Problem 4.10

(a) Check that $Arj_1(kr)$ satisfies the radial equation with $V(r) = 0$ and $\ell = 1$.

(b) Determine graphically the allowed energies for the infinite spherical well, when $\ell = 1$. Show that for large N, $E_{N1} \approx \left(\hbar^2\pi^2/2ma^2\right)(N + 1/2)^2$. *Hint:* First show that $j_1(x) = 0 \Rightarrow x = \tan x$. Plot x and $\tan x$ on the same graph, and locate the points of intersection.

Solution

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

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2M}\nabla^2\Psi + V\Psi$$

If the potential energy function is spherically symmetric $V = V(r)$, then the Laplacian operator is expanded in spherical coordinates (r, θ, ϕ), where θ is the angle from the polar axis.

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2M}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right] + V(r)\Psi(r,\theta,\phi,t)$$

The aim is to solve for $\Psi = \Psi(r,\theta,\phi,t)$ in all of space ($0 \le r < \infty$, $0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$) for $t > 0$. Since Schrödinger's equation is linear and homogeneous, the method of separation of variables can be used to solve it: Assume a product solution of the form $\Psi(r,\theta,\phi,t) = R(r)\Theta(\theta)\xi(\phi)T(t)$ and plug it into the PDE.

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}[R(r)\Theta(\theta)\xi(\phi)T(t)] = -\frac{\hbar^2}{2M}&\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}[R(r)\Theta(\theta)\xi(\phi)T(t)]\right)\right. \\ &+ \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}[R(r)\Theta(\theta)\xi(\phi)T(t)]\right) \\ &\left.+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}[R(r)\Theta(\theta)\xi(\phi)T(t)]\right] + V(r)[R(r)\Theta(\theta)\xi(\phi)T(t)] \end{aligned}$$

$$\begin{aligned} i\hbar R(r)\Theta(\theta)\xi(\phi)T'(t) = -\frac{\hbar^2}{2M}&\left[\frac{\Theta(\theta)\xi(\phi)T(t)}{r^2}\frac{d}{dr}\left(r^2R'(r)\right)\right. \\ &+ \frac{R(r)\xi(\phi)T(t)}{r^2\sin\theta}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) \\ &\left.+\frac{R(r)\Theta(\theta)T(t)}{r^2\sin^2\theta}\xi''(\phi)\right] + V(r)[R(r)\Theta(\theta)\xi(\phi)T(t)] \end{aligned}$$

In order to separate variables, divide both sides by $R(r)\Theta(\theta)\xi(\phi)T(t)$.

$$i\hbar\frac{T'(t)}{T(t)} = -\frac{\hbar^2}{2M}\left[\frac{1}{r^2R(r)}\frac{d}{dr}\left(r^2R'(r)\right) + \frac{1}{r^2\Theta(\theta)\sin\theta}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{1}{r^2\xi(\phi)\sin^2\theta}\xi''(\phi)\right] + V(r)$$

The only way a function of t can be equal to a function of r, θ, and ϕ is if both are equal to a constant.

$$i\hbar\frac{T'(t)}{T(t)} = -\frac{\hbar^2}{2M}\left[\frac{1}{r^2R(r)}\frac{d}{dr}\left(r^2R'(r)\right) + \frac{1}{r^2\Theta(\theta)\sin\theta}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{1}{r^2\xi(\phi)\sin^2\theta}\xi''(\phi)\right] + V(r) = E$$

Multiply both sides by $-2Mr^2/\hbar^2$.

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2R'(r)\right) + \frac{1}{\Theta(\theta)\sin\theta}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{1}{\xi(\phi)\sin^2\theta}\xi''(\phi) - \frac{2Mr^2}{\hbar^2}[V(r) - E] = 0$$

Bring the θ- and ϕ-dependent terms to the right side.

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2R'(r)\right) - \frac{2Mr^2}{\hbar^2}[V(r) - E] = -\frac{1}{\sin^2\theta}\left[\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{\xi''(\phi)}{\xi(\phi)}\right]$$

The only way a function of r can be equal to a function of θ and ϕ is if both are equal to a constant.

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2R'(r)\right) - \frac{2Mr^2}{\hbar^2}[V(r) - E] = -\frac{1}{\sin^2\theta}\left[\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{\xi''(\phi)}{\xi(\phi)}\right] = F$$

Multiply both sides by $-\sin^2\theta$.

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + \frac{\xi''(\phi)}{\xi(\phi)} = -F\sin^2\theta$$

Bring the θ-dependent terms to the left side.

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + F\sin^2\theta = -\frac{\xi''(\phi)}{\xi(\phi)}$$

The only way a function of θ can be equal to a function of ϕ is if both are equal to a constant.

