Basic Quantum Mechanics

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Module No # 02

Simple Solutions of the one Dimensional Schrodinger Equation

Lecture No # 06

One Eigen Values and Eigen Functions of the one Dimensional Schrodinger Equation

Welcome to the ninth lecture on basic quantum mechanics. Today we will be discussing some general issues regarding the Eigen values and Eigen functions, for the one dimensional Schrodinger equation. In my last lecture we had solved the problem of an electron or a proton confined in a potential well of infinite depth. Essentially, we had solved the Schrodinger equation for a particular form of the potential. And as I had mentioned earlier a major part of quantum mechanics, non relativistic quantum mechanics is essentially obtaining the solution of the one dimensional and the three dimensional Schrodinger equation for different forms of the potential.

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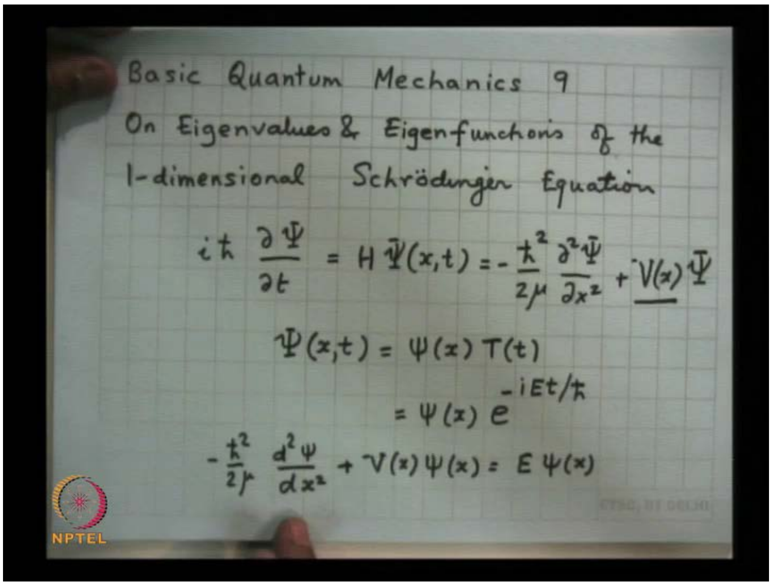

So, as we had discussed in our earlier lectures that the one dimensional Schrodinger equation is given by I H cross delta psi by delta t is equal to H psi psi as a function of x and time and H psi of x t is equal to H cross square by 2 mu delta 2 psi by delta x square plus v of x times psi. This is known as the one dimensional Schrodinger equation for the free particle for the particle in a potential energy function v of x. We assume that the potential energy function is independent of time, depends only on the space coordinates.

And then as we had discussed earlier we can write down the solution using the method of separation of variables, which is given by psi of x and t of t. We have done this before and we found that the variables indeed separated out and the time dependent part was given by E to the power of minus I E t by H cross, where E is a constant. So, if we indeed substitute this we would obtain the following equation that minus H cross square by 2 mu d 2 psi by d x square because now the small psi depends only on the x coordinate plus v of x.

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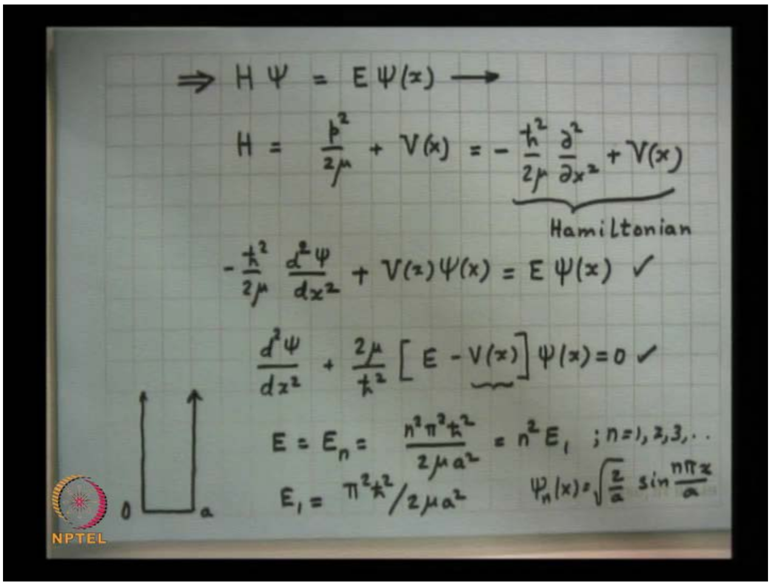

Psi of x is equal to E of x E of psi. So, this equation is actually an Eigen value equation because we can write this equation in the following form. That H psi is equal to E psi and where H is the Hamiltonian operator which is the kinetic energy p square by 2 mu plus v of x and if I substitute for p is equal to minus H cross delta by delta x. So, we will get minus H cross square by 2 mu delta 2 by delta x square plus v of x. This operator representation for the total energy this is known as the Hamiltonian this is known as the Hamiltonian of the system. So, my Schrodinger equation is usually written as is written the time independent Schrodinger equation is written as an Eigen value equation.

So, if I substitute this here. So, as was obtained a few minutes back minus H cross square by 2 mu since psi depends only on the x coordinate. I can replace the partial differential operator by a total differential operator d 2 psi by d x square plus v of x psi of x is equal to E times psi of x. As I had mentioned earlier this is an Eigen value equation. This is a even this equation is an Eigen value equation. We will find that for a given potential energy distribution only certain discrete or continuum values of E are allowed those are the Eigen values of the problem and corresponding to each Eigen value. There is a wave function those are known as the Eigen functions on the system.

