Advanced Mathematical Methods for Chemistry
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Module - 09
Lecture - 05
Recap of Module 9, Practice Problems

Now this will be the fifth lecture of module 9. And in this lecture I will recap module 9 and then we will do some practice problems. The practice problems that I will be doing will actually be related to certain topics in physical chemistry. So, you will see you will see how what we are doing has direct applications in physical chemistry.

So, they will actually be examples that you or they will show you ways to understand something that you learn in your quantum mechanics courses. So, now, let us recap module 9.

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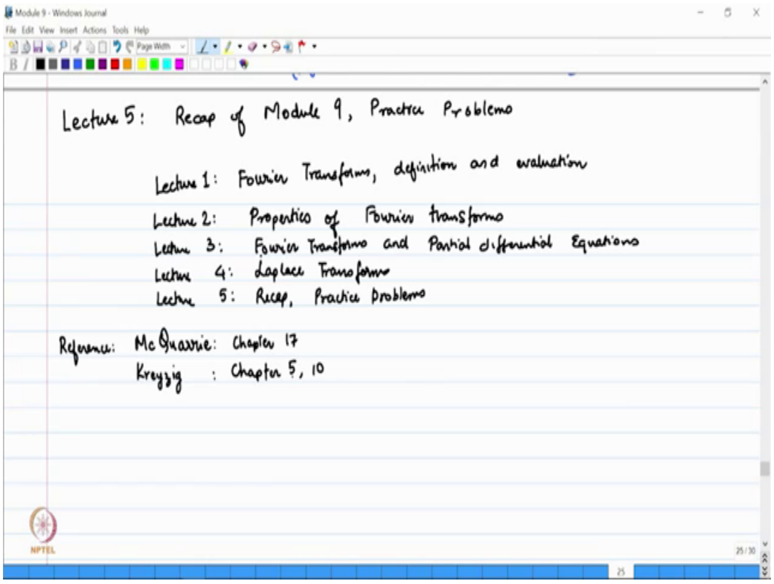

So, in first lecture I talked about Fourier transforms we talked about the definition and how you evaluate them. Then in lecture 2 we looked at various properties of Fourier transforms including things like derivatives shifting etcetera lecture 3 I did Fourier transforms and partial differential equations how you can solve partial differential equations using Fourier transforms in lecture four we looked at Laplace transforms. So, we looked at the other in as one of the other integral transforms and we quickly went through how you can solve problems using Laplace transforms.

So, in today's lecture I am going to do some practice problems. So, the reference in this is nicely covered in my quarry chapter seventeen is dedicated to integral transforms in crazy Laplace transforms has done in chapter 5 and chapter ten has a good description of Fourier transforms. Now, let us go to some practice problems.

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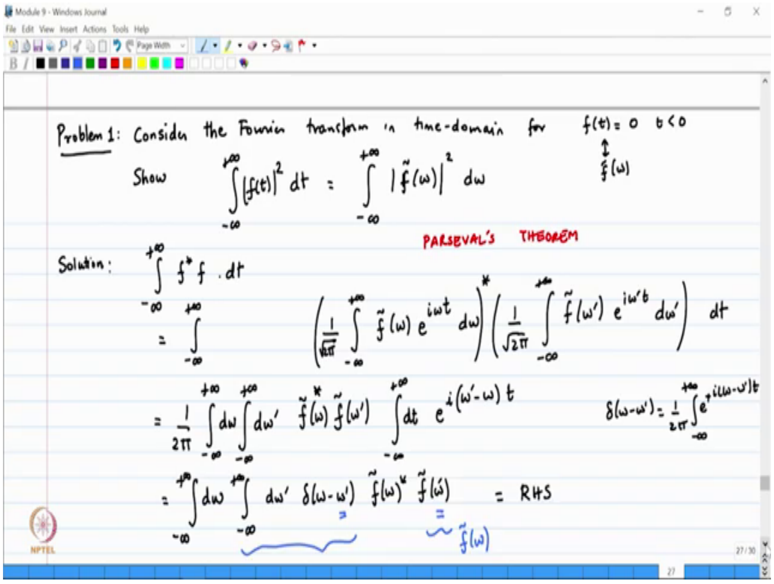

Now, the first problem if this problem is I mean actually what I am trying to show is a very simple theorem, but this has this is of extreme importance to spectroscopy. So, I will illustrate this in a in a few seconds.

So, let us look at the problem. So, the problem says consider the Fourier transform in time domain for a function f of t such that f of t is equal to 0 for t less than 0 and let us say the Fourier transform of this function is f tilde of omega. So, I am using t even though I am do using a Fourier transform. So, now, what I am ask what I am asking you to show is that integral from minus infinity to plus infinity ft square dt is equal to integral from minus infinity to plus infinity f tilde omega square d omega, this is known as Parseval's theorem. So, let us prove this now I am allowing f of t to be complex I am allowing f of t to be complex therefore, I written an absolute modulus square.

