Chemical Applications of Symmetry and Group Theory
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Lecture – 17

Welcome back. So, today is the day 2, of week 4. So, we were discussing about the properties of the characters of the square matrices and we said that for conjugate matrices we had identical character. So, we proved that point and today I am going to show you real example of that. So, now, if you concentrate on this here, this matrix represents the C 3 symmetry operation.

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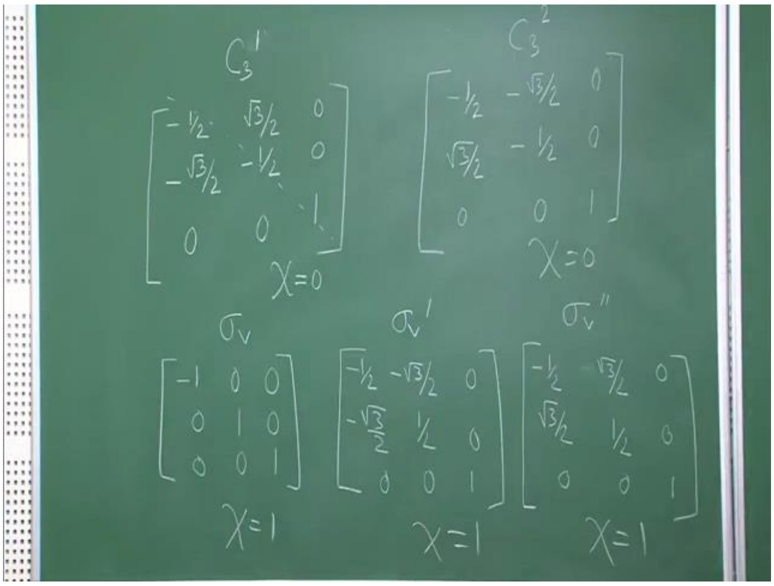

So, C 3 1 means just C 3 and this matrix represents C 3 2, that means, operates C 3 in twice. So, we know when we discussed about the ammonia problem, quite sometime back we said that in a C 3 and C 3 square they form a class; that means, C 3 and C 3 are conjugate elements of that group.

So, now the matrix representation of C 3 and C 3 square, which are given here, they should also follow this, there you know, their own, follow the characteristics of the symmetry operations. That means, this 2 also should form a class, therefore, this 2 element, this 2 matrices should be conjugate, if that is true and if whatever we learnt in the last class if it is true, then their character should be identical. Let us have a look at this. So, the character is the sum of the diagonal element, right? So, in this way, minus half, minus half, plus 1 ; that means, that the character for this one is 0, character is given by this chi. So, here again if we look at, this minus half, minus half, 1, again, the chi is 0.

So, that proves our point, that conjugate matrices have identical character. Let us have a look at some more. So, for the same problem of C 3 v, I have 3 sigma v's and we also said at that point of time that, these 3 sigmas, they form a class, therefore, this matrices representing sigma v, sigma v prime and sigma v double prime, they are conjugate with each other therefore, their character should be identical. Let us verify that. So, here the character is minus 1, plus 1, plus 1, means 1. Here minus half, plus half, plus 1, means character is again 1, here same. So, again we have proved that point, that conjugates matrices which represents the conjugate symmetry operations, they are, they have identical characters.

So, therefore, we can see the importance of the character. If you think carefully, when we say that you know some particular symmetry operations, belonging to a particular group, form a class, they must be something similar in them, in certain properties and that those properties should be also reflected by the matrix representation and thereby, the characters, as per the definition. Now we obtain the, you know, conjugate elements of the group by symmetry transformation, similarly I can use the symmetry transformation on the matrix representation, to find the conjugate matrices. Now the characters of these matrices, which represents the symmetry operations, belonging to a particular class and we know that there are something similar in this, you know, symmetry operations, that is exactly reflected here, when you look at that characters. All the characters are identical. So, we used to say that there is some similarity in this symmetry operations belonging to a class and we see here, that their characters are exactly same.

So, that is an important lesson that you should, you know, take.

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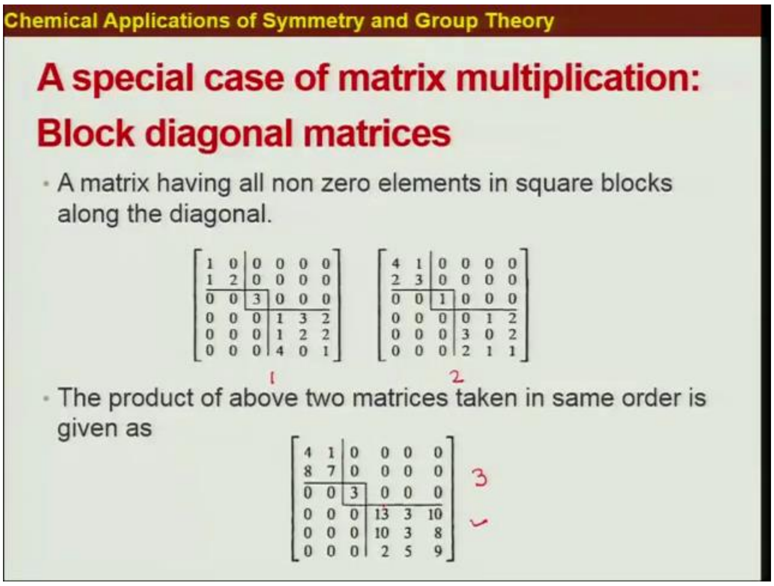

Now very often we are dealing with, you know, combining symmetry operations and thereby combining matrices, while you are talking about matrix representation. And we say that matrix representation can be very large, we can have you know like n by n, n can be like you know 30, 40, 50, 60, whatever numbers. Now if we want to combine 2 such matrices, it is really cumbersome.

