Time Dependent Quantum Chemistry
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Lecture 10 Module 02
Expectation Value and its Time Evolution

Welcome back to module 2 we are continuing the classical quantum correspondence. And next, what we are going to study is how many ways I can present quantum dynamics maintaining classical flavor in it. Which means that I would like to know the trajectory and if I am presenting trajectory what does it mean by that trajectory in quantum dynamics.

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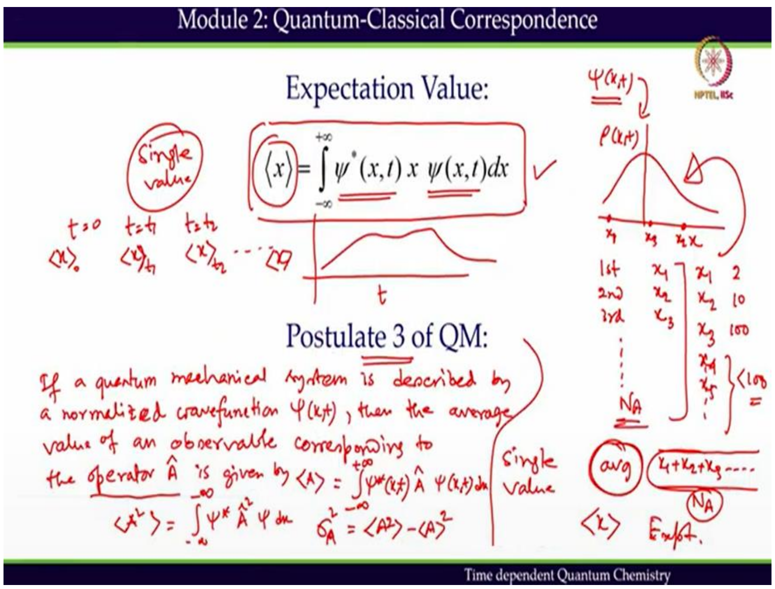

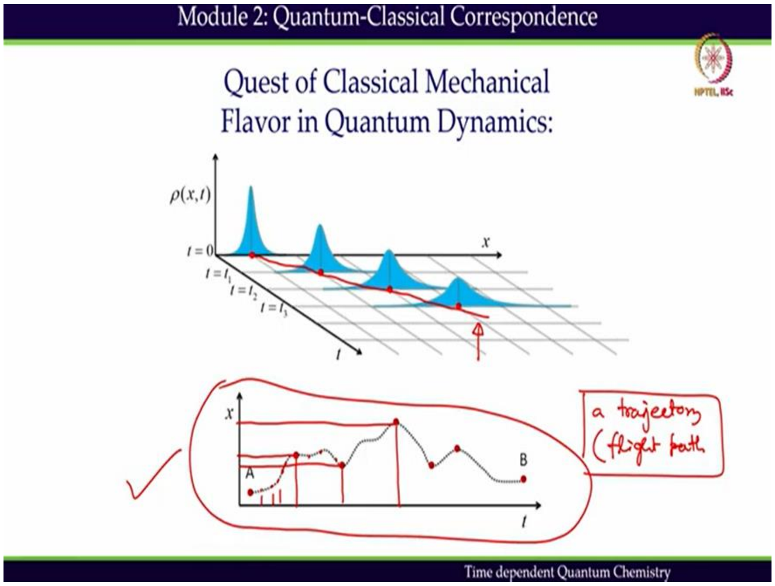

So, we will begin with Ehrenfest theorem although wave function $\psi(x,t)$ an associated probability density distribution for a particle in position space at a given time is always global or delocalized in nature. One can very easily determine the average position of the particle at a given time from the normalized wave function using this expression and this is called the expectation value what does it mean I will present it.

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) x \psi(x,t) dx$$

The average position obtained using the average using this equation is called the expectation value of the position. In fact, for a given normalized wave function ah the expectation value of a physical or dynamical quantity provides a way to compute the average of repetitive experimental measurements. So from wave function I get the density and I have mentioned the density as a distribution in position space.