Now, if you do this integral what you will what you will get is integral minus infinity to plus infinity and because I said this f of t equal to 0 for t less than 0 that is just 2 because you know we want time domain function a function of time, but you know it is not defined for negative time. So, we just arbitrarily choose it to be 0. So, that the Fourier transform is defined. So, I can write this as f star f dt and on the right hand side I will get. So, this is the left hand side and this is equal to integral minus infinity to plus infinity now if I write the complex.

So, what I am going to try write? I am going to write f as integral minus infinity to plus infinity I will I will write f tilde of omega e to the I omega t d omega. So, this is f now what will f f star be so and I have a I have a 1 by square root of 2 pi. So, this is my f now f star will be complex conjugate of this. So, the complex conjugate of this what I will just put a star here we will evaluate that and then I have 1 by root 2 pi integral minus infinity to plus infinity f tilde. Now what I am going to do is I am going to use a different variable I mean this omega is just a dummy variable it is integrated over. So, let me call it omega prime here e to the I omega prime t d omega prime.

So, this is what this integral looks and what I am going to do is to integrate this over dt. So, this is this is what the total integral looks like now what I can do is I will leave this as it is. So, what I am going to do is the t integration I will take the integration over time inside all these integrals. So, I will just change the order of integration. So, let me have and let me take the 2 pi. So, have 1 over 2 pi and then I have integral minus infinity to plus infinity I have d omega then I have integral minus infinity to plus infinity d omega prime and what I will write is f tilde of omega f tilde of omega prime omega star.

So, I had take the complex conjugate of this. So, I will have a complex conjugate of this and then and then what I have is this multiplied by an integral over minus infinity to plus infinity dt and what I have is e to the I omega prime minus omega, I got the minus omega because I took a complex conjugate t. So now, this quantity this quantity is nothing but a delta function. So, this is like the Fourier transform of 1 which is a delta function. So, it is that is. So, this divided by 2 pi is just delta of omega o minus omega prime. So, we use delta omega minus omega prime is equal to 1 over 2 pi integral minus infinity to plus infinity e to the minus I e e to the plus I omega minus omega prime.

So, you use this relation and. So, this is just we replace by delta of omega minus omega prime and what I will have is 1 over 2 pi I do not have 1 over 2 pi anymore. So, I have integral minus infinity to plus infinity d omega. Now what I have is integral minus infinity to plus infinity d omega prime delta omega minus omega prime f f of omega star f tilde of omega prime. Now I can integrate over omega prime, because using this delta function using this delta delta function I can integrate over omega prime all that will happen is this will become omega omega.

So, I just have f tilde of omega star f tilde of omega which is nothing but the right hand side. So, what you are going to do is you are going to use you are going to do this integral and this integral only omega prime appears only here. So, what you are going to do is this whole integral this whole integral is just replaced by f tilde of omega. So, we just since that is how you do integrals involving the Dirac delta function. So, you get this result.

Now, this is a really interesting result this is actually I want to emphasize a few things about this result.

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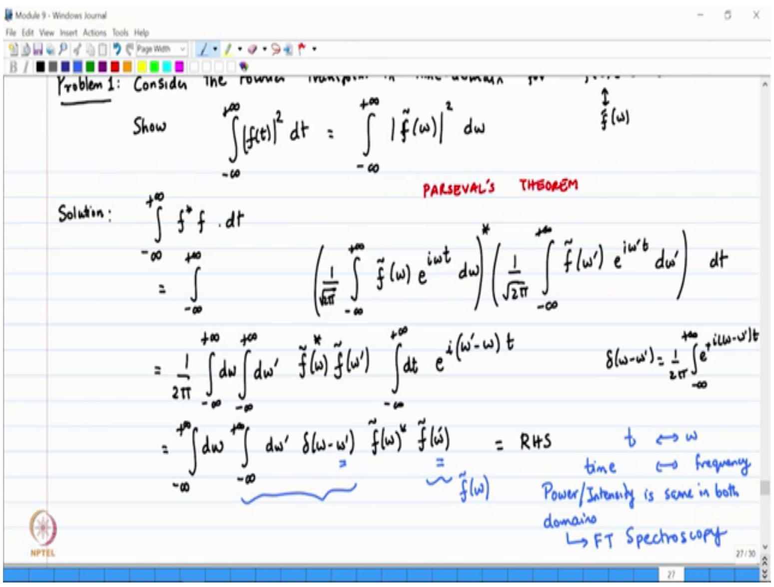

So, what we did is we went from time to omega this is actually from time to frequency and this; what we what we showed is that the total ft square. So, the total square amplitude in time domain is the same as the square amplitude in frequency domain and so this power or intensity is same in both domains.

