Statistical Thermodynamics for Engineers
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Lecture 20
The Steady State Schrodinger Equation: Single Particle Analysis

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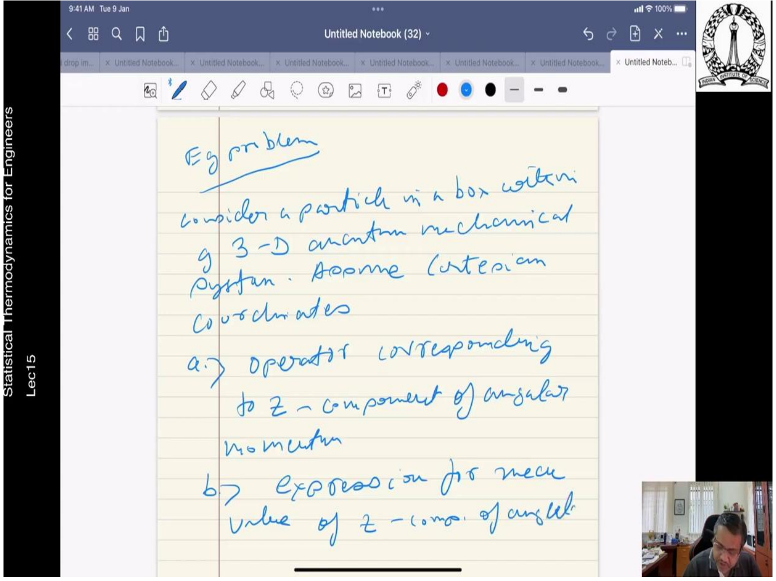
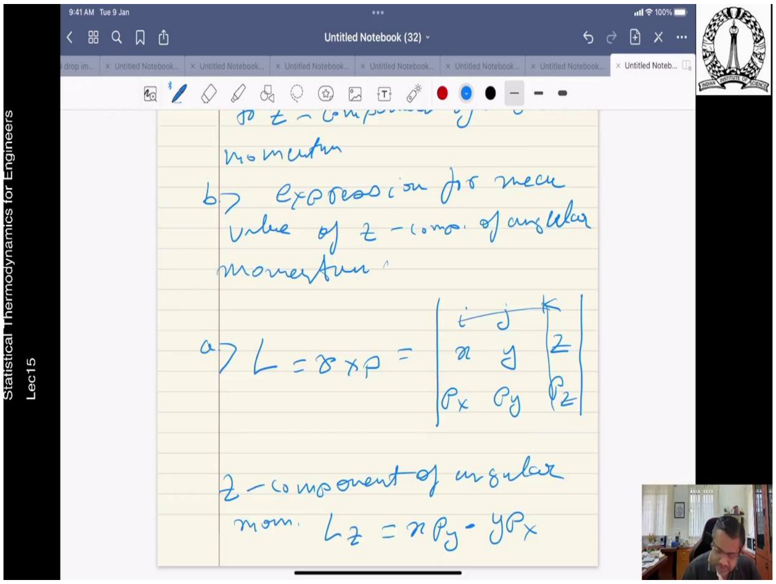


Eg problem

consider a particle in a box within 3-D quantum mechanical system. Assume Cartesian coordinates

a.) operator corresponding to z-component of angular momentum

b) expression for mean value of z-comp. of angular

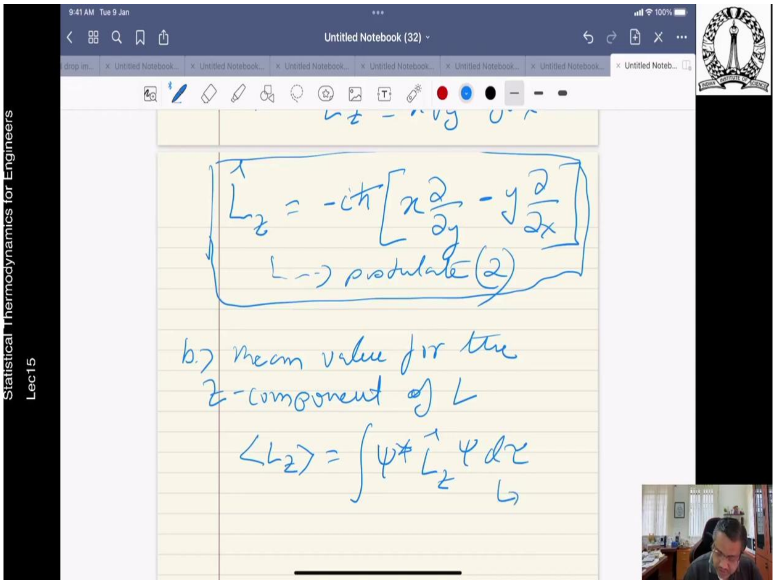


momentum

b) expression for mean value of z-comp. of angular momentum

a) $L = r \times p = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$

z-component of angular mom. $L_z = x p_y - y p_x$

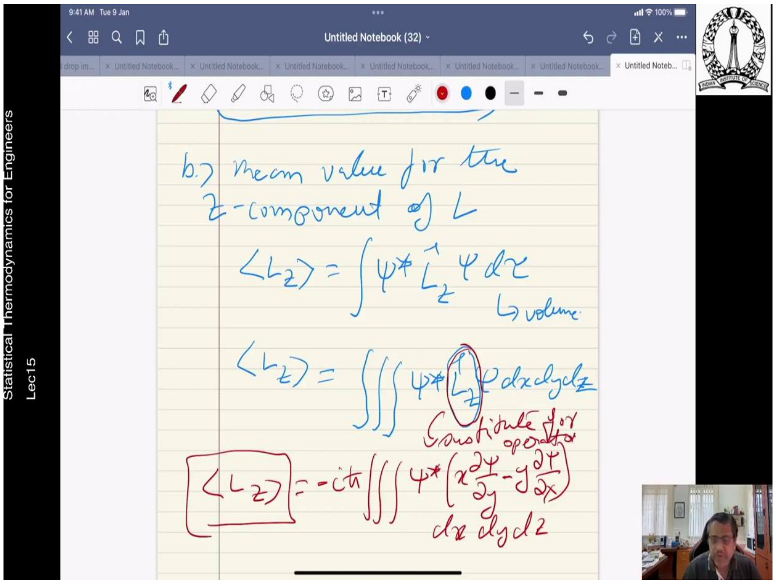


$$\boxed{\hat{L}_z = -i\hbar\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right]}$$

