Quantum Mechanics and Molecular Spectroscopy

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Lecture-36
Selection Rules for Particle in a Box

Hello, welcome to the lecture number 36 of my course quantum mechanics and molecular spectroscopy. Essentially until the lecture number 35 I have covered the derivation of the transition moment integral, relationship of the transition moment integral with various experimental quantities such as the lifetime, line w8s and also the absorption spectrum and in turn related to Einstein's coefficients a and b.

Later we looked at the transition moment integral and derived the selection rules for the rotations vibrations and electronic transitions. Towards the end we also looked at the rotations of the polyatomic molecules. However the vibrations and the electronic spectroscopy of polyatomic molecules will require a knowledge of group theory. Since I have assumed that you will not need any other prerequisites than basic quantum mechanics.

The vibration spectroscopy and the electronic spectroscopy of the polyatomic molecules will be skipped. You can look at some other courses on molecular spectroscopy which include group theoretical treatment for the vibrations and electronic spectroscopy of polyatomic molecules. That in a sense completes the course contents. Now in the next few lectures I would like to look at some of the tutorial problems.

See spectroscopy simply does not mean transient moment integral ok, you can it also looks at how one interprets a spectra to be able to arrive at some useful atomic and molecular parameters. So, over the next few classes I am going to teach you or we are going to solve some very simple problems as a tutorials ok, to begin with I will start with a particle in a box.

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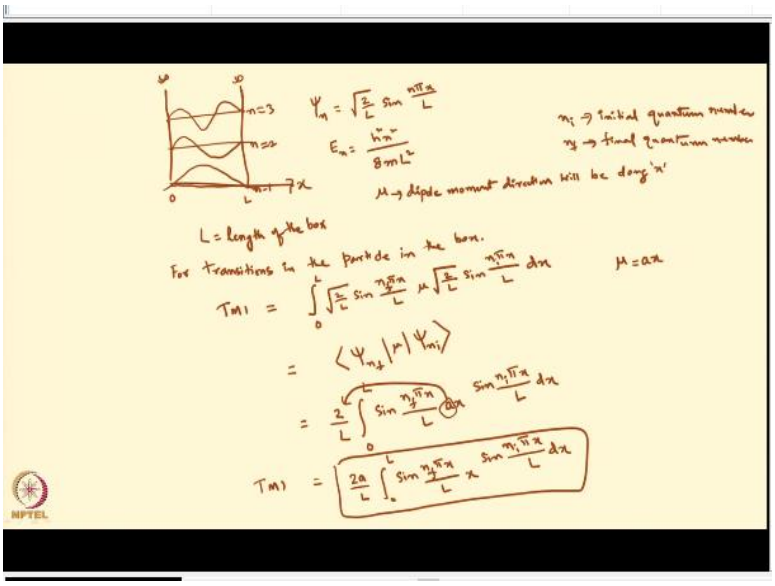

A particle in a box is nothing but something that you know you all might have learned is there as levels n = 1 have a wave function like this, then there will be n = 2 will have a function something like that and n = 3 will have wave function something like that and the wave function psi of n is given by rho 2 by L, by the way this is 0 and this is L where capital L is the length of the box ok.

One more thing is that in a particle in a box these walls extend to infinity, because any particle that is trapped inside this particle in this well or in this box cannot get out sine n pi x by L okay. That is your wave function and the corresponding energy value will be E n = h square n square by 8 m L square. Now one thing that is let us look at this dimension as x. So, the box is along the x axis ok.

So, if the box is along the x axis so the dipole moment direction the mu this moment will be along x, therefore for a transitions in the part in a box ok, you can write T m I as equals to integral, of course particle in a box is limited from the between 0 and L. So, the integral will be 0 to L ok. Now let us say you go from n = there is a n i that is the initial quantum number and you go to n f that is the final quantum number ok.

So, what you have is you have 2 wave functions square root of 2 by L sine n f pi x by L, your dipole moment mu root 2 by L sine n i pi x by L dx. So, this is your transient moment integral. Simply put if I have to write this will be nothing but psi n f mu psi. So, this is the integral that we need to solve ok. So, I am going to rearrange this integral slightly, there is a square root of know 2 by L. So, that can come out because 2 and L are constants for a given particle in a box.

So, that will get is 2 by L integral 0 to L, this will be sine of n f pi x by L okay or dipole moment is along the direction x, it could have some multiplier. So, if I take mu is equal to some constant a into x ok, then this will be a into x sine n i pi x by L dx. Now a is also a constant, so that also I can bring it out. So, this will be nothing but 2 a by L 0 to L sine n f pi x by L x sine n i pi x by L dx. So, essentially your transient moment integral will look something like that ok which is what we need to solve to get the selection rules. So, let us look at them little more carefully.

