Mathematics for Chemistry
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Lecture - 35

Today, we are going to study how symmetry is used in quantum mechanics. In order to do this, first we will revise some of the basic postulates of quantum mechanics and this will set us up for using symmetry arguments.

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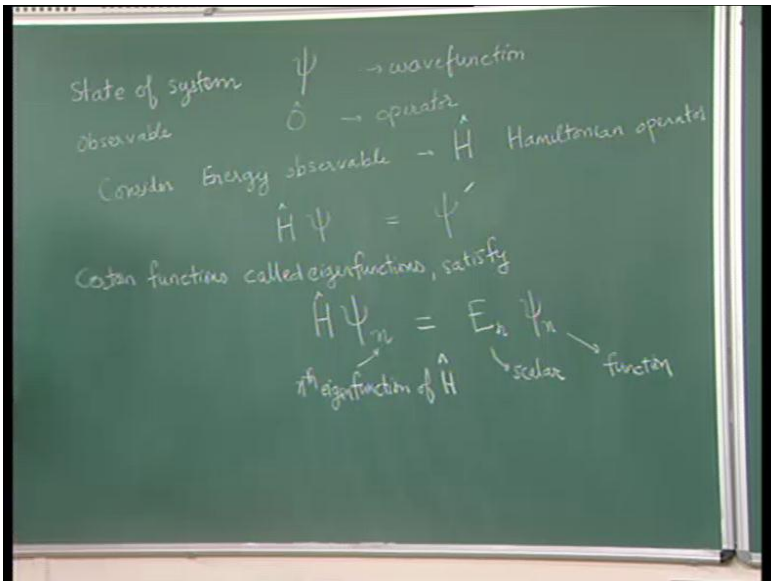

State of system ψ → wavefunction
Observable $\hat{O}$ → operator
Consider Energy observable → $\hat{H}$ Hamiltonian operator

$$\hat{H}\psi = \psi'$$

Certain functions called eigenfunctions, satisfy

$$\hat{H}\psi_n = E_n \psi_n$$

n^{th} eigenfunction of $\hat{H}$
scalar
function

So, if you recall the basic postulates of quantum mechanics, it says that the state of the system is described by an object call the wave function, and it is denoted by psi, so psi is called the wave function. So, the state of the system is denoted by a wave function and this is the function of the coordinates of all the particles. Then you know that an observable, a physical observable corresponds to an operator.

So, corresponding to every physical observable their exists an operator, now there are certain important features of this operator and this is what I want to focus on. Now, let us consider energy observable, so the operator is called the Hamiltonian operator. So, corresponding to the energy observable there is an operator called the Hamiltonian operator.

Now an operator if you remember operator acts on a wave function, to give you some other wave function. So, psi prime of r, I would write the r coordinate, I will just say it acts on psi to give you psi prime, so an operator acts on a wave function to give you another wave function. Now, so certain functions called Eigen functions and these satisfy Hamiltonian operator operating on an Eigen function. So, this is a nth Eigen function of Hamiltonian operator, so it is an Eigen function of the Hamiltonian operator.

So, psi n is the Eigen function of the Hamiltonian operator, so if it satisfies H times psi n, is equal to E n times psi n where, E n is a scalar, so it is just a number. This is a function and this is a number, so this is called the Eigen value equation.

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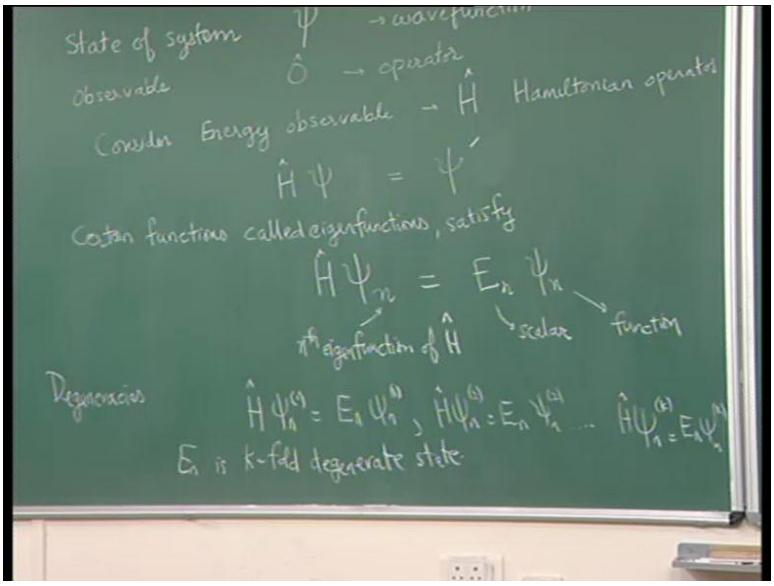

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Degeneracies $\hat{H}\psi_n^{(1)} = E_n \psi_n^{(1)}, \hat{H}\psi_n^{(2)} = E_n \psi_n^{(2)} \ldots \hat{H}\psi_n^{(k)} = E_n \psi_n^{(k)}$

E_n is k-fold degenerate state

Now it is possible that you can have degeneracies, so when we have degeneracies then we say that H times psi n 1 is equal to E n times psi n 1 and you have H times psi n 2 is equal to E n times psi n 2 and so on up to H times psi n k is equal to E n times psi n k. So, then you say that E n is k fold degenerate state.

So, all these Eigen functions psi n 1 psi n 2, psi n 3, up to psi n k they all have the same Eigen value E n. And since there are k of them, you say E n is k fold degenerate state. Now, according to the postulates of quantum mechanics corresponding to every observable and let us take the example of the energy observable.

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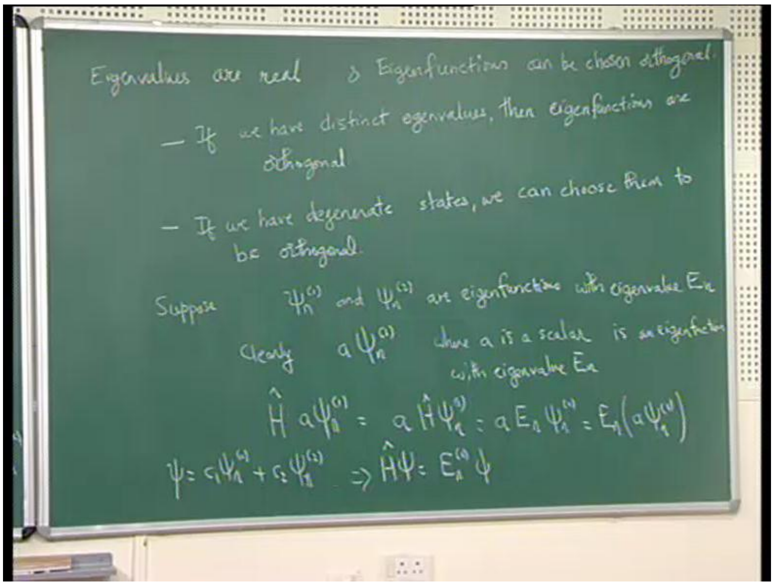

Eigenvalues are real & Eigenfunctions can be chosen orthogonal.

- If we have distinct eigenvalues, then eigenfunctions are orthogonal
- If we have degenerate states, we can choose them to be orthogonal.

