Mathematics for Chemistry

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Lecture - 32

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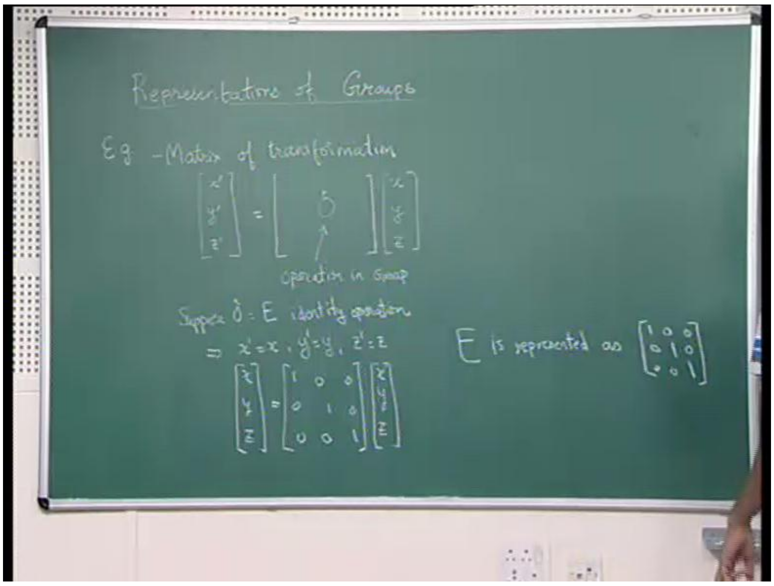

We have seen various symmetry operations in various symmetry groups, now what we want to do is to work away towards writing what is called the character table of a group. So, the character table of a group is how groups are typically represented, and the character table gives you all the information you need to know about the group. So, we will try to work away towards that. One important concept in order to understand the character table is what is called as representations of groups.

So, representations of groups is one important idea and to illustrate at this I am going to go back to something that you have already seen before which is the matrix of transformation of the group. And this is something that you seen before suppose I have an arbitrary point and I operate it this is an operation in the group suppose I perform an operation on an arbitrary point, then I get some resulting point x prime, y prime and z prime. So, any operation in a group can be thought of as something that transforms one point to another point, and the most general object one very general object that transforms vector into another vector or a point in Cartesian coordinates to another point is what is called a matrix. So, you can imagine that if I multiply this by a matrix, then I will get this new point.

And in fact these are the kinds of operations that we will be considering, these are linear operations and so these are the operations that turn out to be related to the various symmetries of the various symmetry elements. So for examples, suppose operator is the identity operation, so the identity operation you can immediately see the x prime y prime z prime is equal x, y, z. So, this implies x prime equal to x, y prime equal to y, z prime equal to z, so this is very clear.

And what you can say is that you are, so you have x, y, z and the matrix that accomplishes this transformation x, y, z. So, if you want to multiply a matrix to x, y, z to get x, y, z that matrix has to be the identity matrix, so this is your identity matrix. So, then you say that identity is represented as 1 1 1 0 0 0. In other words, this matrix is a representation of the identity operation, so this matrix's are presentation of this identity operation; now suppose the group has other operations.

