Electronic Properties of the Materials: Computational Approach
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Lecture: 09
The WKB Approximation Method (Part 1)

Hello friends we already have learned about solving the time independent Schrodinger equation numerically using the Numerov method. In this lecture we are going to learn about WKB method for obtaining approximate solution to the time independent Schrodinger equation in one dimension. It is very useful to get the bound state energies and tunnelling rate through a potential barrier.

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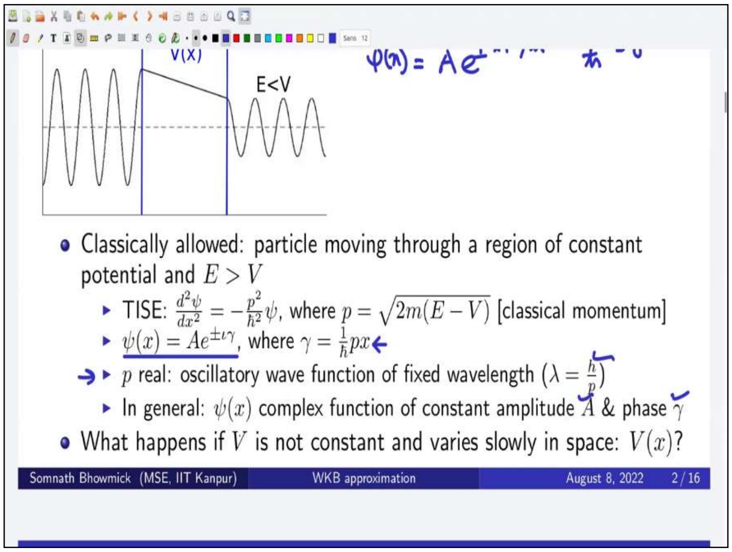

- Classically allowed: particle moving through a region of constant potential and $E > V$
  - TISE: $\frac{d^2\psi}{dx^2} = -\frac{p^2}{\hbar^2}\psi$, where $p = \sqrt{2m(E-V)}$ [classical momentum]
  - $\underline{\psi(x) = Ae^{\pm\iota\gamma}}$, where $\gamma = \frac{1}{\hbar}px \leftarrow$
  - $\rightarrow$ p real: oscillatory wave function of fixed wavelength ($\lambda = \frac{h}{p}$)
  - In general: $\psi(x)$ complex function of constant amplitude A & phase γ
- What happens if V is not constant and varies slowly in space: $V(x)$?

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First let us consider a classically allowed case where particle is moving through a constant potential such that E is greater than V we write the time independent Schrodinger equation - h cross square by 2 m d 2 psi dx square + V of psi is equals to E of sine. Now we just rewrite the above equation as d 2 psi dx square is equals to - 2 m E - V divided by h cross square psi and we just write this equation as - p square by h cross square psi where p is the classical momentum.

Solution for this equation is psi of x is equals to a E power + - I E x by h cross we can rewrite the exponent as p x by h cross is equals to gamma. In that case we see that the solution can be written as psi of x is equals to a E power + - I gamma where gamma is equals to 1 by h bar t times x. Since E is greater than V, E is real and we get oscillatory wave function of fixed wavelength lambda is equals to h by p.

In general psi of x is a complex function of constant amplitude a and this gamma. It is very easy to find the solution when V is a constant. However let us try to understand what happens when V is not a constant but it varies slowly in space.

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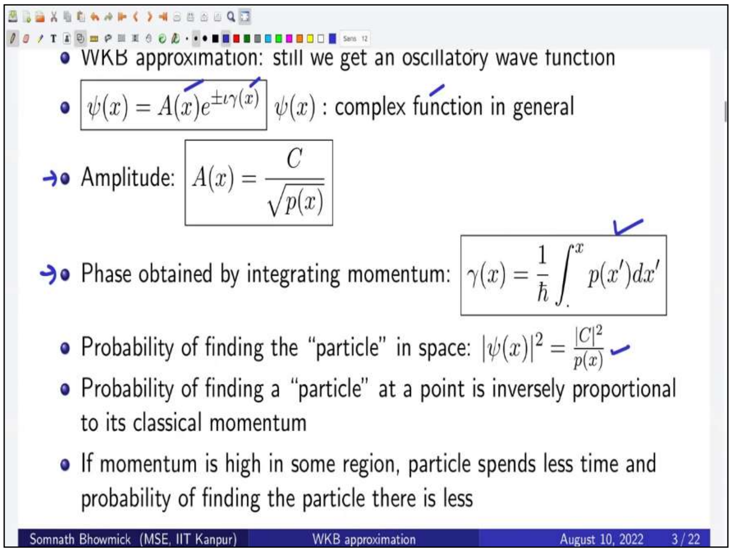

