Statistical Thermodynamics for Engineers
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Lecture 24
The Steady State Schrodinger Equation Multi-particle analysis

Welcome to lecture number 16 on the statistical thermodynamics course for engineers, So, previously we have seen the steady state version of this Schrodinger's wave equation.

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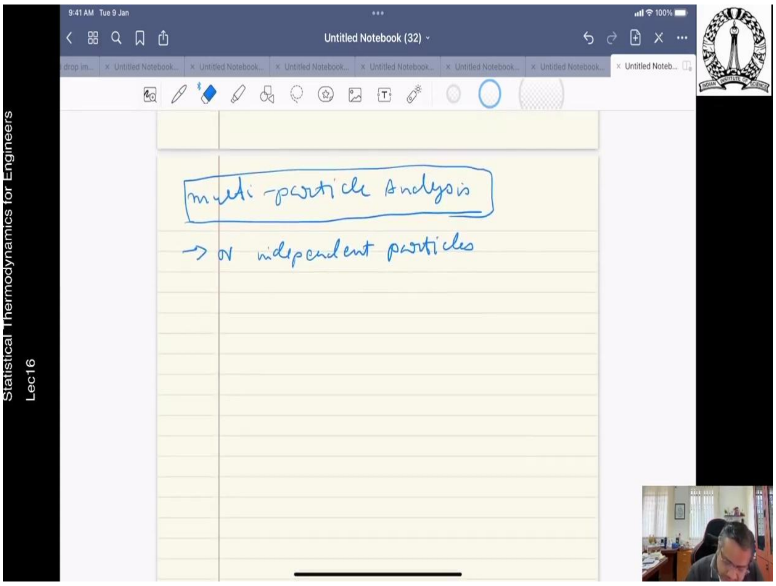

In this case, we are going to now write the first multi-particle analysis using this Schrodinger's wave equation. So, by multi-particle analysis, we mean that there are n independent particles. This is multi-particle. So, previously we looked at single particle, remember the previous forms whatever we did were all corresponded to the single particle, a single particle.

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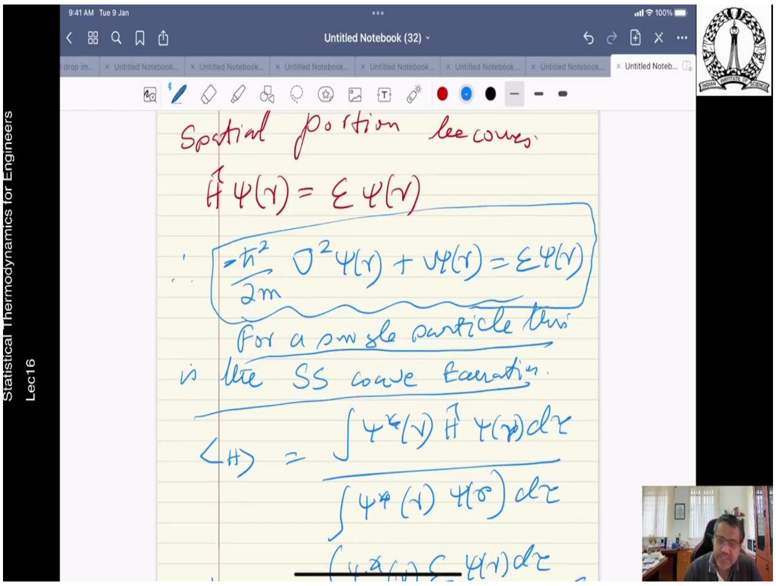

For the single particle, this was the steady state wave function.

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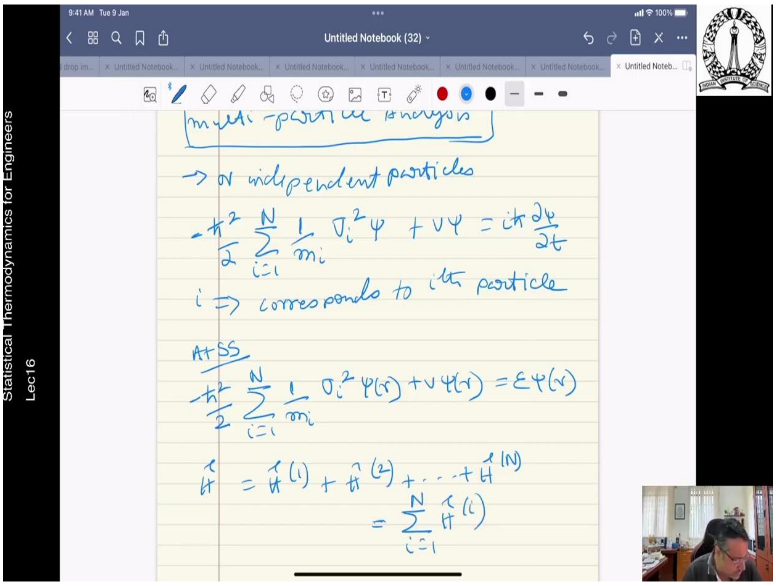

