Quantum Chemistry of Atoms and Molecules
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Lecture-6
Particle in a Box: Part I

Welcome back to the second week of quantum chemistry of atoms and molecules. In the next couple of modules we are going to discuss a rather simple model called particle in a box which helps us understand several nuances of quantum mechanics.

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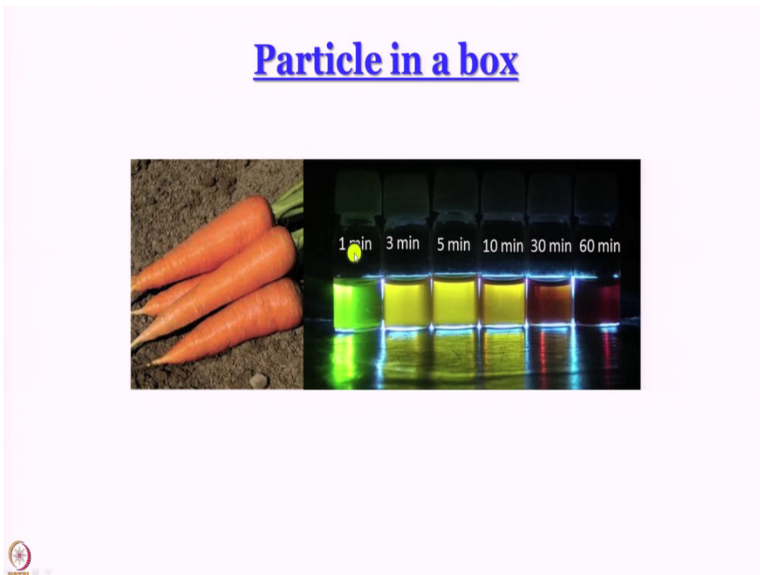

Not only that this model also helps us understand the color of carrots it also helps us understand why is it that the color of semiconductor quantum dots really, really small particles nano crystals of semiconductors. Why they change color upon changing size but that all in good time.

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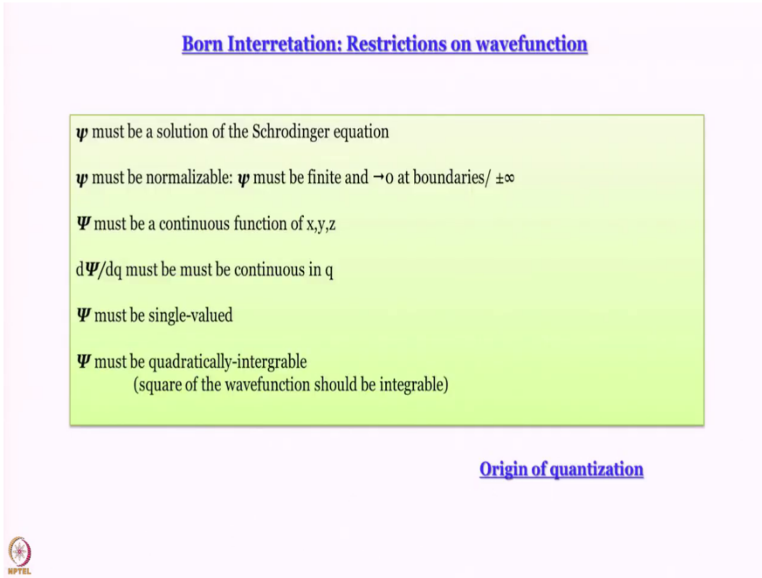

Let us just recapitulate what we have learned so far. We have talked about Schrodinger wave equation and we got this strange enigmatic parameter called wave function for from Schrodinger wave equation and even though the wave function makes perfect sense in the classical waves it was only after Born provided his interpretation sorry about the error in spelling of interpretation in the slide. Only after bond provided his interpretation that one can start making sense of the wave function but Born said if you remember is that amplitude in a regular wave.

If you take the regular wave and take its amplitude and take mod square of it then you get intensity. So, for matter wave also mod Psi square should give you a measure of intensity and then Born said that intensity of matter wave is nothing but the probability density. So, probability of finding a particle in 1 dimensional space let us say between x and x + dx is given by Psi Psi star dx.

And this probabilistic interpretation of wave function led to several restrictions on wave functions as we are studied already. We know by now that of course Psi a solution of Schrodinger equation but it has to be normalizable. What's the meaning of normalizable? Integrate Psi Psi star data over all space that integral has to be equal to 1 because the total probability of finding the particle somewhere in space has to be 1.

