Spectroscopic Techniques for Pharmaceutical & Biopharmaceutical Industries
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Lecture 5
Introduction to Spectroscopy 5

Hello Students, welcome to the fifth lecture of this course. Till last lecture I was discussing about basic of spectroscopy and quantum mechanics. The basics needed to understand different kind of spectroscopy and your its uses and its applications. So in the last lecture I started with postulates of quantum mechanics, I will continue with that and I will try to cover the all the postulates of quantum mechanics in this lecture.

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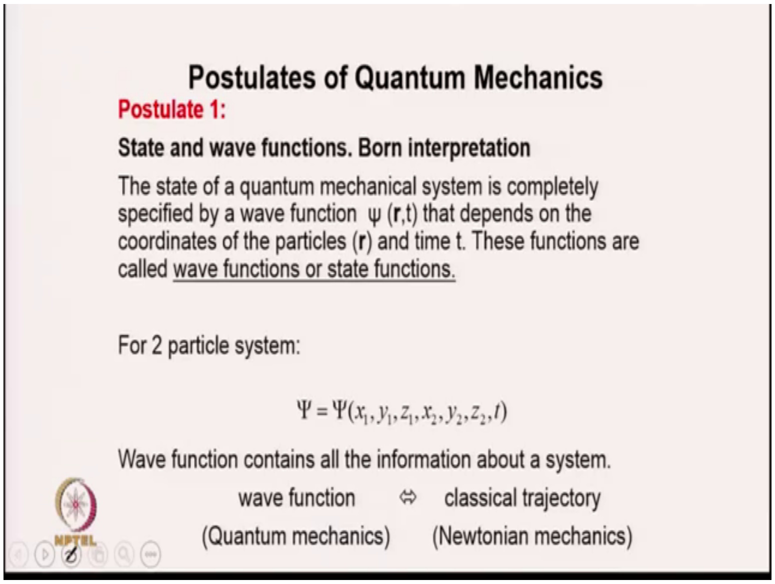

Postulates of Quantum Mechanics

Postulate 1:

State and wave functions. Born interpretation

The state of a quantum mechanical system is completely specified by a wave function ψ (**r**,t) that depends on the coordinates of the particles (**r**) and time t. These functions are called wave functions or state functions.

For 2 particle system:

$$\Psi = \Psi(x_1, y_1, z_1, x_2, y_2, z_2, t)$$

Wave function contains all the information about a system.

wave function	⇔	classical trajectory
(Quantum mechanics)		(Newtonian mechanics)

So postulate 1, it tells you that state of a quantum mechanical system is completely specified by a wave function, this wave function depends on coordinates of the particle and time t. So for a one particle quantum mechanical system this wave function will depend on position of that particle x, y, z and time t.

For 2 particles system it will depend on position of particle 1 x1, y1, z1 and position of particle 2 that is x2, y2, z2 and time t. Important point about this wave function is it contains all the information about a system. It basically tells you about the trajectory of the atom in quantum mechanics, in the quantum mechanics.

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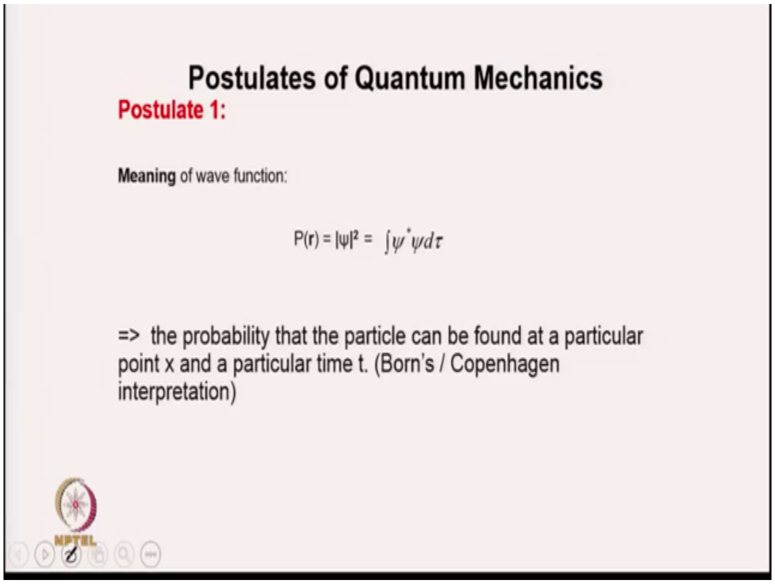

Postulates of Quantum Mechanics

Postulate 1:

Meaning of wave function:

$$P(r) = |\psi|^2 = \int \psi^* \psi d\tau$$

=> the probability that the particle can be found at a particular point x and a particular time t. (Born's / Copenhagen interpretation)

The physical significance of this wave function is that square of the wave function, the square of the wave function is related to your probability, related to probability. This is synonymous to your intensity being proportional to, intensity being proportional to amplitude square.

So here your probability is also proportional to your psy square, since psy can be a complex number so psy square is given by psy z Psy star psy, psy star multiplied by psy. So complex conjugate of a wave function multiplied by a wave function and psy star into psy is called probability density.

So it is similar to mass density where if you multiply mass density by volume element you will get your mass. Similarly if you apply probability density with volume element you will get probability.

So probability is not only dependent on probability density it is also dependent on volume element. Probability is going to be proportional to volume element since larger the volume there is more probability of finding a particle in that volume. So probability is given by integral of psy star psy theta and this equation can be used to find probability of particle being in a particular region.

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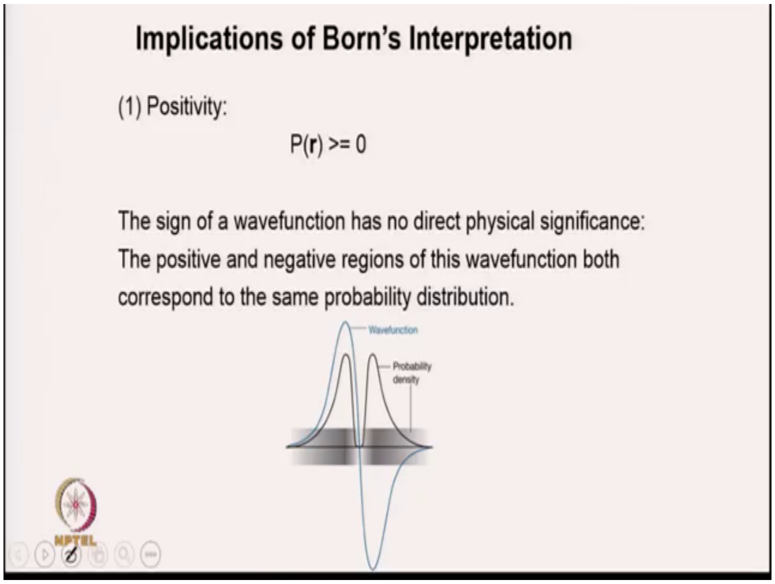

Implications of Born's Interpretation

(1) Positivity:

$$P(\mathbf{r}) >= 0$$

The sign of a wavefunction has no direct physical significance: The positive and negative regions of this wavefunction both correspond to the same probability distribution.

Probability must be greater than equal to 0, it cannot be negative and so it is not the wave function which is going to tell you about a probability. So the sign wave function has no direct physical significance.

The positive and negative regions of this wave function corresponds to same probability distribution. So you can see this blue one is the wave function and this is your positive region, this is your negative region but if you multiply or square it you will get the positive number which is your probability density. So probability must be a positive number.

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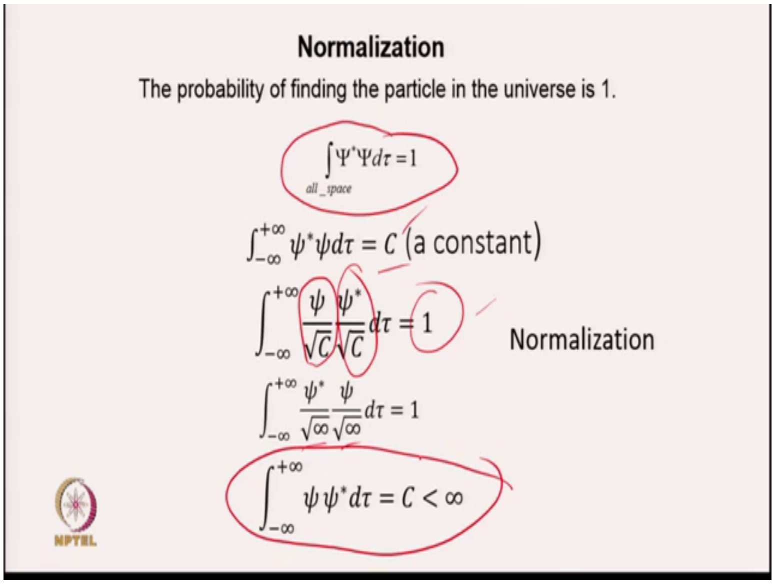

Normalization

The probability of finding the particle in the universe is 1.

$$\int_{all\_space} \Psi^* \Psi d\tau = 1$$

$$\int_{-\infty}^{+\infty} \psi^* \psi d\tau = C \text{ (a constant)}$$

$$\int_{-\infty}^{+\infty} \frac{\psi}{\sqrt{C}} \frac{\psi^*}{\sqrt{C}} d\tau = 1$$

Normalization

$$\int_{-\infty}^{+\infty} \frac{\psi^*}{\sqrt{\infty}} \frac{\psi}{\sqrt{\infty}} d\tau = 1$$

$$\int_{-\infty}^{+\infty} \psi \psi^* d\tau = C < \infty$$

The second important point about probability is that if you try to find out probability over all the space it should be equal to one. What does that mean is psy star Psy d tau over all space should be equal to 1. So you have to choose wave function such that this Psy star Psy d tau when you integrate over all space it must be equal to 1. Now question is suppose I do that and I get a value of C which is a constant, so is it acceptable wave function? So let us think about this.

If suppose this value is C now what I do is, I divide this by root C, divide this Psy star by root C and C by root C multiplied by root C so that will be equal to 1. So a wave function whose value Psy star into Psy d tau integrated over minus infinity to plus infinity is a constant can be normalized such that if you multiply this normalized wave function which is Psy by root C with Psy star divided by root C and then you integrate over a volume element from minus infinity to plus infinity it will come out to be 1. So whatever wave function you are getting you have to normalized it.

Now question is, can C take all the values? For example can this C will be equal to infinity? Which is not true, if suppose it is infinity C has a value of infinity then what you need to do for normalization? You have to divide by root infinity wave function by root infinity the second wave function by root infinity for its normalization. When you do that it will the wave function or normalized wave function will turn out to be a 0 and so your Psy star Psy d tau when integrated over all space so not be equal to infinity, it should be less than infinity.

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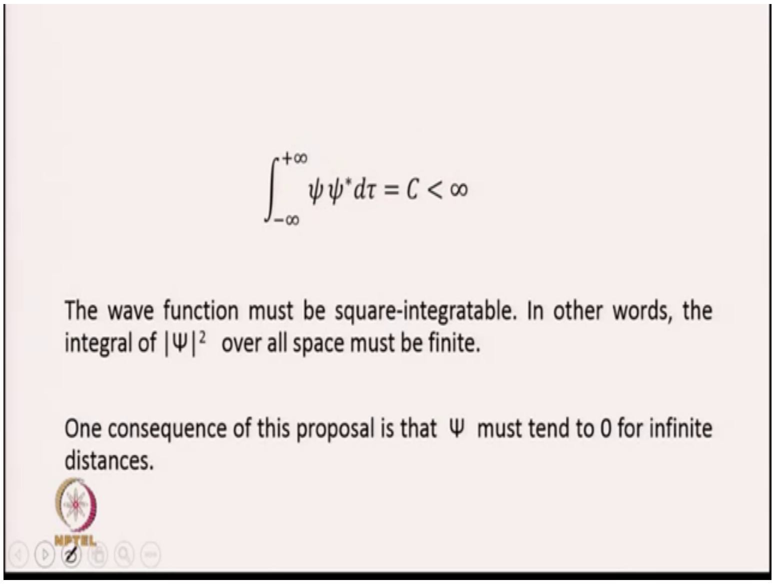

$$\int_{-\infty}^{+\infty} \psi \psi^* d\tau = C < \infty$$

The wave function must be square-integratable. In other words, the integral of $|\Psi|^2$ over all space must be finite.

One consequence of this proposal is that Ψ must tend to 0 for infinite distances.

And when you have this thing then, if you have Psy-Psy star d tau when you integrate this from minus infinity to plus infinity it is equal to C which is less than infinity you say that wave function is square integrated.

So in other words your wave function must be a square integratable and in integral of Psy square over all space must be finite, must be finite. One consequence of this proposal is that Psy must tend to 0 for infinite distances. If it does not then this integral will be equal to infinity. So Psy must tend to 0 for infinite distances.

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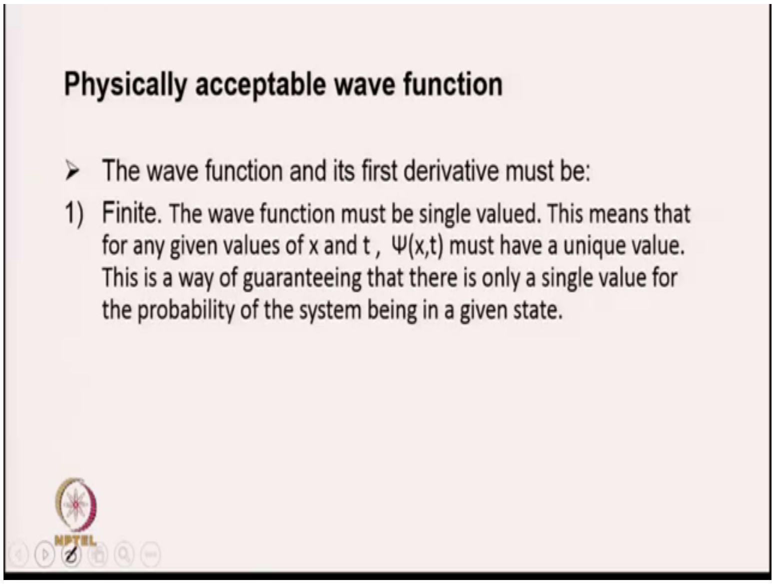

Physically acceptable wave function

- The wave function and its first derivative must be:

1) Finite. The wave function must be single valued. This means that for any given values of x and t , Ψ(x,t) must have a unique value. This is a way of guaranteeing that there is only a single value for the probability of the system being in a given state.

