58) (a) $L_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$ where we will need to write

$$\frac{\partial\psi}{\partial x} = \frac{\partial\psi}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial\psi}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial\psi}{\partial\phi}\frac{\partial\phi}{\partial x} \quad \text{etc}$$

So we need $\frac{\partial r}{\partial x} = \frac{\partial}{\partial x}\left[x^2+y^2+z^2\right]^{\frac{1}{2}} = \frac{1}{2}(2x)\left(x^2+y^2+z^2\right)^{-\frac{1}{2}} = \frac{x}{r}$.

Similarly $\frac{\partial r}{\partial y} = \frac{y}{r}$

Next $\frac{\partial\theta}{\partial x} = \frac{\partial}{\partial x}\tan^{-1}\frac{z}{[x^2+y^2]^{\frac{1}{2}}} = \frac{1}{1+z^2/(x^2+y^2)}(z)\left(-\frac{1}{2}\right)\left(x^2+y^2\right)^{-\frac{3}{2}}(2x)$

$$= \frac{x^2+y^2}{x^2+y^2+z^2}\,(-)\frac{zx}{(x^2+y^2)^{3/2}} = -\frac{xz}{r^2}\frac{1}{\sqrt{x^2+y^2}}$$

Similarly $\frac{\partial\theta}{\partial y} = -\frac{yz}{r^2}\frac{1}{\sqrt{x^2+y^2}}$

Finally $\frac{\partial\phi}{\partial x} = \frac{\partial}{\partial x}\tan^{-1}\frac{y}{x} = \frac{1}{1+(y/x)^2}\left(-\frac{y}{x^2}\right) = -\frac{y}{x^2+y^2}$

$$\frac{\partial\phi}{\partial y} = \frac{\partial}{\partial y}\tan^{-1}\frac{y}{x} = \frac{1}{1+(y/x)^2}\left(\frac{1}{x}\right) = +\frac{x}{x^2+y^2}$$

$$L_z\psi = \frac{\hbar}{i}\left\{\left[x\frac{\partial r}{\partial y}\frac{\partial\psi}{\partial r} - y\frac{\partial r}{\partial x}\frac{\partial\psi}{\partial r}\right] + \left[x\frac{\partial\theta}{\partial y}\frac{\partial\psi}{\partial\theta} - y\frac{\partial\theta}{\partial x}\frac{\partial\psi}{\partial\theta}\right]\right.$$
$$\left. + \left[x\frac{\partial\phi}{\partial y}\frac{\partial\psi}{\partial\phi} - y\frac{\partial\phi}{\partial x}\frac{\partial\psi}{\partial\phi}\right]\right\}$$

$$= \frac{\hbar}{i}\left\{\left[x\cdot\frac{y}{r} - y\frac{x}{r}\right]\frac{\partial\psi}{\partial r} + \left[x\left(-\frac{yz}{r^2}\frac{1}{\sqrt{x^2+y^2}}\right) - y\left(-\frac{xz}{r^2}\frac{1}{\sqrt{x^2+y^2}}\right)\right]\right.$$
$$\left.\cdot\frac{\partial\psi}{\partial\theta} + \left[x\left(\frac{x}{x^2+y^2}\right) - y\left(\frac{-y}{x^2+y^2}\right)\right]\frac{\partial\psi}{\partial\phi}\right\}$$

$$= \frac{\hbar}{i}\left\{0\frac{\partial\psi}{\partial r} + 0\frac{\partial\psi}{\partial\theta} + 1\frac{\partial\psi}{\partial\phi}\right\} = \frac{\hbar}{i}\frac{\partial\psi}{\partial\phi} \Rightarrow \boxed{L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}}$$

(b) $$L_x = +\frac{\hbar}{i}\left[-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right]$$

