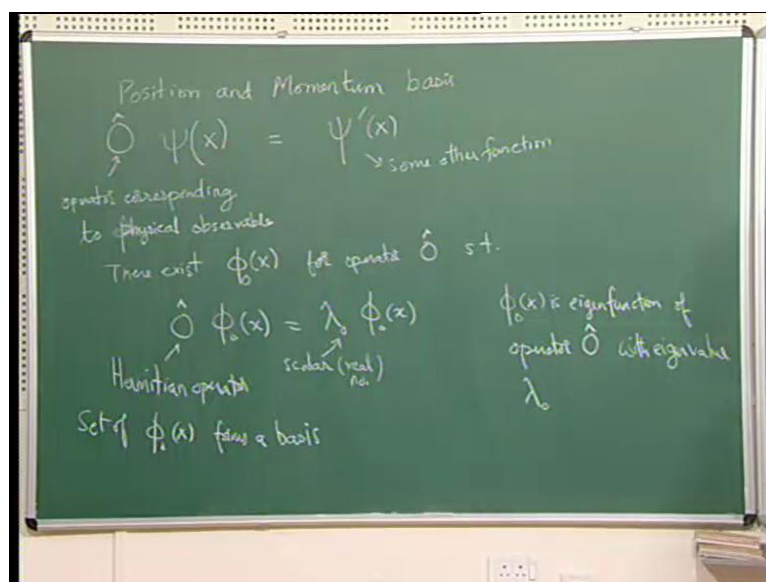


**Mathematics for Chemistry**  
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**Lecture - 24**

Today's class we will look at some examples of the use of Fourier transforms, we already saw in the last class, one example of how you can use Fourier transforms to solve differential equations. Now, today we will look at an example where, which has an important role in quantum mechanics and this has to do with what is called the position in momentum basis.

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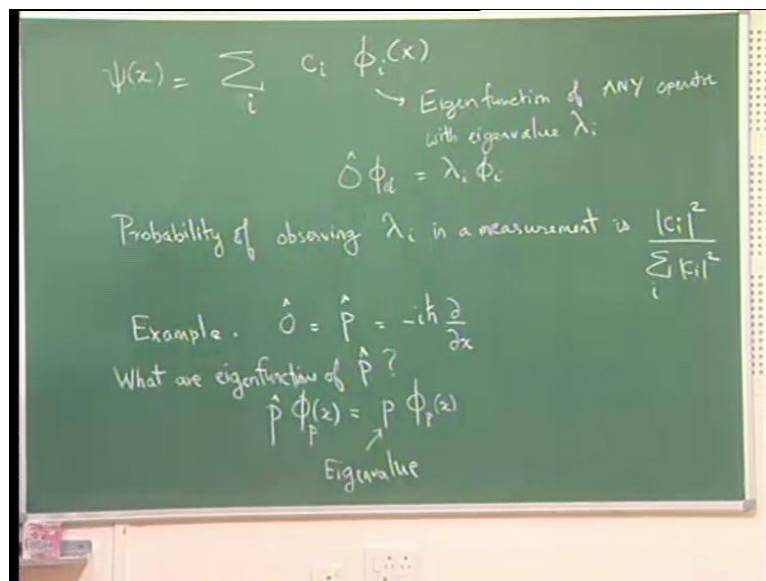
So, one of first postulates of quantum mechanics is that you describe the state of a system by a wave function  $\psi$ , that is the function of the spatial coordinates. So, if you have a one-dimensional system, this will be a function of just  $x$  the spatial coordinate.

So, this describes the state of the system, and if you have any observable then that observable corresponding to that there exists an operator, so this corresponds to this is operator corresponding to observable to... And I will say physical observable. And this physical observable could be the energy of a system, could be the momentum, could be the angle of momentum, could be anything.

So, these is the operator corresponding to the physical observable and if you have operator acting on wave function, then this give you some other functions, gives you psi prime of x. So, just gives you some other function, but corresponding to psi but there exist phi of x phi also phi O of x for operator O, such that operator acting on phi of x is equal to lambda O times phi O of x a, lambda a is scalar; and it is a real number. So, if this corresponds to physical observable this is a real number, and this operator is what is called Hermitian, so this is a Hermitian operator, this is a scalar or real number.

Then phi 0 is called the, is Eigen function of operator O with Eigen value lambda O. So, this is one of the postulates of quantum mechanics is it corresponding to every physical observable there exists an operator. And this operator has Eigen functions and Eigen values, the Eigen values real and it for the more these Eigen functions, they form basis. So, Eigen function set of phi 0 of x forms a basis.

