Time Dependent Quantum Chemistry

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Lecture No. 02

Solution to TDSE, Stationary and Non-stationary States

Welcome back to Module 1 of the course Time Dependent Quantum chemistry. We have so far introduced time dependence Schrodinger Equation and then we have to some extent discussed or given an idea the meaning of quantum particle and classical particles, so with that idea will move forward.

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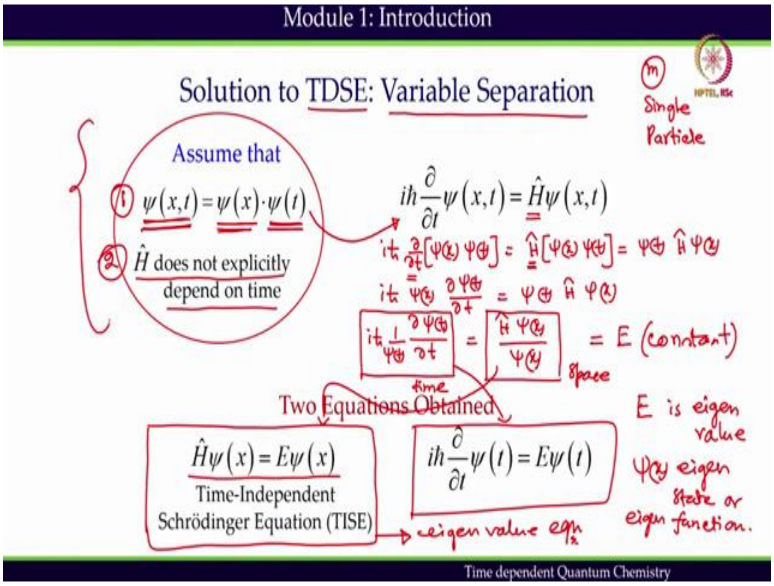

Module 1: Introduction

Solution to TDSE: Variable Separation

ⓜ Single Particle

Assume that

① $\psi(x,t)=\psi(x)\cdot\psi(t)$

② $\hat{H}$ does not explicitly depend on time

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

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

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

$$\boxed{i\hbar\frac{1}{\psi(t)}\frac{\partial\psi(t)}{\partial t}}=\boxed{\frac{\hat{H}\psi(x)}{\psi(x)}}=E\ (\text{constant})$$

time Space

Two Equations Obtained

$$\boxed{\hat{H}\psi(x)=E\psi(x)}$$

Time-Independent Schrödinger Equation (TISE) → eigen value eqn

$$\boxed{i\hbar\frac{\partial}{\partial t}\psi(t)=E\psi(t)}$$

E is eigen value

$\psi(x)$ eigen state or eigen function.

Time dependent Quantum Chemistry

We will move on to the solution of TDSE and we will find out the solution of TDSE time dependent Schrodinger Equation assuming that for a single particle we are considering, so we have particle of mass m and we will assume that the total wave function again I point out that rigorous meaning of wave function and density and its meaning in terms of experimental observable will be discussed very soon in this module and also later in this course.

So far it may appear little mathematical, but we will try to understand the meaning behind it. So, the total wave function $\psi(x,t)$, we will assume that when we are solving time dependent Schrodinger Equation we will assume that we can express this total wave function as a product of the space and time part we can separate it and we can express in terms of this product.

So, that is our first assumption in the to find out the solution. Second assumption we will make which we have already pointed out that $\hat{H}$ that Hamiltonian operator does not explicitly depend on time that is also another assumption we will make to solve this TDSE.

So, what we will do if it is can be used in the product form I will be able to insert this product form to this equation and if I insert it, then what I get is that $\psi(x)$ equals the product form I have inserted, now we know that this is time independent, Hamiltonian is time independent that is the way we have assumed.

Do not think that Hamiltonian is going to be always time independent, there are ways to solve it in a different way but so far we will use variable separation method to solve TDSE and we will get an very simplified expression for the wave function very soon. What we are assuming that Hamiltonian is time independent and because it is time independent I will be able to take out time dependent part out of this Hamiltonian operator and it is acting only on the space dependent wave function.

