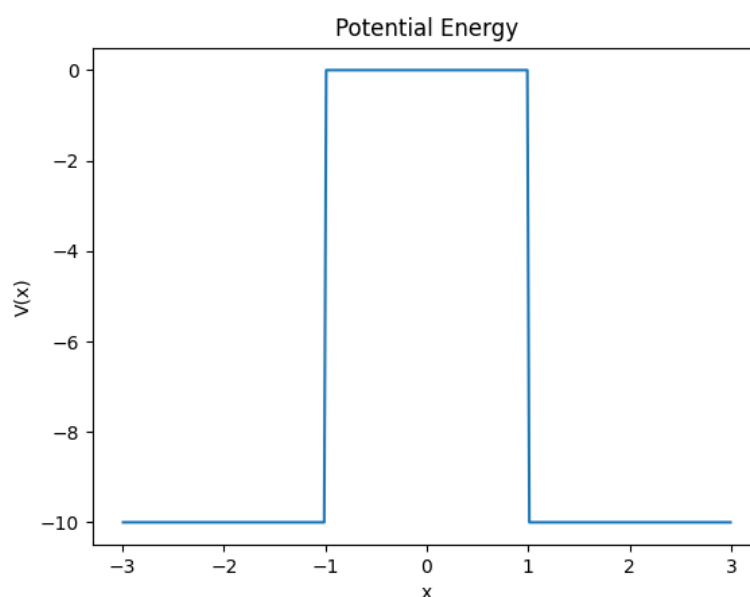


## Problem Set 2

*Student Name: Noah Reef***Problem 2.1****Part a****Figure 2.1.** Sketch of  $V(x)$  for  $a = 1, b = 3$ , and  $V_0 = 10$ 

The time-independent Schrodinger's equation is given by

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} + V(x)\phi(x) = E\phi(x)$$

**Part b**

If we consider the bounded state where  $-V_0 < E < 0$ , and  $0 < x < a$ , then we get that  $V(x) = 0$  and

$$-\frac{\hbar^2}{2m} \phi''(x) = E\phi(x) \implies \phi''(x) = \frac{2m|E|}{\hbar^2} \phi(x)$$

solving the differential equation above gives the general solution,

$$\phi(x) = Ae^{\kappa x} + Be^{-\kappa x}$$

where

$$\kappa = \sqrt{\frac{2m|E|}{\hbar^2}}$$

however since it is symmetric we get that

$$\phi(x) = Ae^{\kappa x} + Ae^{-\kappa x} = 2A \cosh(\kappa x)$$

now if we consider the case where  $a \leq x \leq b$ , we have that  $V(x) = V_0$  and get

$$-\frac{\hbar^2}{2m}\phi''(x) - V_0\phi(x) = E\phi(x) \implies \phi''(x) = -\frac{2m(E + V_0)}{\hbar^2}\phi(x)$$

solving the above differential equation yields the following general solution

$$\phi(x) = C \cos(\xi(b - x)) + D \sin(\xi(b - x))$$

where

$$\xi = \sqrt{\frac{2m(E + V_0)}{\hbar^2}}$$

then since  $V(b) = \infty$  we require that  $\phi(b) = 0$  and hence

$$\phi(x) = D \sin(\xi(b - x))$$

now  $x = a$  we have that

$$2A \cosh(\kappa a) = D \sin(\xi(b - a))$$

taking the derivatives

$$2A\kappa \sinh(\kappa a) = -D\xi \cos(\xi(b - a))$$

then dividing both equations yields

$$\frac{\kappa \sinh(\kappa a)}{\cosh(\kappa a)} = -\frac{\xi \cos(\xi(b - a))}{\sin(\xi(b - a))} \implies \kappa \tanh(\kappa a) = -\xi \cot(\xi(b - a)) = -\xi \frac{1 + \tan(\xi a) \tan(\xi b)}{\tan(\xi b) - \tan(\xi a)}$$

thus

$$\kappa \tanh(\kappa a) + \xi \frac{1 + \tan(\xi a) \tan(\xi b)}{\tan(\xi b) - \tan(\xi a)} = 0$$

letting  $v = \xi b$  and  $a = \gamma b$  then we get that

$$\kappa \tanh(\kappa a) + (v/b) \frac{1 + \tan(\gamma v) \tan(v)}{\tan(v) - \tan(\gamma v)} = 0$$