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + F\sin^2\theta = -\frac{\xi''(\phi)}{\xi(\phi)} = G$$

As a result of using the method of separation of variables, Schrödinger's equation has reduced to four ODEs—one in r, one in θ, one in ϕ, and one in t.

$$\left.\begin{aligned} i\hbar\frac{T'(t)}{T(t)} &= E \\ \frac{1}{R(r)}\frac{d}{dr}\left(r^2R'(r)\right) - \frac{2Mr^2}{\hbar^2}[V(r) - E] &= F \\ \frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\Theta'(\theta)\sin\theta\right) + F\sin^2\theta &= G \\ -\frac{\xi''(\phi)}{\xi(\phi)} &= G \end{aligned}\right\}$$

The strategy is to solve the fourth eigenvalue problem first to get G, then to solve the third eigenvalue problem for F, then to solve the second eigenvalue problem for E, and then finally to solve the first eigenvalue problem to get $T(t)$. In Problem 4.4 it was found that $F = \ell(\ell+1)$, $G = m^2$, $\xi(\phi) = C_1 e^{im\phi}$, and $\Theta(\theta) = C_2 P_\ell^m(\cos\theta)$, where $\ell = 0, 1, 2, \ldots$ and $m = -\ell, -\ell+1, \ldots, -1, 0, 1, \ldots, \ell-1, \ell$. As a result, the second eigenvalue problem is

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2 R'(r)\right) - \frac{2Mr^2}{\hbar^2}[V(r) - E] = \ell(\ell+1).$$

Multiply both sides by $R(r)$.

$$\frac{d}{dr}\left(r^2 R'(r)\right) - \frac{2Mr^2}{\hbar^2}[V(r) - E]R(r) = \ell(\ell+1)R(r) \tag{1}$$

For the infinite spherical well in particular,

$$V(r) = \begin{cases} 0 & \text{if } r \leq a \\ \infty & \text{if } r > a \end{cases}.$$

If $r > a$, then equation (1) becomes

$$\frac{d}{dr}\left(r^2 R'(r)\right) - \frac{2Mr^2}{\hbar^2}(\infty - E)R(r) = \ell(\ell+1)R(r), \quad r > a.$$

The only way both sides of this equation can be satisfied is if $R(r) = 0$. The wave function is required to be continuous at $r = a$, so $R(a) = 0$ is a boundary condition. If $r \leq a$, then equation (1) becomes

$$\frac{d}{dr}\left(r^2 R'(r)\right) - \frac{2Mr^2}{\hbar^2}(0 - E)R(r) = \ell(\ell+1)R(r), \quad r \leq a$$

$$r^2 R''(r) + 2rR'(r) + \left[\frac{2ME}{\hbar^2}r^2 - \ell(\ell+1)\right]R(r) = 0. \tag{2}$$

This is the spherical Bessel equation, and the physically relevant solution is

$$R(r) = C_3 j_\ell(kr), \quad \text{where } k = \frac{\sqrt{2ME}}{\hbar}.$$

To get the so-called radial equation, make the change of variables $u(r) = rR(r)$ in equation (2).

$$r^2\left[\frac{u(r)}{r}\right]'' + 2r\left[\frac{u(r)}{r}\right]' + \left[\frac{2ME}{\hbar^2}r^2 - \ell(\ell+1)\right]\frac{u(r)}{r} = 0$$

$$r^2\left[\frac{r^2u''(r) - 2ru'(r) + 2u(r)}{r^3}\right] + 2r\left[\frac{ru'(r) - u(r)}{r^2}\right] + \left[\frac{2ME}{\hbar^2}r^2 - \ell(\ell+1)\right]\frac{u(r)}{r} = 0$$

$$r^2u''(r) - \cancel{2ru'(r)} + \cancel{2u(r)} + \cancel{2ru'(r)} - \cancel{2u(r)} + \left[\frac{2ME}{\hbar^2}r^2 - \ell(\ell+1)\right]u(r) = 0$$

Divide both sides by r^2 to get the radial equation for the infinite spherical well.

$$u''(r) + \left[\frac{2ME}{\hbar^2} - \frac{\ell(\ell+1)}{r^2}\right] u(r) = 0$$

Part (a)

The aim is to check that $u(r) = rR(r)$ satisfies the radial equation for $\ell = 1$.

$$\begin{aligned} u(r) &= C_3 r j_1(kr) \\ &= C_3 r \left[\frac{\sin kr - kr\cos kr}{(kr)^2}\right] \\ &= \frac{C_3}{k^2}\left(\frac{\sin kr - kr\cos kr}{r}\right) \end{aligned}$$

Evaluate the left side.

