Chemical Applications of Symmetry and Group Theory
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Lecture - 16

Hello every one welcome to the day 1 of week 4 of this course. So, in the last week we looked at the matrix representations of various symmetry operations.

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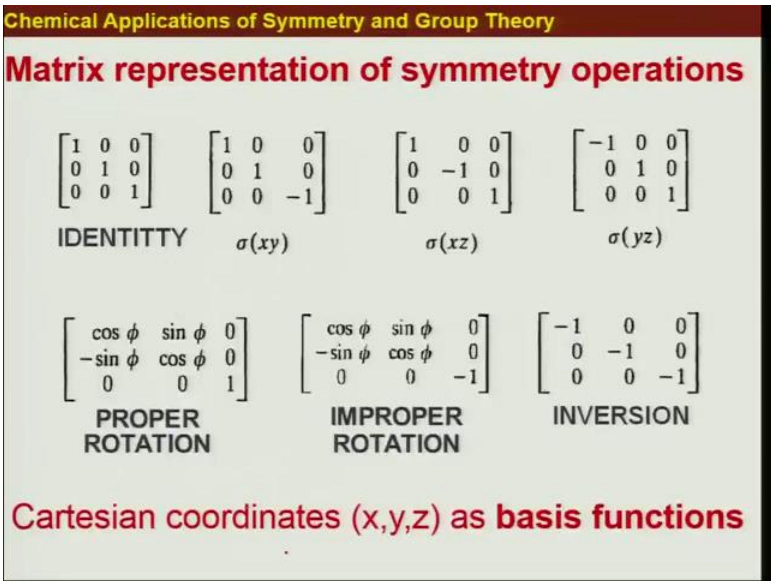

And on your screen you can see all the matrix representations that we form for different symmetry operations. For example, identity difference sigma planes, proper rotation and improper rotation as well as inversion symmetry operations. In order to form this representations we choose x, y and z coordinates of the Cartesian coordinate system. So, x, y, z acted as a basic set for forming these representations. So, you can look at all these representations that we formed in the last class.

Now, after we form these representations we can cross check, whether these representations are capable of acting just like the symmetry operations themselves. So, we used x, y, z as the basics functions. So, if you form a column vector by taking this x, y and z and then occurred this matrices on that we will find, what we will be the outcome. So, we can verify whether these matrix representations are giving back the same modifications of this x, y, z column vector as that would be given by the symmetry operators itself.

So, for that if we look at the screen. So, this one is identity matrix, which represents the identity operation. So, when it operates on the x, y, z column vector it gives back x, y, z column matrix itself. So, it retains its property. So, if we look at other symmetry operators and their matrix representation and then operate on this x, y, z coordinates, we will find out whether really all of this matrix representations they what parallel to this symmetry operators. So, here this matrix responds to the inversion operator. So, when it operates on this x, y, z column vector we get a column vector for which all x, y and z coordinates they are inverted; that is where I have minus signs. So, which is the signature of the inversion operation? So, if you verify all of them you can figure out that truly these matrix representations are capable of functioning just like the symmetric operators themselves.

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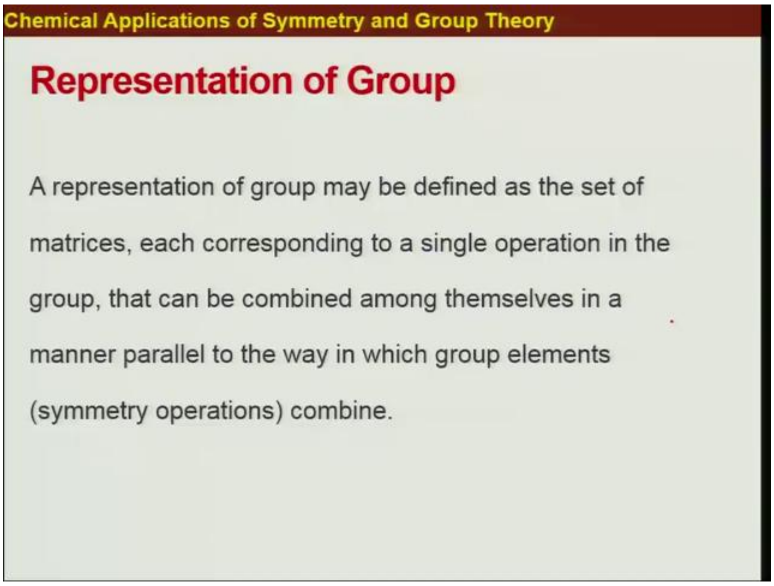

So, they are adequate representation for these operators, symmetry operators. Now after we learned how to form these representations for the symmetry operators, now we are in a condition to form the representation of a group. So, what is the definition of our group representation? So, a representation of a group is defined as follows. So, this representation of a group is the set of matrices each corresponding to a single operation in the group. That can be combined among themselves in a manner parallel to the way in which group elements that is; the symmetry operators operations here they combined right. So, we already stated that these matrices that we found for each symmetry operators they truly act like the symmetry operators.

