Electronic Properties of the Materials: Computational Approach
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Lecture: 07
Numerov Method: Algorithm

Hello friends in this lecture we are going to learn about solving time independent Schrodinger equation using some numerical technique. First let us understand why do we need this. So, far we have solved analytically for example we have solved for particle in a box we have solved for harmonic potential we have solved for free particle etcetera. However, if I have to solve for a double well potential like this, we cannot just solve using the analytical method we have to use some numerical technique for that.

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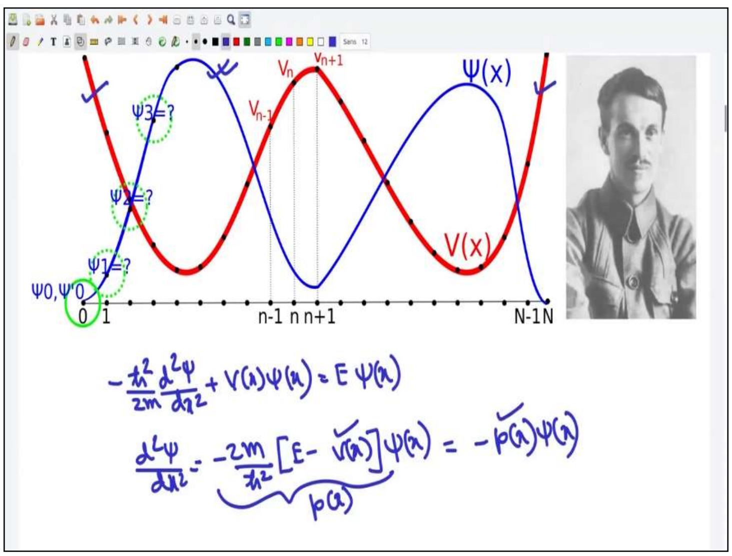

The method that we are going to learn was given by Nemerov although this is a method which can generally be used to solve any second order differential equation our discussion will remain focused on solving the time independent Schrodinger equation. So, let me again state the problem. For example let us assume that this red line is the potential given to us and this looks like some double well potential and as I just mentioned we cannot solve the time independent Schrodinger equation analytically for such a potential.

So, the potential is given to us and then we have to find the solution the psi of x for this given potential numerically. So, let us see that how do we approach the problem. So, the time independent Schrodinger equation is - h cross square by 2m d 2 psi dx square + v of x psi of x is equals to E times psi of x. Now as we did before we just rewrite this d 2 psi d x square is equals to - 2 m by h cross square E - v of x psi of x and this part we just write it as p of x right such that we can just write - p of x psi of x. Now keep in mind that v of x is given to us. So, that means t of x is also given to us.

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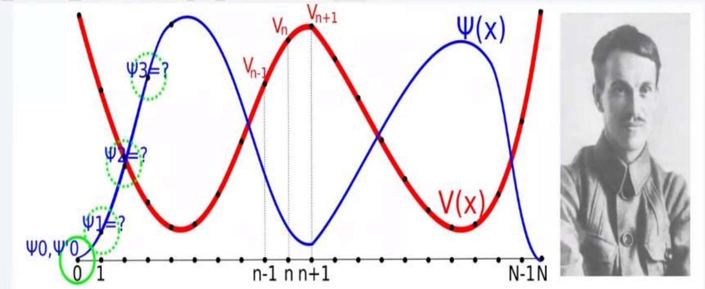

- $\frac{d^2\psi}{dx^2} = -p(x)\psi(x)$
- $p(x) = \frac{2m}{\hbar^2}[E - V(x)]$
- Entire region divided in finite number of grids with $\Delta x = x_n - x_{n-1}$
- Value of potential known at every grid point $V(x_n) = V_n$
- Value of p known at every grid point $p(x_n) = p_n$

Thus we have to solve psi of x from this equation and v of x is given that means if I know E then p of x is also given to me. The first step that we take is we divide the entire region in finite number of grids. So, you see this is the entire region you see this straight line this defines the region where we have to solve psi of x and then the entire region is divided in small regions of width delta of x. And then since the function v x is given to us we know the value of the potential at every great point.