$x = r\sin\theta\cos\phi \qquad y = r\sin\theta\sin\phi \qquad z = r\cos\theta.$

$$\frac{\partial\psi}{\partial\theta} = \frac{\partial\psi}{\partial x}\frac{\partial x}{\partial\theta} + \frac{\partial\psi}{\partial y}\frac{\partial y}{\partial\theta} + \frac{\partial\psi}{\partial z}\frac{\partial z}{\partial\theta}$$

$$= r\cos\theta\cos\phi\frac{\partial\psi}{\partial x} + r\cos\theta\sin\phi\frac{\partial\psi}{\partial y} - r\sin\theta\frac{\partial\psi}{\partial z}$$

$$\frac{\partial\psi}{\partial\phi} = \frac{\partial\psi}{\partial x}\frac{\partial x}{\partial\phi} + \frac{\partial\psi}{\partial y}\frac{\partial y}{\partial\phi} + \frac{\partial\psi}{\partial z}\frac{\partial z}{\partial\phi}$$

$$= -r\sin\theta\sin\phi\frac{\partial\psi}{\partial x} + r\sin\theta\cos\phi\frac{\partial\psi}{\partial y} + 0$$

$$L_x = \frac{\hbar}{i}\left\{-\sin\phi\left(\cancel{r\cos\theta\cos\phi\frac{\partial\psi}{\partial x}} + r\cos\theta\sin\phi\frac{\partial\psi}{\partial y} - r\sin\theta\frac{\partial\psi}{\partial z}\right)\right.$$

$$\left. - \frac{\cos\theta}{\sin\theta}\cos\phi\left(\cancel{-r\sin\theta\sin\phi\frac{\partial\psi}{\partial x}} + r\sin\theta\cos\phi\frac{\partial\psi}{\partial y}\right)\right\}$$

$$= \frac{\hbar}{i}\left\{-r\cos\theta(\sin^2\phi + \cos^2\phi)\frac{\partial\psi}{\partial y} + r\sin\theta\sin\phi\frac{\partial\psi}{\partial z}\right\}.$$

$$= \frac{\hbar}{i}\left\{-z\frac{\partial\psi}{\partial y} + y\frac{\partial\psi}{\partial z}\right\} \Rightarrow \boxed{L_x = \frac{\hbar}{i}\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]}$$

59) Lets begin with L_x^2. From 58

$$L_xL_x\psi = -\hbar^2\left[-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right]\left[-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right]\psi$$

$$= -\hbar^2\left\{\sin\phi\frac{\partial}{\partial\theta}\sin\phi\frac{\partial\psi}{\partial\theta} + \sin\phi\frac{\partial}{\partial\theta}\cot\theta\cos\phi\frac{\partial\psi}{\partial\phi}\right.$$

$$\left. + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\sin\phi\frac{\partial\psi}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\cot\theta\cos\phi\frac{\partial\psi}{\partial\phi}\right\}$$

$$\frac{\partial}{\partial\theta}\cot\theta = \frac{\partial}{\partial\theta}\frac{\cos\theta}{\sin\theta} = -\frac{\sin\theta}{\sin\theta} - \frac{\cos\theta}{\sin^2\theta}\cdot\cos\theta = -\frac{\sin^2\theta+\cos^2\theta}{\sin^2\theta}$$
$$= -1/\sin^2\theta.$$

So

$$L_x^2\psi = -\hbar^2\left\{\sin^2\phi\frac{\partial^2\psi}{\partial\theta^2} + \sin\phi\cos\phi\left[-\frac{1}{\sin^2\theta}\frac{\partial\psi}{\partial\phi} + \cot\theta\frac{\partial^2\psi}{\partial\theta\partial\phi}\right]\right.$$
$$+ \cot\theta\cos\phi\left[\cos\phi\frac{\partial\psi}{\partial\theta} + \sin\phi\frac{\partial^2\psi}{\partial\phi\partial\theta}\right]$$
$$+ \cot^2\theta\cos\phi\left[-\sin\phi\frac{\partial\psi}{\partial\phi} + \cos\phi\frac{\partial^2\psi}{\partial\phi^2}\right]$$