So, what that means is this really this really opens a door for Fourier transform spectroscopy. So, you can look at the spectrum and frequency domain and convert it to time domain or vice versa and; obviously, doing a Fourier transform in an experimentally it not a straightforward thing. However, there are there are you can make you can make circuits that will convert your signal which will allow you to convert from time domain to frequency domain so, but it is really this Parsable serum that allows you to change your spectrum from a time domain to a frequency domain.

So, what is done for example, is suppose you have a sample and you want to measure its spectrum then what you do is you shine light through it you shine light through it. And see now if you wanted to do in time domain what you will do is you will shine monochromatic light you shine light of one frequency and you will see the absorption then you will shine light of a different frequency. And you will do the absorption it will keep doing this for all frequencies and this is generally a very slow process because you need you need to generate light of only a given frequency and you need to be able to tune that frequency.

So, instead of that what is done is you essentially change to time domain where you generate pulses of light and these pulses actually have a have a combination of frequencies and you shine these pulses and you take pulses of different durations and each pulse, you know the set of frequencies it has and so and so using this using this time domain information you can convert to frequency domain information and you can get the spectroscopy.

So, this is actually this is something that is that has really made spectroscopy much quicker and much more efficient and that is why it is one of the reasons why it is so widely used.

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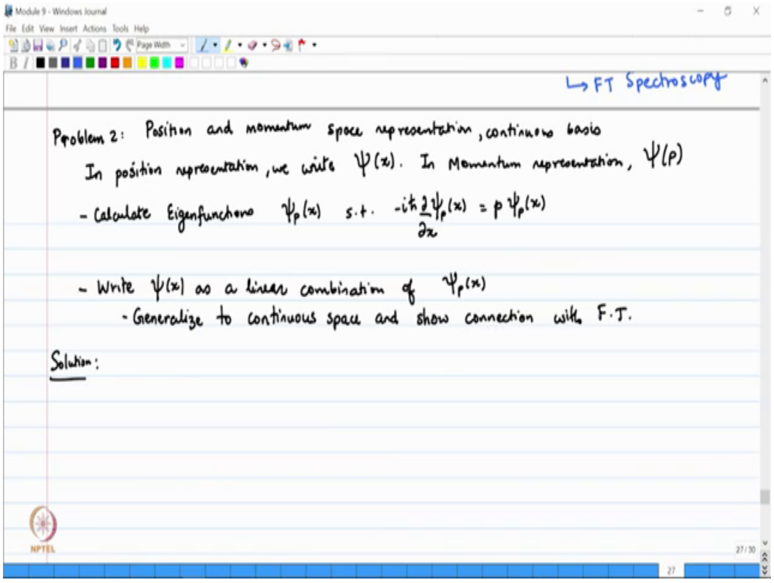

Let us go to the next topic I should emphasize that there are lot more there are lot more details that go into Fourier transform spectroscopy which we will not get into, but essentially it is based on this Parseval's theorem.

Now, the next problem is has to do with position and momentum space representation and continuous basis in quantum mechanics. So, in position representation we write the wave function as a function of position psi of x in momentum representation you write the wave function as a function of momentum in this problem what you do is to calculate Eigen functions of psi of x such that minus i h cross d by dx of psi of x equal to p times ip of x.

So, what a what you are what I am asking to do is to calculate the Eigen functions of the momentum operator in one dimension then write psi x as a linear combination of Eigen functions of momentum operator and generalized to continuous space and show the connection with Fourier transforms. So, let us go ahead and work this out. So, the first part is straightforward this is just a first order differential equation the solution the since a coefficients are constant.

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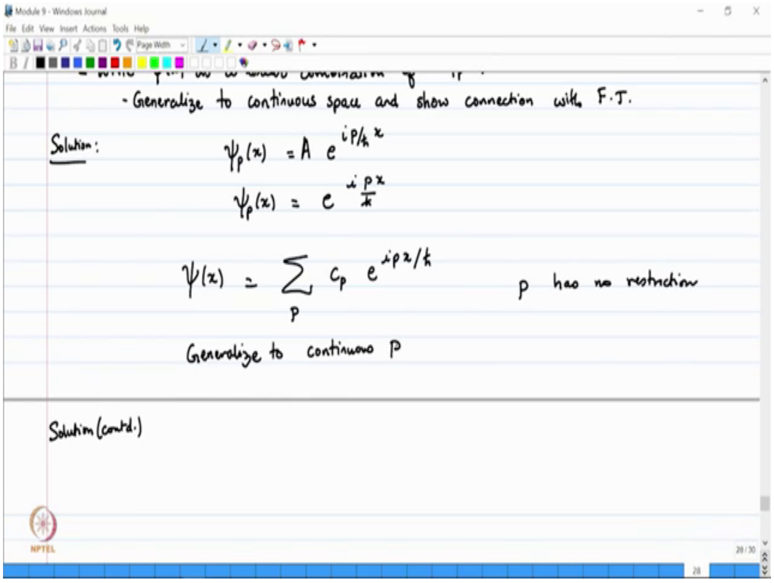

The solution is just e to the ip by h cross x times a constant where the constant is determined by the conditions at x equal to 0. So, this is the solution. So, now, your Eigen functions. So, now, this is just a constant independent of x. So, your Eigen functions are just given by is equal to e to the ipx by h bar. So, you do not need to write this constant in Eigen functions. So, for different values of p you will get different Eigen functions.

