, that is a question. So, if gamma 1 is equal to E. Then, E cross E direct product is gamma 1. It will be 4 0 4 0 0.

(Refer Slide Time: 17:41)



So, E cross E will have character 4 0 4 0 0. Now, the question is, does this contain the totally symmetric representation? So, does E cross E contain A 1? It does not. This is where we use our earlier theorem. So, we want to know how many times A 1 appears in the irreducible representation E cross E. So, we will go back to our earlier theorem which we said, in an irreducible representation, how many times does A 1 appear in E cross E?

(Refer Slide Time: 18:32)



So, E cross E is this. E cross E has these characters, A 1 has these characters and if you want to find out how many times A 1 appears in E cross E, then the answer is a is equal to 1 by h sum over all R times of A1 of R psi E cross E of R. So, you just take the product of these characters in A 1 and E and you can immediately see I take 4 into 1 plus 0 into 1 plus 4 plus 4 into 1. So, you have 4 into 1 plus 0 into 1 plus 4 into 1 plus 0 into 1 plus 0 into 1.

So, h is equal to 8. So, this is equal to 1. So, that means E cross E contains A 1. Since, E cross E contains A 1, that means A 1 cross E cross E contains A 1. That means psi 1 can be in E. So, what we conclude from this is that the dipole allowed transitions are there. There are two possible dipole allowed transitions, psi 1 can belong to A 1 and that will be a dipole polarized along the z direction or psi 1 can be E psi 1 can be E. That will be polarized in the x y plane.

So, these are the two possible dipole allowed transitions. Just as we did this, we can also find what are the other transitions, those that are Raman spectroscopic and so on by looking at the products to find out which of the products appear in which representations. So, clearly if psi 1 is in A 1, then you can have transitions involved in x square plus y square and z square. Else, if psi 1 is in E, you can have transitions involving x z, y z, and so on.

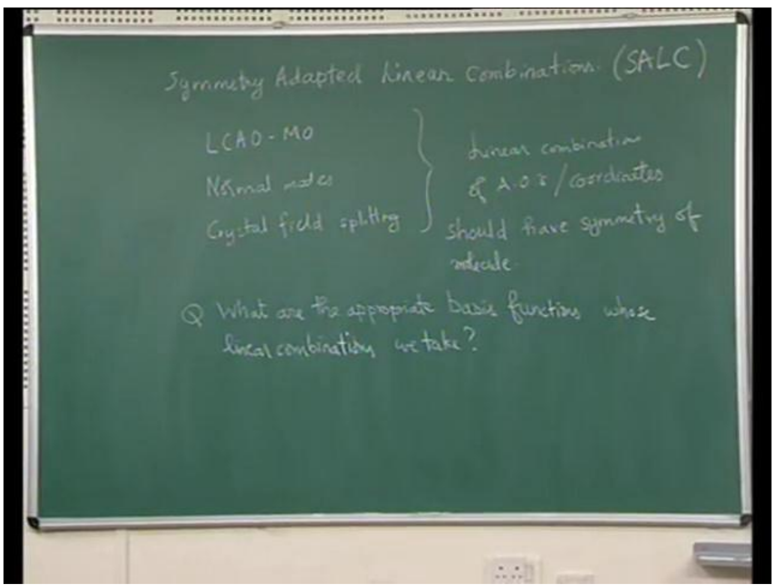
So, this method of identifying which transitions are allowed and which are not allowed is something that can be done extremely easily by using the character table. So, this is one of the the most important applications of group theory. What we should mention here is that, we just ask the question to which representations psi 1 can belong. So, we just ask, to which of the irreducible representation can psi 1 belong?

Now, this is only part of the story. So, they are still in A, in any real molecule belonging to C 4 V. Then, what you have as molecules are what are called normal modes. So, you have normal modes of vibration and in each normal mode of vibration it could be things like symmetric stretch, anti symmetric stretch, it could be bends and you know these are the various normal modes vibration. So, what you have to identify is, now you have to look at the normal modes. You have to see which normal modes belong to which of these representations.

