Advanced Mathematical Methods for Chemistry
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Module - 08
Lecture - 04
Recap of Module 8, Practice Problems

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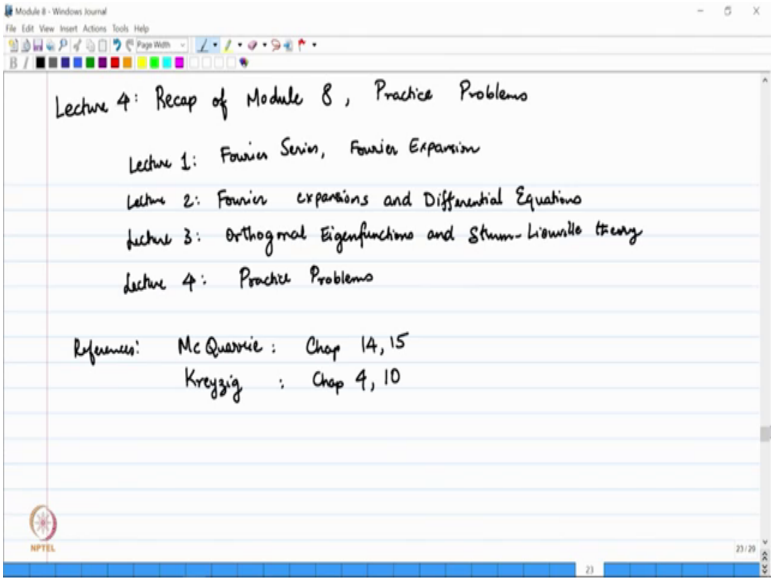

Lecture 4: Recap of Module 8, Practice Problems

Lecture 1: Fourier Series, Fourier Expansion
Lecture 2: Fourier expansions and Differential Equations
Lecture 3: Orthogonal Eigenfunctions and Sturm-Liouville theory
Lecture 4: Practice Problems

References: McQuarrie : Chap 14, 15
Kreyszig : Chap 4, 10

So this will be the last lecture of module 5. And in this lecture I will first of module 8. And in this lecture I will first a recap what we have done in module 8. And then and then we will discuss some practice problems. So, let us see what all we learnt in this module in this module this module. We basically learnt about Fourier series and about orthogonal Eigen function expansion.

So, in the first lecture, we discussed Fourier series and Fourier expansions. We saw how we can write a function in terms of it is Fourier series, we saw what a Fourier series. Then we looked more at Fourier expansions we looked at various functions and what their Fourier expansions look like. And then we also saw how to solve differential equations using Fourier expansions. This part I should emphasize is something that is very useful; we would not be doing practice problems on this, because this is especially useful in numerical solutions of differential equations. Then in the next lecture we saw orthogonal Eigen functions and the Sturm Liouville theory. So, they were only 3 lectures because some of these lectures were little longer. So, we saw the Sturm Liouville theory and how to analyze in terms of orthogonal Eigen functions.

So, today I will do some practice problems. Now this material is there is explained wave very nicely and Macquarie in chapter 14 and 15. And kreyzig has a lot of has some discussion on these things in part of Sturm Liouville theory is there in chapter 4. And then Fourier series is discussed in chapter 10 where actually partial differential equations are discussed. But again I should emphasize that these books have a lot more than what we are doing, but nevertheless they are useful references.

So now, so now, let us go and start working out a few practice problems. So, the first problem this is a quantum mechanical free particle problem.

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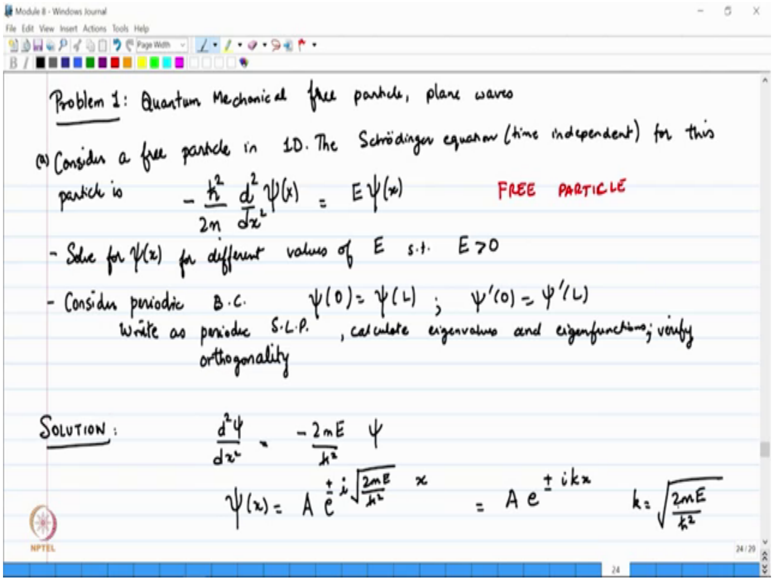

Problem 1: Quantum Mechanical free particle, plane waves

(a) Consider a free particle in 1D. The Schrödinger equation (time independent) for this particle is $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$ FREE PARTICLE

