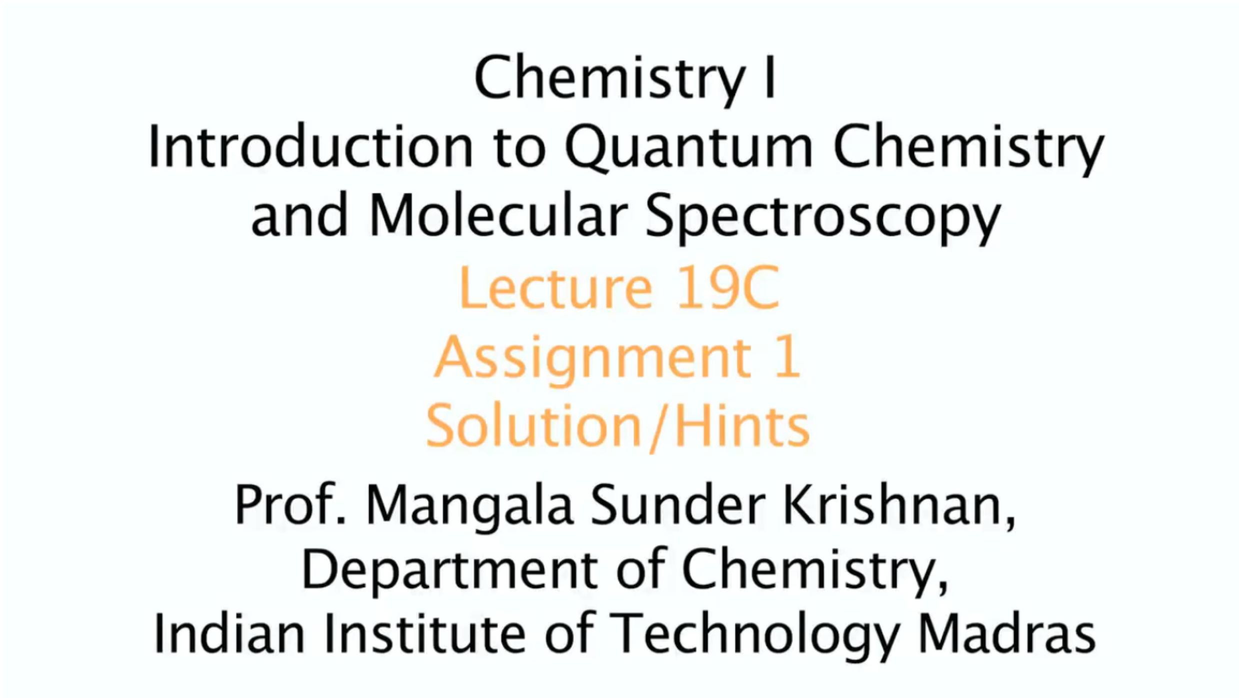
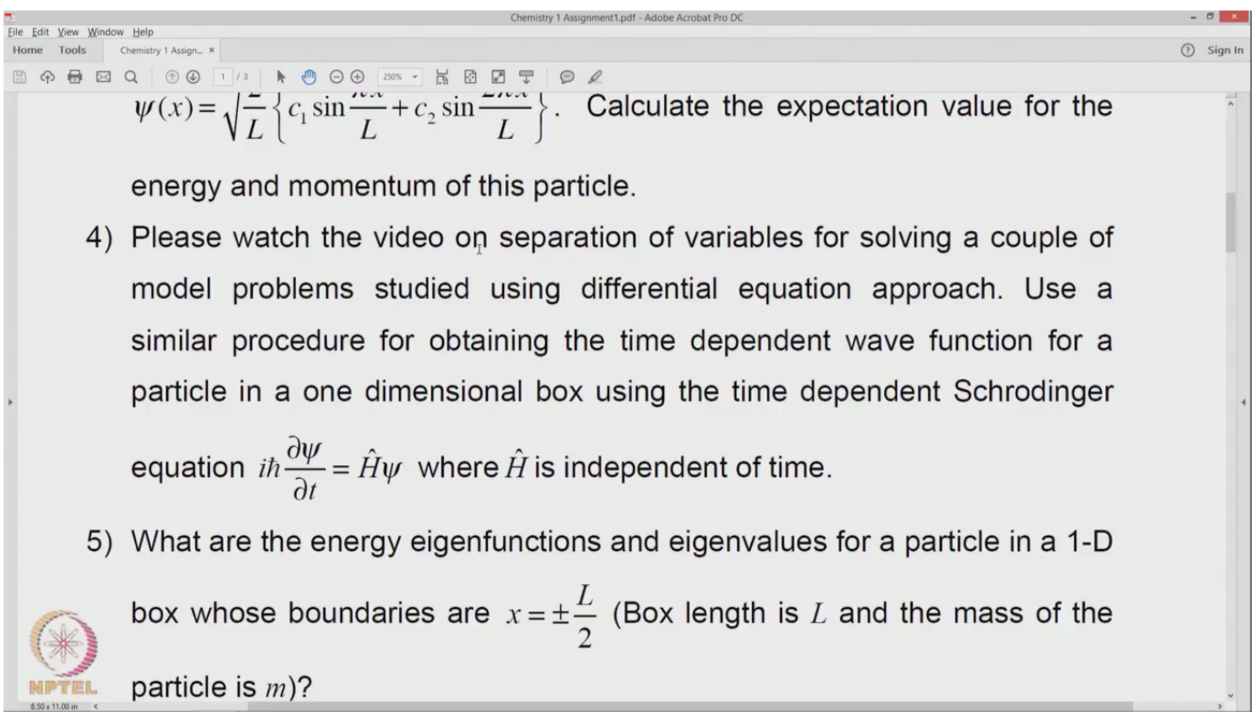