note that if we define

$$S = \frac{b\sqrt{2mV_0}}{\hbar}$$

then we have that

$$\begin{aligned} \kappa &= \sqrt{\frac{2m|E|}{\hbar^2}} = \sqrt{\frac{2m(V_0 - (E + V_0))}{\hbar^2}} = \sqrt{\frac{2mV_0}{\hbar^2} - \xi^2} \\ &= \sqrt{\frac{2mV_0}{\hbar^2} - \frac{v^2}{b^2}} \\ &= \frac{1}{b} \sqrt{S^2 - v^2} \end{aligned}$$

therefore we have that

$$\sqrt{S^2 - v^2} \tanh(\gamma \sqrt{S^2 - v^2}) - v \frac{1 + \tan(\gamma v) \tan(v)}{\tan(\gamma v) - \tan(v)} = 0$$

and hence our eigenvalues are given by

$$E + V_0 = \frac{\hbar^2 \xi^2}{2m} = \frac{\hbar^2 v^2}{2mb^2} \implies \frac{E}{V_0} = -1 + \frac{v^2}{S^2}$$

### Part c

Solving for  $v$  from the equation below we get

$$v_1 = 9.87725$$

$$v_2 = 6.84406$$

$$v_3 = 3.46525$$

plugging these values into the equation

$$\frac{E}{V_0} = -1 + \frac{v^2}{S^2}$$

yields

$$\begin{aligned} \frac{E}{V_0} &= -1 + \frac{(9.87725)^2}{S^2} \approx -0.0244 \\ \frac{E}{V_0} &= -1 + \frac{(6.84406)^2}{S^2} \approx -0.5316 \\ \frac{E}{V_0} &= -1 + \frac{(3.46525)^2}{S^2} \approx -0.8799 \end{aligned}$$

as the eigenvalues of the even bounded state problem.

### Part d

### Part e

To show the odd parity of the wave function we will get a similar result as in part b. However we notice that since the wave is odd we get that in the case  $|x| < a$  the wave function is given by

$$\phi(x) = Ae^{\kappa x} - Ae^{-\kappa x} = 2A \sinh(\kappa x)$$

and in the case  $a < x < b$  we have that

$$\phi(x) = D \sin(\xi(b - x))$$

as before. Then we have that

$$\begin{aligned} 2A \sinh(\kappa a) &= D \sin(\xi(b - a)) \\ 2A \kappa \cosh(\kappa a) &= -D \xi \cos(\xi(b - a)) \end{aligned}$$

then dividing the two equations yields

$$\frac{\kappa \cosh(\kappa a)}{\sinh(\kappa a)} = -\frac{\xi \cos(\xi(b-a))}{\sin(\xi(b-a))} \implies \kappa \coth(\kappa a) = -\xi \cot(\xi(b-a))$$

then by doing similar algebra and substitutions as in part b we get that

$$\frac{\sqrt{S^2 - v^2}}{\tanh(\gamma\sqrt{S^2 - v^2})} - v \frac{\tan(\gamma v) \tan(v) + 1}{\tan(\gamma v) - \tan(v)} = 0$$

and hence the eigenvalues are given by

$$\frac{E}{V_0} = -1 + \frac{v^2}{S^2}$$

as desired.

## Part f

Solving for  $v$  from the equation below, using  $S = 10$  and  $\gamma = 0.2$  we get that

$$v_1 = 6.96192$$

$$v_2 = 3.49913$$

plugging these values into the equation gives the following eigenvalues

$$\frac{E}{V_0} = -1 + \frac{(6.96192)^2}{S^2} \approx -0.5153$$

$$\frac{E}{V_0} = -1 + \frac{(3.49913)^2}{S^2} \approx -0.8775$$

## Part g

The parity of the ground-state wavefunction is even.

