Time Dependent Quantum Chemistry
Professor. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru
Lecture 11
Equation of Continuity

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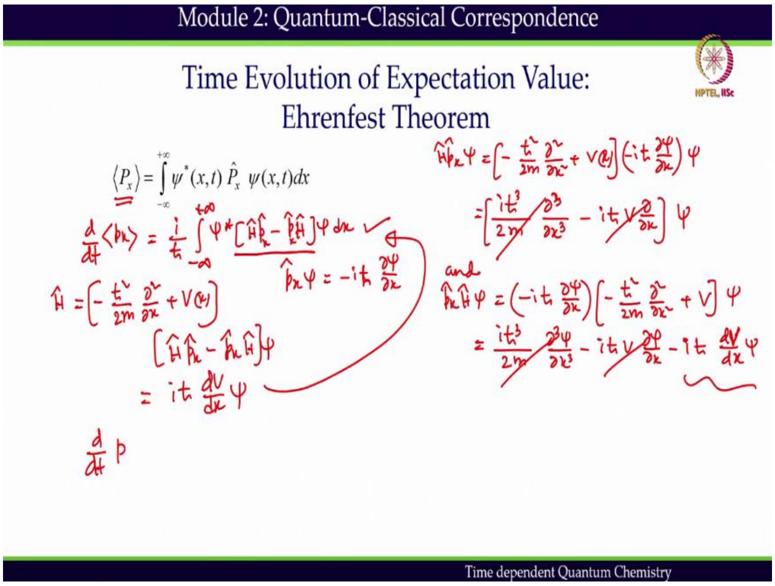

Module 2: Quantum-Classical Correspondence

Time Evolution of Expectation Value: Ehrenfest Theorem

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

$$\frac{d}{dt}\langle p_x \rangle = \frac{i}{\hbar}\int_{-\infty}^{+\infty} \psi^* [\hat{H}\hat{p}_x - \hat{p}_x\hat{H}]\psi dx$$

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

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

$$[\hat{H}\hat{p}_x - \hat{p}_x\hat{H}]\psi = i\hbar\frac{dV}{dx}\psi$$

$$\frac{d}{dt}p$$

$$\hat{H}\hat{p}_x\psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\left(-i\hbar\frac{\partial\psi}{\partial x}\right)\psi$$

$$= \left[\cancel{\frac{i\hbar^3}{2m}\frac{\partial^3}{\partial x^3}} - \cancel{i\hbar V\frac{\partial}{\partial x}}\right]\psi$$

and

$$\hat{p}_x\hat{H}\psi = \left(-i\hbar\frac{\partial\psi}{\partial x}\right)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right]\psi$$

$$= \cancel{\frac{i\hbar^3}{2m}\frac{\partial^3\psi}{\partial x^3}} - \cancel{i\hbar V\frac{\partial\psi}{\partial x}} - i\hbar\frac{dV}{dx}\psi$$

Time dependent Quantum Chemistry

Welcome back to module 2, we are trying to find out how trajectories can be constructed in quantum dynamics and we are going through Ehenfest Theorem, we have seen that average position is following classical trajectory in quantum dynamics.

Similar way we can follow what would be the average or the expectation value of the momentum and we can calculate it very easily right now, because we have seen the derivation for the position space. So, similar derivation can be used for the momentum and we will be able to write down this

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

Previously we had position space this is x because it is one dimensional, we are working on previously we have seen similar expression for x and we have proved it that this is the expression we can get it. So, we have directly written it a little bit of derivation can be done and because $\hat{H}$ is a Hamiltonian operator which can be written as

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

Again, we are considering the time independent potential and because px is nothing but

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

we can write down first, as we did before first, we have to find out this commutator and if we know the commutator, then we will be able to get the solution. So, first part of the commutator is which is nothing but

$$\begin{aligned}\hat{H}\hat{p}_x &= \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\left(-i\hbar\frac{\partial\psi}{\partial x}\right)\psi\\ &= \left[\frac{i\hbar^3}{2m}\frac{\partial^3}{\partial x^3}-i\hbar V\frac{\partial}{\partial x}\right]\psi\end{aligned}$$