Suppose $\psi_n^{(1)}$ and $\psi_n^{(2)}$ are eigenfunctions with eigenvalue E_n

Clearly $a\psi_n^{(1)}$ where a is a scalar is an eigenfunction with eigenvalue E_n

$$\hat{H}\, a\psi_n^{(1)} = a\hat{H}\psi_n^{(1)} = aE_n\psi_n^{(1)} = E_n(a\psi_n^{(1)})$$

$$\psi = c_1\psi_n^{(1)} + c_2\psi_n^{(2)} \Rightarrow \hat{H}\psi = E_n^{(1)}\psi$$

So, the according to the postulates of quantum mechanics, so Eigen values are real, so corresponding to a physical observable, your operator is hermitian. So, the Eigen values are real and Eigen functions can be chosen orthogonal, so I will just expand this a bit. So, your Eigen values for any hermitian operator, they have to be real Eigen values, the Eigen functions they can be chosen to be orthogonal. Now, I am using the word can be chosen that is to emphasize that if we have distinct Eigen values, then Eigen functions are orthogonal.

So, if your Eigen values, so if you have two different Eigen values the corresponding functions will be orthogonal, so that is the first part. Now the second part is if we have degenerate states, we can them to be orthogonal, so in such a case where, the all these Eigen functions have the same Eigen value E n, You can choose different once to be orthogonal. Now, why do I say you can choose them to be orthogonal is it is fairly easy to see. The suppose psi 1 psi n 1 and psi n 2 are Eigen functions with Eigen value E n, so psi n and psi 2 are two different Eigen functions, there Eigen value is they have the same Eigen value E n.

Now, the first thing is that clearly a times psi n 1, so if I multiply psi n by a where a is a scalar, so in any case if I take a times psi n it will have the same, it will be an Eigen function of H with Eigen value E n. So, is an Eigen function with Eigen value E n, this is very easy to see, so you can see this by saying that H times H operated on a psi n 1. Now the hermitian operator is a linear operator, so H operated on a times psi and is a times H operated on psi n psi n 1.

And this is equal to a times E n psi n 1 is equal to E n times a psi n 1, so the Hamiltonian operated on a times psi n 1 is nothing but E n times k psi n 1; so therefore, a times psi n 1 is an Eigen value with the same is an Eigen function with the same Eigen value. More over you can easily show that if I take combination of these functions, I will get an Eigen function.

So, suppose I take psi is equal to c 1 psi n 1 plus c 2 psi n 2, now it is important that both these have the same Eigen values. So, psi n 1 and psi n 2 have the same Eigen value then this implies H times psi is equal to E n 1 times psi. So, the point is you can take a linear combination and you can extend this from two to many more Eigen functions.

And this sort of relation will hold that if you had a set of Eigen functions with the same Eigen values. So, they should have the same Eigen value E n, they should not have distinct Eigen values, if they have distinct Eigen values they are orthogonal. If they are the same the n any linear combination of them is also an Eigen function with the same Eigen value. So, then the question how can we get Eigen functions, that are orthogonal and you can use an orthogonalization procedure.

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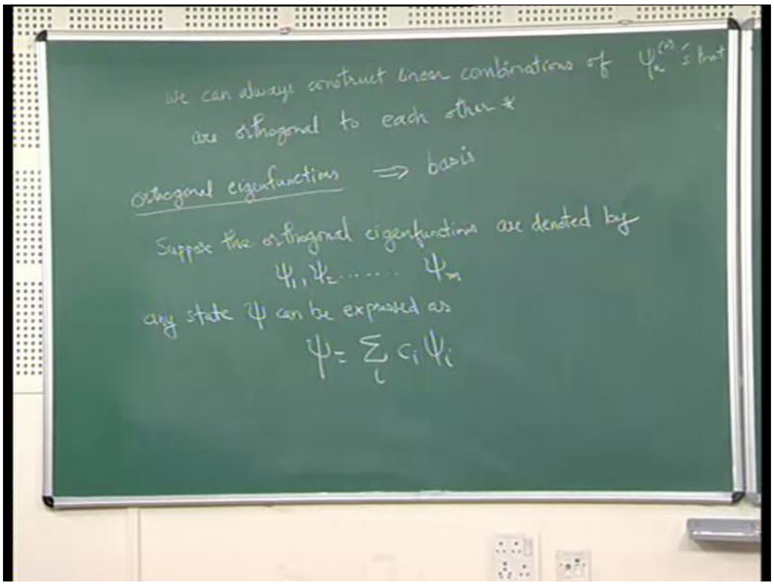

We can always construct linear combinations of $\psi_n^{(\alpha)}$'s that are orthogonal to each other *

orthogonal eigenfunctions $\Rightarrow$ basis

Suppose the orthogonal eigenfunctions are denoted by

$\psi_1, \psi_2 \ldots\ldots \psi_m$

any state ψ can be expressed as

$$\psi = \sum_i c_i \psi_i$$

So, we can always construct linear combinations of psi n k that are orthogonal to each other, so this is one of the postulates of quantum mechanics, that if you look at Eigen functions of any hermitian operator. If you look at Eigen values that are distinct, then the Eigen functions will always be orthogonal. If you look at the degenerate case where, you have a whole range of Eigen values whole range of Eigen function to choose. In that case then you can always select such Eigen functions that are orthogonal to each other.

So, this is a very important point and this is one of the central postulates of quantum mechanics. So, orthogonal Eigen functions, so the net result is that your Eigen functions for a hermitian operator are orthogonal. And when you see the phrase orthogonal Eigen functions, you should immediately thing of basis. So, if you have a set of functions that are orthogonal you can use them as a basis, you can use them as a basis and you can represent any function as a linear combination of these orthogonal Eigen functions.

So, suppose we have the functions are denoted by psi 1 psi 2 up to psi m. So, these are the orthogonal Eigen functions any state psi can be expressed as psi is equal to sum over i c i psi i. So, any state can be expressed as a linear combination of these basis functions. So, this is the meaning of a basis and so your Eigen of the Hamiltonian operator can be used as a basis for representing any wave function, so this is something that we are going to use in the treatment of symmetry.

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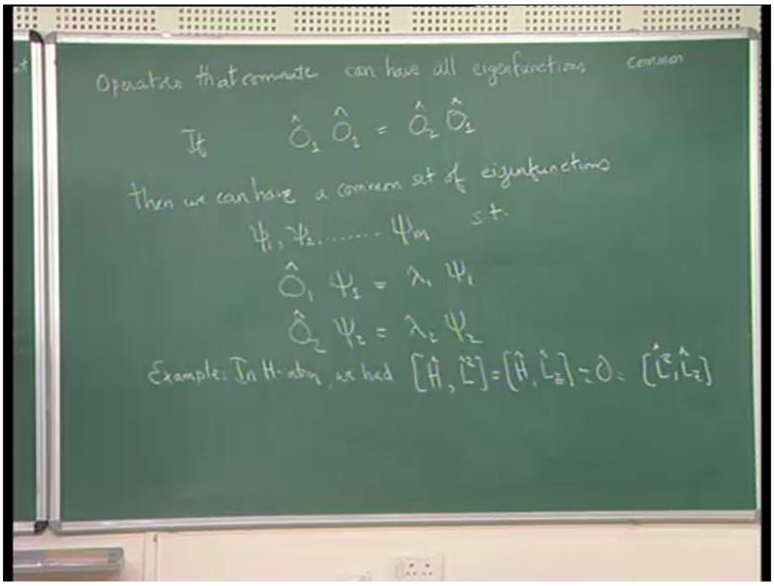

Operators that commute can have all eigenfunctions common

If $\hat{O}_1 \hat{O}_2 = \hat{O}_2 \hat{O}_1$

then we can have a common set of eigenfunctions

$\psi_1, \psi_2 \ldots\ldots \psi_m$ s.t.

