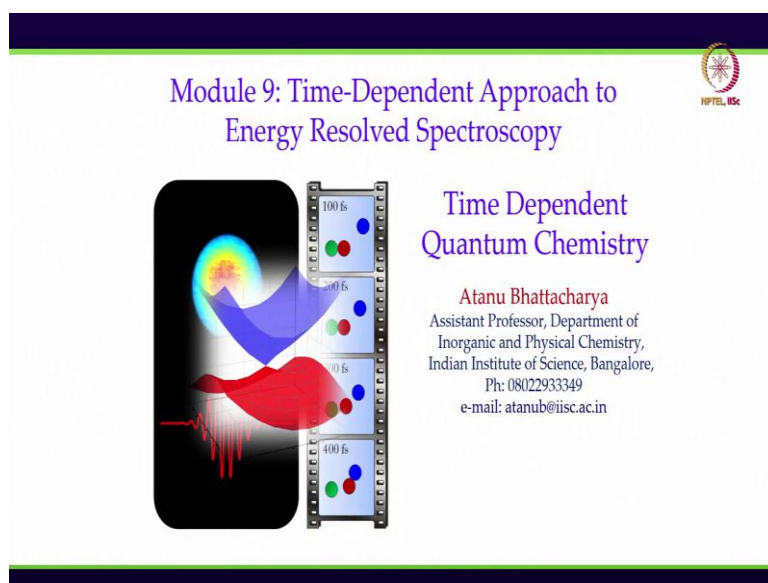


Time Dependent Quantum Chemistry
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Module 9

Time-Dependent Approach to Energy Resolved Spectroscopy

Welcome to module 9 of the course, Time Dependent Quantum Chemistry. In this module, we will go over Time-Dependent Approach to Energy Resolved Spectroscopy.

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Module 9: Time-Dependent Approach to Energy Resolved Spectroscopy

Time Dependent Quantum Chemistry

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In general, we need to think about TDSE Time-Dependent Schrodinger Equation, we get a feelings that it is going to give me a time dependent wave function. And if I have time dependent wave function, I do not have any access to the spectrum of the system. On the contrary, in this module, we will find out that solution to the TDSE can give us the spectrum as well and that is what we are going to go over.

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Module 9: Time-Dependent Approach to Spectroscopy

Conventional Approach to Energy Resolved Spectroscopy

HPTCL, IISc

Obtain Solution to TISE

$$\langle \psi_m | \psi_n \rangle = \delta_{mn}$$

$$\delta_{mm} = 1$$

$$m = n$$

$$\delta_{mn} = 0$$

$$m \neq n$$

Stationary States

Spectrum $\sigma(\omega)$

Time dependent Quantum Chemistry

So, conventional approach to energy resolved spectroscopy, when I say energy resolved spectroscopy, I would like to know the spectrum of the system. If we follow the conventionally what we do and what we have already realized that time independent Schrodinger equation which is given by this equation, time independent independent Schrodinger equation for a quantum system provides stationary eigen states, eigen state energy E_n and eigen state with function $\psi_n(x)$ is provided, they are provided by the time independent Schrodinger equation $H(x)\psi_n(x) = E_n\psi_n(x)$.

These eigen state wave functions are orthonormal in nature that also we have understood generally this is going to be orthonormal in nature which means, this is going to be $\langle \psi_m | \psi_n \rangle = \delta_{mn}$, $\delta_{mm} = 1$, when, $m = n$ and $\delta_{mn} = 0$, when, $m \neq n$.

So, each state, which is a solution to the TDSE are actually orthonormal, the solution to the TDSE provides the spectrum, a structure featuring where the energy states are. So, this is a typical example, if the energy states are here, so, I can get a structure here if energy state is here, I can get a structure here if the energy state is here, I can get structure here and so, on.

So, solution to the TDSE provides the spectrum of the quantum system because it gives me the energy states and that is exactly what is important in energy resolved spectroscopy or in frequency resolved spectroscopy of this frequency and energies, they are related by ω , equals

if it is E_n energy, then $\omega_n = \frac{E_n}{\hbar}$.

So, the basic idea of the energy resolved spectroscopy is that we need to know the energy states and then those energy states can be obtained from time dependent time independent Schrodinger equation that is something which we have understood from very basic quantum chemistry class.