So what are physically acceptable wave function? First thing is that wave function must be single valued and it must be single valued this means for any given value of x and t, Psy must have unique value. Now you will think why? This is because there is only a single value for the probability of system being in a given state.

So at this point suppose you are talking about an electron being in this room and suppose this is a point, here is a point . Now at this point probability of electron being must be a single value, must be a single value and for it being a single value your wave function and its fist derivate must be finite, must be finite.

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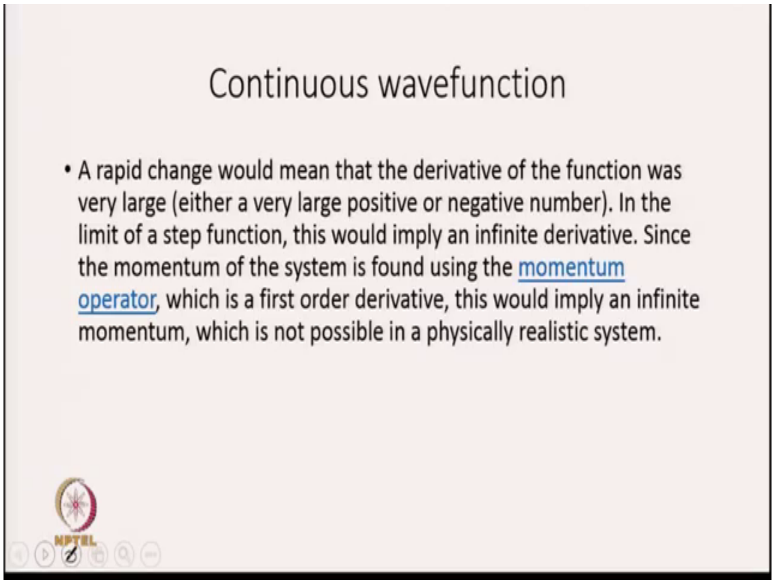

Continuous wavefunction

- A rapid change would mean that the derivative of the function was very large (either a very large positive or negative number). In the limit of a step function, this would imply an infinite derivative. Since the momentum of the system is found using the momentum operator, which is a first order derivative, this would imply an infinite momentum, which is not possible in a physically realistic system.

Now second criteria is that ok now wave function must be a single valued, what are other criteria for an acceptable wave function? So later on you will see that, that momentum of the system quantum mechanical system is found using the momentum operator which is a first order derivative, first order derivative.

So first order derivative should not be infinite, should not be infinite, so derivative of function not be very large, large positive or large negative and this in turn means that there should not be a rapid change in wave function and in other words you can say your wave function must be continuous. Your wave function must be continuous otherwise you will get infinite momentum which is not possible in a physically realistic system.

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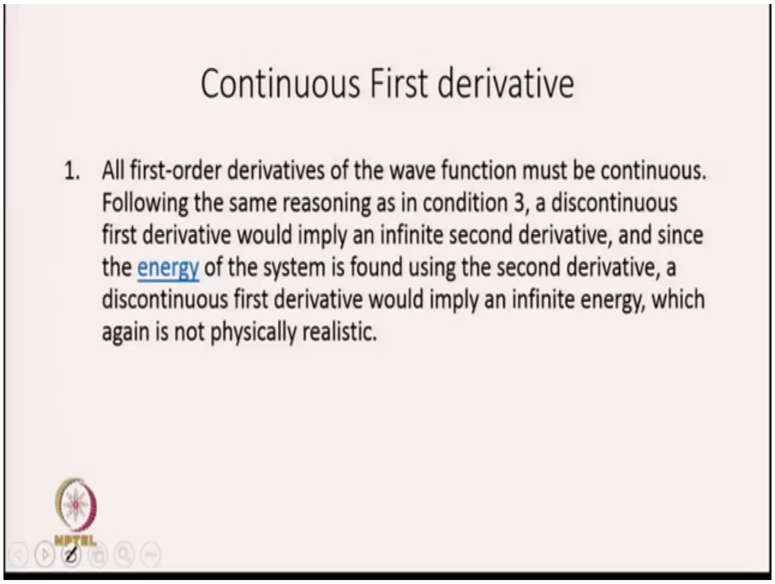

Continuous First derivative

1. All first-order derivatives of the wave function must be continuous. Following the same reasoning as in condition 3, a discontinuous first derivative would imply an infinite second derivative, and since the energy of the system is found using the second derivative, a discontinuous first derivative would imply an infinite energy, which again is not physically realistic.

Now similarly as we discussed about your momentum, energy of the system is found using second derivative and what does that mean is that if I do not want very large value of energy, energy being infinite value if you do not want energy to be infinite then your first ordered derivative of wave function must be continuous.

Discontinuous first derivate imply an infinite second derivative and which will imply energy of system being infinite which again is not physically realistic. So wave function must be continuous it’s first derivate also should be continuous.

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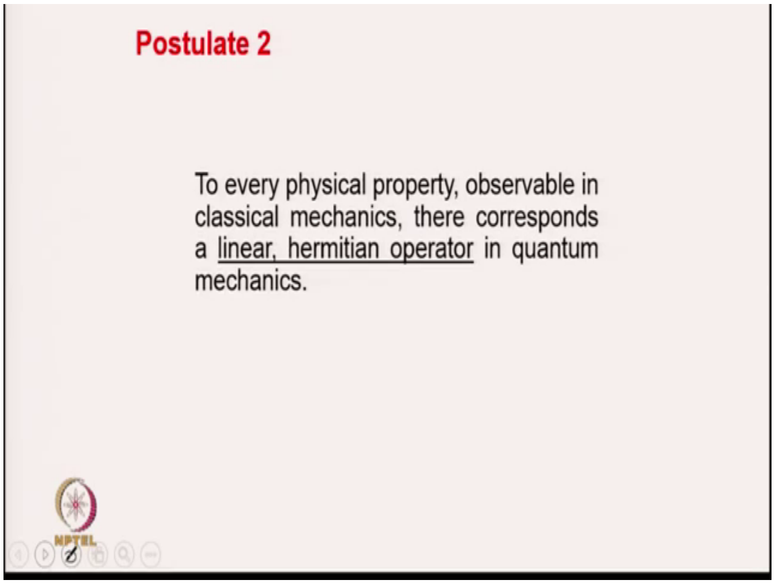

Postulate 2

To every physical property, observable in classical mechanics, there corresponds a <u>linear, hermitian operator</u> in quantum mechanics.

Now will go to postulate 2, postulate 2 tells you that to very physical property observable in classical mechanics there corresponds a linear hermitian operator in quantum mechanics. So there are few terms for example observable, operator, linear operator and hermitian operator we will discuss that before again trying to understand this postulates.

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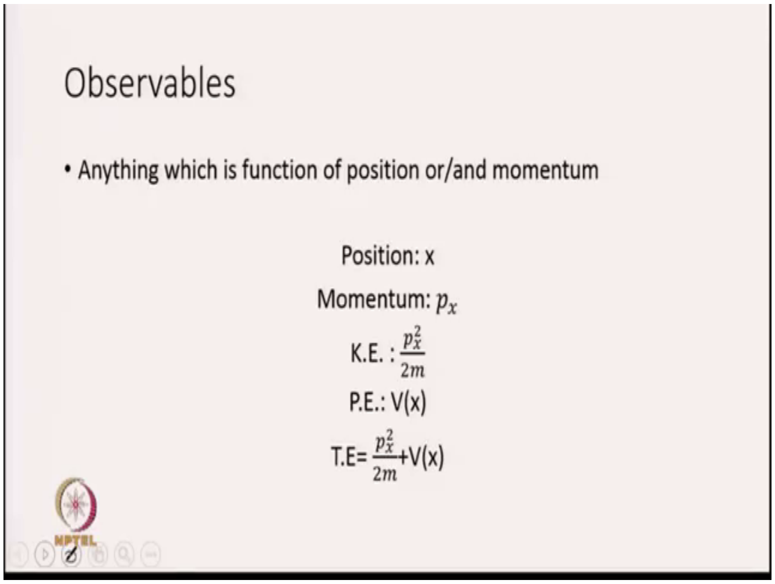

Observables

- Anything which is function of position or/and momentum

Position: x

Momentum: p_x

K.E. : $\frac{p_x^2}{2m}$

P.E.: V(x)

T.E= $\frac{p_x^2}{2m}$+V(x)

So what is observable? Observable is a function of position or and momentum for example position of a particle that is given by x, momentum of the particle P x, kinetic energy P x square by 2 m so kinetic energy is a function of momentum, potential energy it depends on position and total energy is sum of kinetic energy plus potential energy, so it depends both on momentum and position and these are the observables. So corresponding to each of this observables there is a operator, an operator must be linear and your hermitian operator, operator must ne linear and hermitian operator.

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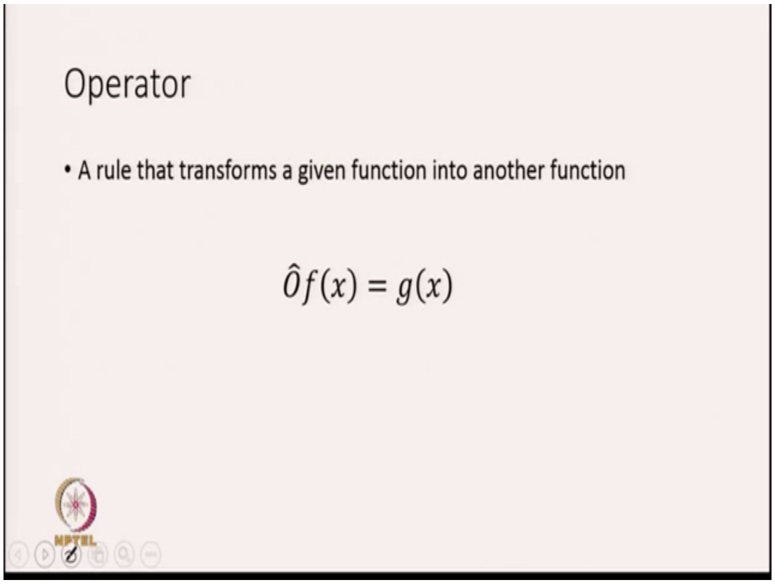

Operator

- A rule that transforms a given function into another function

$$\hat{O}f(x) = g(x)$$

Now let us go and understand what I mean by operator? So operator is a rule that transforms a given function into another function. So if you apply operator to a function for example here f x you will get another function which is g x. So if I apply an operator to a function it should give another function that is what we mean by operator.

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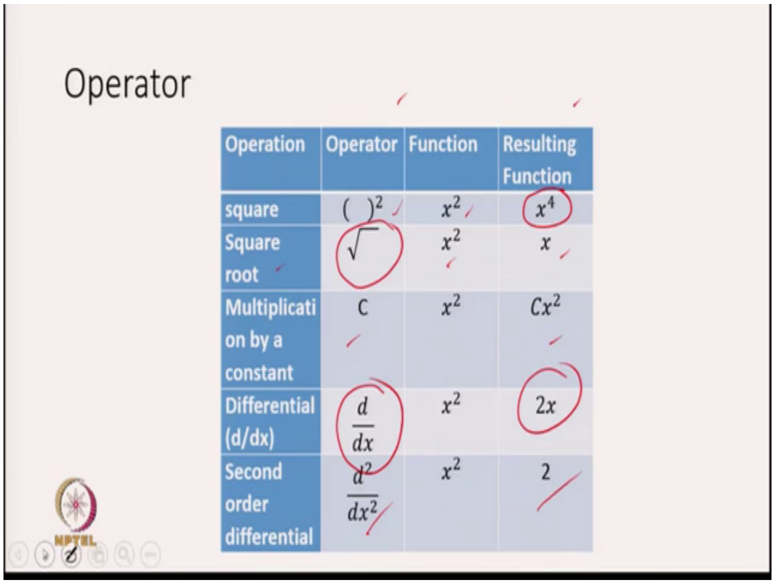

Operator

Operation	Operator	Function	Resulting Function
square	$(\ )^2$	x^2	x^4
Square root	$\sqrt{\ }$	x^2	x
Multiplication by a constant	C	x^2	Cx^2
Differential (d/dx)	$\frac{d}{dx}$	x^2	$2x$
Second order differential	$\frac{d^2}{dx^2}$	x^2	2

So let us understand that, so here is some operation, operator, function and resulting function. So square is a operation and this is shown by this operator. If suppose function is x square so if I apply square operator on a function x square what I am going to get is another function which is x power 4.

Similarly square root can be an operation so you are taking square root of a function and this operator will be given by this sign. If suppose I apply this operator square root operator on x square I am going to get another function x.

Third operator you can think of is multiplication by a constant, here constant is C if I multiply this constant to a function x square what I am going to get is C x square, differential can be another operation and operator will be d by d x if I apply d by d x operator to x square I am going to get the function 2 x and second order differential can be another operation, an operator will be d 2 by dx square if I apply this operator to x square I am going to get the value of 2. So I hope that now you understand operator let us go and understand linear operator.