Second part of the commutator-

$$\begin{aligned}\hat{p}_x\hat{H} &= \left(-i\hbar\frac{\partial\psi}{\partial x}\right)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\psi\\ &= \frac{i\hbar^3}{2m}\frac{\partial^3\psi}{\partial x^3}-i\hbar V\frac{\partial\psi}{\partial x}-i\hbar\frac{\partial V}{\partial x}\psi\end{aligned}$$

So, we get these two expressions and ultimately, we are interested in this commutator.

$$[\hat{H}\hat{p}_x-\hat{p}_x\hat{H}]\psi = i\hbar\frac{dV}{dx}\psi$$

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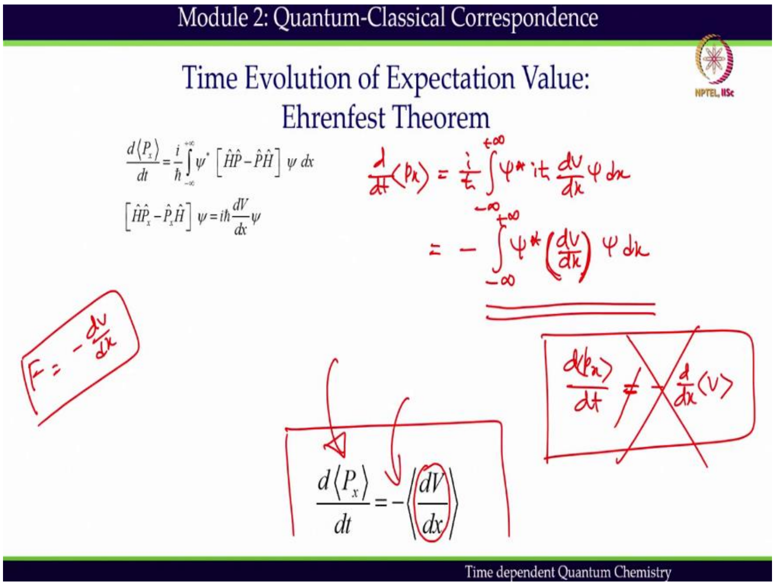

Module 2: Quantum-Classical Correspondence

Time Evolution of Expectation Value: Ehrenfest Theorem

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

$$\left[\hat{H}\hat{P}_x-\hat{P}_x\hat{H}\right]\psi = i\hbar\frac{dV}{dx}\psi$$

$$\frac{d}{dt}\langle p_x\rangle = \frac{i}{\hbar}\int_{-\infty}^{+\infty}\psi^*\, i\hbar\,\frac{dV}{dx}\psi\,dx$$

$$= -\int_{-\infty}^{+\infty}\psi^*\left(\frac{dV}{dx}\right)\psi\,dx$$

$$\boxed{F = -\frac{dV}{dx}}$$

$$\boxed{\cancel{\frac{d\langle p_x\rangle}{dt} \neq \frac{d}{dx}\langle V\rangle}}$$

$$\boxed{\frac{d\langle P_x\rangle}{dt} = -\left\langle\frac{dV}{dx}\right\rangle}$$

Time dependent Quantum Chemistry

$$\frac{d}{dt}\langle p_x \rangle = \frac{i}{\hbar}\left[\int_{-\infty}^{\infty} \psi^* i\hbar \frac{dV}{dx} \psi \, dx\right]$$

$$= -\left[\int_{-\infty}^{\infty} \psi^* \frac{dV}{dx} \psi \, dx\right]$$

Again, we have got a form of typical form of the expectation value, but this time it is the expectation value of the derivative of the potential and that is why we will write this.

$$\frac{d}{dt}\langle p_x \rangle = -\left\langle \frac{dV}{dx} \right\rangle$$

Change of the momentum is the gradient of the potential but, but we have to remember this is not like this

$$\frac{d}{dt}\langle p_x \rangle = -\frac{d\langle V \rangle}{dx}$$

Form expectation value of the derivative of the potential and this is something which we study in classical mechanics very frequently. Force is nothing but negative gradient of the potential is given by force that is in classical mechanics.

