Problem 2.45

In this problem you will show that the number of nodes of the stationary states of a one-dimensional potential always increases with energy.[58] Consider two (real, normalized) solutions (ψ_n and ψ_m) to the time-independent Schrödinger equation (for a given potential $V(x)$), with energies $E_n > E_m$.

(a) Show that

$$\frac{d}{dx}\left(\frac{d\psi_m}{dx}\psi_n - \psi_m\frac{d\psi_n}{dx}\right) = \frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n.$$

(b) Let x_1 and x_2 be two adjacent nodes of the function $\psi_m(x)$. Show that

$$\psi_m'(x_2)\psi_n(x_2) - \psi_m'(x_1)\psi_n(x_1) = \frac{2m}{\hbar^2}(E_n - E_m)\int_{x_1}^{x_2}\psi_m\psi_n\,dx.$$

(c) If $\psi_n(x)$ has no nodes between x_1 and x_2, then it must have the same sign everywhere in the interval. Show that (b) then leads to a contradiction. Therefore, between every pair of nodes of $\psi_m(x)$, $\psi_n(x)$ must have *at least* one node, and in particular the number of nodes increases with energy.

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 that the number of nodes in any stationary state increases with increasing energy. Suppose there are two real linearly independent solutions to the TISE, $\psi_n(x)$ and $\psi_m(x)$, with corresponding energies, E_n and E_m, such that $E_n > E_m$.

$$\begin{aligned} \frac{d^2\psi_n}{dx^2} &= \frac{2m}{\hbar^2}[V(x) - E_n]\psi_n \\ \frac{d^2\psi_m}{dx^2} &= \frac{2m}{\hbar^2}[V(x) - E_m]\psi_m \end{aligned}$$

[58] M. Moriconi, *Am. J. Phys.* **75**, 284 (2007).

Multiply both sides of the first equation by ψ_m, and multiply both sides of the second equation by ψ_n.

$$\psi_m \frac{d^2\psi_n}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E_n]\psi_m\psi_n$$
$$\psi_n \frac{d^2\psi_m}{dx^2} = \frac{2m}{\hbar^2}[V(x) - E_m]\psi_m\psi_n$$

Subtract the respective sides of these equations.

$$\begin{aligned}\psi_n \frac{d^2\psi_m}{dx^2} - \psi_m \frac{d^2\psi_n}{dx^2} &= \left\{\frac{2m}{\hbar^2}[V(x) - E_m]\psi_m\psi_n\right\} - \left\{\frac{2m}{\hbar^2}[V(x) - E_n]\psi_m\psi_n\right\} \\ &= \cancel{\frac{2m}{\hbar^2}V(x)\psi_m\psi_n} - \frac{2m}{\hbar^2}E_m\psi_m\psi_n - \cancel{\frac{2m}{\hbar^2}V(x)\psi_m\psi_n} + \frac{2m}{\hbar^2}E_n\psi_m\psi_n \\ &= \frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n\end{aligned}$$

Add and subtract the same quantity on the left side.

$$\psi_n \frac{d^2\psi_m}{dx^2} + \frac{d\psi_n}{dx}\frac{d\psi_m}{dx} - \psi_m \frac{d^2\psi_n}{dx^2} - \frac{d\psi_m}{dx}\frac{d\psi_n}{dx} = \frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n$$

Use the product rule twice.

$$\frac{d}{dx}\left(\psi_n \frac{d\psi_m}{dx}\right) - \frac{d}{dx}\left(\psi_m \frac{d\psi_n}{dx}\right) = \frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n$$

Factor the derivative operator.

$$\frac{d}{dx}\left(\psi_n \frac{d\psi_m}{dx} - \psi_m \frac{d\psi_n}{dx}\right) = \frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n$$

Integrate both sides with respect to x from x_1 to x_2, where x_1 and x_2 are the locations of two adjacent nodes in $\psi_m(x)$.

$$\begin{aligned}\int_{x_1}^{x_2} \frac{d}{dx}\left(\psi_n \frac{d\psi_m}{dx} - \psi_m \frac{d\psi_n}{dx}\right) dx &= \int_{x_1}^{x_2} \frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n \, dx \\ \left(\psi_n \frac{d\psi_m}{dx} - \psi_m \frac{d\psi_n}{dx}\right)\Bigg|_{x_1}^{x_2} &= \frac{2m}{\hbar^2}(E_n - E_m)\int_{x_1}^{x_2} \psi_m\psi_n \, dx\end{aligned}$$