Now, we are going to write psi of x is equal to sum over all values of momentum some coefficient which depends on momentum times e to the ipx by h bar at this point p has no restriction. So, it looks like a sum now we suppose we generalize to continuous p then I can write psi of x. So, if p was a continuous variable.

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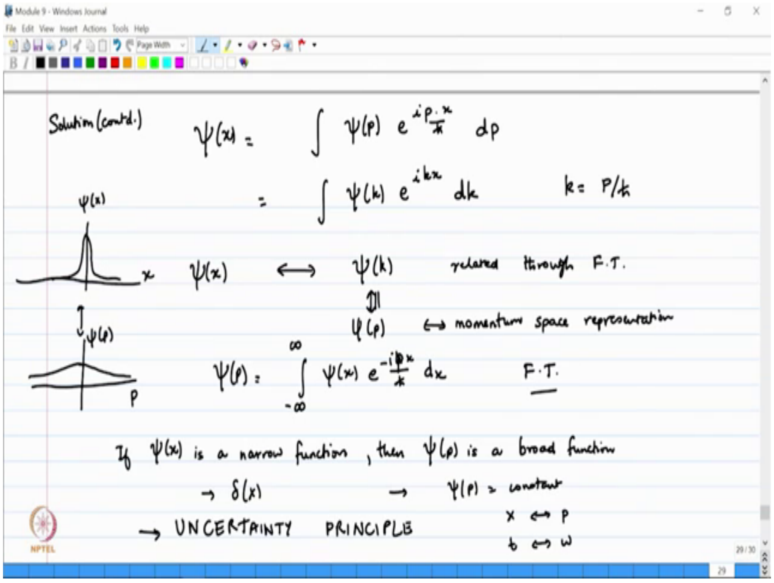

So, you did not have discrete piece to sum over then I will replace this sum by an integral and the what I will call I will call cps psi tilde or psi of p e to the ipx divided by h bar dp if I just I have I have this h bar. So, if I just want to absorb this h bar then I can write this as integral psi k e to the ikx dk where k is equal to p by h bar or psh bar k. So, this is this is how you write in terms. So, basically what we see is that psi of x and psi of p related through Fourier transform. So, this is nothing but a Fourier transform.

I just I mean I mean whether I say p or k I am going to use them interchangeably and psi k is called psi k or psi p or psi p this is equivalent to psi p this is called the momentum space representation and you can write psi p I am not bothering with the constants. So, that is I can write it as integral psi of x e to the minus ikx I ipx by h bar dx. So, I can write it in this way with some constants 1 by root 2 pi and all those factors. So, this is a momentum space representation of the wave function and if you have a function in position space you can always convert it to momentum space using this representation using this using this integral. So, this is directly related to Fourier transform.

Now, one of the things one of the things that you learnt is that is that if psi of x if psi of x is a very narrow function then psi of p is broad. So, if psi of x is narrow function. So, we saw that a Fourier transform for Gaussian is a Gaussian where the width is inverse then psi of p is a broad function. In fact, if it is infinitely narrow if psi of x is a delta function then psi of p is a constant. So, that is infinitely broad.

So, if this is a delta function then this is a constant which is infinitely broad and so there is an inverse relation between the between the nature of the functions of psi of x and psi of p and this is what is enshrined in something called the uncertainty principle. So, the uncertainty principle basically says that if you have a very if you have a very sharply peaked function; that means you can exactly identify the location of the particle the position of the particle.

So, this case you have psi pfp psi x of x, but if you can locate if you can locate the particle very precisely in position then it is very spread out in momentum. So, you cannot locate its momentum very precisely. So, the uncertainty principle of quantum mechanics is actually a direct consequence of the Fourier transforms it is a direct consequence of the fact that the position representation and momentum representation at are related through a Fourier transform.

And in fact this uncertainty principle also, so, you have x and p position and momentum you can also have time and its Fourier transform variable frequency. So, you can also have a time and frequency uncertainty principle in quantum mechanics and you know that that is something that you use in spectroscopy. So, again Fourier transforms is a very useful way to look at some of these principles.