And what does it mean by this distribution? I have performed the experiment let us say and first experiment has given me a position x1 lets say here. Second experiment I have got position x2 which is here let us say third experiment i have got x3 which is let us say here. So, this is x1 this x2 this x3 and like this way and if we keep repeating after the repeating after let us say avogadro number of times I have repeated the experiment.

After repeating the experiment all I am doing is trying to organize my data I am just trying to find out how many counts I have for this positions. I will see that for x1 I have let us say 2 counts for x2 I have let us say 10 counts and I for x3 let us say I have hundred counts and x4 I can have x4, x5 so on everything are actually less than 100. Because the maximum number of counts I have and that is the meaning of the distribution function that is the meaning it is carrying the distribution function carrying the meaning.

Now after doing this experiment I can also find out the average of that value. Average is going to be x1 plus x2 plus x3 all these positions divided by how many times I have repeated the experiment. Here I am considering Avogadro number of times I have repeated the experiments that is why I am dividing by N_A. This is going to be the average value of the of the measurement and that average value would be the expectation value in the distribution.

So, this is nothing but this can be calculated theoretically so this is theory and this is experiment average value of the repetitive measurement is nothing but the expectation value can which can be calculated theoretically from its wave function. If the normalized wave function is known. If I know the normalized wave function, then its average value can be obtained average value of the position can be obtained.

The expectation value of a position represents a point in position space it is going to be a single value average value is going to be single value because I am summing them and dividing by number of times I have done the experiment. So, average value is a single value point. Similarly, expectation, expectation value is actually a single value. So, if I have a single value at a particular time, then this particular value at t equals 0 I will get some value at equals t1 I will get some value at equals t2 I will get some value this expectation value and so on.

So finally, what I can do if I plot x average value as a function of time I will see a trajectory just like classical trajectory I will be able to construct the trajectory. And that is the basic idea of this and the what I have presented right now it is based on postulate 3 another postulate of quantum mechanics which shows that which we states that.

If a quantum mechanical system is described by a normalized wave function $\psi(x,t)$ then the average value of an observable, observable which can be observed experimentally like position, momentum they can be experimentally observed that is why they are observables. Average value of an observable corresponding to the operator a is given by so for every classical observable which can be experimentally observed in quantum mechanics I get the operator corresponding operator I have to take that operator.

I can determine the expectation value by

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\hat{A}\psi(x,t)dx$$

this integration I have to find out. And also similar way I can use a square expectation value of the square of that operator

$$\langle A^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\hat{A}^2\psi(x,t)dx$$

And finally, variance of the measurement you can say standard deviation of the measurement is given by this expression-

$$\sigma_A^2 = \langle A^2 \rangle - \langle A \rangle^2$$

This comes from postulate, one of the postulates of quantum mechanics so if I use that postulate and try to find out the expectation value from the wave function where function is global but expectation value would be single value at a particular time.

Then I can get its ah how that that is moving and that can give me classical flavor and exactly what we have shown here if I this red dots these red dots let us say presenting the expectation value at different time then these points if I connect this points in xt diagram what I am seeing this line is nothing but the trajectory just like a classical trajectory. So, I have some way to present quantum dynamics in terms of classical trajectory. If I consider the average of the distribution.

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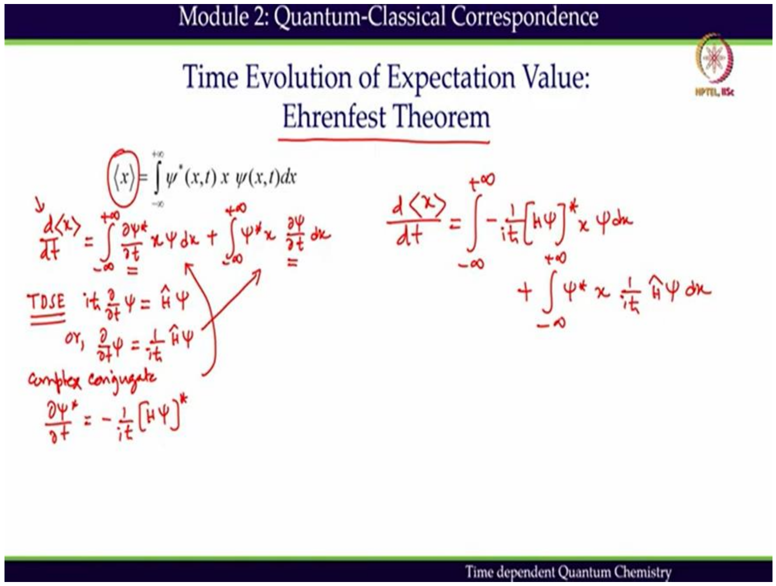