↳ postulate (2)

b.) mean value for the z-component of L

$$\langle L_z\rangle = \int \psi^* \hat{L}_z \psi \, d\tau$$



b.) mean value for the z-component of L

$$\langle L_z\rangle = \int \psi^* \hat{L}_z \psi \, d\tau$$

↳ volume

$$\langle L_z\rangle = \iiint \psi^* \hat{L}_z \psi \, dx\,dy\,dz$$

substitute for operator

$$\boxed{\langle L_z\rangle} = -i\hbar \iiint \psi^* \left(x\frac{\partial \psi}{\partial y} - y\frac{\partial \psi}{\partial x}\right) dx\,dy\,dz$$

So, welcome to lecture number 15. In this particular lecture, we already have seen the four postulates. In this lecture let us start with an example problem. So, let us consider in this example consider a particle in a box within 3D quantum mechanical system. So, you can assume our Cartesian coordinates. So, first and foremost we need to determine the operator corresponding to Z component angular momentum, fair enough and b will be what will be the mean value of expression for the mean value of Z component angular momentum.

So, let us look at a the problem. Number a what is angular momentum? Angular momentum is r into p, p in the linear momentum. So, if you put this in a matrix form j k its Cartesian x, y, z, r has the form x, y, z and this is px by the x component of the linear momentum py and pz. So, the

Z component angular momentum will be Lz which is nothing but x py minus y px it is just from the matrix manipulation. We can write this so that is what it is (())(02:50).

So, as per postulate 1 we have to find out the operator. So, we have to find out Lz hat operator. So, from postulate one the operator will be minus i h bar x d by dy minus y d by dx this is the operator. This comes from your postulate 2 that we described (())(03:29) product and so, this is the expression for the operator for the angular momentum that is a quantum mechanical(())(03:38) Hermitian operator.

So, therefore, now if you have to find out the mean value or the Z component of angular momentum Lz (())(03:56) what we do, is that we basically find out the average of this Z component of the angular momentum. So this is written as star Lz is the operator function is acts on psi into d tau, tau being the volume. So in a sense (())(04:33) is basically it is a triple integral psi star L z that is means the hat psi dx dy dz. If I now substitute the operator value, if this is the operator.

So, Lz bar will remain as (())(05:01) as minus i h bar triple integral psi star x psi by dy d psi by dy minus y d psi by dx dy dz. So, this is the mean value and this is given when you substitute for the quantum mechanical operator substitute for the operator. So, this gives us this enormous power that you know this is how you should solve, for example, if we want to find out the mean value of this component of angular momentum then this is the way you calculate it. Remember which is the operator is acting on the wave function as we saw (())(06:02).

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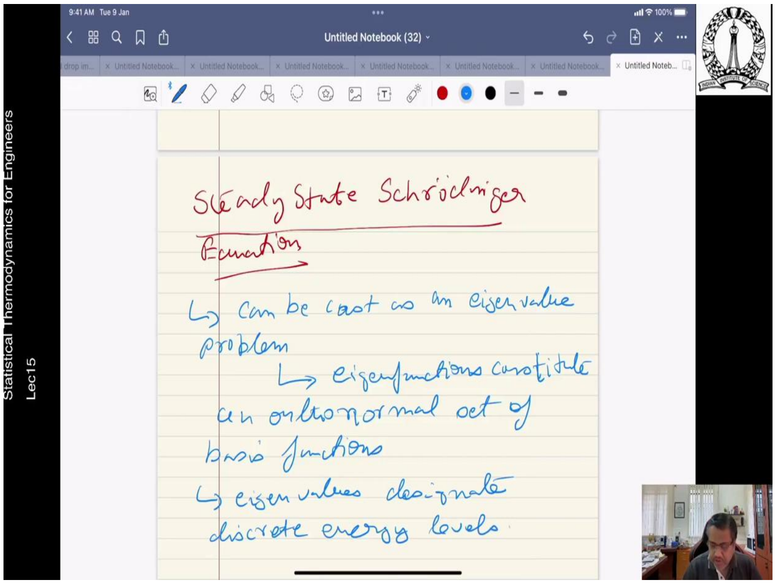
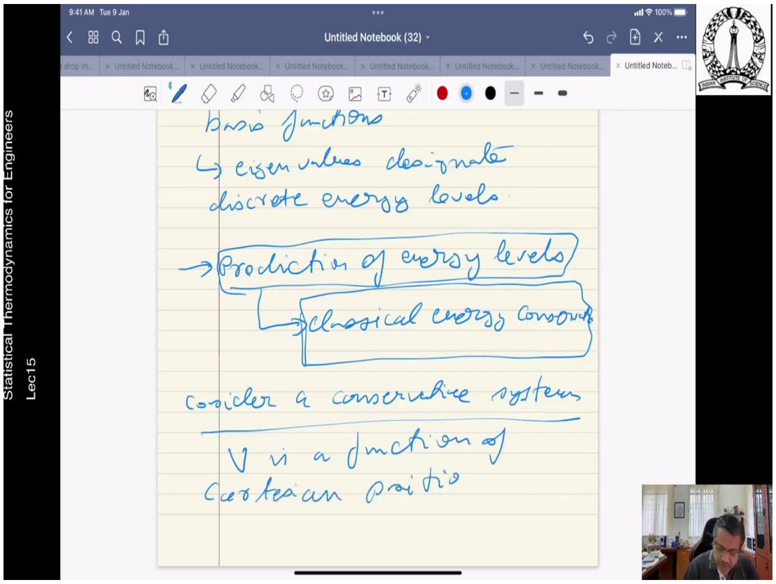


