Statistical Thermodynamics for Engineers
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Lecture 19
The Postulates of Quantum Mechanics

So, welcome to lecture number 14 of Statistical Thermodynamics for Engineers.

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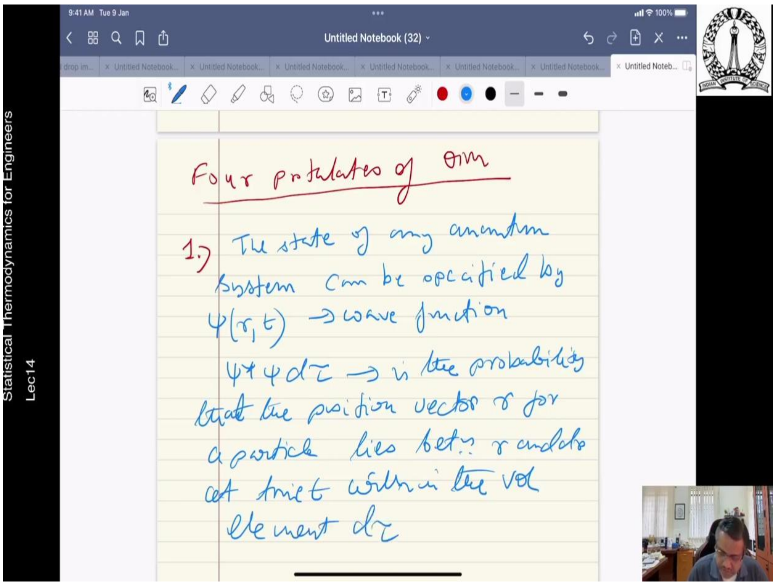
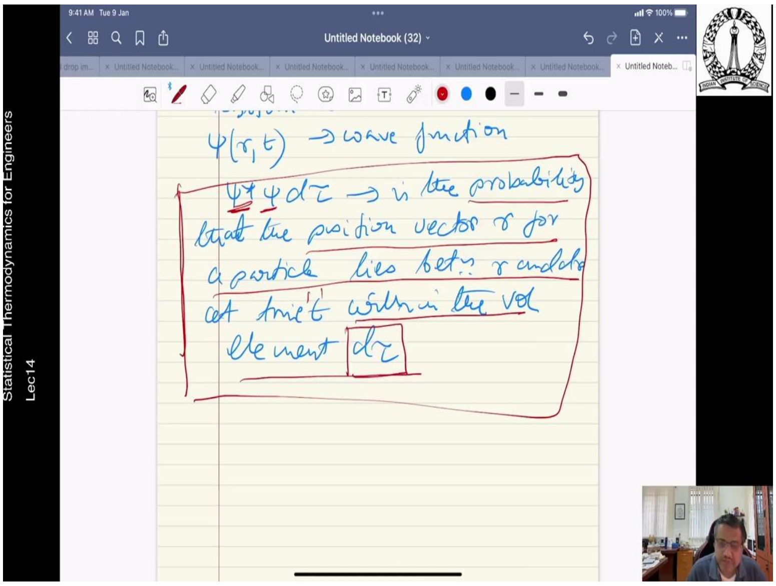


Four postulates of QM

1.) The state of any quantum system can be specified by $\psi(r,t)$ → wave function

$\psi^* \psi \, d\tau$ → is the probability that the position vector r for a particle lies betn r and r+dr at time t within the vol element $d\tau$



$\psi(r,t)$ → wave function

$\psi^* \psi \, d\tau$ → is the probability that the position vector r for a particle lies betn r and r+dr at time t within the vol element $\boxed{d\tau}$

So, as stated before, we said that we are going to cover four postulates of quantum mechanics QM which will be essential for our stat thermo course(())(0:26). So, the first postulate, a postulate number 1 is that the state of any quantum system and this is what we covered in the previous class also any quantum system can be specified by psi r comma t which is quite a function which is called the wave function this is what Schrodinger proposed, the quantity psi into d tau is the probability that the position vector r for a particle lies between r and dr at time t within the volume element d tau.

So, this is the first postulate that the conjugate multiplication of the wave function and its complex conjugate is the probability that the position vector r for a particle lies between r and dr at any time t within the volume element d tau. So, this is the first postulate.

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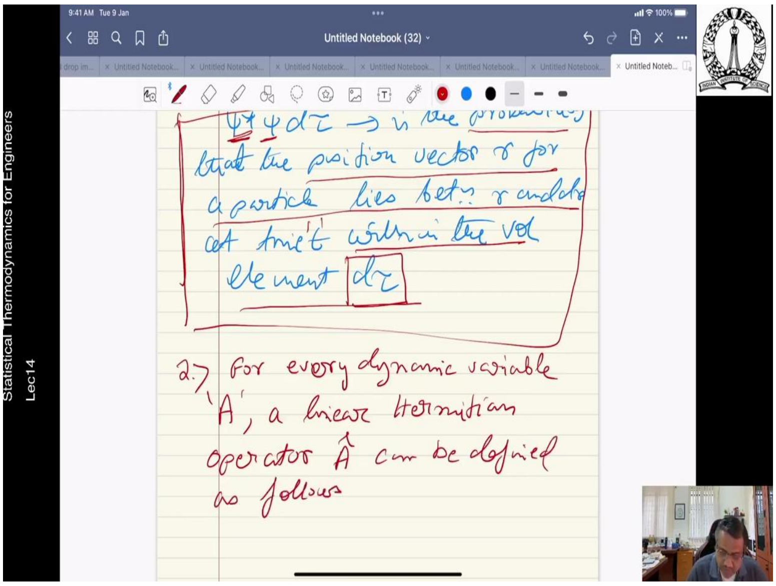

$\Psi^*\Psi\, d\tau \rightarrow$ is the probability that the position vector r for a particle lies betn r and dr at time t within the vol element $\boxed{d\tau}$

2) For every dynamic variable 'A', a linear Hermitian operator $\hat{A}$ can be defined as follows

The second postulate has got sub parts. So, let us take for every dynamic variable and A let us say A is any dynamic variable that we can talk about linear Hermitian operator A hat can be defined as follows.