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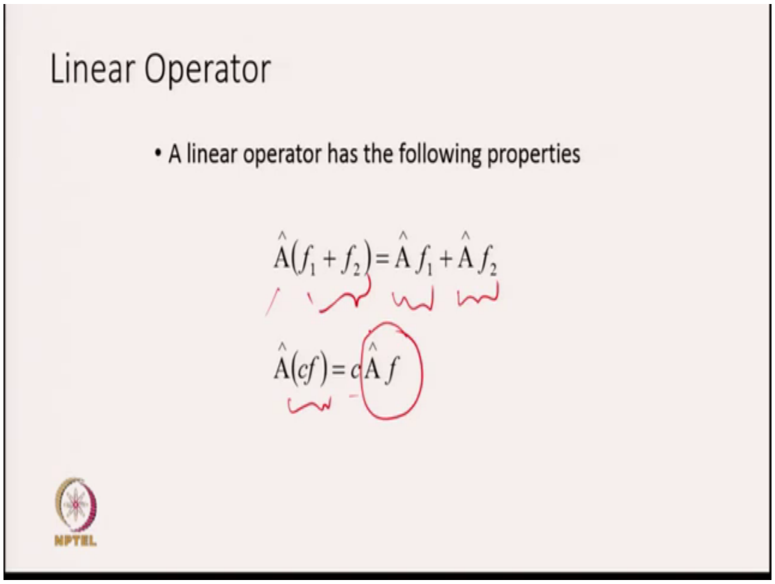

Linear Operator

- A linear operator has the following properties

$$\hat{A}(f_1+f_2)=\hat{A}f_1+\hat{A}f_2$$

$$\hat{A}(cf)=c\boxed{\hat{A}f}$$

Any operator cannot be a linear operator, a linear operator has the following property. So here is a operator is suppose it is a linear operator then when you apply this operator to the sum of two function f1 and f2 that should be equal to operator applied on function 1 plus operator applied on function 2. So A operator applied on f1 plus f2 should be equal to A operator applied on f1 plus A operator applied on f2.

The second criteria is suppose I apply this linear operator on a function multiplied by a constant it must be equal to constant multiplied by your operator when it is applied on that function. So these are the two different properties which is needed for an operator being a linear operator.

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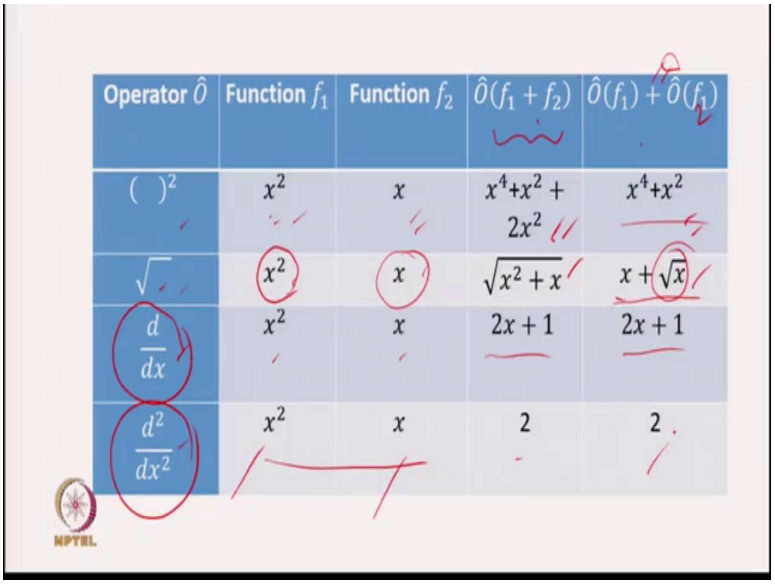

Operator $\hat{O}$	Function f_1	Function f_2	$\hat{O}(f_1+f_2)$	$\hat{O}(f_1)+\hat{O}(f_1)$
$(\ )^2$	x^2	x	$x^4+x^2+2x^2$	x^4+x^2
$\sqrt{\ }$	x^2	x	$\sqrt{x^2+x}$	$x+\sqrt{x}$
$\frac{d}{dx}$	x^2	x	$2x+1$	$2x+1$
$\frac{d^2}{dx^2}$	x^2	x	2	2

Now let us see whether all the operator are linear operators or not and what are some examples operator which are linear operator. So again I will go and discuss four different kind of operator, one is a square operator and let us choose two functions x square and x. Now if you calculate operator on sum of function f1 and f2.

So what you are going to do, you are adding a x square plus x and now you are doing a square of that, what you will get it? x 4 plus x square plus 2 x square. Now you apply this square operator on function 1 then you will get x4, if you apply this operator on function 2 you will get x square and so your operator f1 plus operator f2, this is f2 will be equal to x4 plus x square.

Now you see this two quantities are not equal for this operator, this operator, what does that mean is square operator is not a linear operator. Now think about x square root and same function we are taking x square is a function f1, x as a function f2. Now when you sum this and take under root what you will get, a square root of x square plus x.

Now when you take square root of this x square you will get x and if you take a square root of this x you will get root x. So x plus root x will be for this sum of this two operations okay.

So now you will see that the value of this is not equal to value of this, what does that mean is your operator square root is not a linear operator. Now you think about d by dx same function I have taken x square and x.

So differential x square plus x with respect to x, what you will get is 2 x plus 1 and if you do it separately again you are going to get same thing what does that mean? That mean is d by dx is a linear operator and similarly you can see about this double differential you apply to x square plus x you will get 2, if you apply separately first on x square then on x and submit, you will gain get 2.

So d square by dx square is a linear operator, so in this slide what we are able to see is that first two operator are not linear operators whereas last two first differential and second differential is example of linear operator.

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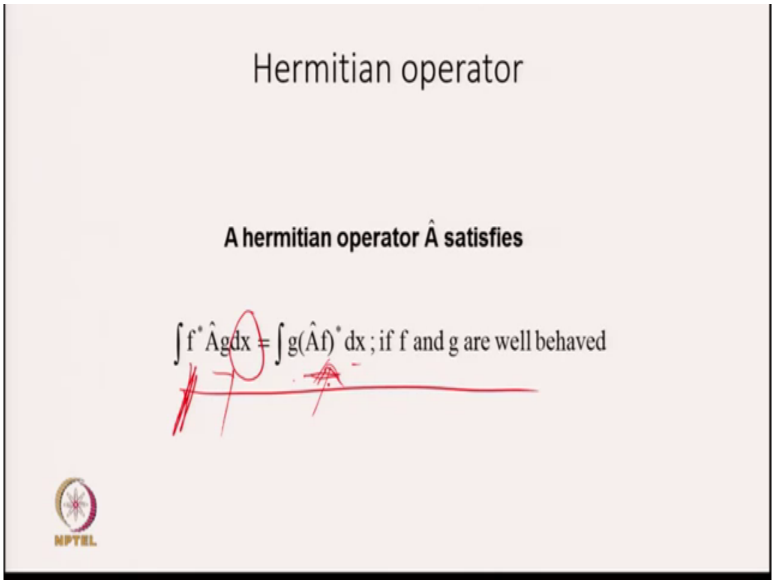

Hermitian operator

A hermitian operator $\hat{A}$ satisfies

$$\int f^* \hat{A} g dx = \int g(\hat{A} f)^* dx \text{ ; if f and g are well behaved}$$

Now after linear operator will go to Hermitian operator, what do we mean by a hermitian operator? A hermitian operator suppose A is a hermitian operator it must satisfy this condition. So now you have a two function f and g, suppose I apply this hermitian operator to g then multiply by conjugate of the second wave function f star and then multiply by volume element and integrate it, what I will get is your g multiplied by your this operator A of f. Now take the conjugate of a value which you get after operation and then dx.

So now see the difference, here what we are trying to do? You see this is initially you have you are taking conjugate of f and you are applying operator on g, now what result you should you get? You are now applying operator on f not on g and then you are taking the conjugate of this operation. The value obtained by this operation and then multiplying by g into d dx and if this is true then your operator A is a hermitian operator. So what is the importance of this hermitian operator?

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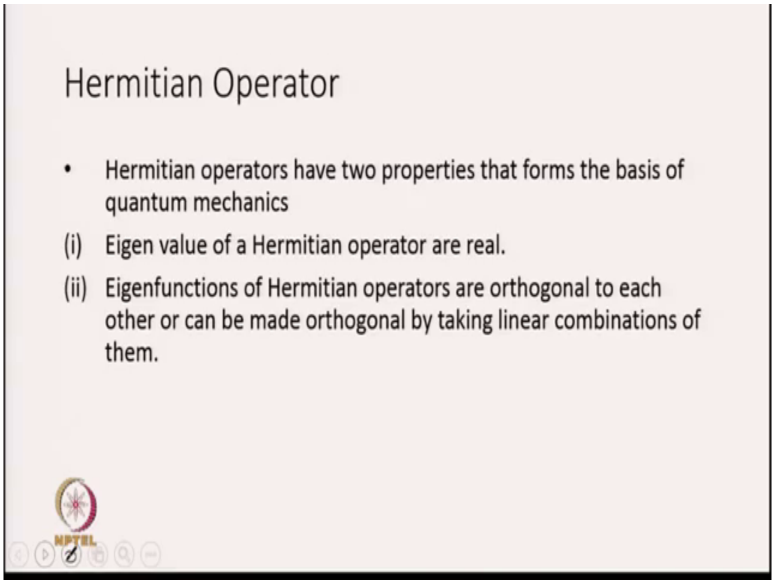

Hermitian Operator

- Hermitian operators have two properties that forms the basis of quantum mechanics

(i) Eigen value of a Hermitian operator are real.

(ii) Eigenfunctions of Hermitian operators are orthogonal to each other or can be made orthogonal by taking linear combinations of them.

Hermitian operators are very important because the eigen value of a hermitian operator are real, will discuss about this in eigen value of the operators in the next postulate. But important thing is that eigen value are real, eigen values of hermitian operator are real. The second important property about hermitian operator is eigen function of hermitian operators are orthogonal to each other or can be made orthogonal by taking linear combinations of them, linear combinations of them.

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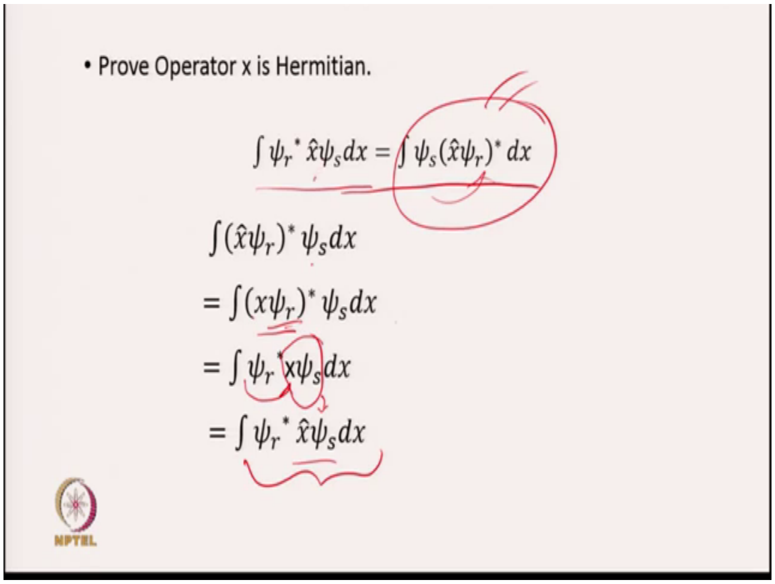

- Prove Operator x is Hermitian.

$$\int \psi_r^* \hat{x}\psi_s dx = \int \psi_s(\hat{x}\psi_r)^* dx$$

$$\int (\hat{x}\psi_r)^* \psi_s dx$$

$$= \int (x\psi_r)^* \psi_s dx$$

$$= \int \psi_r^* x\psi_s dx$$

$$= \int \psi_r^* \hat{x}\psi_s dx$$

Now let us think of can we see that whether how can we see whether a particular operator is a hermitian or not? So let us think about the operator x ok, so this is your thing you have taken two wave function Psy r and Psy s ok and now we are calculating Psy r star into x operator applied on Psy s wave function into dx.

If x is a hermitian operator then you this equation must be true. So now you see here operator is applied on Psy s now you are applying operator on Psy r and taking complex conjugate of this and then multiply Psy s dx.

If this is equal then you say that x operator is a hermitian operator, so let us star with this, so Psy s, so what we did? We took this Psy s this side so this is x operator Psy r conjugate of this multiplied by Psy x into dx. Now you see this, x operator into Psy r is simply x into Psy r and then star Psy s dx now x can come out x star is x so simply you can put this x, x from here to this point. So Psy r star which come from here multiplied by x, x takes to this side and Psy s dx.

Now this x Psy s is your can be written as x operator into Psy s. So x is a operator into Psy s is basically x multiplied by Psy s and that is what we are writing here. So we started with right hand side and we showed that this is equal to left hand side, you see this is the left hand side you see this is the left hand side and what does that mean is operator x is a hermitian operator.

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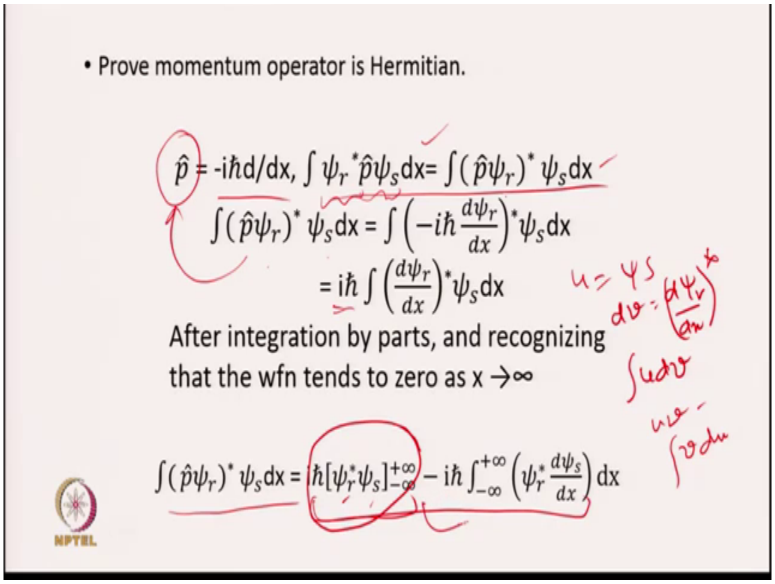

- Prove momentum operator is Hermitian.