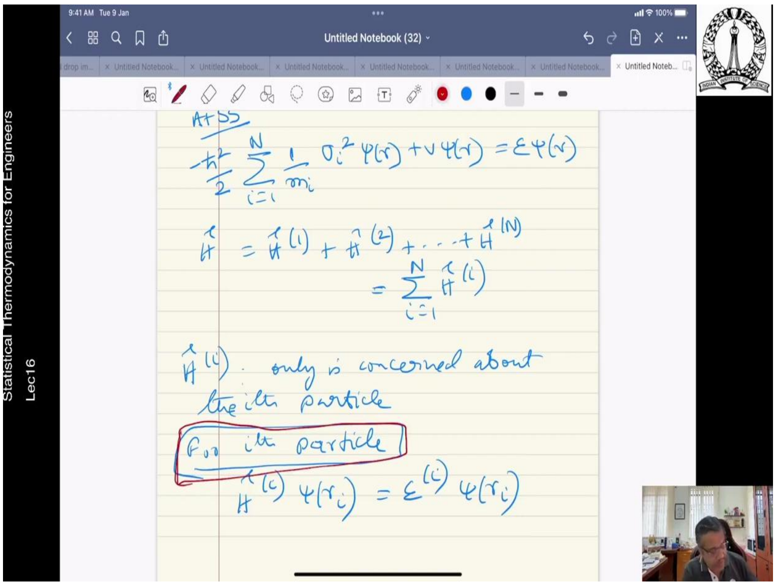

So, for multi-particle because these particles are independent in nature, the multi-particle analysis would be minus h2 summation i equal to 1 mi square. So, these are independent particles, so they have I corresponds to the ith particle. So, if we apply the steady state at steady state wave function, what happens is minus h2 by 2 equal to 1 to N. That is the steady state, steady state, using the steady state Schrodinger's wave equations. So, this is the total expression that you can write where h bar is h bar for particle 1 plus h hat for particle 2 plus HN expressed as summation of all h bars h hats sum over i.

So, hi, only coordinates about the ith particle, only is concerned about the ith. So, for ith particle – H i chi I is equal to EI chi I, this is for the ith particle only. And remember these particles are all independent, mutually independent. So, that is for the ith particle.

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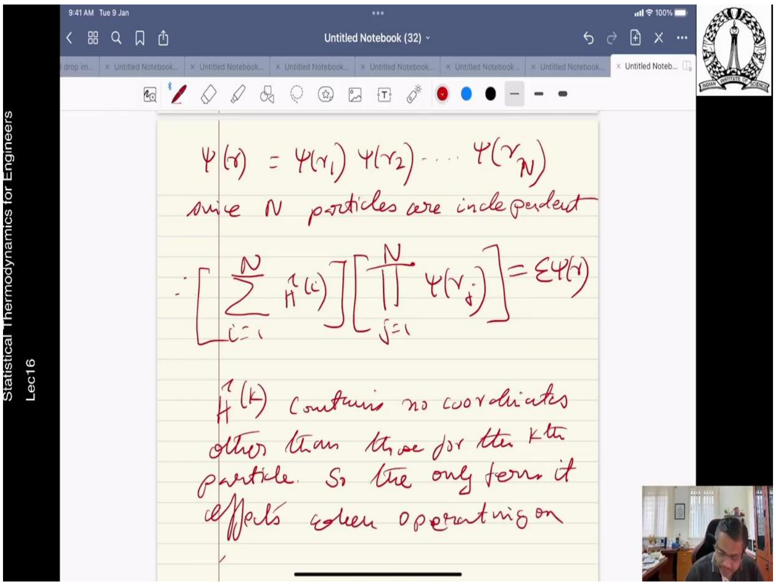

