Quantum Mechanics and Molecular Spectroscopy

Prof. G Naresh Patwari
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture-01
Schrodinger Equation

Hello my name is G Naresh Patwari and I am at the department of chemistry IIT Bombay. I am going to teach quantum mechanics and molecular spectroscopy course. You can reach me at naresh@chem.iitb.ac.in or g.naresh.patwari@gmail.com. Apart from me there are 2 teaching assistants for this course Ms. Namitha Brijit Bijoy who can be reached at namithabrijit@gmail.com and Ms. Sumitra Singh who can be reached at sumitrasingh1412@gmail.com. If you have any queries regarding those course please write an email to one of us, let us get started.

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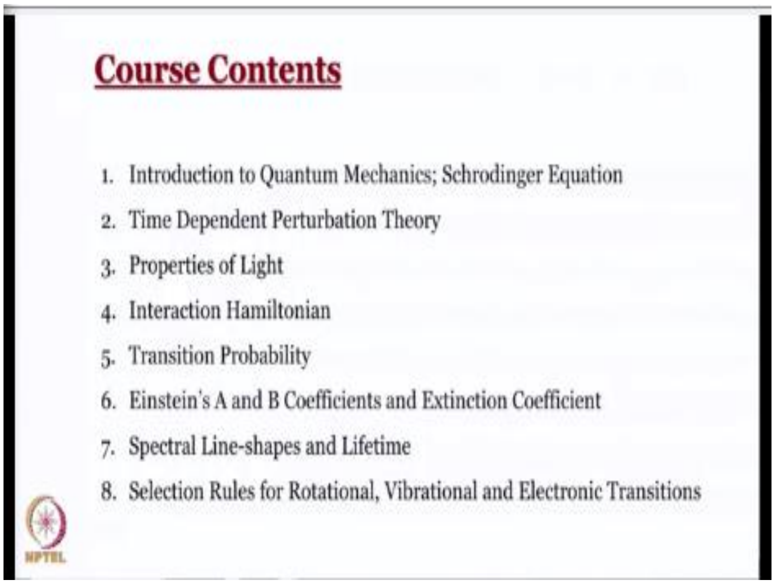

Course Contents

1. Introduction to Quantum Mechanics; Schrodinger Equation
2. Time Dependent Perturbation Theory
3. Properties of Light
4. Interaction Hamiltonian
5. Transition Probability
6. Einstein's A and B Coefficients and Extinction Coefficient
7. Spectral Line-shapes and Lifetime
8. Selection Rules for Rotational, Vibrational and Electronic Transitions

This course contains of 8 parts which may not be equally divided, however we will start with introduction to quantum mechanics and arrive at the Schrodinger equation. Then we will look at the time dependent perturbation theory following which we will also look at properties of light in a classical manner. In the interaction Hamiltonian we will interacts the classical light with the quantum mechanical molecule and that leads to a semi classical picture.

Following which you will evaluate the transition probability and this transition probability will be related to Einstein's A and B coefficients. Following the evaluation of Einstein A and B coefficients these will be related to the extinction coefficient which can be experimentally measured. We will also look at the line shapes and the lifetimes both of which can be evaluated experimentally and theoretically.

We will look at the connection between the experiment and the theory. Finally we will quickly derive the selection rules for rotation, vibration and electronic transitions, all of this we hope to cover in 8 weeks. Today in the first lecture we will start with introduction to quantum mechanics and arrive at the Schrodinger equation. To arrive at the Schrodinger equation we will start with something very simple called classical wave equation.

