Time Dependent Quantum Chemistry
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Lecture 38
Quantum Adiabatic Theory

Welcome back to module 6 of the course, Time Dependent Quantum Chemistry. In this module we are discussing analytical methods to solve to TDSE. There are two ways one can solve the TDSE Of course, one analytical method and another one is numerical method, but most of the solution will come from numerical methodology. However, there are few, very few analytical methods available to solve TDSE. One of them we have already understood it is time dependent perturbation theory. Next, what we will be going over is called Quantum Adiabatic Theory.

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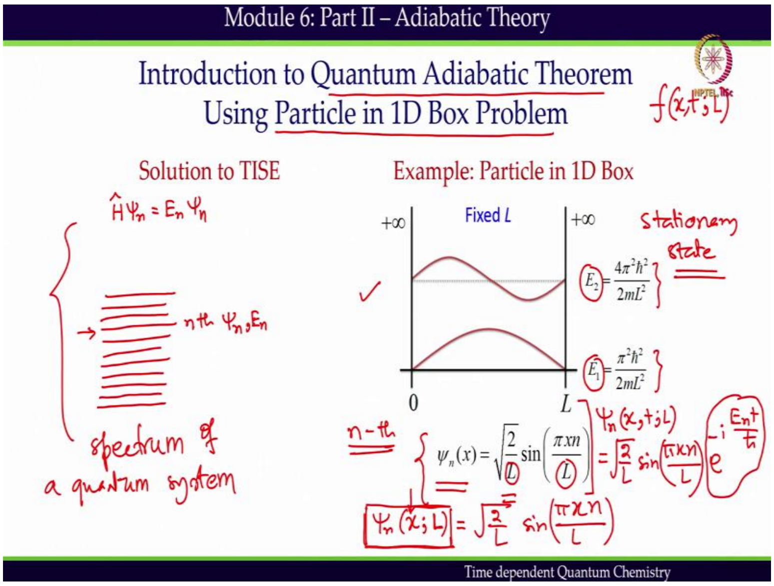

Module 6: Part II – Adiabatic Theory

Introduction to Quantum Adiabatic Theorem Using Particle in 1D Box Problem

$f(x,t;L)$

Solution to TISE

$\hat{H}\Psi_n = E_n\Psi_n$

nth Ψ_n, E_n

spectrum of a quantum system

Example: Particle in 1D Box

Stationary state

$$E_2 = \frac{4\pi^2\hbar^2}{2mL^2}$$

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2}$$

n-th

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x n}{L}\right)$$

$$\Psi_n(x,t;L) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x n}{L}\right)e^{-i\frac{E_n t}{\hbar}}$$

$$\boxed{\Psi_n(x;L)} = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x n}{L}\right)$$

Time dependent Quantum Chemistry

In this to present this quantum adiabatic theory, we will we will make use of the particle in one dimensional box problem, if we if we present the quantum adiabatic theory in along with this example of particle in one dimensional box, it will help us understand the fundamental principle of this theory adiabatic theory very easily. So, we will begin we have already realized that the solution to the time independent Schrodinger equation provides a set of stationary state wave functions represented by Ψ_n.

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So, if I have this time independent Schrodinger equation which is given by this we get actually so, when I solve time independent Schrodinger equation, we get the entire spectrum of the system which means Eigen states of the system. And the n th Eigen state let us say this one is the n th Eigen state and that Eigen state can be has an inner Eigen the wave function Ψ_n and its energy En that is the energy and that is the way we get that is the inter spectrum of a quantum system is often from the solution of time independent Schrodinger equation.

As an example, one may consider the classic problem of particle in one dimensional box of length L. So, this is what we have the example 0 to L and we have and this problem is also known as particle in infinite square will potential the stationary state the n th wave function the n th wave function stationary state of course, these are all stationary states they are stationary states because not because wave function does not have time dependence but it is probability density is time independent that is why stationary state.

So, all the stationary state solutions we get from time independence Schrodinger equation and the n th wave function is given by this expression, the expression which is very well known to us because this is a very frequently taught problem in quantum mechanics. And the energy states are following the first energy state is having energy this one, the second energy state having energy this one and we go on like this way.

So, when we represent the stationary state wave function of the particle in one dimensional box, here n can be 1, n can be 2, n can be 3 this is the quantum number and you can go up to infinity. So, all states can be explored from this wave function. When we express the wave function following using this form, we assume that mostly we probably have not noticed it, but we assume that the length this L term in this equation remains fixed.

In fact, the L term acts as a parameter in in this equation, this is why the n th stationary state wave function of the particle in one dimensional box should be more appropriately represented by this we can use x then semicolon and then $\sqrt{\frac{2}{L}}\sin(\frac{\pi x n}{L})$.

$$\Psi_n(x; L) = \sqrt{\frac{2}{L}}\sin(\frac{\pi x n}{L})$$

What we are doing here to define the notation of this wave function, what we have used is that, we have used L as a parameter and anything we are writing as a parameter will be separated from the variable, variable is the x coordinate here.

The position coordinate is the variable, but the parameter is separated from the variable by a semicolon. That is the convention will follow. So, if I have two parameters of a function two variables in a function, let us say x and t are variables, they are separated by comma but then the parameter if I have a parameter in it, so it will be separated by a semicolon that is the convention we will follow.

So, if we have So, more specifically this is not done very quickly, very frequently in in the textbook, the popular textbook when we represent the one-dimensional box problem. Because it is assumed that L is constant but more specifically and with regard to the presentation of quantum Adiabatic theorem, we will actually specify that this wave function parametrically depends on L. If I change the L my wave function will change but it is not our variable it is parameter.