$\hat{O}_1 \psi_1 = \lambda_1 \psi_1$

$\hat{O}_2 \psi_2 = \lambda_2 \psi_2$

Example: In H-atom, we had $[\hat{H}, \hat{L}^2] = [\hat{H}, \hat{L}_z] = 0 = [\hat{L}^2, \hat{L}_z]$

Next let us talk about operators that commute, so what we are going to show is that if 2 operators they commute with each other, then they can have all Eigen functions as common. This is another important idea that if two operators commute with each other, then we can choose their Eigen functions as common Eigen functions. So, we already saw that you could choose them to be orthogonal any one operator, but if you have two operators that commute then all there Eigen functions can be chosen as common Eigen functions. So, if we have operator 1 if operator 1 times operator 2 is equal to operator 2 times operator 1.

Then we can have a common set of Eigen functions, so I will say psi 1 psi 2 up to psi m, such that O 1 psi 1 is equal to lambda 1 psi 1 and operator 2 psi 2 is equal to lambda 2 psi 2. So, you can choose a set of Eigen functions that are common to both the operators, so this is the other important idea. Now typically if you remember you choose when you are in the inlet us say the hydrogen atom problem, you looked at operators that commuted with the Hamiltonian operator. And we said that you can have a common Eigen function, those operators in the case of hydrogen atom where, the square angular momentum and the z component of the angular momentum.

So, we said that the you can have common Eigen function of both these operators, so just give this example in hydrogen atom we had H comma L square operator is equal to H comma L z operator equal to 0. So, where this a commutator of H and L square that is H times L square minus L square times H. So, if H L square is equal to L square H if the operators commute and this is 0. So, this means H commutes with L square H commutes with L z and we also had L square L z commute with each other which is a trivial identity, so what we had is that we had all these identities.

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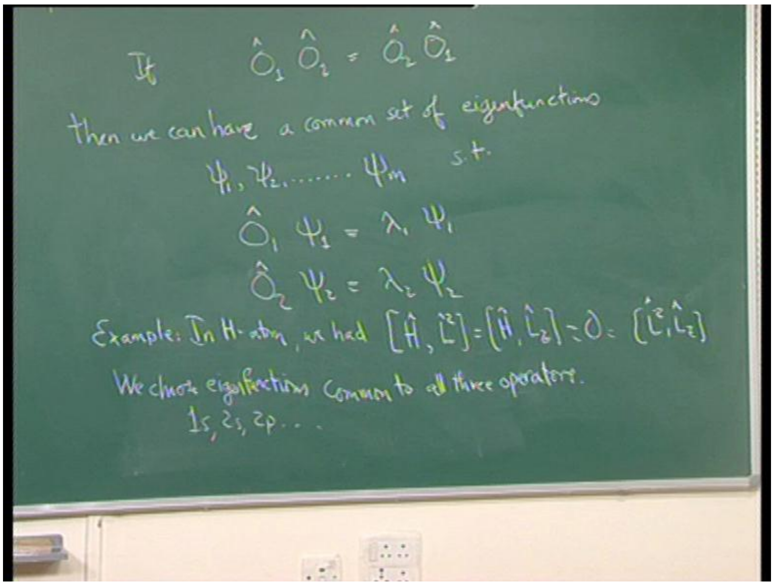

If $\hat{O}_1 \hat{O}_2 = \hat{O}_2 \hat{O}_1$

then we can have a common set of eigenfunctions

$\psi_1, \psi_2, \ldots\ldots \psi_m$ s.t.

$\hat{O}_1 \psi_1 = \lambda_1 \psi_1$

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Example: In H-atom, we had $[\hat{H}, \hat{L}^2] = [\hat{H}, \hat{L}_z] = 0 = [\hat{L}^2, \hat{L}_z]$

We chose eigenfunctions common to all three operators.

1s, 2s, 2p . . .

And therefore, we choose Eigen functions common to all of all 3 operators for chosen, then these are 1 s, 2 s, 2 p, etcetera, 2 p, and so on. So, for example, if you take 1 s your I the you had a specific Eigen value of energy you had a specific Eigen value of L square and you had a specific Eigen value of L z.

So, then we can choose our Eigen functions to be common Eigen functions of all the 3 operators, so with this back ground we can start applying our ideas of symmetry that we have learnt so far in constructing wave functions. So, the so the important point is these linear combinations will be constructed by using wave functions that obey certain symmetry properties.

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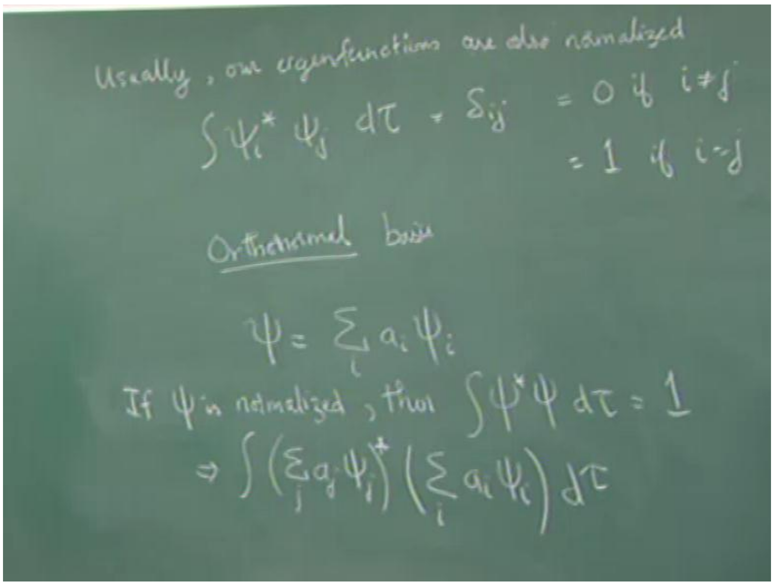

Usually, our eigenfunctions are also normalized

$$\int \psi_i^* \psi_j \, d\tau = \delta_{ij} \quad = 0 \text{ if } i \neq j$$
$$= 1 \text{ if } i = j$$

Orthonormal basis

$$\psi = \sum_i a_i \psi_i$$

If ψ is normalized, then $\int \psi^* \psi \, d\tau = 1$

$$\Rightarrow \int \Big(\sum_j a_j \psi_j\Big)^* \Big(\sum_i a_i \psi_i\Big) d\tau$$

So, now let us mention one more thing that usually our Eigen functions are also normalized. So, they are normalized means the their integral with themselves is 0, so effectively we can write psi i star psi j integral d tau equal to delta i j. Delta I j is 0, if i not equal to j equal to 1, if i equal to j, so we use a orthonormal basis. So, we say that the basis is orthonormal.

Typically, we construct our basis, so that it is orthonormal, we have already seen that you can choose them to be orthogonal and once they are orthogonal it is not hard to normalize each of them. So, if your wave functions are orthonormal, then they satisfy this property. Now suppose you write wave function psi as linear combination as of orthonormal wave function.

