Symmetry and Group Theory
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Lecture -63
Spectral Transition Probabilities Part- I

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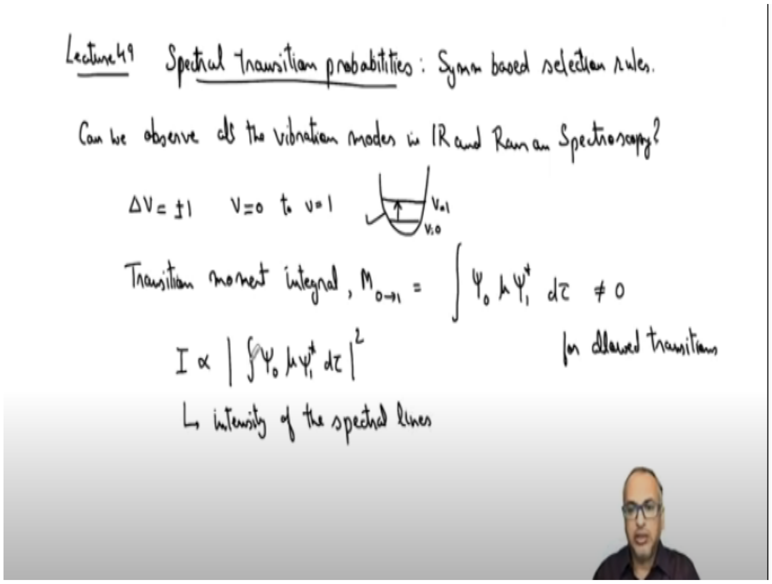

Lecture 49 Spectral transition probabilities : Symm based selection rules.

Can we observe all the vibration modes in IR and Raman Spectroscopy?

$\Delta V = \pm 1$ $V=0$ to $v=1$

Transition moment integral, $M_{0\to 1} = \int \psi_0 \mu \psi_1^* \, d\tau \neq 0$ for allowed transitions

$I \propto \left| \int \psi_0 \mu \psi_1^* \, d\tau \right|^2$

↳ intensity of the spectral lines

So, welcome back guys. Today is the last lecture of this course, and we will be discussing one last application within application of group theory to spectroscopy, which is spectral transition probabilities and symmetry-based selection rules. So, we have done a brief discussion on this when we were discussing direct product applications. So, where we actually looked at whether a particular transition moment integral will survive or not based on.

So, we will see that and then we will go into more details of what spectral transition probabilities are and how do we calculate exactly those probabilities using group theory rules. So, let us start with the spectral transition probabilities, and in this we will be discussing symmetry-based selection rules. So, we have already seen that various normal modes of a molecule can be catalogued using group theory.

And we can also analyze whether what will be the symmetry of those normal modes and all. But now whether we can observe those vibrations in IR and Raman spectra? Because IR and Raman spectra are the one, where we are expected to see such vibrational modes. So, the question is can we observe all the vibration modes in IR and Raman spectroscopy? So, how do we do that? So, we know what the selection rule is.

We know that the change in vibrational quantum number should be plus/minus 1 and only these transitions are allowed. So, we can say v is equal to 0 to v is equal to 1 transition is allowed and so on so forth like 1 to 2, 2 to 3 and so on so forth. So, pictorially you can see that if this is my simple harmonic potential surface and this is v equal to 0, v equal to 1 then this transition is allowed. So, this transition is allowed transition.

Now if I want to write the transition moment integral for this, this we have already seen. So, I am just repeating this. But we will go into more details of this. So, transition moment integral we can write it as M 0 to 1 will be given by psi of 0 mu and psi of 1 to star and d tau and this should not be equal to 0 for a transition, we can say for allowed transitions. Now the intensity of the spectral line we can also measure the intensity.

We can say proportional to not equal to will be proportional to the square of this integral. So, this is the intensity. But of course, you need to know in the exact form of this psi wave function which we will also discuss today, spectral lines.

