Quantum Mechanics and Molecular Spectroscopy
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Lecture-02
Operators and Integrals

Hello I am G. Naresh Patwari and I am teaching quantum mechanics and molecular spectroscopy course, welcome to the lecture number 2. Before we go into lecture number 2 we will have a quick recap of what we have done in lecture number 1.

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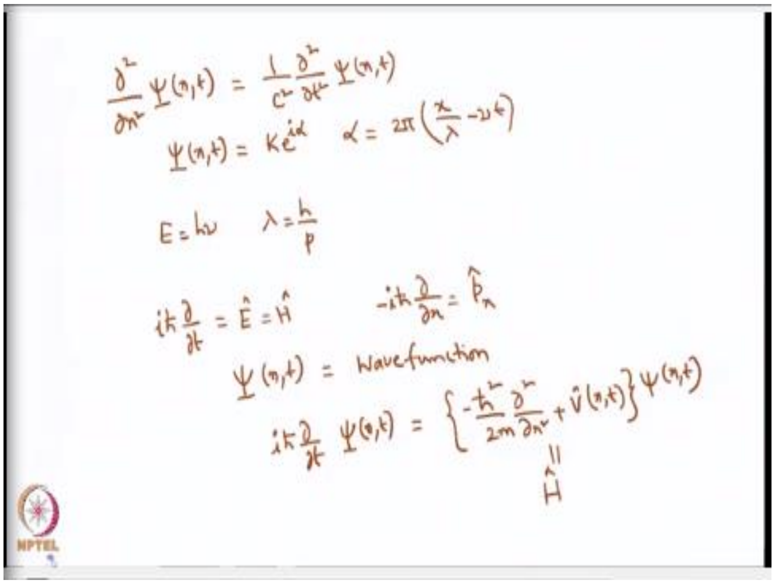

$$\frac{\partial^2}{\partial x^2}\Psi(x,t) = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\Psi(x,t)$$

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

$$E = h\nu \qquad \lambda = \frac{h}{p}$$

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

$\Psi(x,t)$ = Wavefunction

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

In the lecture number 1 starting with classical wave equation which is nothing but d square by dx square of psi of x, t is equal to 1 over c square d square by dt square psi of x, t where psi of x, t is equal to Ke to the power of i alpha and alpha is equal to 2 pi x by lambda - nu t. Using this information from classical equations combined with E equals to h nu and lambda is equal to h by P is Planck Einstein equation and the de Broglie equation.

We arrived at 2 operators i h bar d by dt is equal to operator E or operator h - h bar d by dx is equal to operator p x. We further developed that the psi of x t is equal to wave function and is governed by the time dependent Schrodinger equation which says i h bar d by dt of psi of x, t is equal to - h bar square by 2m t square by dx square + V of x, t acting on psi of x, t. Therefore the time dependence of the wave function psi of x t will depend on the Hamiltonian equation and this is called Hamiltonian operator H ok.

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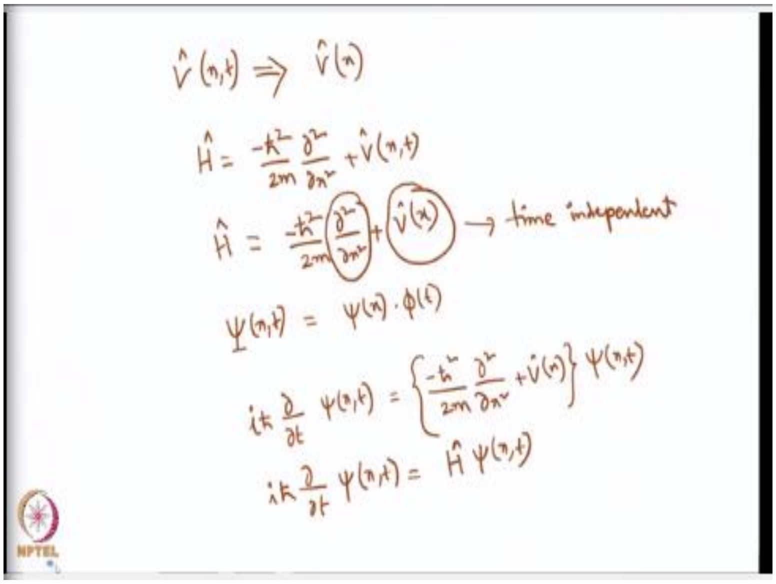