It has to be somewhere otherwise what are we talking about Psi must be finite because if it is infinite even one point then the integral of Psi Psi star d tau is not going to be 1 and also it must vanish at the boundaries this is something that we are going to make use of in the discussions henceforth. Psi must vanish at the boundaries whatever the boundaries of the system are or at least Psi should vanish at + minus infinity then only it is a so it is a good solution acceptable solution of Schrodinger equation.

Then Psi must be continuous we are going to make use of this as well in the present module. It must be a continuous function of spatial coordinates that might be involved because if there is a discontinuity then probability density and therefore probability of the particle at that particular point is undefined this is not acceptable. The first derivative I will not say must be continuous in q we are going to discuss an example today for particle in a box itself where the first derivative is actually not continuous.

But Psi must be single valued if for a given value of x, Psi has three four different values then it means that probability of finding the particle in that place is well three four what does that mean? That does not make sense so Psi has to be single-valued this is something that will make use of when we talk about particle in a ring and hydrogen atom. And Psi must be quadratically integrable otherwise you cannot really have it as a solution of Schrodinger equation.

And today we are going to establish among other things that all these restrictions that are imposed on the wave functions by on Born interpretation these restriction lead to quantization. If you remember so far we have not really got quantization in Schrodinger's method we only have a classical wave equation for de Broglie waves there is no quantum number there. Whatever wave function that we have discussed so far has no quantum number.

So, where do the quantum numbers come from and remember one of the objections against Bohr theory is that the quantum numbers fell from the sky. There was no logical explanation it is just that Bohr invoke quantum numbers because that was the only way of explaining experimental results. As we will see in Schrodinger's treatment quantum numbers arise naturally the moment will incorporate Born interpretation.

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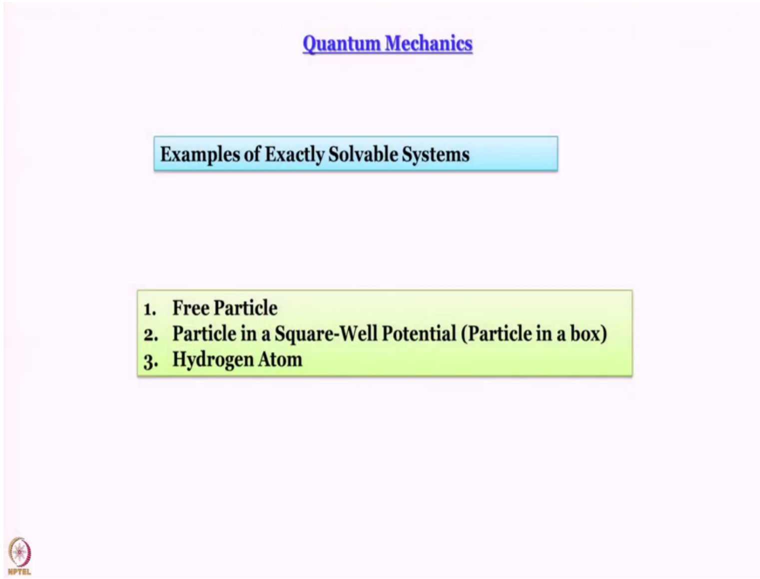

Here actually well we said this that we are going to start with talk about exactly solvable systems, systems in which Schrodinger equation can be solved exactly without using any approximation.

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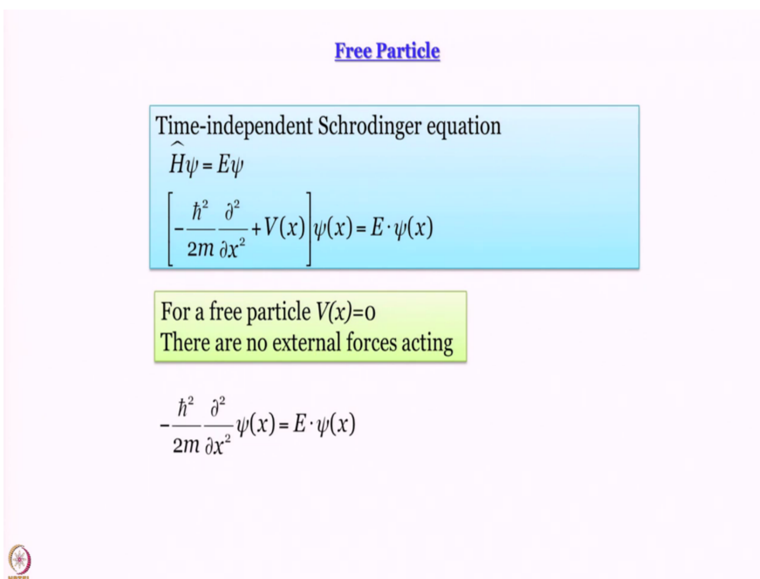