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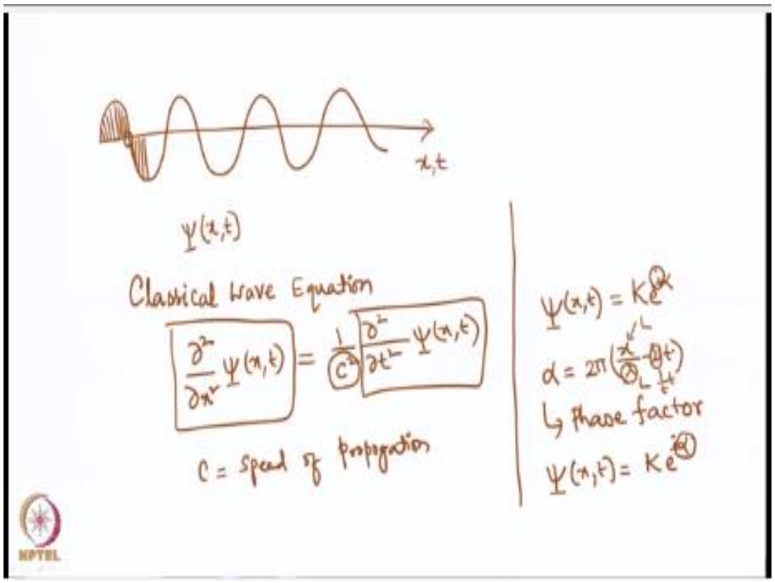

$\psi(x,t)$

Classical Wave Equation

$$\boxed{\frac{\partial^2}{\partial x^2}\psi(x,t)} = \frac{1}{c^2}\boxed{\frac{\partial^2}{\partial t^2}\psi(x,t)}$$

c = Speed of propagation

$\psi(x,t) = Ke^{i\alpha}$

$\alpha = 2\pi\left(\frac{x}{\lambda} - \nu t\right)$

↳ Phase factor

$\psi(x,t) = Ke^{i\alpha}$

For example if you have a wave that is travelling like this ok and this is the direction of propagation. So, as a time progresses it the wave progresses both in the space x and t. And this wave of course has amplitude which is time dependent, so the amplitude keep goes up it will reach a maximum value and then keeps going down and then we will go to negative values as well. And at some instances the amplitude is 0 as in this case.

So, the amplitude depends on both the position and the time. So, if we defined psi as an amplitude, so psi of x, t because it depends both on space or the coordinate and the time, the amplitude depends both on position and time. The variation of amplitude in space and time is given by classical wave equation which says that d square by dx square of psi of x, t equals to 1 over c square d square by dt square psi of x, t.

Now the classical wave equation relates the second derivative of the amplitudes with respect to space or coordinate to the second derivative of the amplitude with respect to time and the proportionality constant is 1 over c square. And in this case c happens to be speed of propagation or velocity of propagation ok. Now you can see that the classical wave equation is a second order partial differential equation in t and x.

So one can quickly realize that since this is a second order partial differential equations one of the possible solutions for psi is equal to ke to the power of i alpha ok, it is an exponential function i out (()) (05:56) because it is periodic nature it has to have this i ok. Now in this case alpha is given by 2 pi x pi lambda - mu t and it is called phase factor ok. Now you should understand that a phase factor is in the exponent here.

So, you can see psi of x, t is equal to k e to the power of i alpha and your alpha is in the exponent, if something is an exponent it must be dimensionless. So, you will see that x is length unit, lambda is length unit. So, x by lambda is going to be dimensionless because lambda is the wavelength it is in length units. Now in the case of frequency nu it is 1 over t, t that is the time is t. So, this nu t also will be dimensionless. So, alpha is a dimensionless quantity therefore can be used as an exponent.