So, if I have this wave functions written like this, then the time dependent wave function as we know this is time independent part so, time dependent wave function can be written as follows I have n th wave function as x comma t then parameter is equals to $\sqrt{\frac{2}{L}}\sin(\frac{\pi x n}{L})$, then I have this time dependent phase factor which is $\exp\left(-i\frac{2\pi E_n t}{h}\right)$.

$$\Psi_n(x,t;L) = \sqrt{\frac{2}{L}}\sin(\frac{\pi x n}{L})\exp\left(-i\frac{2\pi E_n t}{h}\right)$$

So, that is the way we should represent more, we can maintain the notational accuracy with the help of this. Where E_n denotes the energy of the n th stationary state of the particle. So, what we see from this expression is that the time dependence comes entirely from and this is this is the way this is what we have this is a concept which we have developed so, far that the time dependence comes from this time dependent phase factor time dependence of the wave function comes from this time dependent phase factor. And this is what we have developed since module one.

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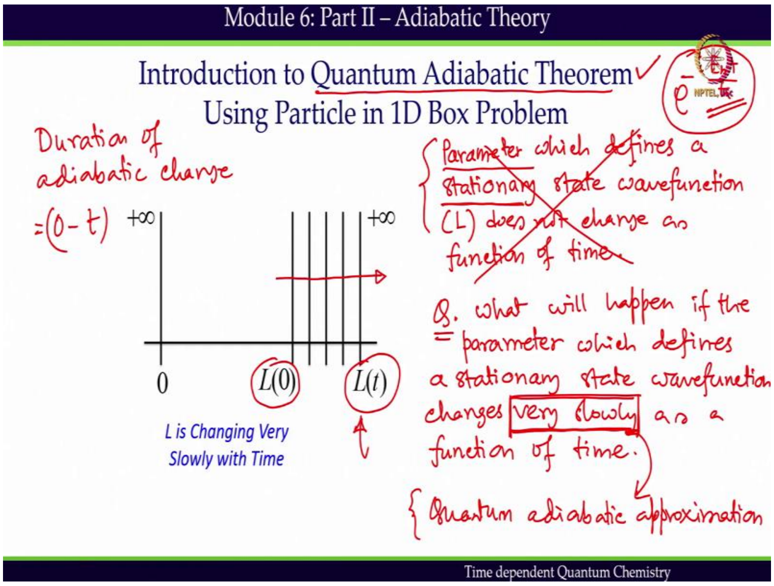

Module 6: Part II – Adiabatic Theory

Introduction to Quantum Adiabatic Theorem ✓
Using Particle in 1D Box Problem

$e^{-\frac{iEt}{\hbar}}$

Duration of adiabatic change
$=(0-t)$

~~Parameter which defines a stationary state wavefunction (L) does not change as function of time~~

Q. what will happen if the parameter which defines a stationary state wavefunction changes $\boxed{\text{very slowly}}$ as a function of time.

{ Quantum adiabatic approximation

L is Changing Very Slowly with Time

Time dependent Quantum Chemistry

Now, in all the hitherto treated time dependent problems we have assumed that the parameter what was the assumption we have made so, far always the parameter which defines a stationary state wave function for example, here it is the L in this example and that is why we are when you will be representing quantum a adiabatic theorem, we will be giving an example So, that one can directly connect the meaning of the mathematical expressions or the state which we are making that will be that this will make our learning process very easy going.

So, far in all the treatment, what we have done time dependent treatment, we have assumed that the parameter which defines a stationary state where function does not change as a function of time. This is the assumption we have made. So, the time dependence term in the wave function comes entirely from this phase factor this is what we have seen. On the contrary, when we are presenting this quantum activity theorem, we will say that this part is not right.

We will say that quantum adiabatic theory which is the subject of the current discussion, it will try to find an answer to an unexplored question the question is following question is what will happen if the parameter which defines our stationary state wave function changes very slowly as a function of time. So, in time dependent perturbation theory, when we have imply time dependent perturbation theory, we have assumed that the stationary state the parameter which is defining the stationary state is not changing.

So, entire time dependence came from the time dependent phase factor, but on the contrary to this picture, when we are presenting this quantum adiabatic theorem, this is also another dynamical evolution of a quantum system. We are saying that we are asking this question what will happen if the parameter which defines a stationary state wave function changes very slowly.

So, one approximation is that the change has to be very slow the parameter which is changing has to be very very slow, then we will be able to explore this quantum adiabatic theorem. If it is fast, then we cannot explore quantum adiabatic theorem, but if it is slow then it is well so, quantum adiabatic theorem of quantum adiabatic theorem is actually based on an approximation that is called adiabatic approximation adiabatic approximation assumes that the parameter is changing very slowly.

So, we our target is not the time dependent phase factor our target is actually the parameter which is changing as a function of time very slowly. And this slow temporal change this is an approximation in quantum adiabatic theorem, this is called quantum adiabatic approximation so, we will under this approximation so, if we come connected to our example, we will say that at time t equals 0 initial time the length was L 0 and it is slowly changing the expanding the box and at time t is for the final time is t.

So, the duration of that adiabatic change of when I say adiabatic change, it is a slow change and every change is 0 to t during this time and the aim of quantum adiabatic theorem is at exploring the wave function after the adiabatic processes turned off. So, that is the problem we have at hand.