So, the ground state of one normal mode might belong to 1 1 representations. The excited state of a normal mode might belong to a different representations and so on. So, it is not as straight forward as just saying, that you know that this way function is symmetric and so on. You really have to look at each normal mode and you have to see to which representation each normal mode belongs. But once you have identified to which representation each normal mode belongs.

Then you can go ahead, use this simple rules to to identify which of the spectroscopic transitions are allowed and which are not allowed. So far, we have seen two two applications of these character tables. One is identifying which integrals which overlap. Integrals relating to energy are non zero and the second is to identify which are the spectroscopic transitions that are allowed or disallowed. So, now we are going to discuss the concept that is widely used in various applications of groups. Here, in quantum chemistry this is called symmetric, that are linear combination and sometimes is noted by SALC.

(Refer Slide Time: 24:15)



Now, you might have seen some. You might have already seen some applications of this and we also have seen how to use some applications. You might have heard of linear combinations of atomic orbital and molecular orbital. So, this is theory called LCAO-MO. Here, what you do is, you take your atomic orbital and by making suitable linear combinations of those atomic orbital, you can set to molecular orbital.

So, then the question is, which atomic orbital is used to construct which molecular orbital? So, suppose I want a certain molecular orbital, which are the atomic orbital which used these linear combinations? One of the things that we will use is the atomic orbital that are used to make linear combinations should have the appropriate symmetry of the molecule. We will see examples of this.

The other problem in which symmetry adapted linear combination are widely used, is in study the normal modes of vibration. So, suppose you have a polyatomic molecule, then you have a large number of vibrations. Degrees of freedom are the independent vibration and are called normal modes. So, which are the coordinates within the molecule which we have independently, during these vibration?

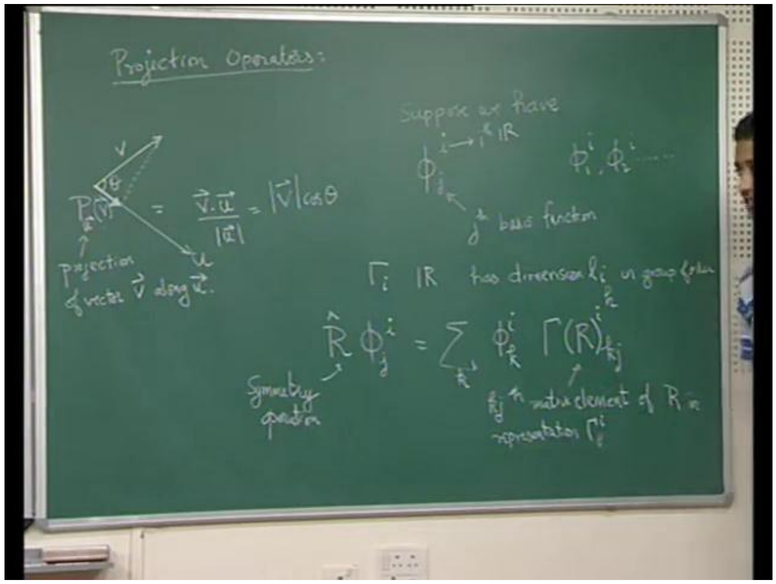
So, which are the coordinates in the molecule corresponding to these normal modes? It turns out that the normal modes are nothing but linear combination of the coordinates of the atoms. Then, we need those linear combination that again satisfy the symmetry of the molecule. So, another example is let us say you have an atom in a crystal field. You are in the field and you know that in the legan field there is splitting that takes place and how should this splitting take place?

So, what is the basis for this splitting, that is another place where these symmetry adapted linear combinations and so, what the common feature is that you have linear combinations of various atomic orbital or coordinates. These linear combinations should have symmetric which shows in the molecule. So, you should choose those appropriate linear combinations that has the symmetry which the molecule shows.

So, this is the idea behind symmetry adopted linear combinations and it will become clear as we look at more examples. So, the question is how do you the appropriate orbital's of which you should take a linear combinations or how do you find appropriate basis vectors in which you take the linear combinations. So, what are the appropriate basis functions whose linear combinations we must take? So, the answer to this is that you choose those basis functions that are symmetry adapted.