## Part h

## Part i

Here we assume that the wavefunction is given in the form

$$\psi(x, t) = c_1(t)\psi_1(x) + c_2(t)\psi_2(x)$$

then we get that from the time-dependent Schrodinger's equation, that

$$i\hbar \frac{d\psi}{dt} = \hat{H}\psi$$

$$i\hbar \frac{d}{dt}(c_1(t)\psi_1(x) + c_2(t)\psi_2(x)) = \hat{H}(c_1(t)\psi_1(x) + c_2(t)\psi_2(x))$$

which gives us

$$i\hbar \left( \frac{dc_1}{dt} \psi_1(x) + \frac{dc_2}{dt} \psi_2(x) \right) = \hat{H}(c_1(t)\psi_1(x) + c_2(t)\psi_2(x))$$

next we can multiply by  $\psi_1^*(x)$  and  $\psi_2^*(x)$  separately and integrate over all space to get the following

$$\begin{aligned} i\hbar \dot{c}_1(t) &= \hat{H}c_1(t) = E_1 c_1(t) \\ i\hbar \dot{c}_2(t) &= \hat{H}c_2(t) = E_2 c_2(t) \end{aligned}$$

solving the above differential equations gives us that

$$c_1(t) = c_1(0)e^{-iE_1 t/\hbar} \quad c_2(t) = c_2(0)e^{-iE_2 t/\hbar}$$

using the boundary conditions we get that

$$c_1(0) = \frac{1}{\sqrt{2}} \quad c_2(0) = \frac{1}{\sqrt{2}}$$

and thus the full solution is given by

$$\psi(x, t) = \frac{1}{\sqrt{2}} \left( e^{-iE_1 t/\hbar} \psi_1(x) + e^{-iE_2 t/\hbar} \psi_2(x) \right)$$

## Part j

If we suppose that the wavefunction is normalized at  $t = 0$  then we have that

$$\int_{-\infty}^{\infty} |\psi(x, 0)|^2 dx = 1$$

and thus for  $t > 0$  we have that

$$\begin{aligned} \int_{-\infty}^{\infty} \psi^*(x, t) \psi(x, t) dx &= \frac{1}{2} \int_{-\infty}^{\infty} \psi_1^*(x) \psi_1(x) + \psi_2^*(x) \psi_2(x) + \psi_1^*(x) \psi_2(x) e^{i(E_1 - E_2)t/\hbar} \\ &\quad + \psi_2^*(x) \psi_1(x) e^{i(E_2 - E_1)t/\hbar} dx \end{aligned}$$

and since  $\psi_1$  and  $\psi_2$  are orthogonal we get that

$$\int_{-\infty}^{\infty} \psi^*(x, t) \psi(x, t) dx = \frac{1}{2} \int_{-\infty}^{\infty} |\psi_1(x)|^2 + |\psi_2(x)|^2 dx = 1$$

and hence the wavefunction is normalized for all time.

**Part k**

If we consider the probability density of  $\psi$  we get that

$$\begin{aligned} |\psi(x, t)|^2 &= \frac{1}{2}(|\psi_1(x)|^2 + |\psi_2(x)|^2 + \psi_1^*(x)\psi_2(x)e^{i(E_1-E_2)t/\hbar} + \psi_2^*(x)\psi_1(x)e^{i(E_2-E_1)t/\hbar}) \\ &= \frac{1}{2}(|\psi_1(x)|^2 + |\psi_2(x)|^2 + 2 \operatorname{Re}(\psi_1^*(x)\psi_2(x)e^{i(E_2-E_1)t/\hbar})) \end{aligned}$$

Then we see that when  $t = \pi\hbar/(E_2 - E_1)$  we have that

$$|\psi(x, t)|^2 = \frac{1}{2}|\psi_1(x) + \psi_2(x)|^2$$

and for  $t = -\pi\hbar/(E_2 - E_1)$  we have that

$$|\psi(x, t)|^2 = \frac{1}{2}|\psi_1(x) - \psi_2(x)|^2$$

and hence has a period

$$T = \frac{2\pi\hbar}{E_2 - E_1}$$

**Part l****Problem 2.2****Part a**

Recall that the expectation value of the electron distance from the nucleus in state  $\psi_{nlm}$  is given by

$$r_{nlm} = \int r |\psi_{nlm}|^2 d\mathbf{r} = n^2 \left\{ 1 + \frac{1}{2} \left[ 1 - \frac{l(l+1)}{n^2} \right] \right\} a_0$$

where  $a_0$  is the Bohr radius. For s-states we have that  $l = 0$  and hence  $m = 0$  and thus  $r_{n00} = \frac{3}{2}n^2a_0$ . So we have that the expectation value of the electron distance from the nucleus are

$$\begin{aligned} r_{100} &= \frac{3}{2}a_0 \\ r_{200} &= 6a_0 \\ r_{300} &= \frac{27}{2}a_0 \end{aligned}$$

for the  $1s$ -,  $2s$ -,  $3s$ -states respectively.