The result for $L_y^2\psi$ is similar except for some $\cos\phi \leftrightarrow \sin\phi$ interchanges and sign changes. I get

$$L_y^2\psi = -\hbar^2\left\{\cos^2\phi\frac{\partial^2\psi}{\partial\phi^2} - \sin\phi\cos\phi\left[-\frac{1}{\sin^2\theta}\frac{\partial\psi}{\partial\phi} + \cot\theta\frac{\partial^2\psi}{\partial\theta\partial\phi}\right]\right.$$
$$-\cot\theta\sin\phi\left[-\sin\phi\frac{\partial\psi}{\partial\theta} + \cos\phi\frac{\partial^2\psi}{\partial\phi\partial\theta}\right]$$
$$\left.+\cot^2\theta\sin\phi\left[\cos\phi\frac{\partial\psi}{\partial\phi} + \sin\phi\frac{\partial^2\psi}{\partial\phi^2}\right]\right\}.$$

When we combine the two parts, many terms cancel and we have

$$(L_x^2+L_y^2)\psi = -\hbar^2\left\{(\sin^2\phi+\cos^2\phi)\frac{\partial^2\psi}{\partial\theta^2} + \cot\theta(\cos^2\phi+\sin^2\phi)\frac{\partial\psi}{\partial\theta}\right.$$
$$\left.+\cot^2\theta(\cos^2\phi+\sin^2\phi)\frac{\partial^2\psi}{\partial\phi^2}\right\}$$
$$= -\hbar^2\left\{\frac{\partial^2\psi}{\partial\theta^2} + \cot\theta\frac{\partial\psi}{\partial\theta} + \cot^2\theta\frac{\partial^2\psi}{\partial\phi^2}\right\}$$

$$L_z^2\psi = -\hbar^2\frac{\partial^2\psi}{\partial\phi^2} \Rightarrow$$

$$L^2\psi = -\hbar^2\left\{\frac{\partial^2\psi}{\partial\theta^2} + \cot\theta\frac{\partial\psi}{\partial\theta} + \left(\frac{\cos^2\theta}{\sin^2\theta}+1\right)\frac{\partial^2\psi}{\partial\phi^2}\right\}$$

$$L^2 = -\hbar^2 \left\{ \frac{\partial^2}{\partial\theta^2} + \cot\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right\}$$

Notice that

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\psi}{\partial\theta} = \frac{1}{\sin\theta}\left[\cos\theta\frac{\partial\psi}{\partial\theta} + \sin\theta\frac{\partial^2\psi}{\partial\theta^2}\right]$$

$$= \cot\theta\frac{\partial\psi}{\partial\theta} + \frac{\partial^2\psi}{\partial\theta^2}$$

so our L^2 can be written in "standard" form

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

60) (a) We have eigenfunctions of L_z which look like this

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}}\frac{x+iy}{r} \;;\quad Y_1^0 = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \;;\quad Y_1^{-1} = \sqrt{\frac{3}{8\pi}}\frac{x-iy}{r}$$

Since

$L_z = xp_y - yp_x$ and $L_x = yp_z - zp_y$ (cyclic permutation)

it makes sense to propose L_x eigenfunctions of the form

$$F_1^1 = -\sqrt{\frac{3}{8\pi}}\frac{y+iz}{r} \qquad F_1^0 = \sqrt{\frac{3}{4\pi}}\frac{x}{r} \qquad F_1^{-1} = \sqrt{\frac{3}{8\pi}}\frac{y-iz}{r}$$

