Problem 1

(a) • $Y_{00}(\theta,\phi) = 1/\sqrt{4\pi}$, hence

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \; Y_{00}^*(\theta,\phi)\, Y_{00}(\theta,\phi)$$

$$= \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \; 1/4\pi = \frac{1}{4\pi}\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi$$

$$= \frac{1}{4\pi} \times 2 \times 2\pi = 1. \checkmark$$

• $Y_{11}(\theta,\phi) = -\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\phi}$, hence

$Y_{11}^*(\theta,\phi)\, Y_{11}(\theta,\phi) = \frac{3}{8\pi}\sin^2\theta$, and

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \; Y_{11}^*(\theta,\phi)\, Y_{11}(\theta,\phi) = \frac{3}{8\pi}\int_0^\pi d\theta \sin^3\theta \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

$$= \frac{3\times 2\pi}{8\pi}\int_{-1}^1 du\,(1-u^2) \qquad \text{with } u=\cos\theta$$

$$= \frac{3}{4}\left(u - \frac{u^3}{3}\right)\Big|_{-1}^{1} = \frac{3}{4}\times 2\times\left(1-\frac{1}{3}\right) = \frac{3}{2}\times\frac{2}{3} = 1. \checkmark$$

(b) • $Y_{1-1}^*(\theta,\phi) = \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\phi}$, hence

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \; Y_{1-1}^*(\theta,\phi)\, Y_{11}(\theta,\phi) = \frac{-3}{8\pi}\int_0^\pi d\theta \sin^3 \int_0^{2\pi} d\phi\, e^{2i\phi}$$

Now, $$\int_0^{2\pi} d\phi\, e^{2i\phi} = \frac{1}{2i}\, e^{2i\phi}\Big|_0^{2\pi} = \frac{1}{2i}\left(e^{4i\pi}-1\right)$$

$$= \frac{1}{2i}(1-1) = 0. \checkmark$$

- $Y^*_{21}(\theta,\phi) = -\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta\, e^{i\phi}$, hence

$$\int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi\, Y^*_{21}(\theta,\phi)\, Y_{11}(\theta,\phi)$$

$$= \sqrt{\frac{15}{8\pi}}\sqrt{\frac{3}{8\pi}} \int_0^{\pi} d\theta \sin^3\theta\cos\theta \underbrace{\int_0^{2\pi} d\phi\, e^{-i\phi} e^{i\phi}}_{=2\pi}$$

$$= \frac{\sqrt{45}}{4}\int_{-1}^{1} du\,(1-u^2)u = \frac{\sqrt{45}}{4}\left(\frac{u^2}{2} - \frac{u^4}{4}\right)\Big|_{-1}^{1}$$

$$= \frac{\sqrt{45}}{4}\left[\left(\frac{1}{2}-\frac{1}{4}\right) - \left(\frac{1}{2}-\frac{1}{4}\right)\right] = 0. \checkmark$$

(c) Since the spherical harmonics are written in terms of the complex exponentials $e^{i\phi}$ and $e^{-i\phi}$, we first write $\cos\phi$ as $\frac{1}{2}(e^{i\phi}+e^{-i\phi})$. Then, clearly,

$$\cos\theta\sin\theta\cos\phi = \frac{1}{2}\cos\theta\sin\theta\, e^{i\phi} + \frac{1}{2}\cos\theta\sin\theta\, e^{-i\phi}$$

$$= \frac{1}{2}\left(-\sqrt{\frac{8\pi}{15}}\, Y_{21}(\theta,\phi) + \sqrt{\frac{8}{15}}\, Y_{2-1}(\theta,\phi)\right).$$

Note: This calculation illustrates the general result that any regular function of the polar angles θ and ϕ can be written as a linear combination of spherical harmonics.