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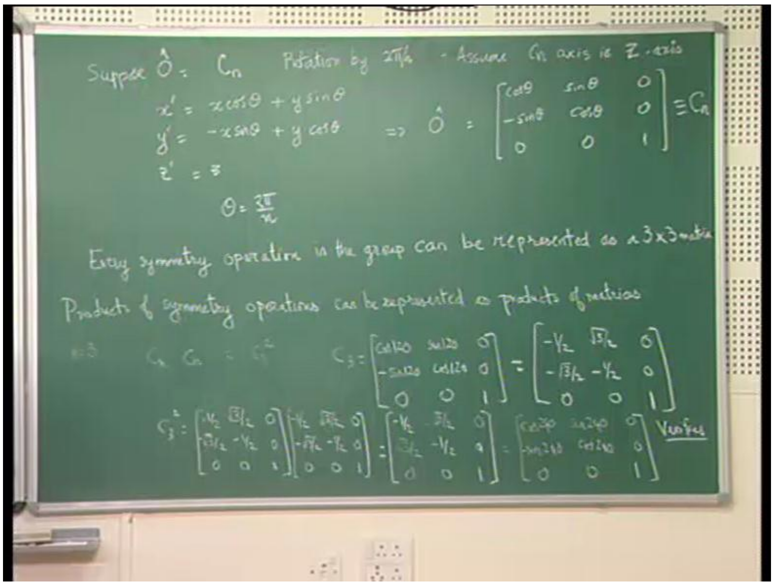

So, let us take another example suppose O is equal to C n, so rotation 2 pi by n. So, then you can show that when you rotate, so this is rotation by 2 pi by n by this angle, now when you rotate by this angle you can clearly see what will happen. Suppose I take a point x, y, z and I rotate by 2 pi by n I rotate by 2 by n and let us say assume C n axis is z axis. So, you are rotating about the z axis by 2 pi by n and when you do that then you know that your x prime is equal to x cos theta plus y sin theta, y prime is equal to minus x sin theta plus y cos theta and z prime equal to z. So, immediately this implies where O operation is represented by cos theta sin theta 0 minus sin theta cos theta 0 1.

So, this is a representation of C n for where you should mention so theta equal to 2 pi by n so this with theta equal to 2 pi by n is a representation the C n operation. So, the C n symmetry operation it is represented by this matrix the identity is represented by this matrix. Similarly, we can represent other operations also by this matrix but I would not go into the details, you can take a group and you can represent every operation in a group in this matrix form. So, every symmetry operation in the group can be represented as a 3 by 3 matrix, now there is one more thing about this representation and that has to do with the products.

So, products of symmetry operations, so products operations means you first you operate by one symmetry operation and then by the other. So, that corresponds to first operating by one matrix and then by another matrix, so you operate by one matrix to get this then you operate on this matrix to get on this vector to get the final vector. And this can be represented as products of matrices, so that means the representation of a product of operations is nothing but the product of the representations and you can see this very easily.

Suppose, I take C n multiplied by C n and let us say for convenience we take n equal to 3 if n equal to 3 then C n times C n, so this is C of 2 pi by 3 this is rotation by this is equal to C 3 square. Now, C 3 square corresponds to rotation by minus 120 degrees, so C n is rotation by 120 degrees our C 3 is rotation by 120 degrees C 3 square is rotation by minus 120 degrees. And C 3 square can be calculated in this way, so you start with C 3 is nothing but cos 120, sin 120 0 minus sin 120 cos 120 0 0 0 1.

Now, cos 120 is minus half sin 120 is root 3 by 2 0 minus root 3 by 2 minus half 0 0 0 1, so C 3 is by this matrix. So, the next question is what about C 3 square, so C 3 square will just be this matrix multiplied by itself, so you can evaluate so C 3 square is equal to minus half root 3 by 2 0 root 3 by 2 minus root 3 by 2 minus half 0 0 0 1. And if you do this so this multiplied by itself and if you take this product you can see what you get, so the first term will be plus 1 by 4 minus 3 by 4, so plus 1 by 4 minus 3 by 4 that is minus half.

So, you can easily see plus 1 by 4 minus 3 by 4 that is minus half the second term will be minus root 3 by 4 minus root 3 by 4, so that is minus root 3 by 2 and the third term you can see it is just 0. Similarly, what you can show is that this term is plus root 3 by 4 plus root 3 by 4 that is root 3 by 2 this is again minus half 0 0 0 1. Now, you can immediately look at this and you can see that this is cos of minus 120, so cos minus 120, this is or you can say cos 240 sin 240 0 minus sin 240 cos 240 0 0 0 1.