Steady State Schrödinger Equation

↳ can be cast as an eigenvalue problem

↳ eigenfunctions constitute an orthonormal set of basis functions

↳ eigenvalues designate discrete energy levels



basis functions

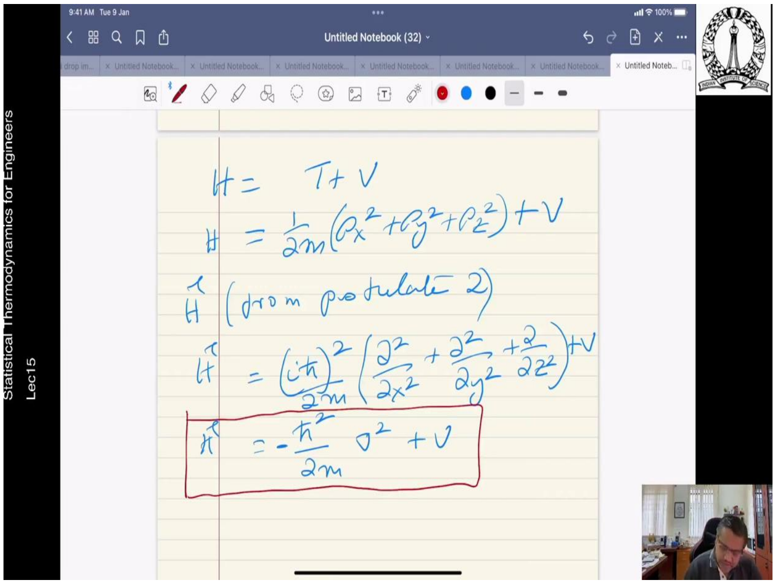
↳ eigenvalues designate discrete energy levels

→ Prediction of energy levels

↳ classical energy conserv

Consider a conservative system

V is a function of Cartesian positio



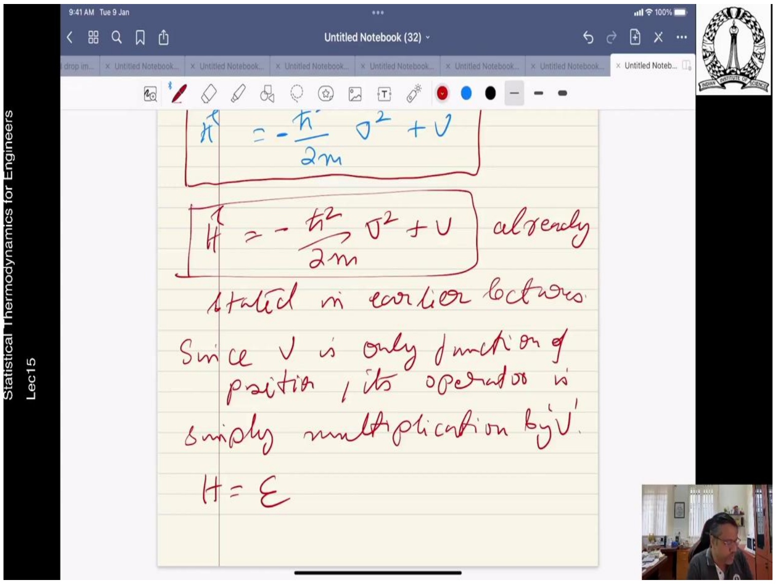
$$H = T + V$$

$$H = \frac{1}{2m}\left(p_x^2+p_y^2+p_z^2\right)+V$$

$\hat{H}$ (from postulate 2)

$$\hat{H} = \frac{(i\hbar)^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V$$

$$\boxed{\hat{H} = -\frac{\hbar^2}{2m}\nabla^2+V}$$



$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2+V$$

$\boxed{\hat{H} = -\frac{\hbar^2}{2m}\nabla^2+V}$ already stated in earlier lectures.

Since V is only function of position, its operator is simply multiplication by 'V'.

$H = E$

Now, let us take the next journey be the steady state Schrodinger equation the steady state. So, what are the things that we know about the Schrodinger wave equation first it can be cast as an eigenvalue problem. In this Eigen value problem, the wave functions Eigen functions constitute an orthonormal set of basis functions. Eigen functions constitute an orthonormal set of basis functions. The Eigen values will be (())(07:26) designated as district energy levels (())(07:34).

So, this was what we knew this is what we thought. So, also if you look at it carefully, we saw that this prediction of energy levels using the Schrodinger wave equation is very well connected or affiliated with you know with a classical energy conservation. So, what we are saying is that Schrodinger wave equation is used for prediction of energy levels that we have seen already.

Now, this has got some connection with the classical energy conservation principle as well. So, let us do a very quick verification of this by considering a conservative system, consider conservative system and it can be where the by conservative system we mean the potential function V is a function of Cartesian coordinates only. So, if I look at it now, the resultant Hamiltonian in normal parlance is given as T plus V, which is equal 1 by 2m it takes a three dimensional system px square plus py square plus pz square plus V.