Now, there are ways to reduce our workload here, how? We can have these square matrices, such that, all the nonzero elements, of those matrices are you know, kind of blocked as a square block, along the diagonal and rest of diagonal elements are 0. Such matrices are called block factored matrix or block diagonal matrix. So, on your screen, you can see such example of block factor matrix or block diagonal matrix. So, say this is matrix 1, this is matrix 2 and you can see that, you know, this square block along this diagonal, again this square block, this square block, they are all along diagonal and only this blocks have nonzero elements and you know this part or this part, they are all 0s.

So, this is 1 block factor matrix, this is another 1 and they are block factored in this, very same way. So, that is what we have right now. Now if we want to combine this 2 matrices; that means, if we want to have the product of this 2 matrices, which are block diagonalized, then we find this matrix, which is I say matrix 3. So, what are the things that are important to find in this case? So, the main important thing is that, the resultant matrix that we get, is blocked out or block factored, in exactly he same way as the constituent matrices here. So, that is very obvious.

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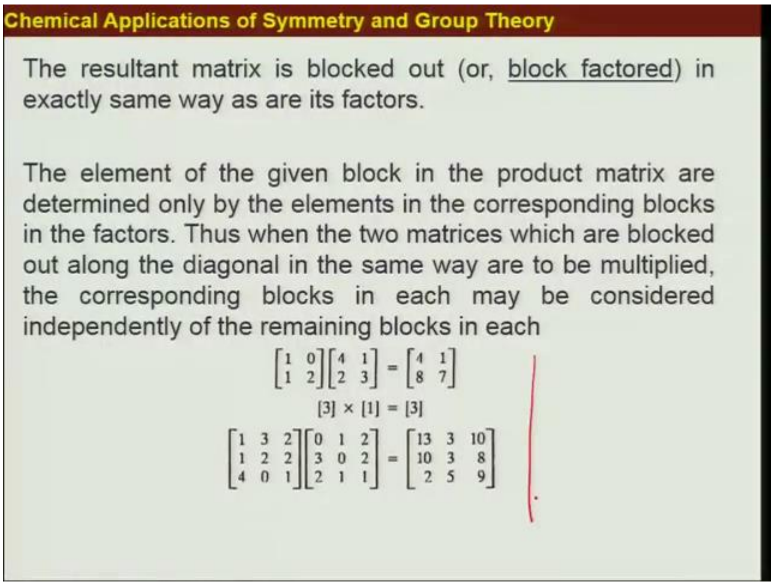

More over the element of the given block, we have 3 blocks there, so, element of the given block in the product matrix, are determined only by the elements in the corresponding blocks, in the factors. Thus when 2 matrices, which are blocked out along the diagonal in the same way, are to be multiplied, the corresponding blocks in each, may be considered independently, of the remaining blocks in each. So, what that it mean, I have a overall matrix suppose I have 1, 2 and 3 blocks in the matrix, rest of the elements are 0. I have another matrix of the, which is block factored in the same way and if I want to multiply them I do not need to consider anything else.

So, I choose the first block here, first block here, do the multiplication and you put it in the same block in another third matrix, you do the same thing for the second block, multiply with the second block of this matrix, third block and third block here and then put the resultant in the respective place in another matrix. So, thereby you will get the, you know, matrix multiplication. So, exactly that is what is shown here in this image. So, you just multiply in this block, you know and get the overall multiplication, overall product.

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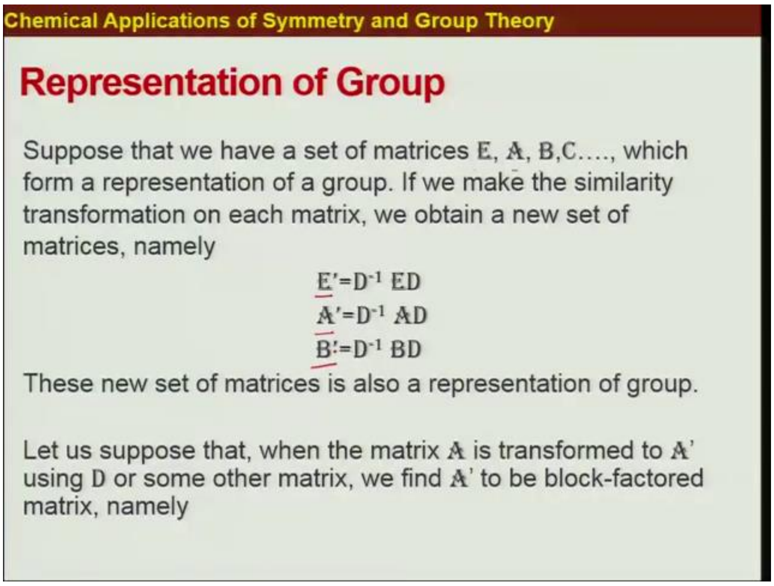

So, suppose we have a group and we have this matrix representation and matrices are you know E, A, B, C and so on and that represents a group. Now if I do similarity transformation on each of this matrices, we, we, we can find any matrix within the group, which we will you know use for the similarity transformation.

