Problem 2.3

Show that there is no acceptable solution to the (time-independent) Schrödinger equation for the infinite square well with $E = 0$ or $E < 0$. (This is a special case of the general theorem in Problem 2.2, but this time do it by explicitly solving the Schrödinger equation, and showing that you cannot satisfy the boundary conditions.)

Solution

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

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

Here it will be solved with the infinite square well potential,

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

and the associated boundary conditions,

$$\begin{aligned} \Psi(0,t) &= 0 \\ \Psi(a,t) &= 0. \end{aligned}$$

Because Schrödinger's equation and the boundary conditions are linear and homogeneous, the method of separation can be applied to solve the PDE: Assume a product solution of the form $\Psi(x,t) = \psi(x)\phi(t)$ and plug it into the PDE

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

and the boundary conditions.

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

Separate variables in the PDE by dividing both sides by $\psi(x)\phi(t)$.

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

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

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

Values of E for which the boundary conditions of this second equation are satisfied are known as eigenvalues (or eigenenergies in this context), and the nontrivial solutions $\psi(x)$ that satisfy this second equation are known as eigenfunctions (or eigenstates in this context).

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

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

This second equation is the time-independent Schrödinger equation and can be written as

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E]\psi \quad \Rightarrow \quad \begin{cases} \dfrac{d^2\psi}{dx^2} = -\dfrac{2mE}{\hbar^2}\psi & \text{if } 0 \le x \le a \\ \dfrac{d^2\psi}{dx^2} = \dfrac{2m}{\hbar^2}(\infty)\psi & \text{if } x < 0 \\ \dfrac{d^2\psi}{dx^2} = \dfrac{2m}{\hbar^2}(\infty)\psi & \text{if } x > a \end{cases}.$$

It must be solved on the intervals where the potential energy has been defined over. For the intervals, $x < 0$ and $x > a$, only the trivial solution $\psi(x) = 0$ satisfies the ODE and the boundary conditions at $x = 0$ and $x = a$. Therefore, $\Psi(x,t) = 0$ if $x < 0$, and $\Psi(x,t) = 0$ if $x > a$. All that remains is

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi, \quad 0 \le x \le a.$$

Check to see if there are any positive eigenvalues: $E = \mu^2$.

$$\frac{d^2\psi}{dx^2} = -\frac{2m\mu^2}{\hbar^2}\psi$$

The general solution can be written in terms of sine and cosine.

$$\psi(x) = C_1 \sin\left(\frac{\sqrt{2m}\mu}{\hbar}x\right) + C_2 \cos\left(\frac{\sqrt{2m}\mu}{\hbar}x\right)$$

Apply the two boundary conditions to determine C_1 and C_2.

$$\begin{aligned} \psi(0) &= C_2 = 0 \\ \psi(a) &= C_1 \sin\left(\frac{\sqrt{2m}\mu}{\hbar}a\right) + C_2 \cos\left(\frac{\sqrt{2m}\mu}{\hbar}a\right) = 0 \end{aligned}$$

Since $C_2 = 0$, this second condition reduces to

$$C_1 \sin\left(\frac{\sqrt{2m}\mu}{\hbar}a\right) = 0.$$

In order to avoid the trivial solution, we insist that $C_1 \neq 0$.

$$\begin{aligned} \sin\left(\frac{\sqrt{2m}\mu}{\hbar}a\right) &= 0 \\ \frac{\sqrt{2m}\mu}{\hbar}a &= n\pi, \quad n = 0, \pm 1, \pm 2, \ldots \\ \mu_n &= \frac{\hbar}{\sqrt{2m}}\frac{n\pi}{a} \end{aligned}$$

Therefore, there are positive eigenvalues,

$$E_n = \mu_n^2 = \frac{\hbar^2\pi^2 n^2}{2ma^2}, \quad n = 1, 2, \ldots,$$

and the eigenfunctions associated with them are

$$\psi(x) = C_1 \sin\left(\frac{\sqrt{2m}\mu}{\hbar}x\right) \quad \Rightarrow \quad \psi_n(x) = A \sin\frac{n\pi x}{a}.$$

Note that the negative values of n have been dropped because they lead to redundant eigenvalues. $n = 0$ is also excluded because it leads to the zero eigenvalue, which will be checked later. This factor A is a normalization constant and is determined by requiring the integral of $|\psi(x)|^2$ to be 1.

