Symmetry and Group Theory
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Lecture -33
Group Theory and Quantum Mechanics

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So, we have now seen all the rules of symmetry and how to apply those rules to actually get to the stage of symmetry operations followed by character table and all. So, given a molecule we can identify what are the symmetry elements present, what are the symmetry operations present in the molecule, what is the point group of the molecule. And then using the rules of great orthogonality theorem or using unit vector transformations etcetera we can identify what are the IR representations.

And we have also seen if we write the reducible representation how to convert that into a irreducible representations. So, all those rules form the first part of this course and now the second part is the applications part. So, let us start seeing applications of group theory now in chemistry. So, a few applications we have already discussed for example the first one was dipole moment whether a molecule has dipole moment or not we can predict based on the rules of symmetry.

And then similarly we have also seen whether a molecule is optically active or not, optical activity we tested again using the rules of symmetry and group theory. So, these two applications we have already seen. So, now let us look at Group Theory and Quantum Mechanics. So, why are we discussing quantum mechanics? We will first introduce not introduce we will just revise; you all must be aware of this famous equation H psi equal to E psi. So, what is H psi equal to E psi, it is a eigenvalue equation.

It is also called as Schrodinger wave equation. So, what are different parts or different components here? So, psi is a state function also called as wave function which tells you about the state, all the properties of that particular state. Then H is Hamiltonian operator that also we know, we might have studied at some point. Hamiltonian operator operates on a function and if it is a eigen function then it generates eigenvalue which is energy of the system. So, basically it is an operator to measure energy.

So, these are the main components, so we have an operator, we have a function and then operator operates on a function to give a constant value which is energy in this case, because the operator is Hamiltonian. So, now why are we discussing Hamiltonian in group theory. So, if we see that there is a very important property which is if we replace, let us stick to the word replace so if we replace identical particles in a molecule with the same particles or with identical particles.
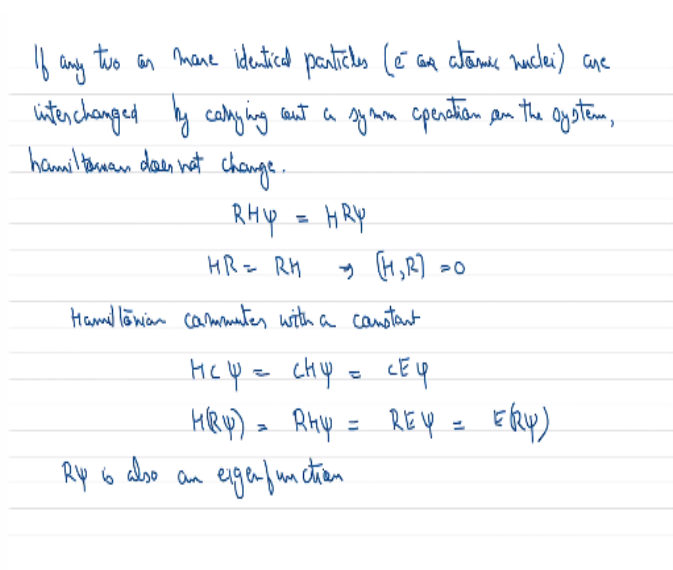
For example, if we have electron and one electron is replaced with the same electron then the energy of the system is invariant. So, what do I mean by that, so let us say if we have a molecule let us take an example of methane. And let us call this configuration as configuration 1. If I am doing any symmetry operation R it goes to equivalent configuration and let us call this equivalent configuration as 2.

Now if you look at, let us say that the symmetry operation is C3. So, then we will be rotating this molecule about the CH bond by 120 degree angle. So, now if you see that this atom is replaced with this, this with this and so on. So, basically particle which is the atomic nuclei here, each of this is replaced with the identical ones. And thus, the energy of the system if we measure energy

of system 1 configuration 1 should be equal to energy of the system 2. Similarly, we can say about the bonds also.

