# Quantum Mechanics and Molecular Spectroscopy
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## Lecture – 32
## Vibrational Selection Rules

Hello, welcome to the lecture number 32 of the course Quantum Mechanics and Molecular Spectroscopy. In the previous lecture, we were looking at the harmonic oscillator because harmonic oscillator is a good approximation for a chemical bond at the equilibrium distance and we will use harmonic oscillator to derive the selection rules rather we will use harmonic oscillators wavefunctions to derive the selection rules for the vibration spectroscopy.

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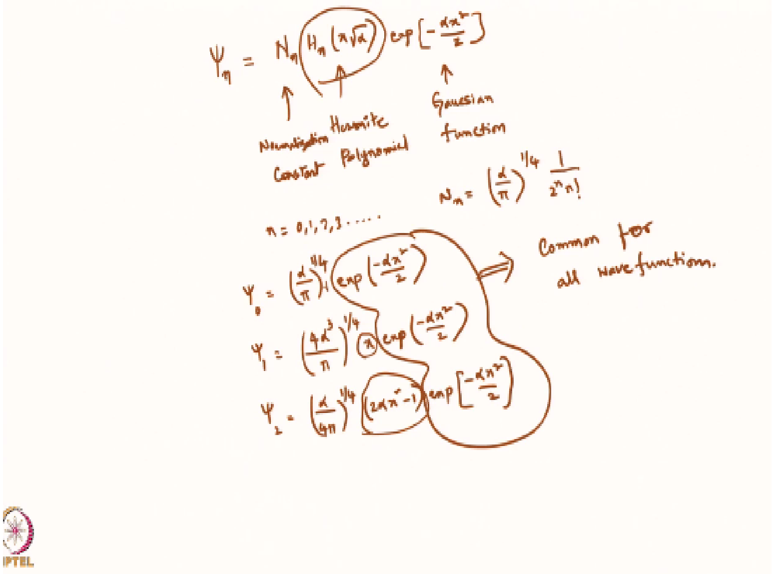

In the last class, I told you the solutions of the harmonic oscillator are of the form psi n = N n some normalization constant H n of x root alpha this is the Hermite polynomials multiplied by a Gaussian function exponential – alpha x square / 2 this is the Gaussian function and this is your normalization constant. Now, where n will take the values of 0, 1, 2, 3 etcetera and your N n is given by alpha / pi to the power of 1 / 4, 1 over 2 to the power of n n factorial.

Now if I use this and then I can write a wavefunction psi 0 will be = alpha / pi to the power of 1 / 4 exponential – alpha x square / 2. Here psi 1 will be equal to 4 alpha cube divided by pi to the power of 1 / 4 x exponential – alpha x square / 2 and psi 2 will be equal to alpha / 4 pi to the power of 1 / 4 2 alpha x square – 1 exponential – alpha x square / 2. Now what you can see this exponential alpha x square / 2 is going to be common for all wavefunctions.

So, essentially the shape of the wavefunction will be dictated by the Hermite polynomial this one. So, in this case this is into 1, in this case this is x and in this case this is 2 alpha x square – 1.

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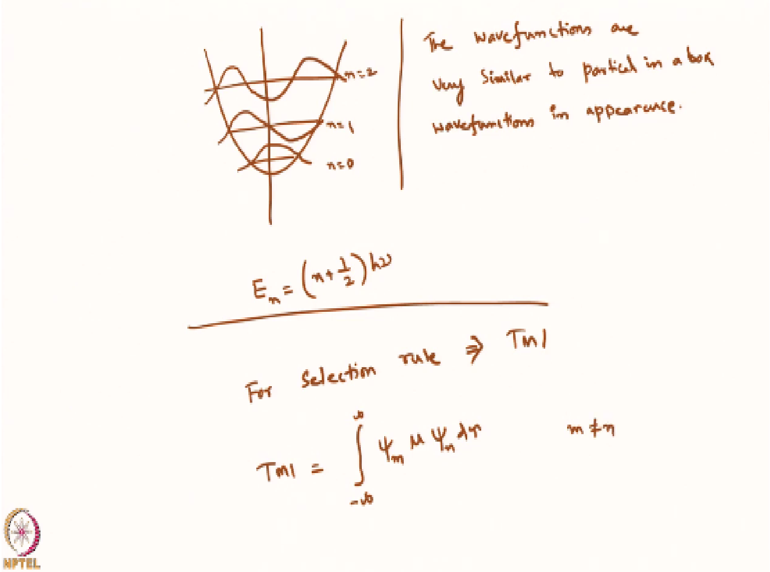