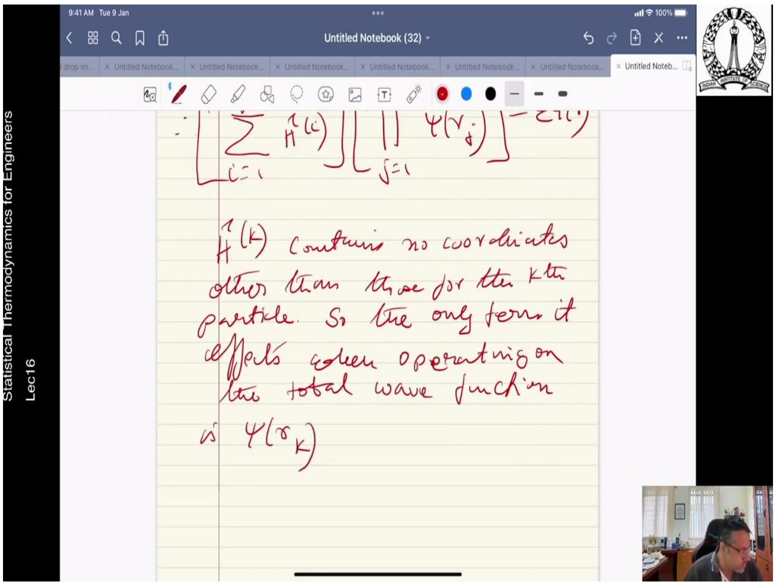

Now, a wave functions we write it(())(4:17) chi r should be now chi r1 chi r2 chi rN, that is because since N particles, it is independent. So, N particles are independent. So, how do you write it final expression? Final expression would be hi I, the first expression is multiplicated J equal to 1 to phi j is equal to, so, we already know that the only effect… so, you can see from this particular expression that this is the total expression, because h just note here, h for example, K contains no coordinates other than those for the Kth particle. So, the only term it affects when operating, so, the only term it affects when operating on the total wave function is phi rK.

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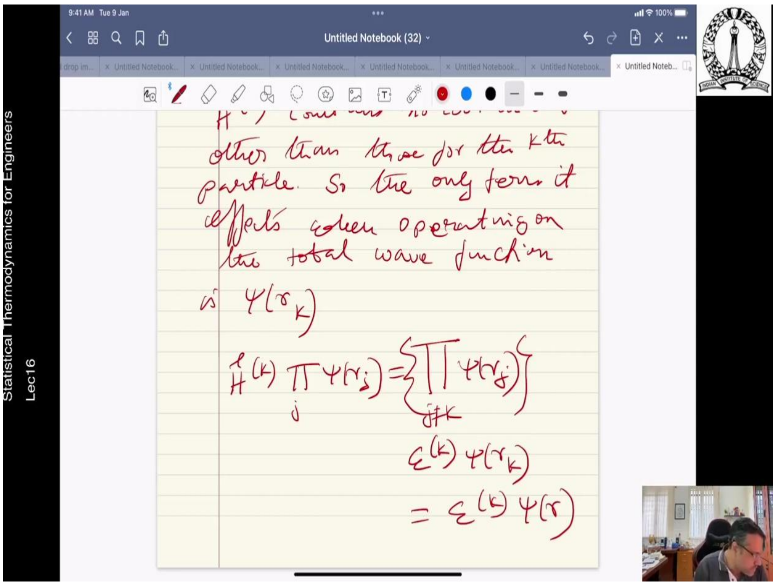

So, in other words, we can write H K and j is equal to, now look at this j is not equal to K Chi r j K chi is equal to K into… So, we have seen, so, this is what it is. So, you can work this out independently as well. So, this actually states the full function.

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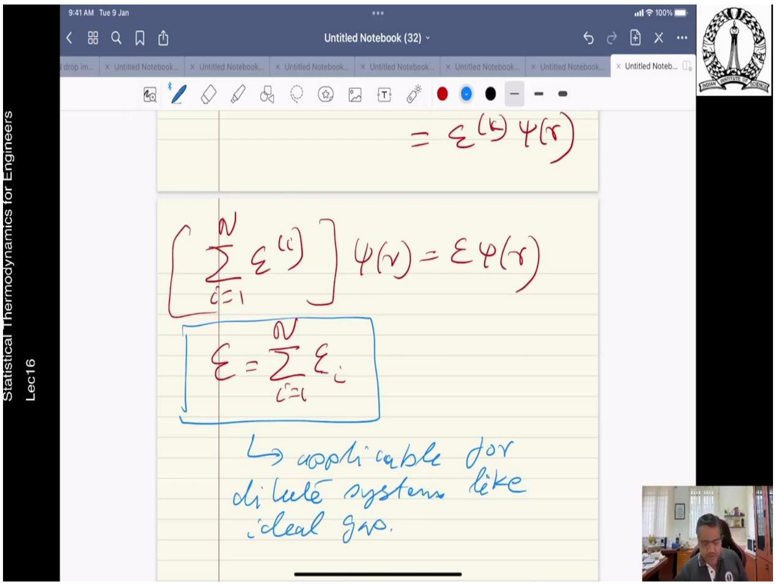

Substituting all of this this, you can kind of get, you can write another expression i equal to 1 to N I wave function is equal to chi. So, that also can be done. And the energy is the sum total of i equal to 1 to N Ei. So, this is for example is applicable for dilute system like ideal gas is one of the example of a dilute system.

