Statistical Thermodynamics for Engineers

Professor Saptarshi Basu
Indian Institute of Science, Bengaluru
Lecture 18
Heuristic Introduction to the SchrodingerEquation

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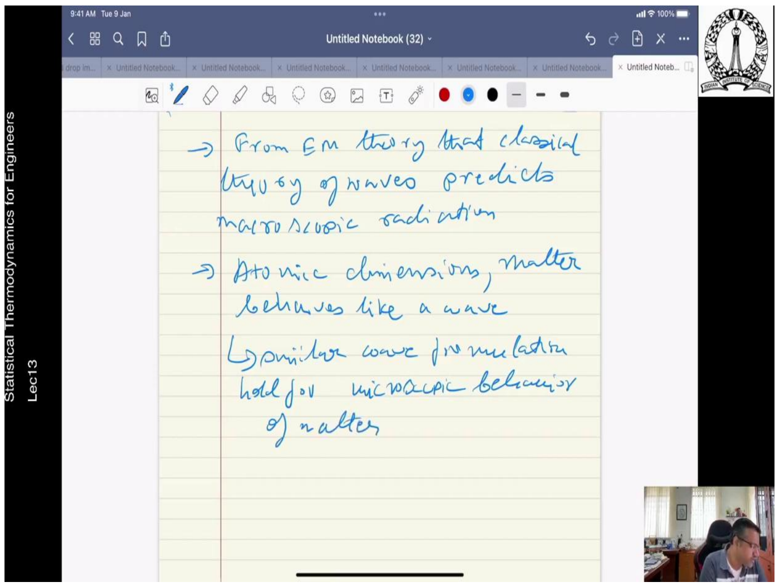

Welcome to Lecture 13 of the course Statistical Thermodynamics for Engineers. So, as we saw already that the Bohr's model, while it was good it felt a little add hoc because it had part classical part quantum mechanics in it. So, as we know that from standard electromagnetic theory, that macroscopic radiation can be modeled successfully by a classical wave equation that we know find that from electromagnetic theory that classical theory of waves predicts the macroscopic radiation.

Now should not for atomic dimensions matter behaves like a wave and so should not similar wave formulation is applicable to a macroscopic behavior of matter hold for microscopic behavior of matter.

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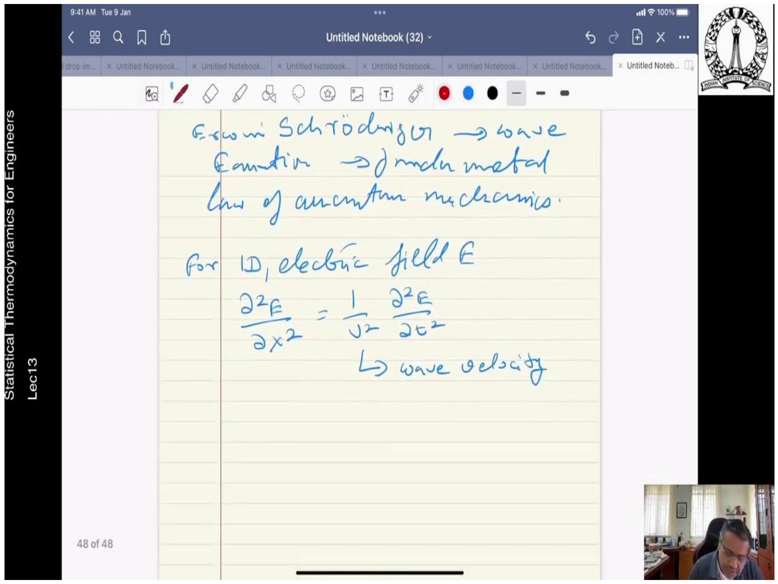