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Module 9: Time-Dependent Approach to Spectroscopy

Conventional Approach to Energy Resolved Spectroscopy

Best Example: Particle in 1D Box

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

$$\begin{cases} V(x;L) = 0 & \text{when } 0 \leq x \leq L \\ V(x;L) = +\infty & \text{otherwise} \end{cases}$$

TISE Explored the Spectrum of a Quantum System

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x n}{L}\right) \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Time dependent Quantum Chemistry

This is just an example following the same conventional approach. We are very much familiar with this particle in 1 dimensional box problem, we have been doing it for a long time. And in the particle 1 dimensional box problem the Hamiltonian is given by this $H(x;L) = \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x;L) \right]$, where more specifically we have written the parameter L. So, it depends on the parameter L controls the overall Hamiltonian the potential which will be experienced.

So, the basic idea is that if it is a free particle in a box problem, then $V(x;L) = 0, 0 \leq x \leq L$ and $V(x;L) = +\infty, \text{otherwise}$, we should remember the semicolon we have used always in the adiabatic theory, we have used it to separate the variable and the parameter.

So, it is going to be $+\infty$ when otherwise. So, this is the definition of the potential, like the particle in 1 dimensional box is experiencing this potential, and that is why we get the wave function, the nth wave function and nth energy state $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x n}{L}\right), E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$ and

if we know the energy states $E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$, $E_2 = \frac{4\pi^2 \hbar^2}{2mL^2}$, we know what kind of transition in the spectroscopy we can have. Different transition we can have.

These transitions occurs within the eigen states, that is why in energy resolved spectroscopy, knowing the energy states are very, very important. So, this is a very general consensus, we have been using this general consensus for very frequently in quantum chemistry on the contrary to the our conventional approach based on time independent Schrodinger equation. What we are going to now present and we are going to realize that it is possible to determine the eigen values and eigen states for any 1 dimensional potential.

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Module 9: Time-Dependent Approach to Spectroscopy

Time Dependent Approach to Energy Resolved Spectroscopy

Can TDSE Explore the Spectrum of a Quantum System ? ✓

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

solution to this may give us eigenstate energy and eigenstate wavefunction for given \hat{H} .

Time dependent Quantum Chemistry

We are continuing with the when 1 dimensional problem. So, this is possible to explore directly from the solution to the time dependent Schrodinger equation.

$i\hbar \frac{\partial \psi(x,t)}{\partial t} = H(x)\psi(x,t)$ So, this is called time dependent Schrodinger equation, we are very

much familiar with it and we will see that this solution to this may give us eigen state energy and eigen state wave function for given Hamiltonian. So, yes, it can TDSE can explore the spectrum of a quantum system, this is what we are going to see.

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Wavepacket Correlation Function ✓

For a given initial wavepacket $\psi(x,0)$: analytical or numerical solution to TDSE gives the wavepacket $\psi(x,t)$ at any later time t . Correlate the initial and final wavepackets.

Wavepacket correlation function

$$c(t) = \langle \psi(x,0) | \psi(x,t) \rangle = \int_{-\infty}^{+\infty} \psi^*(x,0) \psi(x,t) dx$$

Expand the wavefunction using the orthonormal stationary eigen states

$$\psi(x,t) = \sum_n c_n(t) \psi_n(x) e^{-i E_n t / \hbar}$$

$$\psi(x,0) = \sum_m c_m(0) \psi_m(x)$$

TDSE

And in order to realize that what we need to understand is called wavepacket correlation function. What is wavepacket correlation function? We have understood that for a given initial wavepacket, let us say I have a particle initially, the wavepacket is representing that particle. So, I know initial wavepacket which is $\psi(x,0)$, this is the initial wavepacket. For a given, for this given initial wavepacket.

Either I can do analytical solution or numerical. Most of the problems needs to be solved numerically, but we can have analytical solution particularly Gaussian wavepacket we have seen that analytical solution is possible for Gaussian wavepacket. Now, for the translational motion. So, for a given initial wavepacket $\psi(x,0)$ analytical or numerical solution to TDSE gives the wavepacket $\psi(x,t)$ at any later time t that we have seen that.

Now, our task for this present module is to correlate, correlate the initial and final wavepackets. So, what we need to do? Is that we have to do the correlation, how they are correlating that is exactly what we are going to find out. And that is given by this correlation function, this is called wavepacket correlation that is the integration over the entire space.

