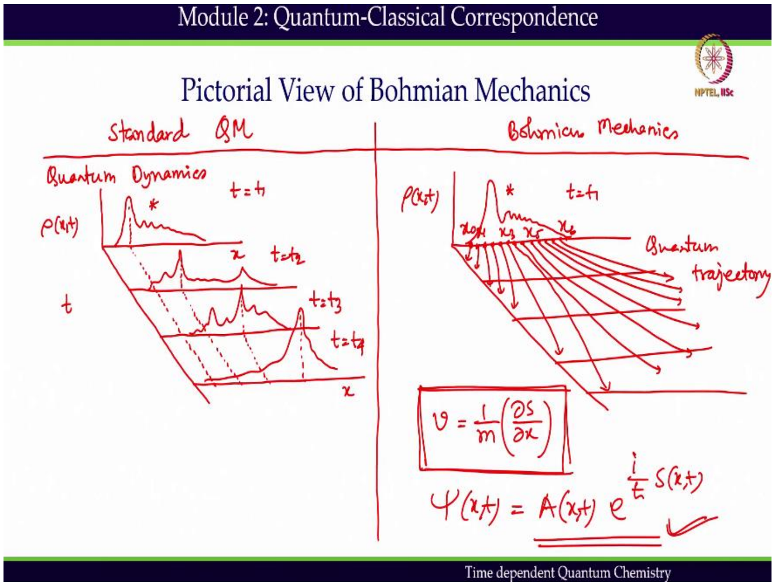
Time Dependent Quantum Chemistry
Professor. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru
Lecture 13
Bohmian Mechanics and Standard Interpretation

Welcome back to module 2 of this course Time Dependent Quantum Chemistry. In this module we are continuing discussion of Bohmian mechanics and in Bohmian mechanics we have assumed certain trial function for the wave function which will give me time dependent probability density, which is important to have to represent quantum dynamics and when we have discussed when we have used that trial function in time dependent quantum, time dependence Schrodinger equation, we have got one velocity information, what does it mean by this velocity?

(Refer Slide Time: 1:11)



Module 2: Quantum-Classical Correspondence

Pictorial View of Bohmian Mechanics

$$\boxed{v = \frac{1}{m}\left(\frac{\partial S}{\partial x}\right)}$$

$$\Psi(x,t) = \underline{\underline{A(x,t)\, e^{\frac{i}{\hbar}S(x,t)}}}$$

Time dependent Quantum Chemistry

We will go over it soon, but before we do that we will look at the one pictorial representation of what we have understood so far. This is standard quantum mechanics standard interpretation of quantum mechanics and this is Bohmian mechanics. It is just different form of viewing the same problem on a different footings.

So, in standard interpretation of quantum mechanics, quantum dynamics is represented in following way, I have a density which is (x,t) dependent and this is space at time t equals t1 I have certain density, let us say I have this density and this is the time axis so I will call it and different time I can plot how the densities would look like.

So, what we are seeing here if we look at it carefully with the help of standard interpretation of quantum mechanics we have to present it in terms of density that is the only way I can have interpretation of the wave function and we see that at different time this is t equals t2, this is t equals t3, this is t equals t4, at different time densities are changing these are just to for our eye to have a feel how it is changing, this is x axis.

So, what we see that densities are changing and that is the way we have to represent the quantum dynamics this is one dimensional representation one dimensional in terms of space in terms of position space that is why it is one dimensional and this is the way we represent the quantum dynamics.

On the other hand, in Bohemian mechanics we have quantum trajectory, so I had this initial distribution of the wave function I have tried to present this distribution and this distribution to be the same. So, this is my t equals t1 time and this distribution in Bohmian mechanics I do not have any wave function anymore, initial distribution can give me different position of the particle different possible position of the particle and it shows at different time how this individual particles are moving with a velocity, each position will have certain trajectory and these are called quantum trajectories this is called these are called quantum trajectory.