So, what it means is that this is nothing but the matrix representation of C 3 square and so this matrix product is a valid way of doing the matrix representation. So, this verifies that this is nothing but a representation of c three square, so C 3 square is represented by this matrix, so what we notice is that this matrix representation preserves the products, so this is the valid representation. Now, the other property of this representation has to do with the nature of these matrices.

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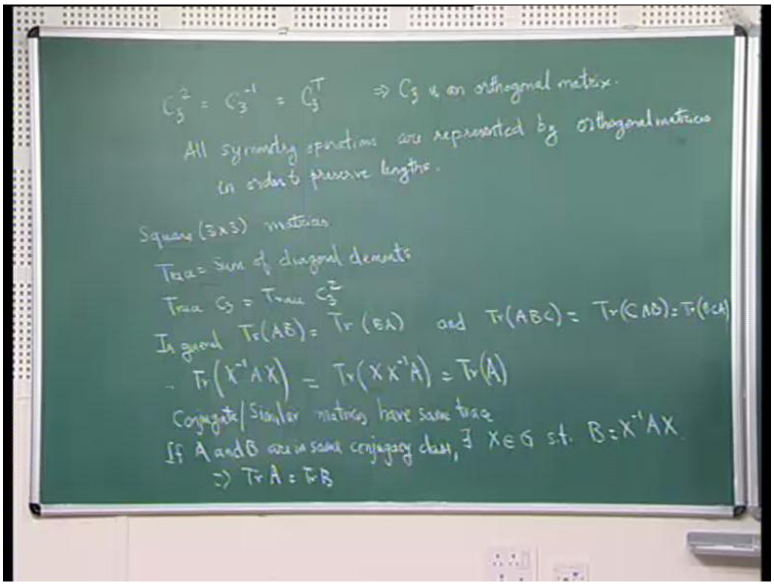

And what we notice is that if I take, so you notice that C 3 square has to be equal to C 3 inverse and what you notice is the following, this is nothing, so you look at C 3 inverse, so C 3 inverse is this, C 3 square is C 3 inverse and you notice C 3 inverse and C 3. So, you notice that C 3 inverse looks exactly like C 3 only these two elements are shift switched and in fact you can see that since the since the other half diagonal elements are the same.

So, you see that C 3 inverse is equal to C 3 transpose, so C 3 inverse so the inverse of C 3, which is c three square is C 3 transpose this implies C 3 is an orthogonal matrix. And you recall when you were doing the matrix of rotations that orthogonal matrices they preserve the dot product, they preserve the length of a vector. So, transformation by an orthogonal matrix preserves the length of a vector and it is very important that all the symmetry operations should preserve the length of this vector x, y, z.

So, all symmetry operations are represented by orthogonal matrices, in order to preserve lengths, this is a feature of all the matrix representations of symmetry operations. The other feature that we see in this representation is that these are square matrices square or 3 by 3 matrices. Now for square matrices a property of a matrix that is very useful is called the trace is equal to sum of diagonal elements. So, this is the definition of the trace and what you notice is that trace of C 3 is equal to trace of C 3 square so trace of C 3 in this representation trace of C 3 is trace of C 3 square.

And there is a deeper meaning to this, so in general trace of A B is equal to trace of B A and trace of A B C is equal to trace of C B A of B C A, it should be B C A. So, you can do a cyclic permutation, so you can get C A B is equal to trace of B C A, so the trace has this cyclic property. Now, this tells you something very useful see suppose i take… So therefore, trace of X inverse A X is nothing but trace of X X inverse A is equal to trace of A X X inverse is just identity, so trace of identity times a identity times a is just a so trace of X inverse A X is just trace of A.

So, this implies that conjugate or similar matrices have same trace, so the trace of two matrices which are related through the similarity transformation are identical. And so what we have already seen is that elements belonging to a class, so various elements belonging to a class are related to each other through this similarity transformation. So, if A and B are in same class same conjugacy class then there exists x belonging to group G such that B is equal to X inverse A X, so we immediately see that therefore, if A and B are in the same class.

