**Mathematics for Chemistry**
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**Lecture - 34**

We have seen how to derive the character table using the great orthogonality theorem. Now, will go to one another application of this, this is for cyclic groups, and in cyclic groups there is relatively easier way to derive the character table and this is what we will see.

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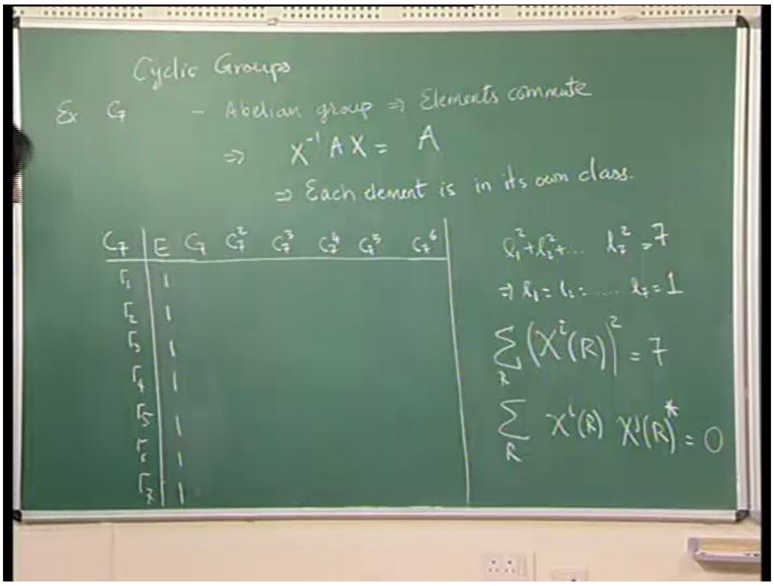


So, cyclic groups let us take the example of C 7 and in a cyclic group it is an Abelian group, every cyclic group is Abelian that implies elements commute. So, all operations of the groups they commute with each other, and that implies that X inverse A X is equal to A, X inverse A is same as A times X inverse, so A times X inverse X is nothing but A. So, this implies each element is in it is own class, so for example if you take C 7. So, C 7 the elements are C 7 C 7 square.

So, all these are not only the elements these are also their classes, C cube. So, these are the 7 elements and they are all in their own class, so the classes are these and since there are 7 classes there should be 7 irreducible representations, the sum of their squares. So, l 1 square plus l 2 square up to l 7 square is equal to 7 the order of the group, so this implies l 1 equal to l 2 equal to l 7 equal to 1. So, there are 7 one-dimensional representations.

So, we can say gamma 1, gamma 2, gamma 3, gamma 4, so I have missed the identity I have to show the identity element. So, there should be identity, so identity is also an element, so then you have gamma 1, gamma 2, gamma 3, gamma 4, gamma 5, gamma 6, and gamma 7. So, these are the 7 one dimensional representations and since, they are one dimensional representations, the character of identity is 1 in each representation. Now, we need to fill in all these values and we need to fill them in such a way, so that any 2 rows treated as vectors will be orthogonal and the sum of squares of across any row of the element should be equal to 1.

So, sum over all operations in any representation it should get 1, so will see that sum over R in this case since all are one dimensional representations chi is same as gamma. So, chi in the ith representation of R square equal to 7 sum overall all operations. Similarly, sum over all operations of chi in ith representation times, chi in the j th representation star equal to 0.

So, we need these to, so if you treat this row as a vector then these 2 vectors are orthogonal to each other. So, you take a dot product of these vector; that means, you take product of any 2 of these 2 elements plus these 2 elements and so on add it up you will get 0. Similarly, you take a dot product of any vector with itself you should get 7, so these are the conditions and we can see that there is a simple way to satisfy all these conditions.

So, these are the conditions that should be satisfied more over the products should also satisfy the relation like C 7 times C 7 square should give you C 7 4. So, whatever the character here multiplied by the character of this should give you the character of this and one easy way to satisfy them is shown right here.

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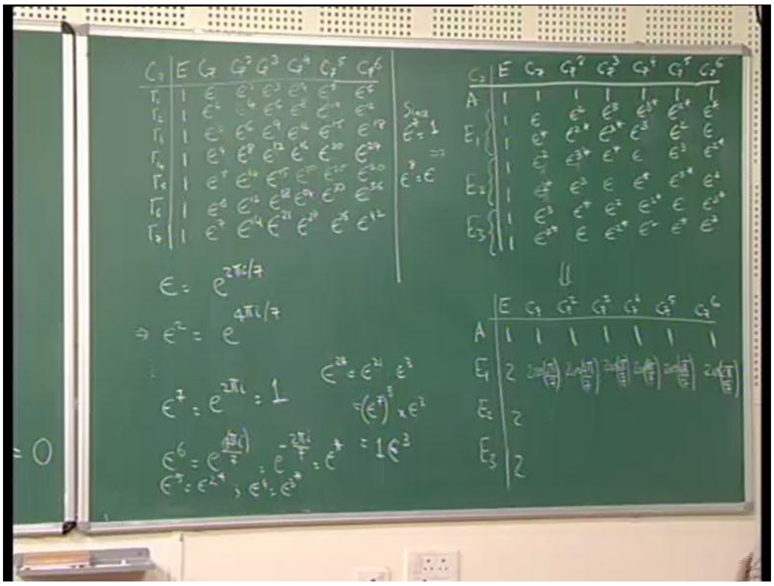

Where epsilon is equal to e to the 2 pi i divided by 7 epsilon is chosen as exponential of 2 pi i divided by 7. So, this implies epsilon square is equal to e to the 4 pi i over 7 and so on. And epsilon is to 7 equal to e to the 2 pi i equal to 1. So, epsilon denotes one of the 7 th roots of identity and what you notice here is that if you have if you define epsilon in this way then I can choose my elements this way I choose C 7 as epsilon then C 7 square is C 7 times itself. So, it should be epsilon square epsilon cube, epsilon 4, epsilon 5, epsilon 6 and you notice that epsilon rise to 7 is 1.