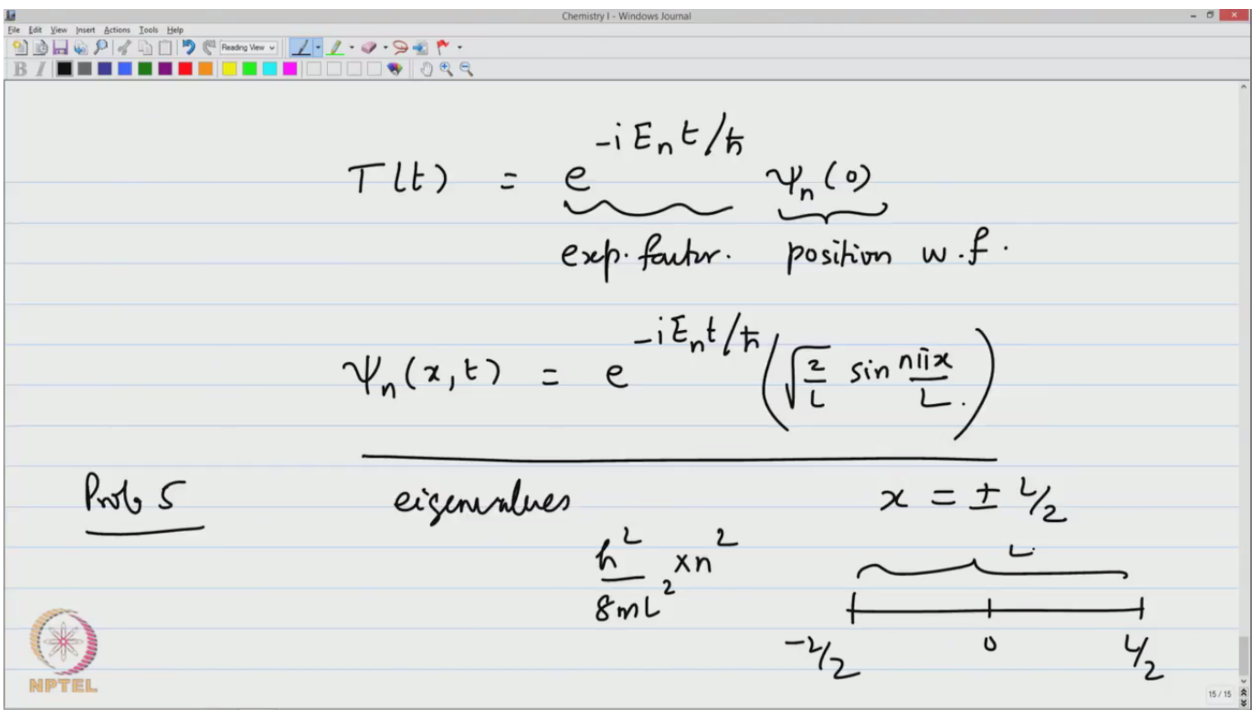
$\psi(x) = \sqrt{\frac{2}{L}}\left\{c_1 \sin\frac{\pi x}{L} + c_2 \sin\frac{2\pi x}{L}\right\}$. Calculate the expectation value for the energy and momentum of this particle.

