Solar Photovoltaics :
Fundamental Technology and Applications
Prof. Soumitra Satapathi
Department of Physics
Indian Institute of Technology-Roorkee

Lecture - 04
Introduction of Quantum Mechanics in Solar Photovoltaics - II

Welcome everyone to the fourth module of our course. In the last class we have learnt about Schrodinger equations. And we gave a very simple example of solving Schrodinger equation in particle in a box. In today's lecture we will see that how to solve this equation with appropriate boundary condition. And also in the second part, we will learn about particle in a finite potential box.

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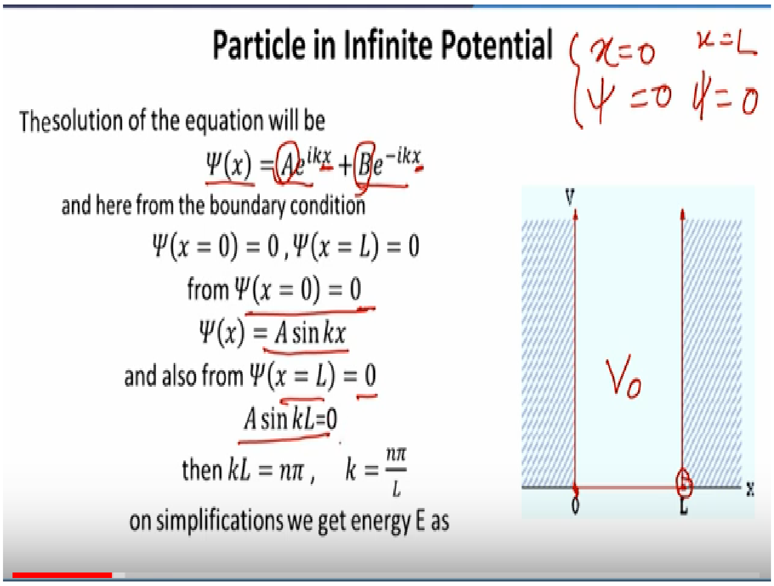

To recapitulate the last class, this is a finite potential, infinite potential well, where the potential energy between 0 to L we said that V naught and the potential blows at the two walls that means at x is equal to zero and at x is equal to L. And in the last class we have written how does the Schrodinger equation looks like in this particular case and what we get that the solution of the Schrodinger equation in this particular problem.

And the solution is psi x, the wave function, this is equal to Ae to the power ikx plus B e to the power –ikx. Where this A and B these are two arbitrary constants. Now we need to find out the value of these two constants and also we have to impose certain boundary condition to see that what are the solution are physically meaningful and what are the solution we have to discuss.

Now if we look to this particular problem, what are the boundary condition here? At this point x is equal to zero, and at this point at x is equal to L, the wave function is non-existent. Because, since the potential blows out here, so according to the postulate of quantum mechanics, the wave function cannot exit here. So that is why we write that at x is equal to zero the wave function psi should be zero.

And that exactly we have written in our first boundary condition. The similarly our second boundary condition is that at x equal to L, the potential blows out so the wave function will also be zero. So at x is equal to L wave function psi is also zero. This is our second boundary condition. Okay, now let us see if we apply this two boundary condition what will happen to the fate of Schrodinger equation.

If we apply the first boundary condition, that is psi x is equal to zero is equal to zero. So what we will get is that if we plug in x is equal to zero in this equation, and x is equal to zero in this equation, what we will get that psi x is equal to A sin kx. And at x is equal to L psi x is also zero. So if we apply that boundary condition we will get A sin kL is equal to zero.

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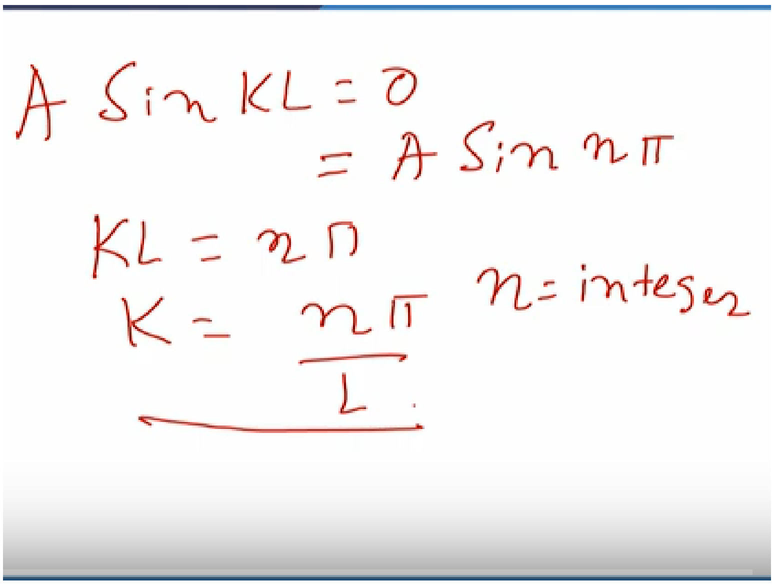

Which will give that since A sin kL is equal to zero, we can also write this let us say A sin kL is equal to zero. When sin becomes zero? When sin is zero, pi 2 pi, 3 pi, 4 pi etc. So in general, we can write that this is A sin n pi where n is any integer. Now if we equate the left hand side and the right hand side, so what we get that KL is equal to n pi or K is equal to n pi over L where n is any integer.

