Problem 2.29

Analyze the *odd* bound state wave functions for the finite square well. Derive the transcendental equation for the allowed energies, and solve it graphically. Examine the two limiting cases. Is there always an odd bound state?

Solution

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

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

For a finite square well,

$$V(x,t) = V(x) = \begin{cases} -V_0 & \text{if } -a \leq x \leq a \\ 0 & \text{if } |x| > a \end{cases},$$

which means the PDE becomes

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi(x,t).$$

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 (Ψ and its derivatives tend to zero as $x \to \pm\infty$) are linear and homogeneous. Assume a product solution of the form $\Psi(x,t) = \psi(x)\phi(t)$ and plug it into the PDE.

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

Evaluate the derivatives.

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

Divide both sides 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

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

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

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(-E)\psi, \quad |x| > a \qquad\qquad \frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}(V_0 + E)\psi, \quad -a \leq x \leq a$$

Bound states have energy $-V_0 < E < 0$, or $V_0 + E > 0$; in this case, the general solution is

$$\psi(x) = \begin{cases} C_1 \exp\left(\frac{\sqrt{-2mE}}{\hbar}x\right) + C_2 \exp\left(-\frac{\sqrt{-2mE}}{\hbar}x\right) & \text{if } x < -a \\ C_3 \cos\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right] + C_4 \sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right] & \text{if } -a \leq x \leq a \\ C_5 \exp\left(\frac{\sqrt{-2mE}}{\hbar}x\right) + C_6 \exp\left(-\frac{\sqrt{-2mE}}{\hbar}x\right) & \text{if } x > a \end{cases}.$$

In order for $\Psi(x,t) = \psi(x)\phi(t)$ to be zero as $x \to \pm\infty$, we require that $C_2 = 0$ and $C_5 = 0$.

$$\psi(x) = \begin{cases} C_1 \exp\left(\frac{\sqrt{-2mE}}{\hbar}x\right) & \text{if } x < -a \\ C_3 \cos\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right] + C_4 \sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right] & \text{if } -a \leq x \leq a \\ C_6 \exp\left(-\frac{\sqrt{-2mE}}{\hbar}x\right) & \text{if } x > a \end{cases}$$

To obtain the odd bound states in particular, set $C_3 = 0$ and $C_1 = -C_6$.

$$\psi(x) = \begin{cases} -C_6 \exp\left(\frac{\sqrt{-2mE}}{\hbar}x\right) & \text{if } x < -a \\ C_4 \sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right] & \text{if } -a \leq x \leq a \\ C_6 \exp\left(-\frac{\sqrt{-2mE}}{\hbar}x\right) & \text{if } x > a \end{cases}$$

The wave function [and consequently $\psi(x)$] is required to be continuous at $x = \pm a$.

$$\lim_{x\to\pm a^-} \psi(x) = \lim_{x\to\pm a^+} \psi(x): \quad C_4 \sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] = C_6 \exp\left(-\frac{\sqrt{-2mE}}{\hbar}a\right)$$

Solve for C_6.

$$C_6 = C_4 \sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] \exp\left(\frac{\sqrt{-2mE}}{\hbar}a\right)$$

As a result, the odd bound state for the finite square well is

$$\psi(x) = \begin{cases} -C_4 \sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]\exp\left[\frac{\sqrt{-2mE}}{\hbar}(x+a)\right] & \text{if } x < -a \\ C_4 \sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right] & \text{if } -a \le x \le a \\ C_4 \sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]\exp\left[-\frac{\sqrt{-2mE}}{\hbar}(x-a)\right] & \text{if } x > a \end{cases}.$$

C_4 is arbitrary because the TISE is homogeneous, but it's chosen so that the integral of $[\psi(x)]^2$ over the whole line is 1. This makes it so that $|\Psi(x,t)|^2$ has the usual probabilistic interpretation.