- Solve for $\psi(x)$ for different values of E s.t. $E > 0$
- Consider periodic B.C. $\psi(0) = \psi(L)$; $\psi'(0) = \psi'(L)$
  Write as periodic S.L.P., calculate eigenvalues and eigenfunctions; verify orthogonality

SOLUTION:

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi$$

$$\psi(x) = A e^{\pm i\sqrt{\frac{2mE}{\hbar^2}}\,x} = A e^{\pm ikx} \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

And this gives the idea of plane waves. But the problem is considered a free particle in 1D the Schrödinger equation the time dependent time independent Schrödinger equation for this particle is given by this. Minus h cross square by 2 m d square by dx square psi x equal to e psi of x. Solve for psi of x for different values of e such that e is greater than 0. Then the next part is to consider periodic boundary condition psi 0 equal to psi l. Psi prime of 0 equal to psi prime of l. And you write this as a periodic sturm devil problem. Calculate Eigen values and Eigen functions I mean verify orthoganality, let us solve this.

So, the first part is to is to do the free particle. So, the free particle part. So, this is the free particle. So, the free particle part I can, I can just write this out this is a simple second order differential equation. So, I can write I can write d square psi by dx square is equal to minus 2 m E by h cross square psi. So, I can write as psi of x as constant I will just write A e to the i and you have square root of 2 m E by h cross square times x. And I will I will use a notation I will write this as and it can be it can be either plus or minus, both the solutions are valid. So, it can be plus or minus.

Now, I will I will write this as I will write this as A e to the plus minus i k x. Where k is equal to square root of 2 m E by h cross square e is greater than 0. So, this is the square root of that.

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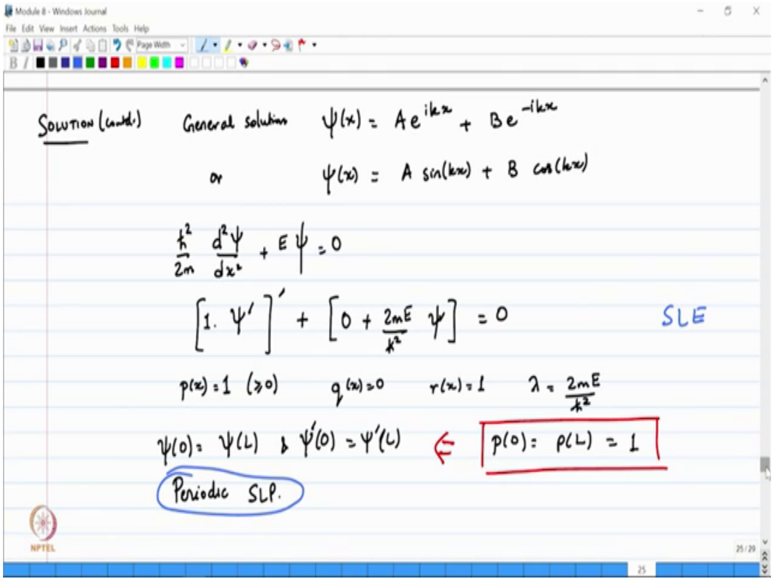

Solution (contd.) General solution $\psi(x) = Ae^{ikx} + Be^{-ikx}$

or $\psi(x) = A\sin(kx) + B\cos(kx)$

$$\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + E\psi = 0$$

$$\left[1.\,\psi'\right]' + \left[0 + \frac{2mE}{\hbar^2}\psi\right] = 0 \qquad \text{SLE}$$

$p(x) = 1\ (\geq 0)$ $q(x) = 0$ $r(x) = 1$ $\lambda = \frac{2mE}{\hbar^2}$

$\psi(0) = \psi(L)$ & $\psi'(0) = \psi'(L)$ $\Leftarrow$ $\boxed{p(0) = p(L) = 1}$

Periodic SLP.

So now, This is a solution for e greater than 0. So, the general, general solution psi of x is equal to A e to the i k x, plus B e to the minus i k x. So, e to the kx e to the i k x and e to the minus i k x are linearly independent functions. So, you can write the general solution as a linear combination of these. Alternatively or you can write phi of x as a sin kx plus b cos kx. So, if you do not want to deal with sins and cosines you can also write in. If you do not want to deal with imaginary functions you can also write in this form. You can easily verify that sin and cosine will also satisfy this equation.

So, that is the that is the first part where you solve for different values of e such that e is greater than 0. Now I consider the periodic boundary conditions. So, psi of 0 equal to psi of l and psi prime of 0 equal to psi prime of l. So now, if I take this differential equation. So, let me take this h cross square by 2 m to the right. So, I will write equal to 0. So, I can or I can write this as x square let me let me just write this as 1D psi by dx the whole thing prime. Or you know just to keep the notation short I will just write psi prime plus 0 plus 2 m E by h cross square psi equal to 0. I wrote it in this form you can immediately see that p of x is equal to 1 which is greater than equal to 0 q of x equal to 0 which is again greater than or equal to 0, r of x equal to 1 lambda is equal to 2 m E by h cross square.