The wavefunctions are very Similar to partical in a box wavefunctions in appearance.

$$E_n = \left(n+\frac{1}{2}\right)h\nu$$

For Selection rule ⇒ TMI

$$TMI = \int_{-\infty}^{\infty} \psi_m \mu \psi_n \, d\tau \qquad m \neq n$$

So, one can plot the harmonic oscillator wavefunctions as this is n = 0 as something like that n = 1 something like that and n = 2 will be something like that. So they look very similar to the wavefunctions or very similar to particle in a box wavefunctions in appearance only for the appearance sake they look same.

And of course there is a energy value E n = n + 1 / 2 h nu. Now we must always remember that the wavefunctions will look very similar to the particle in a box, but they are not exactly mathematically very same because these are Gaussian functions multiplied by Hermite polynomials and those are sinusoidal function. Now when we are now looking at spectroscopy so what we will need is a transition moment integral.

So for selection rule what we need is transition moment integral. Now transition moment integral basically connects two states with two different quantum numbers. So one can think of TMI will be nothing, but integral in the case of harmonic oscillators these will be – infinity to + infinity. Now the wavefunction that we will have is psi m mu psi n d tau so that will be my transition moment integral where m and n will be different quantum numbers when m is not equal to n.

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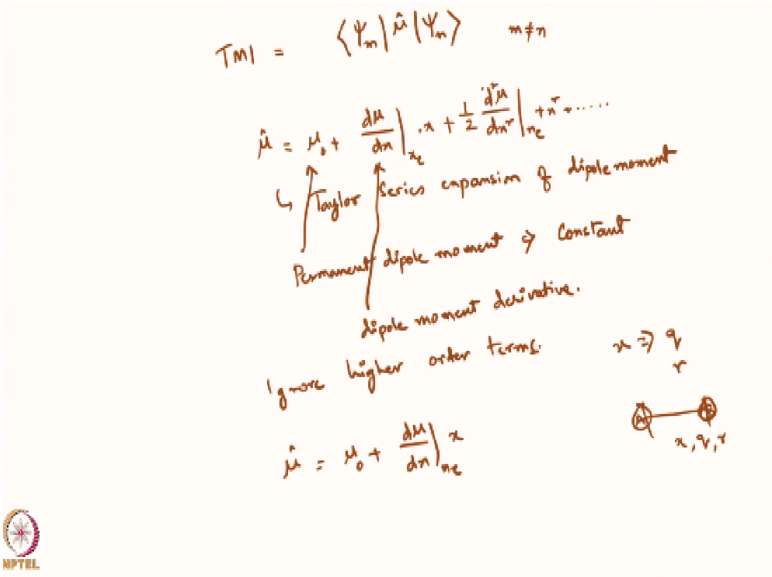

$$TMI = \langle \psi_m | \hat{\mu} | \psi_n \rangle \quad m \neq n$$

$$\hat{\mu} = \mu_0 + \left.\frac{d\mu}{dx}\right|_{x_e} \cdot x + \frac{1}{2} \left.\frac{d^2\mu}{dx^2}\right|_{x_e} + x^2 + \ldots\ldots$$

↳ Taylor Series expansion of dipole moment

Permanent dipole moment ⇒ Constant

dipole moment derivative.

Ignore higher order terms.

$x \Rightarrow q$

$r$

$$\hat{\mu} = \mu_0 + \left.\frac{d\mu}{dx}\right|_{x_e} x$$

The TMI is equal to I can write in terms of bracket notation this will be psi m mu psi n where m is not equal to n. Now we know that mu itself can be written as operator mu itself can be written as mu 0 + d mu / d x evaluated x e into x + 1 / 2 d square mu / d x square evaluated at x e + x square + etcetera. So, this is nothing but your Taylor series expansion of dipole moment.

Now you will realize this is nothing, but your permanent dipole moment and this is a constant. So mu 0 for a molecule is constant the permanent dipole moment is constant and this is nothing, but the dipole moment derivative. Now what we will do is we will ignore higher order terms and we will take just mu will be = mu 0 + d mu / d x evaluated x e into x. Now one thing that I must x is (()) (09:22) generic coordinate.