So you choose A, so this linear combinations is called the symmetry adapted linear combinations. Now, in order to identify this and to work out these symmetry adapted linear combinations, we shall use a very useful concept which you have seen before when you are doing vectors, that was called the projection operators.

(Refer Slide Time: 29:08)



So, you might have seen this and in quantum mechanics. You have definitely seen projections where you are dealing with vectors. So, the way to think of it is that if you have a vector v, you want to find the projection of this vector along another vector u. Suppose, you want to find the projection of this vector along another vector u, then you just see the component of this symbols direction. So this is the projection of vector v along direction u. So this is the projection of vector v along vector u.

So, that is a general idea of projections you are dealing with, right? Now, this also you can write it is as v dot u. So, v dot u is v times u times cos theta. So, you have to divide this by the length of u so that you will need a projection along this strategy. So, we can work this out. Then if the angle is theta, then this tends to be the length of v times cos theta. So, this is the usual projection we talk about when we are dealing with vectors. Now, when we were discussing linear algebra we said that you know this vectors can be generalized. The idea of the vector can be generalized. You can have functions treated as vectors depending of the state that you are interested in.

So, in such cases you want some more general definitions of the projection operator and especially when we use it as a basis. So, that is what we are going to look at next. So, suppose you have a wave function denoted by pi j I. So, this is basically the wave function of the form pi

1 I, pi 2 i and so on. The whole setup re-functions. Now, what this stands for is this is the j th basis function and this is the ith irreducible representation.

So, you have a irreducible representation denoted by gamma i. In this irreducible representation, there is a set of basis function denoted by pi j i. So, pi 1 I, pi 2 i and so on. Now, so these basis function are denoted in this way. Now, let us say that the group dimension of gamma i has dimension l i in group of order h. So, h is the order of the group and l i is the dimension of gamma i. So, you have a gamma i which has the representation of dimension l i.

So, for example l i could be a one dimensional representation. This l i could be a two dimensional representation like we are seeing the various representation A 1, A 2 and E. So, this is one of those representation and the dimension is l i. So, A 1 could be a one dimensional, A 2 would also be one dimensional representation, whereas E would be a two dimensional representation. The order of the group is h.

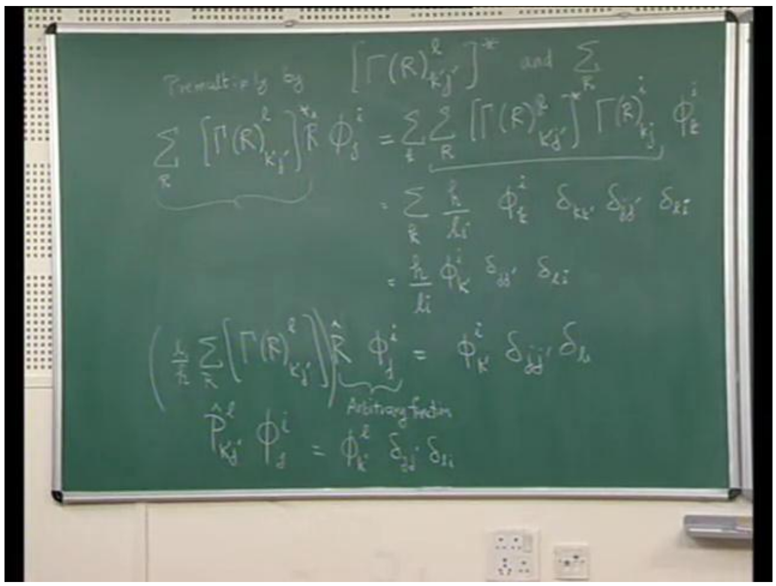
Now, if you have this, then corresponding to any symmetry operation you write and the operator operating on some arbitrary function I, we will just denote it by phi dot i. So, when a symmetry operator operates on some function, what you get is some linear combinations of the basis function. So, the effect of a symmetry operation on a basis function is to give linear combinations of basis functions. So, you can write this is as i A i. So, in the representation you have a linear combinations of sum overall.

