SOLUTIONS: PROBLEM SET 1

1. (i) $\Psi(x) = N \tan ax$.

This is not an acceptable wavefunction as at $\tan(\pi/2)$ the value of the function is undefined. So the function has a discontinuity at $x = \frac{\pi}{2}, \frac{3\pi}{2}, \ldots$

(ii) $\Psi(x) = N x^{1/2} e^{-ax}$ is not an acceptable wavefunction as $\sqrt{x}$ factor gives both a positive and negative value for the same x. So the function is not single-valued.

(iii) $\Psi(x) = N \sin(ax)$ is an acceptable wavefunction as it is singlevalued, continuous and bound between $+N$ and $-N$, no matter what the value of x is.

So, Stephanie is correct.

2.

function	finite?	continuous?	first derivative continuous?	single-valued?	quadratically integrable?
$u = x$, $x \geq 0$, and $u = 0$ otherwise	not for $x=+\infty$	yes	not at $x=0$	yes	no
$u = x^2$	not for $x=\pm\infty$	yes	yes	yes	no
$u = e^{-\|x\|}$	yes	yes	not at $x=0$	yes	yes
$u = e^{-x}$	not for $x=-\infty$	yes	yes	yes	no
$u = \cos(x)$	yes	yes	yes	yes	yes
$u = \sin(\|x\|)$	yes	yes	not at $x=0$	yes	yes
$u = \exp[-x^2]$	yes	yes	yes	yes	yes
$u = 1-x^2$, $-1 \leq x \leq +1$, $u = 0$ otherwise	yes	yes	not at $x=\pm1$	yes	yes

3 (a) $N^2 \int_0^b \sin^2\left(\frac{2\pi z}{b}\right) dz = 1.$

[From our trigonometric knowledge:-

$\cos 2x = \cos^2 x - \sin^2 x$

$\cos 2x = (1 - \sin^2 x) - \sin^2 x$

$\cos 2x = 1 - 2\sin^2 x.$

$\sin^2 x = \frac{1 - \cos 2x}{2}.$]

$N^2 \frac{1}{2}\int_0^b 1 - \cos\left(\frac{4\pi z}{b}\right) dz = 1.$

$\frac{N^2}{2}\left[\int_0^b dz - \int_0^b \cos\left(\frac{4\pi z}{b}\right) dz\right] = 1$

or, $\frac{N^2}{2}\left[b - 0 - \left\{\frac{b}{4\pi}\left[\sin 4\pi - \sin 0\right]\right\}\right] = 1.$

or, $\frac{N^2}{2} b = 1$, $N^2 = \frac{2}{b}$, $N = \sqrt{\frac{2}{b}}$

The normalized wavefunction is:-

$\sqrt{\frac{2}{b}} \sin\left(\frac{2\pi z}{b}\right)$

(b) This is a typical wavefunction for the first excited state of a particle in a 1D box of length b

(b) $N^2 \int_0^b \left[\sin\left(\frac{2\pi z}{b}\right) + 2\sin\left(\frac{3\pi z}{b}\right)\right]^2 dz = 1$

The integral is:—

$$\int_0^b \left[\sin^2\left(\frac{2\pi z}{b}\right) + 4\sin^2\left(\frac{3\pi z}{b}\right) + 4\sin\left(\frac{2\pi z}{b}\right)\sin\left(\frac{3\pi z}{b}\right)\right] dz$$

<u>Term I</u>

$$\int_0^b \sin^2\left(\frac{2\pi z}{b}\right) dz = \frac{b}{2}$$

<u>Term II</u>

$$4\int_0^b \sin^2\left(\frac{3\pi z}{b}\right) dz = 2\int_0^b 1 - \cos\left(\frac{6\pi z}{b}\right) dz.$$

$$= 2b$$

<u>Term III</u>

$$4\int_0^b \sin\left(\frac{2\pi z}{b}\right)\sin\left(\frac{3\pi z}{b}\right) dz$$

Now,

$\{ 2\sin x \sin y = \cos(x-y) - \cos(x+y)$.