So, that is what is shown here, say like you know I find a matrix D and use that to do the similarity transformation on each of the elements of this group, here it is the each of the matrix. So, I do a similarity operation on the matrix E, on matrix A, on matrix B and so on and I get a matrix out of it. So, I call it E prime, A prime, B prime and so on. Now this new set of matrices that I will get, by doing the similarity transformation, will also form a representation, why so? It is very easy to proof. So, let me do that real quick say.

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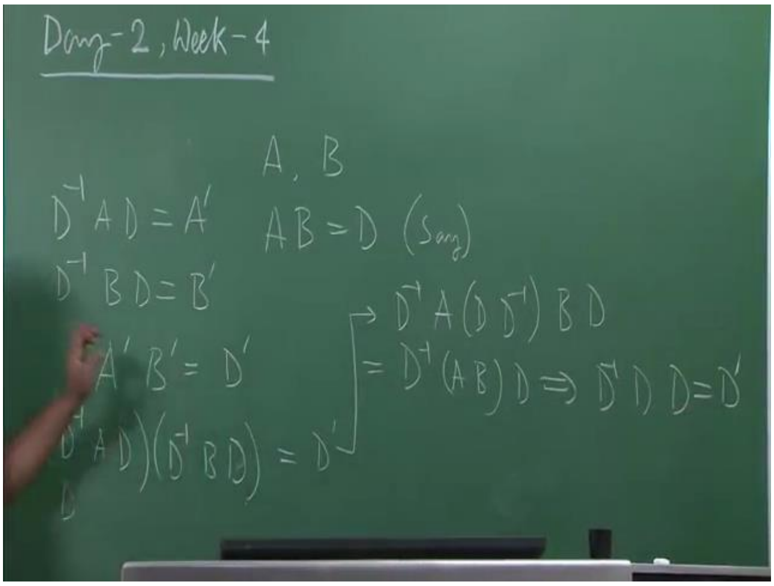

I have 2 elements A and B and I do this similarity transformation, like, using this matrix D. Now suppose I have a matrix A and matrix B, such that A and B, if I combine gives D, suppose I have this condition. So, say, now I find, I use this D, to do the similarity transformation on you know, on this product.

So, if A and B are 2 matrices and D is another matrix. Now if I do, say, a similarity transformation as D inverse A D, equals to A prime, as we have just shown in the on your screen and D inverse D is B prime and we want to show that this A B, they are part of the group that we are considering. And this all this matrices A B C, all this forming a representation and we want to show that, upon this similarity transformation, we are finding this new matrices, A prime, B prime, C prime and so on, they also altogether form a representation of the group.

So, now if we combine A prime and B prime in the same fashion, A prime and B prime I will get something like D prime, I should get. So, now, if I do a similarity transformation on this product, so what is A prime B prime? So, A prime B prime is D inverse A D and D inverse B D, right? That is my D prime. So, this one, I can rewrite as D inverse. So, may I should write here so that you can see. So, D inverse A, D, D inverse B D so this part is identity, therefore, I can write this is equals to D inverse, A B, D, fine which means I have D inverse, D D. So; that means, this is the similarity transformation of D, what I get is D prime correct? So, therefore, I can see that, this D prime, which is the newly formed matrix after the similarity transformation, can also act as the representation.

So, that is what is that, what is written here. Now having said that, if we suppose that when we are transforming, we are doing the similarity transformation on this matrices a B C and all, the new matrices A prime, B prime C prime, you know that we are getting they are block factored and they are block factored in a same way, all of them are block factored in a same way then, we are talking about some situation like this.

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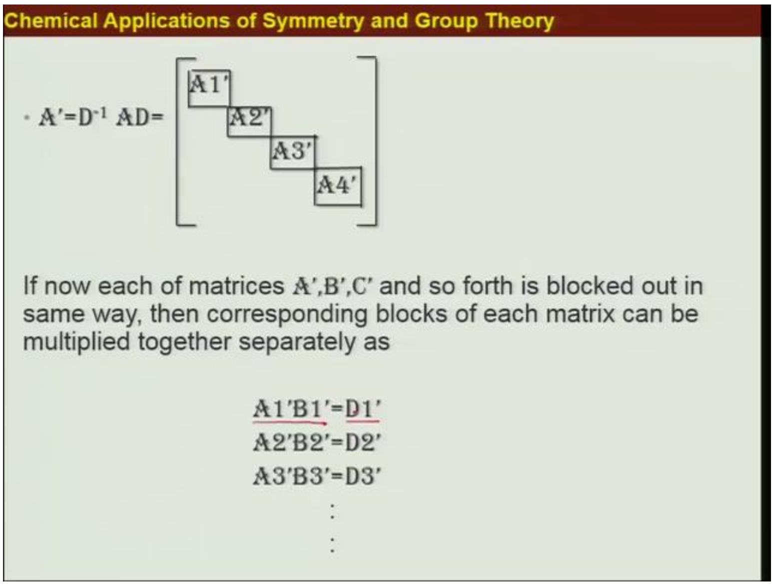

So, this A prime, is a similarity transformation by, by this particular matrix D and this is block factor in this fashion. So, I have say form example here 4 blocks, A 1 prime, A 2 prime, A 3 prime, A 4 prime and all the other you know matrices that are generated, say for example, B prime or C prime, F prime so on, they will be also block factored in the same way.

Now, in that case, what we can have, we can again you know, combine this newly form matrices in, you know, very easily, how? Because we have just seen, that you know block factored matrices, which are block factored in the same way, we have to just consider you know, individual blocks and then multiply this with the corresponding block in another matrix. So, here if I have to find, you know, the you know, the matrix form of D prime, then I just have to multiply this blocks A 1 prime and B 1 prime, we get D 1 prime and we can get other block also in the same way.

