Time Dependent Quantum Chemistry
Professor. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science Bengaluru
Fourier Transform of Time Corelation Function

Welcome back to Module 9 of the course Time Dependent Quantum Chemistry. We have represented, we have represented time correlation function and we have seen that the Fourier transform of the time correlation function is actually giving the spectrum of the system. In order to get that spectrum, I do not need to solve TISE, just solving TDSE I can get that. So, it is a very interesting perspective we have developed for the time dependent Schrodinger equation.

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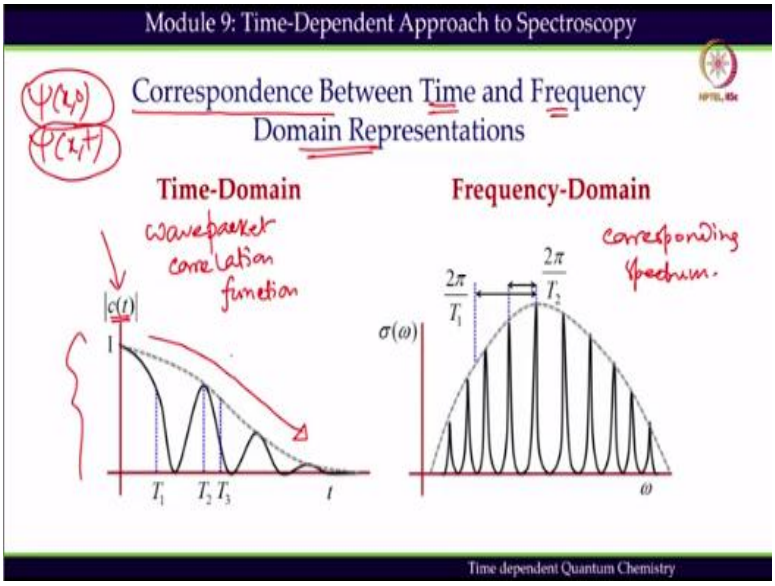
Module 9: Time-Dependent Approach to Spectroscopy

Correspondence Between Time and Frequency Domain Representations

Time-Domain

Frequency-Domain

Time dependent Quantum Chemistry

What you are seeing is that there is close correspondence between the close correspondence between the time and frequency domain representation. So, we will look at this. In the time domain, what is important to know is the correlation function,c(t). So, this is a typical example of wavepacket correlation function, do not expect that this is the way always correlation function will work, this is just an one example of correlation function. So, this is called wavepacket correlation function and corresponding spectrum by doing the Fourier transform.

So, we have to do this Fourier transform this correlation function we will get that. So, question is, how the correlation function varies with respect to time, can we have some idea generic idea how it is varying and the entire discussion is developed based on the first proposal given by Heller in 1981. And, we are following that approach very closely.

So, if we look at the typical behavior of a correlation function, we see that the correlation function is actually always decays, and it should be, it should always decay, why it should decay, because, I start with an initial function $\psi(x,0)$ and I am trying to correlate with a function at later time $\psi(x,t)$. So, it is quite obvious that at later time this function will be moving away from the initial function and if it is moving away, then effective overlap will go down slowly.

So, correlation function, time domain correlation function will always decay, but nature of the decay has characteristic timescales. There are three different kind of decays are will be going on in the, it can be 1, it can be 2, but this particular examples we have, we are giving is 3 different times. So, 3, maximum 3 different possibilities I can see in the correlation function decay, but in some situation I can have only 1 decay. So, we need to define what kind of decays we are talking about.

And depending on the situation I can have 2 different decays, so I can have 3 different decays, I can have 1 decay. So, let us look at what kind of decays we have, but it is quite clear that in the end correlation function has to decay, because more I time more time I spend so, if I start with let us say that, so, if this is your first sorry initial wavepacket and if the final wavepacket is moving away, slowly, then obviously, the overlap between the initial and final is going down and overlap is extent of overlap is representing the c(t) is representing the extent of overlap.

So, that is the correlation function. So, it is quite obvious that it should decay, but nature of the decay will depends on what kind of potential the particle is experiencing and many other factors. This is just an example we have shown in this example we are showing the 3 different decays are possible.

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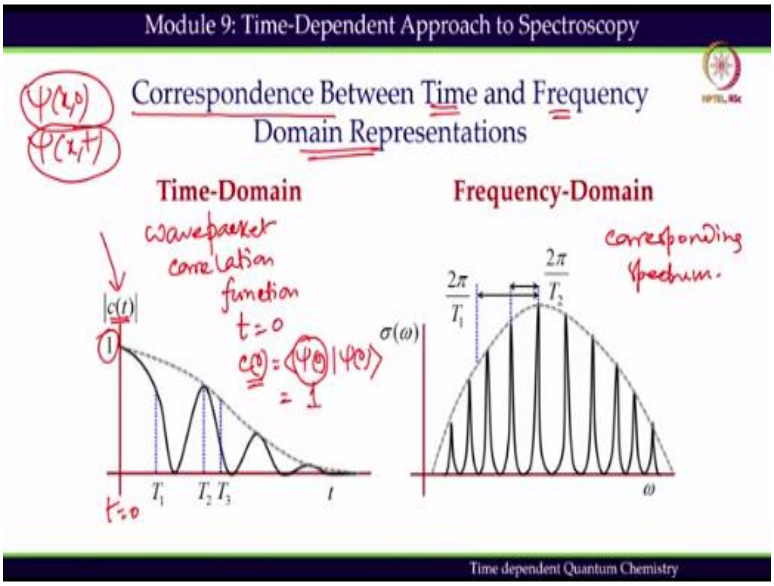

Module 9: Time-Dependent Approach to Spectroscopy

Correspondence Between Time and Frequency Domain Representations

Time-Domain

Frequency-Domain

$\psi(x,0)$

$\psi(x,t)$

wavepacket correlation function

t = 0

$c(0) = \langle \psi(0) | \psi(0) \rangle = 1$

corresponding spectrum.

Time dependent Quantum Chemistry

So, what we are going to look for here the first thing we will take a look at it is that at t = 0, my correlation function is nothing but $c(0) = \langle \psi(0) | \psi(0) \rangle$. I am just have removed the x dependency here for notation only, notational clarity, but it depends on x basically because this integration is over the x, we have to remember, I have just removed this x from this bracket to make it simple.

So, if we look at this correlation function at t = 0, so this is your t = 0 time, we see that this is going to be 1 because this is normalized (see slide figure), we start with normalized wave function, we start with initial normalized wave function, that is the first criteria we have set to solve time dependent Schrodinger equation.

So, because it is normalized, the first, the initial value of the correlation function magnitude would be always 1, there is no exception for that, and which means that from 1 value, unity, it will just decay. Now different ways it can dacay one examples, we have said just three examples we have shown. So, what are the possible decays we can have that is exactly what we are going to take a look at it closely.