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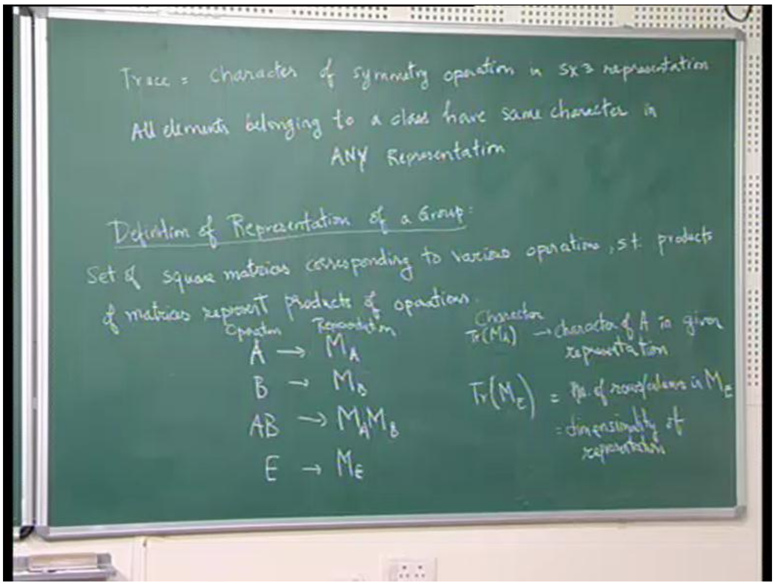

So this implies trace of A is equal to trace of B where A is the matrix representation of A matrix representation of B so the matrix representations of A and B have identical traces matrix representations of operations that are in the same class have identical traces. I want to emphasize right now, that this 3 by 3 matrix that we have been talking about is just an example of a representation, will also see other representations that are possible. But but the 3 by 3 matrix since you have seen this before that I want to use this example to motivate the representations. So, now trace is also called character of symmetry operation in the 3 by 3 representation.

So this so when you represent the symmetry operation as a 3 by 3 matrix then the trace is said to be the character of that symmetry operations. So, what we notice is that all elements belonging to a class have same character and I will mention this is we will say they have the same character in any representation; and here I have generalized from the 3 by 3 matrix to the to a more general representation. So, now we are all said to actually go towards character tables.

So what we want to lead towards is something called character tables, which are like the group multiplication tables but they are represented in terms of conjugacy classes and representations.

So now let us go to a more general definition of representation of a group, so we have look at this example and we have seen and we have seen how to use the 3 by 3 matrix. So, the definition of representation of a group, the general definition is that these as a set of square matrices corresponding to various operations, so that means, each operation has a square matrix associated with it, such that products of matrices represent products of operations.

So, if I have two symmetry operations A and B, then suppose I have A and I have M A is the representation of A, this is representation, so this is the matrix that represents A. So, if I had A is an operation and M A is it is representation; similarly, if I had B, which had a representation M B. So, A is represented by a matrix M A, B is represented by a matrix M B, then the product A B should be represented by first operate to by B, so it is this way M B M A. So, A B is represented by M A M B and if this is true for all elements of the group then this is a valid representation.

So, you have to have this satisfied for all the elements all the symmetrical operations of the group and then it becomes a valid representation. So, now once we have the representation it is very obvious to say what is the character of a representation and a character is nothing but the trace of character of A, so if is a trace of M A this is the character of A in given representation. So, if you have a representation when in which A is represented by a matrix, then the trace of M A is called the character of A in that representation. Similarly, for trace of B and trace of M A M B.

Now, suppose I take the identity and this is represented by a matrix M E, then clearly if M E. So, the trace of trace of this matrix is just going to be the number of rows, so is just equal to the number of rows or columns in M E so the trace of identity is just the size of the matrix. So, if it is a 3 by 3 matrix the trace of the identity will just be 3 because you can see that identity corresponds to 1 along the diagonals and 0 everywhere else, so the trace is just number of rows.