And now as I said that if we know E then we also know this function t at every grid point. Now also we can represent the differential equation in discretized form at every grid point. So, you see that this is like d 2 psi dx square is equals to - px psi of x. So, how do we write the discretized equation. So, for example I can take some grid point and say I take this quick point and at this grid point we can write this equation as psi 2 dash 10 the second derivative of psi at the point n and this is equal to – p n.

So, this is the value of the function at point n times psi of n this is the function at point n which we have to solve. For example if I take grid point number 2 the discretized equation looks like this psi 2 dash is equals to - p 2 psi 2 for and then similarly at grid point 3 the this equation is like this at grid point 4 the equation is psi 4 2 dash is equals to - p 4 psi 4 etc.

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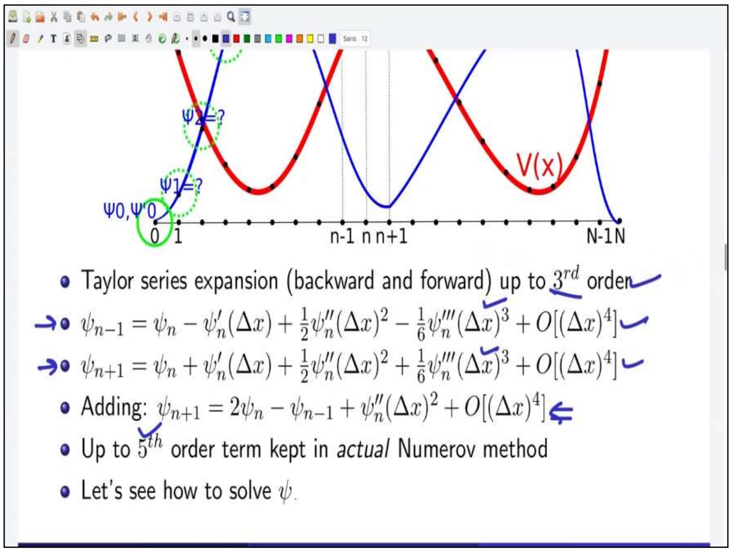

Let us assume that we know the value of function at this point the function as well as its derivatives. Now the question is based on this information can we know about the function at adjacent points for example at point n + one or at point n – 1. Taylor series expansion will help us to achieve this. Let us write the first derivative psi n + 1 - psi of n divided by delta of x this is the first derivative at this point.

Now let us assume that I know everything about the function at this point n. So, that means I can write psi n + 1 is equals to psi n + psi n dash delta x and then I can even add additional terms higher order terms for example psi n 2 dash delta x whole square so on. So, this is known as Taylor series expansion and as you see that if you know about psi of n psi of n dash psi of n 2 dash etc then you can know about the value of the function at the point psi n + 1.

So, this is known as the forward expansion. We can do it for this point also and then that will be known as the backward expansion. Thus, what we do is that we take the function psi and we write the backward Taylor series expansion and forward Taylor series expansion for this.

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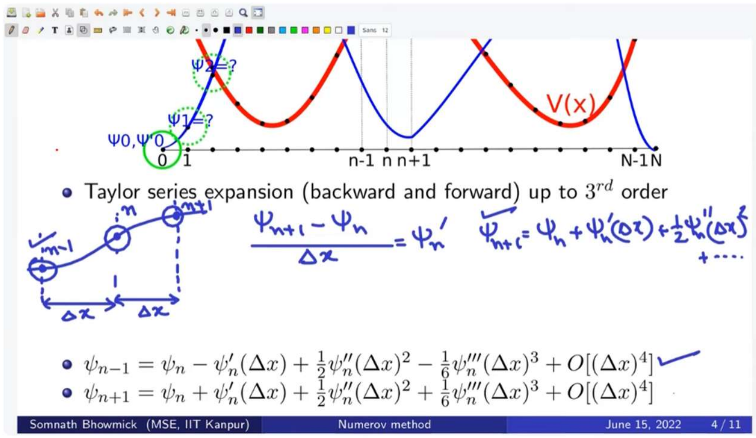

After we do backward and forward Taylor series expansion up to the third order we just add them up right. So, if we add this term and this term this is the equation that we get remember that in actual numerable method up to fifth order term are kept.

However we will keep only up to third order term and that will be sufficient to understand the concept. Now let us see that how do we solve psi from this.