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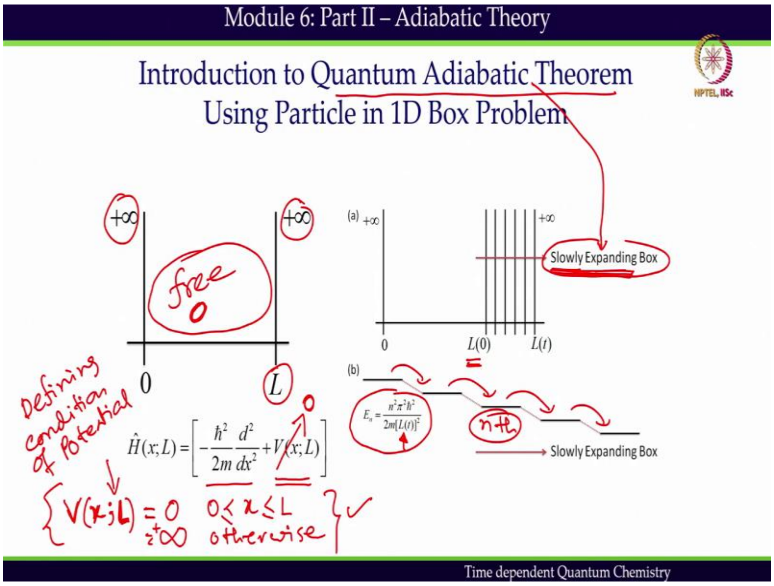
Module 6: Part II – Adiabatic Theory

Introduction to Quantum Adiabatic Theorem Using Particle in 1D Box Problem

$$\hat{H}(x;L) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \overset{0}{\cancel{V}}(x;L)\right]$$

Defining condition of Potential

$$\left\{ V(x;L) = 0 \quad 0 \le x \le L; \quad = +\infty \quad \text{otherwise} \right\} \checkmark$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2m[L(t)]^2}$$

Time dependent Quantum Chemistry

The Hamiltonian of our particle particularly in one dimensional box of length L, let us say is given by this

$$H(x;L) = [-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + V(x;L)]$$

we have kinetic energy and potential energy I have deliberately given potential energy term here, because although generally this is we write as 0 because particle inside the box the potential energy is 0, outside the box potential energy is infinite. So, that is why we make it 0, but we cannot directly write and 0.

We will say that it has a potential function, which will be defined like this way, we this is more specific definition to maintain the notational accuracy. We can we can already see that the potential I am writing it has x dependence as a variable, and it has a parameter dependency L, that is why they are separated by a semicolon. So, what we are saying is that this V would be the defining condition of the potential for the free particle in the box is given by V would be $0 \leq x \leq L$.

So, it has to be greater than equals to 0 to 0 and less than equals to L. And this is going to be infinite last infinite otherwise. So, this is the definition we are giving. So, we are we are not usually from if you when the popular quantum chemistry books, they present particularly in one dimensional box problem, they directly take this V to be 0, we are also taking V to be 0 but we are explicitly writing down to maintain the notational accuracy.

These notations needs to be clearly written to understand this quantum adiabatic theory otherwise things can be a little confusing for the for a person who is learning this theory for the first time. So, what we are writing is that this is the defining condition of the potential where the potential is actually 0 inside the box and outside the box it is the infinite plus infinite.

We have included this L term here to maintain the notational accuracy here. In general, this is not done actually in the popular quantum mechanics booth because they assume that L is constant and also V is 0 we directly write it down like that way. The defining condition of the potential term, which I have written here, mandates the fact that the particle remains completely free inside this box.

So, inside the box, it will be completely free. It is a free particle, but is it confined within the box. Outside the box you have potential infinite potential that is why this infinite potential it prevents it this infinite potential prevents its escape from the boss box. So, the particle cannot go outside the box like this way because of the infinite potential. Now, for the demonstration of quantum adiabatic theory using particle in one dimensional box problem, we assume that this L changes as a function of time very slowly.

So, it is a slowly expanding box and this slow expansion this is the adiabatic expand adiabatic approximation. That is why it is called adiabatic theory quantum adiabatic theory. As a result, the defining condition of the potential, So, what is L? L is actually controlling the defining condition of the potential it is the defining and that defining condition is also changing because L if it if the L is changing, the dimension of the box is changing.

So, potential the behavior of the potential is also changing slowly of course. And because potential is changing and then if we look at the energy expression for particle in 1 dimensional box, we see that if L is changing as a function of time, then E_n in n th energy state will also change very slowly. And because, if L is increasing, that means for the expanding box energy is slowly going down for the for the same n th excited state sorry for the same n th energy level of the particle. So, these are the facts which one can immediately conclude from this from this expanding box problem employing this quantum adiabatic theorem, where adiabatic approximation is the slow expansion of the box.