Here because it is a partial derivative with respect to t, I will be also able to take out space dependent part and we can keep time dependent part as it is. So, I get finally this equation;

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

little bit rearrangement is needed, I do that then what I get is;

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

equals, so what I get is that I have managed to reconfigure TDSE such a way that the left hand side of this equation is only time dependent and right hand side of this equation is only space dependent, and time and space they are independent variables in TDSE.

So, in order to have this relation, to hold this relation all we need to consider is that this is going to be always constant, two different variables cannot be equal, it has to be constant. And constant can be taken anything, for convenience we have taken E because later we will find out that E this constant will be expressing the energy of that particle. That is why because we knew that that is why we are considering otherwise you can take any constant, so this is actually a constant.

$$i\hbar \frac{1}{\psi(t)}\frac{\partial \psi(t)}{\partial t} = \frac{\hat{H}\psi(x)}{\psi(x)} = E$$

And once we take this constant will be able to split separate these two variables and we get one equation like this that is called time independence Schrodinger equation another one we get is time dependent part, this part. So, this part comes here and this part comes here; time independent Schrodinger equation.

This time independent Schrodinger equation $\hat{H}\psi(x) = E\psi(x)$ here there is no time dependent part this equation is an important equation is called Eigen value equation, and this E is called Eigen value and $\psi(x)$ is called Eigen state or Eigen function. So, there are two equations we get from this variable separation method under this assumption. There are two assumptions we have taken.

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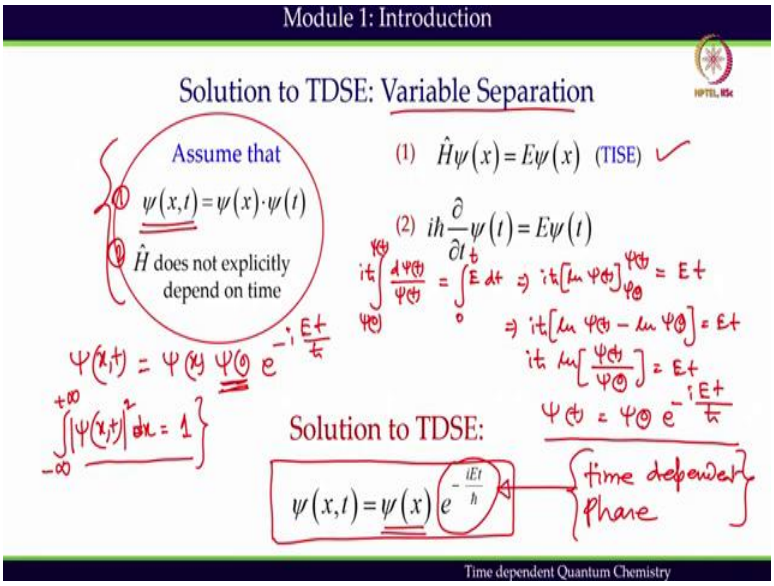

Module 1: Introduction

Solution to TDSE: Variable Separation

Assume that

① $\psi(x,t) = \psi(x)\cdot\psi(t)$

② $\hat{H}$ does not explicitly depend on time

(1) $\hat{H}\psi(x) = E\psi(x)$ (TISE) ✓

(2) $i\hbar\frac{\partial}{\partial t}\psi(t) = E\psi(t)$

$$i\hbar\int_{\psi(0)}^{\psi(t)} \frac{d\psi(t)}{\psi(t)} = \int_0^t E\,dt \Rightarrow i\hbar\left[\ln\psi(t)\right]_{\psi(0)}^{\psi(t)} = Et$$

$$\Rightarrow i\hbar\left[\ln\psi(t) - \ln\psi(0)\right] = Et$$

$$i\hbar\ln\left[\frac{\psi(t)}{\psi(0)}\right] = Et$$

$$\psi(t) = \psi(0)\,e^{-i\frac{Et}{\hbar}}$$

$$\psi(x,t) = \psi(x)\,\psi(0)\,e^{-i\frac{Et}{\hbar}}$$

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

Solution to TDSE:

$$\boxed{\psi(x,t) = \psi(x)\,e^{-\frac{iEt}{\hbar}}}$$

{time dependent Phase}

Time dependent Quantum Chemistry

Now, TISE is a well-known, time-independent Schrodinger equation but the time dependent part if I consider now will be able to integrate that time dependent part and we will do that integration here. When I integrate it, I will be able to write down this equation as equals

$$i\hbar\int_{\psi(0)}^{\psi(t)} \frac{d\psi(t)}{\psi(t)}dt = \int_0^t E dt$$

$$i\hbar\left[\ln(\psi(t))\right]_{\psi(0)}^{\psi(t)} = Et$$

$$i\hbar\left[\ln(\psi(t)) - \ln(\psi(0))\right] = Et$$

$$i\hbar\ln\frac{\psi(t)}{\psi(0)} = Et$$

$$\psi(t) = \psi(0)e^{-\frac{iEt}{\hbar}}$$

We know that total wave function have to be product of this-

$$\psi(x,t) = \psi(x)\psi(0)e^{-\frac{iEt}{\hbar}}$$

Now the $\psi(0)$ is just a multiplicative factor and in the end always we have to normalize the wave function. The wave function must satisfy this normalization condition all the time.

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

This is called normalization condition and with function has to satisfy this condition all the time because if a wave function is not satisfying normalization condition it means that we have failed to give the statistical interpretation.

And that is the only interpretation we have by for the meaning of the quantum particle. So, if statistical interpretation fails then there is no meaning of quantum mechanics anymore, so in order to have that meaningful statistical interpretation of the wave function in quantum mechanics the wave function at every time at for any time it has to be normalized. So, in the end we have to normalize the wave function and any multiplicative factor can be included in the normalization condition.

So, what we can do is that instead of taking this multiplicative factor we can generalize the solution and we can say that this is what we have;

$$\psi(x,t) = \psi(x)e^{-\frac{iEt}{\hbar}}$$

the solution to TDSE under variable separation method which means that I have assumptions; these two assumptions, so I have been able to separate space dependent function and our time dependent part.

This time dependent part behaves like a time dependent phase factor. What does it mean by phase? We will discuss very soon phase is a physical quantity which is very difficult to understand but we will spend some time on understanding this phase.

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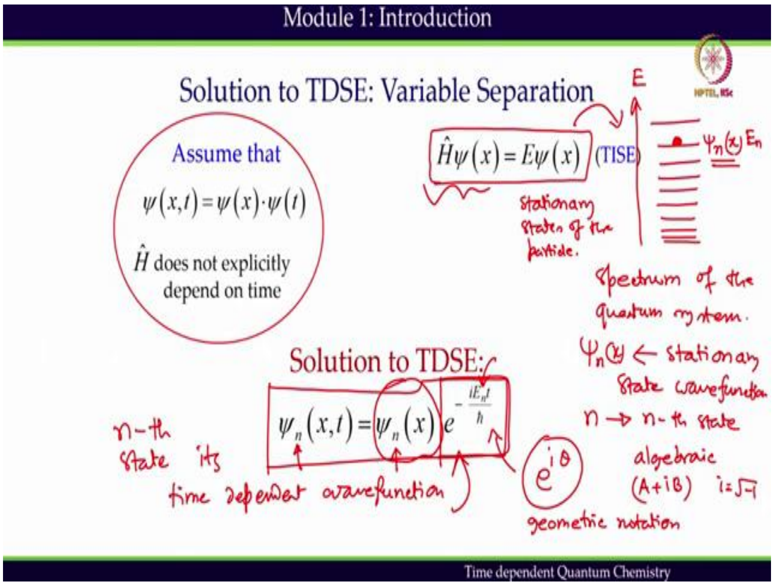

Module 1: Introduction

Solution to TDSE: Variable Separation

Assume that

$\psi(x,t)=\psi(x)\cdot\psi(t)$

$\hat{H}$ does not explicitly depend on time

$\hat{H}\psi(x)=E\psi(x)$ (TISE)

Solution to TDSE:

$\psi_n(x,t)=\psi_n(x)e^{-\frac{iE_nt}{\hbar}}$

Time dependent Quantum Chemistry

In general, when you talk about the general solution TDSE, TISE;

$$\hat{H}\psi(x)=E\psi(x)$$

this TISE when you solve this TISE if we recall that one-dimensional box for particle in one-dimensional box we have solved it and when we have solved it we have seen that we are not finding one solution; we said we get a set of solutions. And this wave function is given by $\psi_n(x)$, if we can recall.