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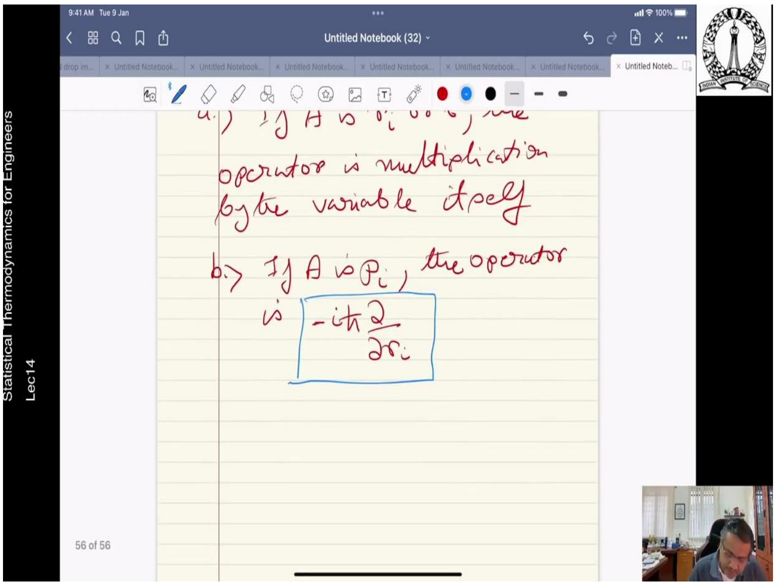

a.) If A is [illegible], the operator is multiplication by the variable itself

b.) If A is p_i, the operator is $\boxed{-i\hbar \frac{\partial}{\partial r_i}}$

And what are those linear Hermitian operators, now see if A is r i or t then the operator is multiplication by the variable itself so, we will see what Hermitian operators are we will do a separate class altogether where we will see that what are those Hermitian operators, what are the operators in general and what are linear Hermitian operators in general. So, but this is the second postulate and out of that, so, every dynamic variable, we can define a linear Hermitian operator which is A hat. Now, then let us look at b, b is if A is p i which is basically the linear momentum the operator is minus i h prime d pi. So, this is the operator.

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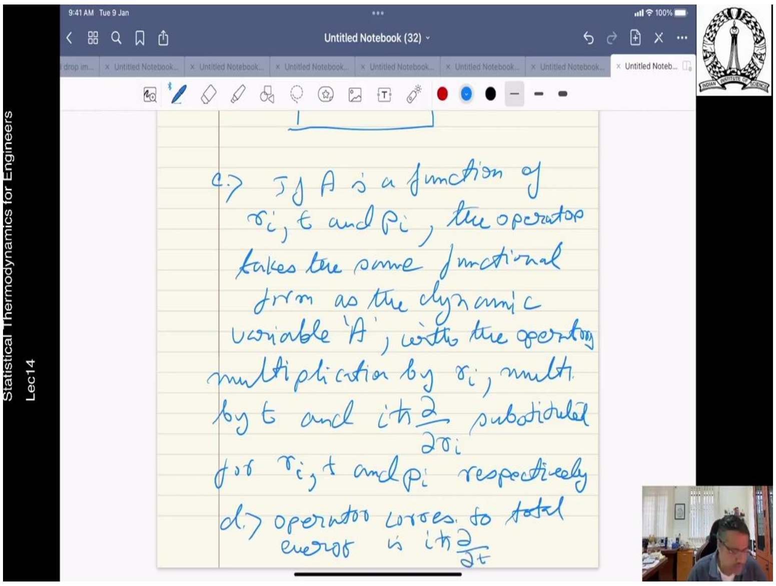

c.) If A is a function of r_i, t and p_i, the operator takes the same functional form as the dynamic variable 'A', with the operators multiplication by r_i, mult. by t and $i\hbar\frac{\partial}{\partial r_i}$ substituted for r_i, t and p_i respectively

d.) operator corres. to total energy is $i\hbar\frac{\partial}{\partial t}$

Now, c, number c, if A is a function of r i t and p i then the operator takes same functional form listen to this carefully same functional form as the dynamic variable. A functional form is the same as functional to dynamic variable A with the operators multiplication by r i, multiplication by t and i h bar by d by dr i substituted for r i, t and p i respectively so, and lastly the operator for energy operator corresponding to total energy is i h bar d by dt. So, this is the second postulate. So, this is about operators the linear Hermitian operators.

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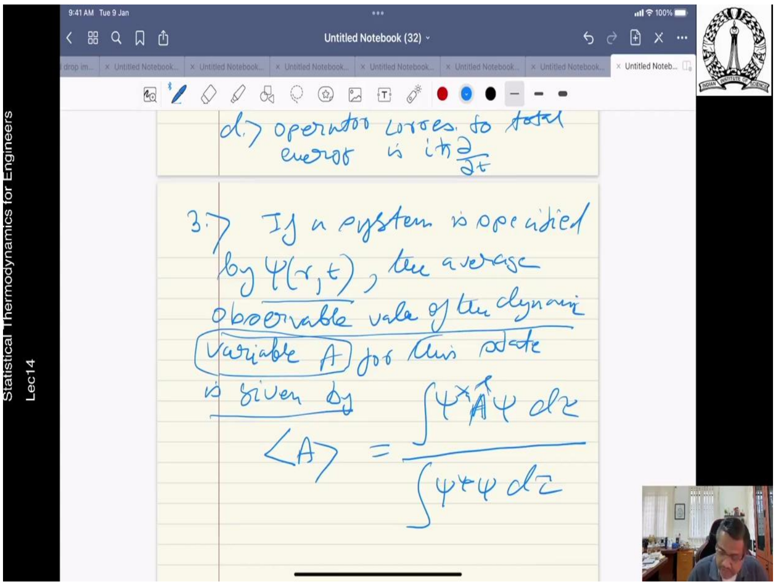

d.) operator corres. to total energy is $i\hbar\frac{\partial}{\partial t}$

3.) If a system is specified by $\psi(r,t)$, the average observable value of the dynamic variable A for this state is given by

$$\langle A\rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

Postulate number 3, if a system is specified by psi r comma t the average observable value of the dynamic variable A for this state is given by A average nothing but acting on this, d tau divided by. So, if a system is specified by this with the average observable value of any dynamic variable A which is in this space is given by this. So, there is an operator. This is the operator, not A and which is acting on the wave function and then you have this and divided by the total probability. So, probability across the entire volume for any given time.