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So, this is one of the fundamental postulates of quantum mechanics and when you say it forms a basis that mean, if you have arbitrary psi of x, you can write this as sum over all the what would, I called the Eigen values all the lambda was are sum over I just say i lambda i phi i of x. So, that means, phi i of x where, this is Eigen function of any operator with Eigen value lambda i. So, you can choose any operator you choose Eigen functions of any operator, that corresponds to physical observable to do this basis

expansion, this is the user basis, it should call the  $\lambda_i$  this should be  $C_i C_i^\dagger$ , so  $C_i C_i^\dagger \phi_i$ , now since this is this is an Eigen function of any operator.

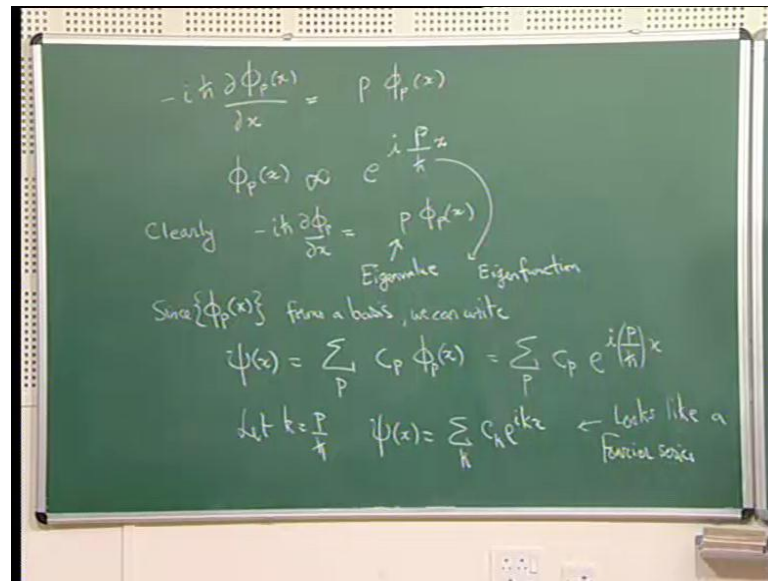
So, if that operator so we will just leave it at this, so in other words operator on  $\phi_0$  on  $\phi_i$  is equal to  $\lambda_i \phi_i$ , then the further about the theorem of quantum mechanics says it said, when you take system in this state, you measure a value of operator. So, operator a operator  $O$  corresponds to the physical observable when you measure that physical observable, you will see one of the Eigen values. So, in any measurement you see one of the Eigen values.

And the probability of seeing this Eigen values  $\lambda_i$ , so probability of measuring of rather let say observable of observing  $\lambda_i$  in a measurement is  $C_i^2$ , that corresponds to absolute value of  $C_i^2$  so absolute value of  $C_i^2$  divided by  $\sum_i C_i^2$ , it is suitably normalized. So, you take absolute value of  $C_i^2$  divided by sum over  $i C_i^2$  and the this will just be some constant number. So, it will just be in just be a it is proportional to absolute value of  $C_i^2$ .

So, let us look specific example of this, so let us take example, operator is equal to  $p$  operator in 1 dimension. So, I will use  $p$  this is  $-\hbar \frac{d}{dx}$  so it is a operator corresponding to. So, that is the form of the operator so what are the Eigen values are Eigen functions of  $p$  operator so the general form. So, the general form is the following, so what we will say is that  $p$  operator on  $\phi$ , I will call it  $\phi_p$  of  $x$  is equal to Eigen value the Eigen value of  $p$  just call  $p \phi_p$  of  $x$ , this is a Eigen value.

So, Eigen value is some momentum that means, you make measurement and your value of momentum is  $p$  so there  $p$  is an Eigen value so now you are solve this equation substituting this value for operator  $p$ .

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So, you have minus  $i\hbar$  cross  $d\phi_p$  of  $x$  by  $dx$  is equal to  $p\phi_p$  of  $x$  and if, you doing the  $\phi_p$  on this side you take the  $dx$  that side you integrated what we will get is the following,  $\phi_p$  of  $x$  is equal to  $e$  to the  $i p$  divided by  $\hbar$  cross  $x$ , now it is proportional to this right.

So, you take this values now, if you take this when you this, when you can clear see that if you take the derivative, you will get  $i p$  by  $\hbar$  cross and if you multiplied by minus  $i$ , you will get one and  $\hbar$  cross you just get  $p$ . So, clearly is equal to  $p\phi_p$  of  $x$  therefore,  $p$  operator and  $\phi_p$  of  $\hbar$  is just  $p$  times  $\phi_p$  of  $x$  so this is Eigen values and this is the Eigen function.