So, the operator again from postulate 2 which we just did a few moments ago. So, H bar operator becomes minus ih square d square plus dx square plus d square d y square (())(10:07) plus V. So the operator essentially become h bar square minus (())(10:24) sorry miss the 2m here (())(10:33) plus V (())(10:42). So, therefore, as we can see that this is the operator this is the corresponding operator. We knew that Hamiltonian which is basically like the total energy and if this is the operator H hat. Now, if you look at it. So, this is the operator function that we have.

So, this is already we knew about this operator if you recall the past lectures that the Hamiltonian operator we say it is trying to be minus h square by 2m laplace (())(11:18) plus V this we knew this was already proceed it. Already stated in earlier lectures. But because potential energy is only a function of position. So, it is just the function itself which is multiplication by V. Since V is only a function of position, so the operator was operator is simply multiplication by V. Now, we also know that H is nothing but the total energy.

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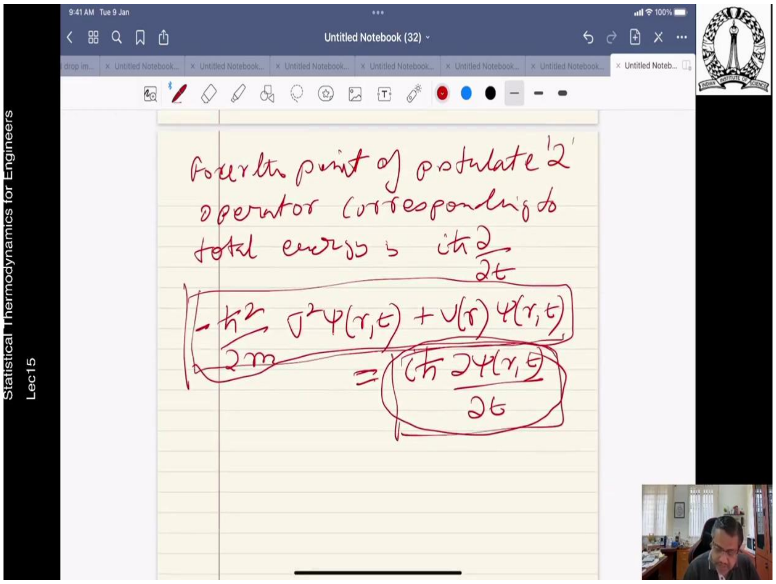
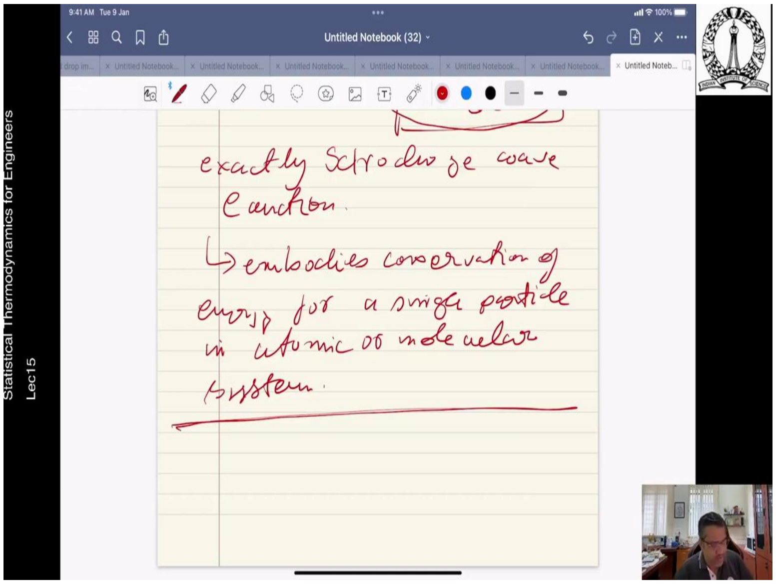


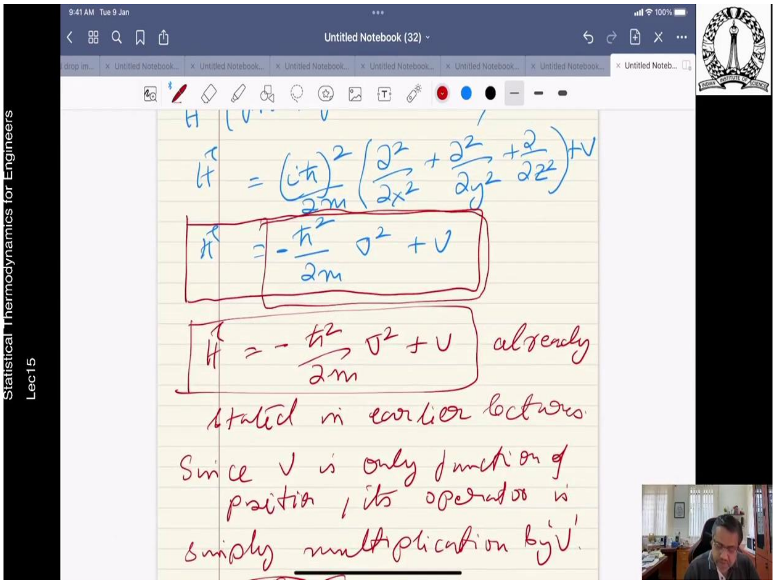
Fourth point of postulate '2'
operator corresponding to
total energy is $i\hbar\frac{\partial}{\partial t}$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi(r,t)+V(r)\,\psi(r,t)} = \boxed{i\hbar\frac{\partial\psi(r,t)}{\partial t}}$$



exactly Schrodinger wave Equation.