Now if I use this value of K in the solution of the Schrodinger equation, what we will get is the following. We will get k is equal to n pi L.

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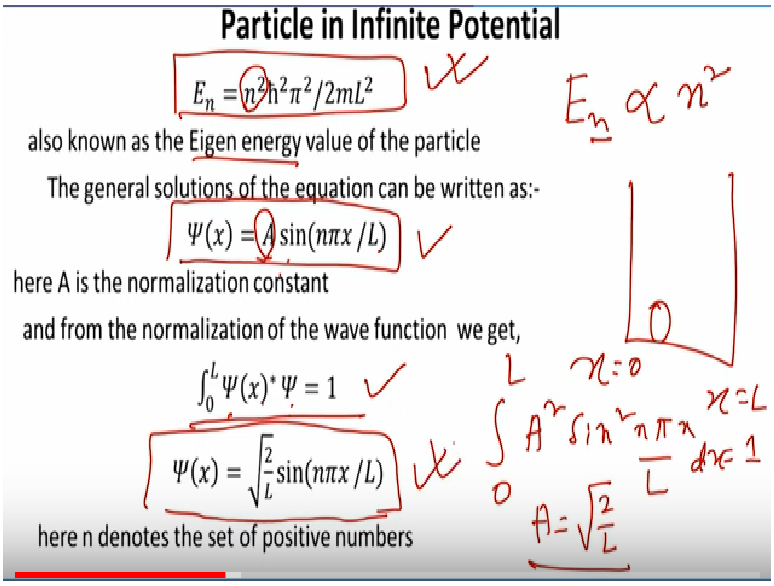

And if we substitute that what we will get is the value of energy in this infinite square well potential and that is E n is equal to n square pi square h bar square divided by 2mL square and this is known as the Eigen energy value of the particle. It is very interesting to see that this energy is proportional to n square. So we can write the energy E n is proportional to n square.

So that means, so the value of the energy at any particular level n is proportional to the square of that number. So energy is quantized in this level and we can write the general solution as psi x is equal to A sin n pi x divided by L, but still we have an unknown constant A. And this constant is called the normalization constant. Now how can I find out the value of this constant?

So from the definition or some of the fundamental postulate of the quantum mechanics, we know that every wave function in a particular area is normalized. So if I apply the fundamental postulates of quantum mechanics, and since in this particular case, our electron is confined between zero and L, which is the dimension of this box.

So we can write that integration 0 to L the wave function times the complex conjugate of wave function, that must be equal to 1.

What is the physical significance of this mathematical equation? It means that the probability of finding the electron somewhere between this box should be equal to 1. That means, if somebody wants to find out the particle between x is equal to zero and x is equal to L, and if I integrate the probability, so we must find the particle somewhere in this box.

And that statement is mathematical written by this equation. If I plug in here the value of psi from this equation, so what I will get is that psi x is A sin n pi x by L and the complex conjugate of psi is again A sin n pi x by L. So basically we are getting if we use this equation it is integration 0 to L A square sin square n pi x by L dx is equal to 1.

And if we carry out this integration we will find out the value of this constant A as root 2 by L and we will leave this calculation to you. If you substitute this value of this constant to the original solution of our Schrodinger equation we will get psi x is equal to root 2 by L sin n pi x by L. And that is our i n function or the wave function of this particular case.

So we get two special case. One is the energy i n value and another is the energy i n function for a particle in a box problem. And it is very interesting to note that the energy i n value is proportional to n square.

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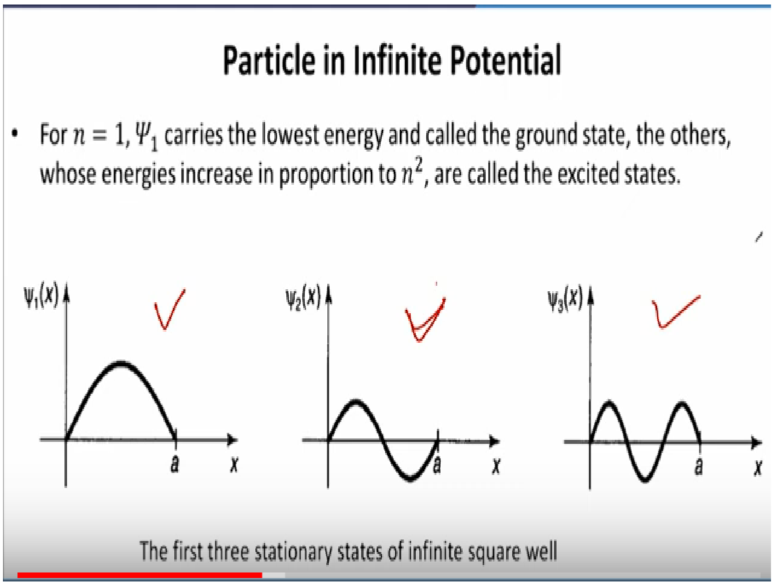

Now if I put the value of n is equal to 1, then the corresponding wave function psi 1 called the ground state wave function. Subsequently the value of n is equal to 2, n is equal to 3. They gives us different excited state energy level. And the energy at all the state is proportional to n square. For example, in this particular case, we are showing how the ground state wave function psi 1 x is plotted as a function of x.

And you can see that as we go to n is equal to 2 or n is equal to 3 we have further nodes in our solutions. And we can also calculate what will be the corresponding energy for this wave function. So this particular case is our ground state and all these are example of first excited or second excited state and so on. So these are different excited state.