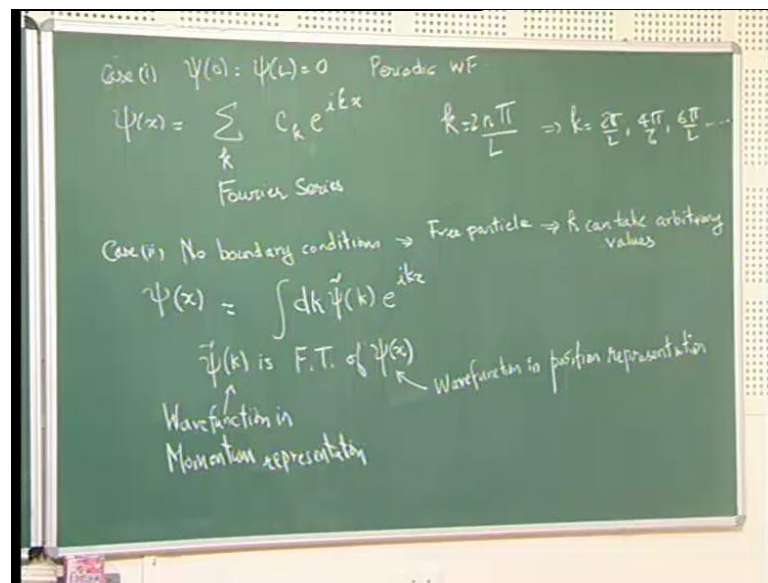
So, you notice that the Eigen functions are just  $p$  to  $i$ , this Eigen value divided by  $\hbar$  cross times  $x$ , now this is looks the lot like  $ikx$  that you were doing in Fourier series. So, let us go ahead and see what this implies so since  $\phi_p$  of  $x$ , since the set of all  $\phi_p$  of  $x$  forms a basis. So, what I mean just call the bracket is a set of  $\phi_p$  s of  $x$  this forms a basis, we can write  $\psi$  of  $x$  any arbitrary wave function is equal to sum over all values of  $p$   $C_p \phi_p$  of  $x$ .

So, you can write it in this form so this is just sum over  $p$   $C_p e$  to  $i p$  by  $\hbar$  cross  $x$ , now again this looks very much like the Fourier transform instead of having, if you had  $p$  by  $\hbar$  cross here and  $p$  by  $\hbar$  cross here, anything would have been the same. So, we say let  $k$  is equal to  $p$  by  $\hbar$  cross then I can write this expansion in the following form  $\psi$  of  $x$  is

equal to sum over  $k$   $C_k e^{i k x}$ . So this looks exactly like a Fourier series, this looks like a Fourier series only thing is a we have an put any boundary conditions, we have not specified, what the boundary conditions on this wave function is.

Now in case, you say that the wave function should be periodic with some time period, then this will be a exactly the Fourier series with that period. In case we say that the wave function did not be periodic, it can be the space is infinite, then what we show that this sum becomes an integral.

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So, we have 2 cases, case one  $\psi(0)$  is equal to  $\psi(L)$  is equal to 0 so this would be one case, when the wave function is periodic. So, this is periodic wave function, so in this case your  $\psi(x)$  into  $\frac{1}{L}$  or  $\frac{2}{L}$  integral 0 to L in  $\psi(x)$  look like sum over  $k e^{i k x}$  where,  $k$  equal to  $n \pi$  by L sorry,  $2 n \pi$  by L  $2 n \pi$  by L because L by 2 is the is the periodicity. So, then this is exactly the  $k$ . So, implies  $k$  is equal to  $2 \pi$  by L  $4 \pi$  by L  $6 \pi$  by L and so on; so this becomes exactly so this is a Fourier series.

