Time Dependent Quantum Chemistry
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Lecture No. 02
Introduction to TDSE

Welcome to module 1 of the course Time Dependent Quantum Chemistry. In this course, in this module we will first introduce time dependent Schrodinger equation and then we will closely inspect that equation to find out the meaning of that equation. And we will introduce Quantum Dynamics from viewpoint of quantum superposition. So, let us begin.

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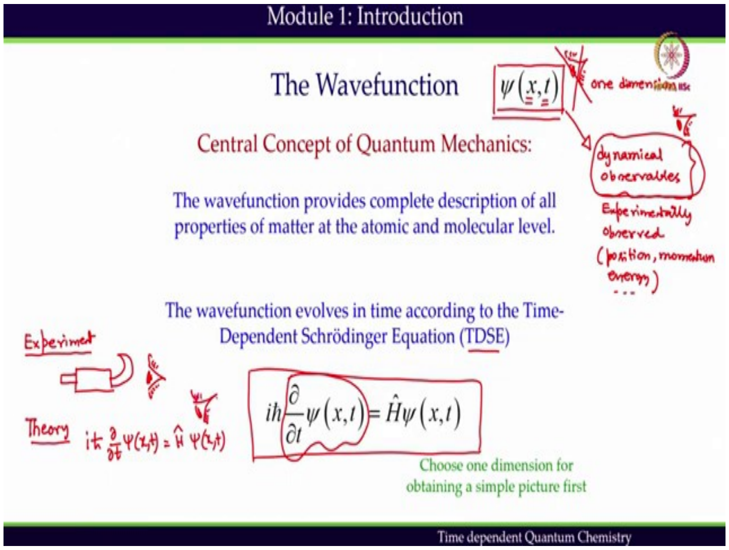

Module 1: Introduction

The Wavefunction $\boxed{\psi(\underline{\underline{x}},\underline{\underline{t}})}$ one dimension

dynamical observables

Experimentally observed (position, momentum energy) ...

Central Concept of Quantum Mechanics:

The wavefunction provides complete description of all properties of matter at the atomic and molecular level.

The wavefunction evolves in time according to the Time-Dependent Schrödinger Equation (TDSE)

Experiment

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

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

Choose one dimension for obtaining a simple picture first

Time dependent Quantum Chemistry

Quantum mechanics governs structure, dynamics, physical and chemical properties of matter at the atomic and molecular level. In quantum mechanics the wave function denoted by $\psi(x,t)$ for simplicity we have considered one-dimension and once we understand the one-dimensional problem, we will be able to move on to three-dimensional problem. So, to get the idea, basic idea, fundamental ideas clear we will continue with one dimension.

So, this wave function in quantum mechanics, this wave function provides a complete description of all properties of matter at a given time and gives information about a matter's dynamical observable. So, from quantum mechanics we get this wave function, from the wave function we will be able to calculate dynamical observable.

Dynamical observables, this dynamical observable can be any physical quantity which can be experimentally measured or observed such as; so this is something which can be experimentally observed such as position, momentum, energy of the particle etcetera. Any physical quantity which can be experimentally observed is called dynamical observable.

Now, this wave function can be connected to the dynamic dynamical observable, we cannot observe wave function directly this is something which we will always remember in this class that we cannot observe wave function directly. Wave function has to be converted to a certain way to connect to this dynamical observable, this is dynamical observable which we can observe through an experiment.

The wave function, what is the meaning of the wave function? Will discuss in this class because clarification of the meaning of this wave function is very important for rest of the class. The wave function which is a function of position and time. The function of a quantum system evolves in time according to time dependent Schrodinger Equation that is given here time dependent Schrodinger Equation this is one dimensional often abbreviated as TDSE.

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

As we can note here is that TDSE time dependence Schrodinger equation is first order in time this is first order in time. So, in general what happens in the experiment when we perform an experiment what we do in general we keep an eye on the apparatus, we try to find out the sensitivity of the apparatus ,the performance of the operators and we acquired the data and analyse the data that is what exactly what we do in the experiments we always keep an eye on the apparatus.

