Problem 2.44

If two (or more) distinct[56] solutions to the (time-independent) Schrödinger equation have the same energy E, these states are said to be **degenerate**. For example, the free particle states are doubly degenerate—one solution representing motion to the right, and the other motion to the left. But we have never encountered *normalizable* degenerate solutions, and this is no accident. Prove the following theorem: *In one dimension*[57] $(-\infty < x < \infty)$ *there are no degenerate bound states.* [*Hint*: Suppose there are *two* solutions, ψ_1 and ψ_2, with the same energy E. Multiply the Schrödinger equation for ψ_1 by ψ_2, and the Schrödinger equation for ψ_2 by ψ_1, and subtract, to show that $(\psi_2 d\psi_1/dx - \psi_1 d\psi_2/dx)$ is a constant. Use the fact that for normalizable solutions $\psi \to 0$ at $\pm\infty$ to demonstrate that this constant is in fact zero. Conclude that ψ_2 is a multiple of ψ_1, and hence that the two solutions are not distinct.]

Solution

The one-dimensional Schrödinger equation is

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

If $V(x,t) = V(x)$, then applying the method of separation of variables results in 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 ODE in x is the time-independent Schrödinger equation (TISE) and can be written as

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

The aim is to show there are no degenerate bound states. Suppose there are two linearly independent eigenstates, $\psi_1(x)$ and $\psi_2(x)$, with the same energy E.

$$\begin{aligned} \frac{d^2\psi_1}{dx^2} &= \frac{2m}{\hbar^2}[V(x) - E]\psi_1 \\ \frac{d^2\psi_2}{dx^2} &= \frac{2m}{\hbar^2}[V(x) - E]\psi_2 \end{aligned}$$

Multiply both sides of the first equation by ψ_2, and multiply both sides of the second equation by ψ_1.

$$\begin{aligned} \psi_2\frac{d^2\psi_1}{dx^2} &= \frac{2m}{\hbar^2}[V(x) - E]\psi_1\psi_2 \\ \psi_1\frac{d^2\psi_2}{dx^2} &= \frac{2m}{\hbar^2}[V(x) - E]\psi_1\psi_2 \end{aligned}$$

[56]If two solutions differ only by a multiplicative constant (so that, once normalized, they differ only by a phase factor $e^{i\phi}$), they represent the same physical state, and in this sense they are *not* distinct solutions. Technically, by "distinct" I mean "linearly independent."

[57]In higher dimensions such degeneracy is very common, as we shall see in Chapters 4 and 6. Assume that the potential does not consist of isolated pieces separated by regions where $V = \infty$—two isolated infinite square wells, for instance, would give rise to degenerate bound states, for which the particle is either in one well or in the other.

Subtract the respective sides of these equations.

$$\psi_2 \frac{d^2\psi_1}{dx^2} - \psi_1 \frac{d^2\psi_2}{dx^2} = 0$$

Add and subtract the same quantity on the left side.

$$\psi_2 \frac{d^2\psi_1}{dx^2} + \frac{d\psi_2}{dx}\frac{d\psi_1}{dx} - \psi_1 \frac{d^2\psi_2}{dx^2} - \frac{d\psi_1}{dx}\frac{d\psi_2}{dx} = 0$$

Use the product rule twice.

$$\frac{d}{dx}\left(\psi_2 \frac{d\psi_1}{dx}\right) - \frac{d}{dx}\left(\psi_1 \frac{d\psi_2}{dx}\right) = 0$$

Factor the derivative operator.

$$\frac{d}{dx}\left(\psi_2 \frac{d\psi_1}{dx} - \psi_1 \frac{d\psi_2}{dx}\right) = 0$$

Integrate both sides with respect to x.

$$\psi_2 \frac{d\psi_1}{dx} - \psi_1 \frac{d\psi_2}{dx} = C \tag{1}$$

This equation must hold for any value of x, so set $x = \infty$ to determine C.

$$\psi_2(\infty) \frac{d\psi_1}{dx}\bigg|_{x=\infty} - \psi_1(\infty) \frac{d\psi_2}{dx}\bigg|_{x=\infty} = C$$

Use the boundary conditions, $\psi_1(x) = 0$ and $\psi_2(x) = 0$ as $x \to \pm\infty$.

$$0 = C$$

Consequently, equation (1) becomes

$$\psi_2 \frac{d\psi_1}{dx} - \psi_1 \frac{d\psi_2}{dx} = 0$$

$$\begin{aligned} \psi_2 \frac{d\psi_1}{dx} &= \psi_1 \frac{d\psi_2}{dx} \\ \frac{\frac{d\psi_1}{dx}}{\psi_1} &= \frac{\frac{d\psi_2}{dx}}{\psi_2} \\ \frac{d}{dx}\ln\psi_1(x) &= \frac{d}{dx}\ln\psi_2(x). \end{aligned}$$

Integrate both sides with respect to x.

$$\ln\psi_1(x) = \ln\psi_2(x) + D$$

Exponentiate both sides.

$$\begin{aligned} \psi_1(x) &= e^{\ln\psi_2(x) + D} \\ &= e^{\ln\psi_2(x)} e^D \\ &= A\psi_2(x) \end{aligned}$$

As a result, $\psi_1(x)$ is a constant multiple of $\psi_2(x)$. This contradicts the assumption that $\psi_1(x)$ and $\psi_2(x)$ are linearly independent. Therefore, there are no degenerate bound states in one dimension.