So, I had, let us say initial this is $-\infty$ to $+\infty$ for x space we have. Initial wavepacket was this, this was $\psi(x,0)$ and final wavepacket, let us say this one, $\psi(x,t)$, all we need to find out we have to correlate it and this kind of correlation is nothing but the overlap between these two functions. So, basically is trying to explore this overlapping regime how they are correlated whether they are fully overlap, partially overlap.

So, this is what we are going to find out this is what is the meaning of it. So, if we can correlate it, we will be able to get an information of the eigen state energy and how we can do that. And that is the, that is the exercise we will go over.

So, we have seen, so, the correlation function, $c(t) = \langle \psi(x,0) | \psi(x,t) \rangle = \int_{-\infty}^{+\infty} \psi^*(x,0) \psi(x,t) dx$,

wavepacket correlation function is nothing but finding out how much they are correlated, how much they are overlapping with each other over the space, so, extent of overlap is going to be calculated through this correlation function. So, in order to do that, what we will do? We will follow the approach we have always taken up in this course, we know that this $\psi(x,t)$ with function of the particle of a quantum system at time t, one can say this is the wavepacket can be expressed as a linear combination of orthonormal eigen states.

So, let us say I have an Hamiltonian, that Hamiltonian is giving me should give me if I solve TISE through TISE, it can give me all these energy states. So, let us say one energy state ψ_n . So, this is going to be ψ_{n-1} and so on. All these energy states are given an energy there eigen values are E_n then this is going to be E_n minus 1 like this way. So, associated eigen state or eigen state energies are there, these are stationary eigen state.

So, basically what you are going to do is that, expand represent or expand, represent or expand the wave function in using, you are going to use that using the orthonormal stationary they are all stationary because TISE gives me stationary states orthonormal stationary eigen states, eigen states of the quantum system, $\psi(x,0) = \sum_m c_m(0) \psi_m(x)$, so that is the way we are going to expand.

If we expand it, then we can have we know that it is going to be c_n expansion coefficient, which means that at time this is a non stationary wave function. This non stationary wave function are represented in the, using the linear combination of stationary wave functions and what contribution which stationary state contributes the most at time t that is controlled by this c_n .

So, c_n is giving you the population at the nth state these are usual meaning we have been using this meaning for a long time in this course. So, this is the, so we have the time independent part, time dependent phase factor and associated expansion coefficient, which is

going to control the population at time t and in that state. So, this is the way we can expand

$$\text{the total wave function at time } t. \psi(x, t) = \sum_n c_n(t) \psi_n(x) e^{-iE_n t / \hbar}$$

And as a result, at times 0, t = 0 time, I will be able to represent the entire thing. So, in that case t = 0, so, this phase factor will be gone, what I am going to do is that to make it as a general, I will just change the index the designation or the notation of the index it, so just to make it a general, because it will be useful to use these things and theoretically, we know that m will be extending index would be extending from so 0 to ∞ , n would be 0 to ∞ , basically, all states possible states, stationary states will be added together, and c_m is showing the population at that state.

So, I have just what I have done is that I have selected two different indices for my convenience, one to represent this one, another to represent this one, but the meaning of these indices is the same, there is no change in the meaning of the indices. So, I have these two functions, so all we need to do is that to find out this time correlation function, I need to add these two into the, into this function, so I have to include it.

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Module 9: Time-Dependent Approach to Spectroscopy

Wavepacket Correlation Function

$$c(t) = \langle \psi(x, 0) | \psi(x, t) \rangle = \int_{-\infty}^{+\infty} \psi^*(x, 0) \psi(x, t) dx$$

$$= \int_{-\infty}^{+\infty} \sum_m c_m^*(0) \psi_m^*(x) \sum_n c_n(t) \psi_n(x) e^{-iE_n t / \hbar} dx$$

$$= \sum_m \sum_n c_m^*(0) c_n(t) e^{-iE_n t / \hbar} \int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx$$

$$= \sum_m \sum_n c_m^*(0) c_n(t) e^{-iE_n t / \hbar} \delta_{mn}$$

$$= \sum_n c_n^*(0) c_n(t) e^{-iE_n t / \hbar}$$

$$c(t) = \sum_n c_n^*(0) c_n(t) e^{-iE_n t / \hbar}$$

$\psi_m^* \psi_n$

$m=n$

✓

Time dependent Quantum Chemistry

So, that is exactly what we are going to do now, I have these two functions now. And I am going to now insert them here, if I insert it, then what I get here is that

$$= \int_{-\infty}^{+\infty} \sum_m c_m^*(0) \psi_m^*(x) \sum_n c_n(t) \psi_n(x) e^{-iE_n t / \hbar} dx. \text{ So, this is what we get after inserting these two}$$

expressions into the time correlation function.