We have started our discussion of free particle a free particle means something that moves without any interaction with anything else so in this equation of Schrodinger time independent Schrodinger equation we have to set Vx to be equal to 0 because it is a free particle it does not interact with anything else and potential energy if it is there has to arise from interaction with something else so potential energy is 0, no external force. So this is what Schrodinger equation has the used to as we have discussed in the last module.

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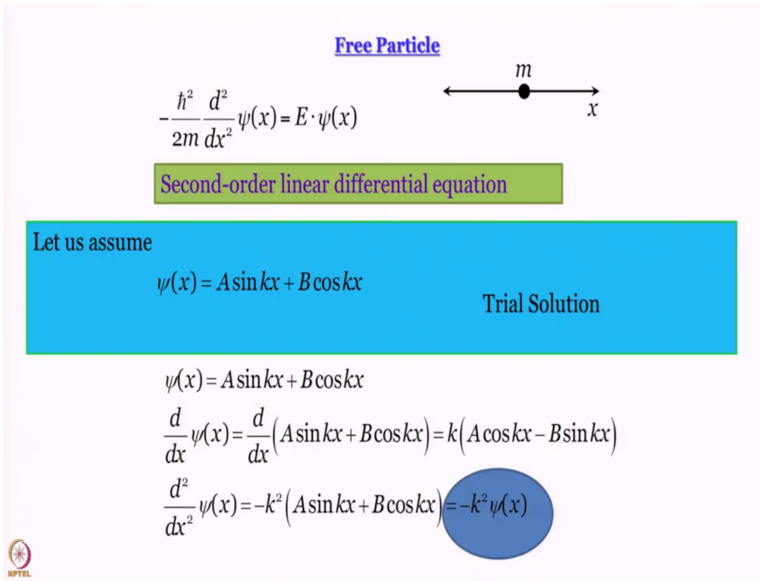

And then we actually went ahead and solved it we proposed a trial solution of A sine kx + B cos kx and we verified that this trial solution actually is an eigenfunction of Schrodinger equation if you differentiate it twice you will get minus k square A sine kx + B cos kx so that means minus k square multiplied by Psi of x if you plug it back here multiplied by minus h cross by 2m you get an expression of energy to be minus h cross square by 2 m multiplied by minus k square.

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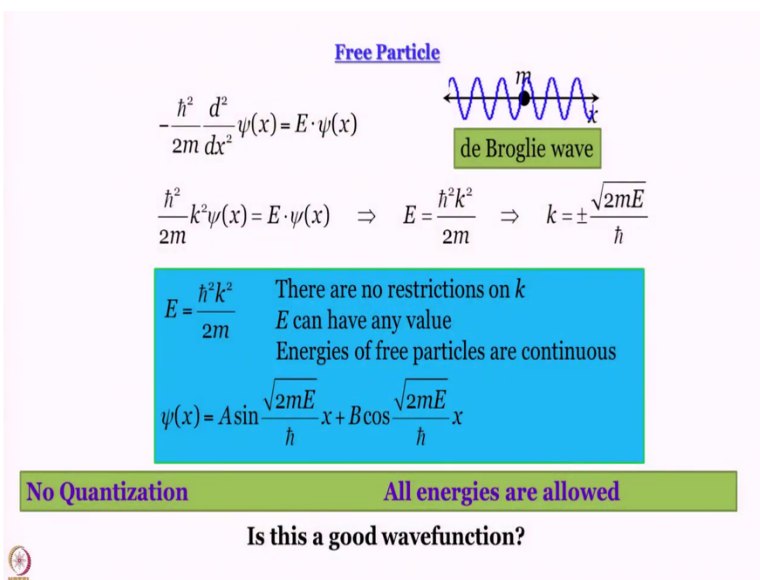

So, this is what we get a plus h cross square k square divided by 2m that is the energy value that we have got and k has turned out to be plus minus root over 2 mu by h cross we did not say anything about this k we are going to talk about a little more it turns out that this k gives you what the momentum is and as you can see for momentum there is a plus minus sign that means the particle can move in this direction or in this direction in both the directions as shown in this figure.