So, in Bohmian mechanics, we can directly get certain kind of trajectory equivalent to classical mechanics but only difference is that remember we have only one particle and this many trajectory what does it mean it means that if the particle was at this point there was a possibility because this is the distribution function distribution function is showing how possible positions are applicable to that particle the particle exactly where it is, I do not know but there are possible positions and if I pick up one of the possible position what kind of velocity it will have that will be given by the Bohmian velocity which is nothing but the space derivative of the phase function where we have assumed that the wave function had following form.

One can argue that instead of taking this kind of form what about if I take this kind of form

$$\psi(x,t) = A(x,t)e^{-i\hbar S(x,t)}$$

that is also fine, probably will end up with some other interesting information. So any kind of form one can use we have used this form because this conveniently leads to certain useful information and if I use this kind of form

$$\psi(x,t) = A(x,t)e\frac{-iS(x,t)}{\hbar}$$

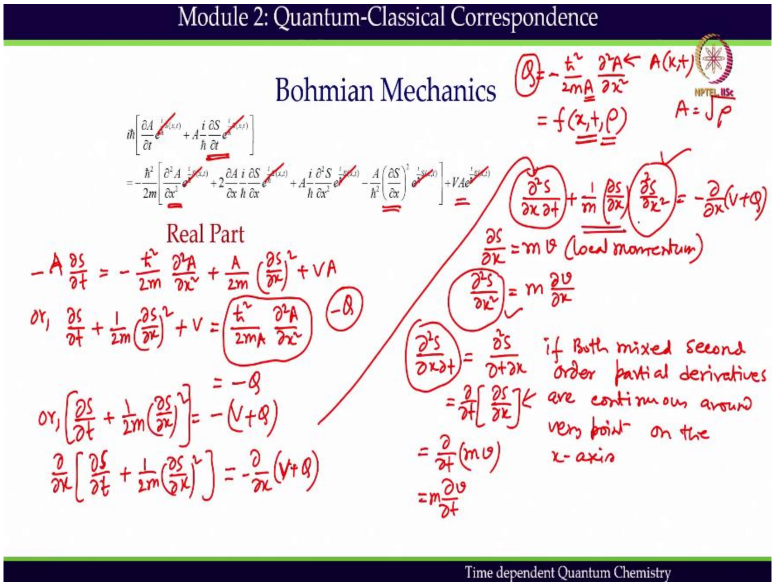
then I get the velocity of individual velocity of the particle for individual possible position initial position.

So, if I start with this x0 initial position, its velocity as well as the trajectory will be different than x1 position then x3 position x5 position x6 position all these different positions of initial positions will be giving me different trajectory.

So, that is the difference between Bohmian mechanics and standard interpretation of quantum mechanics and standard interpretation of quantum mechanics will always deal with the wave function and because wave function cannot be observed directly we have to convert it to density and we will see how density is changing as a function of time that is the manifestation of quantum dynamics in standard interpretation.

In Bohmian mechanics on the other hand, we pick up the possible position initial position and then each position will be now giving me individual trajectory and finally all this trajectory collectively shows how they are behaving.

(Refer Slide Time: 9:06)



Module 2: Quantum-Classical Correspondence

Bohmian Mechanics

$$i\hbar\left[\frac{\partial A}{\partial t}\cancel{e^{\frac{i}{\hbar}S(x,t)}}+A\underline{\frac{i}{\hbar}\frac{\partial S}{\partial t}}\cancel{e^{\frac{i}{\hbar}S(x,t)}}\right]$$

$$=-\frac{\hbar^2}{2m}\left[\underline{\frac{\partial^2 A}{\partial x^2}}\cancel{e^{\frac{i}{\hbar}S(x,t)}}+2\frac{\partial A}{\partial x}\frac{i}{\hbar}\frac{\partial S}{\partial x}\cancel{e^{\frac{i}{\hbar}S(x,t)}}+A\frac{i}{\hbar}\frac{\partial^2 S}{\partial x^2}\cancel{e^{\frac{i}{\hbar}S(x,t)}}-\underline{\underline{\frac{A}{\hbar^2}\left(\frac{\partial S}{\partial x}\right)^2}}\cancel{e^{\frac{i}{\hbar}S(x,t)}}\right]+VA\cancel{e^{\frac{i}{\hbar}S(x,t)}}$$