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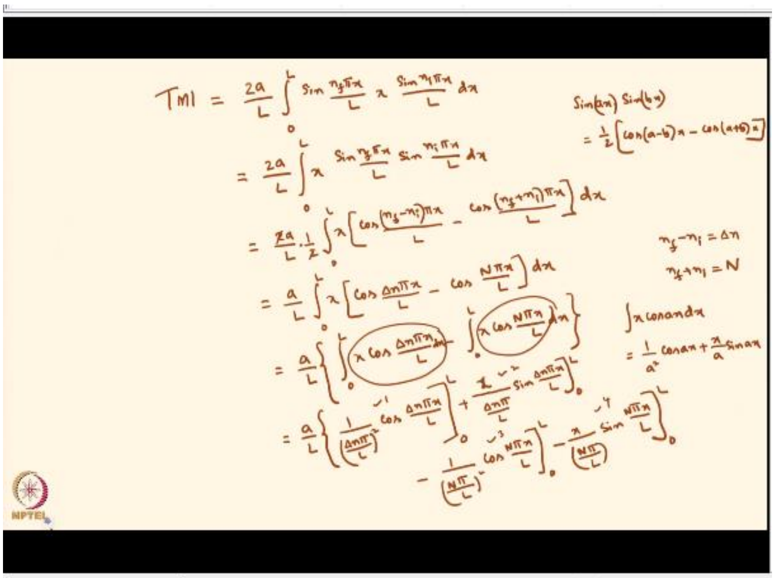

The transition moment integral will be now will be equal to 2 a by L integral 0 to L now because these are product function what you had is the sine n f pi x by L x sine n i pi x by L dx. So, this I can slightly rewrite as 2 a by L 0 to L x sine n f pi x by L sin n i x by L dx. Now I am going to use a small transformation that is if you have sine a x multiplied by sine dx ok, this will be nothing but half of cos a - b x - cos a + b x okay.

So, I am going to use this trigonometry transformation. So, this will be equal to this will be half. So, 2 a by L into half integral 0 to L x into cos of n f - n i pi x by L - cos of n f + ni pi x by L dx okay. So, this I can write this 2 and this 2 I can cancel. So, what you will get is a by L 0 to L x cos of now what I will call it as n f - n i, that is the difference between the quantum numbers of the initial state and final state.

So, that I will call it as delta n. So, this will be delta n pi x by L - cos of so other thing is n f + ni. So, that is the sum of the quantum numbers of the initial and final state I will call it as a capital N ok. So, that will be nothing but capital N pi x by L dx okay. Now we will see this will be nothing but a by L whole thing multiplied by 0 to L x cos delta n pi x by L - 0 to L x cos capital N pi x by L dx ok.

Now you can see this as a these 2 integrals, they are x cos a x type. So, integral x cos a x dx has to be integrated by part. So, this will come out to be 1 over a square cos a x + x by a sine dx. So, this integral is given by this. So, we just have to plug it in. So, this will come out to be this is equal to a by L okay. Now the first integral is 1 over a square, 1 over a square will be 1 over delta n pi by L whole square cos delta n pi x by L okay evaluated from 0 to L + 1 by delta n pi by L into x sine delta n pi x by L evaluated from 0 to L.

Similarly the next integral will be negative of 1 over n pi by L whole square cos n pi x by L 0 to L minus again minus of minus x by n pi by L into sine n pi x by L evaluated from 0 to l. So, you need to get this 4 times 1 2 3 4 ok.

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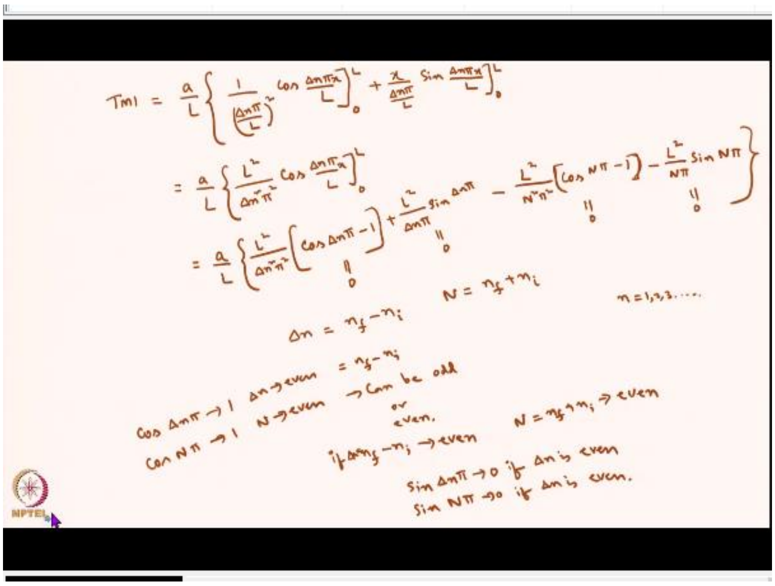

So, now your transition moment integral will be equal to a by L thing multiplied by the first term will be was 1 over delta n pi by L whole square cos delta n pi by L evaluate from 0 to n that was my first term I am going to go one term at a time. So, this will be equal to a by L integral. So, this will be L square divided by delta n square pi square cos of delta n pi by L. So, there is an x here, x 0 to l ok.

