Problem 2.48

Consider a particle of mass m in the potential

$$V(x) = \begin{cases} \infty & x < 0, \\ -32\hbar^2/ma^2 & 0 \le x \le a, \\ 0 & x > a. \end{cases}$$

(a) How many bound states are there?

(b) In the highest-energy bound state, what is the probability that the particle would be found *outside* the well ($x > a$)? *Answer:* 0.542, so even though it is "bound" by the well, it is more likely to be found outside than inside!

Solution

The governing equation for the wave function $\Psi(x,t)$ is the Schrödinger equation.

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

Split it up over the intervals where the given potential is finite and infinite.

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

The only solution for the PDE over $x < 0$ is $\Psi(x,t) = 0$. Because the wave function is continuous, $\Psi(0,t) = 0$ becomes a boundary condition for the remaining PDE on $x > 0$.

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

Since information about the eigenstates and their corresponding energies is desired, the method of separation of variables is opted for. This method works because Schrödinger's equation and its associated boundary conditions are linear and homogeneous. Assume a product solution of the form $\Psi(x,t) = \psi(x)\phi(t)$ and plug it into the PDE

$$i\hbar\frac{\partial}{\partial t}[\psi(x)\phi(t)] = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}[\psi(x)\phi(t)] + V(x)[\psi(x)\phi(t)]$$

$$i\hbar\psi(x)\phi'(t) = -\frac{\hbar^2}{2m}\psi''(x)\phi(t) + V(x)\psi(x)\phi(t)$$

and the boundary conditions.

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

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

$$i\hbar\frac{\phi'(t)}{\phi(t)} = -\frac{\hbar^2}{2m}\frac{\psi''(x)}{\psi(x)} + V(x)$$

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

$$i\hbar\frac{\phi'(t)}{\phi(t)} = -\frac{\hbar^2}{2m}\frac{\psi''(x)}{\psi(x)}V(x) = E$$

As a result of using the method of separation of variables, the Schrödinger equation has reduced to two ODEs, one in x and one in t.

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

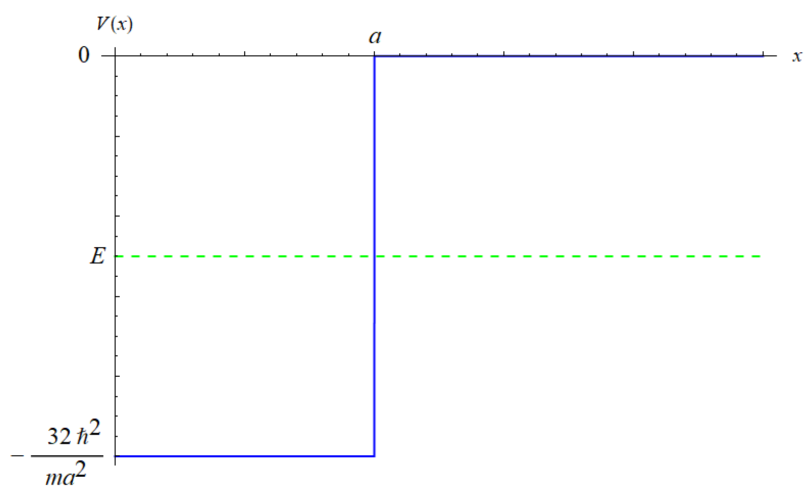
Values of E for which the boundary conditions are satisfied are called the eigenvalues (or eigenenergies in this context), and the nontrivial solutions associated with them are called the eigenfunctions (or eigenstates in this context). The ODE in x is known as the time-independent Schrödinger equation (TISE) and can be written as

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi, \quad x > 0.$$

Split it up over the intervals that $V(x)$ is defined on.

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}\left(\frac{32\hbar^2}{ma^2} + E\right)\psi, \quad 0 \le x \le a; \qquad \frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(-E)\psi, \quad x > a$$

Bound states have energy $-32\hbar^2/(ma^2) < E < 0$, or $32\hbar^2/(ma^2) + E > 0$, as illustrated below.