So, and So, this now we also notice that that since psi of 0 equal to psi of l, this is by demand we have demanded this. And psi of prime of 0 equal to psi prime of l. Now we notice that p of 0 equal to p of l equal to 1. So, this is a periodic, So actually just by just by this equation we can, we can, we can, we can look for solutions that satisfy this. So, this is a periodic Sturm Liouville problem. This is a Sturm Liouville equation and this is a this these boundary conditions imply that it is a periodic Sturm Liouville problem. So, what that means, is that you can have solutions ok.

So those the lambda equal to 2 m E by h cross square is real.

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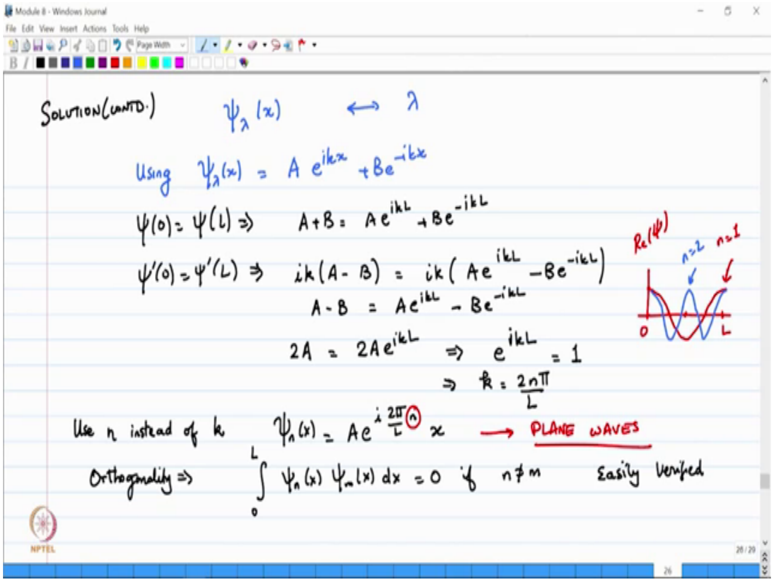

SOLUTION (CONTD.) $\psi_\lambda(x) \longleftrightarrow \lambda$

Using $\psi_\lambda(x) = A e^{ikx} + Be^{-ikx}$

$\psi(0) = \psi(L) \Rightarrow A+B = Ae^{ikL} + Be^{-ikL}$

$\psi'(0) = \psi'(L) \Rightarrow ik(A-B) = ik(Ae^{ikL} - Be^{-ikL})$

$A-B = Ae^{ikL} - Be^{-ikL}$

$2A = 2Ae^{ikL} \Rightarrow e^{ikL} = 1$

$\Rightarrow k = \frac{2n\pi}{L}$

Use n instead of k $\psi_n(x) = Ae^{i\frac{2\pi}{L}\textcircled{n}x} \longrightarrow$ PLANE WAVES

Orthogonality $\Rightarrow \int_0^L \psi_n(x)\,\psi_m(x)\,dx = 0$ if $n \neq m$ Easily Verified

So, you can have various solutions, you can have various solutions. So, you can have solution psi lambda of x corresponding to eigenvalue lambda. And basically each you can have you can have different values of e and each of those will be orthogonal. You need you need your psi lambda of x to satisfy the boundary conditions. Now we saw that we saw that in general, we have we you can write psi of x in this form kx. So now, psi of So psi 0 equal to psi l implies A plus B is equal to A e raise to I kl plus B e raise to minus i k l. And psi prime of 0 equal to psi prime of l implies i k times A minus B is equal to i k times A e raise to i k l, minus B e raise to minus i k l.

So, these are the 2 conditions that should be satisfied. And So, if I just if I just cancel this I will get A minus B is equal to A e raise to I kl minus B e raise to minus i k l. And if I add these 2 what I will get is that. So, I will get 2 a is equal to 2 A e raise to I kl this implies e raised to i k l is equal to 1, implies k is equal to 2 n pi by l.

So, the solutions So now, So now, instead of k. So, use n instead of k and you can writes psi n of x is equal to A e raised to I 2 pi by l n x. And your orthogonal or orthoganality relation implies integral 0 to l psi n of x psi m of x dx equal to 0 if n is not equal to n m, this can be easily verified. This is easily verified this is nothing but a Fourier series ok.

So, this is nothing but a Fourier series, because these are these suggest the coefficients in a Fourier expansion. And So and So, you can easily verify these now these functions are referred to as plane waves. Now if I take different values of n then I will get different functions now all these functions are periodic in the interval 0 to l. So, if I plot them 0 and l these will be periodic functions. So, whatever the value is at 0 you will have the same value. So, you might have you will have, you will have both the real and imaginary parts of this function be periodic.

So, for example, if you look at the real part real part is cosine. So, what it will look like is it is a it is a cosine with this period. So, it will look it look like this. This is for n equal to 1, n equal to 2 n equal to 2, it will look it will look again like a cosine. So, this is a real part out of psi, n equal to 2 it will again look like a cosine, but it look it will have a different period. So, it will have this is n equal to 2.