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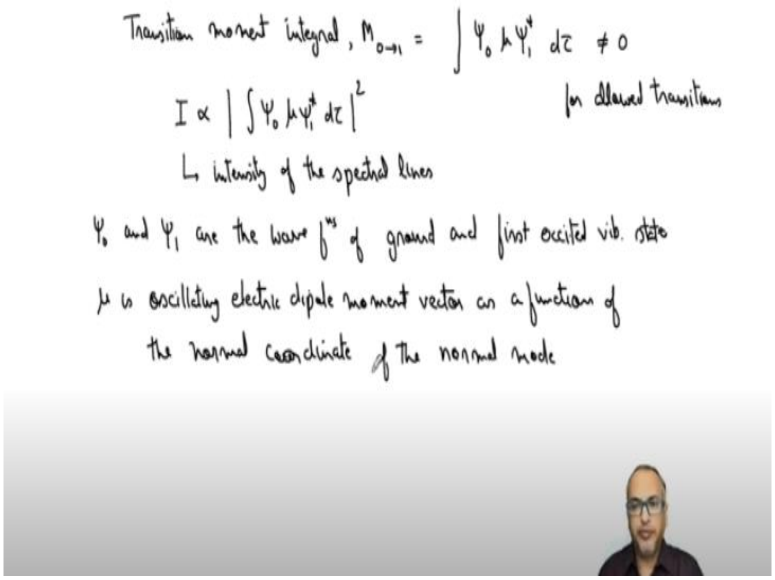

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↳ intensity of the spectral lines

ψ_0 and ψ_1 are the wave f^{ns} of ground and first excited vib. state

μ is oscillating electric dipole moment vector as a function of the normal coordinate of the normal mode

So, we know psi 0 and psi 1 are the wave functions of ground state and first excited state vibrational state and what is mu? So, mu is again we have seen this earlier. Mu is an oscillating electric dipole moment vector as a function of the normal coordinate of the normal mode. So, what is the normal coordinate of the normal mode? Let us also look at that.

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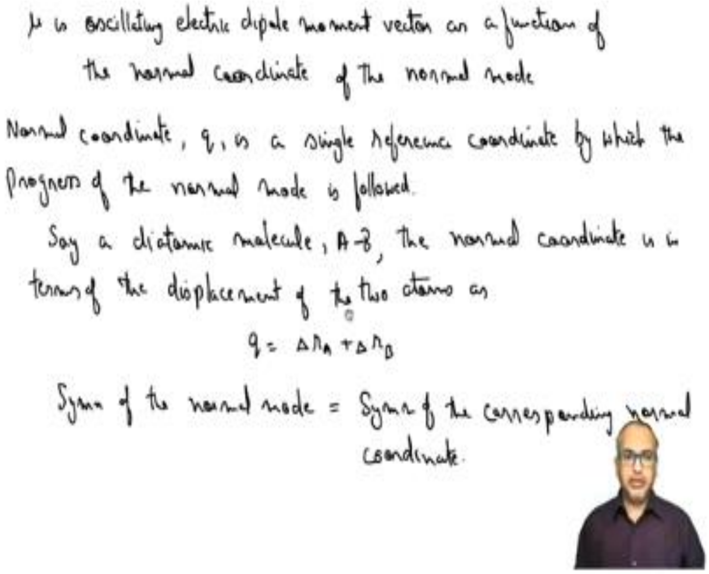

μ is oscillating electric dipole moment vector as a function of the normal coordinate of the normal mode

Normal coordinate, q, is a single reference coordinate by which the progress of the normal mode is followed.

Say a diatomic molecule, A-B, the normal coordinate is in terms of the displacement of the two atoms as

$$q = \Delta r_A + \Delta r_B$$

Symm of the normal mode = Symm of the corresponding normal coordinate.

So, let us define this quantity normal coordinate by q. So, normal, you can say q is a single reference coordinate by which the progress of the normal mode is followed. So, how that particular vibration is changing the bond length, for example, that is followed by a single reference coordinate which is called as normal coordinate. So, let us say a diatomic molecule A-B, the normal coordinate is in terms of the displacement of the two atoms.