So, they retain all the properties of any symmetry operation. For example, when we operate on any particular function it act exactly like the symmetry operator. More over when we combine 2 such matrices which represents 2 symmetry operations, the resultant matrix is a representation for the symmetry operator that would have that we could find upon the combination of the original tool symmetry operators.

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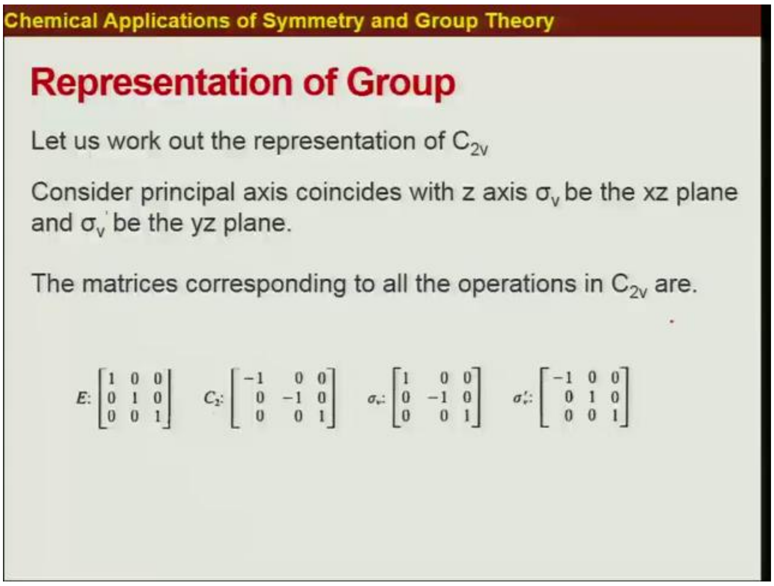

So, we can cross sector, we can work out particular case of C 2 v point group. So, in this case, so we will consider that the principal axis of rotation that coincides with the z axis in the of the Cartesian coordinate system and the sigma v plane C 2 v has 2 sigma planes and both are vertical planes.

Now, we differentiate them as sigma vs, sigma v prime. So, here we choose sigma v to be the x z plane in the coordinate system and sigma v prime to be the y z plane. Now after considering this, we can get the matrices as follows. So, this is for the identity, this is for C 2 rotation axis sigma v and sigma v prime. So, now, we have to cross check whether it really acts like the symmetry operations for the point group C 2 v.

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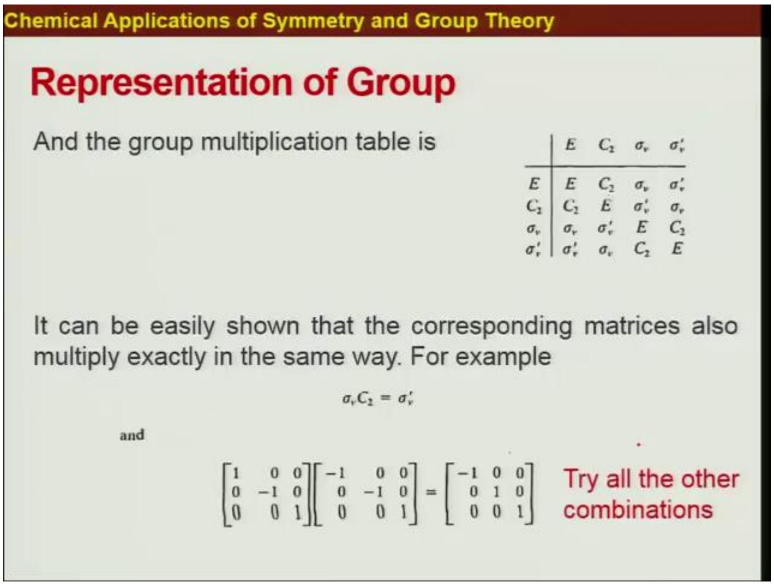

So, now, here we have the group multiplication table here. So, that will help us in proving our point. So, if we take 2 symmetry operations sigma v and C 2. Here C 2 is C 2 z and combines them, and then the resulting should be sigma v prime. As I can easily, find out from this group multiplication table.