So, n equal to 1 looks like this n equal to let me show in blue n equal to 2. So, if n equal to 2 then it will look n equal to 2 and So on. And you can easily verify that each of these are orthogonal. So, these are plane waves that with this periodicity of l. This is a very useful way of writing solutions for wave functions of solids. So, for periodic solids or periodic systems and solid wave the wave function in a solid is expressed as a linear combination of plane waves. And we show the one dimensional plane wave by taking product of plane waves as in different directions we can construct 3 dimensional plane wave. So, we can multiply a plane wave in x by a plane wave in y, by a plane wave in z and you know these are 3 independent directions, So you can get these 3 dimensional plane waves ok.

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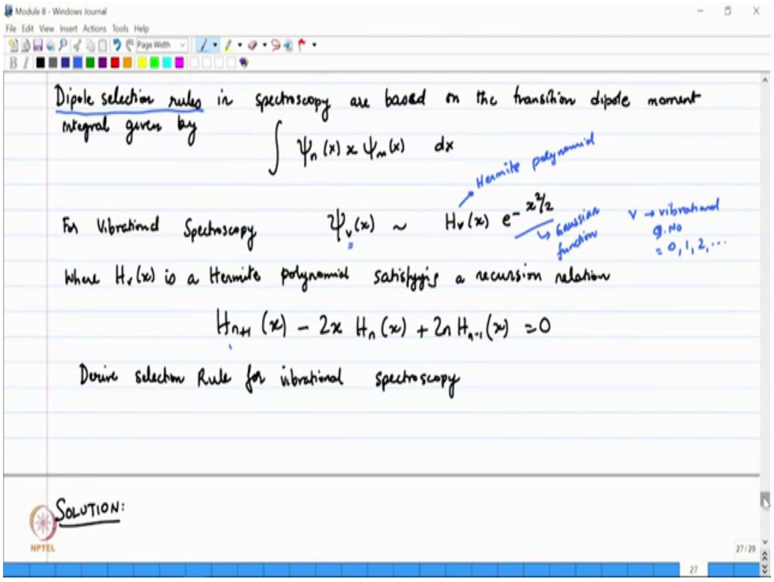

Dipole selection rules in spectroscopy are based on the transition dipole moment integral given by

$$\int \psi_n(x)\, x\, \psi_m(x) \quad dx$$

For Vibrational Spectroscopy $\psi_v(x) \sim H_v(x)\, e^{-x^2/2}$

Hermite polynomial

Gaussian function

v → vibrational q. No = 0, 1, 2, ...

Where $H_v(x)$ is a Hermite polynomial satisfying a recursion relation

$$H_{n+1}(x) - 2x\, H_n(x) + 2n\, H_{n-1}(x) = 0$$

Derive selection Rule for vibrational spectroscopy

SOLUTION:

Now, the next problem this is, this is another very practical application of orthogonal Eigen functions. So, this is in deriving spectroscopic selection rules from orthoganality of Eigen functions and recursion relations. So, the dipole selection rule is one of the most commonly used selection rule in spectroscopy. So, this is based on the transition dipole moment integral. So, there this integral is a you take a wave function multiplied by x and you and you and you multiplied by another wave function. Where x is basically some I mean, you can you can think of x as a some coordinate it might be a spatial coordinate it might also be an angular coordinate.

For vibrational spectroscopy psi v of x the wave function is indexed by a quantum number v. So, v is the vibrational quantum number, quantum number and equal to 0 1 2 and so on. And this function is given by H v, this is the Hermite polynomial. So, it is a hermite polynomial multiplied by this exponential function, by this Gaussian function e to the minus x square by 2 this is called a Gaussian function ok.

So, H v of x is the hermite polynomial the Hermite polynomial satisfies a recursion relation. Now the recursion relation says that h of n plus 1 corresponding to n plus 1 hermite polynomial. Minus 2 x into h n the n hermite polynomial plus 2 n into h n minus 1. So, the n plus 1 n 10 n minus 1 hermite polynomial are related by this recursion relation. And what we are to do is to use this to derive the selection rule for vibrational spectroscopy. Now to solve this is not very difficult you just take this integral. So, let us write this integral. So, the transition dipole moment.

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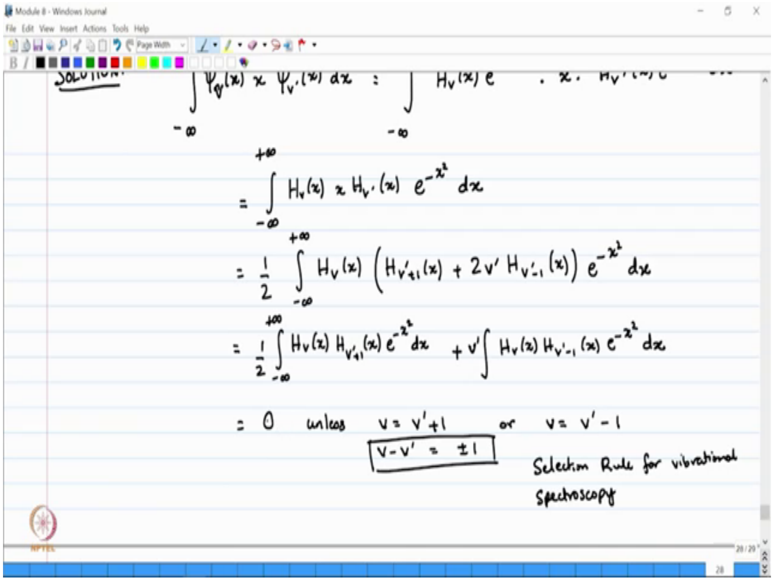