Problem 2

(a) We need to show that the integral of $|\psi_{100}(\vec{r})|^2$ over the whole space is 1.

$$\iiint |\psi_{100}(\vec{r})|^2 r^2 \sin\theta \, dr\, d\theta\, d\phi = 4\int_0^\infty e^{-2r} r^2 dr \underbrace{\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \, Y}_{=1}$$

$$= 4\times\left(\frac{1}{2}\right)^3 \times 2! \times 1 = 4\times\frac{1}{8}\times 2 = 1. \checkmark$$

We also need to show that the integral of $\psi^*_{200}(\vec{r})\psi_{100}(\vec{r})$ over the whole space is 0.

$$\int \psi^*_{200}(\vec{r})\psi_{100}(\vec{r})\, d^3r = \frac{2}{\sqrt{2}}\int_0^\infty \left(1-\frac{r}{2}\right) e^{-\frac{r}{2}} e^{-r} r^2 dr \times 1$$

$$= \sqrt{2}\left[\int_0^\infty e^{-3r/2} r^2 dr - \frac{1}{2}\int_0^\infty e^{-3r/2} r^3 dr\right]$$

$$= \sqrt{2}\left[\left(\frac{2}{3}\right)^3 \times 2 - \frac{1}{2}\times\left(\frac{2}{3}\right)^4 \times 6\right] = 0. \checkmark$$

(b) By $\exp(-iE_{1s}t/\hbar)$, where E_{1s} is the eigenenergy of the 1s state.

(c) A stationary state is a state in which the energy is well defined, i.e., an eigenstate of the Hamiltonian (see Section 3.11 of the QM Primer). Since the 1s and 2s states have different energies (they correspond to different values of the principal quantum number n), making a linear combination of these wave functions cannot give a state with a single, well defined energy. The answer is no.

(d) The probability is found by projecting $\Psi(\vec{r}, t=0)$ onto the ground state wave function and taking the modulus squared of the projection:

$$P = \left| \int \psi^*_{100}(\vec{r}) \, \Psi(\vec{r}, t=0) \, d^3r \right|^2$$

$$= \left| \int_0^\infty dr \, r^2 \, 2e^{-r} \frac{1}{\sqrt{2}} e^{-r/2} \underbrace{\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \, |Y_{00}(\theta,\phi)|^2}_{=1} \right|^2$$

$$= \left| \frac{2}{\sqrt{2}} \int_0^\infty e^{-3r/2} r^2 dr \right|^2$$

$$= \left| \frac{2}{\sqrt{2}} \times \left(\frac{2}{3}\right)^3 \times 2 \right|^2 = \frac{2^9}{3^6}$$ (which is less than 1, as should be expected).

Problem 3

The probability P that the electron is somewhere in space, irrespective of where, is given by the equation

$$P = \int_0^\infty dr\, r^2 \, |R(r)|^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \; |Y_{10}(\theta,\phi)|^2 ,$$

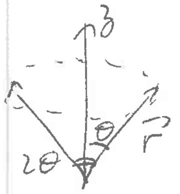
and this probability must be 1. Since the spherical harmonics are normalized,

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \, |Y_{10}(\theta,\phi)|^2 = 1,$$

which means that in order for P to be 1 we must have

$$\int_0^\infty dr\, r^2 \, |R(r)|^2 = 1.$$

To calculate the probability that the electron is in the cone mentioned in the question, we should integrate over θ from 0 to $\pi/3$ only, not from 0 to π:



max $(\theta) = 60°$ for a total aperture of 120 deg, i.e., max $(\theta) = \pi/3$.

Hence, $$P_{cone} = \underbrace{\int_0^\infty dr\, r^2 \, |R(r)|^2}_{=1} \int_0^{\pi/3} d\theta \sin\theta \int_0^{2\pi} d\phi \; |Y_{10}(\theta,\phi)|^2$$

$$= \frac{3}{4\pi} \int_0^{\pi/3} d\theta \sin\theta \cos^2\theta \int_0^{2\pi} d\phi$$

$$= \frac{3}{2} \left. \frac{u^3}{3} \right|_{\cos\frac{\pi}{3}}^{1} = \frac{1}{2}\left[1 - \left(\frac{1}{2}\right)^3\right] = 7/16 .$$

