Chemical Applications of Symmetry and Group Theory
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Lecture - 23

Hello everyone. So, it is a third day of the fifth week. So, today we are going to start with to find out representation of any giving molecule belonging to any particular point group without moving about formation of matrix. This will be necessary in the next part of this class. We will be talking about forming symmetry adapted linear combination or in the next part when we go to the case of spectroscopy because it is not always possible to form a huge matrix and ultimately we are going to use the characters, not the matrix. So, if by some way, if you can wait forming a large matrix and directly you can find out the character that will be immediately helpful, so quickly I will give you an example how to do that?

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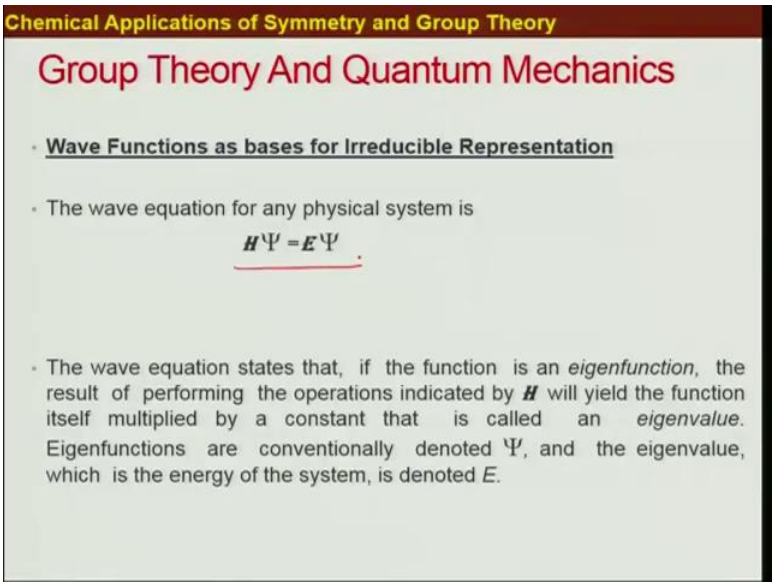

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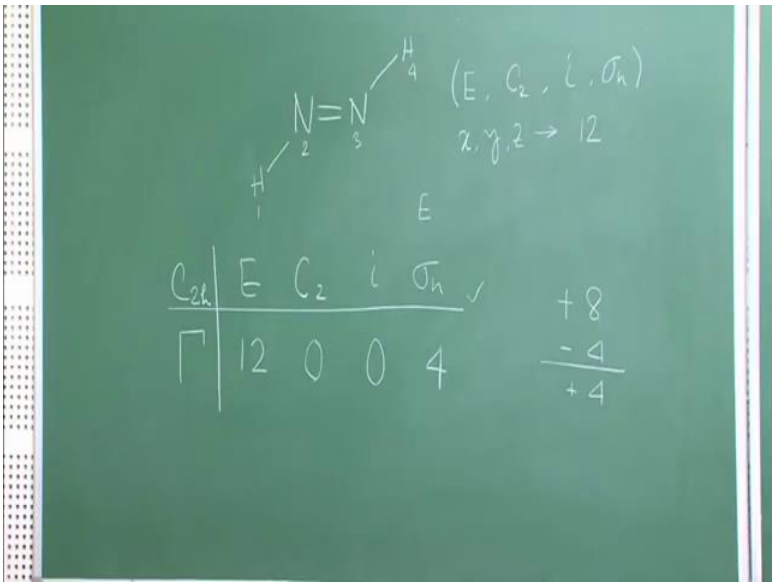

So, let us start with particular molecule, say for example N to F 2 which has a trans configuration and it is a planar molecule. So, without moving about the lone pair of electrons we will try to find out, how we can finally, presentation in terms of character, not worrying about the matrices. So, how to do that? So, there is a concept which is also known as the concept of unshifted atom. So, what does it tell you? That is once you know the structure and know the point group and the corresponding symmetry operations in it, you apply the symmetry operations on this molecular structure. Now you can choose your basis function, whatever you can.

For example I can choose all the its orbitals of 1 S of this 2 hydrogen and 2 S of this 2 Nitrogen's and that can act as my basis set having 4 basis functions. I can still have all the x, y, z coordinates of all the atoms in this molecule as my basis functions. So, if I say consider all the x, y, z coordinates. So, for x, y, z coordinate system I will have total 4 into 3, 15 this is functions in a set. Now earlier what we did? We tried to form matrix which 12 by 12 for each and every operation and from there we found out its in a character and then we reduced it and whatever we did. So, here what we are going to do? We are still taking this x, y, z, coordinates of each atoms as well this S function.