Because that will lead to the stretching or compression of this bond which is one of the vibrational modes. Displacement of the two atoms, as we can write as delta rA plus delta rB. So, how much A is moving from its mean position, how much B is moving from its mean position that is called as delta r A and delta r B and the total sum of that will be called as q. So, q is a normal coordinate to define that particular normal mode which is the vibrational mode.

So, every vibrational mode can be expressed in terms of a normal coordinate which is a single reference coordinate. So, what is the idea behind it? So, the idea is that the symmetry of the normal mode. So, if we, why are we doing this? So, symmetry of the normal mode which we already know from the character table. We have learnt in the last lecture how to find out the symmetry of normal mode, is equal to the same as symmetry of the corresponding normal coordinate.

Again, we will see why we need the symmetry of the normal coordinate? It will come in the hermite polynomial later. So, the idea is that symmetry of the normal mode which we already know, we have seen in the last lecture. How do we find out the symmetry of normal mode, is basically same as the symmetry of the corresponding normal coordinates. So, the symmetry of q is same as the symmetry of the corresponding vibrational mode. So, now let us see what is mu?

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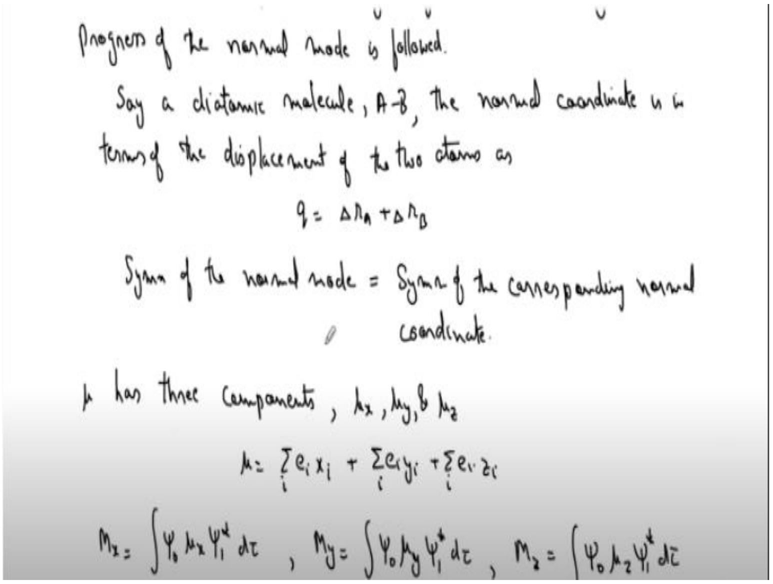

Progress of the normal mode is followed.

Say a diatomic molecule, A-B, the normal coordinate is in terms of the displacement of the two atoms as

$$q = \Delta r_A + \Delta r_B$$

Symm of the normal mode = Symm of the corresponding normal coordinate.

μ has three components, μ_x, μ_y & μ_z

$$\mu = \sum_i e_i x_i + \sum_i e_i y_i + \sum_i e_i z_i$$

$$M_x = \int \psi_0 \mu_x \psi_1^* d\tau \quad , \quad M_y = \int \psi_0 \mu_y \psi_1^* d\tau \quad , \quad M_z = \int \psi_0 \mu_z \psi_1^* d\tau$$

So, now mu has three components. That also we have learnt earlier. You can express mu as a summation of mu x, mu y and mu z and basically mu is nothing but summation of charges present at different Cartesian coordinate values. So, you have x i over i summation of all the charges and their corresponding distance from origin. Let us say e i y i summation e i z i. So, that is why mu can be expressed as mu x which is this part, mu y which is this part, mu z which is this part.

Now if mu has three components, so then the transition moment integral will also have three components. So, you can say that the M x is psi 0 mu x psi 1 star d tau. Similarly, M y is psi 0 mu y and psi 1 star d tau. M z is equal to psi 0 mu z psi 1 star d tau. Now if any of these three is non-zero then the overall M will be non-zero and thus the integration or the transition moment integral will be non-zero.