$$\hat{V}(x,t) \Rightarrow \hat{V}(x)$$

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

$$\hat{H} = \frac{-\hbar^2}{2m}\boxed{\frac{\partial^2}{\partial x^2}} + \boxed{\hat{V}(x)} \rightarrow \text{time independent}$$

$$\Psi(x,t) = \psi(x)\cdot\phi(t)$$

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

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

It turns out that in many problems that we deal in chemistry, the potential energy operator V is of x t can be termed as V of x because has no time dependence. For example you will take a hydrogen atom and hydrogen atom will remain as hydrogen atom in for the infinite time because the potential is time independent. Similarly harmonic cost arrival will continue to remain harmonic oscillator.

So, most of the problems or the systems that we deal in quantum chemistry in chemistry in particular have no time dependence on the potential. Therefore H which was - h bar square by 2m b square by dx square + V of x, t can be written as - h bar square by 2m d square by dx square + V of x. You will see that the kinetic energy operator which is nothing but - h bar square by 2m d square by dx square has no time dependence.

Similarly the potential energy also has no time dependence hence the Hamiltonian becomes time independent. In such a scenario the wave function psi of x t can be written as product of psi of x multiplied by pi of t. Because if you see Hamiltonian only depends on the coordinate any partial derivative with respect coordinate will have time as a constant. Therefore pi of t can be bought out of the wave function.

If you go back to the Schrodinger equation which is nothing but i h bar d by dt of psi of x, t is equal to - h bar square by 2m d square by dx square + V of x psi of x, t. I will write it as i h bar d by dt psi of x, t is equal to h psi of x, t but your psi of x t is now a product of psi of x into pi of t.

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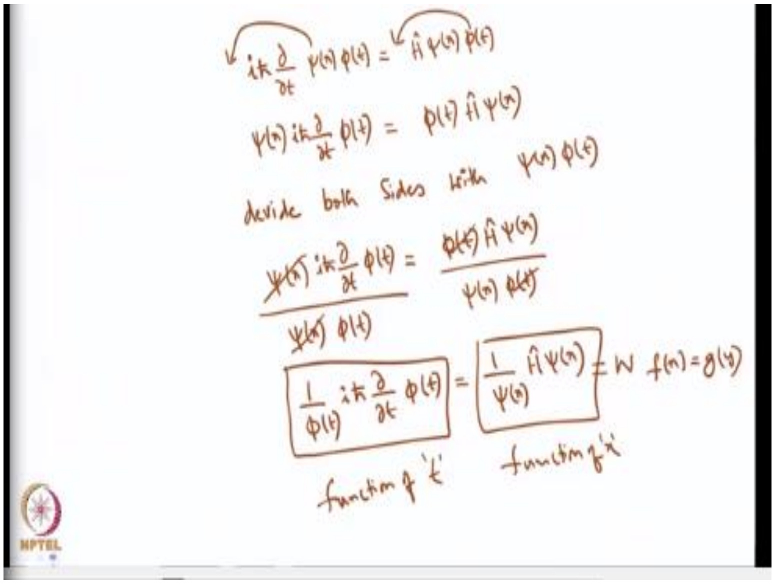

$$i\hbar \frac{\partial}{\partial t} \psi(x)\phi(t) = \hat{H}\psi(x)\phi(t)$$

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

divide both Sides with $\psi(x)\phi(t)$

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

$$\boxed{\frac{1}{\phi(t)}\, i\hbar \frac{\partial}{\partial t} \phi(t)} = \boxed{\frac{1}{\psi(x)} \hat{H}\psi(x)} \neq W \quad f(x) = g(y)$$

function of 't' function of 'x'

So, the Schrodinger equation now becomes i h bar d by dt of psi of x into pi of t is equal to h times pi of x t ok. Now d by dt on the left hand side d by dt when it acts on psi of x psi of x becomes a constant. Similarly h which only depends on the coordinates acts on pi of t pi of t becomes constant. Therefore one can get psi of x outside and pi of t outside, so when I do that I can write this equation as psi of x i h bar d by dt of pi of t is equal to pi of t H psi of x.

What I am going to do is I am going to divide both sides with psi of x pi of t, when I do that psi of x i h bar d by dt of pi of t is equal to pi of t H psi of x divided by psi of x to pi of t divided by psi of x to pi of t or this pi of t will cancel on both sides on the numerator and denominator this psi of x will cancel on the both numerator and denominator. So, what you will get is 1 over pi of t i h bar d by dt of pi of t is equal to 1 over psi of x H psi of x.