So, if this bond the electron density here is replaced with this electron density versus electron density here is replaced with that electron density. So, these are all identical particles, because they have similar location with respect to any particular point in the molecule. So, that means that we are moving these identical particles around and in the process we are not perturbing the energy of the system.

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If any two or more identical particles ($\bar{e}$ or atomic nuclei) are interchanged by carrying out a symm operation on the system, hamiltonian does not change.

$$RH\psi = HR\psi$$

$$HR = RH \quad \rightarrow \quad (H,R) = 0$$

Hamiltonian commutes with a constant

$$HC\psi = CH\psi = cE\psi$$

$$H(R\psi) = RH\psi = RE\psi = E(R\psi)$$

$R\psi$ is also an eigenfunction

So, if I want to write this statement what do I say that any two, so Hamiltonian does not change our energy does not change. So, that means whether I am measuring energy first or doing a symmetry operation first it does not matter. So, in other words what we can do is we can say that if we first measure energy on this and then carry out symmetry operation that should be equal to if we first carry out symmetry operation on this and then measure energy.

So, there is no difference if we first measure energy versus if we first do the symmetry operation. The energy of the system remains invariant. So, that tells you that H R is basically equal to RH which means that H and R commute with each other. So, we know what is the meaning of commutation now. So, H and R basically Hamiltonian commutes with all the symmetry operations present in the given molecule.

So, we can also say that in a similar way we can say that Hamiltonian commutes with a constant. So, we can write HC psi is equal to CH psi is equal to CE psi. So, similarly here we can write H R psi, the only difference is that now R is not a constant R is a operator in itself and we can say that it is RH psi and this now gives you energy. So, RE psi and we can actually take E out of this operator, because now operator will not act on constant so we will say that ER psi, that is very straightforward to see.

So, now we can see that since psi is an eigen function, R psi is also an eigen function. So, we can say R psi is also an eigen function. So, that is easy to see now we also know that psi is normalized.

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So, now if we want R psi also to be normalized what condition we will have, so we will have R psi should be equal to plus minus 1 psi. So, that means if we operate a symmetry operation onto a wave function which defines the state of the molecule and the symmetry operation must belong to the molecule. So, then that state, that symmetry operation will generate a character which is plus or minus 1 because of the above condition.

So, this means that if we are carrying out given that a molecule has certain set of symmetry operations if we carry out all those symmetry operations on psi we will get tau psi. So, let us say

that if we have E, A, B, C and so on symmetry operations in a general group G then we will get plus minus 1. So, here we will always get plus 1 because it is the dimension but we will get plus minus 1. So, any symmetry operation if we do we will either get plus 1 or minus 1.

I mean of course if there is mixing of two states involved then we might get higher state higher dimensional representation. But mostly we will see that this will be a irreducible representation. Because we are getting one dimensional matrix and one dimensional matrix we will not be able to reduce it further. So, this would then be a irreducible representation. So, now let us take an example to show what we are saying here. So, let us take an example of C3v only we have been looking at this molecule since we started this course, so we know in and out of all the character table and symmetry operations and everything so it will be easier to see.

So, now if we look at the central atom which is nitrogen it has 2px and 2py orbitals. So, we can take these as the basis set this is our basis set. So, like we took psi as the basis set here and developed a irreducible representation. So, this is also a wave function we can write the wave function for Px orbital and Py orbital.

And we can treat that as basis set and see what representation do we get, whether it is reducible irreducible and so on. So, Px orbital has the functional form of psi R sine theta cos phi and Py has the functional form of psi R sine theta sine phi. So, I am not going to discuss how we get this Px and Py that is discussed elsewhere in quantum mechanics course. So, we will not go into those details, so let us see what is the meaning of this r, theta and phi.

So, let us say if we have a point in 3-dimensional space the coordinates are x, y, z and length of that vector from origin is R. So, theta here is the angle with which it is going away from z axis. So, that angle which this vector is making in three-dimensional coordinate system with z axis, so how far down basically that vector has fallen from z axis will be called as theta. And now if you take a projection of this vector onto X Y plane, so this is the projection here.