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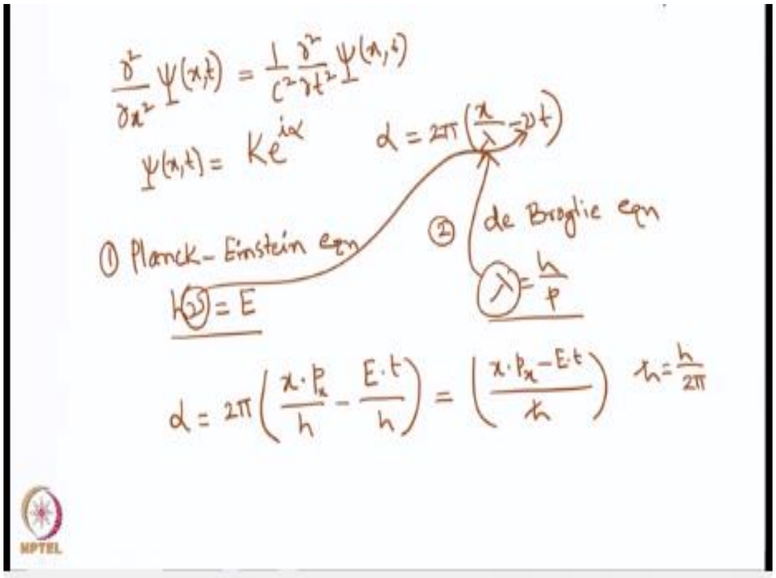

$$\frac{\partial^2}{\partial x^2}\psi(x,t) = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\psi(x,t)$$

$$\psi(x,t) = Ke^{i\alpha} \qquad \alpha = 2\pi\left(\frac{x}{\lambda} - \nu t\right)$$

① Planck- Einstein eqn

$$h\nu = E$$

② de Broglie eqn

$$\lambda = \frac{h}{p}$$

$$\alpha = 2\pi\left(\frac{x\cdot p_x}{h} - \frac{E\cdot t}{h}\right) = \left(\frac{x\cdot p_x - E\cdot t}{\hbar}\right) \qquad \hbar = \frac{h}{2\pi}$$

So, what we have is the classical wave equation d square by d x square psi of x, t equals to 1 over c square d square by dt square psi of x, t and psi of x, t is equal to ke to the power of i alpha where k is a constant ok. Now this is from very old classical mechanics, in the late 19th century and early 20th century when the quantum mechanics was developing then 2 major equations came into force.

And one of them is Planck Einstein equation, that is nothing but h nu is equal to E and the second one is de Broglie equation lambda is equal to h by p. Now these 2 equations are epitome of wave particle duality ok. In the first case light waves behave as particles that is what Einstein said and in the second case lambda is equal to h by p de Broglie said that ok matter can behave as wave and will have corresponding wavelength depending on its momentum.

Now we know that in the classical wave equation alpha equals to 2 pi x by lambda - nu t. So, what I am going to do is that I am going to take this nu ok and substitute in this equation alpha. And similarly I am going to take this lambda and substitute here and when I do that I will get alpha is equal to 2 pi x into p by h - E into t by h ok where x is the coordinate p is the momentum.

However, you will know that the momentum is along a particular direction, because 3 moments along x y z or orthogonal to each other. Therefore this x when multiplied by p can be written as p x ok, now this can be equal to because h by 2 pi this 2 pi one can take into the denominator of over h. So, one can write this as x dot p x – E dot t by h bar, where h bar equals to h by 2 pi ok.

Now in some sense we have quantized the alpha, alpha which was from the classical wave equation is now written in quantum mechanics ok.

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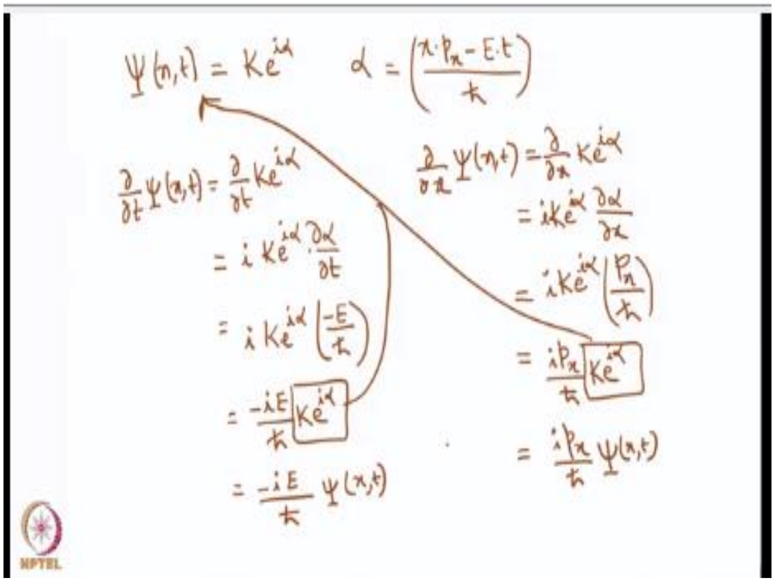

