1. a) $\frac{d}{dx} e^{-ax^2} = -2ax\, e^{-ax^2}$

$\frac{d^2}{dx^2} e^{-ax^2} = -2a\, e^{-ax^2} + 4a^2x^2 e^{-ax^2} = (4a^2x^2 - 2a) e^{-ax^2}$

not an eigenfunction

b) $\frac{d\cos bx}{dx} = -b \sin bx$ not an eigenfunction

$\frac{d^2}{d^2} \cos bx = -b^2 \cos bx$ eigenfunction, eigenvalue $= -b^2$

c) $\frac{d}{dx} e^{ikx} = ik\, e^{ikx}$ eigenfunction, eigenvalue $= ik$

$\frac{d^2}{dx^2} e^{ikx} = -k^2 e^{ikx}$ eigenfunction, eigenvalue $= -k^2$

2. a) $\frac{d}{dx}(c_1 f_1 + c_2 f_2) = \frac{d}{dx} c_1 f_1 + \frac{d}{dx} c_2 f_2 = c_1 \frac{d}{dx} f_1 + c_2 \frac{df_2}{dx^2}$

linear

b) $\sqrt{(c_1 f_1 + c_2 f_2)} \neq c_1 \sqrt{f_1} + c_2 \sqrt{f_2}$ $\therefore$ not linear

c) $e^{c_1 f_1 + c_2 f_2} \neq e^{c_1 f_1} + e^{c_2 f_2}$ $\therefore$ not linear

d) $\int (c_1 f_1 + c_2 f_2)\, d\tau = c_1 \int f_1 d\tau + c_2 \int f_2 d\tau$ linear

3) $(\cos\theta - i\sin\theta)(\cos\theta + i\sin\theta) = \cos^2\theta + \sin^2\theta = 1$

$$e^{-x^2} \cdot e^{-x^2} = e^{-2x^2}$$

4) $[\hat{L}_x, \hat{L}_y] = \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x$

$$(-i\hbar)\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right](-i\hbar)\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right] - (-i\hbar)\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right]$$
$$(-i\hbar)\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]$$

Use an arbitrary function 'f' to show this equals

$$(i\hbar)(-i\hbar)\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right] = i\hbar\hat{L}_z$$

5) $[\hat{L}_x y - y\hat{L}_x]f = -i\hbar\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]yf - y(-i\hbar)\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]f$

$$= -i\hbar\left[\left\{y\frac{\partial(yf)}{\partial z} - z\frac{\partial(yf)}{\partial y}\right\} - y^2\frac{\partial f}{\partial z} + yz\frac{\partial f}{\partial y}\right]$$

$$= -i\hbar\left[y f\frac{\partial y}{\partial z} + \cancel{y^2\frac{\partial f}{\partial z}} - \cancel{zy\frac{\partial f}{\partial y}} - zf - \cancel{y^2\frac{\partial f}{\partial z}} + \cancel{yz\frac{\partial f}{\partial y}}\right]$$

zero ∵ y & z are orthogonal

$$= +i\hbar z f$$

6) operate the functions to get $\hat{L}_z f(\theta,\phi) = k f(\theta,\phi)$

eigenvalue equation

7) $\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$

operate on $(3\cos^2\theta - 1)$ to get an eigenvalue equation

8) Use $\int_0^{\pi}\left[\sin\theta\, d\theta \int_0^{2\pi} d\phi\ Y_1^{-1}(\theta,\phi)^* \ Y_1^{-1}(\theta,\phi)\right]$

It should integrate to 1.

Useful $\sin^3 x = \frac{3}{4}\sin x - \frac{1}{4}\sin 3x$

Show $\int_0^{\pi}\left[\sin\theta\, d\theta \int_0^{2\pi} d\phi\ Y_1^{1}(\theta,\phi)^* \ Y_2^{1}(\theta,\phi)\right] = 0$

9) $I = \mu r^2$

$H^{35}Cl$ $\frac{1}{\mu} = \frac{1}{1} + \frac{1}{35} = \frac{36}{35}$; $I = \frac{35}{36} \times 1.67\times10^{-27} \times 1.275\times10^{-10}$ kg m^2 $= 2.639\times10^{-47}$ kg m^2

$H^{37}Cl$: $I = \frac{37}{38} \times 1.67\times10^{-27} \times 1.275\times10^{-10}$ kg m^2 $= 2.643\times10^{-47}$ kg m^2

$D^{35}Cl$: $I = \frac{70}{37} \times 1.67\times10^{-27} \times 1.275\times10^{-10} = 5.136\times10^{-47}$ kg m^2

Rotational constant $B = \frac{h}{8\pi^2 I}$; $H^{35}Cl \rightarrow 3.179\times10^{11}\ s^{-1}$

$D^{35}Cl \rightarrow 1.634\times10^{11}\ s^{-1}$

first three rotational transitions $\rightarrow$ 2B, 4B, 6B

$H^{35}Cl$: 6.359×10^{11} Hz, 12.716×10^{11} Hz, 19.076×10^{11} Hz

$D^{35}Cl$: 3.268×10^{11} Hz, 6.536×10^{11} Hz, 9.803×10^{11} Hz

frequency halves as the mass doubles from H to D. Could be useful to distinguish!