In the theory, we have this equation for an example, here for this course the most important equation the master equation is going to be time dependence Schrodinger Equation in one-dimension meaning of each part of the equation will be given very soon, but I have this equation and what is our task? We have to keep an eye on this equation try to understand the meaning of this equation first as I have told that this equation is first order in time.

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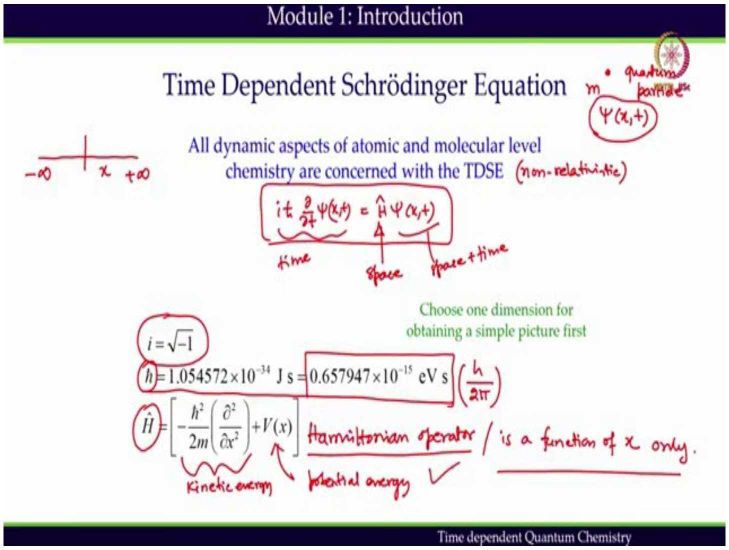

Module 1: Introduction

Time Dependent Schrödinger Equation

All dynamic aspects of atomic and molecular level chemistry are concerned with the TDSE

Choose one dimension for obtaining a simple picture first

$i = \sqrt{-1}$

$\hbar = 1.054572 \times 10^{-34}$ J s $= 0.657947 \times 10^{-15}$ eV s

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

Time dependent Quantum Chemistry

So let us begin, we have one particle let us say a simple particle quantum particle, we have one quantum particle and this quantum particle because it is a sub-atomic I mean atomic or molecular level particle, it is expressed by its wave function $\psi(x,t)$ having mass m the particle mass m and the TDSE of this particle in one dimension is written as-

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

That is one dimensional TDSE because this equation TDSE of the particle single particle m that is the mass of the particle single particle m and we have assumed that the particle velocity is much less than speed of light, so it is a non-relativistic problem we are dealing with.

Non-relativistic particle moving in x dimensional space, let us say I have a space defined by x axis minus infinity to plus infinity and the particle is moving on this x dimensional space its wave function is given by $\psi(x,t)$ and the equation TDSE which governs all dynamical aspects of that system is given by this equation, where-

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

$$\hbar = 1.054572 \times 10^{-34} Js = 0.657947 \times 10^{-15} eVs$$

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

We might want to remember this value in eV because it becomes very useful in many calculations we will be doing in this class. So this is reduced plank constant which is plank constant divided by 2 pi and $\hat{H}$ is the Hamiltonian operator. Many details of the operator quantum mechanical operators will be given, so operator the meaning of operator in quantum mechanics everything will be discussing but to directly come to this TDSE.

In TDSE we have this Hamiltonian operator that is total energy operator which will include kinetic energy part, the first part is called kinetic energy part and second part is the potential energy part. In quantum mechanics $\hat{H}$ this Hamiltonian operator what we can see here the way we have presented so far $\hat{H}$ Hamiltonian operator is a function of space only.

It is not necessary that total Hamiltonian has to be always function of space that is x for one dimension it can be function of time as well but for the time being we will forget time dependence, we will just think about space dependent Hamiltonian, so our Hamiltonian is space dependent.

Wave function is both space and time dependent and this part is time evolution of that wave function and the wave function finally the wave function which is going to describe the particle at the atomic and molecular level that will solely depend on this Hamiltonian operator.