SOLUTION:

$$\int_{-\infty} \psi_v(x)\, x\, \psi_{v'}(x)\, dx = \int_{-\infty} H_v(x)\, e \cdot x \cdot H_{v'}(x)\, e$$

$$= \int_{-\infty}^{+\infty} H_v(x)\, x\, H_{v'}(x)\, e^{-x^2}\, dx$$

$$= \frac{1}{2} \int_{-\infty}^{+\infty} H_v(x) \left(H_{v'+1}(x) + 2v' H_{v'-1}(x) \right) e^{-x^2}\, dx$$

$$= \frac{1}{2} \int_{-\infty}^{+\infty} H_v(x)\, H_{v'+1}(x)\, e^{-x^2} dx + v' \int H_v(x)\, H_{v'-1}(x)\, e^{-x^2} dx$$

$= 0$ unless $v = v'+1$ or $v = v'-1$

$$\boxed{v - v' = \pm 1}$$

Selection Rule for vibrational spectroscopy

So, integral psi n psi v of x, x psi v prime of x dx from minus infinity to plus infinity. This is a range of range of x for a for a hermite polynomial, or for the vibrational quantum number. This is equal to integral ok.

Now, I can write this as H v of x e to the minus x square by 2 times x times H v prime of x e to the minus x square by 2 dx, from minus infinity to plus infinity. Now I cannot use any orthogonality relation because I have an x here. So, let me write this out in the following form I should I should mention that they should be a complex conjugate here. Now these are real function. So, the complex conjugate is nothing but the function itself.

So, let us just go ahead and write this out. So, this is equal to integral minus infinity to plus infinity. Now what we have is H v of x, x H v prime of x e to the minus x square dx. Now what will do is we will take this x we will take x times v H v prime of x. We will use the recursion relation in the following form. So, if you rewrite this what you will what you can show is that this is equal to half integral minus infinity to plus infinity H v of x. Now I take the x h n on the right. So, I will get H v plus 1 of x plus 2 v or v prime plus 1 2 v prime H v prime minus 1 of x, and then I have e to the minus x square dx. So, I took the half factor down.

So, what you get is that you will get 2 terms. So, the first term is half integral minus infinity to plus infinity, H v of x H v prime plus 1 of x e to the minus x square dx plus integral, I have a v prime I will just take the v prime outside it is independent of x, and what I have is H v of x H v prime minus 1 of x e to the minus x square dx. So, you have these 2 terms.

Now, now using the orthoganality of hermite polynomials. So, this is equal to 0 unless v equal to v prime plus 1. So, the first term goes to 0 unless v equal to v prime plus 1, second term goes to 0 unless v equal to v prime minus 1. This equal to 0 unless v equal to v prime plus 1 or v equal to v prime minus 1. So, the selection rules. So, I can write v minus v prime is equal to plus minus 1, this is the selection rule ok.

So, this is this the selection rule for vibrational spectroscopy. So, under the harmonic oscillator approximation, your vibrational spectroscopy you we you will not have a vibrational spectrum. So, this transition dipole moment integral. So, this will be equal to 0 unless you have this condition. So, if you do not have this condition you would not have any spectrum. So, if this transmission dipole moment goes to 0 then there is no spectrum. So, the condition for having a spectrum is that your v minus v prime should be plus minus 1 or the difference between difference between these 2 states n and m should be should be that there their vibrational quantum number should be either should they should differ by one. So, this is a very practical use of or very commonly used a very common application of these orthogonal Eigen functions ok.

So, next problem is the Legendre equation and rotational spectroscopy. So, with So, we will So, we will do it in various steps this problem. So, the first step is to is to write the Legendre differential equation which is given by 1 minus x square y double prime minus 2 xy prime plus n, n plus 1 y equal to 0 as a Sturm Liouville problem.

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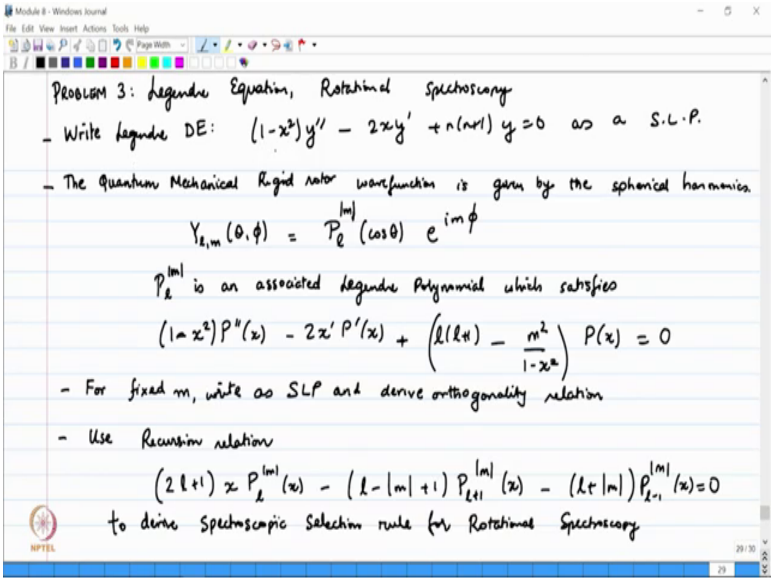