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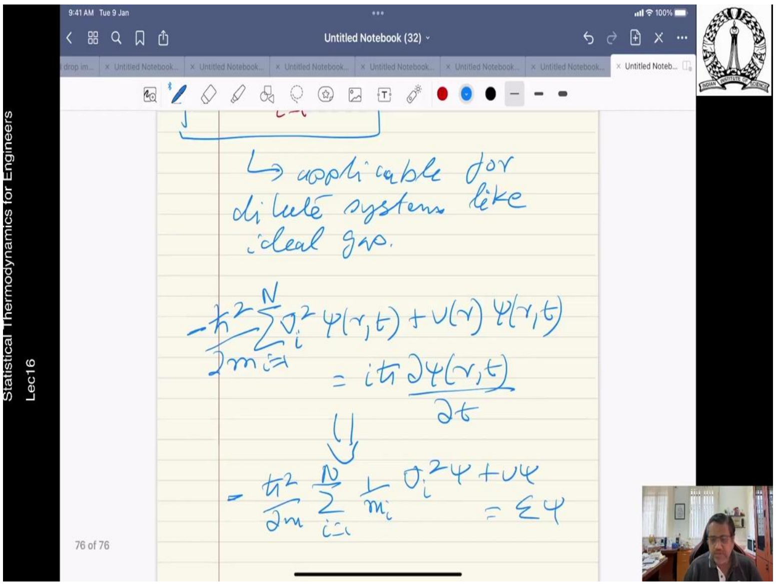

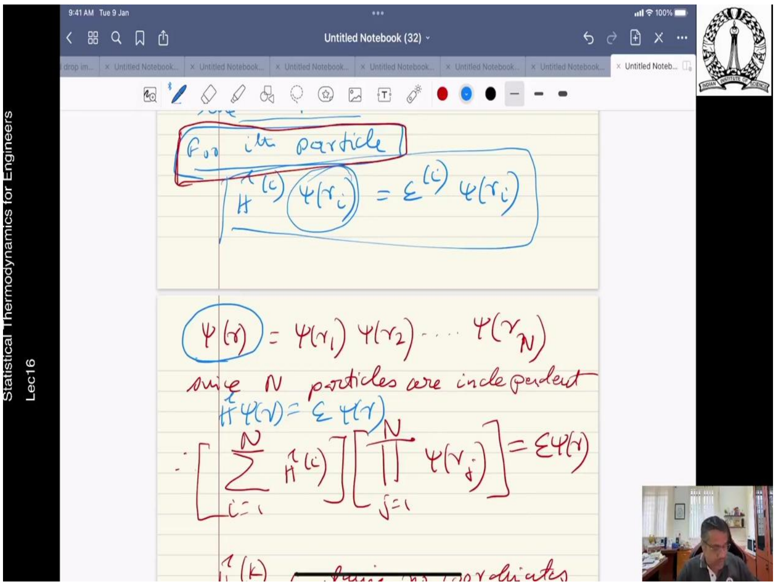

So, let us do a very quick recap that you have a system of simple multi-particle system which is composed of N independent particles. So, if you look at that kind of an expression and if you just recap, if you look at the total Schrodinger's wave equation, then for a single particle, we wrote it like that, this was a time dependent.

So, 2m chi r comma t plus vr phi r t equal to ih bar chi r comma t by dt. So, this was a single particle. When you write it for a multi-particle system this becomes simply i, that there is a summation that comes into the picture what i equal to 1 to N because now this is applicable. This is for the individual particles. So, at steady state, a steady state version of this then becomes minus h square by 2m, again you sum it over 1 to N and 1 over mi, now it becomes mi.

So, the previous one as you saw was mi comes because it is a individual particle ones. So, this was chi plus hi is equal to… So, this was what we wrote in the steady state, but this was the steady state. So, now, you can also now see the Hamiltonian operator now can be separated into a number of terms which is exactly what we did. The Hamiltonian operator was separated into a bunch of terms which is simply put.

So, here we say that hi is only concerned about the ith particle, it is only contains the co-ordinates of the ith particles. Therefore, based on this, the consequently the operators hi can be only used to obtain the wave function phi r and this gives rise, for the ith particle of the system, this is the expression, but the overall wave function, that means the global wave function will just chi r okay therefore must satisfy h chi r is equal t, this should be satisfied. So, the overall wave function should satisfy this particular expression.

For independent particles, the wave function becomes something like that, because it is a multiplicative of multiple particles in a single, single particle wave functions are written as this chi r1 r2 and r3. So, now if we substitute this particular expression as well as, this particular expression, these two if you substitute in this expression, here, you get this. And however, then we argue that hK contains no coordinates other than those for the particle. So, the only term that it affects is chi rK.

So, therefore, you can write it in a slightly modified version like this and then it follows all the other terms that we get. So, this gives for a multi-particle analysis, what should be the procedure.