$\hat{p}$ = -iℏd/dx, $\int \psi_r{}^* \hat{p}\psi_s dx = \int (\hat{p}\psi_r)^* \psi_s dx$

$$\int (\hat{p}\psi_r)^* \psi_s dx = \int \left(-i\hbar \frac{d\psi_r}{dx}\right)^* \psi_s dx$$

$$= i\hbar \int \left(\frac{d\psi_r}{dx}\right)^* \psi_s dx$$

$u = \psi_s$

$dv = \left(\frac{d\psi_r}{dx}\right)^*$

$\int u\,dv$

$uv - \int v\,du$

After integration by parts, and recognizing that the wfn tends to zero as x →∞

$$\int (\hat{p}\psi_r)^* \psi_s dx = i\hbar[\psi_r^* \psi_s]_{-\infty}^{+\infty} - i\hbar \int_{-\infty}^{+\infty} \left(\psi_r^* \frac{d\psi_s}{dx}\right) dx$$

Now let us go and see second example, for example can we prove that momentum operator is a hermitian operator? Momentum operator is a hermitian operator, so this is your momentum operator and this is equal to minus i h bar d by dx ok or h cross, sometime people say h bar or sometimes people say h cross. I will use h bar so minus i h bar d by dx and if I want to prove that momentum operator is a hermitian operator then I need to prove this thing.

So see again there are two wave function r and s, first is your momentum operator applied to Psy s multiplied by the conjugate of Psy r and what we should get is momentum operator applied to Psy r take the complex conjugate multiplied by Psy x dx.

Now let us start again from right hand side, so p momentum operator into Psy r complex conjugate Psy s dx is equal to let us put the operator is equal to minus i h cross d Psy r by dx star into Psy x dx.

Now complex conjugate of i is minus i and so what you will get is minus i will give you i and h bar is a constant so it is simply h bar and then you can simply put d Psy r by dx star into Psy x dx, now you have to solve this integral, what we will do? Will do integration by part to solve this integral.

So how does integral by part goes? So you see this is equal to what is your d Psy r by dx star into Psy s. So suppose this take as U is equal to Psy s, U is equal to Psy s and dv is equal to d Psy r by dx star ok and so what you are going to do is, U into dv ok. When you do integral by part what you will get? U into v first, so you see u is your Psy s so this is Psy s and dv is this so v is your Psy r star and then this i h cross minus infinity to plus infinity. So you are integrating from minus infinity to plus infinity. So first thing is this, this is u into v minus what you will get? Minus, so u into v minus what you will get?

Your v into du and that is what you did, v is your you see again Psy r star and du is d Psy s by dx into d. So this when you do that you will get this two terms and this function tends to 0 so what you are left with is the second part.

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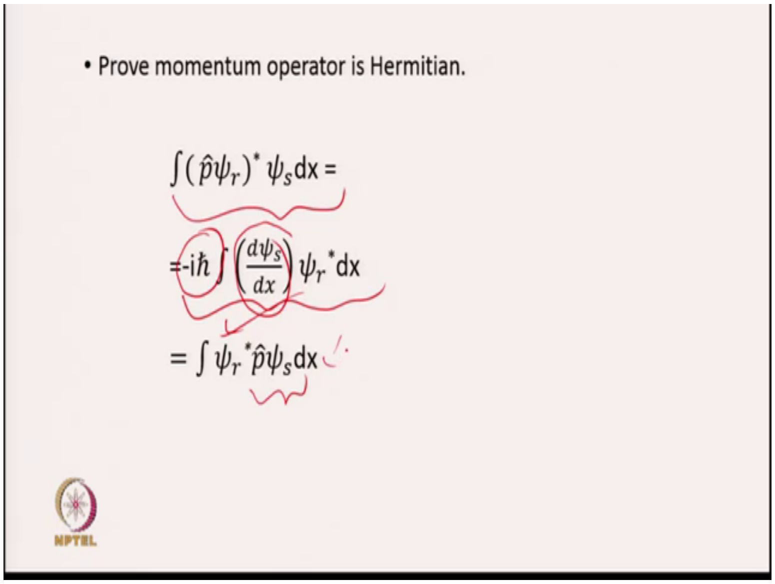

- Prove momentum operator is Hermitian.

$$\int (\hat{p}\psi_r)^* \psi_s dx =$$

$$= -i\hbar \int \left(\frac{d\psi_s}{dx}\right) \psi_r^* dx$$

$$= \int \psi_r^* \hat{p}\psi_s dx$$

And that is what it is written that this should be equal top minus h cross d Psy x by integral of d Psy x by dx Psy r star into dx and again this is Psy r star you put it here and this multiplied by this can be written as momentum operator applied on wave function Psy s and then dx and that is what we wanted to prove. So here we have proved that momentum operator is also an hermitian operator, momentum operator is hermitian operator.

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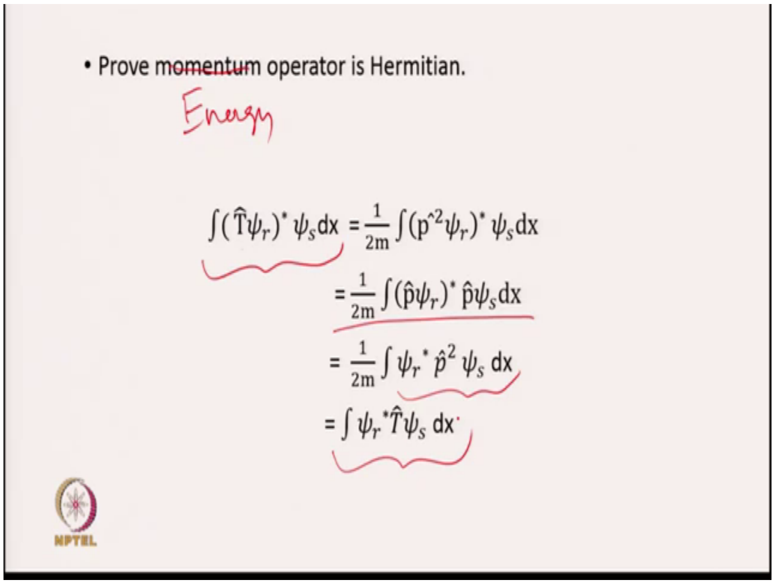

- Prove ~~momentum~~ operator is Hermitian.

Energy

$$\underbrace{\int (\hat{T}\psi_r)^* \psi_s dx}_{} = \frac{1}{2m}\int (p^{\wedge 2}\psi_r)^* \psi_s dx$$

$$= \underline{\frac{1}{2m}\int (\hat{p}\psi_r)^* \hat{p}\psi_s dx}$$

$$= \frac{1}{2m}\int \psi_r{}^* \underbrace{\hat{p}^2 \psi_s dx}_{}$$

$$= \underbrace{\int \psi_r{}^* \hat{T}\psi_s dx}_{}$$

So this is your, now we are going to prove energy operator ok, energy operator is hermitia. So your this is the energy operator and if you try to calculate the right hand side the way we did for other one so this is total energy operator applied on Psy r and then you take complex into Psy s dx your total energy operator is p square by 2 m, so you can simply write p square by 2m Psy r star Psy x dx.

First operator if you that then you will get this thing 1 by 2 m p Psy r star P Psy s dx and then when you do the second operator you will get this thing and that tells you that your energy operator is also hermitian operator. So we talked about what we mean by operator, what we mean by a linear operator, what we mean by a hermitian operator.

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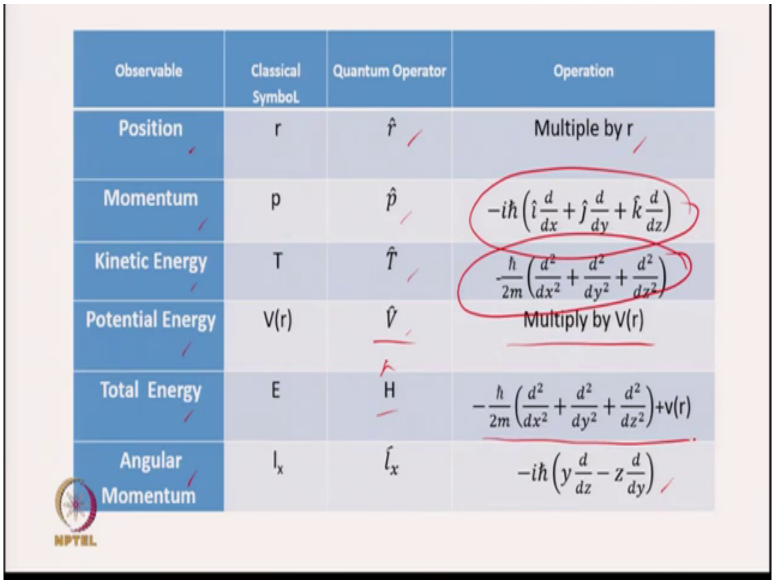

Observable	Classical SymboL	Quantum Operator	Operation
Position	r	$\hat{r}$	Multiple by r
Momentum	p	$\hat{p}$	$-i\hbar\left(\hat{\imath}\frac{d}{dx}+\hat{\jmath}\frac{d}{dy}+\hat{k}\frac{d}{dz}\right)$
Kinetic Energy	T	$\hat{T}$	$-\frac{\hbar}{2m}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)$
Potential Energy	V(r)	$\hat{V}$	Multiply by V(r)
Total Energy	E	$\hat{H}$	$-\frac{\hbar}{2m}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)+v(r)$
Angular Momentum	l_x	$\hat{l}_x$	$-i\hbar\left(y\frac{d}{dz}-z\frac{d}{dy}\right)$

So In quantum mechanics for every observables, position, momentum, kinetic energy, potential energy, total energy and angular momentum there is a quantum operator r, P, T, V, H and this lx which is your angular momentum operator and that is simply multiplication by r, this is applying this thing to the function, energy operator is or applying this operator on wave function, potential energy operator is this and what it does is it multiplies the function by V r and then Hamiltonian operator is basically sum of kinetic energy operator plus potential energy operator and this is the angular momentum operator.

This are all linear and harmitian operator, linear and harmitian operator and they when they are applied to the acceptable wave function they will give position, momentum, kinetic energy, potential energy, total energy and angular momentum.

So if you know the acceptable wave function, you can apply this operators to get different observable, so getting a right wave function is very important because that tells you about each and every observable.

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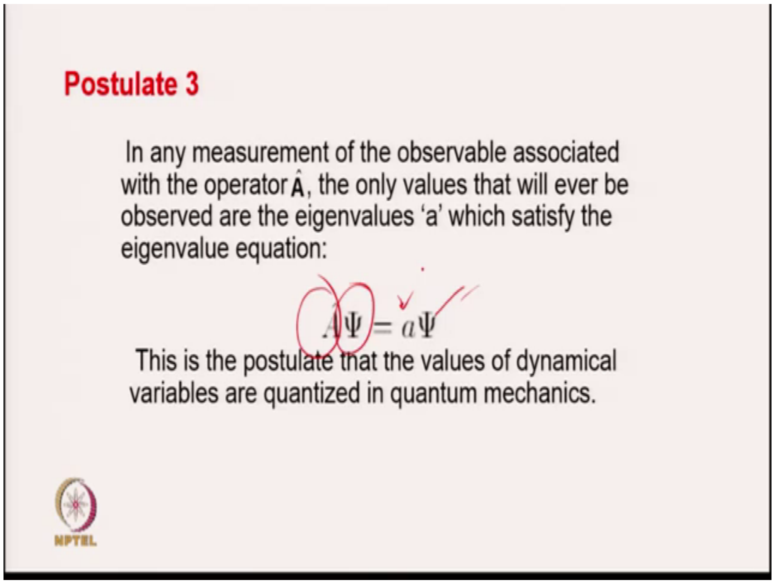

Postulate 3

In any measurement of the observable associated with the operator $\hat{A}$, the only values that will ever be observed are the eigenvalues 'a' which satisfy the eigenvalue equation:

$$A\Psi = a\Psi$$

This is the postulate that the values of dynamical variables are quantized in quantum mechanics.

So now we will go to postulate 3, according to postulate 3, in any measurement of observable associated with the operator A the only value that will ever be observed are the eigen value A is satisfy this condition.

So if you apply this operator on a wave function you are going to get wave function multiplied by a constant which is known as eigen value. If it is a real then only it can be the solution, it can be the solution.

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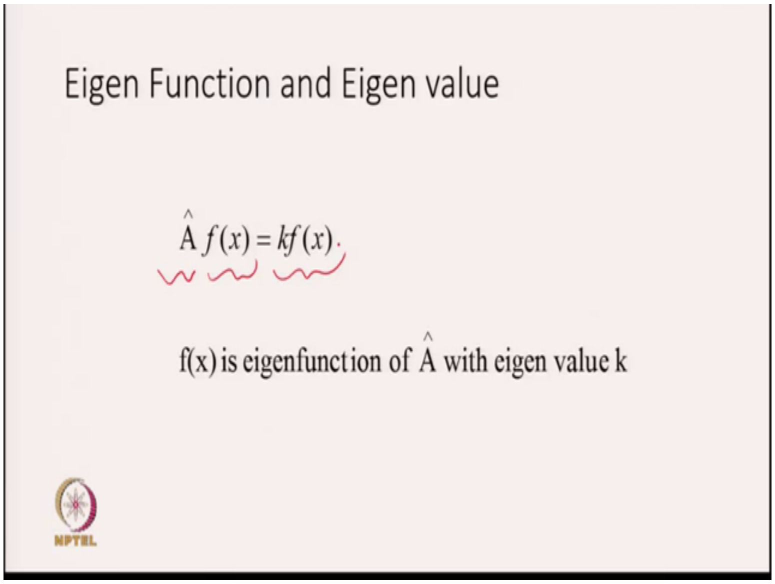

Eigen Function and Eigen value

$$\hat{A} f(x) = kf(x)$$

f(x) is eigenfunction of $\hat{A}$ with eigen value k

Okay and so here is your operator A when you apply to a function f x it will give a constant multiplied by f x. If it does that then f x is called eigen function of A with eigen value k..