I could call it as x could be called as q or r depending on the r is nothing but radial vector connecting two atoms. So, when I have A and B bond this distance I could call it as x or q or r does not really matter they are just variables. So, in the previous classes if I have used r I can interchangeably used r and x.

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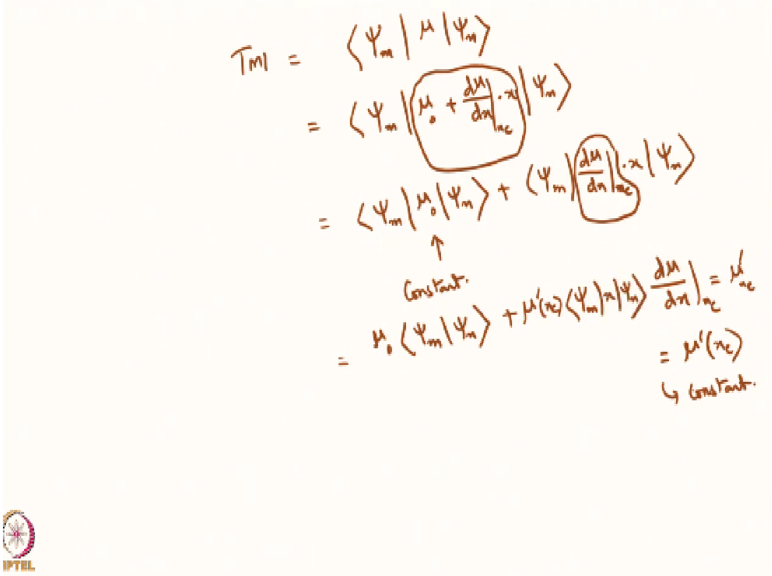

So, my TMI will now become integral psi m mu psi n which will be nothing, but psi m mu 0 + d mu / d x into x evaluated at x e psi n. So, the operator now has two terms. I can evaluate this as two integrals that is nothing, but psi m mu 0 psi n + psi m d mu / d x evaluated at x e multiplied by x psi n. Now I told you mu 0 is a constant so one can bring out the constant out of the integral.

So this will be nothing, but mu 0 psi m psi n + okay when you look at this particular derivative that is nothing, but the integral or sorry the differential first derivative of mu with respect to x evaluated at x e that means d mu / d x whatever that derivative is if I evaluated x e so I will call it as mu prime x e or rather I can call it as mu prime evaluated x e and this again is a constant mu prime evaluated at x e psi m x psi n. So you have two integrals so essentially now my transition moment integral.

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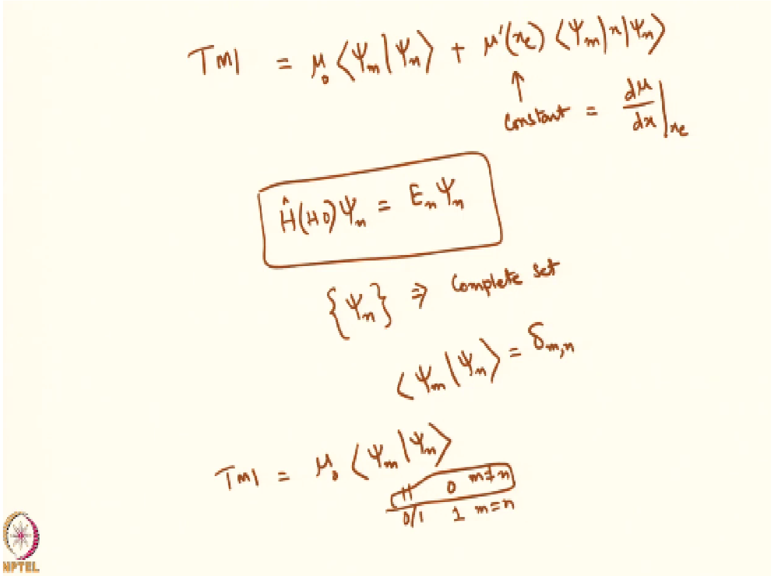

$$TMI = \mu_0 \langle \psi_m | \psi_n \rangle + \mu'(x_e) \langle \psi_m | x | \psi_n \rangle$$

$$\uparrow \text{ constant } = \left.\frac{d\mu}{dx}\right|_{x_e}$$

$$\boxed{\hat{H}(HO)\psi_n = E_n \psi_n}$$

$$\{\psi_n\} \Rightarrow \text{Complete set}$$

$$\langle \psi_m | \psi_n \rangle = \delta_{m,n}$$

$$TMI = \mu_0 \underbrace{\langle \psi_m | \psi_n \rangle}_{0/1} \quad \begin{matrix} 0 & m \neq n \\ 1 & m = n \end{matrix}$$