So, C 7 rise to 7 is nothing but the identity. So, that is also satisfied similarly, I can take C 7 as epsilon square and go ahead then this will become epsilon 4 6 8 10 12 if I take it as cube then it should be 3 6 9 12 15 18 and so on. Now since epsilon rise to 7 equal to 1 epsilon rise to 8 is equal to epsilon, so epsilon rise to 8 is epsilon rise to 7 times epsilon that is just epsilon. So, wherever you see epsilon 8 you replace it by epsilon, epsilon rise to 10 is nothing but epsilon cube because epsilon rise to 7 plus 3.

So, it is epsilon cube, epsilon 12 is epsilon 5 and so on. And you can go ahead and take all these elements and you can replace them replace all these higher numbers by epsilon 8 by epsilon, epsilon 10 by epsilon cube, epsilon 12 by epsilon 5. Further more you can do that you can go ahead and do that so if you take epsilon rise to 24 is 21 plus 3. So, epsilon rise to 21 epsilon rise to 21 is epsilon 7 cube, so epsilon 7 cube is nothing but identity, so it is just epsilon rise to 3.

So, you can do this for all the elements epsilon rise to 2 4 is equal to epsilon rise to 21 times epsilon rise to 3 is equal to epsilon rise to 7 cube times epsilon cube is equal to 1 times epsilon cube. So, you can express all the numbers in terms of epsilon powers which are less than or equal to 7 less than or equal to 6. So, further you can do one more manipulation which you can see this epsilon rise to 6 is equal to e to the 6 pi i 6 into 2 pi i by 7 is equal to e to the minus 2 pi i by 7 is equal to epsilon star.

So, you can easily see this because this is 12 pi i by 7 that is 14 pi i by 7 minus 2 pi i by 7 that is e to the minus 2 pi i by 7. So, we notice that epsilon star similarly, epsilon 5 is equal to epsilon 2 star and epsilon 4 is equal to epsilon 3 star. So, star refers to the complex conjugate, so then you can write this as epsilon, epsilon square, epsilon square epsilon 4, epsilon 4 is epsilon 3 star, epsilon 4 is nothing but epsilon 3 star, epsilon 6 is nothing but epsilon star epsilon 8 is epsilon rise to 1 epsilon 8 using this relation it is epsilon rise to 1 epsilon rise.

So, an epsilon 4 is epsilon 3 star. Now you notice in this representation that the 7 th representation is 1, epsilon 7 which is 1, epsilon 14 which is also 1, epsilon 21 which is also 1, epsilon 28 which is also 1 and so on. So, then what is done is you write this element on top this is just a totally symmetric representation which is always one of the possible representations for any group. So, you always have the totally symmetric irreducible representation, then you write these 2 gamma 1 and gamma 6.

So, gamma 1 as 1 epsilon, epsilon square now notice this is 1 epsilon rise to 6, epsilon rise to 6 is nothing but epsilon star, epsilon rise to 12 is epsilon 5 which is epsilon 2 star epsilon rise to 18 is epsilon rise to 4 which is epsilon 3 star, so I write it in this form. So, 1 epsilon square epsilon 3 the epsilon 4 is epsilon 3 star epsilon 5 is epsilon 2 star then epsilon 6 is epsilon star. So, I write it just in terms of epsilon, epsilon square epsilon cube and their complex conjugates. So, then I can show that I order the table in this way.

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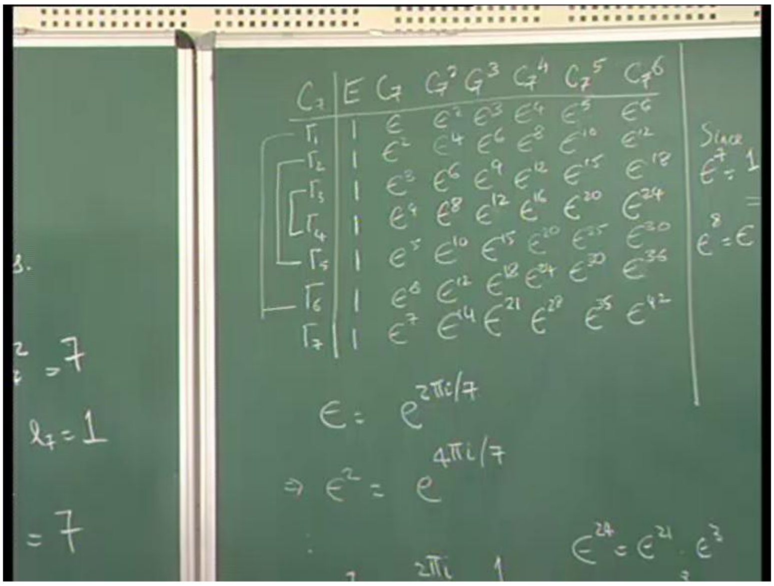

So, I collect gamma 1 and gamma 6 I collect gamma 2 and gamma 5 I collect gamma 3 and gamma 4, so gamma 1 gamma 6 gamma 2 gamma 5 gamma 3 gamma 4. So, I write it in this form and now what you notice is something very interesting if you look at this row and this row this row is just a complex conjugate of this row above. So, you have epsilon, epsilon square epsilon cube epsilon star epsilon 2 star epsilon 3 star epsilon 3 star epsilon 2 star epsilon star epsilon 3 epsilon 2 epsilon.