Now for example, if somebody wants to calculate what will be the energy at this wave function where n is equal to 2. We know that the energy is proportional to n square. So we have to go back to our previous slide and what we can do in the case of n we can substitute the value n is equal to 2 and we will get energy is equal to n square that is 2 square that is 4 pi square h bar square divided by 2m L square.

Now if you consider this is a case of an electron, so we know what is the mass of an electron. So we can substitute the mass of the electron here. Even we can put the value of the Planck's constant H. We know the value of pi. So if we know the dimension L of the box, we can exactly find out what is the energy of this electron in n is equal to 2 state and so on.

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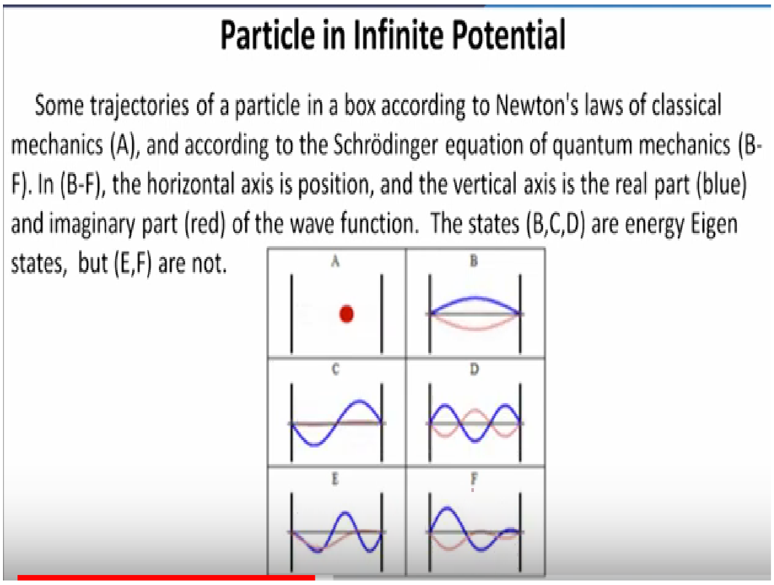

This state sometimes are also called the stationary states. Now this was the explanation or derivation according to the quantum mechanics. If we consider the similar case from a Newtonian mechanics point of view, how does it will look like. In this particular case, we are showing that the trajectories of the particle in a box according to the Newton's law of classical mechanics in A where you can see the ball the red color ball is bouncing back and forth between the two walls of the this well.

But if you consider to the quantum mechanics here, which is showing from B to F; B, C, D, E and F, where horizontal axis is the positions and vertical axis for blue color it is the real part and for the red color it is the imaginary part of the wave function. And this wave functions is fluctuating and they have different nodes as you increase the quantum number n.

And the states B, C, D they are energy Eigen states, but E and F they are not. So this was the particular case when we considered a particle in a box. But in most of the realistic case, we have an example where particle is confined in a finite potential box. Let us say I have an electron in a piece of metal L where I know exactly the length of the metal.

And also at the end of this metal box or metallic box the potential does not blow out. So in that particular case we cannot use our infinite potential square well solutions. So that problem is particle in a finite potential well.

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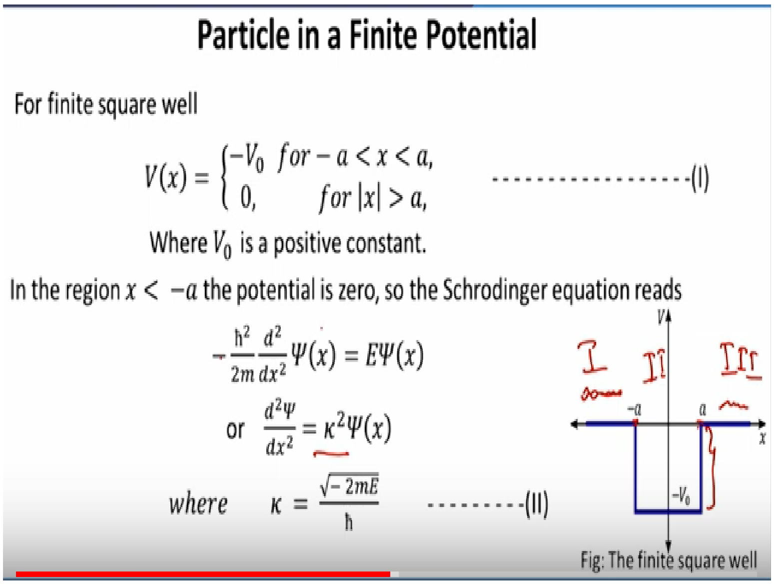

So let us look at this problem because that is more realistic when we talk about the motion of any charged particle or motion of any subatomic particle in a real potential. For a particle in a finite square well potential, the potential is defined like the following. The V x where the potential is a function of the position x it is minus V naught when the value of x is between - a to + a.

You can see the depth of this well is –V naught. And when mod of x that means when the value of x is greater than a this mean in this region or the value of x is less than - a that means in this region, the potential is zero. So one second the potential exists only in between - a and + a and it is zero everywhere else. This type of potential distribution is called a square well potential.

And we need to solve the differential equations for this particular potential case again, the solution is very simple, we need to write the Schrodinger equations for this particular potential case. Again, the solution is very simple. We need to write the Schrodinger equations and all we need to play around with the potential. So there we have to replace the value of V with this particular potential form. Okay, let us do this.