So, we have we can write this equation rewrite this equation just a simple ordering d 2 psi by d x square plus 2 mu, where mu is the mass of the particle E minus v of x. In most textbooks the equation is write at the written either in this form or in this particular form. Now, in my last lecture I had assumed v of x to correspond to a particle in a one dimensional box. And we had assumed the particle to be confined between x is equal to 0 and x is equal to a. Let us suppose and we had found that the energy Eigen values are given by E n, which was equal to n square pi square H cross square by 2 mu a square.

This is equal to n square E 1, where E 1 is the energy level corresponding to n equal to 1. So, that is the ground state energy value 2 pi square H cross square by 2 mu a square. And the corresponding wave function was given by psi n of x was equal to under root of 2 by a sin n by x by a where n takes the values 1 2 3 etcetera. Today we will discuss some general properties of the Eigen values and Eigen functions for a given potential energy function v of x for example, we will show that all Eigen values must necessarily be real. Secondly, we will show that Eigen functions corresponding to different Eigen values are necessarily orthogonal. So, let us first prove that the Eigen values are always real.

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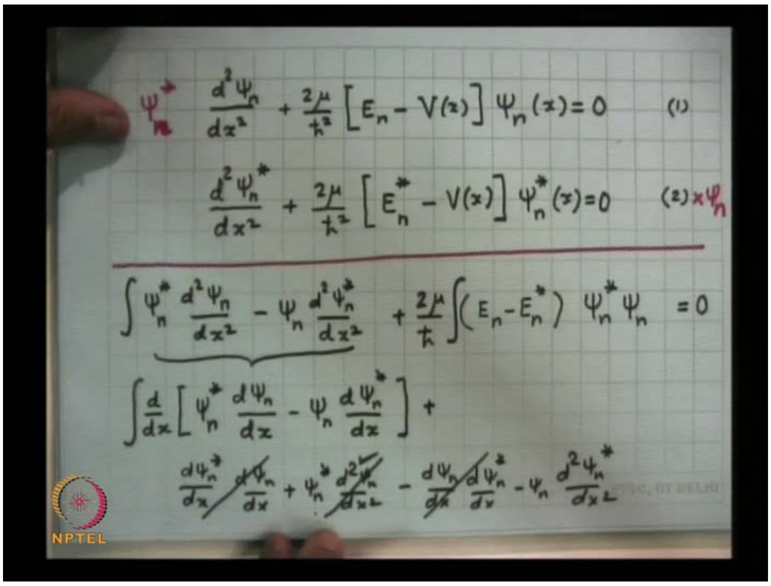

So, we write the Eigen value equation. So, d 2 psi by d x square. Let us suppose for the not state in my previous problem. You remember that we had explicitly determined the energy Eigen values.So, this is my ground state, this is the first excited state, this is second excited state, this is the third excited state n equal to 1, n equal to 2, n equal to 3, n equal to 4 etcetera. So, we assume we do not take a specific form of v of x for a general v of x. We assume that that psi n of x is an Eigen function belonging to the Eigen value 2 mu by H cross square E n minus v of x psi n of x is equal to 0 I now write the complex conjugate of this equation.

So, if I take the complex conjugate. So, we will have d 2 psi n star by d x square mass and H cross are necessarily real quantities. So, you will have 2 mu by H cross square and let us suppose E n can take complex values E n star, but the potential energy function is a real function of x. So, the complex conjugate of that is the same as v star of x is equal to v of x multiplied by psi n star of x. So, the second equation number 1 is the Schrodinger equation corresponding to the not Eigen state equation number 2 is the complex conjugate of equation 1. Where we have assumed that the potential energy function is a real function.

What I do is I multiply the first equation and usually the convention is you multiply on the left by psi m psi sorry psi n star. And the second equation on the right by psi n and then subtract. So, the left hand side. So, the left hand side the first term will be if you see this carefully psi n star d 2 psi n by d x square minus psi n d 2 psi n star by d x square plus 2 mu by H cross square. Please see this here also it is psi n star psi n here also it is psi n star psi n. So, if we subtract this from this the v will cancel out. We will have E n minus E n star multiplied by psi n star psi n equal to 0 this term. If you write carefully then it would be a total differential d d x of please see this psi n star d psi n by d x minus psi n d psi star by d x.

Straight forward differentiation of this equation will give the first term will be d psi n star d x d psi n by d x. And then the second term will be psi n star d 2 psi n by d x square and the if you differentiate these two terms, then it would be minus d psi n by d x d psi n star by d x. And then this term will come minus psi n d 2 psi n star by d x square. So, obviously, these two terms will cancel out sorry I am sorry this two terms will cancel out .This term will remain I am sorry. So, these two terms will be psi n star d 2 psi n by d x square minus this. So, this quantity is rigorously equal to this. So, what I do is I integrate this plus I integrate this plus I integrate this. So, I will obtain I will if I if I integrate a total differential of a quantity multiplied by d x of course.

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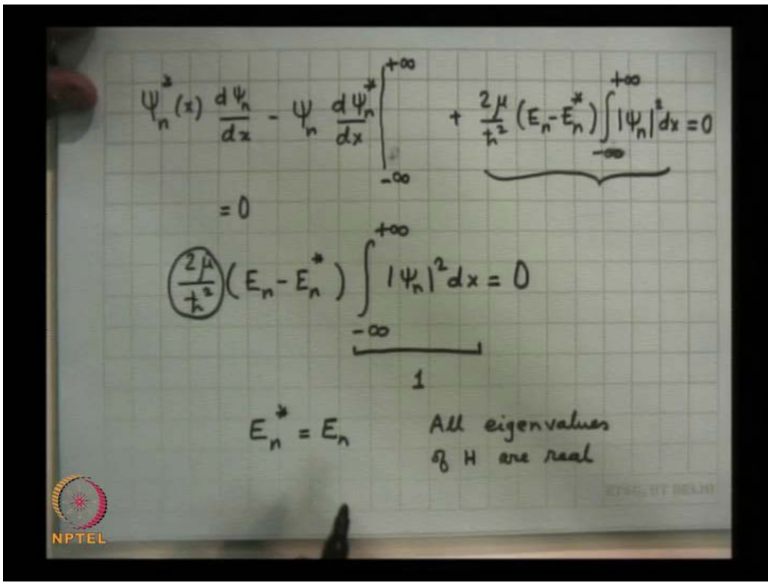