So and this will be true in any representation, if we have a 2 by 2 representation the trace of identity will be 2, if you have a just one dimensional representation then the trace of identity will just be 1 and this is also called dimensionality of representation. So, the number of rows or columns of M E is called the dimensionality of that representation, so if you have a three dimensional representation. So the 3 by 3 matrix was an example of a three dimensional representation, where the trace of identity was 3.

So, it will turn out that the character or the trace of various symmetry operations is what will enter the character table and you can immediately see that, since all elements of the same class have the same characters. So, we like to group the group the operations based on classes and then will write that trace of those, we will write the character of each of those classes.

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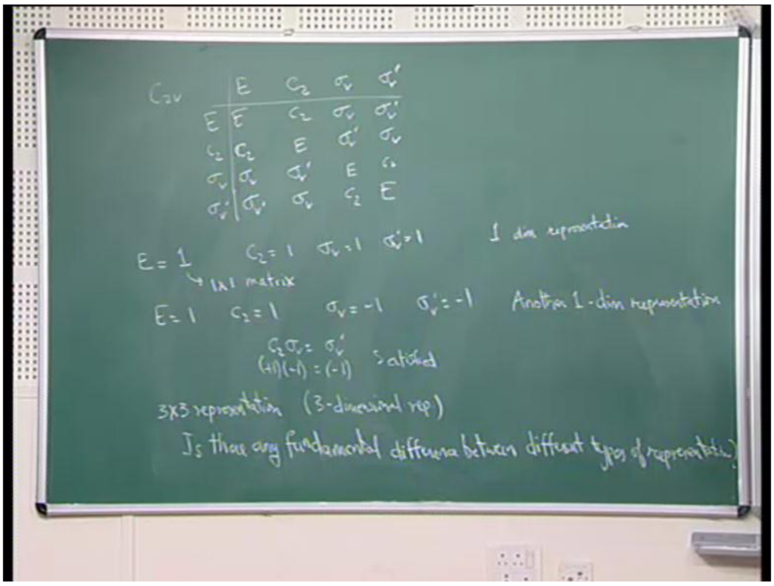

So, let us take a very simple example, let us take C 2 v, C 2 v consists of four operations it consists of E, C 2, sigma v and sigma v prime. So, then we can do the group multiplication table will be times sigma v times this should be identity sigma v should be C 2 times C 2 is identity C 2 times sigma v is sigma v prime sigma v times sigma v, so this is the multiplication table of this C 2 v group. And what we what, we can immediately see is that now we want a representation that maintains all these products.

So, let us looks at various representations, first let us look at a very trivial representation, so E is equal to 1, so 1 is a is basically a 1 by 1 matrix, E is 1, C 2 is 1. So if E equal to 1 C 2 equal to 1, sigma v equal to 1, sigma v prime equal to 1, then you can clearly see that E times C 2 or suppose I take C 2 times sigma v prime, then that we will be E 2 times sigma v is sigma v prime and sigma v prime representation of sigma v prime is 1. So, clearly in this way a very trivial way the products of operations they correspond to the products of representations.

So, this clearly satisfies this condition, this is a one dimensional representation, now you can have other one dimensional representations. So, for example, you could have the following E equal to 1 C 2 equal to 1 sigma v equal to minus sigma v prime equal to minus 1. Now, what you can see is that suppose I take E times C 2 I get C 2 E times sigma v, I get 1 times minus 1, which is minus 1 and all that works. Now, suppose I take C 2 square C 2 square is just 1 square that is 1.

Similarly, if I take sigma v square that is 1, which is identity so sigma v times sigma v should be identity, so sigma v square should be 1 and so on. But, you can also see that suppose I take C 2, suppose I take sigma v times C 2 sigma v times C 2 should be sigma v prime so if I take sigma C 2 equal to sigma v prime, now sigma v has a representation minus 1 C 2 has plus 1 and this is equal to minus 1.