If psi is normalized then psi star psi d tau equal to 1, so this implies integral. So, psi star as sum over j a j psi j star times sum over i a i psi i d tau, it is important to used to use different indices for both of these, because this is the sum of various terms this is also a sum of various terms and when you multiply them together you will get all kinds of cross terms and that is best done if you use different indices.

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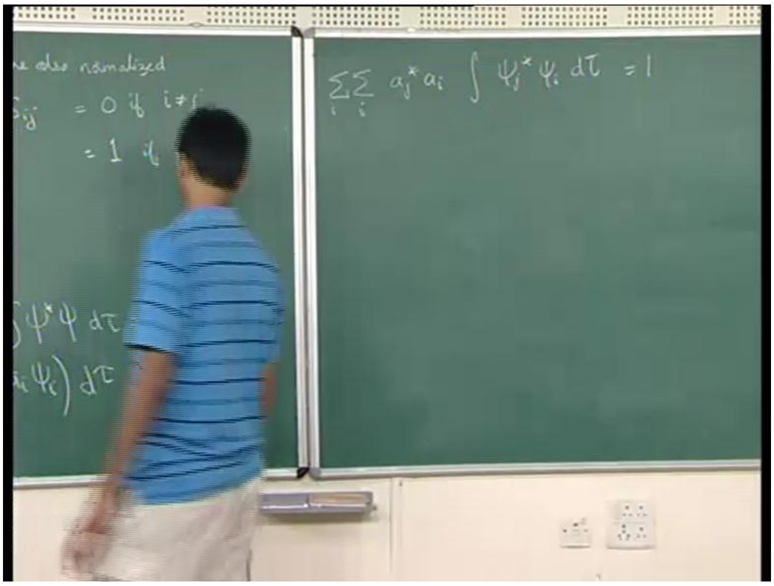

Now, you can expand this and you can write this as integral I write the sum over sum over j sum over i and write this as a j star a i times integral psi j star psi i d tau. So, this is this has to be equal to 1.

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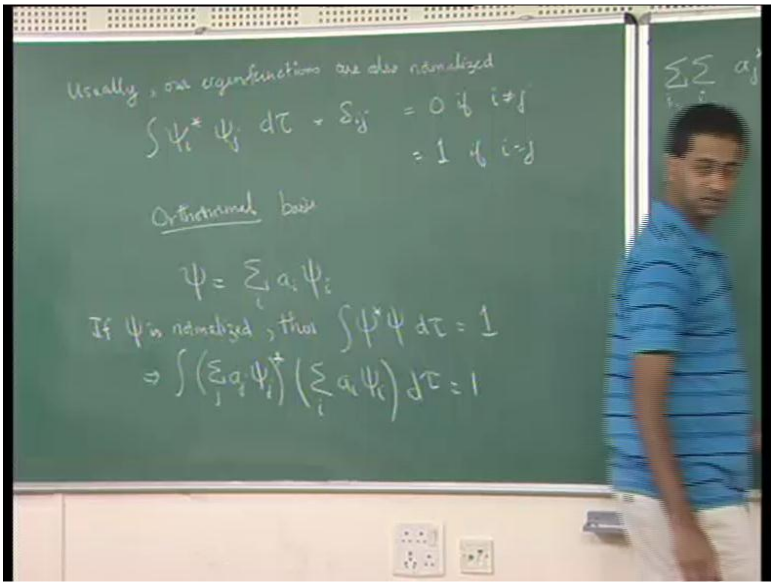

So, since your psi was normalized this has to be equal to 1 and this implies, so if this is has to be equal to 1 this you already know the value of this, because our psi’s are orthonormal this will this is just delta i j And a j star a i delta i j.

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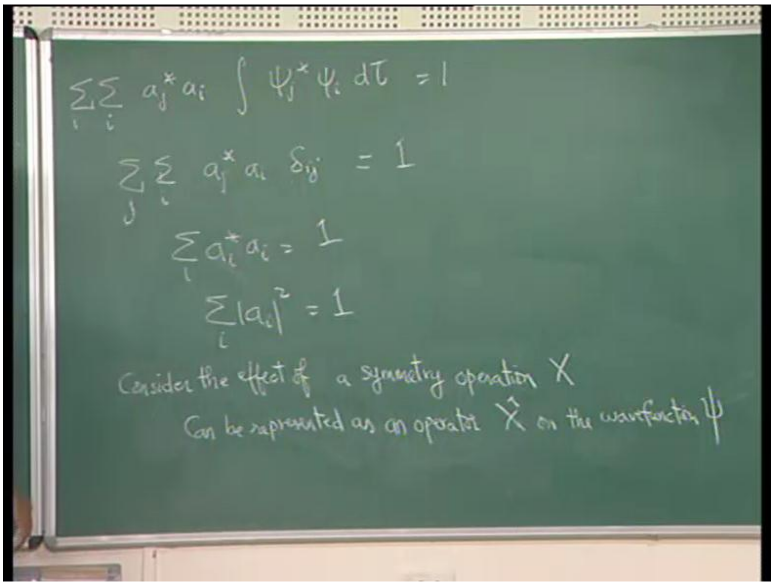

$$\sum_i \sum_i a_j^* a_i \int \psi_j^* \psi_i \, d\tau = 1$$

$$\sum_j \sum_i a_j^* a_i \, \delta_{ij} = 1$$

$$\sum_i a_i^* a_i = 1$$

$$\sum_i |a_i|^2 = 1$$

Consider the effect of a symmetry operation X

Can be represented as an operator $\hat{X}$ on the wavefunction ψ

Now if you sum over j the only term that will appear is when j is equal to i. So, I can write this as sum over i a i star a i is equal to 1 or in other words you can write sum over i a i absolute value square equal to 1, so the condition that psi when you expand psi in an orthonormal basis then the coefficients of the expansion should square up to 1. So, the sum of squares of the coefficient should be equal to 1.

So, this is another point that we will be using, so if you know all the coefficients are not completely independent of each other, if you know all expect one of them you can find the last one. Next we want to consider the effect of a symmetry operation x. So, what we want to say is that you have your symmetry operation x and you are going to operate this on the wave function. Now how do you our symmetry operations, if you remember they correspond to things like rotations about axis or reflections and so on.

Now the question is how do you decide what happens when you operate a symmetry operation on a wave function. So, this can be represented as an operator x on the wave function psi, so the symmetry operation x has an operator that operator x operator and so corresponding to the symmetry operation there exists an operator x 1 the wave function. Now what can you say about this x operator and it turns out that you can say a few things and we will investigate that so what can we say about this operator x.