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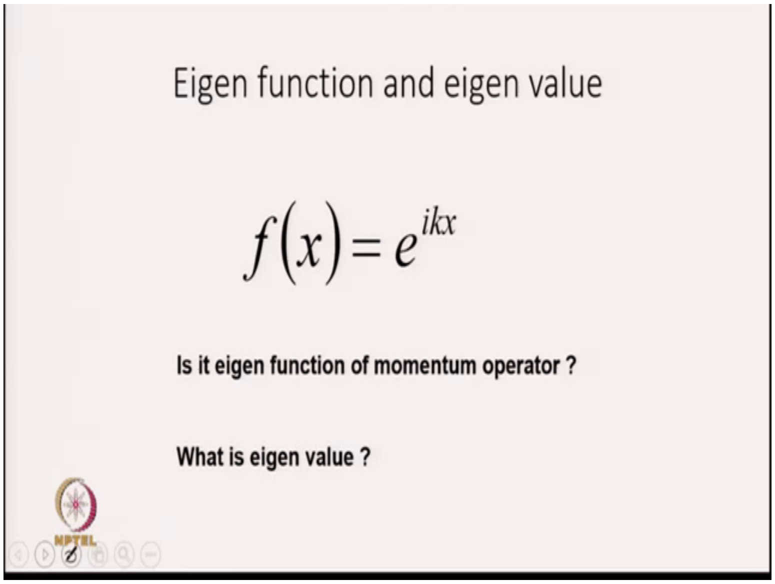

Eigen function and eigen value

$$f(x) = e^{ikx}$$

Is it eigen function of momentum operator ?

What is eigen value ?

And so let us think of a function f x is equal to exponential i k x, now first thing we have to know whether this function is eigen function of momentum operator or not and the other question we can ask is, if this is the eigen value of momentum operator then what is the eigen value?

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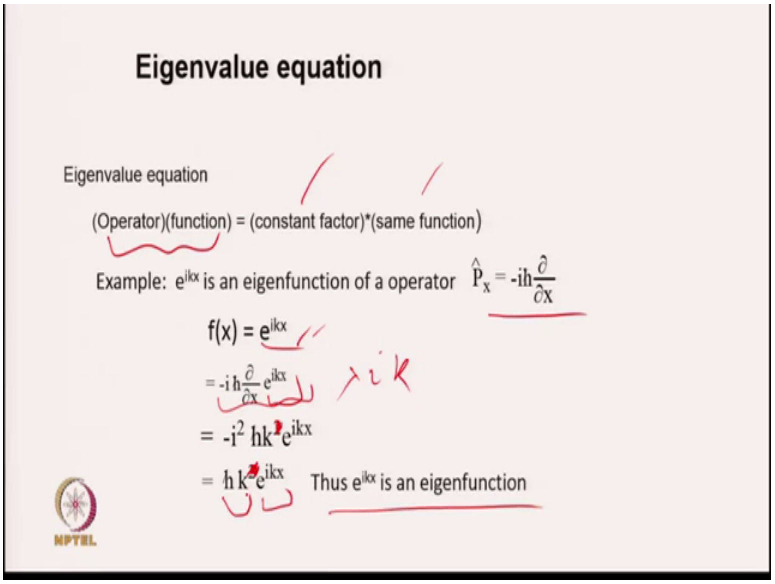

Eigenvalue equation

Eigenvalue equation

(Operator)(function) = (constant factor)*(same function)

Example: e^{ikx} is an eigenfunction of a operator $\hat{P}_x = -i\hbar\frac{\partial}{\partial x}$

$$f(x) = e^{ikx}$$

$$= -i\hbar\frac{\partial}{\partial x}e^{ikx} \quad \times ik$$

$$= -i^2 \hbar k^{\cancel{2}} e^{ikx}$$

$$= \hbar k^{\cancel{2}} e^{ikx}$$

Thus e^{ikx} is an eigenfunction

So let us see, so now what we are going to do is we are going to apply the momentum operator which is i h cross del by del x, on the function e i k x and see whether we are going to get constant multiplied by the exponential i k x.

If we get it then we will say or will say that this function is eigen function of momentum operator. So let us apply operator to this function, what you will get is i minus i h cross del by del x of this function.

When you differentiate this what you are going to get is this multiplied by this total thing multiplied by your ik and if you multiply by this you will get this will be i h cross just remove this, this is minus i square h cross k exponential I k x and so you will get minus i square is 1, so h cross k exponential I k x.

Now you see this is h cross k multiplied by this wave function, what does that mean is exponential i k x is and eigen function of momentum operator and eigen value is h bar multiplied by k.

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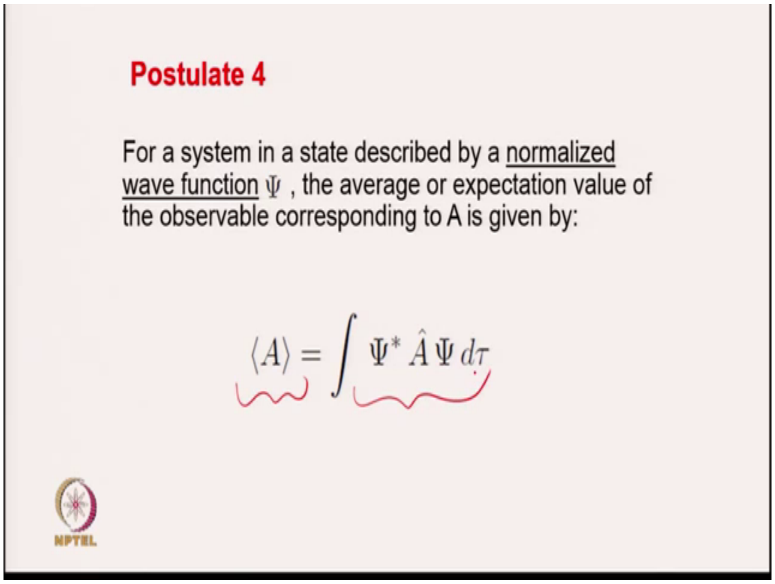

Postulate 4

For a system in a state described by a normalized wave function Ψ , the average or expectation value of the observable corresponding to A is given by:

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

Now we will go to next postulate which is postulate number 4, which tells you for a system in a state described by a normalized wave function Psy, the average or expectation value of the observable corresponding to A is given by this is the average value of A will be given by Psy star A Psy d tau.

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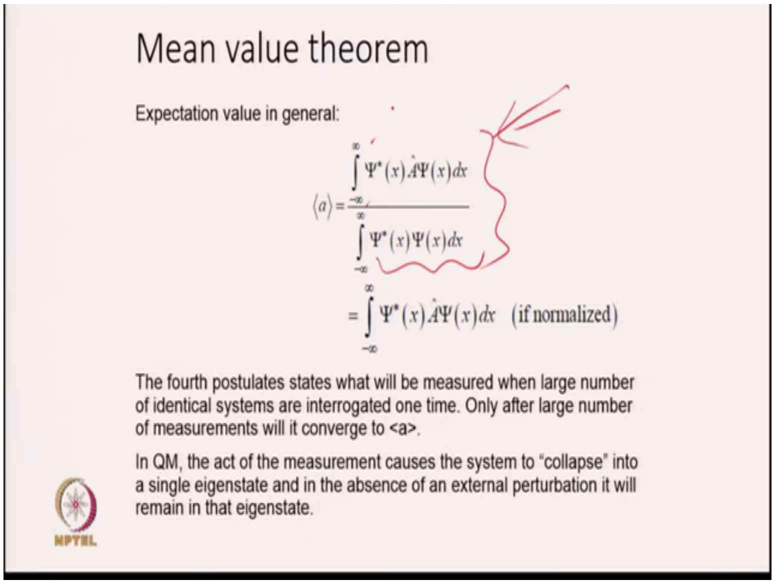

Mean value theorem

Expectation value in general:

$$\langle a \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x) \hat{A} \Psi(x) dx}{\int_{-\infty}^{\infty} \Psi^*(x) \Psi(x) dx}$$

$$= \int_{-\infty}^{\infty} \Psi^*(x) \hat{A} \Psi(x) dx \quad \text{(if normalized)}$$

The fourth postulates states what will be measured when large number of identical systems are interrogated one time. Only after large number of measurements will it converge to <a>.

In QM, the act of the measurement causes the system to "collapse" into a single eigenstate and in the absence of an external perturbation it will remain in that eigenstate.

Expectation value in general is given by this thing, this will be equal to 1 for a normalized wave function and so for a normalized wave function the average value of A will be given by Psy star x operator A on Psy x dx integrated over minus infinity to plus infinity. So this is the way you can calculate the mean value of A.

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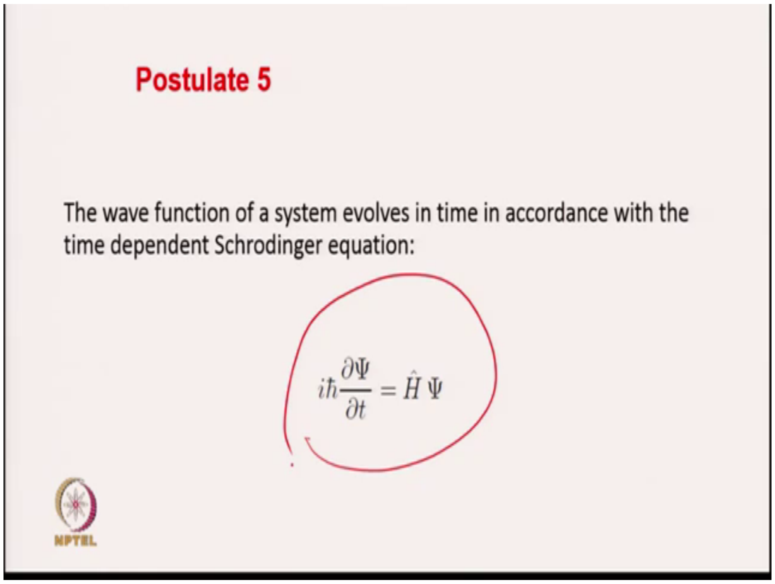

Postulate 5

The wave function of a system evolves in time in accordance with the time dependent Schrodinger equation:

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

Now postulate 5, here again we are going discuss Schrodinger equation as a part of postulate 5 and what does this tells you that wave function of a system evolves in time in accordance with time dependent Schrodinger equation and that is i h cross del Psy by del t is equal to H Psy okay, last time we discussed time independent Schrodinger equation now we will discuss how to get this time dependent Schrodinger equation.

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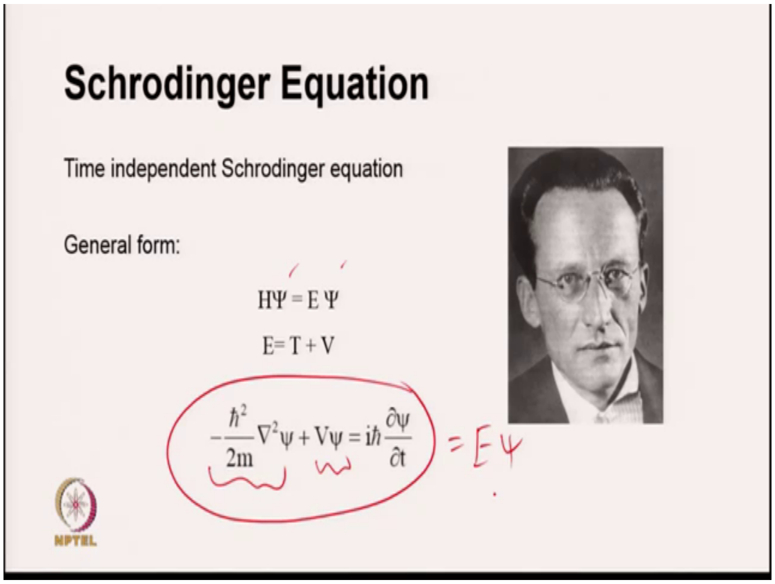

Schrodinger Equation

Time independent Schrodinger equation

General form:

$$H\Psi = E\Psi$$

$$E = T + V$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} = E\psi$$

So time dependent Schrodinger equation is given by this equation, this is your kinetic energy operator on Psy and this is plus potential energy operator applied on Psy should be equal to i h bar d Psy by dt and we know that Psy is equal to E Psy so we can simply write this is also equal to E Psy.

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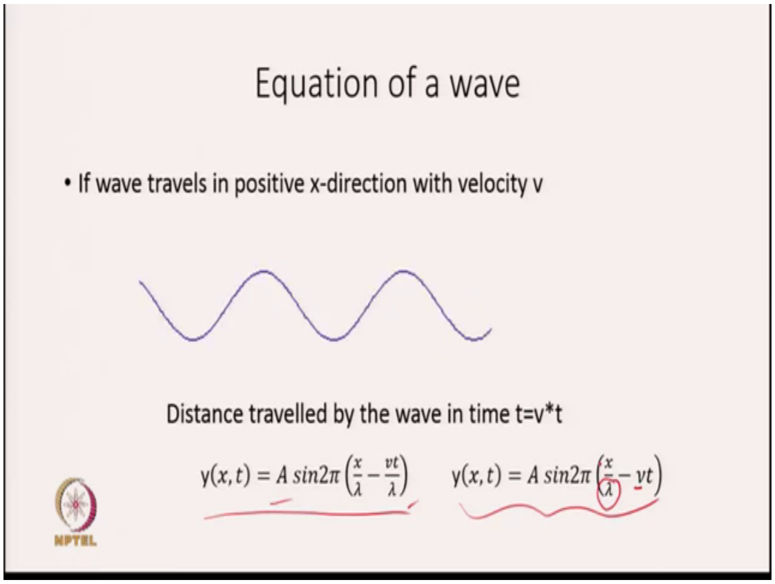

Equation of a wave

- If wave travels in positive x-direction with velocity v

Distance travelled by the wave in time t=v*t

$$y(x,t) = A\sin 2\pi\left(\frac{x}{\lambda} - \frac{vt}{\lambda}\right) \qquad y(x,t) = A\sin 2\pi\left(\frac{x}{\lambda} - \nu t\right)$$

Now we will show you how to derive this equation using a wave equation. So if you recall in the last lecture I told you that a wave travelling in positive x direction with velocity V will be given by this Sin function. So this is vertical displacement in Y direction will be given by A is a constant multiplied by sin 2 Pi x by lambda minus vt by lambda, x by lambda minus vt by lambda and your (vt) v lambda is equal to frequency for a wave travelling with a velocity C, a velocity applied. So this is your equation and I showed you that double differential of this equation and the plug in of value of lambda by H by P will give Schrodinger equation or time independent Schrodinger equation.