So, you can clearly see that this is satisfied, so you can have, so this is also another one dimensional representation, you can construct many more such representations, I would not bother with all the details. But, basically it shows that you can construct two dimensional, you can construct three dimensional representations and so on and there is really no restriction on what you can do. So, let us, so this shows that we have seen that this 3 by 3 representation, or the three-dimensional representation so you can always use this three dimensional representation.

So, if I had used a three dimensional representation for this group then what you can show is that it will actually factor so the set of three dimensional matrices can be factor into a smaller matrices. So, we could have used a three dimensional representation, we could have used and here we used one dimensional representations and what we want to see is that is there any fundamentals difference between various representations so is there any fundamental difference between, I will say different types of representations.

And the other question we want to ask is you know since I have one dimensional representation I can always construct higher order representations very easily. If we know I can always make a if since I can construct a 3 by 3 representation I can construct a 6 by 6, 9 by 9, 12 by 12, I can construct any representation any dimensional representation I want. So, suppose I have this one dimensional representation then i can always construct a two-dimensional representation.

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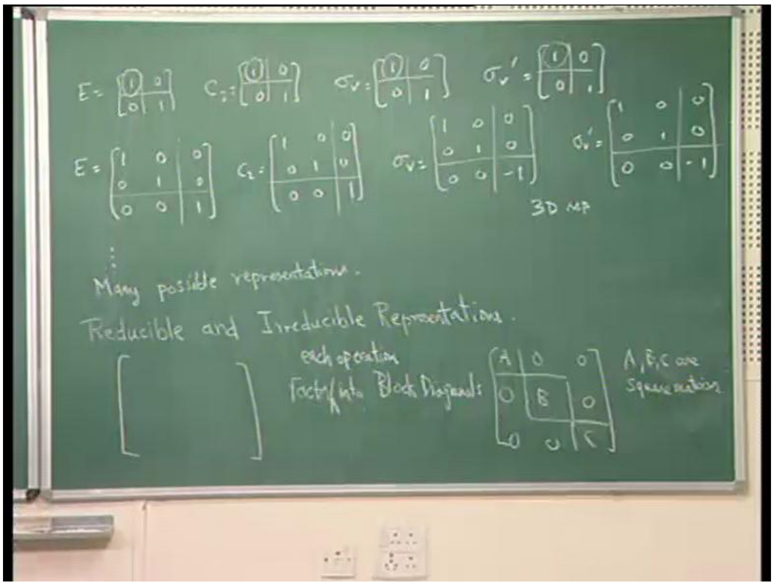

For example, I can say E is equal to 1 1 0 0 C 2 is equal to C 2 is I am using, so I can construct a two dimensional representations starting from this, so 1 1 0 0, sigma v 1 1 0 0, sigma v prime equal to 1 1 0 0. So, you can see that again everything is nothing but the identity matrix and products will also be identity matrix this is a two dimensional representation. Similarly if you want I can construct three-dimensional representations by just putting the this or I can put this and the other one.

So, just to make, so I put 0 1 0, so identity will always be this way C 2 for C 2 again I will just take 1 1 1 for C 2 prime I can take for sigma v, I can take 1 0 0 0 1 0 0 0 minus 1 and sigma v prime I can take as the same. So, I can always take this representation and you can clearly see that since 1 1 1 1is a representation and 1 1 1 1 is a representation and 1 1 minus 1 minus 1 is also a representation. So, this will also be a representation and I can keep doing this, I can keep doing this on and on and I can make all kinds of representations.

So, this is a 3D representation alternatively, I can also use the usual 3D matrix representation of the usual 3 by 3 matrix representation, so there are many possible representations. Now, we will distinguish something called we will say, we will distinguish between reducible and irreducible representations and this can be seen. So, let us take this representation, so 1 1 1 1 so this would be what is called an irreducible representation.