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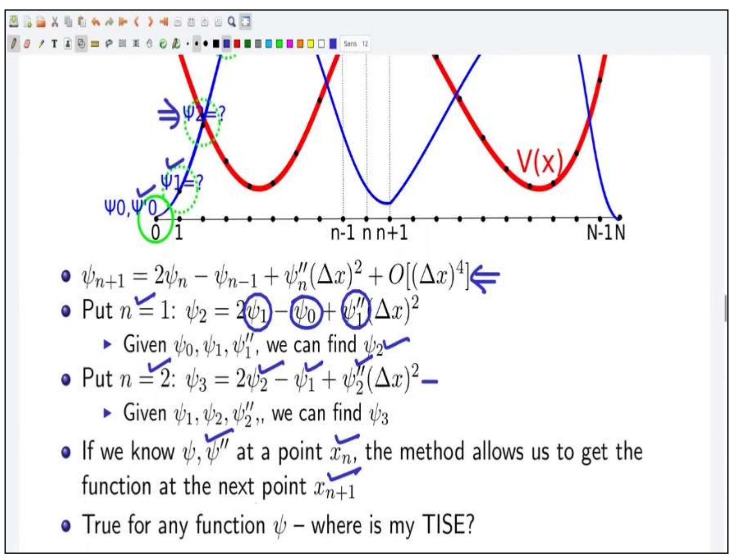

So, we got this equation by adding the forward and backward Taylor series. Now if we put n equal to 1 in this equation what we get is psi 2 is equals to 2 psi 1 - psi naught + psi 1 2 dash delta x square. So, that means if someone gives me the value of psi naught psi 1 and psi 1 2 dashed I can find the value of psi 2. So, that means if I know these 2 values psi naught and psi 1 I can get the value of psi 2.

Similarly you put n equal to 2 and this is the equation that you get and then again you see that to get psi 3 what I need I need psi 2 psi 1 and psi 2 2. So, that means if I knew about the function at psi 1 and psi 2 I can get the value of psi 3 and so on. So, we can keep doing this and then you will see that you will generate the entire blue curve by doing this. So, essentially what we are telling is that if we know psi and psi 2 dash at a point x n then the method will allow us to get the function at the next point x n + 1.

So, far what we have done is true for any function psi then the question is where is my; time independent Schrodinger equation. Remember that we are looking to solve discretized time independent Schrodinger equation given by this. And now via forward and backward Taylor series expansion what we obtained is this equation. Now note this second derivative term in this equation and note the discretized time independent Schrodinger equation. So, that means in place of psi and 2 dash we can replace this. So, let us do that.

So, psi of n + 1 is equals to 2 psi n - psi of n - 1 and in place of this I replace this equation. So, this is like - p n psi n delta x whole square and then we can just rearrange this equation and write psi of n + 1 is equals to 2 - p n delta x whole square psi n - psi n - 1.

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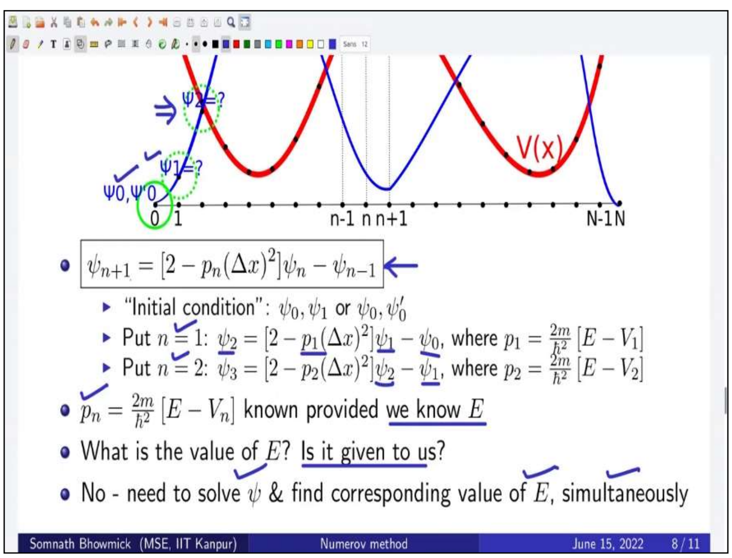

So, we are going to use this equation repeatedly to solve for the wave function. Let us put n equal to 1 and that gives us psi 2 is equals to 2 – p 1 delta x square times psi 1 - psi naught. So, that means if I know the value of psi naught and psi 1 using these 2 values I can get the value of psi 2. And similarly put n equal to 2 and then you see that value of psi 3 can be obtained if

I know the value of psi 2 and psi 1 and we keep doing this and then that will give us the entire curve.