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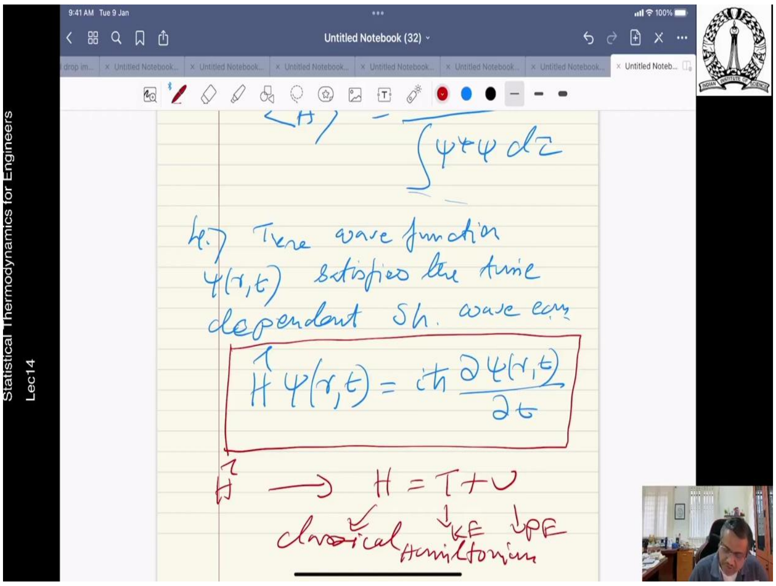

4.) The wave function $\psi(r,t)$ satisfies the time dependent Sh. wave eqn

$$\boxed{\hat{H}\psi(r,t) = i\hbar\frac{\partial \psi(r,t)}{\partial t}}$$

$\hat{H} \longrightarrow H = T + V$

classical Hamiltonian KE PE

Now, the fourth postulate the wave function psi r comma t satisfies the time dependent Schrodinger wave equation which is basically this operator r comma t equal to i h bar psi r comma t divided by. So, this is the, this is this we already know where the Hamiltonian operator h bar corresponds to the classical Hamiltonian operator. That is the classical Hamiltonian operator which is which acts on T plus, so, this is like the correspondence to the classical Hamiltonian. T is kinetic energy, V is the potential energy. So, this is a classical Hamiltonian classical Hamiltonian.

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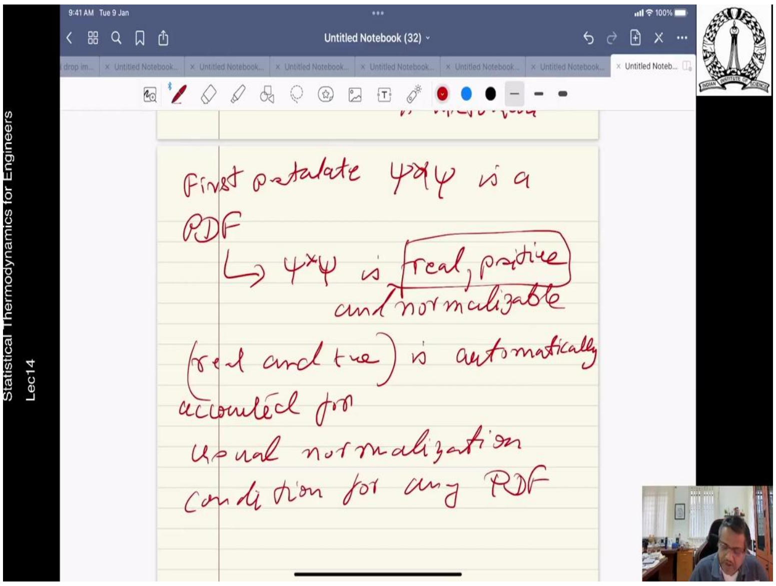
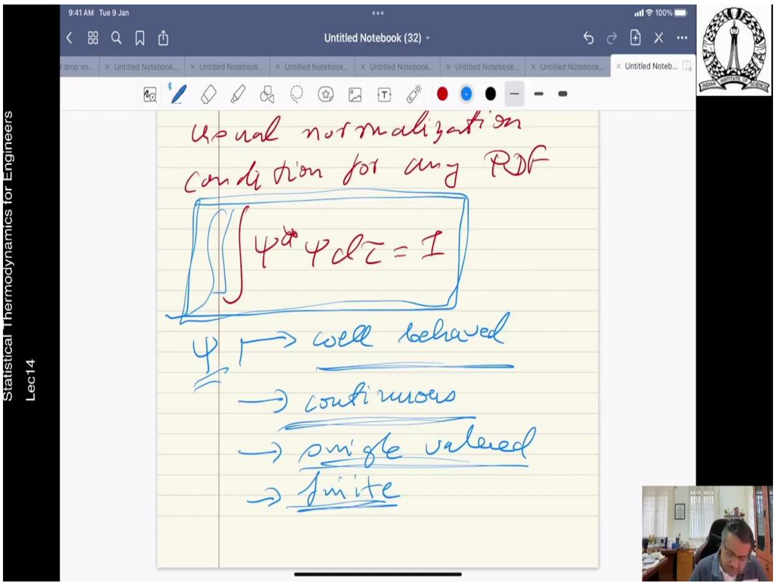


First postulate $\psi^*\psi$ is a PDF

↳ $\psi^*\psi$ is $\boxed{\text{real, positive}}$ and normalizable

(real and +ve) is automatically accounted for

usual normalization condition for any PDF



usual normalization condition for any PDF

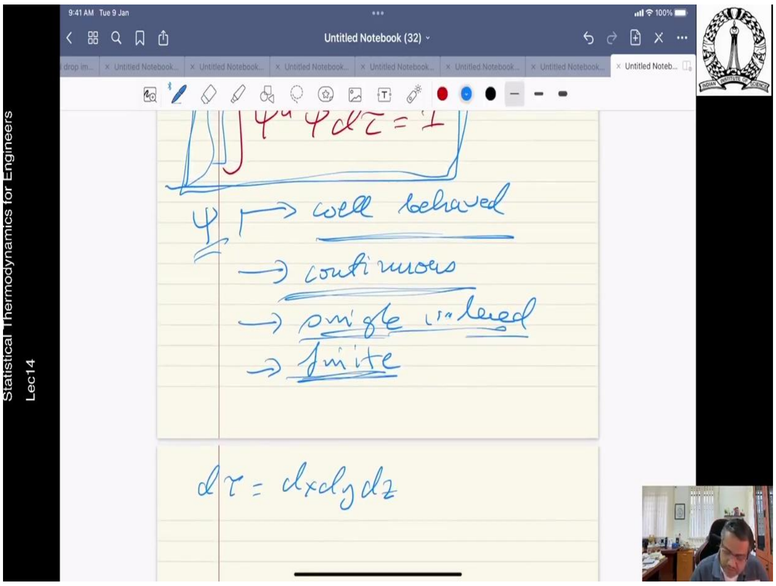
$$\boxed{\iiint \psi^* \psi \, d\tau = 1}$$

ψ → well behaved

→ continuous

→ single valued

→ finite



$\iiint \psi^* \psi \, d\tau = 1$

ψ → well behaved

→ continuous

→ single valued

→ finite

$d\tau = dx\,dy\,dz$

So, these are the four postulates of quantum mechanics. So, these four postulates require some additional stuff as well. So, as we can see, the first postulate essentially dictates that psi star into psi is a PDF or a probability density function. So, this indicates further few things. So, this indicates that this quantity that means psi star by psi is actually real must be positive and should be normalizable. So, the real and the positive part is automatically satisfied because you are any variable when it is multiplied, which is complex conjugate is always real and positive. So, real and positive is automatically accounted for because product of a variable with its complex conjugate is always real and positive.