$$\psi(x,t) = Ke^{i\alpha} \qquad \alpha = \left(\frac{x \cdot p_x - E \cdot t}{\hbar}\right)$$

$$\frac{\partial}{\partial t}\psi(x,t) = \frac{\partial}{\partial t}Ke^{i\alpha} = iKe^{i\alpha}\frac{\partial \alpha}{\partial t} = iKe^{i\alpha}\left(\frac{-E}{\hbar}\right) = \frac{-iE}{\hbar}\boxed{Ke^{i\alpha}} = \frac{-iE}{\hbar}\psi(x,t)$$

$$\frac{\partial}{\partial x}\psi(x,t) = \frac{\partial}{\partial x}Ke^{i\alpha} = iKe^{i\alpha}\frac{\partial \alpha}{\partial x} = iKe^{i\alpha}\left(\frac{p_x}{\hbar}\right) = \frac{ip_x}{\hbar}\boxed{Ke^{i\alpha}} = \frac{ip_x}{\hbar}\psi(x,t)$$

Now we have psi of x, t is equal to ke to the power of i alpha and alpha which is now written in terms of quantum mechanics is nothing but x dot p x – E dot t by h bar. Let us now take partial derivatives of psi with respect to t and x. So, first taking d by dt of psi of x t, this is equal to d by dt of ke to the power of i alpha. So, this will be equal to when you take d by dt of ke to the power of a i alpha, so i ke to the power of i alpha into d alpha by dt.

Similarly, if I take d by dx of psi of x, t is equal to d by dx of ke to the power of i alpha, this is equal to i ke to the power of i alpha, t alpha by dx. Now when I take d alpha by dt. So, if you take d alpha by dt the first part x p x will be a constant and what is it is going to derivate is E t by h bar. So essentially what you will get is i Ke to the power of i alpha - E by h bar.

Similarly this will be i K e to the power of i alpha, in this case x dot p x will be the function and e dot t will be a constant, therefore what we will get is p x by h bar. So, if I slightly rearrange this will become - i E by h bar Ke to the power of i alpha and this will become i p x by h bar Ke to the power of i alpha. But Ke to the power of i alpha is nothing but your psi of x t ok. So, I am going to replace that, so this will become - i E by h bar psi of x, t, this is nothing but - p x h bar psi of x, t, so this is ok. So, all I have done is taken the partial derivatives of psi with respect to t and x ok.

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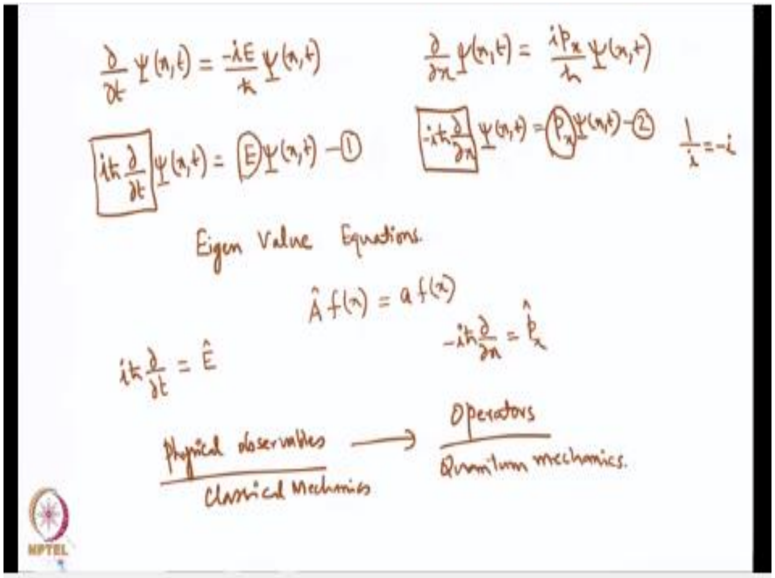