You will see that the left hand side is a function of t and the right hand side is a function of x. So, I am equating 2 functions of 2 different variables, for example if I equate f of x with g of y this will be only possible if both the functions, this will be possible only a both the functions are equal to a constant and that constant I will call it as w.

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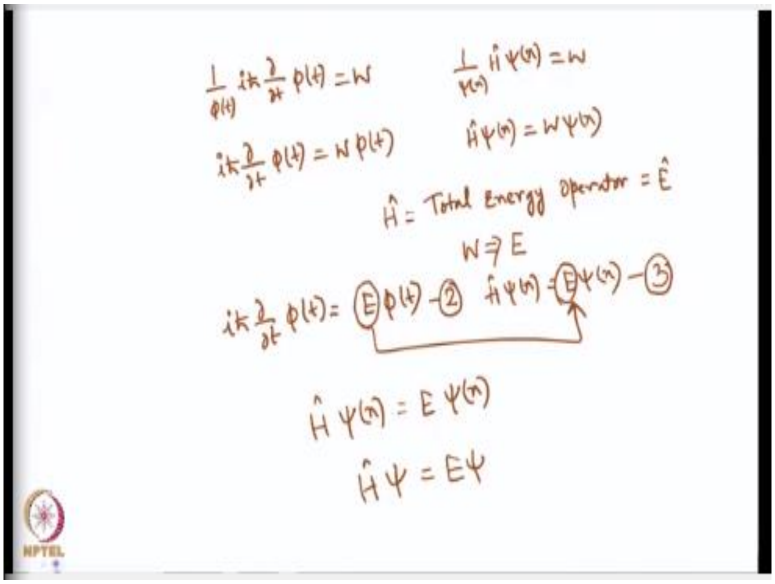

$$\frac{1}{\phi(t)} i\hbar \frac{\partial}{\partial t}\phi(t) = W \qquad \frac{1}{\psi(x)}\hat{H}\psi(x) = W$$

$$i\hbar \frac{\partial}{\partial t}\phi(t) = W\phi(t) \qquad \hat{H}\psi(x) = W\psi(x)$$

$\hat{H}$ = Total Energy Operator = $\hat{E}$

$W \Rightarrow E$

$$i\hbar \frac{\partial}{\partial t}\phi(t) = \textcircled{E}\,\phi(t) - ② \qquad \hat{H}\psi(x) = \textcircled{E}\,\psi(x) - ③$$

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

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

So, you end up getting 2 equations because of that one t and one is x 1 over pi of t i h bar d by dt of pi of t is equal to w, 1 over psi of x h psi of x is equal to w. So, when I rewrite i h bar d by dt of pi of t is equal to W pi of t, H psi of x is equal to w psi of x. Now we know Hamiltonian is nothing but the total energy operator. So, H is equal to and this is also equal to operator E that is something that we have discussed in class number 1 ok.

So, it is easy to replace w with t there, when I do that what I get is i h bar d by dt of pi of t is equal to e pi of t and H psi of x is equal to E psi of x. So, I get 2 equations for which both cases E is the Eigen value. So, the Eigen value E will depend on the time dependence of the system and Eigen value E will depend on the coordinates of the system. However, in the first case it will depend on the time dependent operator d by dt.

And in the second case it depends on the Hamiltonian ok and these 2 anyway you can see are equal. And this equation called this equation as 2 and this as 3, we will realize that equation number 3 is nothing but time independent Schrodinger equation which is nothing but equation number 2 will be h psi of x is equal to E psi of x generically written as h psi equals to E psi and this equation is nothing but your time independent Schrodinger equation.