So, as point pointed out earlier the expectation value of the position which is calculated from a global function wave function represents a point in position space. First question is how does the expectation value of position change as a function of time? So, what I would like to know I am convinced right now we are convinced that yes it is possible to draw a trajectory for quantum dynamics. But question is how that is evolving as a function of can I get an equation for that and that is the task we are taking up that equation is called the Ehrenfest theorem. So, Ehrenfest theorem is showing how the expectation value will evolve as a function of time.

So, we will begin with taking the first derivative of this expectation value it is total derivative not partial derivative because expectation value does not depend on space so if I take this first derivative. Then remember here this is total derivative but I have to inside the integrand I have to use partial derivative because wave function depends on both space and time. This is simple derivative product rule we do not need to take first derivative of x because it is going to be 0.

$$\frac{d\langle x\rangle}{dt} = \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial t} x\psi\, dx + \int_{-\infty}^{\infty} \psi^* x \frac{\partial \psi}{\partial t} dx$$

Now I have to use TDSE because from TDSE I will be able to get the first derivatives and TDSE can be written as

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

So, this is TDSE I can rearrange little bit like this

$$\frac{\partial}{\partial t}\psi = \frac{1}{i\hbar}\hat{H}\psi$$

And I will take the complex conjugate also complex form of the TDSE complex conjugate form of the TDSE that is going to be

$$\frac{\partial}{\partial t}\psi^* = -\frac{1}{i\hbar}\left[\hat{H}\psi\right]^*$$

So, this is we are going to insert now this is going to be here and this going to be here. If I insert it, I will get this equation

$$\frac{d\langle x\rangle}{dt} = \int_{-\infty}^{\infty} -\frac{1}{i\hbar}\left[\hat{H}\psi\right]^* x\psi\, dx + \int_{-\infty}^{\infty} \psi^* x \frac{1}{i\hbar}\hat{H}\psi\, dx$$

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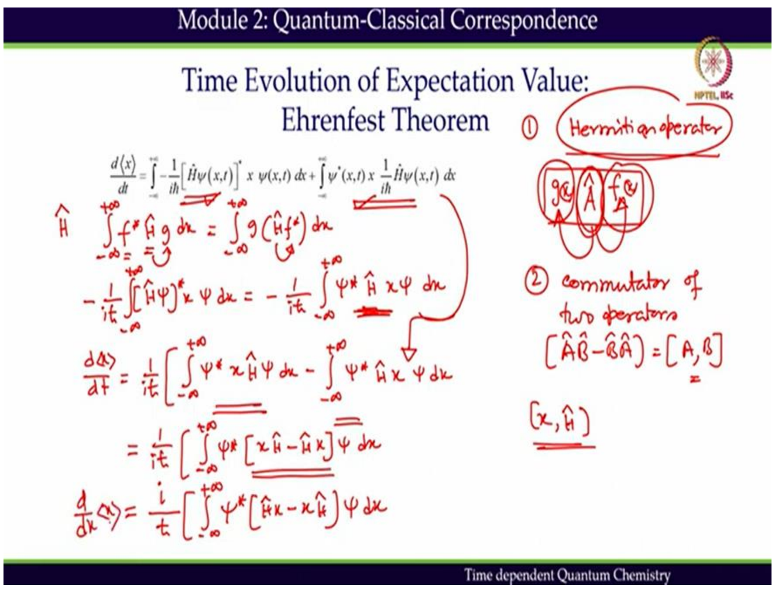

And one thing we will introduce right now is called Hermitian operator.We will regressively rigorously we will go over Hermitian operator again in this class in a different module. What is the property of Hermitian operator what is the matrix representation of Hermitian operator all those things will be studying but right now will just mention one thing is the Hermitian operator the property of a Hermitian operator is following.