So, sigma v C 2 this combination if I go by acting the row operation first, then sigma v and for by C 2 here it gives me sigma v prime, that is what we have here. So, you can choose any other symmetry operations and combine them and you can find the result of that combination from the group multiplication table that we have already learned. So, now, we take the matrix representations for this sigma v and C 2 z as it is written here. Combine them and we get this matrix. Now what this matrix transfer? If we just go back we see that, this corresponds to sigma v prime right. We can find the similar; you can find that this matrix is exactly same as what we get here.

So, we can see the law of this combination, it holds exactly the same way as that symmetry operations would follow. So, what you can do? You can try out all other combinations and verify whatever we just said.

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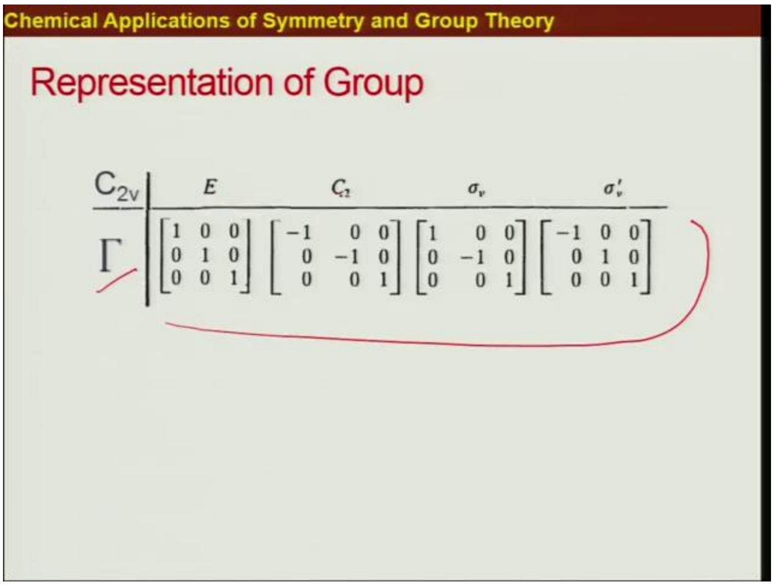

Now, once we have verified all these things then, we can say that all this matrix representations if we use all together we can find a representation of the group itself. So, that is what is shown here. So, here we have found a kind of table here where, this top left corner we have the symbol of this point group on the consideration C 2 v and here you have all the symmetry operations written. Now this is our representation, this whole thing is our representation. Name of the representation that we have given here is Gamma. That is normally people use for any such representation.

So, each matrix corresponds to each symmetry operation and as a whole this is a representation of group verifying.

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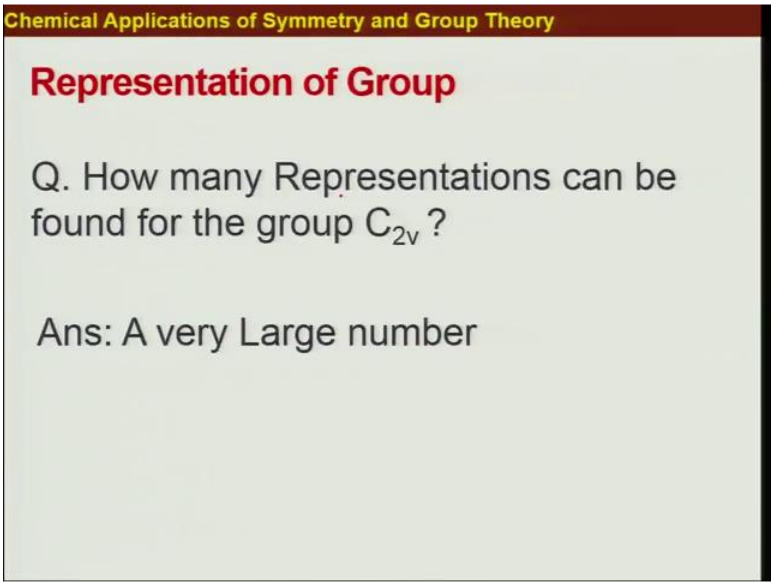

Now, we have a genuine question here; that I took x, y, z as my basis set and found the matrix representations put all the matrix representations against the symmetry operations in a table and we call it a representation. Now how many such representation one can find? So, the clear answer is very very large number of representations can be found. It completely depends on you, what basis set you choose? Based on that, you can find the representation. So, here we took x, y, z as my basics set I could choose I could select any particular molecule. Suppose I am trying to find out the representation for the molecule water.