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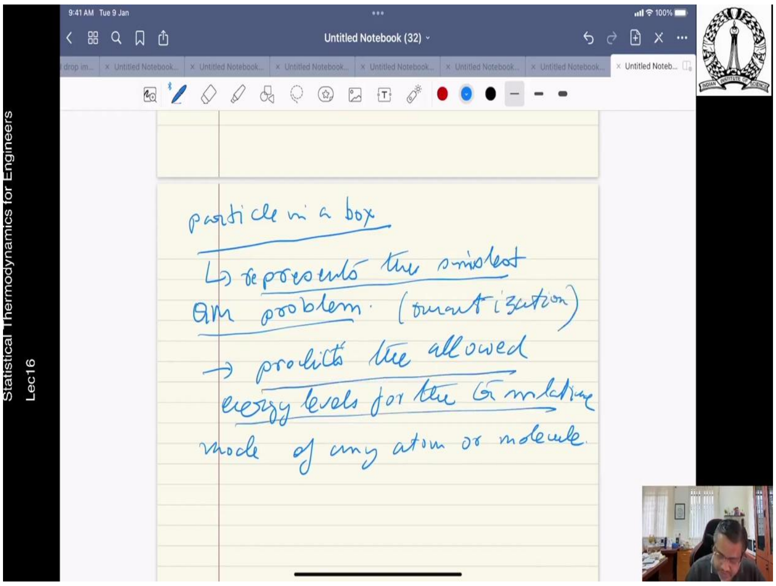

Now, we are going to do particle in a box. So, what is particle in a box? Particle in a box represents the simplest quantum mechanical, it represents the simplest Qm problem. Moreover, it also demonstrates many interesting effects of quantization, the solution is also important because it predicts the allowed energy levels for the translational mode. So, it predicts the allowed energy levels energy for the translational mode of any atom or molecule.

So, this is important because it represents (())(14:19) a very simple problem, but it also predicts that how quantization happens, we will see that shortly and it also predicts the allowed energy levels, what is the concept of microstates and macro states? So, all these things will come in very handy when we actually do this particular problem. For doing this let us look at a cubical box.

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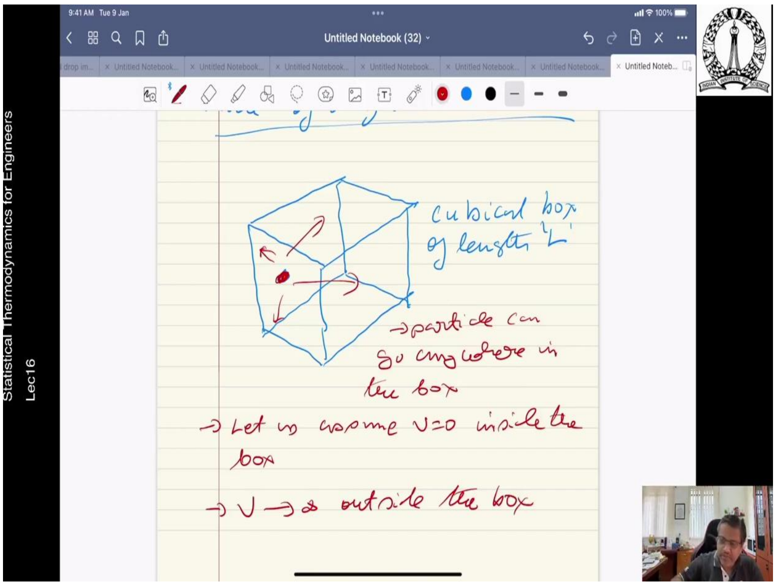

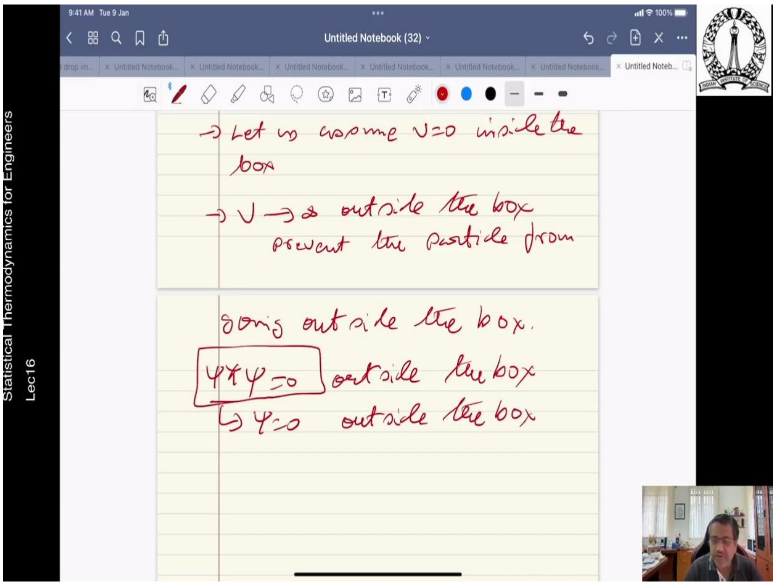

This is a box, cubical box. So, the particle, if this is a particle assume that this is a guy, it can go anywhere in the box. It can go anywhere in the box anywhere within this space. So, it can go, the particle can go anywhere in box, there is no restriction on the particles where it can go. Let us just assume that if V is equal to 0 inside the box it is V0 and V goes to infinity outside the box. So, this actually represents a potential well, so the particle cannot go outside, it is like a barrier.