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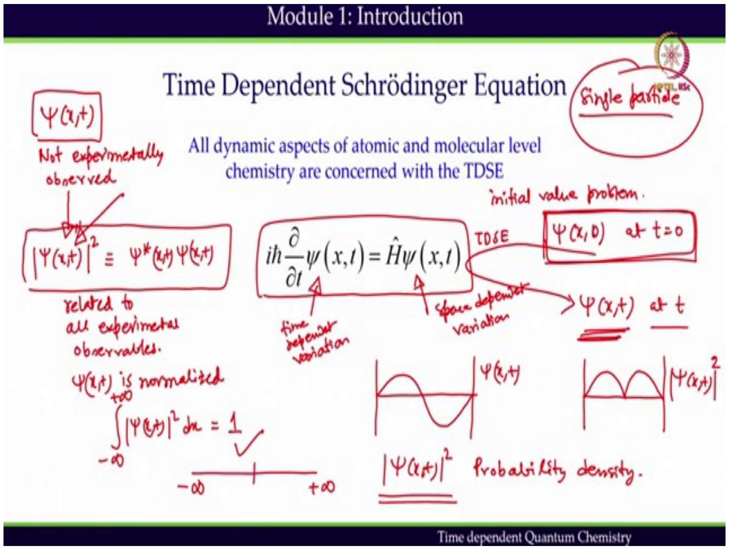

Module 1: Introduction

Time Dependent Schrödinger Equation

Single particle

All dynamic aspects of atomic and molecular level chemistry are concerned with the TDSE

$\psi(x,t)$

Not experimentally observed

$|\psi(x,t)|^2 \equiv \psi^*(x,t)\psi(x,t)$

related to all experimental observables.

$\psi(x,t)$ is normalized

$\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx = 1$ ✓

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

time dependent variation

space dependent variation

TDSE

initial value problem.

$\psi(x,0)$ at $t=0$

$\psi(x,t)$ at t

$|\psi(x,t)|^2$ Probability density.

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So, the way we have seen the problem it is called and in mathematics if we have an equation like this where left hand side is time dependent variation, right hand side is space dependent variation this is called space dependent variation and this is time dependent variation this is called initial value problem.

It means that if I know $\psi(x,0)$ at t=0, If I know the initial wave function then through TDSE using this TDSE I will be able to find out what would be the wave function at time t, so initial value has to be given initial condition has to be given for to figure out what is going to happen at a particular later time, but as I mentioned previously quantum mechanics deals directly with this wave function, wave function of the particle.

What is the meaning of a wave function? It is a physical quantity which is representing the quantum particle, this is what we get from quantum mechanics but this is not something which you can experimentally observe. This is not something which can be observed experimentally all we observe every experimental observable is connected to this quantity the density which is expressed by modular square which is nothing but $\psi^*(x,t)$ complex conjugate of that wave function multiplied by its own form.

$$\left|\psi(x,t)\right|^2 = \psi^*(x,t)\psi(x,t)$$

So, this is what is related to every experimental observable this is related to all experiments and that is something which we always remember in this class in this time dependent quantum chemistry course that wave function is not directly observable in the experiment. So, this is just a simple example. If I have a function like this at a particular time t then experimental observable will be connected to its density which looks like this.

And if this $\psi(x,t)$ is normalized wave function then one can write that in the entire space total probability of finding that particle is going to be 1 because we have single particle, we are dealing with single particle the total probability of in the entire space here it is x space, so minus infinity to plus infinity total probability of finding that particle is going to be always 1.

$$\int_{-\infty}^{+\infty} \left|\psi(x,t)\right|^2 dx = 1$$

And this $\psi(x,t)$ will have elaborate discussion of this probability density very soon just to give you an initial sketch what we can observe and what we do not observe and what physical quantity connected to the experimental observable we are just giving demonstrating this one. This part this square modulus of the wave function is called probability density.