So, what I can do? I can take all the x, y, z coordinates of the 3 atoms 2 hydrogen oxygen and then we can find the matrix representation of the symmetry operations. So, when we took just x, y, z we got 3 by 3 matrices for each of this symmetry operations. For x, y, z coordinates for all 3 atoms together I should have 9 by 9 matrices. Suppose I have molecule which as 10 atoms in it and I choose all the x, y, z coordinates of all the atoms then, my number of the dimension of my matrix representation would be 30 by 30.

So, it depends in that way. So, we are also not limited by this coordinate system, we can take anything we can take any given function. For example, I can take any bond vector. I will give you very quick example, say for it.

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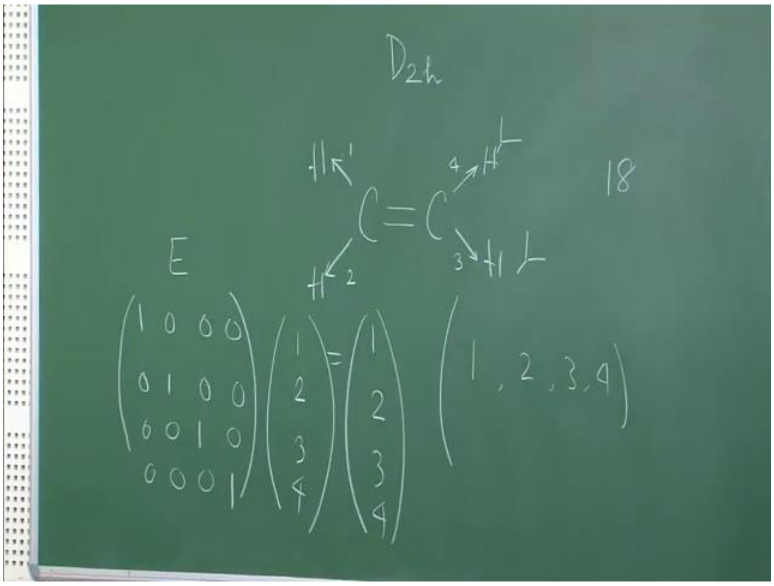

I can take say this molecule. So, what point group it belongs? So, it belongs to D 2 h point group right. So, I can find various different representations for D 2 h, that is we can prove. So, one way I showed by x, y, z, another way I can take that for each one of this atoms I can use their coordinates. So, this hydrogen atom it will have its own coordinate x, y, z coordinate, this one will have its own x, y, z coordinate. So, this carbon, this carbon, this hydrogen, this hydrogen all of them will have their x, y, z coordinates. So, total I have 6 atoms 6 into 3; 18 coordinates all together right.

So, I will get if I use all the x, y, z coordinates for all the atoms then I will get an 18 by 18 matrices for each of the symmetry operations, but as I said I am not limited to this x, y, z coordinate system. I can choose anything whatever I want and which is capable of representing this molecular structure someway. So, for example, I can consider this CH bond. So, I can choose the CH bond vector. So, I can choose this 4 bond vectors, I can put their names like 1, 2, 3 and 4 or I can write A, B, C, D. Now this 4 bond vectors I can use as my basis function right. So, my basis set will be 1, 2, 3, 4. Then what I have to do? I have to operate all the symmetry operations on this structure, on this bond vectors and see how this bond vectors that, how this basics set that is formed out of this bond vectors they are getting modified. So, in this particular case my bond my basics set is something like this 1, 2, 3, 4 and that I can represent in terms of a column vector like 1, 2, 3 and 4 and suppose I operate identity operation on this. So, identity operation we will have it is matrix.

So, upon operation, upon this identity operation I will get my original column vectors back 1, 2, 3, 4. How can that be possible? If I have an identity matrix where, all the diagonal elements has 1 while non off diagonal elements are all 0. Similarly I can find what will happen if I operate C 2. So, in case of C 2 1 will go in the place of 3, it will come here and this one will go here 2 will come to this place. So, I will know exactly how my column vector is getting modified after a particular operation and then correspondingly I can find the matrix form of that symmetry operation. So, this is the matrix form for the identity operation. Similarly I can find for the C 2 operation, I can find other C 2 primes here which are perpendicular C 2s. I can find the matrix form for the sigma h plane, we have a sigma h here.