- WKB approximation: still we get an oscillatory wave function
- $\boxed{\psi(x) = A(x)e^{\pm\iota\gamma(x)}}$ $\psi(x)$: complex function in general
- Amplitude: $\boxed{A(x) = \frac{C}{\sqrt{p(x)}}}$
- Phase obtained by integrating momentum: $\boxed{\gamma(x) = \frac{1}{\hbar}\int^{x} p(x')dx'}$
- Probability of finding the "particle" in space: $|\psi(x)|^2 = \frac{|C|^2}{p(x)}$
- Probability of finding a "particle" at a point is inversely proportional to its classical momentum
- If momentum is high in some region, particle spends less time and probability of finding the particle there is less

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We consider a case where potential V is not a constant but varies slowly in space as a result momentum p also varies slowly in space. By slowly varying I mean Vx and px vary slowly compared to the wavelength of the wave function psi of x. The time independent Schrodinger equation is given by V 2 psi dx square is equals to - p square by h + square psi where px is equals to square root of 2m times E - Vx that is px is equivalent to the classical momentum.

We do not have any analytical solution in this case so we have to use WKB approximation which tells that the wave function is still oscillatory. The form of the wave function is psi of x is equals to A of x times E power + - I gamma of x psi of x is a complex function in general. Thus psi remains same qualitatively as it was for constant V. However the amplitude and wavelength of the rapidly oscillating wave function changes slowly in space.

The amplitude A of x is equal to C divided by square root of p of x square C is a constant and p of x is equivalent to classical momentum. The phase can be obtained by integrating the momentum probability of finding the particle in space is given by mod of psi x square is equals to C square divided by p of x. Thus if p of x is high probability of finding the particle is less and vice versa.

Note that this is exactly what you expect classically probability of finding a particle at a point is inversely proportional to its classical momentum. If momentum is high in some region particle spends less time and probability of finding the particle there is less. On the other hand if momentum is low in some region particle spends more time there and probability of finding the particle is more.

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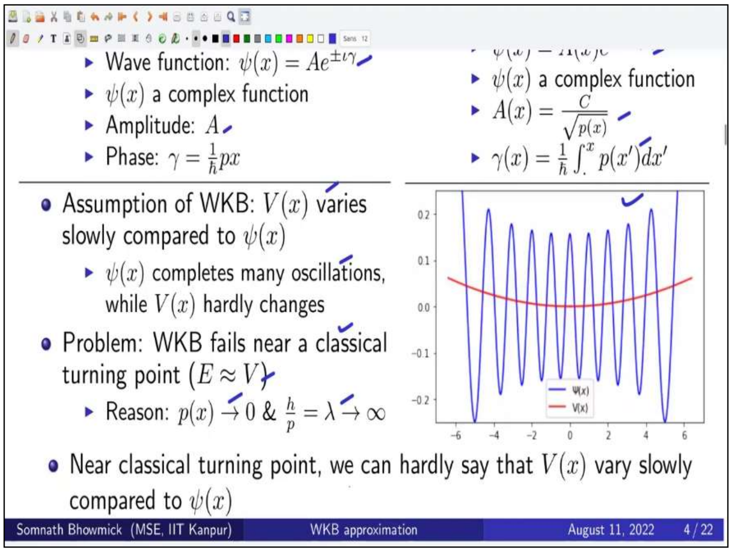