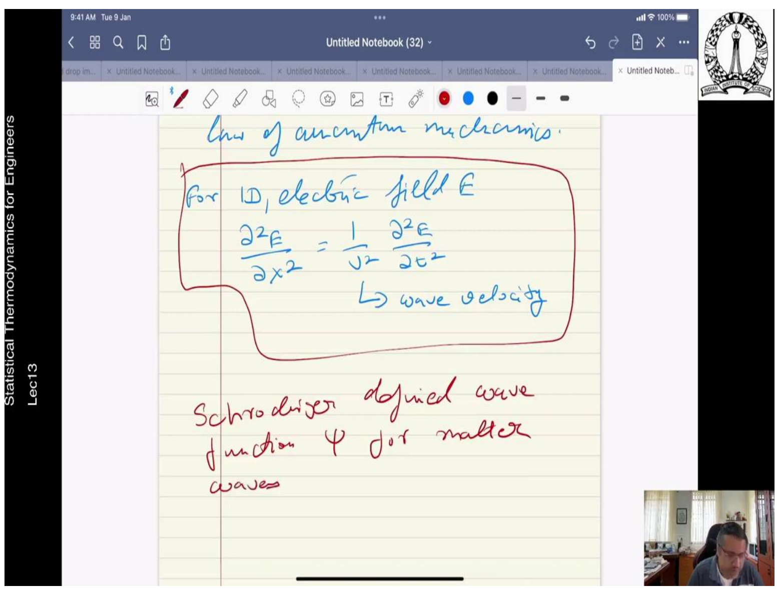

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Schrodinger defined wave function ψ for matter waves

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \psi}{\partial t^2}$$ ..... many solutions

we consider the most well known soln.

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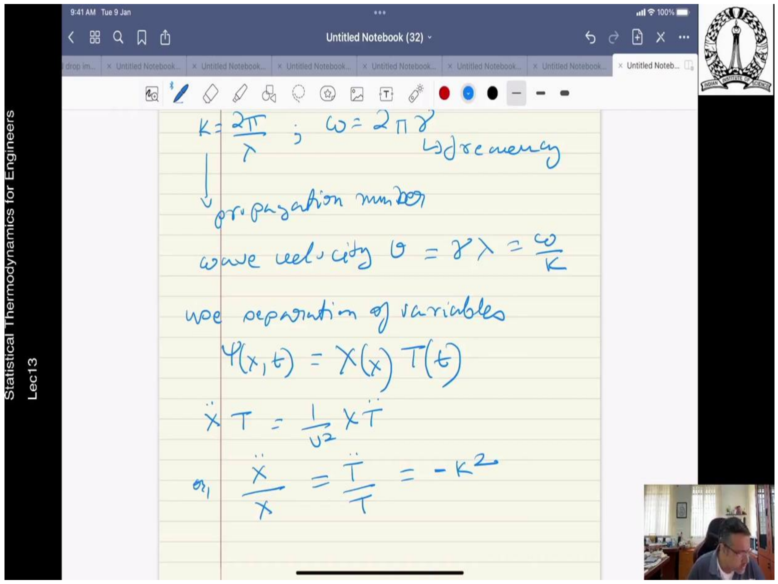
known soln.

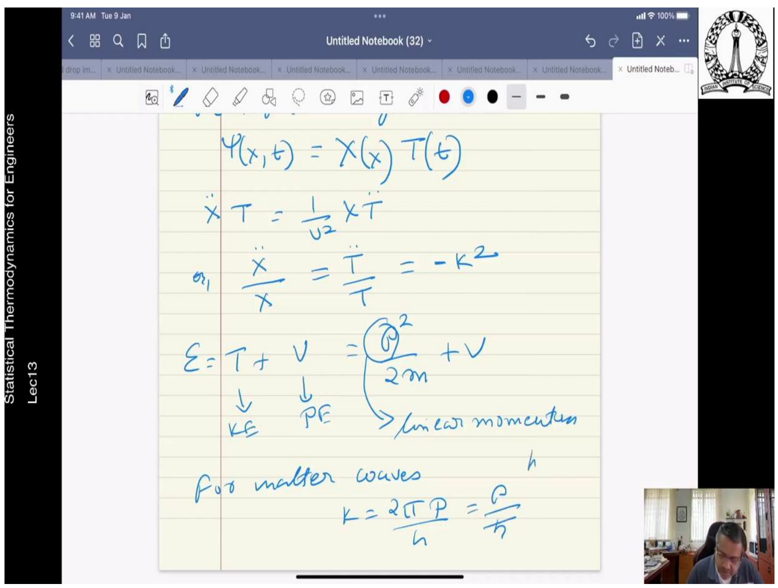
$$\psi(x,t) = C e^{i(kx - \omega t)}$$

$k = \frac{2\pi}{\lambda}$; $\omega = 2\pi\nu$ → frequency

k → propagation number

wave velocity $v = \nu\lambda = \frac{\omega}{k}$





So, unlike this part, classical part, quantum mechanics actually have more can there be more uniform framework which can be used in this particular context. So, this actually set the stage for Erwin Schrodinger Austrian physicist he formulated what is called the wave equation, now this wave equation is now one of the cornerstone, the wave equation is one of the cornerstone of the fundamental law of quantum mechanics.

But we are not going to do a full derivation; we are going to have a Heuristic understanding of Schrodinger wave equation in general. So, let us start to do that for 1D, electric field E, this is like a analogy, electric field E is given as partial for this one dimension 1 by v square delta square E by delta t square, v is basically nothing but a wave velocity.