That means the transition will be allowed. So, you need to find out all three and if any of these three survives then you have allowed transition.

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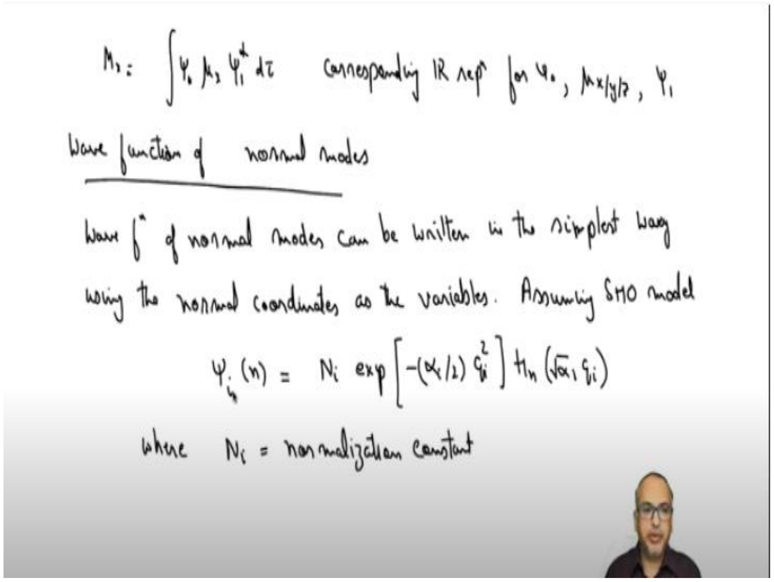

$M_x = \int \psi_0 \mu_x \psi_1^* d\tau$ corresponding IR rep^n for ψ_0, $\mu_{x/y/z}$, ψ_1

Wave function of normal modes

Wave f^n of normal modes can be written in the simplest way using the normal coordinates as the variables. Assuming SHO model

$$\psi_{i_n}(n) = N_i \exp\left[-(\alpha_i/2) q_i^2\right] H_n(\sqrt{\alpha_i}\, q_i)$$

where N_i = normalization constant

So, now when I say this integral let us say if I am talking about M x psi 0 mu x psi 1 star d tau. So, I need to know if you remember the direct product applications. So, I need to know the corresponding IR representation for psi 0 mu x y z and psi 1. All three we must know and then only we should be able to find out those corresponding IR representation, and find out the direct product of all three and that direct product if it corresponds to if it contains a totally symmetric representation the integral will be non-zero, remember that.

So, now how do I find out, what is the IR representation for this psi 0 and psi 1? So, we have discussed a few examples earlier where it was given to you that psi 0 is this and psi 1 is this. But now let us say if we want to know how do we identify what will be IR representation? So, let us see what is the wave function of a normal mode. So, wave function of a normal mode or of normal modes in general we can say can be written in the simplest way using the normal coordinates which we have just learned what is normal coordinate.

So, if we know the symmetry of normal coordinates, we can back calculate the symmetry of wave function. So, that means we should know the symmetry of the normal mode and correspondingly symmetry of the normal coordinate can be predicted and from there the symmetry of wave function can be predicted. So, now let us see normal coordinates have the variables and this will be assuming a simple harmonic oscillator model.

So, we can write down any general wave function psi in can be written as N i exponential of minus alpha i by 2 and q i square H n. See I am not asking you to remember this expression. I am just giving you this expression and if I ask in exam I will give you this expression. So, do not worry about it. It is a long expression I know. But just understand the maths behind it. Now where N i, so let us try to explain all of this.

So, psi i is the wave function of the normal mode. N i this N i is normalization constant. So, it does not affect the symmetry. Now what is the next one?