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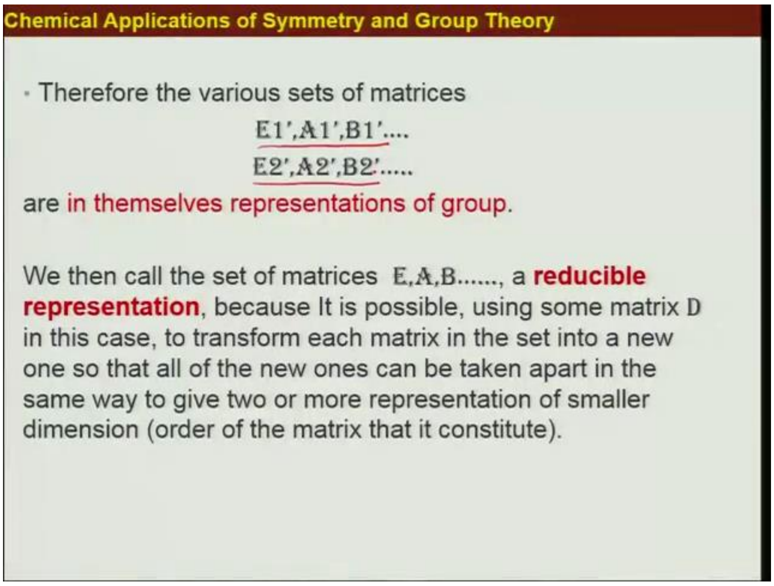

So, I get this newly, you know, form representations in terms of you know like, A prime or B prime or C prime, all this thing they form representation of group, we just saw that. Now once we see that it is possible to take a representation like A B C, that we started with and then by doing some similarity transformation, if possible, we can block factored, we can block factored all these matrices and those also act as the representation of the group, then we can take each blocks and form a representation. So, for example, this E 1 prime, A 1 prime, B 1 prime, they are just the you know blocks taken out from each of this you know, matrices that are formed out of similarity transformation.

So, another block is E 2 prime, A 2 prime, B 2 prime so on, A 3 prime, B 3 prime, E 3 prime so on. So, each of this, you know, this set of this, you know, blocks, are also the representations. When we can do this thing, then we say this original representation that we form, that is matrices A, E, A, B and so on, they are reducible representations, meaning that I can reduce them into smaller blocks, smaller dimensions. I started with say, you know, 9 by 9 matrices, for each representations and I can do the similarity transformation, I can get you know, say you know, 3 by 3, 2 by 2 and 1 by 1 matrices, which themselves form the representation, in the original representation that I form is called reducible representation.

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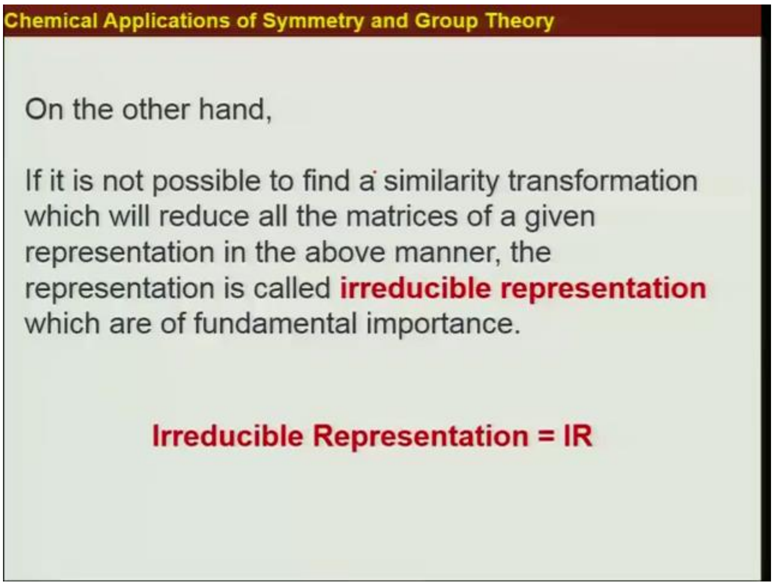

And on the other hand, if it is not possible to find a similarity transformation, which will reduce the matrices of a given representation, that representation is called irreducible representation or in short IR. We will be using this term very often, henceforth that irreducible representation or in short, IR.

Now, just like the characters, this irreducible representation, they contain a lot of information and they can be actually used for the, you know, practical application purposes. So, we will see that in greater detail probably in a following class or next to next, when we learned about the particular theory called great orthogonality theorem. We will know how to you know deal with this irreducible representation, what are their properties and we will learn about you know, how this irreducible representations, they actually represents, you know, say, in a given molecular state or in other words the wave functions of, you know, any particular given state of the molecule.

So, those things we will start discussing in you know, in the next class of the next to next.