Now you know that I must know the value of pn at every grid point. Now this value is known provided we know the value of E. Now what is the value of E is it given to us the answer is no we have to solve psi as well as the corresponding value of E simultaneously. So, we already know how to solve for psi. Let us see that how do we simultaneously solve for the corresponding value of E.

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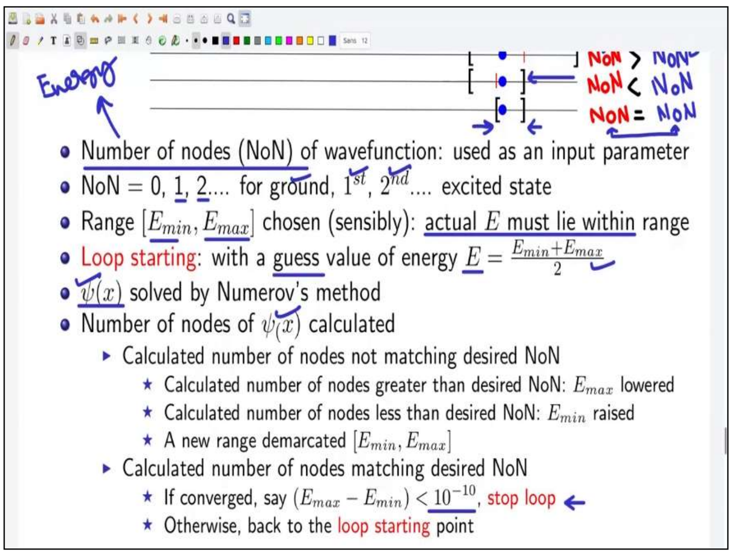

To solve for the energy eigen value we use number of nodes of the wave function as an input parameter. Why do we do this because we know that the number of nodes of the wave function they are related to the energy of the particle. For example number of nodes is equals to zero for the ground state number of nodes is equals to one for the first excited state number of nodes equal to 2 for the second excited state etc.

Now we take some initial guess that the energy lies within this range E min and E max in this figure you can see that the initial guess the E min and the max values are here. And then the assumption is that the actual E must lie within this range. Then we start a loop with the guess value of energy and that value is taken to be the average of mean and max. So, for example if E min is here and E max is here then the guess value of energy is here. So, that is given by this red line.

Now with this value of energy what we do is that we solve psi of x by using Numerov's method. And once we calculate the psi of x then we calculate the number of nodes of that particular psi of x and that number of nodes in this figure is written in red. And now what we know we already have set the value of nodes that I want in the actual wave function and that number is set by or that number is shown by this blue colour.

So, number of nodes NoN in red that is something that I get from my guess solution and NoN in blue that is the actual number of nodes that I am looking to find. And then you see that in the general they will not be equal for example in this case you see. Let us assume that the actual energy value the actual value of energy is given by this blue dots right. So, you see the guess energy is less than the actual energy.

So, that means the number of nodes that I get from this guess wave function will be less than the actual number of nodes that should be there in the wave function and then in this case what we have to do. So, that means I need to increase the energy. So, how do I do that I shift the lower limit to here okay and in the next cycle this is my energy range right. So, this is my E min and this is the E max and then what is the guess value of energy.

And then the guess value of energy is now lying here and again I solve the phi x using the Numerov's method and again I calculate the number of nodes and then again I check whether that is matching with the actual number of nodes or not and in this case also it will not match but because still the guess value of energy is less than the actual value of energy. And then what I have to do again I have to increase the energy that means I just shift the lower limit to the higher value.

And then again I calculate the average and now you see that the guess value of energy now is more than the actual value. So, that means with this value of gas value of energy if I solve then the number of nodes that I get is now actually higher than the actual number of nodes. So, in that case what we have to do. Now we have to shift the upper limit to a lower value and so on. So, this will keep going as long as my number of nodes right the NoN is equal to NoN right.

So, when we achieve this at that point we are going to stop the loop and also you see that as we keep doing this the lower limit and upper limit they will keep moving towards each other. Aand when we say that the calculation has converged when the difference between this upper limit and lower limit is sum it is a very small number for example 10 power -10 right. At that point I say that okay the wave function has converged because the lower limit and upper limit they are very close to each other.