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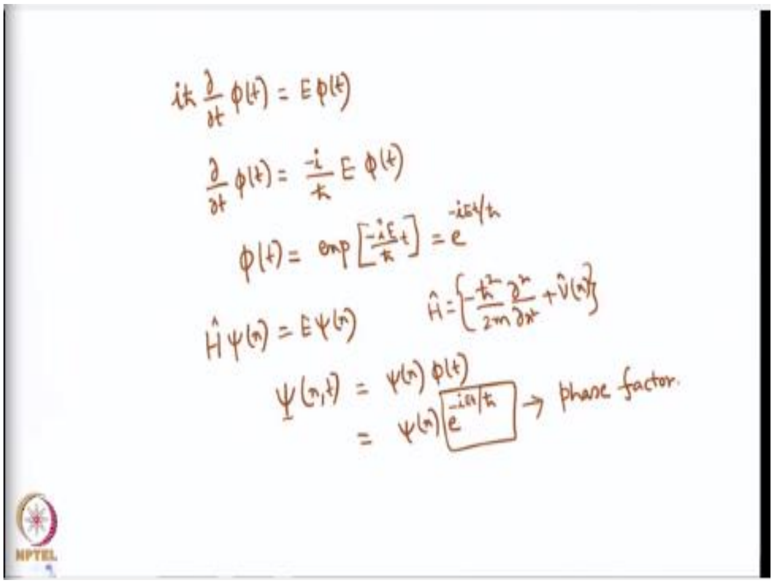

$$i\hbar \frac{\partial}{\partial t}\phi(t) = E\phi(t)$$

$$\frac{\partial}{\partial t}\phi(t) = \frac{-i}{\hbar}E\,\phi(t)$$

$$\phi(t) = \exp\left[\frac{-iE}{\hbar}t\right] = e^{-iEt/\hbar}$$

$$\hat{H}\psi(x) = E\psi(x) \qquad \hat{H} = \left\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}(x)\right\}$$

$$\psi(x,t) = \psi(x)\,\phi(t)$$

$$= \psi(x)\boxed{e^{-iEt/\hbar}} \rightarrow \text{phase factor.}$$

Now, the time dependent equation what you have is i i h bar d by dt of pi of t is equal to E pi of t. So, if I slightly rewrite this d by dt of pi of t equals to when I go on the other side i becomes - i. So, - i h bar will go to denominator E pi of t, so essentially when I operate d by dt operator on pi of t I will get - i by h bar E as a Eigen value ok. Now this means I can solve this first order differential equation very easily ok. And when I solve it the solution will be pi of t equal to exponential - i pi h bar E times t or simply written as E to the power of - i E t by h bar ok.

Now the other equation is h psi of x is equal to E psi of x but my H is nothing but - h bar square by 2m d square by dx square + V of x solution to this is going to be much more complicated ok and I have not solved it. We will come to the solutions of it in a minute but the total wave function that is psi of x, t can now be written as psi of x to pi of t which is nothing but psi of x into e to the power of - i E t by h bar ok and in this case this is called phase factor.

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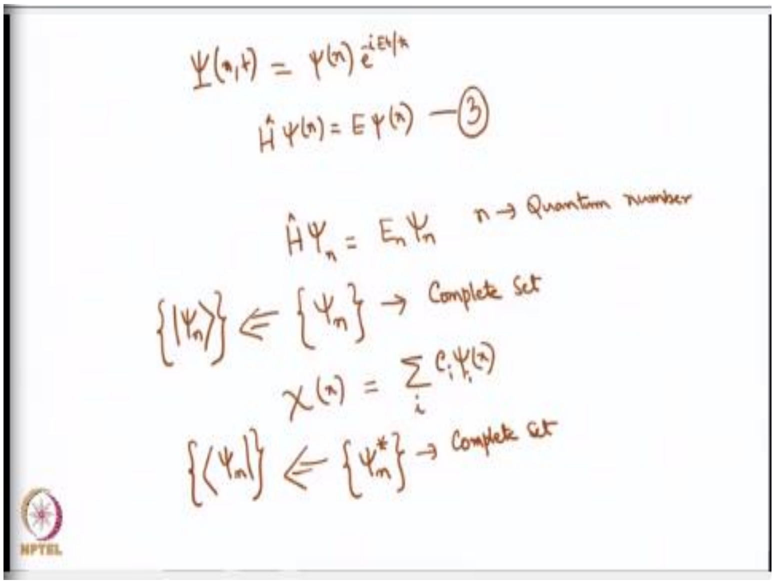

$$\Psi(x,t) = \psi(x)\, e^{-iEt/\hbar}$$

$$\hat{H}\psi(x) = E\psi(x) \quad \text{—③}$$

$$\hat{H}\Psi_n = E_n\Psi_n \quad n \rightarrow \text{Quantum number}$$

$$\{|\Psi_n\rangle\} \Leftarrow \{\Psi_n\} \rightarrow \text{Complete Set}$$

$$\chi(x) = \sum_i C_i \Psi_i(x)$$

$$\{\langle\Psi_m|\} \Leftarrow \{\Psi_m^*\} \rightarrow \text{Complete Set}$$

Total functions wave functions psi of x, t is equal to psi of x e to the power of - i E t by h bar. Unfortunately I still do not know how to solve for psi of x because for that I need to solve h psi of x is equal to E psi of x ok. Solution to this equation or the time independent Schrodinger equation is beyond the purview of this course. If you want to know how to solve this equation then you might want to look up other NPTEL courses such as introduction to quantum chemistry by Professor K.L Sebastian.