So energy is defined completely magnitude of momentum is defined completely direction of momentum can be either this or that plus or minus we have not really talked about the momentum operator so far we will do it once you get into particle in a box. All right so this is what it is now there is no restriction on k which means there is no quantization and all energies are allowed. Now let us ask the question is it really a good wave function does it satisfy all the conditions imposed by Born interpretation.

And right away I hope you can see that the answer is no; yes it is continuous no problem with that but does it vanish at the boundaries? Where is the boundary? Boundary in this case might be at plus infinity and minus infinity does it vanish? Thus I vanished? It does not can you normalize it to be very honest you cannot because limits will be minus infinity to plus infinity that is not going to be one but what one does to circumvent this problem is that for a free particle this wave function is what is called box normalized.

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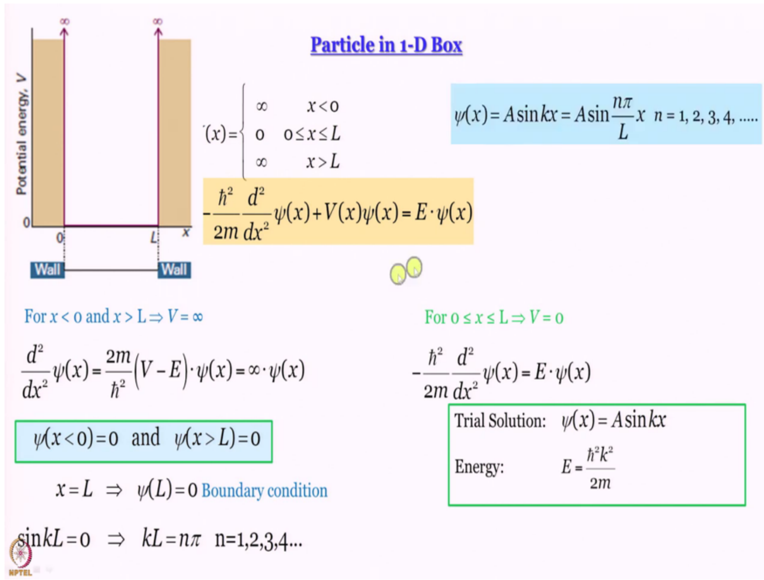

You have to perform box normalization what does that mean take this wave function let it go to some distance large distance and then you say that this is minus infinity that is plus infinity. And this may not be such a bad approximation after all because we're talking about molecular systems atomic systems if you go to even 10 angstroms there is no interaction between two atomic particles at a atomic-level particles.

So infinity does not mean that you have to travel a few light-years so that way it is fine but still very strictly speaking it is not such a great wave function but that's what we have got to start with anyway. So, with that let us move on a little bit and let us see what happens if you restrict the freedom of the particle. Let us say we restrict it in a box of a finite length and that takes us to this model of particle in a box that we promised to discuss today.

What is the model the model is that as long as the particle is between say x equal to 0 and x equal to L the potential energy is 0 which means it is a free particle. The moment you go beyond x equal to 0 or beyond x equal to L potential energy is infinity which means that you can think that if you plot potential energy there will be an infinitely high wall at x equal to 0 infinitely high wall at x equal to L. So, it is as if some selfish giant has entered this quantum mechanical system and will really, really tall walls that nobody can climb infinite potential barrier is what we have here.

And this model right now we are considering only one dimension x so this is called particle in a 1d box because it looks like a box and the other name that one can use is a quantum mechanical well with infinitely high potential barrier infinitely high walls alright. So, let us see what happens to Schrodinger equation for different values of x. This is Schrodinger equation that's where we start from for x less than 0 and x greater than L we said that V equal to infinity so we have to substitute infinity for V of x let us do that this is what the equation becomes.

So if this is the equation then you will get something like infinity multiplied by Psi x nothing else matters and then this equation makes sense only when Psi of x is equal to 0 right. So, in other words what we are saying is that the particle cannot exist outside the box and even physically thinking it makes sense that if there is a an infinitely high potential energy surface how is it possible potential energy wall?