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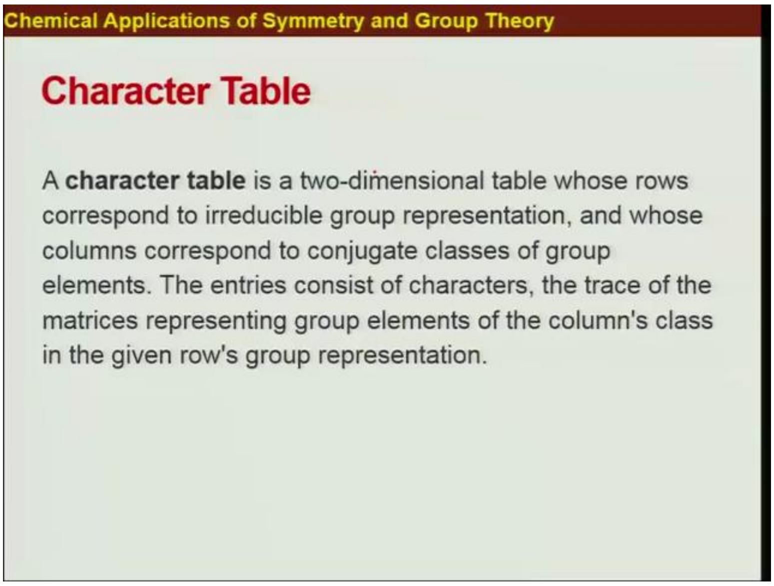

Now after learning the about the character, we will just mention to you about the table called character table, which is extremely important for to us. So, what is the character table? Obviously, it is a table, which is a two dimensional table, whose rows corresponds to irreducible group representations or simply irreducible representations and the columns corresponds to the conjugate classes of the group elements. The entries consist of characters, the trace of the matrices representing group elements of the columns, class, in the given rows group representation. So, let us have a look at, that particular table, which is known as character table and that is on your screen. So, this is the so called character table, of one particular point group.

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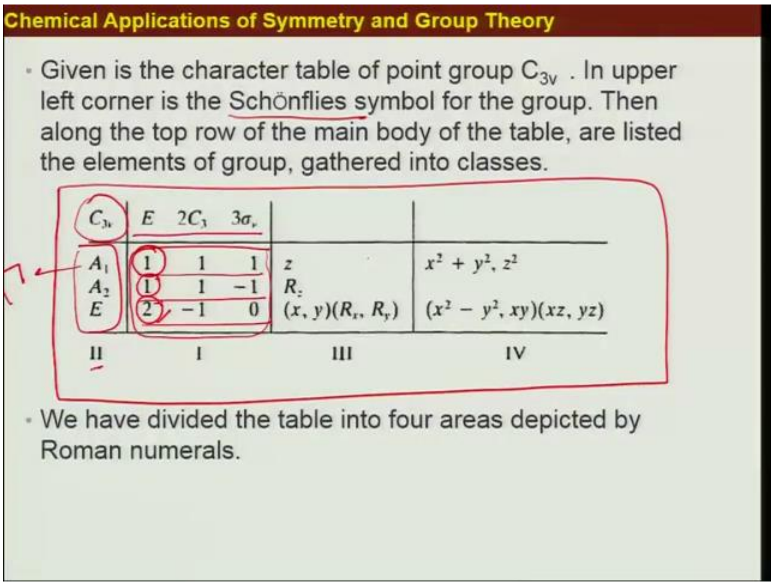

So, essentially, this particular tables, you know, tells us a lot about this, about the symmetry of the particular, you know, molecule which belongs to this particular point group C 3 v here. So, a quick look at this table, will tell you that there are several areas, several sections, in this table, you know, at a very beginning you can see, the top left corner, you have the symbol of the point group which is given by the Schonflies notations. And then next to that, you have the symmetry elements, which are clubbed in classes. And then we have the characters, then we have certain other symbols and some you know functions, linear or you know non-linear functions are there in different, different areas, which we have you know classified as area 1, area 2, area 3, area 4 and so on.

So, we will talk about this, you know, detail divisions of the character tables and we learn those things in big greater detail.

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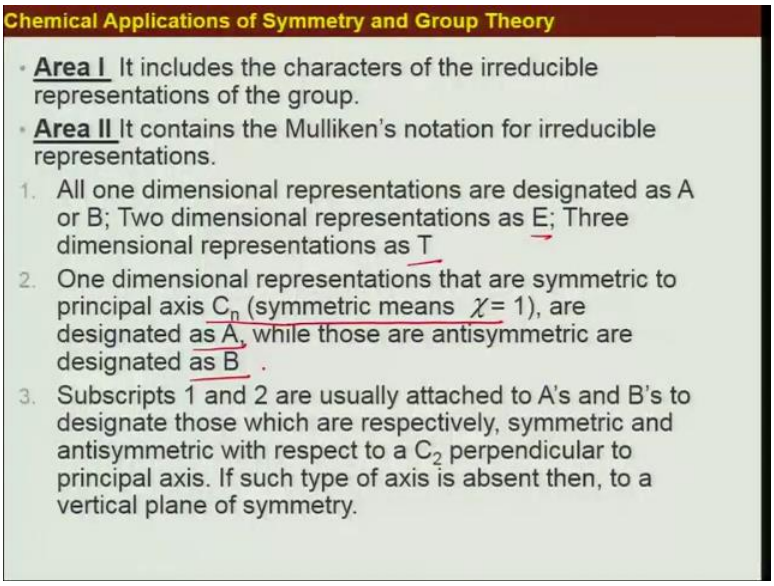

So, first is the area 1. So, what does area 1 give me? So, let us have a look at the area 1. So, here we have all the characters given here. So, each one, each row, this row or this row or this row, they give me the characters of irreducible representations, different irreducible representations. We can see here that there are 3 rows so, then; that means, we have 3 irreducible representations. So, any character table deals with irreducible representations, it does not deal with reducible representation, that we must be very clear about. And this number of rows that is the number of IRs, that are possible for a particular point group is fixed.