For example, if I have sigma h what will be the matrix form? The sigma h is not going to change any of this bond vectors right. So, it will be exactly same as this. So, in that way I can find one particular representation. I can choose other things for example, I can find, I can use the orbitals, various different orbitals say I can choose the P Z orbitals of this carbons or I can choose the S orbitals of hydrogen. I can constitute basics set having n numbers of the basics function in it and then I can form these representations. So, that is why we say that, we can form a very large number of representation for any giving point group and we will see after few classes that this up to us that, what basics function that we will choose? It will more over depend on the problem that we are going to address. So, based on that we have to choose the basics functions and then we have to form the representations and then we have to work with those.

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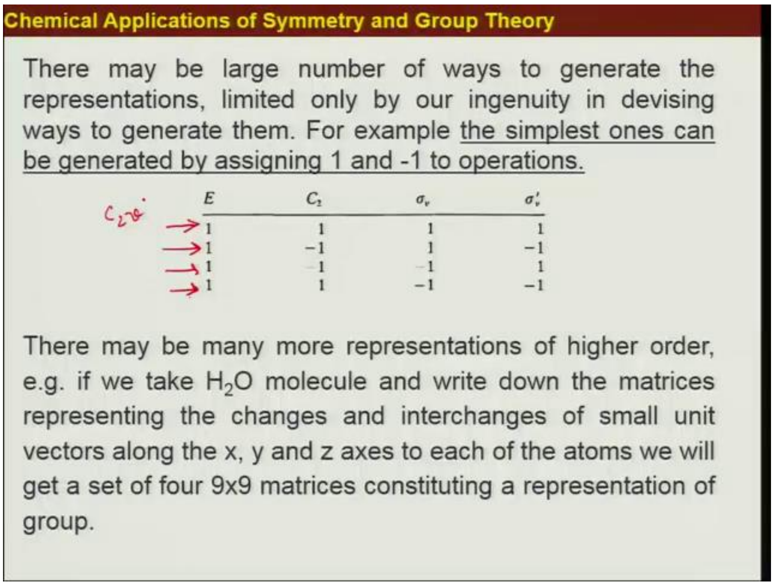

So, some more examples here, as we said that large number of representation can be formed. So, the smallest representations with smallest dimension that one can have, is one dimensional matrix right. So, I can have a one dimensional matrix, say for example, in this particular case if I take this particular double bond as my basics function and operate everything. So, I will get only 1 element there right. So, every time if I get element ultimately my matrix will be a 1 dimensional matrix. So, I will have a matrix representation like one of these. So, each one of these are some matrix representations. So, say here we are giving an example of C 2 v right. So, this is for C 2 v. So, for example, like water. So, if I just take the specific example here, instead of this large molecule let us take a molecule like water, which has a C 2 v point group.

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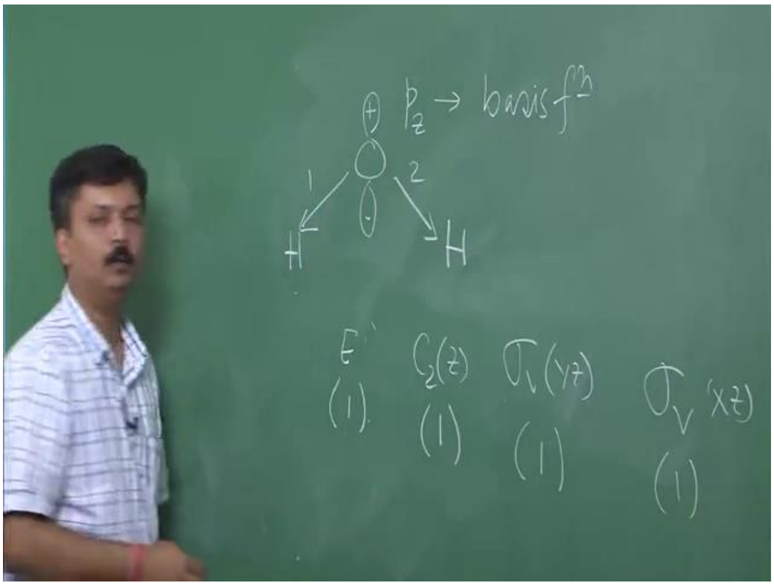

So, what I can do? I can take the say P Z orbital here. So, this P Z orbital will act as my basis function and I have only one function. So, this only single function will form a basics set. So, when we operate say identity on this one. What is going to happen upon or identity operation? Nothing is going to change. So, that we have 1, if I operate say for example, C 2 is not going to change anything right. So, C 2 which is along say Z axis that we also give a matrix which has the element as 1.