How in the particle go outside? It cannot. As we see later on if the height is not infinite but finite then the particle can tunnel through it does not have to climb the wall and it tunneling becomes easier if the wall is shorter but let that be the story for another day. Let us now think what happens when the particle is inside the box, x has values between 0 and L. For this interval the particle behaves like a free particle so as long as it is inside the box its free but it cannot go outside the box that is all.

So that is sort of restricted mobility. So, now see free particle means as we know already V equal to 0 let us put V equal to 0 in the equation we get our own we get back our familiar equation for the free particle just remember now the only difference with the real free particle equation is that it is valid only for x values between 0 and L, 0 less than equal to x, x is less than equal to L. In this interval V is equal to 0 and when V equal to 0 we already know the solution of Schrodinger equation and this is what it is A sine kx + B cos kx they are not normalized yet but let us start from here A sine kx + B cos kx.

And energy we know is h cross k square by 2m do you have quantization yet not yet but we are not very far away from there. Now we know what happens outside the box we know what happens inside the box let us worry about the boundary. What happens at the wall at x equal to 0 and x equal to L? That is what we want to now consider. Now see outside the box at x less than 0 x greater than L the wave function is 0.

And we know one of the conditions imposed by your born approximation born interpretation is that the wave function must be continuous. So, since you go a little early if you go a little bit distance beyond x equal to 0 beyond x equal to L since the wave function is 0 the condition of continuity requires that at x equal to 0 and at x equal to L the wave function has to be 0 right. So, we will take this x equal to 0 situation first for x equal to 0, Psi of x equal to 0 this is required by the boundary condition these are called boundary conditions.

The boundary condition that the wave function must be continuous, all right now what happens to this trial solution if you are; if we use this boundary condition what is the value of Psi at x equal to 0, it has to be 0 but then you see when I put x equal to 0 what is sine kx? Sine kx is also 0 so the first term vanishes no problem with however what about the second term in the second term we have B cos kx if you put x equal to 0 then cos 0 is equal to 1 so you are left with Psi of x is equal to B in which condition when x equal to 0.

So, you can say Psi at x equal to 0 is equal to B but then we know already from the boundary condition that Psi at x equal to 0 has to be 0 so since Psi at x equal to 0 is B it is not difficult to see that B has a value of 0. Remember B is a constant a is a constant they are not dependent on the value of x so when B equal to 0 it is 0 for all values of x it is independent of x anyway right that is sort of nice because now the wave function that we have got by using this boundary condition no longer has two terms.

The second term is eliminated since cos kx is multiplied by B we are left with only one term Psi of x is equal to A sine kx okay wave function is simplified do we have quantization not yet but as we said earlier we are not very far away from it right. Let us now try to use the second boundary condition well I mean the nature of the boundary condition is the same continuity is what we are looking for but we are looking at the other end of the box.

We have got rid of the cos term by looking at x equal to 0. Now what happens if you look at x equal to L, even at x equal to L Psi has to be equal to 0, same boundary condition continuity? So, if we put x equal to L then what is the value of Psi at L that has to be equal to A sine kL which means since Psi at x equal to L equal to 0 A sine kL has to be equal to 0 when sine kL equal to 0 means what? What are the possible values? kL then must be equal to n pi where n is equal to 1, 2, 3, 4 and so on and so forth integers right.

So we can now modify this equation and we can write that Psi of x is A sine n pi by n pi x by L where n is equal to 1, 2, 3, 4 so on and so forth. Now for students on the other side of the screen unfortunately I can cannot see you but I hope that you have a question at this point of time and the question that you ought to have at this point of time is that what happened to 0? I mean when x equal to 0 then also Psi of x is equal to 0 there is no problem with that.

However mathematics is the tool by which we want to understand the subject it is not the be-all and end-all so we have to use mathematics and we also have to think what we are dealing with and we are dealing with wave functions. We are dealing with wave functions that must satisfy Born interpretation. So, what happens if we put x equal to 0 sorry n equal to 0 here if you put n equal to 0 then irrespective of the value of x Psi becomes 0 right that means within the box Psi 0 everywhere which means mod Psi square well there is no mod here it is a real wave function Psi square dx is equal to 0 which means the probability of finding the particle even inside the box is 0 there is no particle what are we talking about.