So, this is from traditional electric fields, this is well known what Schrodinger did was that he defined wave function psi for matter waves following De Broglie wave hypothesis so it defined wave function for matter waves. So, this wave function is nothing but this 1 by v square t square so this is a wave function and very similar to this he kind of you can take an analogy see, what does it actually look like?

Now, many solutions are possible for this particular equation and have many solutions. We consider the most well known solutions, so that well known solution is psi x comma t equal to C e to the power i kx minus omega t, k is equal to 2 pi by lambda, omega is equal to 2 pi frequency this is a frequency this is like a propagation number.

So, this is quite clear so, the wave velocity v, wave velocity v is equal to gamma into lambda which is basically a (())(06:24) propagation number so, this is the solution so, once the solution is set now we solve this equation to use the separation of variables, that mean psi x comma t is equal to X of x into T of t well known separation variable. So this is substituted in the Schrodinger's wave equation to get x double dot T equal to 1 by v square x T double dot so double dot signifies the second derivative. Or in other words x double dot by x equal to T double dot by T equal to minus k square.

So, that is what it is. So, now the total energy, energy is T plus V this is kinetic energy this is potential energy now, this can be represented as p square by 2 m plus v, p is nothing but a linear energy, linear momentum. For matter waves k equal to 2pi p by h which is p by h bar, where h bar is equal to h by 2 pi (())(08:39).

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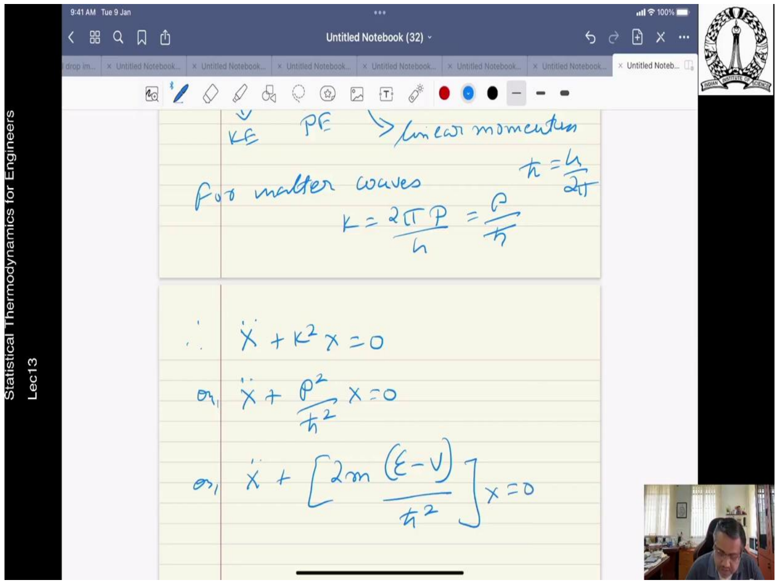

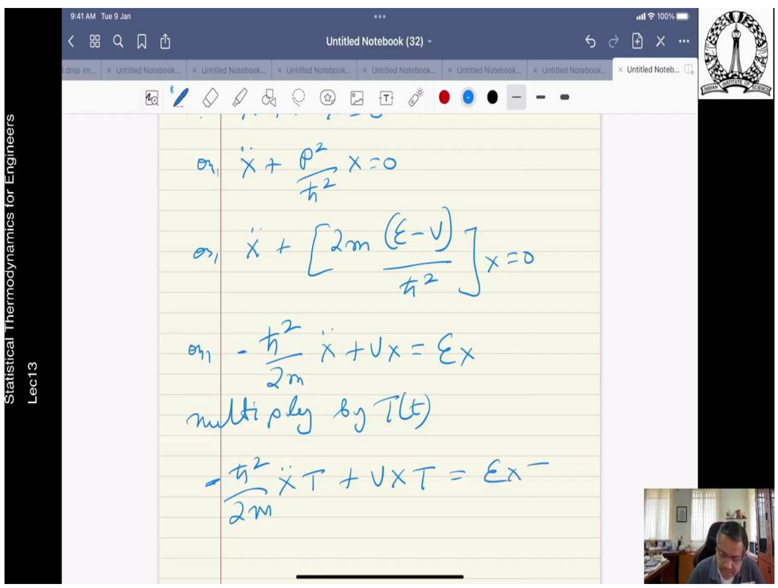

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multiply by $T(t)$

$$-\frac{\hbar^2}{2m}\ddot{X}T + VXT = \mathcal{E}XT \qquad (XT = \psi)$$

or
$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = \mathcal{E}\psi$$

General soln
$$\psi(x,t) = Ce^{i(kx-\omega t)}$$

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$$\frac{\partial\psi}{\partial t} = Ce^{i(kx-\omega t)}(-i\omega)$$