$$\begin{aligned} u''(r) + \left[\frac{2ME}{\hbar^2} - \frac{\ell(\ell+1)}{r^2}\right] u(r) &= \left[\frac{C_3}{k^2}\left(\frac{\sin kr - kr\cos kr}{r}\right)\right]'' + \left[\frac{2ME}{\hbar^2} - \frac{1(1+1)}{r^2}\right]\frac{C_3}{k^2}\left(\frac{\sin kr - kr\cos kr}{r}\right) \\ &= \frac{C_3}{k^2}\left[\left(\frac{\sin kr - kr\cos kr}{r}\right)'' + \left(\frac{2ME}{\hbar^2} - \frac{2}{r^2}\right)\left(\frac{\sin kr - kr\cos kr}{r}\right)\right] \\ &= \frac{C_3}{k^2}\left[\left(\frac{kr\cos kr + (k^2r^2 - 1)\sin kr}{r^2}\right)' + \left(\frac{2ME}{\hbar^2} - \frac{2}{r^2}\right)\left(\frac{\sin kr - kr\cos kr}{r}\right)\right] \\ &= \frac{C_3}{k^2}\left[\frac{(2 - k^2r^2)(\sin kr - kr\cos kr)}{r^3} + \left(\frac{2ME}{\hbar^2} - \frac{2}{r^2}\right)\left(\frac{\sin kr - kr\cos kr}{r}\right)\right] \\ &= \frac{C_3}{k^2}\left[\left(\frac{2}{r^2} - k^2\right)\left(\frac{\sin kr - kr\cos kr}{r}\right) + \left(\frac{2ME}{\hbar^2} - \frac{2}{r^2}\right)\left(\frac{\sin kr - kr\cos kr}{r}\right)\right] \\ &= \frac{C_3}{k^2}\left(\cancel{\frac{2}{r^2}} - \cancel{k^2} + \cancel{\frac{2ME}{\hbar^2}} - \cancel{\frac{2}{r^2}}\right)\left(\frac{\sin kr - kr\cos kr}{r}\right) \\ &= \frac{C_3}{k^2}(0)\left(\frac{\sin kr - kr\cos kr}{r}\right) \\ &= 0 \end{aligned}$$

Part (b)

In order to find the allowed energies when $\ell = 1$, apply the boundary condition $R(a) = 0$.

$$\begin{aligned} R(r) = C_3 j_1(kr) \quad \Rightarrow \quad R(a) = C_3 j_1(ka) &= 0 \\ j_1(ka) &= 0 \\ \frac{\sin ka - ka\cos ka}{(ka)^2} &= 0 \end{aligned}$$

Multiply both sides by $(ka)^2$.

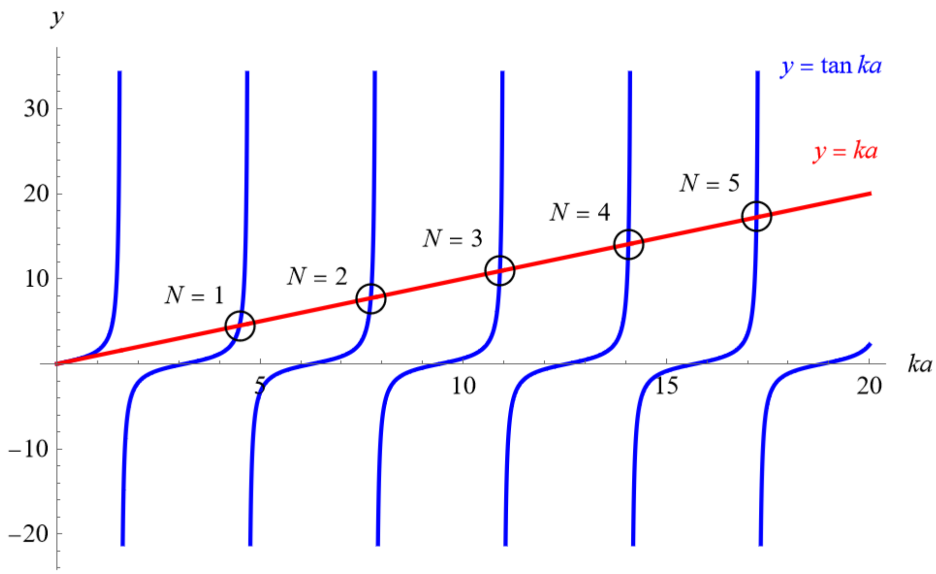
$$\sin ka - ka\cos ka = 0$$

$$\sin ka = ka\cos ka$$

$$\frac{\sin ka}{\cos ka} = ka$$

$$\tan ka = ka$$

To solve for k, plot $y = \tan ka$ and $y = ka$ versus ka and see where the curves intersect.



This graph shows the first five intersections ($k = 0$ doesn't count). Notice that as N increases, the intersections occur closer and closer to the asymptotes of the tangent function. For large N, then,

$$ka \approx \frac{\pi}{2} + N\pi, \quad N = 1, 2, \ldots.$$

Write k in terms of E and factor the right side.

$$\frac{\sqrt{2ME}}{\hbar}a \approx \pi\left(N + \frac{1}{2}\right)$$

Solve for E.

$$\sqrt{2ME} \approx \frac{\pi\hbar}{a}\left(N + \frac{1}{2}\right)$$

$$2ME \approx \frac{\pi^2\hbar^2}{a^2}\left(N + \frac{1}{2}\right)^2$$

Therefore, for $\ell = 1$ and large N,

$$E_{N1} \approx \frac{\pi^2\hbar^2}{2Ma^2}\left(N + \frac{1}{2}\right)^2.$$