So my transition moment integral now will be equal to mu 0 psi m psi n + mu prime evaluated at x e psi m x psi n and I told you this is a constant which is nothing, but d mu / d x evaluated at x e. Now I have two integrals and these integrals must be evaluated. Now one thing we know is that H harmonic oscillator psi n = E n psi n where this is the harmonic oscillator Schrodinger equation and I told you that whenever we have a Schrodinger equation all the solutions that means the solutions psi n form a complete set.

And integral psi m psi n will be equal to delta m, n that means they are mutually orthogonal. So, the first integral if that is the case then your TMI will now become mu 0 psi m psi n and this integral will be either 0 or 1 it will be 0 when m is not equal to n will be equal to 1 when m is equal to n. So, when m is not equal to n it will go to 0 because we are looking for transition from state one state to other state that mean we are also considering this option. When you consider this option this integral will go to 0 and will not contribute to the TMI.

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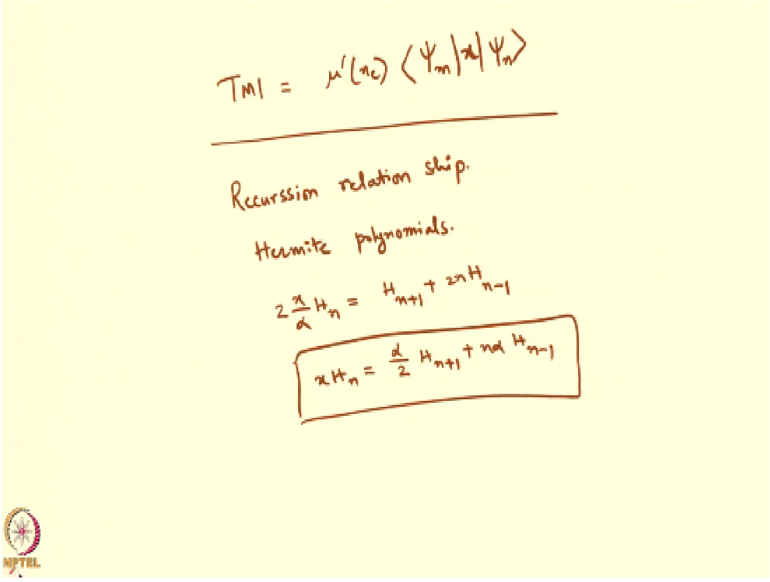

TMI = $\mu'(x_e)\langle\psi_m|x|\psi_n\rangle$

Recurssion relation ship.

Hermite polynomials.

$$2\frac{x}{\alpha}H_n = H_{n+1} + 2nH_{n-1}$$

$$\boxed{xH_n = \frac{\alpha}{2}H_{n+1} + n\alpha H_{n-1}}$$

So, now your TMI is left with only one integral that will be nothing, but mu prime at x e psi m x psi n this is x okay. Now, this integral needs to be evaluated, but fortunately for us this is not a very difficult to integrate because there is something called recursion relationship. Now what is this recursion relationship? In the case of Hermite polynomials one can write two times x / alpha of H n will be equal to H n + 1 + 2 times n H n – 1.

So, I will slightly rewrite this now what I am going to do is I am going to multiply this equation in a slightly different way oh sorry not rearrange this so this times x times H n will be equal to alpha / 2 H n + 1 + n alpha H n – 1. So this relationship I want to remember. Now let us go and write the transition moment integral.