$$\int_0^a |\psi(x)|^2\,dx = 1 \quad \to \quad \int_0^a A^2 \sin^2\frac{n\pi x}{a}\,dx = 1 \quad \to \quad A^2\left(\frac{a}{2}\right) = 1 \quad \to \quad A = \sqrt{\frac{2}{a}}$$

Since the positive eigenvalues are relevant, solve the ODE in t with this formula for E.

$$i\hbar\frac{\phi'(t)}{\phi(t)} = \frac{\hbar^2\pi^2n^2}{2ma^2}$$

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

The left side can be written as the derivative of a logarithm by the chain rule.

$$\frac{d}{dt}\ln\phi(t) = -i\frac{\hbar\pi^2n^2}{2ma^2}$$

Integrate both sides with respect to t.

$$\ln\phi(t) = -i\frac{\hbar\pi^2n^2}{2ma^2}t + C$$

Exponentiate both sides.

$$\phi(t) = \exp\left(-i\frac{\hbar\pi^2n^2}{2ma^2}t + C\right) = e^C\exp\left(-i\frac{\hbar\pi^2n^2}{2ma^2}t\right) \quad \Rightarrow \quad \phi_n(t) = \exp\left(-i\frac{\hbar\pi^2n^2}{2ma^2}t\right)$$

Now check to see if zero is an eigenvalue.

$$\frac{d^2\psi}{dx^2} = 0$$

The general solution is a straight line.

$$\psi(x) = C_3x + C_4$$

Apply the boundary conditions to determine C_3 and C_4.

$$\psi(0) = C_4 = 0$$
$$\psi(a) = C_3a + C_4 = 0$$

Since $C_4 = 0$, the second equation reduces to $C_3a = 0$, which means $C_3 = 0$. This results in the trivial solution $\psi(x) = 0$; consequently, zero is not an eigenvalue.

Now check to see if there are negative eigenvalues: $E = -\gamma^2$.

$$\frac{d^2\psi}{dx^2} = \frac{2m\gamma^2}{\hbar^2}\psi$$

The general solution can be written in terms of hyperbolic sine and hyperbolic cosine.

$$\psi(x) = C_5 \sinh\left(\frac{\sqrt{2m}\gamma}{\hbar}x\right) + C_6 \cosh\left(\frac{\sqrt{2m}\gamma}{\hbar}x\right)$$

Apply the boundary conditions to determine C_5 and C_6.

$$\begin{aligned}
\psi(0) &= C_6 = 0 \\
\psi(a) &= C_5 \sinh\left(\frac{\sqrt{2m}\gamma}{\hbar}a\right) + C_6 \cosh\left(\frac{\sqrt{2m}\gamma}{\hbar}a\right) = 0
\end{aligned}$$

Since $C_6 = 0$, this second equation reduces to

$$C_5 \sinh\left(\frac{\sqrt{2m}\gamma}{\hbar}a\right) = 0.$$

Unfortunately, there is no nonzero value of γ that makes the hyperbolic sine zero, so $C_5 = 0$ is necessary. This leads to the trivial solution $\psi(x) = 0$, which means there are no negative eigenvalues. According to the principle of superposition, the general solution to Schrödinger's equation is a linear combination of the product solutions (or stationary states in this context) $\Psi_n(x,t) = \psi_n(x)\phi_n(t)$ over all the eigenvalues.

$$\begin{aligned}
\Psi(x,t) &= \sum_{n=1}^{\infty} B_n \Psi_n(x,t) \\
&= \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} B_n \exp\left(-i\frac{\hbar\pi^2 n^2}{2ma^2}t\right) \sin\frac{n\pi x}{a}
\end{aligned}$$

The point of including the normalization constant A is so that the stationary states are normalized.

$$\begin{aligned}
1 &= \int_0^a |\Psi_n(x,t)|^2\,dx \\
&= \int_0^a \Psi_n(x,t)\Psi_n^*(x,t)\,dx \\
&= \int_0^a [\psi_n(x)e^{-iE_n t/\hbar}][\psi_n(x)e^{-iE_n t/\hbar}]^*\,dx \\
&= \int_0^a [\psi_n(x)e^{-iE_n t/\hbar}][\psi_n^*(x)e^{iE_n t/\hbar}]\,dx \\
&= \int_0^a |\psi_n(x)|^2\,dx
\end{aligned}$$