Similar thing we are getting here in quantum mechanics which shows that the expectation value of the momentum as a function of time that derivative will depend on the spatial derivative of the potential negative of the spatial derivative of the expectation value of the negative derivative or the potential.

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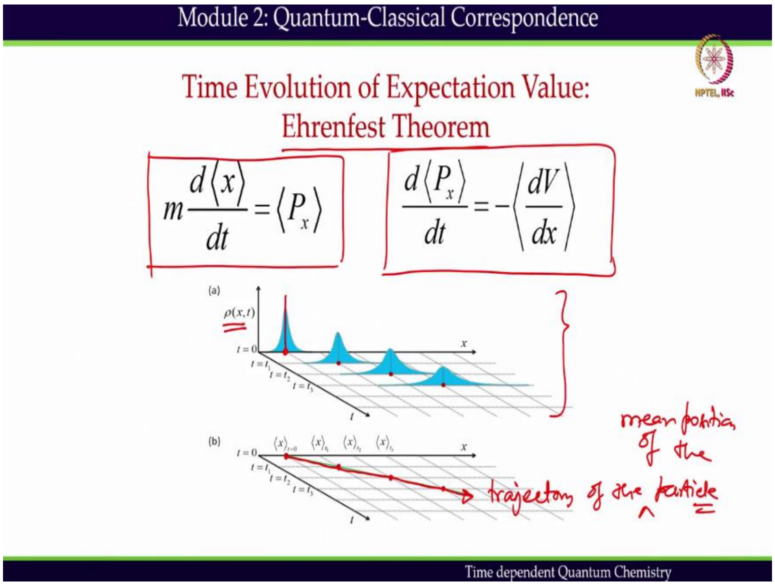

Module 2: Quantum-Classical Correspondence

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Time Evolution of Expectation Value:
Ehrenfest Theorem

$$\boxed{m\frac{d\langle x \rangle}{dt} = \langle P_x \rangle} \qquad \boxed{\frac{d\langle P_x \rangle}{dt} = -\left\langle \frac{dV}{dx} \right\rangle}$$

mean position of the

trajectory of the particle

Time dependent Quantum Chemistry

So, these two equations comprising the Ehrenfest theorem how the expectation value of position and momentum is changing in quantum dynamics and based on Ehrenfest theorem,

$$m\frac{d}{dt}\langle x\rangle = \langle P_x\rangle \qquad \frac{d}{dt}\langle p_x\rangle = -\left\langle \frac{dV}{dx}\right\rangle$$

the example which we have shown before the dynamics of the particle, probability distribution particle is moving that is where probability distribution is changing as a function of time in this 3D plot.

We have given the change we are showing the change and if we take the expectation value at each time, then I get a single point in the position space and that points if I plot them and connect them I get the trajectory of the particle but, this is not a trajectory of the particles. This is the trajectory of the mean position of the particle, calculated from the probability distribution function of the particle. So, some kind of trajectory can be constructed with the help of Ehrenfest theorem.

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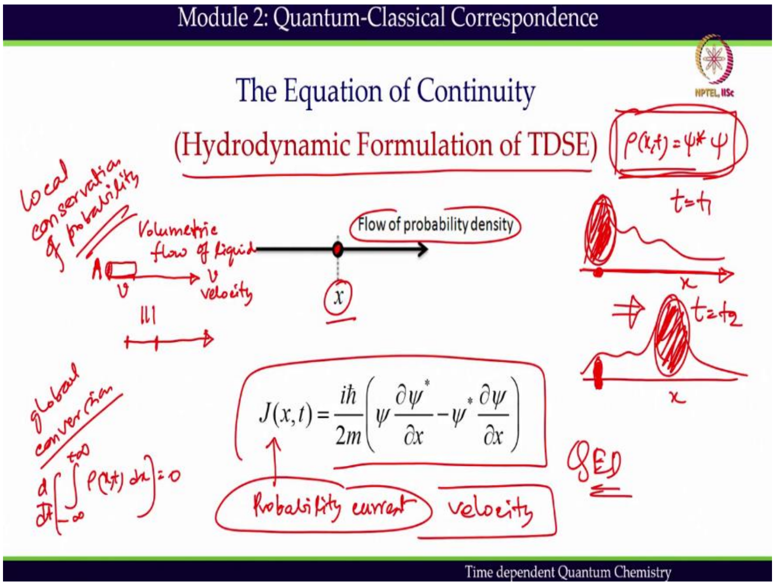