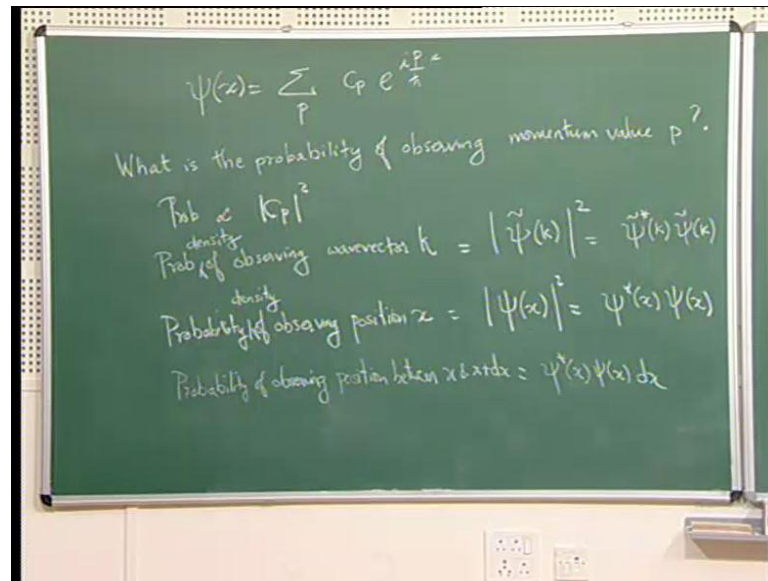
So, if you have a system that with such conditions. So, that is can find to some length then you can expand wave function as a Fourier series and this is the typical, this is very common in seeing the one-dimensional problems, there you do not have any potential then you often represented by a travelling wave, this corresponds to the travelling wave solutions.

So, this is your travelling wave with momentum  $p$  so that is your  $\phi$  of  $x$  now case 2 3 no boundary conditions, free particle and now in this case your  $\phi$  of  $x$  so free particle and this implies your  $k$  can take any values arbitrary values and in this case your  $\phi$  of  $x$  since  $k$  can take arbitrary values your sum over  $k$  can be continuously varied. So, sum over  $k$  becomes, an integral  $\int dk$  know  $C_k$ ,  $C$  is a, since  $k$  is a continuous function, I can write  $C$  of  $k$  as  $e^{ikx}$  and instead of  $C$  of  $k$   $C$  of  $k$  varies continuously, I will just call it some function of  $k$ .

So, this is some function of  $k$ , let me look  $\psi$  and use  $\tilde{\psi}$  and you can clearly see what to what we are trying to do so from going from this continuous in this discrete when the  $k$  values, where discrete you had a sum when naturally corresponded to Fourier series. Now, in the case when there are no boundary condition free particle  $k$  can take arbitrary values, this sum becomes an integral and this  $C_k$  gets changes to sum function of  $k$  because  $k$  is continuously varying you have so  $C_k$  can be represented as some function of  $k$ , we call that function is  $\tilde{\psi}$  of  $k$  and it is clear what  $\tilde{\psi}$  of  $k$  is. So,  $\tilde{\psi}$  of  $k$  is Fourier transform of  $\psi$  of  $x$   $\tilde{\psi}$  of Fourier transformed of  $\psi$  of  $x$  and this is called wave function in momentum representation.

And this is your wave function in position representation, so this is wave function and position representation. So, what you see that the wave function in the momentum representation is the Fourier transform of wave function in position representation, now physically what this means is that what you are  $\psi(k)$  corresponds to  $\psi(x)$  you should think of it as a coefficients. Now, what is the  $C_k$  correspond to you if you have discrete, then if you have a discrete set of  $k$  values then  $C_k^2$   $C_k^2$  corresponds to the probability that in a measurement you will observe value of momentum of  $k$ .

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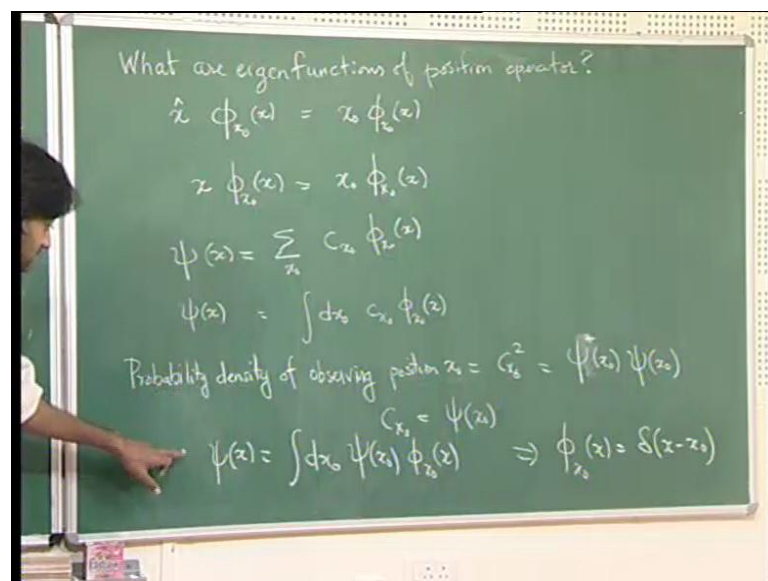
So, remember this C of k. So, let us so psi when we write psi phi of x is equal to sum over, I will go back to my p, if here is C p into the i p x by h cross, we had this right that means, your wave function is written as super position of Eigen functions of momentum, the Eigen value of momentum corresponding to e to i p x is just p. So, then you also question what is the probability of observing momentum value so that means, you make measurement you will get one of the Eigen values, what is the probability of getting momentum value p; the answer is just C p square, it is proportional to C p C p x C p square. So, probability proportional to C p square this is a probability of observing momentum p.