So, by doing an exhaustive analysis, you know, people have already figured out, that these are the you know numbers of irreducible representation, that is possible, that is which is maximum possible irreducible representation for the particular point group and you consult any standard text book of our group theory or symmetry, you will find this character table there or even you can get it in many books of quantum mechanics. Now we will we will talk about this different irreducible representations and all this things in greater details, when we come to the great orthogonality theorem. Now that is about area I.

Now, let us look at the area II. So, area II it contains several symbols. So, earlier when we were forming the representation of group, we said that, the name of the representation of group is gamma. So, we use the term gamma instead of these things. So, we said gamma and we found that, those representations are probably reducible, may not be reducible, may be irreducible, but if we have you know more than you know more than 1 representations so, we use to differentiate by gamma 1, gamma 2, gamma 3, so, that is a generalized term. Here we can see there are some specific terms like A 1, A 2, E and if you go to many other character tables, for many other point groups, you will see there are various different terms. So, like A prime, B prime, A 1, A 2, A g, E g, B g and all those things au.

So, what are this term that are written in area II? So, these are the symbols which is called Mullikan symbol, named after RS Mullikan. Now these symbols are not given arbitrarily, they are there is definite convention of using this particular symbols. So, let us see what are the particular rules or conventions that are followed, to this nomenclature. So, when we look at any irreducible representation, in the character table, we can find out their dimensionality. So, dimensionality of any irreducible representation is the, the number or the character, corresponding to the identity operations, that is the dimensionality. So, for example, if I just quickly look back, so, here I see that, you know, for the first representation, we have the character as 1, for identity operation, for the irreducible representation the second irreducible representation also has a character 1, corresponds to identity operation, while the third irreducible representation has character 2 corresponding to identity.

So, the first two are the one dimensional irreducible representation, while the third one is a two dimensional representation. So, we have to see what are the relation between different irreducible representation, their dimensionalities or the certain other aspects and how can we form, how can we name them, by using Mullikan symbol. So, all the one dimensional representations, they are given the symbols as a or b. So, if you find, an irreducible representation, which has a character as 1, for identity operations, then you know that this particular irreducible representation will be either A type or B type. So, any irreducible representation which has a dimension 2, then that is termed as E, while irreducible representation having dimension 3, will be termed as T, as it is written here. Now after assigning this A or B or T or E, for this particular IR, based on their dimensionality we move a little further.

So, let us see what are those for one dimensional irreducible representations, after we are assigned that they will be either A or B, how do we know whether it will be A or B? We have to look at the character correspond to the principle axis symmetry. If the character corresponding to the principle axis of symmetry C n is symmetric, meaning positive 1, then this particular IR will be termed as A and if it is negative 1, then it will be termed as B. So, for symmetric character with respect to C n is A, while anti symmetric character with respect to C n, will be as, termed as B. So, next we look at the, you know, characteristic of the irreducible representations, with respect to the perpendicular C 2's, perpendicular to the principle axis of symmetry.

So, if the you know characters of the representations, which are one dimensional, if the characters are with respect to the C 2 primes, are symmetry; that means, plus 1, then they will be given subscript to 1, if it is anti symmetric, then a subscript 2 will be given. So, once we are designated whether it is, it will be A or B, then we have to look at the behaviour of the characters, with respect to the perpendicular C 2. If it is symmetric with respect to perpendicular C 2s, meaning if the character of, character is plus 1, corresponding to C 2 prime, then it is A 1 or B 1, otherwise if it is the character is minus 1, with respect to C 2 prime, then it is A 2 or B 2. In case there are no C 2 primes, then 1 has to look at, the character corresponding to the vertical plane of symmetry and we will follow the same trend.

So, with respect to sigma v, if the character is plus 1, then the subscript 1 will be used, if it is anti symmetric that is minus 1, then subscript 2 will be used.

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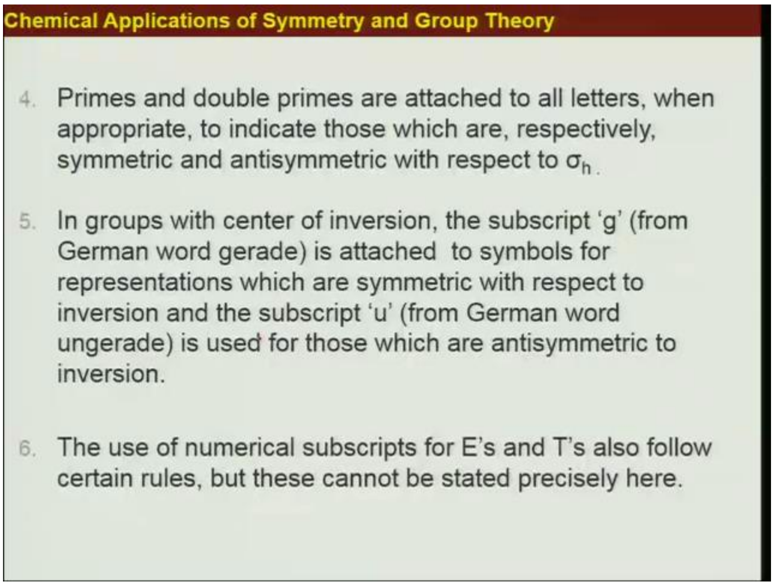

And in many cases primes and double primes attached. So, primes and double primes are attached to all this letters A, B or E, when act you know, appropriate, to indicate, those which are respectively symmetric or anti symmetric, with respect to sigma h. So, if the character corresponds to you know sigma h, if it is positive then you have prime, if it is negative, you will have a double prime. In certain cases we will have a point groups, with inversion symmetry as a one of the symmetry elements present.