So, TISE generally gives a set of solutions which are physically meaningful solution to the equation and to the TISE equation and this set of solution actually represents possible states, stationary states of the particle. Particle can stay here, particle can stay here, particles can stay here all possible steps but they are their energies are different.

So, each particle depending on where they stay the energies can be different, so this way energies are, energy is increasing and this kind of states are actually called the spectrum of the quantum system. So, each solution is represented by $\psi_n(x)$ and that is called stationary state wave function and n represents the quantum state which means nth state, energy state.

$$\psi_n(x,t) = \psi_n(x)e^{-\frac{iEt}{\hbar}}$$

In chemistry, often we use this kind of energy states to express the spectrum of the atom and molecules using this stationary state obtained from TISE time independent Schrodinger equation and so because time independent Schrodinger equation gives a number of states we can final solution to TDSE can also be denoted with respect to its own state.

So, if the particle is staying at nth state then its time dependent wave function is given by this equation where, as I have told you this is the stationary state where the particle is, let us say particle is in this state, that is why I have taken $\psi_n(x)$ and its associated energy E_n, but if we look at this time dependent part is nothing but it looks like a complex number denoted by $e^{i\theta}$.

A complex number can have different notation. I can have algebraic notation of complex number, algebraic notation is A+ iB that is the way we express, i is the complex number and geometric notations the same number, same physical quantity can be expressed in terms of this polar coordinate $e^{i\theta}$, so this is a geometric representation, geometric notation of the complex number.

And this notation, this complex number shows that this is the time dependent phase factor. So, time dependent phase factor in the total wave function comes as a complex quantity and the complex quantity is basically representing the geometric notation of a complex number. What is the meaning of this phase?

We will discuss because phase has a very important effect phase is a physical quantity which will discuss very soon and it carries important information when two wave functions are compared, when two functions are interacting at that time phase becomes an important issue otherwise phase will not be an issue that will be demonstrated in the next slide.

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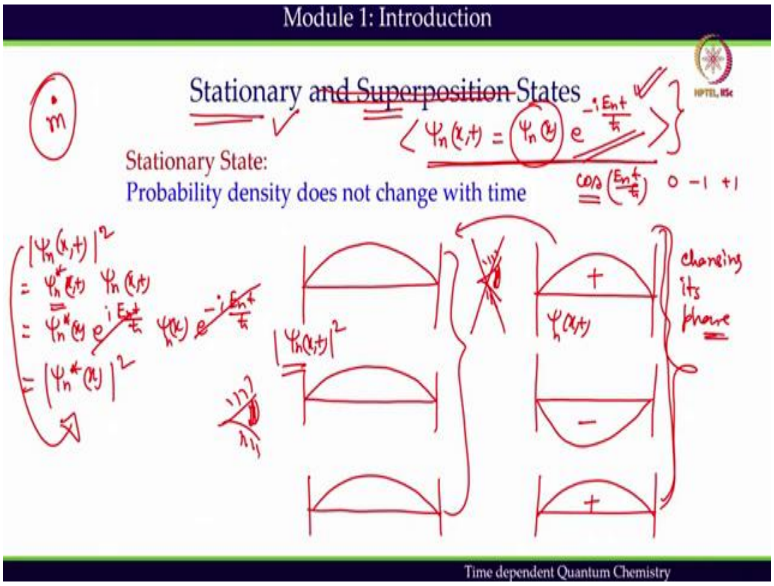

Module 1: Introduction

Stationary ~~and Superposition~~ States

Stationary State:

Probability density does not change with time

Time dependent Quantum Chemistry

So, if we look at total wave function for a particular state is expressed by its space dependent part and time dependent part comes into the picture as a phase, the complex temporal phase of the wave function.

$$\psi_n(x,t) = \psi_n(x)e^{-\frac{iEt}{\hbar}}$$

So this is the, if the particle is staying at the nth stationary state. So, we will distinguish two different states right now stationary states and superposition state.

