Problem 2.57

Find the first four allowed energies (to five significant digits) for the infinite square well, by wagging the dog. *Hint:* Refer to Problem 2.55, making appropriate changes to the differential equation. This time the condition you are looking for is $u(1) = 0$.

Solution

The governing equation for the wave function is Schrödinger's equation.

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x,t)\Psi(x,t), \quad -\infty < x < \infty,\ t > 0$$

For an infinite square well, the potential energy function is

$$V(x,t) = \begin{cases} 0 & \text{if } 0 \le x \le a \\ \infty & \text{if } x < 0,\ x > a \end{cases}.$$

Split up the PDE over the intervals that $V(x,t)$ is defined on.

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + (\infty)\Psi(x,t), \quad x < 0,\ x > a; \qquad i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}, \quad 0 \le x \le a$$

Only $\Psi(x,t) = 0$ satisfies the PDE over $x < 0$ and $x > a$. Because the wave function must be continuous, $\Psi = 0$ at $x = 0$ and $\Psi = 0$ at $x = a$ are boundary conditions for the remaining PDE over $0 \le x \le a$.

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}, \quad 0 \le x \le a,\ t > 0$$
$$\Psi(0,t) = 0$$
$$\Psi(a,t) = 0$$

Substitute $\xi = x/a$ in order to make the position variable dimensionless. Use the chain rule to find out what the second derivative is in terms of ξ.

$$\frac{\partial\Psi}{\partial x} = \frac{\partial\Psi}{\partial\xi}\frac{\partial\xi}{\partial x} = \frac{1}{a}\frac{\partial\Psi}{\partial\xi}$$
$$\frac{\partial^2\Psi}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial\Psi}{\partial x}\right) = \frac{\partial\xi}{\partial x}\frac{\partial}{\partial\xi}\left(\frac{1}{a}\frac{\partial\Psi}{\partial\xi}\right) = \frac{1}{a^2}\frac{\partial^2\Psi}{\partial\xi^2}$$

As a result, the transformed boundary value problem is

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2ma^2}\frac{\partial^2\Psi}{\partial\xi^2}, \quad 0 \le \xi \le 1,\ t > 0$$
$$\Psi(0,t) = 0$$
$$\Psi(1,t) = 0.$$

Use the method of separation of variables now: Assume a product solution of the form $\Psi(\xi,t) = \psi(\xi)\phi(t)$ and plug it into the PDE

$$i\hbar\frac{\partial}{\partial t}[\psi(\xi)\phi(t)] = -\frac{\hbar^2}{2ma^2}\frac{\partial^2}{\partial\xi^2}[\psi(\xi)\phi(t)] \quad \to \quad i\hbar\psi(\xi)\phi'(t) = -\frac{\hbar^2}{2ma^2}\psi''(\xi)\phi(t)$$

and the boundary conditions.

$$\begin{aligned} \Psi(0,t) = 0 \quad &\to \quad \psi(0)\phi(t) = 0 \quad \to \quad \psi(0) = 0 \\ \Psi(1,t) = 0 \quad &\to \quad \psi(1)\phi(t) = 0 \quad \to \quad \psi(1) = 0 \end{aligned}$$

Divide both sides of the PDE by $\psi(\xi)\phi(t)$ in order to separate variables.

$$i\hbar\frac{\phi'(t)}{\phi(t)} = -\frac{\hbar^2}{2ma^2}\frac{\psi''(\xi)}{\psi(\xi)}$$

The only way a function of t can be equal to a function of ξ is if both are equal to a constant E.

$$i\hbar\frac{\phi'(t)}{\phi(t)} = -\frac{\hbar^2}{2ma^2}\frac{\psi''(\xi)}{\psi(\xi)} = E$$

By separating variables, Schrödinger's equation has reduced to two ODEs, one in t and one in ξ; the latter is known as the time-independent Schrödinger equation (TISE).

$$\left.\begin{aligned} i\hbar\frac{\phi'(t)}{\phi(t)} &= E \\ -\frac{\hbar^2}{2ma^2}\frac{\psi''(\xi)}{\psi(\xi)} &= E \end{aligned}\right\}$$

Multiply both sides of the TISE by $(-2ma^2/\hbar^2)\psi(\xi)$.