And after that we can reduce it very easily we can reduce it very easily in the following way,

$$\text{I can have this two summations together} = \sum_m \sum_n c_m^*(0) c_n(t) e^{-iE_n t/\hbar} \int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx.$$

$$= \sum_m \sum_n c_m^*(0) c_n(t) e^{-iE_n t/\hbar} \delta_{mn} = \sum_n c_n^*(0) c_n(t) e^{-iE_n t/\hbar}$$

So, if there is, if the system is representing an Hamiltonian and still we are considering it is our time independent Hamiltonian, so, I have an Hamiltonian which is time independent and that is giving me not explicit time dependent. So, that is the way we should put together.

So, for this Hamiltonian I have this eigen states all these eigen states and the population is changing as a function of time and that is exactly what we are trying to find out. So, I have this ψ_m and ψ_n they are actually representing this stationary states. That is why this part can be approximately a sorry, not can be represented as a delta function.

So, only terms which will be, which will exist in the end in this summation is going to be when $m = n$ and which means that I have this summation remaining

$$c(t) = \sum_n c_n^*(0) c_n(t) e^{-iE_n t/\hbar}.$$

So, finally, the another form of the time correlation function which you get is this one, this is the form of the time correlation function.

So, this summation this particular summation will be all 0, all terms of this summation would be 0, except for the, that term for which $m = n$. And that is why this summation will exist. We are writing here, but this summation when we are writing explicitly, each term, all terms should be 0, except for m equals n term which will exist. So, we have been able to get another form of the time correlation function which is correlating the wave function at equals 0 and wave function at a later time t .

(Refer Slide Time: 21:50)

Time → Freq.

Fourier Transform of Wavepacket
Correlation Function

$$f(\omega) = \int_{-\infty}^{+\infty} f(t) e^{i\omega t} dt$$

$$\sigma(\omega) = \int_{-\infty}^{+\infty} c(t) e^{i\omega t} dt$$

$$c(t) = \sum_n c_n^*(0) c_n(t) e^{-\frac{E_n t}{\hbar}} = \sum_n c_n^*(0) c_n(t) e^{-i\omega_n t}$$

Time → Freq.

Fourier Transform of Wavepacket
Correlation Function



$$\sigma(\omega) = \int_{-\infty}^{+\infty} c(t) e^{i\omega t} dt$$

$$c(t) = \sum_n c_n^*(0) c_n(t) e^{-\frac{E_n t}{\hbar}} = \sum_n c_n^*(0) c_n(t) e^{-i\omega_n t}$$

$$= \int_{-\infty}^{+\infty} \sum_n c_n^*(0) c_n(t) e^{-i\omega_n t} e^{i\omega t} dt$$

$$= \sum_n c_n^*(0) c_n(0) \int_{-\infty}^{+\infty} e^{i\omega t} e^{-i\omega_n t} dt$$

C_n(t) is slowly varying w.r.t. e^{iωt} or e^{-iω_nt}.

Time → Freq.

Fourier Transform of Wavepacket
Correlation Function



$$\sigma(\omega) = \int_{-\infty}^{+\infty} c(t) e^{i\omega t} dt$$

$$c(t) = \sum_n c_n^*(0) c_n(t) e^{-\frac{E_n t}{\hbar}} = \sum_n c_n^*(0) c_n(t) e^{-i\omega_n t}$$

$$= \int_{-\infty}^{+\infty} \sum_n c_n^*(0) c_n(t) e^{-i\omega_n t} e^{i\omega t} dt$$

$$= \sum_n c_n^*(0) c_n(0) \int_{-\infty}^{+\infty} e^{i\omega t} e^{-i\omega_n t} dt$$

$$= 2\pi \delta(\omega - \omega_n) = \int_{-\infty}^{+\infty} e^{i\omega t} e^{-i\omega_n t} dt$$