Real Part

$$-A\frac{\partial S}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 A}{\partial x^2}+\frac{A}{2m}\left(\frac{\partial S}{\partial x}\right)^2+VA$$

$$\text{or, } \frac{\partial S}{\partial t}+\frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2+V = \boxed{\frac{\hbar^2}{2mA}\frac{\partial^2 A}{\partial x^2}} \quad \boxed{-Q}$$

$$= -Q$$

$$\text{or, } \left[\frac{\partial S}{\partial t}+\frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2\right] = -(V+Q)$$

$$\frac{\partial}{\partial x}\left[\frac{\partial S}{\partial t}+\frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2\right] = -\frac{\partial}{\partial x}(V+Q)$$

$$\boxed{Q} = -\frac{\hbar^2}{2m\underline{A}}\frac{\partial^2 A}{\partial x^2} \leftarrow A(x,t)$$

$$= f(\underline{x,t},\underline{\rho}) \qquad A = \sqrt{\rho}$$

$$\boxed{\frac{\partial^2 S}{\partial x\partial t}}+\frac{1}{m}\underline{\left(\frac{\partial S}{\partial x}\right)}\boxed{\frac{\partial^2 S}{\partial x^2}} = -\frac{\partial}{\partial x}(V+Q)$$

$\frac{\partial S}{\partial x} = mv$ (local momentum)

$$\boxed{\frac{\partial^2 S}{\partial x^2}} = m\frac{\partial v}{\partial x}$$

$$\boxed{\frac{\partial^2 S}{\partial x\partial t}} = \frac{\partial^2 S}{\partial t\partial x}$$

if Both mixed second order partial derivatives are continuous around very point on the x-axis

$$= \frac{\partial}{\partial t}\left[\frac{\partial S}{\partial x}\right] \leftarrow$$

$$= \frac{\partial}{\partial t}(mv)$$

$$= m\frac{\partial v}{\partial t}$$

NPTEL IISc

Time dependent Quantum Chemistry

So, this is the primary difference between the standard interpretation of quantum mechanics and Bohmian mechanics will move forward and we will look at the real part. Now real part would be this part would be real now this part is real and this part is real and this part is real and remember we are we have remove this exponential term because this we can take it out.

So, the real part if I write down the real part is going to be

$$-A\frac{\partial S}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2 A}{\partial x^2}+\frac{A}{2m}\left(\frac{\partial S}{\partial x}\right)^2+VA$$

$$\frac{\partial S}{\partial t}+\frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2+V=\frac{\hbar^2}{2mA}\frac{\partial^2 A}{\partial x^2}=-Q$$

Where, $Q=-\frac{\hbar^2}{2mA}\frac{\partial^2 A}{\partial x^2}$

There is a particular meaning of this Q term we will get to know very soon, it is a function of x t and ρ, why? Because A is f(x,t) that is why it is function of x t and I have this a term A which is nothing but-

$$A=\sqrt{\rho}$$

So that is why Q term I have introduced this Q function is a function of (x,t) and its density, I will rearrange this equation-

$$\frac{\partial S}{\partial t}+\frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2=-(V+Q)$$

Now we will take the position derivative of this entire part,

$$\frac{\partial}{\partial x}\left[\frac{\partial S}{\partial t}+\frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2\right]=-\frac{\partial}{\partial x}(V+Q)$$

$$\frac{\partial^2 S}{\partial x\partial t}+\frac{1}{m}\left(\frac{\partial S}{\partial x}\right)\frac{\partial^2 S}{\partial x^2}=-\frac{\partial}{\partial x}(V+Q)$$