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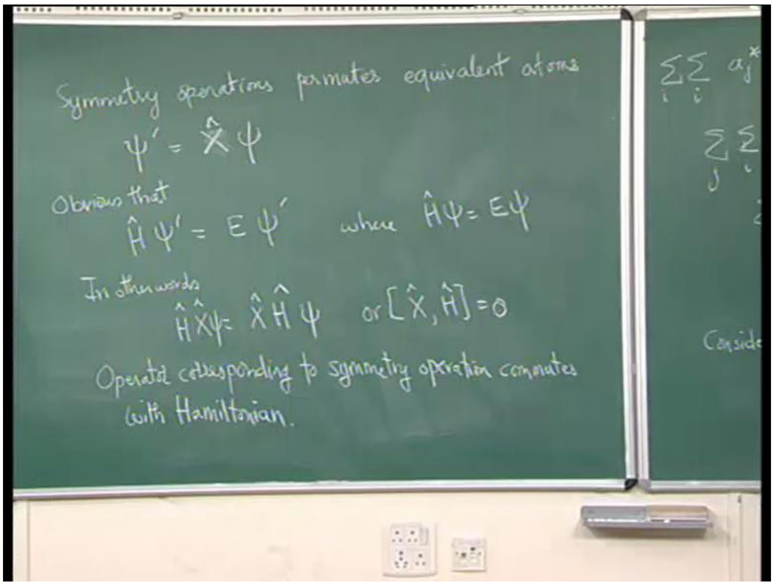

Symmetry operations permutes equivalent atoms

$$\psi' = \hat{X}\psi$$

Obvious that

$$\hat{H}\psi' = E\psi' \quad \text{where} \quad \hat{H}\psi = E\psi$$

In other words

$$\hat{H}\hat{X}\psi = \hat{X}\hat{H}\psi \quad \text{or} \; [\hat{X}, \hat{H}] = 0$$

Operator corresponding to symmetry operation commutes with Hamiltonian.

So, first of all symmetry operation physically what would you expect is symmetry operation to do, it will it will move the equivalent atoms. So, it tends to permutes equivalent atoms, so suppose I do suppose I say psi prime equal to r psi or x psi. So, then your psi prime will look a lot like psi, but only thing the there will be some permutation of atoms, some of the atoms will be permuted with each other.

And the atoms that will be permitted will be equivalent atoms, so only the atoms that are equivalent will be permitted with each other. And then it becomes so then it is obvious that H times psi prime is equal to E times psi prime, where H psi is equal to E psi, so the point is that if you just permute equivalent atoms. So, just changing equivalent atoms will not change the energy.

So, you will have the same energy as you had in the case where, you did not permit the equivalent atoms. So, this is an important point it is that permuting equivalent atoms is not going to change the energies, so this wave function should have the same Eigen values, same energy E. So, in other words H x is equal to x H, so H times psi prime psi prime is x psi, so H times x, x times psi. So, this is H times x times psi and this is psi prime, psi prime is x i. So, it is x times H times psi, so E times psi prime that is E times x psi is x operator on E psi.

So, x that is x times H operator on psi, so or x comma H equal to 0. So, the operator corresponding to symmetry operation commutes with Hamiltonian, and so we are going to use this because this implies that now the Hamiltonian and your symmetry operator, they can have common Eigen functions. So, you can choose your wave functions to be those functions, so you can choose your Eigen functions of the Hamiltonian to be specifically, those that is that are also Eigen functions of the symmetry operator.

Now, you can ask yourself what are the Eigen functions of this symmetry operator, so the Eigen functions of symmetry operator are typically those are functions that have the symmetry. So, the functions should have the symmetry of the molecule, so if you take your C H 4 molecule. Then your Eigen function corresponding to that molecule should have the symmetry of the molecule; that means, you swap the edges you permit the hydrogen’s and your wave function should remain the same and this should be reflected in the wave function for the methane molecule.

So, essentially now we have a procedure in which we say which Eigen functions should be used to as appropriate Eigen functions for the Hamiltonian operator. And we say that we will use only those that have the symmetry of the molecule, so we will choose our Eigen functions to be those that are simultaneous Eigen functions of the Hamiltonian all the symmetry operations and those that are Eigen functions of all the symmetry operations of the group.

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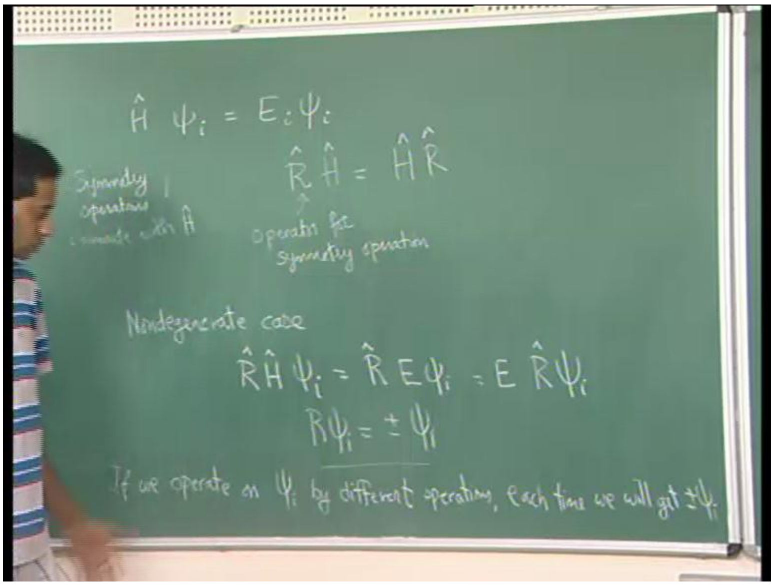

$$\hat{H}\,\psi_i = E_i\psi_i$$

Symmetry operations commute with $\hat{H}$

$$\hat{R}\hat{H} = \hat{H}\hat{R}$$

operator for symmetry operation

Nondegenerate case

$$\hat{R}\hat{H}\psi_i = \hat{R}E\psi_i = E\hat{R}\psi_i$$

$$R\psi_i = \pm\psi_i$$

If we operate on ψ_i by different operations, each time we will get $\pm\psi_i$

So, we have seen that the Eigen operator they can be chosen to be orthonormal Eigen functions and what this means is that if you have 2 Eigen functions with different Eigen values, then the wave then the functions will be a orthogonal, similarly if you even if you have a degenerate Eigen values, you can choose the wave functions to be orthonormal. Now we also know that the symmetry operation of the group they commute with commute with H.

So, what that means, is that if you had a symmetry operation R you could represented by an operator and this operator can for a symmetry operation commutes with the Hamiltonian operator that means, R H equal to H R. What this means is physically it means that if you form a symmetry operation on a molecule. If you perform a symmetry operation on a molecule, then you do not change the energy levels of that state.

So, if you take a molecule in a certain state and you operated by a symmetry operation, then you do not change the energy of that state. So, you reach another state with the same energy, so that is what it means and now suppose you take the non degenerate case, so in the non degenerate, we if a symmetry operation has to commute with the Hamiltonian. Then we can say that that R H psi i is equal to R operator on E psi i E psi i.

And this is same as E times R psi i. So, the then what we conclude is that R times psi i is equal to plus or minus psi i, that is the only choice for R times psi. So, then the effect of the symmetry operation on the wave function has to be either R leaving it as it is or changing the sign of the wave function. So, this is something we can immediately see and this is impact shows that if we operate on psi on a wave function by on psi i by different or different operations each time we will get plus or minus psi i. So, some operations will give plus psi i some operations will give minus psi i.