PROBLEM 3: Legendre Equation, Rotational Spectroscopy

- Write Legendre DE: $(1-x^2)y'' - 2xy' + n(n+1)y = 0$ as a S.L.P.
- The Quantum Mechanical Rigid rotor wavefunction is given by the spherical harmonics

$$Y_{l,m}(\theta,\phi) = P_l^{|m|}(\cos\theta)\, e^{im\phi}$$

$P_l^{|m|}$ is an associated Legendre Polynomial which satisfies

$$(1-x^2)P''(x) - 2x'P'(x) + \left(l(l+1) - \frac{m^2}{1-x^2}\right)P(x) = 0$$

- For fixed m, write as SLP and derive orthogonality relation
- Use Recursion relation

$$(2l+1)\,x\,P_l^{|m|}(x) - (l-|m|+1)\,P_{l+1}^{|m|}(x) - (l+|m|)\,P_{l-1}^{|m|}(x) = 0$$

to derive Spectroscopic Selection rule for Rotational Spectroscopy

The second part has to do with the quantum mechanical rigid rotor wave function, and this is given by spherical harmonics. So, spherical harmonics. So, there are 2 quantum numbers l and m ok.

So, Y l m of theta and phi theta and phi are the angular coordinates. This is given by this is called an associated Legendre polynomial P l m of cos theta absolute value of m of cos theta is an associated Legendre polynomial; it is a function of cos theta and this satisfies so if the variable was x then this P l m would satisfy this equation. So, it looks like a Legendre differential equation 1 minus x squared p double prime of x minus 2 x p prime of x. So, which is which is exactly the same as these 2 terms. And then plus l, l plus 1 which is again very similar to the Legendre equation, but you have an additional term, m square over 1 minus x square px. So, it is it only slightly differs from the Legendre differential equation and therefore, this solution is called the associated Legendre polynomial.

Now, what I am asked to do is, what I am asking you to do is for fixed m right as a right as a Sturm Liouville problem and derive the orthoganality relation, which is fairly straightforward. And then the last part is to use the recursion relation. So, the associated Legendre polynomials they satisfy this recursion relation. So, 2 l plus 1 x into P l m of x minus l minus absolute value of m plus 1 times pl plus 1 l plus 1. So, instead of l I had l plus 1 I always have m everywhere. And I have and in the last term I have l minus 1. And you use this to derive the spectroscopic selection rule for rotational spectroscopy. Now you can see that the last part will be exactly the same as the as we did for the vibrational spectroscopy.

So, let us first write the Legendre differential equation as a Sturm Liouville problem. So, to do this, so if I take 1 minus x square y prime the whole prime, this is equal to 1 minus x square y double prime minus 2 x y prime.

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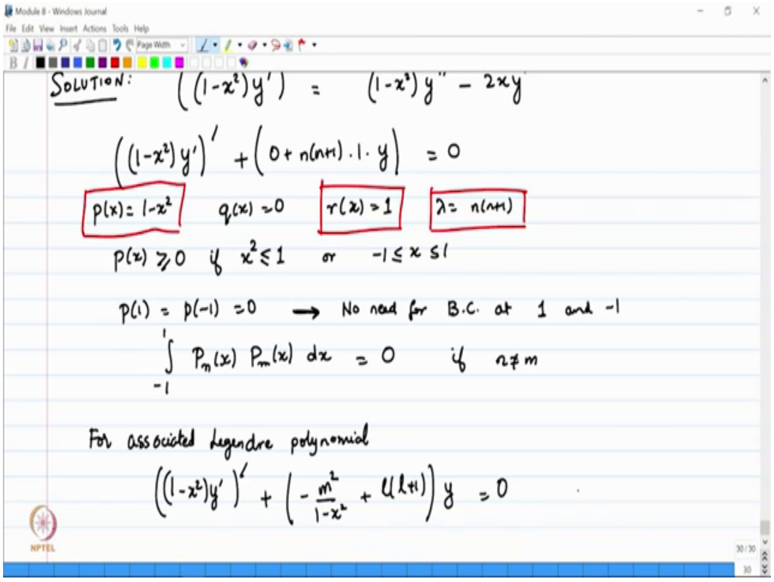

SOLUTION: $\left((1-x^2)y'\right) = (1-x^2)y'' - 2xy$

$$\left((1-x^2)y'\right)' + \left(0 + n(n+1)\cdot 1\cdot y\right) = 0$$

$\boxed{p(x) = 1-x^2}$ $q(x) = 0$ $\boxed{r(x) = 1}$ $\boxed{\lambda = n(n+1)}$

$p(x) \geq 0$ if $x^2 \leq 1$ or $-1 \leq x \leq 1$

$p(1) = p(-1) = 0 \longrightarrow$ No need for B.C. at 1 and -1

$$\int_{-1}^{1} P_n(x)\, P_m(x)\, dx = 0 \quad \text{if} \quad n \neq m$$

For associated Legendre polynomial

$$\left((1-x^2)y'\right)' + \left(-\frac{m^2}{1-x^2} + l(l+1)\right)y = 0$$

So, I can write the Legendre differential equation as 1 minus x square y prime the whole prime plus 0 plus n, n plus 1 times 1 times y equal to 0. So, this is a Sturm Liouville problem p of x is equal to 1 minus x square q of x equal to 0 r of x equal to 1 lambda equal to n, n plus 1.

