Quantum Mechanics and Molecular Spectroscopy
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Lecture-03
Time Evolution

Hello, welcome to the lecture number 3 of quantum mechanics and molecular spectroscopy course. Before we get on with this lecture I would like to have a quick recap of what we have done in the previous lecture.

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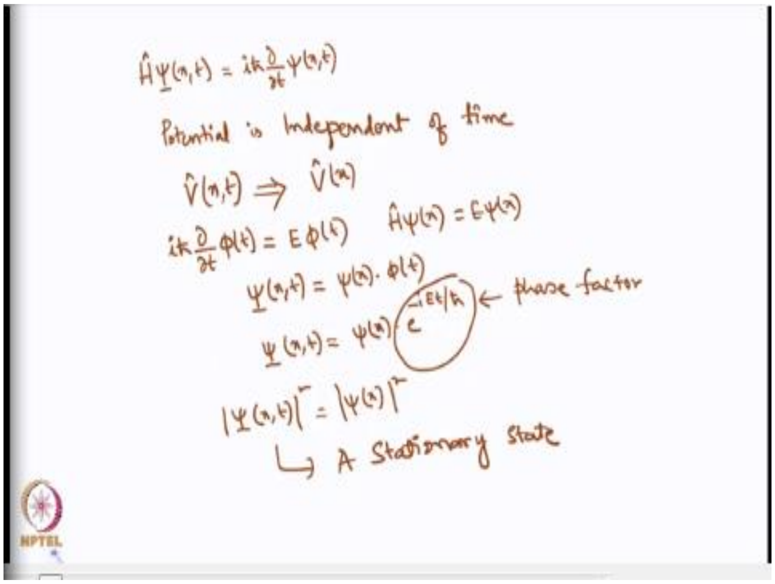

$\hat{H}\underline{\Psi}(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$

Potential is Independent of time

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

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

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

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

$|\underline{\Psi}(x,t)|^2 = |\psi(x)|^2$

↳ A Stationary state

In the previous lecture we found that H of psi of x, t is equal to i h bar d by dt of psi of x, t, this is the Schrodinger equation. However, when the potential is independent of time that is V of x, t can be written as just V of x, this is something we have discussed. Because many problems in chemistry or many systems in chemistry have potential that is independent out of time ok such as particle in a box or hydrogen atom or harmonic oscillator.

In such scenario we can get 2 different equations one 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. Such that psi of x, t is equal to psi of x multiplied by pi of t. And we also showed that psi of x, t is equal to psi of x into e to the power of - i E t by h bar and this we called as the phase factor. Further we also said psi of x, t represents a stationary state because modulus of psi of x, t square is equal to just psi of x square. So, this represents a stationary state.

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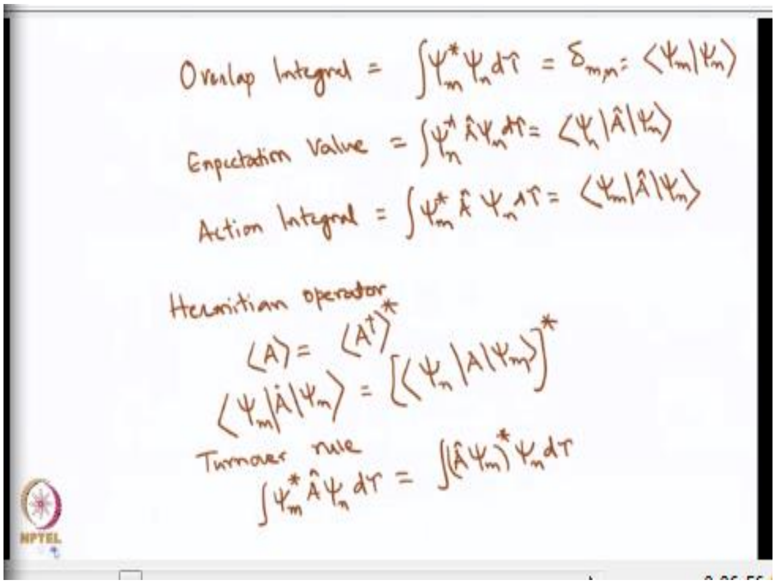

Overlap Integral = $\int \psi_m^* \psi_n \, d\tau = \delta_{mn} = \langle \psi_m | \psi_n \rangle$

Expectation Value = $\int \psi_n^* \hat{A} \psi_n \, d\tau = \langle \psi_n | \hat{A} | \psi_n \rangle$

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

Hermitian operator

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

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

Turnover rule

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

Apart from that we also define some integrals, overlap integral, this was nothing but integral psi m star psi n d tau this is equal to delta m, n also could be written as in bracket notation psi m psi n. Similarly we have expectation value, this is nothing but integral psi m star operator A psi n d tau, expectation value is always with respect to an operator psi m A psi n. Similarly we had defined something called action integral, integral psi m ok.