So, we will get psi n star of x d psi n by d x minus psi n d psi n star by d x this plus 2 mu by H cross square. I can take this outside and then integral mod psi n square d x. So, this is equal to 0. So, from minus infinity to plus infinity. So, this I take the limits from minus infinity to plus infinity for any practical problem. When you have a localized particle the wave function and it is derivative must go to 0 at the boundary these are the boundary conditions of the problem. So, this quantity at both the limits will be 0. So, this will be 0.

So, we will obtain this quantity as 0. So, we will have 2 mu by H cross square which is just a number, which can be removed E n minus E n star integral minus infinity plus infinity mod psi n star d x is equal to 0. Now, this quantity is positive definite because the this is the square of a wave function. In fact, the wave function we always assume to be normalized. So, that this quantity is always equal to 1 we can always assume to be equal to 1.So, therefore, and this is a constant. So, you must have E n star must be equal to E n that is all Eigen values of the Schrodinger equation must necessarily be real.

All Eigen values all this is an important result all Eigen values we will come back to it when we discuss the deducts bra and ket algebra, but, all Eigen values of H the Hamiltonian are real and as we will discuss later that if you make a measurement of energy then you will obtain one of the Eigen values of H. So, these are the possible values that we will measure if we make a precise measurement of energy.

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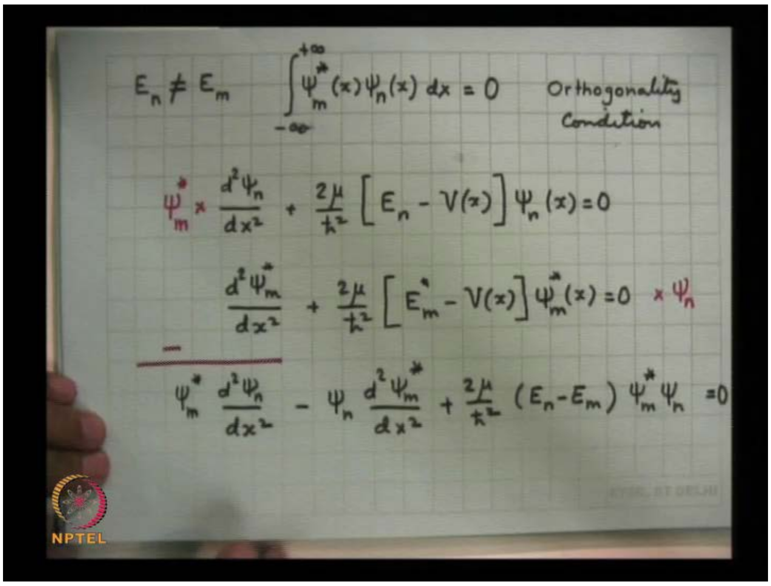

So, we have proved that the energy Eigen values are real what we will next prove is that that if E n, if there are two Eigen values E n and E m and if these two are not equal then the corresponding wave functions psi n and psi m. So, we will have psi m star x psi n of x d x taken between minus infinity to plus infinity. This will be equal to 0, when this condition is satisfied we say that the two functions are orthogonal. So, this is known as the orthogonality condition orthogonality condition.

Now, the proof is very simple we write Schrodinger equation for the n th state d 2 psi n by d x square plus 2 mu by H cross square mu is the mass of the particle E n minus v of x psi n of x is equal to 0 then I write for the mth state. So, d 2 psi m by d x square plus 2 mu by H cross square E m minus v of x psi m of x is equal to 0. What we do is we take the complex conjugate of the second equation. So, I take the complex conjugate of the second equation. Of course mu and H cross are real quantities numbers E m we have proved just now to be real.

So, E m star is equal to E m. So, we do not have to do anything there and then we take the complex conjugate here. There is nothing here sorry. So, because E m is a real number and then what we do is do the same trick. As we had done before multiply this by psi m star on the left the whole equation and multiply this equation by psi n on the left right. So, if you subtract if you multiply the second equation by psi n of x and then subtract then as we had obtained in my earlier slide. We will obtain psi m star d 2 psi n by d x square minus psi n d 2 psi m star by d x square plus 2 mu by H cross square please see this psi m star psi n psi m star psi n.

So, v and v are the same. So, these two terms will cancel out. So, I will be left with E n minus E m psi m star psi n equal to 0. So, what we do next is as we had done in the previous slide I write this as a total differential d by d x psi m star d psi n by d x minus psi n d psi m star by d x let me leave some space here and the same quantity 2 mu by H cross square E n minus E m psi m star psi m I now multiply by d x and integrate from minus infinity to plus infinity.

I now integrate from minus infinity to plus infinity d x this is equal to 0. I had done this in my last slide that if you expand this out there will be four terms two of them will cancel out and the remaining two terms will be this. So, this will be psi m star d 2 psi n by d x square minus psi n d 2 psi m star by d x square and then there will be a terms like d psi m star by d x d psi n by d and d psi n by d x these two terms will cancel out. So, this is the differential of a of a quantity. So, that the integral is just this quantity and.