or
$$i\hbar\frac{\partial\psi}{\partial t} = (-i\omega)(i\hbar)Ce^{-i(kx-\omega t)}$$

or
$$i\hbar\frac{\partial\psi}{\partial t} = (\omega\hbar)Ce^{i(kx-\omega t)}$$

or
$$i\hbar\frac{\partial\psi}{\partial t} = (\omega\hbar)\psi(x,t)$$

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$$\frac{\partial \psi}{\partial t} = C e^{i(kx-\omega t)}(-i\omega)$$

or $$i\hbar \frac{\partial \psi}{\partial t} = (-i\omega)(i\hbar)\, C e^{i(kx-\omega t)}$$

or $$i\hbar \frac{\partial \psi}{\partial t} = (\omega\hbar)\, C e^{i(kx-\omega t)}$$

or $$i\hbar \frac{\partial \psi}{\partial t} = (\omega\hbar)\, \psi(x,t)$$

Now $\varepsilon = h\nu = \hbar\omega$

$$\therefore \quad i\hbar \frac{\partial \psi}{\partial t} = \varepsilon\, \psi(x,t)$$

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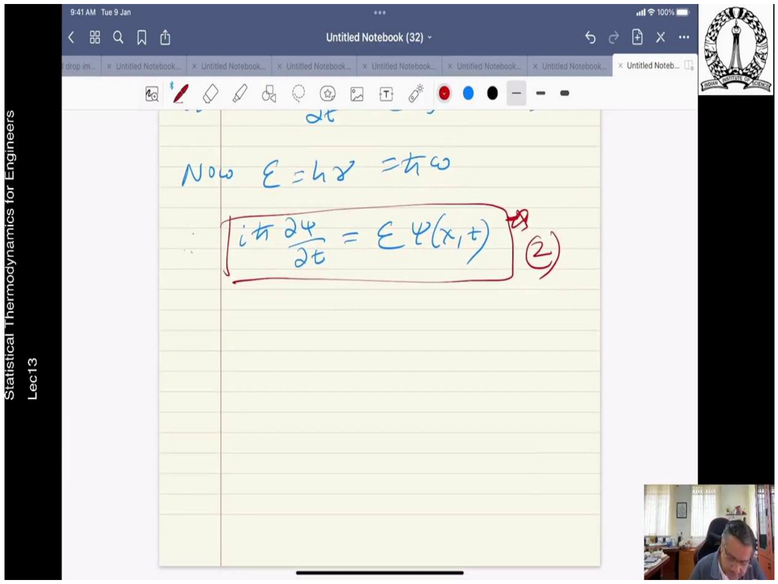
multiply by $T(t)$

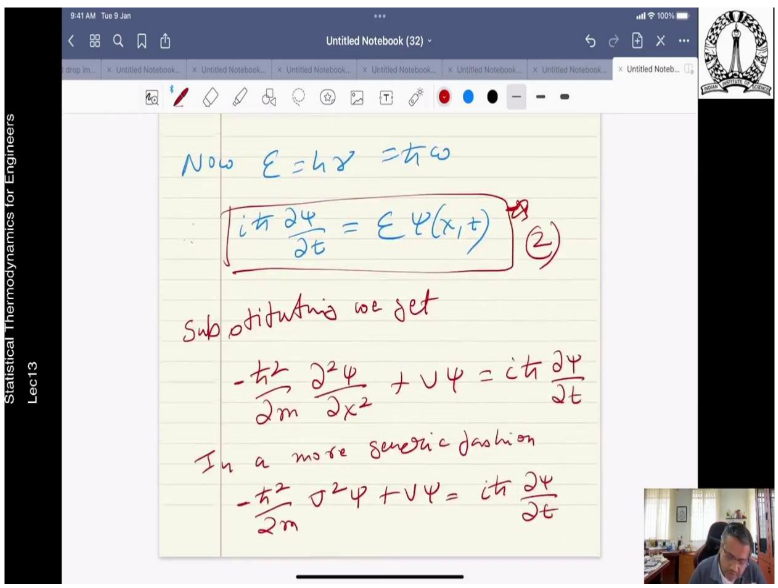
$$-\frac{\hbar^2}{2m}\ddot{X}\,T + V X T = \varepsilon X T$$

or $$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi = \varepsilon\psi \quad (1)$$

General soln:
$$\psi(x,t) = C e^{i(kx-\omega t)}$$

$$\frac{\partial \psi}{\partial t} = C e^{i(kx-\omega t)}(-i\omega)$$





So, now that we have it so, the first expression to look at it is x double dot plus k square x equal to 0 or in other words x double dot plus p square by h bar square x equal to 0, is the first after the separation of variables one is spatial and one is (())(09:00) in other words x double dot plus 2m E minus v E being the total energy divided by h bar square x equal to 0.