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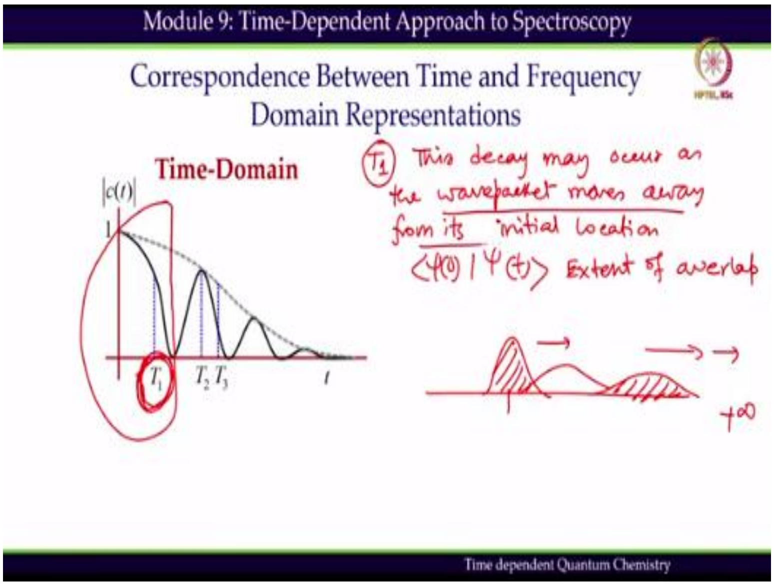

Module 9: Time-Dependent Approach to Spectroscopy

Correspondence Between Time and Frequency Domain Representations

Time-Domain

T_1 This decay may occur as the wavepacket moves away from its initial location

$\langle \psi(0) | \psi(t) \rangle$ Extent of overlap

Time dependent Quantum Chemistry

Initial decay of c(t) may correspond to the timescale T_1 so I can have a timescale T_1 and what is this timescale? We will mention that, this decay, so this is 1 decay associated with this T_1 timescale. Now, this decay occurs, this decay may occur as the wevepacket moves away from its initial location. So, because this $\langle \psi(0) | \psi(t) \rangle$, again, I have removed this x dependency here for clarity, that is all, but it is the integration over the space the $\langle \psi(0) | \psi(t) \rangle$, it is the it representing the extent of overlap, extent of overlap.

So, it is extent of overlap between the initial and the final wavepackets and as a result, as the wavepacket moves away from its initial location in position space, it is actually moving away. So, my initial position wavepacket was this and then at a later time, it is like this, it is like this, it is moving away. Because it is moving away, the overlap between the initial wavepacket and the final wavepacket is we are losing that overlap, and that is why it should decay.

So, this decay is quite inherent decay of the time correlation function. It should decay because, so, in I can have a situation where I have only this part, for a, for a given system where correlation function just decays. There is no other reoccurrence, like the examples we have given here, this is just a generic view. So, I can have no reoccurrence. So, the wavepacket is actually moving away from this initial position to let us say $+\infty$ it is moving away.

If it is moving away, then there is no reoccurrence. And we will have only characteristic timescale of the of this decay time of this decay inherent decay, this decay occurs because the wavepacket moves away from its initial location. So, this is one type of decay we can have.

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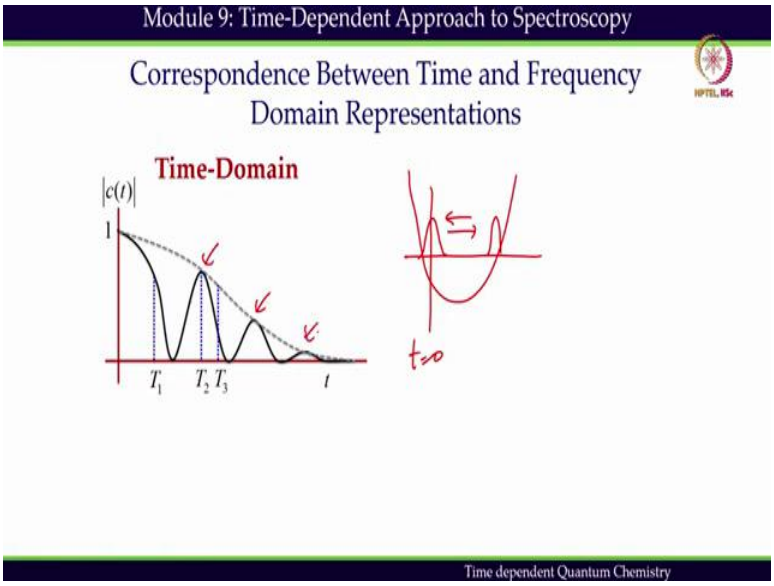

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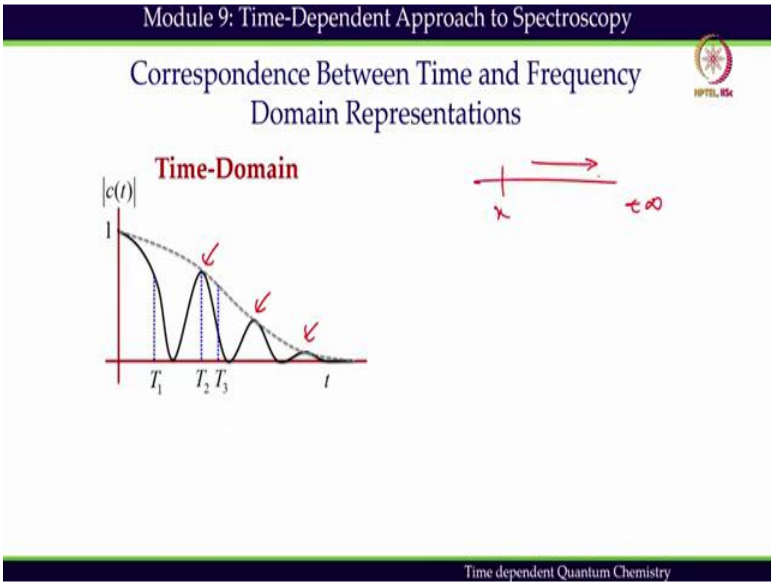
Correspondence Between Time and Frequency Domain Representations

Time-Domain

Time dependent Quantum Chemistry



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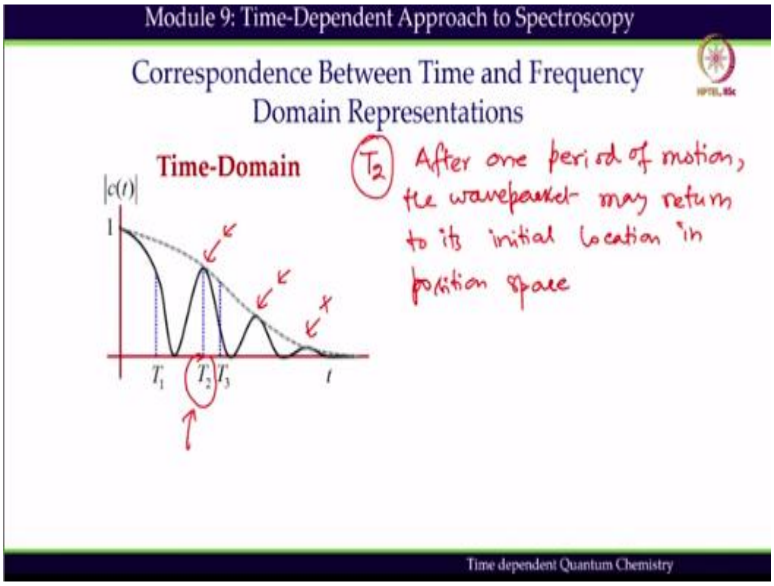

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Correspondence Between Time and Frequency Domain Representations

Time-Domain

T_2 After one period of motion, the wavepacket may return to its initial location in position space

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Another situation, we may have where after one period of motion and that is happening particularly in this kind of harmonic potential where I have a wavepacket here, it can go and it can come here and again it can come back and if it is coming back, my starting point was here (see slide figure). So, it is actually again having higher overlap. So, this is the reoccurrence I can have and if I have reoccurrence, then this is another situation it is not that for all wavepacket will have a reoccurrence.

Let us say I have a particle, free particle moving from $x = 0$ position to $+\infty$,it is actually moving away from the wavepacket. So, it will just decay if there is no reoccurrence. But, if it is in the harmonic potential kind of thing, then it can reoccur. So, the situation I can have another situation which will be defined by the characteristic times equal T_2, after one period of motion the wavepacket may return to its initial location in position space and if that happens, then what will happen?