Problem 4

(a) We use $Y_{1,1} = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}$ and $Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi}$.

$$-\frac{1}{\sqrt{2}}\left[Y_{11} - Y_{1-1}\right] = -\frac{1}{\sqrt{2}}\sqrt{\frac{3}{8\pi}}\left[-\sin\theta e^{i\phi} - \sin\theta e^{-i\phi}\right]$$

$$= \sqrt{\frac{3}{16\pi}} \sin\theta \left(e^{i\phi} + e^{-i\phi}\right)$$

$$= \sqrt{\frac{3}{16\pi}} \sin\theta \; 2\cos\phi = \sqrt{\frac{3}{4\pi}} \sin\theta\cos\phi = \sqrt{\frac{3}{4\pi}} \frac{x}{r}.$$

$$\frac{i}{\sqrt{2}}\left[Y_{11} + Y_{1-1}\right] = \frac{i}{\sqrt{2}}\sqrt{\frac{3}{8\pi}} \sin\theta\left(-e^{i\phi} + e^{-i\phi}\right)$$

$$= -i\sqrt{\frac{3}{16\pi}} \sin\theta \; 2i\sin\phi = \sqrt{\frac{3}{4\pi}} \sin\theta\sin\phi = \sqrt{\frac{3}{4\pi}} \frac{y}{r}.$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \quad \text{since } z = r\cos\theta.$$

(b) $$\frac{1}{\sqrt{2}} L_x\left[Y_{11} - Y_{1-1}\right] = -i\hbar\sqrt{\frac{3}{4\pi}}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\sin\theta\cos\phi$$

$$= -i\hbar\sqrt{\frac{3}{4\pi}}\left(-\sin\phi\cos\phi\cos\theta - \frac{\cos\theta}{\sin\theta}\cos\phi\sin\phi(-\sin\phi)\right)$$

$$= -i\hbar\sqrt{\frac{3}{4\pi}}\left(-\sin\phi\cos\phi\cos\theta + \sin\phi\cos\phi\cos\theta\right) = 0$$

$$= 0 \times \left(-\frac{1}{\sqrt{2}}\left[Y_{11} - Y_{1-1}\right]\right)$$

Thus $-1/\sqrt{2}\left[Y_{11} - Y_{1-1}\right]$ is an eigenfunction of L_x and the eigenvalue is zero.

$$\frac{i}{\sqrt{2}} L_y\left[Y_{11} + Y_{1-1}\right] = -i\hbar\sqrt{\frac{3}{4\pi}}\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)\sin\theta\sin\phi$$

$$= -i\hbar\sqrt{\frac{3}{4\pi}}\left(\cos\phi\sin\phi\cos\theta - \frac{\cos\theta}{\sin\theta}\sin\phi\cos\phi\sin\theta\right) = 0$$

Thus $i/\sqrt{2}\left[Y_{11} + Y_{1-1}\right]$ is an eigenfunction of L_y and the eigenvalue is also zero.

Finally,

$$L_z Y_{10} = -i\hbar\sqrt{\frac{3}{4\pi}}\frac{\partial}{\partial\phi}\cos\theta$$

$$= 0 \text{ since } \cos\theta \text{ is constant in } \phi.$$

As seen in previous courses, Y_{10} is an eigenfunction of L_z and the corresponding eigenvalue is zero.

(c) The first person is right. The third person is wrong: working with eigenfunctions of L_z, rather than eigenfunctions of L_x or L_y or some other projection of $\vec{L}$, is merely a convention, not a mathematical necessity. Likewise, the second person is wrong, too: working with normalized wave functions, rather than unnormalized wave functions, make calculations a bit easier, but again this is not essential. The first person is right because any set of three linearly independent linear combinations of Y_{10}, Y_{11} and Y_{1-1} form a basis set for $l=1$ states, hence using the linear combinations specified in the question (with or without an overall factor of $\sqrt{3/4\pi}$) is as good as using Y_{10}, Y_{11} and Y_{1-1}.