So, when I evaluate this, this will be nothing but 0 to L ok. Now if I take L square by delta n square pi square as a common then what I will get is cos L is when I plug it in L here, L will go. So, you will get cos delta n pi okay. Then cos 0 is 1. So, this is - 1 ok. Now the second term was + x by delta n pi by L sine delta n pi x by L, you add it from 0 to L ok. So, this will be nothing but plus okay.

Now if I plug L value then x will be L and this term will go to, so this will be L square by delta n pi ok sine of L. So, this will be sine of delta n pi because when x = l this will be delta sine delta n pi ok, when x = 0 of course this term will go to 0. So, there will be nothing left ok, this is your second term. Similarly you have the other 2 terms, so when I simply write this as L square by n square pi square cos n pi - 1 - L square by n pi sine capital N pi this whole thing.

So, this is the equation that we get ok, it is a bit complicated you can see there is a L square everywhere, so one can but I do not have to really worry about L square and all. So, there is a formula, so sorry this is not 0 this is a. Now you can see that there are 2 factors, one is delta n and that is nothing but f - n i and other one is capital N that is nothing but n f + n i. Now there are if you take any 2 quantum numbers by the way in the case of particle in a box n can only take values of 1 2 3 etc.

So, they are now integers, real I mean positive integers. So, n f - n i will only be equal, can either be odd or even. So, if n i so n f - n i can be odd or even okay. Now if n f - n i is even when that will happen? When both n i and n f are odd or that both n f and n i are even. So, that will give even. So, when if n f - n i is even it turns out that even n which is nothing but n f + n i is also equal to even ok.

So, if both of them if the difference between the n i or delta n n f that is nothing but your delta n, sorry if a delta n is even then your n also is even. So, when you have even okay then you can see that sine n pi delta n pi ok. So, that will be sine 2 pi 4 pi etc. will go to 0. So, sine delta n pi ok will go to 0, if delta n is even. Similarly sine n pi will also go to 0 if delta n is even.

Similarly you can see that cos delta n pi ok cos delta n pi or will go to 1 if delta n is even and cos capital N pi will also go to 1 when n is even. So, if this goes to 1, so 1 - 1 is 0, this is 0 1 -

1 is 0 and this is 0. So, for this will go to 0, this will go to 0, this will go to 0, this will go to 0. So, all the term will go to 0 when n f - n i or delta n i = even and capital N is even.

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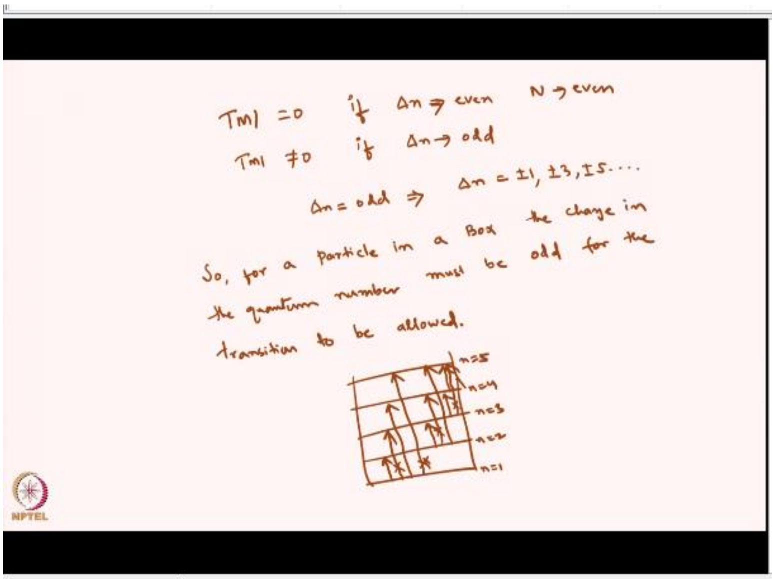

So, your TMI will go to 0 if delta n = even and n is also even. So, you can go back and work out that TMI will not be equal to 0 if delta n is odd ok. If delta n = odd implies delta n must be equal to + - 1 + - 3 + - 5 etc. So, for a particular box the change in the quantum number must be odd for the transition to be allowed ok. So, now which means if you have a particle in a box so n = 1 n = 2 n = 3 n = 4 and = 5.

So, this will be allowed, this will not be allowed, this will be allowed, this not be allowed. So, every alternate will not be allowed. So, every alternate, so similarly this will be allowed, this will not be allowed and this will be allowed. Similarly this will be allowed and this will be allowed, this will not be allowed ok. So, I will stop here, will continue the next lecture, thank you.