Now, we see that p of x is greater than equal to 0 if x is less if x square is less than equal to 1 or minus 1 less than x less than equal to x less than equal to 1. And we also notice that p of 1 equal to p of minus 1 equal to 0. So, therefore, I can write this as So, this is a this So, no need for boundary condition at 1 and minus 1 and I can write the orthoganality relation as minus 1 to 1. Now the solutions for a given value of n are denoted as pn of x pm of x dx equal to 0 if n is not equal to m ok.

So, this is how you can write the Legendre equation as a Sturm Liouville problem. Notice that I am using n instead of lambda, but that does not matter, you know that n, n plus 1 is nothing but lambda. So, lambda is n, n plus 1 and p of x is 1 minus x square. Your weight function r of x is equal to 1. So, I do not need to have any weight function here. So this shows how you can write various equations as Sturm Liouville problems ok.

Now, let us look at the next part. Next part is to take this equation for the associated Legendre polynomial. So, for the associated Legendre polynomial, now I can do a exactly the same thing as I did before. So, I can write 1 minus x square y prime the whole thing prime plus my q, q in this case is m I can write as minus m square over 1 minus x square and plus l, l plus 1 y equal to 0 ok.

So now, remember the Sturm Liouville problem conditions. So, if you go back to the if you go back to the previous lecture so, the Sturm Liouville problem conditions. The Sturm Liouville problem condition it there is the condition is that p should be greater than or equal to 0 r of x should be greater than or equal to 0. There is no condition on q, q can be anything. So, in this case q is actually negative.

So, so what we identify is that p of x equal to 1 minus x square.

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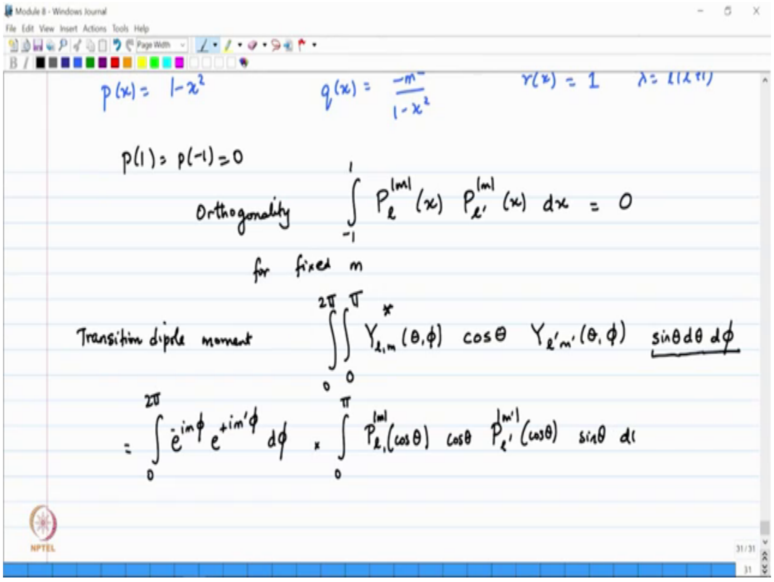

$p(x) = 1-x^2$ $q(x) = \frac{-m^2}{1-x^2}$ $r(x) = 1$ $\lambda = l(l+1)$

$p(1) = p(-1) = 0$

Orthogonality $\int_{-1}^{1} P_l^{|m|}(x)\, P_{l'}^{|m|}(x)\, dx = 0$

for fixed m

Transition dipole moment $\int_0^{2\pi}\int_0^{\pi} Y_{l,m}^*(\theta,\phi)\, \cos\theta\, Y_{l'm'}(\theta,\phi)\, \underline{\sin\theta\, d\theta\, d\phi}$

$= \int_0^{2\pi} e^{-im\phi} e^{+im'\phi}\, d\phi \times \int_0^{\pi} P_{l,}^{|m|}(\cos\theta)\, \cos\theta\, P_{l'}^{|m'|}(\cos\theta)\, \sin\theta\, d($

Q of x equal to minus m square over 1 minus x square, r of x is equal to 1 lambda equal to l, l plus 1. And we can immediately write the solutions. So, again we have p of 0 p of 1 equal to p of minus 1 equal to 0. So, we can write the orthoganality condition as before P l m of x p l prime m of x dx equal to 0. This is for a given value of l, for a given value of m for fixed m. So, that is the that is the orthoganality relation and this completes the second part.