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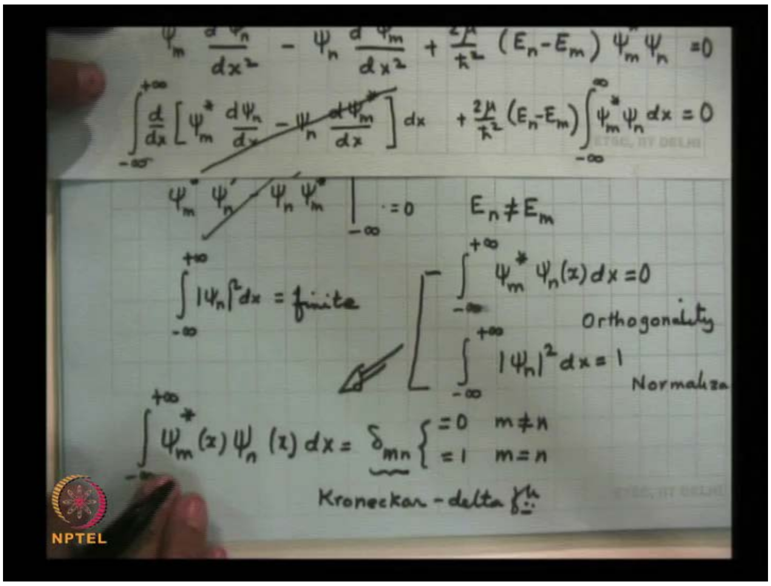

So, therefore, the left hand side after carrying out the integration will be just psi m star psi n prime that is the differential of psi n prime psi n minus psi n psi m star prime. Take it between minus infinity to plus infinity. Now, this is 0 because the wave function vanishes at infinity for to be for them to be square integrable and normalisable they must vanish at infinity. So, by square integrable I mean any function psi n of x is square integral means mod psi n square d x from minus infinity to plus infinity must be finite.

And I will choose a multiplicative constant. So, that this is equal to one. So, a function, which satisfies this equation or this actually the equation. That this quantity the intergral should be finite is known as the square integrable function and for a square integrable function. The function itself must vanish at infinity otherwise it is it will not be a square integrable function.So, therefore, the wave function and its derivative must vanish at infinity and. So, therefore, this term will be 0 this will be equal to 0.

So, we will have only. So, if this term is 0. So, I can cancel this out I will get this is equal to zero. So, I will have product of two terms product of two terms if I write this E n minus E m multiplied by this, but, I have initially assumed that E n is not equal to E m, therefore, this integral must be 0 and this integral minus infinity to plus infinity psi m star of x psi n of x d x must be 0 when E n is not equal to E m. This condition as I had mentioned earlier is known as the orthogonality condition orthogonality condition.

I am assuming that the wave functions are normalized therefore, minus infinity to plus infinity mod psi n square d x is equal to one. So, this is known as the normalization condition and I can combine both of them to write down this equation integral from minus infinity to plus infinity psi m star of x psi n of x d x is equal to delta m n. Where this term delta m n is known as the kronecker delta function and this is equal to 0 if m is not equal to n and is equal to 1 if m is equal to n.

So, we have derived an extremely important result. That the wave functions belonging to different Eigen values wave functions belonging to different Eigen values are necessarily orthogonal and this is the orthogonality condition. There is one more thing that I would like to mention that we will use this that the that the wave function that the Eigen functions of the Hamiltonian form a complete set of functions; that means.

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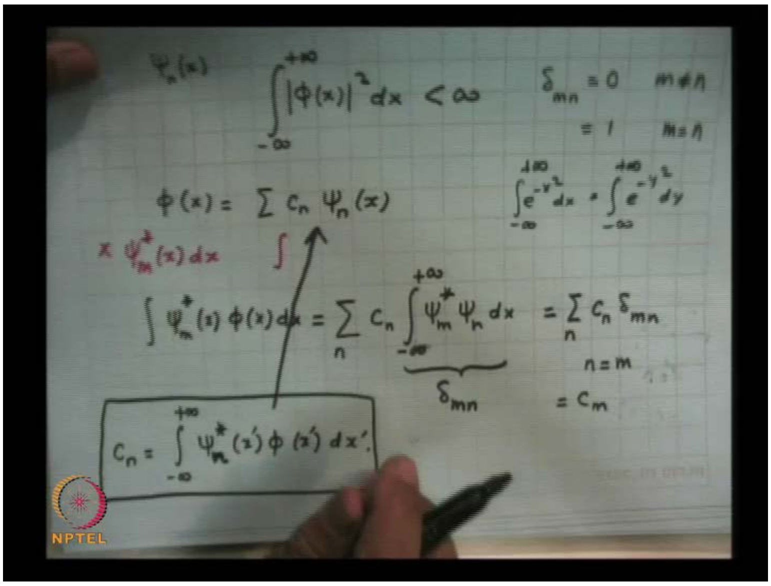

If psi n of x that is suppose the in a particular problem we have a set of wave functions, which are the Eigen functions of the H of the operator H. Then any arbitrarily function say phi of x any arbitrarily well behaved. Well behaved means it has to be single value it should not be infinite anywhere and it should be a square integrable function. So, that is the meaning of the word well behaved. That it should be single valued function at a particular value of x phi of x must have an unique value.

It must not have any infinities it must not go to infinity in at any point and it is a square integrable function that is phi of x d x integral from minus infinity to plus infinity must be less than infinity.This symbol means this inequality means that this integral is finite.

So, such a function is known as a well behaved function and I state without proof that the Eigen functions form a complete set of function that is arbitrary function can be. I will give you examples of that c n psi n of x.