So, this is used to prevent particle from exiting the box, going outside the box. So, it essentially also translates to the chi into complex conjugate is equal to 0 outside the box and just because it represents probability, then there is no chance that the particle can be outside the box, it is an improbable event. It is 0 outside the box. We also assume chi equal to 0 outside the box. So, this is the probability being equal to 0 as we know that this represents a PDF, position of the particle, but, so, this is 0 outside the box.

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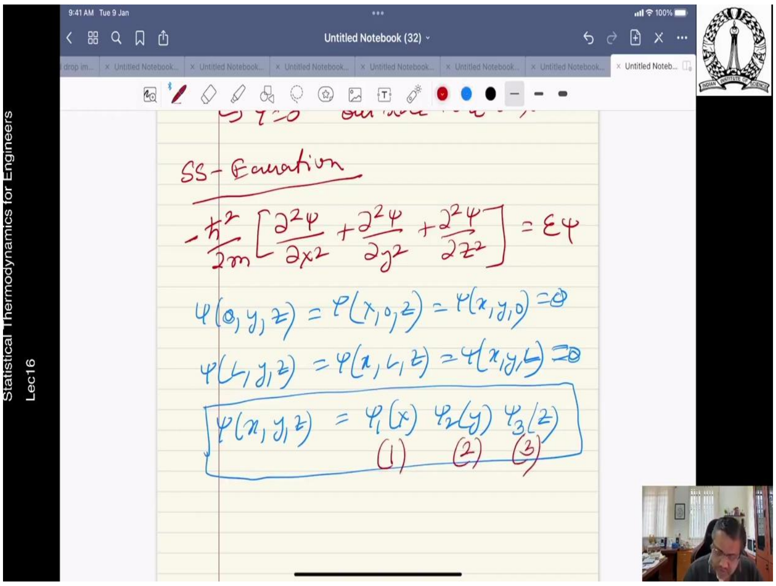

So, if we now assume the steady state equation or the Schrodinger steady state equation, what we will get? There are three coordinates remember, because this is a cuboidal system, so it should have a xyz system. So, this is minus h square by 2m. (())(17:50) So, this is the steady state version of the Schrodinger's wave equation. Now, this equation, of course, this is a three-dimensional system now.

So, what are the boundary conditions? Because this is a partial differential equation, as we can see a chi 0 y z, that means that it is equal to 0 equal to chi, x 0 z is equal to chi x y 0 is equal to 0. And after a length L, that is also equal to 0, and x, y, z, this is equal to chi 1 x plus chi 2 y plus chi3 z because each of the three directions are independent with respect to each other. So, this is at one corner, this is at the other corner. So, the probability is 0 anywhere from those corners and it has a finite probability inside the box, inside the cubicle box.

And the total probability is given as a multiplicative of these three terms which corresponds to the different directions. So, as we know that the particle in a box is very important, because it will allow us to get the energy levels and the quantum numbers for the translational mode. So, let us see how this works.

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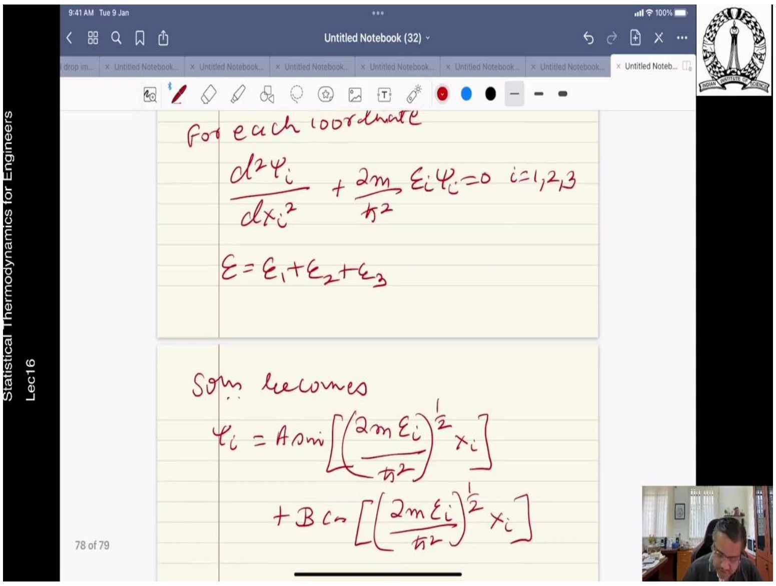

So, for each coordinate, we can say chi i and we are dropping the X Y because this is assumed that this is face dependent only 2m h bar square(())(20:06) is equal to 0 I equal to 1, 2, 3. E equal to E1 plus E2 plus E3. So, the solution for this particular problem, it becomes chi i is equal to A sine 2m Ei… So, this is one of the solution it should become.