In the case of expectation value this is n ok, I beg your pardon ok psi m star A psi n d tau this is nothing but psi m A psi n. Now expectation value is a special case of action integrals ok, then we also define something called Hermitian operator. And if an operator A is Hermitian then average value of A should be equal to average value of A transpose star ok. In terms of integral one can write it as psi m A psi n equals to psi n A psi m star ok.

There is one important thing that is about Hermitian operator is called turnover rule. And turnover rule simply says that psi m star A psi n d tau equals to integral A psi m whole star psi n d tau ok. Now this tells us that Hermitian operators can operate in both direction forward as well as backward ok.

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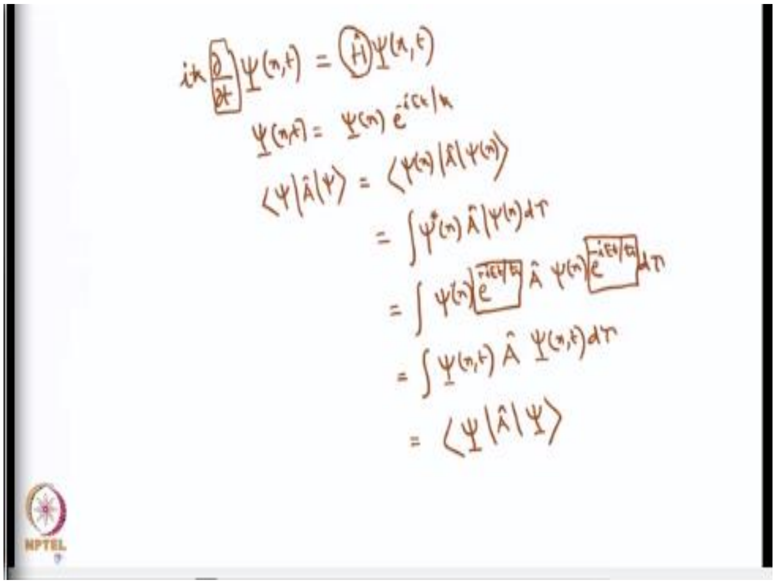

$$i\hbar \boxed{\frac{\partial}{\partial t}} \Psi(x,t) = \enclose{circle}{\hat{H}}\, \Psi(x,t)$$

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

$$\langle \psi | \hat{A} | \psi \rangle = \langle \psi(x) | \hat{A} | \psi(x) \rangle$$

$$= \int \psi^*(x)\, \hat{A}\, |\psi(x)\, d\tau$$

$$= \int \psi(x) \boxed{e^{+iEt/\hbar}}\, \hat{A}\, \psi(x) \boxed{e^{-iEt/\hbar}}\, d\tau$$

$$= \int \Psi(x,t)\, \hat{A}\, \Psi(x,t)\, d\tau$$

$$= \langle \Psi | \hat{A} | \Psi \rangle$$

Now let us look at the some important aspect called time evolution ok. Now the Schrodinger equation is i h bar d by dt of psi of x, t is equal to h psi of ok which means the psi of x and t will evolve in time. The time derivative simply says that how it will evolve in time and that will depend on the Hamiltonian ok. Now we also know that if you have a time independent potential then your psi of x t is equal to psi of x multiplied by e to the power of - i E t by h bar.

And an average value of an operator A is defined as one expectation value of an operator A is defended as psi A psi, this is nothing but psi of x A psi of x. You can see that if I take this integral this will be integral psi star of x A psi of x d tau. So, this is nothing but ok psi of x, I can always multiply by e to the power of - sorry + i E t by h bar A and psi of x multiplied by e to the power of - i e d by h bar d tau.

Because when I multiply this and this ok and of course I am multiplying by e to the 0 that is equal to 1 ok. So, this is nothing but integral psi of x, t A psi of x, t d tau which is equal to psi A psi ok.