Check:

$$L_x = \frac{\hbar}{i}\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]$$

$$L_x F_1^1 = -\frac{\hbar}{i}\sqrt{\frac{3}{8\pi}}\left\{y\left[\frac{i}{r} + (y+iz)\frac{\partial}{\partial z}\left(\frac{1}{r}\right)\right] - z\left[\frac{1}{r} + (y+iz)\frac{\partial}{\partial y}\left(\frac{1}{r}\right)\right]\right\}$$

$$\frac{\partial}{\partial z}\left(\frac{1}{r}\right) = \frac{\partial}{\partial z}\left(x^2+y^2+z^2\right)^{-\frac{1}{2}} = \left(-\frac{1}{2}\right)\left(x^2+y^2+z^2\right)^{-3/2}\cdot(2z) = -\frac{z}{r^3}$$

Similarly $\quad \frac{\partial}{\partial x}\left(\frac{1}{r}\right) = -\frac{x}{r^3}$ and $\frac{\partial}{\partial y}\left(\frac{1}{r}\right) = -\frac{y}{r^3}$

So

$$L_x F_1^1 = -\frac{\hbar}{i}\sqrt{\frac{3}{8\pi}}\left\{\frac{iy}{r} - \frac{z}{r} + (y+iz)\left[\cancel{y\left(-\frac{z}{r^3}\right)} - \cancel{z\left(-\frac{y}{r^3}\right)}\right]\right\}$$

$$= -\sqrt{\frac{3}{8\pi}}\,\hbar\left\{\frac{y}{r} - \frac{z}{ir}\right\} = -\sqrt{\frac{3}{8\pi}}\,\hbar\left\{\frac{y+iz}{r}\right\} = \hbar F_1^1 \checkmark$$

Next

$$L_x F_1^0 = \frac{\hbar}{i}\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]\sqrt{\frac{3}{8\pi}}\left(\frac{x}{r}\right)$$

$$= \frac{\hbar}{i}\sqrt{\frac{3}{8\pi}}\left\{yx\frac{\partial}{\partial z}\left(\frac{1}{r}\right) - zx\frac{\partial}{\partial y}\left(\frac{1}{r}\right)\right\}$$

$$= \frac{\hbar}{i}\sqrt{\frac{3}{8\pi}}\left\{yx\left(-\frac{z}{r^3}\right) - zx\left(-\frac{y}{r^3}\right)\right\} = 0 \quad \checkmark$$

$$L_x F_1^{-1} = \frac{\hbar}{i}\sqrt{\frac{3}{8\pi}}\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]\frac{y-iz}{r}$$

$$= \frac{\hbar}{i}\sqrt{\frac{3}{8\pi}}\left\{y\left(-\frac{i}{r}\right) - z\left(\frac{1}{r}\right) + (y-iz)\left[\cancel{y\left(-\frac{z}{r^3}\right)} - \cancel{z\left(-\frac{y}{r^3}\right)}\right]\right\}$$

$$= \hbar\sqrt{\frac{3}{8\pi}}\left\{-\frac{y}{r} - \frac{z}{ir}\right\} = \hbar\sqrt{\frac{3}{8\pi}}\left(\frac{-y+iz}{r}\right) = -\hbar F_1^{-1} \checkmark$$

(b) If $L_z = \hbar$ and $L^2 = 2\hbar^2$ then the electron's wave function is

$$\psi = Y_1^1 = -\sqrt{\frac{3}{8\pi}}\,\frac{x+iy}{r}$$

To answer the question we need to write ψ as an expansion over L_x eigenfunctions.

