Infinite Well Ground State Energy

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Analytical Derivation of Ground State Energy

A particle of mass m is confined to move inside of an infinitely deep symmetric potential well. Outside the well the potential is infinite, thus the particle is confined to move only within the boundaries of the well of length a centered at the origin. The potential, which depends only on the position (x), is given by

$$V(x) = \begin{cases} +\infty, & x < 0 \\ 0, & -\frac{a}{2} \leq x \leq \frac{a}{2} \\ +\infty, & x > a \end{cases}$$

Since the potential is independent of time, the equation of state of the particle must be a superposition of stationary states of the form

$$\Psi(x,t) = \psi(x)\phi(t) = \psi(x)e^{\frac{iEt}{\hbar}}$$

$\phi(t) = e^{\frac{iEt}{\hbar}}$ with E being the energy associated with the stationary state, which is constant. $\psi(x)$ satisfies the time-independent Schrodinger equation, which is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{1}$$

For the case of a one-dimensional infinite square well, $V = 0$ inside the well. It follows from (1) that inside the well, the motion of the particle satisfies

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \tag{2}$$

with

$$k^2 = \frac{2mE}{\hbar^2}$$

The general solution to (2) is

$$\psi(x) = A\sin kx + B\cos kx$$

Since the well is a symmetric well, $\psi(x) = \psi(-x)$. Since ψ is an even function, $A = 0$ and the general solution for a symmetric potential well is given by:

$$\psi(x) = B \cos kx \tag{3}$$

The probability density of the position of the particle is given by

$$\Psi^2(x,t) = \left(\psi(x) e^{\frac{iEt}{\hbar}}\right)\left(\psi(x) e^{\frac{-iEt}{\hbar}}\right) = \psi(x)^2$$

Since the particle cannot be found at or beyond the boundaries of the well, the probability density at $x \pm a/2$ is be equal to 0.

$$\psi\left(\pm\tfrac{a}{2}\right) = B\cos\left(\pm k\tfrac{a}{2}\right) = 0$$

Since k is a positive constant,

$$k = n\frac{\pi}{a} = \frac{\sqrt{2mE}}{\hbar} \tag{4}$$

The value of the constant B is determine by the normalization condition:

$$1 = \int_{-\frac{a}{2}}^{\frac{a}{2}} (\psi(x))^2 dx = \int_{-\frac{a}{2}}^{\frac{a}{2}} B^2 \cos^2\left(\frac{n\pi}{a}x\right) dx = \frac{B^2}{2}a$$

$$B = \sqrt{\frac{2}{a}} \tag{5}$$

From equations (2),(4), and (5), the solution to the time-independent Schrodinger equation is

$$\psi(x) = \sqrt{\frac{2}{a}} \cos\frac{n\pi x}{a} \tag{6}$$

for $n = 1, 2, 3, \ldots$. And from equation (4), the allowable values of the Energy E are given by

$$E = \frac{n^2\pi^2\hbar^2}{2a^2m}, \;\; n = 1, 2, 3, \ldots$$

To simplify the numerical calculation, a, m and $\hbar$ will each be given the value 1. The ground state energy, which is the energy value for the state in which $n = 1$ is

$$E_{ground} = \frac{\pi^2}{2} \tag{7}$$

and the solution to the Schrodinger equation, equation (6), simplifies to

$$\psi(x) = \sqrt{2}\cos n\pi x \tag{8}$$

Numerical Approximation of Ground State Energy

The starting point for the numerical calculation of the ground state energy of the solution to the Schrodinger equation (equation (8)). Since the ground state is characterized by $n = 1$, the ground state solution to the Schrodinger equation is

$$\psi(x) = \sqrt{2}\cos \pi x \tag{9}$$

Discretized Numerical Approximation of Schrodinger Equation

The Schrodinger equation is a continuous function, but in other to derive approximate solutions, it must be made discrete. This is done using Euler's method of iterative linear approximations as follows.

$$\begin{aligned}
\psi_0 &= \psi_1 = 1 \\
\frac{d\psi_1}{dx} &= 0 \\
\psi_{i+2} &= 2\psi_{i+1} - \psi_i - 2(\Delta x)^2 E_{ground}\psi_i
\end{aligned}$$

If we increment the argument of the Schrodinger equation by $\Delta x = .001$, equation (12) will be iterated 500 times between the boundaries of the well. The value of the Schrodinger equation, ψ, for the 500th iteration depends on the value of the ground state energy, E_{ground} and must be equal to 0. Since it is impractical to expect a numerical approximation to arrive at exactly zero, a value within $\pm 10^{-3}$ will be allowed.

The iterated calculation in Python will start with $E_ground = 0$. If the value of ψ for the 500th iteration is not within $\pm 10^{-3}$, the value of E_{ground} will be increased slightly. The energy will continue to be adjusted by this amount until ψ is within 10^-3 units of 0.

Python Algorithm

```
import numpy as np
import math
import matplotlib.pyplot as plt

delta_x = .5/500
x = np.arange(0,.5+delta_x,delta_x) #array of values of independent variable
psi = np.zeros(len(x)) #array of values for psi
energy = 0 #starting value for energy
theoretical_energy = (np.pi**2) / 2
error = 0.001
psi[0] = math.sqrt(2)
psi[1] = math.sqrt(2)
loop_continue = True
```

```
while loop_continue:
    for i in range(0,len(x) - 2):
        psi[i+2] = 2*psi[i+1] - psi[i] - 2*(delta_x**2)*energy*psi[i]
    if abs(psi[i+2]) > error:
        energy += 0.001
    else:
        difference = abs(energy - theoretical_energy)
        plt.plot(x, psi, 'b')
        print("""
        The estimated energy is {}.
        The difference between this estimation of the energy and the theoretical value of the
energy is {}
        When the energy is {}, the value of psi when x = 0.5 is
{}""".format(energy,difference,energy,psi[i+2]))
        loop_continue = False
plt.plot(x,math.sqrt(2)*np.cos(np.pi * x),'r')
plt.show()
```

Numerical Results

The numerical approximation for the ground state energy, 4.930, is within 0.0038 units of the result derived analytically. The discrete, iterated solution to the Schrodinger equation based on the numerically calculated ground state energy is a nearly perfect fit to the analytical solution. The analytical and numerical curves overlap closely, as shown in the figure below.