$$\begin{aligned}
1 &= \int_{-\infty}^{\infty} [\psi(x)]^2\,dx \\
&= \int_{-\infty}^{-a} [\psi(x)]^2\,dx + \int_{-a}^{a} [\psi(x)]^2\,dx + \int_{a}^{\infty} [\psi(x)]^2\,dx \\
&= \int_{-\infty}^{-a} \left[-C_6 \exp\left(\frac{\sqrt{-2mE}}{\hbar}x\right)\right]^2 dx + \int_{-a}^{a} \left\{C_4 \sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right]\right\}^2 dx + \int_{a}^{\infty} \left[C_6 \exp\left(-\frac{\sqrt{-2mE}}{\hbar}x\right)\right]^2 dx \\
&= C_6^2 \int_{-\infty}^{-a} \exp\left(2\frac{\sqrt{-2mE}}{\hbar}x\right) dx + C_4^2 \int_{-a}^{a} \sin^2\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right] dx + C_6^2 \int_{a}^{\infty} \exp\left(-2\frac{\sqrt{-2mE}}{\hbar}x\right) dx \\
&= C_6^2\left[\frac{\hbar}{2\sqrt{-2mE}} \exp\left(2\frac{\sqrt{-2mE}}{\hbar}x\right)\bigg|_{-\infty}^{-a}\right] + 2C_4^2 \int_0^a \frac{1}{2}\left\{1 - \cos\left[2\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right]\right\} dx \\
&\qquad + C_6^2\left[-\frac{\hbar}{2\sqrt{-2mE}} \exp\left(-2\frac{\sqrt{-2mE}}{\hbar}x\right)\bigg|_a^{\infty}\right] \\
&= C_6^2\left[\frac{\hbar}{2\sqrt{-2mE}} \exp\left(-2\frac{\sqrt{-2mE}}{\hbar}a\right)\right] + C_4^2\left\{x - \frac{\hbar}{2\sqrt{2m(V_0+E)}} \sin\left[2\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right]\bigg|_0^a\right\} \\
&\qquad + C_6^2\left[\frac{\hbar}{2\sqrt{-2mE}} \exp\left(-2\frac{\sqrt{-2mE}}{\hbar}a\right)\right] \\
&= C_6^2\left[\frac{\hbar}{\sqrt{-2mE}} \exp\left(-2\frac{\sqrt{-2mE}}{\hbar}a\right)\right] + C_4^2\left\{a - \frac{\hbar}{2\sqrt{2m(V_0+E)}} \sin\left[2\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]\right\} \\
&= C_4^2 \sin^2\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] \exp\left(2\frac{\sqrt{-2mE}}{\hbar}a\right)\left[\frac{\hbar}{\sqrt{-2mE}} \exp\left(-2\frac{\sqrt{-2mE}}{\hbar}a\right)\right] \\
&\qquad + C_4^2\left\{a - \frac{\hbar}{2\sqrt{2m(V_0+E)}} \sin\left[2\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]\right\} \\
&= C_4^2\left\{\frac{\hbar}{\sqrt{-2mE}} \sin^2\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] + a - \frac{\hbar}{2\sqrt{2m(V_0+E)}} \sin\left[2\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]\right\}
\end{aligned}$$

Solve for C_4.

$$C_4 = \frac{1}{\sqrt{\frac{\hbar}{\sqrt{-2mE}}\sin^2\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] + a - \frac{\hbar}{2\sqrt{2m(V_0+E)}}\sin\left[2\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]}}$$

To determine the energy corresponding to the eigenstate $\psi(x)$, integrate both sides of equation (1) with respect to x from $a-\epsilon$ to $a+\epsilon$, where ϵ is a really small positive number.

$$\begin{aligned}
\int_{a-\epsilon}^{a+\epsilon} \frac{d^2\psi}{dx^2}\,dx &= \int_{a-\epsilon}^{a+\epsilon} \frac{2m}{\hbar^2}[V(x)-E]\psi(x)\,dx \\
\left.\frac{d\psi}{dx}\right|_{a-\epsilon}^{a+\epsilon} &= \int_{a-\epsilon}^{a} \frac{2m}{\hbar^2}[-V_0-E]\psi(x)\,dx + \int_{a}^{a+\epsilon} \frac{2m}{\hbar^2}(-E)\psi(x)\,dx \\
&= \frac{2m}{\hbar^2}[-V_0-E]\psi(a)\int_{a-\epsilon}^{a} dx + \frac{2m}{\hbar^2}(-E)\psi(a)\int_{a}^{a+\epsilon} dx \\
&= \frac{2m}{\hbar^2}[-V_0-E]\psi(a)\epsilon + \frac{2m}{\hbar^2}(-E)\psi(a)\epsilon
\end{aligned}$$

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 continuous at $x = a$ (and $x = -a$) as well.

$$\lim_{x\to a^-}\frac{d\psi}{dx} = \lim_{x\to a^+}\frac{d\psi}{dx}: \quad C_4\frac{\sqrt{2m(V_0+E)}}{\hbar}\cos\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] = C_4\sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]\left(-\frac{\sqrt{-2mE}}{\hbar}\right)$$

Bring quantities with V_0+E to the left side.

$$-\frac{\sqrt{2m(V_0+E)}}{\hbar}\cot\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] = \frac{\sqrt{-2mE}}{\hbar}$$