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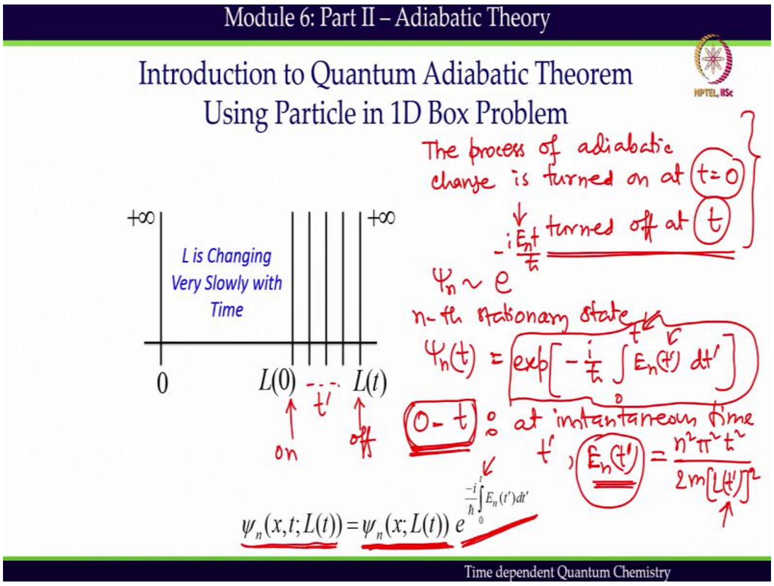

Module 6: Part II – Adiabatic Theory

Introduction to Quantum Adiabatic Theorem Using Particle in 1D Box Problem

The process of adiabatic change is turned on at $\boxed{t=0}$ turned off at $\boxed{t}$

$\Psi_n \sim e^{-\frac{iE_n t}{\hbar}}$

n-th stationary state

$\Psi_n(t) = \exp\left[-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right]$

$\boxed{0-t}$: at instantaneous time t', $E_n(t') = \frac{n^2\pi^2\hbar^2}{2m[L(t')]^2}$

$\psi_n(x,t;L(t)) = \psi_n(x;L(t))\, e^{\frac{-i}{\hbar}\int_0^t E_n(t')dt'}$

Time dependent Quantum Chemistry

Now, here we may assume that the adiabatic process of slow temporal change of length L of the box is turned on. So, what you will do, the assumption is that the process of adiabatic change the process of adiabatic change is turned on at t equals 0 that is the initial time it was turned on. And then the same thing is turned off at a later time t, t can be anything I mean one can choose what kind of t one would like to have.

So, t has it is an arbitrarily chosen by time later time. So, it is turned off at t and the entire so, if it is turned off at t then what happens that the of the wave function the Ψ_n wave function n th Eigenstate wave function of the particle, we said that it has an temporal phase factor $\exp\left(-i\frac{2\pi E_n t}{h}\right)$, it has a temporal phase factor. Now, the time it is evolving from 0 to t time, because it is evolving from 0 to t time n th stationary state.

So, this is the n th stationary state this n th stationary state wave function Ψ_n due to this adiabatic expansion, which is occurring from 0 to t after immediately after the adiabatic process is turned off the I will call this to be at time t when just I have turned off the adiabatic process and I am trying to find out what is the nature of the n th stationary state of wave function then that would be that will have an accumulated phase total accumulated phase which should be given

$$\Psi_n(t) = \exp\left[-i\frac{2\pi}{h}\int_0^t E_n(t')dt'\right]$$

I am just separating this integration variable from its limit. So, that is where you have used t'. So, what is the basic idea? Because when this adiabatic change is occurring, the parameter itself is changing the parameter controls E_n and if the parameter is controlling E_n during that during the time this 0 to t time interval during which the adiabatic change is going on and instantaneous time.

So, for in this duration and instantaneous time at instantaneous time t' any instantaneous time t' within this time interval during which the energy E n would depend on that time at that time, at that time at that t' time what is my energy that is defined already by this expression, this is going to

$$E_n(t') = \frac{n^2h^2}{8m[L(t')]^2}$$

So, at that time what would be the length, that length will decide what would be the energy state for the n th Eigenstate the energy of the n th Eigenstate So, and it is evolving from 0 to t, that is why total accumulated phase has to be of this factor is the total accumulated phase. And because this accumulate this phase is accumulated by the n th stationary state in the end, we can write down the n th stationary state as follows n th stationary state is actually the n th stationary state at the that particular time so, if I consider at t time the adiabatic process has turned off.

So, this is the time when it is turned off and this is the time when it was turned on and any time in between is the t' time. So, at the time, immediately after the adiabatic process is turned off at that time, if I try to find out the wave function of the n th Eigen state of the particle it is going to be this where I have this total accumulated phase given by this one. So, the wave function each n th Eigen state wave function is accumulating our temporal total temporal phase and that is given by this expression.

$$\Psi_n(x,t;L(t)) = \Psi_n(x;L(t))e^{-\frac{i2\pi}{h}\int_0^t E_n(t')dt'}$$

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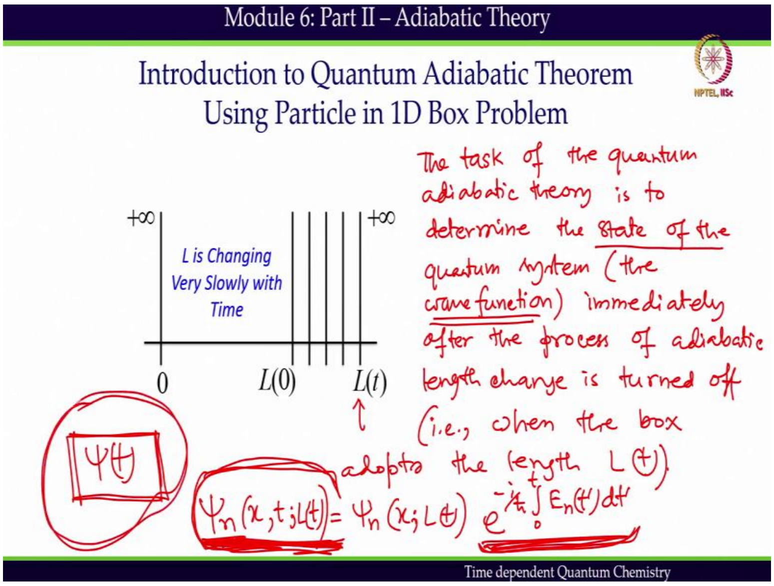