↳ embodies conservation of energy for a single particle in atomic or molecular system.

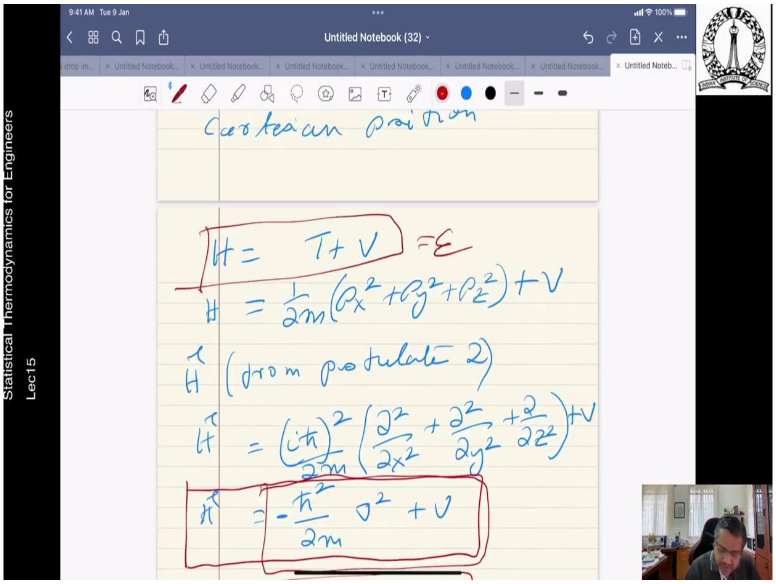


$$\hat{H} = \frac{(i\hbar)^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V$$

$$\boxed{\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V}$$

$$\boxed{\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V}$$ already stated in earlier lectures.

Since V is only function of position, its operator is simply multiplication by 'V'.



Cartesian position

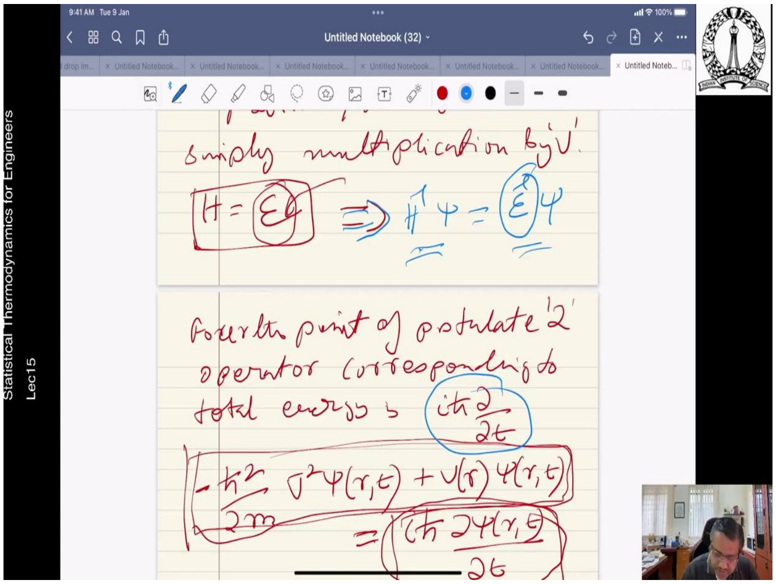
$$\boxed{H = T + V} = E$$

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V$$

$\hat{H}$ (from postulate 2)

$$\hat{H} = \frac{(i\hbar)^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V$$

$$\boxed{\hat{H} = \boxed{-\frac{\hbar^2}{2m}\nabla^2 + V}}$$



simply multiplication by 'V'.

$$\boxed{H = E} \Rightarrow \hat{H}\psi = \hat{E}\psi$$

Fourth point of postulate '2'
operator corresponding to
total energy is $i\hbar\frac{\partial}{\partial t}$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi(r,t) + V(r)\psi(r,t)} = \boxed{i\hbar\frac{\partial\psi(r,t)}{\partial t}}$$

So, therefore, your postulates 2 for the fourth point in postulate 2 you remember the fourth point. Fourth point of postulate 2 fourth point in postulate 2 says that the operator corresponding to total energy is i h bar by dt and H is equal to E because that is the H is a total Hamiltonian. So, now, if you look at the form that we have already said so, postulate 2d. If we apply postulate 2d you will now see this expression becomes 2m square psi (())(13:40) r comma t plus V is only a function of r (())(13:48) r, t is now this is applied in the wave function this is equal to i h because that is a total energy now, psi r comma t divided by dt.

So, you see this was the wave function and this was the total energy operator because H is E. So, in one case the operator act on H on E so, we get this and the lefthand side is a standard operator that we derived the Hamiltonian operator that we derived. So, this proves a point that if you look at this particular equation now, this produces this is exactly the Schrodinger wave equation, or how we have done it? We have done it for the energy conservation. We started with this. So, that is the energy conservation that we said. So, in essence what we have see is that. The Schrodinger wave equation actually embodies the conservation of energy. It embodies conservation of energy conservation for a single particle in atomic molecular system.

So, this is rather this is the most one of the most illuminating part that this is how the Schrodinger wave equation can be cast and this is how it is says this embodies conservation of energy. So, just to give there is one more thing in case you guys a kind of worked on this. So, therefore, this should be equal to (())(16:08) whereas this is the same as this. So, basically we are applied so this operator function is nothing but this, so this should be absolutely clear to you, so, this embodies the conservation of energy principle.