Notice that

$$F_1^1 - F_1^{-1} = -\sqrt{\frac{3}{8\pi}}\,\frac{2y}{r}$$

$\Rightarrow$

$$\frac{i}{2}\left(F_1^1 - F_1^{-1}\right) = -\sqrt{\frac{3}{8\pi}}\,\frac{iy}{r}$$

$$-\sqrt{\frac{3}{8\pi}}\,\frac{x}{r} = -\frac{1}{\sqrt{2}}F_1^0$$

so by inspection

$$Y_1^1 = \frac{i}{2} F_1^1 - \frac{1}{\sqrt{2}} F_1^0 - \frac{i}{2} F_1^{-1}$$

The squares of the expansion coefficients give the probabilities

$$\boxed{\begin{aligned} P(L_x = \hbar) &= \left|\frac{i}{2}\right|^2 = \frac{1}{4} \\ P(L_x = 0) &= \left|-\frac{1}{\sqrt{2}}\right|^2 = \frac{1}{2} \\ P(L_x = -\hbar) &= \left|-\frac{i}{2}\right|^2 = \frac{1}{4} \end{aligned}}$$

6i) In general we have

$$\langle r \rangle = \langle \psi | r | \psi \rangle = \int_0^\infty R_{n\ell}^*(r)\, r\, R_{n\ell}(r)\, r^2 dr$$

2s: $R = 2\left(\frac{1}{2a_0}\right)^{3/2}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$

$\Rightarrow$

$$\langle r \rangle = 4\left(\frac{1}{2a_0}\right)^3 \int_0^\infty \left(1 - \frac{r}{2a_0}\right)^2 r\, e^{-r/a_0}\, r^2 dr$$

Let

$$x = \frac{r}{a_0} \quad r = a_0 x \quad dr = a_0 dx \Rightarrow$$

$$\langle r \rangle = 4\left(\frac{1}{2a_0}\right)^3 a_0^4 \int_0^\infty \left(1 - \frac{x}{2}\right)^2 x^3 e^{-x} dx$$

$$= \frac{a_0}{2} \int_0^\infty \left(x^3 - x^4 + \frac{x^5}{4}\right) e^{-x} dx$$

$$= \frac{a_0}{2}\left\{3! - 4! + \frac{5!}{4}\right\} = \frac{a_0}{2}\left\{6 - 24 + 30\right\} = \boxed{6a_0}$$

Now 2p:

$$R(r) = \frac{1}{\sqrt{3}}\left(\frac{1}{2a_0}\right)^{\frac{3}{2}} \frac{r}{a_0} e^{-r/2a_0}$$

$\Rightarrow$

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

$$= \frac{1}{3}\left(\frac{1}{2a_0}\right)^3 a_0^4 \int_0^\infty x^2 e^{-x} x^3 dx$$

$$\langle r \rangle = \frac{1}{3}\left(\frac{1}{2}\right)^3 a_0 \cdot 5! = \boxed{5a_0}$$

62) (a) $V = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r}$ $\qquad R_{10}(r) = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

so

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0}\left\langle \frac{1}{r} \right\rangle = -\frac{e^2}{4\pi\epsilon_0}\int_0^\infty R_{10}^*(r)\,\frac{1}{r}\,R_{10}(r)\,r^2 dr.$$

$$= -\frac{e^2}{4\pi\epsilon_0}(4)\frac{1}{a_0^3}\int_0^\infty e^{-2r/a_0}\,r\,dr.$$

Let

$$x = 2r/a_0 \qquad r = \frac{a_0}{2}x \qquad dr = \frac{a_0}{2}dx$$

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0}(4)\frac{1}{a_0^3}\left(\frac{a_0}{2}\right)^2\int_0^\infty x e^{-x}dx$$

$$= -\frac{e^2}{4\pi\epsilon_0}\frac{1}{a_0} \times 1! \qquad a_0 = \frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{m}$$

so

$$\boxed{\langle V \rangle = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{m}{\hbar^2} = -27.2\,\text{eV}} = -(1.44\,\text{eV}\cdot\text{nm})^2\frac{5.11\times10^5\,\text{eV}}{(197.3\,\text{eV}\cdot\text{nm})^2}$$

(b) $\langle T \rangle + \langle V \rangle = E = -\frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{m}{\hbar^2}$

so

$$\langle V \rangle = -\langle V \rangle + E = \boxed{+\frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{m}{\hbar^2} = +13.6\,\text{eV}}$$