Module 6: Part II – Adiabatic Theory

Introduction to Quantum Adiabatic Theorem Using Particle in 1D Box Problem

The task of the quantum adiabatic theory is to determine the state of the quantum system (the wave function) immediately after the process of adiabatic length change is turned off (i.e., when the box adopts the length L(t))

$\boxed{\Psi(t)}$

$\Psi_n(x,t;L(t)) = \Psi_n(x;L(t))\, e^{-\frac{i}{\hbar}\int_0^t E_n(t')dt'}$

Time dependent Quantum Chemistry

Now, the task the overall task the task of the quantum adiabatic theory is to determine the state off the quantum system the wave function immediately after the process of adiabatic length change is turned off that is when the box adopts the length L(t). So, the impact task of quantum adiabatic theorem is to determine the state which is nothing but the wave function I need to find out the wave function at this time the wave function of the system.

So, psi t this is what I have to find out. **Ψ**(t) at time t immediately after the adiabatic change has been turned off what is the wave function of the system what wave function is representing the current system immediately after the adiabatic change is turned off. And we can remind ourselves that we have already seen that for each n th state wave function that can be expressed already we have understood that can be expressed as this L is actually depends on t at that time that depends on psi n x L t.

So, it has accumulated some kind of minus i by h cut 0 to t E n t dash dt dash.

$$\Psi_n(x,t;L(t)) = \Psi_n(x;L(t))e^{-\frac{i2\pi}{h}\int_0^t E_n(t')dt'}$$

So, this much temporal phase it has already accumulated due to the adiabatic change. So, each one has accumulated. And we have to understand how to express the final wave function at that time one may say that the final wave function is given already here, this is not the final function this is each state how it is behaving, we do not know what will happen to the particle after the expansion, whether it will stay in the same state or it will go to some other states we do not know.

So, this only information we have is that the state each available state is accumulating some energy to accumulating the certain temporal phase already each state is accumulate has accumulated temporal phase and we have to find out what would be the final wave function the total wave function of the system.

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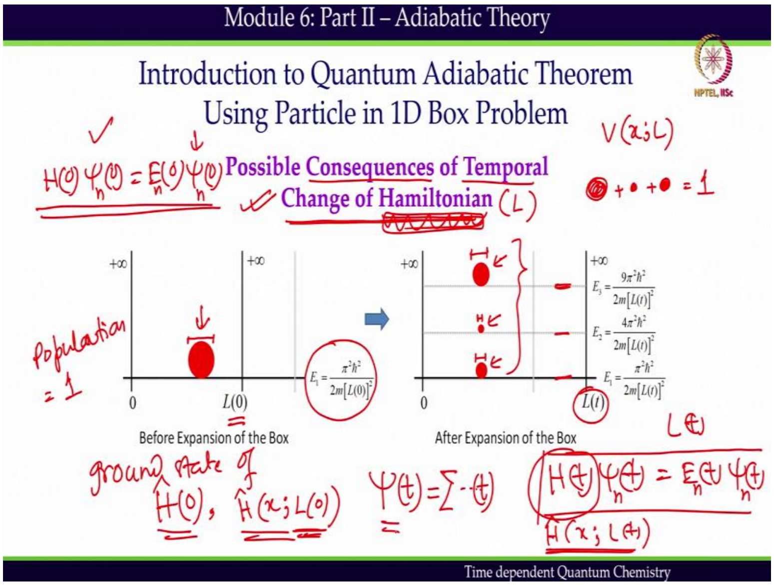


Module 6: Part II – Adiabatic Theory

Introduction to Quantum Adiabatic Theorem Using Particle in 1D Box Problem

Possible Consequences of Temporal Change of Hamiltonian (L)

$H(0)\Psi_n(0) = E_n(0)\Psi_n(0)$

$V(x;L)$

$\bullet + \bullet + \bullet = 1$

Population = 1

ground state of $H(0)$, $\hat{H}(x;L(0))$

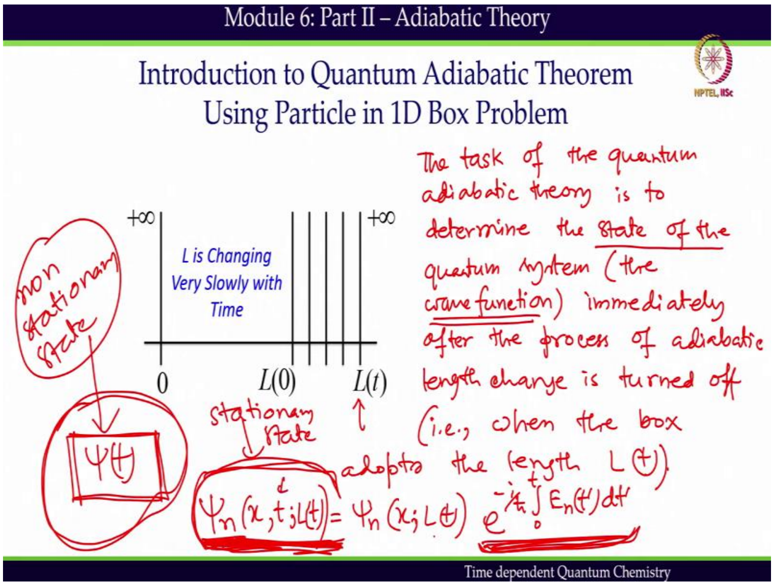
$\Psi(t) = \sum \cdot (t)$

$\boxed{H(t)}\Psi_n(t) = E_n(t)\Psi_n(t)$

$\hat{H}(x;L(t))$

$L(t)$

Time dependent Quantum Chemistry



Module 6: Part II – Adiabatic Theory

Introduction to Quantum Adiabatic Theorem Using Particle in 1D Box Problem

The task of the quantum adiabatic theory is to determine the state of the quantum system (the wave function) immediately after the process of adiabatic length change is turned off (i.e., when the box adopts the length L(t))