- Wave function: $\psi(x) = Ae^{\pm\iota\gamma}$
- $\psi(x)$ a complex function
- Amplitude: A
- Phase: $\gamma = \frac{1}{\hbar}px$

- $\psi(x)$ a complex function
- $A(x) = \frac{C}{\sqrt{p(x)}}$
- $\gamma(x) = \frac{1}{\hbar}\int_{.}^{x} p(x')dx'$

- Assumption of WKB: $V(x)$ varies slowly compared to $\psi(x)$
  - $\psi(x)$ completes many oscillations, while $V(x)$ hardly changes
- Problem: WKB fails near a classical turning point $(E \approx V)$
  - Reason: $p(x) \to 0$ & $\frac{h}{p} = \lambda \to \infty$

- Near classical turning point, we can hardly say that $V(x)$ vary slowly compared to $\psi(x)$

Before proceeding further let me quickly show the case of constant and varying potential side by side. Time independent Schrodinger equation is d 2 psi dx square is equals to - p square by h + square times psi where p square is greater than 0. Since p square is greater than 0 t which is equivalent to the classical momentum is real as a result the wave function is oscillatory in both the cases. Psi of x is a complex function its amplitude A is constant in case of a constant potential but it varies slowly in space in case of a slowly varying potential.

Phase can be calculated by integrating the function p of x keep in mind the assumption of WKB approximation Vx varies slowly compared to psi of x. By this I mean that psi of x completes many oscillations while V of x hardly changes. For example in this diagram the blue line shows the psi of x and the red line shows the potential V of x. Note that while the wave function oscillates rapidly in space V of x varies very slowly in space.

Whenever this assumption fails WKB approximation does not work anymore. For example WKB approximation fails near a classical turning point where E is almost equal to V. Since E is almost equal to V near a classical turning point p tends to 0 and the wavelength becomes infinity. Since the wavelength becomes infinity near a classical turning point we can hardly say that Vx very slowly compared to psi of x.

Let us now solve a problem using WKB approximation. We select particle in a box problem for this purpose because we can compare with the analytical result.

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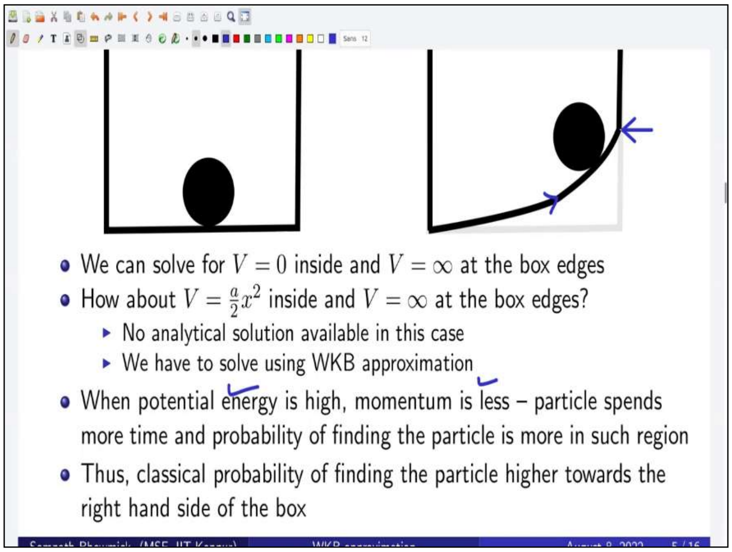

- We can solve for $V = 0$ inside and $V = \infty$ at the box edges
- How about $V = \frac{a}{2}x^2$ inside and $V = \infty$ at the box edges?
  - No analytical solution available in this case
  - We have to solve using WKB approximation
- When potential energy is high, momentum is less – particle spends more time and probability of finding the particle is more in such region
- Thus, classical probability of finding the particle higher towards the right hand side of the box

We know how to solve analytically for V equal to 0 inside and V equal to infinity at the box edges. Let us try to solve for V equal to a by 2 x square inside and V equal to infinity at the box edges that means the potential is increasing as you go from the left hand side of the box to the right hand side of the box and the potential is increasing quadratically. Note that in this case we do not have any analytical solution and we have to solve using WKB approximation.