So, this row is nothing but a complex conjugate of this row similarly, this row is a complex conjugate of this row and this row is a complex conjugate of this row. So, basically what we notice is that these 2 one dimensional representations these are 2 one dimensional representations it make sense to combine them into a two-dimensional representation. This is a 2 dimensional representation the 2 components are nothing but complex conjugates of each other.

This is also taught of as a 2 dimensional representation. So, in some books you will find this group represent the character table represented in this format, in some other books what is done is these two are added together. So, if you add these two together you will get 2 if you add these two together you will get epsilon plus epsilon star.

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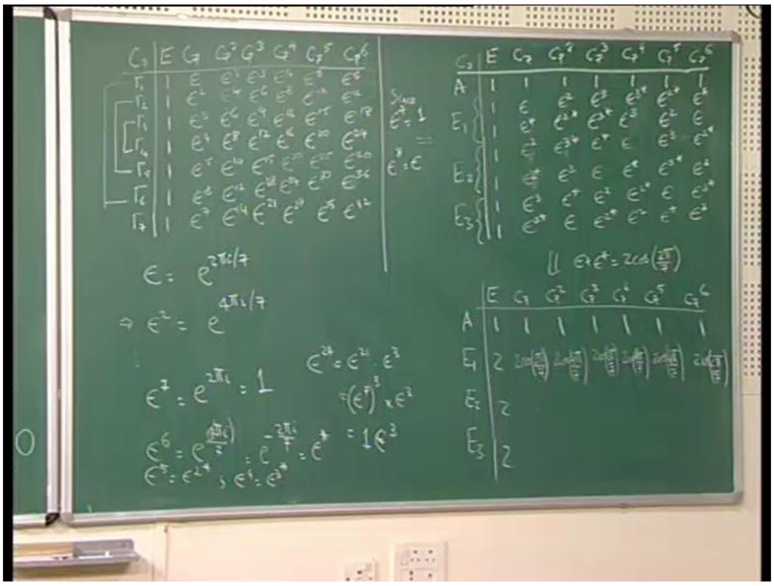

So, epsilon plus epsilon star is equal to 2 cos 2 pi by 7. Epsilon is e to the 2 pi i by 7 epsilon star is e to the minus 2 pi i by 7. So, if you add them up you will get twice cos of 2 pi by 7. So, you can fill up this row in this form, so you have 2 cos 2 pi by 7 2 cos 4 pi by 7 2 cos 6 pi by 7 epsilon 3 star plus epsilon 3 is same as this. So, 2 cos 6 pi by 7 2 cos 4 pi by 7 and 2 cos 2 pi by 7 and similarly, you can fill in for e 2 and e 3. So, there are 2 alternate ways in which character table of cyclic groups are represented.

And you find both of these used you can show that this satisfies all the transformation properties that this other representation also satisfy. So, both these representations are used but you should be a little careful when you use either of them. So, that is about what I want to say about character tables for cyclic groups. Next we have looked at parts of character table but we want to now look at the character table in it is entirety with all the various parts of the of the character tables.

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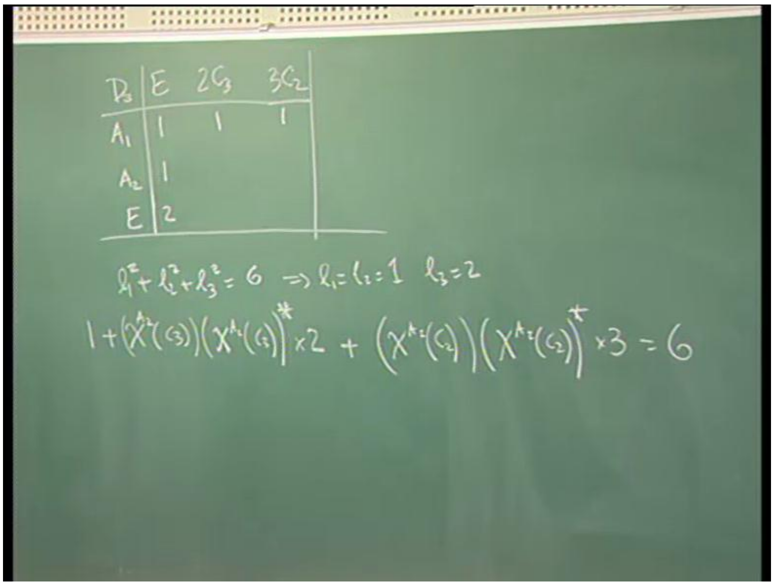

So, let us look at the group D 3, now D 3 has 3 different has 3 classes the identity element which is in one class. Then there are 2 C 3 they C 3 and C 3 square and then there are 3 C 2, so there are 3 C 2 operations they belong to one class. Now D 3, so you can say that number of classes is 3 since, so you have number of irreducible representations as 3. So, l 1 square plus l 2 square plus l 3 square is equal to 6 this implies l 1 equal to l 2 equal to 1 l 3 equal to 2.

So, you have 2 one dimensional representations and one 2 dimensional representations, so I can call it A 1 A 2 and E. So, these are the 2 one dimensional representations and this is the two dimensional representation. Now, the character of identity will be 1 1 and 2 there will always be a totally symmetric representation. Now you have to work out what are the remaining characters, so to work that out you use a great orthogonality theorem.

So, if I call this as suppose i call this chi of C 3 in representation A 2 chi of C 3 in A 2, now it should satisfy 2 properties first is that if you take the dot product of 1 row with itself you should get 6. So, then this will be 1 plus chi A 2 chi A 2 of C 3 square and there will be 2 of these. So, into 2 plus chi A 2 in A 2 of C 2 into chi in A 2 of C 2 star and this should be multiplied by 3. So, this sum should add up to 6 more over it should be orthogonal to this row.