What we see that wave function is time dependent and if wave function is time dependent; this is a complex phase if I try to think about real part it is going to be $\cos\left(\frac{E_n t}{\hbar}\right)$ some kind of a function of cos and cos function is becoming 0,-1, +1 all these values it will take depending on what time it is.

So, if you look at this wave function for an example at a particular time the wave function may look like this, next time though a function may look like this, again the wave function may look like this (look at the slide picture). So, if we look at the wave function its continuously changing as a function of time, changing what? Changing its phase, changing its phase.

Phase is some kind of colour one can say, so some kind of sign. So, let us say if it is above this bar I get positive, if it is below it is negative, if it is above; is positive some kind of like this phase is changing. But as I mentioned before that in the wave function is not something which we can directly observe through experiment. Can I observe it? No, it is not possible.

Only thing what I can observe is its density, what would be the density of this wave function? Like this, this is $\psi(x,t)$, this is $\psi_n(x,t)$, so experimentally relevant quantity density always be like this. It will be always like this, why it will be always like this? It is because density is nothing but-

$$|\psi_n(x,t)|^2 = \psi_n^*(x,t)\psi_n(x,t)$$

$$= \psi_n^*(x)e^{\frac{iEt}{\hbar}}\psi_n(x)e^{-\frac{iEt}{\hbar}}$$

We see that the moment we take the complex conjugate and multiply with its own these two factors goes out phase factor will go out finally what I get is a time independent although I started with time dependent wave function in the end it is giving me time independent physical quantity.

$$|\psi_n(x,t)|^2 = |\psi_n(x)|^2$$

So, density for a stationary state and that is why this this state is called stationary state. I have not discussed superposition state yet I am discussing stationary state and a state of the particle described by this equation is called stationary state because its density is not changing as a function of time; its wave function is changing as you can see, wave function is changing is changing its phase all the time.

But its density is not changing as a function of time and if the density is not changing as a function of time, experimental observables, any experiment I perform I will not be able to see any change in the particle, so there is no way I can see that change in the particle because I cannot observe the wave function.

So, I repeat, I have a quantum particle mass m represented by staying in the stationary state $\psi_n(x,t)$ its wave function is time dependent, it is changing the phase all the time as a function of time, it is changing the phase but there is no way I can see any change in the particle, the particle will look stationary because it looks stationary this state represented by this wave function is called stationary state.

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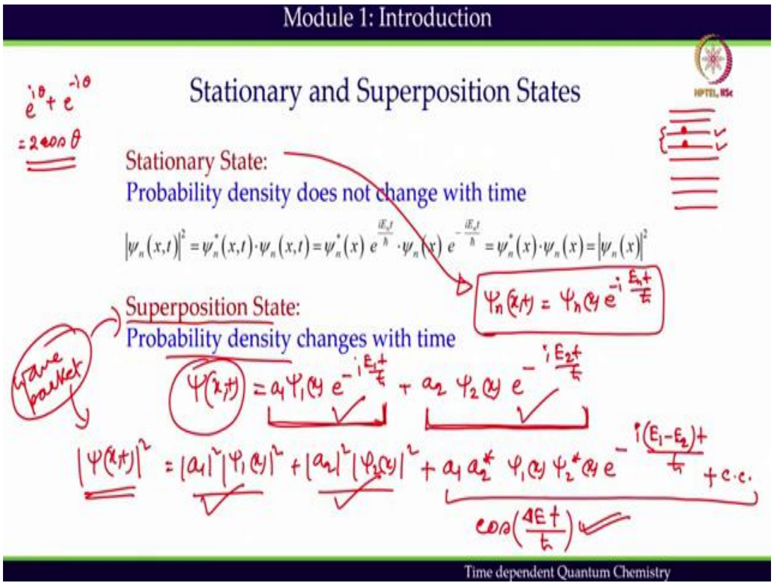