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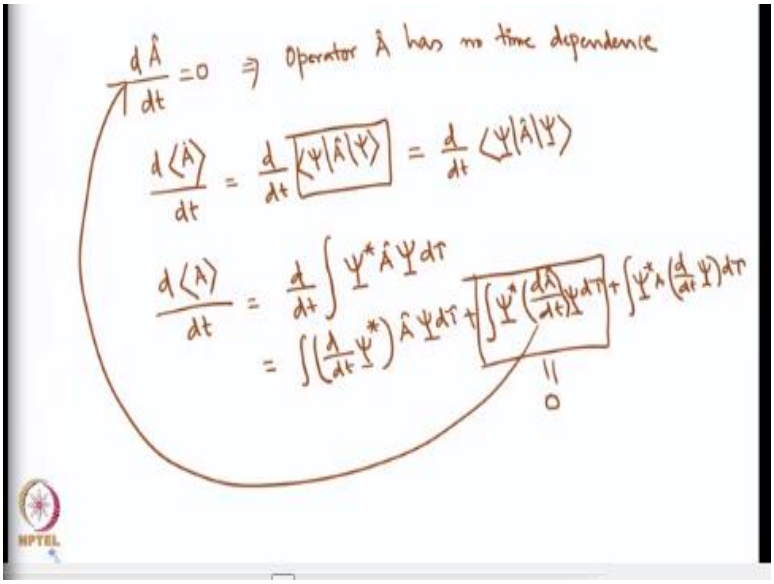

$$\frac{d\hat{A}}{dt} = 0 \Rightarrow \text{Operator } \hat{A} \text{ has no time dependence}$$

$$\frac{d\langle \hat{A}\rangle}{dt} = \frac{d}{dt}\boxed{\langle \psi|\hat{A}|\psi\rangle} = \frac{d}{dt}\langle \psi|\hat{A}|\psi\rangle$$

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

$$= \int\left(\frac{d}{dt}\psi^*\right)\hat{A}\psi \, d\tau + \underset{0}{\underset{\parallel}{\boxed{\int \psi^*\left(\frac{d\hat{A}}{dt}\right)\psi \, d\tau}}} + \int \psi^* \hat{A}\left(\frac{d}{dt}\psi\right) d\tau$$

Now let us start with an operator A such that operator A does not have any time dependence which means d by dt of A equals to 0, this simply means operator A has no time dependence ok. Now even though A may not have time dependence what will happen to the expectation value of the operator A ok. So, what I want to now evaluate is that I want to evaluate the expectation value of operator A it is time dependence.

Now this is given by d by dt of expectation value of A is nothing but psi A psi I had shown a minute back that this integral is equal to d by dt of psi A psi ok. So, let us expand this, so d A by dt equals to d by dt of integral psi star A psi d tau. Now we have to differentiate because psi A and psi R3 either operators you know functions. So, one can write this as this is equal to integral of d by dt of psi star.

So, I am using a product rule for differentiation A psi d tau + integral of psi star d a bye by dt psi d tau + integral of psi star A d by dt of psi d tau, so this I will write is 3 integrals ok. Now we will see that the second integral this one ok this is equal to 0. Because we said d to begin with we said that d A by dt is equal to 0, so now I am left with only 2 integrals.

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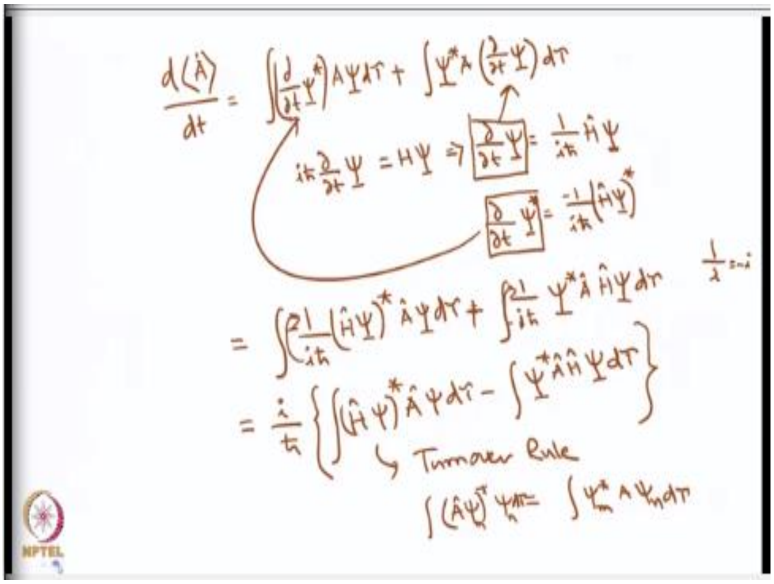

$$\frac{d\langle \hat{A}\rangle}{dt} = \int \left(\frac{\partial}{\partial t}\Psi^*\right) A\Psi\, d\tau + \int \Psi^* A \left(\frac{\partial}{\partial t}\Psi\right) d\tau$$

$$i\hbar \frac{\partial}{\partial t}\Psi = H\Psi \Rightarrow \boxed{\frac{\partial}{\partial t}\Psi} = \frac{1}{i\hbar}\hat{H}\Psi$$