This length and that projection if the angle between that projection and the positive side of the x-axis is called as phi. So, this is phi, theta, and r. Now let us see that what happens under different

symmetry operations present in C3v on to these theta, phi and R. Because we need to calculate the effect of those symmetry operations onto Px, so we should know the effect of symmetry operations onto theta, phi, and r.

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So, let us say the symmetry operations what we have here is, C3v and let us discuss only one of the class elements. And let us call this as xz and this will be our term. So, let us say what happens to r, so psi (r) under E does it change. So, because r is a constant r is the length of the vector and as such E does not do anything so psi (r) remains as psi (r). So, we do not need to consider any effect of identity on to psi (r).

Now C3 on psi r now this is just the rotation so rotation is not going to change the length so again this will be psi r. And similarly, the reflection is also not going to change the length, so this will also be psi r. So, basically psi r is invariant under any of these symmetry operations so that means the character will be plus 1 in for psi r. So, now let us see what happens to theta, so if we see carefully theta is the angle which is between the vector and the z axis.

Now all our rotations are with respect to z axis, because our C3 is lying along z axis so all our rotations are about z axis. So, no matter how much you rotate this angle above z axis the theta will not change. So, that means theta 1 must always be equal to theta 2 where this is angle before symmetry operation and this is angle after symmetry operation is performed. So, this means

other component sin theta that will also not change, so that will also remain same under both c 3 as well as sigma xz.

Now because sigma xz, why sigma xz will also not change? because sigma xz contains the z axis, so the theta with respect to z axis will not going to be different. So, now let us look at phi so phi 2 if we are doing a C3 rotation what happens to phi 2. So, phi 2 becomes phi 1 + 2 pi by 3, so we are taking this vector and rotating it by 120 degrees. So, that means your new phi will be phi plus 2 pi by 3, phi plus 120 degree.

So, we can say that phi 2 is equal to phi 1 + 2 pi by 3. Now this means that what happens to cos phi, cos phi 2 will be cos phi 1 + 2 pi by 3. And we can always write this as cos phi 1 cos 2 pi by 3 minus sine phi 1 sine 2 pi by 3. So, this is cos a plus b is equal to cos a cos b minus sin a sin b. So, now what happens to cos 2 pi by 3 this is minus half, so you have minus half cos phi 1 and sin 2 pi by 3 is plus root 3 by 2.

So, you have minus root 3 by 2 sin phi 1, so cos phi 2 is equal to this when I am doing a C3 operation. So, this is for C3 operation. Now let us see okay we also have to calculate for sine phi. Because there was one more term in phi which is sine phi.

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$$C_3 - \quad \phi_2 = \phi_1 + \frac{2\pi}{3} \quad Sin\phi_2 = Sin\left(\phi_1 + \frac{2\pi}{3}\right)$$

$$= Sin\phi_1 \, Cos\frac{2\pi}{3} + Cos\phi_1 \, Sin\frac{2\pi}{3}$$

$$= -\frac{1}{2} Sin\phi_1 + \frac{\sqrt{3}}{2} Cos\phi_1$$

$$\sigma_{xz} \quad \phi_2 = -\phi_1 \quad Cos\phi_2 = Cos(-\phi_1) = Cos\phi_1$$

$$Sin\phi_2 = Sin(-\phi_1) = -Sin\phi_1$$

$$\hat{E} \, P_x = \hat{E}\left[\psi_n \, Sin\theta \, Cos\phi\right] = \psi_n \, Sin\theta \, Cos\phi = P_x$$

$$C_3 \, P_x = C_3\left(\psi_n \, Sin\theta \, Cos\phi\right) = \psi_n \, Sin\theta \left(-\frac{1}{2} Cos\phi - \frac{\sqrt{3}}{2} Sin\phi\right)$$

So, let us also calculate for sin phi. So, under C3 phi 2 equal to phi 1 + 2 pi by 3. So, if we have sine phi 2 this will be equal to sine phi 1 + 2 pi by 3. Now this is sine a plus b which will be sine a cos b plus cos a sine b. So, this again becomes minus half sine phi 1 and this becomes plus root 3 by 2 cos phi 1. Now let us calculate under sigma xz what happens to phi 2. So, let us go back to the coordinate system so if you are having sigma xz, phi will be reflected to minus phi.