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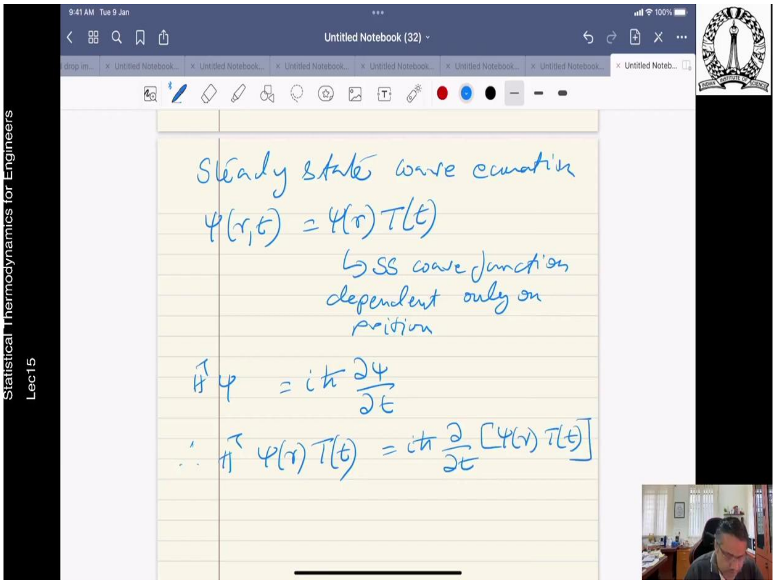


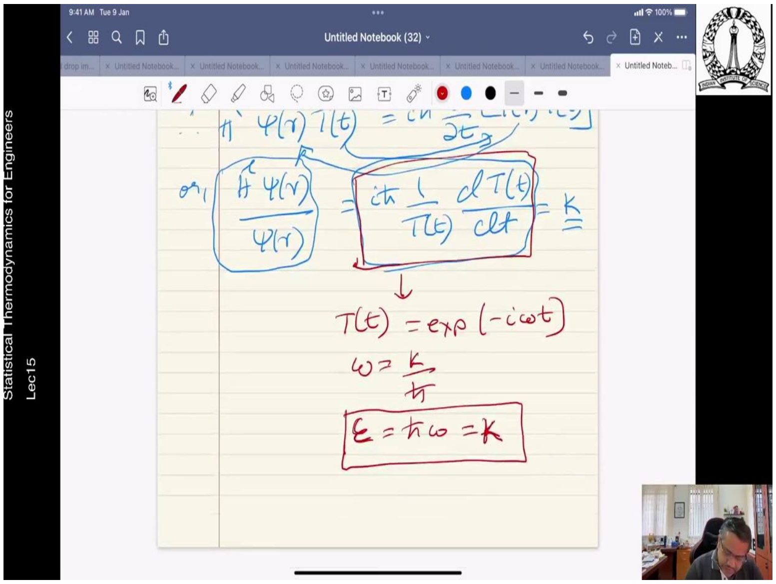
Steady state wave equation

$\psi(r,t) = \psi(r)T(t)$

$\hookrightarrow$ SS wave function dependent only on position

$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$

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



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

$$\text{or,}\quad \boxed{\frac{\hat{H}\,\psi(r)}{\psi(r)}} = \boxed{i\hbar\,\frac{1}{T(t)}\,\frac{dT(t)}{dt}} = K$$

$$T(t) = \exp(-i\omega t)$$

$$\omega = \frac{K}{\hbar}$$

$$\boxed{E = \hbar\omega = K}$$

Now, let us now we are in a position to tackle the Schrodinger the steady state Schrodinger wave equation. So, let us state we started with this we got distracted a little bit. Let us state wave equation psi r comma t equal to psi r this is like a separation variable this is the steady state wave function which is dependent only on position dependent only on the position (())(17:18).

Now H hat we need acts on a wave function multiply h bar d psi by dt this we already know therefore H acting on psi r (())(17:37). Something like this we write it like that then this will be something like this so this psi r basically comes out and goes to the side this comes to this side and this must be equal to because this side is a function of time this side function of space therefore this should be equal to a constant that is the only way that this equality can be attained. Now if we look at this part now only this part a wave function we find that T t is given as exponential minus i omega t, while omega is equal to k by h bar therefore E is equal to (())(19:11) h omega is equal to k omega is k by h bar and energy is nothing but h bar by omega as we know. So, that is equal to K.

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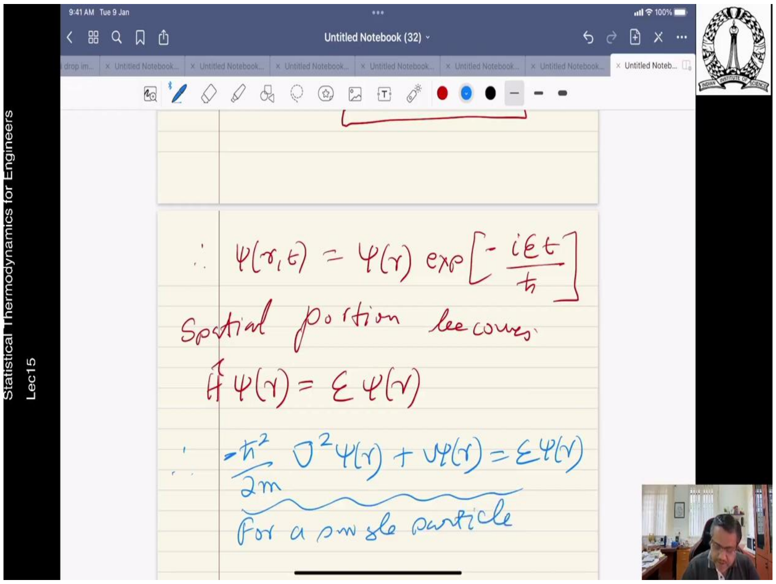