Module 1: Introduction

Stationary and Superposition States

Stationary State:

Probability density does not change with time

$$|\psi_n(x,t)|^2 = \psi_n^*(x,t)\cdot\psi_n(x,t) = \psi_n^*(x)\, e^{\frac{iE_nt}{\hbar}}\cdot\psi_n(x)\, e^{-\frac{iE_nt}{\hbar}} = \psi_n^*(x)\cdot\psi_n(x) = |\psi_n(x)|^2$$

$$\boxed{\Psi_n(x,t) = \Psi_n(x)\, e^{-i\frac{E_nt}{\hbar}}}$$

Superposition State:

Probability density changes with time

$$e^{i\theta}+e^{-i\theta} = 2\cos\theta$$

wave packet

$$\Psi(x,t) = a_1\Psi_1(x)\, e^{-i\frac{E_1t}{\hbar}} + a_2\Psi_2(x)\, e^{-i\frac{E_2t}{\hbar}}$$

$$|\Psi(x,t)|^2 = |a_1|^2|\Psi_1(x)|^2 + |a_2|^2|\Psi_2(x)|^2 + \underbrace{a_1a_2^*\,\Psi_1(x)\Psi_2^*(x)\, e^{-\frac{i(E_1-E_2)t}{\hbar}} + c.c.}_{\cos\left(\frac{\Delta E t}{\hbar}\right)}$$

Time dependent Quantum Chemistry

We will move to superposition state now. What does it mean by superposition state? If we want to describe motion of a quantum particle we have to describe the motion of the quantum particle not by the particular solution. So, we have expressed that particle is staying in this state,

$$\psi_n(x,t) = \psi_n(x)e^{-\frac{iEt}{\hbar}}$$

if the particle is staying in this state it is a stationary state, its density does not change as a function of time.

In order to observe a change in probability density, the particle has to be in a superposition state and superposition state what does it mean? I will be expressing this state of the particle so a function will be expressed as;

$$\psi(x,t) = a_1\psi_1(x)e^{-i\frac{E_1t}{\hbar}} + a_2\psi_2(x)e^{-i\frac{E_2t}{\hbar}}$$

a linear combination of two stationary states I have to add, at least two stationary states need to be added to express the state of the particle.

So, let us say, I had a particle and these are the stationary states I had somehow I have manage if the particle is staying only in this state, then density will never change as a function of time but if I somehow manage to prepare a state where these two states are excited simultaneously or in other words there is a possibility the particle will be staying here and also particle will be staying here.

Single particle but there is a possibility that particle will be staying in both states that is called superposition state and the whole quantum dynamics, basics of quantum dynamics depends on this superposition state. We have to create superposition state to observe temporal change in the particle density, the probability density and that we can express very easily by taking only two states, we are linearly combining these two states.

If we linearly combine these two states then what is the probability density we get? We can see very easily that finally I will get individual contributions plus both are time independent plus there is a cross term which will come.

$$\psi(x,t)=|a_1|^2|\psi_1(x)|^2+|a_2|^2|\psi_2(x)|^2+a_1a_2^*\psi_1(x)\psi_2(x)e^{-i\frac{(E_1-E_2)t}{\hbar}}+c.c$$

Often we write down complex conjugate as c dot c in this class in the ultra-first optics and spectroscopy which I teach in NPTEL in that course also you must have noticed that this complex conjugate comes into the picture.

Because whenever we use some complex number its associated complex conjugate we do not write it directly but we just mention that is there is a complex conjugate part. So, what we see here is that

$$e^{i\theta}+e^{-i\theta}=2\cos\theta$$

we get the real part. So, these two together will give me the real part which is going to be $\cos\left(\frac{\Delta Et}{\hbar}\right)$ and this is time dependent, so density becomes time dependence.