The usual normalization condition for any PDF any PDF it's basically integral psi star psi d tau is equal to 1. So, this essentially warrants two other things that the wave function psi should be well behaved because you are integrating. It is continuous single valued and finite. So, the psi automatically has so this requires this particular thing requires that the wave function must be well behaved. It must be continuous. It must be single valued and it must be finite to begin with.

So, the volume integrals are basically, this is basically a triple integral in three dimensional system, this is basically three integrals this is it is over the in Cartesian coordinate system of course, d tau is basically dx dy dz. So, it all subsequent integrations coupling over the region defined by the finite values of this. So, as you can see, this has to be finite, well behaved, single valued, continuous and everything that you can think of. So, and it is a triple integral essentially.

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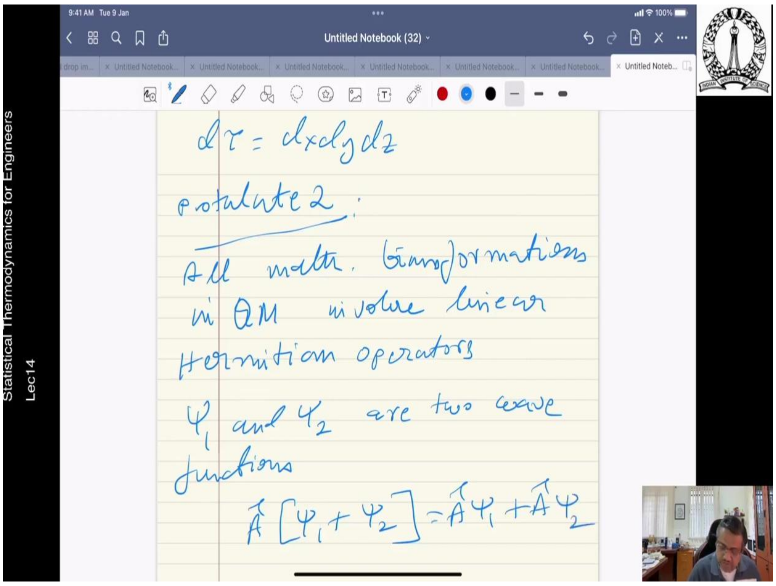


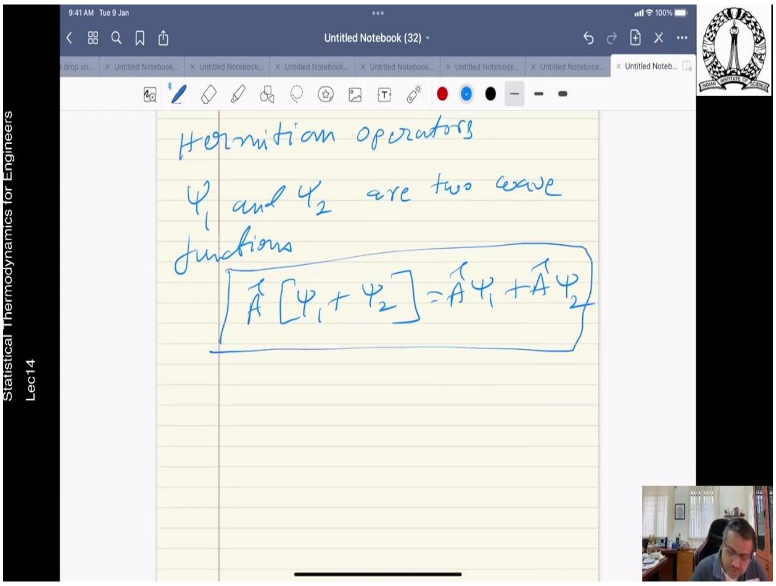
$d\tau = dx\,dy\,dz$

postulate 2 :

All math. transformations in QM involve linear Hermitian operators

ψ_1 and ψ_2 are two wave functions

$$\hat{A}[\psi_1 + \psi_2] = \hat{A}\psi_1 + \hat{A}\psi_2$$



Hermitian operators

ψ_1 and ψ_2 are two wave functions

$$\boxed{\hat{A}[\psi_1 + \psi_2] = \hat{A}\psi_1 + \hat{A}\psi_2}$$

So, what about postulates 2, postulate 2, the one that you have did that all mathematical transformations in QM in quantum mechanics involve linear Hermitian operators, operator theory and that is we are going to cover that in a separate lecture altogether. So, if we have two wave functions, the psi 1 and psi 2 are two wave functions. Then operator A acting on psi 1 plus psi 2 is basically you can write it as psi 1 plus psi 2. So, this is what linearity actually dictates. So, this is this is a condition that is usually followed.

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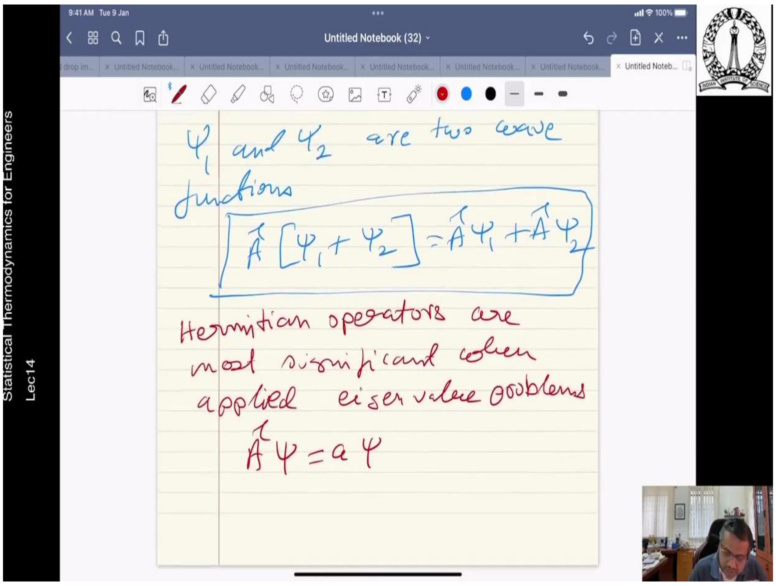