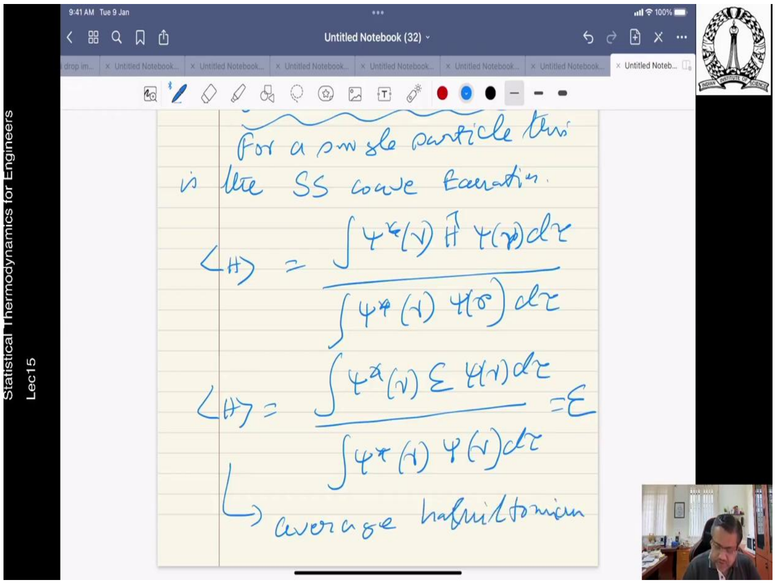
$$\therefore \ \psi(r,t) = \psi(r)\exp\left[-\frac{iEt}{\hbar}\right]$$

Spatial portion becomes:

$$\hat{H}\psi(r) = E\psi(r)$$

$$\therefore \ \underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V\psi(r) = E\psi(r)}$$

For a single particle

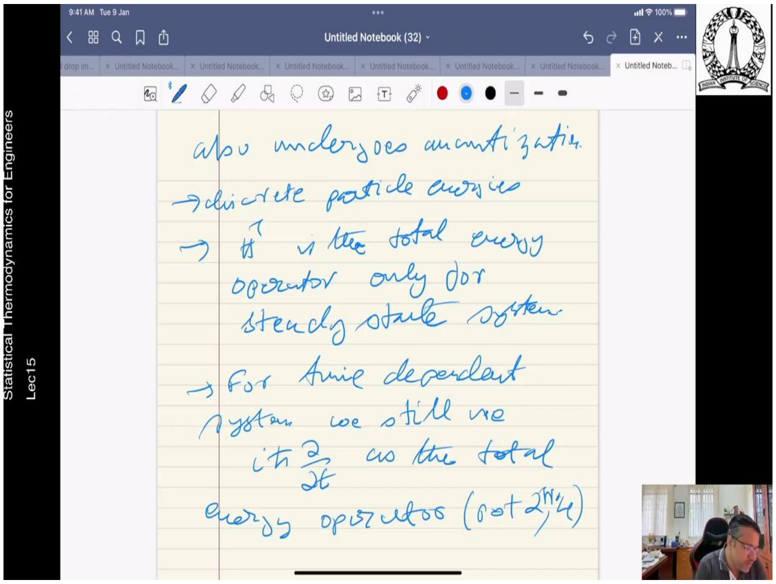


For a single particle this is the SS wave Equation.

$$\langle H\rangle = \frac{\int \psi^*(r)\hat{H}\psi(r)\,d\tau}{\int \psi^*(r)\psi(r)\,d\tau}$$

$$\langle H\rangle = \frac{\int \psi^*(r)E\psi(r)\,d\tau}{\int \psi^*(r)\psi(r)\,d\tau} = E$$