So, in those cases particularly, we look at the characters for this inversion operation and if the character is you know, symmetric that is you know, plus 1, then we will have you know the subscript g, with respect to the terms like A, B or E and if it is anti symmetry, that is minus 1, then I will have subscript as u. So, this g and u are coming from the German word Gerade Ungerade. So, apart from this, these are the most commonly used symbols for irreducible representations, but other than, this they are certain you know numeric subscript that are used for the symbols E and T, but we lot discussed those things right here and for most of our purpose those will not be very much required.

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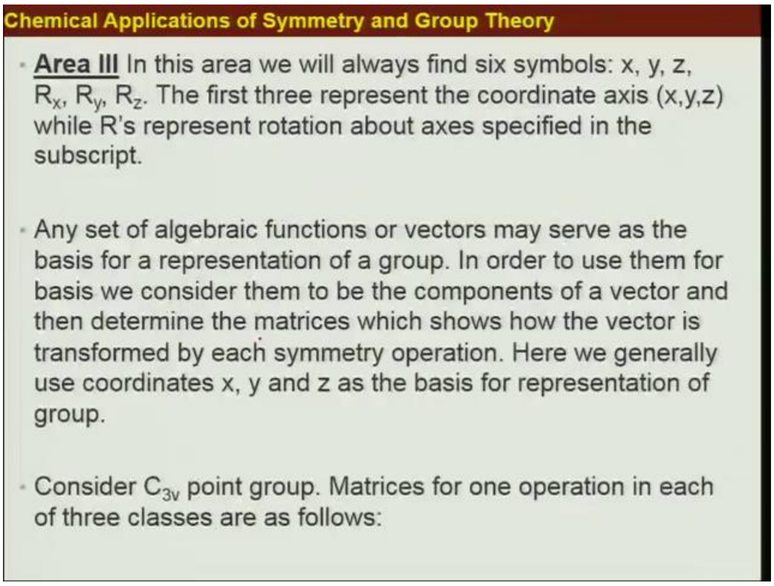

Next we look at the area III, so area III if you look at, what we have? We have 6 different symbols.

So, let us have a look at area 3. So, this is the region we are talking about. So, have total 6 symbols, 1, 2, 3, 4, 5, 6. So, x y z and R x, R y, R z - xyz are the Cartesian coordinates and this R's are the rotational symmetries, which respect to each axis, which is given as the subscript. So, about x axis if the rotation is there, then I have R x, otherwise R y or R z, fine. So, you will find that, these are the only 6 symbols that you have in area 3 always, in all of the character tables. Now their positions will, know, you know, they will be placed against certain irreducible representations. So, that will depend on the particular property of the irreducible representation, corresponding to that particular point group, those we will discuss in detail, at a later stage.

So, as we said that you know, any algebraic function can act as a basis you know, function and we can form any basis set out of those functions and we can use any vector also, you know talked about the bond vectors. So, we showed earlier the examples, we taking x y z for example, C 2 v point group. Now we are discussing with respect to one particular point group here C 3 v, for this particular character table. So, now, if I consider that C 3 v point group, the matrices for you know, one operation, operation each, from the 3 classes that we can have, we can have 3 classes for C 3 v as you know. So, then we can get the matrix is as follows.

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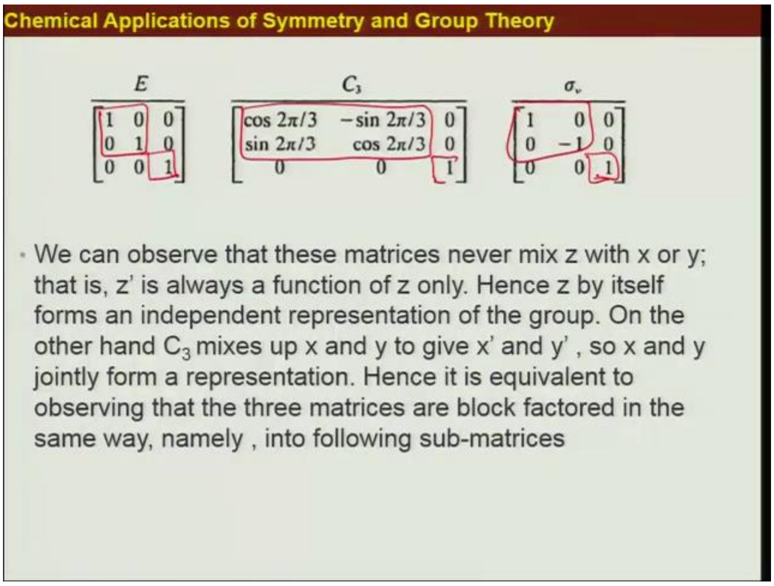

So, this is corresponding to E, C 3 and sigma v.

So, now here what we can see is that, this you know, in this case, in this matrices this z is always you know separated from x and y. So, z never mixes with x and y, but x and y, they mix, because you cannot get any particular one dimensional representations for x or for y, but you can get it for z. x and y always transform together, they always transform together, to form a representations. So, that is why when you formed the matrix representation, if you remember then we form for x y and separately z and altogether we put all x y z and get this 3 by 3 matrix. So, here can see that you know C 3 mixes of x and y, to give x prime and y prime. So, x and y jointly form a representation, hence it is equivalent to observing, that the 3 matrices are block factored in the same way. So, I can think about that. So, you can see this is the block and this is another block. So, here also, I can think about, that I have same block, same way. So, here and here, I have 3 matrices, block factored, in the way same way.