**Part b**

Recall that  $a_0 = 0.0529177\text{nm}$  and hence we get that the expectation values in part a are

$$\begin{aligned} r_{100} &= 0.07937655\text{nm} \\ r_{200} &= 0.3175062\text{nm} \\ r_{300} &= 0.71438895\text{nm} \end{aligned}$$

**Part c**

To show that the 1s-state and 2s-state are orthogonal we check to see if their inner product is 0. First notice that

$$\begin{aligned}\psi_{100} &= R_{10}(r)Y_{00}(\theta, \phi) \\ \psi_{200} &= R_{20}(r)Y_{00}(\theta, \phi)\end{aligned}$$

then we have that

$$\begin{aligned}\int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin(\theta) \psi_{100}^* \psi_{200} dr d\theta d\phi &= \int_0^\infty \int_0^\pi \int_0^{2\pi} R_{10}^* R_{20} r^2 |Y_{00}|^2 \sin(\theta) dr d\theta d\phi \\ &= \int_0^\infty R_{10}^* R_{20} dr\end{aligned}$$

and note that

$$\begin{aligned}R_{10} &= 2a_0^{-3/2} e^{-r/a_0} \\ R_{20} &= \frac{1}{\sqrt{2}} a_0^{-3/2} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}\end{aligned}$$

and hence our integral becomes

$$\int_0^\infty R_{10}^* R_{20} dr = \frac{2a_0^{-3}}{\sqrt{2}} \int_0^\infty r^2 \left(1 - \frac{r}{2a_0}\right) e^{\frac{-3r}{2a_0}} dr$$

using Mathematica to evaluate the integral, we get that

$$\int_0^\infty r^2 \left(1 - \frac{r}{2a_0}\right) e^{\frac{-3r}{2a_0}} dr = 0$$

and hence

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin(\theta) \psi_{100}^* \psi_{200} dr d\theta d\phi = 0$$

thus  $\psi_{100}$  and  $\psi_{200}$  are orthogonal.

**Part d**

To show that the 2s-state and the 2p-states are orthogonal we aim to show that their inner product is zero. First recall that

$$\begin{aligned}\psi_{200} &= R_{20}(r)Y_{00}(\theta, \phi) \\ \psi_{21m} &= R_{21}(r)Y_{1m}(\theta, \phi)\end{aligned}$$

then we have that

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin(\theta) \psi_{21m}^* \psi_{200} dr d\theta d\phi = \int_0^\infty \int_0^\pi \int_0^{2\pi} R_{20}^* R_{21} r^2 Y_{00}^* Y_{1m} \sin(\theta) dr d\theta d\phi$$

and since

$$\int_0^\pi \int_0^{2\pi} Y_{00}^* Y_{1m} \sin(\theta) d\theta d\phi = \delta_{01} \delta_{m0} = 0$$

and hence our above integral becomes

$$\delta_{01} \delta_{m0} \int_0^\infty R_{20}^* R_{21} r^2 dr = 0$$

thus  $\psi_{200}$  and  $\psi_{21m}$  are orthogonal for all  $m$ .

## Problem 2.3

### Part a

We consider

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} + e\epsilon x \right] |\psi\rangle = E |\psi\rangle$$

and assume that  $\psi = c_1 \psi_{1s} + c_2 \psi_{2x}$ . Then we have that  $\langle \psi_{1s} | \psi \rangle = c_1$  and  $\langle \psi_{2x} | \psi \rangle = c_2$  since the  $\psi_{1s}$  and  $\psi_{2x}$  are orthonormal. Then we have that

$$\langle \psi_{1s} | H | \psi \rangle = c_1 \langle \psi_{1s} | H | \psi_{1s} \rangle + c_2 \langle \psi_{1s} | H | \psi_{2x} \rangle = \langle \psi_{1s} | E | \psi \rangle = c_1 E$$

and

$$\langle \psi_{2x} | H | \psi \rangle = c_1 \langle \psi_{2x} | H | \psi_{1s} \rangle + c_2 \langle \psi_{2x} | H | \psi_{2x} \rangle = \langle \psi_{2x} | E | \psi \rangle = c_2 E$$