So, this is known as the completeness condition that any arbitrary function can be represented as a sum as a linear combination of the Eigen functions of H. So, how do I determine c n what we do is I multiply this equation I multiply this equation by psi m star of x d x and then integrate. So, what we will have is that the left hand side becomes psi m star of x phi of x d x is equal to summation the sum is over all values of n the c n psi m star of x psi n d x integral from minus infinity all limits are from minus infinity to plus infinity.

But this I have just now proved to be equal to delta m n. So, therefore, this equation becomes right hand side becomes c n delta m n sum the summation is over all values of n. So, only the n equal to m term will survive because for all other terms this kronecker delta function is 0. As I had mentioned that delta m n is equal to 0 for m not equal to n and is equal to 1 if m is equal to n. So, therefore, the summation is our n. So, when n takes the value m that term survives.

So, this will be equal to c m. So, this is how we will determine the coefficient as I have indicated in my earlier lectures also. So, c m is equal to or I can write down c n, c n is equal to integral. And this limits are also from minus infinity to plus infinity psi m star of x phi of x d x sorry n this should be n.Now, what I do is next step is I substitute for c n from here to here, but you must be careful because this is a definite integral over x. This x should not get confused with this x, but since this is a definite integral I can quietly put a prime here.

And then this x and this x can be differentiated. I hope it is clear because this is a function of x and c n is a constant and c n is a definite integral. And in a definite integral it does not matter ,whether you put write x or y or z. For example, E to the power of minus x square d x from minus infinity to plus infinity is the same as E to the power of minus y square d y. It does not really matter what you what is in both of them are equal to square root of pi.So, this x should not get confused with this x and. So, therefore, I quietly put a prime and then I substitute this here. So, I will substitute this expression for c of n in this equation.

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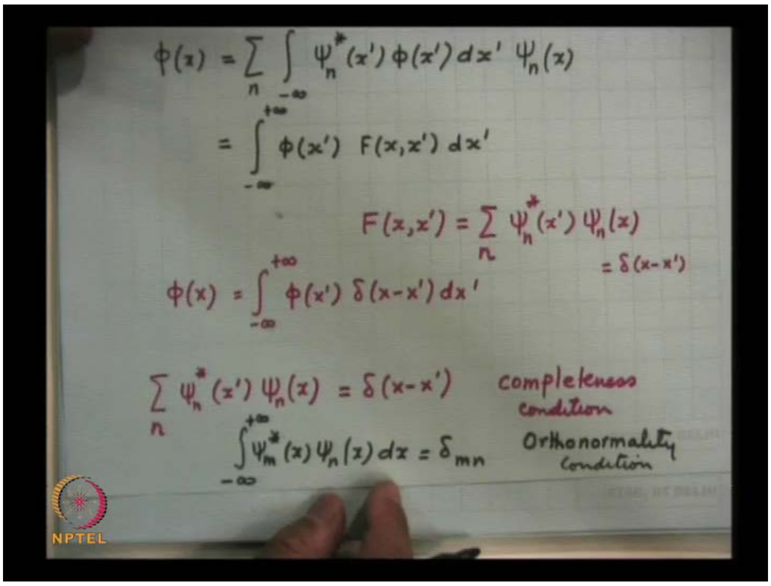

So, I will obtain please see this carefully that phi of x phi of x is equal to summed over n and c n and what is the value of c n as we had determined earlier minus infinity to plus infinity psi n star x prime phi of x prime d x prime multiplied by psi n x.What I will do is I will first carry out the summation and then the integration. So, that all these quantities, which are dependent on n I take this. So, I get is equal to integral from minus infinity to plus infinity please see this carefully phi of x prime phi of x prime and then some function of x, x prime d x prime. And as you would have noticed that f of x prime f of x, x prime is the summation of psi n star x prime multiplied by psi n of x summed over n.

If you would recall the earlier lectures 1 of the earlier lectures in, which we had derived the we in, which we had defined the Dirac delta function and that was phi of x will be equal to minus of infinity to plus infinity phi of x prime delta of x minus x prime d x prime. So, it picks up the value at x only no matter what the function phi mean phi is. So, therefore, this function has to be 0 for all values of x other than x prime and. So, therefore, this quantity must be the Dirac delta function this condition is often known as the completeness condition. The that is the wave functions the Eigen functions of the Hamiltonian operator form a complete set of orthonormal function.

And we say this through the following equation that summation psi n star of x prime psi n of x summed over n is equal to delta of x minus x prime.So, we have derived two very important relations this is known as the completeness condition. And the other is other is that psi m star of x psi n of x d x is equal to delta m n. This is known as the orthonormality condition it combines the orthogonality condition and the normalization condition. So, this is known as the orthonormality condition. So, these limits are also from minus infinity to plus infinity. So, now, in the example that we had discussed in my last lecture lecture 8.

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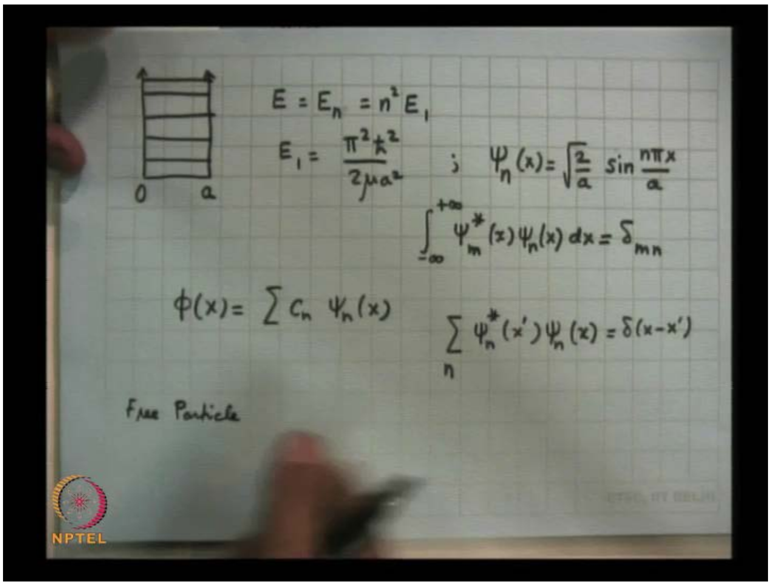