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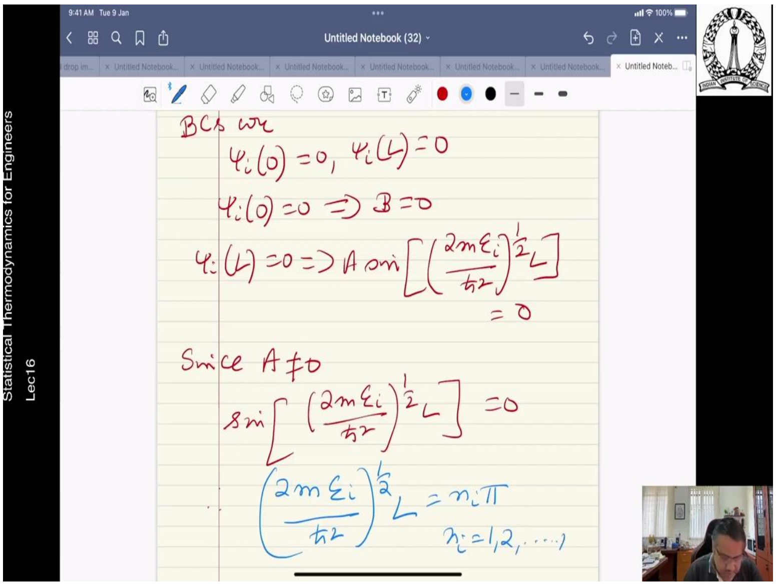

So, the boundary conditions phi I is 0 is equal to 0, phi i L is equal to 0, these are the two extremes. So, this chi i equal to 0 needs to be equal to 0. Chi i is equal to 0 at xi equal to 0. So, this term will become 0, this term becomes 1. So, E equal to 0 and chi i L equal to 0 weights to A sine theta as 2mEi h bar square half into L is equal to 0. Since A cannot be equal to 0, this would mean A cannot be, then it becomes a trivial, if A equal to 0 then chi is equal to 0. So, that is a trivial solution.

So, this becomes 2m Ei square is equal to 0. Therefore, 2m Ei h bar square half into L is equal to nip u where ni equal to 1, 2, 3. So, this being equal to 0 proves this is the point. This, we are going to leave it, there is already quantization that you see coming right over there.

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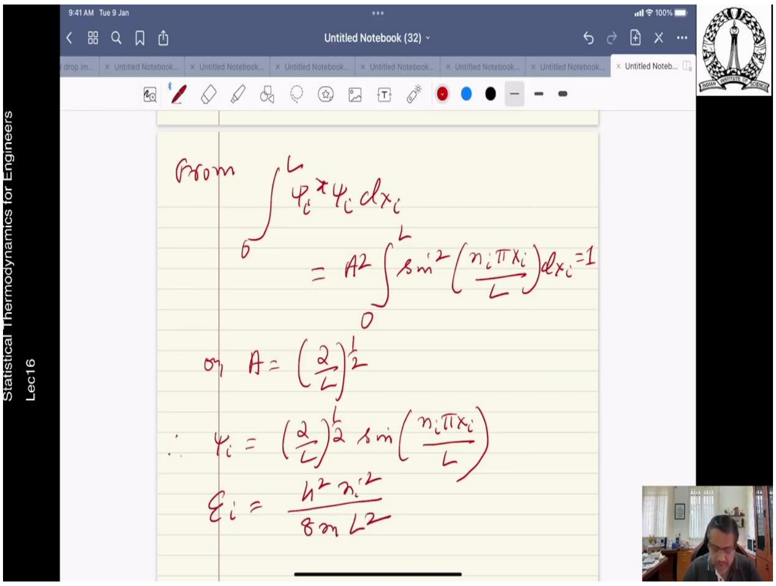

Now from 0 to L, chi i star phi I dxi, this is we are integrating to xi, this is A square 0 to L sine square ni pi xi by L into dxi is equal to 1. That should be equal to 1 because the total probability when you integrate it should be equal to 1. So, this gives you A is equal to 2 by L into half.

Therefore, chi i becomes 2 by L sine ni pi xi divided by L. And Ei therefore becomes h square ni square divided by 8m L square. That is a particle maps. So, these two are two vitally important. So, we have found out the wave function in the ith coordinate system in the ith direction. We have found out the energy in the ith direction also.

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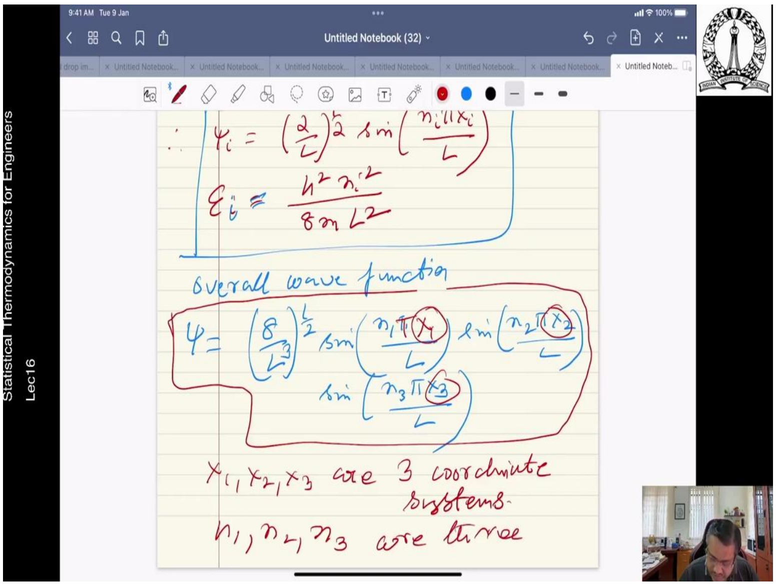