$$\frac{\partial}{\partial t}\Psi(x,t) = \frac{-iE}{\hbar}\Psi(x,t) \qquad \frac{\partial}{\partial x}\Psi(x,t) = \frac{ip_x}{\hbar}\Psi(x,t)$$

$$\boxed{i\hbar\frac{\partial}{\partial t}}\Psi(x,t) = \textcircled{E}\,\Psi(x,t) \ \text{—①} \qquad \boxed{-i\hbar\frac{\partial}{\partial x}}\Psi(x,t) = \textcircled{p_x}\,\Psi(x,t) \ \text{—②} \qquad \frac{1}{i} = -i$$

Eigen Value Equations.

$$\hat{A}f(x) = a\,f(x)$$

$$i\hbar\frac{\partial}{\partial t} = \hat{E} \qquad -i\hbar\frac{\partial}{\partial x} = \hat{p}_x$$

$$\frac{\text{Physical observables}}{\text{Classical Mechanics}} \longrightarrow \frac{\text{Operators}}{\text{Quantum mechanics.}}$$

So, at the end of last slide what we had is d by dt of psi of x, t is equal to - i E by h bar psi of x, t. The other equation is d by dx of psi of x, t equals to i p x h bar psi of x, t right. Now what we can do is slightly rearrange this equation ok. Now one thing remember is that 1 over i equals to – i ok, if I remember that and rearrange these 2 equations what I will get is i h bar d by dt of psi of x, t equals to E psi of x, t similarly - i h bar d by dx of psi x, t is equal to p x psi x, t.

Now these 2 equations which I will call it as 1 and 2, these 2 equations are Eigen value equations, what are Eigen value equations. If you take a mathematical operation say an operation in this case you take the derivative with respect to time and multiplied by i h bar, so that is some kind of operator. Let us say if we have an operator A and it is acts on a function f of x then what you get is a constant multiplied by the same function such an equation is called Eigen value equation.

And you will see that equations 1 and 2 are Eigen value equations, how so. If I have this operator i h or d by dt and I take that operator and act on psi of x, t will gives me the Eigen value.

Similarly you have an operator - i h bar d by dx and operate on psi then I will get the Eigen value p x and I will get back the same function back in both the cases. Therefore in the first case i h bar d by dt will correspond to the operator energy because it gives me energy Eigen value.

Similarly - i h bar d by dx operator will corresponding to the momentum operator because it will give me momentum Eigen value when you operate it on psi of x, t ok. Now we have used the concept of operator E and p x and these operators i h bar d by dt is equal to operator E - i h bar d by dx is operator p x ok. Now in quantum mechanics the concept of operators is very crucial. One of the postulates of quantum mechanics says all physical observables must have a corresponding operator.

This is in classical mechanics, this will have corresponding operators in quantum mechanics ok. So, in the case of energy the quantum mechanical operator will be i h bar d by dt and in the case of momenta the quantum mechanical operator will be - i h bar d by dx ok.