We consider a particle in a one dimensional box and the domain that we consider was between 0 and a. And he we had found that the energy Eigen values are E is equal to E n square of E 1, where E 1 is equal to pi square H cross square by 2 mu a square these are the Eigen values and as you can see all Eigen values are real.We had also derived that the wave functions are given by under root of normalized wave functions sin of n pi x by a. And if you use this you can immediately show that psi m star of x psi n of x if m and n are different then it will be 0.So, this is equal to delta m n. So, we have E 1 E 2 E 3 E 4 E 5 and so on there are infinite number of states.

Infinite number of discrete states and any function, any well behaved function in the region from 0 to a can be represented by can be approximated and this is my Fourier series that c n psi n of x.So, this is something like the Fourier series that you must have learnt in your college. So, the wave functions also form a complete set of functions and. So, therefore, psi n star x prime multiplied by psi n of x summed over n equal to 1 2 3 infinity is equal to delta of x minus x prime. So, this was the particle in a box problem that we had done yesterday. Let me consider another problem about 4 5 3 4 lectures back I had discussed the free particle problem now in the free particle problem let me do it on an another sheet v of x is 0 everywhere.

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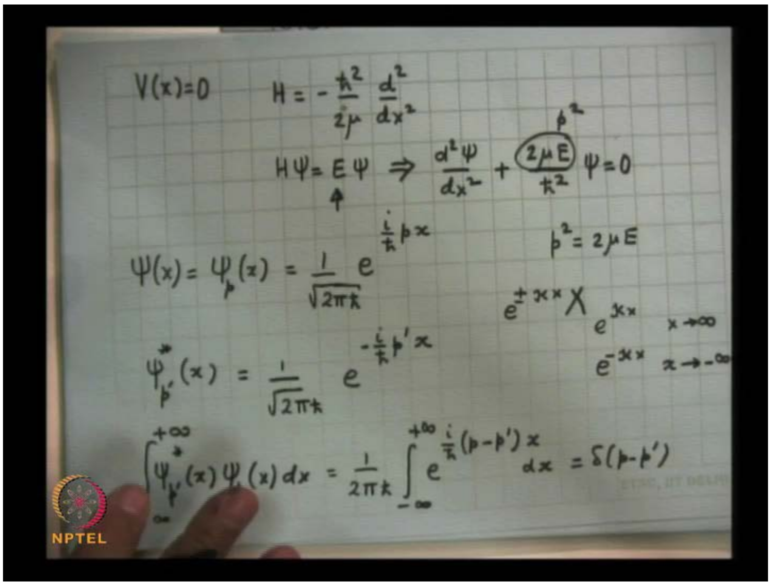

So, it is a free particle and the Hamiltonian operator, which is equal to minus H crosses p square by 2 m H cross square by 2 mu d 2 by d x square plus v of x, but, v of x is 0. So, we had solved this equation and we had found that if I write H psi is equal to E psi then we will get d 2 psi by d x square plus 2 mu E by H cross square psi is equal to 0. So, if I write H psi is equal to E psi then simple manipulations will give this where E is now the Eigen value where it is a number.

So, we write this as p square this quantity as p square and the Eigen functions are psi of x becomes psi p of x this is equal to E to the power of I by H cross p times x.Now, I put because I know this I put a factor 2 pi H cross. So, what are the values of p E has to be positive E has to be positive because I have put because if p if E becomes negative as you can as you can see p square is equal to 2 mu e. So, if p E becomes negative then p will become imaginary if p will become imaginary then times I will be something like either plus or minus kappa x.

When this happens then the wave function either goes to infinity at plus infinity or minus infinity E to the power of plus kappa x will blow up at x is equal to infinity as x tends to infinity E to the power of minus kappa x will blow up as x tends to minus infinity. So, that is not possible because the if the wave function becomes infinity it is no more square integrable you can no more normalize the wave function.So, therefore, E has to be positive, but, p can be plus or minus. So, for a given value of E there are 2 values of p 1 plus 1 minus we say that there is a 2 fold degeneracy.

So, if you work this out then I can write down that psi p prime of x will be equal to 1 by 2 pi H cross E to the power of I by H cross p prime x. Please see this if I take a star here make the complex conjugate then this will be minus here and I can write down psi p prime star x psi p x d x minus infinity to plus infinity I multiply this. So, I get 1 over 2 pi H cross E to the power of I by H cross p minus p prime time has x d x from minus infinity to plus infinity. So, this is the Dirac delta function delta of p minus p prime. This is an example, where the Eigen functions form a continuum. In the previous example we had a discrete set of energies we had a discrete set of energies only certain values of energy were allowed in this case we have all possible values of energy from 0 to infinity.