Or in other words minus h bar square by 2 m x double dot plus vx equal to Ex multiply by (())(09:42) minus h bar square by 2m x double dot T plus vxT is equal to ExT or in other words this actually becomes minus h bar square by 2m (())(10:06) x square plus v psi (())(10:12) is equal to E psi. Now recall the general solution general solution was psi x comma t equals Ce to the power i k x minus omega t so d psi by dt equal to ce to the power i kx minus omega t into minus i omega, or in other word i h bar d psi by dt is equal to minus i omega i h bar c e to the power minus i k x minus omega t or i h bar d psi by dt equal omega h bar c e to the power of i kx minus omega t or i h bar d psi by dt equal to omega h bar psi x comma t.

Now E equal to h mu which is equal to h bar omega therefore i h bar d psi by dt is equal to E psi x comma t. Now if you can take this expression now and you take this all the way and apply h here you take this so, let us call this 2 and if you call this 1 we take 2 and apply into 1. And substituting therefore we get minus h bar square by 2m d square psi by d x square plus v psi is equal to i h bar d psi by dt (())(13:01) in a more generic way, in a more generic fashion, all you can do is that, equal minus h bar square, this is the Laplace psi plus V psi is equal to ih (())(13:28).

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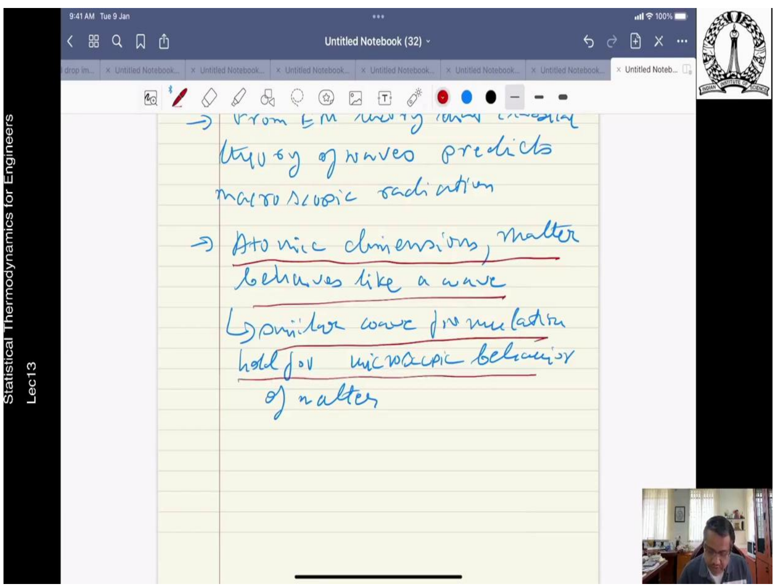

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Erwin Schrödinger → wave Equation → fundamental law of quantum mechanics.

For 1D, electric field E

$$\frac{\partial^2 E}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 E}{\partial t^2}$$

↳ wave velocity

Schrodinger defined wave function ψ for matter waves

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Schrodinger defined wave function ψ for matter waves

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \psi}{\partial t^2}$$

.... many Solutions

we consider the most well known soln.

Solutions

we consider the most well known soln.

$$\Psi(x,t) = C e^{i(kx-\omega t)}$$

$k = \frac{2\pi}{\lambda}$; $\omega = 2\pi\nu$ (frequency)

↓ propagation number

wave velocity $v = \nu\lambda = \frac{\omega}{k}$

↓ propagation number

wave velocity $v = \nu\lambda = \frac{\omega}{k}$

use separation of variables

$$\Psi(x,t) = X(x)\,T(t)$$

$$\ddot{X}\,T = \frac{1}{v^2} X \ddot{T}$$

or, $$\frac{\ddot{X}}{X} = \frac{\ddot{T}}{v^2 T} = -k^2$$

$$E = T + V = \frac{p^2}{2m} + V$$

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or, $\frac{\ddot{X}}{X} = \frac{\ddot{T}}{v^2 T} = -k^2$