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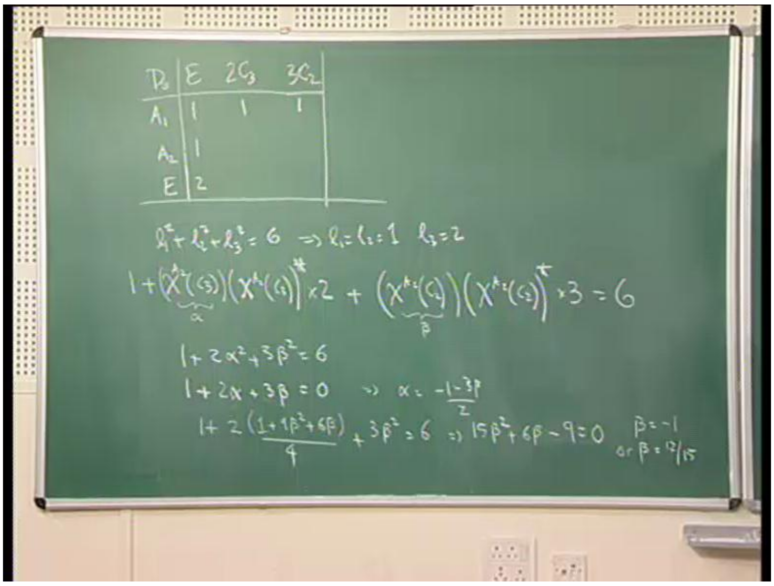

So, I will just denote this by alpha and this by beta, so then you will say 1 plus 2 alpha square plus 3 beta square equal to 6 similarly, it should be orthogonal to this. So, I take dot product of these 2, so this will be 1 plus now, I will get alpha into 1. So, and this will be multiplied by factor of 2. So, 2 alpha plus 3 beta equal to 0. So, you have these 2 equations and you can solve this for alpha and beta. So, you have alpha and beta are the unknowns.

So, let us work it out, so one solution if you just try to solve this what you will get from the second one is that alpha is equal to minus 1 minus 3 beta by 2 and if you substitute this in the first equation what you will get is 1 plus 2 into 1 plus 9 beta square plus 6 beta divided by 4 plus 3 beta square into 6. Now if you rewrite this what you will find is the following, so what we will do is multiply this by 2. So, get 9 plus 6 15 beta square.

So, the beta square term will be 9 plus 3 times to 6 15 beta square and then you have 6 beta plus 6 beta minus 9 equal to 0. So, you have 1 plus 2 is 3 and here you have minus 12 oh you have 12, so 3 minus 12 is minus 9, so you will get this equation and if you solve this you will get beta is equal to minus 1 or beta equal to 12 by 15. So, if you solve this you will get these 2 possibilities of beta. So, if beta is minus 1 let us take the case where beta is minus 1 then clearly by using this equation alpha has to be equal to plus 1.

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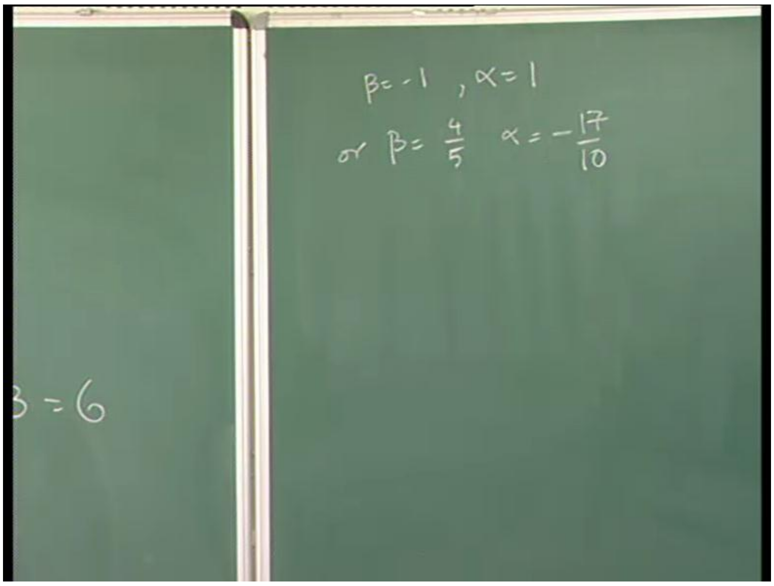


So, 2 solutions are beta equal to minus 1 alpha equal to 1 or 12 by 15 is 4 by 5, so beta is 4 by 5 what should alpha B. So, if beta is 4 by 5 then 3 into 4 is 12 by 5 17 by 5. So, minus 17 by 10 beta is 4 by 5, so you can check again 4 into 3 is 12 plus 5 is 17 and this is minus 17 by 10. So, these are the possibilities, so these 2 choices first of all they will be normalized. So, if you sum the squares you will get 1 secondly they will be orthogonal to this, so no if you sum the squares you will get 6.

Secondly if you take the dot product of this you will get 0, so these are the 2 possible choices now, the question is how do you know which one to put here and the answer to that is you have to have this second set you have to work out the 2 dimensional representation.