This perhaps a fourth time I have said what are we talking about in this course but well that is what I feel what are we talking about if Psi is equal to 0 everywhere that does not make sense that is why n equal to 0 is not what we accept. Okay even though it is a valid mathematical solution it is eliminated by Born interpretation. So, n equal to 1 2 3 4 5 does that ring a bell whatever we achieve, they receive quantization.

We have said that only certain wave functions are allowed those wave functions in which n is a positive integer all other wave functions are not allowed. As we will see this will lead to quantized energies as well because you might remember that every Psi is associated with a particular energy state. We will come to that before that let us get done with Psi. Let us first determine what the value of A is and let us see what these wave functions would look like for different values of n right.

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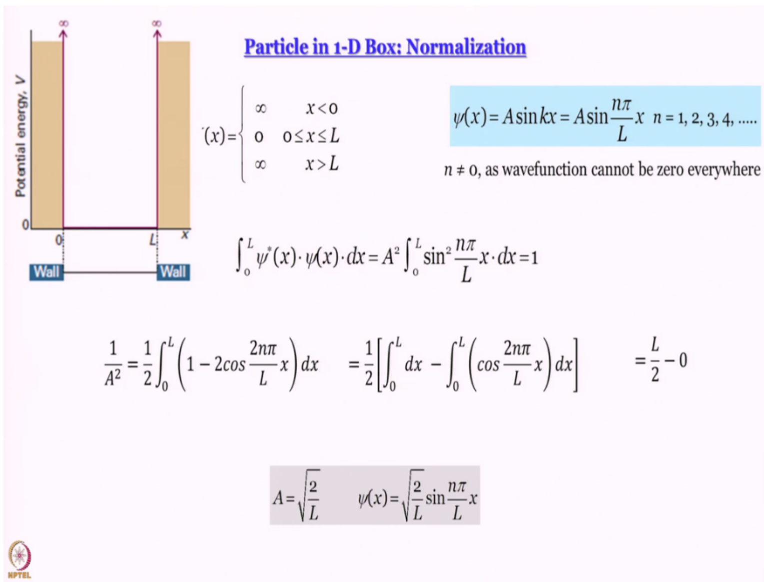

To get a value of A what we need to do is normalization. When we normalize and now see we have said the generic definition is for normalization the integral has to be from minus infinity to plus infinity but then we know already that from minus infinity to x equal to 0 Psi equal to 0 any way from x equal to L to plus infinity Psi equal to 0 anyway so we do not really have to go from minus infinity to plus infinity it is enough if you integrate between the limits 0 to L.

So you integrate between 0 to L Psi star of x x Psi of x dx we get A square integral 0 to L sine square n pi by L x dx equal to 1, now usually students are better than me at mathematics I am sure all of you are and it is not very difficult for you to integrate it but I still do it in steps what we do is we know very well what is the relationship between sine square theta and cos 2 theta we use that relationship.

And instead of sine square n PI by L x we write 1 - cos 2 n PI by L into x multiplied by 1/2 and then we work out this integral what will the integral be I have two terms now right the first one is integral 0 to L dx that is very simple that gives me L and if you take this half it gives me L by 2 the first term becomes L by 2, what about the second term integral of cos kx will give me sine kx multiplied by some constant.

Now sine kx integrated from 0 to L or what do I get what is the value of sine kx at x equal to 0 it is 0, what is it at x equal to L, 0 now remember the integral has the same form as a wave function here. So, and the wave function vanishes at x equal to 0 and x equal to L so the second term turns out to be 0. So, right hand side becomes L by 2 - 0 now it is very simple we just change the subject of formula A turns out to be root over 2 by L and when we substitute it in the expression for the wave function we get the normalization constant as we said is root 2 by L Psi of x turns out to be root 2 by L sine n PI x divided by L. So we have got the wave function.