4) Please watch the video on separation of variables for solving a couple of model problems studied using differential equation approach. Use a similar procedure for obtaining the time dependent wave function for a particle in a one dimensional box using the time dependent Schrodinger equation $i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$ where $\hat{H}$ is independent of time.

5) What are the energy eigenfunctions and eigenvalues for a particle in a 1-D box whose boundaries are $x = \pm\frac{L}{2}$ (Box length is L and the mass of the particle is m)?

Welcome back to the lectures on quantum chemistry and molecular spectroscopy. This is the assignment solutions continued into the third part, the part C and let us look at the problems of the assignment four and five. Problem four in the assignment given in your website tells you to watch the video on separation of variables for solving a couple of model problems studied using differential equation approach. I gave this as one lecture to tell you how the time dependent Schrodinger equation can be separated out when the Hamiltonian does not depend on time. It use that same procedure or a similar to see just for obtaining the time-dependent wave functions for a particle in a one dimensional box using the time dependent Schrodinger equation. It's a very simple problem I don't think I need to do that. The Hamiltonian that you have to do H Ψ is equal to E Ψ that you're write that Hamiltonian is actually the particle in a box Hamiltonian so I think the solution for this problem is immediate. So if I have to solve this ih bar bar dau Ψ by dou t is equal to H for the particle in a box then all I need to do is to write the Ψ of x,t which we did because the wave function is a function of both the coordination time as the Ψ n of x the particle in a box eigenfunctions and the time only function where Ψ n of x is obviously the solution of the Hamiltonian H Ψ n of x is equal to En Ψ n of x. Therefore you know these. These are root 2 by l L sine n π x by l and these are h square n square by 8 ml square. So what is T of t? it's also very simple. T of t is exponential minus iEnt by h bar Ψ n of 0. So this is the position dependent wave function or the position based on some that you have. This is the exponential factor. So the wave function Ψ n of x,t is E to the minus iEnt by h bar square root of 2 by l sine n π x by l. So this is the Ψ n of 0. So the solution should be immediate.

The general wave function for a particle in a box system will be a linear combination of all these functions Ψ n of x of t but that if you want to do it's in the next course when you look at probabilities and overlaps that might be useful. But this is the simplest solution for the time dependent Schrodinger equation for the particle in the box.