So, now you go back to this, so when we say that psi tilde of k is the Fourier transform of psi of x then we have this sort of representation, so that means, probability of observing wave vector k is equal to psi tilde of k square, when this is just so what is the probability that we will observe wave vector k, that is just tilde of k star psi tilde of k, which is just based from, by comparing with this. Now, you understand why psi tilde of k is called the wave function in momentum representation, because if you want to find out the probability of find a certain momentum. And just use psi star psi in this representation, just as probability of observing position x that is the probability that your particle is at x this is just psi of x square is equal to psi star of x psi of x.

So, now you can see why this is called wave function in momentum representation, this is wave function and position representation because of probability of observing position  $x$  is just  $\psi^* \psi$ , probability of observing position  $x$  is what is the probability that you are particle located of  $x$ , there or located between  $x$  and  $x + dx$  that is  $\psi^* \psi dx$ . So, this is it should be a little corrected so this is now it is this is density, so this becomes probability density. Now, when you go to discrete variables, when you are values of momentum can take only certain values you can talk about probability but when your values of momentum can be continuous, when we are talk about probability density.

So, all these are so just as  $\psi^* \psi$  representation of probability density, that means probability of observing position between  $x$  and  $x + dx$  is equal to  $dx$ . So this is a probability of observing position between  $x$  and  $x + dx$  here. So, because  $x$  is the continuous variable, you cannot ask what is the probability of observing position  $x$ , you have you ask what is the probability density of observing position  $x$  how they can ask what is the probability density at  $x$ . So, what we have seen is that this momentum representation is and is Fourier transform of the position representation. And now we can go ahead and ask next question, what is what are the Eigen function of position vector or what are the Eigen functions of position operator. So, what are the Eigen functions of position operator.

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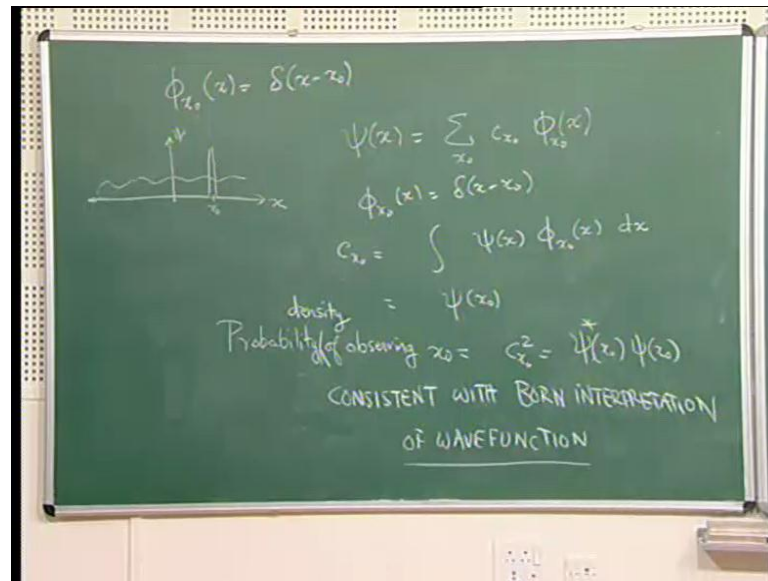
So, let us take the case there we have no boundary conditions and we want to find out what are the Eigen functions of the position operator what are of position operator. So, then if you have  $\psi(x)$  of  $\psi(x_0)$  of  $x$  so we will say  $x$  operator in  $\psi(x)$  of  $0$  of  $x$  should be  $x_0$  times  $\psi(x_0)$  of  $x$ . So, this is the Eigen value equation, now  $x$  operator is just  $x$ . So,  $x$  multiplied by  $\psi(x_0)$  of  $x$  is equal to  $x_0$  times  $\psi(x_0)$  of  $x$ .

So, the Eigen functions of position operator and such that when you multiplied by  $x$  is same as multiplying by  $x_0$ . So, this is the Eigen value that means, when you make a measurement of position you ask where the particle is your answer is  $x_0$  this is. So, the probability of getting  $x_0$  is your get at to  $\psi(x_0)$  square are the coefficient of  $\psi(x_0)$  square.