Before we try to solve let us try to understand what do we expect classically. We know that if the potential energy is high the momentum is going to be less that means the particle will spend more time and probability of finding the particle is more in a region where the momentum is less. Thus classical probability of finding the particle is higher towards the right hand side of the box then compared to the left hand side of the box.

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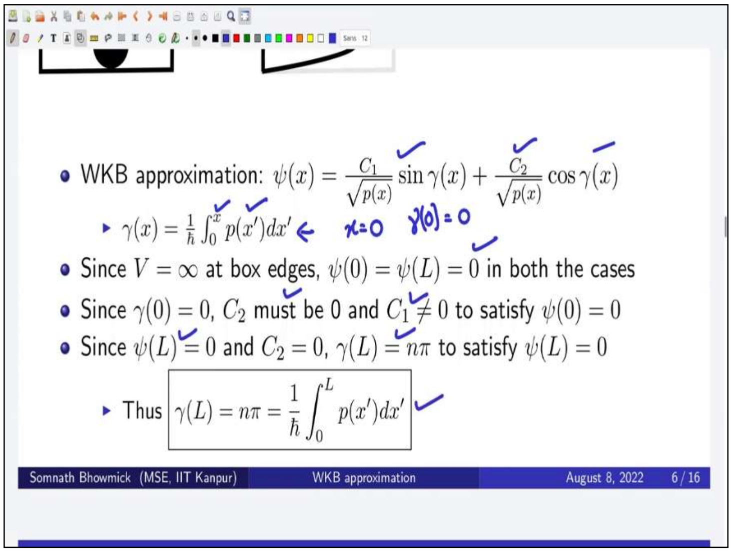

- WKB approximation: $\psi(x) = \frac{C_1}{\sqrt{p(x)}}\sin\gamma(x) + \frac{C_2}{\sqrt{p(x)}}\cos\gamma(x)$
  - $\gamma(x) = \frac{1}{\hbar}\int_0^x p(x')dx' \leftarrow$ $x=0$ $\gamma(0)=0$
- Since $V = \infty$ at box edges, $\psi(0) = \psi(L) = 0$ in both the cases
- Since $\gamma(0) = 0$, C_2 must be 0 and $C_1 \neq 0$ to satisfy $\psi(0) = 0$
- Since $\psi(L) = 0$ and $C_2 = 0$, $\gamma(L) = n\pi$ to satisfy $\psi(L) = 0$
  - Thus $\boxed{\gamma(L) = n\pi = \frac{1}{\hbar}\int_0^L p(x')dx'}$

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Let us apply the boundary condition in WKB wave function. We write the general solution as psi of x is equals to C 1 divided by square root of px e power i gamma of x + C 2 by square root of p of x e power - i gamma x. Note that we are using the classical analogy while we are writing the amplitudes of the wave function. Classically we know that the probability of finding the particle is more when momentum is less.

Since the probability of finding the particle is related to the amplitude of the wave function we are doing the same thing here that is the amplitude of the wave function is more when momentum is less and vice versa. Now we can just use e power i gamma is equals to cos gamma + i sin gamma and write the wave function in this form psi of x is equals to C 1 divided by square root of p of x times sine gamma of x + C 2 divided by square root of p of x times cos gamma of x where gamma of x can be calculated by calculating this integral.

Since V is equal to infinity at the box edges psi of 0 and psi of l should be equal to 0 in both the cases. Now gamma of x is given in this form that means if we put x equal to 0 in the upper limit of the integral gammas of 0 is equals to 0. Thus the constant in front of the cosine term 2 must be equal to 0 to ensure psi of 0 is equals to 0. Wave function must be 0 at the other boundary also that is psi of l is equals to 0.

Since C 1 is not equal to 0 and C 2 is equals to 0 this is only possible if gamma of l is equals to n pi because sine of n pi is equals to 0 for any integral value of n. This gives us the quantization condition gamma of l is equals to n pi is equals to this integral.