And also the number of nodes they are also matching with the desired number of nodes that I set initially. In that case I say that the loop has converged and then the solution has been achieved.

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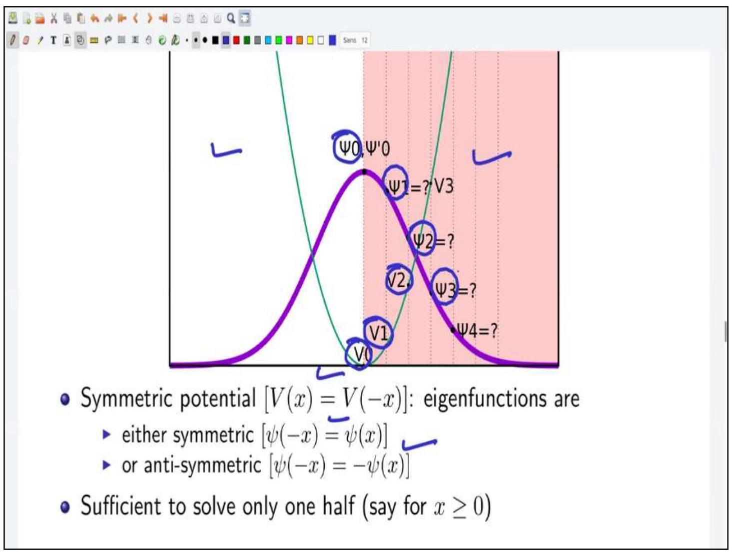

We are going to sort the time independent Schrodinger equation numerically for 2 symmetric potentials the first one is harmonic potential for which we know the analytical solutions we can match the numerical and analytical results to verify whether code is written correctly or not. In case of a symmetric potential v of x is equals to v of - x and as a result the eigen functions are either symmetric that is psi of - x is equals to psi of x or they are anti-symmetric that is psi of - x is equals to - psi of x.

Thus it is sufficient to solve for only one half say x greater than equal to zero because the other half is related by symmetry. For example if we solve for x greater than 0 that is in the shaded region we also get the eigen function in the unshaded region that is x less than or equal to 0 because of the symmetry of the potential. The values of the potential v 0 v 1 v 2 etc are known to us.

If we start with some reasonable initial guess of psi then we can get the eigen function at psi 1 psi 2 psi 3 etc using the Numerov's method and that will give us the entire eigen function.

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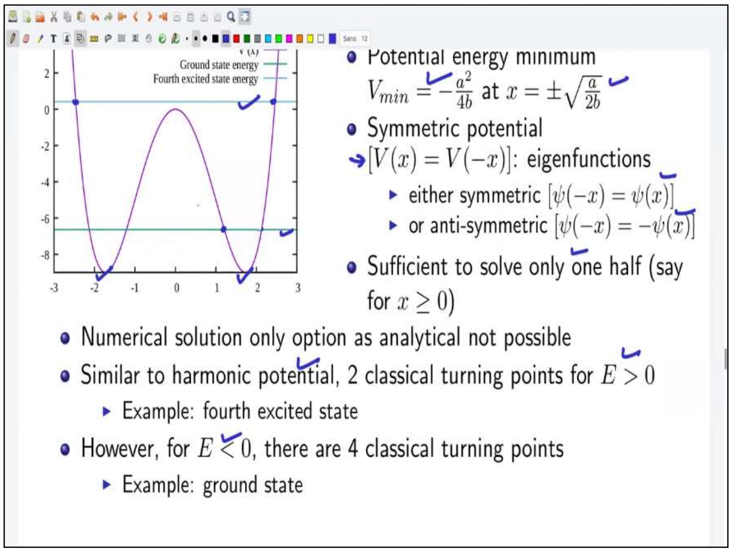

We are going to solve for another symmetric potential the double well potential which has a general form of v x is equals to - a x square + d x to the power 4. The plot shown here is for a is equals to 6 and b equal to 1 unlike harmonic potential which has only one energy minimum at x equal to 0 we have 2 different energy minima at x is equals to + - square root of a by 2 b. So, 1 minima is here then another one is here.