where

$$H = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} + e\epsilon x$$

Note that

$$(\langle \psi_{1s} | H | \psi_{2x} \rangle)^* = \langle \psi_{2x} | H | \psi_{1s} \rangle$$

and hence by letting

$$\begin{aligned} h_{11} &= \langle \psi_{1s} | H | \psi_{1s} \rangle \\ h_{22} &= \langle \psi_{2x} | H | \psi_{2x} \rangle \\ h_{12} &= \langle \psi_{1s} | H | \psi_{2x} \rangle = e\epsilon \langle \psi_{1s} | x | \psi_{2x} \rangle \end{aligned}$$

we get that

$$\begin{pmatrix} h_{11} & h_{12} \\ h_{12}^* & h_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$



**Part b**

Recall that

$$\begin{cases} \psi_{1s} &= R_{10}(r)Y_{00}(\theta, \phi) \\ \psi_{2px} &= \frac{R_{21}(r)}{\sqrt{2}} (Y_{1,-1}(\theta, \phi) - Y_{1,1}(\theta, \phi)) \end{cases}$$

Note that

$$\begin{aligned} R_{10}(r) &= 2a_0^{-3/2} e^{-r/a_0} \\ R_{21}(r) &= \frac{1}{\sqrt{6}} a_0^{-3/2} \left( \frac{r}{2a_0} \right) e^{-r/2a_0} \\ Y_{1,-1} &= \sqrt{\frac{3}{8\pi}} e^{-i\phi} \sin(\theta) \\ Y_{1,1} &= -\sqrt{\frac{3}{8\pi}} e^{i\phi} \sin(\theta) \\ Y_{0,0} &= \sqrt{\frac{1}{4\pi}} \end{aligned}$$

and so we have that

$$\begin{cases} \psi_{1s} &= \frac{2}{\sqrt{4\pi}} a_0^{-3/2} e^{-r/a_0} \\ \psi_{2px} &= \frac{1}{\sqrt{32\pi}} a_0^{-3/2} \left( \frac{r}{a_0} \right) e^{-r/2a_0} \sin(\theta) \cos(\phi) \end{cases}$$

so then we have that

$$\begin{aligned} \langle \psi_{1s} | x | \psi_{2px} \rangle &= \int_0^\infty \int_0^\pi \int_0^{2\pi} r \sin(\theta) \cos(\phi) \psi_{1s}^* \psi_{2px} r^2 \sin \theta dr d\theta d\phi \\ &= \left( \frac{2}{\sqrt{4\pi}} \right) \left( \frac{1}{\sqrt{32\pi}} \right) a_0^{-4} \int_0^\infty r^4 e^{-3r/2a_0} dr \int_0^\pi \sin^3(\theta) d\theta \int_0^{2\pi} \cos^2(\phi) d\phi \\ &= \frac{128\sqrt{6}}{243} a_0 \end{aligned}$$

and hence  $e\varepsilon \langle \psi_{1s} | x | \psi_{2px} \rangle = \frac{128\sqrt{6}}{243} e\varepsilon a_0$

**Part c**

We compute the eigenvalues of the matrix above by

$$\det \left( \begin{bmatrix} h_{11} - E & h_{12} \\ h_{12}^* & h_{22} - E \end{bmatrix} \right) = 0 \implies (h_{11} - E)(h_{22} - E) - |h_{12}|^2 = E^2 - E(h_{11} + h_{22}) + h_{11}h_{22} - |h_{12}|^2 = 0$$

solving the above equation gives us the eigenvalues of the matrix as

$$E = \frac{h_{11} + h_{22}}{2} \pm \sqrt{\left( \frac{h_{11} - h_{22}}{2} \right)^2 + |h_{12}|^2}$$

we take the  $(-)$  term to get the lower energy eigenvalue. Then we get that

$$\begin{aligned} c_1 h_{11} + c_2 h_{12} &= E c_1 \\ c_1 h_{12}^* + c_2 h_{22} &= E c_2 \end{aligned}$$

Letting  $c_1 = 1$  we get that

$$c_2 = \frac{E - h_{11}}{h_{12}}$$

and hence we have

$$\psi = \psi_{1s} + \frac{E - h_{11}}{h_{12}} \psi_{2p_x}$$

then normalizing the wavefunction gives us that

$$\psi = \frac{1}{\sqrt{1 + \frac{(E - h_{11})^2}{h_{12}^2}}} \left( \psi_{1s} + \frac{E - h_{11}}{h_{12}} \psi_{2p_x} \right)$$