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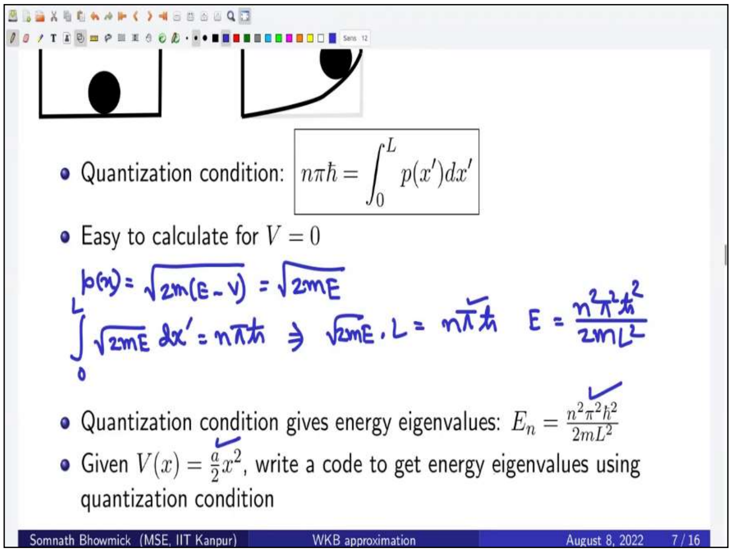

- Quantization condition: $\boxed{n\pi\hbar = \int_0^L p(x')dx'}$
- Easy to calculate for $V = 0$

$p(x) = \sqrt{2m(E-V)} = \sqrt{2mE}$

$\int_0^L \sqrt{2mE}\, dx' = n\pi\hbar \Rightarrow \sqrt{2mE}\cdot L = n\pi\hbar \quad E = \frac{n^2\pi^2\hbar^2}{2mL^2}$

- Quantization condition gives energy eigenvalues: $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$
- Given $V(x) = \frac{a}{2}x^2$, write a code to get energy eigenvalues using quantization condition

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Let us apply the quantization condition for b is equals to 0 in this case p of x is equal to square root of 2 m E - V and C since V is equals to 0 this is just equal to square root of 2m E. Thus we can write integral 0 to l p of x is square root of 2 mE dx is equals to n pi h bar which implies square root of 2 mE times l is equals to n pi h bar. Now we can just rewrite this equation as E is equals to we have to square this part n square pi square h bar square divided by 2m L square.

Thus the quantization condition gives the energy eigen values for particle in a box E n is equals to n square pi square h + square divided by 2m L square. We already know this from our analytical solution of particle in a box. Now given V of x is equals to a by 2 x square let us write a code to get the energy eigen values using the quantization condition. Quantization condition tells us the integral of momentum over the entire box of length l is equal to n pi h bar.

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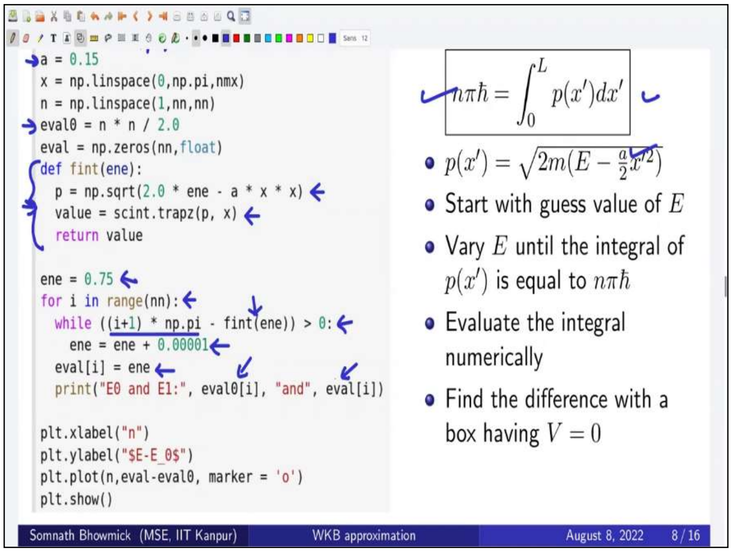

```
a = 0.15
x = np.linspace(0,np.pi,nmx)
n = np.linspace(1,nn,nn)
eval0 = n * n / 2.0
eval = np.zeros(nn,float)
def fint(ene):
  p = np.sqrt(2.0 * ene - a * x * x)
  value = scint.trapz(p, x)
  return value

ene = 0.75
for i in range(nn):
  while ((i+1) * np.pi - fint(ene)) > 0:
    ene = ene + 0.00001
  eval[i] = ene
  print("E0 and E1:", eval0[i], "and", eval[i])

plt.xlabel("n")
plt.ylabel("$E-E_0$")
plt.plot(n,eval-eval0, marker = 'o')
plt.show()
```