We have already understood that

$$\frac{\partial S}{\partial x} = mv\ ,\ \frac{\partial^2 S}{\partial x^2} = m\frac{\partial v}{\partial x}$$

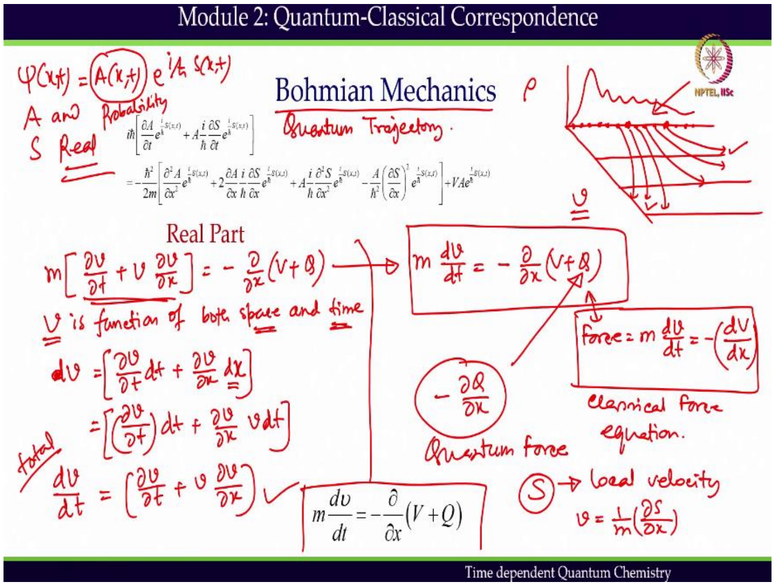
$$\frac{\partial^2 S}{\partial x \partial t} = \frac{\partial^2 S}{\partial t \partial x} = \frac{\partial}{\partial t}\left(\frac{\partial S}{\partial x}\right) = \frac{\partial}{\partial t}(mv) = m\frac{\partial}{\partial t}v$$

this $\frac{\partial S}{\partial x}$ is called local momentum, why it is local momentum? Because this is a momentum represented by the particle for each individual initial position coming from the initial distribution.

So, if we do that local momentum and we can take the second derivative and that is going to be m dx, so we have to use this because this is a term which we have here so we are going to use this one here and as a result another thing which we have to do here is this one can write to be equal if both mixed second order partial derivative are continuous around every point on the x axis.

So, as long as s is continuous, function will be able to write down this one, so if we write down this one, then what we have is this is nothing but time derivative of and we know that this is related to momentum, so this is going to be mv which is time derivative of this.

(Refer Slide Time: 18:31)



Module 2: Quantum-Classical Correspondence

Bohmian Mechanics

Quantum Trajectory.

$\psi(x,t) = \boxed{A(x,t)}\, e^{i/\hbar\, S(x,t)}$

A and S Real

Probability

$$i\hbar\left[\frac{\partial A}{\partial t}e^{\frac{i}{\hbar}S(x,t)} + A\frac{i}{\hbar}\frac{\partial S}{\partial t}e^{\frac{i}{\hbar}S(x,t)}\right]$$

$$= -\frac{\hbar^2}{2m}\left[\frac{\partial^2 A}{\partial x^2}e^{\frac{i}{\hbar}S(x,t)} + 2\frac{\partial A}{\partial x}\frac{i}{\hbar}\frac{\partial S}{\partial x}e^{\frac{i}{\hbar}S(x,t)} + A\frac{i}{\hbar}\frac{\partial^2 S}{\partial x^2}e^{\frac{i}{\hbar}S(x,t)} - \frac{A}{\hbar^2}\left(\frac{\partial S}{\partial x}\right)^2 e^{\frac{i}{\hbar}S(x,t)}\right] + VAe^{\frac{i}{\hbar}S(x,t)}$$