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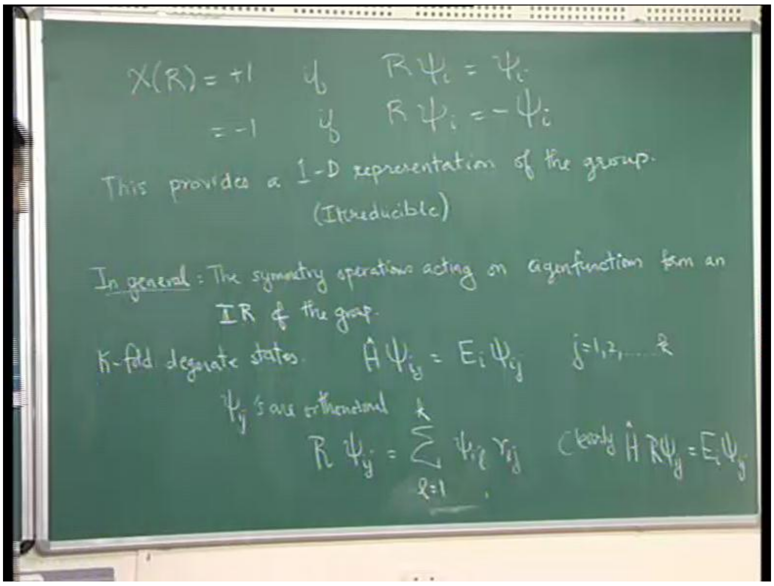

$\chi(R) = +1$ if $R\psi_i = \psi_i$

$= -1$ if $R\psi_i = -\psi_i$

This provides a 1-D representation of the group.

(Irreducible)

In general: The symmetry operations acting on eigenfunction form an IR of the group.

K-fold degenerate states. $\hat{H}\psi_{ij} = E_i\psi_{ij}$ $j = 1, 2, \ldots k$

ψ_{ij}'s are orthonormal

$R\psi_{ij} = \sum_{l=1}^{k} \psi_{il} r_{lj}$ Clearly $\hat{H}R\psi_{ij} = E_i\psi_{ij}$

So, the operations that give plus psi i, so chi of R equal to plus 1 if R psi i equal to psi i and chi of R equal to minus 1, if r psi i equal to minus psi i. Now this is how we define chi R I chi R and in fact it is not it is easy to see that chi did this provides a one dimensional representation of the group. And since it is a one dimensional representation it has to be irreducible, so what we are say and seen is that in the non degenerate case the effect of operating on the wave function by all the symmetry operations gives you these Eigen values which form a one dimensional representation of the group.

Now we can prove this is in more general in general. So, we can generalize this is the non degenerate case. We can generalize it to the degenerate case and other cases, so the symmetry operations acting on wave functions on Eigen functions form an irreducible representation of the group. So, we will show this shortly we have already seen in the non degenerate case, we can easily see this.

In fact, the wave what you would say is that if you have two operations and then the then there effect of the product of the operations just gives the product of the characters. So, that is what shows that this indeed is a valid representation, in general what you can say is that if you have the symmetry operations acting on Eigen functions. They form an irreducible representation of the group.

Let us take an example k fold degenerate states, so you have h operator on psi i psi i j is equal to E i psi i j equal to 1 2 up to k. So, there are k such equations all of them have the same Eigen value E i. Now you ask yourself what will happen? If you operate by one of the symmetry operations on psi i j, psi i j is are orthonormal. Now suppose I say I operate by R on psi i j, so suppose I operate by a symmetry operation on psi i j.

Now you know that whatever you get has to have the same Eigen value E i, so since R commutes with the Hamiltonian. When it operates on psi i j you will get another wave function, which also has the same Eigen value E i. And now if you want a wave function with Eigen value E i, you can just take it as a linear combination of these of all the all these wave functions.

So, I can write it as sum over psi i j and I will just say R, so this is j equal to 1, so psi i l, l equal to 1 to k. And then there is a coefficient corresponding to each l, so let say r l j. So, I can just write it this way. So, I just wrote it as a linear combination of all the wave functions all these basis functions. So, it is just a linear combination of those, so if I choose a wave function like this then you can clearly see H times R psi i j is equal to E i psi i j. So, I will, so you can easily see this that x times R psi i j is E i times psi i j, because each of these Eigen functions has the same Eigen value E i. So, the energy Eigen value is not changed and this is a most general representation of this operation.

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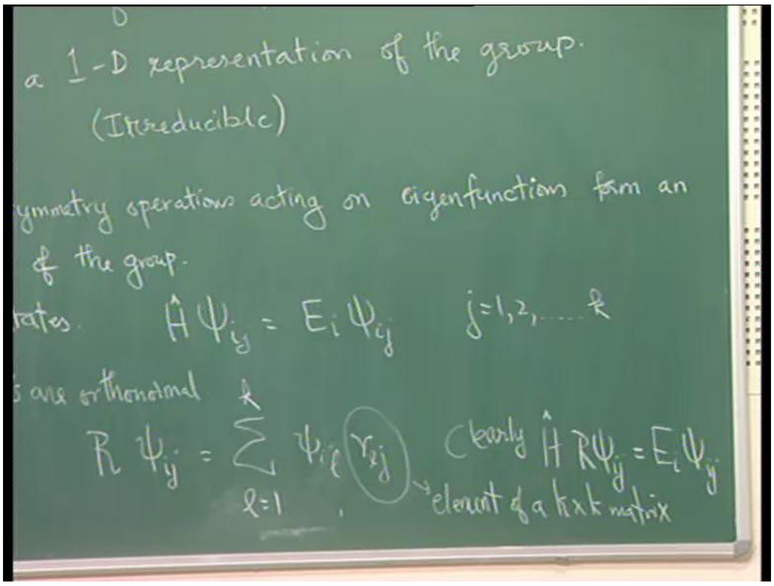

a 1-D representation of the group.

(Irreducible)

ymmetry operations acting on eigenfunctions from an

of the group.

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s are orthonormal

$R\psi_{ij} = \sum_{l=1}^{k}\psi_{il}\, r_{lj}$ Clearly $\hat{H}R\psi_{ij} = E_i\psi_{ij}$

element of a k×k matrix

And now you instantly see this quantity r L j, this looks like an element of a matrix, it will be a k by k, k times k matrix. So, this is element of a k cross k matrix. And in fact this element is what we will call k dimensional representation of the operation r.

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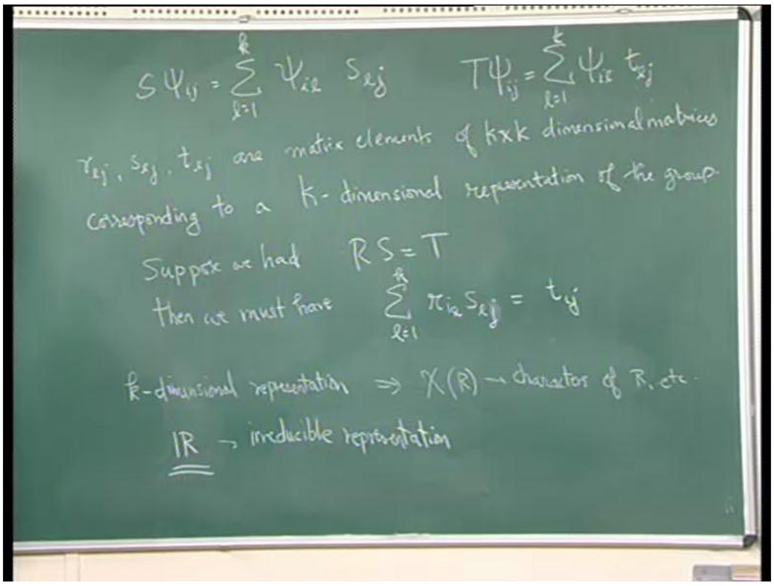

$$S\psi_{ij} = \sum_{l=1}^{k} \psi_{il} \, s_{lj} \qquad T\psi_{ij} = \sum_{l=1}^{k} \psi_{il} \, t_{lj}$$

r_{lj}, s_{lj}, t_{lj} are matrix elements of $k \times k$ dimensional matrices corresponding to a k- dimensional representation of the group.