Problem 5

(a) $\int \psi^*_{211}(\vec{r})\, H'(r)\, \psi_{200}(\vec{r})\, d^3r$

$$= \int_0^\infty dr\, r^2 \frac{1}{\sqrt{24}} r e^{-r/2} \left[-V_0 \frac{e^{-3r}}{r}\right] \frac{1}{\sqrt{2}}\left(1-\frac{r}{2}\right) e^{-r/2}$$

$$\times \underbrace{\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, Y^*_{21}(\theta,\phi)\, Y_{00}(\theta,\phi)}_{=0}$$

= 0 because the spherical harmonics Y_{00} and Y_{21} are orthogonal to each other.

↳ The whole integral is zero.

(b) $\int \psi^*_{200}(\vec{r})\, H'(r)\, \psi_{200}(\vec{r})\, d^3r$

$$= \int_0^\infty dr\, r^2 \frac{1}{2}\left(1-\frac{r}{2}\right)^2 e^{-r}\left[-V_0 \frac{e^{-3r}}{r}\right] \times \underbrace{\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, Y^*_{00} Y_{00}}_{=1}$$

$$= -\frac{V_0}{2}\int_0^\infty dr \left(r - r^2 + \frac{r^3}{4}\right) e^{-4r}$$

$$= -\frac{V_0}{2}\left(\frac{1}{16} - \frac{2}{64} + \frac{6}{4\times 256}\right) = -V_0 \frac{38}{2048} = -\frac{19}{1024} V_0 .$$

$\int \psi^*_{21m}(\vec{r})\, H'(r)\, \psi_{21m}(\vec{r})\, d^3r$

$$= \int_0^\infty dr\, r^2 \frac{1}{24} r^2 e^{-r}\left[-V_0 \frac{e^{-3r}}{r}\right] \times \underbrace{\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, Y^*_{1m} Y_{1m}}_{=1}$$

$$= -\frac{V_0}{24}\int_0^\infty dr\, r^3 e^{-4r} = -\frac{V_0}{24}\frac{6}{4^4} = -\frac{1}{1024} V_0$$

(c) The 2p wave functions are much smaller in magnitude than the 2s wave function for $r \ll 1$ a.u., i.e., in the region of space where $H'(r)$ is largest. To see this, just note that $\psi_{21m}(\vec{r}) = 0$ at $r=0$ whereas $\psi_{200}(\vec{r}) \neq 0$ at $r=0$. In other words, $H'(r)$ is largest in a region of space where the electron has a smaller probability of entering when the atom is in the 2p state than when it is in the 2s state.

(d) See Section 6.3 of the QM Primer for the method. The first step is to calculate the matrix elements of $H'(r)$ between all the degenerate states. Some of these matrix elements were already calculated in (a) and (b) above. Similarly, one finds

$$\int \psi_{21m}^* H' \psi_{200}\, d^3r = \int \psi_{200}^* H' \psi_{21m}\, d^3r = 0 \quad \text{for all } m$$

$$\int \psi_{21m'}^* H' \psi_{21m}\, d^3r = 0 \quad \text{if } m' \neq m.$$

Hence, the determinant equation is

$$\begin{vmatrix} -\frac{19V_0}{1024} - E^{(1)} & 0 & 0 & 0 \\ 0 & -\frac{V_0}{1024} - E^{(1)} & 0 & 0 \\ 0 & 0 & -\frac{V_0}{1024} - E^{(1)} & 0 \\ 0 & 0 & 0 & -\frac{V_0}{1024} - E^{(1)} \end{vmatrix} = 0$$

Therefore either $E^{(1)} = -\frac{19V_0}{1024}$ or $E^{(1)} = -\frac{V_0}{1024}$, which means that this energy level splits into two sub-levels.

(e) No, the off-diagonal matrix elements with $l' \neq l$ or $m' \neq m$ are all zero, by orthogonality of the spherical harmonics.