$$\mathcal{E} = T + V = \frac{p^2}{2m} + V$$

T → KE, V → PE, p → linear momentum

$\hbar = \frac{h}{2\pi}$

For matter waves

$$k = \frac{2\pi p}{h} = \frac{p}{\hbar}$$

$\therefore \ddot{X} + k^2 X = 0$

or, $\ddot{X} + \frac{p^2}{\dots}$

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multiply by $T(t)$

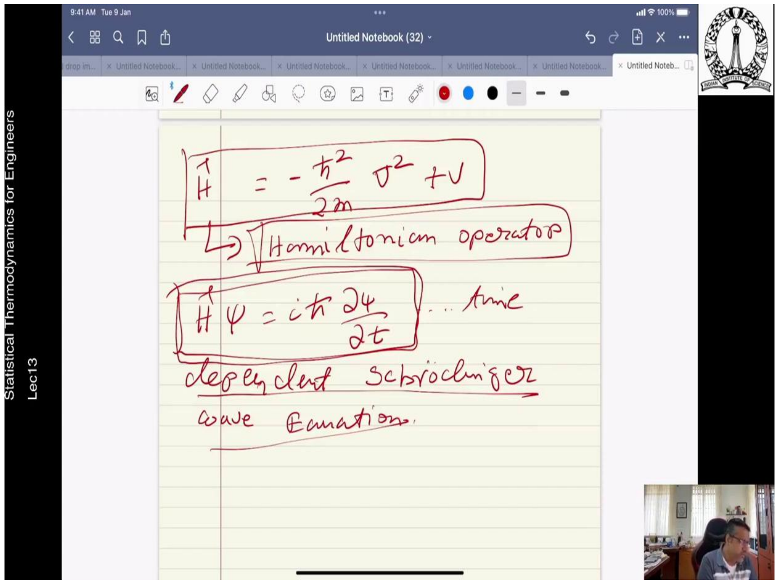
$$-\frac{\hbar^2}{2m}\ddot{X}T + VXT = \mathcal{E}XT \qquad (XT = \psi)$$

or, $$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = \mathcal{E}\psi \qquad (*)$$

General soln.

$$\psi(x,t) = Ce^{i(kx-\omega t)}$$

$\frac{\partial\psi}{\partial t} = Ce^{i(kx-\omega t)}(-i\omega)$



Now, if we define H hat, H hat is defined as minus h bar square by 2m the laplace plus V. So, this particular operator is called Hamiltonian operator, so, therefore, once you have passed it in terms of the Hamiltonian operator is equal to i h bar d psi at dt. So, this is the time dependent, Schrodinger wave equation, so let us see that if we have missed anything here.

So, once again it is a heuristic way of understanding the whole thing. So, we have done a lot of math, just let us just a very quick recap. So, we had, atomic dimensions matter, should behave like a wave. So, therefore, similar wave formulation can be done for matter. So, Schrodinger by taking analogy from the one dimensional electric field equation, Schrodinger defined the wave function or matter waves and of course, this is the wave function this is the wave equation many solutions are possible, but we take the most well known solution, which is this and then what we did we did what we call separation variables and separation of variables. So this is the most common solution as we say, so we did a separation of variable, so this is very spatial and temporal, so this was the solution, this was the solution that we got a solution.

So, the total energy was taken as kinetic energy plus potential energy. So, this is given in terms of momentum for matter waves the K can be written like this in terms of the linear momentum and so, then we went through the motion, we substituted this and when we also get the, multiply this by the T, the time dependent portion and we got this was expression, once we got that expression, we took a temporal derivative we took the temporal derivative and we showed that this is what it is the temporal derivative is given as this.

Now, we took this temporal derivative now, and we substituted it here because this was exactly the same as this. So, this part that is basically substituted, that is what we have done and therefore, we get this and now, then we say that this let us consider this as a Hamiltonian operator and this Hamiltonian operator that locates the final form of the equation, which is basically time dependent Schrodinger's wave equation.

So, this is a heuristic development does not constitute a proof of this Schrodinger's wave equation, but instead a rational, for its formulation, ultimately its veracity depends solely on its utility, how well it is able to address the atomic of the molecular dynamics.

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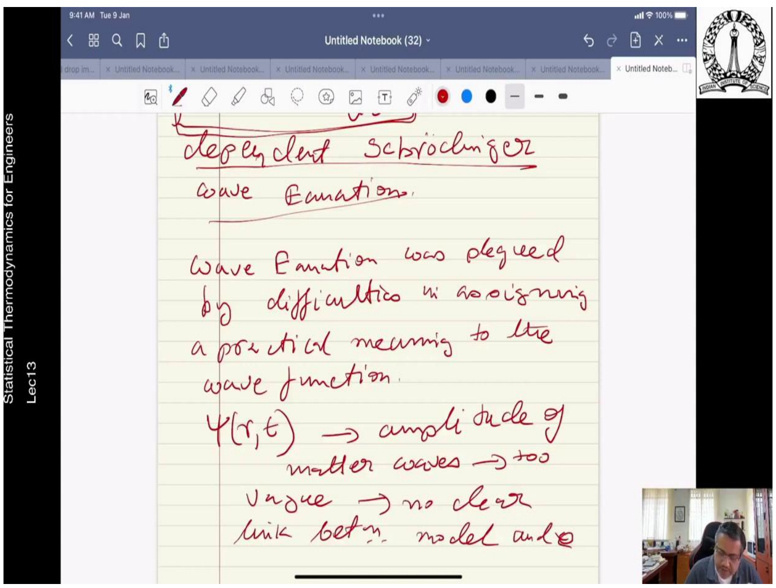