All is the symmetry operation. So, all is the symmetry operation and so that sum of bases function you get typical linear combinations. So, you have sum over k pi k i times the coefficient and the coefficient is nothing but the matrix elements of this symmetry operation, which matrix element is it? So, it is you are getting elements for the representation i corresponding to a irreducible representation I and matrix element should be pi j j. This is the basis. So, the appropriate matrix elements will be the k j matrix element.

So, how in this representation i, the matrix elements are defined in this form matrix element of any operator. So, this is in some sense that the definition of your gamma or pi k j. If you recall this was the object that appeared in the theorem, so every operator can be represented by a matrix. Whose dimension will be l i in the representation and this is the k j element of that matrix. So, this is the k j matrix element of R in the representation gamma R. So, what I mean is that, you have R in this representation gamma i r which can represented as matrix and this is the k j matrix element.

So, this is the usual definition of the matrix elements, but what we have seen is we have looked at it as how the operator acts on a on a basis function. Now, we will use this to motivate the definition of the projection operator. In order to define the projection operator, let R E be multiplied on both sides. So, pre multiplied on both sides by the complex conjugate of one other matrix element. Then, we use the great theorem. So, what we do is as shown here.

(Refer Slide Time: 38:03)



So, first we pre multiply by gamma R in the 10 representation and in the k prime j prime element. So, notice that here you have the i th representation and there you have the j th representation, here you have k j and there you have k prime j prime. So, we multiplied by the complex conjugate on that and then you sum over all the operations. Now, you do this on both sides. So, on the left hand side what you have is this object. So, you have sum over R gamma R l k prime j prime star and you have A R pi i R pi j i. So, this R pi j I, you have it here.

On the right hand side, when you do this , I inturn take the sum over k and sum over R and i. I write it in this form, so I have the sum over R coming from gamma R l k prime j prime coming from here with the star. I have the gamma R i k j which came from here. I have the phi k I, which is right here. So, this is the usual way in which you calculate coefficient in any basis function expansion. This is the way you calculate the coefficient, but you are going to use this as a motivation to define the projection operators.

So, now you can use the great orthogonality theorem for this. What you will be left with, when you use this whole object can be similar pi. What you get is h by l i, where l i is the dimension of of the i irreducible representation. This phi k i is as it is and then you have these three delta function. So delta k k prime has to be equal to k j prime has to be equal j l has to be equal to i. So, this is the expression and you have a sum over k of phi k i delta k k prime. So, you can do this sum over k. You will get x by l i phi k prime of i delta j for different delta li.

So, this is actually not very complicated. Now, what we do is we look at the right hand side and we take this l i by j to the right hand side through the left hand side. So, when you take l i by h to the left hand side, what you can have is l i by h sum over R. You have gamma R the one, the representation k prime j prime r which was the operation that we consider this whole thing operating on pi j i. So, operating on phi j i and now you can actually think of it in a slightly different way. You can put this here. You can imagine that this whole thing you can have this. I am operating on R pi i.

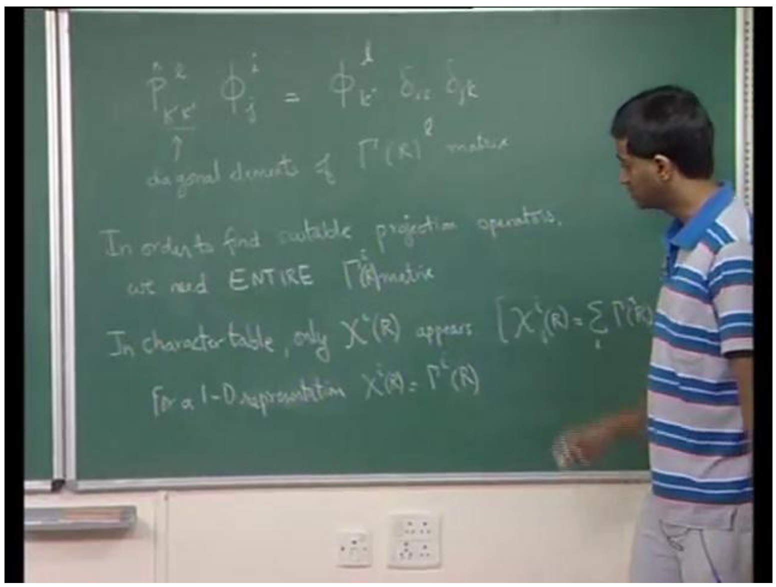
At the right hand side, there is phi k prime i delta j j prime delta l i. So, what is happening here is, this is an arbitrary function. So, you can think of this arbitrary function, then this operator reading on this arbitrary function. This gives you this various delta functions and it gives this function in i. The representation in the i th irreducible representation and gives something that is related to the k prime basis function. So, this operator is called as a projection operator. So, the way you think of this as E, this is our projection unto the l th irreducible representation.