The general solution for ψ can be written as

$$\psi(x) = \begin{cases} C_1\cos\ell x + C_2\sin\ell x & \text{if } 0 \le x \le a \\ C_3 e^{-\kappa x} + C_4 e^{\kappa x} & \text{if } x > a \end{cases},$$

where

$$\kappa = \frac{\sqrt{-2mE}}{\hbar} \quad \text{and} \quad \ell = \sqrt{\frac{2m}{\hbar^2}\left(\frac{32\hbar^2}{ma^2} + E\right)}.$$

Apply the boundary condition at $x = 0$ to determine one constant.

$$\psi(0) = C_1 = 0.$$

To satisfy the boundary condition at $x = \infty$, set $C_4 = 0$.

$$\psi(x) = \begin{cases} C_2 \sin \ell x & \text{if } 0 \leq x \leq a \\ C_3 e^{-\kappa x} & \text{if } x > a \end{cases}$$

Use the fact that the wave function [and consequently $\psi(x)$] must be continuous at $x = a$ to determine another constant.

$$\lim_{x \to a^-} \psi(x) = \lim_{x \to a^+} \psi(x) : \quad C_2 \sin \ell a = C_3 e^{-\kappa a} \tag{1}$$

Finally, integrate both sides of the TISE with respect to x from $a - \epsilon$ to $a + \epsilon$, where ϵ is a really small positive number.

$$\begin{aligned} \int_{a-\epsilon}^{a+\epsilon} \frac{d^2\psi}{dx^2}\, dx &= \int_{a-\epsilon}^{a+\epsilon} \frac{2m}{\hbar^2} [V(x) - E] \psi(x)\, dx \\ \left. \frac{d\psi}{dx} \right|_{a-\epsilon}^{a+\epsilon} &= \int_{a-\epsilon}^{a} \frac{2m}{\hbar^2} \left(-\frac{32\hbar^2}{ma^2} - E \right) \psi(x)\, dx + \int_a^{a+\epsilon} \frac{2m}{\hbar^2} (-E) \psi(x)\, dx \\ &= \frac{2m}{\hbar^2} \left(-\frac{32\hbar^2}{ma^2} - E \right) \psi(a) \int_{a-\epsilon}^{a} dx + \frac{2m}{\hbar^2} (-E) \psi(a) \int_a^{a+\epsilon} dx \\ &= \frac{2m}{\hbar^2} \left(-\frac{32\hbar^2}{ma^2} - E \right) \psi(a) \epsilon + \frac{2m}{\hbar^2} (-E) \psi(a) \epsilon \end{aligned}$$

Take the limit as $\epsilon \to 0$.

$$\left. \frac{d\psi}{dx} \right|_{a^-}^{a^+} = 0$$

It turns out that $\partial \Psi / \partial x$ is also continuous at $x = a$.

$$\lim_{x \to a^-} \frac{d\psi}{dx} = \lim_{x \to a^+} \frac{d\psi}{dx} : \quad C_2 \ell \cos \ell a = -C_3 \kappa e^{-\kappa a} \tag{2}$$

Substitute equation (1) into equation (2).

$$C_2 \ell \cos \ell a = -C_2 \kappa \sin \ell a$$

To avoid the trivial solution, assume that $C_2 \neq 0$.

$$\ell \cos \ell a = -\kappa \sin \ell a$$

Multiply both sides by a.

$$\ell a \cot \ell a = -\kappa a \tag{3}$$

Note that

$$\kappa^2 + \ell^2 = \frac{-2mE}{\hbar^2} + \frac{2m}{\hbar^2} \left(\frac{32\hbar^2}{ma^2} + E \right) = -\frac{2mE}{\hbar^2} + \frac{64}{a^2} + \frac{2mE}{\hbar^2} = \frac{64}{a^2}.$$

Multiply both sides by a^2 and then solve for κa.