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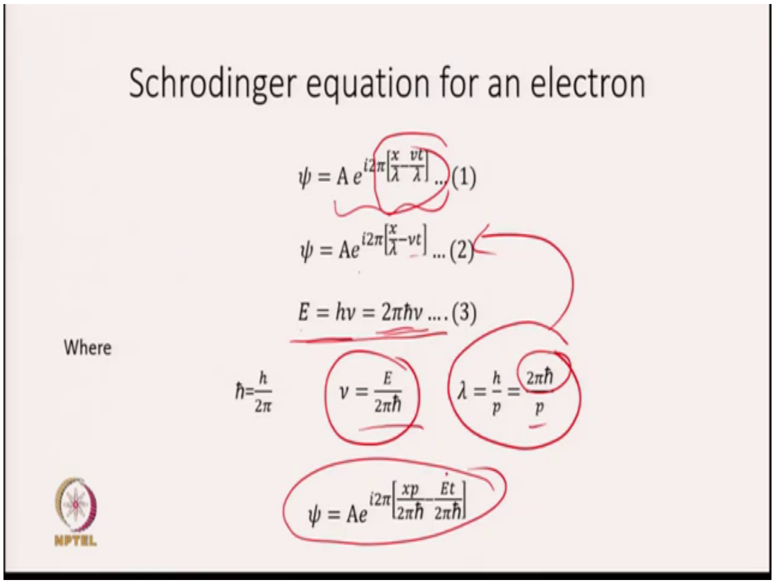

Schrodinger equation for an electron

$$\psi = A\, e^{i2\pi\left[\frac{x}{\lambda} - \frac{vt}{\lambda}\right]} \ldots (1)$$

$$\psi = A e^{i2\pi\left[\frac{x}{\lambda} - vt\right]} \ldots (2)$$

$$E = hv = 2\pi\hbar v \ldots. (3)$$

Where

$$\hbar = \frac{h}{2\pi} \qquad v = \frac{E}{2\pi\hbar} \qquad \lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$$

$$\psi = A e^{i2\pi\left[\frac{xp}{2\pi\hbar} - \frac{Et}{2\pi\hbar}\right]}$$

Now we will go and see in a detail that what this equation which I showed you as a postulate 5, how we can derive it. So the wave function associated with electron can be a complex number and so it will be better to express Psy as a function of r Psy as this, A exponential i 2 Pi x by lambda minus vt by lambda this is same what we used for the sin function.

Only thing now we are taking exponential as representation of a wave, representation of a wave, exponential function as a representation of wave. Okay so this is similar Psy is equal to A exponential i 2 Pi x by lambda minus v by lambda is your nu frequency into t and now we know that E is equal to h nu and we can write like 2 Pi h bar nu ok so you divide by 2 Pi, multiply 2 Pi, h by 2 Pi is h bar, so you can write energy as 2 Pi h bar nu.

So nu will be given by E divided by 2 Pi h bar and we know that lambda is equal to h by p, what does that mean is that this is h can be written as 2 Pi h bar divided by p. So now this two value I am going to plug in the equation 2, when you plug this two values, what you are going to get is Psy is equal to A exponential i 2 Pi x by lambda so in place of lambda you put p by 2 Pi h bar and here for nu you are putting E by 2 Pi h bar, so this is your equation for wave function associated with an electron.

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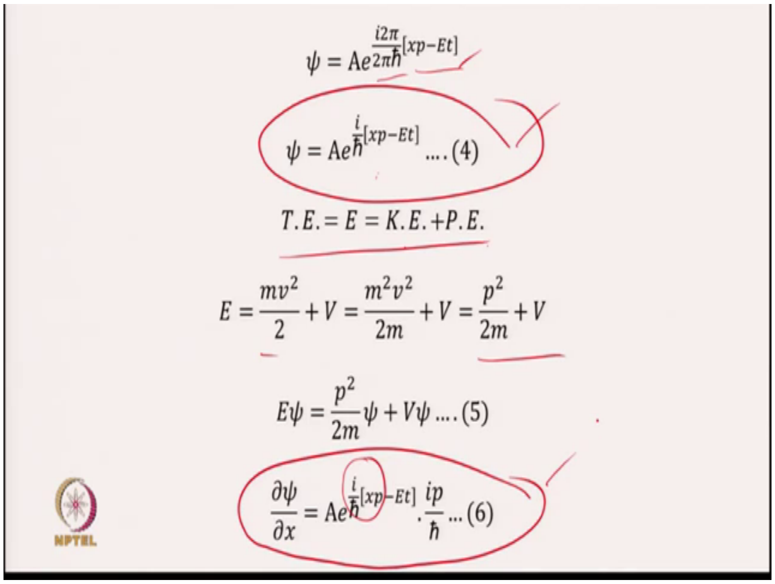

$$\psi = Ae^{\frac{i2\pi}{2\pi\hbar}[xp-Et]}$$

$$\psi = Ae^{\frac{i}{\hbar}[xp-Et]} \ldots.(4)$$

$$T.E. = E = K.E. + P.E.$$

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

$$E\psi = \frac{p^2}{2m}\psi + V\psi \ldots.(5)$$

$$\frac{\partial\psi}{\partial x} = Ae^{\frac{i}{\hbar}[xp-Et]} \cdot \frac{ip}{\hbar} \ldots(6)$$

So same equation I have written here only thing I took 2 Pi h bar out so you can simply write A exponential i 2Pi by 2 Pi h bar xp minus E t, 2 Pi, 2 Pi cancels out so this is your equation for a wave function. Now let us go and see the energy, this energy. So energy is basically your kinetic energy plus potential energy, kinetic energy is mv square by 2 plus v and p square by 2m plus v and if I put E Psy is equal to then what you are going to get is p square 2m Psy plus v Psy, I am simply differentiating this with respect to x if you do that A exponential i by h cross xp minus E t ok the this term if you differentiate that then you will going to get i p by h cross, so that is what is differential with respect to x d Psy by dx. So what I did simply, I took this and differentiated this ok.

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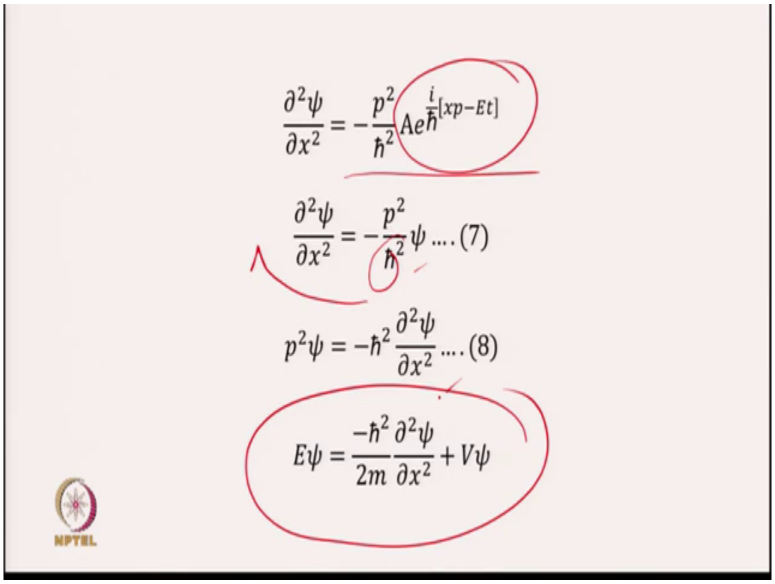

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{p^2}{\hbar^2} A e^{\frac{i}{\hbar}[xp-Et]}$$

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\psi \ldots.(7)$$

$$p^2\psi = -\hbar^2\frac{\partial^2\psi}{\partial x^2}\ldots.(8)$$

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

Now if you do double differential, so differential of Psy with respect to x, with respect to x double differential of Psy with respect to x what we are going to get is minus p square by h cross square and this whole wave function and this is simple, you can see basically this is square of i p by h cross square, i p by h cross square so minus p square by h cross square and this is your wave function so you can write del square Psy by del x square is equal to minus p square by h cross square into Psy. So p square Psy is equal to minus h cross square, minus h cross square you take this side so minus h cross square del square Psy by del x square.

And if you remember E Psy is equal to p square by 2m Psy plus v Psy ok, so E Psy is equal to p square Psy by 2m plus v Psy and this is our time independent Schrodinger equation, this we derived earlier by using a function of form sin, function of sin waveform okay. Now we can we have shown here is exponential if we take a function like this we can have the same time independent Schrodinger equation.

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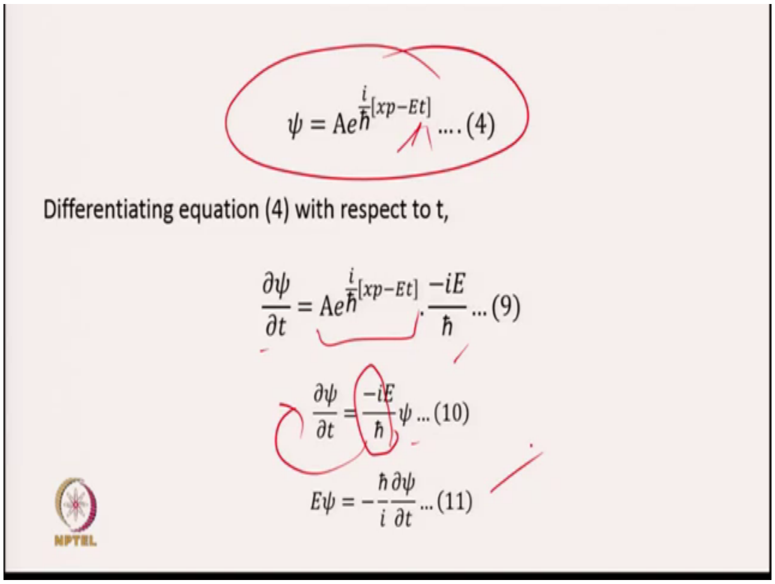

$$\psi = Ae^{\frac{i}{\hbar}[xp-Et]} \ldots.(4)$$

Differentiating equation (4) with respect to t,

$$\frac{\partial\psi}{\partial t} = \underbrace{Ae^{\frac{i}{\hbar}[xp-Et]}}_{}.\frac{-iE}{\hbar}\ldots(9)$$

$$\frac{\partial\psi}{\partial t} = \frac{-iE}{\hbar}\psi\ldots(10)$$

$$E\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}\ldots(11)$$

Now let us go and see that what we get if we differentiate this wave function with t, so we have seen how wave function changes with position x, now we will see how wave function changes with time. So wave function this already we have discussed how this wave function is given, now if I differentiate this with respect to time what am going to get is, this whole expression multiplied by now you see you have to differentiate this, so i h cross i E divided by h cross okay.

So d Psy by dt is equal to minus i E by h cross Psy or simply you can write E Psy is equal to if you take this whole this side then minus h cross by i del Psy by del t. You remember we have calculated E Psy here also and we have now another E Psy, if we differentiate del Psy by del t,we differentiate with Psy with time t. So now differential of Psy with respect to x and differential of Psy with respect to t has relationship.

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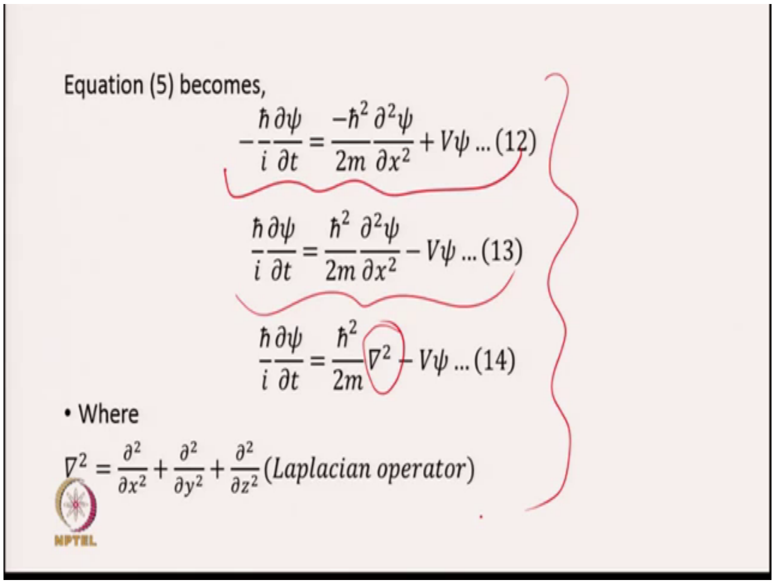

Equation (5) becomes,

$$-\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi \ldots (12)$$

$$\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = \frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} - V\psi \ldots (13)$$

$$\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = \frac{\hbar^2}{2m}\nabla^2 - V\psi \ldots (14)$$

- Where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} (Laplacian\ operator)$$

What is that relationship? Is this, minus h cross by i del Psy by dt is equal to minus h cross by 2m del A square Psy by del x square plus v Psy if you multiply this you will get this, this can be written as a Laplacian operator I have discussed that earlier also.

So this is your Schrodinger equation, this is your Schrodinger equation. So what you need to do is, you need to take a proper function for wave function associated with electron and then what you need to do is you differentiate that with respect to x, we differentiate that with respect to t and then you plug in the value of lambda from the (())(48:59) equation and you can get Schrodinger equation.