If I operate sigma v in this way say sigma v say x, z this is say y, z. So, sigma v, y, z this is not going to altered this P Z orbital. So, this plus will remain plus minus will be remain minus. So, one half is just a where image of other half. So, this will also give a matrix having element only as 1 and sigma v, x, z which is the molecular plane that will also do the same thing. So, I get I representation for which all the matrices are 1 dimensional and the elements are just unit.

Similarly, I can choose any other thing and find another representation. I can choose this bond vectors say 1 and 2 and I can find representation where, each of this matrices will be 2 dimensional. So, 2 by 2 matrix, I can find many many such representations and say for example, here I said like with x, y, z for water I will get 9 by 9 matrices.

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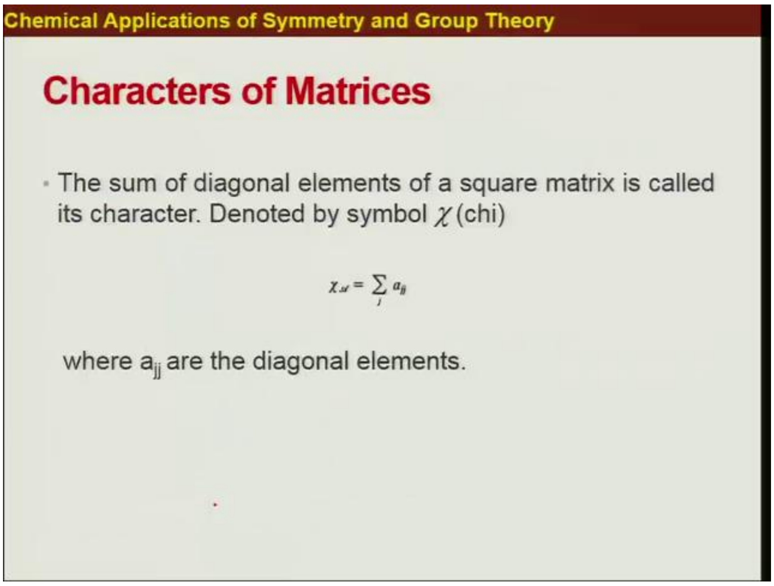

And I can choose many many such things. Now this particularly matrix representation what does it do? So, matrix representation or the matrix, it contains all the necessary information's and all the necessary properties of all the symmetry operations. We are convinced about that.

Now, after we can form the representation of the group so; that means, this matrices all together they give us certain information which are condensed in those matrix from. Now what is more intriguing about this representation by using matrices is the trace of the matrix. So, what is the trace of the matrix? Trace of the matrix is the sum of all the diagonal elements of a square matrix. So, here this Chi symbol is used for the trace of the matrix and you can see that all the diagonal elements are somewhat here.

Now, in case of square matrix this sum of these diagonal elements that is the trace is also called the character and there is a definite reason for calling the character. This is the matrix itself contain all the information or all the properties of the symmetry operation, but moreover this trace of this matrix it contains all those information and properties in even more condensed form. So, instead of using the whole matrix representation I can use just the trace of that matrix and get all the characteristics of the matrix which intern give me all the characteristics of the symmetric operation. So, that is why this trace of these square matrices which represents these matrix operations is called the characters.

So, we will be using these characters throughout this course hence forth and that is very important.

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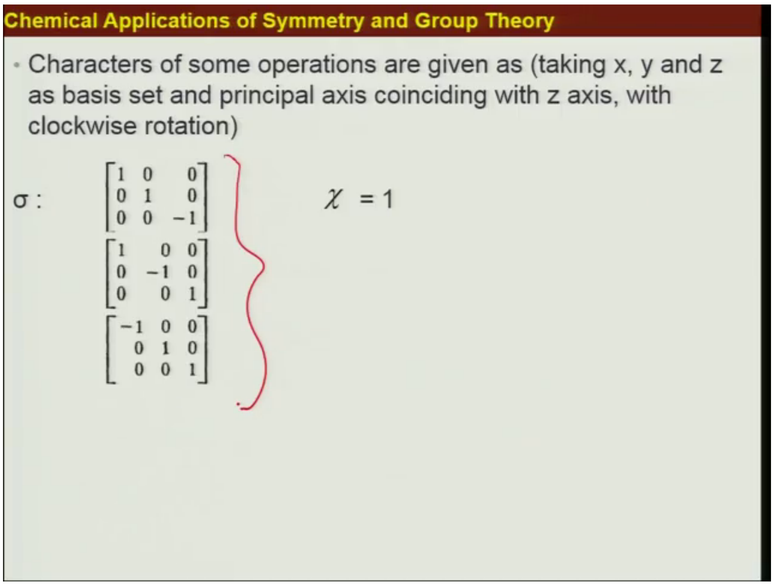

Now, let us look at some of the characters of different representations that we can form. So, some of this matrix represents sigma planes that, we have already seen in our earlier part of this lecture.