Now, the last part is to use a recursion relation for p to derive spectroscopic rules for rotational spectroscopy. Now in this case you are transition dipole moment So, that will look like y phi. And then now actually the there is a term that looks like cos theta and I have y l prime m prime of theta phi integral and the and the and the integral is over sin theta d theta d phi. So, this is what this integral looks like and there are 2 limit is are from d theta goes from 0 to pi d pi goes from 0 to 2 pi.

So, this sin theta d theta d phi is the Jacobean for in this for converting to spherical polar coordinates. So, we are converting to these angles theta and phi. So, this is the this is what your transition dipole moment looks like, now you can clearly see that if I write if I expand for Y l m of theta phi. If I write this Y l m of theta phi in terms of in terms of a theta part that is P l m cos theta and e to the im phi. Then what I can see is that the phi integral 0 to 2 pi the phi integral the integral over phi will just have e to the i m phi e to the and I should put a complex conjugate here. E to the minus i m phi times e to the plus i m prime phi.

So, the minus came because you took a complex conjugate d phi. And then I have a theta integral that looks like integral 0 to pi, and what I have is P l m cos theta times cos theta l prime m prime cos theta sin theta d theta. What you can see from the first integral is that is that this looks like integral.

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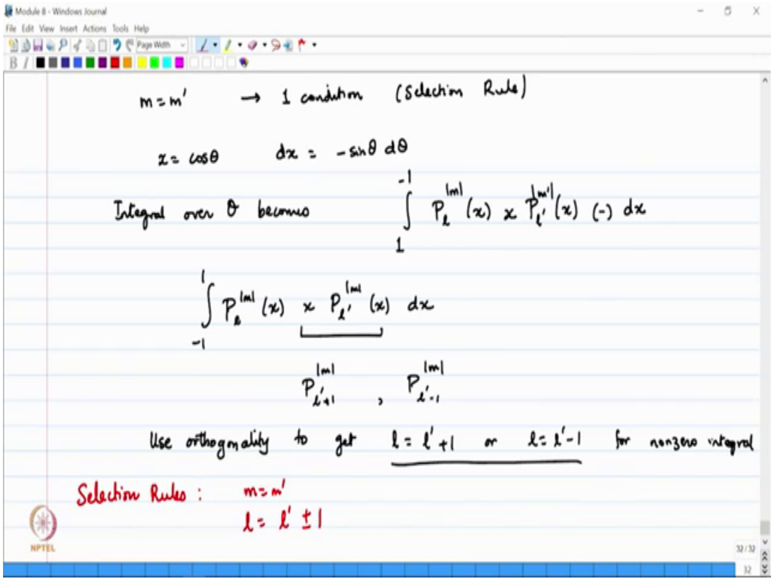

$m = m'$ → 1 condition (Selection Rule)

$x = \cos\theta \qquad dx = -\sin\theta \, d\theta$

Integral over θ becomes $\int_{1}^{-1} P_l^{|m|}(x) \, x \, P_{l'}^{|m'|}(x) \, (-) \, dx$

$$\int_{-1}^{1} P_l^{|m|}(x) \, \underbrace{x \, P_{l'}^{|m|}(x)} \, dx$$

$$P_{l'+1}^{|m|} \, , \quad P_{l'-1}^{|m|}$$

Use orthogonality to get $\underline{l = l'+1 \text{ or } l = l'-1}$ for nonzero integral

Selection Rules : $m = m'$

$l = l' \pm 1$

0 to 2 pi e to the i m minus m prime phi d phi and this equal to 0 unless m equal to m prime.

So, if m is not equal to m prime, then you can easily show that this goes to 0. So, that is the first one. So, the So, the first integral is just this so. So therefore, what we will what we will say that m equal to m prime is one condition or selection rule. Now the second condition we can get by putting m equal to m prime in this, what you will get is and then and then you will put x equal to cos theta dx equal to minus sin theta d theta x so what I will get is. So, this second integral So, integral over theta becomes integral, now aqh when theta equal to 0 x equal to 1 theta equal to pi x equal to minus 1. Now I have pl m of x times cos theta is x and I have pl prime m prime of x. Now sin theta d theta is minus d x minus d x. So, what I can do is I can just change the limit is and I can write this as P l m of x x p l prime m of x dx from minus 1 to 1.

Now, we already saw So now, now let us use the recursion relation, using this recursion relation. So, the recursion relation says that 2 l plus 1 times x pl, is given by some quantity l minus m r and sun p l plus 1 and some constant times p l minus 1. We can replace this by 2 terms one that involves p l prime plus 1 and another that involves p l prime minus 1 of m. And use orthoganality just like hermite polynomials l equal to l prime plus 1 or l equal to l prime minus 1 So, for non 0 integral. So, unless l equal to l prime plus 1 or l equal to l prime minus 1 your integral will be non 0.

So, the final selection rules for rotation for rotational spectroscopy m equal to m prime l equal to l prime plus minus 1. So, what I have shown you through these problems this is again you know very, very useful selection rule for rotational spectroscopy. So, we can see the applications of this orthogonal Eigen functions in actually deriving selection rules for spectroscopy. So, I will conclude this module on ah module 8 with this and next week we will start module 9.

Thank you.