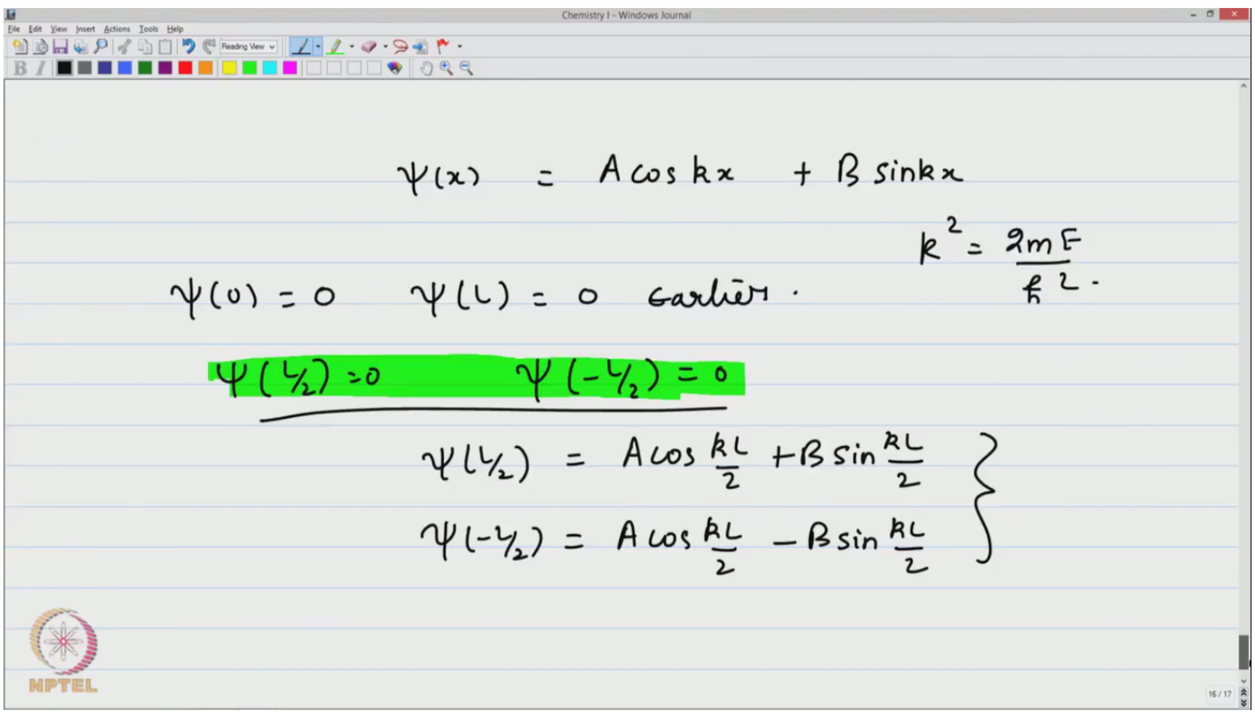


Let's look at the next problem. It's asking you to calculate the energy eigenfunctions and eigenvalues for a particle in the 1-D box whose boundaries are different. They are plus minus L by 2. The box length is still the same l and mass of the particle is m. It's important to recognize these are the parameters of the problem. The energy eigenfunctions and eigenvalues if you look at them energy eigenvalues do not depend on the coordinates. Remember the Ens are h square by

8 ml square times n square. The coordinates has been integrated out. Therefore, as long as the length of the box is l and as long as the particles mass is m the energy eigenvalues do not change. It doesn't matter where you put your coordinate if the box width or the box length is the same as before. Therefore, the answer to the question about the eigenfunctions is slightly different but the eigenvalues problem 5, eigenvalues for x is equal to plus or minus L by 2 the eigenvalues are still h square by 8 ml square n square since the box width is from minus L by 2 this is 0 this is plus l by 2 the box width is l. That doesn't change. What about the eigenfunctions? Interesting.

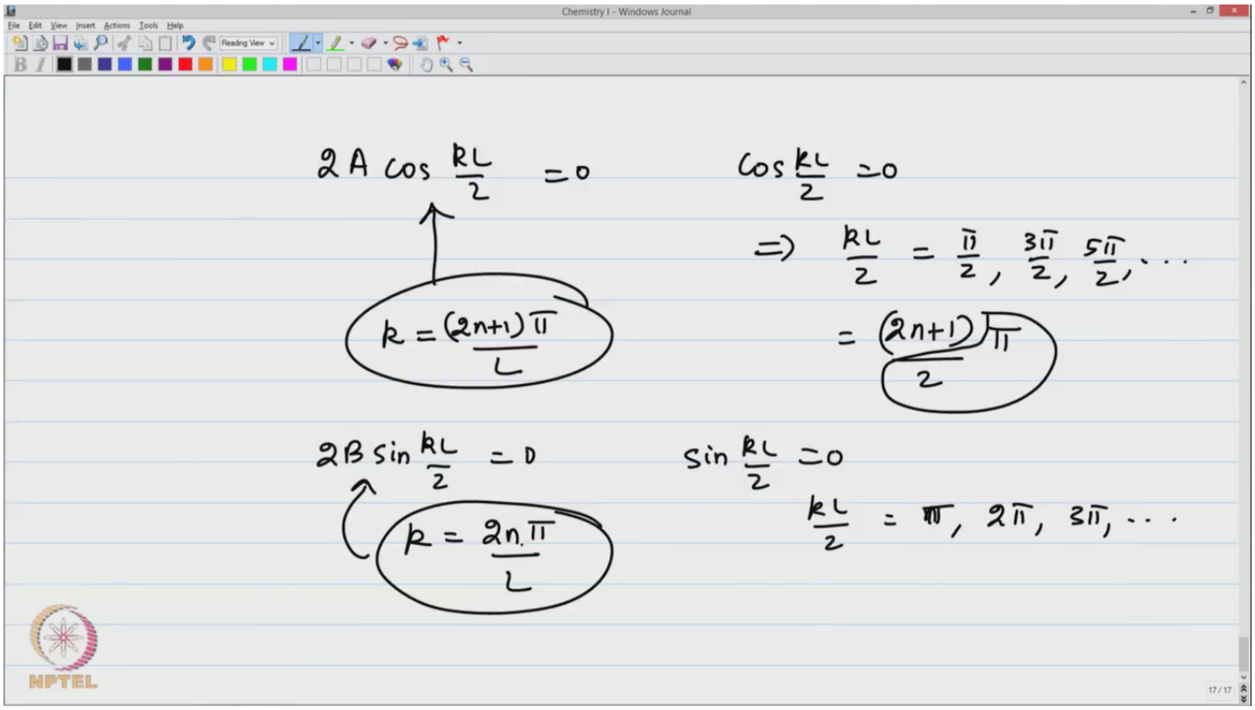
Remember the wave function that we solve for Ψ of x is equal to Acoskx plus B sinekx where k square is 2mE by h bar square and then we use the boundary conditions Ψ of x is equal to 0 is 0. Ψ of l x is equal to l is zero earlier. Now we are told Ψ of l by 2 is 0 and Ψ of minus L by 2 is 0. So these are the two conditions that we have to use instead of the conditions that we used earlier because the physical boundary is shifted. But the physics will not change. The wave function of course depends on the coordinate and therefore the wave function representation will be slightly different. You should see that.