The aim now is to write everything in terms of the cotangent's argument. Start by multiplying both sides by a.

$$\begin{aligned}
-\frac{\sqrt{2m(V_0+E)}}{\hbar}a\cot\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] &= \frac{\sqrt{-2mE}}{\hbar}a \\
&= \left[\sqrt{\frac{2mV_0}{\hbar^2} - \frac{2m(V_0+E)}{\hbar^2}}\right]a \\
&= \sqrt{\frac{2mV_0}{\hbar^2}a^2 - \frac{2m(V_0+E)}{\hbar^2}a^2} \\
&= \sqrt{\left(\frac{\sqrt{2mV_0}}{\hbar}a\right)^2 - \left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]^2}
\end{aligned}$$

Introduce the variables,

$$z_0 = \frac{\sqrt{2mV_0}}{\hbar}a \quad \text{and} \quad z = \frac{\sqrt{2m(V_0+E)}}{\hbar}a,$$

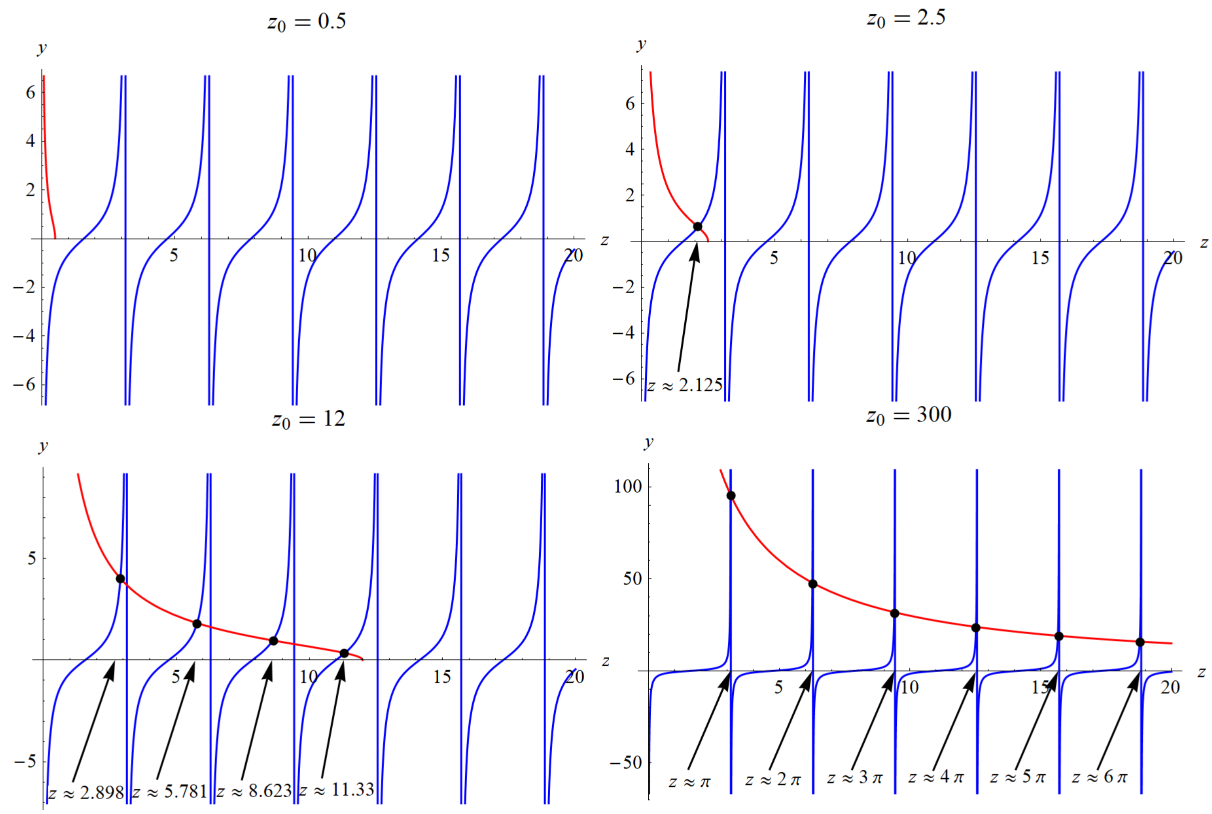
to get a transcendental equation for the eigenvalues.

$$-z\cot z = \sqrt{z_0^2 - z^2}$$

Divide both sides by z to get an equation analogous to Equation 2.159 (page 72) in the textbook.

$$-\cot z = \sqrt{(z_0/z)^2 - 1}$$

Below are plots of $y = -\cot z$ (in blue) and $y = \sqrt{(z_0/z)^2 - 1}$ (in red) versus z for various values of z_0. The number of intersections indicates the number of legitimate odd bound states.