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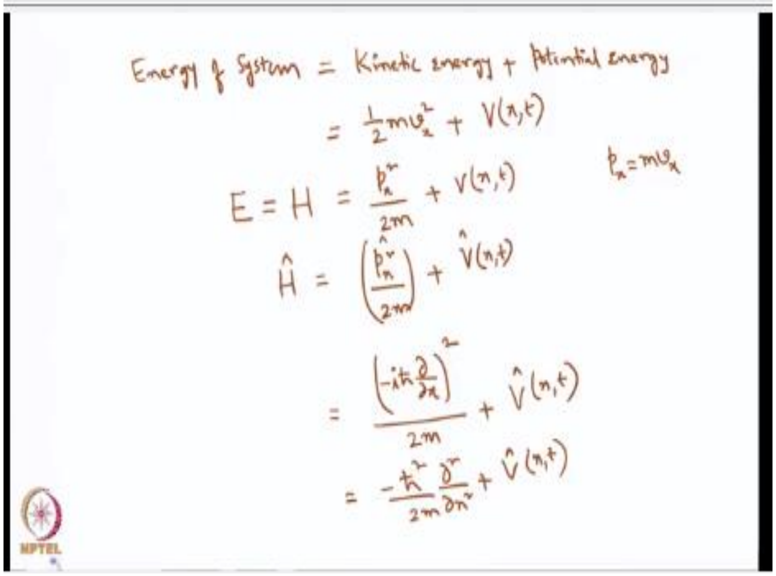

Energy of System = Kinetic energy + Potential energy

$$= \frac{1}{2} m v_x^2 + V(x,t)$$

$$E = H = \frac{p_x^2}{2m} + V(x,t) \qquad p_x = m v_x$$

$$\hat{H} = \left(\frac{\hat{p}_x^2}{2m}\right) + \hat{V}(x,t)$$

$$= \frac{\left(-i\hbar \frac{\partial}{\partial x}\right)^2}{2m} + \hat{V}(x,t)$$

$$= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x,t)$$

Now if you take energy of a system, what is the energy of the system, energy of the system is nothing but kinetic energy + potential energy ok. So, in classical mechanics kinetic energy will be equal to 1/2 m v of course if is along the x axis it is v x square + some potential capital V of x, t ok, I will come back to the potential energy in a minute but let us look at this. So, this can also be rewritten as P x square by 2 m because p x is equal to m into v x in classical mechanics + V of x, t.

And this total energy of the system is also called Hamiltonian h ok. Now in classical mechanics E and H can be interchangeably used E is in a total energy of the system and it is also called Hamiltonian ok. Now if I want to convert this into operator then I must take h convert into operator this is equal to p x square by 2 m operator corresponding to that + V of x t operator corresponding to that.

Now p of x operator I already know that is nothing but - i h bar d by dx that is a operator corresponding to p x take a square of it divided by 2m + potential energy operator V of x, t. So, when I expand this I will get - h bar square by 2m t square by dx square + V of x, t.

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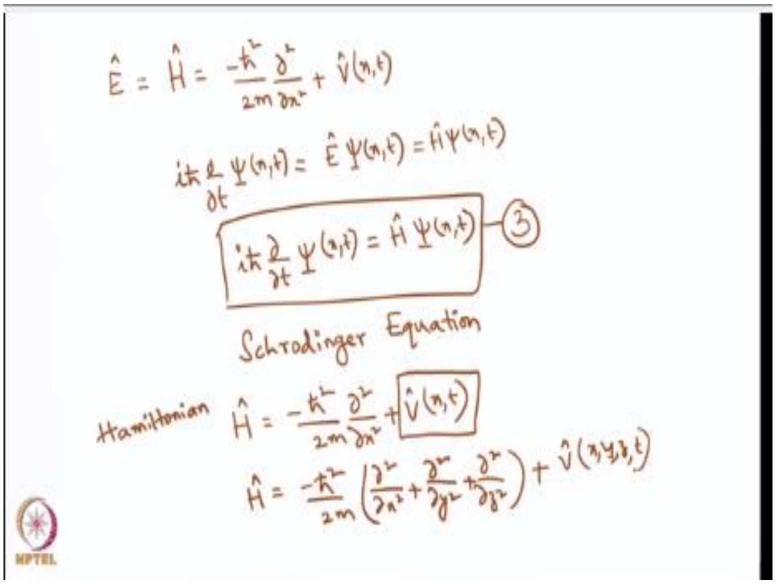

$$\hat{E} = \hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}(x,t)$$

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

$$\boxed{i\hbar\frac{\partial}{\partial t}\psi(x,t) = \hat{H}\psi(x,t)} - ③$$

Schrodinger Equation

Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \boxed{\hat{V}(x,t)}$

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

So, your Hamiltonian operator H will be nothing but - h bar square 2m t square by dx square + V of x, t this also equal to of course total energy operator E. Now if you take equation 1 ok what was our equation 1 i h bar d by dt of psi of x t is equal to operator E psi of x t, this is nothing but operator h psi of x t, no. If I write only like this ih bar d by dt of psi of x, t is equal to h psi of x, t.