Now for Ψ L by 2 equal to 0 you have Ψ of l by 2 if you substitute x is equal to L by 2 you have A cos kl by 2 plus B sine kl by 2 and Ψ at minus L by 2 remember cos of minus x is the same as cos of x therefore this doesn't change. This is still A cos kl by 2 minus kl by 2 is the same as cos kl by 2 but the sine function changes the sign therefore you have B sine kl by 2 with a minus sign. So these are the boundary conditions now.



Now the boundary conditions are such that you have two equations A plus B and A minus B and therefore if you add you get one equation. If you subtract you get the other equation. So if you add you get 2 A cos kl by 2 is 0 and if A is not zero that means cos kl by 2 is 0 which implies kl by 2 is either π by 2 or 3 π by 2 or 5 π by 2 and so on so I would write this in general as to n plus 1 by 2 π that is it's an odd number, odd integral multiple of π by 2 that will make cos kl by 2 to 0.

So A is not zero. If you subtract you get 2 B sine kl by 2 and that's equal to 0 and this implies that sine kl by 2 0 or kl by 2 is n π namely π, 2 π, 3 π, and so on. Therefore kl is 2 π, 2 π, 3 π etc. so you can see that the wave functions are slightly different because if kl by 2 is 2n plus 1 then what is k? K is 2n plus 1 π by l that's for this solution. And here k is equal to 2 n π by l that is for this solution. Therefore depending on the n value you have two solutions.



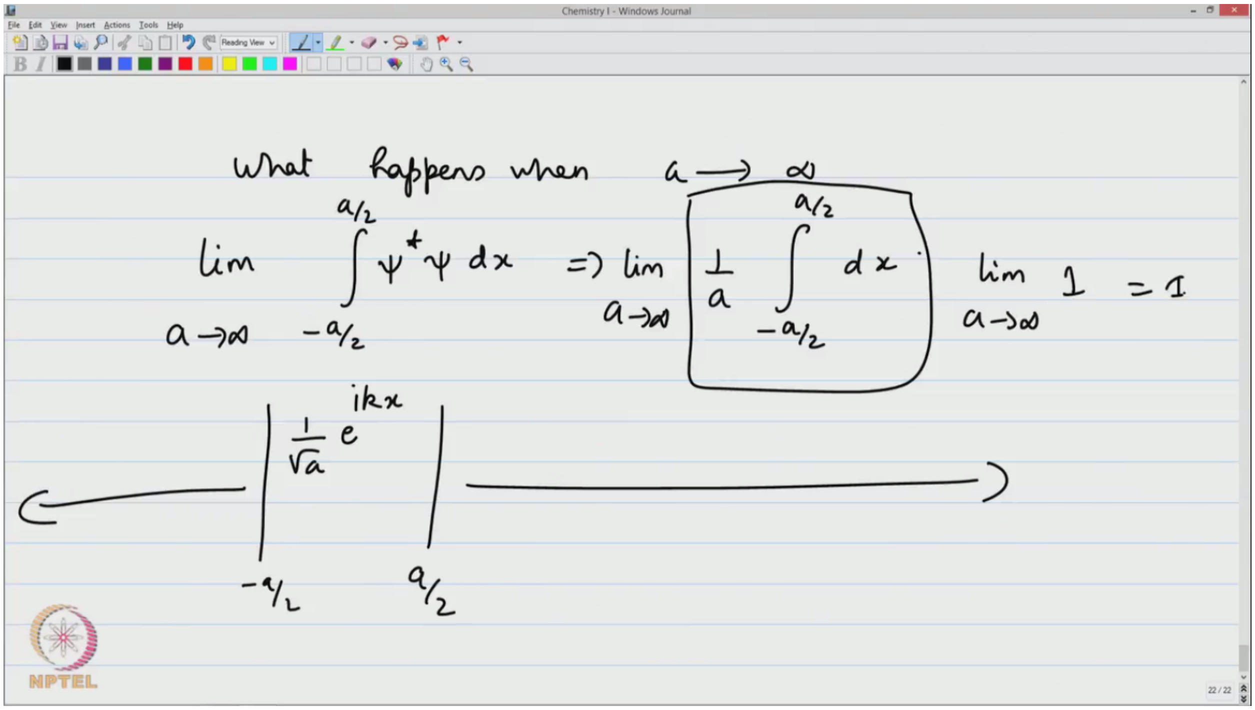
So let me summarize the solution. Ψ of x is equal to some normalization constant cos 2 n plus 1 π by l x and this is for n equal to 1, 2, 3, etc. or it is A sine 2 n π by l x again n equal to 1, 2, 3, etc. and the energy of course En is the same. It doesn't change. It is h square n square by 8 ml square. So all that happens is that the functional representation changes because the coordinates and the boundary conditions have been shifted but the physics mainly the energy eigenvalue and where is the particle the average value for the position of the particle is in the middle of the box. So therefore that will become l equal to 0 not like the l by 2 in the previous problem. Those are quite obviously the results of the mathematical consequences. This is the other problem.