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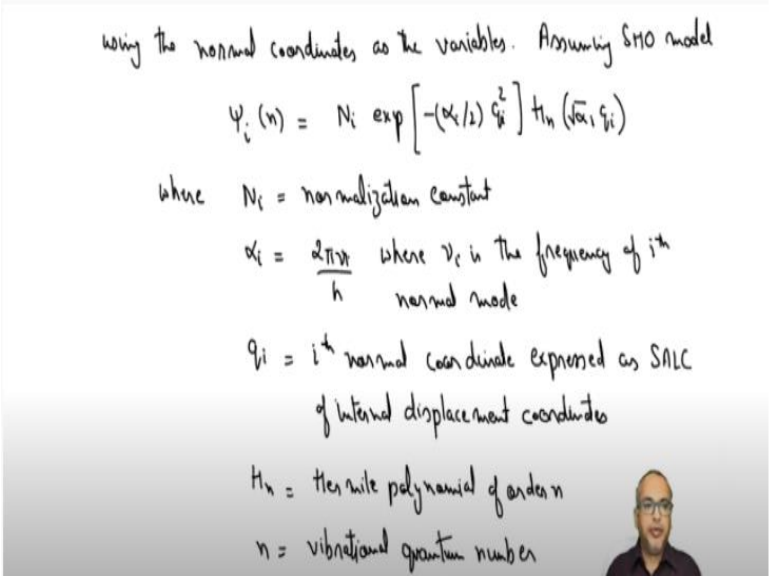

using the normal coordinates as the variables. Assuming SHO model

$$\psi_i(n) = N_i \exp\left[-(\alpha_i/2)\, q_i^2\right] H_n(\sqrt{\alpha_i}\, q_i)$$

where N_i = normalization constant

$\alpha_i = \frac{2\pi\nu_i}{h}$ where ν_i is the frequency of i^{th} normal mode

q_i = i^{th} normal coordinate expressed as SALC of internal displacement coordinates

H_n = Hermite polynomial of order n

n = vibrational quantum number

Alpha i is 2 pi nu i by h, where nu i is the frequency of ith normal mode. So, now next is q i. So, q i is ith normal coordinate. We just learned what is normal coordinate, and how is this expressed? This is expressed as SALC of internal displacement coordinates, basically how the atoms are moving? So, that will be internal displacement coordinates. So, a linear combination of internal displacement coordinates gives you a particular q i which is normal coordinate of that particular normal mode.

We have already seen this example. Now H n is a hermite polynomial of order n. We will see what that is, n is a vibrational quantum number. So, if you are talking about the ground state, n will be 0. Let us see how do we write Hn.

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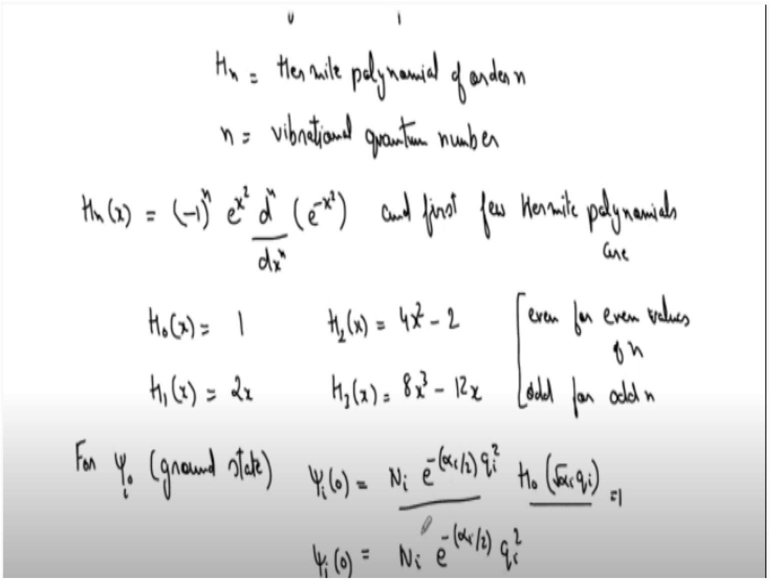