So, if you look at each one of this matrix, this is x y, x z, y z. So, when you sum all these diagonal elements what you get 1 plus 1 minus 1 equals to 1, here again 1 minus 1 plus 1 equals to 1 and here also minus 1 plus 1 plus 1 equals to 1. So, for all these 3 different sigma 3 depend representation of 3 different sigma planes sigma x y, sigma x z, sigma y z they have same characters this is something which you should note.

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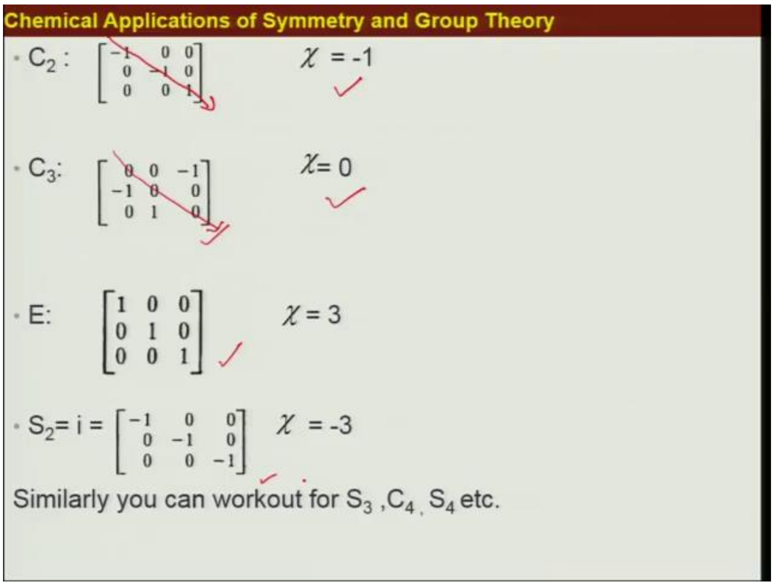

Now again, just look at the character of C 2 representation, so when you have this C 2 the representation of C 2 found by using x, y, z basics set, what I get if I sum all these diagonal element? Then I get the character as minus 1.

Similarly, if I form matrix for C 3 operation then I sum up all these characters and I get the character as 0 and I can find the identity and for inversion operation or (Refer Time: 23:39) operation. So, in this way we can find the characters. Now you have been dealing with matrix representations. So, that we can come to this particular thing called trace and also character. I will very soon in show tell you how without even forming the matrix representation you can find out the character because our ultimate aim is to find this character because it is the entity which contains all the necessary information and all the necessary properties of the symmetry operations, in a most condensed form.

So, our aim is to get those characters. So, I can go that get those characters by forming the matrices, summing up all the diagonal elements, but also there are ways that I can get the characters directly. So, we will talk about those things later, but to begin with I will urge you to work out the representations for different symmetry operations not only by taking this only Cartesian coordinate system x, y, z, but also like a putting Cartesian coordinate system for all the atoms taking them all together as the basis set and forming the representations or in the way I should it for say water or it ethylene using various different type of basics set and finding out the representations and there by finding out the characters of each of the matrix representation corresponding to each of this symmetry operations.

Now, just look at some beautiful properties of these characters. So, one most important property of this character just trace what the character, we are going to discuss.

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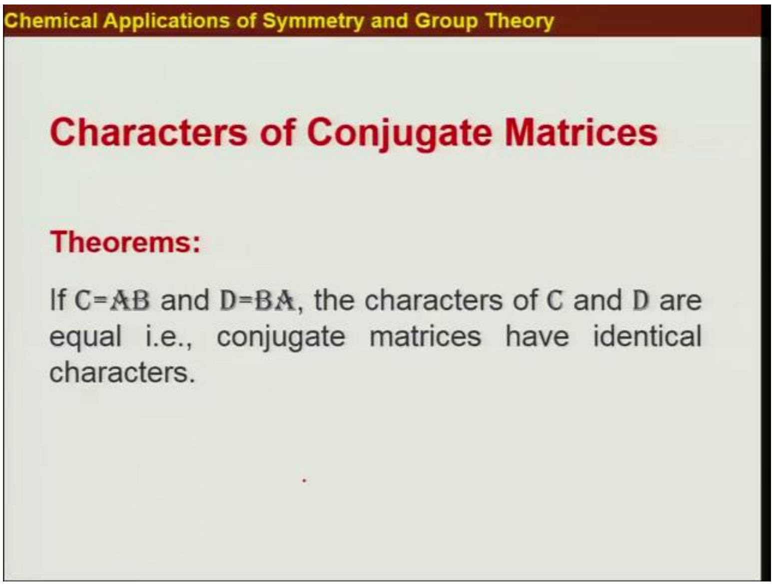