10) $H^{79}Br$. series of lines $\Rightarrow 2\tilde{B} = 16.72\ cm^{-1} = 1672\ m^{-1}$

$$2\tilde{B} = \frac{2h}{8\pi^2 I c} = \frac{6.626\times10^{-34}}{4\pi^2 I \times 3\times10^8} = 1672$$

$$I = 3.346\times10^{-47}\ kg\ m^2$$

$$\mu = \frac{79}{80} m_p \qquad r = \sqrt{I/\mu} = \sqrt{\frac{80}{79}\times\frac{3.346\times10^{-47}}{1.67\times10^{-27}}} = 1.424\ \mathring{A}$$

11) Classically forbidden region $\rightarrow$ KE < 0

total E = PE $\quad \dfrac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2} = \dfrac{e^2}{4\pi\varepsilon_0 r}$

$\therefore r = 2\cdot\dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = 2a_0$ ← classically forbidden for $r > 2a_0$

G.S. $R_{10}(r) = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

Probability $\displaystyle\int_{2a_0}^{\infty} |R_{10}(r)|^2 r^2 dr$ $\quad$ Use $\boxed{\displaystyle\int x^2 e^{cx} dx = e^{cx}\left(\frac{x^2}{c} - \frac{2x}{c^2} + \frac{2}{c^3}\right)}$

$$= \int_{2a_0}^{\infty} \frac{4}{a_0^3} e^{-2r/a_0} r^2 dr = \frac{1}{2}\int_4^{\infty} x^2 e^{-x} dx = -\frac{1}{2}\left[x^2 + 2x + 2\right]e^{-x}\Big|_4^{\infty}$$

$$= 13e^{-4} = 0.238$$

(Put $2r/a_0 = x$, $\frac{2}{a_0}dr = dx$)

12) $\langle r \rangle = \int_0^\infty r \cdot r^2 |R|^2 \, dr$ average

$r_{m.p.} \Rightarrow \frac{d}{dr}(r^2|R|^2) = 0$ gives $r_{m.p.}$

$r_{rms} \rightarrow \sqrt{\langle r^2 \rangle} = \left(\int_0^\infty r^2 \cdot r^2 |R|^2 \, dr \right)^{1/2}$

for 1s. $\langle r \rangle = \frac{3}{2} a_0$

$r_{mp} = a_0$

$r_{rms} = \sqrt{3}\, a_0$

for 2p

$\langle r \rangle = 5a_0$

$r_{mp} = 4a_0$

$r_{rms} = \sqrt{30}\, a_0$

$r_{mp} < \langle r \rangle < r_{rms}$ $\because$ the $r^2|R|^2$ curve is not symmetric.

13) $\int_0^\infty r^2 dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \; \psi_{n\ell m}^* \; \psi_{n'\ell' m'} = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}$

Calculate these integrals to show normalization or orthogonalization

14) $\int_0^{a_0} r^2 \frac{4}{a_0} e^{-2r/a_0} dr = \frac{1}{2}\int_0^2 x^2 e^{-x} dx = 0.323$

(see Q. 10)

15) $r^2 \psi_{2s}^2(r) = r^2 \left[\frac{1}{\sqrt{8}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \right]^2$

Put $\frac{d[r^2 \psi_{2s}^2(r)]}{dr} = 0$ and $\frac{d^2}{dr^2} r^2\psi^2 < 0$ for maxima

or $\frac{d}{dr}\left[rf(rf' + f) \right] < 0$

Apart from constants,

$$r^2\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0} = \left(2r-\frac{r^2}{a_0}\right)^2 e^{-r/a_0}.$$

differentiate to get

$$2\left(2r-\frac{r^2}{a_0}\right)\left(2-\frac{2r}{a_0}\right)e^{-r/a_0} + \left(2r-\frac{r^2}{a_0}\right)^2\left(\frac{-1}{a_0}\right)e^{-r/a_0}$$

$$\left(2r-\frac{r^2}{a_0}\right)\left(4-\frac{4r}{a_0}-\frac{2r}{a_0}+\frac{r^2}{a_0^2}\right)e^{-r/a_0}$$

gives $r = 2a_0,\ (3+\sqrt{5})a_0,\ (3-\sqrt{5})a_0$

Now use second derivative to get the maxima and minima. $2a_0$ is a minima.

$(3+\sqrt{5})a_0,\ (3-\sqrt{5})a_0$ are maxima.