$$\boxed{\frac{\partial}{\partial t}\Psi^*} = \frac{-1}{i\hbar}(\hat{H}\Psi)^*$$

$$\frac{1}{i} = -i$$

$$= \int -\frac{1}{i\hbar}(\hat{H}\Psi)^*\hat{A}\Psi\, d\tau + \int \frac{1}{i\hbar}\Psi^*\hat{A}\hat{H}\Psi\, d\tau$$

$$= \frac{i}{\hbar}\left\{\int(\hat{H}\Psi)^*\hat{A}\Psi\, d\tau - \int \Psi^*\hat{A}\hat{H}\Psi\, d\tau\right\}$$

Turnover Rule

$$\int (\hat{A}\Psi_m)^* \Psi_n\, d\tau = \int \Psi_m^* A \Psi_n\, d\tau$$

So, d of A dt equals to integral of d by dt of psi star A psi d tau + integral of psi star A d by dt of psi d tau. Now here we are going to invoke the Schrodinger equation, what does Schrodinger equation says i h bar d by dt of psi equals to H psi, this implies d by dt of psi is equal to 1 over i h bar H psi. Now if I take a complex conjugate of this ok d by dt of psi star equals to i h bar h psi star and with a negative sign because i will become - i ok.

Now I am going to plug in, so I am going to plug in d psi by dt here and d by dt of psi star here ok. Now if I do that then I will get integral - 1 by i h bar H psi whole star multiplied by A psi d tau equals sorry + integral 1 over i h bar psi star A H psi d tau ok. Now 1 over i equals to – I, so if I use that I can take this ith numerator and this also I can take numerator. So, this will become i by h bar I can take here integral H psi star A psi d tau **+** - integral psi star A H psi d tau ok.

Now we have these 2 integrals ok, now if I use turnover rule here says integral A psi star whole star psi m psi n equals to integral d tau equals to psi m star A psi n d tau.

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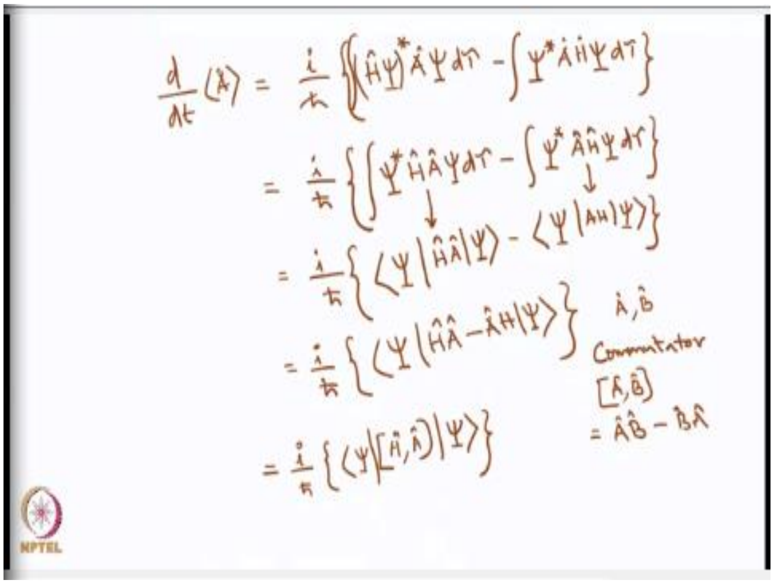

$$\frac{d}{dt}\langle \hat{A}\rangle = \frac{i}{\hbar}\left\{\int(\hat{H}\Psi)^*\hat{A}\Psi\,d\tau - \int\Psi^*\hat{A}\hat{H}\Psi\,d\tau\right\}$$

$$= \frac{i}{\hbar}\left\{\int\Psi^*\hat{H}\hat{A}\Psi\,d\tau - \int\Psi^*\hat{A}\hat{H}\Psi\,d\tau\right\}$$

$$\downarrow \qquad\qquad \downarrow$$

$$= \frac{i}{\hbar}\left\{\langle\Psi|\hat{H}\hat{A}|\Psi\rangle - \langle\Psi|AH|\Psi\rangle\right\}$$

$$= \frac{i}{\hbar}\left\{\langle\Psi|\hat{H}\hat{A}-\hat{A}H|\Psi\rangle\right\}$$

$$= \frac{i}{\hbar}\left\{\langle\Psi|[\hat{H},\hat{A}]|\Psi\rangle\right\}$$

$\hat{A},\hat{B}$

Commutator

$[\hat{A},\hat{B}]$

$= \hat{A}\hat{B} - \hat{B}\hat{A}$

If I use that turnover rule and then I can write d by dt of average value of A equals to i by h bar integral h psi whole star A psi d tau – integral psi star A H psi d tau, this is nothing but i h bar integral H A psi d tau - integral psi star AH psi d tau ok. So, this is nothing but this is equal to I can think of it like this ok i by h bar, now this is nothing but integral.