So, I repeat one more time, TDSE gives me wave function. Wave function cannot be observed experimentally I have to convert that wave function to its own density and that density is somewhat connected to the experimental observable. In order to get the wave function through TDSE I need to know the initial wave function at t = 0.

So, with this preliminary idea although we have not discussed how that wave function should look like in quantum mechanics even for single particle that we have not discussed yet but, we will just move on to the solution to TDSE.

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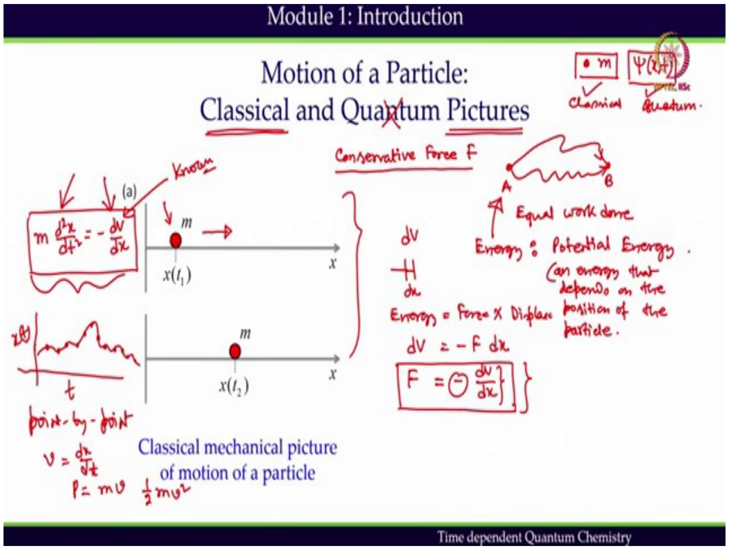

Module 1: Introduction

Motion of a Particle: Classical and Qua~~x~~tum Pictures

Classical mechanical picture of motion of a particle

Time dependent Quantum Chemistry

Conservative Force F

Equal work done

Energy : Potential Energy. (an energy that depends on the position of the particle.

Energy = Force x Displac

$dV = -F\,dx$

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

$m\frac{d^2x}{dt^2} = -\frac{dV}{dx}$

$v = \frac{dx}{dt}$

$P = mv$ $\frac{1}{2}mv^2$

But before we give the solution we should clarify one more conceptual idea here, the classical particle and quantum particle we have shown that this is a particle m and that when we show that the this is the particle of mass m we are showing actually classical particle, the same particle idea in quantum mechanics will be the in quantum mechanics the particle will be expressed in terms of wave function.

So, what is the meaning what is the difference between these two pictures? One picture is this one this is the classical picture, and this is quantum mechanical picture. So, what is the difference between quantum mechanical particle and classical particle? Will go over classical particle first; let us assume that a particle of mass m is under the influence of conservative force.

So, we are focusing on classical particle right now not quantum particle quantum particle will come in the next slide. So, we will assume that the particle here I have a particle shown by this ball and particle having mass m it is moving under the conservative force F. So, what is conservative force? In classical mechanics, conservative force is defined as the force for which work done in moving particle between two points is independent of the path taken between two points.

I have let us say two points A and B, if I take two different path then these two paths are different but still the energy or the work done would be the same. So, for both paths equal work is done. So, it depends on its position such as for an example gravitational force is a conservative force and that is why the energy associated with this height does not depend how we reach that height it depends on directly the height.

And this kind of energy is called when the energy of the particle subjected to a conservative force depends only on its position not on the path taken by the particle to reach that position this energy is called potential energy. So, the energy associated with that particle that energy is called potential energy, an energy that depends on position of the particle.

So, now if I consider infinitesimal change in position let us say dx if the potential energy change is dv then under the conservative force one can write down energy is nothing but force multiplied by displacement which is nothing but $dV = -Fdx$, so if it is a conservative force then one can very easily write down that the force is given by negative gradient of the potential energy.