So since we have three different regions, like we can consider as a region 1, this is region 2, and this is region 3. And potential distribution is different in this three regions. Of course, it is same in region 1 and 3, but it is different from 1 to 2. So we have to solve the Schrodinger equation in all three different regions. In the region x less than - a that means in the region 1 the potential is zero.

So if I write V = 0, in the Schrodinger equation it will look like – h bar square by 2m d 2 psi dx 2 psi x is equal to E psi x. And the solution of the Schrodinger equation will be d 2 psi dx 2. We can take this minus on the right hand side and multiply this 2m by E. So what we will get is 2mE by h bar square. And this 2mE by h bar square we can equate to a constant called kappa. Where kappa is equal to root over – 2mE by h bar.

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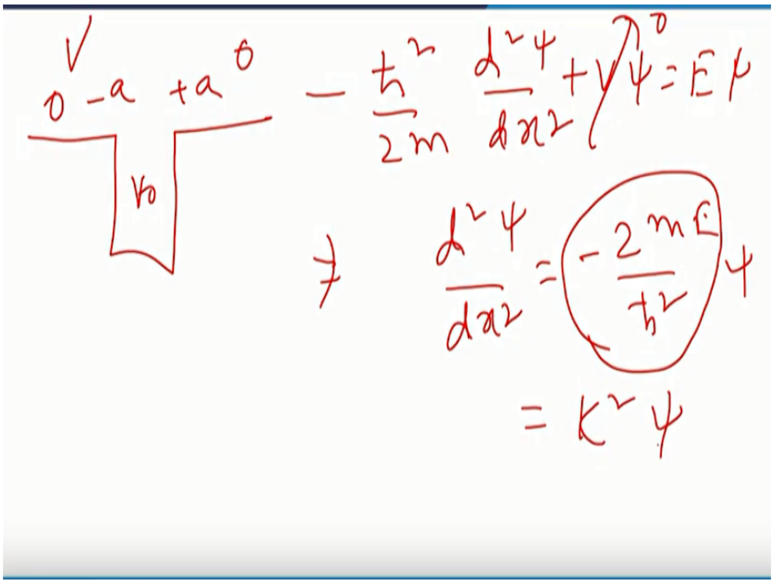

So to write it in a better way let us say minus h bar square by 2m d 2 psi dx 2 plus V psi is equal to E psi, right? So in the region x less than my – a, you remember there are three regions here. This is – a, this is + a. Here the potential is V naught but here it is 0, here it is 0. So we are considering in this region. In this region potential is zero. So we can write d 2 psi dx 2 is equal to – 2mE by h bar square psi.

Now if we consider whole this thing as a constant kappa square, so we can write this is kappa square psi.

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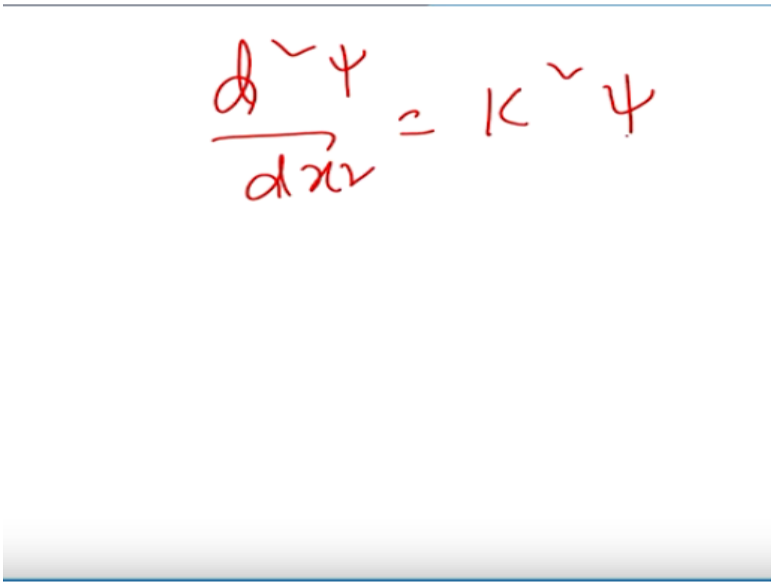

So the equations will become d 2 psi dx 2 is equal to kappa square psi. Let us come back here. So that is what we have written here, kappa is equal to square root of – 2mE by h bar.

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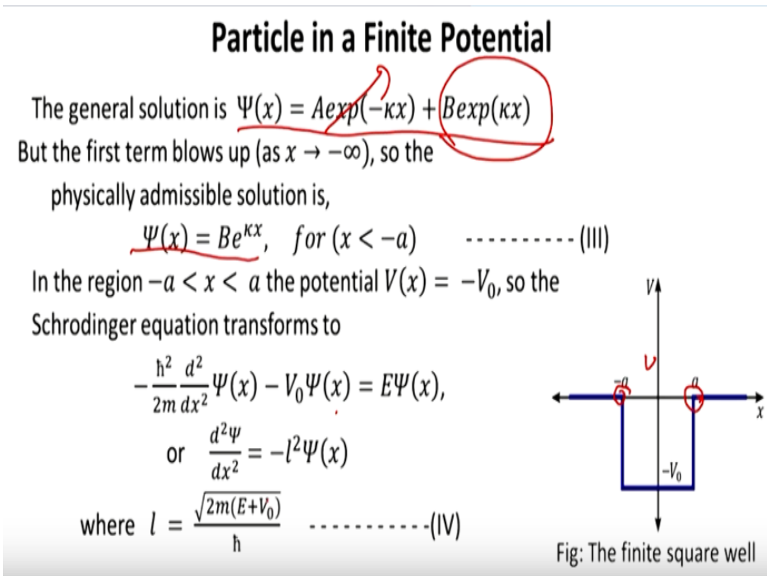

And if we substitute that the general solutions will be psi x is equal to A exponential minus kappa x plus B exponential plus kappa x. But again, we know that we have certain boundary condition and we need to apply those boundary condition. Now what are the boundary condition? Now at this region when we go towards the infinity x tends to minus infinity, we know that the first term blows out.