Suppose we had $RS = T$

then we must have $\sum_{l=1}^{k} r_{il} s_{lj} = t_{ij}$

k-dimensional representation $\Rightarrow \chi(R) \rightarrow$ character of R, etc.

IR $\rightarrow$ irreducible representation

Now, if we had another operation S such that S times psi i j is equal to sum over l equal to 1 to k psi i l S l j and you had T operator on psi i j is equal to sum over l equal to 1to k psi i l t l j. So, if we had something like this, so then S i j is a matrix element of the k dimensional representation of psi i of S of operation S. Similarly, T l j is a matrix element of the matrix representation of T and this, so we can show that r l j, s l j, t l j are matrix elements of k cross k dimensional matrices corresponding to a k dimensional representation of the group.

So, the point I want to make is that this is a way to get, so if you have k fold degenerate states then you can generate a k dimensional representation of the group using this procedure. Now suppose we had R times S equal to T. suppose the product of these 2 operations was equal to T, so in the group R times S was equal to T.

Then we must have and this is again not hard to work out, but I will just write the answer sum over l equal to 1 to k r i l l S l k S l j is equal to t I j. So, the matrix corresponding to this operator matrix corresponding to t should be a matrix product of these 2 matrices. So, if we had this for operations it should also be true for the matrices, in order for the matrices to be a valid representation for the group. And this is very easy to verify you can show this by using these equalities.

So, the point we are point I want to make is that this is the way to generate a valid representation of this group and what we get is a k dimensional representation. So, this is the way to generate a k dimensional representation, we will look at a specific example of this next, so k dimensional representations and this you can get characters in this k dimensional representation character of R etcetera.

So, you can generate the characters of each of the elements and this will be an irreducible representation. Now why this should this be an irreducible representation? it is not immediately obvious why this should be an irreducible representation, but in fact, if you look at it more closely. You can show that this since you have k fold degenerate states.

So, the and the k Eigen functions are chosen to be orthonormal to each other, then you can show that this will indeed form an irreducible representation. So, let us take a specific example of this we look at the N H 3 molecule.

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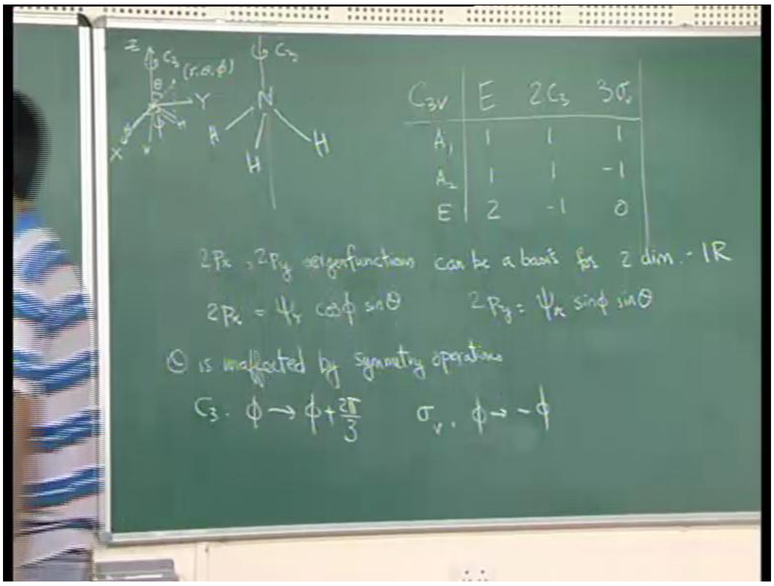

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$2p_x$, $2p_y$ eigenfunctions can be a basis for 2 dim. - IR

$2p_x = \psi_r \cos\phi \sin\theta$ $\quad$ $2p_y = \psi_r \sin\phi \sin\theta$

θ is unaffected by symmetry operations

$C_3 . \ \phi \rightarrow \phi + \frac{2\pi}{3}$ $\quad$ $\sigma_v . \ \phi \rightarrow -\phi$

So, the N H 3 molecule this belongs to group C 3 v this has 1 C 3 axis. So, this is the C 3 axis and there are 3 sigma planes containing the C 3 axis and one of the hydrogen. So, the elements of the group are E 2 C 3 and 3 sigma 3 sigma v, so there are 3 sigma v planes and you can easily work out, since the dimension of the group is 6. You can easily work out that there have to be 3 representations the, so there will be the completely symmetric representation. Then there will be 1 with this and there will be a two dimensional representation.

So, will be 2 minus 1 0, so that is the that can be worked fairly easily, now what we will show is that our p x 2 p x and 2 p y are Eigen functions can be a basis for this irreducible representation for two dimensional irreducible representation. To show this what we will say we have to set up our coordinate systems. So, we will choose this as a z axis this and it will be centered as the at the center of this, it will be center on the nitrogen, so the origin will be on the nitrogen. This is the x this is the y and we will choose, so that one of the hydrogen's lies in the x z plane.

So, one of the 1 nitrogen is at the center one of the hydrogen's is in the x z plane, the other 2 hydrogen's are somewhere else and z axis is the C 3 axis. So, then any arbitrary point you can have a polar representation r theta phi, where theta is this angle, phi is this angle r theta phi. And now in this polar representation your psi of 2 p x wave function is equal to a radial part psi r times cos phi sin theta, so the angular part is cos phi times sin theta and the 2 p y will be a radial part times sin phi sin theta.

So, 2 p x and 2 p y will have this form, we would not bother about the pre-factor of psi of r, because what we will see is that would not be affected. So, any symmetry operation will not change r, so we are not bothered about that r part. Now each of these operations, so E C 3 and sigma v if you notice if you do a C 3 rotation this point will rotate, but this angle theta with the z axis will not change.

So, theta is the theta angle will not change, so even if this point rotates here the theta, but the phi angle will change as you change this C 3, similarly when you reflect about a plane containing the z axis. And either the one of the hydrogen atoms again you will find that theta is not changed, so theta is unaffected by symmetry operations. Now when you rotate operate by C 3.

So, C 3 takes phi to phi plus 2 pi by 3, so C 3 is rotation about the z axis. So, this angle phi will change to phi plus 2 pi by 3 and it changes and then sigma v and let us take for convenience, let us take sigma v as the x z plane. So, if you take it as a x z plane when you reflect about this phi this H will come on this side, so or this phi will become minus phi, sigma v takes phi to minus phi. And this is all we need to derive the characters of this irreducible representation. So, we will see that in a minute.