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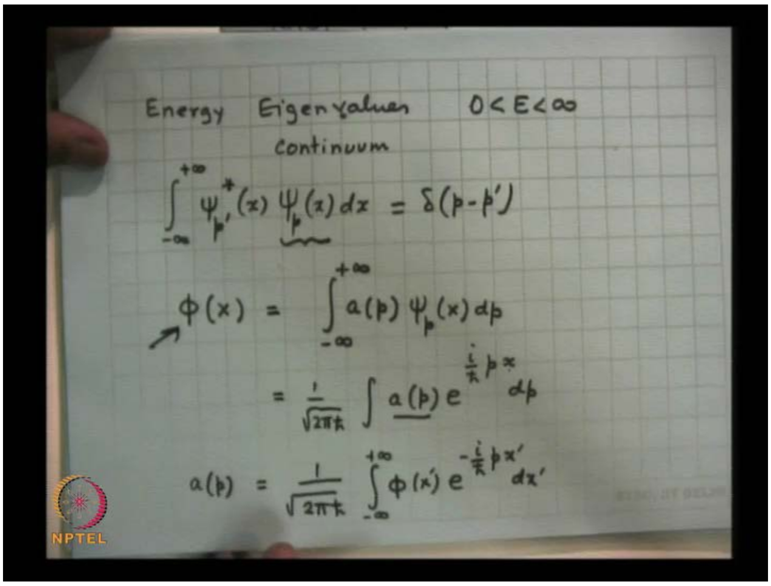

So, we say that the energy Eigen values form a continuum energy Eigen values are 0 less than E can take all values between 0 and infinity. So, they form a continuum and when this happens the orthogonality. Orthonormality condition is represented by this equation psi p prime star of x psi p of x d x the kronecker delta symbol is replaced by the Dirac delta function.Also these functions of course, these they are they form a complete set of functions. So, that any arbitrary function phi of x can be written as a of p superposition times psi p of x psi p of x d p and. So, therefore, these limits are also from minus infinity to plus infinity. So, what is psi p of x psi p of x is 1 over root 2 pi H cross integral a of p E to the power of I by H cross p x d p.

So, this is the Fourier transform. So, it is a superposition of the moment of these wave functions and. So, therefore, a of p is given by the inverse Fourier transform which we had discussed in quite a bit of length this will be phi of x E to the power of minus I by H cross p x d x all limits are from minus. So, for any well behaved function phi of x I can always make this expansion because I can always find a of p by carrying out the inverse Fourier transform now I can substitute for a of p in this equation, but, I have to be careful once again this is a definite integral over x and this x should not be confused with this x. So, I must quietly once again put a prime here and I when I substitute that I will obtain if you see this carefully that.

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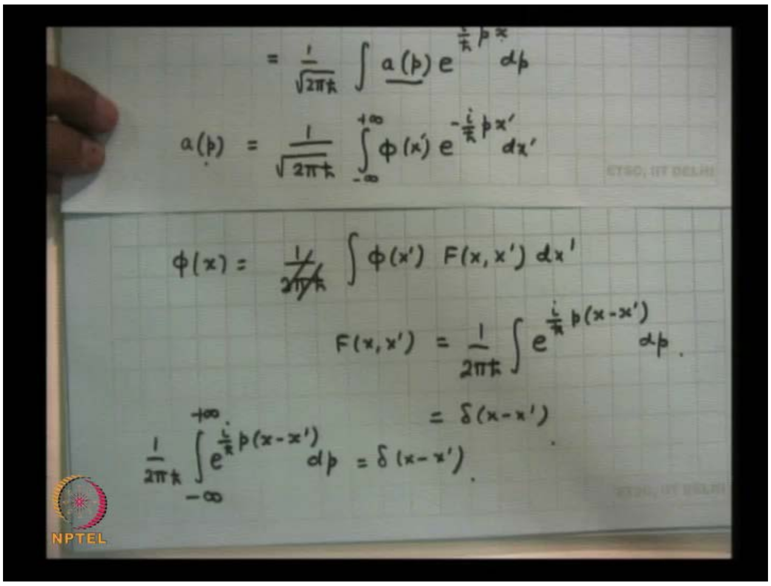

That if I substitute a of p from here there then you will get phi of x is equal to 1 over twp pi H cross phi of x prime and then there will be another function x comma x prime d x prime where f of x prime comma x prime is equal to I will take the 1 over 2 pi H cross here 1 over 2 pi H cross integral E to the power of I by H cross p x minus x prime d p.

This we know that this is the delta function. So, as soon as I substitute it here I get psi of x. So, this is my completeness condition is no more a sum it is an integral. So, psi this condition that I represent this is the completeness condition integral E to the power of I by H cross p d p from minus infinity to plus infinity is equal to delta of x minus x prime this is the continuum Eigen function of the of this is the completeness condition for the Eigen functions of the operator H.

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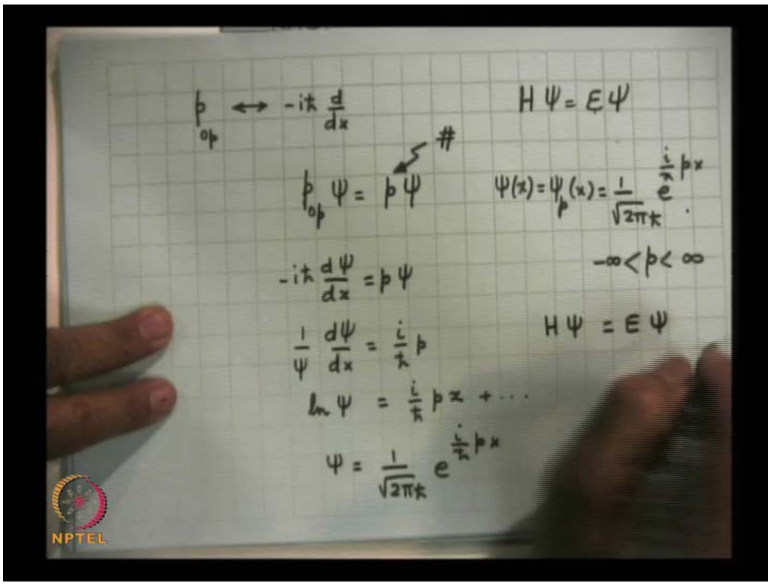

I would like to mention one more thing and that is let me consider the momentum operator p op the momentum operator. We had said that the momentum operator can be represented by minus I write it as a total differential and let us try to find out the Eigen functions of the momentum operator. So, I write this as op of psi is equal to p psi this is an Eigen value equation for the momentum operator where p is an Eigen value which is just a number. So, we had the Eigen value equation H psi is equal to E psi this is the Hamiltonian which is an operator and you find that only certain values of E are allowed these are the Eigen values.