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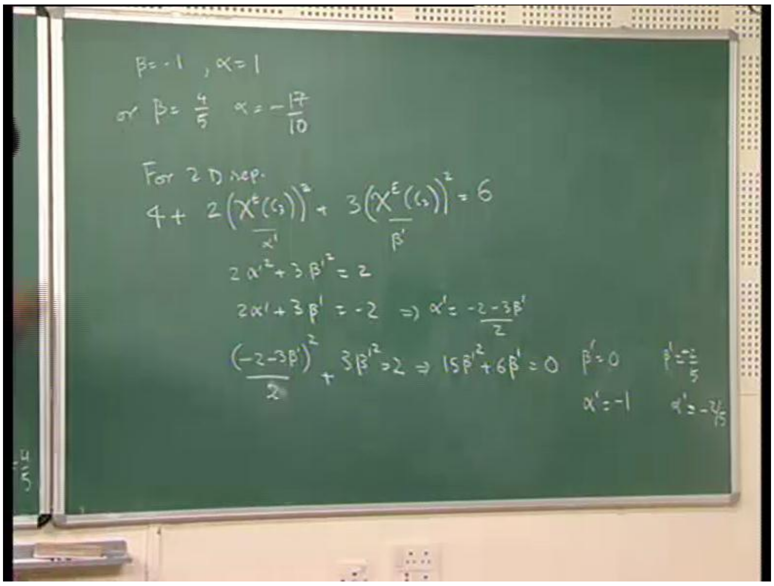


So, for two dimensional representation what you will say is that first is the sum of squares here should be 4 plus 2 chi e of C 3 square plus 3 chi e of C 2 square equal to 6. So, this I can write as if I call this alpha prime and this as beta prime. So, I can write this as 2 alpha prime square plus 3 beta prime square is equal to this is 4. So, that is 2 the other relation you can also write, so this is 2 plus so you can write 2 alpha prime plus 3 beta prime equal to minus 2.

So, you can write these two relations and this can also be solved again using the same method you can solve this. So, what you will get is equal to minus 2 minus 3 beta prime by 2 and if you substitute in here what you will get is by 2 plus 3 beta prime square equal to 2. So, this implies, so 4 and in this case you have a 4 on the right. So that one will give 0, so you will get 9 beta square plus 3 beta square 12 beta prime square, and you have 6 beta prime 9 plus 6 15 beta prime square plus 6 beta prime equal to 0.

So, that will be the final result. So, this implies beta prime equal to 0 or beta prime is equal to 6 by 15 6 by 15 is just 2 by 5 and this implies alpha prime is equal to minus 1. So, beta prime is 0 then clearly alpha prime has to be minus 1 beta prime is should be minus 2 5th if beta prime is minus 2 by 5 then this is minus 2 into 3 is minus 6 by 5 minus 6 by 5, so if you take that away. So, you will give you minus 4 by 5 minus 2 by 5. So, alpha prime should be minus 2 by 5 these are the two possibilities.

So, both these are equal to minus 2 by 5 then clearly this is 5 into minus 2 by 5 that is minus 2. So, you can have either of these possibilities are allowed, so you had two possibilities for alpha and beta and you have possibilities for here.

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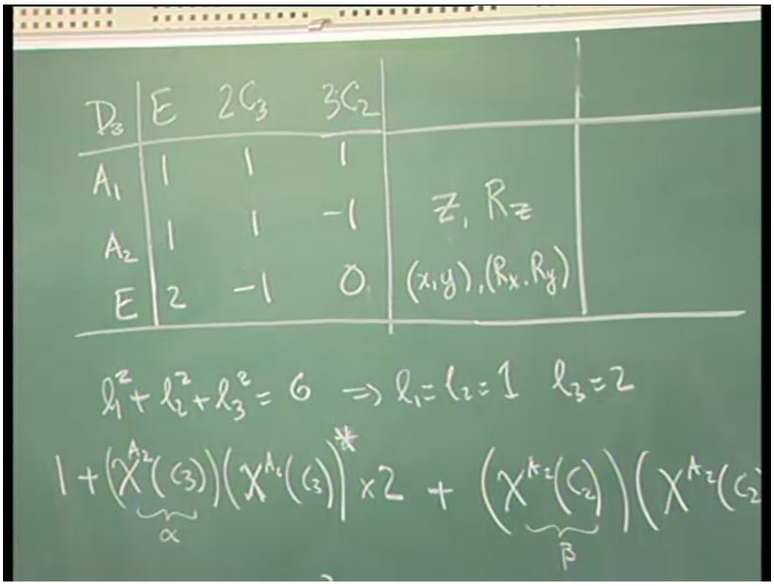


So, I will just write it here, so you can have 1 minus 1 or you can have minus 17 by 10 and 4 by 5. Now this will satisfy orthogonality with this then you can also have in this case you can have minus 1 0 or you can have minus 2 by 5 minus 2 by 5, so these are the 2 possibilities here. Now it is also important that these 2 should be orthogonal to each other and if you impose that condition you can clearly see that if I take this and this if i take these 2 they will clearly not be orthogonal. If I take these 2 also they are not orthogonal.

So, basically this second choice is not valid. So, you can directly eliminate this choice and also you see that you can eliminate this choice because this is not orthogonal to this these 2 are not orthogonal to each other. So, this choice can also be eliminated and so you have left with only one choice that is 1 minus 1 and 2 minus 1 0. So, this is important it has to be these 2 rows also have to be orthogonal and this is the only choice that satisfies that these 2 rows are also orthogonal and these 2 are orthogonal and these 2 are orthogonal.

This is the basic only possible choice for your characters. Now the now if you look at a character table there are 2 more parts of the character table. So, there are some things there are these 2 parts of the character table there are 2 additional parts of the character table, and what appears here is the following in this path what appears is one of the following either either x y z R x R y R z. So, one of these one or more of these will appear for the group I will illustrate this with an example.

So, for this group D 3 what will appear here is z and R z and here what will appear is x y R x R y. So, what appears for D 3 is z and R z here x y or x y in one bracket and R x R y in other bracket, so what does this signify is the following. So, when you imagine that you have x y and z axis, so you have x y and z axis, now when you operate by e by C 3 and by C 2 on the z axis. When you operate by e C 3 and C 2 on the z axis C 3 will not do anything to the z axis because C 3 axis coincides with the z axis those C 2 s; however, will change z to minus z.