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

This is a pure classical concept. The force is related to negative gradient of the potential energy, dV is the potential energy change this negative sign comes from the fact that potential energy increases when displacement increases but the force is active on the opposite direction to reduce the potential energy so that is the basic idea, we have this negative sign.

So, now let us assume that the particle is moving along the positive x direction here as I have shown here under the conservative force when is moving at that time I can use Newton's equation of motion which is $m\frac{d^2x}{dt^2} = -\frac{dV}{dx}$ that is the force coming from the potential energy which is related to Newton's equation of motion.

And if we know the potential, then we get to know will be able to solve this equation as long as potential is known, so for a known potential I will be able to solve it and the moment I solve it I will be able to get the trajectory how x(t) is changing as a function of time. So, what is very important to note here is that classical mechanics or classical picture of motion of a particle gives me exactly point by point information.

At what time the particle would be at what position that is known, every time and every position is correlated and the moment it is known I will be able to find out the position is known so I will be able to find out velocity which is nothing but dx/dt, I will be able to momentum which is P=mv and kinetic energy. Every experimental observables are now known because its position at different time is known.

Our classical local notion of motion of a particle is depicted in this figure so it shows that at a particular time I know exactly where the particle is. Let us say we are flying and we are flying from Bangalore to Kolkata and if we ask the airlines will be able to get to know exact location of the position of that flight.

But, in quantum mechanics the moment we jump to quantum mechanics and try to describe the motion of a particle this local information is lost completely, local information or point by point information is lost. If I think about quantum particle flying from Bangalore to Kolkata and if I ask the airline where is that flight? There is no definite answer be given to me.

Only answer which can be given to me only legitimate or acceptable answer which can be given to me for a quantum particle is that the most probable position of the flight is probably near Vizag and when we get this kind of delocalized information not a very local information, we feel very uncomfortable.

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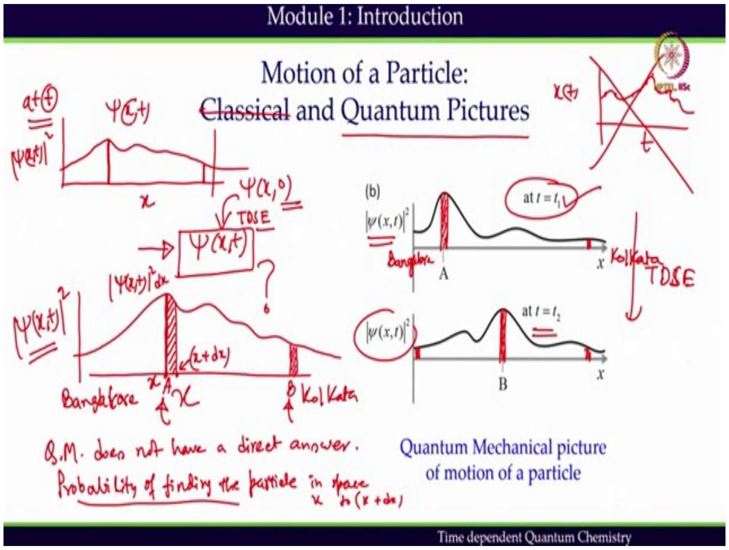

Module 1: Introduction

Motion of a Particle:
~~Classical~~ and Quantum Pictures

Q.M. does not have a direct answer.
Probability of finding the particle in space x to $(x+dx)$

Quantum Mechanical picture of motion of a particle

Time dependent Quantum Chemistry

So, moving from classical concept to quantum concept this uncomfort, this discomfort actually hindered the progress of quantum mechanics for a long time. To accept this idea that it is possible that we will not be able to tell where exactly the particle is, classically we cannot imagine, classically if I am sitting in this room in front of you it means that I am sitting here but quantum mechanically, I have a probability of sitting here, there is a probability of sitting somewhere else as well. But most probable probability is here, that is why I am here.

So, this concept needs to be switched and we will move to now classical to quantum picture of the particle as I have told you in quantum mechanics there is nothing which I can show by a point. Always there is a distribution, always though a function is delocalized all the time, so this is wave function. At a particular time though a function of the particle is given like this way and if the particle is given by this wave this is x axis, at a particular time let us say, at time t and if we so this is wave function from wave function will be able to calculate the density because that is related to the experimental observable.