Time → Freq. Fourier Transform of Wavepacket
Correlation Function

$$\begin{aligned}
 \sigma(\omega) &= \int_{-\infty}^{+\infty} c(t) e^{i\omega t} dt \\
 c(t) &= \sum_n c_n^*(0) c_n(t) e^{-i\frac{E_n t}{\hbar}} = \sum_n c_n^*(0) c_n(t) e^{-i\omega_n t} \\
 &= \int_{-\infty}^{+\infty} \sum_n c_n^*(\omega) c_n(t) e^{-i\omega_n t} e^{i\omega t} dt \\
 &= \sum_n c_n^*(\omega) c_n(t) \int_{-\infty}^{+\infty} e^{i\omega t} e^{-i\omega_n t} dt \\
 &= 2\pi \sum_n c_n^*(\omega) c_n(t) \delta(\omega - \omega_n)
 \end{aligned}$$

$\omega_n = \frac{E_n}{\hbar}$

This time correlation function now what we will do is that we will Fourier transform the wavepacket correlation function, so we have this wavepacket correlation function $c(t)$ and we will Fourier transform it, this is the way we do Fourier transform, it is just a convention.

So, if we have a function, let us say if we have a function, and I am converting into frequency domain time to frequency domain, so it is going to be time to frequency. If we do the Fourier transform, we will see what we have basically what information is hiding within this function

$c(t)$ that we will be able to explore in the frequency domain, $f(\omega) = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt$

On the other hand, if we take this representation where time to frequency domain representation is loss, then frequency to time during the presentation when we will do inverse Fourier transform of these, then we will have to use $e^{i\omega t}$.

So, whether to use $e^{i\omega t}$ or $e^{-i\omega t}$ it depends entirely on the convention or the representation of the Fourier transform we are going to use and corresponding inverse Fourier transform has to be selected accordingly. So, here we are considering $e^{i\omega t}$ there is a reason why we are doing it because it will give me and very interesting outcome very interesting information will which will emerge which is hiding within this time correlation function.

So, let us do that. So, if we do this integration, we have to just now insert

$c(t) = \sum_n c_n^*(0) c_n(t) e^{-i\omega_n t}$ This is going to be over the time and as we can see that one can say

that this the $c(t)$, this is an more like an envelope function. So, I have let us say

$$\sigma(\omega) = \int_{-\infty}^{+\infty} \sum_n c_n^*(0) c_n(t) e^{-i\omega_n t} e^{i\omega t} dt = \sum_n c_n^*(0) c_n(t) \int_{-\infty}^{+\infty} e^{i\omega t} e^{-i\omega_n t} dt, .$$

So, what do you see here is that recollect this information from a pulse, we had envelope function which was represented by $a(t)e^{-i\omega t}$ and then I will clearly write it when if you recollect the pulse formation, we had all the wavepacket information, we had an envelope function $a(t)$ in the time domain, we considered in the pulse and then $e^{-i\omega t}$, that is the way we have represented which was slowly varying and fast varying components we have got, and we said that this part is very slowly varying component.

So, if this, I mean following the similar note, if we consider that the $c(t)$ although it is time dependent, but it is varying very slowly as compared to these terms, these two oscillatory terms, then we can take it out from the integration and we can actually write down

$$\sigma(\omega) = \int_{-\infty}^{+\infty} \sum_n c_n^*(0) c_n(t) e^{-i\omega_n t} e^{i\omega t} dt = \sum_n c_n^*(0) c_n(t) \int_{-\infty}^{+\infty} e^{i\omega t} e^{-i\omega_n t} dt$$

And if we can take it out, then

what will happen, we can recall the definition of the delta function we have already given when we have, when we are dealing with translational motion or wavepacket dynamics, delta function has one representation which is $\delta(\omega - \omega_n) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} e^{-i\omega_n t} dt$ that was the representation.

And if we in the present context, if we try to do similar representation what we have here we

$$\text{have } 2\pi\delta(\omega - \omega_n) = \int_{-\infty}^{+\infty} e^{i\omega t} e^{-i\omega_n t} dt = 2\pi \sum_n c_n^*(0) c_n(t) \delta(\omega - \omega_n), \omega_n = \frac{E_n}{\hbar} \text{ that is the}$$

representation we have. So, this equation this integration is actually representing our delta function, how we are going to write it down and if it is delta function,

So, we can write it down in terms of delta function, this is nothing but summation of

$$\sigma(\omega) = 2\pi \sum_n c_n^*(0) c_n(t) \delta(\omega - \omega_n)$$

So, what we see that this $\sigma(\omega)$ which is representing the

Fourier transform of the, Fourier transform of the correlation function it is given by this and

there is a meaning which you can immediately find out from this where, $\omega_n = \frac{E_n}{\hbar}$