I will have a reoccurrence of c(t), just like here, what you are seeing here it is reappearing for three times. And this reoccurrence time is defined by this T_2. So, this is the time of the reoccurrence time which is characterised by T_2 time.

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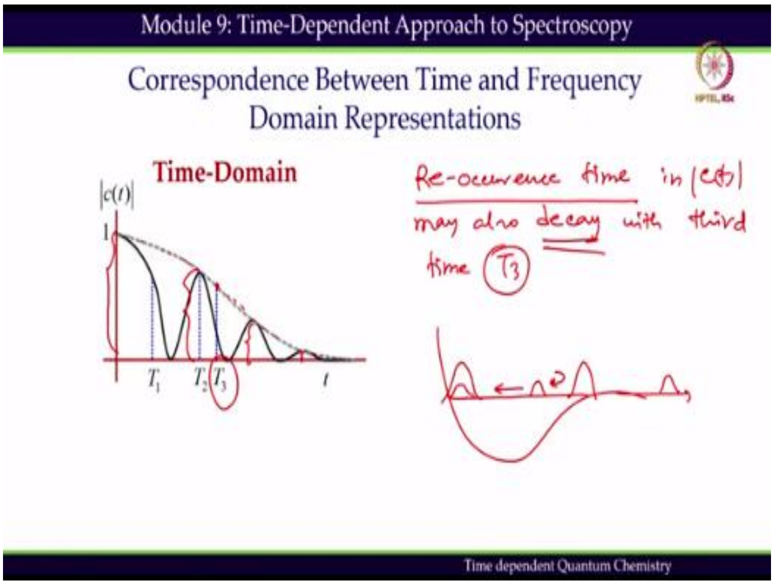


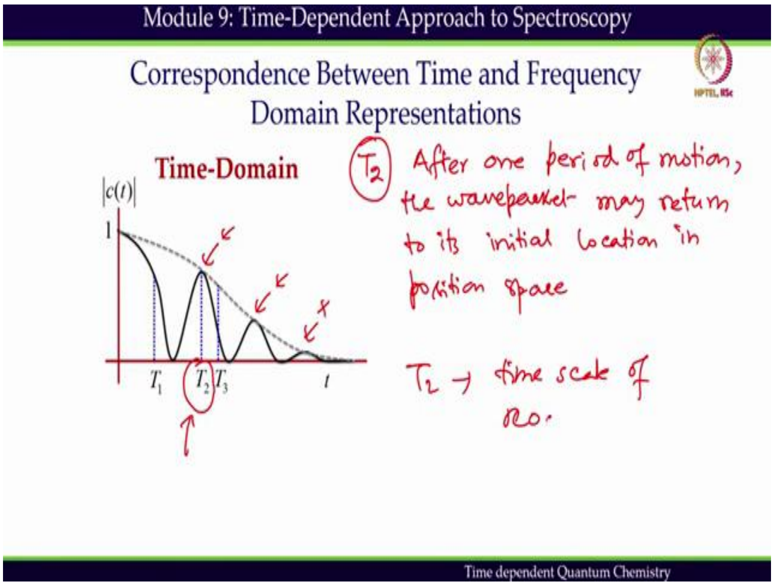
Module 9: Time-Dependent Approach to Spectroscopy

Correspondence Between Time and Frequency Domain Representations

Time-Domain

Re-occurence time in |c(t)| may also decay with third time T_3

Time dependent Quantum Chemistry



Module 9: Time-Dependent Approach to Spectroscopy

Correspondence Between Time and Frequency Domain Representations

Time-Domain

T_2 After one period of motion, the wavepacket may return to its initial location in position space

T_2 → time scale of RO.

Time dependent Quantum Chemistry

We can have another situation when there is a reoccurrence of the wavepacket, then I may have another situation the situation is following this reoccurrence time, when it is reoccurring, reoccurrence time in c(t) may also decay with third timescale.

These are the all possibilities it is not necessary that our quantum system has to follow always this, there is a third timescale I can have T_3 where reoccurrence is decaying as you can see this amplitude the first amplitude was 1, the reoccurrence first reoccurrence amplitude is less, second reoccurrence amplitude has less has become less and third reoccurrence amplitude has less amplitude.

So, it is slowly decaying this reoccurrence time is decaying and if it is decaying, then this particular decay is defined by this dotted line…. and this decay will have a characteristic timescale and this characteristic timescale I can call it as T_3, one can define that characteristic timescale as full width a half max (FWHM) at the time when the decay has gone to the amplitude of half of the maximum or it can be defined by some other characteristic timescale but that will have a timescale characteristics timescale that is T_3 and this is because of the reoccurrence decay, decay of the reoccurrence.

T_2 was just time of reoccurrence timescale of occurrence. So, how quickly it is reoccurring, that timescale is T_2 and how quick how quickly this reoccurrence is decaying that is defined by T_3. So, this kind of decay can possible, is possible in an harmonic kind, not harmonic, anharmonic oscillator where things can decay slowly due to dissociation, let us say so, I am here.

So, I can have a situation like this which is going this way, but when and then part of the wave function is going away and second part of the wavefunction is coming back and that is why we can have a less overlap and we can have a decay in the time correlation function. So, this is also possible. So, these are the three possibilities we have possible possibilities for the decay timescale of the time correlation functions we have shown.

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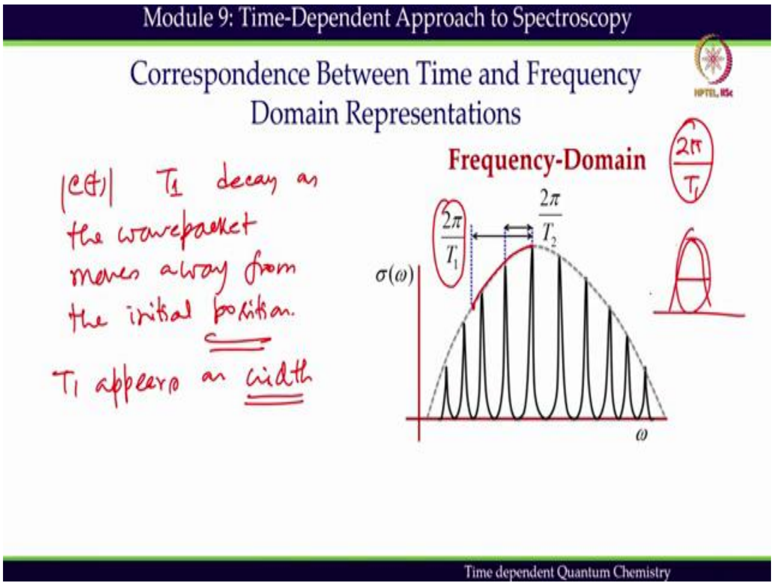


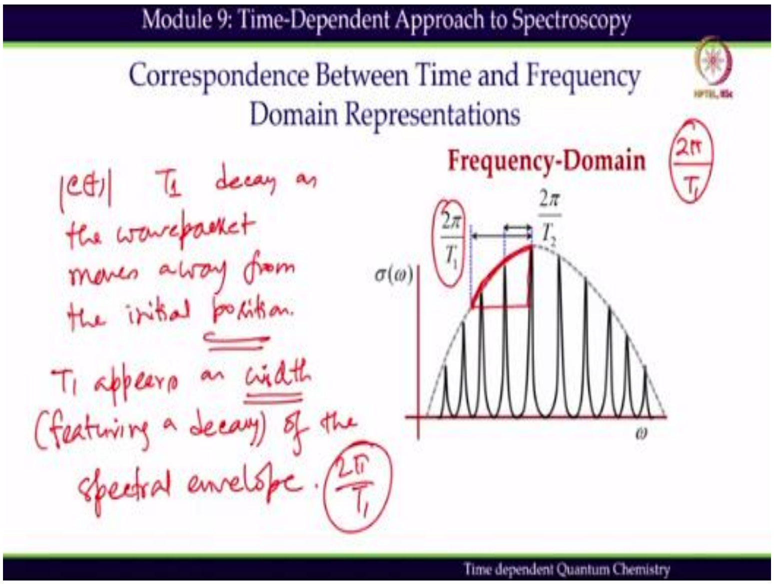
Module 9: Time-Dependent Approach to Spectroscopy

Correspondence Between Time and Frequency Domain Representations

$|c(t)|$ T_1 decay as the wavepacket moves away from the initial position.

