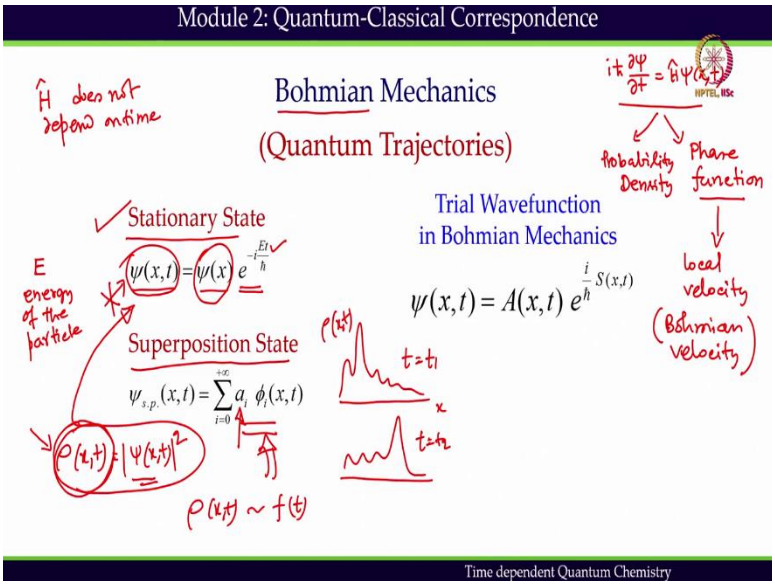
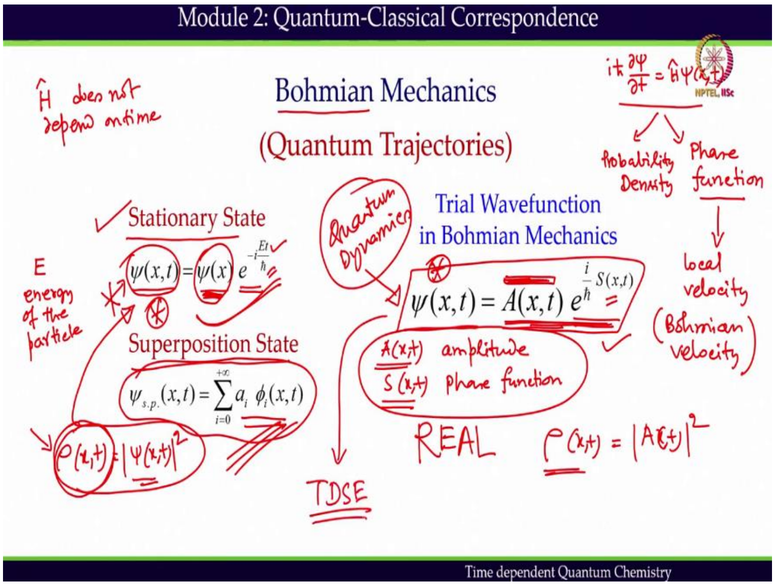
Time Dependent Quantum Chemistry
Professor. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru
Lecture 12
Bohmian Mechanics

Welcome back to module 2 of the course, Time Dependent Quantum Chemistry. In this module, we have gone over, we have tried to find out classical mechanical flavour in quantum dynamics. We have gone over Ehrenfest theorem and hydrodynamic formulation of TDSE.

(Refer Slide Time: 00:49)





Next, we will go over Bohmian mechanics, this is the third topic which we will cover in this in this module. In the Bohemian formulation, what we will do, we will rewrite the TDSE as two equations. So,we started with TDSE these are all different formulation of TDSE, we started with TDSE Time Dependence Schrodinger Equation, here ψ function of x and t.

And we will rewrite this equation into two equations. One for the probability density another one for the phase function and this phase function we will see that in Bohmian mechanics. This phase function will give me the velocity or the local velocity, it is called local velocity or Bohmian velocity, what does it mean? I will discuss that one. So, from phase function, we will get them local velocity.

We have understood that variable separation method which we have previously used under the assumption that Hamiltonian of the system it does not depend on time. Under this assumption, we have done variable separation method and from variable separation method, we have been able to get the solution to the TDSE and we have got one solution which is called Stationary State solution we have got by this where we have this time dependent phase factor introduced and e represents the energy of the particle.

This is just a review of what we have already understood. This $\psi(x)$ is position dependent stationary state of the particle. As all experimental observables are associated with the probability density of the particle. Probability density of the particle is represented by this $\rho(x,t)$ which is nothing but $\psi(x,t)$ absolute square. So, every experimental observable is actually related to this $\rho(x,t)$ not to the $\psi(x,t)$.

The probability density of the particle expressed by this equation which is coming from this $\psi(x,t)$ does not depend on time and that is why it is called Stationary State. So, Stationary State has time dependency for the wave function, but not for the density. And because density is something which we observe experimentally; experimentally, we do not see any time dependence.

Time dependence, in order to observe time dependence, we have understood that superposition state is very important and is expressed by this linear combination of different states, stationary states with its expansion coefficient. Now, this is we have already understood and that makes $\rho(x,t)$ to be dependent on time. It can be function of time for only superposition state.