If I have let us say a function and if I take the derivative I have let us say two functions one is this one this form we know that this operator is going to act on this function only.

$$g(x)\frac{d}{dx}f(x)$$

It is not going to act on this function. So, it is more like we three are sitting together on my right hand side one person and on my left hand side one person is sitting and I am just talking I can I am allowed to talk to only one person let us say on the right hand side so I can talk to him only I cannot talk to the left hand person.

That is the way the operator is working and if the operator is working following that principle then it is not an Hermitian operator. This part is not Hermitian operator Hermitian operator can talk to both basically. So if I am if I am allowed to talk to both the right hand the person sitting on my right hand side and the person sitting on my left hand side if I can talk to both then it is called Hermitian operator.

So, $\frac{d}{dx}$ only differential operator is not Hermitian operator if an operator is Hermitian, then it can act on right hand part it can act on left hand part without any constraint. And one more important point will remember we will discuss that in details later that all quantum mechanically acceptable operators has to be Hermitian operator.

Which means that all quantum mechanically acceptable operators can talk to right hand person or left hand person both. So, $\hat{H}$ is an Hermitian operator it is the Hamiltonian operator because it is Hermitian operator we can write down

$$\int_{-\infty}^{\infty} f^*\hat{H}g dx = \int_{-\infty}^{\infty} g(\hat{H}f^*)dx$$

They are equal you can see that h is acting on g here and here h is acting on f star which was on the on this side.

So, which way its acting that order does not matter because it is Hermitian operator do not think that every mathematical operator is Hermitian operator. For an example $\frac{d}{dx}$ is not an Hermitian operator $\frac{d}{dx}$ only acts on the right hand side what I have in the right hand side. So, mathematically, that is why this operator cannot be accepted in quantum mechanics we do not consider it in quantum mechanics. So, all Hermitian operators should be able to act on both side, so if it is so we can rewrite this equation as follows. I can write down

$$-\frac{1}{i\hbar}\int_{-\infty}^{\infty}\left[\hat{H}\psi\right]^* x\psi dx = -\frac{1}{i\hbar}\int_{-\infty}^{\infty}\psi^*\hat{H}x\psi dx$$

You see I have now change the position of Hermitian operator and that is possible this is the way Hermitian operator will work.

And if it is so, then I can rewrite this as follows

$$\frac{d\langle x\rangle}{dt} = \frac{1}{i\hbar}\left[\int_{-\infty}^{\infty}\psi^* x\hat{H}\psi dx - \int_{-\infty}^{\infty}\psi^*\hat{H}x\psi dx\right]$$
$$= \frac{1}{i\hbar}\left[\int_{-\infty}^{\infty}\psi^*[x\hat{H} - \hat{H}x]\psi dx\right]$$

This difference is called another concept we are going to.

So, these are pending topics we are just using them we will discuss it in details another topic is going to be commutator of two operators it is written as $[\hat{A}\hat{B} - \hat{B}\hat{A}]$ in the shorthand it is written as within bracket $[\hat{A}, \hat{B}]$ with a comma we use this comma sine to to represent it so this is called commutator of two operators. So, if it is like that so this part is nothing but $[x, \hat{H}]$. I will just change it I will make it

$$= \frac{i}{\hbar}\left[\int_{-\infty}^{\infty}\psi^*[\hat{H}x - x\hat{H}]\psi dx\right]$$

So, we have this form of the time derivative of the expectation value.

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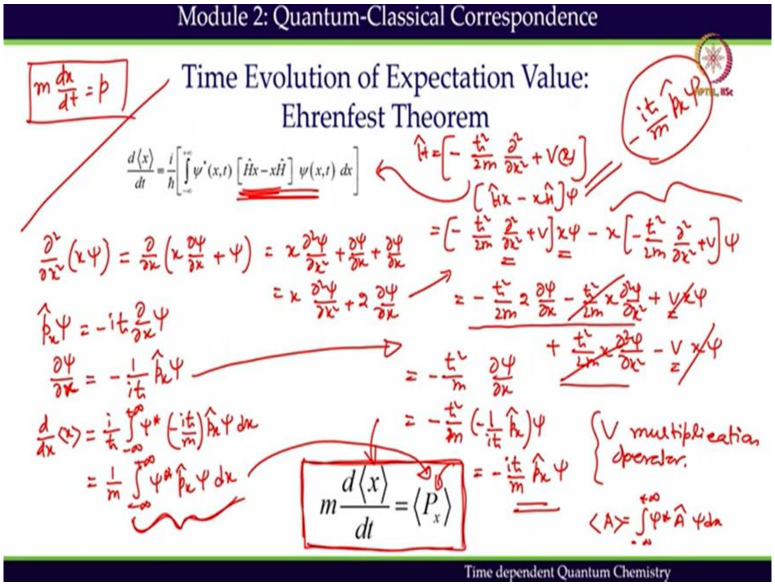