T_1 appears as width

Time dependent Quantum Chemistry



Module 9: Time-Dependent Approach to Spectroscopy

Correspondence Between Time and Frequency Domain Representations

Frequency-Domain

$|c(t)|$ T_1 decay as the wavepacket moves away from the initial position.

T_1 appears as width (featuring a decay) of the spectral envelope. $\frac{2\pi}{T_1}$

$\frac{2\pi}{T_1}$

Time dependent Quantum Chemistry

We will take a look at now what are the possibilities I can have for the frequency domain. So, those timescales which we have defined all the, in the time domain, how does it look like in the frequency domain, and we will see that always there is a close correspondence between time and frequency domain. The first, if we recall that the first decay of c(t) we have characterized as the timescale T_1, which is the decay as the wavepacket moves away from the initial position.

So, that is the way in the time domain we have understood that decay time. Here, we will have that time will have will correspond to some frequency and that frequency is going to be represented by $\frac{2\pi}{T_1}$ that frequency is given by this decay in the spectrum and this part is going to represent that T_1 decay time. Now, T_1 decay time has to be represented in the time domain, in the frequency domain we will call it this T_1, T_1 appears as width and remember width is also features a decay.

So, when we think about a width, this width is actually featuring how things are decaying. So, width and decay they are synonymous in this problem. So, we will call it width or decay featuring a decay, but mostly decay we consider in the time domain and in the frequency domain it is decay because it is decaying, but we call it with in terms of width. So, T_1 appears as width of the spectral envelope. So, what we get is that $\frac{2\pi}{T_1}$ this is representing the width of the spectral envelope. So, T_1 is appearing as a, as the width of the spectral envelope in the frequency domain.

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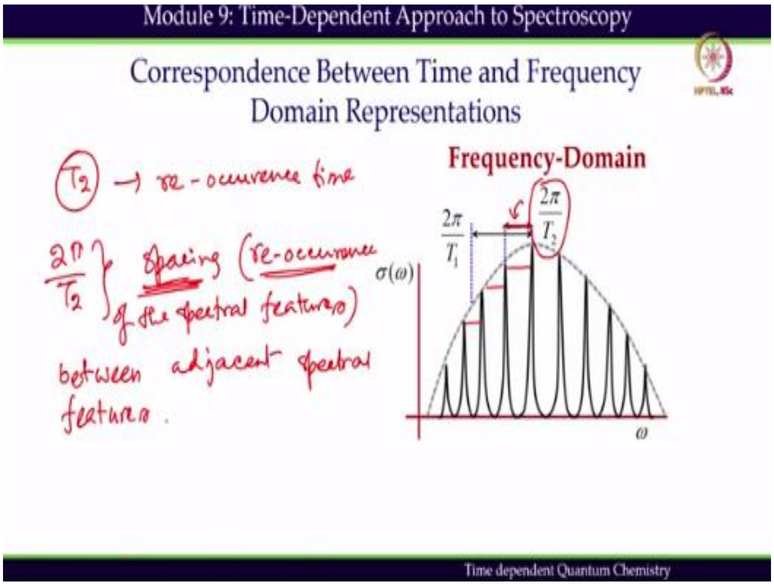

Module 9: Time-Dependent Approach to Spectroscopy

Correspondence Between Time and Frequency Domain Representations

T_2 → re-occurrence time

$\frac{2\pi}{T_2}$ } Spacing (re-occurrence of the spectral features) between adjacent spectral features.

Frequency-Domain

Time dependent Quantum Chemistry

What about T_2, what we have defined T_2, this T_2, reoccurrence time we have reoccurrence time as T_2, reoccurrence time of T_2 in time domain. So, that T_2 will correspond to the spacing. So, in the time, in the frequency domain it is going to be $\frac{2\pi}{T_2}$ and $\frac{2\pi}{T_2}$ is going to correspond to the spacing which is nothing but spacing but when you say spacing between two spectral lines, the spacing between two spectral line when you says spacing it is actually representing the reoccurrence of the spectral features here. So, there is a direct correspondence between these two, reoccurrence of the spectral features.

So, it is going to control this $\frac{2\pi}{T_2}$ is going to control the spacing between adjacent spectral features so, this is what we have shown, this part is going to represent, this arrow is going to represent, this spacing is going to represent $\frac{2\pi}{T_2}$. So, it is showing the reoccurrence of the spectral features, but reoccurrence this terminology we use in the time domain, in the frequency domain we call it the spacing the spectral how does spectrum are, spectral features are separated in the frequency domain.

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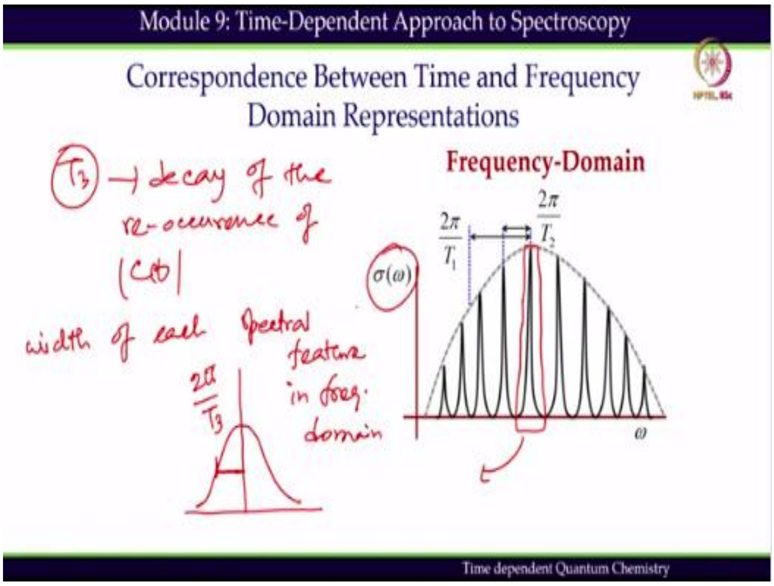

Module 9: Time-Dependent Approach to Spectroscopy

Correspondence Between Time and Frequency Domain Representations

T_3 → decay of the re-occurrence of $|C(t)|$

width of each spectral feature in freq. domain

$\frac{2\pi}{T_3}$

Frequency-Domain

Time dependent Quantum Chemistry

The third timescale, we talked about T_3, which is the decay in the time domain it was associated with decay of the reoccurrence features of c(t) that was the meaning in time domain. In the frequency domain, what it does mean? It means that this T_3 appears as the width again width is decay in the time domain of each spectral feature in the frequency domain.

So, this part I have to magnify. So, I will magnify this part first, I will magnify this entire spectrum spectral features, I will magnify it, it will be like this and this T_3 is indicating how, what is the width of each spectral feature, this is $\frac{2\pi}{T_3}$. So, in the frequency domain this what you call T_3 in time domain it is going to be frequency, in the frequency domain is going to be $\frac{2\pi}{T_3}$ and $\frac{2\pi}{T_3}$ is going to be again the width of each spectral feature in the frequency domain.

Now, it is not necessary that width will be same for each spectral feature, in that case you will have more number of timescale and each timescale in the time domain is now going to correspond to the 2 pi by that time in the frequency domain and that is the way we get the close correspondence between the time domain and frequency domain representation. Time domain representation of the correlation function and frequency domain representation of that correlation function, which is nothing but the, the spectrum.