ψ_1 and ψ_2 are two wave functions

$$\boxed{\hat{A}[\psi_1+\psi_2] = \hat{A}\psi_1 + \hat{A}\psi_2}$$

Hermitian operators are most significant when applied eigen value problems

$$\hat{A}\psi = a\psi$$

The Hermitian operators are however has another significant Hermitian operators proved to be more significant are most significant when they are applied to eigenvalue problems. So, I request you guys to go and tell a little bit of eigenvalues if you brush up things from your undergraduate math or graduate level math. So, eigenvalue problem and the eigenvalue problem is this acting on the wave function is equal to a psi.

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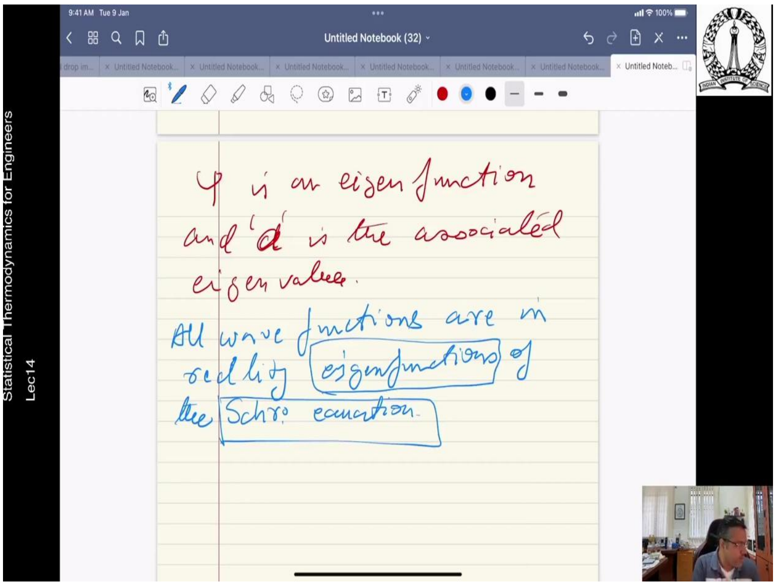

ψ is an eigen function and 'a' is the associated eigen value.

All wave functions are in reality $\boxed{\text{eigenfunctions}}$ of $\boxed{\text{the Schro equation.}}$

Now, here of course, as you can see, psi is an eigen function and a this a that you see here this a is associated eigenvalue. So, you can pause a little bit and you can think, does this mean that the Schrodinger wave equation is actually an eigenvalue problem? It is actually a disguised eigenvalue problem. So, all wave functions that we see all wave functions are in reality all wave functions are in reality eigen functions of the Schrodinger equation. So, all wave functions are in reality eigen functions of the Schrodinger equation, so, that is good.

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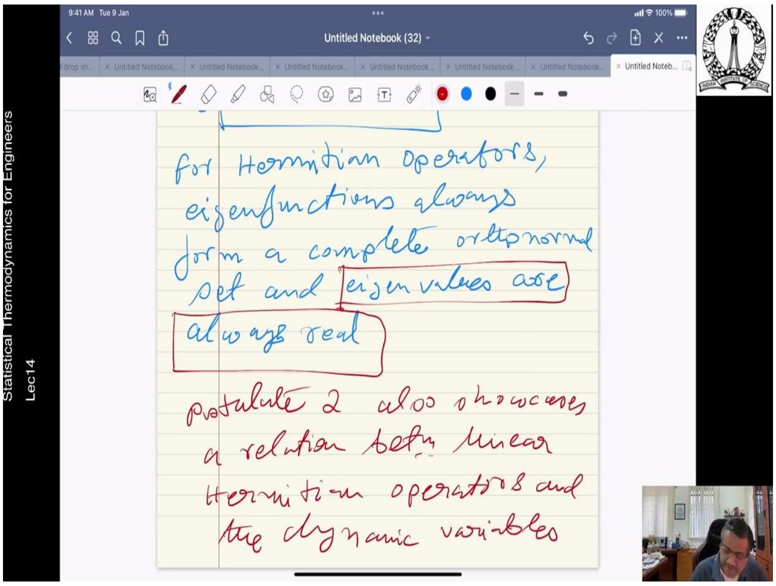

for Hermitian operators,
eigenfunctions always
form a complete orthonormal
set and eigen values are
always real

postulate 2 also showcases
a relation betn linear
Hermitian operators and
the dynamic variables

So, for Hermitian operators, Eigen functions, they always form a complete orthonormal set and Eigen values are always real, Eigen values which means a are always real that is important are always real. So, as a result, the normalization condition is essentially guaranteed by the Hermitian nature of all quantum mechanical operators because the quantum mechanical operators are all Hermitian in nature normalization and the real nature of the values always are always ensured(())(18:49).

So, there is also postulate 2 also showcases a relation between relation between a linear Hermitian operators and the dynamic variables, that we are interested in. So, association comes from applying the wave equation to matter waves by the de Broglie hypothesis so on and so forth. So, it is to find the real set of Hermitian operators is not always very easy, which operator is associated with which dynamic variable and so the difficulties mainly arises is basically because the multiplication is inherently commutative for dynamic variables, but not so for the Hermitian operators. The multiplication of Hermitian operators are not always commutative. We will see that in a companion lecture, why that is so.