In this course of course we will assume that we know the solutions typically for a time dependence, typically for a time independent Schrodinger equation. There are many solutions and are of the form H psi n is equal to E m psi n ok where n is the quantum number ok. Now you get many such solutions for this in fact in some cases you get infinite number of solutions. And if you take a set of all the psi n's this will form what is known as complete set ok.

This complete set simply means that any arbitrary function chi of x can be written as a summation over i C i psi i of x ok. So, any arbitrary function can be written as a linear combination of elements of this complete set. I will give you an example you have a CARTESIAN coordinates x, y and z, any point in the Cartesian space can always be written as a linear combination of x, y and z.

Therefore the Cartesian coordinates x, y, z or the vectors corresponding to x, y, z form a complete set ok. In quantum mechanics for every psi and there is another set complete set which is made of complex conjugates of psi of n ok. That is because there are no rules on the wave function as to whether it should be real or complex. In general if a function can be complex. So, when you have complex wave function then there exists a complex conjugate of it.

In the (()) (19:37) notation this is written as a (()) (19:51) function de Broglie function ok. Now in this case we of course assumed that we all know what psi n's are. For example if we take a hydrogen atom problem the psi n's will be all the orbitals 1s, 2s, 2p, 3s, 3p, 3d etc. If we take harmonic oscillator functions will be equal to the V is equal to 0 v is equal to 1 or vibrational quantum number S equal to 0, the function corresponding to that second and third and etc.

If you have particular in a box and then there is a n is equal to 1, n is equal 2, n is equal to 3 function etc ok. In this course of course we will assume that all the solutions are already known, before I move on there are a few things that I would like to define ok.

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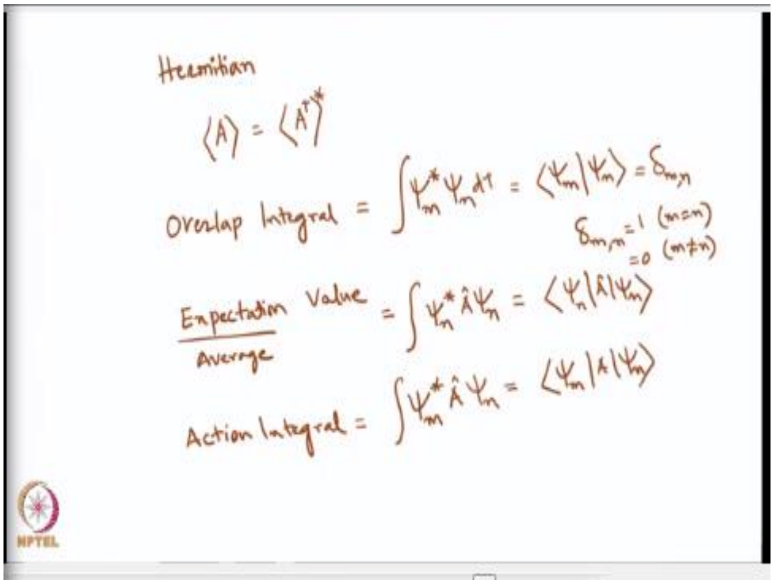

Hermitian

$$\langle A \rangle = \langle A^{\dagger} \rangle^{*}$$

Overlap Integral $= \int \psi_m^{*} \psi_n \, d\tau = \langle \psi_m | \psi_n \rangle = \delta_{m,n}$

$\delta_{m,n} = 1 \; (m=n)$
$= 0 \; (m \neq n)$

Expectation Value / Average $= \int \psi_n^{*} \hat{A} \psi_n = \langle \psi_n | \hat{A} | \psi_n \rangle$

Action Integral $= \int \psi_m^{*} \hat{A} \psi_n = \langle \psi_m | A | \psi_n \rangle$

In quantum mechanics any operator corresponding to a physical observable is Hermitian. Hermitian means operator is a self adjuvant of itself ok which means A average value, I will come to what average value means average value of an operator A is equal to it is transpose complex conjugate that is Hermitian. Now I will define a few integrals ok and integrals are definite integrals in quantum mechanics generally the integrals are definite integrals.