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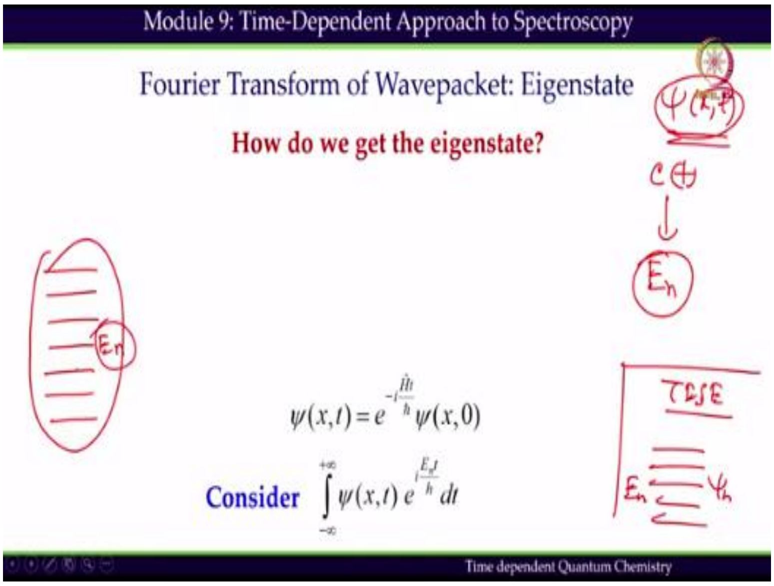


Module 9: Time-Dependent Approach to Spectroscopy

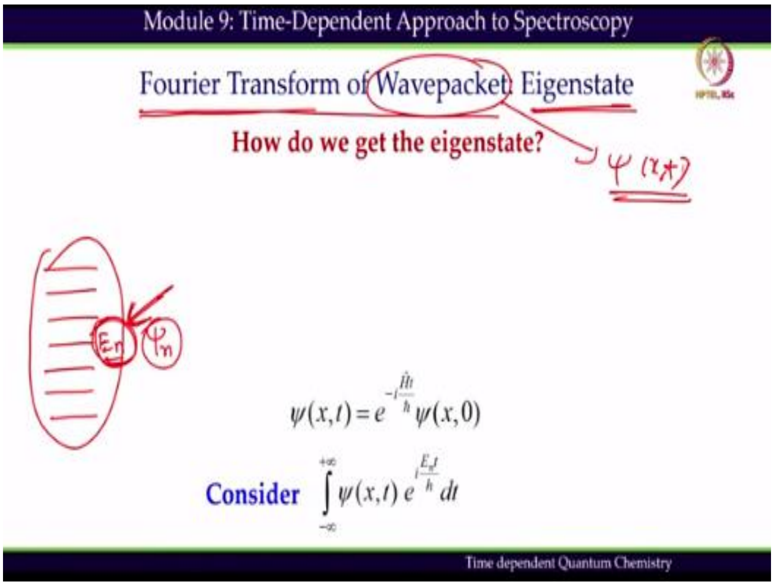
Fourier Transform of Wavepacket: Eigenstate

How do we get the eigenstate?

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

Consider $\int_{-\infty}^{+\infty} \psi(x,t)\, e^{i\frac{E_n t}{\hbar}}\, dt$

Time dependent Quantum Chemistry



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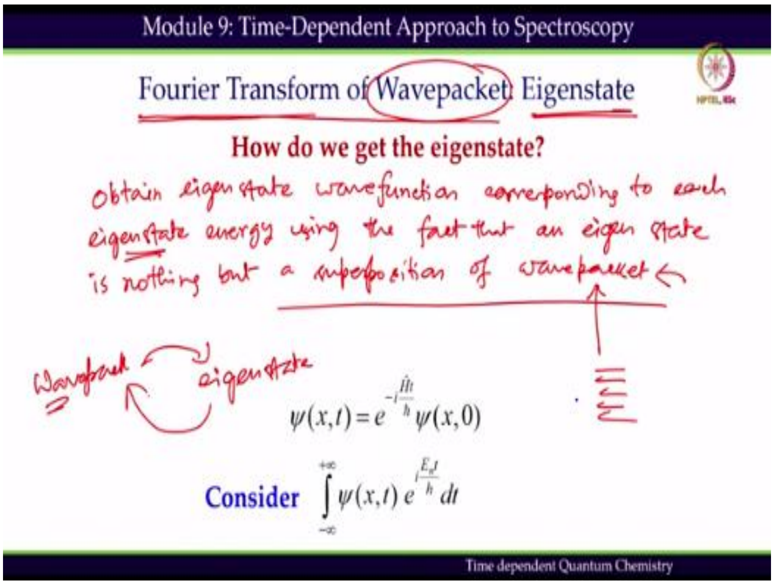
Time dependent Quantum Chemistry



Module 9: Time-Dependent Approach to Spectroscopy

Fourier Transform of Wavepacket: Eigenstate

How do we get the eigenstate?

obtain eigenstate wavefunction corresponding to each eigenstate energy using the fact that an eigen state is nothing but a superposition of wavepacket

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

Consider $\int_{-\infty}^{+\infty} \psi(x,t)\, e^{i\frac{E_n t}{\hbar}}\, dt$

Time dependent Quantum Chemistry

So, what we have realized that if I know the correlation functions c(t), I will be able to get to know its Eigen state energies. So, I will be able to explore the eigen state energies of a system. All I need to do is that I have to play with the propagation of the wave function. I can start with this a particular wave function and then I have to propagate it for a long time or convenient time so that I can see, I can include the eigen state energies of interest.

But then question is once we get these Eigen states, I would like to know because TISE will give me if I solve TISE, it will give me Eigen states and Eigen functions. So, E_n $\psi(x,t)$ both will be getting back from TISE. Now, so far with the help of TDSE, I have been able to get this Eigen state energies, question is what is the function we get, Eigen state function?

And for that we have to go over another, we have to explore another realisation that the Fourier transform of the wavepacket at that Eigen state so, if I am interested to find out the Eigen state wave function associated with the Eigenvalue E_n, I want to find out ψ_n, then all I need to do is that Fourier transform of the wavepacket, wavepacket is $\psi(x,t)$. That is the packet I have. I have to Fourier transform that wavepacket at that energy E_n energy to get that Eigen state that is the basic idea.

$$\psi(x,t) = e^{-iHt/\hbar}\psi(x,0),$$
$$consider \int_{-\infty}^{+\infty} \psi(x,t) e^{iE_n t/\hbar}\, dt$$

So, I will first prove this idea whether this is mathematically justified or not. So, bottom line what we are trying to make here is that one may obtain Eigen state wavefunction corresponding to each Eigen state energies, each Eigen state energy using the fact that an Eigen state is nothing but a superposition of wavepacket. This is an interesting statement. So far, we have seen that wavepacket is created by taking superposition of stationary states.

Similarly, there is another theory which can be proved that if we take the linear combination of the wavepacket I get back the Eigen state. So, both are possible. So, wavepacket to Eigen state conversion is possible by taking linear combination of the wavepacket and I can again, wavepacket can be constructed by taking a linear combination of the Eigen states both are possible.

One possibility we have already seen combining eigen states we have created wavepacket in many occasions. And but the reverse we have not seen and we will check this reverse is true for getting the Eigen state.