## Part d

## Part e

Computing the dipole moment  $\mu$  we get that

$$\begin{aligned} \mu &= -e \langle \psi | x | \psi \rangle = -e \left[ \langle \psi_{1s} | x | \psi_{1s} \rangle + M^2 \langle \psi_{2p_x} | x | \psi_{2p_x} \rangle + M \langle \psi_{1s} | x | \psi_{2p_x} \rangle + M \langle \psi_{2p_x} | x | \psi_{1s} \rangle \right] \\ &= -2eM \langle \psi_{1s} | x | \psi_{2p_x} \rangle \end{aligned}$$

where

$$M = \frac{h_{12}}{h_{11} - h_{22}}$$

and get

$$\mu = \frac{-e^2 \varepsilon}{h_{11} - h_{12}} \left( \frac{128\sqrt{6}}{243} a_0 \right)^2$$

## Problem 2.4

Let  $\hat{P}$  be the parity operator, that is  $\hat{P}f(r) = f(-r)$ . Then if  $f$  is an eigenfunction of  $\hat{P}$  with eigenvalue  $p$  then we have that

$$\hat{P}f(r) = f(-r) = \lambda f(r)$$

and

$$\hat{P}^2 f(r) = f(-(-r)) = f(r) = \lambda^2 f(r) \implies \lambda^2 = 1$$

and hence  $\lambda = \pm 1$ . In the case  $\lambda = 1$  we have that

$$f(r) = f(-r)$$

which implies that  $f$  is an even function. Similarly for the case  $\lambda = -1$  we have that

$$-f(r) = f(-r)$$

which implies that  $f$  is an odd function. Thus our eigenvalues are  $\pm 1$  and the eigenfunctions are even and odd functions respectively.

## Problem 2.5

### Part a

If an operator  $\hat{A}$  has eigenstates  $|a\rangle$  with eigenvalues  $\alpha$  then we have that

$$\hat{A}|a\rangle = \alpha|a\rangle$$

additionally recall that the Taylor Expansion of  $e^x$  is given by

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$$

and so

$$e^{\hat{A}}|a\rangle = \sum_{n=0}^{\infty} \frac{\hat{A}^n}{n!}|a\rangle = \sum_{n=0}^{\infty} \frac{\alpha^n}{n!}|a\rangle = e^{\alpha}|a\rangle$$

### Part b

Recall that  $z$  component of the angular momentum operator is given by  $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$ . Additionally recall that a wavefunction is given by

$$\psi(r, \theta, \psi) = \sum_{lm} R_{lm}(r)Y_{lm}(\theta, \psi)$$

and hence we have that

$$\hat{L}_z\psi(r, \theta, \psi) = \sum_{lm} R_{lm}(r)\hat{L}_zY_{lm}(\theta, \psi)$$

and since  $Y_{lm}(\theta, \psi)$  are eigenfunctions of  $\hat{L}_z$  we have that

$$\hat{L}_zY_{lm}(\theta, \psi) = m\hbar Y_{lm}(\theta, \psi)$$

and hence

$$\hat{L}_z\psi(r, \theta, \psi) = \sum_{lm} R_{lm}(r)m\hbar Y_{lm}(\theta, \psi)$$

and thus

$$e^{i\hat{L}_z\phi_0/\hbar}\psi(r, \theta, \psi) = \sum_{lm} R_{lm}(r) e^{im\phi_0} Y_{lm}(\theta, \psi)$$

However note that

$$e^{im\phi_0} Y_{lm}(\theta, \psi) = (-1)^{(m+|m|)/2} \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos(\theta)) e^{im\phi+\phi_0} = Y_{lm}(\theta, \psi + \phi_0) \quad (2.1)$$

and hence

$$e^{i\hat{L}_z\phi_0/\hbar}\psi(r, \theta, \psi) = \sum_{lm} R_{lm}(r) Y_{lm}(\theta, \psi + \phi_0) = \psi(r, \theta, \psi + \phi_0)$$

and hence the operator  $e^{i\hat{L}_z\phi_0/\hbar}$  is the operator that rotates the wavefunction by an angle  $\phi_0$  about the  $z$ -axis.