So, what does it mean? It means that at t equals t1 time I have some density this is rho versus x. Again, at t equals t2 time I have some other density. So, then density is changing as a function of time, x and t as a function of time density is changing it means that I have the dynamics in the quantum system. Now, when you said that this linear combination can be used this equation itself even if I take two stationary states this equation can be very complicated.

So, instead of such a complicated wave function which will represent the dynamics of quantum system one can propose that. Let us assume that the trial wave function looks like this; trial function has amplitude as well as time dependent phase.

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

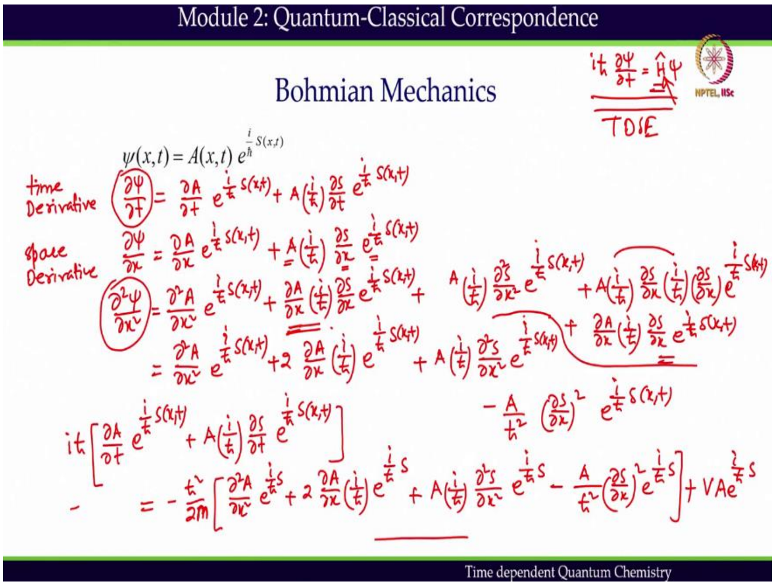
So, this A(x,t) is the amplitude and S(x,t) is the phase function and, we will assume that both of these functions are real.

This is the assumption we are making for the time dependent wave function, because this time dependent function remember, we will if I take the $\rho(x,t)$ of this time dependent function, I still get time dependency in the density. And time dependence in in the density it means that this wave function is suitable to represent quantum dynamics as opposed to this stationary state wave function.

Although note the similarity between this wave function and this wave function, it has a time dependent phase factor it has time dependent phase factor, it has some kind of amplitude which is time independent, but here the only difference is that I have time dependent amplitude. So, both are changing as a function of time and that kind of wave function can be very useful to represent my quantum dynamics.

So, instead of taking this superposition state wave function complicated linear combination of wave function one can propose that one can use this as a trial function and then plug that in to TDSE and get the solution for that for the particular system. So, because this A and S they are unknown function, we have to find out what kind of form we have in this function. So, we have to plug that in this wave function is to be plugged into the into them TDSE, Time Dependent Schrodinger Equation and that is exactly what we are going to do.

(Refer Slide Time: 09:33)



So, Schrodinger equation. TDSE

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

So, what we will do right now, we will take the time and space derivative separately So, first we will take the time derivative.

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

So, this is time derivative and then we will go for the space derivative.

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

Then I have to take the second derivative because Hamiltonian operator has second derivative in it,

$$\frac{\partial^2}{\partial x^2}\psi = \frac{\partial^2 A}{\partial x^2}e^{i\frac{S(x,t)}{\hbar}} + \frac{\partial A}{\partial x}\left(\frac{i}{\hbar}\right)\frac{\partial S}{\partial x}e^{i\frac{S(x,t)}{\hbar}} + A\left(\frac{i}{\hbar}\right)\frac{\partial^2 S}{\partial x^2}e^{i\frac{S(x,t)}{\hbar}} + A\left(\frac{i}{\hbar}\right)\frac{\partial S}{\partial x}\left(\frac{i}{\hbar}\right)\frac{\partial S}{\partial x}e^{i\frac{S(x,t)}{\hbar}} + \frac{\partial A}{\partial x}\left(\frac{i}{\hbar}\right)\frac{\partial S}{\partial x}e^{i\frac{S(x,t)}{\hbar}}$$

So, now we will reduce it further.