It projects the k prime j prime element onto the k prime j prime element. This, when operated on on some function pi j I, this projection and this operator acts on the function. So, it takes it from the basis function in the i th representation. It takes to the l th representation. So, what you get out of this is a pi k prime I, which is same as pi k prime l. So, I can write this as pi k prime l. So, I wrote from the l th representation to the i th representation. What I have is delta j delta and delta i.

So this is the basic idea of projection. So you project an arbitrary vector and you project it and you get a vector in this representation. So, from an arbitrary vector you can extract what is the component of that vector in the particular representation. So, this is the list of this. So, just in this case you will have arbitrary vector v and you found the projection along u. So, the same way we had a basis function in some representation or you could even have taken an arbitrary basis function.

You can take a arbitrary function and you could project it you could find what is the projection onto the certain representation. So, this is an object that turns out to be very useful in constructing the symmetry adapted linear combinations. Now, let us consider a case where k prime and j prime are the same.

(Refer Slide Time: 44:57)



So, when k prime and j prime are the same then this has the expression, so p l k k prime phi j prime phi j i this is equal to phi k prime i. This k prime and you have delta i. You have it delta j j prime j k in this. So, j prime is just k. So, it is delta j k. So, instead of je prime, you have k. So, what you have in the right hand side is prime l k prime ok delta. So, instead of j prime here we take k. So, it is delta j k delta I knot. So, this is k prime. So, this is the diagonal elements. So, notice now we had A. So, even the expression for the projection operator diagonal elements of the matrix.

So, this involves only the diagonal elements of the matrix and gamma matrix. So, in this matrix representation, this involves only the diagonal elements. This expression also turns out very extremely useful. So, just using the diagonal elements of the matrix you can find a projection operators. So, this is something we will see and one point we should make here is that, in order to find projection operators we need the entire gamma matrix. So, that means you need the entire matrix. You need the entire matrix for the representation operation.

So, in any irreducible representation, you stage a matrix corresponding to that irreducible representation and you need all the elements. If you recall in the character table, you only have a trace. So, in the character table only psi square times of R appears. Also, psi of R is equal to gamma psi of R n l sum over l. So, it is sum of the diagonal element of this matrix, okay? But now in order to find the proportional projection, what you find is that it is not enough to know just a trace, but you need the entire matrix.

So, in a sense you truly want to find out all these projections and to the symmetry at arbitrarily linear combinations which is not sufficient to have just a character table with the group. You need more information than just the character table of the group. But what we see in some application is that, because you can use the diagonal elements you can find that with few manipulation. You know that just starting with the character table, you can get a large number of projection of operators. There are just a few others projection operators for which you need to do something more than just using the character table.

So, that is what we are going to see next. Another point I want to make is that, if you have a one dimensional representation, so for a one dimensional representation psi square r is equal to gamma to the power l of R. So, the matrix is a one dimensional matrix. It is just a scalar. So, the trace is nothing but the scalar itself and so knowing the traces are sufficient, so for a one dimensional representation you can entirely calculate all the projection operators. But for higher dimensional representation you need more than just a trace.

You need more than just a trace. You need to know the actual matrix elements. You need to know the actual matrix elements in order to in order to delight the projection operators. So, in the next class we will look at some examples of actual calculation on the projection operators. Then, we will go into it and see how they are used to construct previous linear combinations.