$$\boxed{n\pi\hbar = \int_0^L p(x')dx'}$$

- $p(x') = \sqrt{2m(E - \frac{a}{2}x'^2)}$
- Start with guess value of E
- Vary E until the integral of $p(x')$ is equal to $n\pi\hbar$
- Evaluate the integral numerically
- Find the difference with a box having $V = 0$

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Note that this is irrespective of the form of the momentum p of x we already have verified that the quantization condition gives us the correct result for V equal to 0. Now we shall consider the case where V is equals to a by 2 x square. In this case since we do not know E we have to start with some guess value of E. Energy of the ground state for V equal to 0 which is known analytically can be a good case value. Because the energy for V greater than 0 will always be more than the ground state energy for V equal to 0.

We have to evaluate the momentum integral with the guess value of e if it is not equal to n pi h bar we increase the value of E and again evaluate the momentum integral. We keep doing this until the momentum integral becomes equal to n by h bar for some value of E. The value of E for which the quantization condition is satisfied is the energy eigenvalue. We are going to use trapezoidal rule to evaluate the integral numerically.

Finally we are going to plot the difference of energy eigen values with particle in a box with b equal to 0 the code will compare the energy difference with b equal to 0 for n equal to 1 2 3 etc. So, this is what is defined here. The value of a defines the strength of the harmonic potential we shall compare the results for different values of a. Eval 0 is the energy eigen value for particle in a box having V equal to 0.

I take the box length L is equals to pi and I also take m and h bar to be equal to 1 in that case the energy eigen value is given by n is equals to n square by 2. We have a user defined function which evaluates the momentum integral over the 1d box t is the momentum in this step we calculate the momentum integral. We start with a guess value of energy 0.75. The for loop is for getting the energy eigenvalue for different eigen states starting from the ground state.

The while loop checks whether the momentum integral is satisfying the quantization condition or not. If quantization condition is not satisfied for the guess value of the energy we increase the guess value of the energy and try again. In this step we call the user defined function with guess value of energy and then compare whether the quantization condition is satisfied or not. In case the quantization condition is not satisfied we change the guess value of energy and again check whether the quantization condition is satisfied or not.

We keep doing this as long as the quantization condition is not satisfied. Once the quantization condition is satisfied the while loop stops and we get the energy eigenvalue and finally we compare between the results of V equal to 0 and V equal to ax square by 2. By printing the respective eigen values and also plotting the difference.

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We are going to find the energy eigen values for five different eigen states starting from the ground state the strength of the potential is given by a and we start with a value of a equal to 0.1 eval 0 is the energy eigenvalue with b equal to 0. Here we have a user defined function to evaluate the momentum integral and here we run a loop to find the energy eigenvalue for different eigen states.

Let us run the code and check the output. So, here the code is printing the energy eigen values so 0.5 is the energy eigen value for a box with potential V equal to 0 and this is for a box with harmonic potential and the first row is for the ground state. The second row is the energy difference for the first excited state third row is for the second excited state fourth row is for the third excited state and so on.

And finally we plot the energy difference where E is the energy eigen value for the box with harmonic potential and E naught is the energy eigen value for the box with potential equal to 0 inside the box. And we see that the difference between the 2 decreases with increasing value of n. So, we try for another value of a let us take a equal to 0.15 and the guess value of energy to be equal to 0.75.