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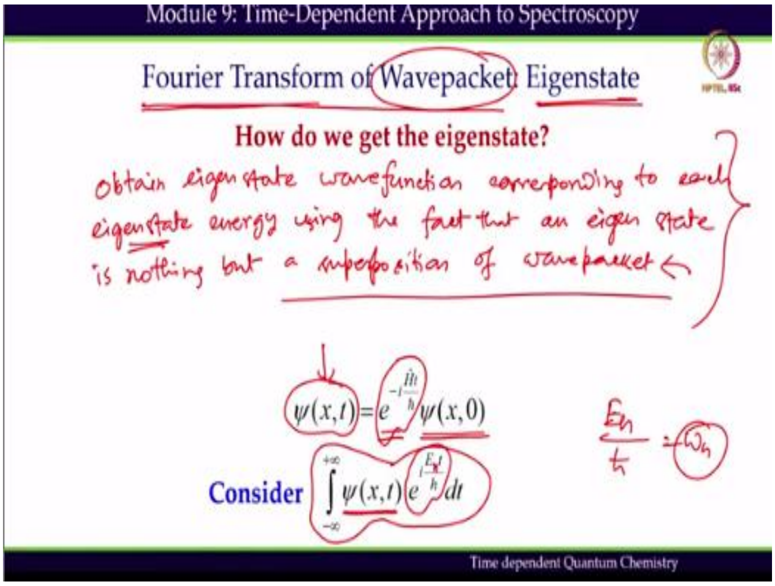

Module 9: Time-Dependent Approach to Spectroscopy

Fourier Transform of Wavepacket: Eigenstate

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obtain eigenstate wavefunction corresponding to each eigenstate energy using the fact that an eigen state is nothing but a superposition of wavepacket

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

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

Consider $\int_{-\infty}^{+\infty}\psi(x,t)\,e^{i\frac{E_n t}{\hbar}}\,dt$

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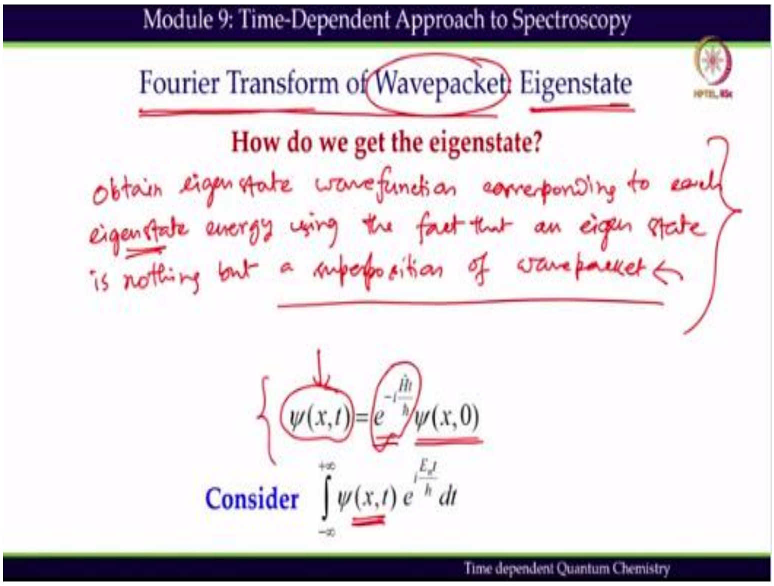

Module 9: Time-Dependent Approach to Spectroscopy

Fourier Transform of Wavepacket: Eigenstate

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Consider $\int_{-\infty}^{+\infty}\psi(x,t)\,e^{i\frac{E_n t}{\hbar}}\,dt$

Time dependent Quantum Chemistry

We have already seen that time evolution operator can give me $\psi(x,t)=e^{-iHt/\hbar}\psi(x,0)$, $\psi(x,t)$ time evolution operator, this is represented by this exponential operator, this part can give me the wave function at time t, if I know the initial wavefunction $\psi(x,0)$. So, we will make use of this time evolution operator and we will try to find out what we try to mean here.

So, for that we have to consider this integration what is the meaning of this integration we will get to know later not now, we just move forward with this integration. This integration, this is very interesting integration, this integration is in mathematical language this integration is nothing but getting a Fourier transform of this wavepacket at time t at the energy E_n we have considered E_n energy.

$consider \int_{-\infty}^{+\infty} \psi(x,t) e^{iE_n t/\hbar} dt$,I am taking the Fourier transform. So, that is the meaning of this integration, but instead of finding out the meaning of this integration, we can just move forward with this integration and we try to understand the meaning of this integration and this $\psi(x,t)$ will be represented in terms of the time evolution operator.

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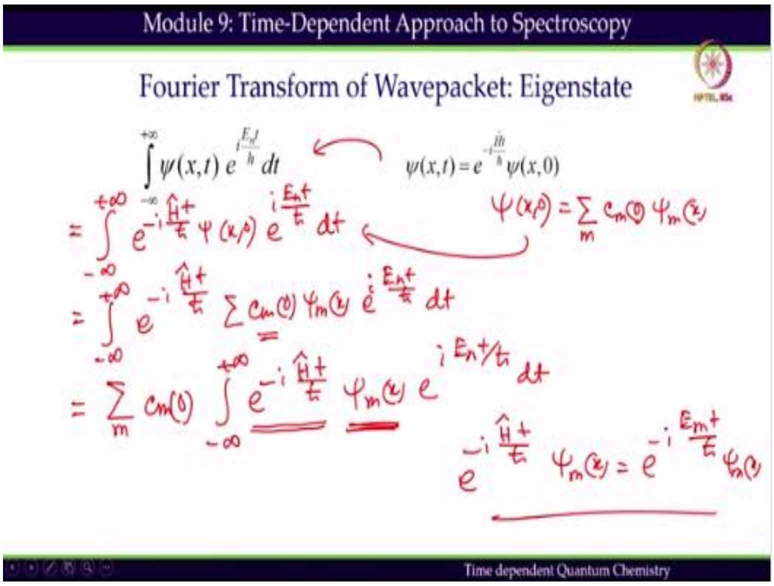

Module 9: Time-Dependent Approach to Spectroscopy

Fourier Transform of Wavepacket: Eigenstate

$$\int_{-\infty}^{+\infty} \psi(x,t)\, e^{i\frac{E_n t}{\hbar}} dt \qquad \psi(x,t) = e^{-i\frac{\hat{H}t}{\hbar}} \psi(x,0)$$

$$= \int_{-\infty}^{+\infty} e^{-i\frac{\hat{H}t}{\hbar}} \psi(x,0)\, e^{i\frac{E_n t}{\hbar}} dt \qquad \psi(x,0) = \sum_m c_m(0) \psi_m(x)$$

$$= \int_{-\infty}^{+\infty} e^{-i\frac{\hat{H}t}{\hbar}} \sum \underline{\underline{c_m(0)}} \psi_m(x)\, e^{i\frac{E_n t}{\hbar}} dt$$

$$= \sum_m c_m(0) \int_{-\infty}^{+\infty} \underline{\underline{e^{-i\frac{\hat{H}t}{\hbar}}}} \underline{\underline{\psi_m(x)}}\, e^{iE_n t/\hbar} dt$$

$$e^{-i\frac{\hat{H}t}{\hbar}} \psi_m(x) = e^{-i\frac{E_m t}{\hbar}} \psi_m(x)$$

Time dependent Quantum Chemistry

So, we will do that we will insert that expressions $\psi(x,t)$ into this integration and we will see that it is we have to insert it and we insert $\int_{-\infty}^{+\infty} \psi(x,t) e^{iE_n t/\hbar} dt = \int_{-\infty}^{+\infty} e^{-iHt/\hbar} \psi(x,0) e^{iE_n t/\hbar} dt$

Now, this $\psi(x,0)$, we have already seen that this can be expanded in terms of the Eigen functions like this. It does not have the time dependent face factor because t = 0. So, this expansion we have already done. So, we will insert this expansion here. If we insert it $\psi(x,0) = \sum_m c_m(0) \psi_m(x)$, then what I get is. Or this is not time dependent.