Real Part

$m\left[\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial x}\right] = -\frac{\partial}{\partial x}(V+Q) \rightarrow \boxed{m\frac{dv}{dt} = -\frac{\partial}{\partial x}(V+Q)}$

v is function of both space and time

$dv = \left[\frac{\partial v}{\partial t}dt + \frac{\partial v}{\partial x}dx\right]$

$= \left[\left(\frac{\partial v}{\partial t}\right)dt + \frac{\partial v}{\partial x}v\,dt\right]$

total

$\frac{dv}{dt} = \left(\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial x}\right)$ ✓

$$m\frac{dv}{dt} = -\frac{\partial}{\partial x}(V+Q)$$

$\boxed{\text{force} = m\frac{dv}{dt} = -\left(\frac{dV}{dx}\right)}$

classical force equation.

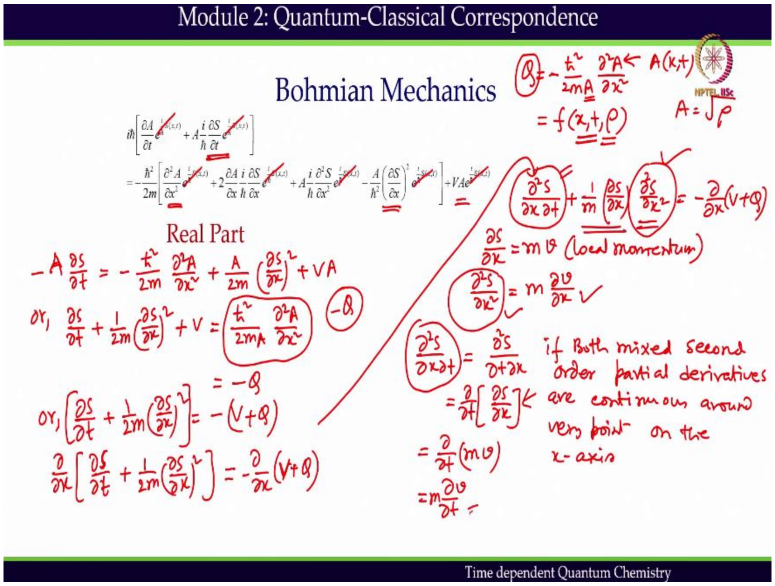
$-\frac{\partial Q}{\partial x}$

Quantum force

$S \rightarrow$ local velocity

$v = \frac{1}{m}\left(\frac{\partial S}{\partial x}\right)$

Time dependent Quantum Chemistry



Module 2: Quantum-Classical Correspondence

Bohmian Mechanics

$Q = -\frac{\hbar^2}{2mA}\frac{\partial^2 A}{\partial x^2} \leftarrow A(x,t)$

$= f(x,t,\rho)$

$A = \sqrt{\rho}$

$$i\hbar\left[\frac{\partial A}{\partial t}\cancel{e^{\frac{i}{\hbar}S(x,t)}} + A\frac{i}{\hbar}\frac{\partial S}{\partial t}\cancel{e^{\frac{i}{\hbar}S(x,t)}}\right]$$

$$= -\frac{\hbar^2}{2m}\left[\frac{\partial^2 A}{\partial x^2}\cancel{e^{\frac{i}{\hbar}S(x,t)}} + 2\frac{\partial A}{\partial x}\frac{i}{\hbar}\frac{\partial S}{\partial x}\cancel{e^{\frac{i}{\hbar}S(x,t)}} + A\frac{i}{\hbar}\frac{\partial^2 S}{\partial x^2}\cancel{e^{\frac{i}{\hbar}S(x,t)}} - \frac{A}{\hbar^2}\left(\frac{\partial S}{\partial x}\right)^2 \cancel{e^{\frac{i}{\hbar}S(x,t)}}\right] + VA\cancel{e^{\frac{i}{\hbar}S(x,t)}}$$

Real Part

$-A\frac{\partial S}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 A}{\partial x^2} + \frac{A}{2m}\left(\frac{\partial S}{\partial x}\right)^2 + VA$

or, $\frac{\partial S}{\partial t} + \frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2 + V = \boxed{\frac{\hbar^2}{2mA}\frac{\partial^2 A}{\partial x^2}}$ $\quad (-Q)$