$$2\sin\left(\frac{2\pi z}{b}\right)\sin\left(\frac{3\pi z}{b}\right) = \cos\left(\frac{2\pi z - 3\pi z}{b}\right) - \cos\left(\frac{2\pi z + 3\pi z}{b}\right)$$

$$= \cos\left(-\frac{\pi z}{b}\right) - \cos\left(\frac{5\pi z}{b}\right)$$

$$= \cos\left(\frac{\pi z}{b}\right) - \cos\left(\frac{5\pi z}{b}\right)$$

$$\therefore \; 2\int_0^b \cos\left(\frac{\pi z}{b}\right) dz - 2\int_0^b \cos\left(\frac{5\pi z}{b}\right) dz.$$

$$= 2\left[\frac{b}{\pi} \sin\left(\frac{\pi z}{b}\right) \Big|_0^b\right] - \left[\frac{2b}{5\pi} \sin \frac{5\pi z}{b}\right]\Big|_0^b$$

$$= \quad \underset{0}{\parallel} \qquad\qquad \underset{0}{\parallel}$$

$$= 0.$$

$$\therefore N^2\left[\frac{b}{2} + 2b\right] = 1. \qquad \frac{N^2 5b}{2} = 1.$$

$$N = \sqrt{\frac{2}{5b}}$$

The normalized wavefunction is:-

$$\sqrt{\frac{2}{5b}}\left[\sin\left(\frac{2\pi z}{b}\right) + 2\sin\left(\frac{3\pi z}{b}\right)\right]$$

(C) $$N^2 \int_{-\infty}^{+\infty} e^{-2az^2} dz = 1.$$

$$N^2 \, 2\int_0^{\infty} e^{-2az^2} dz = 1.$$

$$N^2 \cancel{\chi} \cdot \frac{1}{\cancel{\chi}(2a)^{(0+1)/2}} \Gamma\left(\frac{0+1}{2}\right) = 1.$$

$$N^2 \frac{1}{(2a)^{1/2}} \Gamma\left(\frac{1}{2}\right) = 1.$$

$$N^2 \frac{\sqrt{\pi}}{\sqrt{2a}} = 1. \qquad N^2 = \left(\frac{2a}{\pi}\right)^{1/2}.$$

$$N = \left(\frac{2a}{\pi}\right)^{1/4}.$$

The normalized wavefunction is:-

$$\left(\frac{2a}{\pi}\right)^{1/4} e^{-az^2}$$

These are typical wavefunctions for the ground state of a 1D simple harmonic oscillator.

*[Here the Gamma-functions have been used.

$$\int_0^\infty x^n e^{-ax^2} dx = \frac{1}{2a^{(n+1)/2}} \Gamma\left(\frac{n+1}{2}\right)$$

$$\Gamma(n+1) = n! = n\Gamma(n)$$

$$\Gamma\left(\tfrac{1}{2}\right) = \sqrt{\pi}.$$

(d) $N^2 \int_0^{2\pi} (e^{ia\phi} + e^{-ia\phi})^2 \, d\phi = 1$

$N^2 \int_0^{2\pi} (\cos a\phi + \cancel{i \sin a\phi} + \cos a\phi - \cancel{i \sin a\phi})^2 \, d\phi =$

$N^2 4 \int_0^{2\pi} \cos^2 a\phi \, d\phi = 1.$

$N^2 2 \int_0^{2\pi} 2\cos^2 a\phi \, d\phi = 1.$

[Now, $\cos^2\phi - \sin^2\phi = \cos 2\phi$

$2\cos^2\phi - 1 = \cos 2\phi.$

$2\cos^2\phi = 1 + \cos 2\phi$]

$\therefore 2N^2 \int_0^{2\pi} 1 + \cos 2a\phi \, d\phi = 1.$

$2N^2 \left[\int_0^{2\pi} d\phi + \int_0^{2\pi} \cos 2a\phi \, d\phi \right] = 1.$

$2N^2 \left[2\pi - 0 + \left. \frac{\sin 2a\phi}{2a} \right|_0^{2\pi} \right] = 1$

$2N^2 \left[2\pi + \frac{1}{2a} \left\{ \underbrace{\sin 4(a\cancel{\phi}\pi)}_{= 0} - 0 \right\} \right] = 1.$