H_n = Hermite polynomial of order n

n = vibrational quantum number

$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2})$ and first few Hermite polynomials are

$H_0(x) = 1$ $\quad H_2(x) = 4x^2 - 2$

$H_1(x) = 2x$ $\quad H_3(x) = 8x^3 - 12x$

[even for even values of n

odd for odd n

For ψ_0 (ground state) $\psi_i(0) = \underline{N_i e^{-(\alpha_i/2)q_i^2}} \underline{H_0(\sqrt{\alpha_i} q_i)}_{=1}$

$\psi_i(0) = N_i e^{-(\alpha_i/2)q_i^2}$

Hn can be written as Hn of x let us say is minus 1 to the power of n, e to the power of x square nth derivative dx n e to the power minus x square. And the first few hermite polynomials are, so let us try to write down. So, H0 of x is 1. H1 of x is equal to 2x. You can calculate it yourself. It is easy. I am just giving you a first few so that we do not need to calculate every time. Then H2 x is 4 x square minus 2. H3 x is 8x cube minus 12x.

So, if you see there is a trend. It is even for even values of n and it is odd for odd n. That trend can be seen. So, n equal to 0 the function is even, n equal to 1 the function is odd, n equal to 2 the function is even, again n equal to 3 the function is odd again. So, all we care about is whether it is even and odd because we are talking about the integration and we are interested in symmetry. We are not exactly interested in what is the functional form of this.

Now let us try to calculate the symmetry of ground state. Because let us say if we are interested in ground state and the first excited set. So, of course you can calculate for the second excited state, third excited set. All those calculations can be done. Let us try to calculate for psi i 0, the ground state. So, psi i 0 is equal to N i e to the power minus alpha i by 2 and q i square H0 x is square root of alpha and q i.

Now it does not matter what x is. H of 0 goes to 1. So, this quantity is equal to 1. And now we are left with this quantity. So, what is this over here? Let us see. So, you have psi i 0. So, you are left with N i e to the power minus alpha by 2 and q i square. So, this thing goes to 1. So, we are left with only this. So, now let us see what is the symmetry of psi i. So, we know the symmetry of q i and we know the symmetry of q i square, so we will know the symmetry of psi i. Let us see how to do that.

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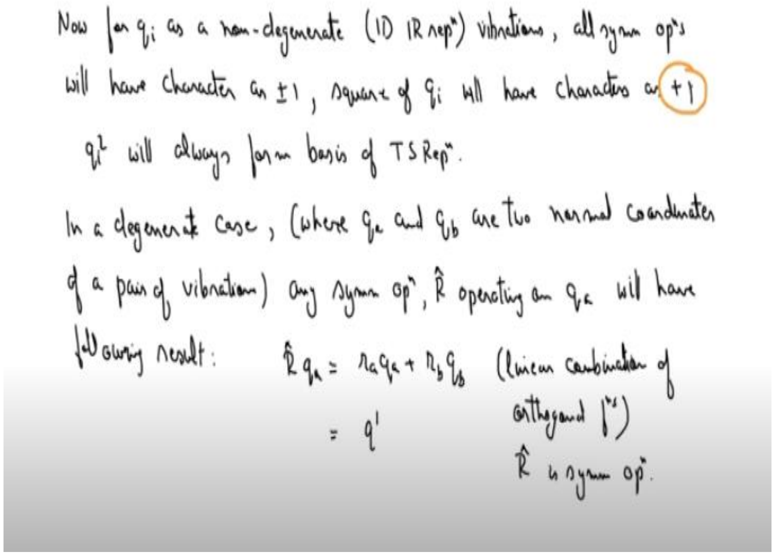

Now for q_i as a non-degenerate (1D IR rep^n) vibrations, all symm op^{n}s will have character as ±1, square of q_i will have characters as +1

q_i^2 will always form basis of TS Rep^n.