Now, we are going to use this unshifted atom concept here. So, what it tells is, when I operate all the symmetry operations say for example, I what are the symmetry operations that I have? I have identity C 2, I have inversion symmetry and I have sigma h. So, these

are the 4 symmetry operations that possible over here. So, for example, if I operate C 2 which is here, on this molecule which either atom are shifting from it is position will contribute nothing to the diagonal of the matrix that I can form. So, if suppose us when we are dealing with characters, it is the diagonal element which matters off diagonal element does not contribute anything, sot it, to that overall character.

So, once the atoms say if I mark this one like 1, 2, 3 and 4 upon a symmetry operation. If one is shifted to some other atom then this will not contribute anything to the overall character. Now if my basis function is such that. So, here it is like x, y, z. So, on this atom I have 3 basics function right. So, I have x, y and z. So, the same thing will be applicable to the basics function as well. So, that is means all 3 basis function, suppose this x 1, y 1 and z 1 each one of them will contribute 0, to the overall character. In case the atom is not shifted, the atom remains there then this any basis function on that atom that you are taking will contribute 1 to the diagonal.

So, for example, for any operation take in example of identity. So, if I operate identity on this 1 and let us concentrate only on this hydrogen, this one will remain unchanged, unshifted right. So, this atom and any basics functions on that atom we will contribute 1 each to the overall character. So, x 1, y 1 and z 1, they will contribute to 1 each. So, from this hydrogen atom I will get a contribution of 3 to the overall character because x 1 is giving 1, y 1 is giving 1 and z 1 is giving 1. Suppose I would have the 1 is orbital as my basics function here instead of this x, y, z then that will contribute a character of 1 to the overall character of the representation.

So, now let us start with all the symmetry operations. So, that it becomes more clear right. So, we will start with the identity operation and we will directly go to the representation right. So, this molecule has point with C 2 h we have seen that and let me write down all the operations here. So, and let me call my representation is Gamma right. So, identity operation will not shift any one of them correct. So, each one of them will contribute in the diagonal. Now each of the atoms contains 3 axes which we are using as basics function. So, each atom will contribute 3 to the overall character, so 3, 3, 3 and 3. So, total 12 will be contributed to the diagonal.

Now, you will remember when we form the matrix for identity we had a unit matrix of order that is given by the number of basics function in the basics set that you choose. So,

here also we are getting the same result. So, overall the character should be 12. So, see I do not have to formulate this. Now E is very easy, but let us see what are the other symmetry operations that you have? So, for example, C 2 is in this direction. So, if I operate C 2 1 will go to the place of 4, 4 will go to the place of 1 and 2 and 3 also will interchange.

So, none of the atoms are remaining in their space; that means, none of the basics function will contribute any positive value to the overall character bringing the total character of the presentation corresponding to C 2 operation will be 0.

Now, let us look at i. So, what it does i do? So, i does this, putting the same thing as C 2 does. So, 1 and 4 gets interchanged 2 and 3 gets interchanged. So, there is no unshifted atom meaning every basics function will contribute 0 to the diagonal leading to overall character of the presentation to be 0. Now what about sigma h? So, sigma h will be in this plane. So, what it will do? It will keep all the atoms in their place.

Now, here we have to worry about something. We are considering x, y and z axis right. So, if this direction is z axis then, the molecule is x, y plane. So, sigma h will not do anything to x and y, x and y will remain as it is. So, overall each atom will contribute 1 for x and 1 for y. So, all together I have 2 into 4 eight plane contributed by the x and y coordinates of all atoms correct. So, I have plus 8 contributions. Now what about the contribution of z? So, when I reflect on this plane plus z will become minus z correct. So, each one of this z coordinates will contribute 1 to the diagonal, but with a negative sign right. So, 4 z coordinates z 1, z 2, z 3, z 4 will contribute minus 4 to the diagonal.

So, over all the character may be plus 4. So, this is what I get. So, see how easily I can find out the representation of a molecule in terms of their character without knowing about the (Refer Time: 10:44) representation. So, once you find out the representation of any given point group, you can do whatever you want in the next step. So, for example, if I want to know about say the vibrational nodes. So, what I have to do? I have to next see if it is reducible or irreducible and by now you know that this representation is clearly reducible because the square of the characters, some of the square of the characters of this representations is higher than the or other group. So, this is reducible. So, you can reduce it by using the formula that we have all ready talked about in the last couple of classes.