So, psi H A - psi AH psi ok this integral I have written like this and this integral I have written like this in terms of bracket notation. So, there is an HA operator that is going to operate over integrate over psi star psi. So, HA operator integrating over psi star psi similarly AH operator integrating over psi star psi ok, this is equal to i h bar. Now these are 2 different integrals which I can combine into 1 integral that is nothing but psi HA - AH psi ok.

Now you can see that HA – AH, I have 2 operators ok. Let us say you have an operator A and operator B then we can define what is known as a commutator which says commutator A, B is equal to AB operator - BA operator ok. Of course this one thing that I want to tell you is that commutators have to be evaluated with respect to some function ok. But nonetheless it is just the AB - BA.

Now if you have A and B as a numbers or functions then commentator AB will always be 0 but that is not necessarily true for operators ok. So a commutator maybe equal to 0 or may not be equal to 0 of 2 operators A and B ok. So this is equal to i by h bar psi commutator H, A psi ok, this is one of the very interesting results in quantum mechanics and is very useful for spectroscopy ok.

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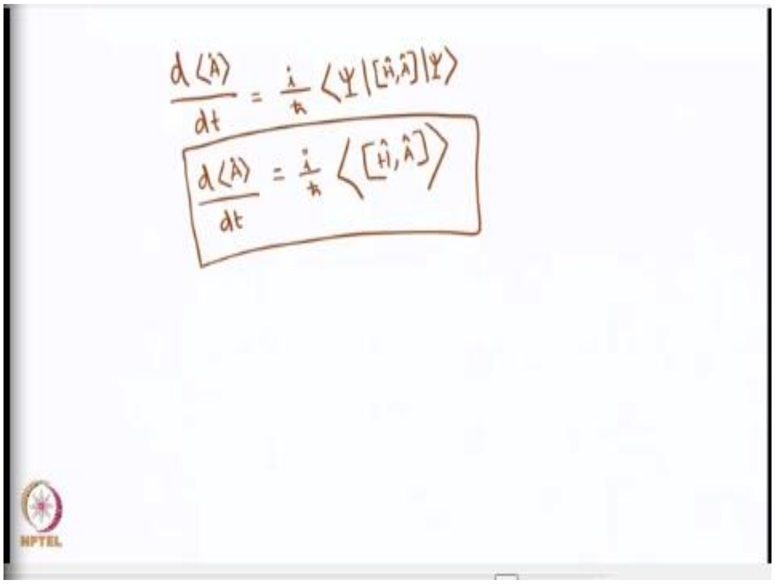

$$\frac{d\langle \hat{A}\rangle}{dt} = \frac{i}{\hbar}\langle \Psi|[\hat{H},\hat{A}]|\Psi\rangle$$

$$\boxed{\frac{d\langle \hat{A}\rangle}{dt} = \frac{i}{\hbar}\left\langle [\hat{H},\hat{A}]\right\rangle}$$

Now I am going to rewrite that equation once more d A by dt is equal to i by h bar average value of psi H, A commutator psi. So, this is in short can be written as i by h bar average value of H A commutator d A by dt ok, what does it mean. This is a very important formula, it says that if a operator A commutes with H of course if it is commutes with H this will go to 0 HA commutator will go to 0 then d A by dt will be equal to 0.

So, the average value of A, the time dependence of it will depend on whether A commutes with the Hamiltonian or not. If operator A commutes with the Hamiltonian then it is average value or expectation value does not have any time dependence. But if operator A does not commute with Hamiltonian then it is average value will have some time dependence ok. In spectroscopy this is very interesting because if you start with the molecules and interact with the light.

And if you write an operator corresponding to light it does not commute with Hamiltonian. If it does not commute with Hamiltonian it is expectation value will show time dependence. That means for example you start with the hydrogen atom and you apply this operator A correspondent to the light, interaction of light. Then what happens is that the average value will change with time because it has time dependence.

So, something that started with 1 will end up with some other expectation value corresponding to either 2s or 2p or 3s or 3p depending on the nature of your operator. So, it is very important that a state will move, this means that the state will move to a different value. You can move a state or a initial state from one expectation value to different expectation value only if you apply an operator that does not commute with the Hamiltonian ok. I will stop for this lecture, we will continue in the next lecture, thank you.