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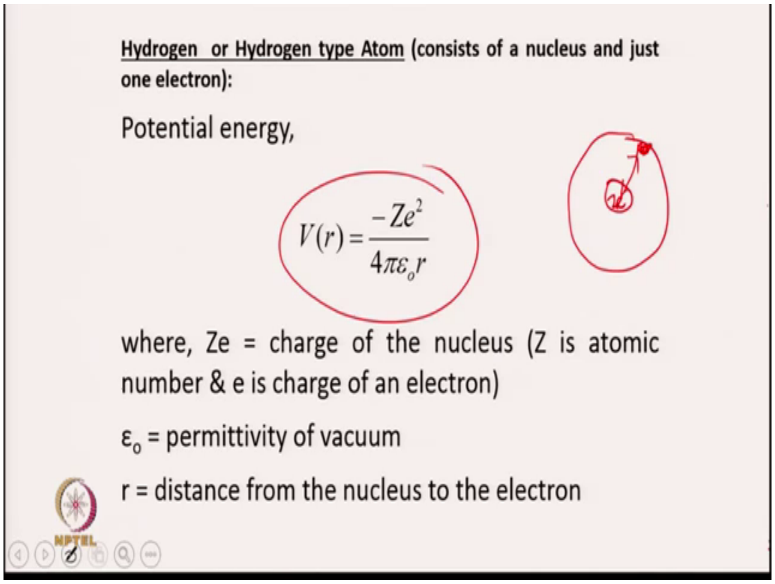

Hydrogen or Hydrogen type Atom (consists of a nucleus and just one electron):

Potential energy,

$$V(r) = \frac{-Ze^2}{4\pi\varepsilon_o r}$$

where, Ze = charge of the nucleus (Z is atomic number & e is charge of an electron)

ε_0 = permittivity of vacuum

r = distance from the nucleus to the electron

Now you know Schrodinger equation, now we will see how to write a Schrodinger equation for atom. So for example you start with hydrogen or hydrogen atom then it has a potential energy part, it has a kinetic energy part, Hamiltonian operator at both part, kinetic energy and potential energy, so first thing how to express your potential energy? So think of hydrogen atom it has nucleus which has charge Ze here Z is 1 for a proton , for a hydrogen atom and then there is 1 electron here. So this is 1 electron system we are talking about and there is a force of attraction and force of attraction can be calculated and that will be your Ze square divided by 4 Pi epsilon knot r square and from that you can calculate potential energy and potential energy is minus Ze square 4 Pi epsilon knot r.

Here Z is 1, since we are talking about hydrogen atom but Z is generally as such we are writing as a charge of the nucleus, epsilon knot is permittivity of the vacuum, r is distance from the nucleus, the distance of electron from the nucleus.

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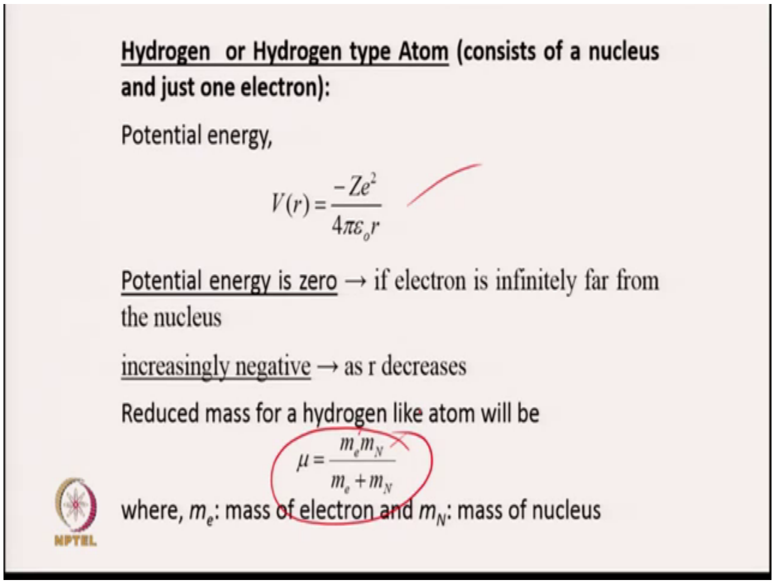

Hydrogen or Hydrogen type Atom (consists of a nucleus and just one electron):

Potential energy,

$$V(r) = \frac{-Ze^2}{4\pi\varepsilon_o r}$$

Potential energy is zero → if electron is infinitely far from the nucleus

increasingly negative → as r decreases

Reduced mass for a hydrogen like atom will be

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

where, m_e: mass of electron and m_N: mass of nucleus

So potential energy is given by this equation, if r is in infinity what does that mean is potential energy is zero if r decreases then this increasingly more negative okay and then you can write reduce mass for this kind of system and that will be given by m e in to m n by m e into m n so you have two things nucleus, one electron and so mass will be given by reduced mass and where m e is mass of electron m n is mass of nucleus.

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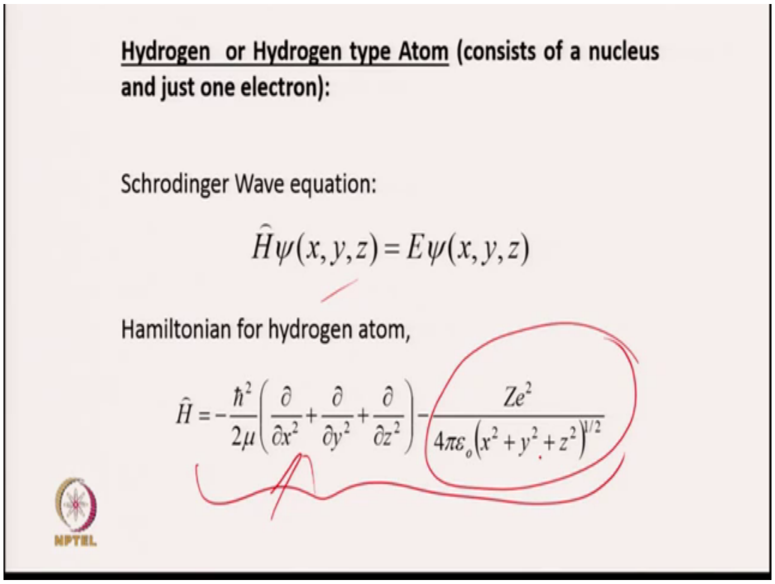

Hydrogen or Hydrogen type Atom (consists of a nucleus and just one electron):

Schrodinger Wave equation:

$$\hat{H}\psi(x,y,z) = E\psi(x,y,z)$$

Hamiltonian for hydrogen atom,

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right) - \frac{Ze^2}{4\pi\varepsilon_o\left(x^2+y^2+z^2\right)^{1/2}}$$

Once you get this v and then you can just simply put in the Schrodinger equation to get the energy of different orbital. So Hamiltonian is this for hydrogen atom so this is your kinetic energy part and this is your potential energy part so r is basically written as x square plus y square z square power half or square root of x square plus y square plus z square.

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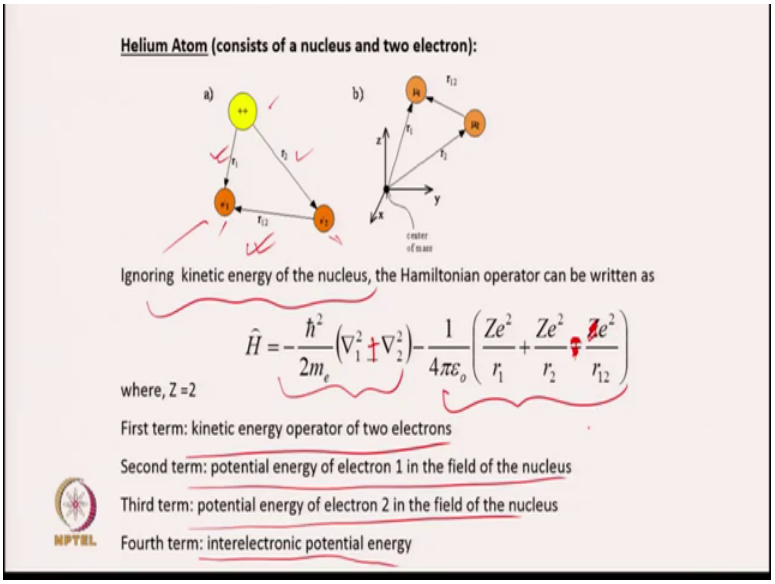

Helium Atom (consists of a nucleus and two electron):

Ignoring kinetic energy of the nucleus, the Hamiltonian operator can be written as

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right)}_{} - \underbrace{\frac{1}{4\pi\varepsilon_o}\left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} - \frac{\cancel{Z}e^2}{r_{12}}\right)}_{}$$

where, Z =2

First term: kinetic energy operator of two electrons

Second term: potential energy of electron 1 in the field of the nucleus

Third term: potential energy of electron 2 in the field of the nucleus

Fourth term: interelectronic potential energy

For helium atom, helium atom not only have 1 nucleus it has 2 electrons and so it is shown here that these are the 2 electrons this is nucleus which has two positive charge and then Hamiltonian can be written as minus h cross square by 2 m e and del 1 square plus del 2 square, so what we have done is we are ignoring kinetic energy of nucleus in that case your kinetic energy operator comes from electron 1, electron 2 and that is what we have written here and now you have potential energy part.

Potential energy part will be your Ze square by r1, you are talking about this interaction then your Ze square by r2 you are talking about this interaction and then there is a repulsion between this two electrons and so you have Ze square by r12. So this should be sorry this should be E square and here it should be minus because you have a repulsion here because of repulsion. So you have a kinetic energy part, you have a potential energy part and this is the way you write a Hamiltonian for a system.

First term, kinetic energy operator have 2 electrons, second term potential energy of electron 1 in the field of nucleus, potential energy of electron 2 in the field of nucleus and this is inter-electronic potential energy and that is minus Ze square by r12.

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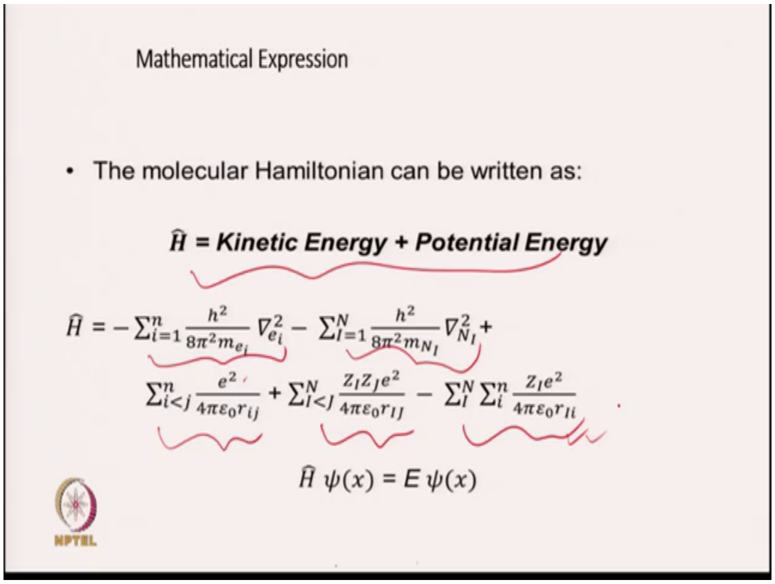

Mathematical Expression

- The molecular Hamiltonian can be written as:

$$\hat{H} = \textit{Kinetic Energy} + \textit{Potential Energy}$$

$$\hat{H} = -\sum_{i=1}^{n} \frac{h^2}{8\pi^2 m_{e_i}} \nabla_{e_i}^2 - \sum_{I=1}^{N} \frac{h^2}{8\pi^2 m_{N_I}} \nabla_{N_I}^2 + \sum_{i<j}^{n} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{I<J}^{N} \frac{Z_I Z_J e^2}{4\pi\varepsilon_0 r_{IJ}} - \sum_{I}^{N} \sum_{i}^{n} \frac{Z_I e^2}{4\pi\varepsilon_0 r_{Ii}}$$

$$\hat{H}\,\psi(x) = E\,\psi(x)$$

Okay so similar way in a similar way you can write Hamiltonian for hydrogen molecule and for that again Hamiltonian can be written as sum of kinetic energy term and potential energy term, Hamiltonian for kinetic energy term for electron is given like this and this is your again for nucleus so one is for electron, another is for nucleus okay and then and this would be i is equal to 1 to n and this is i is equal to 1 to n so for two hydrogen atom there will be two terms and then this is your potential energy term, this three are potential energy term and you can see that this is E square by so this you are talking about repulsion between two electrons, this is between two nucleus Zi, Zj E square so this is potential energy due to interaction between two nucleus and then this is potential energy due to interaction between nucleus and electron.

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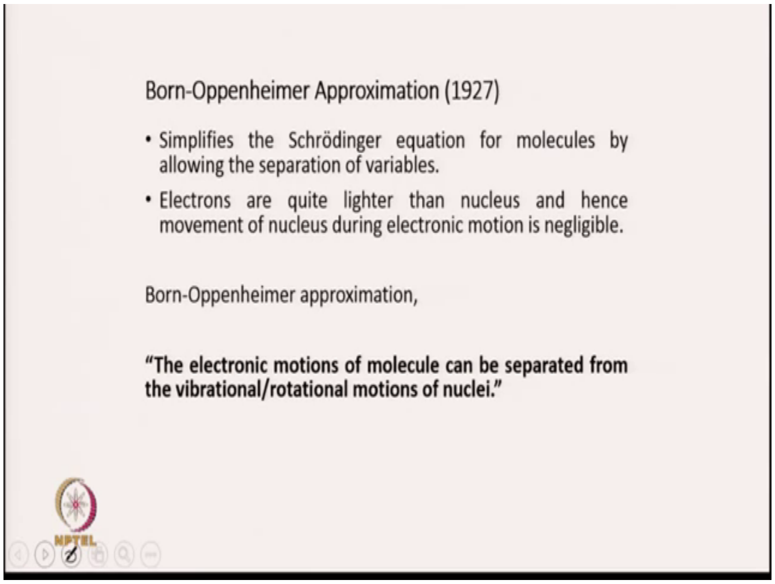

Born-Oppenheimer Approximation (1927)

- Simplifies the Schrödinger equation for molecules by allowing the separation of variables.
- Electrons are quite lighter than nucleus and hence movement of nucleus during electronic motion is negligible.

Born-Oppenheimer approximation,

"The electronic motions of molecule can be separated from the vibrational/rotational motions of nuclei."