So, you can find out how many times one irreducible presentation occurs in this particular representation? So, there will be 4 irreducible presentations for this one, that also we seen earlier for C 2 h point group. So, say (Refer Time: 11:48), A 2 G, B 1 G, B 2 G. So, how many times A 1 G will occur? How many times A 2 G will occur? How many times B 1 G, (Refer Time: 11:59) will occur. So, that you can find out and from there we can go on and solve the problem that you are trying to solve.

So, with is we are pretty much in a position to deal with a actual applications of this symmetric properties of a molecule and you are going to look at one of these which is known as symmetry adapted linear combination, but in order to be able deal with this kind of linear combination of atomic orbital which is very very vital to find out the, which atomic orbital will contribute to the formation of certain MOs or hybrid orbitals we need to know about the relation between good theory and quanta mechanics. There is a list all these orbitals that we will be talking about, they are the characterized by the wave functions. So, we need to know about these wave functions and how you know these wave functions, their properties are related to the symmetry properties of that particular molecular structure.

So, in the next step we will look at that. So, now for this we do not need to have very detailed idea of quanta mechanics, but if you have some basic knowledge about wave equation and little bit of quanta mechanics that will be very much helpful. So, for any moving physical system the wave equation is given by this relation. This is the (Refer Time: 14:03) equation while we do not talk about any time. So, Psi is a wave function which defines the state of a system and which is the Hamiltonian operator. This is an energy operator right.

So, when H operates on this weight function Psi it gives a value which is a constant value, which is the H or giving us E. So, this wave equation says that the function is an Eigen function and the result of performing the operation which is Hamiltonian here we produce the function itself and which will be multiplied by a constant, which is also known as an Eigenvalue. So, (Refer Time: 15:00) of you have gone through the basic quantum mechanics, that this Eigen function and Eigen value equation and here exactly by this quantum equation we are finding that Psi is an Eigen function of Hamiltonian operated for the system and E is the energy Eigen value.

So, normally this is how it is represented. Now there are certain properties of this Eigen functions and this operators in the Eigen values. So, suppose I am considering one particular molecule. So, molecule will be composed of certain atoms. So, these atoms if I consider them as particles, what a symmetry operation does? It interchanges some of these particles. So, we are in (Refer Time: 16:02) to give an indistinguishable structure. So, for a system where 2 or more particles are inter changed by carrying out this symmetry operation on the system, the Hamiltonian remains unchanged which is quite easily understood because a symmetry operation it does not, make any change in a molecule. It merely re (Refer Time: 16:28) I mean it inter change certain atoms, certain bonds and ultimately it gets indistinguishable structure.

So, 2 D indistinguishable structures cannot have two different energies. So, Hamiltonian operator which gives us the energy when it is operating on the Eigen function of the system, this Hamiltonian is (Refer Time: 16:52) by any symmetry operation. Therefore, symmetry operation if I write symmetry operation by the term R and Hamiltonian as it is by H then, H and R they also commute right because symmetry operation does not do anything. So, here that expression is written here that is R H is equals to H R.

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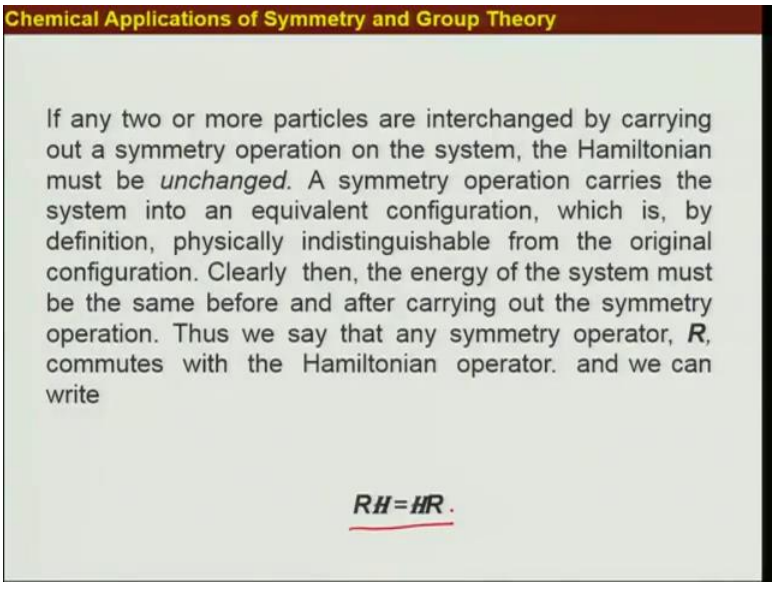

Because they do not interfere in to each other worlds, operating Hamiltonian on those molecular wave function is not going to do anything to the symmetric operators these are the molecules and vice versa correct.