Now let's look at the next problem. For the one dimensional box obtain an expression for the maxima of the probability densities P is equal to Ψ of n x whole square for all the n. It can be written down analytically but let's explain the problem a bit. Recall that sine n of x hold the absolute square for the particle in the 1-D box if you remember the picture that I had for the wave functions and the wave function square. For n equal to 1 something like that it's a sine square for n equal to 2 if you remember it's a full wave so the square of the function gained something like that two nodes. So there is one maximum another maximum here. That is one more maximum here and this is for one n equal to 2 and for n equal to 3 of course you will have three of these and for n equal to 4 you will have four of these and so on. The problem asks you to calculate this maxima in a formal way. So what is the maximum? If the probability is given by Ψ n of x whole square and that's essentially sine square n π x by l times 2 by l then you know this is the maxima or minima is obtained by taking the derivative of this probability with respect to the position and setting that equal to zero and whatever value that we get for x if we substitute that in the second derivative if this is less than zero then it's a maximum for this value of x satisfied by this equation and if it is greater than zero it's a minimum. That's easy to see because you see the function have the minimum here and here namely zeros and in the middle it has that L by 2 this has a minimum and you can see that the number of minima also increases for n equal to 3. There are two minima and three maxima for n equal to 4 there are three minima and four maxima so on so what's the formula for this.