So, now we have to find out  $\psi(x_0)$  is and we can do it the following way so i to do it this is  $\psi(x)$  is equal to sum over  $x_0$   $C(x_0)$   $\psi(x_0)$  of  $x$  and since  $x_0$   $x_0$  can take all values so this is becomes equal to integral  $d x_0$   $C(x_0)$ , I will just call it as, I will just say  $C(x_0)$   $\psi(x_0)$  of  $x$  this is  $\psi(x)$  so probability density of observing position  $x_0$  is equal to  $C(x_0)$  square but you know that  $C(x_0)$  square is nothing should be equal to  $\psi(x_0)$  star  $\psi(x_0)$   $C(x_0)$  square should be nothing but  $\psi(x_0)$  star  $\psi(x_0)$ . So, in other words  $C(x_0)$  should be equal to  $\psi(x_0)$  right.

So, in other words  $c(x)$  should be nothing but  $\psi(x_0)$ . So, that  $c(x_0)$  square is  $\psi(x_0)$  star or  $\psi(x_0)$  square so in other words you have  $\psi(x)$  is equal to integral  $d x_0$   $\psi(x_0)$   $\psi(x_0)$  of  $x$  and when, you look at this form you would immediately recognize that this is satisfied if so implies  $\psi$  of the function that satisfies this, if you remember when we will discussing delta functions, we said that are delta function is one such that when you integrate  $d x_0$  of  $\psi(x_0)$   $\delta(x - x_0)$  you get  $\psi(x)$  so that means,  $\psi(x_0)$  of  $x$  is equal to  $\delta(x - x_0)$ .

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So, what we have concluded is that the position basis functions, your basis function of the position operator with Eigen value  $x_0$  are just delta functions of  $x$  minus  $x_0$  and this makes sense physically also, because if you had  $\delta(x-x_0)$  if you want to say that you are in a state, which has a very fixed value of the position, then we have only the state that can have fixed values of position is where you are probability finding the particle is only non 0 at one point  $x_0$ ,  $\psi$  has to be equal to  $\delta(x-x_0)$ .

So, suppose you have a wave function, this is your  $x$  variable and this was a wave function, now if you had a wave function like this then you have a certain probability of finding the particle everywhere but if your wave function looks like a delta function at  $x_0$  then the only place where you can find the particle is that  $x_0$ .

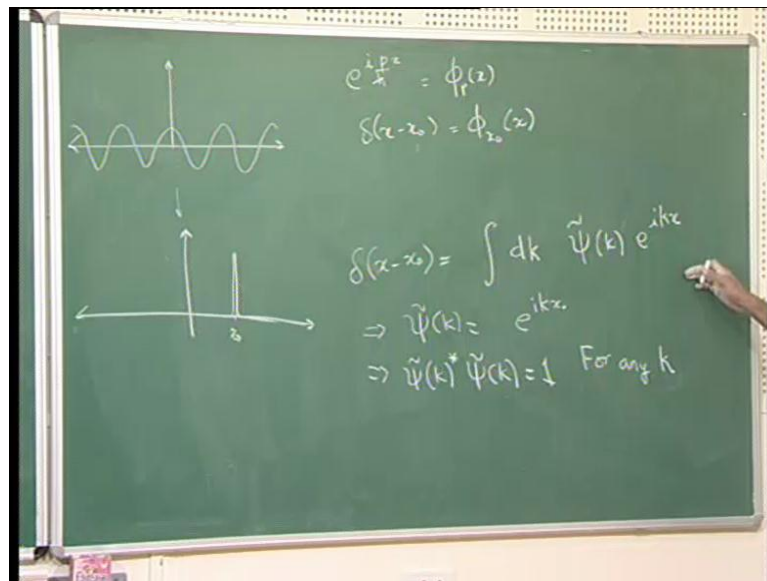
Therefore when you make a measurement you will get one specific value of  $x_0$  and that is why this is an Eigen function of the position operator, so Eigen functions of the position operator are delta functions and you can easily see that if you write  $\psi(x)$  is equal to  $\sum c_{x_0} \delta(x-x_0)$  you can trivially see that if you put delta functions then this equality gets satisfied.