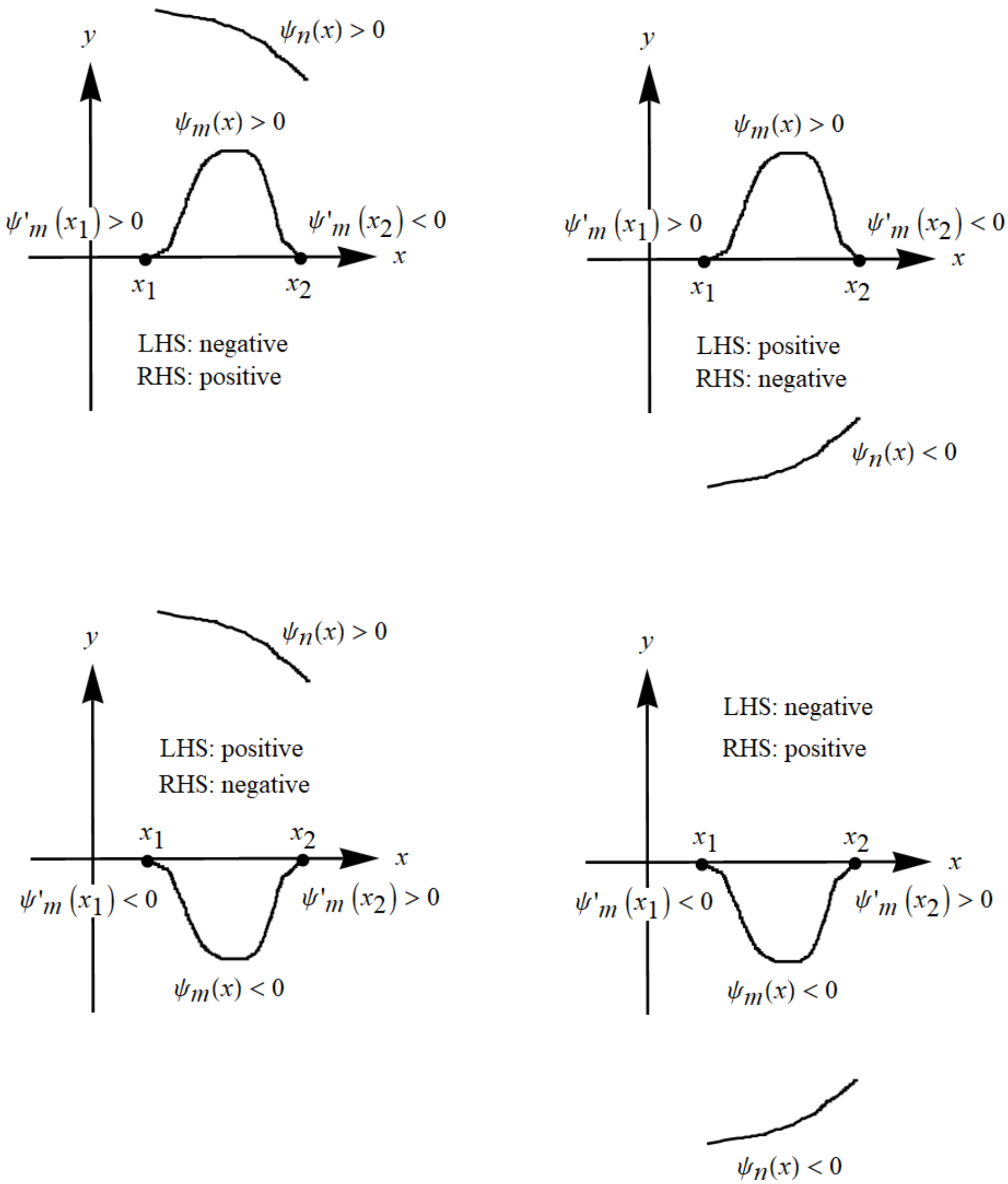
Expand the left side, noting that nodes are where a function is zero.

$$\psi_n(x_2)\frac{d\psi_m}{dx}(x_2) - \underbrace{\psi_m(x_2)\frac{d\psi_n}{dx}(x_2)}_{=0} - \psi_n(x_1)\frac{d\psi_m}{dx}(x_1) + \underbrace{\psi_m(x_1)\frac{d\psi_n}{dx}(x_1)}_{=0} = \frac{2m}{\hbar^2}(E_n - E_m)\int_{x_1}^{x_2} \psi_m\psi_n \, dx$$

$$\psi_m'(x_2)\psi_n(x_2) - \psi_m'(x_1)\psi_n(x_1) = \frac{2m}{\hbar^2}(E_n - E_m)\int_{x_1}^{x_2} \psi_m\psi_n \, dx \tag{1}$$

Assume that $\psi_n(x)$ has no nodes in $x_1 \le x \le x_2$. Then $\psi_n(x)$ has the same sign in $x_1 \le x \le x_2$. Since $\psi_m(x)$ has no nodes in $x_1 < x < x_2$, $\psi_m(x)$ has the same sign in $x_1 < x < x_2$. In addition, because the two adjacent nodes are at x_1 and x_2, $\psi_m'(x_1)$ and $\psi_m'(x_2)$ have opposite signs.

Below are graphs that illustrate the different possibilities for the left-hand side (LHS) and the right-hand side (RHS) of equation (1).



Whatever the case may be, equation (1) implies that a positive number is equal to a negative number, a contradiction. Therefore, $\psi_n(x)$ has at least one node between x_1 and x_2. However many nodes $\psi_m(x)$ has, $\psi_n(x)$ will have more, meaning that the number of nodes in any eigenstate increases with increasing energy.