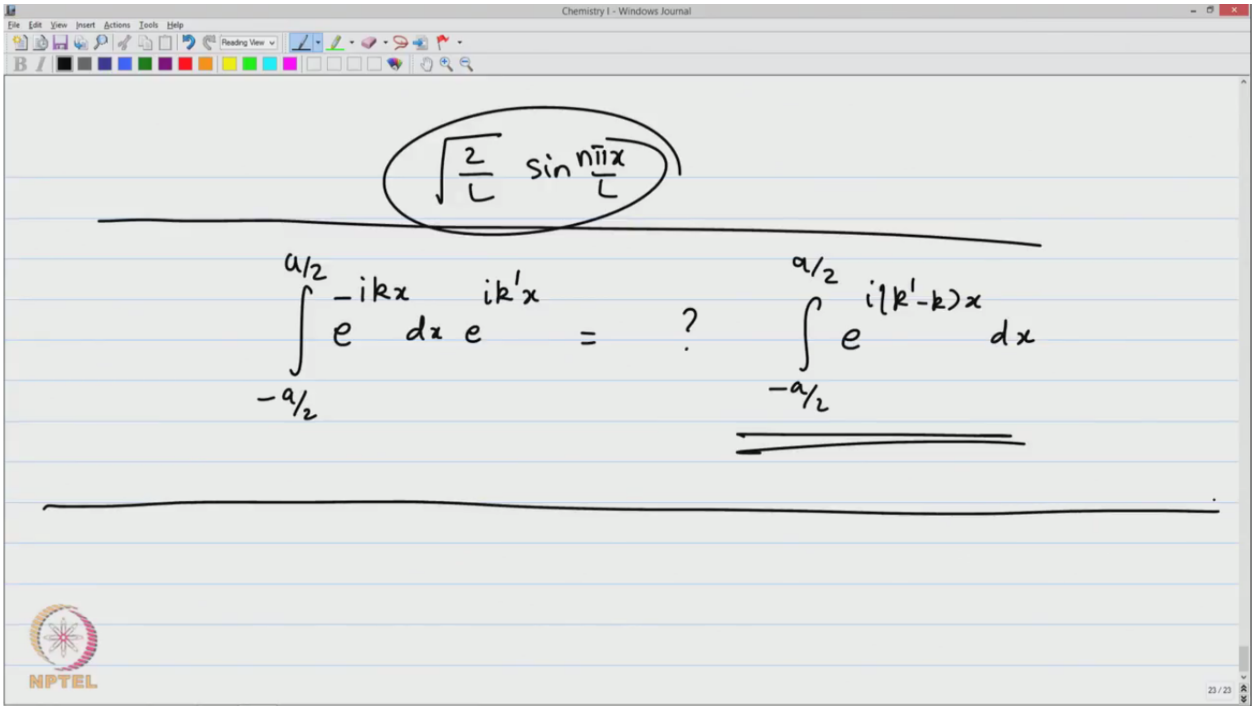
So you take the derivative of this. The derivative of dP by dx is equal to 0 is 1 by L sine n π x by l cos n π x by l and that should be equal to zero. This is 1 by 2 l sine 2 n π x by l. So you can see immediately that this function has a maximum at for n equal to 1, for n equal to 1 the maximum is at x is equal to l by 2 and if it is n equal to 2 the maximum happens at l by 4 and 3 l by 4 because for n equal to 2 the probability density goes like this and this point is l by 4, this is l by 2 and this point is 3 l by 4. So now you can in principle write the general formula on what is the expression for the number of maxima and number of minima and L by 2 is a minimum, L by 4 and 3 l by 4 are maxima. So this is a simple way of differentiating the function to obtain maximum in probabilities and minimum in probabilities.

Let's go to the next problem. The next problem tells us whether asks us to find out whether the wave function given by this formula Ψ of k of x is equal to 1 by root Ae to the ikx in the interval minus A by 2 plus A by 2? Are these day functions normalized and orthogonal in the limit of A is equal to infinity? Show your answer. The first thing is to see whether these functions are normalized.

So Ψ k of x is 1 by root Ae to the ikx and the region is minus a by 2 x less than a by 2. Therefore the normalization integral is Ψ k of x star Ψ k of x dx. The star is very important here. It's from minus a by 2 to plus a by 2. Why the star is important because the function is complex. Therefore the absolute square is the probable -- represents the probability density. So if you do that the integral is minus a by 2 plus a by 2 1 by a it is e to the minus ikx times e to the ikx dx and this integral is 1. Therefore this is normalized. What happens when we take the limit a tending to infinity. You can see that the wave function Ψ star Ψ dx from minus a by 2 to plus a by 2 gives you 1 by a times minus a by 2 plus a by 2 dx. Now you want to take the limit a tending to infinity that is you are extending this finite limit minus a by 2 box plus a by 2 by opening it up all the way with this function namely 1 by square root of a e to the ikx you will see that there is no problem with that because this integral when limit of a tends to infinity please note that this integral is actually independent of a because a get canceled out. Therefore, you have limits of a tending to infinity one doesn't change it's one.



So this is a beautifully normalized box normalized free particle wave function. So this function 1 by root a to the e ikx is known as box normalized free particle wave function. It's not a surprise if you remember the functions that you were used it's the root 2 by L sine n π x by l is already there. Similar things have been done except that this is the imaginary part of the e to the ikx. You have otherwise functionally there is no difference in the concept. What about the orthogonality? The integral a to the ikx minus dx e to the ik prime x from minus a by 2 to plus a by 2. I would like you to calculate this integral and tell me and find out what the behavior of this is. Of course minus a by 2 to plus a by 2 e to the ik prime minus k x dx and you know that this is not orthogonal, the integral is not 0 for finite a. So you can do this integral.



The next problem is a slightly longer problem. We will do that in the next part.