So, I will be able to take it out and if I take it out, then what I get is $\int_{-\infty}^{+\infty} \psi(x,t) e^{iE_n t/\hbar} dt = \int_{-\infty}^{+\infty} e^{-iHt/\hbar} \psi(x,0) e^{iE_n t/\hbar} dt = \sum_m c_m(0) \int_{-\infty}^{+\infty} e^{-iHt/\hbar} \psi_m(x) e^{iE_n t/\hbar} dt$

And $e^{-iHt/\hbar} \psi_m(x) = e^{-iE_m t/\hbar} \psi_m(x)$

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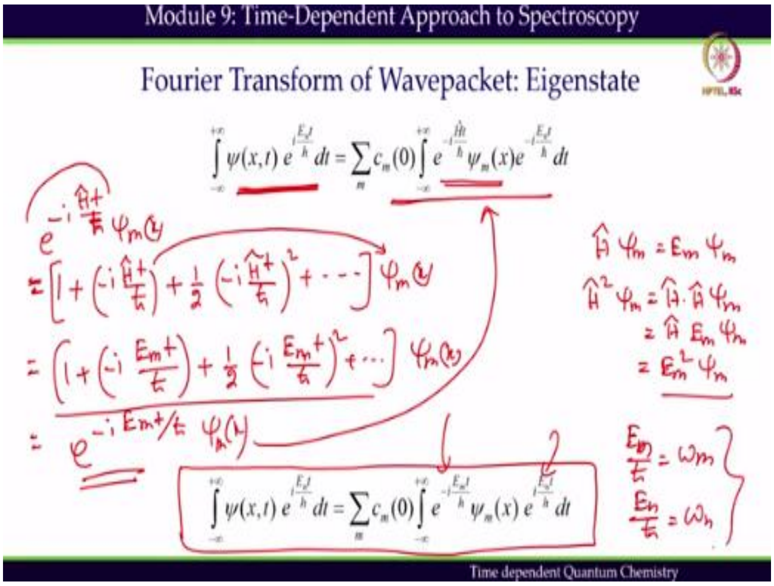

Module 9: Time-Dependent Approach to Spectroscopy

Fourier Transform of Wavepacket: Eigenstate

$$\int_{-\infty}^{+\infty} \psi(x,t)\, e^{i\frac{E_n t}{\hbar}}\, dt = \sum_m c_m(0) \int_{-\infty}^{+\infty} e^{-i\frac{\hat{H}t}{\hbar}} \psi_m(x) e^{-i\frac{E_n t}{\hbar}}\, dt$$

$$e^{-i\frac{\hat{H}t}{\hbar}} \psi_m(x) = \left[1 + \left(-i\frac{\hat{H}t}{\hbar}\right) + \frac{1}{2}\left(-i\frac{\hat{H}t}{\hbar}\right)^2 + \cdots\right]\psi_m(x)$$

$$= \left(1 + \left(-i\frac{E_m t}{\hbar}\right) + \frac{1}{2}\left(-i\frac{E_m t}{\hbar}\right)^2 + \cdots\right]\psi_m(x)$$

$$= e^{-iE_m t/\hbar}\, \psi_m(x)$$

$$\boxed{\int_{-\infty}^{+\infty} \psi(x,t)\, e^{i\frac{E_n t}{\hbar}}\, dt = \sum_m c_m(0) \int_{-\infty}^{+\infty} e^{-i\frac{E_m t}{\hbar}} \psi_m(x)\, e^{i\frac{E_n t}{\hbar}}\, dt}$$

$$\hat{H}\psi_m = E_m \psi_m$$

$$\hat{H}^2\psi_m = \hat{H}\cdot\hat{H}\psi_m = \hat{H}E_m\psi_m = E_m^2\psi_m$$

$$\left.\begin{aligned}\frac{E_m}{\hbar} &= \omega_m\\ \frac{E_n}{\hbar} &= \omega_n\end{aligned}\right\}$$

Time dependent Quantum Chemistry

So, this integration this is what we started with is nothing but now this integration as we have taken the time evolution operator and now we will be able to prove that $e^{-iHt/\hbar}\psi_m(x) = e^{-iE_mt/\hbar}\psi_m(x)$, this time evolution operator can be very easily find out what is the value.

And in order to find out the value, we will use the Taylor series expansion that we have always done for the time evolution operator because in an exponential operator, we take the Taylor series expansion and we get

$$e^{-iHt/\hbar}\psi_m(x) = \left[1 + (-iHt/\hbar) + \frac{(-iHt/\hbar)^2}{2} + \ldots.\infty\right]\psi_m(x),.$$

And if we and we see that if this operator is acting on t $H\psi_m(x) = E_m\psi_m(x)$,

that is the time independent Schrodinger equation. Similarly, $H^2\psi_m(x) = HH\psi_m(x) = HE_m\psi_m(x) = E_m^{\,2}\psi_m(x)$. So, what I get here this is nothing

$$e^{-iHt/\hbar}\psi_m(x) = \left[1 + (-iE_mt/\hbar) + \frac{(-iE_mt/\hbar)^2}{2} + \ldots.\infty\right]\psi_m(x) = e^{-iE_mt/\hbar}\psi_m(x)$$

So, what we have done, we have proved that this part, this part can be written in terms of the, this is simplified form and as a result we get this form where we do not have time evolution operator we have now time dependent phase factors, these two time dependent phase factors, because we going to insert this one here and we get the time dependent phase factor. Once we get this time dependent phase factor we know that $\frac{E_m}{\hbar} = \omega_m$ and $\frac{E_n}{\hbar} = \omega_n$. So, we can insert that.

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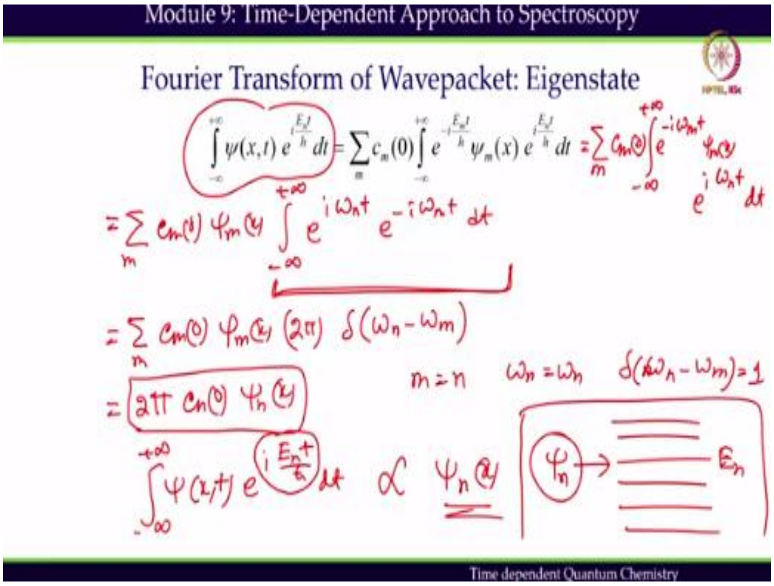

Module 9: Time-Dependent Approach to Spectroscopy

Fourier Transform of Wavepacket: Eigenstate

$$\int_{-\infty}^{+\infty}\psi(x,t)\,e^{i\frac{E_n t}{\hbar}}dt = \sum_m c_m(0)\int_{-\infty}^{+\infty} e^{-i\frac{E_m t}{\hbar}}\psi_m(x)\,e^{i\frac{E_n t}{\hbar}}dt = \sum_m c_m(0)\int_{-\infty}^{+\infty} e^{-i\omega_m t}\,\psi_m(x)\,e^{i\omega_n t}dt$$

$$= \sum_m c_m(0)\,\psi_m(x)\underbrace{\int_{-\infty}^{+\infty} e^{i\omega_n t}\,e^{-i\omega_n t}\,dt}$$

$$= \sum_m c_m(0)\,\psi_m(x)\,(2\pi)\,\delta(\omega_n-\omega_m)$$

$$= \boxed{2\pi\, c_n(0)\,\psi_n(x)}$$

$m = n \quad \omega_n = \omega_n \quad \delta(\omega_n-\omega_m) = 1$

$$\int_{-\infty}^{+\infty}\psi(x,t)\,e^{\boxed{i\frac{E_n t}{\hbar}}}dt \propto \underline{\underline{\psi_n(x)}}$$