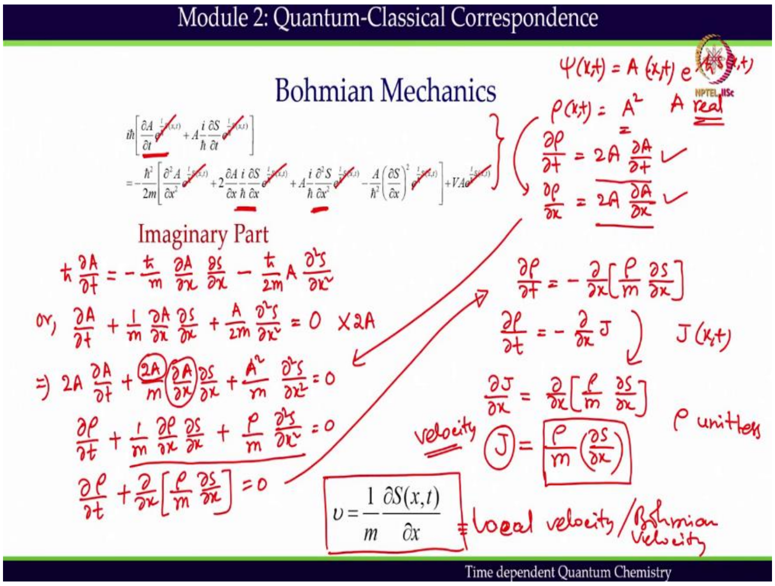
$$= \frac{\partial^2 A}{\partial x^2}e^{i\frac{S(x,t)}{\hbar}} + 2\frac{\partial A}{\partial x}\left(\frac{i}{\hbar}\right)\frac{\partial S}{\partial x}e^{i\frac{S(x,t)}{\hbar}} + A\left(\frac{i}{\hbar}\right)\frac{\partial^2 S}{\partial x^2}e^{i\frac{S(x,t)}{\hbar}} - \frac{A}{\hbar^2}\left(\frac{\partial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

So, this is what we have reduced this is just tedious one can do it very quickly. And all we have to do is that now, we have second derivative with respect to space and time derivative we have so, we will be able to plug that in TDSE.

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

This is the final form of the TDSE. So, all we need to do now, in this equation on the left-hand side I have some real part and on the right-hand side I have some real part. So that needs to be equal. On the other hand. On the left-hand side, I have some imaginary part on the right-hand side we have imaginary part we will make them equal.

(Refer Slide Time: 19:31)



So, we will just equate separately real and imaginary part we will look at the imaginary part first. So, this was the equation which we have got in the previous slide. And if we look at the imaginary part, imaginary part is going to be following. This part is going to multiplied by i h cut. So, this part is going to be real part and imaginary part is going to be this part.

One can also notice that I can remove this exponential part from each term they can actually be eliminated. So, I will just go ahead and equate the imaginary parts

$$\hbar\frac{\partial A}{\partial t}=-\frac{\hbar}{m}\frac{\partial A}{\partial x}\frac{\partial S}{\partial x}-\frac{\hbar}{2m}A\frac{\partial^2 S}{\partial x^2}$$

$$\frac{\partial A}{\partial t}+\frac{1}{m}\frac{\partial A}{\partial x}\frac{\partial S}{\partial x}+\frac{A}{2m}\frac{\partial^2 S}{\partial x^2}=0$$

For this particle probability density will be represented by,

$$\psi(x,t) = A(x,t)e^{i\frac{S(x,t)}{\hbar}}$$
$$\rho(x,t) = A^2$$

I said that A is going, is real that was the assumption we have made.

So, because it is real it is nothing but the A square and if it is a square I will be able to find out time derivative of the probability density that is going to be

$$\frac{\partial}{\partial t}\rho(x,t) = 2A\frac{\partial A}{\partial t}$$

and, similarly, space derivative is going to be,

$$\frac{\partial}{\partial x}\rho(x,t) = 2A\frac{\partial A}{\partial x}$$

So, now what we will do, here we will just multiply this equation by 2A. If we multiply this equation by 2A than what I get?

$$2A\frac{\partial A}{\partial t} + \frac{2A}{m}\frac{\partial A}{\partial x}\frac{\partial S}{\partial x} + \frac{A^2}{m}\frac{\partial^2 S}{\partial x^2} = 0$$

Now, I can insert this one and this one here. If we do that, then I can see that

$$\frac{\partial}{\partial t}\rho(x,t) + \frac{1}{m}\frac{\partial}{\partial x}\rho(x,t)\frac{\partial S}{\partial x} + \frac{\rho(x,t)}{m}\frac{\partial^2 S}{\partial x^2} = 0$$
$$\frac{\partial}{\partial t}\rho(x,t) + \frac{\partial}{\partial x}\left[\frac{\rho(x,t)}{m}\frac{\partial S}{\partial x}\right] = 0$$
$$\frac{\partial}{\partial t}\rho(x,t) = -\frac{\partial}{\partial x}\left[\frac{\rho(x,t)}{m}\frac{\partial S}{\partial x}\right]$$

Now, we will recall the hydrodynamic formulation of TDSE previously, we have done that. Hydrodynamic formulation where we have presented rho, density change of density as a function of probability current.

So, we have shown that change your probability density is nothing but negative of the gradient of the current at that point and particular definition of J has been given already.

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

So, we are not giving it right now. So, one can say that this is nothing but rho by m dx or J has now new definition in Bohmian mechanics J is nothing but this part. So, we can recall that $\rho(x,t)$ is unitless. It is a probability density, this is unitless quantity. And J represents some kind of velocity in one dimension.

So, if this is velocity, then one can say that this entire term which is given here is representing the velocity of the particle this is called local velocity or Bohman velocity. So, what we have got is some kind of velocity information we have got for the particle which is moving and what does it mean by this velocity. We will go over it in the next session.