The, in this expression the first term originates from the pure $\psi_1(x)$ state; second term comes from $\psi_2(x)$ states and the third one develops an interference between two stationary states. The interference term is a result of having a superposition of the Eigen states with different energies and this is called wave packet. The moment I create the superposition state this wave function is called wave packet.

And I need a wave packet to observe quantum dynamics, anything I observe in the density change temporal change in density for that I need the wave packet which means that the particle has to be in a superposition state. How do we create a superposition state? Simply by linearly combining two states with its characteristic phase factor. Characteristic phase factor should be also added together.

The wave packet which originates from superposition of stationary states having different energies is required in order to have a time dependence in probability density and in other experimental observables such as average position, average momentum of the particle, so superposition state is very important.

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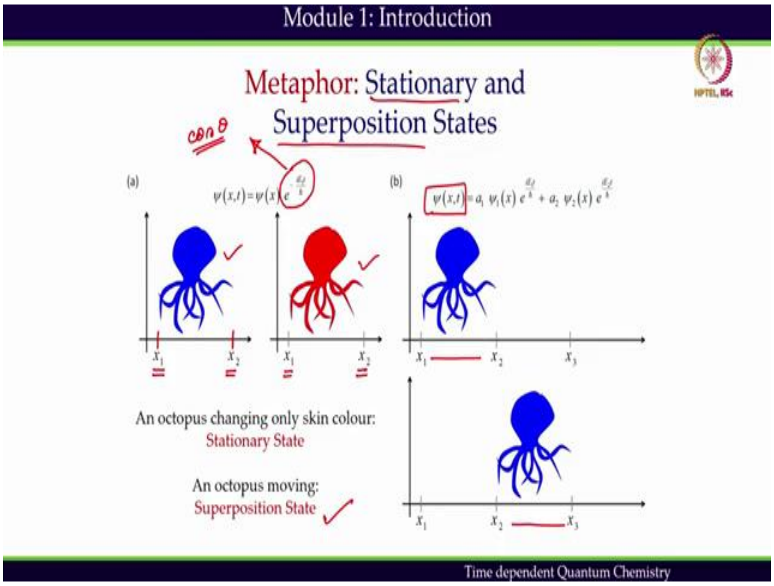

Module 1: Introduction

Metaphor: Stationary and Superposition States

cos θ

(a) $\psi(x,t)=\psi(x)e^{-\frac{iEt}{\hbar}}$

(b) $\boxed{\psi(x,t)}=a_1\,\psi_1(x)\,e^{-\frac{iE_1t}{\hbar}}+a_2\,\psi_2(x)\,e^{-\frac{iE_2t}{\hbar}}$

An octopus changing only skin colour: Stationary State

An octopus moving: Superposition State ✓

Time dependent Quantum Chemistry

What we will do we will just quickly give a metaphor, these kind of examples are not directly related but we get to understand the meaning of stationary and superposition states in quantum mechanics. We all know that an octopus can change skin colour to adapt its local environment, so that we cannot recognize it and that is the kind of nature has given protecting ability to the species octopus.

Now let us assume that the octopus is staying localized in this space between x1 to x2 and octopus is changing the colour that is exactly octopus is doing. It is not moving, it is staying at the same place but changing the colour; periodically let us say. Changing colour periodically is represented by this phase factor. Phase factor this is an oscillatory factor, this is a complex representation of an oscillatory part which is nothing but a $\cos\theta$ or cos kind of an function in a real sense.

So, when I say stationary state it means that octopus is changing the colour being in the same position, position between x1 to x2, here also you see it is staying in the same position and that's called stationary state. Wave function is changing colour but, the total density is not moving, the octopus itself is not moving. But if I see octopus is moving now from position between x1 to x2 to x2 to x3 position it is moving it means that it is in the superposition state and that is why we see the movement of the octopus body.

So stationary state; it is stationary not because the wave function is time independent but because its density is timed independent, probability density is time independent. Something is superposition state which is created by a wave packet and a wave packet must be created to, the wave packet is created through the super superposition state and a superposition state is absolutely needed to observe the quantum dynamics, to observe a change in the overall density. We will stop here and will continue this module in the next session.