So, the overall wave function now that we know overall wave function, it is written chi, it is multiplicative of all these, sine n1 pi x1, x1 is like your x sine n2 pi x2 by L divided by sine n3 pi x3 L. So, this is the total wave function, which involves now three coordinates – x1, x2, x3. So, x1, x2, x3 are 3 coordinate systems. And n1, n2, n3 are 3 distinct numbers that we are dealing with, 3 distinct numbers of three degrees of freedom also we can say.

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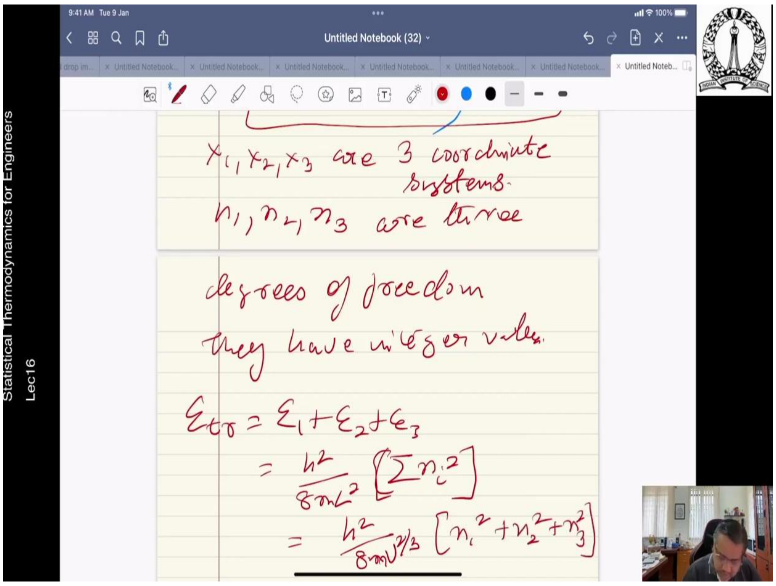

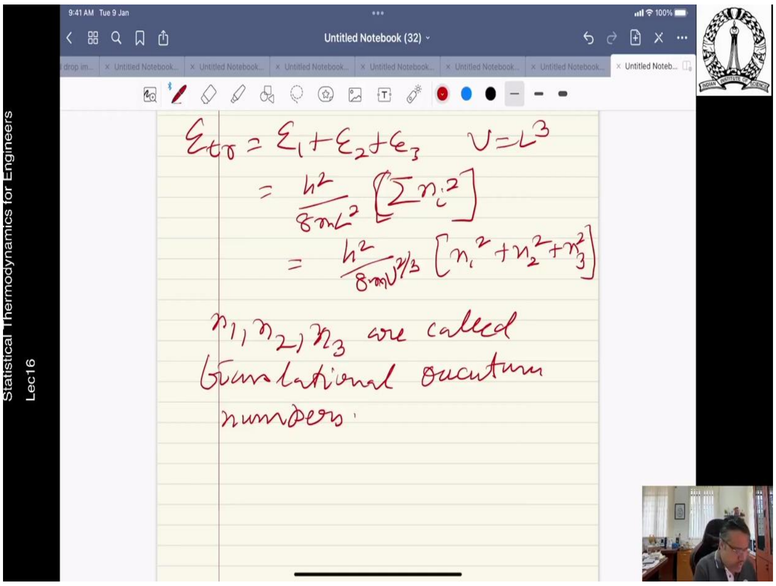

Degrees of freedom and they have integer values. So, you can see that there is a total also. The total translational energy is there for E1 plus e2 plus E3, which is basically the h square 8 n L square summation of ni square which is h square divided by 8m keeping the volume by third n1 square plus n2 square plus n3 square, where n1, n2, n3 are feasible to L cube which basically the volume.

So, these ns, therefore n1, n2, n3, they are called translational quantum numbers, which is also connected to something like the degree of freedom of the system. So, this is rather interesting. So, this is how we found out. This is a very pretty straightforward process to find the translational quantum numbers.

The equation is most significant, because there will be multiple interpretations of this system because we saw that the energy was quantized and we can make five observations on this, which we will cover in the next class based on this analysis. It is a simple analysis but it has got a profound effect that what is actually meant by doing this because we have got three translational quantum numbers readily popping out of this particular context. So, thank you, we will see you in the next class.