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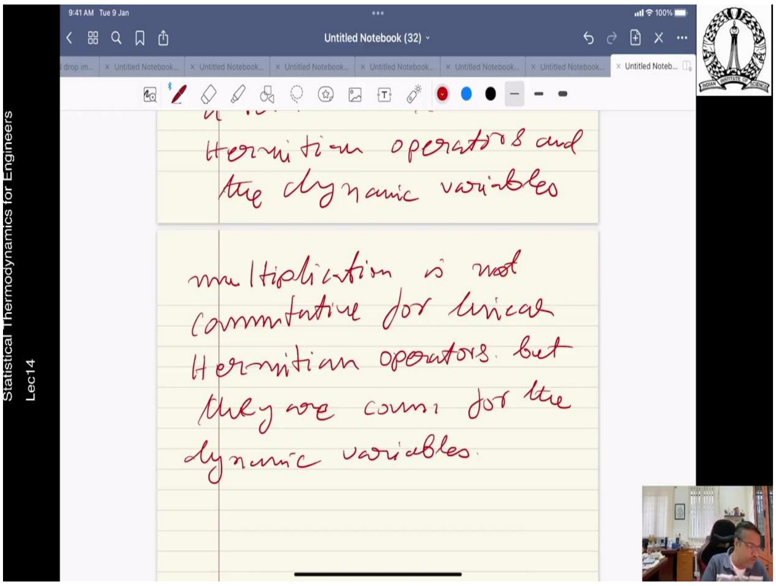
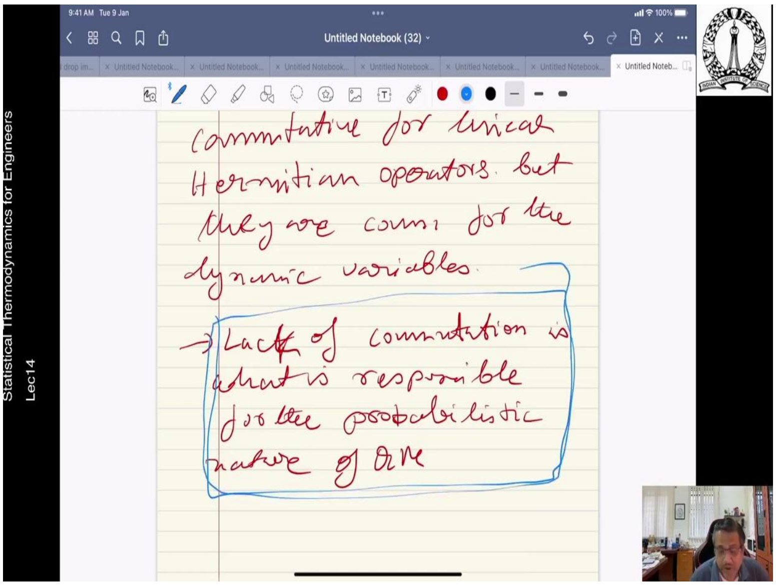


Hermitian operators and the dynamic variables

multiplication is not commutative for linear Hermitian operators. but they are comm: for the dynamic variables.



commutative for linear Hermitian operators. but they are comm: for the dynamic variables.

→ Lack of commutation is what is responsible for the probabilistic nature of QM

So, multiplication, we can just note it down here multiplication is not commutative for linear Hermitian operators, they are commutative for the dynamic variables but they are commutative for the dynamic variables.

So, actually this lack of commutation is also responsible we will show later. This lack of commutation is what is responsible for the probabilistic nature of a quantum mechanical system QM. This is the important point. So, putting it in a box.

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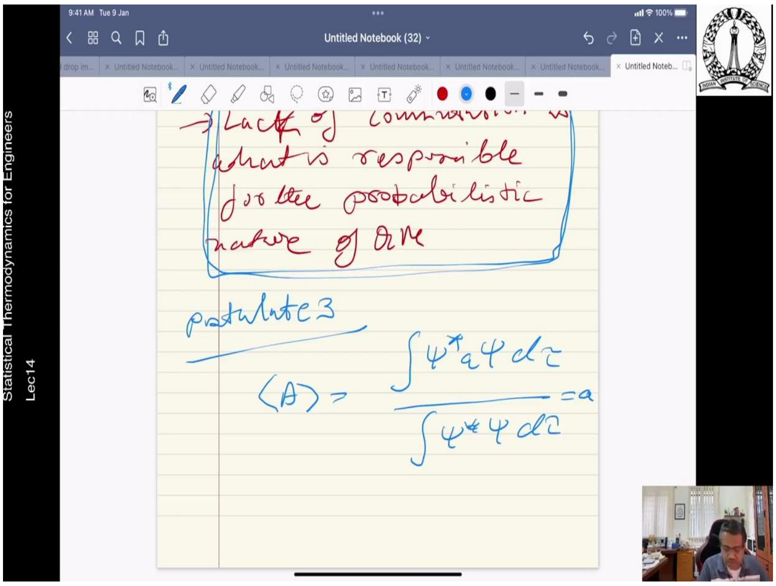

→ Lack of commutation is what is responsible for the probabilistic nature of QM

postulate 3

$$\langle A \rangle = \frac{\int \psi^* a \psi \, d\tau}{\int \psi^* \psi \, d\tau} = a$$

So, the postulate 3 now, I mean to postulate 3, so, we have covered now postulate 1, 2. Postulate 3 means that the physical means physical observations to both PDF defined by postulate 1, linear Hermitian operator by postulate 2 and requires that a operate on wave function and not on the conjugative wave function. So, it is basically means this a psi d tau divided by equal to a something like this, where the denominator is force it is previously normalized so, we do not need that. We know that the mean collapses to an Eigen value of its associated Hermitian operators.

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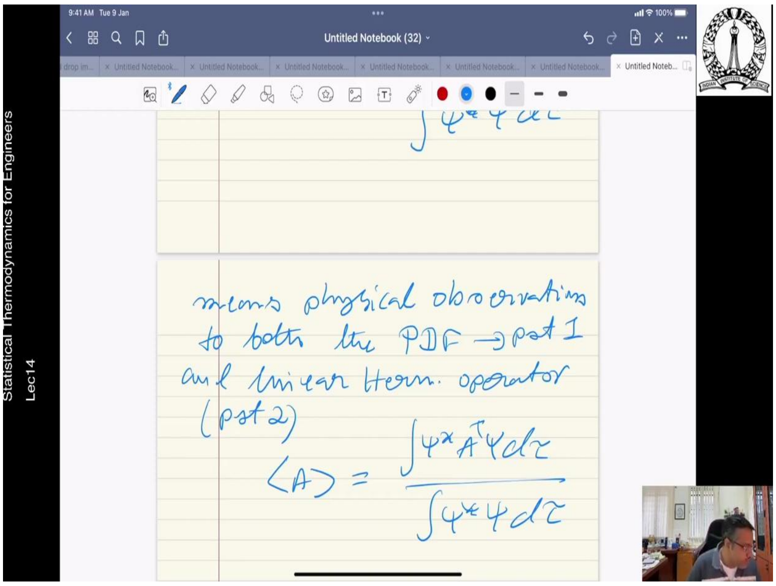
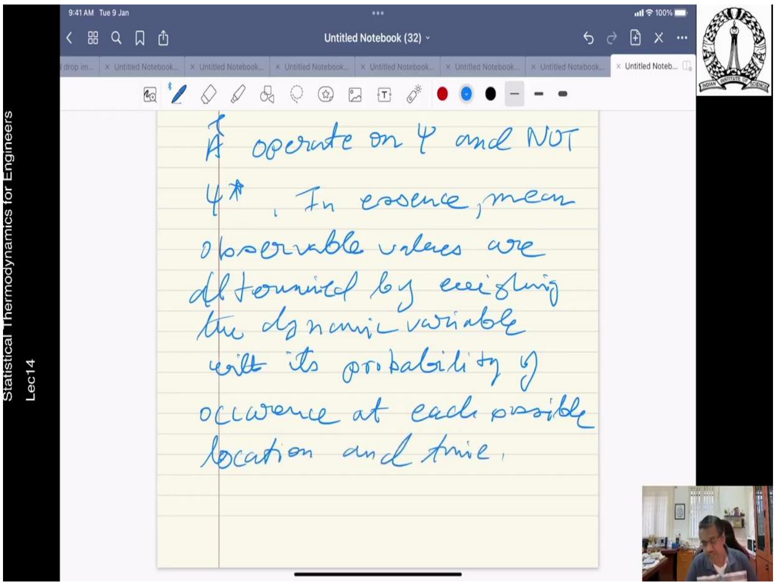