$= -Q$

or, $\left[\frac{\partial S}{\partial t} + \frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2\right] = -(V+Q)$

$\frac{\partial}{\partial x}\left[\frac{\partial S}{\partial t} + \frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2\right] = -\frac{\partial}{\partial x}(V+Q)$

$\boxed{\frac{\partial^2 S}{\partial x\partial t}} + \frac{1}{m}\left(\frac{\partial S}{\partial x}\right)\boxed{\frac{\partial^2 S}{\partial x^2}} = -\frac{\partial}{\partial x}(V+Q)$

$\frac{\partial S}{\partial x} = mv$ (local momentum)

$\boxed{\frac{\partial^2 S}{\partial x^2}} = m\frac{\partial v}{\partial x}$ ✓

$\boxed{\frac{\partial^2 S}{\partial x\partial t}} = \frac{\partial^2 S}{\partial t\partial x}$ if Both mixed second order partial derivatives are continuous around very point on the x-axis

$= \frac{\partial}{\partial t}\left[\frac{\partial S}{\partial x}\right]$

$= \frac{\partial}{\partial t}(mv)$

$= m\frac{\partial v}{\partial t}$

Time dependent Quantum Chemistry

So, we have now this term evaluated we have already evaluated this term, so we can plug that in these two if we plug that in, we get back a simple equation like,

$$m\left[\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial x}\right] = -\frac{\partial}{\partial x}(V+Q)$$

So this part is velocity v this part is given here and this part is given here. Now because velocity is a function of both space and time, why? I have showed already if this is the initial distribution function, then these are the possible positions I have for the particle anywhere it can stay but at the same time I have to mention here that although there is a possibility of the particle staying anywhere in this but there is a mean position also that is given by expectation value.

So, those are the standard interpretation of quantum mechanics, here we have this possible positions and each position will be now undergoing some motion and this motion is represented by the quantum trajectory. So, this velocity in the end depends on its position from where it is starting, if it is starting from here, then it will end up with going somewhere else if it is starting from here it will go somewhere else.

So, it is it depends on velocity depends on both space and time velocity has to depend on time also, so because it depends on both space and time this total derivative which is not partial derivative total derivative will be given by partial derivative summation of these two partial derivative and that is exactly what we have here.

$$dv = \left[\frac{\partial v}{\partial t} dt + \frac{\partial v}{\partial x} dx \right]$$

$$= \left[\frac{\partial v}{\partial t} dt + \frac{\partial v}{\partial x} v dt \right]$$

And this dx can be represented as vdt that the displacement you will have or by this mathematical trick what I get is the total derivative total time derivative of the velocity I get and that can be represented by summation of these two partial derivatives

$$\frac{\partial v}{\partial t} = \frac{\partial v}{\partial t} + v \frac{\partial v}{\partial x}$$

And this exactly what we have here.

So, this equation can be simplified as follows is going to be

$$m \frac{\partial v}{\partial t} = -\frac{\partial}{\partial x} \left(V + Q \right)$$

We get so what it suggest if it is was a classical particle moving under conservative force, then we write that force which is nothing but

$$Force = m\frac{\partial v}{\partial t} = -\frac{\partial V}{\partial x}$$

So, this is the classical force equation and in Bohmian mechanics what we get is this equation which is very comparable very close to the classical equation except for the fact that I have now additional term which is Q, so it is not just the potential there is another potential which is introduced and this part is called quantum force $\frac{\partial Q}{\partial x}$ this part is called quantum force.