So, what we saw was the following  $\psi(x)$ , if you write  $\psi(x)$  is equal to  $\sum_{x_0} c_{x_0} \phi_{x_0}(x)$  this is a basis function expansion. Now, we saw that  $\phi_{x_0}(x)$  is equal to  $\delta(x-x_0)$  and what we will say is that  $c_{x_0}$  is equal to  $\int \psi(x) \phi_{x_0}(x) dx$ , and this is nothing but  $c_{x_0}$  is nothing but  $\psi(x_0)$  so now probability of observing  $x_0$  is equal to  $c_{x_0}^2$ .

square and this is equal to  $\psi(x=0)$  star  $\psi(x=0)$ . So, this is consistent with the with bond interpretation of wave function.

So, this is completely consistent with bond interpretation of wave function and the last thing, I want say is that in this aspect is that we saw that the position representation and a momentum representation or Fourier transforms of each other.

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Now that can be understood in a very simple way so momentum representation so if you look at the Eigen functions of momentum, they are  $e^{i p x / \hbar}$ . So, this is your Eigen functions of momentum Eigen functions of positions are  $\delta(x-x_0)$  so what that means, is the following the Eigen functions of momentum, so if you definite value of momentum, if you want to have a state where, the value of momentum is definite that state should look like this and if you just think real part of this it is just looks like a cosine wave. So, it look like it this, so this is the state with a definite value of momentum.

So, notice that if you have a state to the definite value of momentum it can be found anywhere, so the particle can be anywhere it could has to have a definite value of momentum it has to be it can be anywhere that means, you know nothing about its position. So, that means you if you have a definite value of momentum you know nothing about the position of particle because it can be anywhere on the other hand if

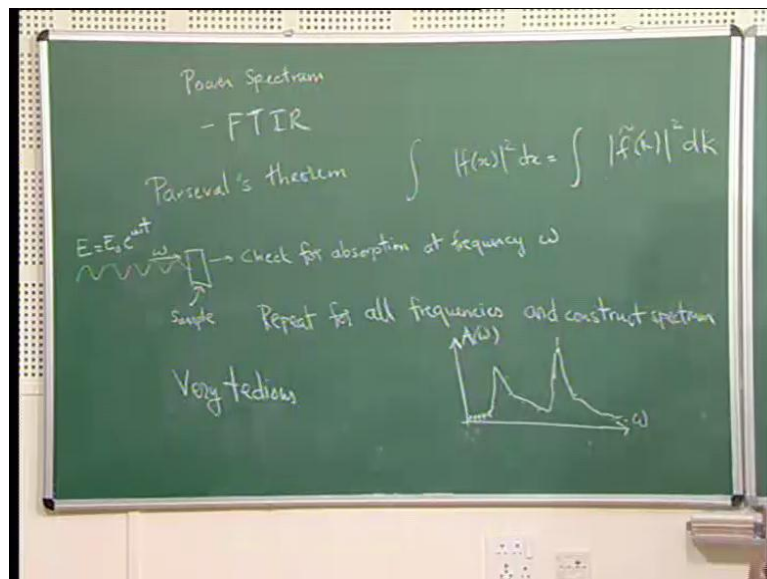
you have a definite value of position then what you do is the Fourier transform what you do is a definite value of position will look like this is  $x_0$ .

So, this is a wave function that has a definite value of position so what you can show is that, if you want to write this in terms of momentum basis you have write this in terms of infinitely many momentum, so if you have definite value position you can write  $\delta(x - x_0)$  is equal to  $\sum c_p e^{i k x}$ , we can write this as  $\int dk \tilde{\psi}(k) e^{i k x}$ .

So, I can write it in this form and basically what it means is that in order to represent this function, you will need infinitely many wave vectors. So, what we will find with this is  $\tilde{\psi}(k)$  is equal to  $x_0$  that means, for any value of momentum, so this implies  $\tilde{\psi}(k)$  is equal to one for any  $k$  that means you can have wave vector  $k$  any value in other word you can have more momentum take any values all values of momentum are possible.

So, if you fix your position that  $x_0$ , then you can get any value of position momentum possible, so in a see the whole idea of uncertain principle is contain in this Fourier transforms.

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So, this is one very common application of Fourier transform the other application that, .I will just mention briefly about Fourier transforms is the powers spectrum so the last

application I will just mention this briefly this is the power spectrum this is example as, F T I R or F T N M R and so on. So, you might have heard this is Fourier transform infrared spectroscopy.

So, for what is the role of Fourier transforms in spectra scoping and this I will just mention it briefly, I want going to too many details, this is based on the Parseval's theorem so Parseval's theorem says that  $\int f(x)^2 dx$  is equal to  $\int \tilde{f}(k)^2 dk$  when you do a in any spectra scoping, so in any spectra scoping what is done is following, you have a sample you shine light of a certain frequency.