$\psi_n \rightarrow E_n$

Time dependent Quantum Chemistry

And what we get here is that this part is nothing

$$\int_{-\infty}^{+\infty}\psi(x,t)e^{iE_n t/\hbar}dt = \sum_m c_m(0)\int_{-\infty}^{+\infty} e^{-iHt/\hbar}\psi_m(x)e^{iE_n t/\hbar}dt = \sum_m c_m(0)\int_{-\infty}^{+\infty} e^{-i\omega_m t}\psi_m(x)e^{i\omega_n t}dt$$

$$= \sum_m c_m(0)\psi_m(x)\int_{-\infty}^{+\infty} e^{i\omega_n t}e^{-i\omega_m t}dt = \sum_m c_m(0)\psi_m(x)(2\pi)\delta(\omega_n-\omega_m) = 2\pi c_n(0)\psi_n(x)$$

Only term exists when $m = n, \omega_n = \omega_m, \delta(\omega_n - \omega_m) = 1$, all other terms is going to be 0.

So, that is why it is summation will end up with this simplified form and what is the simplified form? We have seeing that we actually calculating this integration. So, what we are getting this integration $\int_{-\infty}^{+\infty}\psi(x,t)e^{iE_n t/\hbar}dt \propto \psi_n(x)$. What is $\psi_n(x)$? $\psi_n(x)$ is the Eigen state, this is the Eigen state with functions $\psi_n(x)$ and I am doing this Fourier transform at E_n.

So, corresponding to our Eigen value, I am now getting an Eigen state wavefunction and that is exactly what we wanted to do because TISE has given me these two informations together now, I am looking at through TDSE and through TDSE we are now seeing that the Fourier transform of the wavepacket at the energy.

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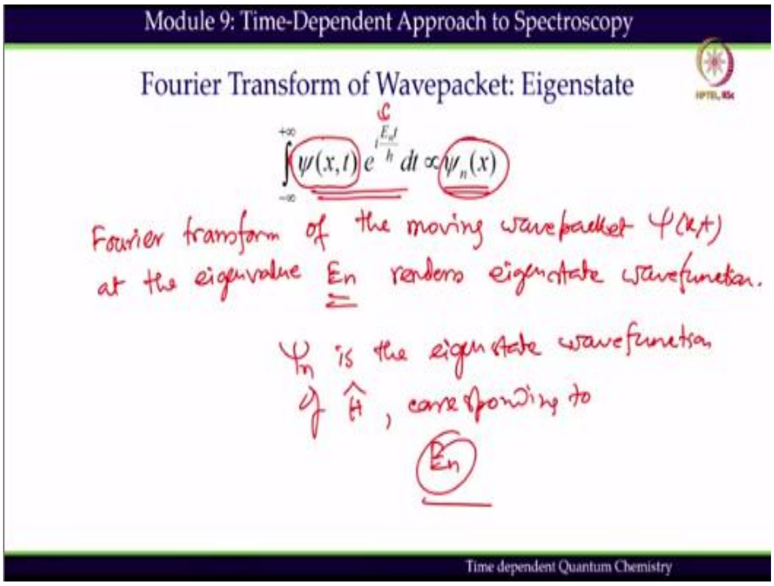

Module 9: Time-Dependent Approach to Spectroscopy

Fourier Transform of Wavepacket: Eigenstate

$$\int_{-\infty}^{+\infty} \psi(x,t)\, e^{i\frac{E_n t}{\hbar}}\, dt \propto \psi_n(x)$$

Fourier transform of the moving wavepacket $\psi(x,t)$ at the eigenvalue E_n renders eigenstate wavefunction.

ψ_n is the eigenstate wavefunction of $\hat{H}$, corresponding to E_n

Time dependent Quantum Chemistry

So, the basic idea is that the meaning of this integration is that the Fourier transform of the moving wavepacket which is $\psi(x,t)$ moving wavepacket at the Eigen value E_n is actually giving me renders eigen state wave function. So, if I Fourier transform that entire wavepacket at that energy E_n, then I get back corresponding eigen state wavefunction which is $\psi_n(x)$ and $\psi_n(x)$, here $\psi_n(x)$ is the Eigen state wavefunction of a Hamiltonian corresponding to the eigenstate energy E_n.

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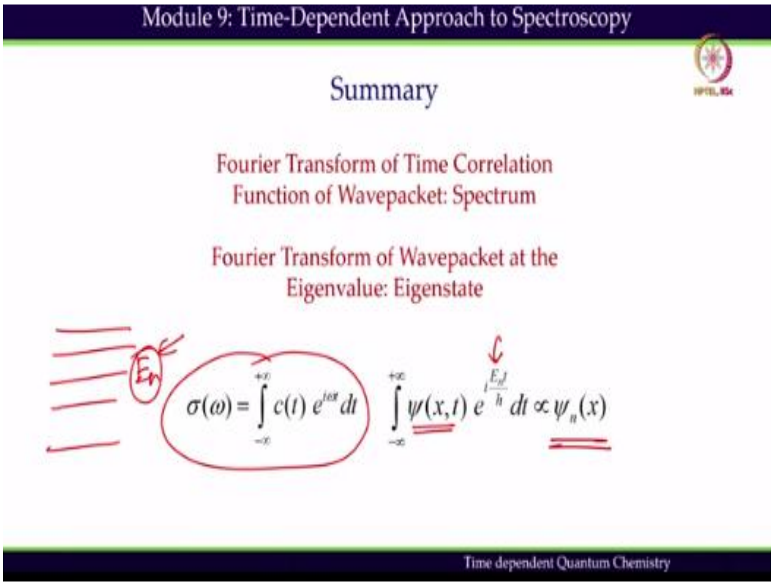

Module 9: Time-Dependent Approach to Spectroscopy

Summary

Fourier Transform of Time Correlation Function of Wavepacket: Spectrum

Fourier Transform of Wavepacket at the Eigenvalue: Eigenstate

E_n

$$\sigma(\omega) = \int_{-\infty}^{+\infty} c(t)\, e^{i\omega t}\, dt \qquad \int_{-\infty}^{+\infty} \psi(x,t)\, e^{i\frac{E_n t}{\hbar}}\, dt \propto \psi_n(x)$$

Time dependent Quantum Chemistry

So, we have come to the end of this module. In this module we have gone over and a very interesting perspective of the TDSE. Generally, we think that TISE I need time independent Schrodinger equation I need to find out the spectrum of a system which is energy level of the system and corresponding eigen states and of wavefunctions.

But, what we see here from this exercise from the in this module that TDSE, solution to TDSE can give me an wavepacket at time t and I can correlate that wavepacket with the initial wavepacket to get the correlation function, time correlation function and Fourier transform of the time correlation function gives the spectrum of the system.

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

And spectrum has all this information energy, level information, E_n information is taken from the spectrum, can be taken from spectrum. On the other hand, the same wavepacket at t equals time t later time t, if I Fourier transform that wavepacket at that particular energy, then I get back the wavefunction corresponding to that Eigen state $\int_{-\infty}^{+\infty} \psi(x,t) e^{iE_n t/\hbar} dt \propto \psi_n(x)$. We will stop here and we will meet again for the next module.