So, e will not do anything C 3 will not do anything C 2 will change that to minus z. So, this A 2 this irreducible representation is exactly how z transforms how the z axis transforms under these operations is exactly how this A 2 representation characters behave. Therefore, z is put here similarly, rotation about z axis will also not be affected by C 3 and C 2 will change the rotation to minus of that rotation, so these characters are like the characters of this of z or R z, so z and R z behave exactly like A 2.

So, in other words these various representations they are like different ways to express various operations and this way of expressing operations is consistent with z and R z. Now, let us take the 2 dimensional representation, so the 2 dimensional representation e, now what this does to your identity is nothing happens to identity. Now what you notice is that C 3 that character is minus 1 and C 2 the character is 0 you can think of it in this way, so x and y what happens to x and y under C 3.

So, when you operate by C 3 x and y get mixed into each other, so C 3 mixes x and y. So, C 3 does not change z but it mixes x and y and C 2 will not do anything to x and y but it will change that to minus z depending on which way C 2 is oriented it might also affect x and y but in general it changes z to minus z. So, the point is if you work out the character if you work out the matrix of transformation for x and y and work out for R x and R y what you will find is that there characters are exactly represented by these 2 minus one 0.

So, and what this represents is that x and y gets mixed R x and R y gets mixed but together in this is the 2 dimensional representation which transforms exactly like these characters. So, will illustrate right here, so you can think of it this way, so suppose I take x y and I imagine that I have a 2 dimensional vector x y with components x and y and I operate it by c 3 c 3 is about the z axis.

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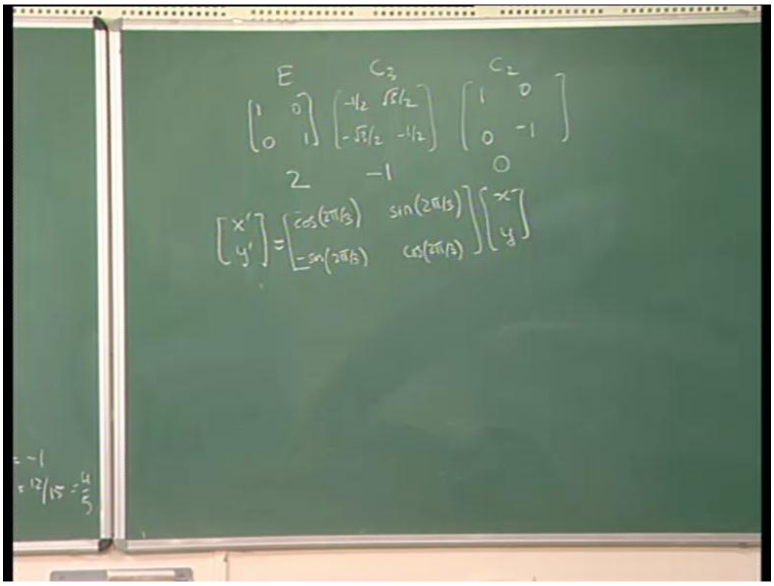


Then the new vector will be x prime y prime and this can be written as cos 2 pi by 3 sin 2 pi by 3 minus sin 2 pi by 3 and cos 2 pi by 3 times x y. So, the transformation from x y to x prime y prime under rotation under C 3 is this matrix. So, C 3 the matrix corresponding to C 3 is this.

Now what is the trace of this matrix is minus 1 the matrix corresponding to the identity is just. That has trace 2 now the matrix corresponding to C 2, so let us take, so this has 3 C 2 axis which are perpendicular to the z axis. So, if you take one of them along the x axis then the matrix of transformation will be shown as this because the x coordinate is not changed y coordinate changes to minus y z of course changes to minus z but we are not showing z we are just showing x y.

So, the trace of this is 0, so what this means is that if you think of a vector like x y or 2 dimensional vector x y that will transform exactly like this representation. So, this representation is how a vector a 2 dimensional vector x y transforms similarly, R x R y these rotations will also transform according to these with just these characters. So, this is the third part of the character table which is where only these 6 elements will appear and each of them will tell us how these operations transform under these symmetry operations. There is a 4th part of the character table, so here we only use x y z R x R y R z. Now sometimes there are various products of like x into y or x square plus y square which transforms exactly according to certain representations.

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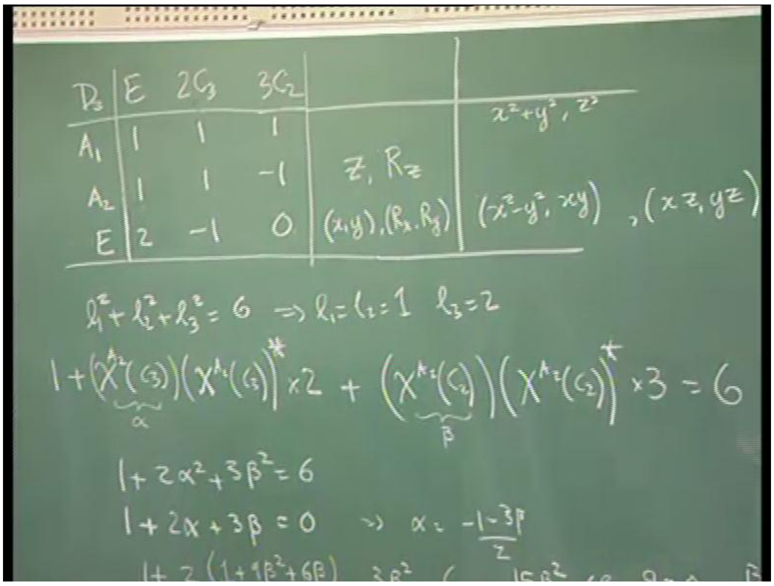

So, for example, this in this case I will be x square plus y square and z square. So, if you take z square if you operate C 3 on z square that trace will be identity C 2 on z square the trace I means you can easily show that c 2 takes z to minus z. So, z square will nothing will happen to z square similarly, C 2 will preserve x square plus y square and C 3 will also preserve x square plus y square. So, these are preserved and so they transform like A 1, so this product appears in the first row.