So, at the same time at the same time we but there is there is a nice using de-Broglie's platform we have been able to get to this time dependent Schrodinger's analysis. Now that, now, the problem that plagued this particular wave equation so, this wave equation was plagued by difficulties, basically the difficulties came in assigning, practical meaning, to the wave function, we could not assign practical meaning to the wave function it was like that so, like for example, if we say that this is the wave function, and then we exceed (())(18:53) say defining as the amplitude say this is the amplitude, of say this is the amplitude of matter waves, it is too vague, to vague the definition, and did not offer a clear link between, model and experiment.

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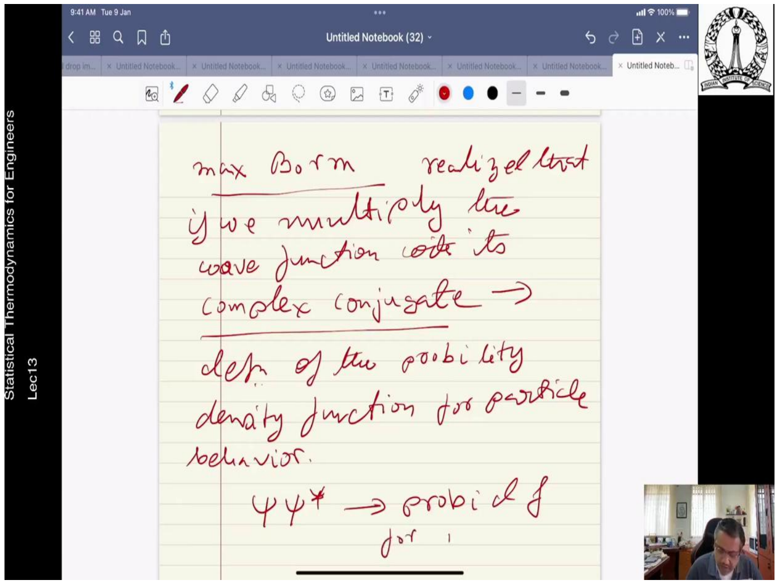

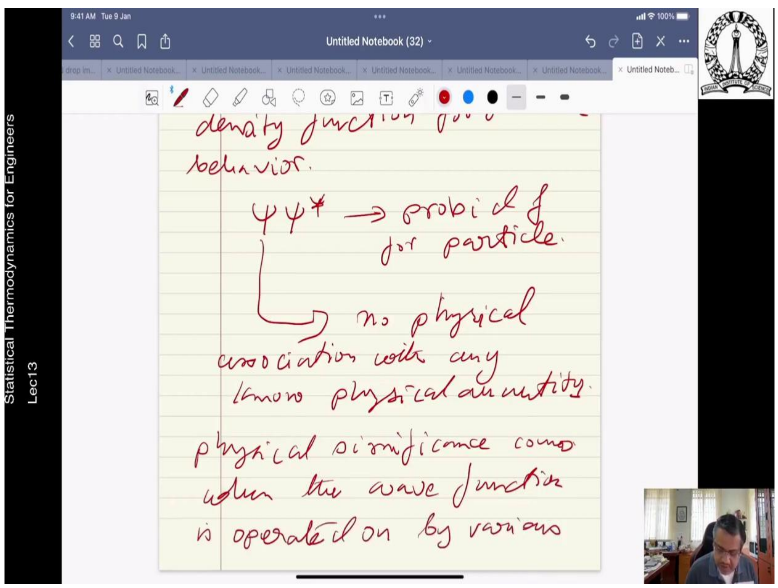

So, let us do that there is no clear link between the model and experiment. So, it is offered really no real insights and it was a there was no physical meaning to it. So, what happened after that was that Max Borm the German physicist ultimately provided a rational to it, so he said he ultimately realized that if we multiply the wave function with its complex conjugate it basically defines, it basically let us do a definition of the probability density function, to a probability density function for particle behavior.