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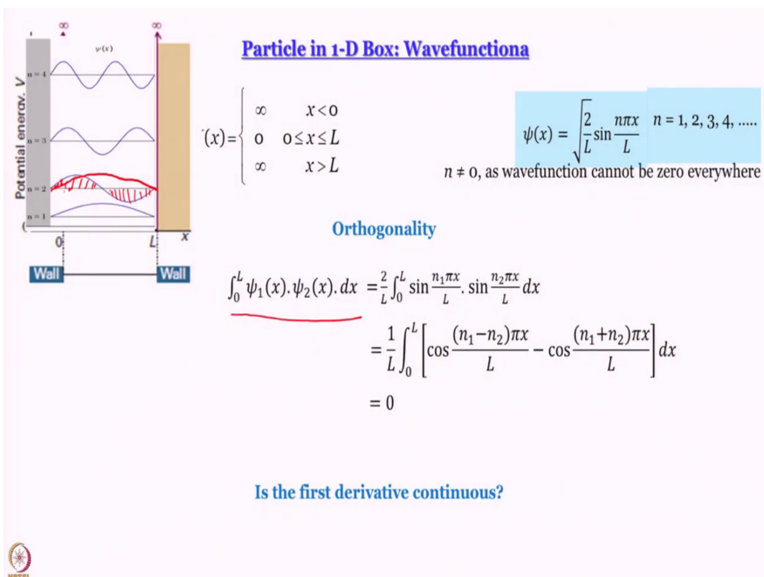

If I plot the wave functions what do I get these are the wave functions for n equal to 1 what will happen x equal to 0 only at x sorry Psi equal to 0 only at x equal to 0 and x equal to L this diagram is a little bit off sync with the labeling here sorry about that and there will be no node, node means a point at which the wave function changes sign. If I take n equal to 1 then what will happen the wave function will become 0 not only at the ends but also at L by 2.

Sorry what am I saying when n equal to 1 there is no node this is a wave function that you get when n equal to 2 then the wave function is root 2 by L sine 2 n PI x divided by L so that function will become 0 even at L by 2, so you will get this you get the full wave earlier we had only half a wave for n equal to 2 we get a full wave. For n equal to three we get three half waves, for n equal to 4 we get to full waves which means for half waves.

So what we see is that n also stands for the number of half wave lengths that are present for that particular wave function inside the box. Remember we have said that the wave functions must be orthogonal for a particular system are these wave functions orthogonal well it is very easy to see that if we just plot them. Let me plot the n equal to one well the n equal to 1 wave function is there already. Let me actually plot here the n equal to wave function on top of the n equal to 2, wave function.

It will be something like this forgive my poor artistic skills but tell me when I want to search for orthogonality when I want to look for this kind of when I want to look for orthogonality I want to evaluate this integral what does it actually mean? It means that for the 2 wave functions have chosen for every point for every value of x, I have to multiply this value of Psi, Psi 1 with Psi 2 and I keep on doing that for all and then add up the products that is essentially what I am doing.

Now it is not very difficult to understand that for x equal to 0 to L by 2 product of Psi 1 and Psi 2 is going to be positive products are going to be all positive. For x equal to 0 to sorry for x equal to L by 2 to L these products are all going to be negative, so when we add up all the products what do we get we get 0 right. So, I do not even have to evaluate the integral to say that indeed the wave functions are orthogonal.

I leave it to you to work this out for any pair of wave functions you desire and then quickly if we want to work it out not by a diagram but actually by evaluating the integral the hard way this is what you do you know that we know the relationship between sine c, sine d and cos c + d and cos c – d, we use that relationship work it out and once again since integral of course is a sine and since of sine functions we know are 0 at x equal to 0 and x equal to L we get is 0.

Hence it is proved that the wave functions are orthogonal. So, what have we got we have got wave functions that are normalized and which form an orthogonal set, are they continuous? Yes there are continuous. So, so far everything looks hunky-dory let me ask a question now, is a first derivative are the first derivatives continuous? Obviously not because just let us look at this first wave function n equal to 1.

What is the first derivative here Psi equal to 0 right it is a flat line so first derivative will also be equal to 0 for all these values. What is the first derivative here at x equal to L and x equal to L your it is the sine function right Psi is still 0 but then go a little bit in what will happen it will be the derivative is going to be cos theta right. So, if sine is Theta is equal to 0 what is cos theta, 1, sine square theta + cos square theta equal to 1.

So suddenly at x equal to L there will be a discontinuity and the value will be 1 of the first derivative. So, what am I plotting here I am plotting d Psi dx against x so and then it will go something like this. So, there are discontinuities at the boundaries, so that is what we have been saying that this continuity of first derivative is not really an essential requirement for the wave function to satisfy Born interpretation even though it is put that way in many textbooks. We stop here today and then we will come back and talk about the energies of these wave functions.