Module 2: Quantum-Classical Correspondence

The Equation of Continuity

(Hydrodynamic Formulation of TDSE)

Flow of probability density

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

Time dependent Quantum Chemistry

We have understood that a practically realisable interpretation of the wave function is obtained only by using the concept of probability density. Probability density which is expressed as $\rho(x,t) = \psi^*\psi$. And we have to get the probability density idea because that is the only way I can get the practically useful interpretation of the wave function in quantum mechanics.

This probability distribution function, I have also mentioned that at t equals t1 time, the probablity distribution function can be like this and at t equals t2 time probably distribution function will come like this. When the probability distribution function is changing as a function of time, it is manifesting the quantum dynamics, this is the x space.

So, probability distribution function has to change as a function of time to manifest the quantum dynamics and this idea that probability density is changing as a function of time this idea can be reviewed in terms of hydrodynamic formulation or hydrodynamic flow or liquid flow through space.

One can say that, as if probability is flowing through space, because see probability density has changed, the maximum density was here now, maximum density is here. So, this has changed the position. So, as the probability is flowing through the x space or the position space. So, one may conveniently represent the time dependent change of the probability density at a particular position x as a flow or probability density through that point x if we consider the liquid flow as if liquid is flowing through space.

And this idea will give me the local conservation of probability. Global conservation of probability we have seen, global conservation of probability is probability total probability density has to be constant at any time. So, first derivative with this time is going to be 0. That is the conservation of total probability density.

But local probability density at this point locally probability is changing. For example, here probability was high at a particular time, then on the same time on a different time, at a different time, on the same point, the probability density has changed as if there is a big wave of liquid was here. And then now, that wave has gone out. And that is why I have less amount of liquid at this point.

And that is why at a particular point, liquid is flowing through that point as a function of time. So, the flow of probability density through a point is called probability current, which is expressed, this is called probability current which is expressed by this expression.

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

This expression has its origin in quantum electrodynamics, we will not go over the origin we will use this equation, this representation of the probability current and we will try to find out hydrodynamic formulation of TDSE.

This is another formulation another way to look at the Time Dependent Schrodinger Equation. In fluid dynamics, volumetric flow rate. So, let us say a volume of liquid is flowing through space. This is A cross sectional area and v is the velocity. So, first second, it will make v distance advancement. So, this is called volumetric flow. And this is three-dimensional volumetric flow.

But, if we consider the same thing if we equivalent form in one dimension, then this flow is nothing but the velocity. Because in one dimension I do not have cross section is representing the velocity. So, J this probability current in one dimension is simply representing the velocity.

Velocity of the probability going through does position space, what is the velocity with which this probability is changing as a function of time or flowing through this space as a function of time. So that is the kind of hydrodynamic formulation the basic idea behind the hydrogen hydrodynamic formulation. In order to get that, what we will do.