Because if we put x is equal to minus infinity, so minus and minus plus and exponential plus infinitive means infinity, which makes whole the solution goes towards the infinity. And we know from the postulate of quantum mechanics that is not physically admissible. So this term must be vanish, which left out with the right hand side the second term.

So we get the solution psi x is equal to B kappa x for x less than – a. That is the solution of the Schrodinger equation for finite square well potential in the first region. Now let us look for the second regions. So in this regions. Now we are between x is equal to - a and x is equal to + a. In this region potential is minus V naught.

So the Schrodinger equation will be minus h bar square by 2m d 2 psi dx 2 minus V naught psi is equal to E psi. And or you can write it d 2 psi dx 2 is equal to minus L square psi x where here the constant l is square root of 2m E plus V naught by h bar.

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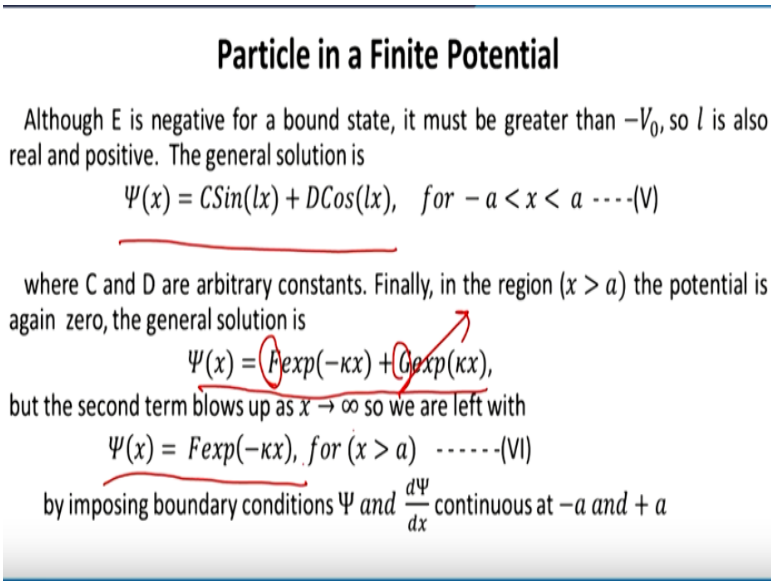

What will be the general solution here. We will come to the general solution, but before that have a look on the constant l. Now since this is a bound state, the energy must be negative value. So E is negative for a bounced state and it must be greater than minus V naught. So if we consider that, that E is greater than minus V naught so l should be a real and positive constant.

So if l is a real and positive constant the solutions of this equations d 2 psi dx 2 plus l square psi x is equal to plus l square psi x is equal to 0 will be psi x is C sin lx plus D cosine lx for x less than – a to + a. That means where the potential is minus V naught.

Now here C and D are two arbitrary constant and we need to find out what is this arbitrary constant. We will come to this point later on.

Now next consider the last region or the third region. So in this region x greater than a the potential is again zero and the general solution will be we know in this case, we change the constant psi x is F exponential minus kappa x plus G exponential kappa x where F and G is an arbitrary constant. And again we need to apply the boundary condition. But here what is the boundary condition?

Here as we go x to positive infinitive, the second term will blow out. Because if we put x equal to plus infinity here, exponential plus infinitive, this whole terms goes to infinity, but that is not possible according to the postulate of quantum mechanics. So these terms must cancel leaving out the first term. So the general solution of the third region will be psi x is F exponential minus kappa x for the region x greater than a.

Okay, so we have found out the solution in x less than - a and x less than + a by applying the boundary condition. We have solved the case of x between – a and + a but so far we have not applied any boundary condition. Now let us look at that. So here we have two different boundary condition. The first boundary condition is that psi is continuous at - a and + a and also the first derivative of psi that is d psi dx that is also continuous at - a and + a.

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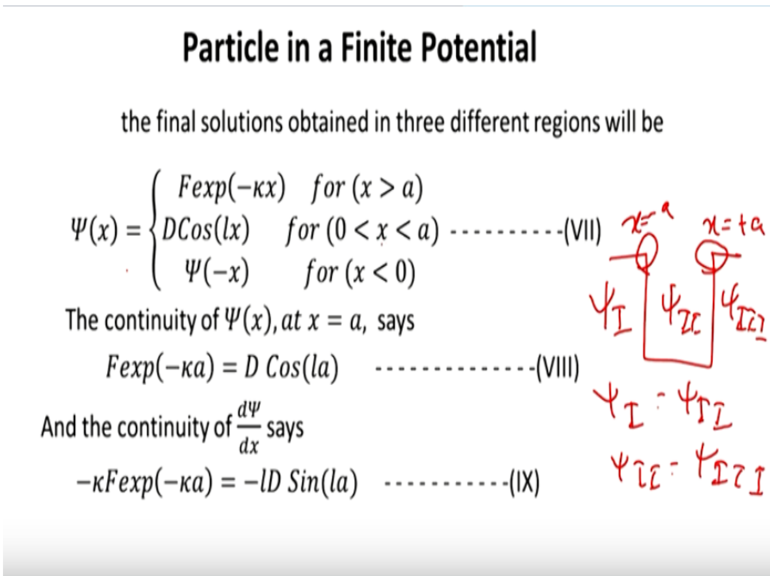