$$\Psi_n(x,t;L(t)) = \Psi_n(x;L(t))\, e^{-\frac{i}{\hbar}\int_0^t E_n(t')dt'}$$

Time dependent Quantum Chemistry

Now, this is what we are going to clarify here when will just look at the general consequence of a temporal change of an Hamiltonian, Hamiltonian depends on L. So, it depends on L because it depends on the V and V has a parameter which is L that is why Hamiltonian depends on the parameters. So, this is the parameter which is controlling the Hamiltonian. So, we are talking about only parametric change the change in the parameter.

So, when we when we are looking at the general consequences of temporal change of an Hamiltonian before the expansion of the box, let us assume that the particle was in the ground state. So, this is the particle which I am showing and the circle is showing the population is a full population I have in the ground state, the circle the diameter showing what kind of population I have let us diameter is this entire diameter is actually representing population equals 1.

So, entire population of the particle is on the ground state and its energy is given here, at L equals 0 time the length is L, L_0 we are specifying and that is why it is in the ground state. Now, what ground state of what ground state of which Hamiltonian, Hamiltonian H(0). Or specifically, if we want to be notationally very correct, then it is going to be H (x;L(0)) that is the Hamiltonian we have. So, at t equals 0 the Hamiltonian would be H(0), and for that H(0), I will have these equations. So,

$$H(0)\boldsymbol{\Psi}(0)=E(0)\boldsymbol{\Psi}(0)$$

Here, I am just not mentioning the coordinate space here, all our all depends on coordinate space as well, except for E, but it has a parameter so that parameter dependency I am looking at. So, before the adiabatic change occurred, it has the from this TDSE I will be able to get different states and we are saying that in the ground state it is present and the particle is present in the ground state.

Now, after the expansion of the box, it may so happened this is a quite general consequence we are writing it means what happened that the particle is no longer staying in the ground state anymore. It may so, happen the general consequence of this kind of adiabatic this kind of have the change temporal change of Hamiltonian, the temporal change of the parameter which controls the Hamiltonian is following.

The particle may not be staying in the ground state anymore, it may so, happen that the there is a probability or population in the ground state, there is a probability in the excited states like this. And now the diameters are showing relative diameters are showing what kind of population I have then total this 1 plus this 1 plus this 1, total probability is 1 definitely. But now, due to this change, Hamiltonian change of Hamiltonian it is not necessary that it is an adiabatic change.

So, far we have not concluded what will happen if it is adiabetic change, we are just saying that if it is a change, then then the change of the Hamiltonian then the general consequence is that the particle may not be staying in the ground state it can go to the to the excited state as well and there can be a development of population in states other than the ground state of the final, what is the grounds to final H(t).

So, for final H(t), I will have this TISE Time Independent Schrodinger Equation, which is this t this is the final and we have this in in n n E n here also we have n n. So, this is the Time Independent Schrodinger Equation at time t immediately after the adiabatic expansion has turned off and just before the adiabatic expansion was initiated at that time TISE is given by this.

$$H_n\boldsymbol{\Psi}_n(t)=E_n(t)\boldsymbol{\Psi}_n(t)$$

So, if I solve this equation, at that time, there will be an L for that L if I solve it, I will be able to get different energy states and those energy states may have certain population because of the change temporal change of the Hamiltonian. This is the very general concept of temporal change of Hamiltonian. Now, when the Hamiltonian of a quantum system changes as a function of time.

In principle, the particle which was present in the n th discrete non-degenerate stationary state have initial H 0. So, this is the Hamiltonian may undergo the transition and in that case there can be development of probability of finding the particle in states other than that, n th discrete non degenerate stationary state of final H(t). So, when I say finally stay more specifically it is actually H(x;L(t)) that is the Hamiltonian.

So, for this particular Hamiltonian, I will be able to get different states and it may so, happen that these states are populated in a certain way does the temporal evolution of Hamiltonian creates a non-stationary state of the particle. So, it is quite clear that because Hamiltonian is changing as a function of time the state is a non-stationary state and non-stationary state of a particle we know that any non-stationary state of the particle.

So, in the previous slide we said that we have to find out **Ψ**(t), this is actually non-stationary state wave function the particle can actually be in the non-stationary state after the expansion it may not be the in the stationary state that is the general consequence of any time evolving system. Because the system is evolving in time and whenever the system is evolving in time, the system cannot stay in the stationary state.

These are stationary states this stationary state this is a stationary state at time t, which means at for a particular length of the box, this is a stationary state, but particle because of this expansion, because of this possibility of development of the population in different states, the states which is defined by H(t). Now, because of this development of this population, one can say that the particle is not in a stationary state anymore it is in a non-stationary state which is defined by **Ψ**(t).

And this non-stationary state we know that it can be represented as a linear combination of the stationary state at time t. So, all the stationary states at that time whatever I can get those stationary states I can collect with a with a corresponding phase factor and then linearly combine them to get the non-stationary state.