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Module 9: Time-Dependent Approach to Spectroscopy

Fourier Transform of Wavepacket
Correlation Function: Spectrum

at $t=0$

$\psi(x,t)$

$\psi(x,0)$

$$\sigma(\omega) = 2\pi \sum_n c_n^*(0) c_n(t) \delta(\omega - \omega_n)$$

$\omega = \omega_n$

Fourier transform of the wavepacket correlation function renders the spectrum of the quantum system

Time dependent Quantum Chemistry

So, what we get is that this Fourier transform of the correlation function gives me a spectrum because this is actually representing a spectrum this is representing a spectrum. Why this is representing a spectrum? This, this will exist this delta function will exist only when ω is ω_n .

What is ω_n ? ω_n is those states representing those eigen states. So, whenever ω and ω is continuously varying, so, I am going to vary ω continuously and I will have function value only when these states are matching with this omega. So, I will get a spectrum and that is all about the spectrum spectroscopy, energy resolved spectroscopy, I get the energy states, which is modulated by this function.

So, I will be able to plot now, this $\sigma(\omega)$ as a function of ω and I get the max, function value, this is the, this is kind of in this envelope is represented by $c_n^*(0) c_n(t)$. That is the way it is representing. So, what I need to do is that at I need to find out at time $t, \psi(x, t)$, what is my wavepacket and correlated with respect to $\psi(x, 0)$.

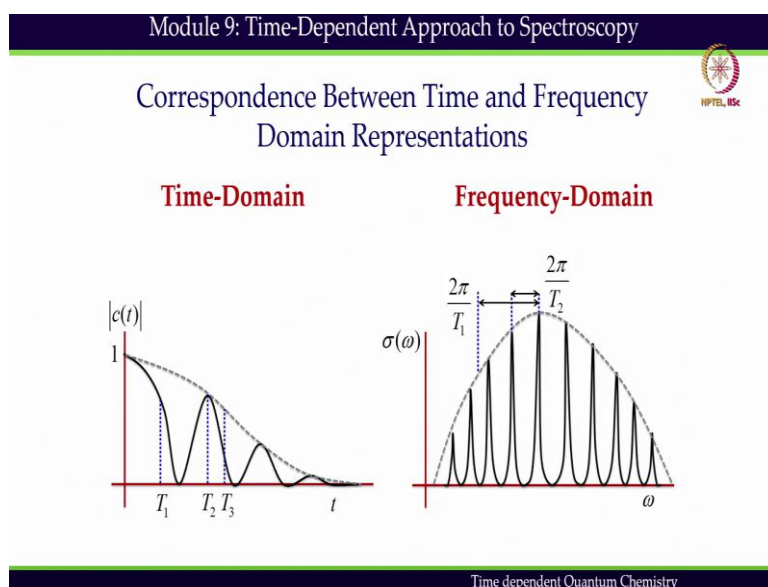
Once we correlate it, I can Fourier transform that correlation function and I get back the spectrum. This is the way I get the spectrum. This function exist only when I have this is matching ω_n , and ω_n representing the wave function stationary states, each stationary state of the of the Hamiltonian.

So this is the way we are getting it. So, this exercise demonstrate that the Fourier transform of the wavepacket, Fourier transform of the wavepacket correlation function, wavepacket correlation function renders the spectrum of the quantum system and this is called time dependent approach to the energy resolved spectroscopy.

It is quite interesting that through TDSE we are actually extracting the information of the eigen states we are not solving TISE time independent Schrodinger equation to get this we are actually solving TDSE time dependent Schrodinger equation, we are starting with an initial wave function and we are allowing the system to evolve following time dependent Schrodinger equation and we are then after a certain time, we have to select this wave function at time t.

Then correlate them correlate which means that we have to find out the extent of overlap and that overlap is going to now, if I Fourier transfer that overlap has that information, how many states are there and what states we have, but we cannot see it in time domain, we have to, we have to see that we have to go to the Fourier domain or frequency domain and immediately we will be able to see that. So, this entire exercise gives us an interesting perspective of the time dependent Schrodinger equation.

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We have been finding out the correspondence between time and frequency. We will stop here and we will continue this discussion in the next lecture.