So, let us define the first one called overlap integral, this integral is given by integral psi m star psi n d tau, d tau is the corresponding volume element or the surface element or length element in for integration. So this is equal to in bracket notation will be psi m psi n and this is given by for a given system given by delta m, n ok, delta m, n is nothing but Kronecker delta. So, delta m, n is equal to 1 if m is equal to n and d is equal to 0 if m is not equal to in such case we get what is known as the orthonormal set ok.

But overlap integral is delta m, n only if all of psi m and psi n belong to the same system wave functions of the same system. If they are wave functions of different systems then of course you will have to really evaluate the overlap ok. Then other reason expectation value, it is also called average value ok this is given by and this will correspond an operator ok average value of an operator A, expectation value of an operator A for a given system.

So, this will come out as psi n star A psi n in terms of bracket rotation this is return as psi N A psi n ok. I do not know what how much you did, I know that it is a number because you know it is a definite integral. But I do not know what is it is value, I have to evaluate this number or this integral to get the value it could be 0 as well, expectation value can be 0 ok. And the other one I will call it as an action integral.

Now what is this action integral, I will define this as psi m star A psi n, so what does it do, A acts on psi n and the resulting function gets projected on to the psi m ok. So, the bracket notation it is psi m A psi n. For example if I act light on hydrogen atom which is in 1s orbital whatever resulting function you can now project onto either 2s or 2p and in generally this will give us transitions. So, these action integrals are very important in spectroscopy.

Now the other thing that I want to tell you is about the Hermitian operators ok. As I told you that all operators corresponding to physical variables or Hermitian in quantum mechanics.

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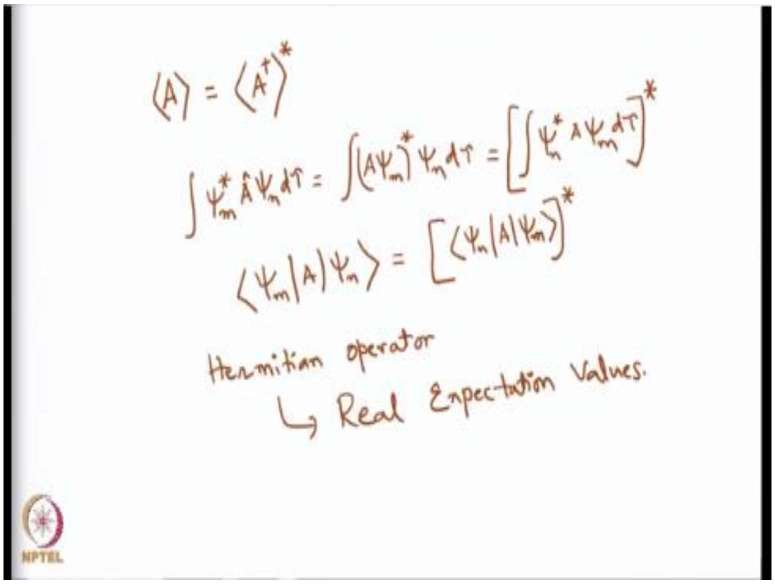

$$\langle A\rangle = \langle A^{\dagger}\rangle^{*}$$

$$\int \psi_m^{*}\hat{A}\psi_n\,d\tau = \int (A\psi_m)^{*}\psi_n\,d\tau = \left[\int \psi_n^{*}A\psi_m\,d\tau\right]^{*}$$

$$\langle \psi_m|A|\psi_n\rangle = \left[\langle \psi_n|A|\psi_m\rangle\right]^{*}$$

Hermitian operator

↳ Real Expectation Values.

So, we just said that A average is equal to A average transpose star. Now if I write in terms of integrals then this will be in the case of Hermitian operators will be integral psi star m A psi n d tau equal to integral A psi m whole star psi n d tau is also equal to psi n star A psi m d tau whole star ok. In bracket notation one can write psi m A psi n is equal to psi n A psi m star ok. Now this is properties of Hermitian operator ok and Hermitian operators give real expectation values ok.

So, because all physical observables were correspond to some real expert values. So, when you measure momentum it should be a real number, when you measure kinetic energy it should be real number, if you measure position it should be real number. So, operators that correspond to momentum, position, kinetic energy or Hermitian operators. We will stop it here, we will continue with the in the next lecture.