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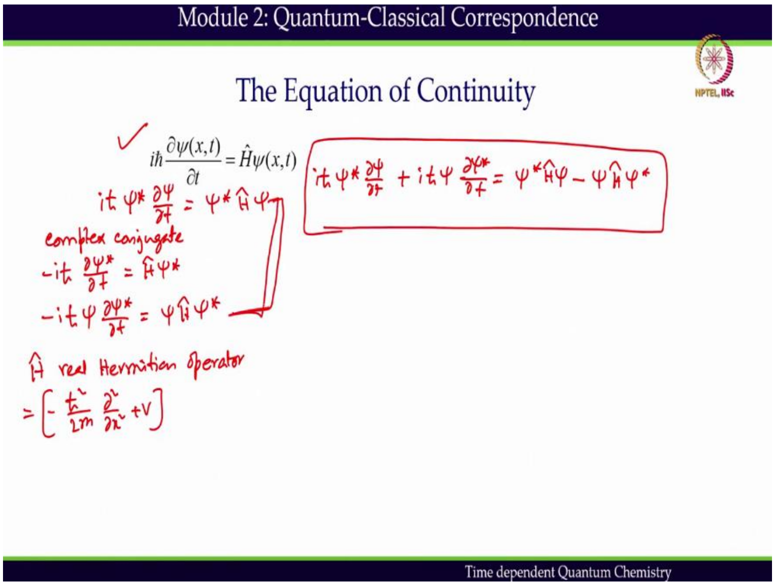

Module 2: Quantum-Classical Correspondence

The Equation of Continuity

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

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

complex conjugate

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

$$-i\hbar\,\psi\frac{\partial\psi^*}{\partial t}=\psi\hat{H}\psi^*$$

$\hat{H}$ real Hermitian operator

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

$$\boxed{i\hbar\,\psi^*\frac{\partial\psi}{\partial t}+i\hbar\,\psi\frac{\partial\psi^*}{\partial t}=\psi^*\hat{H}\psi-\psi\hat{H}\psi^*}$$

Time dependent Quantum Chemistry

We will start with TDSE, Time Dependent Schrodinger Equation,

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

and then we will multiply this equation by its complex conjugate of the wave function from the left-hand side. So, I will write down this one

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

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

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

And for that also, I will multiply the wave function, and remember this $\hat{H}$ is a Hermitian operator which is expressed by,

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

Again time independent potential you have considered. So, we will this one will be subtracted from this one, we get

$$i\hbar\psi^*\frac{\partial}{\partial t}\psi+i\hbar\psi\frac{\partial}{\partial t}\psi^*=\psi^*\hat{H}\psi-\psi\hat{H}\psi^*$$

So, this is the subtracted form, I am just subtracting these two expressions.

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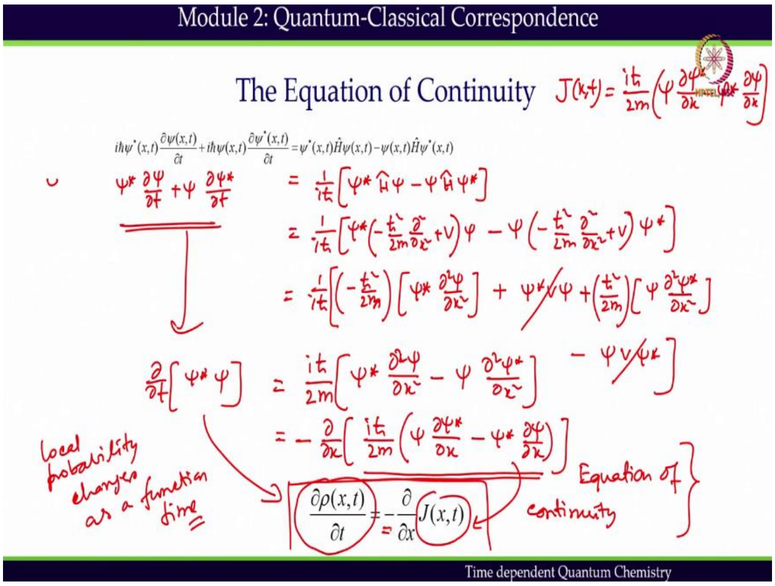

Module 2: Quantum-Classical Correspondence

The Equation of Continuity $J(x,t) = \frac{i\hbar}{2m}\left(\psi\frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}\right)$