Whereas something like this would be what is called a reducible representation, the reason why this is called a reducible representation is the following that if you factor these into blocks then each of these is also a representation. So, each of the blocks is also a representation, similarly, I can factor this in to blocks I can factor it either into blocks this way, so if I have factor it this way then I get a one dimensional representation.

So, we already saw that this is a one dimensional representation 1 1 minus 1 minus 1 and this is an example of two dimensional representation, so this 2 by 2 matrix is an example of two dimensional representation and everywhere else you have diagonals. So, basically if I take a product of any two elements, I can do a product of this matrix and I can do a product of this and I can put 0 everywhere. So these are examples of reducible representations, whereas this is an example of an irreducible representation in the sense you cannot reduce it to smaller dimensional representations.

So, the way to do it formally is to see that, suppose you had a representation suppose you had a general representation and if you could… So you keep trying to factor it in to block diagonal forms into block diagonal form diagonals then you will get something that looks like this A, might get something like this B, C and you will get 0's everywhere else so you get 0's for all the. So, this is a general this is one part of the matrix this is another piece of a matrix, so all these are square matrices.

So, A B C are square matrices, so you keep doing this, you keep breaking in to block diagonals till you cannot break it anymore and then what you find is that each of these A B C 's are also representations. And if you cannot factor it anymore then they are called irreducible representations, so I will just give an example of a matrix.

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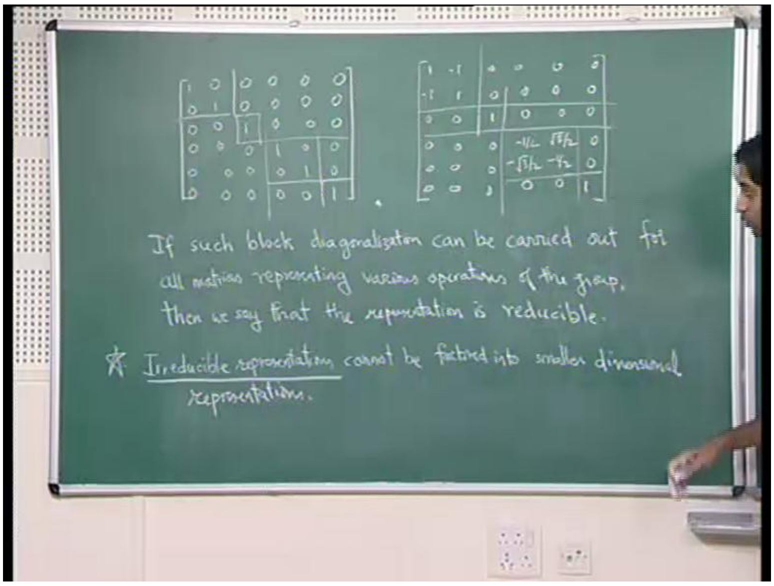

So, here is an example of we will start with a matrix, so the important part is each operation should be factored into such block diagonals. So, factor each operation, so if you can factor every operation in the group in to such block diagonals, then that representation is called a reducible representation, because you can reduce it to smaller representation; then each of these is also a valid representation. So, let us take an example suppose I had a matrix, suppose my various operations of the group they can be fact. So, one example let us say, so the identity operation will always be block diagonal.

So, the identity will always be diagonal, now if I had other operation and they had this structure, so this is one operation, this is another operation I will just take 1 minus 1 minus 1 1 0 0 0 0. And then I had let us say 1 0 0 1 I have one and let me take minus half root 3 by 2 0 root 3 by 2 minus half 0 0 0 1. So, suppose I had something like this, so if this is a representation of one operation and if all the operations, so I see that I can immediately factor this into this form so this immediately factors into something like this.