$$\frac{d^2\psi}{d\xi^2} = -\frac{2ma^2E}{\hbar^2}\psi(\xi)$$

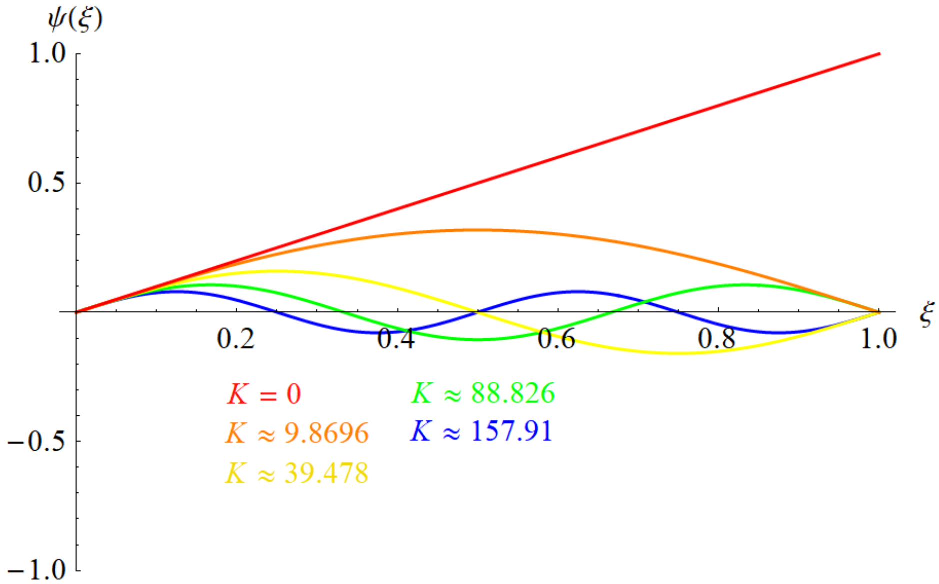
Introduce the dimensionless energy K for $2ma^2E/\hbar^2$ and bring both terms to the left side.

$$\frac{d^2\psi}{d\xi^2} + K\psi(\xi) = 0, \quad \psi(0) = 0, \ \psi(1) = 0$$

This is the dimensionless TISE for the infinite square well. Unfortunately, solving this numerically using these boundary conditions results in only the trivial solution. Since the eigenstates ψ_n are all odd functions, replacing $\psi(1) = 0$ with $\psi'(0) = 1$ is the way to go. The eigenvalues will be the values of K for which the graph of $\psi(\xi)$ passes through zero at $\xi = 1$. The code to use in Mathematica is as follows.

```
Manipulate[
  Plot[
    Evaluate[
      u[x]/.
        NDSolve[
          {u''[x] + L*u[x] == 0, u[0] == 0, u'[0] == 1}, u[x], {x, 0, 1}
        ]
      ],
    {x, 0, 1}, PlotRange -> {-1, 1}
  ], {L, 0, 160}
]
```

Below is a plot of the numerical solution to the dimensionless TISE with the boundary conditions, $\psi(0) = 0$ and $\psi'(0) = 1$, for several values of K.



Therefore, the energies corresponding to the first four eigenstates are

$$K = \frac{2ma^2E}{\hbar^2} \approx 9.8696 \quad \Rightarrow \quad E_1 \approx \frac{9.8696\hbar^2}{2ma^2} \approx \frac{1^2\pi^2\hbar^2}{2ma^2}$$

$$K = \frac{2ma^2E}{\hbar^2} \approx 39.478 \quad \Rightarrow \quad E_2 \approx \frac{39.478\hbar^2}{2ma^2} \approx \frac{2^2\pi^2\hbar^2}{2ma^2}$$

$$K = \frac{2ma^2E}{\hbar^2} \approx 88.826 \quad \Rightarrow \quad E_3 \approx \frac{88.826\hbar^2}{2ma^2} \approx \frac{3^2\pi^2\hbar^2}{2ma^2}$$

$$K = \frac{2ma^2E}{\hbar^2} \approx 157.91 \quad \Rightarrow \quad E_4 \approx \frac{157.91\hbar^2}{2ma^2} \approx \frac{4^2\pi^2\hbar^2}{2ma^2}.$$