Now as you go for a bigger molecule Schrodinger equation becomes complex so here this Born-Oppenheimer Approximation helps you. What is tells you that electrons are quite lighter than nucleus that we already know so this approximation is fact and tells you that you can neglect the motion of movement of nucleus during electronic motion and what does that mean is that electronic motion of molecule can be separated from vibration rotational motions of nuclei.

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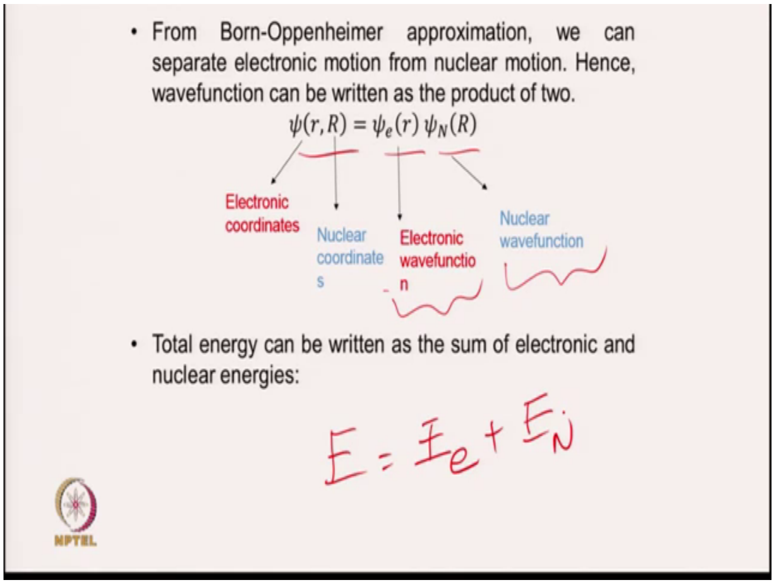

- From Born-Oppenheimer approximation, we can separate electronic motion from nuclear motion. Hence, wavefunction can be written as the product of two.

$$\psi(r,R) = \psi_e(r)\,\psi_N(R)$$

Electronic coordinates

Nuclear coordinates

Electronic wavefunction

Nuclear wavefunction

- Total energy can be written as the sum of electronic and nuclear energies:

$$E = E_e + E_N$$

We can separate the wave function due to electron and wave function due to nucleus. So wave function can be written as wave function due to electron multiplied by wave function due to nucleus and so this is Psy e is called electronic wave function, Psy N called nuclear wave function so your wave function is Psy e multiplied by Psy N and total energy can be written as sum of electronic energy and nuclear energy. So total energy can be written as sum of electronic and nuclear energy.

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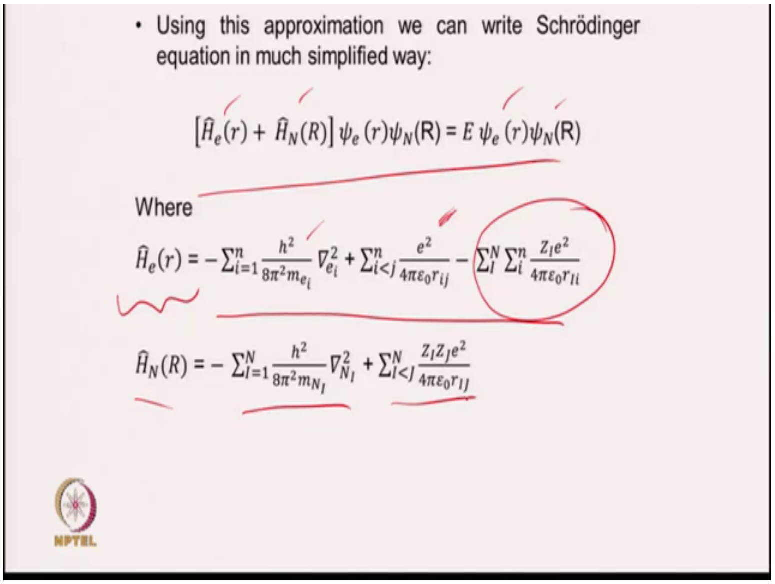

- Using this approximation we can write Schrödinger equation in much simplified way:

$$[\hat{H}_e(r) + \hat{H}_N(R)]\,\psi_e(r)\psi_N(\mathrm{R}) = E\,\psi_e(r)\psi_N(\mathrm{R})$$

Where

$$\hat{H}_e(r) = -\sum_{i=1}^{n}\frac{h^2}{8\pi^2 m_{e_i}}\nabla_{e_i}^2 + \sum_{i<j}^{n}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} - \sum_{I}^{N}\sum_{i}^{n}\frac{Z_I e^2}{4\pi\varepsilon_0 r_{Ii}}$$

$$\hat{H}_N(R) = -\sum_{I=1}^{N}\frac{h^2}{8\pi^2 m_{N_I}}\nabla_{N_I}^2 + \sum_{I<J}^{N}\frac{Z_I Z_J e^2}{4\pi\varepsilon_0 r_{IJ}}$$

So using that equation we can write Schrodinger equation for hydrogen molecule in much simpler way and this is the way you can write Hamiltonian now is written as a two term and then your function is written as multiplication of this two wave function where your Hamiltonian for electrons or electronic Hamilton of electronic wave function is given as this.

This is kinetic energy for the electron, this is potential energy due to repulsion between two electrons and this is your potential energy due to interaction of electron with nucleus and then your Hamiltonian of nucleus will be given by this is the kinetic energy term and this is the interaction between two nucleus.

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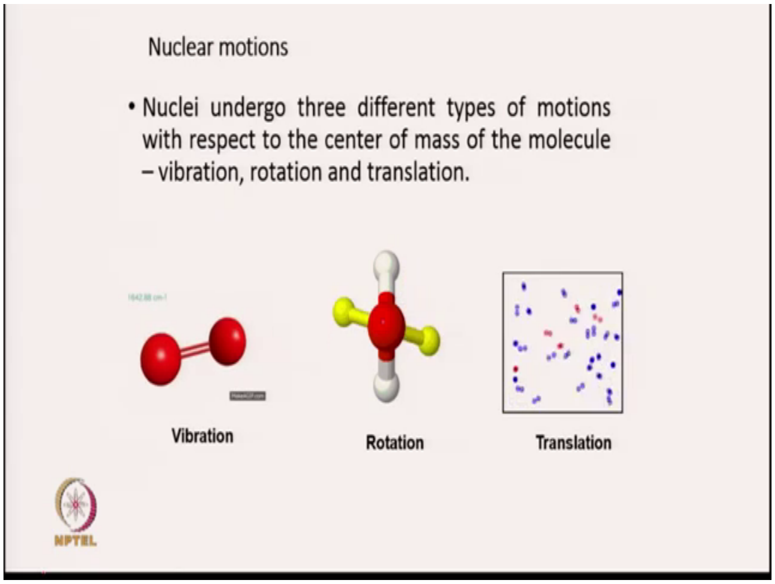

Nuclear motions

- Nuclei undergo three different types of motions with respect to the center of mass of the molecule – vibration, rotation and translation.

Vibration

Rotation

Translation

Now nuclei can undergo three different type of motion with respect to center of mass that is vibration, rotation and translation. So this is your vibration motion, this is your rotation and this is your translation.

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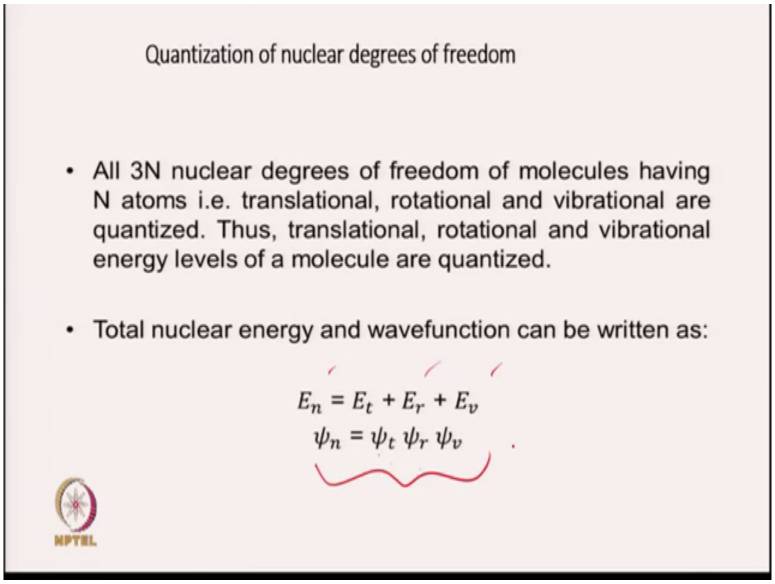

Quantization of nuclear degrees of freedom

- All 3N nuclear degrees of freedom of molecules having N atoms i.e. translational, rotational and vibrational are quantized. Thus, translational, rotational and vibrational energy levels of a molecule are quantized.
- Total nuclear energy and wavefunction can be written as:

$$E_n = E_t + E_r + E_v$$

$$\underbrace{\psi_n = \psi_t \psi_r \psi_v}$$

All these 3N nuclear degree of freedom of molecule having N atoms so if there is a N atom in a molecule there will be 3N nuclear degree of freedom that includes translation, rotational and vibrational. The energy level due to this motions are also quantized. So in a similar way the way we have done for nuclear and electrons, even nuclear energy can be divided into 3 different part, so E n is equal to E t plus E r and E v, nuclear wave function is given by translation wave function multiplied by wave function due to rotation, wave function due to vibration, so they are quantized, this are the simple rules which can be very useful in simplification of Schrodinger equation and it is used to simplify equation and get the energy levels of different of energy levels associated with different quantized levels.

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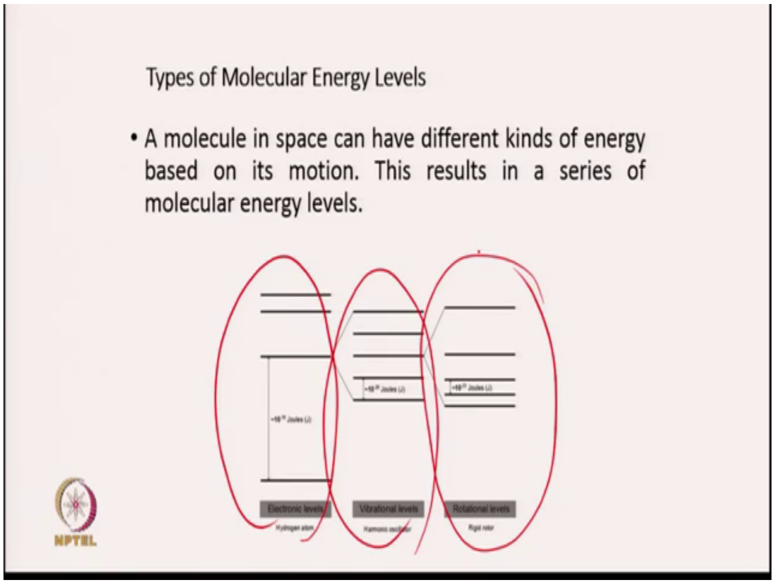

Types of Molecular Energy Levels

- A molecule in space can have different kinds of energy based on its motion. This results in a series of molecular energy levels.

So depending on motion energy can be of different type or quantized energy levels can be of different type, you have electronic levels. Within one electronic levels you have a vibrational levels and within one vibrational level there are several rotational levels and depending on kind of wavelength absorbed or emitted you are either dealing with electronic spectra or rotational spectra or vibrational spectra. So this is the basis of calculating the energy of different quantized level.

So in this lecture I discussed about a wave function and how to calculate the energy associated with different quantized level and now we are set up for discussing different kind of a spectroscopy, different kind of spectroscopy. In the next lecture what I am going to do is, I am going to first discuss about general features of different spectroscopy, general features of different spectroscopy for example intensity, resolution, Fourier transformation these are some general features of the spectroscopy.

Once I discussed that then I will go to each and every spectroscopy for example rotational spectroscopy, vibrational spectroscopy, Roman spectroscopy I will again talk about basics associated with those spectroscopy and then finally we will move to application part.

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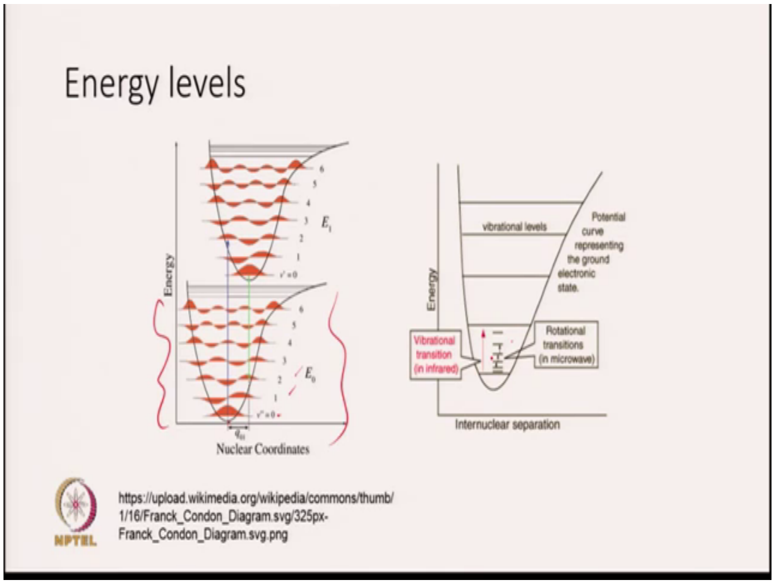

Energy levels

https://upload.wikimedia.org/wikipedia/commons/thumb/1/16/Franck_Condon_Diagram.svg/325px-Franck_Condon_Diagram.svg.png

So these are the different levels, you can see this is your electronic levels and if the transition happens from this to this then you say that you have electronic spectra, if transition happens in between so this are the vibrational levels in between then you are dealing with vibrational spectra. Within each vibrational levels there are rotational level and if transition happens in this you are basically dealing with rotational spectra. So I will stop here, thank you very much, see you in the next lecture, bye these are the some books which I am following and so please have a look at it if you want for the reading and thank you very much.