If I apply those boundary condition that psi x is continuous at the two boundary. So if this is my potential well, this is my first boundary and this is my second boundary. So at this two positions wave function should be continuous. So that means if you call this as psi 1, if you call it as psi 2 and if you call it as a psi 3, so psi 1 must be equal to psi 2 and psi 2 similarly will be equal to psi 3.

If we apply this condition we will get that psi x the value of wave function for x greater than a is F exponential minus kappa x and between x 0 to a it is D cosine lx and for x less than zero it will be psi minus kappa x. The continuity of psi x at x is equal to A that means on the other side of the well gives that F exponential minus kappa is equal to D cosine la.

And the continuity of the first derivative of psi with respect to x that gives us the value minus kappa F exponential minus kappa a is equal to minus lD sin la. So we have now two equations. One comes from the continuity of the wave function another comes from the continuity of the first derivative of the wave function.

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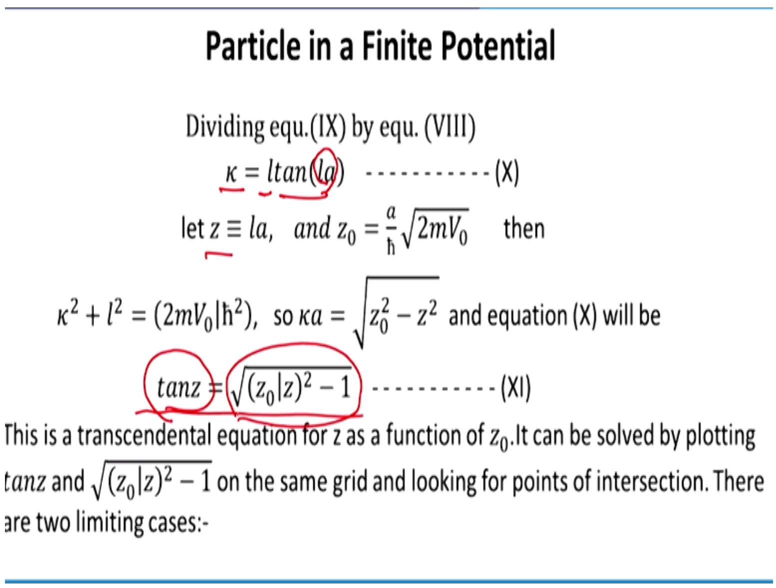

If I divide the first equation by the second we will get the value of the first constant kappa in terms of l and another terms called tangent la. Now if we consider this la or the terms inside the bracket is z. And also further if we define z naught is equal to a by h bar square root of 2m V 0 then what we get, kappa square plus l square is 2m V 0 by h bar square. And the value of kappa a will be root over z 0 square minus z square.

And the equation 10 can be written as tan z is equal to square root of z 0 by z whole square minus 1. This is a transcendental equations as a function of z for a function of z 0. It can be solved by plotting tangent, this is the left hand side first function as a function of the right hand side first function, square root of z 0 by z whole square minus 1 on the same grid and looking for the point of intersections.

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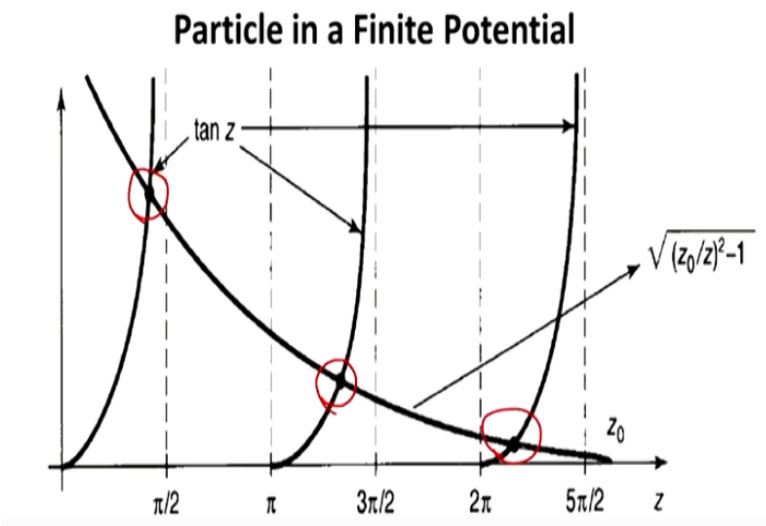

Fig:-Graphical solution of equation (X)

Here we have plotted in this graph. In your y axis we have tangent and in the x axis we have square root of z 0 by z whole square minus 1. And we see that we got certain point of interaction like this at different values of the z like pi by 2, pi, 3 pi by 2, 2 pi, and 5 pi by 2. This is a generic diagram. Now there can be several limiting case happens in this particular problem.