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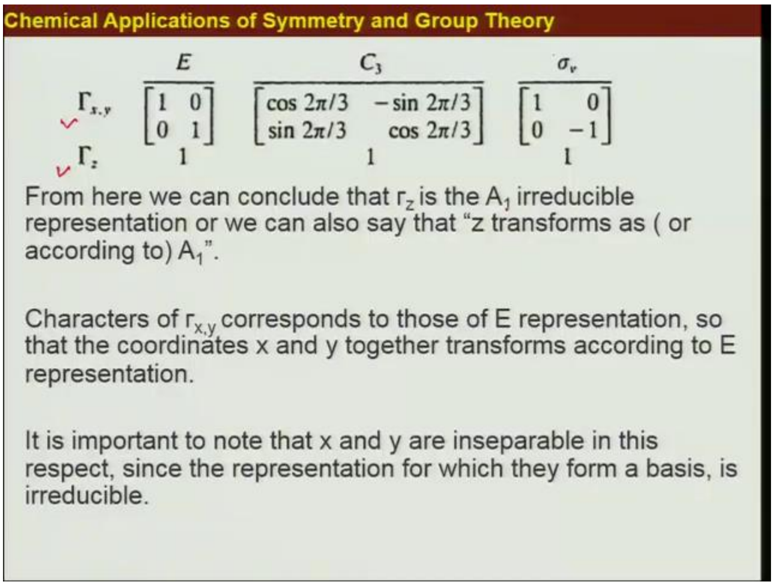

So, therefore, we can form 2 sub matrices, if I consider those 2 blocks individually and I get one representations for z alone, while I get another representations, where x and y transform together. So, we get 2 by 2 matrices. So, from here we can, what we can conclude is that, you know this gamma z, is the A 1 irreducible representation, if you just go back and see the character table, then you will find the realities, that this gamma z is the nothing, but the A 1 reducible representation, while gamma x y, is the E irreducible representation. So and you cannot separate this x and y contributions.

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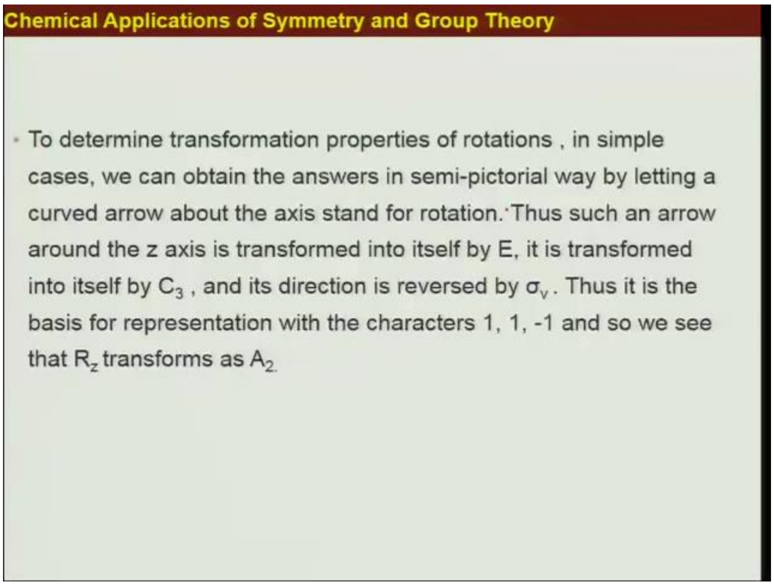

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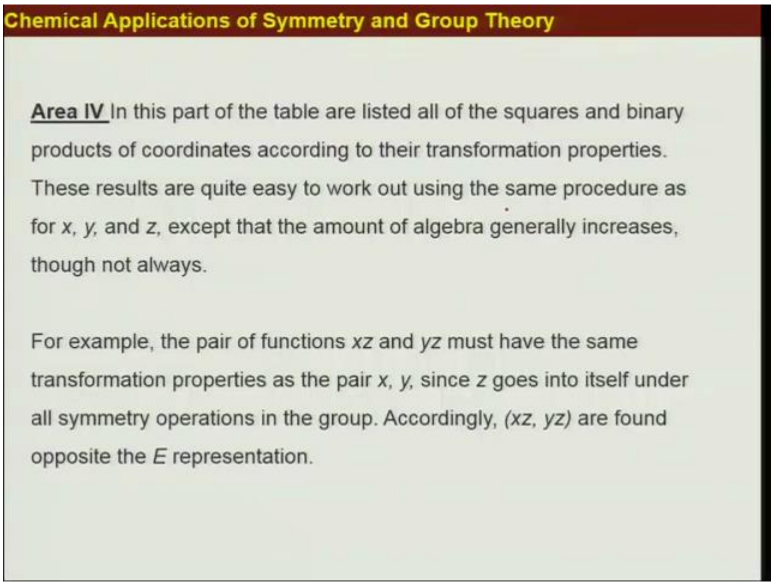

Now let us look at the area IV. So, area IV also you will see certain functions, which are like, you know, binary products of you know x y and z. So, it may be either you know xy, xz, yz or x square, y square, z square and so on. So, this you know pair of functions, they, you know, must have the transformation property, the same transformation properties, as a pair xy, since z goes into itself under all symmetry operations, in the group. So, this binary functions xy, xz or x square, y square, they form basis for certain irreducible representation and this part will be more clear, when we deal with certain, you know, properties or you know observations like Raman spectroscopy and all.

So, we will stop here and in the next class, we will talk more about this irreducible representation and look at their properties by learning this so called great orthogonality theorem.

Thank you very much for your attention, see you tomorrow.