$2N^2 \, 2\pi = 1.$

$N^2 = \frac{1}{4\pi}$ $\qquad N = \frac{1}{\sqrt{4\pi}}$

The normalized wavefunction is:-

$\frac{1}{\sqrt{4\pi}} (e^{ia\phi} + e^{-ia\phi})$

PROBLEM 3 (d) can be also solved as:-

$$N^2 \int \psi^* \psi \, d\tau = 1.$$

$$N^2 \int_0^{2\pi} (e^{ia\phi} + e^{-ia\phi})^* (e^{ia\phi} + e^{-ia\phi}) \, d\phi = 1.$$

$$N^2 \int_0^{2\pi} (e^{-ia\phi} + e^{ia\phi}) (e^{ia\phi} + e^{-ia\phi}) \, d\phi = 1.$$

$$N^2 \int_0^{2\pi} d\phi + \int_0^{2\pi} d\phi + \int_0^{2\pi} e^{i2a\phi} + e^{-i2a\phi} \, d\phi = 1.$$

$$N^2 \left[2\pi + 2\pi + 2\int_0^{2\pi} \cos 2a\phi \right] d\phi = 1$$

$$N^2 \left[4\pi + 2 \left(\sin 2a\phi \right) \Big|_0^{2\pi} \right] = 1.$$

$$N^2 \left[4\pi + 2 (\underbrace{\sin (4a\pi)}_{= 0} - \underbrace{\sin 0}_{= 0}) \right] = 1.$$

$$N^2 = \frac{1}{4\pi} \qquad N = \frac{1}{\sqrt{4\pi}}.$$

(e) This is a 3D problem involving the coordinates r, θ, ϕ.

$$N^2 \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \cos^2\theta \, e^{-2ar} \, r^2 dr \sin\theta \, d\theta \, d\phi = 1.$$

$$N^2 \underbrace{\int_0^{2\pi} d\phi}_{\text{I}} \underbrace{\int_0^{\pi} \cos^2\theta \sin\theta \, d\theta}_{\text{II}} \underbrace{\int_0^{\infty} r^2 e^{-2ar} dr}_{\text{III}} = 1.$$

$$\text{I} \rightarrow \int_0^{2\pi} d\phi = \phi \Big|_0^{2\pi} = 2\pi - 0 = \boxed{2\pi}$$

$$\text{II} \rightarrow \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta$$

Let $\cos\theta = z$

when, $\theta = 0$, $z = 1$

$\theta = \pi$, $z = -1$.

$$dz = -\sin\theta \, d\theta$$

$$\therefore \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta = -\int_1^{-1} z^2 dz = \int_{-1}^{+1} z^2 dz$$

$$= \frac{z^3}{3}\Big|_{-1}^{+1} = \frac{1}{3} - \left(-\frac{1}{3}\right) = \boxed{\frac{2}{3}}$$

4. $\Psi(r) = N \exp[-r/a_0]$, find N

Normalization: $\int\Psi^*\Psi d\tau = 1$

$\int\int\int N^2 \exp[-2r/a_0]\, r^2dr\, \sin\theta d\theta\, d\varphi$

Integrating over $d\varphi$ gives $\varphi\,|_0^{2\pi}$ gives 2π.

Integrating over $\sin\theta d\theta$ gives $-\cos\theta\,|_0^{\pi}$ gives 2.

Finally integrating over r: $4\pi \int_0^\infty N^2 \exp[-2r/a_0]\, r^2dr =1$

Given $\int_0^\infty x^n\exp[-ax]dx = n!/a^{n+1}$ with n=2, a= $2/a_0$ gives $4\pi N^2\, 2!\, (2/a_0)^{-3} = 1$

$N^2 = 1/ \pi a_0^3 \quad N = [\pi a_0^3]^{-½}$

Therefore the normalized function is $\Psi = [\pi a_0^3]^{-½} \exp[-r/a_0]$

The probability of finding the electron within a volume of magnitude $d\tau$ is $\Psi^*\Psi\, d\tau$. The probability of finding the electron inside a small volume of magnitude 1.0 pm^3 located at the nucleus is $[\pi a_0^3]^{-½} \exp[-0/a_0]$ 1.0 pm^3

1 pm = 10^{-10} cm

$[\pi (0.529\times10^{-8})^3]^{-½}\, 10^{-30} = \pi^{-½}\, 10^{-18}/0.529^{3/2} = 1.466 \times 10^{-18}$

The probability of finding the electron inside a small volume of magnitude 1.0 pm^3 located at a distance a_0 from the nucleus is