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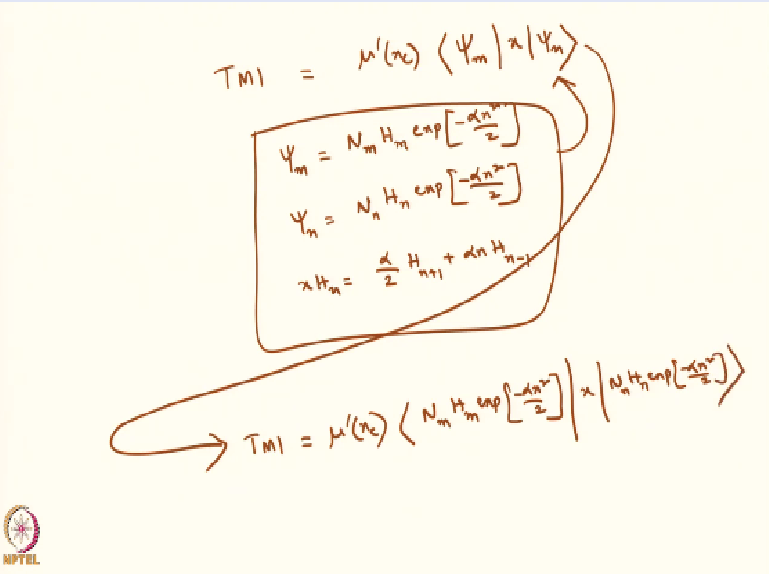

TMI = $\mu'(x_e)\langle\psi_m|x|\psi_n\rangle$

$$\psi_m = N_m H_m \exp\left[\frac{-\alpha x^2}{2}\right]$$

$$\psi_n = N_n H_n \exp\left[\frac{-\alpha x^2}{2}\right]$$

$$xH_n = \frac{\alpha}{2}H_{n+1} + \alpha n H_{n-1}$$

$$\text{TMI} = \mu'(x_e)\left\langle N_m H_m \exp\left[\frac{-\alpha x^2}{2}\right]\middle| x \middle| N_n H_n \exp\left[\frac{-\alpha x^2}{2}\right]\right\rangle$$

So time moment integral TMI this will be equal to mu prime evaluated at x e psi m x psi n and what is your psi m? Psi m = N m H m e to the power of exponential – alpha x square / 2 and your psi n will be equal to N n H n exponential – alpha x square / 2 and we also know that x times H n will be equal to alpha / 2 H n + 1 + alpha times n H n – 1. Now, we will use these three formulae or these three equations and plug it in this.

Let me write this in a slightly different way that is my TMI is now equal to mu prime x e that is the first dipole moment derivative of mu with respect to x and evaluated x e. Now psi m will be equal to N m H m exponential – alpha x square / 2 multiplied by x N n H n exponential – alpha x square / 2 so that is my TMI.

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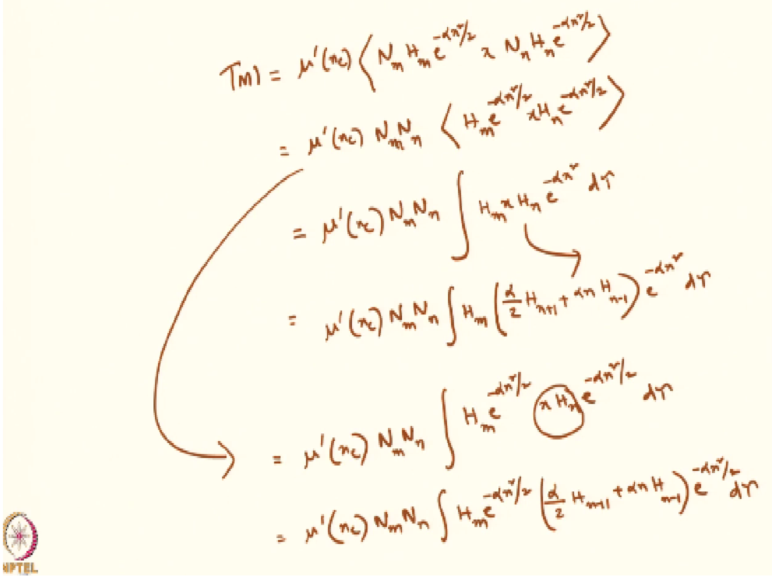

$$TMI = \mu'(x_e)\left\langle N_m H_m e^{-\alpha x^2/2}\, x\, N_n H_n e^{-\alpha x^2/2}\right\rangle$$

$$= \mu'(x_e) N_m N_n \left\langle H_m e^{-\alpha x^2/2}\, x H_n e^{-\alpha x^2/2}\right\rangle$$