It is straightforward to find the minimum value of the potential energy given by V min is equals to - a square by 4b. This is also a symmetric potential that is V of x is equals to V of - x as a result eigen functions are either symmetric that is psi of - x is equals to psi of x or their anti-symmetric that is psi of - x is equals to - psi of x thus it is sufficient to solve for only one half say for x greater than equal to zero.

Note that unlike harmonic potential we do not have any analytical solution thus numerical solution is the only option in this case. Similar to the harmonic potential there are 2 classical points in case of double well potential for energy greater than zero. For example I have shown here the 4th excited state energy which is greater than zero and you see that there are 2 classical turning points in this case.

However for E less than zero there are 4 classical turning points in this plot this is the ground state energy and you see that in this case we have 4 classical turning points, 2 classical turning points for x greater than zero and 2 classical turning points for x less than zero.

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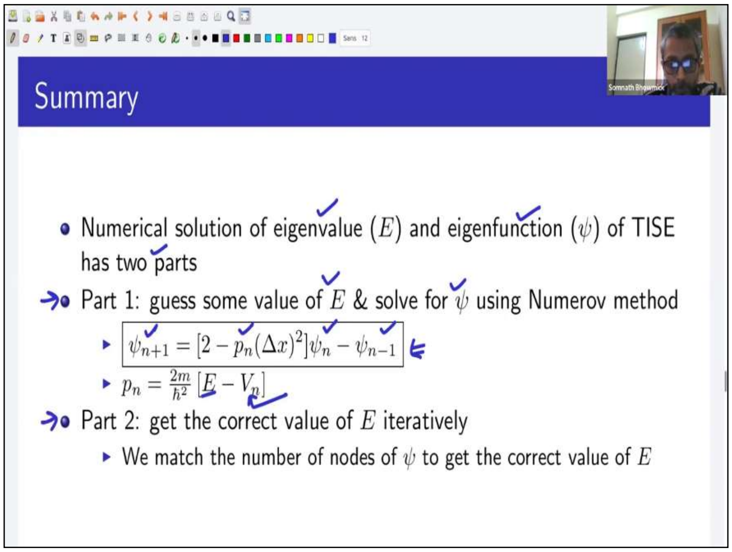

Finally let me quickly summarize what we have done. So, far in this lecture numerical solution of eigenvalue and eigen function of time independent Schrodinger equation has 2 parts. In part one we guess some value for E and solve for psi using numeral of method thus if we know the value of psi at point n and point n - 1 then we can find the value of psi at point n + 1 because we know the function p of n.

The function p of n is given by E - v of n and we know the potential at every point n while calculating p often we start with some guess value of energy. In part 2 we have to get the correct value of energy iteratively and we do this by matching the number of nodes psi to get the correct value of E.

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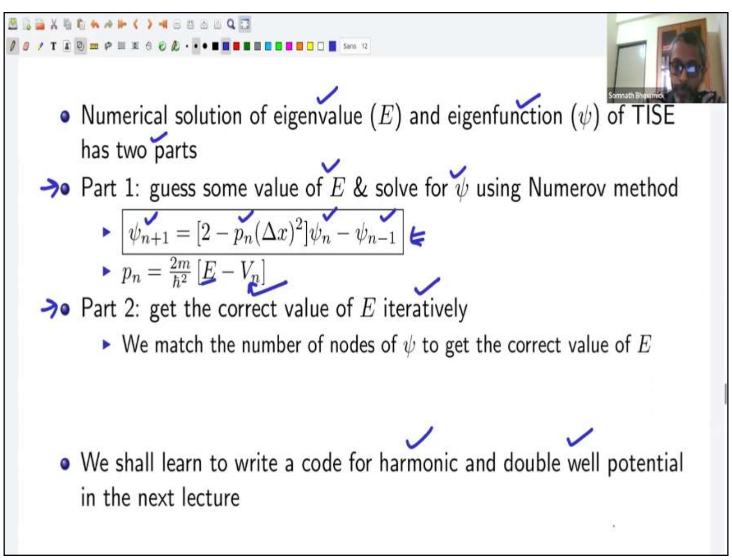

In the next lecture we shall learn to write a code for harmonic potential and double well potential. The analytical results or harmonic potential are known such that we can verify our code by matching the analytical and numerical results. Once we are confident that our code is working fine then we will apply the code for double well potential to get the energy eigen values and eigen functions.