means physical observations to both the PDF → post 1 and linear Herm. operator (post 2)

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$



$\hat{A}$ operate on ψ and NOT ψ^*, In essence, mean observable values are determined by weighing the dynamic variable with its probability of occurrence at each possible location and time.

So, just to take a little bit of a pause, and let us try to work it out in a little bit more details that this means postulate 3 means the physical observations to both PDF as it is defined by postulate 1 and the linear Hermitian operator by postulate 2 basically postulate 2 (())(23:33) Hermitian operator by postulate 2 for a particular dynamic variable. So, based on this that is if you recall that A we wrote it as equal to star A hat tau divided by this we wrote. So, based on this particular equations, the resulting formalism requires this requires that A hat should operate on psi and not psi star. In essence, what does this imply, in essence mean observable values are determined by weighing the dynamic variable with its probability of occurrence at each point i or else at each possible location and there is like a weighting fraction like what we saw in the statistics this like weight.

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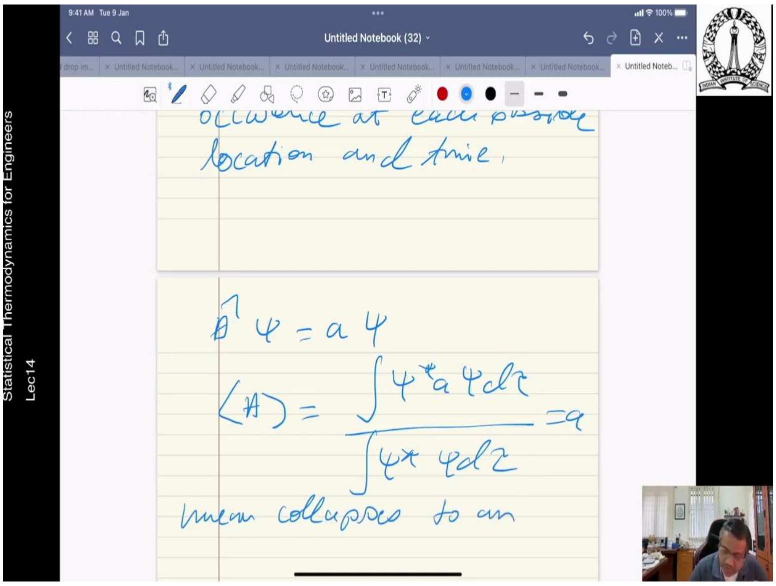
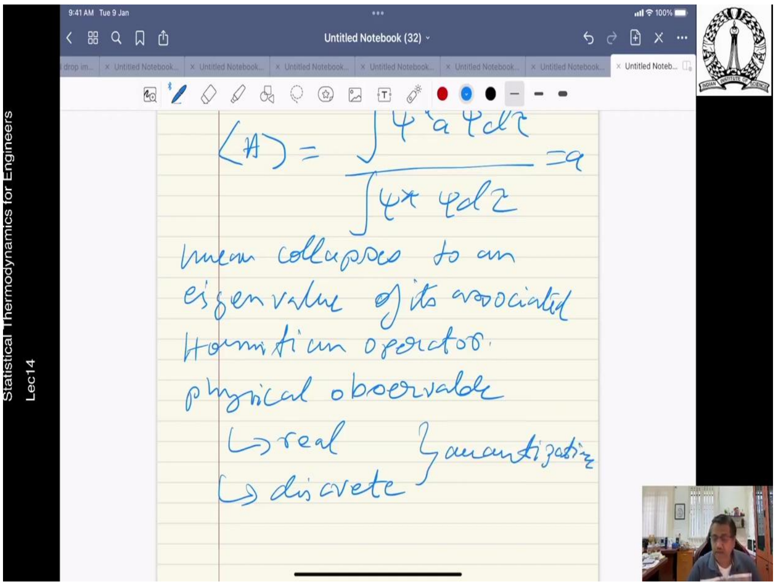


occurrence at each possible location and time.

$$\hat{A}\psi = a\psi$$

$$\langle A \rangle = \frac{\int \psi^* a \psi \, d\tau}{\int \psi^* \psi \, d\tau} = a$$

mean collapses to an



$$\langle A \rangle = \frac{\int \psi^* a \psi \, d\tau}{\int \psi^* \psi \, d\tau} = a$$

mean collapses to an eigenvalue of its associated Hermitian operator.

physical observable

↳ real } quantization

↳ discrete

For a linear Hermitian operator, which satisfies however this a equal to this, we also just observe that a is equal to a star this is what we wrote just a few minutes ago a. Here we note that the mean collapses to an Eigen value of its associated Hermitian operator, so, as a result, the physical observable, as you can see, must be both must be real and discrete because it is an eigenvalue. It collapses to an eigenvalue value such behavior contitutes the genesis of quantization, this is what is the genesis of quantization.

So, you can see how the quantization comes into the picture, because it collapses to an eigenvalue, it collapses the mean collapses to an eigenvalue of the associative Hermitian operator that we are dealing with, all the associated affirmation operator of that dynamic variable.