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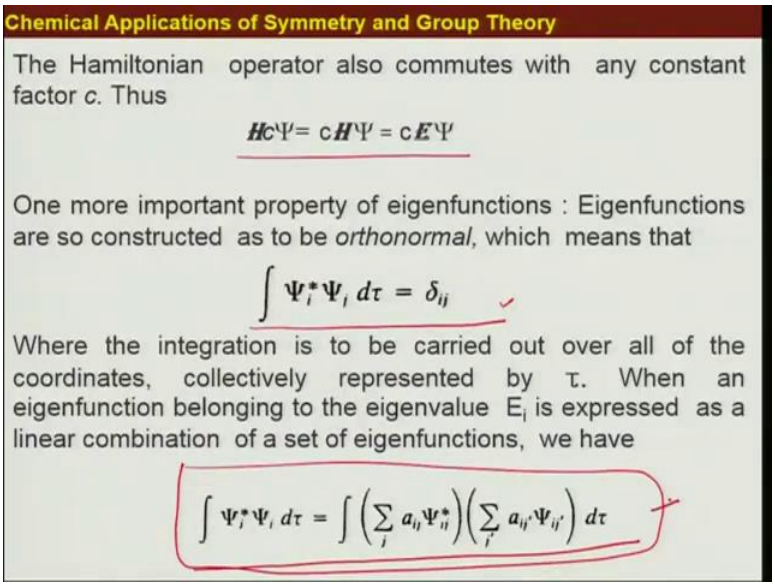

Now, the Hamiltonian operator apart from being commuted they are showing you know commutative property with the symmetry operations. It also commutes with any constant factor right. So, for example, here it is shown like you know wave function is giving a Psi, but if I multiply this Psi by any constant then that also does not change the state of the system. It only the normalizing condition just changes. So, with the (Refer Time: 18:15) is that the Hamiltonian it also commutes with the constant. So, therefore, I can write that if I have a constant c multiplied to the wave function Psi which is an Eigen function of Hamiltonian operator then, c and H they commute. So, this is an important thing that we should note.

Another important property of this Eigen functions are, this Eigen functions are Orthonormal. So, what do you understand by Orthonormal? Means that two Eigen functions say Psi i and Psi j, they are orthogonal to each other and each of them are normalized. So, if I mathematically want to show that, that is shown here. So, if I take Psi i and Psi j and then interpret over all the coordinates given by this tau then, this integral we survive and it is a value of 1 only when the Psi i it is equal to psi j; that means, i equals to j and it will be a delta function provided this Psi i and Psi j they are normalized. So, that is shown here and when an Eigen function having a particular Eigen value say E i is expressed as a linear combination of a set of Eigen functions then we can write like this right. So, what you mean here is that I can write the Eigen function as a

linear combination of several Eigen functions. So, Psi equals to Psi i Psi j psi k and so on.

So, the (Refer Time: 20:27) co efficient like c i, c j, c k and all this things. So, that is given here that this energy also can be expressed as a linear combination of a set of Eigen functions, now in this particular equation.

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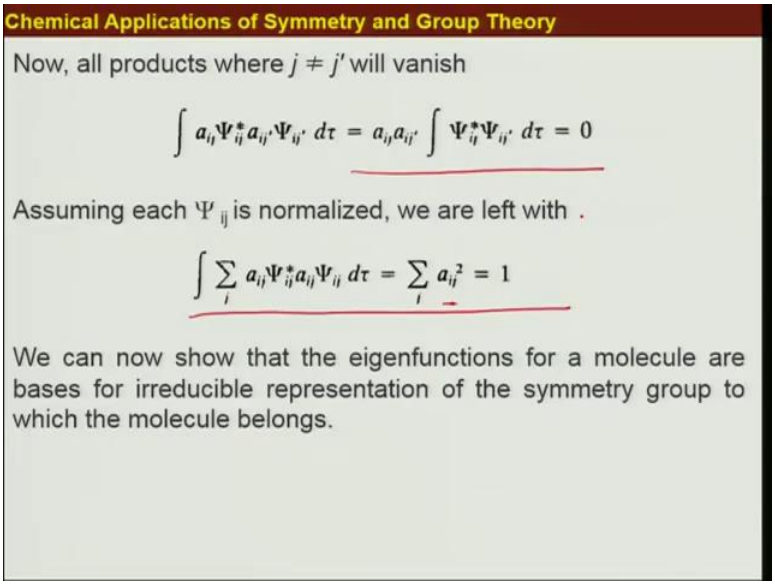

All the products where, this j is not equals to j prime they will vanish. So, this will be the result provided j is not equals to j prime. Now if it is Psi i j is normalized then normalized with normalized to 1 then what we have from here is this. This is the normalization.