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

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

$$= \frac{1}{i\hbar}\left[\psi^*\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\right)\psi - \psi\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\right)\psi^*\right]$$

$$= \frac{1}{i\hbar}\left[\left(-\frac{\hbar^2}{2m}\right)\left[\psi^*\frac{\partial^2\psi}{\partial x^2}\right] + \cancel{\psi^* V\psi} + \left(\frac{\hbar^2}{2m}\right)\left[\psi\frac{\partial^2\psi^*}{\partial x^2}\right] - \cancel{\psi V\psi^*}\right]$$

$$\frac{\partial}{\partial t}\left[\psi^*\psi\right] = \frac{i\hbar}{2m}\left[\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right]$$

$$= -\frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\psi\frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}\right)\right]$$

$$\boxed{\frac{\partial\rho(x,t)}{\partial t} = -\frac{\partial}{\partial x}J(x,t)}$$

Local probability changes as a function time

Equation of continuity

Time dependent Quantum Chemistry

After this subtraction I will further reduce the equation by inserting the Hamiltonian operator here.

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

$$= \frac{1}{i\hbar}\left[\psi^*\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi - \psi\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi^*\right]$$

$$= \frac{1}{i\hbar}\left[\left(-\frac{\hbar^2}{2m}\right)\left[\psi^*\frac{\partial^2\psi}{\partial x^2}\right] + \psi^* V\psi + \left(\frac{\hbar^2}{2m}\right)\left[\psi\frac{\partial^2\psi^*}{\partial x^2}\right] - \psi V\psi^*\right]$$

So, clearly, we are going to cancel this two because potential is a multiplication operator it can be placed anywhere, I can reorganise that expression without any constraint. So, finally what I get is

$$\psi^*\frac{\partial}{\partial t}\psi + \psi\frac{\partial}{\partial t}\psi^* = \frac{i\hbar}{2m}\left[\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right]$$

This is the expression what we get.

$$\frac{\partial}{\partial t}\left[\psi^*\psi\right] = \frac{i\hbar}{2m}\left[\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right]$$

Now, this part can be further reduced in following form

$$\frac{\partial}{\partial t}\left[\psi^*\psi\right]=-\frac{\partial}{\partial x}\left(\frac{i\hbar}{2m}\left[\psi\frac{\partial\psi^*}{\partial x}-\psi^*\frac{\partial^2\psi}{\partial x^2}\right]\right)$$

And we know that this part is what we call the current, probability current which is expressed by

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

this is the probability current. So, I can replace it by probability current and I get this expression where density is here and this part is here.

$$\frac{\partial\rho(x,t)}{\partial t}=-\frac{\partial}{\partial x}J(x,t)$$

So, this equation is another form of TDSE it is called Equation of Continuity which shows that how local probability changes as a function of So, change your probability density as a function of time, it will depend on the negative gradient of the current. So, what does it mean?

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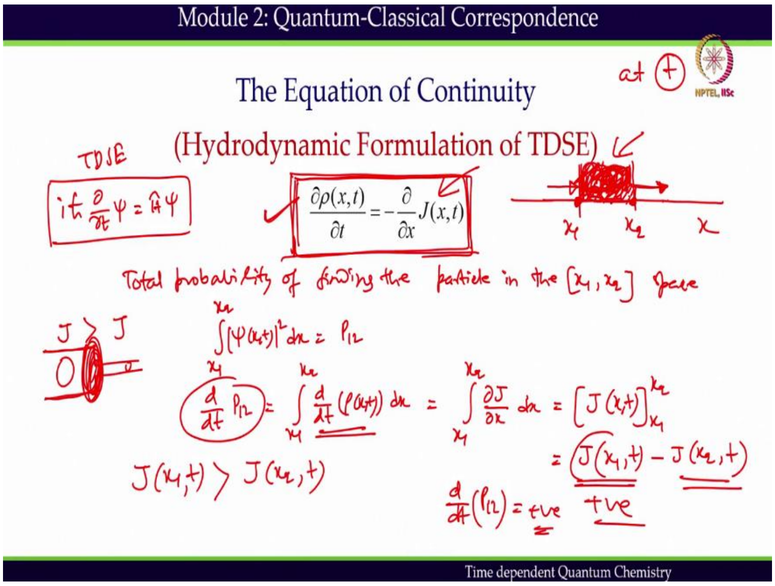

Module 2: Quantum-Classical Correspondence

The Equation of Continuity

(Hydrodynamic Formulation of TDSE)