$$= \mu'(x_e) N_m N_n \int H_m x H_n e^{-\alpha x^2}\, d\tau$$

$$= \mu'(x_e) N_m N_n \int H_m \left(\frac{\alpha}{2} H_{n+1} + \alpha n H_{n-1}\right) e^{-\alpha x^2}\, d\tau$$

$$= \mu'(x_e) N_m N_n \int H_m e^{-\alpha x^2/2}\, \boxed{x H_n}\, e^{-\alpha x^2/2}\, d\tau$$

$$= \mu'(x_e) N_m N_n \int H_m e^{-\alpha x^2/2} \left(\frac{\alpha}{2} H_{m+1} + \alpha n H_{m-1}\right) e^{-\alpha x^2/2}\, d\tau$$

So, TMI now will be equal to okay let me rewrite that equation mu prime x e integral N m H m e to the power of – alpha x square / 2 x N n H n e to the power of – alpha x square / 2 integral. So this will be nothing, but mu prime x e now you see (()) (19:45) is nothing, but your this normalization constant and they are constant so one can bring them out so N n N m now rest is the integral H m e to the power of – alpha x square / 2 H x H n e to the power of – alpha x square / 2.

So this is equal to mu prime x e N m N n okay and I will write in terms of integral H m x H n e to the power of – there is a two of them so this will be – alpha x square d tau so that is my integral that I need to evaluate. So this is nothing, but now we know x H n this is the generating function or the recursion relationship and that is equal to mu prime x e of x N m N n integral H m into x into H m (()) (21:13) alpha / 2 H n + 1 + alpha n H n – 1.

So that is what I have written down in terms of generating recursion relationship e to the power of – alpha x square d tau or one could write it as from here one could write it as this is equal to mu prime x e N m N n integral H m e to the power of – alpha x square / 2 to x H n e to the power of – alpha x square / 2 d tau and now I can plug in the recursion relationship here.

So this will be equal to mu prime x e N m N n integral H m e to the power of – alpha x square / 2. Now this one will be alpha / 2 H n + 1 + alpha n H n – 1 e to the power of – alpha x square / 2 d tau.

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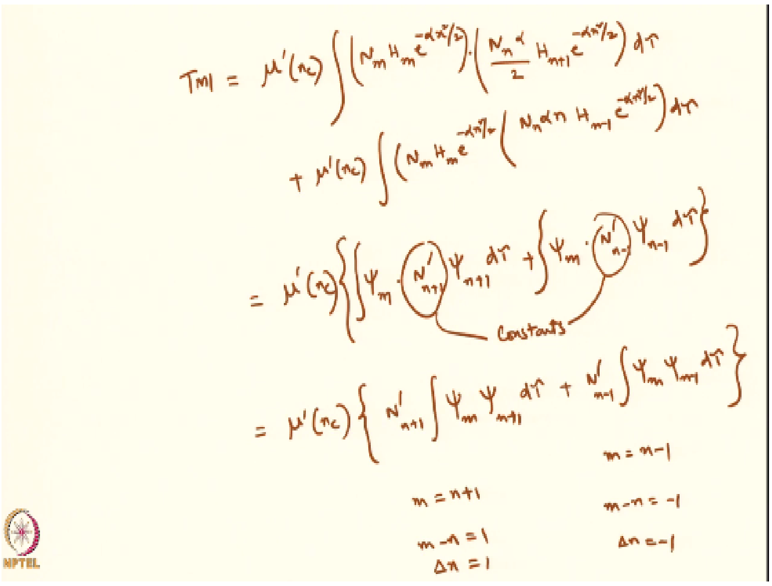

$$TMI = \mu'(x_e)\int \left(N_m H_m e^{-\alpha x^2/2}\right)\cdot\left(\frac{N_n\alpha}{2} H_{n+1} e^{-\alpha x^2/2}\right) d\tau$$

$$+ \mu'(x_e)\int \left(N_m H_m e^{-\alpha x^2/2}\right)\left(N_n \alpha n\, H_{n-1} e^{-\alpha x^2/2}\right) d\tau$$

$$= \mu'(x_e)\left\{\int \psi_m \cdot \boxed{N'_{n+1}}\,\psi_{n+1}\, d\tau + \int \psi_m \cdot \boxed{N'_{n-1}}\,\psi_{n-1}\, d\tau\right\}$$