If I plot the density now then we see that there is a probability; higher probability, there is a lower probability. Particle is delocalized. It can be found anywhere and will discuss the meaning of this density distribution very soon. Quickly what will show that here I will not be able to create a trajectory noise trajectory like previously what I have shown this is x t and this is t.

And this is showing how x is changing as a function of time and each position is known. Here in quantum mechanics, I will not be able to draw such trajectory. There are ways to bypass that problem we will discuss that with the quantum mechanical motion of a quantum particle with a classical flavour that will do in the second module.

But here what we are trying to emphasize is that all physical and chemical description of a particle because it is given by the wave functions $\psi(x,t)$ so and if I know $\psi(x,0)$ at time t what was my wave function; how the particle distribution was; I will be able to get to know this $\psi(x,t)$ with the help of TDSE, that is the basic idea of the quantum dynamics.

The wave function itself whatever wave function I get from TDSE for a given initial value by its very nature is spread out in space, delocalized over space. So how does this wave function look like? Like this, it is everywhere let us say this is Bangalore, this is Kolkata, it is everywhere in x dimensional space. Three dimensional space we have not considered yet it is everywhere.

A particle, this the global or delocalized nature of the wave function of the particle, quantum particle at any given time contradicts our classical or local notion that a wave function, if the wave function representing a particle classically we feel that it must be localized at a particular point. If the particle is in Bangalore we feel that it should be in Bangalore, there is nothing in Kolkata.

But in quantum mechanics the problem becomes following because the wave function is delocalized is nature a function which is describing its all possible positions and that is the only way I can describe the quantum particle, there is no other way I can describe the quantum particle.

So, the first question comes to our mind before we jump into any further details of quantum dynamics; how can a delocalized mathematical function, wave function represent a particle which is supposed to be localized in our classical notion, in our classical concept or classical feelings? And if it is delocalized; what does it mean? Can I answer this question; where the particle is?

So, quantum mechanics does not have any direct answer to the question, where is the particle? If I ask this question; where is the particle, quantum particle, where is my quantum particle? Is in Bangalore? In Kolkata? There is no direct answer. Only answer quantum mechanics gives is a statistical answer; statistical answer what does it mean?

Statistical answer suggest that okay, you have found wave function from TDSE, from wave function find out the density which is $\left|\psi(x,t)\right|^2$. Once you know the density distribution; what does it mean by this density? This density suggest that at a particular position what is the probability of finding that particle?

And the probability of finding the particle, in space x to x+dx within this space. So, let us say I have x here and this one is x plus dx within this dx space what is the probability of finding the particle? That is actually this density multiplied by dx which is nothing but if it is the multiplication part this is the area under the curve.

So, it is clearly suggesting that probability of finding the particle, we are talking about probability you may find there is a possibility of finding that particle. Probability, because that is the only statistical answer we get to the question where is the quantum particle and it does not give the direct answer it gives the statistical answer. Probability of finding the particle is given by this area, so in space A area is higher but here area would be low. So, probability of finding that particle at space A much higher than probability of finding the particle at space B and that is exactly what we have shown.

In quantum dynamics I will not be able to draw this kind of trajectory which we get from classical equation of motion. What we all express is that, the density at a particular time I plot again density at a different time I plot this plots has been done using TDSE time dependence

Schrodinger equation given the initial wave function and what we see that the probability of finding the particle most probable is here it was here at time t1 and now it has come to position B.

Probability; the maximum probability of finding the particle is now moving but still it is the probability of finding the particle here, still there is a finite probability. So, if I consider this is Bangalore and this part is Kolkata, then we see that something, some probability is slowly moving from Bangalore side to the Kolkata side. But still it has always probability near Bangalore, near Kolkata and this is a concept which we need to keep it in mind in this quantum dynamics course. We will stop here and we will continue this module in the next session.