Provided are, so itself it is not it does not mean anything, but it provided a probability so basically to multiply psi by its complex conjugate psi star this offers the probabilistic probability probability density (())(21:19) basically for particle. This is what (())(21:25) but itself, this offers no physical association, no physical association with in known physical forms. So, that was the problem that it did not provide with a physical rational (())(21:59).

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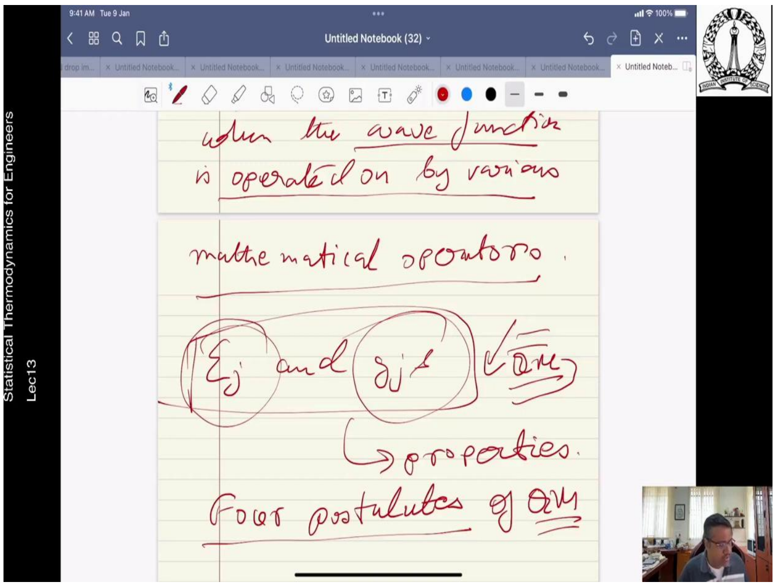

So, the physical significance comes when the wave function is operated on by various mathematical operators, that is where the physical significance, you understand see only the wave function which is operated by different mathematical operators then only we get a physical significance associated with it. So, the general procedures for identifying, assessing solutions to this Schrodinger wave equations are delineated by basically four basic postulates.

So, we are going to deal with the postulates in the next class because there are a set of postulates, but postulate one you can easily see that basically psi star into psi or the wave function multiplied this complex conjugate, is the probability. So, that we already know, we ordered. So, that will be some kind of the first postulates but, it can see once a mathematical operator when the wave function is associated with a mathematical operator then only we get physical significance of that particular quantity.

So, it is almost like a waiting, weightage fraction, some kind of a probability cloud for a particular variable, whatever the variable be it and then only the physical significance arises for any dynamic variable, so, whatever that dynamic variable can be. So, so, in this particular in this particular thing, what we have learned so, far, if we go to the four postulates is that de-Broglie hypothesis that matter wave should be present because it lights can behave like a particle why not matter behave like a wave. So, that set the stage and he showed that for electrons and we showed it by an example, that for an electron in that atomistic atomic dimensions the matter waves are very important because they are almost of the same order as the radii.

So, that actually set the stage for Schrodinger to device a more universal framework, so to say. So, that all these things can be reconciled under one framework and not have this part mechanical part classical approach as was done by Bohr's model. So, there the wave mechanics took ideas from an electric field theory and then it is applied for an arbitrary quantity which is called the wave function the significance of which was done later on by Max Borm, who said, this probably indicates a mathematical probability a mathematical probability of a particle. And then once it is, this is applied to different dynamic variables position momentum, etcetera, then it gives rise to the average position average momentum of all these particles combined. So, and that can be now further used to calculate energies and other types of stuff.

So, so, we can see the progression, there was a historical perspective how the quantum mechanics evolved, because, one had to identify those ejs and gjs if you remember for calculating properties, so, that was the first thing that we did, and so, to get these EJs and GJs, we follow this very elaborate, elaborate understanding of quantum mechanics because this can only come from quantum mechanics as we have said again and again.

So, therefore, we started with Bohr, we showed how the classical model was inappropriate. So, then we have the maxima, how bohr actually, how Einstein used to show the duality than the de-Broglie came into the picture, then how bohr showed it was quantized, orbits are quantized to the angular momentum was quantize. So, the radius which the electrons will recide are also quantized. So, this sets the stage that from an electromagnetic perspective how the wave equation can be used, now, as a cornerstone of quantum mechanics.

So, this is, so in the next class what we are going to do, we are going to advocate four postulates these postulates are postulates of quantum mechanics and then we are going to see how these postulates can be used subsequently to find out about the different dynamic variables and how it can be applied in quantum mechanics analysis that we will do in the next few classes, so, thank you and this is the end of lecture 13.