Constants

$$= \mu'(x_e)\left\{ N'_{n+1}\int \psi_m \psi_{n+1}\, d\tau + N'_{n-1}\int \psi_m \psi_{n-1}\, d\tau\right\}$$

$m = n+1$

$m - n = 1$

$\Delta n = 1$

$m = n-1$

$m - n = -1$

$\Delta n = -1$

So, one can rewrite this integral TMI = mu prime x e N m psi N n N m H m e to the power of – alpha x square / 2 into N n alpha / 2 H n + 1 e to the power of – alpha x square / 2 this is one form integral d tau + mu prime x e integral N m H m e to the power of – alpha x square / 2 N n alpha n H n – 1 e to the power of – alpha x square / 2 d tau so it will come out as 2 integrals.

So this will be nothing, but mu prime of x e if I take common then you see this is they are all constants so this is nothing, but your psi m multiplied by this is nothing, but sum because normalization constant is slightly different than n + 1 so what I will write it as N n + 1 prime okay I do not know what that is what is sum number psi n + 1 d tau + similarly psi m this is the integral into N prime n – 1 psi n – 1 d tau so we will have 2 integrals.

So which means if this so n + 1 is just a constant similarly this N prime n – 1 is also a constant so these two are constants. Therefore, mu prime of x e if this should work then psi m and psi n must so integral so some constant N prime n + 1 times integral psi m and psi n + 1 d tau similarly + N prime n – 1 psi m psi n – 1 d tau. If these have to be but then m must be equal to n + 1 or m must be equal to n – 1.

So then if I bring it rather m – n must be equal to 1 and m – n = - 1. So this is nothing but your delta n = 1 and delta n = - 1.

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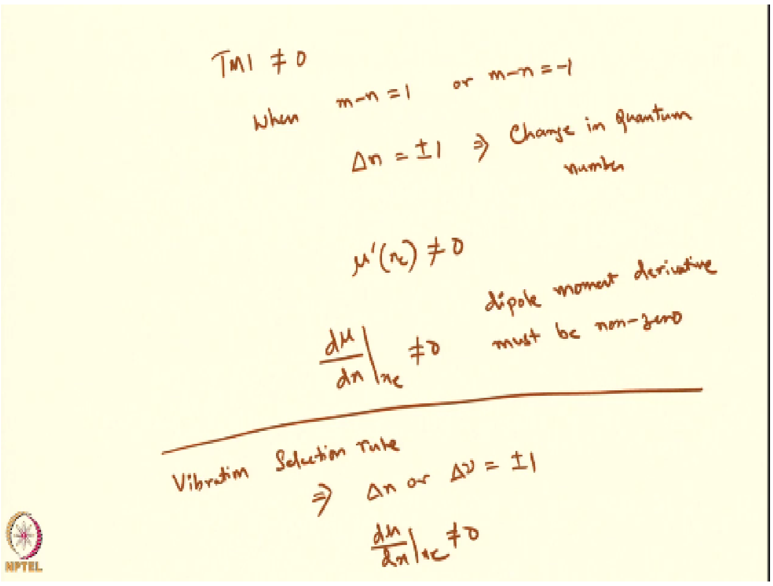

TMI $\neq 0$

When $m-n=1$ or $m-n=-1$

$\Delta n = \pm 1 \Rightarrow$ Change in quantum number

$\mu'(x_e) \neq 0$

$\left.\frac{d\mu}{dx}\right|_{x_e} \neq 0$ dipole moment derivative must be non-zero

Vibration Selection rule

$\Rightarrow \Delta n$ or $\Delta v = \pm 1$

$\left.\frac{d\mu}{dx}\right|_{x_e} \neq 0$

The TMI will be not equal to 0 when m – n = 1 or m – n = - 1 of course both of them simultaneously cannot happen. So that means your delta n that is a change in the quantum number should be equal to + - 1. This is nothing, but change in quantum number. Apart from that your mu prime x e must not be equal to 0 because if this goes to 0 then you are multiplying everything with 0 that means d mu / d x evaluated at x e should not be equal to 0 that means dipole moment derivative must be non-zero.

So this is the vibrational selection rule so summing up we will get delta n or delta mu depending on what the symbol that used this must be equal to + - 1 and d mu / d x evaluated x e must be non-zero. So, that finishes the vibrational selection rules. We will continue in the next class we will stop it here. Thank you.