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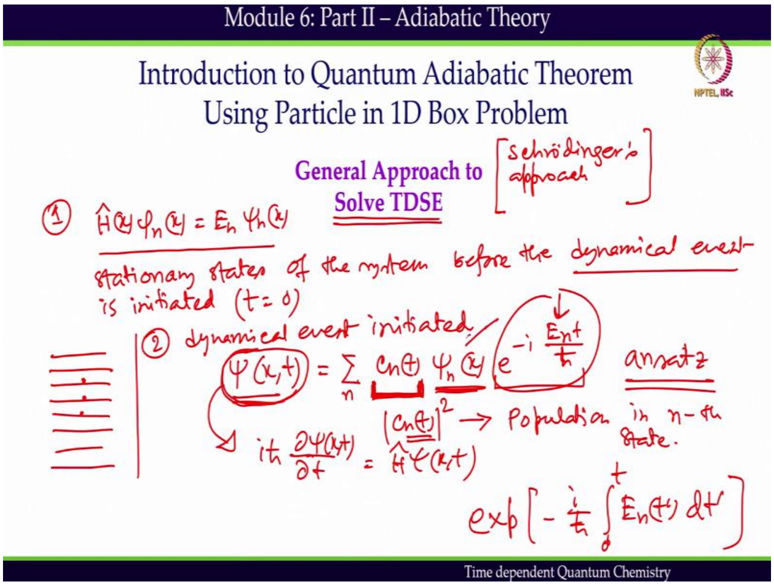


Module 6: Part II – Adiabatic Theory

Introduction to Quantum Adiabatic Theorem Using Particle in 1D Box Problem

General Approach to Solve TDSE [Schrödinger's approach]

① $\hat{H}(x)\psi_n(x) = E_n\psi_n(x)$

stationary states of the system before the dynamical event is initiated $(t=0)$

② dynamical event initiated

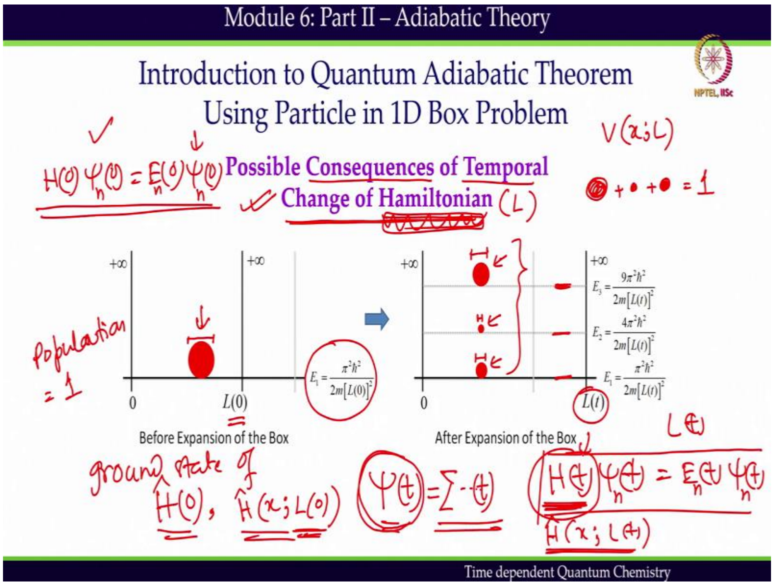
$\Psi(x,t) = \sum_n c_n(t)\,\psi_n(x)\, e^{-i\frac{E_n t}{\hbar}}$ ansatz

$|c_n(t)|^2 \to$ Population in n-th state.

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

$\exp\left[-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right]$

Time dependent Quantum Chemistry



Module 6: Part II – Adiabatic Theory

Introduction to Quantum Adiabatic Theorem Using Particle in 1D Box Problem

Possible Consequences of Temporal Change of Hamiltonian (L)

✓ $H(0)\psi_n(0) = E_n(0)\psi_n(0)$

$V(x;L)$

● + • + ● = 1

Population = 1

Before Expansion of the Box

After Expansion of the Box

ground state of $\hat{H}(0)$, $\hat{H}(x;L(0))$

$\Psi(t) = \sum \cdot (t)$

$L(t)$

$H(t)\psi_n(t) = E_n(t)\psi_n(t)$

$\hat{H}(x;L(t))$

Time dependent Quantum Chemistry

This is a very common approach to solve TDSE. What is the how do you solve TDSE this is something which you should remember, because anytime for an unknown system if we want to solve some dynamical problem, the problem should be viewed like this way first and this is this approach is called Schrodinger approach. So, we will use this approach very common approach to solve the dynamical problem this is called Schrodinger approach.

So, what we do here is that first we solve TISE. If I solve the TISE which means the TISE before the time evolution. So, this is the by solving this TISE I get stationary states of the system before the dynamical event is initiated, which means I can call it, it is a t equals 0 time. So, at t equals 0 before t equals 0 when the dynamical event is not initiated yet I have to what we have to find out I have to find out all possible stationary states.

Then, after the dynamical events has initiated once the dynamical event initiated then we cannot say that the particle of the system in a stationary state it is going to be in the non-stationary state and the non-stationary state is given by

$$\Psi_n(x,t) = \sum_n c_n(t)\,\Psi_n(x)\,e^{-i\frac{2\pi E_n t}{h}}$$

linear combination of all stationary states with its own phase factor and expansion coefficient that is the way we get that non stationary state and this is called trial wave function this is called ansatz or trial wave function.