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TDSE

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

$$\boxed{\frac{\partial \rho(x,t)}{\partial t} = -\frac{\partial}{\partial x}J(x,t)}$$

Total probability of finding the particle in the $[x_1, x_2]$ space

$$\int_{x_1}^{x_2} |\psi(x,t)|^2 dx = P_{12}$$

$$\frac{d}{dt}P_{12} = \int_{x_1}^{x_2} \underline{\frac{d}{dt}(\rho(x,t))}\, dx = \int_{x_1}^{x_2} \frac{\partial J}{\partial x}\, dx = \left[J(x,t)\right]_{x_1}^{x_2}$$

$$= \underline{J(x_1,t)} - \underline{J(x_2,t)}$$

$J(x_1,t) > J(x_2,t)$

$\frac{d}{dt}(P_{12}) = \underline{+ve}$ $\quad$ $\underline{+ve}$

Time dependent Quantum Chemistry

The meaning can be very easily realised if we consider a finite space between x1 and x2 we will show that how within this space in this x diagram within this space how probability is changing that we will calculate. But before we do so, one thing we should remember that this is the hydrodynamic formulation of TDSE or Equation of Continuity although the equation of continuity is just another mathematical form of TDSE.

But there exists an important difference between the Equation of Continuity and TDSE in the sense of interpretation, the equation of continuity as shown here directly deals with the probability density which is an experimentally realisable quantity, but TDSE is dealing with wave function and wave function cannot be observed directly through experiment. It is the density of which we can directly observed.

So, the presentation of your equation of continuity is something which can be directly connected to the experimental observable. So, that is the major difference we have otherwise, they are just simple, simply they are just different mathematical form of the same hypothesis, quantum mechanics.

Now, we will try to understand this equation the meaning of this equation and it will be very easily can be clarified if we consider this finite space between x1 and x2 so, then we can find out the total probability of finding the particle in the x1, x2 space and that is called local probability. It is not going to be 1. If it is, the wavefunction is normalised because it is within this finite.

$$\int_{x1}^{x2} |\psi(x,t)|^2 dx = P_{12}$$

$$\frac{d}{dt}P_{12} = \int_{x1}^{x2} \frac{d\rho(x,t)}{dt}dx$$

$$= \int_{x1}^{x2} \frac{dJ}{dx}dx$$

$$= \left[J(x,t)\right]_{x1}^{x2}$$

$$= J(x1,t) - J(x2,t)$$

If I considered that the J(x1,t) is greater than J(x2,t), then this part is positive and this part is positive It means that $\frac{d}{dt}P_{12}$, local change of probability within this space is going to be positive is developing the probability within this space local probability.

So, what does it mean? at a particular time, at this point, the current and at this point current, they are different, let us say, if the currents are different, if they are equal, then there is no effective change in the probability here prolate is not changing as a function of time. But if they are different, and if we assume that current which is entering into the space and exiting out of the space, if these two currents are different, then there will be probability accumulation in this regime.

And that is exactly what does it mean exactly the meaning exactly transferred from the fluid dynamics. Let us say I have a liquid which is flowing through this tube, but this tube has large diameter here small diameter here. So, there is a current difference now, and if the current here is greater than current here, then there will be an accumulation of liquid here and that is exactly going on here also, the current entering the regime and the current going out of the regime they are different and currently in one dimensional space is nothing but the velocity.

So, the velocity with which probability entering the space and the velocity with which the probability going out of that space that particular regime is different. And if the entering velocity is higher than the exit velocity, then in this regime, there will be a development of the probability density development of the liquid development of the probability density. So, probability density has very close resemblance with the liquid and that is why it is called hydrodynamic formulation of TDSE.

We will stop here we will continue this session, will continue this module in the next session. In the next session, we will consider Bohemian mechanics which is the last topic of this module.

We have studied Ehrenfest theorem, we have just now studied hydrodynamic formulation of the TDSE and a third topic is going to be Bohemian mechanics which can also give us the trajectory feelings in quantum dynamics. We meet again.