Now what are the products that transform like A 2 in this case actually there is no simple product that transforms as A 2 but there are some products that transform as e and that is x square minus y square x y it has to be a 2 dimensional representation or you can have x z y z. So, if you had a vector like x square minus y square and x y. So, which had 2 components x square minus y square and x y you could have done exactly you could have seen what is the effect of identity.

And that will have a character of that will have character 2 what is the effect of C 3 on x square minus y square and x y and you can show that will have character minus 1 similarly, if you take C 2 will you can easily show C 2 will take x to will preserve x and change y to minus y. So, then x square minus y square will be preserved, so and then x y will change sign. So, you have 1 minus 1. So, you will get 0.

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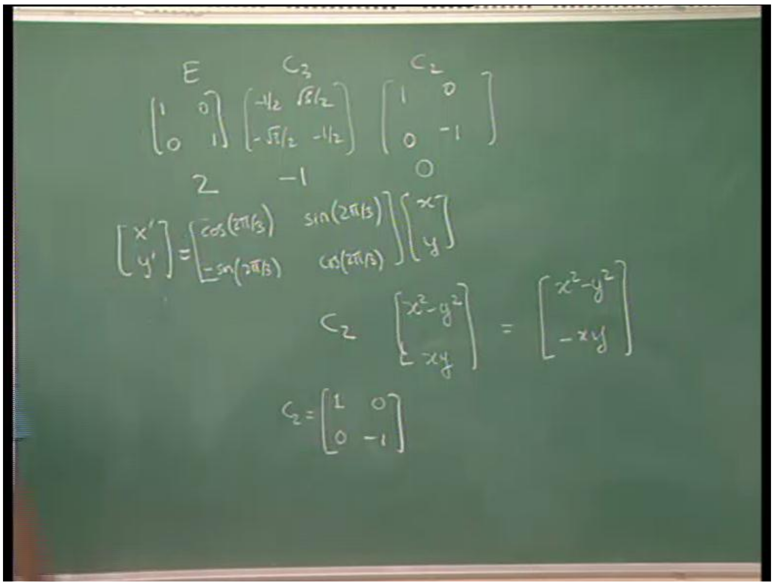


So, you take vector of the form x square minus y square and x y and you operate it with C 2 so then what you will get is the following. So, C 2 will take x to C 2 will keep x as it is, so will get x square C 2 will change the sign of y to minus y. So, x square minus y square will remain x square minus y square x y will become minus x y, so then you can write C 2 is equal to 1 0 minus 1. So, these operations. So, this vector transforms like e.

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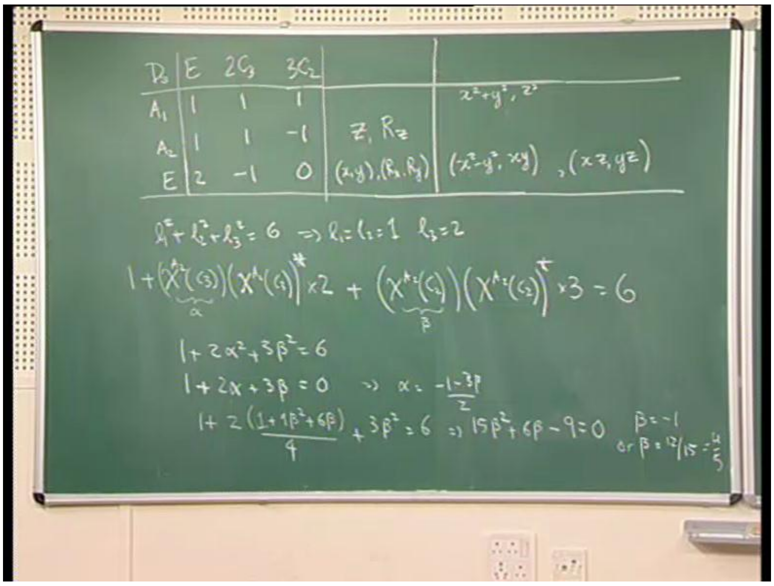


Similarly, you can show that x z y z a vector with components x z and y z will transform exactly like this. So, these products are represented these simple products of various coordinate axis or what is represented in this 4th part of the character table. Now, these will become these are actually extremely important you will notice immediately that these products seen very familiar. So, this looks like you immediately identify you have seen that d x y d y z d x z d x square d y square.

So, you immediately see that there are lots of similarities and in fact one of the major applications of group theory is to find out which orbitals mix with each other which orbitals overlap. And so when we look at an application of group theory in quantum mechanics, all these it is important to know which representations allow various products to mix. So, this concludes the character table and I urge all of you to go back and try look in any book look at a character table of any group and try to identify try to derive it step by step.

And when I say derive all parts not just this part not just characters but also these parts and when you get once if you have done it for 1 or 2 groups then its fairly straight forward to do it for all the other groups. Now I will before I end the discussion on character tables I want to mention one other theorem that is one other relation that is extremely useful in for lot of practical applications.