↳ average hamiltonian

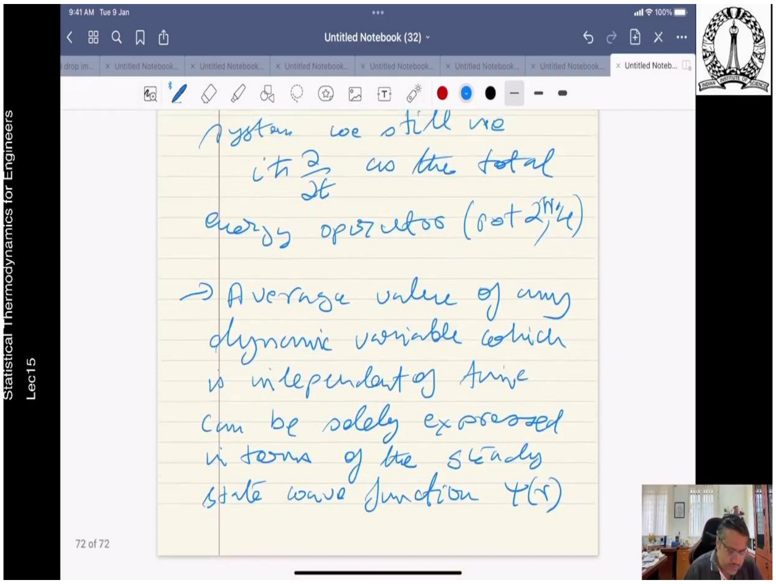


also undergoes quantization

→ discrete particle energies

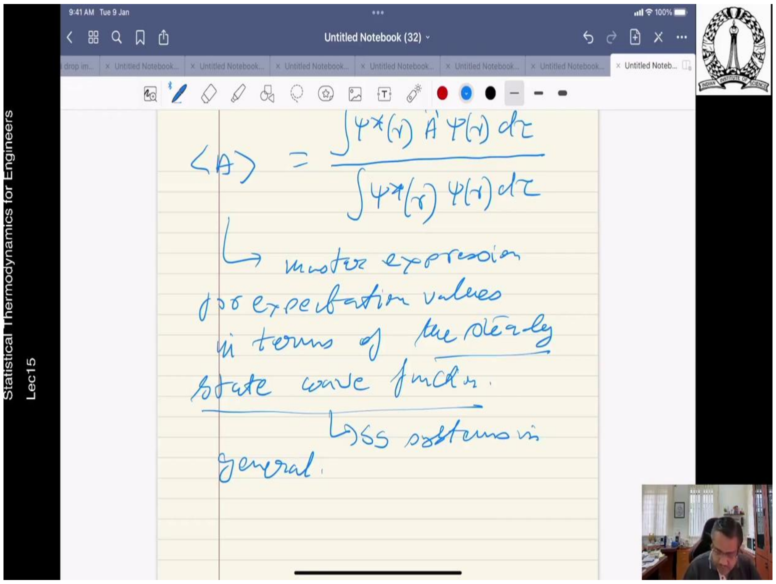
→ $\hat{H}$ is the total energy operator only for steady state system

→ For time dependent system we still use $i\hbar\frac{\partial}{\partial t}$ as the total energy operator (not $\hbar^2/2m$)



system we still use $i\hbar\frac{\partial}{\partial t}$ as the total energy operator (not $\hbar^2/2m$)

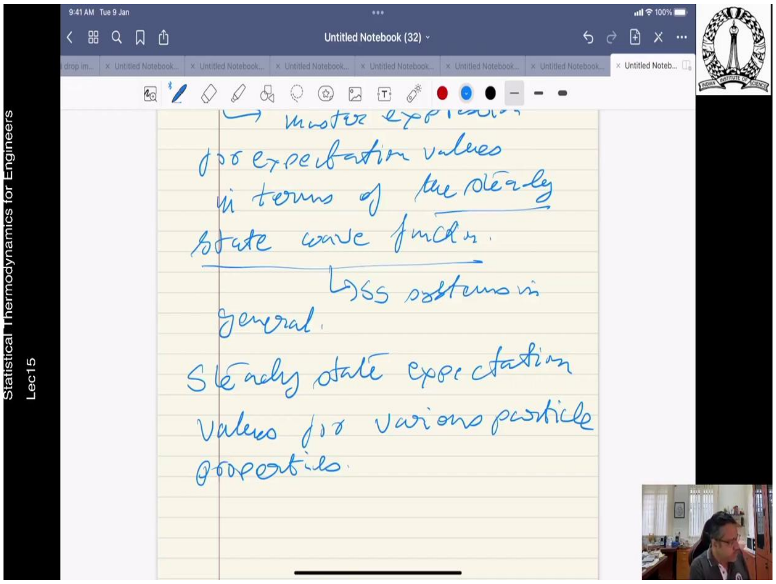
→ Average value of any dynamic variable which is independent of time can be solely expressed in terms of the steady state wave function $\psi(r)$



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

↳ master expression for expectation values in terms of the steady state wave fnctn.

↳ SS systems in general.



↳ master expression for expectation values in terms of the steady state wave fnctn.

↳ SS systems in general.

Steady state expectation values for various particle properties.

So, therefore, psi r comma t is equal to psi r into exponential minus i t by h bar this is exponential omega we are substituting omega by E by h bar essentially. So that is the total expression that we are getting. Now, the spatial portion now, if we just look at the spatial portion then becomes H bar psi r equal to E (())(20:34) this is a spatial portion. So, therefore minus h square by 2m we are just putting in the numbers psi r plus v psi r equal to E. So, for a single particle this is the a steady state SS wave equation.

So, H bar therefore is written as psi star I am just putting the r so, that it is easier for you to differentiate, hope can use a different notation but we are going to stick to this because in writing you cannot replicate such notation. So, H bar is nothing but the total energy r E so that is what it is E is the operator E tau divided by (())(22:15). So, we can see the average Hamiltonian also undergoes quantization (())(22:37).

So, the average Hamiltonian let say this undergoes quantization (())(22:44). So, what happens in this the Hamiltonian that we saw that this now therefore provides the districts particle energies. This is (())(23:12) the total operator energy operator only for steady state systems. For time dependent systems we still use h bar d by dt as the total energy operator.

This comes from your postulate 2. So, (())(24:04) number 4. So this is like the average value average observable value of a dynamic variable which is expressly independent of time and (())(24:22) so, the average value of any dynamic variable which is independent of time can be solely expressed in terms of a steady state wave function psi r which is not dependent on (())(25:08). Say in essence that can be written as this like a master template.

A is the operator (())(25:24). So this is the average observable values this is like a master expression for calculating expectation values, (())(26:04) but in terms of steady state wave function (())(26:25) therefore teady state system in general and it undergoes quantization and we have seen that you know temporary permission in certain cases when you (())(26:44) because we may want to produce steady state expectation values for various particle properties.

So, this allows us to do that because we will not be interested in temporal (())(27:11) at all. So, this provides us with a unique idea that how you can actually do this and we have also seen that the Schrodinger wave equation also is reduces upon embodies the conservation of energy as well.

And we have seen what will be that different operators for say energy, for angular momentum and stuff like that so that example, problem. We will have a full class where we will cover on these Hermitian operators and so, we can cover more in depth analysis of that as well. In the next lesson we are going to look at probably multi particle type a system so multi particle systems which will be interesting so, multi particle systems (())(27:54) stuff like that. So, we will do that in the next class. Thank you.