So, you have the momentum operator p op and this is a I want to solve this Eigen value equation.So, I will have minus I H cross d psi by d x is equal to p psi where p once again is a number.So, I multiply by I by H cross. So, the left had side becomes one. So, I get 1 over psi d psi by d x is equal to I by H cross times p.If you integrate this. So, you get log psi is equal to I by H cross p times x plus a constant.

So, psi becomes the constant I will choose as one over under root of 2 pi H cross E to the power of I by H cross p x. So, these functions psi of x I write this as psi p of x and I have put the factor 2 pi H cross E to the power of I by H cross p x, where p can take any value from plus infinity to minus infinity to plus infinity. These are known as the normalized momentum Eigen functions these are known as the normalized momentum Eigen functions these are the Eigen functions normalized Eigen functions of the momentum operator. Actually these are simultaneous Eigen functions not only of the momentum operator, but H psi is equal to E psi for the free particle.

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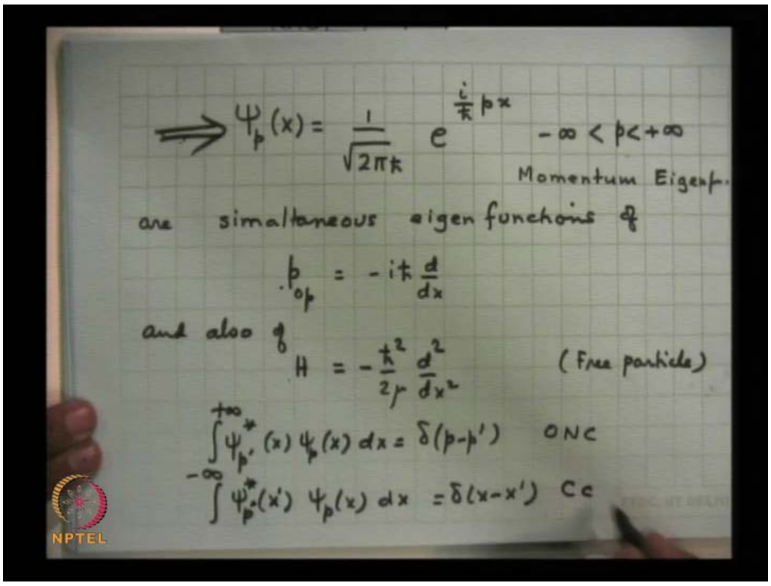

So, therefore, we say that psi p of x is equal to 1 over root 2 pi H cross E to the power of I by H cross p x p going from plus minus infinity to plus infinity they are simultaneous Eigen functions, simultaneous Eigen functions of p op, which is equal to minus I H cross d by d x and also and also of the Hamiltonian. For the free particle Hamiltonian for the free particle is H cross square by 2 mu d 2 by d x square actually the Hamiltonian has a v of x term. But v of x is 0 this is for a free particle and these wave functions these wave functions are therefore, Eigen functions of p op as well as of this. And these wave functions are often known as the momentum Eigen functions momentum Eigen functions.

And they form a orthonormal set that is psi p prime star x psi p x d x is equal to the Dirac delta function p minus p prime and they also all limits are from minus infinity to plus infinity. And they also form and orthonormal the completeness psi p of x psi star p of x p prime psi p of x d x this is equal to delta of x minus x prime sorry psi p’s x prime here and this is the orthonoarmality condition. This is the completeness condition let me rewrite this again this is not I have not written this carefully.

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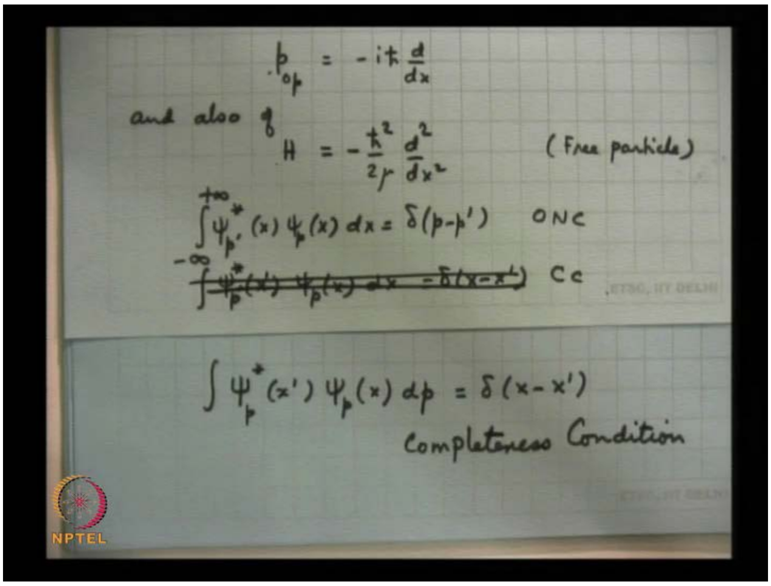

So, this is integral psi p star of x prime time has psi p of x d p is equal to delta of x minus x prime this is the completeness condition. So, this completes the analysis for the free particle problem as well as for the particle in a box. In our next lecture we will discuss first the solutions of the linear harmonic oscillatory problem and then we will derive those solutions thank you.