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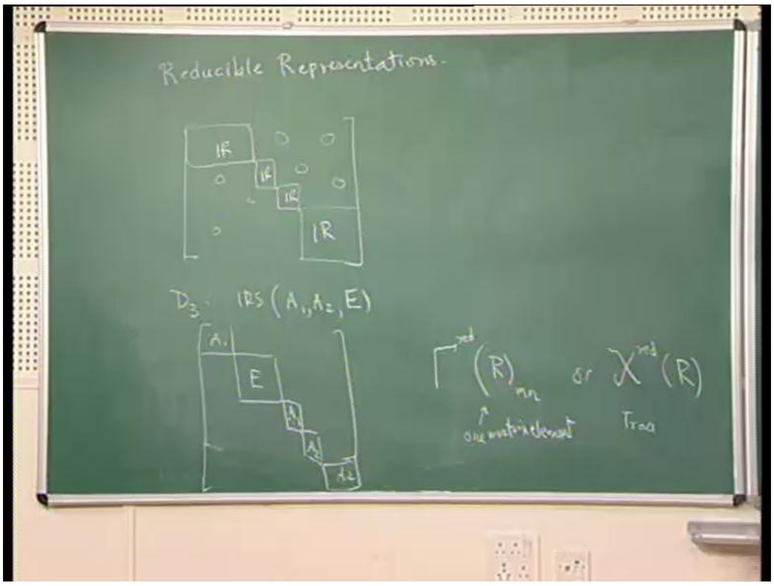


So, now this has to do with reducible representations. So, now if representation is reducible then the matrix corresponding to that representation if it is reducible it factors into various it will factor into various block various other matrix and there will have 0 everywhere else. So, all these will be 0's and will factor into this might be a 3 dimensional this might be a 1 dimensional and so on. So, any reducible representation can be factored into irreducible representation. So, this is this are irreducible representations.

Now if you do any if you do this then sometimes the same irreducible representation might appear multiple times. So, when you take any reducible representation you write it in terms of irreducible representation then sometimes, for certain matrices you can easily imagine that one irreducible representation appears multiple times. For example, if you had the D 3 group had 3 irreducible representations they were A 1 A 2 and E, E was a 2 dimensional representation.

Now if you had a you could imagine that you have a matrix that is reducible, so you have reducible representation and in this when you block diagonalise, it app you have A 1 appearing once E A 1 A 2. So, you could imagine that something like this, so then what you would say is that and once again you have A 2. So, you say that A 2 appears twice A 1 appears twice and e appears once. Now the question is if this if a reducible representation also has even in a reducible representation you can speak of characters.

So, I can ask gamma for a gamma for a reducible representation I can ask what is the character of some operation of m n, I can ask some question like that. So, for a reducible representation what is the character of R m n, how is this related to the characters of the corresponding irreducible representation. So, I can ask m n character or I can ask what is a character the trace of the reducible representation of R. So, in the reducible representation what is the character of a particular operation this is one matrix element.

So, this is the m n th matrix element this is the character of the trace of the matrix corresponding to the reducible representation of operation R. So, how is this related to the trace of the irreducible representations now, you can immediately look at this and you can say the answers.

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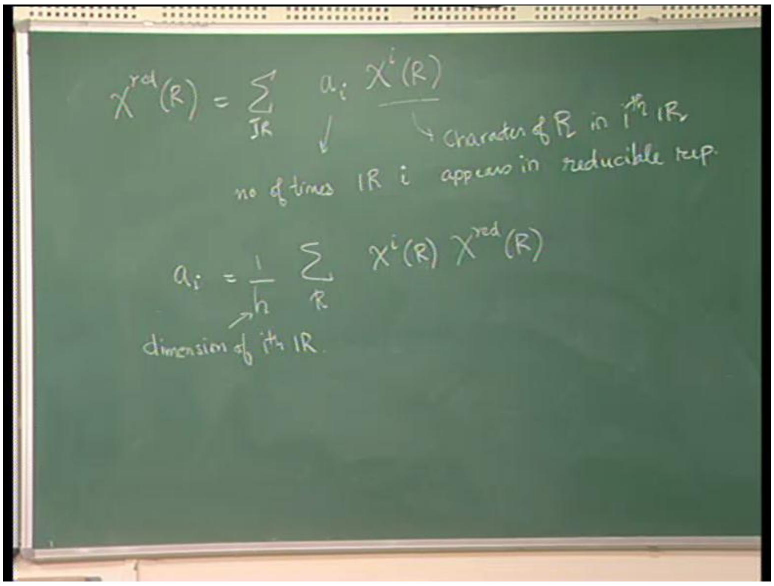


So, chi in the reducible representation of R that has to be, so if you had something like this what you notice is that E appears once. So, the trace of this should be trace of A 1 plus trace of E plus trace of A 1 plus trace of A 2 plus trace of A 2. Trace of this matrix is trace of A 1 plus trace of E plus trace of A 1 plus trace of A 2 plus trace of A 2. So, you can judge generalize this in the following form sum over all irreducible representations a i chi i of R. So, this is the character of R ith irreducible representation and this is the a i is the number of times irreducible representation i appears in their reducible representation. So, how many times thus the irreducible a i.

And here you can use the great orthogonality theorem and you can say that a i is equal to sum over all R. So, it will be chi i of R and chi reducible of R, so and this divided by h i one over h sorry where h is the dimension of i th irreducible representation. So, you can show this relation easily you can just use the great orthogonaliy theorem, if you multiply on the multiply both sides by chi i of R then you can show this you can show such a relation.

So, this is an extremely useful relation it looks very much like the usual you know when you, expand one vector as linear combinations of basis vectors then the coefficients of the basis are got by dot product of this vector with the basis vector and it looks exactly like that and in fact that analogy is useful and correct. The only thing the great orthogonality theorem always has a h factor that appears and so this relation is very useful in application.

So, again when you are doing when you are constricting linear combination of orbitals in various theories, then it is then such relations will prove to be extremely useful. So, with this will close the discussion on the character tables and characters next will go to something called symmetry adopted linear combinations, and this will be this is where we get into the heart of applications of group theory.