There are no intersections below a certain value of z_0. Once z_0 reaches $\pi/2 \approx 1.57$, there is one intersection at $z = \pi/2$. Therefore, if

$$z_0 = \frac{\sqrt{2mV_0}}{\hbar}a < \frac{\pi}{2}$$

$$V_0 < \frac{\pi^2\hbar^2}{2m(2a)^2},$$

then there are no odd bound states. Observe that this is the smallest energy of the infinite square well potential with width $2a$. On the other hand, if z_0 is really high, then the intersections occur at $z \approx n\pi$, where n is a positive integer.

$$z = \frac{\sqrt{2m(V_0 + E)}}{\hbar}a \approx n\pi, \quad n = 1, 2, \ldots$$

$$V_0 + E_n \approx \frac{(2n)^2\pi^2\hbar^2}{2m(2a)^2}$$

Observe that the energies are those of the infinite square well with width $2a$ for even integers.

The continuity of $\partial\Psi/\partial x$ at $x = a$ allows the formula for C_4 to be simplified.

$$\lim_{x\to a^-}\frac{d\psi}{dx} = \lim_{x\to a^+}\frac{d\psi}{dx}: \quad C_4\frac{\sqrt{2m(V_0+E)}}{\hbar}\cos\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] = C_4\sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]\left(-\frac{\sqrt{-2mE}}{\hbar}\right)$$

Rewrite the equation.

$$\frac{\hbar}{\sqrt{-2mE}}\cos\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] = -\frac{\hbar}{\sqrt{2m(V_0+E)}}\sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]$$

Therefore, the normalization constant becomes

$$\begin{aligned}
C_4 &= \frac{1}{\sqrt{\frac{\hbar}{\sqrt{-2mE}}\sin^2\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] + a - \frac{\hbar}{2\sqrt{2m(V_0+E)}}\sin\left[2\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]}} \\
&= \frac{1}{\sqrt{\frac{\hbar}{\sqrt{-2mE}}\sin^2\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] + a - \frac{\hbar}{\sqrt{2m(V_0+E)}}\sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]\cos\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]}} \\
&= \frac{1}{\sqrt{\frac{\hbar}{\sqrt{-2mE}}\sin^2\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right] + a + \frac{\hbar}{\sqrt{-2mE}}\cos^2\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]}} \\
&= \frac{1}{\sqrt{\frac{\hbar}{\sqrt{-2mE}} + a}},
\end{aligned}$$

which means the odd bound state is

$$\psi(x) = \begin{cases} -\frac{1}{\sqrt{\frac{\hbar}{\sqrt{-2mE}}+a}}\sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]\exp\left[\frac{\sqrt{-2mE}}{\hbar}(x+a)\right] & \text{if } x < -a \\ \frac{1}{\sqrt{\frac{\hbar}{\sqrt{-2mE}}+a}}\sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}x\right] & \text{if } -a \le x \le a \\ \frac{1}{\sqrt{\frac{\hbar}{\sqrt{-2mE}}+a}}\sin\left[\frac{\sqrt{2m(V_0+E)}}{\hbar}a\right]\exp\left[-\frac{\sqrt{-2mE}}{\hbar}(x-a)\right] & \text{if } x > a \end{cases},$$

or in terms of z_0 and z,

$$\psi(x) = \begin{cases} -\frac{1}{\sqrt{\frac{a}{\sqrt{z_0^2-z^2}}+a}}\sin z\exp\left[\sqrt{z_0^2-z^2}(x+a)\right] & \text{if } x < -a \\ \frac{1}{\sqrt{\frac{a}{\sqrt{z_0^2-z^2}}+a}}\sin\frac{zx}{a} & \text{if } -a \le x \le a \\ \frac{1}{\sqrt{\frac{a}{\sqrt{z_0^2-z^2}}+a}}\sin z\exp\left[-\sqrt{z_0^2-z^2}(x-a)\right] & \text{if } x > a \end{cases} = \begin{cases} -\frac{\sin z}{\sqrt{a\left(1-\frac{\tan z}{z}\right)}}e^{-(x+a)z\cot z} & \text{if } x < -a \\ \frac{1}{\sqrt{a\left(1-\frac{\tan z}{z}\right)}}\sin\frac{zx}{a} & \text{if } -a \le x \le a \\ \frac{\sin z}{\sqrt{a\left(1-\frac{\tan z}{z}\right)}}e^{(x-a)z\cot z} & \text{if } x > a \end{cases}.$$