So, this has a now if all the operations in the group can factor into the same form for example, I could factor this also in to the same form I can do this for all the operations of the group, then you say that the six dimensional representation is not an irreducible representation so if such block diagonalization can be out for all matrices representing various operations of group of the group. So, if you can do such a block diagonalization for every for the matrix corresponding to each and every symmetry operation then we say that the representation is reducible.

So, we say that it is reducible and each of these individual so you keep doing this until you cannot do it anymore and each of these two by… So, this is an example of an irreducible representation, because you cannot make this into any smaller block, this is an example of an reducible representation because it is one dimensional, one dimensional representation by default is irreducible. Similarly, this is an example of irreducible representation because you cannot break it into smaller blocks for all the elements.

Actually in these two you can you can break it into this, but if there are other elements which mix the others then so you can also break this like this, so you can also go this way but this 2 by 2 representation is an irreducible. So, basically what we try to do is to break up our matrix into blocks such that there is 0, outside the blocks it is 0 and you try to do this for all the elements. So, irreducible representations cannot be factored into smaller dimensional representations, so what we have concluded by all these arguments is that there are two kinds of representations there are reducible and irreducible representations.

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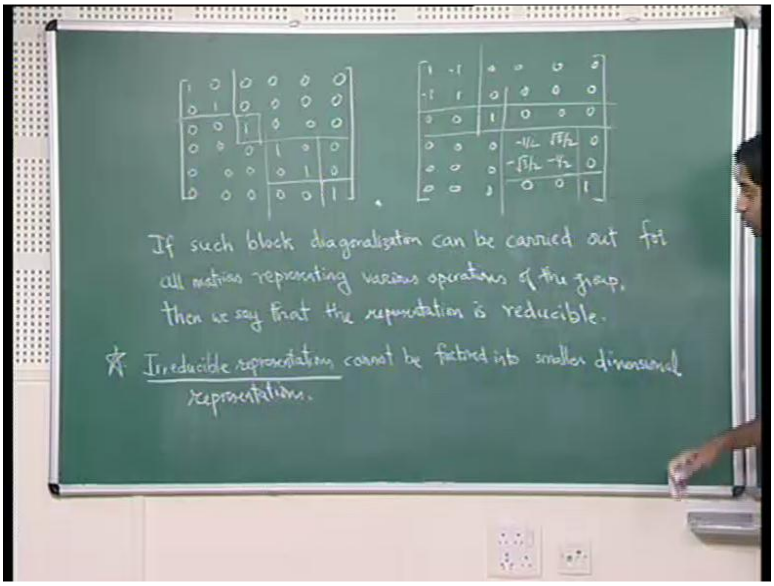

The reducible representations can or those representations which can be factor into smaller blocks, the irreducible representation are those that cannot be factor into smaller blocks. For example, this one is an irreducible representation, but it is very important to keep in mind that this factory has to be possible for all the symmetry operations, it is not if it happens only for one or two symmetry operations is not, you do not say that the that this is a valid factorization.

So, when you are looking to see whether representation is reducible or irreducible you should try to do this block diagonalization for all the elements for matrices corresponding to all the symmetry operations. Now, the irreducible representations or the once that are more relevant, so you can already seen that irreducible representations are the important representations, because I can always using irreducible representations I can always make more and more representations.

So, the relevant representations are the irreducible representations they are like you cannot using those you can always make up see using such irreducible representations I can always make up a bigger reducible representation. So, it is always of interest to know what are the how many fundamental different irreducible representations are there I any in any group. And this will be the topic of something called the great orthogonality theorem, which tells you how may irreducible representations are there so last thing that I will mention is that each of these matrix representations, each of these.

So this is a matrix representation of identity two by in a two dimensional representation this is what ever operation in a two dimensional representation. Now, all of these will have the properties of representations that is that the trace of two elements in the same class or the same so the character of two of any two elements in any representation will be identical if the two elements are in the same class. So, in the next class we will look at the great orthogonality theorem and what it tells you about the various representations that are possible.