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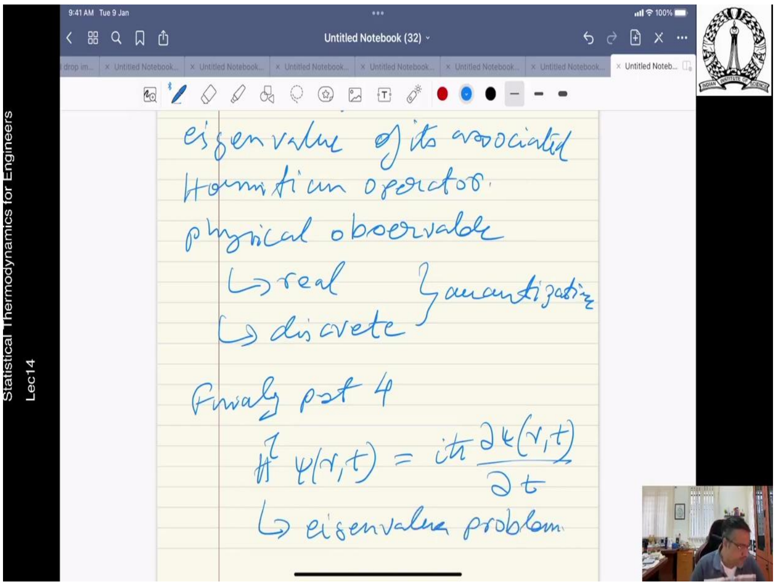

eigenvalue of its associated Hermitian operator.

physical observable

↳ real } quantization

↳ discrete

Finally part 4

$$\hat{H} \psi(r,t) = i\hbar \frac{\partial \psi(r,t)}{\partial t}$$

↳ eigenvalue problem

Finally, finally, postulate 4, identifies equation by 5.32, which is basically this which is basically this is a fundamental equation in quantum mechanics, this is the fundamental equation in quantum fundamental law of quantum mechanics. So, time dependent Schrodinger wave equation in reality is an eigenvalue problem to begin with.

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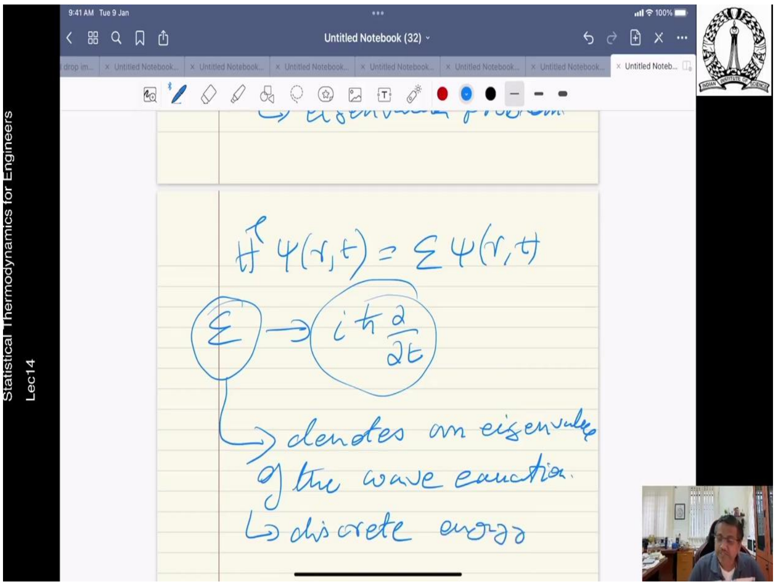


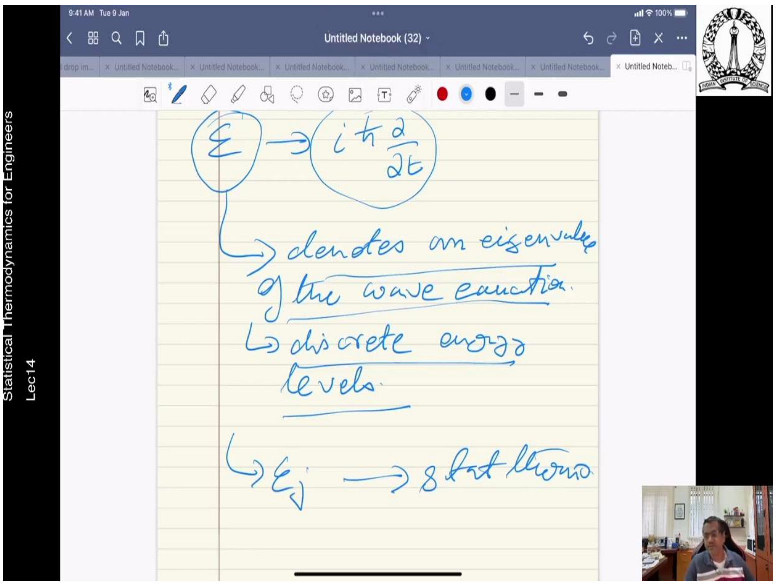
$\hookrightarrow$ eigenvalue problem

$$\hat{H}\psi(r,t) = \varepsilon\psi(r,t)$$

$$\boxed{\varepsilon} \rightarrow \boxed{i\hbar\frac{\partial}{\partial t}}$$

$\hookrightarrow$ denotes an eigenvalue of the wave equation.

$\hookrightarrow$ discrete energy



$$\boxed{\varepsilon} \rightarrow \boxed{i\hbar\frac{\partial}{\partial t}}$$

$\hookrightarrow$ denotes an eigenvalue of the wave equation.

$\hookrightarrow$ discrete energy levels.

$\hookrightarrow \varepsilon_j \longrightarrow$ 8 [illegible]

So, this equation can also be written as remembering that the operator for energy can be also written as it is remembering the operator for energy is, this is energy. So, that is the operator. So, energy denotes an Eigen value of the Schrodinger wave equation, so this denotes if you look at it, it is like an eigenvalue problem denotes and so, the energy denotes an eigenvalue of the wave equation. This is eliminating. So, this further tells you that the energy levels are discrete energy levels, we will thus so the discrete energy levels. So, the wave equation offers us that energy is an eigenvalue of the wave equation and therefore, it should have discrete energy levels the discrete nature is automatically comes out of it.

So, therefore, on our way to calculate the energy levels because we need to calculate these energy levels for step1. So, that is the main purpose that we have done over here. We have gone over the four postulates and we have shown what those postulates are, special consideration on the linear Hermitian operator that you see over here. Thank you so much.