This equation is the Schrodinger equation, it is also called time dependent Schrodinger equation. And H will be equal to - h bar square by 2m d square by dx square + V of x, t ok. Now I know what is the kinetic energy operator, but I still do not know what is the potential energy operator because I am keep on writing V of x, t. Because the potential energy will depend on the problem that I one like to choose.

For example if I take a part linear box the potential is 0 inside the box, if I take a hydrogen atom the potential energy will be 1 over square root of x square + y square + z square. And if I take harmonic oscillator the potential energy will be 1 by 2 kx square. Therefore the potential energy operator will depend on the problem that we will choose. However, the kinetic energy operator will remain always the same - h bar square by 2m d square by dx square.

This kinetic energy operator of course is only the 1 dimension, one can generalize Hamiltonian in 3 dimensions ok by the way H is also called Hamiltonian. So, H in 3 dimensions will be - h bar square by 2m d square by dx square + d square by dy square + d square by dz square + V of x, y, z, the That is the generalization of the Hamiltonian 3 dimensions where the kinetic energy is along x, y and z dimensions.

And they are orthogonal to each other and you take projections of kinetic energy along each dimension and the potential energy also is function of 3 dimensions. But in the present case we will try to limit the Hamiltonian to 1 dimension.

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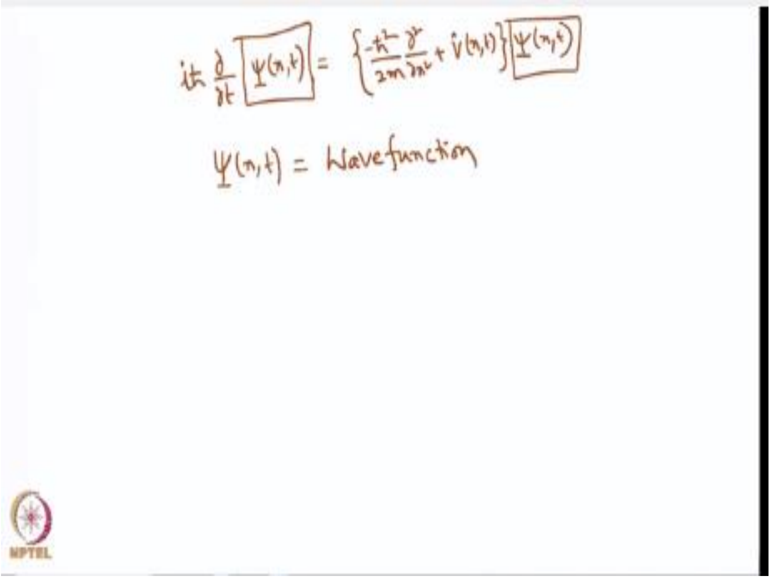

$$i\hbar \frac{\partial}{\partial t} \boxed{\Psi(x,t)} = \left\{ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x,t) \right\} \boxed{\Psi(x,t)}$$

$\Psi(x,t)$ = Wavefunction

So, finally what you have is ih bar d by dt of psi of x, t equals to - h bar square by 2m d square by dx square + V of x, t. So, this is the Schrodinger equation. It says that the influence of time on the psi of x, t is equal to the influence of the total energy operator on psi of x, t ok. So, the time dependence of any psi of x, t will be governed by the total energy operator ok. And in such scenario the psi of x, t is called the wave function.

The name wave function was given by Schrodinger, however the interpretation of the wave function was given by (()) (28:48). Let us stop here for this lecture and we will continue in the next lecture.