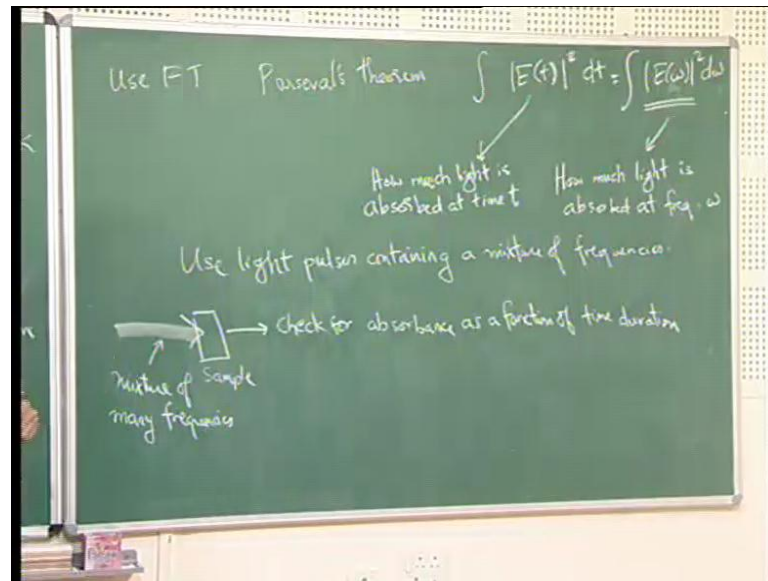
So, you shine light of a certain frequency and light has a certain frequency can be that correspondences to electric field that as the form  $e^{i\omega t}$ . So, the electric field oscillates in time with this frequency with this angle of frequency and you can already see that since the electric field as oscillating function in time, you can already see that something Fourier transform might be useful.

So, when you shine a light now when you record you send one frequency  $\omega$  check for absorption, so you check for absorption and you see that it observes in that frequency then what you do is to change the frequency, check for absorption at  $\omega + \Delta\omega$ . Then what you have do is you need to change the frequency and send another frequency and then again check for absorption, you keep doing so repeat for all frequencies and construct spectrum.

So, for example, you could say the absorption as a function of frequency looks like this, so you have various frequencies you should probably just for them in the positive direction, so you look at a particular frequency you will see low observation may be at some frequency we will see high absorption, you will see you see things like this. So, then you connect all of them and you will get some spectra just look like this.

Now you can see that this is the very previous procedure because you have to say and one light of one frequency then another frequency then you are keep sending light of difference frequencies to measure this. So, this is very theories, not only do you have to send light of one frequency then send light of another frequency then keep changing the frequency and. So, where keep changing the light and check the absorbance now this can be very tedious.

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So, one way to get around this to get around use Fourier transform  $f(t)$  so the idea is and this is where, we use the Parseval's theorem. So, instead of doing it and in the in the time domain we will do it in the frequency domain. So, we use the parseval's theorem says integral is equal to integral  $E$  of  $\omega$  square  $d\omega$ . So, this is how much of the this is the intensity of the electric field how much is absorbed at time that is related to so the integral under that is related to how much light is absorbed at a particular frequency. So, this frequency  $\omega$ .

So, this  $p$  of  $\omega$  square is how much light is absorbed at frequency  $\omega$ , if you integrate over all  $\omega$  that is same as this is how much light at time  $t$ , so then now the strategy is very simple. So, you just send lights you send lights of different time duration so instead of sending light of a single frequency you send lights of various time durations.

So, we send various pulses of different time durations and you program it in such a way that you know that you what this distribution of frequencies is in each pulse and you just measure how much of the total light that is being absorbed, so you measure the total light that is being absorbed as a function of this pulses and you can use the light.

So, use light pulses containing a mixture of frequencies in this case you send a light of only one frequency only one  $\omega$  but in this case your light you are sending a pulse that has a mixture of in the simple mixture of many frequencies and you send you send

the pulse of a certain duration and you measure and you see absorbance as a function of time duration.

So, as a function of the time duration of the pulse you can see how much light is absorbed, then from this you can take the Fourier transform that information to get how much light is absorbed, at a certain frequency. And this will be on the other hand is much easier to do, because you do not have to keep sending different frequency you just send lights of different pulses with a known with a mixture of known frequencies.

So, there are more details in this but I just wanted to mention that Fourier transforms are very useful in spectroscopy, so with this we conclude that the discuss on differential equations and applications and starting from the next class we will start talking about completely different topic that is group theory.