$$\kappa^2 a^2 + \ell^2 a^2 = 64$$

$$\kappa^2 a^2 = 64 - \ell^2 a^2$$

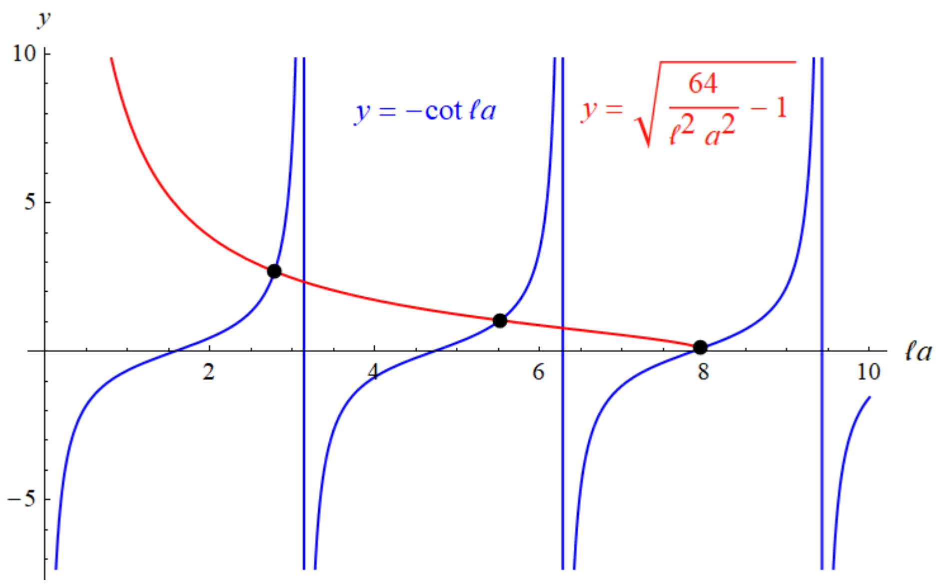
$$\kappa a = \sqrt{64 - \ell^2 a^2}$$

As a result, equation (3) becomes

$$\ell a \cot \ell a = -\sqrt{64 - \ell^2 a^2}$$

$$-\cot \ell a = \sqrt{\frac{64}{\ell^2 a^2} - 1}.$$

Plot the functions on both sides versus ℓa.



Since there are three intersections, there are three bound states. These intersections occur at approximately

$$\ell a \approx 2.78590 \quad \rightarrow \quad \sqrt{\frac{2m}{\hbar^2}\left(\frac{32\hbar^2}{ma^2} + E_1\right)}a \approx 2.78590 \quad \rightarrow \quad E_1 \approx -\frac{28.1194\hbar^2}{ma^2}$$

$$\ell a \approx 5.52145 \quad \rightarrow \quad \sqrt{\frac{2m}{\hbar^2}\left(\frac{32\hbar^2}{ma^2} + E_2\right)}a \approx 5.52145 \quad \rightarrow \quad E_2 \approx -\frac{16.7568\hbar^2}{ma^2}$$

$$\ell a \approx 7.95732 \quad \rightarrow \quad \sqrt{\frac{2m}{\hbar^2}\left(\frac{32\hbar^2}{ma^2} + E_3\right)}a \approx 7.95732 \quad \rightarrow \quad E_3 \approx -\frac{0.340529\hbar^2}{ma^2}.$$

For the highest energy,

$$\kappa = \frac{\sqrt{-2mE_3}}{\hbar} \approx \frac{0.825263}{a} \quad \text{and} \quad \ell \approx \frac{7.95732}{a}.$$

The eigenfunction associated with the highest energy is

$$\begin{aligned}
\psi(x) &= \begin{cases} C_2 \sin \ell x & \text{if } 0 \le x \le a \\ C_3 e^{-\kappa x} & \text{if } x > a \end{cases} \\
&= \begin{cases} C_2 \sin \ell x & \text{if } 0 \le x \le a \\ (C_2 e^{\kappa a} \sin \ell a) e^{-\kappa x} & \text{if } x > a \end{cases} \\
&= \begin{cases} C_2 \sin \ell x & \text{if } 0 \le x \le a \\ (C_2 \sin \ell a) e^{-\kappa (x-a)} & \text{if } x > a \end{cases} \\
&\approx \begin{cases} C_2 \sin \frac{7.95732x}{a} & \text{if } 0 \le x \le a \\ (C_2 \sin 7.95732) \exp\left[-0.825263\left(\frac{x}{a} - 1\right)\right] & \text{if } x > a \end{cases}.
\end{aligned}$$

C_2 is arbitrary and is chosen so that the integral of $[\psi(x)]^2$ over the half-line is 1.

$$\begin{aligned}
1 &= \int_0^\infty [\psi(x)]^2 \, dx \\
&= \int_0^a \left(C_2 \sin \frac{7.95732x}{a} \right)^2 dx + \int_a^\infty \left\{ (C_2 \sin 7.95732) \exp\left[-0.825263\left(\frac{x}{a} - 1\right)\right] \right\}^2 dx \\
&= 1.10587 a C_2^2
\end{aligned}$$

Solve for C_2.

$$C_2 = \frac{0.950930}{\sqrt{a}}$$

Therefore, the eigenstate with the highest energy is

$$\psi(x) = \begin{cases} \frac{0.950930}{\sqrt{a}} \sin \frac{7.95732x}{a} & \text{if } 0 \le x \le a \\ \frac{0.945857}{\sqrt{a}} \exp\left[-0.825263\left(\frac{x}{a} - 1\right)\right] & \text{if } x > a \end{cases}.$$

The probability that the particle is outside the well is 1 minus the probability that it's inside the well.

$$\begin{aligned}
1 - \int_0^a [\psi(x)]^2 \, dx &= 1 - \int_0^a \left(\frac{0.950930}{\sqrt{a}} \sin \frac{7.95732x}{a} \right)^2 dx \\
&\approx 0.542
\end{aligned}$$