So, that means I can say that phi 2 is equal to minus phi 1. So, you can see that my new phi will be somewhere around here. So, this will be my phi so this will be a negative angle so that is why you have phi 2 is equal to negative of phi 1. So, now if you want to calculate for cos phi 2, this will be equal to cos of minus phi 1 and if we want to calculate for sine phi 2 this will be equal to sine of minus phi. So, this will be equal to cos of phi 1 and this will be equal to minus sine phi, so now that we have calculated.

Let us calculate the effect of this different symmetry operations onto all of the elements which is psi r sine theta cos phi and sine theta sine phi. So, now let us calculate the effect of E onto P\x now we can do that. So, E when operated on psi r sine theta cos phi what do I get, so I get the same thing. So, I get psi sine theta cos phi and I can say that this is Px. Now let us do the same thing for C3, if I do C3 on P x, I do C3 on psi r sine theta cos phi and what do I get here.

So, I will just write down the answer here, so psi r does not change and sine theta does not change. So, I will say psi r sine theta and cos phi changes to cos phi 2. Now that cos phi 2 will be given by minus half of cos phi 1 minus root 3 by 2 of sine phi 1. So, I can say that this is minus half cos phi minus root 3 by 2 sine phi.

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$$C_3(P_x) = -\frac{1}{2}\psi_n \sin\theta \cos\phi_1 - \frac{\sqrt{3}}{2}\psi_n \sin\theta \sin\phi_1$$

$$C_3(P_x) = -\frac{1}{2}P_x - \frac{\sqrt{3}}{2}P_y$$

$$C_3(P_y) = C_3(\psi_n \sin\theta \sin\phi) = \psi_n \sin\theta \sin\phi_2$$

$$= \psi_n \sin\theta \left(-\frac{1}{2}\sin\phi_1 + \frac{\sqrt{3}}{2}\cos\phi_1\right)$$

$$= -\frac{1}{2}\psi_n \sin\theta \sin\phi_1 + \frac{\sqrt{3}}{2}\psi_n \sin\theta \cos\phi_1$$

$$= -\frac{1}{2}P_y + \frac{\sqrt{3}}{2}P_x$$

$$\sigma_{xz}(P_z) = \sigma_{xz}(\psi_n \sin\theta \cos\phi)$$

Now I can expand this further and I can say that C3 on to Px will give me psi r sine theta minus half can come out and this will be cos phi 1 and minus root 3 by 2 psi r sine theta and we will have sine phi 1. So, all I have done is I have just expanded this bracket over here to get this. And now what is this, this is minus half of Px minus root 3 by 2 of Py. So, basically upon doing C3 operation on to Px orbital it gets mixed between Px and Py orbital.

Similarly, now we do C3 on to Py and what do we get we will get C3 on to psi r sine theta sine phi. So, this will now be psi r does not change, sine theta does not change and sine phi becomes sine phi 2 which is so I can say this is sine phi 2 and this will be psi r sine theta this, I can write as minus half sine phi 1 plus root 3 by 2 cos phi. So, this again is coming from effect of C3 on to here, effect of C3 onto sine phi 2 which gives you minus half sine phi 1 plus root 3 by 2 cos phi 1.

Now if you expand this what do you get minus half psi r sine theta sine phi 1 plus root 3 by 2 psi sin theta cos phi. And this in turn can be written as minus half Py plus root 3 by 2 Px. Now similarly this is for C3, ideally we should also do it for C3 square. But we will just skip it because we just want to see how the matrix is looking for the C3 operation, for sigma xz what happens if we apply sigma xz on to Px. If we do that, we will have sigma xz applied on psi r sine theta and cos phi.