In a degenerate case, (where q_a and q_b are two normal coordinates of a pair of vibrations) any symm op^n, $\hat{R}$ operating on q_a will have following result:

$$\hat{R} q_a = r_a q_a + r_b q_b \quad \text{(linear combination of orthogonal f}^{n}\text{s)}$$

$$= q'$$

$\hat{R}$ is symm op^n.

So, now for qi as a non-degenerate, or we can say one dimensional IR representation. See the IR representation for qi will be the same as the IR representation for the corresponding normal mode. So, we have seen that the symmetry of normal mode is equal to symmetry of the normal coordinate. So, we know this will have symmetry of the normal mode. Now that symmetry can be one dimensional or two dimensional.

It can be non-degenerate which is 1D IR representation or it can be degenerate and then it will be a 2D IR or 3D IR representation. We have seen that normal modes can have symmetry of 1D IR and 2D IR and 3D IRs. So, now if it is a 1D IR representation, non-degenerate vibrations we can say, all symmetry operations will have character as plus/minus 1. In any 1D IR representation the character is always plus/minus 1.

So, if this is plus/minus 1, the square of qi will have characters as plus 1, only plus one not minus 1, only plus one. So, this is to remember, it is only plus one. So, what does that mean? That means qi square will always form the basis of totally symmetric representation. In most cases it is A1 or A. So, this is for a non-degenerate case. Now let us look for a degenerate case. In a degenerate case, we will also discuss examples. So, do not worry about it if you are not able to follow it.

We will see examples and then it will be very clear. So, in a degenerate case where qa and qb, let us say there are two q values for the corresponding degenerate case, are two normal coordinates of a pair of vibrations. Now degenerate vibrational mode that means two vibrations will have the same frequency. Now those pair of vibrations will have two normal coordinates q a and q b.

Now any symmetry operation on let us say R, operating on qa will have the following result. So, if you operate R on to q a what you will get is you will get a linear combination of q a and q b. Why linear combination? Because both of them are forming the basis of that particular IR representation. It is a degenerate representation. So, for example if you apply C3 on x and if x and y together are forming bases, you will get x plus y, some combination of x and y. r a and r b will be those coefficients. So, you can say that this is my q prime.

Let us see. So, this is a linear combination of orthogonal functions, which together form the basis for a particular IR representation and R is symmetry operation. So, this is understood.

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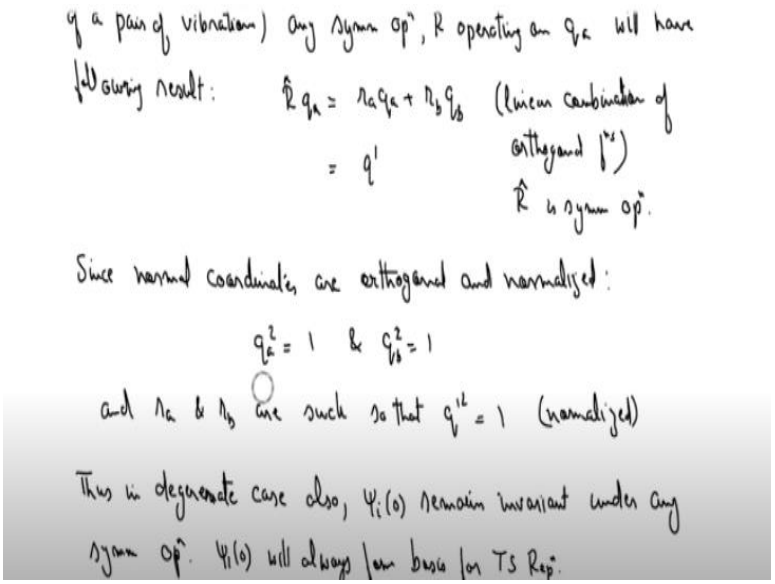

q a pair of vibration) any symm opⁿ, R operating on q_a will have following result: $\hat{R} q_a = r_a q_a + r_b q_b$ (linear combination of orthogonal f^ns)

$= q'$

$\hat{R}$ is symm opⁿ.