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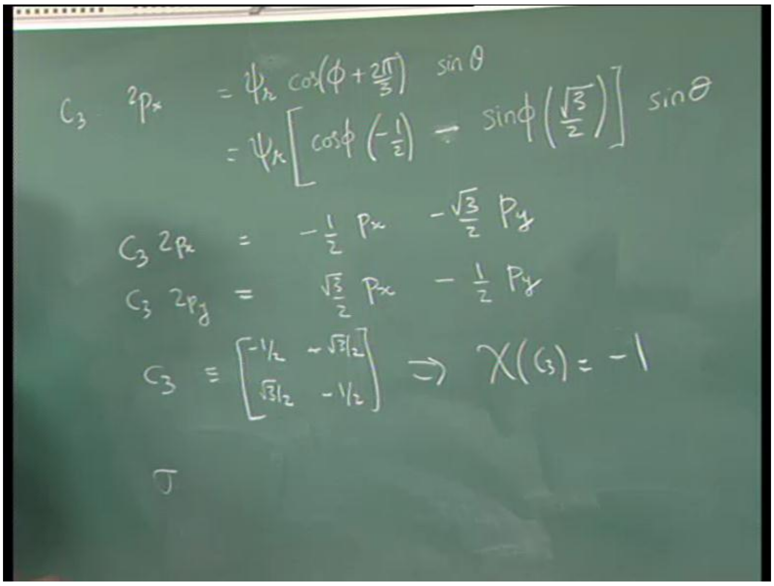

$$C_3 \; 2p_x = \psi_r \cos\left(\phi + \frac{2\pi}{3}\right) \sin\theta$$

$$= \psi_r \left[\cos\phi \left(-\frac{1}{2}\right) \mp \sin\phi \left(\frac{\sqrt{3}}{2}\right)\right] \sin\theta$$

$$C_3 \; 2p_x = -\frac{1}{2} p_x - \frac{\sqrt{3}}{2} p_y$$

$$C_3 \; 2p_y = \frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y$$

$$C_3 \equiv \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix} \Rightarrow \chi(C_3) = -1$$

$$\sigma$$

So, let us look at what happens when C 3 acts on p x 2 p x, so when C 3 acts on 2 p x what you get is, so phi will be changed to phi plus 2 pi by 3. So, you can show this that will become psi of r cos phi plus 2 pi by 3 sin theta, remains the same. And if you work this out this will be a combination of cos phi into cos 2 pi by 3 plus sin phi into sin 2 pi by 3.

So, this is psi r, so cos phi cos 2 pi by 3 is minus half plus or minus sin phi into root 3 by 2 sin 2 pi by 3 is root 3 by 2 sin theta. So, this is equal to you can, so it is minus half p x minus root 3 by 2 p y. So, C 3 operating on 2 p x is this, C 3 operating on 2 p y this will be root 3 by 2 p x minus half p y.

So, therefore, you can say that C 3 is represented by a matrix representation of C 3 is minus half minus root 3 by 2 root 3 by 2 minus half, so this is the two dimensional matrix representation of C 3 implies chi of C 3 is equal to minus 1. The trace of this minus 1, similarly you can show that sigma has a representation sigma will keep just change phi to minus phi. So, when phi changes to minus phi, you can see that 2 p x remains the same, but 2 p y changes sign.

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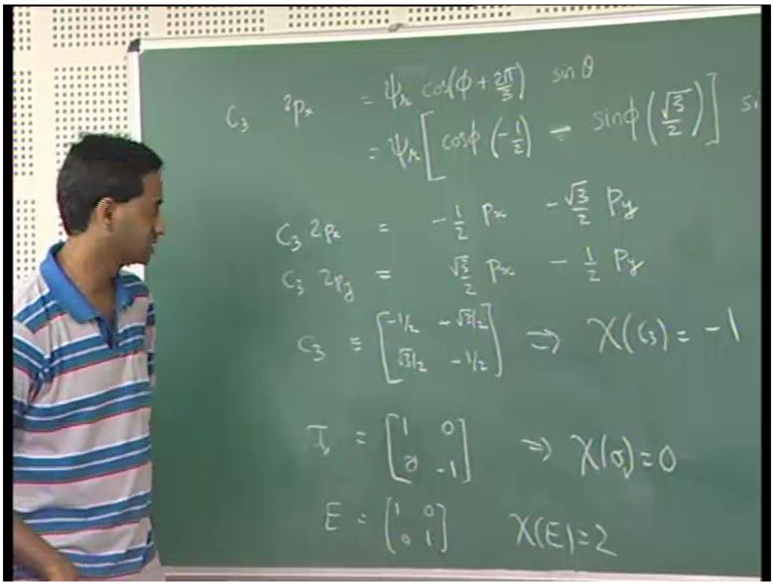

$C_3 \quad 2p_x = \psi_r \cos(\phi + \frac{2\pi}{3}) \sin\theta$

$= \psi_r \left[\cos\phi \left(-\frac{1}{2}\right) - \sin\phi \left(\frac{\sqrt{3}}{2}\right)\right]$

$C_3 \, 2p_x = -\frac{1}{2} p_x - \frac{\sqrt{3}}{2} p_y$

$C_3 \, 2p_y = \frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y$

$C_3 \equiv \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix} \Rightarrow \chi(C_3) = -1$

$\sigma_v = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \Rightarrow \chi(\sigma_v) = 0$

$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad \chi(E) = 2$

So, this is sigma and this implies that chi of sigma equal to 0 sigma v, so and since this is the two dimensional representation clearly E is equal to 1 0 0 1 chi of E equal to 2. And so what you notice is that 2 minus 1 0 which is the same as the dimensional representation, so this is an irreducible representation. This is the two dimensional irreducible representation of this group. So, what we said is that p x and p y form a basis for a two dimensional irreducible representation of this group.

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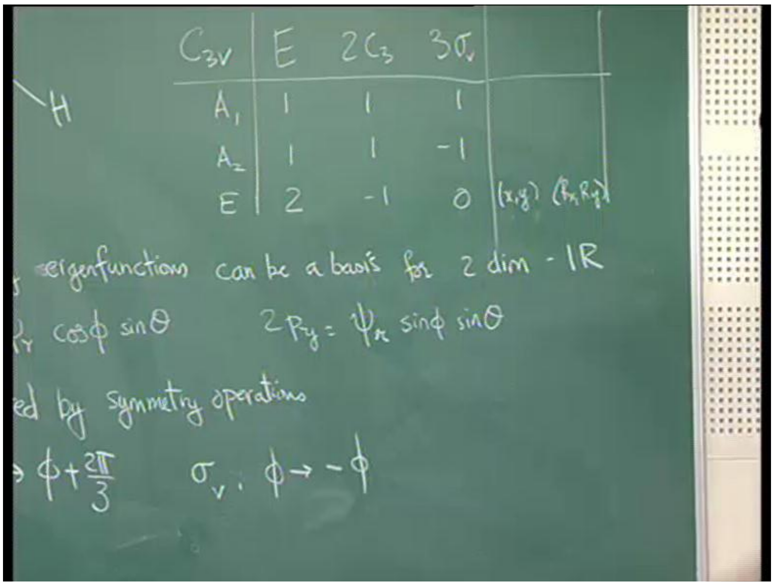

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	(x, y) (R_x, R_y)

H

eigenfunctions can be a basis for 2 dim - IR

$\cos\phi \sin\theta \qquad 2p_y = \psi_r \sin\phi \sin\theta$

ed by symmetry operations

$\phi + \frac{2\pi}{3} \qquad \sigma_v : \phi \to -\phi$

And if you remember in this column of the group, what you will have is x y x and y transform as p x and p y. So, they will be form a two dimensional irreducible representation and you also have R x and R y, so this is one of the things in this you have other things also, but this is one of the things and this is what we have shown using this representation. So, we can use the Eigen functions as to generate a two dimensional irreducible representation of this group.