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$$= \psi_n \, Sin\theta \, Cos\phi_2 = \psi_n \, Sin\theta \, Cos\phi = P_x$$

$$\sigma_{xz}(P_y) : \sigma_{xz}(\psi_n \, Sin\theta \, Sin\phi)$$

$$= \psi_n \, Sin\theta \, Sin\phi_2 = -\psi_n \, Sin\theta \, Sin\phi$$

$$= -P_y$$

$$\Rightarrow E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad C_3 = \begin{bmatrix} -\tfrac{1}{2} & -\tfrac{\sqrt{3}}{2} \\ \tfrac{\sqrt{3}}{2} & -\tfrac{1}{2} \end{bmatrix} \quad \sigma_{xz} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$E \begin{bmatrix} P_x \\ P_y \end{bmatrix} = \begin{bmatrix} P_x \\ P_y \end{bmatrix}$$

$$\Gamma_{P_x P_y} = E$$

C_{3v}	E	$2 C_3$	$3 \sigma_v$	
$\Gamma_{P_x P_y}$	2	-1	0	
E	2	-1	0	(x, y)

So, this gives us so psi r does not change and so is sine theta that also does not change. And we have cos phi 2, cos phi 2 in terms of, when we did sigma xz on cos phi 2, it remained same. So, I can write it as psi r sine theta cos phi which is nothing but Px. So, Px remains as Px now let us do sigma xz on Py. Now we will see that this will be sigma xz on psi r sine theta sine phi and this turns out to be psi r remains as psi r, sine theta and this becomes sine phi 2.

And we are seeing that it was sin phi 2 is equal to sin of minus phi 1 and we get negative sign out. So, psi r sine theta sine phi which is nothing but negative of Py. So, sigma xz on Py gives you negative of Py. So, that means if you want to write the matrix for E what we will get is 1, 0, 0, 1. If you want to write the matrix for C 3 this will be minus half, minus root 3 by 2, root 3 by 2, minus half.

And for sigma xz, this will be 1, 0, 0, minus 1. So, basically this comes if we are doing E on to Px and Py we have to do it together because they are getting mixed. Then what is the form we are getting here in terms of Px and Py and this basically helps you give this matrix. Similarly if we are doing C3 operation here then Px gets transformed into what and Py gets transformed into what and that will give you the matrix for C3 which is this. Similarly for sigma xz.

So, now there is very important thing which we want to see that this actually belongs to if we look at the trace here. This trace over here for E, C3, and sigma xz is nothing but 2, minus 1, and

0, so we can say this tau Px Py for C3v. Now we know that this is the trace for E representation under C3v point group. So, we can say that the tau Px Py is nothing but E representation. And E representation has basis as, like if we write down it here E, 2, -1, 0, the unit vector basis for that is x and y.

So, it is transformed as x and y, so Px and Py orbital because they are lying along x and y. So, they will also transform as x and y. So, they will also form the basis of E representation. Actually, this is the reason why this particular function which is given by Px is called as Px, because to start with we did not know whether this function is lying along x-axis or this function is lying along y-axis. But now as it turns out it lies along x and y axis which is clear from group theory, this character table.

So, this means that we can now name this orbital as Px orbital what I mean is that to start with we only had this functions we did not know whether it is Px or Py. When we get the result of quantum mechanics, when we solve the equation, we will not go into details how we get the Px and Py orbitals but when we solve the equations we get this orbitals. But we do not know whether it is Px and Py orbitals which we get to know from here that this indeed is Px and Py.

Because it is transforming as x and y transforming as E representation under C3v. So, we have seen today the very important role of group theory where wave functions can be taken as basis set and their properties can be discussed whether they are lying along x and y axis or not. We will see more into this when we will move to symmetry adapted linear combinations. So, that is all for today and if you have any questions we will discuss in interaction session.