The potential well can be very wide or it can be also very narrow. If I consider a very wide deep potential well, then z 0 is very large and the intersection in the previous site here the intersection points, if you look at the intersection point where z 0 value is very high they occurs slightly below than n pi by 2 where n is odd.

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Particle in a Finite Potential

1. **Wide, deep well:-** if z_0 is very large, the intersections occur just slightly below $z_n = (n\pi|2)$, with n odd; it follows that

$$E_n + V_0 \cong \frac{n^2\pi^2\hbar^2}{2m(2a)^2} \quad \text{-----------(XII)}$$

Here $(E + V_{0)}$ is the energy above the bottom of the well, and on the right we have precisely the infinite square well energies, for a well width of 2a, since n is odd. So the finite square well goes over to the infinite square well, as $V_0 \to \infty$, however for any finite V_0 there are only finitely many bound states.

So if I again look back to the previous diagram, if n is odd, then it is 3 pi by 2, it is 5 pi by 2. And you see that interaction is happening here, interaction is happening here. So it is less than n pi by 2 where n is equal to odd number if z 0 is large. And we can write E n plus V naught is equal to, almost equal to n square pi square h bar square by 2m 2a square.

So it somewhat looks like an particle in an infinite square well potential. Because there also we found an n square dependence and also there we have a inversely proportional to the dimension square but here the dimension is 2a. Here E plus V naught is the energy above the bottom of the well. And on the right we have precisely the infinite square well energies for a well width of 2a since n is odd.

So the finite square well goes over to the infinite square well as V naught tends to infinity. However, for any finite V naught they are the only finite many bound states.

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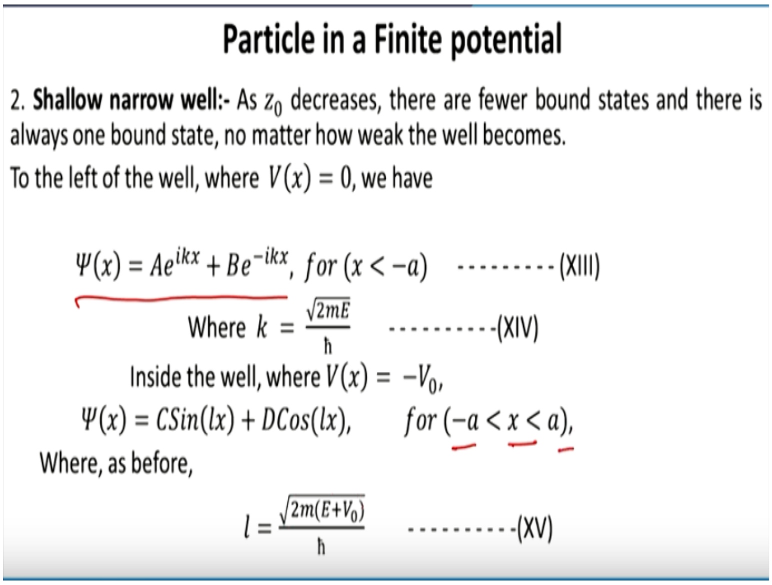

Now consider the other extreme. So far we have considered a well which is very in the previous case we have considered the well was wide, but now consider the other case, the well is here very shallow and narrow. So in that case, if you consider z naught that decreases there are fewer bound states here.

And thus always one bound state no matter how weak the well becomes to the left of the well where V x is 0 we have psi x is A e to the power ikx plus B e to the power –i kappa x for x less than – a where kappa is equal to square root of 2mE by h bar. And inside the well where V x is equal to minus V naught then psi x is C sin lx plus D cosine lx. And where x is between – a and + a. And similarly we have defined l before square root of 2m E plus V naught by h.

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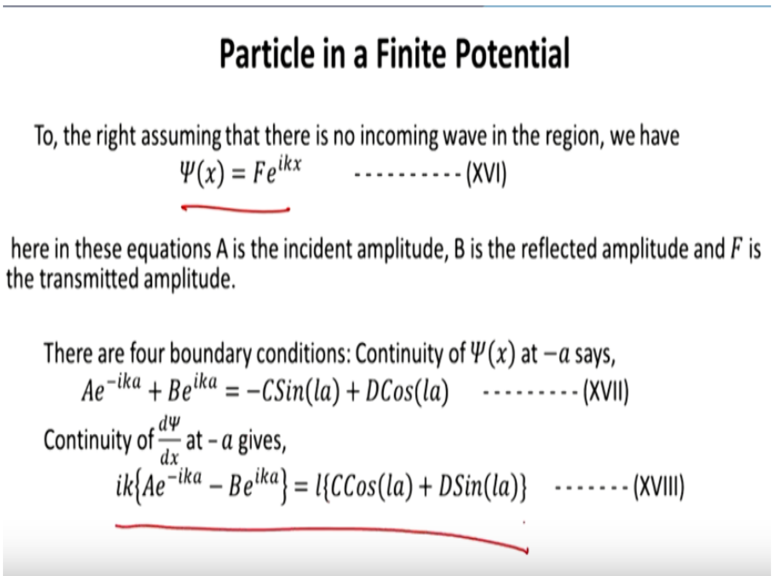

To the right assuming that there is no incoming wave in the region we have psi x is F e to the power i kappa x. Here in this equations A is the incident amplitude B is the reflected amplitude and F is the transmitted amplitude. Now if I apply the four boundary condition continuity of psi x at - a, that gives us this equation A e to the power - ika + B e to the power ika = - C sin la + D cosine la.