We will keep reducing it because $\hat{H}$ is Hamiltonian operator we can write down as

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

So, we can plug that in here and particularly we are interested in knowing this part $[\hat{H}x - x\hat{H}]$ commutator of Hamiltonian operator and position operator. So, for that what I need to do is that

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]x\psi - x\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi$$

So, we can write down this part we take the second derivative of this

$$\frac{\partial^2}{\partial x^2}(x\psi) = \frac{\partial}{\partial x}(x\frac{\partial \psi}{\partial x} + \psi)$$

$$= x\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial \psi}{\partial x} + \frac{\partial \psi}{\partial x}$$

$$= x\frac{\partial^2 \psi}{\partial x^2} + 2\frac{\partial \psi}{\partial x}$$

So this can be plugged in here and I will be able to write down

$$[x, \hat{H}] = -\frac{\hbar^2}{2m}2\frac{\partial \psi}{\partial x} - \frac{\hbar^2}{2m}x\frac{\partial^2 \psi}{\partial x^2} + Vx\psi + \frac{\hbar^2}{2m}x\frac{\partial^2 \psi}{\partial x^2} - Vx\psi$$

Remember V is a multiplication operator and any multiplication operator can be placed anywhere it does not matter what is the order and that is how you can write down. We see that this two will cancel out and we get this is the form we get finally.

$$[x,\hat{H}] = -\frac{\hbar^2}{2m}2\frac{\partial\psi}{\partial x} - \frac{\hbar^2}{2m}x\frac{\partial^2\psi}{\partial x^2} + \frac{\hbar^2}{2m}x\frac{\partial^2\psi}{\partial x^2}$$

Now if we think of the momentum operator acting on ψ it is nothing but this complex derivative operator.

$$\hat{p}_x\psi = -i\hbar\frac{\partial\psi}{\partial x}$$

So, one can write down that this first derivative with respect to x is nothing but

$$\frac{\partial\psi}{\partial x} = -\frac{1}{i\hbar}\hat{p}_x\psi$$

this part also canceling out.

So finally, I get

$$\begin{aligned}[x,\hat{H}] &= -\frac{\hbar^2}{m}\frac{\partial\psi}{\partial x} \\ &= -\frac{\hbar^2}{m}(-\frac{1}{i\hbar}\hat{p}_x)\psi \\ &= \frac{-i\hbar}{m}\hat{p}_x\psi\end{aligned}$$

So, in the end I get the first derivative of the expectation value is nothing but

$$= \frac{i}{\hbar}\int_{-\infty}^{\infty}\psi^*(-\frac{i\hbar}{m})\hat{p}_x\psi\,dx$$

which is nothing but

$$= \frac{1}{m}\int_{-\infty}^{\infty}\psi^*\hat{p}_x\psi\,dx$$

This form is familiar form because I said that for any expectation value of an operator if I have an operator and I want to find out the expectation value of that operator I can get it by taking this integration.

That is exactly what we are seeing here so this is nothing but the expectation value of the momentum. So, what we are seeing finally this is the equation we are finally getting this is Ehrenfest theorem and this equation shows that the this equation is very familiar in classical mechanics. In classical mechanics we often use Newton's equation of motion which is nothing but mv is actually momentum in classical mechanics. In quantum mechanics if we take the average of position and average of the momentum we see the same form of equation of motion.

So, this equation shows that how the average position of the quantum particle will evolve as a function of time. And we see that average position is evolving or following classical trajectory. Next, we will find out how the average momentum will change as a function of time which is part of Ehrenfest theorem will continue in the next session.