Since normal coordinates are orthogonal and normalised:

$q_a^2 = 1$ & $q_b^2 = 1$

and r_a & r_b are such so that $q'^2 = 1$ (normalized)

Thus in degenerate case also, $\psi_i(0)$ remain invariant under any symm opⁿ. $\psi_i(0)$ will always form basis for TS Repⁿ.

Now let us say since my normal coordinates are orthogonal and normalized, I can say q a square is equal to 1 and q b square is also equal to 1 and then my r a and r b are such chosen so that q prime square is also equal to 1. Because this also has to be normalized. This is the normalization condition. So, q i square is also 1. So, that means whatever is the value of q i like if I am operating a symmetry operation on to q prime, so if I square this I will always get 1.

Thus, in degenerate case also psi i 0 remains invariant under any symmetry operation. This should be clear now. So, that means psi i 0 will always form bases for totally symmetric representation. So, whether it is 1D or 2D psi i 0 will always form basis for totally symmetric representation. So, now we know the IR representation for psi i 0. Now let us calculate for the excited state psi i 1.

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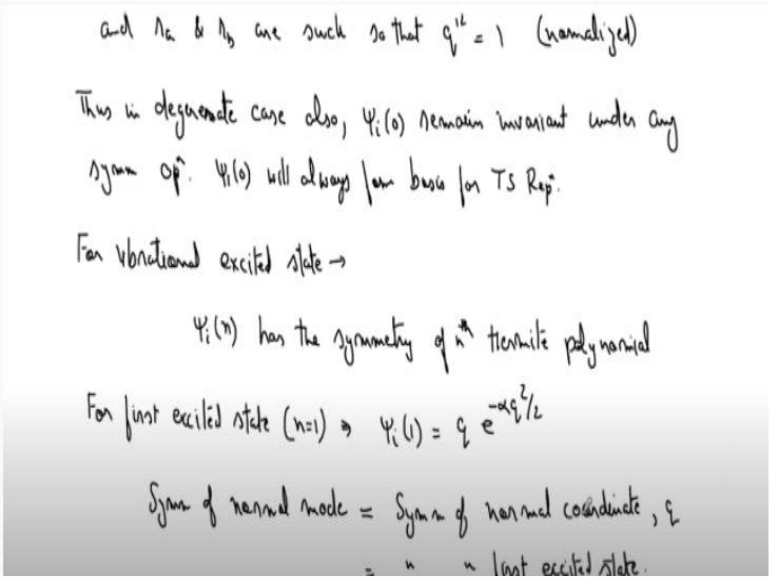

and N_a & N_b are such so that $q'^2 = 1$ (normalized)

Thus in degenerate case also, $\psi_i(0)$ remain invariant under any symm op^n. $\psi_i(0)$ will always form basis for TS Rep^n.

For vibrational excited state →

$\psi_i(n)$ has the symmetry of n^{th} hermite polynomial

For first excited state $(n=1) \Rightarrow \psi_i(1) = q\, e^{-\alpha q^2/2}$

Symm of normal mode = Symm of normal coordinate, q

= " " first excited state.

So, for vibrational excited state, psi i n has the symmetry of nth hermite polynomial. Other than that nothing is contributing to the symmetry. So, let us see how it happens. So, for the first excited state let us say we have n equal to 1. So, psi i 1 can now be written as q e to the power minus alpha q square divided by 2. So, this q is coming from the hermite polynomial after solving for n equal to 1. Now that means q square is nothing but q square is a totally symmetric representation.

So, this does not contribute to symmetry. Now the symmetry contribution comes from q. So, whatever is the symmetry of the normal coordinate that will be the symmetry of the first excited state. So, the symmetry of normal coordinate is coming from symmetry of the corresponding normal mode. So, that means the first excited state will have symmetry of the normal mode itself. So, let us say symmetry of normal mode, which is determined in the last lecture, is equal to symmetry of normal coordinate q and this is equal to symmetry of the first excited state. So, this is clear.