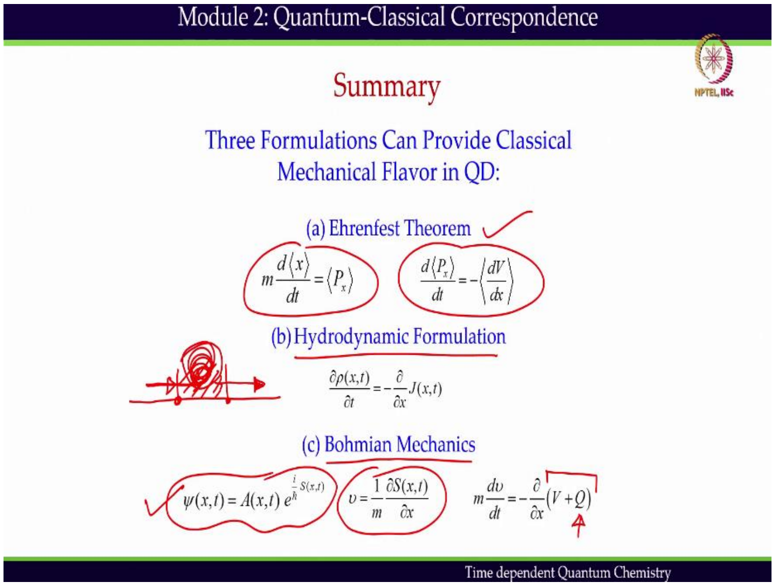
So, what it points out that an important information here is that if a state of a moving quantum particle is represented

$$\psi(x,t) = A(x,t)e\frac{-iS(x,t)}{\hbar}$$

trial wave function where A and S are both we are considering real then A gives me probability density of the particle at a given time.

So, this is related to the probability density, on the other hand S function this gives me the local velocity or Bohmian velocity which is given by the space derivative and that is why Bohmian mechanics gives me quantum trajectory.

(Refer Slide Time: 25:38)



Module 2: Quantum-Classical Correspondence

NPTEL, IISc

Summary

Three Formulations Can Provide Classical Mechanical Flavor in QD:

(a) Ehrenfest Theorem ✓

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

(b) Hydrodynamic Formulation

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

(c) Bohmian Mechanics

$$\psi(x,t) = A(x,t)\, e^{\frac{i}{\hbar}S(x,t)} \qquad \upsilon = \frac{1}{m}\frac{\partial S(x,t)}{\partial x} \qquad m\frac{d\upsilon}{dt} = -\frac{\partial}{\partial x}(V+Q)$$

Time dependent Quantum Chemistry

So, we have pretty much come to the end of the presentation this module we have made an attempt to understand quantum dynamics with classical mechanical flavor with classical mechanical idea and the only difference between classical mechanics and quantum mechanics is that in classical mechanics we can draw a trajectory and trajectory, what does it mean? It means that in (x,t) plot I can find out the particle exact position at different time.

In quantum mechanics, I cannot get that information directly because the particle will be represented by a wave function and wave function itself is a delocalized function, so what can I do? How can I get that classical idea in the quantum dynamics? There are three theorems I have presented, Ehrenfest theorem where I have seen that expectation value is following classical mechanics, what is the definition of expectation value that I have already presented.

Hydrodynamic Formulation second theorem where we have shown that this quantum dynamics can be represented as a flow of density and flow of density solely depends on the probability current at that point. So, if these two points if we consider and this space we consider and if the inner current and outer current are different, then there will be a accumulation or decay of the probability at this region. So, this is called hydrodynamic formulation with the help of probability current.

And the third formulation we have shown is Bohmian mechanics where we are assuming that the wave function which is supposed to present the superposition state but I am intelligently selected a particular trial function for that kind of evolving system time evolving system and then plug that in and I am getting a local velocity and in addition to that I have some additional information which is related to the quantum force as well, what is the meaning of quantum force?

Those are the topics which will not cover in this in this course and will not much discuss about the Bohmian mechanics except for the fact that will be presenting free particle motion the behavior of a free particle motion with the help of Bohmian mechanics is that is the only topic which we will cover in this course but is an open topic and there are many terminology which are used very frequently hidden variables those things will not present here. So we will end this module I will see you again for the next module.