$[\pi (0.529\times10^{-8})^3]^{-½} \exp[-2]\, 10^{-30} = 0.20 \times 10^{-18}$

5. (a) $V = -Ze^2/r_1 + -Ze^2/r_2 + e^2/r_{12}$

(b) $L_z = xp_y - yp_x = x (\hbar/i)\partial/\partial y - y (\hbar/i)\partial/\partial x$

(c) $V = -q\mathbf{r}\bullet\mathcal{E} = -qz\, \mathcal{E}_z$

(d) $T = -(\hbar^2/2m_e) \{\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2 + \partial^2/\partial x_2^2 + \partial^2/\partial y_2^2 + \partial^2/\partial z_2^2\}$

(e) Be^{+3} ion has Z=4 and one electron.

$$\mathcal{H}= -(\hbar^2/2m_e) \{\partial^2/\partial x_e^2 + \partial^2/\partial y_e^2 + \partial^2/\partial z_e^2\} \quad -(\hbar^2/2M_n) \{\partial^2/\partial x_n^2 + \partial^2/\partial y_n^2 + \partial^2/\partial z_n^2\} -Ze^2/r_{en}$$

6. (a) $$-(\hbar^2/2M) \{\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2 + \partial^2/\partial x_2^2 + \partial^2/\partial y_2^2 + \partial^2/\partial z_2^2+ \partial^2/\partial x_3^2 + \partial^2/\partial y_3^2 + \partial^2/\partial z_3^2+ \partial^2/\partial x_4^2 + \partial^2/\partial y_4^2 + \partial^2/\partial z_4^2\} \Psi(x_1,y_1,z_1, x_2,y_2,z_2, x_3,y_3,z_3, x_4,y_4,z_4) = E\, \Psi(x_1,y_1,z_1, x_2,y_2,z_2, x_3,y_3,z_3, x_4,y_4,z_4)$$

(b) He atom has a nucleus of charge 2e and two electrons

$$\{-(\hbar^2/2m) [\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2 +\partial^2/\partial x_2^2 + \partial^2/\partial y_2^2 + \partial^2/\partial z_2^2] -(\hbar^2/2M_n) [\partial^2/\partial x_n^2 + \partial^2/\partial y_n^2 + \partial^2/\partial z_n^2] -2e^2/r_{1n} -2e^2/r_{2n}\}\Psi(x_1,y_1,z_1, x_2,y_2,z_2, x_n,y_n,z_n) = E\, \Psi(x_1,y_1,z_1, x_2,y_2,z_2, x_n,y_n,z_n)$$

(c) $$\{ -(\hbar^2/2m_e) [\partial^2/\partial x_e^2 + \partial^2/\partial y_e^2 + \partial^2/\partial z_e^2] -(\hbar^2/2M_n) [\partial^2/\partial x_n^2 + \partial^2/\partial y_n^2 + \partial^2/\partial z_n^2] - e^2/r_{en} -e\, z_n\, \mathcal{E}_z +e\, z_e\, \mathcal{E}_z\} \Psi(x_e,y_e,z_e, x_n,y_n,z_n) = E\, \Psi(x_e,y_e,z_e, x_n,y_n,z_n)$$

(d) $\{ -(\hbar^2/2m_e) [\partial^2/\partial x_1{}^2 + \partial^2/\partial y_1{}^2 + \partial^2/\partial z_1{}^2 + \partial^2/\partial x_2{}^2 + \partial^2/\partial y_2{}^2 + \partial^2/\partial z_2{}^2]$
$-(\hbar^2/2M_H)[\partial^2/\partial x_H{}^2 + \partial^2/\partial y_H{}^2 + \partial^2/\partial z_H{}^2] -(\hbar^2/2M_D) [\partial^2/\partial x_D{}^2 + \partial^2/\partial y_D{}^2 + \partial^2/\partial z_D{}^2]$
$- e^2/r_{1H} - e^2/r_{2H} - e^2/r_{1D} - e^2/r_{2D} \} \Psi(x_1,y_1,z_1, x_2,y_2,z_2, x_H,y_H,z_H, x_D,y_D,z_D)$
$= E\, \Psi(x_1,y_1,z_1, x_2,y_2,z_2, x_H,y_H,z_H, x_D,y_D,z_D)$