Similarly, like the previous treatment, we can do the first derivative of psi and looks at the continuity at the point x is equal to - a and that will give this equations.

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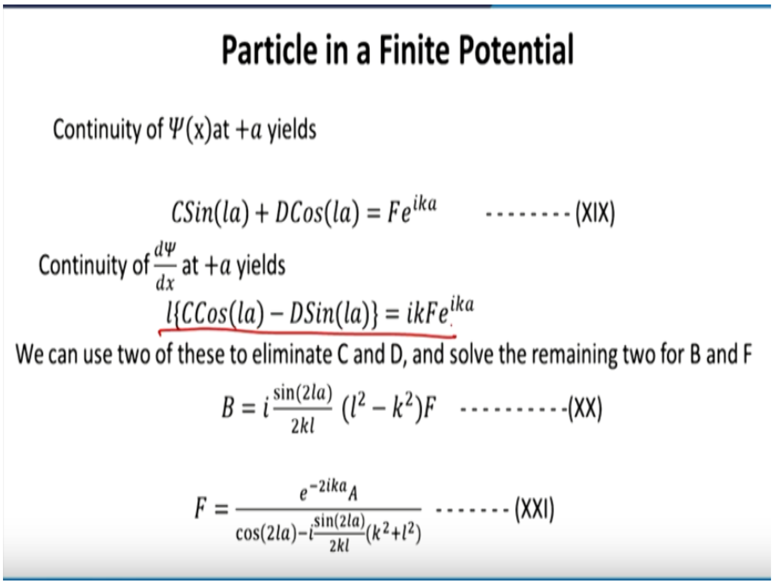

If I apply the third boundary condition that is the continuity of psi x and x is equal to a that will give C sin la plus D cosine la is equal to Fe to the power ika. And the fourth boundary condition is the first derivative of psi with respect to x at a that will give this equation. Now there are four equations and there are four constants. So we use two of these to eliminate C and D and to solve the remaining two for B and F.

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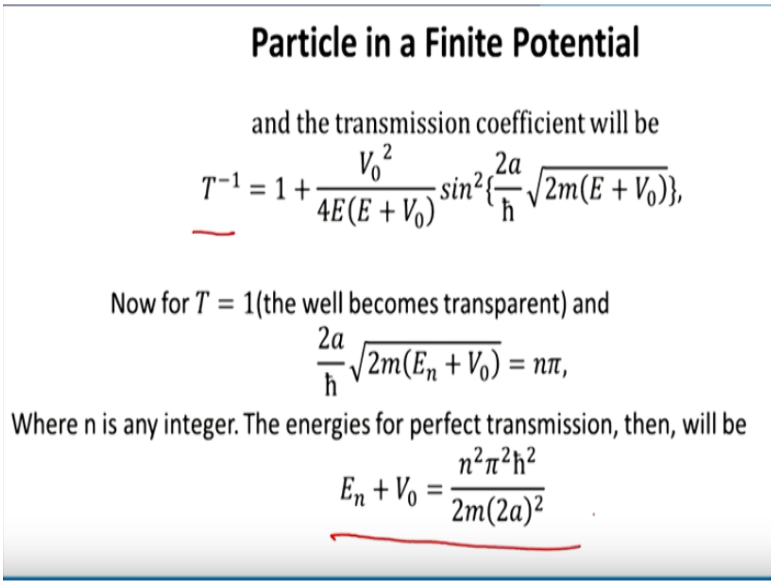

If we do that, what we will get is the following. The T inverse of 1 is equal to 1 plus V naught square by 4E E plus V 0. Sin square 2a by h bar square root of 2m E plus V naught. And T is called the transmission coefficient. It is a very important things which we are going to use experimentally. Now for T is equal to when the well becomes transparent and 2a by h bar square root of 2m E n plus V naught is equal to n pi where n is any integer.

The energy for perfect transmission then will be E n plus V naught is equal to n square pi square h bar square by 2m into 2a square. Again look it is like an infinite potential well where the total energy is proportional to n square and inversely proportional to the dimension square. In this diagram, we have plotted the transmission coefficient versus as a function of the energy.

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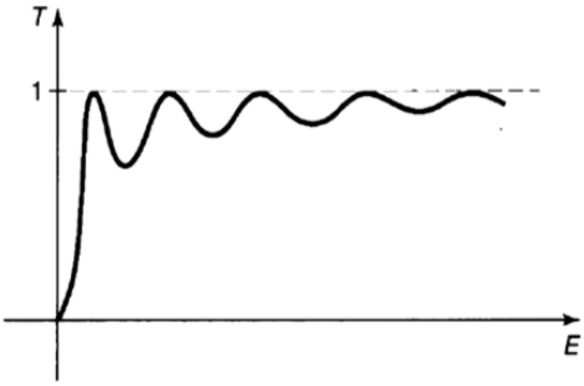
Particle in a Finite Potential



Transmission coefficient as a function of energy

And we are showing this particular case where like the transmission coefficient is asymptomatic functions and it is touching about 1.

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References

- Introduction to Quantum Mechanics: David J. Griffiths
- Quantum Mechanics : Concepts and Applications by Zettli

We can get the basic idea of all of these things in the Griffiths quantum mechanics books. And also there are certain other quantum mechanics books and all of these has an applications in the solid state physics and where we will learn later on about the origin of the band theory. And also we will learn about how these electrons moves in this band which will help us to understand the device physics later on. Thank you.