So, now, if we look at the properties of the conjugate matrices, so what are Conjugate matrices? Let us talk about the matrices which represent the symmetry operations. So, symmetry operations if you consider and if I tell you these are the conjugate symmetry operations, what do you understand by that? You immediately will tell that well those symmetry operations which are connected by simulative transformations are conjugate symmetry operations.

So, in case of matrix representations, it will also follow the same simulative transformation relations as that is followed by the symmetry operation themselves. So, thus matrix representations correspond to the symmetry operations which are conjugate will also be conjugate here fine. So, an important theorem about these conjugate matrices is that their characters are equal or identical.

So, now we have learned that this conjugate elements of a group they form the class right. So, once we do the simulative transformation on all the elements of a group in our case the symmetry operations, we find that certain elements are forming certain classes and what we will are going to see here that the matrix is correspond to, corresponding to those elements belonging to class they give exactly same characters.

Here for example, if I have 2 conjugate matrices A and A corresponding to 2 symmetry operation say, then A and B will have same characters and we are going to prove that. So, what I mean here is for example, say I have A and B are 2 matrices representing to symmetry operations.

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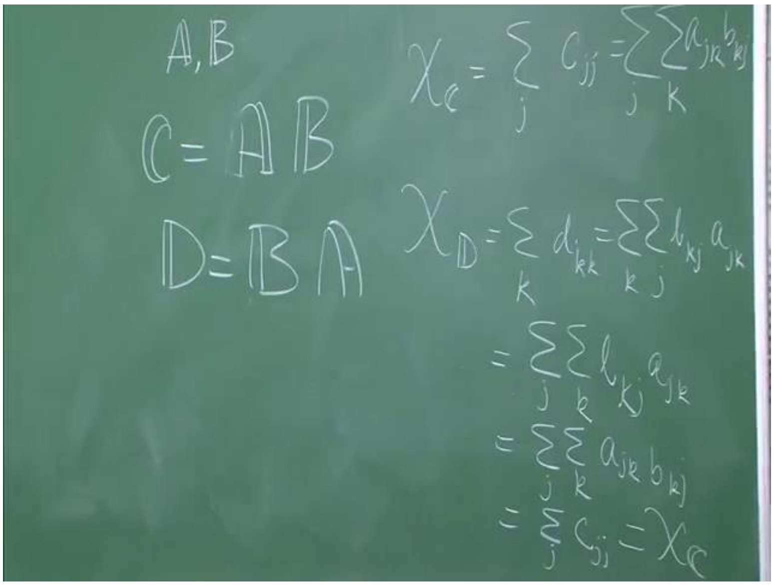

So, if I have a relation like A B and if I have A, then C and D will have their characters identical. So, how do I prove that? So, if I want to find out the character of C so; that means, character of X c equals to the sum of all the diagonal element of the matrix C correct. So, if I write this as sum over j C j j, those are the diagonal elements right.

So, if I get this one further excuse me I can write it as a product of the A and B matrices; that means, the product of the elements a j k at A b k j right. So, a j k b k j I can write that. Now what will be the character of the matrix D, I will have say the diagonal element d k k standing over k right, I can split them again just in the same manner. So, I have sum over k and sum over j then I can have D is B A right. So, I will have b k j and a j k correct.

Now, I can re write this one because this order of the summation is immaterial. So, what I can do is? I can write it in this fashion. So b k j a j k and since we are taking about this, conjugate matrices, I can be always commute. So, what I can do? I can write it like this. So, a j k and b k j which is nothing, but A B here is C will be C j j, which means these are the diagonal elements of the matrix C and I am summing over all j. So, this is nothing, but the character of the matrix c. So, thereby I can see the conjugate matrices will have the identical characters. So, we will stop here and we will start again in the following class.

Thank you very much for your attention.