Let us run the code and it starts printing the energy eigenvalues for the 2 different cases. So, the first row is the ground state second one is the first excited state. And so the code is over now and it has plotted the energy difference as a function of n.

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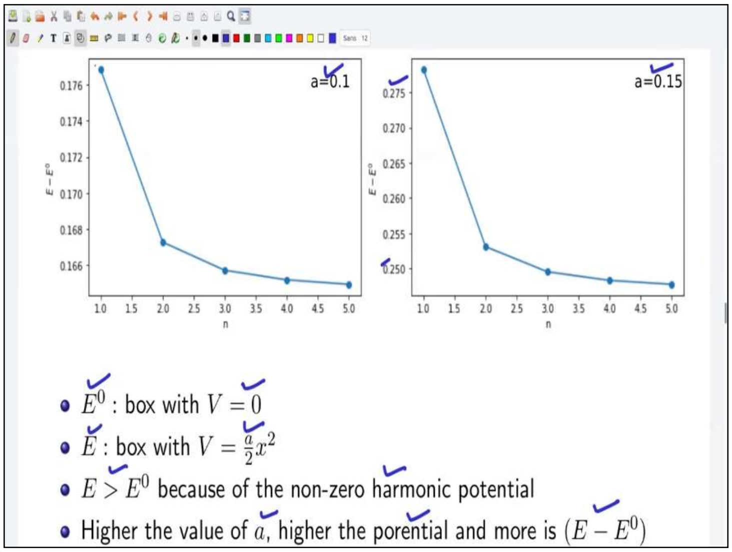

- E^0 : box with $V = 0$
- E : box with $V = \frac{a}{2}x^2$
- $E > E^0$ because of the non-zero harmonic potential
- Higher the value of a, higher the porential and more is $(E - E^0)$

Let us try to compare the results between a equal to 0.1 and a is equals to 0.15. Remember that a represents the strength of the harmonic potential E 0 is the energy eigen value for particle in a box with b equal to 0 and E is the energy eigen value for particle in a box with b equal to a by 2 x square. Note that E is greater than E 0 because we have a non-0 harmonic potential. We also see that higher the value of a higher the potential and more is the energy difference E - E naught.

For example in case of a is equals to 0.1 the energy difference lies approximately in the range of 0.166 to 0.176. On the other hand for a stronger potential the energy difference lies in the range of 0.250 to 0.275. Also note that the energy difference is the highest in case of the ground state and it decreases with the increasing value of n.

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Let us now try to plot the eigen functions for particle in a box with a harmonic potential inside the box and compare the eigen functions for a box with V equal to 0 psi naught x is the eigen function for a box with V equal to 0. In the code we define psi not x here for V equal to ax square by 2 the eigen function is given by the WKB approximation psi of x is equals to C 1 by square root of ex sine com of x.

Now to get psi of x we need to know p of x the momentum function and p of x is given by this and in the code in this step we calculate the p of x. Other than p of x we also need gamma of x to get the WKB wave function and gamma of x is calculated from the numerical integral of p of x and we have a user defined function for this purpose. So, after we get gamma of x and E of x we can plot psi of x.

And then this is where we get psi of x in the code. After we get psi of x we normalize psi of x and once we have the normalized eigen function we can calculate the energy expectation value by evaluating this integral. This is done in this step and then we also evaluate the position expectation value for the ideal case that is V equal to 0. Finally we plot the eigen functions for V equal to 0 as well as V naught 0 in this step.

This is how the code looks like this is where we define the eigen function for particle in a box with V equal to 0. This is where we run a loop to get the value of momentum function this is where we have user defined function to evaluate the momentum integral. Now we run a loop to get the eigen function then we normalize the eigen function after that we calculate the position expectation values and finally we plot the results here.

Let us run the code and see some outputs. So, it is asking for the index of the eigen function let us do it for the first excited state that is the index of the eigen function is equal to 2. Now it is asking for the the eigen value and we use the eigen eigenvalue that we have found in the other code. So, we put the value of eigenvalue and then this eigenvalue was for a is equals to 0.15. So, let us enter 0.15 the value of a and this is how the probability density looks like.