So, this particular coefficient if you take the square of and then sum it over all j values then I will get value of 1. So, having this knowledge, now we can show that the Eigen functions for any given molecule can act as the basis for the irreducible representation of the symmetry point group to which that molecule belong to. This is a very very important class. So, we are going to show that like you know I can tell you at the beginning itself, but yes this Eigen functions of any for a given molecule, for any given operator we act as the basis for the symmetry groups to which that molecule belongs to.

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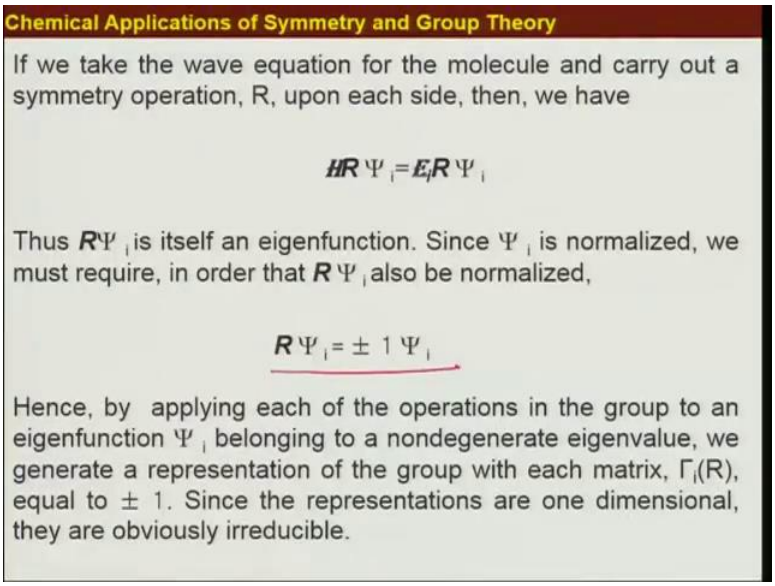

So, now we are going to show that. If we take the wave function for the molecule and carry out the symmetry operations R. So, what we are going to I mean have? So, suppose I have some wave functions Psi i and I operate each symmetry operations, given by R it is i may be in a symmetry operation.

So, what about the resultant? I am operating my Hamiltonian operator on that. Now in that case, what I am going to have? Because H r, H and R they commute. So, therefore, H and R they are not going to interfere with each other's duties right. So, therefore, when I operate Hamiltonian on this R Psi i it is going to give me the same Eigen value E i and return me this R Psi 1. Therefore, this R Psi 1 also act as an Eigen function of the Hamiltonian operator that is obvious here. Now this Psi I each Psi i is normalized. So, therefore, and we said that we are normalizing it to the value of 1. So, now, if we (Refer Time: 24:00) these two facts that when you operate any symmetry operation on this Psi i, but R Psi i is an Eigen function is also an Eigen function of Hamiltonian operator for which Psi i is a Eigen function and next is that if Psi i is normalized.

So; that means, in order to have R Psi i as an Eigen function R Psi i must be normalized. So, it should be such that R Psi i equals to plus minus Psi i. So, either it can be symmetric or anti symmetric, the Eigen value will be either plus 1 or minus 1. So, it simply means from symmetry point of view that is this psi i is either symmetric or anti symmetric with respect to the symmetry operations. So, now, if we apply all the

symmetry operations of the group onto and Eigen function Psi i, which belonging to a non degenerate Eigen value. So, what do you mean by non degenerate? That when we operate Hamiltonian on the Psi i then the Eigen value that is generated is non degenerate.

So, then we can generate a representation of the group as Gamma IR. Now you have just seen that R Psi i equals to plus minus Psi i; that means, the Eigen value is plus minus 1. So, therefore, the elements of this representation Gamma i of any given symmetry operation will be equal to either plus 1 or minus 1. So, the overall representation that I will get for the point group taking this Psi 1 as my basis I will get the characters which are only unity either plus 1 or minus 1.

Therefore, the dimension of the representation is 1. Therefore, it is not further reducible. So, we are getting an irreducible representation right and that is what we said at the beginning, that the wave function of any given molecule can act as basis for the irreducible presentation of the symmetry point group to which the molecule belongs to and that is was is the proof here. So, in the following class, we will look at some more properties of this wave functions of a molecule and we are also try to correlate that, how this wave functions get transformed in to different irreducible presentation and all and we will then, see how this can be actually applied on to the real problems. So, we will back in the fourth day of this class tomorrow. So till then.

Thank you.