This is the wave function which is representing the non-stationary state but because C_n is unknown and we know that C_n the square of absolute value of C_n will give me the population in a n th state a non-stationary state can have several population in different states. So, before the dynamical event started, I may have population only on the single state, but during the dynamical popular dynamical event when it is going on, at that time, the population it can occupy different places the it can have population in different levels.

I can have population here I can have a total population is going to be 0 sorry 1 but I can have population development in different states and that is called non-stationary state. And in order to express that state, I need to know the population and that population can be obtained by inserting this wave function trial wave function to the TDSE, TDSE is

$$i\frac{h}{2\pi}\frac{d\Psi(x,t)}{dt} = H\Psi(x,t)$$

we have to insert that to get this population.

And once we get the population, then what will happen? We will be able to define what is the non-stationary state, this non-stationary state will be defined in terms of stationary states, but I need to know the population relative population for each non-stationary, stationary state which is defining the non-stationary state. Now, this is a very general approach to solve any dynamical problem with the help of TDSE only difference here is that the same thing is happening here also.

We are saying that we started with the ground state and at t equals 0 it evolved up to t equals t time and due to this evolution, I may have population in different states the states are now defined by this H (t) Hamiltonian. And but the overall state overall physical state of the particle not quantum the physical state of the particle is given by psi t which is a non-stationary state which will be expressed in terms of linear combination of the stationary states defined by this H (t).

So, same idea we are implementing only difference is that here we have assumed that E_n does not change, previously we have assumed but here in the problem, we know that E_n is changing as a function of time. So, the total accumulated phase cannot be just $e^{-i\frac{2\pi E_n t}{h}}$ but $e^{-\frac{i2\pi}{h}\int_0^t E_n(t')dt'}$ that is going to be the total phase accumulated by the n th this n th stationary state of H(t).

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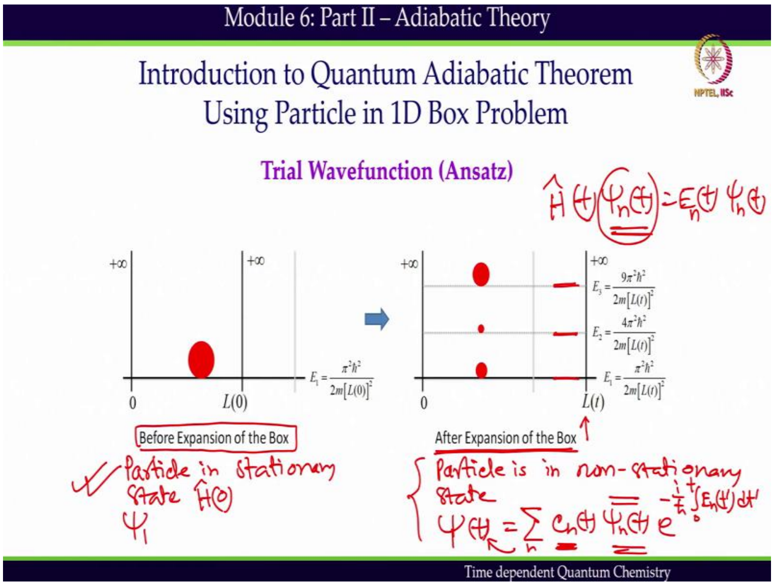

Module 6: Part II – Adiabatic Theory

Introduction to Quantum Adiabatic Theorem
Using Particle in 1D Box Problem

Trial Wavefunction (Ansatz)

$\hat{H}(t)\,\Psi_n(t) = E_n(t)\,\Psi_n(t)$

Before Expansion of the Box

Particle in stationary state $\hat{H}(0)$
Ψ_1

After Expansion of the Box

Particle is in non-stationary state
$\Psi(t) = \sum_n c_n(t)\,\Psi_n(t)\,e^{-\frac{i}{\hbar}\int_0^t E_n(t')dt'}$

Time dependent Quantum Chemistry

So, with these consequences we will move on and we will look at the problem which we have the non-stationary state of the particle. So, basically what we are doing here before expansion of the box the particle is in stationary state and the state is defined by the Hamiltonian H(0), but after the expansion of the box, the state is not a stationary state anymore the particle is in non-stationary state.

So, I have to express it like this way and that non stationary state we have said that following Schrodinger approach can be expressed in terms of linear combination of C_n (t)

$$\Psi_n(t) = \sum_n c_n(t)\Psi_n(t)e^{-\frac{i2\pi}{h}\int_0^t E_n(t')dt'}$$

that is going to be the non-stationary state at this time immediately after the expansion has is over.

So, one key point which you should remember that before the expansion definitely particle was in the stationary state here we are assuming this is in ground state that is why the stationary state can be defined as **Ψ**(1) in the **Ψ**(1) stationary state it was there, but after the expansion because the Hamiltonian has evolved over the time is the dynamical event the particle has to be in the non-stationary state particle cannot be in the stationary state immediately after the entire change is turned off immediately after that.

And that non-stationary state will be defined with the help of the stationary states at that time, and the stationary states at that time will be defined by H(t) that is the stationary state. So, those stationary states I have to collect and then plug that in here. So, this stationary state are obtain like this way.

$$H(t)\boldsymbol{\Psi}n(t)=E_n(t)\boldsymbol{\Psi}_n(t)$$

So, this is the wave function which is representing the stationary state at that time and the stationary state we have given.

And the contribution of each stationary state is given by this expansion coefficient the contribution to the total non-stationary state. So, the key information here we should remember that that non-stationary state is prepared actually after the expansion, we will continue this session in the next class.