The orange line is for the case when V is equals to 0 and I call it ideal. So, you see that it has only one node the blue line is for the harmonic potential within the particle in a box and you see that the blue line significantly differs from the orange line. And also note that the position expectation value for the ideal case is 1.57 which is equal to pi by 2 this is because we have chosen the length of the box to be equal to pi.

Note that the position expectation value also differs from the ideal position expectation value. So, we have obtained the result for a value of a is equals to 0.15 let us run the code for some other value of a for that purpose we need to use the other code and find the eigenvalues. So, now let us use a is equals to 0.1. so, the code is running and here we get the value for the first excited state. Let us use this value in this code.

We again do it for the first excited sets that is the index of the eigen function is 2. Now we enter the energy eigen value for a is equals to 0.1 and we plot the eigen functions and again you see that there is a significant difference between the ideal case where V is equals to 0 and for the case where we have a harmonic potential within the box. Let us try to understand in detail.

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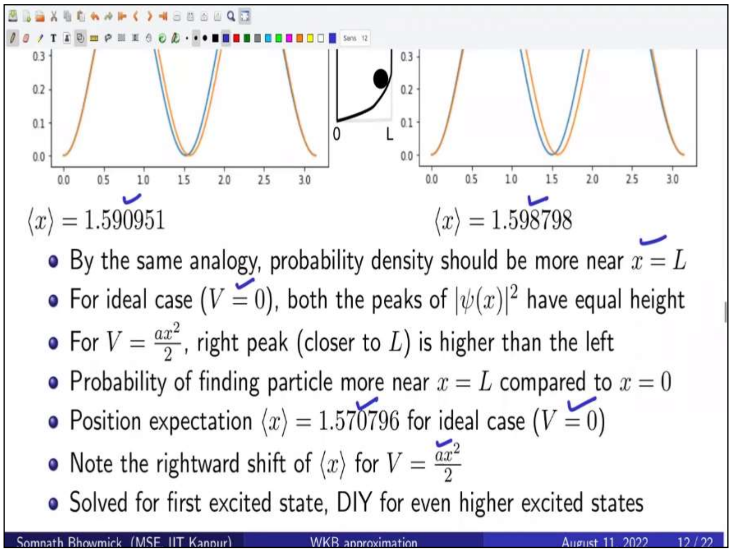

$\langle x \rangle = 1.590951$ $\langle x \rangle = 1.598798$

- By the same analogy, probability density should be more near $x = L$
- For ideal case ($V = 0$), both the peaks of $|\psi(x)|^2$ have equal height
- For $V = \frac{ax^2}{2}$, right peak (closer to L) is higher than the left
- Probability of finding particle more near $x = L$ compared to $x = 0$
- Position expectation $\langle x \rangle = 1.570796$ for ideal case ($V = 0$)
- Note the rightward shift of $\langle x \rangle$ for $V = \frac{ax^2}{2}$
- Solved for first excited state, DIY for even higher excited states

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First let us try to understand what do we expect classical total energy that is kinetic energy + potential energy is conserved. In the region near x equal to l the particle has less kinetic energy because potential energy is high in this region. Thus the particle has less momentum near x equal to L than compared to the region near x equal to 0 as a result particle spends more time near x equal to L then compared to x equal to 0.

Thus classically probability of finding the particle is more near x equal to L than that of x equal to 0. If we use classical analogy then probability density should be more near x equal to L probability densities are plotted in these diagrams. For the ideal case that is V equal to 0 both the peaks of mod psi x square have equal height as shown by the orange line. However for V equal to ax square by 2 the right peak which is closer to L is slightly higher than the left peak.

This implies that probability of finding the particle is more near x equal to L than compared to x equal to 0 same as we would expect classically position expectation value is 1.570796 for the ideal case that is V equal to 0 this is because we have chosen the box length to be equal to pi and the position expectation value is given by pi by 2. However in case of V equal to ax square by 2 the position expectation value has shifted towards the right hand side of the box. Thus we have solved for the first excited state do it yourself for even higher excited steps.